Treatment of Printing Ink Wastewater using High Liquid Carryover mode Flotation

by

Choon Jek ANG

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Environment and Biotechnology Centre Swinburne University of Technology Melbourne Australia
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Choon Jek ANG
Melbourne, August 2004.
I hereby declare that, to the best of my knowledge, this thesis contains no material previously written or published by another person, except where reference is made in the text. I also declare that none of this work has been previously submitted for a degree or similar award at another institution.

Choon Jek ANG
The following papers have been presented or published in support of this work:


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ABSTRACT

The aim of this project is to investigate the feasibility of the use of a novel process of high liquid carryover (HLC) mode flotation to treat wastewater from a cardboard printing and coating plant. This is conducted by characterising the process conditions with the purpose of achieving a set condition that have a low susceptibility to variability in the wastewater composition. Information pertaining to the surface and physical characteristics of the solid contained in the wastewater sample were used to explain the flotation outcomes.

Fe(II) was found to be more suited for industrial use as coagulant over the more commonly known coagulants, Al(III) and Fe(III), as it has the advantages of having a constant optimum flotation pH (6.5) regardless of wastewater characteristics, as well as having a much lower detrimental effect on the flotation outcome when present in excess of the minimum requirement for flocculation of wastewater solids. This allows the setting of a coagulant dose (5 mM) that will treat both high and low solids content wastewater samples.

The use of cationic surfactant (CTAB) was found to require lower coagulant dosages compared to those required for anionic (SDS) or non-ionic (TericG12A8) surfactants in order to achieve good flotation outcomes. A CTAB concentration of 300 ppm was required to achieve a stable foam that can sustain for a prolonged period to allow solid (in foam)/liquid separation.

The optimum batch mode conditions for HLC flotation were found to be pH 6.5, 5 mM Fe(II) and 300 ppm CTAB. This was found to correspond to a small and negative electrophoretic mobility at the wastewater solid surface and large floc size.

Batch mode flotation of individual ink components under the optimum conditions for industrial wastewater treatment revealed that the presence of large quantities of either blue or yellow inks in the wastewater can lead to poor removal. Their combined presence, however, did not have detrimental effects.

Continuous mode flotation at 5 mM Fe(II), 300 ppm CTAB and pH 6.5 was found to remove above 96% of contaminants at cell residence times of 6 minutes and 88% of contaminants at cell residence times of 1.5 minute. Greater than 87% of the initial wastewater volumes were recovered as treated effluent (i.e. <13% disposed as waste foam sludge), yielding a waste foam sludge containing between 12 and 17% solids. The best flotation outcomes were achieved when all the wastewater volume entering the flotation cell leaves the cell with the foam.
Chapter 1: General Introduction

1.1 Industrial Wastewater Management Strategy

The printing ink industry, like all other chemical industries, has its own specific problems in dealing with the toxic nature of its waste and wastewater. In general, industrial pollutants can be managed through the following strategies:

- using different raw materials;
- modifying processes or equipment;
- installing wastewater treatment plants; and
- discharging industrial wastewater to public sewage systems for treatment.

Pollution prevention and waste minimisation at its source is the ultimate goal, as this will prevent or minimise further complex environmental problems such as toxic solid waste disposal. Thus, the first two strategies mentioned above are a priority in dealing with industrial wastewater.

The implementation of waste minimisation may not be adequate in resolving the issue of the adverse environmental impact of industrial wastewater. Thus, the next step is to install a wastewater treatment plant to treat the ink bearing waste at the source prior to discharge to the sewer. This research project deals with the treatment of wastewater from a cardboard printing and coating plant that employs flexographic printing techniques.

1.2 Water-based Flexographic Ink Wastewater Characteristics

The main contaminants in wastewater from cardboard printing processes are the various types of flexographic inks. Ink wastes occur whenever printing machines are washed for colour replacement. It is estimated that more than 5% of the amount of inks used will end up in the wastewater [1].

In the United States, the use of flexographic inks has been increasing at around 6% per year since the early 1980’s [2, 3]; a larger growth than the other various printing processes. Flexographic inks represented about 21% of the printing ink market in 1991 [4] with a market value of US$675 million of flexographic ink usage in 1995 in North America alone [3]. Flexographic inks are used mainly in the printing of packaging and flexible packaging material where they accounted for at least 60% of all packaging printing [2]. The rapid growth in
flexographic ink usage in recent years is due partly to its penetration of the newspaper [5, 6] and commercial markets as new and improved equipment, inks, substrates and inking techniques are developed. This new equipment includes electronic pre-press, printing plates, press construction and register. Elsewhere, flexographic ink has found wide use in the printing of paperback books, labels, disposable products (e.g. paper cups and toilet tissue), and decorative materials such as wallpaper and gift wrap [3, 7, 8].

The trend towards the use of water-based ink as a substitute for organic solvent-based systems has altered both the quality and quantity of wastewater produced. Water is increasingly being used for cleaning instead of organic solvents, resulting in increased quantities of chemicals in the wastewater.

The most unacceptable characteristics of ink waste streams include their relatively high pH, their high levels of chemical oxygen demand, the pigments’ low biodegradability, the high concentrations of metals and suspended solids found within them and their strong colour [9, 10, 11]. The typical metals associated with ink wastewater are aluminium, barium, chromium, copper, iron, lead, zinc and titanium [12, 13]. These metals are found either incorporated in the ink pigment (inorganic pigment) or as trace elements within the ink system. The metals are not in solution but are attached to the colloidal particles. Lead, zinc and chromium are known to be toxic towards humans, animals, plants and the environment and as a result, the use of these heavy metal-containing pigments is slowly being phased out.

Pigment molecules are highly structured polymers that are toxic to micro-organisms [14]. In addition, these ink molecules are designed to withstand harsh conditions [15], and are highly resistant to the effects of chemicals such as acids, alkalis and chlorine. These pigments are therefore resistant to treatment with conventional activated sludge treatment processes. Disposal of these waste streams in an untreated form into the sewer system is, therefore, an unsustainable practice.

A hazard assessment of the wastewater problems associated with the printing industry was conducted by the Danish Environment Protection Authority (Danish EPA) in 1996. It classified the wastewater from the cleaning of flexographic printing machines as a high priority area of intervention for cleaner technology [1]. Similarly, in 1980, the EPA body of the United States classified the concentrated sludge product resulting from the treatment of flexographic wastewater as either a ‘hazardous waste’ or a ‘special waste’, with the constituents used in the manufacture of flexographic inks containing up to 34 priority pollutants [9].
1.3 Choice in Wastewater Treatment System

There are a wide variety of processes available for the treatment of wastewater, each with its own advantages and disadvantages. The exact choice of processes will depend on many factors, including:

- the nature and characteristics of the wastewater;
- the diversity and complexity of the types of pigments in the printing wastewater;
- the relative cost and treatment effectiveness of each treatment system;
- the availability of spaces, especially in urban industrial areas;
- the current and future regulations governing the permissible discharge levels of contaminants in the effluent being discharged into the environment or local sewage systems (more stringent standards can be expected in the near future);
- land disposal and transportation cost; and
- the availability and economics of the water supply. In Australia, this is becoming an increasingly important issue. The recent droughts have heightened public awareness of the need for water conservation. A wastewater treatment system that can produce effluent clean enough for recycling purposes within the printing plant would meet this need.

1.4 Current Technology Employed in Treating Printing and Coating Wastewater

The most common treatment methods used for treating flexographic ink wastes can be divided into two broad categories:

- physico-chemical treatment; and
- physical treatment.

The most prevalent treatment system for ink wastes is a combination of chemical additive to destabilise the emulsion and encourage coagulation and flocculation, followed by the physical separation of solids from the bulk liquid by physical means, such as sedimentation, filtration or centrifugation. Lime, alum, ferric chloride and polyelectrolytes of Al(III) and Fe(III) are used widely as coagulants in water and wastewater treatment to increase the de-waterability of sludge [9, 16, 17].

O’Shaughnessy et al. [18] compared the effectiveness of different physical separation methods (after chemical addition). Filtration, sedimentation and centrifugation were compared by measuring the amount of solids, metal and colour. The authors found that filtration was the best separation method, followed by centrifugation, while sedimentation was the least effective. It
has been reported, however, that regardless of which physical separation method is used, the treated effluent has a slight residual colour associated with dyes used in flexographic inks. The residual colour can be removed through addition of oxidants or methods such as powdered activated carbon treatment and ozonation.

The filtration method is by far the most widely used as it is a simple and effective treatment system that will not be affected by fluctuations in both ink concentrations and volumes in wastewater [19, 20, 21]. Fluctuating wastewater volumes can be overcome easily by increasing or decreasing the number of filter presses in use at the time. Filtration through a 1 µm pore size filter has been found to remove most colour and suspended solids (90 – 100%) [18]. A pressure of 80 psig on the plate-filter press will result in a sludge with up to 50% solids concentration [13, 16]. The main disadvantages of the filtration method, apart from the cost required for machinery (pumps and filters), maintenance and energy, is the constant blinding or clogging of the filter media by the sludge. Recent improvements in filtration technology in (i) overcoming the blinding of the filter media and (ii) achieving a higher waste solids content (up to 50%), had been reported by Hayes (Precoat Rotary Drum Vacuum Filter, [16]) and Fedrigon (Recessed Plate Filter Press, [13]). The waste solids filter cake can be disposed without requiring further chemical stabilisation, as it contains little free water.

Centrifugation is very effective in concentrating sludges for easy disposal, and requires minimal space. However, a high centrifugal speed of 400 g is required [18], consuming a lot of energy. Sedimentation is the cheapest physical separation option, but it is also the least effective method as the resulting waste sludge has a low concentration of solids. In addition, it is a slow process that requires a large space for a sedimentation tank.

Physical treatment methods that do not use any chemical alteration are less common. Stanton and Harvey [11] gave a comprehensive review of the two main physical separation methods used – ultrafiltration and evaporation. The authors then went on to introduce a process they called the ‘Membrane/Drum Dryer System’, which incorporated ultrafiltration and evaporation.

The advantages of ultrafiltration are the resulting high sludge concentration, and that no pH adjustment or coagulant addition is required [18]. The resulting treated effluent is reported to be clean enough to be reused as wash water [22]. It is not, however, a popular treatment technique as a lot of energy is required to achieve a concentrated sludge. There are also recognised problems with membrane fouling and the inability to remove dissolved solids. In general, due to the high latent heat of vaporisation of water, evaporation will only be feasible if (i) there is a readily available source of heat or (ii) when high solids sludge is desirable (70% solids content),
mainly for ease of waste disposal [10]. Physical-chemical process, followed by the evaporation of waste solids sludge will further reduce the water content with little additional cost.

Conventional biological treatment of ink wastewater is reported to be ineffective due to (i) the high metal concentration associated with flexographic inks [9], and/or (ii) the low biodegradability of the carbon compounds associated with the pigment structure, signified by the low value of carbonaceous biochemical oxygen demand (CBOD₅) to chemical oxygen demand (COD) ratio, with typical reported ratios between 0.01 and 0.15 depending on the types of pigments [9, 14]. It may, however, be a valid treatment method in the future if flexographic ink formulation changes to exclude metals and use only organic pigments [9]. For example, Sun Chemical, an organic pigment production plant, uses a biological wastewater treatment system to treat its wastewater, with the resulting treated effluent being clean enough to be recycled for usage within the plant [23]. Among the biological treatment methods reported are absorption using activated brown carbon and oxidation with ozone/UV or UV/H₂O₂ [19].

1.5 Flotation as a Wastewater Treatment Method

Flotation achieves separation by exploiting the surface energy and surface excess charge characteristics of the solids to be removed. In solid-liquid separation, separation can be achieved by modifying the surface affinity of the solids for the liquid medium. Air bubbles are passed through the solution and given the right conditions, solids become attached to the bubbles and are selectively removed from the solution. Flotation has the advantage over sedimentation, as it does not rely on differences in specific gravity. The specific gravity differences required by sedimentation may not be easily modified, especially for colloidal sized suspended solids with high hydrophobicity.

Flotation is used extensively in the mineral industry in the separation of valuable minerals from the gangue. Elsewhere, it has found usage in many applications including protein separation, plastics separation and recycling, deinking of printed paper, and the removal or harvesting of algae or microorganisms [24]. However, despite the potential and proven broad applications, flotation has not been used widely in wastewater treatment systems. There are a number of reasons for this. Firstly, the flotation process is more complex than other separation techniques, requiring more specific process conditions for successful separation. These specific process conditions require an understanding of the surface chemistry involved in the flotation system and how each variable affects the flotation outcome down to the molecular level, before implementation. In addition, the process relies on the surface energy being modified via the adsorption of surfactants onto the solids surface. Anything that can hinder or prevent this
adsorption will interfere with the flotation process. This is especially true in wastewater systems of variable and complex composition. The high degree of complexity makes automation more difficult, and operation of the flotation plants by highly qualified personnel would be necessary. In addition, there are also limitations in the flotation technique, one of which is the high liquid content associated with the concentrated waste sludge. The high liquid content in the waste sludge in conventional mode flotation processes cannot be avoided due to the instability of the foam at low water contents.

Rubio et al. [24] gave a comprehensive review of the applications of the flotation process in wastewater treatment. Flotation has been found to be effective in the removal of solids, ions, oil, grease, macromolecules, dyes and fibres from both municipal and industrial wastewater, such as wastewater from food processing, oil refineries, and pulp and paper mills [25, 26]. The more common flotation processes used in wastewater treatment are:

- dispersed/induced air flotation (IAF), dissolved air flotation (DAF) and electrolytic flotation for removal of colloidal suspended solids; and
- adsorbing colloid flotation (ACF), precipitate flotation and ion flotation for the removal of metal ions.

A list of recent innovations in flotation techniques (with a brief description of each) has been presented by Rubio et al. [24]. These include nozzle flotation (NF), centrifugal flotation (CF) and aggregation-DAF (ADAF).

The main application of flotation in wastewater treatment is in the area of the separation of inorganic metal ions from solution, including (i) 95 – 100% removals of zinc, nickel and chromium from electroplating wastewater [27], (ii) 96% removal of chromium from tannery wastewater [28], (iii) > 99% removal of zinc from radioactive process wastewater [29], and (iv) 92 – 99% removals of arsenic, chromium and lead from mining wastewater [30].

Flotation has also been utilised to remove colloidal suspended solids in water treatment where low settling velocity makes effective sedimentation difficult. For example, for water supply in rural areas, colloidal suspended solids, organic colour (e.g. humic and fulvic acids), algae present in raw surface water are removed with flotation prior to granular filtration [31, 32, 33].

Pulp and paper de-inking treatment, where ink particles are floated and separated from the fibre material, is the main industrial application of flotation on wastewater containing pigments and inks [5, 34]. The use of de-inking flotation has increased from 1.5 million t/year of wastewater to 17.7 million t/year worldwide from 1972 to 1991 [35].
Flotation has proven very effective in removing highly coloured inorganic/organic and anionic/cationic dyes from solution by adsorption or coprecipitation. Sheu and Huang [36], Huang and Huang [37] and Cheng and Huang [38] separately investigated the removal from solution of Basic Violet 14 (organic cationic dye), Acid Red 114 (anionic dye) and Direct Red 1 (anionic dye) respectively, using ferric hydroxide and/or aluminium hydroxide as coagulant and sodium laurylsulfate (SDS) as collector [36, 37, 38]. Removals of 99.6%, 99% and 97% were achieved for Basic Violet 14, Acid Red 114 and Direct Red 1 respectively.

One of flotation’s many advantages is rapid operation, requiring only a small operating space. Cheng and Huang [38], for example, found that 97% of Direct Red 1 could be removed within 3 minutes with ferric hydroxide flocs and SDS as collector and frother.

The total cost of the wastewater treatment process is an important concern. The total cost includes the capital cost and running cost and the cost associated with the ultimate disposal of concentrated sludge. The capital cost involves the cost of fixed equipments (e.g. flotation and flocculation tanks) and mechanicals (e.g. pumps and mixers) while the running cost includes the chemical cost of coagulants and surfactant, energy and labour requirement, and maintenance. The advantage of flotation over treatment techniques such as filtration is that the maintenance cost is low due to the lower number of moving parts within the flotation system. Wilkinson et al. [39] conducted a study on the operating cost of a flotation plant and found that the chemical cost (coagulant and surfactant) comprised a large proportion of the operating cost. Thus, in this study, coagulant and surfactant are important process variables with the aim of understanding and minimising the usage of these raw materials.

Despite its many applications in mineral processing or wastewater treatments, the flotation process has limited application in treating wastewater with high solids content such as the wastewater from the printing ink industry. The disadvantage of conventional mode flotation in this regard is that the increased solids content results in a decrease in the liquid drainage rate and an increase in foam stability, leading to a large amount of liquid entrainment [40]. This, in turn, leads to a sludge that is very wet and necessitates the use of large columns and low wastewater throughputs to allow more time for extensive drainage.

1.6 HLC mode Flotation

The high liquid carryover (HLC) mode flotation is a relatively recent innovation in flotation, where high air throughput is applied during flotation [41]. The foam produced is wet with high liquid entrainment. This foam is then carried over to a collection vessel for extensive drainage.
The success of this method relies on selecting operating conditions such that the hydrophobicity, size and concentration of the solids lead to the formation of a solids-stabilised foam. When this occurs, the solid contaminants are retained in the foam while clean liquid drains out. This process allows for operation at a much faster hydraulic loading than the conventional flotation system, as it eliminates the need to keep the foam water content low, allowing the use of much higher air flow rates. This allows a smaller and less expensive column to be used.

The disadvantages of HLC mode flotation, however, as outlined by Sanciolo et al. [41], are the requirement for more complicated collection/drainage vessels, the difficulty in automation of the process and the operating costs associated with the use of surfactants as higher surfactant concentrations are required.

1.7 Objective of Thesis

The objective of the research in this thesis is to investigate the feasibility of using the high liquid carryover (HLC) mode flotation as a means of treating industrial wastewater generated from a cardboard printing and coating plant. This objective can be subdivided into three main aims:

- to gain a better understanding of the effects of each process variables on the flotation outcome;
- to evaluate the potential of HLC mode flotation in treating high solids content wastewater; and
- to develop a wastewater treatment process that is flexible and robust enough to accommodate changing wastewater characteristics.
Chapter 2: Theoretical Basis of High Liquid Carryover mode Flotation

2.1 Overview

The high liquid carryover (HLC) mode flotation process can be subdivided into three stages: wastewater pre-treatment, flotation, and foam and effluent management as shown in Figure 2.1.

![Figure 2.1: HLC mode flotation process](image)

The aim of pre-treating the sample is to modify the surface chemistry and physical size of the colloidal suspended solids in the printing ink wastewater. The printing ink wastewater consists mainly of finely divided pigment solids suspended in the solution with an average solid size of 0.2 µm [5]. Metal ions are added to destabilise the colloidal suspension through adsorption onto the solid surface, leading to flocculation of the mixed pigment-coagulant solids to a size suitable for flotation, or precipitation in the solution followed by heteroflocculation with the finely divided pigment solids. Surfactant is then added in order to render the surfaces hydrophobic.
and lower the air-liquid interface surface tension such that a foam can be formed during flotation.

In the flotation stage, gas bubbles are introduced through the wastewater and solid-bubble aggregates are formed through the collision and subsequent attachment of the flocculated solids onto the gas bubbles. The foam containing the stable solid-bubble aggregates is pushed up by newly formed foam as it drains, and overflows from the flotation cell into a foam collection vessel where more extensive drainage is allowed. The liquid that drains from the foam, along with the liquid that is left in the flotation cell (after a flotation run), are collected as treated effluent.

The ideal ultimate products of the printing wastewater treatment process using HLC mode flotation are (i) an effluent of low solid contaminant concentration, and (ii) a low water content foam product, which can be disposed of without further treatment. The foam must therefore be able to withstand extensive liquid drainage. This can only be achieved if the surface chemistry and the concentration of solids are such that a solids-stabilised foam is formed.

2.2 Wastewater Pre-treatment

2.2.1 Introduction

Pre-treatment involves the addition of a flocculant (commonly Al(III) and Fe(III) cations) followed by pH adjustment and surfactant addition. The role of the pre-treatment stage is threefold:

- to flocculate the finely dispersed pigment solids so that they are within the optimum size range for flotation;
- to alter the surface charge and hydrophobicity of the pigment solids in order to facilitate their attachment to the bubbles; and
- to lower the surface tension of the wastewater in order to facilitate the formation of a foam.

2.2.2 Surface Characteristics of Solids Prior to Treatment

2.2.2.1 Pigment Chemical Structure

Pigments are the most important constituent in printing inks as they convey the visual identity of the ink. Pigments are also responsible for the many specific properties of the inks, such as specific gravity, opacity/transparency and resistance to light, heat or chemicals.
The main pigments found in the printing ink wastewater samples and their chemical structures are shown in Figure 2.2.

The black pigment most commonly used in the printing ink industry is carbon black [42]. Its structure depends upon the manufacturing process and conditions of operation. It has an intermediate crystallinity (or paracrystalline), between that of crystalline graphite and that of amorphous coal, with a continuous network of distorted graphite layers [42].

It is common practice to mix different types of pigments into an ink formulation in order to obtain the desired colour and characteristics. For example, one of the process inks used as simulated wastewater in Chapter 5 is magenta ink, which comprises mainly a mixture of lithol rubine 4B and rhodamine GG.
The main feature characteristics of the pigments used in cardboard printing inks are very similar, i.e. they exhibit properties that are highly resistant towards heat, light, water, solvents, acids and alkalis [7]. Other similarities include desirable physical properties such as small particle sizes with high particle stability while exhibiting bright shades and high tinting strength.

Despite the similarities in properties, the various types of printing inks can be classified into two main categories, i.e. organic or inorganic pigments. Organic pigments such as diarylide yellow and phthalocyanine blue (see Figures 2.2(a) and (b)) are made up of large, complex molecules and are generally stronger and brighter than the inorganic pigments. Inorganic pigments such as titanium dioxide (see Figure 2.2(e)) are simple chemicals with small molecules. The constituents in inorganic pigments have changed through the years as pigment containing heavy metal pollutants such as lead, cadmium and chromium [18] are slowly being replaced by less toxic or carcinogenic metals.

Real industrial wastewater is a complex mixture of these pigments. It is thus difficult to predict the surface characteristics of the wastewater solids.

2.2.2.2 Pigment Hydrophobicity

Organic pigments such as diarylide yellow (see Figure 2.2(a)) and carbon black tend to contain more hydrophobic sites. Inorganic pigments such as titanium dioxide (see Figure 2.2(e)) are hydrophilic in nature, while organic pigments with ionic functional groups such as lithol rubine 4B (see Figure 2.2(c)) may contain a mixture of hydrophobic and hydrophilic sites.

Surface hydrophobicity can also change in the presence of additives on the pigment surface, such as coating and dispersing agents (e.g. polymers and surfactants). For example, Musselman and Chander [43] found that at high concentrations (> 0.1 mM), the non-ionic acetylenic diol-based surfactants (or derivatives of 2,4,7,9-tetramethyl-5-decyne-4,7-diol) adsorbed through tail-down orientation onto the lampblack and phthalocyanine blue pigments, i.e. with the polyethylene oxide chains extended into the solution, leads to a decrease in the pigment’s hydrophobicity.

2.2.2.3 Pigment Surface Charge

The surface charge of the pigment solids is based on the ‘rule of thumb’ of electrokinetics, i.e. the surface area weighted average of each of the surface components [44]. The surface characteristics of the pigment particles are altered during ink formulation in order to render the
pigment particles dispersible. Therefore, the characteristics at the pigment surface can be very different from the characteristics of the pigment itself. For example, for titanium dioxide pigment particle coated with silica and/or alumina and an adsorbed layer of dispersant (e.g. polymer binders and surfactants) as shown in Figure 2.3, the surface charge is dominated mainly by the dispersant and to a lesser extent, the silica and/or alumina. Titanium dioxide has minimal contribution towards the surface charge as indicated by Taylor et al. [45] who found that the isoelectric point (IEP) of titanium dioxide coated with alumina is much closer to the IEP of alumina than the IEP of titanium dioxide.

![Figure 2.3: Schematic diagram of single titanium dioxide pigment particle, showing the layer structure [Reference: Croll, 46].](image)

The presence of the negatively charged polymer binders and anionic surfactants as dispersing agents allow a more predictable pigment solids surface charge. Fujitani [47], for example, found that a zeta potential value of –19 mV exhibits maximum colloidal stability for pigment particles in water-based system regardless of the types of pigments involved. This zeta potential value can be achieved through surface application with a variety of binders and anionic surfactants of different chemical compositions and concentrations.

Polymer binders commonly used in water-based ink are usually a variety of homo- and co-polymers of esters of acrylic and methacrylic acid resins with styrene and vinyl acetate [5, 6, 48] while for paper and cardboard coating, common polymers include the co-polymers of carboxylic acid with styrene and butadiene mixture or carboxylic acid with acrylic mixture [49]. The charged associated with polymer binders can be attributed to the carboxylate functional group. For example, the ionisation of the carboxylate functional group in polyacrylic and polymethacrylic acids, as shown in Figure 2.4, at pH value above 4.6 (the pKa of carboxyl group) contributes to the increase in negative surface charge of the pigment solids [50, 51].
Anionic surfactants are incorporated into the ink formulation to stabilise the pigment particles through electrostatic repulsion force. This is achieved through the adsorption of these surfactants with the hydrophobic tail orienting towards the pigment surface and the charged head group away from the pigment surface, thereby increasing the negative surface charge at the pigment surface. Gonzalez-Garcia et al. [52], for example, found that the zeta potential of carbon black pigment increases from $-40 \pm 10 \text{ mV}$ to $-80 \pm 10 \text{ mV}$ as the concentration of sodium dodecyl sulphate (SDS) increases from $1.0 \times 10^{-5} \text{ mol/L}$ to $1.0 \times 10^{-3} \text{ mol/L}$. The adsorption of the hydrophobic tail of the anionic surfactants towards the pigment surface can be facilitated with the pre-treatment of the pigment surface, such as the incorporation of a hydrophobic group anchor [53], the pre-adsorption of a cationic surfactant [54] or the surface modification with a coating agent [55]. These pigment surface pre-treatment steps are conducted in particular for the more hydrophilic inorganic pigments.

### 2.2.2.4 Pigment Solids Size

Binders, anionic and non-ionic surfactants stabilise the colloidal suspension in aqueous dispersion by increasing the electrostatic, steric or electrosteric repulsion and/or decreasing the hydrophobicity of the pigment solids [5, 48, 56]. Factors that affect the colloidal stability include (i) the amount of polymer (in binders) that are adsorbed onto the solids thereby creating steric hindrance towards coagulation, (ii) the specific interactions between the solvent and the polymer functional groups [5], (iii) the type and concentration of ions present [6, 57], and (iv) the pH levels [6, 57].

Studies conducted on different flexographic printing inks revealed that 90% of these solids are below 5 $\mu$m with the average size being close to 0.2 $\mu$m [5, 34].
2.2.3 Flocculation of Ink Solids

2.2.3.1 Introduction

The typical solids size range in flotation is 10 – 100 µm [58]. As the majority of the pigment solids are below 5 µm, they are too small to be removed through flotation (see Section 2.3.2.2). The stability created by the presence of the electrostatic, steric or electrosteric repulsion of the pigment solids by the dispersing agents needs to be overcome to allow the formation of large solids before flotation can be conducted.

In order to encourage flocculation, the total interaction energy, $E_{\text{Total}}$, between two solids must be positive. The total interaction energy is the attractive interaction of van der Waals force, $E_{\text{vdw}}$, minus the sum of the repulsive interactions due to the electrical double layer (EDL) force, $E_{\text{edl}}$, and the steric hindrance force, $E_{\text{sh}}$, as shown in equation [2.1].

\[ E_{\text{Total}} = E_{\text{vdw}} - (E_{\text{edl}} + E_{\text{sh}}) \]  
[2.1]

The colloidal nature of printing ink solids can be destabilised through several means, including:

- modifying the pH of the system, since H⁺ and OH⁻ are the potential determining ions of the dispersing agents (such as polymer binders) on the surface of the pigment solids [6]. Bringing the pH closer to the IEP of the solid (with adsorbed dispersing agents) decreases the surface charge and decreases the $E_{\text{edl}}$;
- increasing the ionic strength with monovalent or multivalent ions to compress the EDL leading to a decrease in the repulsive EDL force; and
- adding the appropriate coagulant to decrease the surface charge of the colloidal solids and hence, decreasing $E_{\text{edl}}$.

Of these, pH adjustment and coagulant addition are the most commonly used methods.

2.2.3.2 Flocculation by pH Adjustment

The carboxylate functional group in binders (see Figure 2.4) contributes to the surface charge and hence, to the colloidal nature of printing ink [6]. Other functional groups present can also contribute to the electrostatic charge of the solid. Common anionic surfactants such as sodium dodecyl sulphate (SDS) have been shown by Gonzalez-Garcia et al. [52], for example, to adsorb onto carbon black ink, resulting in an increase in the zeta potential of the ink surface. Also, the functional groups associated with the pigments (e.g. RSO₃⁻ in lithol rubine 4B and R₂NH⁺ in
rhodamine GG, see Figures 2.2(c) and (d)) can also influence the solids charge to a smaller extent (compared to the dispersing agents) as the pigment surface is shielded by the dispersing agents. A typical example of a pigment solid in the presence of these functional groups is illustrated in Figure 2.5.

Figure 2.5: A pigment solid in the presence of surface functional groups.

The decrease in pH level decreases the magnitude of EDL force as the anionic functional groups (e.g. \(\text{RCOO}^-\) and \(\text{ROSO}_3^-\)) become protonated as shown in equations [2.2] and [2.3].

\[
\text{RCOO}^- + \text{H}^+ \rightarrow \text{RCOOH} \quad (\text{pKa} \approx 5) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldot
the offset inks (for newspaper printing) is approximately pH 2.3. The flocculation of pigment solids at pH 2 (or approximately 3 pH points lower than the pKa of the carboxylate functional group) suggests that anionic surfactants such as SDS with pKa of approximately 2 [60] and/or strong acids corresponding to aromatic carboxyl groups with pKa of between 2 – 5 [5] may be responsible for the low flocculating pH value.

2.2.3.3 Flocculation by Metal Ion Addition

Flocculation of inks at close to neutral pH values can be achieved via the addition of multivalent metal ions such as Al(III) and Fe(III). These metal ions can assist flocculation by altering the surface charge characteristics of the inks. One of the mechanisms leading to pigment surface charge reduction is heterocoagulation, i.e. the hydrous metal oxide solids (e.g. Fe(OH)$_3$(s)) precipitates in the bulk solution, and heterocoagulate with the negatively charged pigment solids. This occurs at pH values below the IEP but above the precipitation pH of the hydrous metal oxide solids. The hydrous oxides of Al(III) and Fe(III) have very low solubility at neutral pH values, with an amorphous precipitate forming within 10 – 20 seconds [61].

Another flocculation mechanism is the adsorption or surface precipitation of the metal ions (e.g. Fe$^{2+}$) or its hydrous oxide complexes (Fe(OH)$^+$, Fe(OH)$_2$) onto the negatively charged pigment solid surface sites. This adsorption mechanism occurs through electrostatic attraction and is favourable at pH values below the precipitation pH of the metal hydrous oxide complexes (e.g. approximately pH 7 for hydrous oxides of Fe(II), [62]) and above the pKa of the functional groups (e.g. approximately 4.6 for carboxyl group, [51]).

The reduced negative surface charge can further induce flocculation through the ‘bridging’ mechanism where the tails or loops of the high molecular weight anionic polymer chain (in binders) interact with the solids, effectively functioning as flocculants. The ‘bridging’ flocculation mechanism is discussed in detail in Section 2.2.3.5. For this reason, it is common in wastewater treatment system to add a high molecular weight, low charge density polymers during chemical pre-treatment as coagulant aid to promote flocculation [25]. Also, the resultant large flocs can ‘capture’ fine suspended solids through ‘sweep flocculation’ during contact through Brownian motion, resulting in a growing precipitate.

2.2.3.4 Mechanism of Action of Commonly Used Metal Ion Flocculants

Inorganic metal ions such as Al(III) and Fe(III) salts are widely used as coagulants in water purification and wastewater treatment as they are very effective at removing a broad range of
impurities from water, including colloidal particles and dissolved organic substances, as well as increasing the dewaterability of sludge for ease of filtration [9, 16, 17, 63]. The effectiveness of these metal ions is reflected in the low quantity of metal ions required. Letterman et al. [64], for example, found that at pH 6, the amount of Al(III) needed to bring the particle electrophoretic mobility (EM) to zero was around $4 - 7 \mu$mol per $m^2$ of the particles’ surface in kaolin or silica suspension.

At least part of the ability for metals to act as coagulant can be attributed to the amorphous nature of their hydrous metal oxides solids. The hydrous oxides of Fe(III) remain predominantly in a solid ‘amorphous’ state of ferric hydrous oxide present in two precipitate states of FeO(OH) and hydrated oxide, Fe$_2$O$_3$.nH$_2$O [65], while the ‘amorphous’ state of Al(OH)$_3$ is thought to be formed along with AlO(OH). According to Parks [44], ‘amorphous’ hydrous oxides have higher IEP values and higher positive charges than the more ordered crystalline arrangement. Therefore, heterocoagulation with the negatively charge ink particles occurs more effectively and over a wider pH range.

Recent evidence also suggests that the polymeric intermediate complexes such as Al$_2$(OH)$_4^{4+}$, Al$_3$(OH)$_6^{3+}$, Al$_4$(OH)$_7^{4+}$, Al$_5$(OH)$_9^{3+}$, Al$_7$O$_4$(OH)$_{24}^{7+}$ and Al$_{15}$(OH)$_{32}^{10+}$ for Al(III) and Fe$_2$(OH)$_4^{4+}$ for Fe(III) [25, 32, 63, 66], formed during hydrolysis of the metal ions, are very effective coagulants, especially at low hydrous metal oxide concentrations [67]. There is evidence that these intermediate complexes interact with the carboxylate functional groups through electrostatic attraction and form chemical bonds. Cheng [68], for example, showed the adsorption of Fe(III) hydrous oxide complexes onto humic acid through chemical reaction to form the mixed Fe-humic acid complexes as shown in Figure 2.6. Humic acid contains bidentate carboxylic acid ligands, similar to one of the main functional groups on the pigment surfaces. It is thus possible that a similar chemical reaction can occur leading to a more effective hydrous metal oxide complex adsorption onto the pigment surfaces (compared to heterocoagulation).

![Figure 2.6: Mechanism by which Fe(III) hydrous oxide complex adsorbs onto humic acid](Reference: Cheng, 68)

The hydrous oxides of Al(III) and Fe(III) are not the only coagulants used. A less commonly used coagulant is the hydrous oxide of Fe(II). It is less common as it has been found for some
systems to not be as effective as a coagulant in reducing the surface charge of pollutants compared to the two trivalent metal hydrous oxides [69]. Fe(II) has been known to be used either on its own in the form of ferrous sulphate or copperas (FeSO₄·7H₂O) or in combination with chlorine in the form of chlorinated copperas – Fe₂(SO₄)₃ + FeCl₃ [25]. As it is highly soluble below pH 7 [62], destabilisation of the colloidal solids at low pH values can be attributed to the adsorption of Fe(II) hydrous oxide complexes onto the negative surface sites. These hydrous oxide complexes may be the monomeric Fe(II) or some intermediate complexes formed during the oxidation of Fe(II) to Fe(III), of which Green Rust is an example [70].

The structure and density of the mixed pigment-hydrous metal oxide solids, is dependent on the macroscopic properties of the pigment surfaces. Bache and Papavasilopoulos [71] found that the solids of hydrous Al(III) oxide-humic sludge mixture are much denser and 20 – 30% larger than the corresponding solids in hydrous Al(III) oxide system. Denser solids have the advantages that (i) they retain less water at the periphery of the solids surfaces during foam drainage (see Section 2.4.2), leading to a sludge with a higher solids content for disposal [72], and (ii) larger solids enhance the effectiveness in gathering colloidal particulates through the ‘sweep flocculation’ mechanism.

Pre-formed polymeric salts such as polyaluminium chloride (PACl) and polyferric sulphate (PFS) have been found to be more efficient in removing turbidity, algae, colour and natural organic matter (NOM) than inorganic metal ions [68, 73, 74, 75]. Viraraghavan and Wimmer [75], for example, conducted a case study on the removal of colloidal particles in a water treatment plant and found that the amount of PACl required (70 mg/L) for charge neutralisation is approximately 60% less than that required when alum (180 mg/L) is used. The effectiveness of polymeric salts has been attributed to:

- the controlled polymerisation process, allowing the formation of hydrolysis products that are more effective as coagulant [76];
- the slower rate of hydrolysis, allowing a longer period and greater opportunity for adsorption and/or chemical reaction to occur [77]; and/or
- the ‘bridging flocculation’ through cross-linkages between the polymers [68, 77].

The advantage of adding polymeric salts may not be as pronounced for printing ink wastewater since the ink is formulated with an abundance of polymers (e.g. in binders and thickeners, [7]) that can function as flocculants through ‘bridging flocculation’ mechanism (see Section 2.2.3.3).

Metes et al. [17], however, compared the effectiveness of pre-polymerised and monomeric salts in the flocculation of 2 types of simulated flexographic printing ink wastewater and found that
polymeric salts such as Levafloc R commercial flocculant, PACl and a mixture of polyamine-PACl, produced effluent of higher turbidity (> 1 nephelometric turbidity unit or NTU) than monomeric Al(III) and Fe(III) salt systems (0.4 NTU). In addition, the optimum pH values for the polymeric and monomeric salts systems are in the acidic (< 5) and neutral (7 – 9) range respectively. The reason for the better flocculation performance using monomeric salts in this system is not known.

2.2.3.5 Influence of Wastewater Composition on Flocculation Behaviour of Ink Solids

The coagulant concentration required for charge neutralisation and the extent of flocculation of pigment solids depends on (i) the electrolyte concentration, (ii) the surfactant concentrations in the solution and on the ink surface, (iii) the concentration of polymer binders, (iv) the solids content of the wastewater, and (v) the physical properties of the mixed pigment-hydrous metal oxide solids.

Electrolyte concentration

The electrolyte concentration in a typical ink formulation is kept as low as possible to minimise flocculation as well as to maximise anionic surfactant adsorption onto pigment surface [56]. Typical electrolytes present include the sodium salts of sulphate, phosphorus and chloride [78]. The tendency of hydrous metal oxides to form complex species with these anionic electrolytes can influence the solubility and surface charge of the resultant hydrous oxide complexes. For example, Perry and Shafran [79] observed that the presence of sulfate ions in aluminium ion solution resulted in the formation of monomeric Al(SO₄)⁺ and Al(SO₄)₂⁻ complexes. The reduced charge of the hydrolysis products also allows flocculation to occur over a wider pH range [63, 67].

Anionic surfactant concentration

In the absence of any metal ions addition, the anionic surfactant is adsorbed onto the pigment surface with the charged head group orienting away from the pigment surface as illustrated in the left section of Figure 2.7(a).
It is difficult to predict what effect metal ion addition might have on this system. At pH values where the metal exists as a cation (i.e. at pH below the precipitation pH), adsorption onto both the pigment solids surface may occur directly (on negatively charged surface sites) or via the anionic surfactants (see Figure 2.7(a)).

At pH values where heterocoagulation between the pigment solids and the hydrous metal oxides takes place (i.e. at pH above the precipitation pH), as the pigment surface is fully covered with dispersants, the major interaction may be between the anionic surfactant head group and the hydrous metal oxide solids (see Figure 2.7(b)).

It is important to note that the surfactants are not permanently adsorbed at the pigment surface but are subjected to a continuous adsorption-desorption process. The generation of positively charged hydrous metal oxide solids is therefore likely to deplete the solution anionic surfactant concentration through adsorption. This will, in turn, deplete the anionic surfactant coverage of the pigment solids surface, thereby exposing the hydrophobic pigment surface (for organic pigment) or the hydrophobic anchor group (for inorganic pigment), leading to a more hydrophobic surface. The extent of surfactant depletion will depend on the relative affinity of the anionic surfactant for the hydrous metal oxide surface, and on the quantity of hydrous metal oxide added as illustrated in Figure 2.8.
The shift in equilibrium position of the anionic surfactants, leading to a more hydrophobic surface for both the pigment and hydrous metal oxide solid (see Figure 2.8), can further encourage flocculation by providing additional energy through the diffusional and attractive force between the surfactant molecules to overcome the energy barrier encountered in the thinning of the liquid between the solids prior to coagulation [60]. Israelachvili and Pashley [80] measured the attractive force between two hydrophobic crossed cylinders of mica and found that the attractive force is approximately 10 times larger than the maximum possible van der Waals dispersion force. This attractive force is attributed to the hydrophobic interaction between the two solids and has been reported to function up to a distance of 300 nm [81].

The presence of the hydrophobic attractive force, however, was not observed in the investigation conducted by Schulze [82] who questioned the existence of the force on hydrophobic surfaces. The author argued that the increased interaction is due to the presence of gas nuclei on the hydrophobic surface sites. Ralston et al. [81] tried to reconcile the different findings by claiming that a possible cause of the hydrophobic attraction may be due to the presence of dissolved gas or microbubbles concentrating near the vicinity of the hydrophobic solids. Murphy et al. [86] found that these microbubbles near the vicinity of the hydrophobic surfaces increase the aggregation of surfactants into hemi-micelles or admicelles leading to further coagulation. The claim that the presence of microbubbles contributes to the increased attraction has been further supported by Meagher and Craig [84], who found that degassing a dilute NaCl solution reduces the hydrophobic attraction between the polypropylene solids.

**Presence of polymer binders**

In the absence of metal ions addition, the presence of polymers can lead to *electrosteric stabilisation* (i.e. a combination of electrostatic and steric stabilisation) as illustrated in Figure 2.9(a).
Electrostatic stabilisation (see Figure 2.9(a)) can be achieved with the ionisation of the polymer functional groups at pH values above the pKa of the functional groups. Steric stabilisation, on the other hand, is achieved by the coverage of the pigment particle surface by the polymer chains with a high extension of the polymer stretching into the aqueous phase, thereby inhibiting the approaching particles from reaching a distance where coagulation can occur through van der Waals attractive force. For hydrophobic pigments, adsorption of polymer is most likely through the hydrophobic attraction with the more hydrophobic polymer section such as styrene or butadiene while leaving the less hydrophobic polyacrylic or polymethacrylic acids projecting away from the particle surface into the aqueous dispersion.

The decrease in pH value below the pKa of the polymer functional groups can encourage flocculation due to the reduced electrostatic repulsion, resulting in less extension of the polymer into the aqueous phase as shown in Figure 2.9(b). This allows the particles to approach close enough for flocculation through van der Waals attractive force. The spontaneous flocculation of the carbon black printing ink at pH 2, for example, has been attributed to the protonation of the majority of ionisable functional groups on the pigment surface and the collapse of the polymer chain binders [5]. The closer approach of particles can also allow individual polymer molecules to adsorb onto two or more pigment particles, leading to ‘bridging flocculation’ of the pigment particles.

Figure 2.9: Illustration of the possible flocculation mechanism upon coagulant addition or pH adjustment (a) electrosteric stabilisation in the absence of coagulant or pH adjustment, (b) flocculation in the absence of coagulant at low pH, and (c) ‘bridging’ flocculation or (d) heteroflocculation in the presence of coagulant.
(Note: surfactants not shown here for simplicity. HMO = hydrous metal oxide.)
Upon the addition of metal ions and above the precipitation pH of the hydrous metal oxide, the extent of the adsorption of polymers onto the hydrous metal oxide surface is dependent on their relative charge. Adsorption through hydrophobic attraction is only likely if the hydrophilic hydrous metal oxide solid surface has a good coverage of anionic surfactant (see Figure 2.8(b)). Adsorption through electrostatic attraction can also occur at pH values above the pKa of polymer’s functional groups but below the IEP of the hydrous metal oxide solids. Flocculation is likely to occur through the ‘bridging’ flocculation (see Figure 2.9(c)) and/or heteroflocculation (see Figure 2.9(d)) mechanisms under these conditions. Metes et al. [17] conducted a microscopic examination on the flocculated sludge of a flexographic printing ink wastewater and found specific cross-linking between the ink solids. The authors attributed these cross-linkages to the presence of polymers that act as flocculant aids. The cross-linkages also strengthen the solids and prevent them from breaking-up under shear force. At pH values above the IEP of the hydrous metal oxide solids, the adsorption of polymers onto the hydrous metal oxide solid (through electrostatic attraction) decreases leading to less flocculation.

Alternatively, below the precipitation pH of the metal ions, the adsorption of metal ions (and their hydrous oxide complexes) onto the negatively charged polymers decreases both the net negative charge of the polymer and the affinity for the aqueous phase. This can potentially lead to a reduced spatial extension of the polymers into the aqueous phase resulting in less steric hindrance to coagulation (e.g. through the van der Waals force).

**Physical properties of the mixed pigment-hydrous metal oxide solids**

Further aggregation of solids has also been observed at the particle-bubble interface, during flotation after particle-bubble attachment [85, 86, 87]. This was attributed to the attractive lateral capillary forces that exist between the solids at the air-liquid interface. Drzymala [85] found that the hydrophobic aggregation (interaction) between solids at the particle-bubble interface occurs for the solids with contact angles above 20° and depends on the density of the solids, with no aggregation observed for solids with densities below 2 g/mL. Pigments such as titanium dioxide that have a density of approximately 4.0 g/mL [42] would therefore be expected to aggregate via this mechanism, while less dense organic pigments such as carbon black, which have a density of approximately 2 g/mL [42], would not. Whether or not this mechanism of aggregation takes place in the mixed pigment-hydrous metal oxide systems, however, is not clear.
**Solids content**

The extent of flocculation also depends on the amount of solids in the solution with increased flocculation with the increase in solids content. This can be seen from the simplified version of the Smoluchowski expression shown in equation [2.5].

\[
\ln \left( \frac{N}{N_0} \right) = -\frac{4}{\pi} \alpha \phi G t \quad \ldots \ldots \ldots \ldots \ldots [2.5]
\]

where \(N = \text{total concentration of particles in suspension at time } t\), \(N_0 = \text{initial particles concentration}\), \(\alpha = \text{collision efficiency factor}\), \(\phi = \text{volume fraction of particles}\), \(G = \text{velocity gradient} \) [Reference: Letterman et al., 64].

The extent of flocculation is indicated by the fraction \((N/N_0)\). The fraction \((N/N_0)\) decreases with the increase in flocculation, i.e. from equation [2.5], the extent of flocculation is a function of the collision efficiency factor \((\alpha)\), the volume fraction of particles \((\phi)\), the velocity gradient \((G)\) and the flocculation time \((t)\). The velocity gradient \((G)\) is proportional to the applied stress (from external sources such as stirring during the pre-treatment stage) on the sample, and can be kept constant during experiments by using a fixed stirring speed. According to the Derjaguin-Landau-Verweg-Overbeek (DLVO) theory [88, 89], as the electrophoretic mobility (EM) value of the solids approaches zero, the collision efficiency \((\alpha)\) approaches one. The extent of flocculation at time \(t\) depends on the solids concentration (i.e. the volume fraction of particles, \(\phi\)) in the solution.

**2.2.4 Surfactant adsorption onto the mixed pigment-hydrous metal oxide solids**

**2.2.4.1 Introduction**

When the surface of the solid to be removed is hydrophilic in nature, attachment to a bubble on collision is unlikely. Even in situations where the bubble and the solids have opposite surface charges, attachment is hindered by the difficulty of displacing the water that separates bubble and solid. The displacement of this water is facilitated by lowering the affinity of the solid surface for water (i.e. by rendering the surface hydrophobic). A surfactant is added that adsorbs with its polar head group onto the pigment surface and with its hydrocarbon tails orienting away from the surface towards the solution. This is the approach taken for the removal of hydrophilic solution such as (most) minerals [51, 90] and hydrous metal oxide precipitates [27, 91].

As discussed in Section 2.2.3.5, the situation is considerably more complex in the case of industrial printing wastewater. The pigment particles are inherently hydrophobic and the added
Hydrous metal oxides are inherently hydrophilic, but both surfaces have an unknown and variable quantity of surfactant adsorbed that, in general, renders the pigment particles less hydrophobic and the hydrous metal oxide particles less hydrophilic (see Figure 2.8). Although the hydrophobicity of the mixed pigment-hydrous metal oxide solids in printing wastewater may be sufficient to achieve particle-bubble attachment, surfactant addition may be beneficial to ensure sufficient hydrophobicity for the establishment of a solids-stabilised foam (see Section 2.4.2) and operation of the flotation process in high liquid carryover (HLC) mode (see Section 2.4.3).

2.2.4.2 Mechanisms of surfactant adsorption onto wastewater ink solids

In simple thermodynamic terms, adsorption of surfactant onto the solid surface is spontaneous if the total free energy of adsorption is negative. The total free energy of adsorption consists of all the contributions of the various components of free energy of adsorption. The main components of the free energy of adsorption are shown in equation [2.6] [92].

\[
\Delta G_{\text{adsorption}}^o = \Delta G_{\text{electrostatic}}^o + \Delta G_{c-c}^o + \Delta G_{c-s}^o + \Delta G_{\text{chemical}}^o + \ldots \quad \ldots [2.6]
\]

where \( \Delta G_{\text{adsorption}}^o \) = total free energy of adsorption, \( \Delta G_{\text{electrostatic}}^o \) = electrostatic free energy of adsorption, \( \Delta G_{c-c}^o \) = lateral chain-chain interaction between the adsorbed surfactant molecules, \( \Delta G_{c-s}^o \) = hydrophobic interaction between the hydrocarbon tail of surfactant and the hydrophobic solids, and \( \Delta G_{\text{chemical}}^o \) = chemical interaction between the solids and surfactant leading to covalent bonding or acid-base interaction [Reference: Somasundaran and Krishnakumar, 92].

A large and negative \( \Delta G_{\text{adsorption}}^o \) can often be achieved by selecting a surfactant that has a charge that is opposite to that of the pigment surface, giving a large and negative \( \Delta G_{\text{electrostatic}}^o \). This is done to maximise the electrostatic attraction and to ensure that the surfactant adsorbed with the head group orienting towards the pigment surface, thereby imparting hydrophobicity. When this is not possible, provided that \( \Delta G_{\text{electrostatic}}^o \) is not too large and positive, a large and negative \( \Delta G_{\text{adsorption}}^o \) can still be achieved by selecting a surfactant that can chemically bond with the surface functional groups and/or that has a long hydrocarbon chain, thereby giving a large and negative \( \Delta G_{\text{chemical}}^o \) and/or \( \Delta G_{c-c}^o \) respectively.

An important factor that governs the orientation is the free energy associated with the interaction of the hydrocarbon chain with the solid surface (\( \Delta G_{c-s}^o \)). When the surface is hydrophobic, this term is large and negative and can induce adsorption in the tail-down orientation, thereby giving a less hydrophobic surface.
The pigment surface in the presence of anionic surfactants and ionised polymers is negative in charge and has an IEP of approximately 2 [5, 59]. The introduction of metal ions at pH values below the IEP and above the precipitation pH of the metal hydrous oxides can reduce the negative charge or even cause a charge reversal depending upon the added concentrations. It is expected that for anionic surfactant, adsorption (i.e. with the head-down orientation) is favoured when there is a positive net surface charge of the mixed pigment-hydrous metal oxide solids.

As printing ink wastewater is relatively high in suspended solids content (4 – 10 g/L, [10]), the concentration of metal ions required to dominate the surface characteristics of the mixed solids, is expected to be high. This is not only undesirable in terms of cost effectiveness, but also in terms of the quantity of waste sludge for disposal (after the wastewater treatment process) as well as a greater corresponding foam volume leading to foam handling problems.

A more economical approach is to only add enough hydrous metal oxide to flocculate the solids – not enough to reverse the negative charge of the solids – and to use a cationic surfactant instead. This, too has its disadvantages (e.g. higher cost and toxicity associated with cationic surfactants, [93, 94]) but it minimises sludge volumes and foam handling problems such as channelling and foam overturning due to excessive foam solids content (see Section 2.4.3). Under these conditions, the cationic surfactant will preferentially adsorb onto the negative pigment particles in the mixed pigment-hydrous metal oxide solids rather than the positive hydrous metal oxide particles.

The developments of advanced techniques such as neutron reflection [95, 96], ellipsometry [97, 98], fluorescence spectroscopy [99] and atomic force microscopy [98, 100, 101] have enhanced the knowledge of cationic surfactant adsorption onto surfaces with well-known characteristics (e.g. mica and silica). The surfaces of mica and silica are, however, very different from the surface of printing ink solids that have been flocculated using a metal ion coagulant.

The orientation of the cationic surfactant adsorption, and its effect on the hydrophobicity of these particles, however, is not clear. Figure 2.10 illustrates some of the many possible adsorption outcomes.
Figure 2.10: The possible outcomes after cationic surfactant adsorption on the mixed pigment-hydrous metal oxide (HMO) solids at pH values below the IEP of the HMO solids. The different scenarios, in the presence of anionic surfactants, are (a) and (b) both the pigment and the hydrous metal oxide solid surfaces are hydrophobic, (c) and (d) the pigment surface is hydrophilic while the hydrous metal oxide solid surface is hydrophobic, and (e) both the pigment and the hydrous metal oxide solid surfaces are hydrophilic.

A possible outcome, as illustrated in Figure 2.10(a), is the adsorption of cationic surfactant with head-down orientation through electrostatic attraction force onto the anionic surfactant, thereby imparting hydrophobicity onto the pigment surface. This occurs if the electrostatic attraction force between the anionic and cationic surfactants is larger than the attraction forces due to the hydrophobic interaction between the hydrocarbon tail of the cationic surfactant and the exposed hydrophobic pigment surfaces or the lateral chain-chain interaction between the surfactants. Both the latter interaction forces result in a more hydrophilic pigment surfaces (see Figures 2.10(c) and (e)). An example of the lateral chain-chain interaction force between the hydrophobic surfactant tails (with similar or different surfactant types) playing an important role on surfactant adsorption is illustrated in Figure 2.11.
As depicted in Figure 2.11, direct interaction between the added surfactant’s hydrocarbon tail and the hydrophobic pigment surface would be expected to result in a less hydrophobic pigment surface. Conversely, direct interaction between the surfactant’s head group and the hydrophilic hydrous metal oxide surface would be expected to result in a more hydrophobic hydrous metal oxide surface. It is also noteworthy that the co-adsorption mechanism (i.e. head-down adsorption onto hydrous metal oxide and tail-down adsorption onto pigment surface) depicted in Figure 2.11 is a simplification of the mechanism likely to occur in reality, i.e. a mixture of both adsorption orientations on both the hydrous metal oxide and the pigment surfaces, depending on the surface charge and hydrophobicity of the solids surface.

For pigments with a higher negative surface charge (e.g. at higher pH), adsorption of anionic surfactants from the solution onto the solid surface (with head-down orientation) can be enhanced through the lateral chain-chain interaction with the adsorbed cationic surfactant or vice-versa (see Figure 2.10(b)), hence imparting hydrophobicity onto the pigment surface. Alternatively, the adsorption of anionic surfactant onto the pigment surface can occur through surfactant ‘bilayer’ formation (see Figure 2.10(d)), i.e. through the interaction between the hydrocarbon tails of surfactants, resulting in a more hydrophilic pigment surface. For example, Ninness et al. [54] found that the sodium dodecyl sulphate (SDS) adsorbed immediately and rapidly on the titanium dioxide pigment surface at pH 10.3 in the presence of CTAB and formed an ordered ‘bilayer’ (or admicelle) surfactant structure at the solid surface. The formation of this ‘bilayer’ decreases the hydrophobicity of the pigment surface.
At pH values below the IEP of the hydrophilic hydrous metal oxide solids, the adsorption of anionic surfactant with head-down orientation (see Figure 2.8) imparts hydrophobicity (see Figures 2.10(a) – (d)). Cationic surfactant adsorption is less likely due to unfavourable $\Delta G_{\text{electrostatic}}^\circ$ and $\Delta G_{\text{c-s}}^\circ$ free energies of adsorption.

### 2.2.4.3 Influence of Composition and Characteristics of Wastewater on Surfactant Adsorption Behaviour

The presence of electrolytes decreases the electrostatic repulsion between the adsorbed surfactant head groups, leading to an increase (in negativity) in the free energy associated with the lateral chain-chain interaction between the adsorbed surfactant molecules, $\Delta G_{\text{c-c}}^\circ$ (see equation [2.6]), where the adsorbed surfactant monomers act as nucleation sites for further surfactant adsorption [98].

For hydrophilic surfaces such as the surfaces of the titanium dioxide pigment or the hydrous metal oxide solids, adsorption of cationic surfactant onto these surfaces tends to occur through the head group orienting towards the pigment surface through attractive electrostatic forces at pH values above the IEP of the solids. The free energy associated with the hydrophobic interaction between the hydrocarbon tail of surfactant and the mixed pigment-hydrous metal oxide solids surface, $\Delta G_{\text{c-s}}^\circ$, is expected to be minimal. Below the IEP of the solids, adsorption with head group orienting towards the pigment surface can still occur if the free energy associated with the lateral chain-chain interaction between the adsorbed surfactant molecules, $\Delta G_{\text{c-c}}^\circ$, is large and negative enough and/or if the free energy associated with the chemical interaction of the surfactant functional group with surface functional groups, $\Delta G_{\text{chemical}}^\circ$, is large and negative enough to overcome the free energy due to electrostatic repulsion, $\Delta G_{\text{electrostatic}}^\circ$.

The presence of anionic and non-ionic surfactant within the ink formulation may act to enhance or inhibit the adsorption of cationic surfactant at the solid-liquid and the air-liquid interfaces. The synergistic effects of co-adsorption of ionic and non-ionic surfactants used to increase the hydrophobicity of the solids substrate, especially in the mineral industry, are well known [102, 103]. It must, however, be stressed that the primary purpose of non-ionic surfactant in the ink formulation is that of a dispersing agent, the dispersion achieved through steric repulsion. Thus, any increase in non-ionic surfactant adsorption onto ink surfaces (above a certain surface coverage area) may prove to be detrimental to flocculation. Also, the presence of non-ionic surfactant on the solid surface may shield its negative charge, leading to a decrease in the adsorption effectiveness of cationic surfactant.
The introduction of cationic surfactant has been found to further enhance the adsorption of non-ionic surfactants onto the solid surface and vice-versa [92, 104]. Somasundaran and Krishnakumar [92] found that the presence of cationic surfactant of tetradecyl trimethyl ammonium chloride (TTAC) increases non-ionic pentadecylethoxylated nonyl phenol (NP-15) adsorption on alumina due to the increase in hydrocarbon chain-chain interaction between surfactants. Dixit et al. [104] found that the non-ionic surfactants enhance CTAB adsorption at low CTAB concentration but inhibits adsorption at concentrations above critical micelle concentration (cmc). The authors attributed the decrease in cationic surfactant adsorption to the formation of mixed micellisation of the surfactants. The decrease in cationic surfactant adsorption could also be due to the competition between the surfactants for adsorption sites [92].

Anionic surfactants present within the ink formulation may react with the added cationic surfactant in a number of ways (at the pigment surface) as discussed in Section 2.2.4.2. In addition, in the bulk solution, the reaction between cationic and anionic surfactants through electrostatic attraction can lead to the formation of insoluble complexes with both surfactants possibly losing their surfactant properties (such as the ability to foam or wet) [94, 103].

2.2.4.4 Choice of Cationic Surfactant

Even if the cationic surfactant adsorbs through a ‘head-down’ orientation, the effectiveness of a cationic surfactant in imparting hydrophobicity depends on several factors, the most important being its associated hydrocarbon chain length [51, 98, 105]. A surfactant with a longer hydrocarbon chain tail is more effective in imparting hydrophobicity onto a surface due to:

- a higher number of clathrate bound water molecules required to solubilise its longer tail. The presence of these clathrate bound water molecules lowers the system’s entropy and increases both the hydrophobic interactions between the surfactant molecules and the surface sites, as well as the lateral chain-chain interactions between the adsorbed surfactant molecules. This increase in hydrophobic interaction results in the increase in the adsorption concentration on the surface sites [98]; and

- the lower surfactant concentration required before the surfactants at the solid-liquid interface associate into hemi-micelle formation as a result of the presence of microbubbles near the vicinity of the hydrophobic surfaces. Hemi-micelle formation is found to encourage flocculation of solids [83]. Murphy et al. [83] found that the average size of silica solids increases when longer alkylamine surfactant chain length (above C_{12} alkyl chain) is added.
The length of the hydrocarbon chain of the surfactant is, however, limited due to the increase in insolubility with hydrocarbon chain length. A hydrocarbon chain that is too long loses its ability to function as a surfactant.

The polar head group associated with the surfactant should be sufficiently polar to be soluble in water. Adsorption is also facilitated if the functional group can chemically react with surface groups during adsorption onto surface sites. Adsorption through chemical reaction is much stronger than physical adsorption, as it decreases the possibility of surfactant desorption under circumstances such as changes in process conditions. For example, an acidic shift in pH over time results in an association of hydrogen ions onto the surface groups, lowering the electrostatic attraction with the cationic surfactant. This can potentially lead to polyvalent cations such as sodium or calcium displacing the cationic surfactants from the solids surface through ion-exchange mechanism.

2.3 Flotation

2.3.1 Introduction

The fundamental process in flotation is the collision and attachment of the solids to the gas bubbles, and the formation of a stable particle-bubble aggregate. The prerequisite for this attachment is the rupture of the thin liquid film formed between the solid and the bubble, resulting in a three-phase contact. The foam formed at the liquid-air interface – containing stable particle-bubble aggregate – is stabilised by the presence of surfactants and is removed from the flotation cell to a foam collection vessel for further drainage.

2.3.2 Particle-bubble Attachment

2.3.2.1 Mechanism of Particle-bubble Attachment

The most widely accepted theory is the hydrodynamic three-zone model of particle-bubble interaction around the surface of the bubble [106]. In their analysis, Derjaguin and Dukhin described the bubble under dynamic conditions (i.e. moving through a liquid) with three distinct zones with different forces dominating the particle-bubble interaction as shown in Figure 2.12.
In Zone 1 (> 10 µm from the bubble interface), hydrodynamic forces are dominant. The forces that are found to act on the solids are the drag force, the viscous force, the solid inertia and the gravitational force [107]. Small solids below the solid size limit for flotation (usually < 10 µm) lack the inertia or momentum to deviate from the streamline with no further penetration into Zone 2 [58, 106].

In Zone 2 (1 to 10 µm from the bubble interface), the diffusional and electrophoretic forces are dominant. As the bubble rises through the surrounding liquid to the surface, a tangential stream is created as a result of a net flow of adsorbed ions or surfactants from the upper hemi-surface of the bubble towards the rear of the bubble. This creates a concentration gradient of ions and surfactants with the rear of the bubble being much more concentrated. Consequently, a strong electrical field (or electrophoretic force) exists between the upper bubble surface and the approaching particle. If this electrophoretic attractive force is sufficient to overcome the viscous resistance of the liquid layer, the particle is pulled into Zone 3. Concurrently, the surfactant molecules that are not chemically bonded to the surfactant-rich solid surface can migrate or diffuse to the surfactant-poor upper bubble surface. The bubble surface acquires the surfactant’s charge and can be attracted to the particles of opposite surface charge. The diffusional and electrophoretic forces are, however, negligible for solids with diameter larger than 3 µm [108].

In Zone 3 (< 150 nm from the bubble interface), surface forces such as the EDL interaction, the van der Waals and the hydrophobic attraction forces become dominant. The subsequent rate of thinning of the liquid film (that separates the particle from the bubble) leading to the rupture of the film depends on the net force near the interface. Attachment occurs if the film between the bubble and particle is unstable, leading to its rupture (within the contact time of the approaching particle).
The hydrodynamic three-zone model developed by Derjaguin and Dukhin deals with the simple situation of discrete spherical particles. The flotation of printing ink wastewater, however, deviates from this simple model in that the ‘particles’ are replaced by the mixed pigment-hydrous metal oxide flocs. Although the model explains why it is necessary to flocculate the pigment particles into an aggregate of larger overall dimensions, it does not explain the behaviour of these aggregates when they are subjected to different forces within the three zones.

The particles of newly formed metal hydrous oxide readily aggregate into flocs as large as 2 to 3 mm. These flocs, however, break up to much smaller aggregates under high turbulence conditions and the size of the resultant aggregates is dependent on the forces which hold the aggregates together, the original particle size and the extent of turbulence to which they are subjected. For example, at a high stirrer speed of between 1000 and 5000 rpm, the sizes of the ferric hydrous oxide flocs are between 2 and 90 µm [109, 110]. The size of the flocs under flotation conditions is difficult to measure but is likely to vary and is a function of the turbulence encountered – depending on its position within the flotation cell – ranging from very high turbulence and high degree of floc break up (e.g. near the stirrer or near the air inlets of a flotation cell apparatus) to very low turbulence and larger resultant flocs (e.g. near the eddies or in the upper regions of the flotation froth or foam).

It should be noted that the mixed pigment-hydrous metal oxide flocs, under similar conditions, are likely to be larger than the corresponding metal hydrous oxide flocs due to the electrostatic attraction force involved leading to much denser (and hence, larger) flocs. Therefore, upon particle-bubble attachment, the large attached flocs are likely to penetrate across the three different zones of particle-bubble interaction (see Figure 2.12). As such, different forces (as outlined in the hydrodynamic three-zone model) act on different sections of a floc, depending on the distances from the bubble interface. Although the flocs are stronger and denser, it is possible that the forces acting at different directions can shear off part of a floc. The smaller attached floc can be ineffective towards foam stabilisation and this is to be discussed in detail in Section 2.4.2. Conversely, the attractive lateral capillary forces [85, 86, 87] between the attached flocs (see Section 2.2.3.5) can result in further flocculation on the bubble surface leading to solids-stabilised foam formation.

The presence of adsorbed surfactants (with head-down orientation) and microbubbles on the pigment surface increases the hydrophobic attraction force between the pigment solid and the bubble, leading to the increase in the rate of destabilisation of the thin liquid film that separates the solid from the bubble. For solids with patches of hydrophobic sites, the rupture of the thin liquid film can occur at these localised hydrophobic sites.
The presence of anionic electrolytes such as sulphate and chloride in the printing ink wastewater [46] compresses the EDL, leading to an increased in particle-bubble attachment efficiency. Dai et al. [111] found that increasing the KCl concentration from 0 to 0.01 M increases the attachment efficiency from 0.4 to 0.9 for 40-µm diameter methylated quartz particles with a 74° contact angle hydrophobicity.

The relative surface charges on both the mixed pigment-hydrous metal oxide solids and the bubble can influence the particle-bubble attachment efficiency with electrostatic attraction/repulsion force. As previously discussed in Section 2.2.4.2, the hydrous metal oxide is added in sufficient quantity to flocculate the solids but not to reverse the charge of the negative flocs, in order to maximise $\Delta G_{\text{electrostatic}}^\circ$ for head-down cationic surfactant adsorption. The surface charge of the bubble is, however, difficult to be determined. The charge on the bubble is a function of the pH value and on the effectiveness of the surfactants in functioning as frothers. The ability of the surfactants present in the ink (e.g. anionic and non-ionic surfactants) to function as frothers is not known. These inks are formulated such that foam production is minimised, as foam production during printing is detrimental to the printing quality. It is, however, worth noting that the conditions of the mixed pigment-hydrous metal oxide solids in printing wastewater can be very different from that found in stabilised colloidal ink dispersion. The added cationic surfactant, in general, is not as effective a frother as the anionic or non-ionic surfactants [51].

Bubble charge can also be influenced by the diffusion of the surfactants from the mixed pigment-hydrous metal oxide solids surface to the bubble surface (especially to the surfactant-poor upper bubble surface) when the solid and bubble are within 10 µm (i.e. Zone 2). The loss of the surfactants from the solid surface can change its hydrophobicity and hence, subsequently change its particle-bubble attachment efficiency.

### 2.3.2.2 Particle Size Limit

An important criterion in flotation is the particle size. The typical optimum particle size range in flotation is 10 – 100 µm [58], and depends on the many factors that affect particle-bubble attachment, detachment and stability such as bubble size, solid hydrophobicity, and electrolyte concentration. Particle sizes above the upper limit (usually > 100 µm), with high kinetic energy, may cause considerable deformation on the bubble surface on impact, and then rebound from the deformed surface due to the elastic energy of the surface [111]. Particles with sizes below the lower flotation limit (usually < 10 µm) lack the inertia or momentum to deviate from
the streamline that flows around the bubble and hence, direct contact with the bubble is not possible [106].

The optimum size range for the mixed pigment-hydrous metal oxide floc can differ from that of discrete particles. For a similar equivalent diameter, the conformation of the floc is generally more open with a lower density than a mineral particle. Therefore, the floc may lack inertia to deviate from the streamline. Consequently, a higher minimum size flotation limit (i.e. > 10 µm) may be necessary. For the upper size flotation limit, a larger sized hydrophobic floc is expected to be able to float more effectively (than a similar sized hydrophobic particle) due to their ability to spread out over the surface of the bubble and increasing the area of three-phase contact. Hence a hydrophobic floc is likely to be held more tenaciously onto the bubble than a discrete hydrophobic particle.

The collection efficiency, $E_{col}$, which is the efficiency in the formation of a particle-bubble aggregate and is the product of the efficiencies of the collision, the attachment as well as the stability of this particle-bubble aggregate is shown in equation [2.7].

$$E_{col} = E_c E_a E_s$$  

[2.7]

where $E_{col}$ = efficiency in particle-bubble aggregate formation, $E_c$ = collision efficiency, $E_a$ = attachment efficiency and $E_s$ = stability efficiency of the bubble/particle aggregate [Reference: Dai et al., 111].

These efficiencies represent the particle-bubble aggregate formation at different stages:

- collision efficiency – the efficiency in the hydrodynamic approach and collision of the solid and the bubble;
- attachment efficiency – the efficiency in the attachment of the particle to the bubble, i.e. the displacement of water molecules which separates the particle and bubble; and
- stability efficiency – the efficiency in the stability of the particle-bubble aggregate after attachment. The stability of the particle-bubble aggregate is a function of the external forces that may cause detachment, such as turbulence, gravitational, buoyant, hydrostatic, capillary and other detaching forces in the external flow field.

For coarse particles or aggregates of particles, the probability of collision, $E_c$, and attachment, $E_a$, approaches 1 [85]. This is attributed to the higher collision energy that is able to displace the water molecules and rupture the thin film, leading to attachment. The stability of the particle-bubble aggregate, $E_s$, however, is likely to be significantly reduced due to the increased inertia, causing it to lag behind the accelerating bubble with a consequent straining on the bubble skin [85]. Woodburn et al. [112], for example, found that the probability of detachment
increases with the particle size ($\alpha r^{1.5}$). Thus for coarse particles, the collection efficiency is governed by the stability efficiency, $E_s$, as shown in equation [2.8].

$$E_{col} \approx E_s \quad \ldots \ldots \ldots \ldots [2.8]$$

For fine particles, both the attachment efficiency, $E_a$, and the stability efficiency, $E_s$, approaches 1 for systems with high solids hydrophobicity and high electrolyte concentrations [113, 114]. For example, Dai et al. showed that $E_aE_s \approx 1$ for the flotation of hydrophobised quartz particles ($73^\circ$ contact angle) with diameter 10 – 60 µm in 0.01 M KCl solution. Thus, for fine particles, the collection efficiency is governed by the collision efficiency as shown in equation [2.9].

$$E_{col} \approx E_c \quad \ldots \ldots \ldots \ldots [2.9]$$

In general, the collision efficiency and attachment efficiency are generally found to increase with particle size as demonstrated by, for example, King [105] in equation [2.10].

$$P_{ca}(r) = \frac{12r}{R} \exp(-6V\lambda / 4R) \quad \ldots \ldots \ldots \ldots [2.10]$$

where $P_{ca} = \text{probability of particle-bubble collision and attachment}$, $\lambda = \text{induction period for film rupture}$, $R = \text{bubble radius}$, $V = \text{velocity of approach}$ and $r = \text{particle radius}$ [Reference: King, 105].

From equation [2.10], for a fixed bubble radius, the probability of particle-bubble collision and attachment, $P_{ca}$, is found to be proportional to the particle size. Many studies and models had been developed on the collision efficiency of small and medium sized particles (< 50 µm) and a review was conducted by Dai et al. [108] on many of these models.

Although the collection efficiency, $E_{col}$, and the probability of collision and attachment, $P_{ca}$, shown in equations [2.8] to [2.10] are based on the flotation of discrete particles and not on the flotation of flocs, it is expected that the trends found for discrete particles are applicable for flocs with minor modifications, including:

- the collision efficiency, $E_c$, apart from being dependent on the size as discussed for discrete particles, is also dependent on the density and conformation of the flocs. The increase in density increases the inertia and momentum of the floc and therefore, increases the collision efficiency. Loosely held open flocs are free to move relative to each other and form the conformation which best follows the fluid streamlines, resulting in a decreased collision efficiency;
the attachment efficiency, \( E_a \), depends on the hydrophobicity of the flocs. The increase in floc hydrophobicity increases the attachment efficiency by decreasing the time for the liquid film between the floc and the bubble to thin and rupture; and

- the stability efficiency, \( E_s \), apart from being dependent on the size as discussed for discrete particles, is also dependent on the hydrophobicity and conformation of the flocs. The increase in hydrophobicity and loose floc conformation can increase the stability efficiency by maximising the three-phase contact area by spreading over the surface of the bubble.

2.3.2.3 Bubble Size Limit

The relationship between collection efficiency and the bubble and particle sizes for a discrete particle is shown in equation [2.11].

\[
E_{\text{col}} \propto \frac{d_p^m}{d_b^n}
\]

………………[2.11]

where \( E_{\text{col}} = \) collection efficiency, \( d_p = \) particle diameter, \( d_b = \) bubble diameter, exponent \( m = 1 - 2 \), exponent \( n = 1.5 - 2 \) [Reference: Collins and Jameson, 115].

For a given particle size, the efficiency of particle-bubble attachment is found to increase with the decrease in bubble size as shown in both equations [2.10] and [2.11]. Dai et al. [111] found that the collision efficiency decreased by more than half with bubble size increasing from 0.77 to 1.52 mm. The decrease in collision efficiency for larger bubbles may be caused by the decreased liquid drainage rate and the longer expansion time required for the formation of the three phase contact line. In addition, for a given volume of air, the probability of interaction with solids in the solution decrease with larger bubbles due to the decrease in both the total surface area of air-liquid interface and the number of bubbles produced.

Small bubbles – such as those being used in dissolved air flotation (DAF) (< 100 \( \mu \)m) – however, have the disadvantage of having corresponding small terminal velocities, especially if solids are attached. The lower limit in bubble size is thus dependent on the corresponding size and density of the solids. Larger solids require larger bubbles as the particle-bubble aggregate has to be buoyant enough to be removed from the flotation cell as foam.

The size of the flocs under flotation conditions is likely to vary and is a function of the turbulence conditions encountered in the flotation cell (see Section 2.3.2.1). Applying bubbles of varying sizes [60], or increasing the amount of bubbles by increasing the air flow rate (effectively increasing both the kinetic or collision force and the total bubble surface area) are
two strategies that can further increase the flotation outcome. Increasing the amount of bubbles may also be necessary for printing ink wastewater that has a high suspended solids content to ensure that the bubble surface area is adequate for solids attachment [10]. Coalescence of the bubbles can be minimised with the presence of adequate surfactant concentrations at the bubble surface.

2.3.3 Foam Generation

2.3.3.1 Introduction

Printing ink wastewater contains anionic and non-ionic surfactants which function as dispersing agents in the original printing ink. These can, together with the cationic surfactant added to render the flocs more hydrophobic, adsorb at the air-liquid interface and give rise to a stable foam when air is introduced into the flotation cell. Mixed surfactant foams such as these are often more stable than individual surfactant foams due to better packing of surfactants at the air-liquid interface, resulting in lower surface tension [116], an indication of the increase in the ability to produce and maintain a persistent or stable froth.

The role of the foam in flotation is to hold onto the removed solids, while releasing as much as possible of the liquid, and to move these solids to the foam management and handling stage (see Figure 2.1). The presence of hydrophobic solids in the foam, however, can have a profound effect on the foam stability. The stability of the foam during flotation is a net result of the surfactant adsorption behaviour at the air-liquid interface (i.e. in the absence of solid particles), and the destabilising and/or stabilising effect of the solids in the foam.

2.3.3.2 Foam Characteristics in the Absence of Solids

Solutions that contain surface-active agents form a foam when bubbles are introduced through the solution. This foam is thermodynamically unstable but can be ‘metastable’ depending on the mechanical-dynamical properties of the surface adsorbed layers (surface tension gradients). Factors that contribute towards stability at this stage are the surface elasticity, viscosity (bulk and surface), gravity drainage and capillary suction [116].

Upon extensive drainage, the likelihood of survival of the foam lamellae depends on its ability to resist excessive localised thinning in the lamellae. The foam lamellae's ability to resist excess localised thinning is a function of the elasticity and viscosity at the air-liquid interface, the viscosity of the bulk liquid within the lamellae and the concentration of the surfactants at the
interface. High elasticity and/or low film viscosity ensure that the localised thinning of the film is repaired by the Gibbs-Marangoni effect. The Gibbs-Marangoni effect occurs when the film is prevented from rupture by the surface elasticity pulling the surfactants and the adjacent liquid layer into the thinned section [116]. High liquid viscosity ensures slow drainage and allows a longer period for film healing through the Gibbs-Marangoni effect [117]. The elasticity of the film is a function of the concentration of the surfactant present. However, the presence of a mixture of different types of surfactants at the film interface has been found to minimise the dependence of the surface elasticity on the surfactant concentration [118].

The lifetime of the film has been found to increase exponentially with surfactant concentration [116, 119]. Exerowa et al. [119] found that a stable film of 90 nm thickness can only be obtained in the presence of CTAB concentration above $10^{-4}$ M (or $>36$ ppm). The stable film is the result of increased electrostatic repulsion between the opposing head group during film thinning. This repulsion prevents excessive film thinning, because both film surfaces have a large positive surface potential.

A mixture of surfactants present in the foam film may increase the film’s stability above that of their individual surfactant system. The enhanced stability may be explained through:

- the reduction of a surfactant’s concentration in achieving its critical micelle concentration in the presence of another surfactant, leading to a reduced concentration required for the stable film thinning through stratification (or step-wise film thinning);

- the lowering of film surface tension with a combination of surfactants [120]; and

- the change in mechanical-dynamical properties of the film [116].

The presence of a minute amount of antifoam can greatly destabilise the foam [121]. Antifoams are non-micelle forming surfactants (such as silicone compounds) that are added to the ink formulation to minimise the incorporation of air bubbles during pumping and recirculation of the inks prior to printing [7]. The basic principle of antifoam destabilisation mechanisms is similar – foam rupture is achieved through extensive film thinning in localised area [116, 121, 122]. Higher surfactant concentrations may be necessary to offset the destabilisation effect of the antifoam. These surfactant excesses are required to ensure the effectiveness of the Gibbs-Marangoni mechanism in repairing the localised thinning of film due to the activity of the antifoams.
2.3.3.3 Foam Characteristics in the Presence of Solids

The influence of solids on the foam depends on their shape, size, hydrophobicity and concentration in the foam.

*Hydrophilic* solids of any size or shape do not attach to bubbles, but they can nevertheless be entrained in the foam during foam formation. They do not interact with the foam lamellae and are simply squeezed out into the plateau borders and eventually out of the foam without significantly influencing the lamellae stability and foam drainage rate [105].

*Hydrophobic* particles, however, interact with the lamellae and they can have a destabilising or a stabilising effect on the foam, depending on their shape, hydrophobicity and concentration in the foam.

The key determinant of the influence of hydrophobic particles on foam stability is the rate at which the air-solid interface, first formed during particle to bubble attachment, grows or spreads on particles within the foam. High speed photography studies on low concentrations of smooth spherical glass beads performed by Dippenaar [123, 124] have shown that if the rate of growth of the air-solid interface was less than the rate of natural thinning of the lamella, the particle moves away from the thinning section of the lamella and leaves the film to break at its inherent rupture thickness. If however, the rate of growth of the air-solid interface is faster than the natural thinning rate of the film, the solid particle remains in the thinning section and accelerates film thinning. The particle bridges the lamella and the regions of air-solid interface protruding through the two sides of the lamella rapidly grow until they meet, resulting in premature rupturing of the film. Dippenaar showed that for the spherical glass beads studied, premature rupturing of the film only occurred if the contact angle was greater than 90°. Particles with rough, uneven surfaces have been found to require considerably higher contact angles to achieve foam destabilisation [125, 126], due to the slower rate of growth of the air-solid interface on a rough surface.

It is important to note that for the particle to accelerate film rupture it must bridge both sides of the lamella. If the particle is smaller than the film’s inherent critical film thickness it cannot bridge the lamella and so cannot destabilise the film, regardless of its contact angle.

It is also important to note that the above studies were conducted at low solids concentration in the foam. At high concentrations, both smooth and rough hydrophobic particles can *stabilise* the foam. The formation of a closely packed layer at the film surface slows or impedes the
growth or spread of the air-solid interface on the individual particles. The two sides of the lamella are physically prevented from approaching each other, and attainment of the critical film thickness is prevented [127]. Such foams are often referred to as 'solids-stabilised' and their formation during the flotation process is critical to the success of HLC mode flotation. Further discussion of these foams is reserved for Section 2.4.2.

2.4 Foam and Effluent Management

2.4.1 Introduction

The ability of a solid to attach to a bubble is of little use if the particle-bubble aggregate does not survive long enough for excess liquid drainage from foam and subsequent separation of the solids-rich foam from the solids-poor effluent. In conventional mode flotation, this separation occurs in the flotation cell and the high solids content foam has to be stable until it exits the flotation cell. In HLC mode flotation where the liquid content in the foam carried over from the flotation cell is much higher to overcome problems related to channelling and foam overturning (see Section 2.4.3), this separation occurs externally in a foam collection vessel. In order for this flotation mode to be feasible, a solids-stabilised foam that can withstand extensive liquid drainage is necessary.

2.4.2 Solids-Stabilised Foam

The formation of a solids-stabilised foam requires the following solids characteristics:

- large solids size;
- high solids hydrophobicity; and
- high solids concentration.

Solids-stabilised foam can only be formed when the three criteria are met as depicted diagrammatically in Figure 2.13.

Successful formation of solids-stabilised foam (SSF) is represented in the triple overlap region at the centre (see Figure 2.13) where the solids are numerous, large and hydrophobic. The double overlap regions (denoted 1, 2 and 3) represent conditions where one of the criteria is not met. Failure to meet one (or more) of these criteria is evident in the foam's ability to retain the solids after extensive drainage, as well as in the volume and liquid content of the final foam product.
**Figure 2.13:** A pictorial demonstration of the criteria needed for solids-stabilised foam formation. (Note: SSF = Solids-stabilised foam formation.)

**Region 1 – High concentrations of small hydrophobic solids**

If the particles are too small to bridge the lamellae before the critical film thickness is attained, they will not destabilise the foam. Since HLC mode flotation relies on the use of high air flow rates, this leads to the formation of large volumes of very wet foam that, on drainage, will eventually collapse, giving up its solids in the process.

If the solids are large enough to bridge the lamellae at small film thickness, the delay in the foam’s destructive effect will allow large volumes of wet foam to be generated. On drainage, these foams also give up their solids since film rupture occurs at relatively long time after film formation, when the lamellae are thin and there is relatively little difference in lamellae thickness between top and bottom of foam body. Under these conditions, the release of hydrophobic solids at the top of the foam body will have a devastating effect on all the lamellae it meets on the way down. As the foam drains and collapses, the solids concentration increases but it only becomes great enough to establish solids-stabilised films when the number of surviving films is too small to support the quantity of the solids present. The excess solids drain out of the foam, contaminating the drainage liquid below the foam. These foams are problematic because of their high volumes and the need to separate them from the drainage liquor before they begin to give up their solids, i.e. at relatively high foam liquid content.
Region 2 – High concentration of large solids with low to moderate hydrophobicity

As previously discussed in Section 2.2.3.3, particles with low hydrophobicity tend to move away from the thinning section of the lamellae without disrupting it.

The combination of the use of high air flow rate in HLC mode flotation, the high surfactant content in printing ink wastewater and the lack of destabilisation by the solids give rise to large volumes of very wet foams.

These foams have a longer lifetime than the foams in Region 1 described earlier because of the lack of destabilisation. They, however, never achieve solids-stabilised stage when the concentration of foam solid increases as the foam volume decreases. They collapse completely, giving up their load of solids to the drainage. Like the foams in Region 1, these foams are problematic because of their high volumes and the need to separate them from the drainage liquor before they give up their solids, i.e. at relatively high foam liquid content.

Region 3 – Low concentration of large hydrophobic solids

Foams in Region 3 are characterised by excessive destabilisation of the lamellae by large and very hydrophobic solids. These solids are so large and hydrophobic as to disrupt the lamellae at large thickness, i.e. soon after they are formed. The high film destabilisation rate results in a slow growth in foam volume (in the flotation cell) and a rapid increase in solids concentration at the top of the foam body. The high concentration of large, hydrophobic solids allows the establishment of solids-stabilised films. They, however, are too few to carry the large concentration of solids present and the excess solids drain down to lower region of the foam further destabilising the lamellae there. By the time the foam overflows into the collection vessel, it has a low liquid content and a high solids content, but is not resilient enough to survive the flow. What is collected would more accurately be described as a frothy sludge than a foam. Although a low foam volume, low foam liquid content, high foam solid content product are desirable, these ‘foams’ are problematic in that they do not allow the high liquid carryover with the foam required when conducting flotation in HLC mode (see Section 1.6). These foams are also unsuitable for conventional flotation due to their inherent instability, leading to channeling and foam overturning within the flotation cell.
**SSF region**

The SSF region represents the conditions where the solids are hydrophobic enough to be retained at the air-liquid interface during liquid drainage, numerous enough to form a closely packed layer on the film surface and large enough to physically prevent the opposing air-liquid interfaces from approaching each other.

Dippenaar [127] conducted an experiment on the stability of the 3-phase foam with hydrophobic sulphur particles (contact angle, $\theta = 70^\circ$ and particle size 20 – 140 µm) and found that at high solids concentration, a closely packed layer of solids on the film surface is formed. Upon film thinning, the solids are prevented from moving freely and are surrounded by a film of finite thickness as shown in Figure 2.14.

![Figure 2.14: Solids-stabilised foam with large, hydrophobic solids stabilising the liquid film.](Reference: Dippenaar, 127)

The surface tension of the film at the air-liquid interface prevents further drainage. The interfaces are physically kept apart and bubbles are prevented from coalescing. This foam can be stable for over a long period, and when left standing, evaporates slowly to the point of almost complete dryness. Such foam can have very low water content due to the protrusion of the particles into the gaseous phase, leaving a relatively thin, solids-stabilised, aqueous film [128]. Due to the low water content (i.e. the probability of toxic waste leaching from waste sites is minimum), this foam can be disposed without further treatment.

A typical printing ink wastewater is high in suspended solids concentration (between 4 – 10 g/L, [10]). Under conditions where the suspended solids concentration is relatively low compared to the average loadings, the coalescence rate during the foam drainage stage is higher. The high foam instability (due to foam coalescence) at the initial drainage period does not cause poor solids retention within the foam provided that the solids are large and hydrophobic enough to pierce through the next encountered air-liquid interface, i.e. foam coalescence occurs until a point where the solids are numerous enough to stabilise the foam (as illustrated in Figure 2.14).
2.4.3 HLC Mode Flotation

HLC mode flotation involves increasing the air throughput substantially above that normally applied in conventional mode flotation. One of the many advantages in increasing air throughput is the increase in the turbulence and relative velocity between the particle and the bubble in the flotation stage [129, 130]. Philippoff [129] and Whelan and Brown [130] found that the more force (momentum or kinetic energy) with which a particle collides with a bubble, the greater the chance of particle-bubble attachment, especially for smaller sized particles. Also, the higher air to solids ratio was found by Maddock [131] to assist in the flotation of more dense solids through increased buoyancy as well as to facilitate the drainage and compaction of the sludge – from 3.0% to 3.7% wt/wt of dry solids in foam as the air to solids ratio increased from 5 mL/g to 9 mL/g.

The corresponding rate of particle detachment from the bubble is considerably less studied, as the detachment of small hydrophobic particles from bubbles at typical conventional mode flotation conditions is most likely very low in comparison to its rate of attachment. The rate of particle detachment depends on the relative amount of attached particles, the interaction forces between particles in aggregation and the external forces acting on the particles [132]. The increase in turbulence is expected to increase both the rate of detachment (leading to poor contaminant removals from the flotation cell) and the break up of attached flocs (leading to poor solids retention within the foam). Therefore, there is an upper limit for the amount of air throughput after which the detrimental impact becomes a problem. Nevertheless, this upper air throughput limit in HLC mode flotation is much higher in comparison to the limit found in a typical conventional mode flotation. Operating at a higher air throughput enables higher wastewater throughput [41], potentially allowing the use of a smaller and less expensive flotation cell.

Wilson and Thackston [133] investigated the removal of toxic inorganic metals from industrial wastewater using foam flotation and found that the major detrimental factors contributing to the quality of the treated effluent in conventional flotation are the effects of channelling and foam overturning. Channelling and foam overturning are primarily due to foam instability as a result of excessive foam drainage. The authors found that channelling and foam overturning occurred at high hydraulic loadings (> 4.7 m³/m² hr) and low air flow rates (< 14.6 m³/m² hr). They found that this problem can be overcome by increasing the air flow rate to 29.2 m³/m² hr but the resultant volume of collapsed foam was found to increase from approximately 3% to 9% of the influent volume.
The problems associated with channelling and foam overturning, however, can be avoided using HLC mode flotation. Sanciolo et al. [41] conducted flotation studies on the removal of heavy metals from the electroplating wastewater and found that by increasing the air throughput until all the liquid entering the flotation cell exits with the foam, a much higher hydraulic loading can be achieved without sacrificing the treated effluent quality. The authors increased the air flow rate to 4.8 L/min (or hydraulic loadings of 35.0 m³/m² hr) and even at wastewater flow rate of 3 L/min (or hydraulic loadings of 22.9 m³/m² hr), the heavy metal removals achieved in the liquid drained from the foam were well below the regulatory discharge limits for discharge to the local sewage system, i.e. 1.2 ppm (99% removal), 3.2 ppm (94% removal), and 0.05 ppm (98% removal) for chromium, nickel and zinc respectively. The hydraulic loading of 22.9 m³/m² hr represents a 5-fold increase in wastewater processing speed compared to the hydraulic loadings achieved by Wilson and Thackston [133].

The conventional mode flotation process has limited application in treating wastewater with relatively high suspended solids content (e.g. > 4 g/L) such as the wastewater from the printing ink industry. The high suspended solids content results in a decreased liquid drainage rate (i.e. an increased foam stability) leading to a large amount of liquid entrainment [40]. This, in turn, leads to a waste sludge that is very wet. The air throughput has to be decreased further, increasing the possibility of channelling and foam overturning in the flotation cell. Operating the flotation process in HLC mode not only decreases the problems associated with conventional mode flotation such as wet waste sludge or channelling and foam overturning, but also allowing operation at a much higher wastewater treatment rate.

### 2.5 Summary

The HLC mode flotation process is a modification of the conventional mode flotation process whereby high air throughput is applied through the flotation cell. Extensive drainage of the wet foam is conducted externally from the flotation cell. The success of this method relies on the process conditions whereby the hydrophobicity, size and concentration of the pigment solids are such that a solids-stabilised foam can be formed while relatively clean liquid drains from the foam.

The choice of optimum process conditions leading to the formation of a solids-stabilised foam is favoured by the following conditions:

- the choice of the metal ions as coagulant is one that forms a hydrous metal oxide at a high IEP value and a large positive surface charge at the flotation pH (usually around
neutral pH values) to facilitate electrostatic attraction between it and the negatively charged pigment solids;

- a low surface charge of the mixed pigment-hydrous metal oxide solids. This facilitates flocculation of the solids into size range suitable for flotation. This can occur through heterocoagulation with the hydrous metal oxide solids and/or adsorption with the metal ions or its hydrous oxide complexes;

- a net negative surface charge of the mixed pigment-hydrous metal oxide solids to aid the adsorption of the added cationic surfactant with the head group orienting towards the pigment surface through electrostatic attractive force, i.e. the free energy associated with the electrostatic attraction force is large and negative;

- the choice of a cationic surfactant is one which chemically reacts with the negative solid surface sites to maximise the free energy associated with the chemical interaction between the solids and the surfactant’s head group, thereby imparting hydrophobicity onto the solids surface. Hydrophobic surface encourages flocculation, increases particle-bubble attachment and stability efficiencies, and assists in both the foam stability and the solids retention within foam; and

- a denser and more compact resultant mixed pigment-hydrous metal oxide solids, ensuring that less water is trapped at the periphery of the solids surfaces during foam drainage and less likely to break up due to external forces acting on the solid.

The achievement of as many of these conditions as possible under the restriction of economic and environmental considerations while minimising the susceptibility of the wastewater treatment process to the variability in the wastewater composition will be the aim of the experimental investigation in this thesis.
Chapter 3: Experimental Procedures

3.1 Flotation Studies

3.1.1 Reagents

Flotation studies:
- 40,000 ppm Fe(III) – from AR grade Fe(NO₃)₃·9H₂O (Ajax Chemicals);
- 40,000 ppm Fe(II) – from AR grade FeSO₄·7H₂O (BDH Chemicals) prepared fresh just before each experiment;
- 40,000 ppm Al(III) – from AR grade Al(NO₃)₃·9H₂O (BDH Chemicals);
- 0.05 M CTAB – from GR grade N-cetyl-N,N,N-trimethylammonium bromide (Merck Chemicals);
- 10,000 ppm SDS – from specially pure sodium laurylsulfate (BDH Chemicals);
- 10,000 ppm Teric G12A8 – from ICI Chemicals with no further treatment;
- nitric acid – from AR grade HNO₃ (BDH Chemicals); and
- sodium hydroxide – from AR grade NaOH (BDH Chemicals).

Yellow pigment determination by UV-vis spectroscopy:
- chloroform – from HPLC grade chloroform (BDH Chemicals).

Metal quantification by atomic absorption spectroscopy:
- All standards were prepared from 1000 ppm metal nitrate standard solution (BDH Chemicals); and
- hydrochloric acid – from AR grade HCl (BDH Chemicals).

CTAB quantification:
- 4 mM SDS – from specially pure sodium laurylsulfate (BDH Chemicals);
- mixed indicator solution – from 0.500 g dimidium bromide (Aldrich Chemicals), and 0.250 g acid blue 1 (BDH Chemicals) in 250 mL 10% (v/v) AR grade ethanol (BDH Chemicals); and
- mixed indicator acid solution – from 20 mL mixed indicator solution, and 20 mL AR grade concentrated H₂SO₄ (BDH Chemicals) in 500 mL distilled water.
Chemical Oxygen Demand (COD) determination:
  - digestion solution – from 10.216 g AR grade K$_2$Cr$_2$O$_7$ (BDH Chemicals) previously
dried at 103 °C for 2 hours, 167 mL AR grade concentrated H$_2$SO$_4$ (BDH Chemicals),
and 33.3 g AR grade HgSO$_4$ (Sigma Chemicals) in 1 L distilled water;
  - sulfuric acid reagent – from 5.5 g AR grade Ag$_2$SO$_4$ (BDH Chemicals) in 1 kg AR
grade concentrated H$_2$SO$_4$ (BDH Chemicals); and
  - potassium hydrogen phthalate (KHP) standard – from 765 mg AR grade KHP (BDH
Chemicals) in 1 L distilled water (equivalent to COD level of 900 mg O$_2$/L).

Carbonaceous Biochemical Oxygen Demand (CBOD$_5$) determination:
  - glucose-glutamic acid solution – from 150 mg AR grade anhydrous D-(+)-glucose
(Sigma Chemicals) and 150 mg L-glutamic acid (Sigma Chemicals) in 1 L distilled
water;
  - phosphate buffer solution – from 8.5 g AR grade KH$_2$PO$_4$ (BDH Chemicals), 21.75 g
AR grade K$_2$HPO$_4$ (Ajax Chemicals), 33.4 g AR grade Na$_2$HPO$_4$.7H$_2$O (Aldrich) and
1.7 g AR grade NH$_4$Cl (BDH Chemicals) in 1 L distilled water;
  - magnesium sulfate solution – from 22.5 g MgSO$_4$.7H$_2$O (Sigma Chemicals) in 1 L
distilled water;
  - calcium chloride solution – from 27.5 g CaCl$_2$.2H$_2$O (Sigma Chemicals) in 1 L
distilled water;
  - ferric chloride solution – from 0.25 g LR grade FeCl$_3$.6H$_2$O (Ajax Chemicals) in 1 L
distilled water;
  - CBOD$_5$ dilution water – from 1 mL phosphate buffer solution, 1 mL magnesium sulfate
solution, 1 mL calcium chloride solution, 1 mL ferric chloride solution and 5 mL
activated sludge in 1 L distilled water; and
  - nitrification inhibitor formula 2533 (Hach Chemicals) – containing sodium sulfate and
2-chloro-6-(trichloromethyl) pyridine.

Carbon and nitrogen analysis:
  - 40,000 ppm Fe(III) – from LR grade FeCl$_3$.6H$_2$O (Ajax Chemicals).

3.1.2 Industrial Wastewater Collection and Storage

Wastewater samples were taken periodically from the printing effluent of a cardboard printing
and coating plant at Visy Industries Pty. Ltd., Coolaroo, Victoria, Australia. These samples
were stored in 25 L plastic drums at room temperature until needed. Once collected, the
samples are subjected to periodical testing over time to monitor the changes in their physical
and chemical characteristics as well as the changes in their flotation responses using fixed process variables and process conditions over a set pH range.

3.1.3 Simulated Wastewater Preparation and Storage

The individual inks and coating solutions were supplied by a cardboard printing and coating plant (Visy Industries Pty. Ltd., Coolaroo, Victoria, Australia). They were diluted with distilled water and stored in 10 L plastic drums at room temperature until needed (experiments were conducted within 2 months of sample preparation).

3.1.4 Flotation Studies

3.1.4.1 Batch Mode Flotation

Batch mode flotation experiments were performed using the apparatus shown diagrammatically in Figure 3.1.

![Figure 3.1: Batch mode flotation: (1) compressed air inlet, (2) rotameter, (3) magnetic stirrer, (4) teflon coated magnetic stirrer bead, (5) porous glass frit (medium porosity), (6) flotation cell (4.5 cm internal diameter, 70 cm height), (7) overflow column, (8) foam collector.](image)

A 200 mL volume of wastewater sample was dosed to the required concentration with respect to the metal ions (Fe(II), Fe(III) and/or Al(III)) prior to pH adjustment with NaOH (above native pH) or HNO₃ (below native pH). Gentle mixing was applied throughout the experiment.

A 15-minute aging period was allowed before surfactant addition (usually CTAB). A 20 mL volume of wastewater was taken for analysis. A one-minute equilibration period was allowed
before the remaining wastewater was introduced into the flotation cell. Instrument grade air was introduced into the flotation cell through a porous glass frit of medium porosity. The duration of the flotation process was set at 10 minutes.

After the flotation process was completed, water samples were taken for analysis from (i) the foam drainage liquid, and (ii) the liquid left in the flotation cell, where sufficient volumes were available.

**Rate of Contaminant Removal Studies**

A 200 mL volume of wastewater sample was dosed with the required concentration of metal ions (Fe(II), Fe(III) and/or Al(III)) prior to pH adjustment with NaOH (above native pH) or HNO₃ (below native pH). A 15-minute aging period was allowed before CTAB addition.

A one-minute equilibration period was allowed before the wastewater was introduced into the flotation cell. Instrument grade air was introduced into the flotation cell at 250 mL/min through a porous glass frit of medium porosity. The duration of the flotation process was 10 minutes.

Throughout the flotation run, 1 – 2 mL samples were taken from the liquid in the flotation cell every 30 seconds. These samples were then analysed for turbidity to assess the rate of contaminant removal from the bulk liquid in the flotation cell.

**3.1.4.2 Continuous Mode Flotation**

Continuous mode flotation experiments were performed using the apparatus shown diagrammatically in Figure 3.2. The illustration and dimensions of the foam collection vessel ((14) in Figure 3.2) is shown in Figure 3.3.

Two litre wastewater samples were dosed to the required concentration with respect to Fe(II) prior to pH adjustment with NaOH (above native pH) or HNO₃ (below native pH). A 15-minute aging period was allowed before it was pumped into the flotation cell at a fixed pre-determined flow rate. CTAB was introduced directly into the flotation cell.

Instrument grade air was introduced into the flotation cell through a porous glass frit of medium porosity. During the flotation process, the liquid volume in the flotation cell was kept below 200 mL by removing liquid through outlet B (see Figure 3.2). The duration of the flotation
process depended on the wastewater flow rate. The continuous mode flotation process was run until the full two litres of wastewater samples were treated.

**Figure 3.2:** Continuous mode flotation: (1) compressed air inlet, (2) rotameter, (3) magnetic stirrer, (4) teflon coated magnetic stirrer bead, (5) porous glass frit (medium porosity), (6) flotation cell (4.5 cm internal diameter, 70 cm height), (7) overflow column, (8) surfactant container, (9) surfactant pump, (10) wastewater pre-treatment container, (11) teflon coated magnetic stirrer bead, (12) magnetic stirrer, (13) wastewater pump, (14) foam collector (see Figure 3.3), (15) foam drainage collector, (16) liquid leaving flotation cell collector, (A) treated wastewater – foam drainage, (B) treated wastewater – cell exit liquid.

**Figure 3.3:** A 2-dimensional illustration of the 4-segment foam collector tray (4-SLT). The tray was tilted at an angle of approximately 8° to assist in the flow of the foam through gravity.
Water samples were taken for analysis (where sufficient volumes were available) from (i) the foam drainage liquid, (ii) the liquid leaving the flotation cell through outlet B, and (iii) the liquid left in the flotation cell after the flotation run at the end of the flotation process. These samples, along with a sample of the untreated wastewater, were then analysed for turbidity to assess the effectiveness of the flotation process.

3.2 Electrophoretic Mobility Studies

3.2.1 Sample Preparation

As the amount of suspended solids in the samples was too high, sample preparation involving solids reduction with filtration was required before any mobility studies could be conducted. The sample was filtered with a 0.45 µm Millipore nitrocellulose membrane filter. A few drops of the original sample solution were added to the filtrate to introduce solids into the filtrate.

3.2.2 Electrophoretic Mobility Measurement

A Rank Bros. Mark II Micro-electrophoresis apparatus, fitted with a ‘flat’ cell, was used to measure the electrophoretic mobility of the solids contaminant.

3.3 Analytical Procedures

3.3.1 UV-Visible Spectroscopy

3.3.1.1 Sample Preparation

This procedure allowed the organic pigments to be extracted from the water phase to the organic phase, in order to enable quantitative analysis using UV-Vis spectroscopy. A 1.0 mL aliquot of wastewater sample was added to 100 mL distilled water in a 500 mL separatory funnel. This mixture was then acidified with two drops of 5 M HNO₃, shaken with a 10.0 mL aliquot of chloroform, and allowed to separate. The chloroform layer was removed, and the process was repeated with a further three 10.0 mL aliquots of chloroform. The four volumes of chloroform were then mixed, and analysed using UV-visible spectroscopy.
3.3.1.2 Yellow Pigment Determination

A Varian Cary 3 UV-Visible absorption spectrophotometer was used to quantify the intensity of absorbance by the organic pigments present in the wastewater samples. A type of organic pigment commonly present in the printing ink wastewater is the diarylide yellow pigment contained in yellow ink (CI no. 21100 or CAS no. 6358-85-6, see Figure 2.2(a)). This pigment absorbs strongly between 424 – 426 nm in chloroform medium as shown in Figure 3.4.

![Figure 3.4: UV-Vis absorbance spectrum for the wastewater sample and yellow ink in chloroform phase.](image)

In order to minimise interference caused by the background noise, the average absorbance between 421 – 430 nm was taken when determining the pigment concentration. The extent of pigment removal was determined by comparing the relative pigment concentrations between the treated effluents with its initial concentration in the wastewater sample. The intensity of absorbance represents the amount of pigments present and pigment removal was calculated using equation [3.1].

$$\text{Removal} (%) = (1 - \frac{I_f}{I_i}) \times 100 \quad \text{...............}[3.1]$$

where $I_f$ = absorbance in treated effluent, $I_i$ = absorbance in initial wastewater sample.

3.3.2 Atomic Absorption Spectroscopy (AAS)

3.3.2.1 Sample Preparation

Due to the metals being present as solids within the ink formulation, the samples had to be digested with concentrated HNO$_3$ and HCl prior to analysis according to method 3030 D.
(Preliminary Digestion for Metals) as outlined in the Standard Methods for the Examination of Water and Wastewater [134].

A 3 mL volume of concentrated HNO₃ was added to 10.0 mL of sample. This mixture was heated to boiling and evaporated down to approximately 5 mL. The sample was allowed to cool to room temperature before 5 mL of HNO₃ was added, and again heated and evaporated down to a volume of approximately 5 mL. The whole process of cooling, addition of 5 mL of HNO₃, and boiling, was repeated again before cooling to room temperature. This was followed by the addition of 0.5 mL 50% (w/v) HCl and 0.75 mL distilled water. This mixture was heated for 15 minutes, cooled to room temperature and filtered using a 0.45 µm Millipore nitrocellulose membrane filter. The filtered sample was made up to 50.0 mL with distilled water and analysed using AAS.

### 3.3.2.2 Metal Content Measurement

A Varian SpectrAA-220 atomic absorption spectrophotometer was used to analyse the wastewater samples for metal content. All standards were prepared in 0.01 M HNO₃ from 1,000 ppm metal nitrate standard solutions (BDH Chemicals), acidified with 5% v/v HNO₃ and stored in plastic polythene containers.

A type of pigment commonly present in the printing ink wastewater is the phthalocyanine blue pigment contained in blue ink (CI No. 74160 or CAS No. 147-14-8, see Figure 2.2(b)). The digestion procedure digests the pigment structure and releases the copper contained in it. The extent to which metals were removed was determined by comparing the relative metal concentrations between the treated effluents with its initial concentration in the wastewater sample as shown in equation [3.2].

$$\text{Removal} \ (%) = (1 - \frac{C_f}{C_i}) \times 100 \quad \ldots\ldots\ldots\ldots[3.2]$$

where $C_f$ = metal concentration in treated effluent, $C_i$ = metal concentration in initial wastewater sample.

Copper is used to represent the extent of metal removal over other metals such as aluminium, iron, zinc, chromium or barium, as it is commonly present in high concentrations in the printing ink wastewater (phthalocyanine blue pigment is widely used in blue process ink, [42]), it has a wide detection concentration range and a low detection limit (< 1 ppm) using AAS.
3.3.3 Turbidimetry

3.3.3.1 Sample Preparation

A 1.0 mL aliquot of sample was diluted to 500 mL with distilled water, and sonicated using a 50 Hz sonicator for 2 minutes before turbidity measurements were taken.

3.3.3.2 Turbidity Measurement

The turbidity of the wastewater samples was carried out using a ZBK Turb 500 IR, manufactured by Wissenschaftlich-Technische Werkstatten GmbH (WTW). Turbidity measurements were taken according to the Standard Method ISO 7027 or DIN 27027 where an infra-red (IR-LED) of wavelength 860 nm was passed through the sample [135]. A measurement of the scattered light at an angle of 90° was used to determine the degree of turbidity in the sample, measured in nephelometric turbidity units (NTU).

The extent of turbidity removal was determined by comparing the relative turbidity between the treated effluents and the initial wastewater as shown in equation [3.3].

\[ \text{Removal} \% = (1 - \frac{\text{NTU}_f}{\text{NTU}_i}) \times 100 \]  

where \( \text{NTU}_f \) = nephelometric turbidity unit of treated effluent, \( \text{NTU}_i \) = nephelometric turbidity unit of initial wastewater sample.

3.3.4 CTAB Analysis

3.3.4.1 Sample Preparation

For the analysis of CTAB adsorption and/or precipitation in the presence of waste solid and metal ion coagulant, the sample was dosed with the required concentration with respect to the metal ions prior to pH adjustment. A 15-minute aging period was allowed before CTAB addition. A one-minute equilibration period was allowed before the sample was filtered with a 0.45 μm Millipore nitrocellulose membrane filter. The filtered solution was then analysed for CTAB.

For the analysis of CTAB precipitation in the absence of waste solid or metal ion coagulant, the sample was filtered with a 0.45 μm Millipore nitrocellulose membrane filter before CTAB addition. A one-minute equilibration period was allowed before the filtrate (with added CTAB)
was filtered with a 0.45 µm Millipore nitrocellulose membrane filter. The filtered solution was then analysed for CTAB.

3.3.4.2 CTAB Quantification

CTAB quantification was conducted based on the ISO 2871-2-1990 Part 2 standard method [136]. The cationic-active matter (i.e. CTAB) contained in the sample was titrated in a two-phase (chloroform as organic layer) system against SDS in the presence of a mixed indicator solution (consisting of mixed anionic and cationic dyes). CTAB initially reacts with the anionic dye to form a salt which dissolves in the chloroform layer and imparts a blue colour to this layer. During the titration, SDS displaces the anionic dye and, at the end point, forms a salt with the cationic dye, imparting a greyish-pink colour to the chloroform layer.

A 10.0 mL aliquot of mixed indicator acid solution, 15.0 mL chloroform, and 25.0 mL distilled water were added to 20.0 mL of filtrate. The solution was titrated with 4 mM SDS solution. The end point was reached when the chloroform layer turned from blue to greyish-pink. The amount of CTAB (in ppm) could be obtained through the calibration of its concentration to the amount of SDS required.

3.3.5 Floc Size Analysis

Image analysis was used to determine the average floc size. A small drop of the wastewater sample was placed between the glass slides and cover slips, and then placed into a microscope. A Pulnix TMC-76 camera was used to capture the image at 40 times magnification using Global Lab Image/2 image analysis software. Four images were captured for each sample.

Image analysis software was used to determine the size of each solid using a blob analysis function. This was achieved by utilising the light contrast between each solid and its surrounding background. The average size of the solids in each sample was determined based on the size of all of the solids within the four captured images.

3.3.6 Total Solids Content

A 20.0 mL aliquot of sample was dried in an oven at 60 – 80°C overnight. The sample was then cooled in a desiccator to room temperature and weighed. This cycle of drying, cooling, desiccating and weighing was repeated until a constant weight was obtained or until the weight
change was less than 4% of the previous weight. The total solids content was calculated in grams per litre of sample.

### 3.3.7 Total Suspended Solids Content

A 20.0 mL aliquot of sample was dosed with HNO₃ to a pH of 6.5. The sample was then filtered with a 0.45 µm Millipore nitrocellulose membrane filter. The filtered solids were dried in an oven at 60 – 80°C overnight, cooled in a desiccator to room temperature and weighed. This cycle of drying, cooling, desiccating and weighing was repeated until a constant weight was obtained or until the weight change was less than 4% of the previous weight. The total suspended solids content was calculated in grams per litre of sample.

### 3.3.8 Chemical Oxygen Demand (COD)

A 2.5 mL aliquot of sample, 1.5 mL of digestion solution, and 3.5 mL of sulfuric acid reagent were added to a 10 mL standard ampoule and placed in a block digester that was preheated to 150°C and allowed to reflux for 2 hours. The ampoule was allowed to stand and cooled to room temperature to allow solids to settle before absorbance measurement at 600 nm, using a Varian Cary 3 UV-Visible absorption spectrophotometer. This absorbance was compared to the calibration curve with different dilutions of the potassium hydrogen phthalate standard (equivalent to COD level of 900 mg O₂/L) that had been subjected to the same treatment as the sample.

### 3.3.9 Carbonaceous Biochemical Oxygen Demand (CBOD₅)

The 5-day CBOD measurement was performed using an OxiTop® OC 100 BOD measuring head apparatus manufactured by Wissenschaftlich-Technische Werkstatten GmbH (WTW). According to the manufacturer, this set-up is based on the Standard Method DIN 38409 part 52 [137]. The CBOD₅ was determined by measuring the change in air pressure, caused by a decrease in oxygen gas due to the degradation of organic substances by microorganisms. Nitrification inhibitor formula 2533 was added to prevent nitrification.

A standard volume (as specified by the manufacturer), comprised of a mixture of the sample and the CBOD₅ dilution water, was left in an environment where the temperature was fixed at 20 ± 1°C and under continuous stirring for 5 days. Each set of experiments was conducted in triplicate.
Glucose-glutamic acid checks were conducted in order to check the quality of the seeding material. This check was subjected to the same treatment as the sample and also conducted in triplicate.

3.3.10 Carbon and Nitrogen Analysis

3.3.10.1 Sample Preparation

The samples were concentrated by centrifugation of the flocculated solids (with 250 ppm Fe(III) at 4,000 rpm for 10 minutes) with the Sorvall Centrifuge RC5C and the removal of the supernatant.

3.3.10.2 Carbon and Nitrogen Measurement

The amount of carbon and nitrogen were measured using a LECO CN-2000 carbon/protein/nitrogen elemental analyser. The samples were combusted in pure oxygen environment of the furnace at 1050°C. The carbon content is determined through the infra-red determination of the resulting carbon dioxide formation while the nitrogen content is determined using a thermal conductivity cell to detect N₂ gas after the NOₓ gases had been reduced to N₂ by the catalyst heater. The C/N ratio was determined from the gradient of ‘C and N vs sample concentration’ plots.

3.3.11 pH Measurement

The pH measurement was made using an Ionalyzer model 701A pH/mV meter. Calibration was carried out using pH 4.00 ± 0.02 in 20°C buffer tablets (BDH Chemicals) and 0.01 M pH 9.22 sodium tetraborate (LR Grade, Ajax Chemicals).

3.3.12 Conductivity Measurement

Sample was filtered with a 0.45 µm Millipore nitrocellulose membrane filter. Conductivity measurement was made using a Metrohm 644 Conductometer with a Russell electrode.
Chapter 4: High Liquid Carryover Mode Flotation Studies on Industrial Wastewater

4.1 Introduction

The inks and coatings used in commercial cardboard printing consist of a wide variety of pigments, extenders, surfactants, binders, clays, waxes, antifoam and various other additives. These inks and coatings are routinely washed off the printing machine at the end of each production run and end up in the wastewater, along with washings from the plant floor that may also contain machine oil and lubricants. The composition of this wastewater, therefore, can change with time, depending on the number of printing machines being washed and the colours used in each machine.

The variability of printing wastewater composition poses a major challenge to the treatment process employed, particularly if a flotation separation process is to be used. The first stage of the flotation wastewater treatment process involves the flocculation of the well dispersed negatively charged colloidal pigments. This is most commonly achieved by adding a metal ion coagulant such as alum or ferric chloride [25]. The optimum requirement of coagulant for each wastewater sample varies according to the concentration of solids as well as the type of solid. The minimum requirement of coagulant for the industrial printing ink wastewater is one that does not allow the treatment process to become susceptible to this variability in wastewater composition, i.e. a dose that is sufficiently high to successfully flocculate high concentrations of the highly charged solids. It is important, however, to keep the coagulant addition to a minimum in order to minimise cost and the quantity of sludge for disposal.

Apart from cost and waste disposal considerations, there is another important reason to keep the coagulant dose to a minimum. Although a high coagulant dose ensures flocculation for both high and low solids content wastewaters, it does not ensure similar surface properties for the flocs produced. In the case of the low solids content samples, at high coagulant addition a greater proportion of the mixed pigment-hydrous metal oxide floc is composed of the hydrous oxides of the metal ion coagulant. The surfactant adsorption and flotation behaviour in this case is likely to be different to that achieved for wastewater samples containing high solid content where the mixed pigment-hydrous metal oxide floc contains a higher proportion of pigment particles.
The need to keep coagulant addition to a minimum also dictates the type of surfactant used. The well-dispersed pigment particles in the wastewater are initially negatively charged. Coagulant addition renders them less negatively charged, thus promoting flocculation. Under these conditions, electrostatic forces facilitate adsorption of a cationic surfactant onto the negative mixed pigment-hydrous metal oxide floc. The use of larger doses of metal ion coagulant can further decrease the negative charge of the mixed pigment-hydrous metal oxide floc or impart a net positive charge, thus facilitating the adsorption of anionic surfactants.

In this chapter, the issue of wastewater variability is addressed by investigating the flotation behaviour of a number of samples with varying suspended solids content. The investigation of the influence of different pigment types is reserved for Chapter 5 of this thesis where the flotation behaviour of single and multiple components simulated wastewater samples is studied. This allowed a better understanding the influence of these components on the flotation process.

4.2 Characterisation of Industrial Wastewater Samples

Industrial wastewater discharged to the environment or the local sewage system must comply with the discharge limit set by the local municipal authority. The typical environmental concerns regarding printing ink wastewater are the high pH, the total solids and suspended solids, the metal contents, colour, the oxygen demand and the biodegradability of the ink pigments. The allowable discharge limits of concern to printing wastewater, set by Yarra Valley Water, Victoria, Australia is shown in Table 4.1.

<table>
<thead>
<tr>
<th>Physical characteristics</th>
<th>Discharge limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6 to 10</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>200 kg/day</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>10 g/L</td>
</tr>
<tr>
<td>Metal content</td>
<td>10 ppm (Cu(II), Cr(III) and Zn(II))</td>
</tr>
<tr>
<td>Colour</td>
<td>&lt; 9 Adams-Nickerson units</td>
</tr>
<tr>
<td>Non-biodegradable latex emulsion a</td>
<td>1,000 mg/L</td>
</tr>
</tbody>
</table>

a includes paint, adhesive, rubber, plastic or similar materials.

Four different industrial printing ink wastewater samples were taken from the printing effluent of a cardboard printing plant in Coolaroo, Victoria, Australia. These wastewater samples had very different physical and chemical characteristics. The differences in the flotation outcomes
are compared and discussed, taking into account their respective properties. Due to the large number of experiments required, industrial wastewater samples had to be taken in bulk (e.g. 100 L) in as short a time as possible, to minimise differences in composition between containers (25 L plastic drums) of similar sample batches.

The characteristics of the four wastewater samples that were collected for analysis are shown in Tables 4.2 – 4.4.

**Table 4.2:** pH, turbidity and ionic strength of the wastewater samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH a</th>
<th>Turbidity b (NTU)</th>
<th>CBOD&lt;sub&gt;5&lt;/sub&gt; to COD ratio</th>
<th>Conductivity (µS)</th>
<th>Conductivity equivalent NaCl conc. (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.6</td>
<td>143</td>
<td>-</td>
<td>1,060</td>
<td>0.011</td>
</tr>
<tr>
<td>2</td>
<td>7.7</td>
<td>29</td>
<td>0.045</td>
<td>360</td>
<td>0.004</td>
</tr>
<tr>
<td>3</td>
<td>7.6</td>
<td>81</td>
<td>0.043</td>
<td>880</td>
<td>0.009</td>
</tr>
<tr>
<td>4</td>
<td>7.5</td>
<td>75</td>
<td>-</td>
<td>1,060</td>
<td>0.011</td>
</tr>
</tbody>
</table>

a the native pH of printing wastewater is 9. The pH given is the average pH over 2 months after sampling.
b turbidity taken at 500 times dilution.

**Table 4.3:** Total solids content and total suspended solids of the wastewater samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total solids content (g/L)</th>
<th>Total suspended solids (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.8</td>
<td>46.8</td>
</tr>
<tr>
<td>2</td>
<td>4.8</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>18.7</td>
<td>11.3</td>
</tr>
<tr>
<td>4</td>
<td>18.4</td>
<td>16.2</td>
</tr>
<tr>
<td>Average</td>
<td>28</td>
<td>19</td>
</tr>
</tbody>
</table>

**Table 4.4:** Metal content of the wastewater samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al(III)</th>
<th>Ba(II)</th>
<th>Cr(III)</th>
<th>Cu(II)</th>
<th>Fe(III)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>392</td>
<td>1</td>
<td>1574</td>
<td>51</td>
<td>350</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>43</td>
<td>0</td>
<td>103</td>
<td>4</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>167</td>
<td>7</td>
<td>0</td>
<td>52</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>216</td>
<td>33</td>
<td>0</td>
<td>138</td>
<td>11</td>
<td>34</td>
</tr>
</tbody>
</table>

The carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>), usually a critical discharge limit criteria in wastewater containing organic matter [25], is not a crucial criterion in printing ink wastewater as its CBOD<sub>5</sub> value is low. The low CBOD<sub>5</sub> value is due to a high proportion of
non-biodegradable substances. The non-biodegradability of the substances in the samples is indicated by the low CBOD₅ to chemical oxygen demand (COD) ratio of between 0.043 and 0.045 (see Table 4.2). Results by other authors revealed similarly low values, with CBOD₅/COD ratios ranging between 0.01 and 0.15 [9, 14]. Thus, biological treatment processes, as used in most sewage treatment plants, tend to be ineffective.

A fundamental characteristic of the printing ink wastewater is its high level of metal content (see Table 4.4). All the samples were found to exceed the discharge limit of 10 ppm on one or more types of metal contaminants. The differences in metal content in the various samples indicate a considerable difference in both the types and quantities of the pigments present.

The total solids (TS) values were found to range from as low as 4.8 g/L to as high as 67.8 g/L. The average TS content across the 4 samples was found to be 28 g/L. This average TS value was 3 times higher than the typical flexographic ink wastewater of 8.8 g/L [11]. This difference in TS values is a result of the differences in their respective plant procedures associated with waste minimisation or prevention. This includes basic steps such as minimising water usage during wash down by skimming off ink residues.

The total suspended solids (TSS) values were found to range from as low as 3 g/L to as high as 47 g/L. The average TSS content across the 4 samples was found to be 19 g/L. This average TSS value was higher than that reported for the wastewater of a cardboard printing plant, which is between 4 and 10 g/L [10]. Again, this difference is a result of the differences in their respective plant procedures associated with waste minimisation or prevention.

In order to gain a better understanding of sample to sample variability, and how the four samples listed in Tables 4.2 to 4.4 compare to the typical printing ink wastewater characteristics (in terms of solids loadings), samples of the wastewater were taken for solids content analysis over four days and the results are presented in Figure 4.1 and Table 4.5.

The TS values from 33 samples (i.e. 29 samples over a four-day period and 4 samples listed in Tables 4.2 to 4.4) were found to range from as low as 3.4 g/L to as high as 67.8 g/L. The average TS content in a typical printing ink wastewater is 13.0 g/L with the TS values for 1st and 3rd quartiles being 9.5 g/L and 18.3 g/L respectively (see Table 4.5).
Figure 4.1: Total suspended solids in the wastewater over a four-day period.

Table 4.5: Average TS and TSS content of the wastewater samples over a four-day period.

<table>
<thead>
<tr>
<th></th>
<th>Total solids content (g/L)</th>
<th>Total suspended solids (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>13.0</td>
<td>11.0</td>
</tr>
<tr>
<td>1st quartile</td>
<td>9.5</td>
<td>8.0</td>
</tr>
<tr>
<td>3rd quartile</td>
<td>18.3</td>
<td>14.9</td>
</tr>
</tbody>
</table>

The TSS values from the 33 samples collected were found to range from as low as 2.3 g/L to as high as 46.8 g/L. The average TSS content in a typical printing ink wastewater is 11 g/L with the TSS values for 1st and 3rd quartiles being 8.0 g/L and 14.9 g/L respectively (see Table 4.5). On the fourth day, higher TSS levels were measured (see Figure 4.1) corresponding to the high levels of wastewater discharge from the coating plant during their once a week equipment washing.

Sample 1, with TS and TSS contents of 68 g/L and 47 g/L respectively (see Table 4.3), is the highest solids loading sample recorded while Sample 2, with TS and TSS contents of 5 g/L and 3 g/L respectively, is one of the lowest solids loading samples recorded. Sample 3 represents the average solids loadings while Sample 4 has a solids loading slightly above the corresponding average values.

4.3 Aging Characteristics of Industrial Wastewater Samples

As the industrial wastewater samples had to be taken in bulk, it was necessary to monitor the samples for any change in characteristics over time, to ensure that the results obtained in the flotation studies are not due to these changes. The characteristics of wastewater that were investigated include the pH level, the turbidity, the chemical oxygen demand (COD), the
carbonaceous biochemical oxygen demand (CBOD₅) and the carbon-to-nitrogen ratio (C/N). Flotation experiments with fixed process variables and process conditions were also conducted.

4.3.1 pH

The pH of the sample can be an indicator of change in wastewater composition brought about by microbial activity and by slow chemical interactions within the sample. The pH of samples over the 8-week monitoring period is shown in Figure 4.2.

Figure 4.2: The pH of Samples 2 and 3 as a function of time.

The pH level was found not to change over the 8-week period indicating negligible levels of microbiological activity and consistent with the low BOD₅/COD ratios for these samples (see Table 4.2). The average pH levels for Samples 2 and 3 are 7.7 ± 0.1 and 7.6 ± 0.1 respectively.

4.3.2 Turbidity

Turbidity of the wastewater depends on the amount and size of its dispersed solids content. As the amount of solids for a particular wastewater sample is fixed, a change in turbidity indicates a change in the size of the solids. Floc size can change due to pH fluctuations and the activity of the microorganisms (e.g. by changing the surface characteristics of the solids). The changes in the turbidities of Samples 2 and 3 are shown in Figure 4.3.

The turbidity levels of these samples were not found to change over time. The average turbidities for Samples 2 and 3 are 29.0 NTU and 81.8 NTU respectively with a standard deviation of 2%.
4.3.3 Chemical Oxygen Demand (COD)

The COD is the amount of oxygen needed to oxidise all the carbon compounds in the wastewater. The changes in COD for Samples 2 and 3 are shown in Figure 4.4.

![Chemical Oxygen Demand (COD) of Samples 2 and 3 as a function of time.](image)

The COD levels of these samples were not found to change over time, suggesting a low level of chemical change over time. The average COD levels throughout the aging period for Samples 2 and 3 are 7,300 and 14,600 mg O$_2$/L respectively with a standard deviation of 4%.

4.3.4 Carbonaceous Biochemical Oxygen Demand (CBOD$_5$)

The CBOD$_5$ is the amount of oxygen required by bacteria to decompose its organic matter in the course of 5 days with the samples incubating at 20°C. The changes in CBOD$_5$ over time for Samples 2 and 3 are shown in Figure 4.5.

![Carbonaceous Biochemical Oxygen Demand (CBOD$_5$) of Samples 2 and 3 as a function of time.](image)
Figure 4.5: Carbonaceous Biochemical Oxygen Demand (CBOD$_5$) of Samples 2 and 3 as a function of time.

There is a decrease in the levels of CBOD$_5$ over time, possibly due to the reduction in the amount of organic matter as a result of microbial activity. It should be noted, however, that the starting CBOD$_5$ level of these samples (330 and 620 mg O$_2$/L for Samples 2 and 3 respectively, see Figure 4.5) was low. The halving of the CBOD$_5$ over the 8-week period does not represent a high level of microbial activity.

4.3.5 Carbon-to-Nitrogen ratio (C/N)

The C/N ratio is another indicator of the extent of bacteria activity in the wastewater. Bacteria decompose the organic matter and release inorganic nutrients, such as phosphates and nitrates into the system. The changes in C/N ratio over time for Samples 2 and 3 are shown in Figure 4.6.

Figure 4.6: Carbon-to-Nitrogen (C/N) ratio of Samples 2 and 3 as a function of time.
A slight decrease in C/N ratio over time was found to occur for Sample 3. The slight decrease in C/N ratio confirms the results obtained for CBOD$_5$, indicating that there is a decrease in the amount of organic matter in the wastewater due to microbial activity over time.

4.3.6 Flotation

A flotation run was conducted with one of the coagulants (i.e. Fe(II) hydrous oxide) and surfactants (i.e. CTAB) chosen for investigation in this thesis. Flotation experiments with the addition of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively at various pH levels between 5 and 9 were conducted to detect any changes in the flotation response over time. The flotation responses over time for Sample 3 are shown in Figures 4.7 and 4.8 and for Sample 2, in Figures 4.9 and 4.10 for the contaminant removals achieved in foam drainage and liquid in cell respectively.

For Sample 3 (see Figure 4.7), the flotation behaviour at pH values where high foam drainage removals were observed (i.e. between pH 6 and 7) was found to have minimal change over time. At pH 7, for example, the average foam drainage removal over the 2-month period was found to be 96.9 ± 0.5%. At pH levels where lower foam drainage removals were observed, however, the variability was much higher. At pH values 5 and 8, for example, the average foam drainage removals over the 2-month period were found to be 39 ± 23% and 86 ± 7% respectively. The lack of clear correlation of removal values with time at these pH values suggests that the higher variability was due to a higher sensitivity to small changes in one or more process variables, and not to the aging of the samples.

![Figure 4.7](image_url)

*Figure 4.7: Removal of contaminants in foam drainage for Sample 3 over 2-month period after wastewater sample collection as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: Negative removals were observed at pH 9, i.e. the foam drainage was richer in suspended solids content than the starting wastewater sample.)*
Figure 4.8: Removal of contaminants for liquid in cell for Sample 3 over 2-month period after wastewater sample collection as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

Figure 4.9: Removal of contaminants in foam drainage for Sample 2 over 2-month period after wastewater sample collection as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: A different flotation pH range on x-axis compared to Sample 3, see Figure 4.7.)

Figure 4.10: Removal of contaminants for liquid in cell for Sample 2 over 2-month period after wastewater sample collection as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: A different flotation pH range on x-axis compared to Sample 3, see Figure 4.8.)
For Sample 2 (see Figure 4.9), however, the high variability seen for Sample 3 at low pH value (e.g. pH 5) was not found. This may be attributed to the higher TS and TSS contents in Sample 3 (see Table 4.3) resulting in a requirement for higher coagulant and surfactant concentration. This is an indication of the importance of solids loading in wastewater as a determinant in the flotation outcome and is to be investigated further in Section 4.5.2.5.

The variability in removals for liquid in cell for both Samples 2 and 3 (see Figures 4.8 and 4.10) over the 2-month period was minimal (± 2%), with removals above 90% observed throughout the pH values conducted.

4.3.7 Conclusion – Aging Characteristics of Industrial Wastewater Samples

There were no substantial changes over time in the pH levels, the turbidity and the COD of the wastewater samples. The decrease in CBOD₅ values may be due to the microbial activity that decreases the amount of organic matter in the samples. This is also indicated by the slight decrease in the carbon-to-nitrogen ratio.

The decrease in CBOD₅ and other changes occurring in the sample over time were found not to affect the flotation behaviour.

It is noteworthy that the results from the flotation studies conducted weekly over the 2-month period at identical flotation conditions demonstrate good reproducibility for foam drainage under conditions where high removals are obtained (pH 6 – 7) and poor reproducibility under condition where solids retention in the foam is poor.

4.4 Assessment of Flotation Effectiveness

The turbidity of the wastewater sample is caused by the suspended pigment solids. It is an expression of the optical property where light is scattered and absorbed rather than transmitted through the wastewater sample. Correlation of turbidity with the weight or quantity of suspended pigment solids, however, is made with caution as the size, shape and refractive index of the contained particles also affect the light scattering. The use of this technique for the assessment of the effectiveness of flotation assumes that the size, shape and refractive index of the particles that remain after flotation are essentially the same as those of particles before flotation. This may not be a valid assumption, particularly as large flocs are expected to be removed more effectively and rapidly than small primary particles or aggregates of primary particles (see Section 2.3.2.2).
To test this assumption, flotation was performed using Fe(II) and CTAB, and the contaminant removals were measured by comparing the before and after flotation quantities of yellow pigment and copper content. These are shown, together with the removals determined by turbidity measurements, in Figure 4.11.

Figure 4.11: Removal of contaminants through various assessment methods for Sample 1 as a function of pH for flotation with 5 mM Fe(II) and 300 ppm CTAB.

The flotation responses throughout the pH range investigated for the 3 different assessment methods – yellow pigment (colour), turbidity (suspended solids) and Cu(II) concentration (metal content) – are similar. This indicates that the various types of contaminants are not selectively removed, as is often the case in mineral flotation. Thus, turbidity can be used as the primary assessment method as it is quick and easy. These results also indicate that the turbidity results can safely be used to estimate the removals of pigments, colour and metal contents from the wastewater samples.

The use of turbidity values quantitatively is, however, restricted to the same wastewater sample. Direct comparison of turbidity values of different wastewater samples is not an accurate indicator of their relative suspended solids content (see Tables 4.2 and 4.3).

4.5 Batch Mode Flotation Studies

4.5.1 Surfactant Requirements

4.5.1.1 Introduction

The surface characteristics of the ink solids in the printing ink wastewater are difficult to predict as the wastewater consists of a complex mixture of inks. The hydrophobicity of the solids
depends on the types of pigment present and their adsorbed dispersant (surfactant and polymer binder, see Section 2.2.2.2). Other surface characteristics such as size and charge are more predictable (see Sections 2.2.2.3 and 2.2.2.4). The pigment solids are negative in charge [47] and small in size with the average size being 0.2 μm [5, 34]. The addition of metal ion coagulant is necessary in order to flocculate the solids to a size that will allow collision with and attachment onto bubbles (see Section 2.3.2.2).

Although the wastewater already contains considerable quantities of surfactant, it is not clear whether this surfactant imparts hydrophobicity to the mixed pigment-hydrous metal oxide floc. As previously discussed (see Section 2.2.3.5), the dispersant surfactants are likely to render the pigment surface less hydrophobic and the hydrous metal oxide surface more hydrophobic (see Figure 2.8). Furthermore, the possibility also exists that some of the surfactant adsorbed on the pigment or the hydrous metal oxide solids may be stripped off the particles during interaction with the bubbles (see Section 2.3.2.1).

Regardless of whether the mixed pigment-hydrous metal oxide flocs are sufficiently hydrophobic for removal by flotation at the end of the flocculation stage, reliance on this level of hydrophobicity is likely to render the process susceptible to fluctuations in wastewater surfactant content. This level of hydrophobicity may also be insufficient for the establishment of a solids-stabilised foam (see Section 2.4.2). It may, therefore, be advantageous to add surfactant. The research reported in this section aims to address the issue of surfactant requirements for the removal of contaminants through flotation and for the formation of the clean draining solids-stabilised foam necessary for HLC mode flotation.

Three surfactants of different charge characteristics were investigated: cationic cetyl trimethylammonium bromide (CTAB), anionic sodium dodecyl sulphate (SDS) and non-ionic Teric G12A8.

4.5.1.2 Effect of Surfactant Types

CTAB has been widely used and studied in the modification of negatively charged solid surfaces such as silica [139, 140] and quartz [141]. CTAB is not sensitive to pH variations, the presence of polyvalent anions (e.g. sulphate) or high electrolyte concentrations in solution [142]. It has poor water solubility due to its long hydrophobic tail, thus ensuring high adsorption and maximum surface activity [143], and has a positively charged amine head group that can adsorb strongly on the negatively charged pigment surface groups such as the –COO⁻ functional group as a result of the large and negative ΔG°electrostatic (see equation [2.6]).
The disadvantage of using a cationic surfactant as a collector and/or a frother for printing wastewater, however, is that CTAB may react with the anionic dispersant surfactants present in the ink formulation through electrostatic attraction, resulting in the formation of insoluble surfactant salts, with both the surfactant types losing the ability to produce and stabilise a foam [93, 142].

One of the most widely used anionic surfactants for the flotation of commercial minerals [144, 145], dyes [36, 37, 38] and wastewater treatment [146, 91] is SDS. It is relatively inexpensive and its biodegradation products have low toxicity [147]. The advantage of using an anionic surfactant for printing ink wastewater is that it is less likely to react with the anionic surfactants present in the printing wastewater. The main disadvantage, however, in using SDS is that it has a similar charge to the pigments’ surface. It can also be easily displaced after adsorption onto surface sites by competing anions such as phosphate, fluoride, sulfate, perchlorate or thiocyanate [148]. Anionic electrolytes such as chlorides and hydroxides are commonly used as organic solvents in water-based inks [15].

Non-ionic surfactant can be very effective in lowering the solids surface charge through shielding [126]. Teric G12A8 is a polyethylene oxide derivative with a 12-carbon length chain incorporated with 8 ethylene oxide units (thereby designated G12A8). Teric G12A8 was found to be very effective (more so than CTAB or SDS) in adsorbing onto coal due to its high adsorption density on the negatively charged coal surfaces [149].

**Electrophoretic Mobility of Solids Prior to Surfactant Addition**

The influence of Fe(II) addition to various concentrations (up to 5 mM) on the EM of the solids contained in Sample 2 is shown in Figure 4.12.

![Figure 4.12: EM of solids contained in Sample 2 as a function of pH at various Fe(II) concentrations.](image_url)
In the absence of added Fe(II), the EM of the solids was found to be negative at all pH values, increasing in magnitude with increasing pH values, from $-1 \times 10^{-8}$ m$^2$/s/V at pH 4 to $-2 \times 10^{-8}$ m$^2$/s/V at pH 9. The solids remained well dispersed at all pH values tested.

The addition of Fe(II) was found to give rise to less negative EM values (see Figure 4.12). The extent of surface charge reduction was found to be greatest at lower pH values ($< 7$). This is consistent with the increase in positive EM values of the metal hydrous oxides with the decrease in pH [63] leading to more effective surface charge reduction.

**Flotation**

**System with High Concentrations of Metal Hydrous Oxide**

The flotation outcomes after the addition of Fe(II) to a concentration of 5 mM are shown in Figures 4.13 – 4.15 for 300 ppm CTAB, Teric G12A8 and SDS respectively.

*Figure 4.13:* Removal of contaminants for **Sample 2** as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

*Figure 4.14:* Removal of contaminants for **Sample 2** as a function of pH with 5 mM Fe(II) and 300 ppm Teric G12A8.
Despite the marked difference in surfactant functional groups and head group charges, the flotation outcomes are remarkably similar, suggesting that the lateral chain-chain interaction between the tails of the adsorbed surfactant molecules already on the solid and/or the interaction between the surfactant’s hydrophobic chain with the hydrophobic pigment surface play an important role as shown in Figure 2.11. The high removals achieved for liquid in cell for these systems throughout the pH levels conducted (> 90%, see Figures 4.13 – 4.15) suggests that the co-adsorption mechanism with head-down orientation onto the hydrous metal oxide solid is more prevalent than the tail-down adsorption mechanism onto the pigment surface.

A common feature of the flotation outcomes for the three different surfactant systems is that the highest achievable foam drainage removal was found to occur at pH values 6 – 7 (see Figures 4.13 – 4.15). The decrease in foam drainage quality at low pH values may be tentatively attributable to the low quantity of Fe(II) hydrous oxide solid present at these low pH values [62], resulting in a mixed floc with a higher proportion of pigment solids and hence, tail-down co-adsorption mechanism (see Figure 2.11) – leading to a more hydrophilic surface – is more prevalent. The decrease in foam drainage quality at high pH values, on the other hand, may be attributable to the high EM value of the mixed pigment-hydrous metal oxide solids, potentially leading to a mixed solid that is too small to stabilise a foam and hence, poor solids retention occurs within the foam. The importance of floc size to the flotation outcome is discussed in Section 4.5.2.3.

As well as the co-adsorption mechanism discussed above, the surfactants can also, of course, adsorb via direct electrostatic interaction with the surface. The mixed pigment-hydrous metal oxide floc is negatively charged at all pH values tested (see Figure 4.12), facilitating the adsorption of CTAB via this mechanism, particularly at high pH values.

Figure 4.15: Removal of contaminants for Sample 2 as a function of pH with 5 mM Fe(II) and 300 ppm SDS.
SDS adsorption via electrostatic interaction, however, would be expected to be minimal. Apart from the lateral chain-chain interactions in the co-adsorption mechanism (as illustrated in Figure 2.11), the adsorption of SDS (present in the form of \( \text{RSO}_4^- \)) may occur through intermediate polyvalent cations such as \( \text{Ca}^{2+} \) or \( \text{Al}^{3+} \), which are typically present in industrial wastewater or through adsorbing onto positive surface sites on the predominantly negative charged pigment solids. For example, at neutral pH level, the positive surface sites on pigment solids include the Al(III) oxide, used as a coating agent for titanium dioxide pigment, and Ca(II), present in high concentrations in process inks as clay extenders [42]. Extenders are incorporated into the ink to reduce the cost of the water-based inks while maintaining the solids content.

**System with Low Concentrations of Metal Hydrous Oxide**

The similarity of the removal curves for the three different surfactant types suggests co-adsorption of surfactant onto the hydrous metal oxide solids (see Figure 2.11) may play a major role in the flotation of the mixed pigment-hydrous metal oxide flocs. One of the questions arising from this interpretation of the results is what effect, if any, does the overall charge of the mixed pigment-hydrous metal oxide floc have on the flotation with the three different surfactant types. Knowledge of the role of solids surface charge will give valuable information on the roles of the metal ion coagulant and therefore the quantity required for each surfactant type. To answer this question, flotation was performed at lower hydrous metal oxide concentration. The resulting electrophoretic mobility is shown in Figure 4.12 and the flotation outcomes after the addition of Fe(II) to a concentration of 1.25 mM are shown in Figures 4.16 – 4.18 for 300 ppm CTAB, Teric G12A8 and SDS respectively.

At this lower Fe(II) concentration, the EM of the suspended solids was found to only be slightly less than in the absence of Fe(II). Despite this, good removals for the liquid in cell were observed for CTAB and Teric G12A8 (see Figures 4.16 and 4.17). For SDS, the removal for liquid in cell was not measured due to insufficient liquid quantity. The very low volume of liquid left in cell after the flotation run in the SDS system suggests high solution concentration of surfactants and/or poor floc hydrophobicity. This is consistent with lower SDS adsorption at lower Fe(II) concentrations due to greater electrostatic repulsion with the more negative mixed floc surface (see Figure 4.12).
**Figure 4.16:** Removal of contaminants for Sample 2 as a function of pH with 1.25 mM Fe(II) and 300 ppm CTAB.

**Figure 4.17:** Removal of contaminants for Sample 2 as a function of pH with 1.25 mM Fe(II) and 300 ppm Teric G12A8.

**Figure 4.18:** Removal of contaminants for Sample 2 as a function of pH with 1.25 mM Fe(II) and 300 ppm SDS.
(Note: No liquid left in cell after flotation run.)
The lower Fe(II) dose, however, had a greater effect on solids retention in the foam. For SDS and Teric G12A8 systems, lower Fe(II) concentrations were found to be detrimental to the flotation outcome, with their corresponding maximum foam drainage removals being 69% (at pH 6.5) and 84% (at pH 6) respectively (compare Figures 4.14 and 4.15 with Figures 4.17 and 4.18). A possible explanation for the poor solids retention is that the mixed pigment-hydrous Fe(II) oxide solids are too small – due to the large negative EM values – leading to spontaneous film rupture before a solids-stabilised foam can be formed (refer to Section 2.4.2 for discussion).

Flotation using CTAB, however, was found to be more effective at lower Fe(II) concentrations. The maximum removal at 5 mM Fe(II) was 93% whereas the maximum removal at 1.25 mM Fe(II) was 99%. This is consistent with higher CTAB adsorption (with head-down orientation, see Figure 2.10(b)) at lower Fe(II) concentrations due to greater electrostatic attraction with the more negative mixed floc surface (see Figure 4.12). The reversal in the orientation of the adsorbed anionic surfactant (onto the pigment surface) as depicted in Figure 2.10(b) can occur as a result of a large lateral chain-chain interaction force between the tails of the adsorbed surfactant molecules.

The presence of higher concentrations of Fe(II) (5 mM) can result in a less hydrophobic surface of the mixed floc if it is dominated by the hydrophilic hydrous oxides, leading to poorer particle-bubble attachment efficiency (lower removal for liquid in cell) and poorer solids retention in foam (lower removal for foam drainage).

**Conclusion – Effect of Various Charged Surfactants**

This study has highlighted the importance of tailoring the coagulant metal ion dose to the surfactant type. High doses of coagulant metal ion (5 mM) were found to reduce the surface charge sufficiently to allow the use of cationic, anionic or non-ionic surfactant. Reduction of coagulant dose to 1.25 mM was found to favour the use of cationic surfactant. On the basis of these results, and the need to keep the sludge volume to a minimum to minimise foam handling problems associated with excessive foam solids content (see Section 2.4.3), CTAB was chosen for further studies.
4.5.1.3 Optimisation of CTAB Concentration

Introduction

Surfactants are commonly added to a flotation system prior to flotation to facilitate a more hydrophobic solids’ surface, primarily to increase the particle to bubble attachment efficiency. Secondary gains in cationic surfactant adsorption onto printing wastewater are (i) enhancing further coagulation/flocculation of the mixed pigment-hydrous metal oxide solids through hydrophobic interaction force, and (ii) decreasing the negative EM value of the pigment surfaces leading to a decrease in the coagulant consumption.

Optimisation of Surfactant Concentration in Fe(II) Hydrous Oxide System

The purpose of this study is to gauge the CTAB requirement for samples with different suspended solids content after the addition of 1.25 mM Fe(II) at flotation pH 6.5. Two samples were selected for this study, i.e. Sample 2 (low suspended solids content, see Table 4.3) and Sample 3 (average suspended solids content). The 1.25 mM Fe(II) concentration level was chosen based on the samples’ optimised concentration levels from experiments conducted in Section 4.5.2.2 (see Figures 4.25 and 4.26) while pH 6.5 was found to achieve the highest overall removals for both low (1.25 mM) and high (5 mM) concentrations of added Fe(II) (see Figures 4.13 and 4.16). This CTAB requirement study was not conducted on Samples 1 and 4 as these samples have higher optimum Fe(II) concentration levels (5 mM and above 10 mM respectively, see Figures 4.24 and 4.27). The differences in Fe(II) dosage can influence CTAB requirement.

The flotation removals achieved with CTAB added to various concentrations up to 500 ppm are shown in Figures 4.19 and 4.20 for Samples 2 and 3 respectively. The volumes for the liquid in the flotation cell and the foam in the collection vessel at the end of the flotation run are shown in Table 4.6 (Sample 2) and Table 4.7 (Sample 3).
Figure 4.19: Removal of contaminants for Sample 2 as a function of CTAB concentration with 1.25 M Fe(II) at pH 6.5.

Figure 4.20: Removal of contaminants for Sample 3 as a function of CTAB concentration with 1.25 mM Fe(II) at pH 6.5.

Table 4.6: Flotation behaviour at various CTAB concentrations for Sample 2 at pH 6.5 with the addition of Fe(II) to a concentration of 1.25 mM.

<table>
<thead>
<tr>
<th>CTAB concentration (ppm)</th>
<th>Volume of liquid in cell (mL)</th>
<th>Foam volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>109</td>
<td>0.3</td>
</tr>
<tr>
<td>50</td>
<td>127</td>
<td>0.2</td>
</tr>
<tr>
<td>100</td>
<td>145</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>300</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>500</td>
<td>117</td>
<td>0.4</td>
</tr>
</tbody>
</table>
### Table 4.7: Flotation behaviour at various CTAB concentrations for Sample 3 at pH 6.5 with the addition of Fe(II) to a concentration of 1.25 mM.

<table>
<thead>
<tr>
<th>CTAB concentration (ppm)</th>
<th>Volume of liquid in cell (mL)</th>
<th>Foam volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67</td>
<td>0.6</td>
</tr>
<tr>
<td>50</td>
<td>79</td>
<td>0.4</td>
</tr>
<tr>
<td>100</td>
<td>89</td>
<td>0.2</td>
</tr>
<tr>
<td>300</td>
<td>83</td>
<td>0.4</td>
</tr>
<tr>
<td>500</td>
<td>83</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Sample 2**

In the absence of CTAB, foam can still be produced due to the presence of surfactants (mainly anionic and non-ionic surfactants) functioning as frothers in the samples. High removals were achieved for both the foam drainage (95%, see Figure 4.19) and the liquid in cell (98%) suggesting that the mixed pigment-hydrous metal oxide solids are sufficiently hydrophobic. The anionic surfactant is likely to adsorb with head-down orientation onto the positively charged hydrous metal oxide solid while the surfactant’s concentration at the pigment solids surface is decreased as illustrated in Figure 2.8. Both these actions lead to a more hydrophobic mixed pigment-hydrous metal oxide solid surface.

In the presence of low concentrations of CTAB (100 ppm), the removal for foam drainage decreases from 95% to 50% (see Figure 4.19) with poor solids retention and poor foam stability. The poor foam stability is reflected in (i) a lower final foam volume (< 0.1 L, see Table 4.6) and (ii) a higher final volume of liquid in cell (145 mL).

This foam instability at low CTAB concentrations may be due to the excessive solids hydrophobicity with the enhanced adsorption of anionic surfactants from the solution onto the solids’ surface through the lateral chain-chain interaction with the adsorbed cationic surfactant as illustrated in Figure 2.10(b). The increased hydrophobicity in the presence of CTAB is consistent with literature findings [54] that the above mode of adsorption was more prevalent in the presence of polyelectrolyte sodium polyacrylate (NaPA) than hemimicelle bilayer formation (see Figure 2.10(d)). In printing ink, polyelectrolyte polyacrylate is used as dispersing agent (see Figure 2.4). Copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and sodium methacrylate (MANa), for example, are used as dispersing agents for the aqueous dispersion of the white pigment titanium dioxide [150].
The foam instability may also be attributed to the decrease in surfactant concentration at the foam interfaces resulting from the reaction between the added CTAB and the anionic surfactants to form insoluble surfactant salts, resulting in the loss of both surfactants' ability to form and stabilise a foam [103]. CTAB precipitation is further addressed in Section 4.5.2.3.

The increase in CTAB concentrations above 100 ppm results in higher foam stability (reflected in the lower final volume of liquid in cell and the higher final foam volume, see Table 4.6) and higher solids retention in the foam (reflected in the higher foam drainage removal, see Figure 4.19). The high removal achieved for the liquid in cell at these high CTAB concentrations suggests that the increased foam stability is not due to a decrease in hydrophobicity. The observed foam stability and foam drainage removal trends are consistent with the precipitation of CTAB with the anionic surfactant present in the sample until all the available anionic surfactant is used up. CTAB addition in excess of this, give rise to increase adsorption at the air-liquid interface and greater foam stability.

Sample 3

In the absence of CTAB, the overall removal achieved was only 61% (see Figure 4.20) with relatively poor removals observed for both the foam drainage (29%) and the liquid in cell (93%) in comparison to those achieved for the lower suspended solids content Sample 2 (see Figure 4.19). The lower removals observed for both the foam drainage and the liquid in cell for Sample 3 (with a higher suspended solids content) may be attributed to (i) insufficient level of colloidal pigment flocculation with 1.25 mM Fe(II) coagulant in the absence of CTAB, and/or (ii) insufficient hydrophobicity level at the solids surface, i.e. the anionic surfactant's coverage at the pigment solids surface is not depleted enough to expose the more hydrophobic pigment surface (see Figure 2.8).

Similar to Sample 2, the presence of CTAB at low concentrations (100 ppm) resulted in a decrease in foam drainage removal from 29% to 17% but increased to above 95% removals upon the addition of CTAB to concentrations above 300 ppm. The destabilisation of the foam at low CTAB concentrations is reflected in (i) a lower final foam volume (0.2 L) and (ii) a higher final volume of liquid in cell (89 mL) as shown in Table 4.7. The effect of foam destabilisation is more prominent for the higher suspended solids content Sample 3 (compare Tables 4.6 and 4.7) with a lower foam drainage removal achieved. This may be attributed to the insufficient flocculation of colloidal pigment solids and/or higher anionic surfactant concentrations contained in Sample 3.
It is interesting to note that the increase in CTAB concentration from 300 to 500 ppm was found to decrease the volume of liquid in foam (see Table 4.8). Although the overall removals are similar, the flotation outcome was improved with the production of a ‘drier’ solids-stabilised foam. This is consistent with a higher solids hydrophobicity and the establishment of a solids-stabilised foam (see Section 2.4.2) at high CTAB concentrations, resulting in protrusion of the solids particles into the air phase and greater loss of water. It is also interesting to note that the reduction in foam liquid volume is less for the lower solids content Sample 2.

Table 4.8: A comparison of the liquid volumes in foam at CTAB concentrations of 300 ppm and 500 ppm at pH 6.5 with the addition of Fe(II) to its optimised concentration (1.25 mM).

<table>
<thead>
<tr>
<th>Sample</th>
<th>300 ppm CTAB</th>
<th>500 ppm CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volumes</td>
<td>Volumes</td>
</tr>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>2</td>
<td>38</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>83</td>
</tr>
</tbody>
</table>

A minimum CTAB concentration of 300 ppm was required to achieve overall removals above 95% in the flotation of printing ink wastewater Samples 2 and 3 with Fe(II) as coagulant. For these two samples, the sample to sample variability was minimised by adding CTAB concentrations above 300 ppm (see Figures 4.19 and 4.20). The issue of the CTAB and Fe(II) requirement at various wastewater solids content will be addressed again in Section 4.5.2.5.

Effect of Surfactant Concentration with Different Metal Hydrous Oxide Systems

The purpose of this study is to gauge the CTAB requirement for different metal ion coagulant (dosed to 1.25 mM) at flotation pH 6.5. This study was conducted with the low suspended solids content Sample 2. The 1.25 mM metal ion coagulant concentration level was chosen based on Sample 2’s optimised concentration levels from experiments conducted in Section 4.5.2.4 (see Figures 4.44 – 4.46) while flotation pH 6.5 was found to achieve the highest overall removals from experiments conducted in Section 4.5.2.3 (see Figures 4.36, 4.40 and 4.42). The flotation outcomes after the addition of one of Fe(II), Al(III) or Fe(III) to a concentration of 1.25 mM and CTAB to various concentrations up to 500 ppm are shown in Figures 4.21 – 4.23 respectively.
Figure 4.21: Removal of contaminants for Sample 2 as a function of CTAB concentration with 1.25 M Fe(II) at pH 6.5.

Figure 4.22: Removal of contaminants for Sample 2 as a function of CTAB concentration with 1.25 mM Al(III) at pH 6.5.

Figure 4.23: Removal of contaminants for Sample 2 as a function of CTAB concentration with 1.25 mM Fe(III) at pH 6.5.
Low foam drainage removals were found to occur at low CTAB concentrations (e.g. 100 ppm) in both the iron hydrous oxide systems (i.e. Fe(II) and Fe(III)). The low removals correspond to high foam instability are shown in Table 4.9 by (i) the lower foam volume, and (ii) the higher liquid volume in cell.

Table 4.9: Flotation behaviour at various CTAB concentrations for Sample 2 at pH 6.5 with 1.25 mM coagulant concentration.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>0 ppm CTAB</th>
<th>100 ppm CTAB</th>
<th>300 ppm CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volumes</td>
<td>Volumes</td>
<td>Volumes</td>
</tr>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam drainage (mL)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>35</td>
<td>109</td>
<td>0.3</td>
</tr>
<tr>
<td>Al(III)</td>
<td>37</td>
<td>109</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>38</td>
<td>111</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>117</td>
<td>0.3</td>
</tr>
</tbody>
</table>

It is interesting to note that foam destabilisation is not as pronounced for the Al(III) system. If the observed instability at 100 ppm CTAB was exclusively due to the formation of insoluble CTAB-anionic surfactant salts, the foam instability should be the same for all three hydrous metal oxide solid tested. The fact that foam destabilisation is not pronounced in the Al(III) system suggests that the hydrophobicity of the mixed pigment-hydrous metal oxide flocs in this system is less. The influence of hydrophobic solids on foam stability and on solids retention in the foam is discussed in Section 2.4.2.

For all three coagulant systems, the increase in CTAB concentration above 100 ppm increases the solids retention within the foam (reflected by the increased foam drainage removals, see Figures 4.21 – 4.23). The possible reasons for this are outlined in p.83. A minimum of 300 ppm CTAB is required to achieve overall removals above 95% for all three coagulant systems with Sample 2.

As previously discussed in p.84 where it was observed that the increase in CTAB concentration from 300 ppm to 500 ppm was found to improve the flotation outcome by producing a ‘drier’ solids-stabilised foam for two samples (of different suspended solids content) with Fe(II) system, similar observations were shown for other metal ion coagulant systems (see Table 4.10).
Table 4.10: A comparison of the liquid volumes in foam at CTAB concentrations of 300 ppm and 500 ppm for Sample 2 at pH 6.5 with 1.25 mM coagulant concentration.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>300 ppm CTAB</th>
<th>500 ppm CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volumes</td>
<td>Volumes</td>
</tr>
<tr>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Liquid in foam (mL)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>38</td>
<td>120</td>
</tr>
<tr>
<td>Al(III)</td>
<td>46</td>
<td>111</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>38</td>
<td>117</td>
</tr>
</tbody>
</table>

Conclusion – Optimisation of Surfactant Concentration

For Fe(II) system, a minimum CTAB concentration of 300 ppm is required to overcome the sample to sample variability as well as achieving removals above 95% for both foam drainage and liquid in cell for all the samples tested. At lower CTAB concentrations (e.g. 100 ppm), the foam was found to be unstable. This was attributed to the loss of the sample’s ability to produce and stabilise a foam due to the reduced surfactant concentration (at the air-liquid interface) as a result of the formation of insoluble CTAB-anionic surfactant salts. This foam instability was found to be greater for the higher solids content sample suggesting that high solids hydrophobicity may also be a contributing factor to this instability. At CTAB concentrations above 300 ppm, a ‘drier’ and more compact solids waste were produced.

The optimum CTAB concentration was found to be similar for all three coagulant systems tested, i.e. 300 ppm. The flotation responses for these systems at various CTAB concentrations were generally similar although there was a variation in the extent of foam instability at low CTAB concentration (100 ppm). The foam instability was found to be less pronounced for Al(III) system than Fe(II) or Fe(III) systems. Overall, no distinct advantages can be observed between the three coagulants tested.

4.5.2 Metal Hydrous Oxide Requirements

4.5.2.1 Introduction

The results presented in Section 4.5.1.2 showed that for Sample 2, flotation with CTAB is best performed at low coagulant dose (1.25 mM). This sample, however, is particularly low in suspended solids content (see Table 4.3). In the first section (Section 4.5.2.2), the flotation response for this sample will be compared to that of other samples with higher solids content, using varying quantities of Fe(II) coagulant. In Section 4.5.2.3, the results of Section 4.5.2.2
will be used to select a coagulant dose for a more in-depth study of the influence of pH on the surface charge characteristics and flotation behaviour of printing ink wastewater using Fe(II), Fe(III) or Al(III) as coagulant. In Section 4.5.2.4, the influence of coagulant dose (Fe(II), Fe(III) or Al(III)) will again be assessed at two different pH values on one sample. The aim of this study is to investigate the influence of coagulant addition in excess. Finally, in Section 4.5.2.5, the influence of solids content on the optimum coagulant dose is investigated. This section also includes the investigation into the possibility of overcoming the detrimental effect if the coagulant dose is added in excess.

4.5.2.2 Optimisation of Fe(II) Hydrous Oxide Concentration

Introduction

The primary function of a coagulant is to alter the surface charge of the suspended solids in the wastewater so that they are large enough to be separated easily through physical means such as flotation. One of the challenges in treating industrial wastewater is determining the optimum coagulant concentration required for this purpose. Insufficient coagulant concentration can result in inadequate charge reduction leading to small colloidal solids that can be detrimental towards the flotation outcome. Excessive coagulant concentration above the optimum concentration level increases the amount of waste solids for disposal and may cause charge reversal at the solid’s surface (to positive charge) leading to poorer CTAB adsorption (see Section 4.5.1.2). Also, high concentrations of metal hydrous oxides can change the surface characteristics of the mixed solids, potentially leading to a less hydrophobic surface and hence, higher surfactant concentration may be necessary.

The aim of this section is to determine the optimum coagulant concentration for each samples as well as the minimum coagulant concentration that will treat most wastewater samples. The optimum coagulant concentration depends on types and quantity of pigment present, the ionic strength and the pH levels at which the wastewater samples are treated. Flotation pH 6.5 was chosen for this study as the flotation at this pH was found to yield the highest overall removals for both low (1.25 mM) and high (5 mM) concentrations of added Fe(II) in the presence of CTAB (see Section 4.5.1.2) while Fe(II) was found to give the best overall performance with CTAB as surfactant (see Section 4.5.2.3). A CTAB concentration of 300 ppm was used for each sample prior to flotation as the concentration level was found to result in high overall removals for low to average suspended solids content wastewater (see Section 4.5.1.3).
Effect of Fe(II) Hydrous Oxide Concentration

The flotation outcomes after the additions of Fe(II) to various concentrations and CTAB to a concentration of 300 ppm at flotation pH 6.5 are shown in Figures 4.24 – 4.27 for Samples 1 – 4 respectively.

**Figure 4.24:** Removal of contaminants in foam drainage for Sample 1 as a function of Fe(II) concentration with 300 ppm CTAB at pH 6.5.
(Note: No liquid left in cell after flotation run.)

**Figure 4.25:** Removal of contaminants for Sample 2 as a function of Fe(II) concentration with 300 ppm CTAB at pH 6.5.
Figure 4.26: Removal of contaminants for Sample 3 as a function of Fe(II) concentration with 300 ppm CTAB at pH 6.5.

Figure 4.27: Removal of contaminants for Sample 4 as a function of Fe(II) concentration with 300 ppm CTAB at pH 6.5.

**Liquid in cell**

In the absence of Fe(II), the contaminant removals for liquid in cell were found to remain above 90% for Samples 2, 3 and 4, indicating that the solids are sufficiently large and hydrophobic for particle-bubble attachment (see Section 2.3.2.2). The removal for liquid in cell was not measured for Sample 1 due to insufficient liquid quantity.

In the presence of Fe(II), the removals were found to decrease slightly with the increase in Fe(II) concentration, especially when Fe(II) was added to concentrations above the level where maximum overall removals were achieved. The decrease in removals is greater for the low suspended solids content Sample 2 (from 97% to 78% as Fe(II) is increased to 10 mM, see Figure 4.25), followed by a smaller decrease for the average suspended solids content Sample 3.
The decreased removals with increase in Fe(II) concentration indicate a poorer particle to bubble attachment efficiency, most likely a result of the mixed pigment-hydrous Fe(II) oxide solids’ surface properties becoming increasingly dominated by the less hydrophobic hydrous Fe(II) oxide solids. Lower suspended solids content sample (e.g. Sample 2) is more susceptible to the detrimental effect of high concentrations of Fe(II) than higher suspended solids content sample (e.g. Sample 4) due simply to their lower pigment surface area. The lower surface hydrophobicity is also reflected in the increased foam volume and a higher liquid entrainment (hence, less liquid left in cell) as shown in Table 4.11. A higher CTAB concentration may be required to impart hydrophobicity (through the co-adsorption mechanism, see Figure 2.11) in circumstances where high concentrations of Fe(II) are added.

Table 4.11: Flotation behaviour at various Fe(II) concentration for Sample 3 at pH 6.5 with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Fe(II) conc. (mM)</th>
<th>0</th>
<th>1.25</th>
<th>2.5</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid in cell volume (mL)</td>
<td>87</td>
<td>80</td>
<td>66</td>
<td>66</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>Foam volume (L)</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Foam drainage**

In the absence of Fe(II), the removals for foam drainage vary from 1% to 85% in the following order – Samples 1, 4, 3, and 2. This correlates with the decreases in suspended solids content and ionic strength in the respective wastewater samples (see Tables 4.2 and 4.3), with higher foam drainage removals achieved in lower suspended solids content and lower ionic strength samples.

Low foam drainage removals and the relatively high removals for liquid in cell, achieved for higher suspended solids content and higher ionic strength samples (e.g. Sample 4, see Figure 4.27) suggest that even in the absence of Fe(II), the solids are of sufficient size and hydrophobicity for attachment to bubbles (see Section 2.3.2.2) but not for the establishment of a solids-stabilised foam (see Section 2.4.2).

The optimum Fe(II) concentration for good solids retention in the foam was found to increase with the sample’s suspended solids content (see Table 4.3). Despite the lower solids hydrophobicity at Fe(II) concentrations above the optimum concentration (indicated by the
decrease in removal for the liquid in cell), an increase in Fe(II) dosage above the optimum concentration was not found to affect the solids retention in the foam, i.e. the foam drainage removals remained constant. This result suggests that high solids hydrophobicity may not be the major determinant in achieving high foam drainage removals.

**Optimum Fe(II) concentration**

The optimum Fe(II) concentrations were found to vary between 1.25 mM to above 10 mM Fe(II) as shown in Table 4.12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optimum Fe(II) conc. (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>2</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>1.25</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

The optimum Fe(II) concentration was found to increase with the sample’s suspended solids content (see Table 4.3) and is consistent with the expected higher coagulant concentration required for sufficient flocculation of solids (for flotation purposes) in higher suspended solids content/higher ionic strength samples (e.g. Samples 1 and 4).

The minimum Fe(II) concentration required to treat 3 of the 4 wastewater samples tested (to overall removals above 90%) was found to be approximately 5 mM. This includes samples with up to above average suspended solids content (i.e. Samples 2, 3 and 4, see Table 4.3). At 5 mM Fe(II), the flotation of high suspended solids content Sample 1 was found to yield an overall removal of only 77%.

**4.5.2.3 Single Metal Hydrous Oxide System**

**Introduction**

The use of inorganic metals such as Al(III), Fe(III) and Fe(II) as coagulants is common in water purification and wastewater treatment systems [9, 16, 17, 63]. This section involves studies on the influence of pH on (i) the surface charge characteristics, (ii) the solubility of coagulants, (iii) the CTAB adsorption, and (iv) the flocculation behaviour of printing ink wastewater Sample 2, for each of these coagulants.
These results were then compared with the flotation behaviour observed for Sample 2 with each of these three coagulants. The influence of pH on the flotation behaviour for Samples 1, 3 and 4 was also determined and compared to that of Sample 2. The coagulant dose used in this experiment was 5 mM, a coagulant concentration that allowed good removal of contaminants (>90%) from most wastewater samples (i.e. excluding samples with very high suspended solids loading such as Sample 1) using Fe(II) as coagulant based on experiments conducted in Section 4.5.2.2. The CTAB concentration used was the optimum dose for the flotation of Samples 2 and 3 using 1.25 mM Fe(II) at pH 6.5 (see Section 4.5.1.3).

**Electrophoretic Mobility of Solids**

The influence of coagulant (Fe(II), Al(III) or Fe(III)) and CTAB additions to concentrations of 5 mM and 300 ppm respectively on the EM of the solids contained in Sample 2 are shown in Figures 4.28 – 4.30 respectively. As expected, both the additions of the coagulants and CTAB give rise to less negative EM values.

![Graph: Electrophoretic Mobility of Solids](image)

*Figure 4.28:* EM of solids contained in Sample 2 as a function of pH with subsequent additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively. (Note: Between pH 4 and 6 for 5 mM Fe(II) with 300 ppm CTAB, the EM of the solids is negligible. It is not shown in the graph due to inability to conduct measurements at such low mobility.)
Figure 4.29: EM of solids contained in Sample 2 as a function of pH with subsequent additions of Al(III) and CTAB to concentrations of 5 mM and 300 ppm respectively.

Figure 4.30: EM of solids contained in Sample 2 as a function of pH with subsequent additions of Fe(III) and CTAB to concentrations of 5 mM and 300 ppm respectively.

At all pH values under investigation, in the absence of CTAB, the changes in the negative EM values of the mixed pigment-hydrous metal oxide solids were found to be similar for all the three coagulants tested (compare Figures 4.28 – 4.30). This findings contradicted the results by Black and Willems [69] who found that the trivalent metal hydrous oxides (Al(III) and Fe(III)) were more effective coagulants than the divalent metal hydrous oxide (Fe(II)).

It should be noted that although the net effect on the mixed floc’s EM value is similar, the mechanisms of action for these coagulants can be very different (see Section 2.2.3.4). For Al(III) and Fe(III) systems, it is likely that the destabilisation of the colloidal pigment solids mainly occurs through the heterocoagulation of hydrous metal oxide solids with the pigment rather than the adsorption or surface precipitation of the metal ions (e.g. Fe$^{3+}$ or Al$^{3+}$) or their hydrous oxide complexes (e.g. Fe(OH)$^{2+}$, Fe(OH)$_2^+$ or Al(OH)$^{2+}$). Firstly, the solubility of
hydrous oxides of Al(III) is negligible between pH 5 and 9 while the solubility is negligible throughout the pH values investigated (i.e. between pH 5 and 10) for the hydrous oxides of Fe(III) [62]. Secondly, within these low solubility pH values, the opportunity for adsorption or surface precipitation of metal ions or their hydrous oxide complexes may be limited due to the rapid formation (within seconds) of amorphous precipitates (e.g. FeO(OH) and Fe₂O₃·nH₂O for Fe(III), Al(OH)₃ and AlO(OH) for Al(III)) upon the addition of the coagulant [61, 65, 151].

For the Fe(II) system, the mechanism responsible for the decrease in EM is not clear due to the many forms of Fe complexes that can be formed during hydrolysis and oxidation. In addition, the surface characteristics of Fe(II) hydrous oxides are considerably more complex than the hydrous oxides of Al(III) or Fe(III) due to the low degree of hydrolysis (before precipitation) and the slow rate of oxidation to Fe(III) [62]. In the presence of oxidants, some or all of the Fe(II) may be converted to Fe(III) depending on the solution pH and the quantity of oxidants in the wastewater. The rate of oxidation is faster at neutral and alkaline pH values [152]. Other hydrous oxide complexes may be generated during the oxidation process that have both Fe(II) and Fe(III) within its complex structure such as the intermediate complex Green Rust [70]. The surface characteristics and precipitation behaviour of the Fe(II) hydrous oxides upon addition to wastewater is therefore difficult to predict. They are, however, likely to be somewhere between those of Fe(OH)₂ and those of Fe(OH)₃; Fe(II) precipitates at pH values above 7 with minimum solubility at pH 10 – 11 and an isoelectric point (IEP) of 12, whereas Fe(OH)₃ precipitates at pH values above 3 with minimum solubility at pH 4 – 10 and an IEP of 7 [44, 62]. The lower rate of oxidation and the higher Fe(II) solubility at pH values below 7 [62] suggests that at these pH values, the adsorption or surface precipitation of metal ions or their hydrous oxide complexes onto the pigment surface through electrostatic attraction is the main coagulation mechanism. Above pH 7 where the hydrous Fe(II) oxide precipitates and the oxidation rate to Fe(III) is faster, the destabilisation of the colloidal pigment solids is also likely to occur through the heterocoagulation of Fe(II) and/or Fe(III) hydrous oxide solids with the pigment.

The changes in EM of the mixed pigment-hydrous metal oxide solids for Al(III) or Fe(III) systems in the presence of 300 ppm CTAB were found to be similar over the pH values investigated (see Figures 4.28 – 4.30), with the point of zero charge (pzc) at the solid surface occurring at approximately pH 7. Below pH 7, charge reversal (to positive surface charge) was observed at the solids’ surface indicating that CTAB adsorption occurs even when the electrostatic interaction is not favourable. CTAB adsorption above that required for charge neutralisation may be attributed to the lateral chain-chain interaction (as indicated in Section 4.5.1.2) and/or specific chemical interactions with surface sites. Above pH 7, based on the large negative EM values of the mixed pigment-hydrous metal oxide solids (< −1 x 10⁻⁹ m²/s/V), it is
likely that the CTAB adsorbs with head-down orientation through electrostatic attraction (see Figure 2.10(b)).

For the Fe(II) system, in the presence of 300 ppm CTAB, the decrease in the negative EM values below pH 8 for the mixed pigment-hydrous Fe(II) oxide solids is less than those found in both the Al(III) or the Fe(III) systems (compare Figures 4.28 – 4.30). No charge reversal was observed. At pH values less than 6, the EM values of the solids are negligible (with a very slight negative surface charge). The smaller decrease suggests poorer CTAB adsorption in the Fe(II) system than in the Al(III) or Fe(III) systems at these pH values and/or is attributable to a difference in adsorption mechanism for Fe(II) system due to its higher solubility.

The predominant coagulation mechanism for Fe(II) at low pH values (< 7) is tentatively the adsorption of Fe(II) ions or their hydrous oxide complexes onto the pigment surface (as discussed in p.95). The adsorption of CTAB onto the mixed pigment-hydrous metal oxide solids may have caused a net desorption of Fe(II) ions (or their hydrous oxide complexes) from the solids through an ion-exchange mechanism, possibly as a result of unfavourable electrostatic interaction and high Fe(II) solubility. The desorption of Fe(II) ions or their hydrous oxide complexes is reflected in the presence of Fe(II) in the solution below pH 8 (see Figure 4.31) and the small change in EM of the solids upon the addition of CTAB (see Figure 4.28). Adsorption via ion-exchange mechanism may not be detectable through EM measurement as there may not be any net charge difference as a result of this adsorption. This mode of adsorption would also be likely to impart hydrophobicity to the surface as it results in head-down surfactant adsorption, whereas adsorption that is driven by chain-chain interaction can impart hydrophobicity or hydrophilicity depending on the orientation of the surfactant molecules already present on the surface (see Section 2.2.4.2).

Another possible explanation for the smaller decrease in the negative EM value upon CTAB addition for Fe(II) system is the co-adsorption of negatively charged ions such as hydroxides, chlorides or sulfates commonly found in water-based inks [15].

Evidences of both the adsorption of counter ions and desorption of co-ions has been documented for other pigment system. Pochard et al. [159] found that the adsorption of barium ions onto hematite induces the desorption of sodium ions (co-ions) and coadsorption of chloride ions (counter ions).
Concentration of Metal Ions in Solution

The EM values in the presence of CTAB were found to be very different for Al(III) and Fe(III) systems compared to the Fe(II) system (compare Figures 4.28 – 4.30). It is suggested that the ion-exchange mechanism where the Fe(II) ions or their hydrous oxide complexes are replaced by the CTAB ions at the negative pigment surface sites may have contributed to the smaller decrease in EM values for Fe(II) system. Al(III) and Fe(III), on the other hand, heterocoagulate with the pigment solids and therefore, cannot be displaced by CTAB ions, as reflected in the larger change in EM values upon CTAB addition. To gain more information regarding the role hydrous metal oxide species/solids may be playing in the adsorption of CTAB, solubility studies of the metal ions or their hydrous oxide complex species were conducted by measuring the concentration of these in the wastewater after coagulant and CTAB addition. The results are shown in Figure 4.31.

![Figure 4.31: Concentration of coagulant metal ions in solution in Sample 2 as a function of pH with 5 mM coagulant and 300 ppm CTAB.](image)

The hydrous oxides of Al(III) have negligible solubility in the 5 – 9 pH range, present mainly in the form of the ‘amorphous’ states of Al(OH)$_3$ and AlO(OH). The presence of soluble metal ions above pH 9 is attributed to the formation of the anionic complex species, Al(OH)$_4^-$ [62]. The hydrous oxides of Fe(III) exhibited negligible solubility over the pH range investigated, present predominantly in the solid ‘amorphous’ state of Fe(OH)$_3$ and is found in two precipitate states of Fe$_3$O$_4$.nH$_2$O and FeO(OH) [65]. The negligible solubility of hydrous oxides of both Al(III) and Fe(III) implies that coagulation of colloidal pigment solids occurs mainly through heterocoagulation. CTAB adsorption in this pH range is therefore unlikely to involve exchange of positive metal species.
For Fe(II), the amount of soluble Fe(II) species is low above pH 8. The solubility curve of this system is similar to the solubility curve of Fe(II) in a solution saturated with Fe(OH)$_2$ at 1 M and 25°C [62]. The low solubility above pH 8 and the high rate of oxidation to Fe(III) [152] suggest that colloidal destabilisation is most likely due to the heterocoagulation of the hydrous oxides with the pigment solids. At these pH values, similar to Al(III) and Fe(III) systems, the adsorption of CTAB is unlikely to be via ion exchange mechanism involving positive metal species.

At pH values below 6, however, where both the precipitation of Fe(II) and the rate of oxidation to Fe(III) are low, the decrease in EM (see Figure 4.28) may be due to – apart from CTAB adsorption – the adsorption of positively charged Fe(II) species such as Fe$^{2+}$ and FeOH$^-$ onto the negative surface sites of the pigment solids. The lack of charge reversal and high Fe(II) solubility observed at low pH values in the presence of CTAB suggests the possibility, amongst others, of CTAB adsorption via an ion-exchange mechanism at the expense of the positively charged Fe(II) species as previously discussed in p.96.

The high Fe solubility at low pH values can potentially lead to a treated effluent that has a low pigment residue but high Fe concentration. Below approximately pH 7.5, the Fe concentration in the solution is above the 30 ppm legal limit for Fe discharge to sewer [138].

**CTAB Adsorption/Precipitation**

The primary functions of CTAB are two-fold, to facilitate foam formation (as a frother) and to increase the particle-bubble attachment efficiency (as a collector) during flotation. It was found in Section 4.5.1.3 that high initial foam destabilisation occurred at low CTAB concentration of 100 ppm for all the three coagulant systems tested (see Figures 4.21 – 4.23). It was also suggested that this foam destabilisation could be a result of either excessive solids hydrophobicity or reaction between the added CTAB and the anionic surfactants to form insoluble surfactant salts. Valuable information pertaining to the solids hydrophobicity and the extent of insoluble surfactant salts formation can be gained by measurement of CTAB concentration in solution. The quantity of CTAB present in the solution after equilibration in the presence of the mixed pigment-hydrous metal oxide solids after the addition of coagulant and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 4.32. The CTAB concentration resulting from the addition of CTAB (to 300 ppm with respect to Sample 2) to the filtrate of Sample 2 without coagulant addition is also shown in Figure 4.32.
For all three coagulants in the presence of pigment solids, the amount of CTAB in the solution was found to be negligible at all pH values. This suggests that the role of CTAB is primarily as a collector as its concentration in the solution is too low to contribute towards the frothing ability of the wastewater.

![CTAB concentration in solution for Sample 2 as a function of pH with 5 mM coagulant and 300 ppm CTAB.](image)

**Figure 4.32:** CTAB concentration in solution for **Sample 2** as a function of pH with 5 mM coagulant and 300 ppm CTAB.

As previously discussed in Section 4.5.1.3, the foam stability in the absence of CTAB (see Tables 4.6 and 4.7) showed that the surfactants present in the printing ink wastewater (anionic and non-ionic) can function as frothers.

The addition to 100 ppm CTAB concentration, however, was found to result in foam instability. The low CTAB concentration in the presence of 300 ppm CTAB system shown in Figure 4.32 suggests that this foam instability may be due to high hydrophobicity. It is also important to note, however, that the adsorption of CTAB onto the pigment solids is not the only mechanism by which the CTAB concentration in solution can be depleted. Filtration of the solids with a 0.45 μm Millipore membrane filter before the addition of CTAB to a level of 300 ppm (see Figure 4.32) revealed that between 90 and 145 ppm of the CTAB had precipitated in the absence of solids, possibly due to CTAB reacting with the anionic surfactants present, and/or bulk or surface precipitation as its solubility is reduced in the presence of electrolytes. This amount of precipitated CTAB is consistent with the high foam destabilisation encountered at 100 ppm CTAB for all three coagulant systems tested (see Figures 4.21 – 4.23), i.e. insufficient amount of surfactants to counter the destabilisation effect on the foam by the large hydrophobic solids.
Floc Size

A major role of the added hydrous metal oxides in wastewater treatment by flotation process is to alter the surface charge of the solids to be removed thereby aiding in the flocculation of these solids. Floc size has been found to influence both the efficiency of particle-bubble attachment [114] and foam stability [153]. The average size of the mixed pigment-hydrous metal oxide solids contained in Sample 2 after the additions of coagulant and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 4.33. A comparison of the relative sizes of the mixed pigment-hydrous Fe(II) oxide solids at different pH values is shown in Figure 4.34.

For the Al(III) and Fe(III) systems, the largest average size of the mixed pigment-hydrous metal oxide solids for the three coagulants was achieved at pH 6.5 – 7 and decreased gradually as the pH deviated from 6.5 – 7. Comparison of the floc size with the EM values (see Figures 4.28 – 4.30) showed that the maximum floc size occurs when the EM values of the mixed pigment-hydrous metal oxide solids are small, i.e. $\pm 0.7 \times 10^{-8}$ m$^2$/s/V. The sizes and EM values of the mixed pigment-hydrous metal oxide solids for Al(III) and Fe(III) (see Figures 4.29 and 4.30) are similar throughout the pH values investigated. These similarities, along with the low solubility in the measured pH range and precipitation within seconds upon addition further suggests that the coagulation mechanism is similar, i.e. heterocoagulation, as previously discussed at p.97.

![Figure 4.33: Average floc size in Sample 2 as a function of pH with 5 mM coagulant and 300 ppm CTAB.](image-url)
In contrast, the average size of the mixed pigment-hydrous Fe(II) oxide solids for Fe(II) is about 29 to 68% larger at pH range 6 – 8 than those found in Al(III) and Fe(III) systems. Comparison of the floc size with the EM values of the Fe(II) system showed the expected decrease in floc size with increasing pH and EM values at pH above 7. The floc size at pH values below 7, however, is difficult to explain in terms of the EM values. Between pH values 4 and 6, for example, the EM was found to be close to zero, yet the floc size decreases considerably with decreasing pH. Comparison of the floc size data with the precipitation data (see Figure 4.31) reveals that the increase in floc size may be due to increasing quantities of hydrous metal oxide solid present with increasing pH between 4 and 6. Interestingly, the maximum floc size occurs under conditions where most but not all of the Fe(II) has precipitated. This suggests that the adsorption of Fe$^{2+}$, Fe(OH)$^+$ and/or other hydrous oxide complexes onto the pigment solid’s surface may also be involved. This concords with Licsko’s [61] finding that ionic adsorption is a major mechanism responsible for the destabilisation of the colloidal particulates in the surface water.
Single Metal Hydrous Oxide Flotation

Fe(II) Hydrous Oxide System

The flotation outcomes after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively are shown in Figures 4.35 – 4.38 for Samples 1 – 4 respectively.

**Figure 4.35:** Removal of contaminants for **Sample 1** as a function of **pH** with 5 mM Fe(II) and 300 ppm CTAB.
(Note: No liquid left in cell after flotation run).

**Figure 4.36:** Removal of contaminants for **Sample 2** as a function of **pH** with 5 mM Fe(II) and 300 ppm CTAB.
Figure 4.37: Removal of contaminants for Sample 3 as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: Foam drainage removal at pH 9 is –42%).

Figure 4.38: Removal of contaminants for Sample 4 as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: Foam drainage removal at pH 9 is –59%).

Liquid in cell

Despite the considerable differences in the wastewater characteristics as shown in Tables 4.2 – 4.4, a similar pattern in the flotation characteristics was observed for Samples 2, 3 and 4. The contaminant removal for liquid in cell was found to remain above 90% throughout the range of pH tested, suggesting that the solids are sufficiently hydrophobic. This may be attributed to the adsorption of CTAB with head-down orientation onto the negative adsorption sites of the solids surfaces (see Figure 2.10(b)), and is consistent with the change in EM of the solids upon CTAB addition (see Figure 4.28) and the negligible CTAB concentration in the solution (see Figure 4.32). The removal for liquid in cell could not be measured for Sample 1 as all the liquid was carried over with the foam.
**Foam drainage**

The highest achievable removal for foam drainage was found to occur at the same pH value (6.5) for Samples 2, 3 and 4. This is in spite of the marked differences in the metal contents of these samples (see Table 4.4) – an indication of the considerable difference in both types and quantities of the pigments present. This suggests that the surface characteristics of the solids are dominated by the hydrous oxides of Fe(II), possibly by forming a coating of hydrous oxides. James and Healy [154] have presented evidence which indicates that the adsorption of soluble hydrolysis products leads to the formation of a layer or a partial layer of hydroxide precipitates on the solids surface.

Comparison of the floc size data (see Figure 4.33) and the corresponding foam drainage removal for Sample 2 (see Figure 4.36) suggests a strong correlation between the floc size and the foam solids retention. The higher the floc size the greater the foam drainage removal. The high foam drainage removal (or effective solids retention within foam) and large flocs at pH 6.5 is consistent with the collection of high concentrations of large flocs in the liquid separating the bubbles in the foam, such that the approach of the two films to the critical distance for film rupture is delayed or does not occur (see Section 2.4.2). The size of the flocs can also be a useful visual indicator that may be used for trouble shooting as well as more effective process control during a flotation operation.

Sample 1 behaved differently to the other samples. The curve for Sample 1 is rather flat at the top with a maximum removal of only 77% at pH 6.5 and a more pronounced decrease in removal above pH 6.5. In view of the relatively high solids and suspended solids content in Sample 1 (see Table 4.3), the lower removal can be tentatively attributed to a higher coagulant and/or surfactant requirement than was used in these experiments (i.e. 5 mM Fe(II) and 300 ppm CTAB).

The removals achieved in foam drainage were found to decrease markedly with increasing pH values above 6.5 for all samples. This corresponds to the decrease in the floc sizes (see Figure 4.33) and an increase in the surface charges (see Figure 4.28). Below pH 6.5, the foam drainage removals were found to decrease with the decrease in pH values. This corresponds to a reduction in the floc sizes (see Figure 4.33) and decreasing quantities of adsorbed or precipitated Fe(II) hydrous oxide (see Figure 4.31).
Sensitivity to pH

The rate of decrease in contaminant removals with increasing pH above 6.5 was found to be greater for the high solids content/high ionic strength samples (compare Figures 4.35 – 4.38). Sample 1, which had a high solids content and a high ionic strength, was found to exhibit a dramatic decrease in flotation effectiveness with increasing pH above 6.5 from 77% at pH 7 to negligible removal at pH 8. For Sample 2, which had a low solid content and a low ionic strength, a removal of 86% was maintained even at pH 8. This is consistent with the expected higher demand for coagulant and/or surfactant by samples with a higher solids content [64].

Liquid entrainment

The high solids content/high ionic strength samples were also found to exhibit considerably higher levels of liquid entrainment in the foam. The achieved contaminant removals and volumes for the liquid in cell and the foam drainage at optimum flotation pH (6.5) are shown in Table 4.13.

Table 4.13: Flotation behaviour at optimum pH (6.5) with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TSS (g/L)</th>
<th>Conductivity (µS)</th>
<th>Liquid in cell</th>
<th>Foam drainage</th>
<th>Overall removal (%)</th>
<th>Effluent recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Volume (mL)</td>
<td>Removal (%)</td>
<td>Volume (mL)</td>
<td>Removal (%)</td>
</tr>
<tr>
<td>1</td>
<td>46.8</td>
<td>1060</td>
<td>0</td>
<td>-</td>
<td>75</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>360</td>
<td>120</td>
<td>92</td>
<td>42</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>11.3</td>
<td>880</td>
<td>66</td>
<td>94</td>
<td>76</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>16.2</td>
<td>1060</td>
<td>58</td>
<td>94</td>
<td>88</td>
<td>91</td>
</tr>
</tbody>
</table>

a the total sample volume was 180 mL.
b effluent recovery = 100% x (combined volumes of liquid in cell and foam drainage)/total sample volume.

A comparison of the amount of liquid in cell shows that the amount of liquid carried over with the foam increases with increasing solids content and ionic strength. The observed amount of liquid entrainment is consistent with the destabilisation of the newly formed foam in the flotation cell at low solids concentration and the stabilisation of this foam at high solids content. Stabilisation of the foam at high solids content is a result of the formation of closely packed solids physically separating the air-liquid interfaces, retarding or preventing coalescence [127].
Effluent recovery

The effluent recovery is an indication of the proportion of the treated wastewater relative to the initial wastewater volume. A high effluent recovery is therefore desirable and the primary aim in any wastewater treatment system. From Table 4.13, a comparison of the effluent recovery shows that the amount recovered decreases with increasing solids content and ionic strength. These results highlight the need for extensive dewatering of the foam product for high solids content samples. This level of dewatering is not possible when using conventional mode flotation processes as the high solids content leads to channeling and foam overturning in the foam at low foam water contents [133]. These problems are not encountered in HLC mode flotation and the resulting solids-stabilised foam can survive extensive dewatering [41]. The issue of effluent recovery will be addressed further in Section 4.6.5.3.

Fe concentration in effluent

The optimum flotation pH (6.5) coincides with residual Fe ions in the effluent (see Figure 4.31) for the 5 mM Fe(II) system. It is therefore important to monitor the Fe concentration in the treated effluents to ensure compliance with the discharge limit of 30 ppm for this metal [138]. This experiment was conducted with Fe(II) dosage of 5 mM, the optimum Fe(II) concentration found in Section 4.5.2.2 to result in good contaminant removals (>90%) for most wastewater samples. The Fe concentrations found in the combined effluents (i.e. foam drainage and liquid in cell) for Samples 2, 3 and 4 are shown in Table 4.14.

Table 4.14: Fe ion concentration in the combined effluent at optimum pH (6.5) with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>47</td>
</tr>
</tbody>
</table>

The Fe concentrations for all the three samples tested were found to be above the 30 ppm allowable discharge limit for Fe ions [138]. Despite its effectiveness in removing the solid contaminants from most wastewater samples, flotation conducted with 5 mM Fe(II) at pH 6.5 results in the treated effluent containing a high concentration of Fe ions.
**Al(III) Hydrous Oxide System**

The flotation outcomes after the addition of Al(III) and CTAB to concentrations of 5 mM and 300 ppm respectively are shown in Figures 4.39 and 4.40 for Samples 1 and 2 respectively. Samples 1 and 2 were chosen based on their unusually high and low solids’ content respectively, to obtain an indication of the effectiveness of Al(III) hydrous oxide as a coagulant.

![Graph showing removal of contaminants for Sample 1 as a function of pH with 5 mM Al(III) and 300 ppm CTAB.](image)

**Figure 4.39:** Removal of contaminants for **Sample 1** as a function of **pH** with 5 mM Al(III) and 300 ppm CTAB.
(Note: No liquid left in cell after flotation run).

![Graph showing removal of contaminants for Sample 2 as a function of pH with 5 mM Al(III) and 300 ppm CTAB.](image)

**Figure 4.40:** Removal of contaminants for **Sample 2** as a function of **pH** with 5 mM Al(III) and 300 ppm CTAB.

**Liquid in cell**

Similar to the Fe(II) flotation system (see Figure 4.36), the removals for liquid in cell for Sample 2 (see Figure 4.40), remained high at all pH values investigated below pH 9, indicating
that the solids are sufficiently hydrophobic. At pH 10, however, the removal for the liquid in cell decreases to 70%. This may be attributable to the partial dissolution of the Al(III) hydrous oxide (see Figure 4.31) to form an anionic complex species, Al(OH)$_4^-$.

The dissolution of Al(III) hydrous oxide precipitate, combined with the change in its surface charge above pH 9 (IEP = 8.8, [155]), lead to poor flocculation of ink solids (see Figures 4.33) which, in turn, leads to the decreased flotation efficiency (see Figure 4.40).

**Foam drainage**

The foam drainage removal curve – in the flotation of Sample 2 – for Al(III) system (see Figure 4.40) is similar to that for Fe(II) system (see Figure 4.36), with the highest removals achieved at pH 6 – 6.5. These removals correspond to low positive EM values (< 1 x 10$^{-8}$ m$^2$/sV, see Figure 4.29) and the largest mixed pigment-hydrous Al(III) oxide solids (see Figure 4.33). The removals achieved for foam drainage were found to decrease as the pH deviated further from pH 6 – 6.5. This corresponded to the decrease in floc sizes and an increase in surface charge.

For Sample 1, the optimum flotation pH is below 5 (see Figure 4.39). This represents a shift towards a more acidic pH compared to the optimum pH (6) for Sample 2. A possible reason for this is that the high solids content/high ionic strength sample requires higher concentrations of Al(III) to achieve adequate flocculation of the fine solids. This is consistent with the results reported by Hodgson and Fernandez [5] and Stumm and O’Melia [156] which indicate the existence of a stoichiometric relationship between the solids concentration and the optimum coagulant concentration.

The poorer foam drainage removals in the flotation of Sample 1 for Al(III) system (see Figure 4.39) compared to those achieved for Fe(II) system (see Figure 4.35) below pH 7 suggests that the extent of coagulation in Fe(II) system is greater than that achieved in Al(III) system (note the similarity in trends for foam drainage removals and floc sizes with pH, compare Figures 4.33, 4.36 and 4.40). This indicates that heterocoagulation alone (between hydrous Al(III) oxide solids and colloidal pigment) is not as effective in increasing pigment sizes compared to those achieved for Fe(II) system, i.e. a combination of heterocoagulation (between hydrous Fe(II) oxide solids and colloidal pigment) and adsorption (e.g. Fe(OH)$^+$ onto pigment surface). The differences in foam drainage removals (and the level of coagulation) are most prevalent between pH 6 and 7 where the solubility of Fe(II) ions is not too high (compared to < pH 6) while above pH 7, heterocoagulation becomes prevalent as the rate of oxidation to Fe(III) increases with increase in pH [152].
Fe(III) Hydrous Oxide System

The flotation outcomes after the additions of Fe(III) and CTAB to concentrations of 5 mM and 300 ppm respectively are shown in Figures 4.41 and 4.42 for Samples 1 and 2 respectively.

**Figure 4.41**: Removal of contaminants for **Sample 1** as a function of pH with 5 mM Fe(III) and 300 ppm CTAB. (Note: No liquid left in cell after flotation run).

**Figure 4.42**: Removal of contaminants for **Sample 2** as a function of pH with 5 mM Fe(III) and 300 ppm CTAB.

**Liquid in cell**

The contaminant removals for liquid in cell remained above 90% at all pH levels above 6.5, consistent with the results achieved for both the Fe(II) and the Al(III) systems (compare Figures 4.36, 4.40 and 4.42) and the expected lower initial foam destabilisation ability by the decreasing floc size with increasing pH (see Figure 4.33).
It is, however, interesting to note that below pH 6, in contrast to the results obtained for Fe(II) or Al(III) systems, lower removals were observed for Sample 2 (compare Figures 4.42, 4.36 and 4.40). The low removals below pH 6 are not due to unfavourable EM values since these EM values are found to be similar to those in Al(III) system (compare Figures 4.29 and 4.30) where high liquid in cell removals were observed (see Figure 4.40). The low removals can also not be attributed to the hydrophobicity, as CTAB adsorption and precipitation (see Figure 4.32) for Fe(III) system was found to be similar to Fe(II) or Al(III) where high removals were observed (see Figures 4.36 and 4.40).

**Foam drainage**

It is interesting to note that low removals were observed for foam drainage for Sample 2 at pH values above 6, where the surface charge of the mixed pigment-hydrous Fe(III) oxide solids is negative. This is in spite of the relatively large flocs between pH 6 and 7 (see Figure 4.33), low solubility of hydrous metal oxide between pH 4 and 10 (see Figure 4.31) and apparent hydrophobicity (see Figures 4.30 and 4.32) that were important parameter requirements for the achievement of high solids retention within the foam (see Section 2.4.2). The foam volume data shown in Table 4.15 reveals that the low removals can be attributed to poor foam stability. Above pH 6, the volume of foam remaining at the end of the experiment was found to be extremely low. The foam instability is also reflected in the high liquid volumes left in the cell after the flotation run (155 mL or 86% of the influent volume).

**Table 4.15:** Flotation behaviour for **Sample 2** with 5 mM Fe(III) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>pH</th>
<th>Foam drainage (mL)</th>
<th>Liquid in cell (mL)</th>
<th>Foam (L)</th>
<th>Foam drainage (%)</th>
<th>Liquid in cell (%)</th>
<th>Overall (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>68</td>
<td>67</td>
<td>1.4</td>
<td>93</td>
<td>85</td>
<td>89</td>
</tr>
<tr>
<td>5.5</td>
<td>59</td>
<td>92</td>
<td>0.6</td>
<td>94</td>
<td>71</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
<td>100</td>
<td>0.4</td>
<td>92</td>
<td>83</td>
<td>86</td>
</tr>
<tr>
<td>6.5</td>
<td>10</td>
<td>155</td>
<td>0.05</td>
<td>26</td>
<td>96</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>154</td>
<td>0.05</td>
<td>18</td>
<td>97</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>153</td>
<td>0.1</td>
<td>14</td>
<td>98</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>153</td>
<td>0.2</td>
<td>15</td>
<td>97</td>
<td>92</td>
</tr>
</tbody>
</table>

For Sample 1, the flotation response in Fe(III) system (see Figure 4.41) is similar to that found in Al(III) system (see Figure 4.39) with the optimum flotation pH below 5, representing a shift towards a more acidic pH than the optimum pH for Sample 2 (between 6.5 and 8, see Figure 4.42). As discussed in Al(III) system, p.106, the high solids content/high ionic strength sample
may require higher concentrations of Fe(III) for adequate flocculation of ink solids at neutral pH values [5, 156].

It is interesting to note the differences in flotation outcome as Fe(III) concentrations are varied (compare Figures 4.23 and 4.42 for 1.25 and 5 mM Fe(III) respectively) while other process variables are kept constant (i.e. 300 ppm CTAB at pH 6.5). The increase in the amount of hydrous Fe(III) oxide solids was found to cause foam destabilisation. The reason for this foam destabilisation is not clear. The influence of hydrous metal oxide concentration on the flotation outcome will be addressed further in Section 4.5.2.4.

**Foam Liquid Solids Concentration**

The concentration of solids in the liquid left in the drained foam at the end of the experimental run gives an indication of the foam’s ability to retain the removed solids while liquid drains. A combination of high foam liquid solids concentration and good foam drainage removal indicates good solids retention. On the other hand, a combination of high foam liquid solids concentration and poor foam drainage removal indicates that the foam is overloaded with solids, i.e. inadequate bubble surface area to support the solids contained within the foam, and the unattached solids are washed during liquid drainage. A high foam liquid solids concentration is an indication of high hydrophobicity, with greater loss of water at equilibrium position of the three-phase boundaries on either side of the solids as found in Section 4.5.1.3 where a ‘drier’ foam was achieved as the CTAB concentration was increased from 300 to 500 ppm. A high foam liquid solids concentration can also indicate that the flocs are large in size as less liquid volume is trapped at the periphery of the solids surface. The foam liquid solids concentration for the three coagulants after the additions of coagulant and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 4.43.

![Figure 4.43: Foam liquid solids concentration for Sample 2 as a function of pH with 5 mM coagulant and 300 ppm CTAB.](image)
The highest foam liquid solids concentration was found to occur between pH 5.5 and 6.5 for the Fe(II) system. This corresponds to low solids EM value (see Figure 4.28), large floc size (see Figure 4.33) and high Fe(II) solubility (see Figure 4.31). This concentration decreases as the pH increases above 7, corresponding to high negative solids EM value, small floc size and low Fe(II) solubility. Higher foam liquid solids concentration at pH values where the flocs are large in size is consistent with less liquid volume at the periphery of a smaller solids surface area.

The foam liquid solids concentration for Al(III) system is lower than the other two systems throughout the pH range tested. Although the solids retention within the foam as well as the foam drainage removals are good between pH 5 and 7 (see Figure 4.40), the foam has a relatively high water content potentially resulting in a large sludge volume for disposal. The highest foam liquid solids concentration occurs between pH 8 and 9. This is consistent with a more hydrophobic solid surface than those found at lower pH values. These results suggest that CTAB adsorption, indicated by the large change in EM value at pH value below 7 (see Figure 4.29), was largely in tail-down orientation, resulting in lower solids hydrophobicity.

A similar trend to that observed with the Al(III) system, was observed for the Fe(III) system. In this system, however, the effect is more pronounced. Between pH 7 and 9, the high foam liquid solids concentration, the poor foam drainage removal and the low foam volume generated (see Table 4.15) suggest that the initial foam destabilisation by hydrophobic solids is excessive under these conditions, leading to low foam carryover volume and high liquid in cell volume. The foam carryover is highly loaded with solids and these solids are easily washed from the foam by the drainage of liquid from the fresh foam above.

**Conclusion – Single Metal Hydrous Oxide Flotation**

The surface characteristics of the mixed pigment-hydrous metal oxide solids in the Fe(II) system were found to be different from those in Al(III) or Fe(III) systems. No charge reversal was observed at low pH values for the solids in Fe(II) system (see Figure 4.28) in the presence of CTAB. The solids in Al(III) and Fe(III) systems, on the other hand, exhibit a charge reversal to positive charge below pH 7 and a larger change in EM value (than found in Fe(II) system) upon CTAB addition.

The increase in Fe(II) solubility with the decrease in pH level below pH 8 (see Figure 4.31) suggests that adsorption of Fe(II) ions and their hydrous oxide complexes onto the pigment solids at these pH values played an important part in the coagulation of colloidal pigment.
Above pH 8, the low Fe(II) solubility and the increase in oxidation rate to Fe(III) may result in heterocoagulation being the predominant coagulation mechanism. The coagulation mechanism for Al(III) and Fe(III) systems, on the other hand, is most likely through the heterocoagulation of the hydrous metal oxide with the pigment solids and this is reflected in the low solubility levels for both Al(III) and Fe(III) between pH 5 and 10.

The floc sizes for the three coagulant systems were found to be largest between pH 6.5 and 7 (see Figure 4.33). The flocs decrease in size as the pH deviates from 6.5 – 7. The large flocs correspond to conditions where the EM values are small (see Figures 4.28 – 4.30). At these pH values, the solids contained in Sample 2 in Fe(II) system were found to be between 29 to 68% larger than those found in Al(III) or Fe(III) systems. The adsorption of Fe(II) ions and/or their hydrous oxide complexes onto the pigment solids was suggested as a possible contributing factor to the more effective coagulation.

A reduction of CTAB concentration from 300 ppm to negligible amounts (see Figure 4.32) was found to occur through adsorption and/or precipitation onto the mixed pigment-hydrous metal oxide solid in Sample 2. Approximately 1/3 of the added CTAB was removed from the solution, in the absence of wastewater solids by precipitation. The formation of insoluble CTAB-anionic surfactant salts was suggested as the likely source of this precipitation. The resulting poor foam stability of the newly formed foam at low CTAB concentrations was found to lead to poorer removal. Excess quantities of CTAB were required to restore foam stability and removal.

The surface characteristics data and the flotation results showed that the best foam drainage removal for all the three coagulant systems corresponded to conditions when the solids’ EM value is small and the flocs are large. Large flocs and small solids’ EM values, however, do not always lead to high foam drainage removal as found in the flotation of Sample 2 with Fe(III) as coagulant (see Figure 4.42). The foam instability, giving rise to poor foam solids retention was attributed to excessive solids hydrophobicity in this system.

The results presented in this section showed that the flotation is more effective in Fe(II) system than the flotation in Al(III) or Fe(III) systems for the flotation of printing ink wastewater in HLC mode. The optimum flotation pH for the Fe(II) system (6.5) was found to be similar for all the wastewater samples tested (see Figures 4.35 – 4.38). These wastewater samples represented a wide variation in terms of the suspended solids content (low, average, above average and high TSS) and the ionic strength (see Tables 4.2 and 4.3). A constant optimum flotation pH presents a distinct advantage in wastewater treatment where optimised process
conditions are usually governed by the wastewater characteristics, which changes over time. The optimum flotation pH for Al(III) or Fe(III) systems, however, differs from sample to sample, with lower optimum pH for higher suspended solids content and higher ionic strength sample (compare Figures 4.39 and 4.40, 4.41 and 4.42). A distinct disadvantage for Fe(II) system, however, is the high Fe(II) solubility at the optimum flotation pH (6.5), resulting in a high Fe concentration in solution (see Table 4.14).

Even when the flotation performance is similar (with overall removals of 91 – 92%) as shown in Table 4.16 for Sample 2, Fe(II) system exhibits a better overall flotation characteristic in terms of foam volume produced, foam stability, solids retention within foam and effluent recovery. These characteristics are important for future considerations such as running the flotation system in continuous mode and/or upscaling to an industrial sized process.

Table 4.16: Flotation behaviour for Sample 2 with 5 mM coagulant and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Volume</th>
<th>Removal</th>
<th>Effluent recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>40</td>
<td>120</td>
<td>0.4</td>
</tr>
<tr>
<td>Al(III)</td>
<td>85</td>
<td>45</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>10</td>
<td>155</td>
<td>0.05</td>
</tr>
</tbody>
</table>

* effluent recovery = 100% x (combined volumes of liquid in cell and foam drainage)/total sample volume (180 mL).

From Table 4.16, for the Fe(II) system, the foam volume after the flotation run is manageable at 0.4 L, the solids retention within the foam is high (93% foam drainage removal) and 89% effluent recovery. Although the flotation with Al(III) produces a foam with high solids retention (89% foam drainage removal), the large foam volume (1.4 L) can be difficult to manage, especially in larger scale treatment processes. In addition, the effluent recovery is comparatively low (72%), i.e. the liquid in the foam does not drain out as effectively, potentially leading to a large volume of wet sludge for disposal. For the flotation with Fe(III), the effluent recovery (92%) is the highest amongst the three coagulants tested. In spite of this, the foam produced is very unstable leading to a low foam carryover volume (hence, high liquid in cell volume – 155 mL) and poor solids retention within the foam (26% foam drainage removal). The flotation characteristics shown for Fe(III) system are not suitable for conducting flotation in HLC mode due to poor solids retention within foam and poor foam stability.
4.5.2.4 Effect of Metal Hydrous Oxide Concentration with Different Metal Hydrous Oxide Systems

In Section 4.5.2.2, the Fe(II) concentration requirement was found to vary between 1.25 and > 10 mM, increasing with the increase in ionic strength and suspended solids content (see Tables 4.2 and 4.3). The variation in the coagulant requirement over time and between sample batches causes difficulty in operating a flotation process at optimum level, especially in continuous mode. A minimum Fe(II) concentration of 5 mM was found to be able to treat most wastewater samples to overall removals above 90% (see Section 4.5.2.2). This concentration can, however, be above the optimum requirement level and therefore, detrimental towards the flotation outcome. This detrimental effect was especially evident from the liquid in cell removals (e.g. Samples 2 and 3, see Figures 4.25 and 4.26). The aim of this section is to investigate and compare the effect of excess coagulant dose on the flotation outcome for the three coagulants tested.

Flotation pH 6.5

The flotation outcomes after the additions of Fe(II), Al(III) or Fe(III) to various concentrations and CTAB to a concentration of 300 ppm at pH 6.5 are shown in Figures 4.44 – 4.46 respectively. Flotation pH 6.5 was chosen for this study in Fe(II) and Al(III) systems because this pH level was found to yield maximum overall removals in the flotation of Sample 2 for these two coagulants (see Section 4.5.2.3) while for Fe(III) system, although higher removals can be achieved at pH 6.5, pH 6 was chosen due to the higher solids retention within foam (see Figure 4.42). A CTAB concentration of 300 ppm was dosed on each sample prior to flotation as the concentration level was found to result in overall removals above 95% in the flotation of Sample 2 for all the three coagulant systems tested (see Section 4.5.1.3).

All three coagulant systems exhibit a similar flotation outcome pattern as a function of the coagulant concentration. The increase in the coagulant concentration increases the foam drainage removals but decreases the removals for the liquid in cell. Also, the optimum coagulant concentration required in the flotation of Sample 2 is similar, i.e. 1.25 mM.
Figure 4.44: Removal of contaminants for Sample 2 as a function of Fe(II) concentration with 300 ppm CTAB at pH 6.5.

Figure 4.45: Removal of contaminants for Sample 2 as a function of Al(III) concentration with 300 ppm CTAB at pH 6.5.
(Note: The foam drainage removal at 10 mM Al(III) system is –56%, see also Table 4.17)

Figure 4.46: Removal of contaminants for Sample 2 as a function of Fe(III) concentration with 300 ppm CTAB at pH 6.0.
(Note: The foam drainage removal at 10 mM Fe(III) system is –3%, see also Table 4.17)
**Liquid in cell**

In spite of the similarities in trends and the required optimum concentrations, the flotation behaviour for these systems can be very different. For example, the differences in the detrimental effect of coagulant concentrations added in excess to the flotation outcome as shown in Table 4.17.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Removal for liquid in cell (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.25 mM coagulant conc.</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>95%</td>
</tr>
<tr>
<td>Al(III)</td>
<td>99%</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>97%</td>
</tr>
</tbody>
</table>

The detrimental effect of high coagulant concentrations on the liquid in cell removals was minimal at high Fe(II) concentrations. Fe(III) and Al(III), on the other hand, recorded larger decreases and the reason for this decrease in removal, as previously discussed in Section 4.5.2.3, is not clear. The detrimental effect of 5 mM Fe(II) concentration on lower suspended solids content (than Sample 2) will be addressed in Section 4.5.2.5.

An 8-fold excess of Al(III) or Fe(III) decreases the removals for liquid in cell from 99% and 97% to −56% and −3% respectively (see Table 4.17). Fe(II) was the least affected with the corresponding removals decreasing to 78%. These results are consistent with a decrease in hydrophobicity with increased coagulant doses as the surface characteristics are increasingly dominated by the presence of the hydrophilic hydrous metal oxide. This data also suggests that the flocs in the Fe(II) system at high coagulant dose are more hydrophobic than those found in the Al(III) or Fe(III) systems. The lower hydrophobicity is reflected in larger foam volumes for Al(III) and Fe(III) systems, leading to a higher liquid entrainment (hence, less liquid left in cell) as shown in Tables 4.18 and 4.19 respectively. It is also interesting to note that both the increase in foam volume and the decrease in liquid in cell volume above the optimum coagulant concentration are not gradual, especially for Al(III) and Fe(III) systems. For example, the foam volume increases from 0.5 L to 1.4 L as the Al(III) is increased from 2.5 mM to 5 mM (see Table 4.18).
Table 4.18: Foam volume at various coagulant concentrations for Sample 2 at either pH 6.5 (for Fe(II) and Al(III)) or pH 6 (for Fe(III)) with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Foam volume (L) at various coagulant conc. (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 mM</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.7</td>
</tr>
<tr>
<td>Al(III)</td>
<td>0.7</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 4.19: Liquid in cell volume at various coagulant concentrations for Sample 2 at either pH 6.5 (for Fe(II) and Al(III)) or pH 6 (for Fe(III)) with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Liquid in cell volume (mL) at various coagulant conc. (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 mM</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>84</td>
</tr>
<tr>
<td>Al(III)</td>
<td>84</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>84</td>
</tr>
</tbody>
</table>

Foam drainage

The foam drainage removal was found to increase slightly with the increase in coagulant concentration for the three coagulants tested (see Figures 4.44 – 4.46). The lower hydrophobicity in Al(III) or Fe(III) systems, as suggested from the liquid in cell data (see Figures 4.45 and 4.46), does not lead to poorer solids retention within the foam. The lower hydrophobicity, however, leads to an increase in both the foam volume (see Table 4.18) and the effluent retention within the foam, potentially resulting in a foam sludge that is very wet and low in suspended solids concentration as shown in Figure 4.47.

Figure 4.47: Foam liquid solids concentration for Sample 2 as a function of coagulant concentration with 300 ppm CTAB at either pH 6.5 (for Fe(II) and Al(III)) or pH 6 (for Fe(III)).

The increase in the foam liquid solids concentration as the coagulant concentration is added to its optimum concentration can tentatively be attributed to the increase in floc size, destabilising
the foam at low solids concentration and stabilising the foam at high solids concentration. Above the optimum concentration level, the foam liquid solids concentration decreases with the increase in coagulant concentration. This is consistent with a lower solids’ hydrophobicity, i.e. decreased protrusion of the solid particles into the air phase leading to smaller loss of liquid as previously discussed in Section 4.5.1.3.

**Flotation pH 8**

In this section, the flotation of Sample 2 was conducted at pH 8 with Fe(II), Al(III) and Fe(III) added to various concentrations up to 10 mM and CTAB to a concentration of 300 ppm and the flotation outcomes are shown in Figures 4.48 – 4.50 respectively. Flotation at pH 8 was chosen for this study because this pH level was found to yield maximum removals for liquid in cell for all the three coagulants tested (see Figures 4.36, 4.40 and 4.42). The corresponding flotation behaviour is shown in Tables 4.20 – 4.22.

![Figure 4.48: Removal of contaminants for Sample 2 as a function of Fe(II) concentration with 300 ppm CTAB at pH 8.](image)

**Figure 4.49: Removal of contaminants for Sample 2 as a function of Al(III) concentration with 300 ppm CTAB at pH 8.**
Figure 4.50: Removal of contaminants for Sample 2 as a function of Fe(III) concentration with 300 ppm CTAB at pH 8.

<table>
<thead>
<tr>
<th>Fe(II) conc. (mM)</th>
<th>Volumes</th>
<th>Removals</th>
<th>Effluent recovery a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>0</td>
<td>104</td>
<td>20</td>
<td>1.8</td>
</tr>
<tr>
<td>1.25</td>
<td>52</td>
<td>89</td>
<td>1.1</td>
</tr>
<tr>
<td>2.5</td>
<td>28</td>
<td>129</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>120</td>
<td>0.3</td>
</tr>
<tr>
<td>7.5</td>
<td>56</td>
<td>91</td>
<td>0.6</td>
</tr>
<tr>
<td>10</td>
<td>63</td>
<td>79</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\[ \text{Effluent recovery } a = 100\% \times \frac{\text{(combined volumes of liquid in cell and foam drainage)}}{\text{total sample volume (180 mL)}.} \]

Table 4.21: Flotation behaviour at various Al(III) concentrations with 300 ppm CTAB at pH 8.

<table>
<thead>
<tr>
<th>Al(III) conc. (mM)</th>
<th>Volumes</th>
<th>Removals</th>
<th>Effluent recovery a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>0</td>
<td>104</td>
<td>20</td>
<td>1.8</td>
</tr>
<tr>
<td>1.25</td>
<td>21</td>
<td>135</td>
<td>0.4</td>
</tr>
<tr>
<td>2.5</td>
<td>15</td>
<td>148</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>55</td>
<td>95</td>
<td>0.6</td>
</tr>
<tr>
<td>7.5</td>
<td>60</td>
<td>86</td>
<td>0.8</td>
</tr>
<tr>
<td>10</td>
<td>61</td>
<td>74</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\[ \text{Effluent recovery } a = 100\% \times \frac{\text{(combined volumes of liquid in cell and foam drainage)}}{\text{total sample volume (180 mL)}.} \]
Table 4.22: Flotation behaviour at various Fe(III) concentrations with 300 ppm CTAB at pH 8.

<table>
<thead>
<tr>
<th>Fe(III) conc. (mM)</th>
<th>Volumes</th>
<th>Removals</th>
<th>Effluent recovery a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>0</td>
<td>104</td>
<td>20</td>
<td>1.8</td>
</tr>
<tr>
<td>1.25</td>
<td>40</td>
<td>105</td>
<td>0.7</td>
</tr>
<tr>
<td>2.5</td>
<td>18</td>
<td>132</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>155</td>
<td>0.1</td>
</tr>
<tr>
<td>7.5</td>
<td>33</td>
<td>129</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>46</td>
<td>110</td>
<td>0.6</td>
</tr>
</tbody>
</table>

a effluent recovery = 100% x (combined volumes of liquid in cell and foam drainage)/total sample volume (180 mL).

**Overall removal**

For all three coagulant systems investigated, the optimum coagulant concentration was found to be 2.5 mM (see Figures 4.48 – 4.50). This is double the coagulant required for flotation at pH 6.5 (see Figures 4.44 – 4.46). Also, the corresponding level of removals achieved at pH 6.5 (97% average maximum removals) is higher than that achieved at pH 8 (94% average maximum removals). The higher coagulant concentration required at pH 8 is consistent with the decrease in positive charge of the hydrous metal oxide complexes and hydrous metal oxides solids at higher pH level, leading to a decrease in coagulant effectiveness [63]. In addition, the larger negative EM value at pH 8 in the absence of any coagulants (see Figure 4.12) necessitates a larger surface charge reduction for flocculation than at pH 6.5.

**Liquid in cell**

Removals for liquid in cell increased until the optimum coagulant concentration was reached. This is consistent with an increasing floc size leading to increased particle-bubble attachment efficiency. The lower removals at coagulant concentrations above the optimum level are consistent with a decrease in hydrophobicity as the surface characteristics were increasingly dominated by the presence of the hydrous metal oxides. A 4-fold excess of Fe(II), Al(III) or Fe(III) decreases the removals for liquid in cell to 57%, 40% and 78% respectively (see Tables 4.20 – 4.22). Interestingly, the lower sensitivity of the Fe(II) system to increase in Fe(II) concentration seen at pH 6.5 (see Table 4.17) does not exist at pH 8. This suggests that the main flocculation mechanism for all three systems is similar, i.e. heterocoagulation with the pigment solids, reflected by their low solubilities (see Figure 4.31) and the high rate of oxidation to Fe(III) for Fe(II) hydrous oxide [152].
Foam drainage

The foam drainage removal was found to increase with the increase in coagulant concentration for Fe(II) and Al(III) systems. This is consistent with the results observed for those systems at pH 6.5 (see Figures 4.44 and 4.45). It is interesting to note the differences in behaviour observed for Fe(III) system, i.e. the sharp decrease in foam drainage removal between 2.5 and 5 mM Fe(III) concentration. This decrease corresponds to a high liquid in cell volume and a low resultant final foam volume, suggesting excessive foam destabilisation by the large hydrophobic solids immediately after foam formation and before the conditions leading to solids-stabilised foam can be achieved. The reason for this excessive foam destabilisation for Fe(III) system (and not found in Fe(II) or Al(III) systems), however, is not clearly understood.

For the Fe(II) and Al(III) systems, the increase in coagulant concentration – to an optimum level (i.e. 2.5 mM coagulant concentration) – can result in an increase in floc size through charge reduction of the solids (at pH values < IEP of the metal hydrous oxide) and/or through creating a surface that is less hydrophobic (than the pigment solids’ surface) for possible CTAB (as well as other surfactants) adsorption with head-down orientation (see Figure 2.10(b)). The increased floc size and/or hydrophobicity destabilises the foam at low solids concentration (reflected in the lower foam and liquid in cell volumes, see Tables 4.20 – 4.22) and stabilises the foam at high solids concentration, resulting in increase in both the foam drainage removal and the effluent recovery while the foam volume decreases (see Tables 4.20 and 4.22). Increases in both the foam drainage removal and the effluent recovery are reflected in the increase in the foam liquid solids concentration as shown in Figure 4.51.

![Graph showing foam liquid solids concentration for different coagulant concentrations](image)

**Figure 4.51:** Foam liquid solids concentration for Sample 2 as a function of **coagulant concentration** with 300 ppm **CTAB** at **pH 8**.
The increase in coagulant concentration above the optimum level was found to correspond to a decrease in the foam liquid solids concentration. This may be due to a decrease in the hydrophobicity of the mixed pigment-hydrous metal oxide solids, leading to a foam sludge that is very wet and low in suspended solids content.

For the Fe(III) system, the excessive foam destabilisation found at 5 mM Fe(III) concentration (see Figure 4.50) corresponds to a high foam solids liquid concentration and a low foam drainage removal. This indicates that the foam’s ability in retaining the suspended solids while effluent drains out is limited, possibly due to the high initial foam destabilisation leading to insufficient foam carryover volume which the solids can attach to. These unattached solids will be washed from the foam by the liquid drainage from the fresh foam above. In spite of this, 92% effluent recovery and 93% overall removal were achieved (see Table 4.22), i.e. this condition may be suitable for conventional mode flotation but not HLC mode flotation. A comparison of the two flotation techniques will be conducted with the results obtained in continuous mode in Section 4.6.5.3.

For the Fe(II) and Al(III) systems, although the solids retention within the foam and the foam drainage removal increases with coagulant concentration, the removals are still low (90% and 78% for Fe(II) and Al(III) respectively at 10 mM coagulant concentration, see Tables 4.20 and 4.21) compared to those achieved at pH 6.5 (96% and 93% at 1.25 mM coagulant concentration, see Figures 4.44 and 4.45). A lower foam drainage removal is an indication of a smaller resultant floc size (compare Figures 4.33 and 4.36), i.e. flocculation is less effective at pH 8. A higher coagulant dosage is, therefore required to increase the foam drainage removal and this can result in a higher sludge volume as well as a higher CTAB concentration required to maintain the surface hydrophobicity for flotation purposes. This highlights the disadvantages for conducting flotation in HLC mode at pH 8.

**Conclusion – Effect of Metal Hydrous Oxide Concentration**

In real industrial printing wastewater, the variability in types and concentrations of the ink components in the wastewater over time (see Tables 4.2 – 4.4 and Figure 4.1) cannot be predicted in advance. Thus, it is impossible to implement a wastewater treatment system that can operate at or close to the optimum coagulant concentrations at all times. The ideal coagulant dose is one that will coagulate the finely dispersed solids at most solids concentration range, i.e. a dose that is in excess of the optimum requirement most of the time.
In this regard, Fe(II) was found to hold a significant advantage over Al(III) or Fe(III) in that it had a much lower detrimental effect on the flotation outcome when added in excess of the minimum requirement. This was attributed to the lower concentration of hydrous metal oxide solids generated and the higher metal ion concentration remaining in solution (due to high Fe(II) solubility, low oxidation rate to Fe(III), and poor Fe(II) adsorption when the EM value of the pigment solid is small or positive) at pH 6.5 for the Fe(II) system. Therefore, the increase in Fe(II) dose in excess does not lead to the generation of large quantities of positively charged, hydrophilic hydrous metal oxide solids compared to Al(III) or Fe(III) systems, thereby leading to a mixed pigment-hydrous metal oxide solid that is more hydrophobic and better removal achieved for liquid in cell. A drawback of the Fe(II) system compared to the Al(III) or Fe(III) systems, however, is its high solubility at pH 6.5 (see Figure 4.31) leading to a treated effluent that is high in Fe (see Table 4.14). High Fe(II) dosages (e.g. 10 mM) are likely to result in very high concentrations of soluble Fe and therefore, should be avoided.

In spite of the high Fe concentration in the treated effluent for Fe(II) system, Fe(II) was chosen ahead of Al(III) or Fe(III) as coagulant for future flotation experiments due to the many advantages as outlined above. The problem associated with high Fe concentration in the treated effluent warrants further investigation.

Flotation pH 6.5 was found to be more suitable for HLC mode flotation compared to pH 8 as less coagulant was required (1.25 mM and 2.5 mM at pH 6.5 and 8 respectively). This was attributed to a higher coagulant effectiveness at reducing the negative charge of the solid at lower pH values. In addition, the average maximum removals that can be achieved for the three coagulants tested at pH 6.5 (97%) are higher than the corresponding removals at pH 8 (94%).

4.5.2.5 Effects of Solids Content on Flotation Behaviour

Introduction

The 4 samples studied were found to have different coagulant requirements. The optimum coagulant dose for high solids content samples was higher than for low solids content samples (see Section 4.5.2.2). It was also found that the addition of large quantities of coagulant to low solids content samples could be detrimental (see Section 4.5.2.4). These findings make the selection of a coagulant dose that will be able to treat both high and low solids samples difficult. The aim of this study is to confirm the earlier findings relating coagulant dose to solids content and to investigate the possibility of overcoming the detrimental effect of the use of coagulant dose that is higher than required for low solids samples (but optimum for high solids samples).
by increasing the surfactant concentration. In order to eliminate other variables that may complicate the results, such as anionic surfactant content and pigment type, this study was conducted on one sample. Sample 2 was pre-treated according to Table 4.23 to low, medium and high solids content and then floated at various Fe(II) and CTAB doses.

**Table 4.23:** Solids content and pre-treatment procedure in low, medium and high solids content for Sample 2.

<table>
<thead>
<tr>
<th>Pre-treatment of Sample 2</th>
<th>Dilution of original wastewater with the supernatant from centrifugation (0.6 g/L suspended solids content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low solids content</td>
<td>No pre-treatment (3.0 g/L suspended solids content)</td>
</tr>
<tr>
<td>Medium solids content</td>
<td>Concentration of solids through centrifugation (9.0 g/L suspended solids content)</td>
</tr>
<tr>
<td>High solids content</td>
<td></td>
</tr>
</tbody>
</table>

**Flotation**

The flotation outcomes for the low, medium and high solids content samples after the additions of Fe(II) and CTAB to various concentrations up to 5 mM and 300 ppm respectively at pH 6.5 are shown in Figure 4.52. The corresponding removal outcomes for foam drainage and liquid in cell are shown in Figure 4.53.

**Low Solids Content**

**In the absence of Fe(II)**

In the absence of added Fe(II) or CTAB, the overall removal achieved was found to be poor, with 63% removal as shown in Table 4.24 (see also Figure 4.52(a)).

**Table 4.24:** Flotation behaviour for low solids content with no coagulant addition at pH 6.5.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>0</td>
<td>38</td>
<td>105</td>
</tr>
<tr>
<td>100</td>
<td>41</td>
<td>108</td>
</tr>
<tr>
<td>300</td>
<td>88</td>
<td>68</td>
</tr>
<tr>
<td>500</td>
<td>124</td>
<td>13</td>
</tr>
</tbody>
</table>
Figure 4.52: Overall removal of contaminants for (a) low solids content, (b) medium solids content, and (c) high solids content Sample 2 as a function of Fe(II) and CTAB concentrations at pH 6.5.
Figure 4.53: Removal of contaminants for (i) foam drainage and (ii) liquid in cell for (a) low solids content, (b) medium solids content, and (c) high solids content Sample 2 as a function of Fe(II) and CTAB concentrations at pH 6.5.
The removal outcomes were found to be poor for both the liquid in cell (73%, see Figure 4.53(a)(ii)) and, in particular, the foam drainage (37%, see Figure 4.53(a)(i)). The low removals may be attributable to the inability of the colloidal pigment solids to (i) be retained within the foam structure during drainage and (ii) facilitate particle-bubble attachment, due to small solid size and/or low hydrophobicity.

A small CTAB concentration (100 ppm) was found to increase both the removal outcomes to 95%. This implies that for a low solids content wastewater sample, only a small surfactant concentration is required to impart both the necessary hydrophobicity and flocculation for flotation in HLC mode.

A high CTAB concentration (500 ppm) was found to decrease the foam drainage removal to 87% (see Figure 4.53(a)(i)). A possible reason for this decrease is that high concentrations of surfactants at the air-liquid interfaces retard foam coalescence, creating a metastable foam that has a longer lifetime and keeps the concentration of solids between the lamellae lower than the optimal amount required for the establishment of a solids-stabilised foam (see Section 2.4.2). This is reflected in the higher liquid entrainment volume (only 13 mL left in the cell after the flotation run, see Table 4.24) and a larger surviving foam volume (1.4 L). The larger foam carryover volume has a higher air-to-solids ratio leading to foam destabilisation through coalescence and ruptures during foam drainage in areas with less solids content. In spite of the destabilisation, a large final foam volume (1.4 L) is recorded due to the large initial foam carryover volume produced.

**In the presence of low Fe(II) concentration (1.25 mM)**

A small Fe(II) concentration (1.25 mM) in the absence of CTAB was found to increase the overall removal from 63% to 95% (see Figure 4.52(a)). The corresponding increase in both the removals for foam drainage (from 37% to 94%, see Figure 4.53(a)(i)) and liquid in cell (from 73% to 95%, see Figure 4.53(a)(ii)) is consistent with the formation of larger flocs and/or the changes in the anionic surfactants’ adsorption orientation (from tail-down adsorption onto pigment surface to head-down adsorption onto the more hydrophilic Fe(II) hydrous oxides) leading to a more hydrophobic surface (see Section 2.2.3.5).

**In the presence of high Fe(II) concentration (5 mM)**

High concentrations of Fe(II) (5 mM) without CTAB is detrimental (see Figure 4.52(a)),
especially the removal for liquid in cell (see Figure 4.53(a)(ii)) where only a 42% removal is achieved. The increase in CTAB concentration decreases the detrimental effect of high Fe(II) concentration. At a concentration of 300 ppm CTAB, the lower removal (in the presence of high Fe(II) concentration) concords with the results obtained in Section 4.5.2.2 where an 8-fold excess in Fe(II) concentration decreases the removal for liquid in cell from 95% to 78% (see Table 4.17). The low removal can be attributed to the poor particle-bubble attachment efficiency that results from the low hydrophobicity of the mixed pigment-hydrous Fe(II) oxide solids. The surface properties of the solids contained in the low solids content sample, are likely to be dominated by that of the hydrous oxides of Fe(II), Fe(III) or a combination of Fe(II)-Fe(III), which are hydrophilic. This is further supported by the increased removal for liquid in cell with increasing CTAB concentration (see Figure 4.53(a)(ii)). A CTAB concentration of 500 ppm is required to achieve removals above 95% (see Figure 4.52(a)).

**Optimum Fe(II) and CTAB concentrations**

For the low solids content wastewater sample, the optimum coagulant and surfactant concentrations – achieving 98% removals (see Figure 4.52(a)) – are (i) 1.25 mM Fe(II) with 100 ppm CTAB, and (ii) no added Fe(II) with 300 ppm CTAB.

**Medium Solids Content**

**In the absence of Fe(II)**

In the absence of added Fe(II) or CTAB, the removal achieved was found to be poor with 42% overall removal as shown in Table 4.25 (see also Figure 4.52(b)).

**Table 4.25:** Flotation behaviour for medium solids content with no coagulant addition at pH 6.5.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Removales</th>
<th>Foam drainage (%)</th>
<th>Liquid in cell (%)</th>
<th>Overall (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
<td>Foam drainage</td>
<td>Liquid in cell</td>
</tr>
<tr>
<td>0</td>
<td>80</td>
<td>50</td>
<td>1.8</td>
<td>23</td>
<td>71</td>
</tr>
<tr>
<td>100</td>
<td>82</td>
<td>55</td>
<td>1.8</td>
<td>46</td>
<td>87</td>
</tr>
<tr>
<td>300</td>
<td>60</td>
<td>84</td>
<td>0.7</td>
<td>85</td>
<td>97</td>
</tr>
<tr>
<td>500</td>
<td>117</td>
<td>25</td>
<td>0.9</td>
<td>91</td>
<td>96</td>
</tr>
</tbody>
</table>

The foam drainage removal was found to be poor (23% removal, see Table 4.25) and the large
foam volume (1.8 L) suggests that the solids are small in size leading to high initial foam stability but low foam persistence and poor solids retention within foam.

The increase in CTAB concentration to 500 ppm was found to increase the removals for foam drainage (from 23% to 91%, see Table 4.25). A higher CTAB concentration (500 ppm) was required to achieve high removals (i.e. > 90%). This is considerably higher than the 100 ppm required for similar results in the flotation of the low solids content sample (see Tables 4.24 and 4.25).

*In the presence of low Fe(II) concentration (1.25 mM)*

As previously discussed in Section 4.5.1.2, foam destabilisation was found to occur in the flotation of Sample 2 with low concentrations of Fe(II) (1.25 mM) and CTAB (100 ppm) (see Figure 4.23). Increasing Fe(II) concentration (to 5 mM) stabilises the foam at low CTAB concentration, reflected by the smaller decrease in foam drainage removals as shown in Figure 4.53(b)(i). The increased foam stability in the presence of high Fe(II) concentration (5 mM) suggests that the high foam destabilisation observed at low Fe(II) concentration (1.25 mM) and 300 ppm CTAB is most likely due to excessive solids hydrophobicity (i.e. the higher concentrations of added Fe(II) render the mixed solids surface more hydrophilic, leading to less foam destabilisation) rather than the formation of insoluble surfactant salts from the reaction between CTAB and the anionic surfactants. Foam destabilisation was not observed in the flotation of low solids content wastewater samples (see Figure 4.53(a)(i)) as there were less hydrophobic solids to destabilise the foam.

*In the presence of high Fe(II) concentration (5 mM)*

High concentrations of Fe(II) (5 mM) were found to give rise to high removals, between 92 and 95%, regardless of the surfactant concentration (see Figure 4.52(b)). The low removal for liquid in cell (42%, see Figure 4.53(a)(ii)) achieved in the flotation with a high concentration of Fe(II) (5 mM) and a low concentration of CTAB (0 ppm) for low solids content sample was not found in the flotation of the medium solids content sample (see Figure 4.53(b)(ii)). This indicates that even at high Fe(II) concentration (5 mM), the surface properties of the solids contained in the medium solids content sample are not dominated by the metal hydrous oxides. This can be attributed to the higher pigment surface concentration in medium solids content sample. A much higher concentration of Fe(II) is therefore required for the detrimental effect on the removal for liquid in cell to become apparent (e.g. 10 mM Fe(II), see Figure 4.44).
**Optimum Fe(II) and CTAB concentrations**

The optimum Fe(II) and CTAB concentrations – achieving 97% removals (see Figure 4.52(b)) – are 1.25 mM Fe(II) with at least 300 ppm CTAB. Higher dosages of Fe(II) or CTAB are required for the medium solids content sample compared to the low solids content sample. This is consistent with the higher coagulant/surfactant requirement as the suspended solids content is increased.

**High Solids Content**

**In the absence of Fe(II)**

In the absence of added Fe(II) or CTAB, the removal achieved is poor with 29% overall removal as shown in Table 4.26 (see also Figure 4.52(c)).

**Table 4.26:** Flotation behaviour for **high solids content** with no coagulant addition at **pH 6.5**.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th></th>
<th>Removables</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
<td>Foam drainage (%)</td>
</tr>
<tr>
<td>0</td>
<td>96</td>
<td>17</td>
<td>1.2</td>
<td>18</td>
</tr>
<tr>
<td>100</td>
<td>95</td>
<td>16</td>
<td>1.2</td>
<td>7</td>
</tr>
<tr>
<td>300</td>
<td>92</td>
<td>21</td>
<td>1.1</td>
<td>19</td>
</tr>
<tr>
<td>500</td>
<td>90</td>
<td>25</td>
<td>1.0</td>
<td>31</td>
</tr>
</tbody>
</table>

The poor foam drainage removal (18%), the large foam volume (1.2 L) and the relatively low removal for the liquid in cell (88%), suggest that the solids are small, leading to low initial foam destabilisation but low foam persistence and poor solids retention due to lower than optimal concentration of solids in the lamellae for the establishment of a solids-stabilised foam. In the absence of CTAB, the foam drainage removals in the flotation of various solids content samples were poor (between 18 and 37%, see Figures 4.53(a)(i), 4.53(b)(i) and 4.53(c)(i)). This is an indication that the flocs are small in size, which is expected as the solids contained in the process inks and the coating components that make up the wastewater have a high negative charge. Coagulant addition is therefore necessary regardless of the solids content.

As shown in Table 4.26, the addition of a high concentration of CTAB (500 ppm) in the absence of added coagulant leads to low foam drainage removal (31%), suggesting inadequate reduction of the pigment’s surface charge. This is in contrast to the results achieved for low and medium
solids content samples where CTAB concentrations of 100 ppm and 500 ppm respectively were required to achieve high removals (see Tables 4.24 and 4.25).

In the presence of high Fe(II) concentration (5 mM)

The flotation with a high concentration of Fe(II) (5 mM) was found to achieve high overall removals of between 89 and 95% regardless of the surfactant concentration (see Figure 4.52(c)). This concords with the flotation of the medium solids content sample at similar process conditions where removals between 92 and 95% were achieved (see Figure 4.52(b)) but contrasts with the detrimental effect of high Fe(II) concentration in the absence of CTAB on the flotation of the low solids content sample (see Figure 4.52(a)). The increased removal observed with increased CTAB concentration at high Fe(II) concentration (5 mM) indicates that the detrimental effect of excessive Fe(II) dose for low solids content sample can be overcome with high CTAB additions. These results also confirm the earlier finding relating coagulant dose requirement to the solids content (see Section 4.5.2.2).

A higher pigment solid surface concentration in medium and high solids content samples ensured that the surface properties of the mixed pigment-hydrous Fe(II) oxide solids are not dominated by the less hydrophobic hydrous Fe(II) oxides. Therefore, these samples are less dependent on CTAB (to impart hydrophobicity) compared to low solids content samples. Also, in spite of the high Fe(II) solubility, Fe(II) oxidation (to Fe(III)) followed by precipitation to Fe(OH)₃ may result in the mixed solids (contained in the low solids content samples) being dominated by the positively charged and less hydrophobic hydrous metal oxide, leading to poorer adsorption of CTAB with head-down orientation and poorer removal for liquid in cell (see Figure 4.53(a)(ii)). This situation is similar to those found in Al(III) or Fe(III) systems when these coagulants (of low solubility) were added in excess (see Section 4.5.2.4).

Optimum Fe(II) and CTAB concentrations

The optimum Fe(II) concentration for high solids content sample – achieving 93% removals (see Figure 4.52(c)) – is 5 mM. At this Fe(II) concentration, CTAB was found not to have any influence on the flotation outcome. The Fe(II) optimum concentrations are higher than those found in the flotation of both low or medium solids content samples, consistent with a higher coagulant required for higher suspended solids content (see Section 4.5.2.2). The optimum removal of 93% is lower than the removals that were achieved in the flotation of low or medium solids content samples (98% and 97% respectively). This lower removal can result from the
small number of Fe(II) concentrations tested (i.e. 0 mM, 1.25 mM and 5 mM). The optimised Fe(II) concentration for the high solids content sample may be different from the tested levels.

**Conclusion – Effect of Solids Content on Flotation Behaviour**

The solids content in the wastewater was found to have a major determinant in the flotation outcome as reflected in the differences in the optimum process conditions shown in Table 4.27.

**Table 4.27:** Optimum process conditions and their respective removal of contaminants for different levels of solids content in Sample 2 at pH 6.5.

<table>
<thead>
<tr>
<th>Solids content</th>
<th>Optimum conc.</th>
<th>Removals</th>
<th>Effluent recovery a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe(II) (mM)</td>
<td>CTAB (ppm)</td>
<td>Foam drainage (%)</td>
</tr>
<tr>
<td>Low</td>
<td>1.25</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td>Low</td>
<td>0</td>
<td>300</td>
<td>97</td>
</tr>
<tr>
<td>Medium</td>
<td>1.25</td>
<td>300</td>
<td>96</td>
</tr>
<tr>
<td>High</td>
<td>5</td>
<td>0</td>
<td>95</td>
</tr>
</tbody>
</table>

\[ \text{Effluent recovery} \ = \ 100\% \times \frac{\text{combined volumes of liquid in cell and foam drainage}}{\text{total sample volume (180 mL)}} \]

The increase in solids content from 0.5 g/L to 9.0 g/L was found to cause the optimum Fe(II) concentration to increase gradually from 0 mM to 5 mM. This is consistent with the positive correlation between the coagulant requirement and the surface sites’ concentrations [64].

The effluent recovery shown in Table 4.27 is consistent with the decrease in the effluent volumes recovered with the increase in the wastewater solids content. This observation is consistent with the higher liquid volumes trapped or bound within the solids surface in the foam with increasing solids content samples and in concordance with the results obtained for the various samples with 5 mM Fe(II) and 300 ppm CTAB (see Table 4.13).

As previously discussed (see Section 4.5.2.2), the coagulant dose requirement for an industrial process is one that will effectively treat both low and high suspended solids content samples. This study has shown that this is only possible at high Fe(II) (5 mM) and high CTAB (500 ppm) doses. At these high coagulant and surfactant concentrations, the variation in flotation outcomes due to the fluctuations in solids content in the wastewater is minimised. The detrimental effect of a high Fe(II) dose in low solids content sample was found to be overcome by a high CTAB dose while for high solids content sample, a high Fe(II) dose was required to achieve high foam drainage removal.
**4.5.3 Two-Metals Hydrous Oxide Flotation**

**4.5.3.1 Introduction**

As discussed in Section 4.5.2.3, the flotation of Sample 2 with three different coagulants at pH 6.5 achieved overall removals of between 91 and 92% (see Table 4.16). Their flotation characteristics, however, are very different. For Fe(III) system for instance, the solids retention within foam is poor, with a low foam drainage removal of 26% achieved due to poor foam persistence (negligible foam volume survived at the end of the flotation run). For Al(III) system, although good solids retention within foam and a high overall removal (91%) were achieved, the resulting foam sludge was wet (28% of influent volume) and voluminous (1.4 L recorded at the end of the flotation run). Fe(II) was found to give more favourable flotation characteristics with high removals for both the foam drainage (93%) and the liquid in cell (92%), manageable foam volume (0.4 L) and good effluent recovery (89%). The use of Fe(II), however, leads to an effluent that contains Fe ion concentrations above the 30 ppm legal limit for disposal to sewer (see Table 4.14).

This section involves the study of the possible synergistic outcome when combinations of two types of hydrous metal oxides (of equal concentrations) are used as coagulants, in particular, the mixed systems involving Fe(II) with the aim of reducing Fe concentration in the effluent by replacing some of the Fe(II) with Al(III) or Fe(III). The emphasis of this study, apart from the influence of each coagulant on the removal outcomes, is therefore on the resultant flotation characteristics of the mixed system. The flotation characteristics include the volumes of foam, foam drainage and liquid in cell, the solids retention within the foam as well as the suspended solids and liquid content within the foam.

The influence of pH (between 5 and 10) on the flotation behaviour for the mixed hydrous metal oxide systems will be determined and compared to their individual flotation characteristics. A coagulant concentration of 5 mM was chosen for this study as this concentration was found to yield good removal for most wastewater samples using Fe(II) as coagulant (see Section 4.5.2.2) while the CTAB concentration used was 300 ppm as this concentration level was found to result in good overall removals (> 95%) in the flotation of Sample 2 for all the three coagulant systems conducted individually (see section 4.5.1.3). This experiment was conducted using Sample 2 as extensive surface characterisation was conducted on this sample (see Section 4.5.2.3).
4.5.3.2 Mixed Equal Molar Ratio Metal Hydrous Oxide System of Al(III) and Fe(II)

**Flotation**

The flotation outcomes for Sample 2 after the additions of Al(III) and/or Fe(II) to a total coagulant concentration of 5 mM and CTAB to a concentration of 300 ppm are shown in Figures 4.54 and 4.55.

![Figure 4.54: Removal of contaminants in foam drainage for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(II)) and 300 ppm CTAB.](image)

![Figure 4.55: Removal of contaminants for liquid in cell for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(II)) and 300 ppm CTAB.](image)

For Sample 2, the removals for both foam drainage (see Figure 4.54) and liquid in cell (see Figure 4.55), were similar to their individual coagulant systems, with maximum foam drainage removal occurring at pH 6.5 while removal for liquid in cell is highest between pH 8 and 9. There did not appear to be any synergistic benefits observed for the mixed Al(III)/Fe(II) coagulant system in terms of the removals achieved.
**Flotation characteristics**

The corresponding volumes obtained for the foam drainage, the liquid in cell and the foam at the end of the flotation run, are shown in Figures 4.56 – 4.58 respectively.

**Figure 4.56:** Amount of foam drainage for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(II)) and 300 ppm CTAB.

**Figure 4.57:** Amount of liquid in cell for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(II)) and 300 ppm CTAB.
The volumes for foam drainage, liquid in cell and foam for the mixed Al(III)/Fe(II) coagulant system were found to be between those observed for Al(III) and Fe(II) individually throughout the pH ranges tested. Between pH 5 and 7, however, the volumes for the mixed Al(III)/Fe(II) system are closer to those in Al(III) system than those in the Fe(II) system. This suggests that the surface of the mixed pigment-hydrous metal oxide solids is dominated by the pigment-hydrous Al(III) oxide solids at these pH values and is consistent with the solubility behaviour of the two metals (i.e. high Fe(II) solubility and low Al(III) solubility, see Figure 4.31). Above pH 7, on the other hand, the volumes are closer to those in Fe(II) than in the Al(III) system suggesting that the surface characteristics are dominated by those of the pigment-hydrous Fe(II) oxide solids. This, in turn, suggests that hydrous Al(III) oxide is formed faster than the hydrous Fe(II) oxide leading to a greater concentration of Fe(II) surface sites on the surface.

**Foam Liquid Solids Concentration**

The concentration of solids in the foam liquid at the end of the flotation run for the mixed Al(III)/Fe(II) system as well as their individual systems are shown in Figure 4.59.

The foam liquid solids concentration for the mixed Al(III)/Fe(II) system between pH 5 and 7 are closer to those observed for Al(III) system than Fe(II) system. This is consistent with the flotation characteristics (see Figures 4.56 – 4.58) and the solubility behaviour of the two metals (see Figure 4.31). It is interesting to note that this concentration is higher at pH 8 – 9 for the mixed Al(III)/Fe(II) system than their individual coagulant systems. This corresponds to a lower foam drainage removal (see Figure 4.54), higher liquid in cell volume (see Figure 4.57) and lower foam volume (see Figure 4.58) for the mixed Al(III)/Fe(II) system, suggesting that
the initial foam destabilisation is higher leading to unattached solids being washed from the foam by the drainage of liquid from the fresh foam above (see Section 2.4.2, Region 3 in Figure 2.11).

**Figure 4.59:** Foam liquid solids concentration for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(II)) and 300 ppm CTAB.

**Flotation pH 6.5**

As previously discussed in Section 4.5.2.3, the optimum flotation outcome was achieved at pH 6.5 for the flotation of industrial wastewater Sample 2. The flotation characteristics of the mixed Al(III)/Fe(II) as well as their individual systems at pH 6.5 are shown in Table 4.28.

**Table 4.28:** Flotation behaviour for Sample 2 with 5 mM coagulant (Al(III)/Fe(II)) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Volume</th>
<th>Removal</th>
<th>Effluent recovery a</th>
<th>Conc. b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
<td>Foam drainage (%)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>40</td>
<td>120</td>
<td>0.4</td>
<td>93</td>
</tr>
<tr>
<td>Al(III)</td>
<td>85</td>
<td>45</td>
<td>1.4</td>
<td>89</td>
</tr>
<tr>
<td>Al(III)/Fe(II)</td>
<td>67</td>
<td>75</td>
<td>0.7</td>
<td>94</td>
</tr>
</tbody>
</table>

a effluent recovery = 100% x (combined volumes of liquid in cell and foam drainage)/total sample volume (180 mL).

b foam liquid solids concentration.

The removals for both foam drainage (89 – 94%) and liquid in cell (90 – 93%) are similar for the single or mixed metal coagulant systems. The volumes for foam drainage, liquid in cell and foam for the mixed Al(III)/Fe(II) system is in between those of the individual metal coagulant systems. In spite of the similarity in the effectiveness of contaminant removers, the introduction of Al(III) to Fe(II) system increases the foam volume from 0.4 L to 0.7 L. This can potentially
lead to problems associated with foam management. More importantly, the replacement of half the Fe(II) with Al(III) decreases the effluent recovered from 89% to 79% vol/vol, doubling in the amount of waste for disposal. The increased waste indicates that mixed Al(III)/Fe(II) system may not be a suitable option to reduce the high soluble Fe concentration found in Fe(II) system.

The differences in flotation characteristics indicate that the flotation behaviour with one metal coagulant can be altered in the presence of the other. This suggests that another metal coagulant can be added to a flotation run to improve the flotation characteristics provided the impact of the added metal coagulant on the flotation behaviour is known. This may be beneficial for Fe(III) systems where the foam instability was found to lead to poor foam drainage removals. The two-metal hydrous oxide combinations involving Fe(III) are to be investigated in the next two sections.

4.5.3.3 Mixed Equal Molar Ratio Metal Hydrous Oxide System of Al(III) and Fe(III)

_Flotation_

The flotation outcomes for Sample 2 after the additions of Al(III) and/or Fe(III) to a total coagulant concentration of 5 mM and CTAB to a concentration of 300 ppm are shown in Figures 4.60 and 4.61.

_Figure 4.60:_ Removal of contaminants in foam drainage for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(III)) and 300 ppm CTAB.
Figure 4.61: Removal of contaminants for liquid in cell for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(III)) and 300 ppm CTAB.

The removals for both the foam drainage (see Figure 4.60) and the liquid in cell (see Figure 4.61) for the mixed Al(III)/Fe(III) system were found to be between those of their individual coagulant systems. The low foam drainage removal (due to high initial foam destabilisation) in the Fe(III) system between pH 6.5 and 9 (see Figure 4.42 and Table 4.15) was found to be partially negated by the presence of Al(III), especially between pH 6 and 7 where the removal outcomes are closer to those obtained in the Al(III) system. Between pH 7 and 9, however, the foam drainage removal outcomes are closer to those obtained in the Fe(III) system than the Al(III) system. This behaviour indicates that the surface characteristics are dominated by those of mixed pigment-hydrous Al(III) oxide solids between pH 6 and 7 and those of mixed pigment-hydrous Fe(III) oxide solids between pH 7 and 9. The reason for this is not clear as the total added coagulant concentration (5 mM) and the solubility of these coagulants are the same (see Figure 4.31).

Flotation Characteristics

The corresponding volumes obtained for the foam drainage, the liquid in cell and the foam at the end of the flotation run, are shown in Figures 4.62 – 4.64 respectively.
Figure 4.62: Amount of foam drainage for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(III)) and 300 ppm CTAB.

Figure 4.63: Amount of liquid in cell for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(III)) and 300 ppm CTAB.

Figure 4.64: Amount of foam for Sample 2 as a function of pH with 5 mM coagulant (Al(III)/Fe(III)) and 300 ppm CTAB.
The volumes for foam drainage, liquid in cell and foam for the mixed Al(III)/Fe(III) system were found to be between those observed for their individual Al(III) and Fe(III) systems (see Figures 4.62 – 4.64). For the mixed Al(III)/Fe(III) system, no distinct volume inclination towards the volume characteristics (especially the volumes for foam drainage and liquid in cell) found in their corresponding individual coagulant systems were observed. This is consistent with the low solubility behaviour of both the metals between pH 5 and 10 (see Figure 4.31). The higher foam drainage removal between pH 6 and 7 for the mixed Al(III)/Fe(III) system may be attributed to the high foam stability due to the presence of hydrous Al(III) oxide solid as shown in the high foam volumes (> 1.0 L) recorded for Al(III) system alone (see Figure 4.64). Between pH 7 and 9, the foam stability for Al(III) system decreases (foam volumes of 0.6 – 0.7 L recorded) leading to a lower ability of the hydrous Al(III) oxide solid to negate the high initial foam destabilisation due to the presence of the hydrous Fe(III) oxide solid. Hence, the foam carryover contains a high solid concentration resulting in unattached solids being washed from the foam by the liquid drainage, i.e. the foam drainage removals for the mixed Al(III)/Fe(III) system is closer to those achieved for Fe(III) system (see Figure 4.60).

**Foam Liquid Solids Concentration**

The concentration of solids in the foam liquid at the end of the flotation run for the mixed Al(III)/Fe(III) system as well as their individual systems are shown in Figure 4.65.

![Figure 4.65](image)

*Figure 4.65*: Foam liquid solids concentration for **Sample 2** as a function of pH with 5 mM coagulant (Al(III)/Fe(III)) and 300 ppm CTAB.

The trend in the foam liquid solids concentration for the mixed Al(III)/Fe(III) system was found to be similar to those in their individual coagulant systems, i.e. the concentration increases with the increase in pH value (to 9). This is consistent with a more hydrophobic solid surface at higher pH values as CTAB adsorbed predominantly with head-down orientation. The foam
liquid solids concentration of the mixed Al(III)/Fe(III) system is, however, closer to those observed in Fe(III) system than those in Al(III) system, especially at the pH value where high initial foam destabilisation was observed for Fe(III) system (i.e. between pH 6.5 and 9, see Figure 4.42 and Table 4.15). The higher foam liquid solids concentration, similar foam drainage and overall removals for the mixed system (see Figure 4.60) compared to Al(III) system (at the lower pH range where high initial foam destabilisation was observed for Fe(III) system) may warrant the use of the mixed Al(III)/Fe(III) over Al(III) alone. For example, at pH 6.5 where the foam drainage removal for the mixed Al(III)/Fe(III) system is high (90%, see Figure 4.60), the higher foam liquid solids concentration (26 g/L, see Figure 4.65) gives an added advantage over the use of Al(III) alone (90% foam drainage removal and 12 g/L foam liquid solids concentration) while the overall removals are similar (93% and 91% respectively).

**Flotation pH 6.5**

The flotation characteristics of the mixed Al(III)/Fe(III) as well as their individual systems at pH 6.5 are shown in Table 4.29.

*Table 4.29: Flotation behaviour for Sample 2 with 5 mM coagulant (*Al(III)/Fe(III))* and 300 ppm CTAB at pH 6.5.*

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Volume</th>
<th>Removal</th>
<th>Effluent recovery a</th>
<th>Conc. b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam drainage (%)</td>
<td>Liquid in cell (%)</td>
</tr>
<tr>
<td>Al(III)</td>
<td>85</td>
<td>45</td>
<td>1.4</td>
<td>89</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>10</td>
<td>155</td>
<td>0.05</td>
<td>26</td>
</tr>
<tr>
<td>Al(III)/Fe(III)</td>
<td>53</td>
<td>107</td>
<td>0.5</td>
<td>90</td>
</tr>
</tbody>
</table>

a effluent recovery = 100% x (combined volumes of liquid in cell and foam drainage)/total sample volume (180 mL).
b foam liquid solids concentration.

At this pH value (6.5), although the overall removals are similar (91 – 93%), the choice of coagulant/s is dependent on their flotation characteristics. The increased foam stability in the presence of Al(III) in the mixed Al(III)/Fe(III) system results in greater foam drainage removal (90% compared to 26%, see Table 4.29). This can be attributed to the higher foam stability reflected by the larger foam volume recorded at the end of the flotation run (0.5 L in the presence of Al(III) compared to 0.05 L in its absence). The presence of Fe(III) in the mixed Al(III)/Fe(III) system leads to the increase in the foam liquid solids concentration (23 g/L compared to 10 g/L in its absence) and the decrease in foam volume (0.5 L compared to 1.4 L in its absence).
The flotation characteristics of mixed Al(III)/Fe(III) coagulant are more favourable in the HLC mode flotation of Sample 2 than (i) the Al(III) system as the foam is more manageable (0.5 L to 1.4 L), the effluent recovery is higher (89% to 72%) and the foam liquid solids concentration is higher (23 to 10), or (ii) the Fe(III) system as the foam is more stable leading to higher solids retention within foam and higher foam drainage removal (90% to 26%).

4.5.3.4 Mixed Equal Molar Ratio Metal Hydrous Oxide System of Fe(II) and Fe(III)

Flotation

The flotation outcomes for Sample 2 after the additions of Fe(II) and/or Fe(III) to a total coagulant concentration of 5 mM and CTAB to a concentration of 300 ppm are shown in Figures 4.66 and 4.67.

![Figure 4.66](image-url)  
*Figure 4.66:* Removal of contaminants in foam drainage for Sample 2 as a function of pH with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB.

![Figure 4.67](image-url)  
*Figure 4.67:* Removal of contaminants for liquid in cell for Sample 2 as a function of pH with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB.
Similar to the flotation outcome of the mixed hydrous oxides of Al(III)/Fe(III) system, the initial foam destabilisation in the Fe(III) system above pH 6 is partially reduced by the presence of Fe(II) (see Figure 4.66). The removals for both the foam drainage (see Figure 4.66) and the liquid in cell (see Figure 4.67) for the mixed Fe(II)/Fe(III) system were between those of their individual hydrous metal oxide flotation outcomes.

**Flotation Characteristics**

The corresponding volumes obtained for the foam drainage, the liquid in cell and the foam at the end of the flotation run, are shown in Figures 4.68 – 4.70 respectively.

*Figure 4.68:* Amount of foam drainage for Sample 2 as a function of pH with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB.

*Figure 4.69:* Amount of liquid in cell for Sample 2 as a function of pH with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB.
Figure 4.70: Amount of foam for Sample 2 as a function of pH with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB.

The flotation behaviours for mixed Fe(II)/Fe(III) system are between those observed for Fe(II) and Fe(III) individually throughout the pH ranges tested (see Figures 4.68 – 4.70), an observation similar to the other mixed two-metal coagulant systems discussed previously in Sections 4.5.3.2 and 4.5.3.3. Between pH 5 and 6.5, however, the volumes for the mixed coagulant system are closer to those found in Fe(III) system than in Fe(II) system. This concords with the results in the mixed coagulant system involving Al(III) and Fe(II) at similar pH ranges in Section 4.5.3.2 and is consistent with the solubility behaviour of the respective metal hydrous oxides (i.e. high Fe(II) solubility and low Fe(III) solubility, see Figure 4.31).

Foam Liquid Solids Concentration

The concentrations of solids in the foam liquid at the end of the flotation run for the mixed Fe(II)/Fe(III) system as well as their individual systems are shown in Figure 4.71.

Figure 4.71: Foam liquid solids concentration for Sample 2 as a function of pH with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB.
The trend in the foam liquid solids concentration for the mixed Fe(II)/Fe(III) system was found to follow the that of the Fe(III) system, i.e. the highest concentration occurs between pH 7 and 9. The concentration was also closer to those observed in Fe(III) system than those in Fe(II) system, especially at pH value where high initial foam destabilisation was observed for Fe(III) system (between pH 7 and 9, see Figure 4.42 and Table 4.15). This observation was similar to that found for the mixed Al(III)/Fe(III) system (see Figure 4.65). Even though the foam liquid solids concentration for the mixed Fe(II)/Fe(III) system is higher than those observed for Fe(II) system between pH 7 and 9, the solids retention within foam and the foam drainage removals (see Figure 4.66) are poor and therefore, not suitable for conducting flotation in HLC mode.

Below pH 7, the foam liquid solids concentration for the mixed Fe(II)/Fe(III) system are closer to those observed for Fe(III) system than Fe(II) system. This is consistent with the flotation characteristics (see Figure 4.68 – 4.70) and the solubility behaviour of the two metals (see Figure 4.31).

\textit{Flotation pH 6.5}

The flotation characteristics of the mixed Fe(II)/Fe(III) as well as their individual systems at pH 6.5 are shown in Table 4.30.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Coagulant & Volume & Removal & Effluent & Conc. \textsuperscript{b} \\
 & Foam & Liquid in & Foam & drainage & Liquid in & Overall & \\
 & drainage & cell & drainage & (\%) & cell & (\%) & recovery \textsuperscript{a} & g/L \\
 & (mL) & (mL) & (L) & (\%) & (\%) & (\%) & (\%) & \\
\hline
Fe(II) & 40 & 120 & 0.4 & 93 & 92 & 92 & 89 & 25 \\
Fe(III) & 10 & 155 & 0.05 & 26 & 96 & 91 & 92 & 33 \\
Fe(II)/Fe(III) & 52 & 100 & 0.4 & 95 & 88 & 90 & 84 & 14 \\
\hline
\end{tabular}
\caption{Flotation behaviour for Sample 2 with 5 mM coagulant (Fe(II)/Fe(III)) and 300 ppm CTAB at pH 6.5.}
\end{table}

\textsuperscript{a} effluent recovery = 100\% x (combined volumes of liquid in cell and foam drainage)/total sample volume (180 mL).
\textsuperscript{b} foam liquid solids concentration.

At pH 6.5, although the overall removals are similar (90 – 92\%), their flotation characteristics are very different, especially between the two individual metal coagulants. The increased foam stability in the presence of Fe(II) in the mixed Fe(II)/Fe(III) system results in a higher foam drainage removal (95\% compared to 26\%, see Figure 4.66). This can be attributed to the higher foam stability reflected by the larger foam volume (0.4 L in the presence of Fe(II) compared to 0.05 L in its absence, see Table 4.30) at the end of the flotation run. The reason for the lower
foam liquid solids concentration for the mixed system (14 g/L) compared to both their individual coagulant systems (25 g/L for Fe(II) and 33 g/L for Fe(III)) is not clear. Apart from this, the flotation characteristics for the mixed two-metal coagulant system are similar to those obtained for Fe(II) alone (see Table 4.30). This may offer a potential solution to the problem encountered in Fe(II) system involving high Fe concentration in the effluent and, warrants further investigation.

4.5.3.5 Conclusion – Two-Metals Hydrous Oxide Flotation

The mixed coagulant systems were found not to result in any distinct improvement in the overall removals compared to their individual coagulant systems. They can, however, be beneficial in that the flotation behaviour can be controlled and the flotation outcomes are not too dependent on any one coagulant. This is especially important if the conditions are such that the resulting foam is either too stable (leading to difficulty in foam management as in the flotation of Sample 2 with Al(III)) or too unstable (leading to dirty foam drainage and low foam carryover volume as found in the flotation of Sample 2 with Fe(III)). The flotation characteristics of the mixed systems are generally a compromise of their individual coagulant components.

It was also found that the mixed systems could exhibit more favourable flotation characteristics compared to their individual systems. For example, the presence of Fe(III) increases the foam liquid solids concentration for the mixed Al(III)/Fe(III) and Fe(II)/Fe(III) systems compared to those achieved for Fe(II) or Al(III) systems. Also, the presence of Al(III) or Fe(II) in the mixed systems containing Fe(III) increases the foam stability and the solids retention within the foam compared to those achieved for Fe(III) system.

The results presented in this section show that the flotation characteristics can be improved and controlled when multiple coagulants are used and warrant further future investigation.

4.6 Continuous Mode Flotation Studies

4.6.1 Introduction

The flotation experiments presented in earlier sections of this chapter have all been conducted in batch mode. Batch mode treatment is convenient on a small scale. An alternative mode of treatment is the continuous mode. This mode of operation is more suited to larger scale
industrial applications due to smaller equipment size requirements and easier automation.

Due to the larger sample volumes, the use of an efficient (and larger) foam collection vessel is necessary to ensure smooth continuous operation in the ‘foam and effluent management stage’ (see Figure 2.1). This includes foam collection, foam liquid drainage and separation of aged foam from the fresh foam. Various foam collection vessel dimensions were investigated for this purpose and the results are shown in Section 4.6.3. In addition, the advantage of using a larger foam collection vessel for flotation in continuous mode eliminates the wall effects on the foam and foam drainage characteristics, hence, a more accurate representation to an industrial-sized flotation operation.

In Section 4.6.4, the effects of CTAB concentration and the wastewater flow rate on the flotation outcome are investigated at a fixed air flow rate. The presence of CTAB above 300 ppm had been found to aid flotation (in batch mode with Fe(II) at flotation pH 6.5) with high removals achieved for both the foam drainage and the liquid in cell (see Section 4.5.1.3). This can be attributed to, amongst the many possible contributing factors, a higher volume of foam formation and an increase in particle-bubble attachment efficiency (see Section 2.3.2). Both these factors result in the increase in the rate of solids attachment onto the bubble surface, potentially leading to increases in the wastewater flow rate.

In Section 4.6.5, the influences of the air and wastewater flow rates on the flotation outcomes are investigated. The increase in the air volumes introduced into the flotation cell had been found to increase the amount of sample that can be treated [133].

The optimised process conditions for each wastewater samples conducted in batch mode flotation – i.e. pH 6.5, Fe(II) and CTAB at their optimised concentrations – are replicated in the continuous mode flotation studies. Fe(II) was chosen ahead of Al(III) or Fe(III) for this experiment as it was found to give the highest removal at a constant flotation of pH 6.5 (see Section 4.5.2.3) as well as having a smaller detrimental effect towards the flotation outcome when its concentration is added in excess (see Section 4.5.2.4). Flotation using CTAB was found to perform best at lower Fe(II) dosage compared to the concentration required when SDS or Teric G12A8 was used (see Section 4.5.1.2). The samples used in this study are the average suspended solids content Sample 3 and the above average suspended solids content Sample 4. The Fe(II) concentration dose depended on the optimum requirement for each sample (see Section 4.5.2.2). The influence of suspended solids content contained in the samples on the flotation responses was investigated.
4.6.2 Determination of the Range in Wastewater Residence Time for Flotation in Continuous Mode

The rate of removals from the liquid in cell over time in batch mode operation was conducted to determine the range in residence times required for the wastewater samples in the flotation cell (when conducting experiments in continuous mode). The duration required for maximum removals of the solids contained in three samples, ranging from low to above average suspended solids content, was investigated. For this experiment, the pre-treatment of the samples includes the addition of Fe(II) to the sample’s respective optimum concentrations (see Section 4.5.2.2) and CTAB to 300 ppm. Flotation was conducted at pH 6.5 and the removal results are shown in Figure 4.72.

![Figure 4.72: Removal of contaminants for liquid in cell for Samples 2, 3 and 4 as a function of flotation time at their respectively optimum Fe(II) and CTAB concentrations at pH 6.5.](image)

The times required for maximum removals from liquid in cell for Samples 2 – 4 are shown in Table 4.31.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optimum concentrations</th>
<th>Minimum residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe(II) (mM)</td>
<td>CTAB (ppm)</td>
</tr>
<tr>
<td>3</td>
<td>1.25</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>300</td>
</tr>
</tbody>
</table>

The residence time ranged from 1.0 minute to 4.0 minutes, consistent with higher residence times required for higher solids content/higher ionic strength samples (see Table 4.3). A longer residence time is expected to be required for higher solids content samples because there are...
more solids to be floated with a fixed amount of air (250 mL/min). Longer residence times were chosen for the initial continuous mode experiments (i.e. 1.5 minutes to 6.0 minutes) to allow time for foam carryover as well as avoiding overloading the foam in the cell with solids.

4.6.3 Influence of Foam Collection Vessel

An efficient foam drainage collection vessel is especially important in the continuous flotation operation in HLC mode. The rapid operation in the HLC mode requires equally rapid mode of liquid drainage from the foam. Literature studies have shown that natural drainage is adequate as long as a large area is provided for drainage, for example, a shallow and wide collection vessel [41].

The following foam collection vessel configurations were investigated:

- wide cylindrical (WC) drainage cell with diameter 13.8 cm and cross sectional surface area of 149.6 cm²;
- narrow cylindrical (NC) drainage cell with diameter 9.4 cm and cross sectional surface area of 69.4 cm²;
- long tray (LT) drainage cell with width 10 cm and length 84 cm; cross sectional surface area of 840 cm²; and
- 4-segment long tray (4-SLT) drainage cell with the dimensions of each segment – width 10 cm, length 21 cm, and cross sectional surface area of 210 cm² (See Figure 3.3). The combined 4 segments have a total cross sectional surface area of 840 cm².

Note: The LT and 4-SLT drainage cells were tilted at an angle of approximately 8° to assist in the flow of the aged foam through natural gravity.

The collective foam drainage removals for Sample 4 as a function of time using the various collection vessels are shown in Figure 4.73.

The removals are relatively low at the initial stages (75 – 90% about 5 minutes into the flotation run) for all collection vessels but stabilised at 97% after about 10 minutes into the flotation run, suggesting that the foam is persistent in its drained state but was unstable in the initial stages. That is, the foam drains very cleanly over time despite an initial relatively large collapse of foam. This concords with the findings in the continuous mode adsorbing colloid flotation studies on chromium stream electroplating wastewater where a large release of chromium, nickel and zinc from the foam at the initial stage while the effluent drains cleanly from the foam over time [41]. The foam collapse at the initial stage can be attributed to the higher suspended
solids content contained in the initial foam carryover. Although this foam is stabilised by the high concentrations of hydrophobic solids, its resilience to damage is less than foam of higher liquid content. Subsequent foam carryover has a lower solids and a higher liquid content due to the continuous liquid draining from the foam directly above.

![Figure 4.73: Removal of contaminants in foam drainage for Sample 4 as a function of flotation time with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5, 2 L sample at 36 mL/min wastewater flow rate (total flotation period = 56 minutes at 5 minutes residence time) and 250 mL/min air flow rate.](image)

From Figure 4.73, it can be seen that the removals for NC and WC drainage cells decrease after about 25 and 40 minutes respectively whereas for LT and 4-SLT drainage cells, removals above 95% were maintained until the end of their respective flotation runs. A vessel with a large cross-sectional surface area is essential for effective drainage. This is consistent with the expected higher solids loading per unit cross-sectional area for smaller drainage cells, resulting in foam collapsing under its own weight.

The 4-SLT drainage cell was chosen for further flotation studies as the divided segments enable the monitoring of the rate of natural drainage from the foam and ensures that the foam collected (from the final segment) as waste sludge for disposal has drained extensively. This form of divided segments also assists in the physical separation of the dewatered solids sludge from the incoming fresh foam. If the dried dewatered sludge is not separated from the incoming fresh foam carryover, there is a high possibility of foam collapsing under its own weight.

### 4.6.4 Optimisation of Surfactant Concentration and Wastewater Flow Rate

This section involved the optimisation of the CTAB concentration and the wastewater flow rate. Even though CTAB concentration optimisation has been conducted in batch mode flotation (see section 4.5.1.2), the required concentration for flotation conducted in continuous mode can be
very different. Firstly, the one-minute equilibration period allowed in batch mode can improve surfactant adsorption potentially leading to a smaller surfactant dosage. On the other hand, the equilibrium period can also result in the surfactant being trapped inside the solids with the continuous breaking and reforming of flocs, hence, a higher surfactant dosage may be necessary to impart the required hydrophobicity.

This section also investigates the influence of wastewater flow rate when the air flow rate into the flotation cell is fixed. A high ratio of wastewater-to-air flow rate results in insufficient air interface for the solids to adhere to, potentially resulting in low removals for the effluent leaving the flotation cell via outlet B (see Figure 3.2). In this circumstance, the increase in CTAB concentration may allow an increase in the overall removals by increasing the air-liquid interface area (see Section 2.3.3.3) and/or increasing the particle-bubble attachment efficiency (see Section 2.3.2). Conversely, a low ratio of wastewater-to-air flow rate can lead to a foam carryover that is high in solids content due to destabilisation of the foam in the cell at low solids concentration and the stabilisation of the foam at high solids content. The high solids content foam can potentially lead to a dirty foam drainage (e.g. from mechanical disturbances as liquid that drains from fresh foam washes the unattached solids from the aged foam).

4.6.4.1 Flotation Results for Sample 3

The flotation outcomes for Sample 3 after the additions of Fe(II) to its optimised concentration (1.25 mM, see Section 4.5.2.2) and CTAB up to a concentration of 500 ppm at pH 6.5 with an air flow rate of 250 mL/min through the cell, are shown in Figure 4.74.

![Figure 4.74: Continuous mode flotation – Removal of contaminants for treatment of 2 L of Sample 3 as a function of wastewater flow rate and CTAB concentration with 1.25 mM Fe(II) at pH 6.5, and 250 mL/min air flow rate. The liquid volume in the flotation cell was kept under to 200 mL.](image-url)
Influence of Wastewater Flow Rate

The removal outcomes for the various effluent outlets in the flotation of the average suspended solids content Sample 3 (with optimum CTAB concentration of 300 ppm) as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.32 and 4.33 respectively.

Table 4.32: Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>81</td>
<td>2</td>
<td>10</td>
<td>92</td>
</tr>
<tr>
<td>45</td>
<td>81</td>
<td>4</td>
<td>6</td>
<td>91</td>
</tr>
<tr>
<td>72</td>
<td>77</td>
<td>9</td>
<td>4</td>
<td>89</td>
</tr>
<tr>
<td>120</td>
<td>56</td>
<td>34</td>
<td>2</td>
<td>91</td>
</tr>
</tbody>
</table>

Table 4.33: Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>89</td>
<td>86</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>45</td>
<td>93</td>
<td>81</td>
<td>98</td>
<td>93</td>
</tr>
<tr>
<td>72</td>
<td>94</td>
<td>76</td>
<td>98</td>
<td>93</td>
</tr>
<tr>
<td>120</td>
<td>93</td>
<td>56</td>
<td>99</td>
<td>80</td>
</tr>
</tbody>
</table>

The main effluent outlets are the foam drainage and the liquid leaving the flotation cell via outlet B (see Figure 3.2). For simplicity, the latter effluent is to be denoted as ‘cell exit liquid’. The volume for liquid in cell does not significantly contribute to the overall removal as the liquid was not allowed to exceed 200 mL. This accounts to a maximum of 10% of the total sample volume treated.

A comparison of the removals for the two main effluent outlets showed that the foam drainage removals are generally higher than the removals for cell exit liquid (see Table 4.33). This difference is found to increase with the increase in the wastewater flow rate, mainly as a result of the decrease in the removal for cell exit liquid (to 56% at 120 mL/min wastewater flow rate). This decrease in removal for cell exit liquid can be attributed to the lower residence time and
therefore, the lower probability of particle-bubble attachment within the given time period. The lower overall removal (80%, see Table 4.33) at high wastewater flow rate (120 mL/min) is a result of the higher volume of cell exit liquid (34% of the influent volume, see Table 4.32). A higher volume of cell exit liquid is a result of the higher rate of wastewater entering the cell compared to the rate that can be removed with the foam.

Therefore, for an air flow rate of 250 mL/min, flotation with low to intermediate wastewater flow rates (30 to 72 mL/min) were found to give the best removal outcomes where 90 – 93% removals can be achieved (see Figure 4.74 and Table 4.33).

**Influence of CTAB Concentration**

The removal outcomes for the various effluent outlets in the flotation of Sample 3 (at the optimum wastewater flow rate of 72 mL/min) as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.34 and 4.35 respectively.

**Table 4.34:** Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) at pH 6.5, 72 mL/min wastewater flow rate and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>100</td>
<td>51</td>
</tr>
<tr>
<td>300</td>
<td>77</td>
</tr>
<tr>
<td>500</td>
<td>89</td>
</tr>
</tbody>
</table>

**Table 4.35:** Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) at pH 6.5, 72 mL/min wastewater flow rate and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Removals (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>100</td>
<td>78</td>
</tr>
<tr>
<td>300</td>
<td>94</td>
</tr>
<tr>
<td>500</td>
<td>98</td>
</tr>
</tbody>
</table>

Higher overall removals occurred with increased CTAB concentration (see Figure 4.74 and Table 4.35). A minimum concentration of 300 ppm was required to achieve removals above 90% regardless of the wastewater flow rates.
High concentrations of CTAB (> 300 ppm) were found to aid flotation through an increased rate of liquid entrainment with the foam (see Table 4.34). For example, an increase in CTAB concentration from 100 ppm to 500 ppm results in an increase in the foam drainage volume from 51% to 89% of the total influent volume at the expense of the cell exit liquid which decreased from 35% to 0%. The higher rate of liquid entrainment is consistent with the higher foam stability and reduced bubble coalescence (thereby increasing air dispersion) in the presence of a higher surfactant concentration functioning as frother. Taking into account the relative removals that can be achieved for these two effluent streams, the increased liquid entrainment with CTAB concentration contributes to the increase in the removals from 72% to 98% (see Table 4.35).

The increase in CTAB concentration was also found to increase the foam drainage removal, from 78% to 94% to 98% at CTAB concentration of 100 ppm, 300 ppm and 500 ppm respectively (see Table 4.35). This can be attributed to the increased solids hydrophobicity (as CTAB adsorbs with head-down orientation) resulting in a general increase in foam stability for solids of large sizes (e.g. diameter above 44 µm, [153, 157]) and/or further increases in the degree of solids flocculation possibly through hydrophobic attraction force or presence of gas nuclei on the hydrophobic surface sites [81, 82]. These increases in hydrophobicity and/or floc size were reflected in the corresponding increased rate of contaminant removal from the cell (i.e. higher particle-bubble attachment efficiency) as shown in the increased removal for cell exit liquid (from 60% at 100 ppm CTAB to 72% at 300 ppm CTAB, see Table 4.35).

The increase in solids retention, especially as the CTAB concentration is increased from 100 to 300 ppm, is consistent with the relatively low foam drainage removal at 100 ppm and the increase in foam drainage removals with the increase in CTAB concentration above 100 ppm in the flotation of Sample 3 in batch mode (see Figure 4.20). The destabilisation effect at 100 ppm seen in batch mode sludge at identical process conditions (17%, see Figure 4.20) is, however, not as pronounced for the flotation in continuous mode (78%, see Table 4.35). This difference may be a result of the difference in solid and surfactant concentrations in both the foam and liquid in cell over time.

**Rates of Natural Drainage and Foam Aging**

An important consideration for operating flotation in HLC mode is the management of the large volumes of foam produced. From the experiments conducted in batch mode in Section 4.5, the flotation of a 180 mL sample produces a foam volume of at least a few times the liquid sample
In an up scaled continuous mode flotation with 2 L sample volume, the large volumes of foam produced can be problematic if not managed effectively. An example is shown in Section 4.6.3 where the removals at identical process conditions were different when using different foam collection vessel. Section 4.6.3 also showed that more effective removal from natural drainage occurs with larger foam collection vessel is utilised. A rapid rate of natural liquid drainage from foam is essential to minimise the space area required for foam management as well as to prevent it from being a rate limiting factor in the flotation process.

The foam drainage volumes and their corresponding removals at the different segments of the 4-SLT drainage cell at various wastewater throughputs are shown in Tables 4.36 and 4.37 respectively. The corresponding foam volumes and their solids content are shown in Tables 4.38 and 4.39 respectively.

**Table 4.36:** Foam drainage volumes for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage volumes (%)</th>
<th></th>
<th></th>
<th></th>
<th>Total volumes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
<td>Segment 3</td>
<td>Segment 4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>74</td>
<td>6</td>
<td>1</td>
<td>&lt; 1</td>
<td>81</td>
</tr>
<tr>
<td>45</td>
<td>71</td>
<td>8</td>
<td>2</td>
<td>1</td>
<td>81</td>
</tr>
<tr>
<td>72</td>
<td>59</td>
<td>12</td>
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<td>2</td>
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</tr>
<tr>
<td>120</td>
<td>45</td>
<td>7</td>
<td>3</td>
<td>1</td>
<td>56</td>
</tr>
</tbody>
</table>

**Table 4.37:** Foam drainage removals for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage removals (%)</th>
<th></th>
<th></th>
<th></th>
<th>Average removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
<td>Segment 3</td>
<td>Segment 4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>89</td>
<td>96</td>
<td>94</td>
<td>91</td>
<td>89</td>
</tr>
<tr>
<td>45</td>
<td>93</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>93</td>
</tr>
<tr>
<td>72</td>
<td>93</td>
<td>98</td>
<td>96</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td>120</td>
<td>92</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>93</td>
</tr>
</tbody>
</table>

**Table 4.38:** Foam volumes for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam Volumes (L)</th>
<th></th>
<th></th>
<th></th>
<th>Total volumes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
<td>Segment 3</td>
<td>Segment 4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>45</td>
<td>0.1</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>1.1</td>
</tr>
<tr>
<td>72</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>120</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Table 4.39: Foam solids contents for treatment of 2 L of Sample 3 with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam solids content (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
</tr>
<tr>
<td>30</td>
<td>15.0</td>
<td>16.4</td>
</tr>
<tr>
<td>45</td>
<td>13.9</td>
<td>13.9</td>
</tr>
<tr>
<td>72</td>
<td>8.8</td>
<td>13.0</td>
</tr>
<tr>
<td>120</td>
<td>8.3</td>
<td>12.3</td>
</tr>
</tbody>
</table>

The relatively high volumes of foam drainage collected at the first segment (45 – 74% of the influent volume, see Table 4.36), their high levels of removal (89 – 93%, see Table 4.37), as well as a solids content of 8 – 15 wt% (see Table 4.39), suggest that the natural drainage of liquid from the foam is quick and effective. The high foam drainage removals achieved (> 90%, see Table 4.37) at segments 2 to 4 reflects the persistence of the solids-stabilised foam over time.

The consequence of the high rate of natural drainage, if not managed appropriately, may leave the solids-stabilised foam immobile. The loss of froth mobility has a negative effect on the transportation of the foam to subsequent segments. The likely consequence of this is the continuous piling of fresh foam on top of the aged foam. The liquid drainage from the fresh foam through the aged foam can result in the washing of the solids from the bubble interface leading to poor solids retention in the aged foam. This is especially true at lower wastewater flow rates where lower volumes of foam survived the liquid drainage in the cell consistent with the foam destabilisation at low solids concentration and the foam stabilisation at high solids concentration. Therefore lower foam carryover volumes are produced leading to slower movement of the aged foam to subsequent segments. This loss of foam mobility at low wastewater flow rates is reflected in the higher solids content in the foam at Segment 1 (see Table 4.39). For example, for a wastewater flow rate of 30 mL/min, Segment 1 has an average solids content of 15.0 wt% whereas for wastewater flow rate of 120 mL/min, it is only 8.3 wt%.

The corresponding foam drainage removals in Segment 1 reflect the disadvantage of conducting the flotation at low wastewater flow rates, with the removal at 30 mL/min wastewater flow rate being marginally lower (i.e. 89% as opposed to 92 – 93% at higher wastewater flow rates, see Table 4.37).

The average foam solids content increases with decreasing wastewater flow rate (see Table 4.39). This can be attributed to the longer drainage period due to the longer flotation duration as the wastewater flow rate is decreased. The high foam drainage removals achieved even after the
long flotation duration at low wastewater flow rate of 30 mL/min (see Table 4.37) suggests that the foam stabilised by the presence of solids is very stable.

4.6.4.2 Flotation Results for Sample 4

The flotation outcomes for Sample 4 after the additions of Fe(II) to its optimised concentration (5 mM, see Section 4.5.2.2) and CTAB up to a concentration of 500 ppm at pH 6.5 with an air flow rate of 250 mL/min through the cell, are shown in Figure 4.75.

Influence of Wastewater Flow Rate

The removal outcomes for the various effluent outlets in the flotation of the above average suspended solids content Sample 4 with 5 mM Fe(II) and no added CTAB (as CTAB was found to have negligible influence on the removal outcomes in the flotation with CTAB concentration > 300 ppm, see Figure 4.75) as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.40 and 4.41 respectively.

![Figure 4.75](image)

*Figure 4.75:* Continuous mode flotation – Removal of contaminants for treatment of 2 L of Sample 4 as a function of wastewater flow rate and CTAB concentration with 5 mM Fe(II) at pH 6.5, and 250 mL/min air flow rate. The liquid volume in the flotation cell was kept under 200 mL.
Table 4.40: Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 4 with 5 mM Fe(II) and no surfactant addition at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Volumes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>30</td>
<td>84</td>
</tr>
<tr>
<td>45</td>
<td>83</td>
</tr>
<tr>
<td>72</td>
<td>84</td>
</tr>
<tr>
<td>120</td>
<td>72</td>
</tr>
</tbody>
</table>

Table 4.41: Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 4 with 5 mM Fe(II) and no surfactant addition at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Removals (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>30</td>
<td>98</td>
</tr>
<tr>
<td>45</td>
<td>98</td>
</tr>
<tr>
<td>72</td>
<td>97</td>
</tr>
<tr>
<td>120</td>
<td>91</td>
</tr>
</tbody>
</table>

Flotation runs with wastewater flow rates below 72 mL/min resulted in removals above 95% (see Table 4.41). The high overall removals achieved can be attributed to the high proportion of liquid leaving the cell with the foam (see Table 4.40). No effluent volumes were collected from the cell exit liquid as its volume remained below 200 mL throughout the flotation run. Since the foam drainage is cleaner than the cell exit liquid (see Table 4.33), this gives rise to higher removals. This observation contrasts to the flotation with Sample 3 where even at a low wastewater flow rate of 30 mL/min, there is a small volume collected for cell exit liquid (see Table 4.32). The difference in cell exit liquid volumes for Samples 3 and 4 can be attributed to their differences in the suspended solids content (see Table 4.3) and is consistent with the foam destabilisation at low solids concentration and the foam stabilisation at high solids concentration.

At a high wastewater flow rate of 120 mL/min, however, lower overall removals were achieved at low CTAB concentrations, i.e. < 100 ppm (see Figure 4.75). This can be attributed to the higher rate of wastewater flow into the cell compared to the rate that can be removed with the foam, resulting in liquid buildup in the cell and effluent collected as cell exit liquid. For example, in the absence of CTAB, the cell exit liquid, with a low removal of 37% (see Table 4.41), accounts for approximately 10% of the influent volume (see Table 4.40), thereby causing
the overall removal to decrease to 85%. The slight decrease in foam drainage removal (91%, see Table 4.40) at high wastewater flow rate contributes to the lower overall removal achieved. It is possible that the lower foam drainage removal is a result of a large foam carryover volume (due to foam stabilisation at high solids concentration) leading to mechanical disturbances to the foam structure and foam collapse in the foam collection vessel. The lower foam drainage removal is not observed for Sample 3 (see Table 4.33) and this can be attributable to the less foam carryover volume due to its lower suspended solids content (see Table 4.3).

**Influence of CTAB Concentration**

From Figure 4.75, it is interesting to note that the presence of CTAB was found to have no influence on the flotation outcome except at a high wastewater flow rate of 120 mL/min where higher removals were achieved at CTAB concentrations above 300 ppm. The removal outcomes for the various effluent outlets in the flotation of Sample 4 at the above wastewater flow rate as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.42 and 4.43 respectively.

**Table 4.42:** Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 4 with 5 mM Fe(II) at pH 6.5, 120 mL/min wastewater flow rate and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes (%)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>72</td>
<td>10</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>70</td>
<td>17</td>
<td>2</td>
<td>89</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>75</td>
<td>9</td>
<td>2</td>
<td>85</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>73</td>
<td>13</td>
<td>1</td>
<td>87</td>
</tr>
</tbody>
</table>

**Table 4.43:** Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 4 with 5 mM Fe(II) at pH 6.5, 120 mL/min wastewater flow rate and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Removels (%)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>91</td>
<td>37</td>
<td>96</td>
<td>85</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>91</td>
<td>42</td>
<td>95</td>
<td>82</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>97</td>
<td>72</td>
<td>100</td>
<td>94</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>96</td>
<td>64</td>
<td>98</td>
<td>91</td>
</tr>
</tbody>
</table>

A minimum amount of 300 ppm CTAB was required to increase the foam drainage removal and
the overall removal from 91% to 97% and 82% to 94% respectively (see Table 4.43). This suggests that at a higher CTAB concentration, some of the added CTAB functions as frother, stabilising the foam film as well as minimising the destabilising impact on the foam in the collection vessel by the incoming voluminous fresh foam carryover.

Alternatively, a higher CTAB concentration can result in increased solids’ hydrophobicity (i.e. through adsorption with head-down orientation) leading to an increase in particle-bubble attachment efficiency. The increased particle-bubble attachment efficiency is reflected in the corresponding increase in the removal for cell exit liquid from 42% to 72% (see Table 4.43).

It is interesting to note that the main difference in the continuous mode flotation of Samples 3 and 4 with the increase in CTAB concentration is the rate of liquid entrainment with the foam. The increase in CTAB concentration increases the rate of liquid entrainment for Sample 3 (see Table 4.34) but no noticeable trend is observed for Sample 4 (see Table 4.42). A possible reason for this is the difference in the suspended solids content of the samples (see Table 4.3). Sample 3 has a lower suspended solids content, requiring the presence of CTAB to minimise bubble coalescence (and hence, maximise liquid entrainment) while the higher suspended solids content of Sample 4 does not depend to as great an extent on CTAB for this purpose as the high concentration of solids attached to the bubble interface acts as a barrier to coalescence.

**Rates of Natural Drainage and Foam Aging**

The foam drainage volumes and their corresponding removals at the different segments of the 4-SLT drainage cell at various wastewater throughputs are shown in Tables 4.44 and 4.45 respectively. The corresponding foam volumes and their solids content are shown in Tables 4.46 and 4.47 respectively. The CTAB concentration of 300 ppm was chosen for data representation as it was shown in previous section that 300 ppm can increase the removal outcomes at the high wastewater flow rate of 120 mL/min (see Table 4.43).

**Table 4.44:** Foam drainage volumes for treatment of 2 L of **Sample 4** with 5 mM **Fe(II)** and 300 ppm **CTAB** at **pH 6.5** and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage volumes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
</tr>
<tr>
<td>30</td>
<td>76</td>
</tr>
<tr>
<td>45</td>
<td>75</td>
</tr>
<tr>
<td>72</td>
<td>71</td>
</tr>
<tr>
<td>120</td>
<td>51</td>
</tr>
</tbody>
</table>
Table 4.45: Foam drainage removals for treatment of 2 L of Sample 4 with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage removals (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
</tr>
<tr>
<td>30</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>45</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>72</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>120</td>
<td>96</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 4.46: Foam volumes for treatment of 2 L of Sample 4 with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam volumes (L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
</tr>
<tr>
<td>30</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>45</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>72</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>120</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 4.47: Foam solids content for treatment of 2 L of Sample 4 with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5 and 250 mL/min air flow rate.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam solids content (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segment 1</td>
<td>Segment 2</td>
</tr>
<tr>
<td>30</td>
<td>12.3</td>
<td>15.5</td>
</tr>
<tr>
<td>45</td>
<td>13.7</td>
<td>14.3</td>
</tr>
<tr>
<td>72</td>
<td>11.7</td>
<td>13.0</td>
</tr>
<tr>
<td>120</td>
<td>10.7</td>
<td>9.8</td>
</tr>
</tbody>
</table>

The relatively high volumes of foam drainage collected at the first segment (51 – 76%, see Table 4.44), their high levels of removals (95 – 98%, see Table 4.45) and the corresponding solids content of 10.7 – 12.3 wt% (see Table 4.47), suggest that the natural drainage of effluent from the foam is quick and effective. The high foam drainage removals achieved (> 98%, see Table 4.45) at subsequent segments reflect the stability and persistence of the solids-stabilised foam over time. These observations are similar to that obtained in the flotation of Sample 3 (see Section 4.6.4.1).

4.6.5 Optimisation of Air and Wastewater Flow Rate

Results thus far in the continuous mode flotation studies have shown that the optimum flotation
outcome is obtained when all the liquid leaves the cell with the foam. This implies that the amount of wastewater that can be treated per unit time is limited by the rate at which liquid can leave the cell with the foam. It is well known in flotation that the amount of liquid in the foam can be increased simply by increasing the air flow rate [133]. This section looks at the influence of the air flow rates on the wastewater flow rates and the flotation outcomes.

Samples 3 and 4 were chosen for this experiment. The samples were dosed with their respective optimum Fe(II) concentrations while a CTAB concentration of 300 ppm was chosen for both samples as it was found in Section 4.6.4 to give good overall removals (see Figures 4.74 and 4.75). Although the use of higher concentrations of CTAB above 300 ppm further increases the removals achieved, the small improvements are not enough justification of the higher usage.

4.6.5.1 Flotation Results for Sample 3

The flotation outcomes for Sample 3 after the additions of Fe(II) to its optimum concentration (1.25 mM) and CTAB to a concentration of 300 ppm at pH 6.5 at variable wastewater and air flow rates, are shown in Figure 4.76.

![Figure 4.76: Continuous mode flotation – Removal of contaminants for treatment of 2 L of Sample 3 as a function of wastewater and air flow rates with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5. The liquid volume in the flotation cell was kept below 200 mL.](image)

Influence of Air Flow Rate

The overall removal outcomes, as shown in Figure 4.76, at various wastewater and air flow rates in the flotation of Sample 3 are shown in Table 4.48.
Table 4.48: Removal of contaminants for treatment of 2 L of Sample 3 at 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Air flow rate (150 mL/min)</th>
<th>Air flow rate (250 mL/min)</th>
<th>Air flow rate (400 mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>96</td>
<td>90</td>
<td>74</td>
</tr>
<tr>
<td>45</td>
<td>88</td>
<td>93</td>
<td>74</td>
</tr>
<tr>
<td>72</td>
<td>60</td>
<td>93</td>
<td>87</td>
</tr>
<tr>
<td>120</td>
<td>40</td>
<td>80</td>
<td>88</td>
</tr>
</tbody>
</table>

At a low wastewater flow rate of **30 mL/min**, the corresponding optimum air flow rate was 150 mL/min, with an overall removal of 96%. At a high wastewater flow rate of **120 mL/min**, the corresponding optimum air flow rate was 400 mL/min, with an overall removal of 88% (see Table 4.48). The direct positive correlations between the optimum air and its corresponding wastewater flow rates in the continuous mode flotation in HLC mode are shown in Figure 4.76. These correlation concords with the increase in the required effluent retention time in the cell at a lower air flow rate [132].

**Operation at Low Air Flow Rate**

The removal outcomes at a low air flow rate of 150 mL/min for the various effluent outlets in the flotation of Sample 3 as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.49 and 4.50 respectively.

The advantage of operating at low air flow rates is the relatively low turbulence created, resulting in a high particle-bubble attachment stability [40]. The higher particle-bubble attachment stability leads to higher particle-bubble attachment efficiency for larger sized solids [85]. This is reflected in the high removal achieved (92%, see Table 4.49) for cell exit liquid at a low wastewater flow rate (30 mL/min). At higher wastewater flow rates (> 45 mL/min), however, the removals for cell exit liquid decrease (e.g. 30% removal at the wastewater flow rate of 120 mL/min). This decrease can be attributed to the insufficient air volumes to provide adequate bubble surface areas for solids attachment, thereby decreasing the probability of particle-bubble attachment, reflected in the increase in the proportion of cell exit liquid from 39% to 75% as the wastewater flow rate is increased from 30 mL/min to 120 mL/min (see Table 4.50). As previously discussed in Section 4.6.4.1, the increased proportion of cell exit liquid is detrimental towards the flotation outcome. Operating at low air flow rate, therefore, limits the wastewater throughput.
Table 4.49: Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 3 at low air flow rate of 150 mL/min with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Removals (%)</th>
<th></th>
<th></th>
<th></th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td>Cell exit liquid</td>
<td>Liquid left in cell at end of exp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>98</td>
<td>92</td>
<td>99</td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>45</td>
<td>95</td>
<td>81</td>
<td>99</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>72</td>
<td>88</td>
<td>47</td>
<td>98</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>120</td>
<td>82</td>
<td>30</td>
<td>98</td>
<td></td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4.50: Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 3 at low air flow rate of 150 mL/min with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Volumes (%)</th>
<th></th>
<th></th>
<th></th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td>Cell exit liquid</td>
<td>Liquid left in cell at end of exp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>46</td>
<td>39</td>
<td>10</td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>45</td>
<td>37</td>
<td>47</td>
<td>8</td>
<td></td>
<td>92</td>
</tr>
<tr>
<td>72</td>
<td>20</td>
<td>68</td>
<td>7</td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>120</td>
<td>11</td>
<td>75</td>
<td>5</td>
<td></td>
<td>91</td>
</tr>
</tbody>
</table>

In addition, the decrease in the foam drainage removal at higher wastewater flow rates also contributes (to a small extent) to the low overall removals achieved (see Table 4.49). For example, at 120 mL/min wastewater flow rate, the foam drainage removal achieved is only 82%. This can be attributed to the inadequate bubble surface area to support the solids contained within the foam leading to solids entrainment, i.e. the solids are held loosely with other attached solids (to bubble), possibly through hydrophobic interaction. The liquid drainage from foam above can wash the unattached solids leading to poor solids retention within the foam.

Higher foam stability was observed when the air flow rate is increased as shown in Table 4.51 (i.e. 93% and 88% for 250 mL/min and 400 mL/min respectively). In this circumstance, the bubble surface is not saturated with solids and the entrained hydrophobic solids of an adequate size are likely to penetrate through the three different zones of particle-bubble interaction (see Figure 2.10) and attached directly at a bubble surface.
Table 4.51: Foam drainage removal for treatment of 2 L of Sample 3 at various air flow rates with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5, and 120 mL/min wastewater flow rate.

<table>
<thead>
<tr>
<th>Air flow rate (mL/min)</th>
<th>Foam drainage removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>82</td>
</tr>
<tr>
<td>250</td>
<td>93</td>
</tr>
<tr>
<td>400</td>
<td>88</td>
</tr>
</tbody>
</table>

Operation at High Air Flow Rate

The removal outcomes at a high air flow rate of 400 mL/min for the various effluent outlets in the flotation of Sample 3 as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.52 and 4.53 respectively.

Table 4.52: Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 3 at high air flow rate of 400 mL/min with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Removals (%)</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cell exit liquid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid left in cell at end of exp.</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>73</td>
<td>99</td>
</tr>
<tr>
<td>45</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>72</td>
<td>87</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>88</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.53: Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 3 at high air flow rate of 400 mL/min with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Volumes (%)</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cell exit liquid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid left in cell at end of exp.</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>94</td>
<td>0</td>
</tr>
<tr>
<td>45</td>
<td>94</td>
<td>0</td>
</tr>
<tr>
<td>72</td>
<td>91</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>92</td>
<td>0</td>
</tr>
</tbody>
</table>

When a high air flow rate of 400 mL/min is introduced into the cell during flotation, an increase in the wastewater flow rate was found to increase the overall removals (see Figure 4.76 and Table 4.52). The overall removal increases from 74% to 88% as the wastewater flow rate is increased from 30 mL/min to 120 mL/min. This increase is mainly a result of the increase in the foam drainage removals at higher wastewater flow rates. This increase in foam drainage removals can be attributed to the higher foam stability when the foam carryover has enough
solids to stabilise the foam. Low wastewater flow rates and high air flow rates are detrimental as the bubble coalescence in the cell can lead to foam destabilisation (by the low concentration of large hydrophobic solids) during drainage.

Even though the volume proportion for foam drainage was high (between 91 and 94%, see Table 4.53) in comparison to cell exit liquid or liquid in cell, the resultant corresponding removals are relatively low compared to the foam drainage removals that were found in earlier experiments in Section 4.6.4 when a lower air flow rate of 250 mL/min was used (see Tables 4.33, 4.35 and 4.36). These lower removals indicate that there is an upper limit to the air flow rate for the flotation process in HLC mode. The lower removal at high air flow rate can be attributed to the higher bubble surface area per solids content and a large foam carryover volume, leading to foam destabilisation through coalescence (especially at low wastewater flow rate) in areas with lower concentrations of hydrophobic solids. This foam coalescence may be adequate to disrupt the foam structure leading to poor solids retention. Also, the turbulence created at high air throughput may cause break-up of loosely held solids. Smaller solids are not as effective at stabilising the foam.

### 4.6.5.2 Flotation Results for Sample 4

The flotation outcomes for Sample 4 after the additions of Fe(II) to its optimum concentration (5 mM) and CTAB to a concentration of 300 ppm at pH 6.5 at variable wastewater and air flow rates, are shown in Figure 4.77.

![Figure 4.77](image_url)

**Figure 4.77:** Continuous mode flotation – Removal of contaminants for treatment of 2 L of Sample 4 as a function of wastewater and air flow rates with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5. The liquid volume in the flotation cell was kept below 200 mL.
Influence of Air Flow Rate

The overall removal outcomes, as shown in Figure 4.77, at various wastewater and air flow rates in the flotation of Sample 3 are shown in Table 4.54.

Table 4.54: Removal of contaminants for treatment of 2 L of Sample 4 at 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Air flow rate (150 mL/min)</th>
<th>Air flow rate (250 mL/min)</th>
<th>Air flow rate (400 mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>97</td>
<td>96</td>
<td>75</td>
</tr>
<tr>
<td>45</td>
<td>84</td>
<td>98</td>
<td>77</td>
</tr>
<tr>
<td>72</td>
<td>84</td>
<td>97</td>
<td>79</td>
</tr>
<tr>
<td>120</td>
<td>61</td>
<td>94</td>
<td>90</td>
</tr>
</tbody>
</table>

At a low wastewater flow rate of 30 mL/min, the corresponding optimum air flow rate was 150 mL/min, with an overall removal of 97%. At a high wastewater flow rate of 120 mL/min, the corresponding optimum air flow rate was 400 mL/min, with an overall removal of 90% (see Table 4.48). The direct positive correlation between the optimum air and its corresponding wastewater flow rates (see Figure 4.77) is consistent with the outcomes obtained for the flotation of Sample 3 in Section 4.6.5.1.

Operation at Low Air Flow Rate

The removal outcomes at a low air flow rate of 150 mL/min for the various effluent outlets in the flotation of Sample 4 as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.55 and 4.56 respectively.

Table 4.55: Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 4 at low air flow rate of 150 mL/min with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>97</td>
<td>-</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>45</td>
<td>84</td>
<td>80</td>
<td>94</td>
<td>84</td>
</tr>
<tr>
<td>72</td>
<td>91</td>
<td>69</td>
<td>95</td>
<td>84</td>
</tr>
<tr>
<td>120</td>
<td>66</td>
<td>55</td>
<td>91</td>
<td>61</td>
</tr>
</tbody>
</table>
Table 4.56: Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 4 at low air flow rate of 150 mL/min with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Volumes (%)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>84</td>
<td>0</td>
<td>3</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>52</td>
<td>27</td>
<td>8</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>50</td>
<td>30</td>
<td>6</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>29</td>
<td>57</td>
<td>5</td>
<td>91</td>
<td></td>
</tr>
</tbody>
</table>

The trend in the flotation behaviour at a low air flow rate is similar to that found in the flotation of Sample 3 in Section 4.6.5.1, i.e. the overall removal is found to decrease from 97% to 61% as the wastewater flow rate is increased from 30 mL/min to 120 mL/min (see Table 4.55). The decrease is mainly a result of the decrease in the removal for cell exit liquid and the corresponding increase from 0% to 57% of the influent volume. Compared to Sample 3, the decrease in the overall removal for Sample 4 is less (97% to 61% for Sample 4 and 96% to 40% for Sample 3, compare Tables 4.55 and 4.49). This can be attributed to the higher solids content in Sample 4 (see Table 4.3) leading to higher foam stability (hence, large foam volume) and lower volume proportion of cell exit liquid (57% for Sample 4 and 75% for Sample 3 at 120 mL/min wastewater flow rate, compare Tables 4.56 and 4.50).

An insufficient air flow rate results in decreased foam drainage removal at higher wastewater flow rates (see Table 4.55). For example, at 120 mL/min wastewater flow rate, the foam drainage removal is only 66%. As previously discussed in Section 4.6.5.1, this poor foam drainage can be attributed to the inadequate bubble surface area to support the solids contained within the foam. These unattached solids can be washed from the foam by liquid drainage from fresh foam leading to poor solids retention within the foam. The poor solids retention for entrained solids is also consistent with the lower removal obtained for the higher solids content Sample 4 (66%, see Table 4.55) than the lower solids content Sample 3 (82%, see Table 4.49).

Operation at High Air Flow Rate

The removal outcomes at a high air flow rate of 400 mL/min for the various effluent outlets in the flotation of Sample 4 as well as their volumes (as a percentage of the influent volume) are shown in Tables 4.57 and 4.58 respectively.
Table 4.57: Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of Sample 4 at high air flow rate of 400 mL/min with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>75</td>
<td>-</td>
<td>95</td>
<td>75</td>
</tr>
<tr>
<td>45</td>
<td>77</td>
<td>-</td>
<td>99</td>
<td>77</td>
</tr>
<tr>
<td>72</td>
<td>79</td>
<td>-</td>
<td>-</td>
<td>79</td>
</tr>
<tr>
<td>120</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 4.58: Breakdown of various treated effluent outlet and their respective volumes for treatment of 2 L of Sample 4 at high air flow rate of 400 mL/min with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Wastewater flow rate (mL/min)</th>
<th>Volumes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>30</td>
<td>86</td>
</tr>
<tr>
<td>45</td>
<td>89</td>
</tr>
<tr>
<td>72</td>
<td>86</td>
</tr>
<tr>
<td>120</td>
<td>87</td>
</tr>
</tbody>
</table>

For flotation with a high air flow rate, increased wastewater flow rate increased the overall removals (see Figure 4.77 and Table 4.57). The overall removal increased from 74% to 88% as the wastewater flow rate was increased from 30 mL/min to 120 mL/min. This removal outcome is similar to that obtained for Sample 3 (74% to 88%, see Table 4.52). This increase is mainly a result of increased foam drainage removals at higher wastewater flow rates and can be attributed to the greater foam stability when the foam carryover has enough solids to stabilise the foam.

As found in Section 4.6.5.1 for the high air flow rate of 400 mL/min, the wastewater effluent leaves the flotation cell through entrainment with the foam and this foam drainage effluent has a lower removal outcome compared to the removals achieved (> 90%, see Tables 4.41, 4.43 and 4.45) when a lower air flow rate of 250 mL/min is introduced into the cell.

4.6.5.3 Comparison with Conventional Mode Flotation and Filtration

Comparison between HLC Mode and Conventional Mode Flotation

In conventional mode flotation, a core consideration is in the minimisation of the foam’s liquid content. This limits the amount of air that can be introduced into the cell as the foam sludge
water content increases with the increase in air flow rate [133]. A low air flow rate, in turn, minimises the amount of wastewater that can be treated per unit time as sufficient air volumes are required to provide adequate bubble surface areas for solids attachment. The air and wastewater flow rates used in the experiments presented in this thesis, for example, would be considered excessive for conventional mode flotation as the quantity of liquid in the foam is a large proportion of the total liquid treated. The data for the lowest air and wastewater experiments are shown in Tables 4.59 and 4.60 for Samples 3 and 4 respectively.

**Table 4.59:** Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of **Sample 3** with 1.25 mM Fe(II) and 300 ppm CTAB at pH 6.5, 150 mL/min air and 30 mL/min wastewater flow rate.

<table>
<thead>
<tr>
<th>Volume (%)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal (%)</td>
<td>46</td>
<td>39</td>
<td>10</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>98</td>
<td>92</td>
<td>99</td>
<td>96</td>
</tr>
</tbody>
</table>

**Table 4.60:** Breakdown of various treated effluent outlet and their respective removal of contaminants for treatment of 2 L of **Sample 4** with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5, 150 mL/min air and 30 mL/min wastewater flow rate.

<table>
<thead>
<tr>
<th>Volume (%)</th>
<th>Foam drainage</th>
<th>Cell exit liquid</th>
<th>Liquid left in cell at end of exp.</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal (%)</td>
<td>84</td>
<td>0</td>
<td>3</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>-</td>
<td>97</td>
<td>97</td>
</tr>
</tbody>
</table>

**Sample 3**

In conventional mode flotation, only the effluent from the cell (i.e. cell exit liquid and liquid in cell) is collected. As a result, for Sample 3, only 49% of the influent volume is treated with the remaining 51% being discarded as waste sludge (see Table 4.59). This is not a viable treatment option as the wastewater volume is only reduced by approximately half its original volume. The air throughput has to be reduced further to increase foam dewatering in the cell. The decreased air throughput can potentially lead to a lower optimum wastewater throughput, provided that the applied air volumes are in excess of what is required to remove the solids within the residence time, i.e. if the applied air volumes are in excess, decreasing the air will not have a great effect on the cell exit liquid removal and it will not be necessary to decrease the wastewater throughput. The data in Table 4.49, however, suggest that this is not the case. An increase in wastewater throughput from 30 to 45 mL/min decreases the cell exit liquid removal from 92 to 81%. As a result, a decrease in air flow rate would be expected to decrease the cell exit liquid
removal, thereby requiring a decrease in wastewater throughput to maintain a high removal for the cell exit liquid.

In HLC mode flotation, on the other hand, the overall volume of treated effluent is 94% of the influent volume at 96% removal with the remaining 6% being discarded as waste within the foam structure (see Table 4.59).

**Sample 4**

The conventional mode flotation process is not possible for Sample 4 as no cell exit liquid can be collected (see Table 4.60). A possible reason for this is that Sample 4 has a higher solids content and a higher ionic strength compared to Sample 3 (see Tables 4.2 and 4.3). The higher solids content stabilised the foam produced, consistent with foam stabilisation at higher solids concentration and foam destabilisation at lower solids concentration. Also, the higher ionic strength decreases the contact angle at the solids-liquid interface leading to a high foam stability and higher volumes of foam carryover and liquid entrainment within the foam.

In HLC mode flotation, the overall volume of treated effluent is 87% of the influent volume at 97% removal with the remaining 13% being discarded as waste within the foam structure (see Table 4.59).

**Comparison between HLC Mode Flotation and Filtration**

The flotation results presented thus far in continuous mode flotation showed that flotation in HLC mode can be an alternative treatment option to the more popular form of printing ink wastewater treatment, i.e. filtration. At the right process conditions, the foam is stabilised by the presence of hydrophobic solids while the liquid drains cleanly. In addition, operating at HLC mode allowed higher wastewater throughput without any noticeable decrease in the overall removals (see Tables 4.48 and 4.54) and this can be achieved simply by increasing the air throughput and/or the CTAB concentration. The resulting solids content contained in the foam sludge is between 12 – 17 wt% (see Tables 4.38 and 4.46). This waste solids sludge content of 12 – 17 wt% is lower than the solids content in the waste sludge of a filtration process, which had been reported to achieve up to 50 wt% solids concentration [13, 16]. It is, however, worth noting that other advantages associated with flotation over filtration (e.g. lower energy requirement, less moving parts leading to lower maintenance cost) may outweigh the poorer solids sludge concentration and other disadvantages associated with HLC mode flotation (e.g.
higher surfactant requirement).

4.6.6 Conclusion – Continuous Mode Flotation Studies

The major findings of the continuous mode flotation studies include:

- the rate of natural drainage is quick and effective. Extensive drainage to foam solids content of between 12 – 17% is achieved within the flotation duration;

- the presence of CTAB is essential in improving the flotation outcome by (i) increasing the rate of removals for the liquid in cell, (ii) increasing the removal for foam drainage by increasing the foam stability, and (iii) increasing the rate of liquid entrainment leading to an increase in volume proportion for the foam drainage at the expense of the cell exit liquid;

- based on the results achieved for the 2 main effluent streams (i.e. the cell exit liquid and the foam drainage), all the effluent should leave the cell with the foam and this can be achieved by increasing the air throughput. The air throughput is, in turn, limited by the physical turbulence and foam destabilisation at low foam solids content that are detrimental to the flotation outcome;

- although the optimum air flow rate increases with the increase in wastewater flow rate, better performance can be achieved at lower air and wastewater flow rates (see Tables 4.48 and 4.54); and

- conventional mode flotation is not suitable for the flotation of industrial printing ink wastewater. These wastewaters are high in both the solids content and the ionic strength leading to a foam sludge that is very wet. Increasing the foam dewatering by decreasing the air throughput was not a solution as it results in a further decrease in the optimum wastewater throughput.

4.6.7 Summary

The key findings for this chapter on the HLC mode flotation studies on industrial printing ink wastewater are:
the aging of the wastewater samples is found not to affect the flotation behaviour in spite of the decrease in the CBOD₅ and the carbon-to-nitrogen ratio. The pH level, the turbidity and the COD of the samples are found to show no significant changes over time;

the various pigment components that made up the wastewater sample are not selectively being removed. This is reflected by the similarity in the removals for the three characterisation methods tested, i.e. the turbidity, the yellow pigment and the copper concentration;

the use of CTAB as surfactant requires a lower Fe(II) dosage compared to the concentration required when SDS or Teric G12A8 is used. This was attributed to the higher and more negative surface charge on the mixed pigment-hydrous metal oxide solids at low coagulant dose, facilitating adsorption of cationic surfactant. The charge reduction (i.e. surface charge of solids is less negative) upon the adsorption of CTAB also aids flocculation;

for the samples tested, a minimum CTAB concentration of 300 ppm was generally required to achieve removals of above 90% for foam drainage. Low CTAB concentration of 100 ppm was found to result in foam instability. This was attributed to the reaction with anionic surfactants leading to the surfactants’ inability to form and stabilise a foam in the presence of hydrophobic particles. High CTAB concentration of 500 ppm resulted in less liquid contained in the solid waste;

no charge reversal was observed upon CTAB addition for the solids contained in the sample in the presence of Fe(II) even at low pH level (down to 5) or at high Fe(II) concentrations (5 mM). This is in contrast to the Al(III) or Fe(III) systems where charge reversals were observed. CTAB adsorption studies, however, revealed similar, high levels of adsorption for all three coagulant systems. These observations suggest different CTAB adsorption mechanisms;

the optimum flotation pH for flotation using Fe(II) was found to be 6.5 and this corresponds to the formation of large flocs;

the increase in solids content results in an increase in the Fe(II) requirement. This is consistent with the positive correlation between the coagulant requirement and the
surface sites concentrations [64]. A high Fe(II) dosage (above minimum requirement) is detrimental towards the removal outcome for liquid in cell while a low dosage (below minimum requirement) is detrimental towards the removal outcome for foam drainage;

- Fe(II) was found to have less detrimental effect on the flotation outcome compared to Al(III) or Fe(III) when its concentration is added in excess. This makes Fe(II) more suited for industrial use where the set concentration level needs to be sufficiently high as to flocculate the solids in both high suspended solids as well as low suspended solids content wastewater;

- the mixed two-metal coagulant systems did not result in any distinct improvement in the overall removals compared to their individual coagulant systems. They did, however, improve certain flotation characteristics such as increasing the foam liquid solids concentration (e.g. presence of Fe(III) in mixed coagulant systems), increasing both the foam stability and the foam solids retention (e.g. presence of Al(III) or Fe(II) in mixed coagulant systems containing Fe(III)). They were also found to be a potential solution to the problem encountered in Fe(II) system involving high Fe concentration in the effluent without compromising on the flotation outcome (e.g. presence of Fe(III) in mixed Fe(II)/Fe(III) coagulant system); and

- in continuous mode flotation studies:
  - high overall removals can best be achieved when all the liquid is carried over with the foam;
  - the optimum wastewater flow rate increases with the increase in air flow rate;
  - operation of the flotation process in HLC mode allows much higher foam product dewatering (12 – 17% solids) than is possible with conventional flotation, thereby making flotation an effective option for the treatment of industrial printing ink wastewater.

In conclusion, the high liquid carryover (HLC) mode flotation of printing ink wastewater was found to perform consistently at close to optimum levels at pH 6.5 after the wastewater samples had been pre-treated with a combination of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively. The influences of pH, Fe(II) and CTAB concentrations on the HLC mode flotation of individual simulated wastewater components will be addressed in Chapter 5 of this thesis.
Chapter 5: High Liquid Carryover Mode Flotation Studies on Simulated Wastewater

5.1 Introduction

In Chapter 4, the process variables that affect the flotation behaviour in high liquid carryover (HLC) mode were investigated and optimised on a number of industrial wastewater samples. The main process variables crucial to the flotation outcome were studied, namely the pH, the concentrations of coagulant (Fe(II), Al(III) and Fe(III)) and CTAB. It was found that the removal of pigment contaminants from the flotation cell occurs over a wide range of pH values but the overall flotation outcome using HLC mode was best when using Fe(II) as coagulant under conditions where the floc size is large and where the foam volume is optimal. It was also found that when Fe(II) is used as coagulant, the optimum flotation outcome occurs approximately at pH 6.5. The concentration of Fe(II) required was found to be dependent on the suspended solids content while the factors that affect the optimum dosage of CTAB are unclear. A minimum concentration of 300 ppm CTAB was generally required to ensure optimum outcome.

The aim of this study using simulated wastewater is to better understand how the various wastewater components contribute to the flotation behaviour observed during the flotation of industrial wastewater, and to identify any component or combination of the components that, when present in high concentrations, can lead to poor flotation outcomes.

5.2 Simulated Wastewater Composition

The simulated wastewater was comprised of individual or mixtures of the simulated wastewater components such as the process inks (blue, yellow, magenta, black and white) and the coating (applied to cardboard to facilitate printing). The individual consumption of these simulated wastewater components over a year (based on the source company’s yearly statistics) is as shown in Table 5.1.

It is important to note that the types and concentrations of the components that make up the wastewater vary from time to time and are dependent on both the colours required for each printing job and the frequency of changeover when the printing machine are washed after each print run.
Table 5.1: Relative usage (in quantity) of each simulated wastewater components.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Consumption (wt% of total raw material consumption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>19.3</td>
</tr>
<tr>
<td>White</td>
<td>17.6</td>
</tr>
<tr>
<td>Blue</td>
<td>16.0</td>
</tr>
<tr>
<td>Red</td>
<td>13.3</td>
</tr>
<tr>
<td>Black</td>
<td>6.3</td>
</tr>
<tr>
<td>Coating</td>
<td>14.3</td>
</tr>
<tr>
<td>Other</td>
<td>13.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

5.3 Characterisation of Simulated Wastewater

The characteristics of the six simulated wastewater samples are shown in Tables 5.2 and 5.3.

Table 5.2: pH, turbidity and ionic strength of the wastewater samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Turbidity</th>
<th>Conductivity</th>
<th>Conductivity equivalent NaCl conc.</th>
<th>Total suspended solids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(NTU)</td>
<td>(µS)</td>
<td>(M)</td>
<td>(g/L)</td>
</tr>
<tr>
<td>Blue</td>
<td>7.3</td>
<td>127</td>
<td>1,040</td>
<td>0.011</td>
<td>3.0</td>
</tr>
<tr>
<td>Yellow</td>
<td>7.7</td>
<td>50</td>
<td>840</td>
<td>0.009</td>
<td>4.4</td>
</tr>
<tr>
<td>Magenta</td>
<td>7.4</td>
<td>18</td>
<td>890</td>
<td>0.009</td>
<td>3.8</td>
</tr>
<tr>
<td>Black</td>
<td>8.4</td>
<td>34</td>
<td>470</td>
<td>0.005</td>
<td>2.5</td>
</tr>
<tr>
<td>White</td>
<td>7.1</td>
<td>242</td>
<td>180</td>
<td>0.002</td>
<td>2.5</td>
</tr>
<tr>
<td>Coating</td>
<td>8.3</td>
<td>84</td>
<td>230</td>
<td>0.003</td>
<td>4.9</td>
</tr>
</tbody>
</table>

* Turbidity taken at 500 times dilution.

Table 5.3: Metal content of the wastewater samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al(III)</th>
<th>Ba(II)</th>
<th>Cr(III)</th>
<th>Cu(II)</th>
<th>Fe(III)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>332</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Yellow</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Magenta</td>
<td>32</td>
<td>85</td>
<td>0</td>
<td>2</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Black</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>White</td>
<td>161</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Coating</td>
<td>237</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
These simulated wastewater components were diluted to a total suspended solids (TSS) content (see Table 5.2) close to that of the least concentrated suspended solids industrial wastewater, i.e. Sample 2 (see Table 4.3). A low solids content was chosen for the simulated wastewater in order to ensure good coagulation at 5 mM Fe(II) concentration. This coagulant concentration was found to result in good removal in the flotation of low, average and above average solids content samples at pH 6.5 with CTAB concentration of 300 ppm (see Section 4.5.2.2).

The turbidity of the samples depends on the amount and size of its dispersed suspended solids content. As the TSS contents for these samples are similar (see Table 5.2), the differences in the turbidity levels may be attributable to the differences in particle sizes. It is, however, worth noting that the variation in the turbidity range is too large to be solely a result of the differences in particle sizes. For example, magenta ink has the lowest turbidity reading at 18 NTU while white ink has the highest level at 242 NTU. A possible reason may be due to the different responses of these samples towards the infra-red light source (860 nm) passing through the samples during turbidity measurements.

In spite of this, turbidity is still a valid means of characterising the contaminant removals, as the type and proportion of pigment solids present in a wastewater sample was found not to change during the flotation run. This is shown by the similarities in the removal effectiveness of various types of contaminants from industrial wastewater using different analytical techniques, i.e. Cu(II) content, yellow pigment concentration and turbidity (see Figure 4.11 in Section 4.4).

The metal content of the different simulated wastewater components was found to differ (see Table 5.3). For example, very low concentrations of metals were found in black or yellow inks while other samples have one or more associated metals. The high levels of Cu(II) is attributable to the presence of phthalocyanine blue pigment (see Figure 2.2(b)) in blue ink while the presence of Ba(II) is due to the lithol rubine 4B red pigment (see Figure 2.2(c)) in magenta ink. Al(III), the most abundant metal found in industrial wastewater along with Cu(II) (see Table 4.4), is found in high concentrations in coating and white ink. Alumina has been known to be used as a coating agent to modify the surface characteristics of titanium dioxide pigment present in white ink and coating [55]. Aluminium can also be found in coating as hydrated aluminium silicate and/or aluminium trihydrates [49].
5.4 Single Component Simulated Wastewater

5.4.1 Introduction

The aim of this section is to determine the effect of Fe(II) and CTAB additions on the flotation of the individual simulated wastewater components. The first section involves the study of the influence of Fe(II) on the flotation outcome in the pH range 5 to 9. A Fe(II) concentration of 5 mM was chosen as this concentration was found in Section 4.5.2.2 to be able to treat most industrial wastewater samples to overall removals above 90%. The flotation results in the presence of Fe(II) are then compared with the average sizes and electrophoretic mobility (EM) of the mixed pigment-hydrous Fe(II) oxide solids, and the effect of these surface properties on the trends in the removals as well as the flotation and foam characteristics, are discussed. For industrial wastewater samples, the similarity in trend between the floc size and the foam drainage removal curve as a function of pH (compare Figures 4.33 and 4.36) suggested that floc size is a major determinant in the solids retention within the foam. The best foam drainage characteristics and removal outcomes were found to occur under conditions where the EM value is small, i.e. ± 1 \times 10^{-8} \text{ m}^2/\text{sV} (compare Figures 4.28 and 4.36). Small EM values, however, did not necessary lead to a favourable flotation outcome. The final section involves the study of the influence of CTAB concentration (up to 500 ppm) on the flotation outcome of the individual simulated wastewater components in the presence of 5 mM Fe(II).

5.4.2 Blue Ink

5.4.2.1 Flotation in the Absence and Presence of Fe(II) Hydrous Oxide

The flotation outcomes for blue ink in the absence and presence of 5 mM Fe(II) after the addition of CTAB to a concentration of 300 ppm are shown in Figures 5.1 and 5.2 respectively. The corresponding flotation behaviour is shown in Tables 5.4 and 5.5.
Figure 5.1: Removal of contaminants for blue ink as a function of pH with no coagulant addition and 300 ppm CTAB. (Note: There was hardly any liquid left in the flotation cell after the flotation run (< 5 mL) throughout the pH conducted.)

Figure 5.2: Removal of contaminants for blue ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

Table 5.4: Flotation behaviour for blue ink in the absence of coagulant with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>128</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>121</td>
<td>5</td>
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<tr>
<td>6.5</td>
<td>104</td>
<td>5</td>
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<tr>
<td>7</td>
<td>105</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>71</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 5.5: Flotation behaviour for blue ink with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>129</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>9</td>
</tr>
<tr>
<td>6.5</td>
<td>116</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>119</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>105</td>
<td>33</td>
</tr>
<tr>
<td>9</td>
<td>107</td>
<td>40</td>
</tr>
</tbody>
</table>

In the absence of Fe(II), low removals were observed at high pH values (e.g. < 10% removals above pH 6, see Figure 5.1 and Table 5.4) and an increase in removals as the pH level decreases. The increase in removals at low pH values (e.g. 32% at pH 5) is mainly a result of high foam drainage removals. The increase in removal with decreasing pH is consistent with the expected decrease in EM of the solids as the IEP of the pigment solid is approached (IEP ~ 2, [5]), leading to larger flocs that are easier to float (see Section 2.2.3.2) and which are more conducive to stabilisation of the final foam product.

In addition to the low foam drainage removals, there was very little liquid left in the cell after the flotation run (< 5 mL or less than 3% of the initial sample volume, see Table 5.4) suggesting that the solids are too small in size and/or insufficiently hydrophobic to destabilise the initial foam, i.e. the film takes a long time to thin down to less than the solids own dimensions. This high initial foam stability is also reflected in the high foam volume (> 1.4 L) throughout the pH range tested.

In the presence of 5 mM Fe(II), the removals increased significantly between pH 8 and 9 (compare Figures 5.1 and 5.2) with overall removals of 92 to 97% and foam drainage removals of 90 to 97% being achieved. These higher removals correspond to lower foam volumes recorded at the end of the flotation run (0.7 – 0.8 L, see Table 5.5) and higher liquid in cell volumes (33 – 40 mL).

A comparison of the flotation curve for blue ink (see Figure 5.2) and those for the industrial wastewater samples (see Figures 4.35 – 4.38) in the presence of 5 mM Fe(II) and 300 ppm CTAB showed that the pH region where optimum removals are achieved is very different (pH 6 – 7 for industrial wastewater samples and pH 8 – 9 for blue ink). At the flotation pH (6.5) where optimum removals were achieved when treating industrial wastewater samples (see
Section 4.5.2.3), the flotation of blue ink yields a low removal of 36%. The foam produced is too voluminous due to the high initial foam stability. The ability of solids being retained within the foam is poor as reflected by the low foam drainage removal of 31%. This suggests that the presence of high concentrations of blue ink in industrial wastewater is expected to be detrimental towards the flotation outcome.

5.4.2.2 Floc Size

The average size of the mixed pigment-hydrous Fe(II) oxide solids after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.3.

![Figure 5.3: Average floc size for blue ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.](image)

The flocs in blue ink are large in size at high pH values (between 8 and 9, see Figure 5.3) corresponding to high removals for foam drainage (between 90 and 97%, see Figure 5.2), low foam volumes (0.7 – 0.8 L, see Table 5.5) and relatively high liquid in cell volumes (33 – 40 mL). This result is consistent with the destabilisation of the initial foam by the large hydrophobic solids, followed by high foam stability and good solids retention within the foam upon the establishment of a solids-stabilised foam.

At low pH values (< 7), the mixed pigment-hydrous Fe(II) oxide solids are small in size corresponding to low foam drainage removals (< 36%), high foam volumes (> 1.4 L, see Table 5.5) and low liquid in cell volumes (< 10 mL). This result is consistent with large volumes of foam carryover due to high initial foam stability but low solids retention within the foam as small solids are not as effective in stabilising the foam.

The large differences in floc sizes over the pH range conducted showed that flocculation of the colloidal blue pigment is more effective at high pH values than at low pH values.
5.4.2.3 Electrophoretic Mobility

The EM after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.4.

![Figure 5.4: EM for blue ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: Between pH 6 and 8.5, the EM of the solids was slightly negative. It was not shown in the graph due to inability to conduct measurements at such low mobility.)](image)

The increase in negative EM value of the mixed blue pigment-hydrous Fe(II) oxide solids with the decrease in pH at low pH values (< pH 6) indicates that the adsorption of Fe(II) ions is poor, leading to poor flocculation (see Figure 5.3), poor solids retention within foam and low foam drainage removal (see Figure 5.2).

Between pH 6 and 8.5, the EM values are small and negative. The small EM values at this pH region, however, were found not to necessarily result in large floc formation. Smaller flocs were observed at the lower pH range (between pH 6 and 7) suggesting that the interaction between the colloidal blue pigments is inhibited, most likely by the steric stabilisation of the polymers (e.g. binder, non-ionic surfactant or thickener) present at the pigment surface physically preventing the pigments from reaching a distance where electrostatic or van der Waal forces act. It is interesting to note that much larger flocs were observed between pH 7 and 8.5 compared to those found between pH 6 and 7 even though their EM values were similar. The differences in floc sizes indicated that the mechanism responsible in preventing flocculation between pH 6 and 7 had minimal effect between pH 7 and 8.5. The reason for this is not known.

Above pH 8.5, a sharp increase in the negative EM value is observed in spite of the high ionic strength (see Table 5.2), possibly as a result of small change in surface charge upon the heterocoagulation of the mixed Fe(II)/Fe(III) hydrous metal oxide with the blue pigment as the
IEP of the mixed Fe(II)/Fe(III) hydrous metal oxide is approached (somewhere between that of the hydrous Fe(III) oxide (pH 7, [44]) and that of the hydrous Fe(II) oxide (pH 12). The increase in the negative EM value corresponds to a decrease in the floc size (see Figure 5.3).

5.4.2.4 Effect of Surfactant Concentration

In Section 5.4.2.1, it was found that at the optimum flotation conditions found in treating industrial wastewater samples (see Section 4.5.2.3), i.e. 5 mM Fe(II) and 300 ppm CTAB at pH 6.5, the flotation of blue ink produced a foam that is initially stable (reflected in the high foam volume and low liquid in cell volume, see Table 5.5) but unable to retain the solids within the foam (reflected in the low foam drainage removal, see Figure 5.2). These flotation characteristics can be attributed to the flocs being small in size (15 µm, see Figure 5.3) in spite of the small and negative EM value (approximately –0.5 x 10^{-8} m²/sV, see Figure 5.4). This section involves the investigation on the influence of surfactant concentration to the flotation outcome for blue ink, i.e. whether the low blue pigment removal (36%) achieved at the optimum flotation conditions can be improved by varying the surfactant concentration. This section also determined which simulated wastewater samples are responsible for the high initial foam destabilisation observed at low CTAB concentration (100 ppm) in the flotation of industrial wastewater samples (see Section 4.5.2.3).

The flotation outcome for blue ink after the additions of Fe(II) to a concentration of 5 mM and CTAB up to a concentration of 500 ppm is shown in Figure 5.5. The corresponding flotation behaviour is shown in Table 5.6.

![Figure 5.5: Removal of contaminants for blue ink as a function of CTAB concentration with 5 mM Fe(II) at pH 6.5.](image-url)
Table 5.6: Flotation behaviour for blue ink with 5 mM Fe(II) at optimum pH 6.5.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Removals</th>
<th>Effluent recovery a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam drainage (%)</td>
</tr>
<tr>
<td>0</td>
<td>121</td>
<td>4</td>
<td>1.3</td>
</tr>
<tr>
<td>100</td>
<td>130</td>
<td>2</td>
<td>1.1</td>
</tr>
<tr>
<td>300</td>
<td>116</td>
<td>10</td>
<td>1.4</td>
</tr>
<tr>
<td>500</td>
<td>145</td>
<td>4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

a effluent recovery = 100% x (combined volumes of liquid in cell and foam drainage)/total sample volume.

The increase in CTAB concentration to 500 ppm was found to increase the foam drainage removals from 14 to 78% (see Figure 5.5 and Table 5.6). This increase can tentatively be attributed to, among the many possibilities, greater CTAB adsorption onto the pigment surfaces resulting in a decrease in the negative EM value, similar to the change in EM value upon CTAB addition found for the industrial wastewater Sample 2 (see Figure 4.28). The smaller and less negative EM value of the pigment solid gives rise to larger floc formation and therefore, higher foam drainage removals (deduced from the similarity in trends for the foam drainage removal and the floc size curves, see Figures 5.2 and 5.3).

The greater CTAB adsorption onto the pigment solid can also potentially result in increased hydrophobic interaction between the mixed blue pigment-hydrous Fe(II) oxide solids. The increased hydrophobic interaction may have lead to increased foam drainage removal via large floc formation, i.e. through overcoming the steric stabilisation by the polymer binders or other mechanisms responsible in inhibiting flocculation at lower CTAB concentrations.

Apart from the increase in foam drainage removal, the increase in CTAB concentration from 300 to 500 ppm was found to increase the flotation outcome by increasing the effluent recovery from 70 to 83% of the influent volume (see Table 5.6), representing a 43% decrease in the liquid sludge volume. This trend is consistent with the 18% and 22% volume reduction obtained for industrial wastewater Samples 2 and 3 respectively (see Table 4.8).
5.4.3 Magenta Ink

5.4.3.1 Flotation in the Absence and Presence of Fe(II) Hydrous Oxide

The flotation outcomes for magenta ink in the absence and presence of 5 mM Fe(II) after the addition of CTAB to a concentration of 300 ppm are shown in Figures 5.6 and 5.7 respectively. The corresponding flotation behaviour is shown in Tables 5.7 and 5.8.

![Figure 5.6: Removal of contaminants for magenta ink as a function of pH with no coagulant addition and 300 ppm CTAB.](image1)

![Figure 5.7: Removal of contaminants for magenta ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.](image2)
Table 5.7: Flotation behaviour for magenta ink in the absence of coagulant with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>108</td>
<td>23</td>
</tr>
<tr>
<td>6.5</td>
<td>123</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>143</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>151</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>151</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.8: Flotation behaviour for magenta ink with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>82</td>
<td>55</td>
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<tr>
<td>6</td>
<td>80</td>
<td>56</td>
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<td>85</td>
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<td>72</td>
</tr>
<tr>
<td>9</td>
<td>77</td>
<td>49</td>
</tr>
</tbody>
</table>

In the absence of Fe(II) (see Figure 5.6), the flotation trend is similar to that found in the flotation of blue ink (see Figure 5.1), i.e. low removals were achieved at high pH values (< 20% removals above pH 7) and an increase in removals as the pH level decreases. In contrast to blue ink, however, the pH level where a large increase in removals was observed (i.e. between pH 6 and 7 for magenta ink) was found to be higher than that found in the flotation of blue ink (i.e. < pH 6). This suggests magenta ink has a higher IEP than blue ink, potentially giving rise to larger particle size in the pH range tested. Another possibility is that other interactive forces such as the hydrophobic attraction force between the pigment solids may be more dominant in magenta ink. In order to verify that the pigment solids in magenta ink are more hydrophobic in nature, a qualitative solvent extraction experiment is conducted (see Section 3.2.2.1 for procedures). In this experiment, the degree of ink partition (determined qualitatively through colour intensity) to the organic phase (i.e. chloroform) is an indication of the solids’ hydrophobicity. Magenta ink was found to be more hydrophobic than blue ink as the former can be partially extracted to the chloroform phase while the latter remained either at the water phase or at the aqueous/solvent interface as shown in Figure 5.8.
Figure 5.8: UV-Vis absorbance spectrum for the simulated wastewater samples of magenta and blue inks in chloroform phase. (Note: Negligible absorbance for blue ink. It is expected that the absorbance peak for blue pigment, if any, would occur at the lower visible wavelength range.)

In the presence of Fe(II), the removals increased significantly between pH 6.5 and 8 (compare Figures 5.6 and 5.7) with overall removals of 92 to 97% and foam drainage removals of 90 to 95% being achieved. These higher removals correspond to a lower foam volume recorded at the end of the flotation run (0.6 L, see Table 5.8) and a higher liquid in cell volume (72 – 85 mL). This is consistent with the trends observed for blue ink (see Section 5.4.2.1) i.e. destabilisation of the initial foam by larger hydrophobic solids, followed by the establishment of a solids-stabilised foam on standing (see Section 2.4.2).

A comparison of the flotation curve for magenta ink (see Figure 5.7) and those for the industrial wastewater samples (see Figures 4.35 – 4.38) in the presence of 5 mM Fe(II) and 300 ppm CTAB showed that the pH regions where optimum removals were found to be achieved overlaps at pH 6.5 – 7 (i.e. between pH 6 and 7 for industrial wastewater and between pH 6.5 and 8 for magenta ink). At pH 6.5, for example, the removal achieved was found to be 94% (see Table 5.8). This is within the range of 91 – 96% removals achieved for low to above average solids content industrial wastewater samples under identical conditions (i.e. Samples 2 – 4, see Table 4.13).

In contrast to blue ink, the presence of magenta ink in the industrial wastewater is expected to assist flotation at pH 6.5 (with 5 mM Fe(II) and 300 ppm CTAB) as the foam volume of 0.6 L is moderate (see Table 5.8) compared to 1.4 L for blue ink (see Table 5.5) while the removals for both the overall and the foam drainage are much higher (both removals at 94%) compared to 36% and 31% respectively for blue ink. Even though the liquid in cell removal for blue ink is
higher (98%) than that achieved for magenta ink (93%), the associated volume (10 mL or 6% of the influent volume) for blue ink is too small to warrant any advantage.

5.4.3.2 Floc Size

The average size of the mixed pigment-hydrous Fe(II) oxide solids after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.9.

![Figure 5.9: Average floc size for magenta ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.](image)

The trend in the floc size curve is similar to the foam drainage removal curve (compare Figures 5.7 and 5.9). The flocs in magenta ink are largest (80 to 100 µm) at pH values between 6 and 8, decreasing in size as the pH deviates from these pH values. As was found for blue ink, the pH region where flocs in magenta ink are largest corresponds to high removals for foam drainage (between 75 and 95%, see Figure 5.7), low foam volume (between 0.6 and 0.8 L, see Table 5.8) and relatively high liquid in cell volume (between 56 and 85 mL).

The range in floc sizes achieved for magenta ink between pH 5 and 9 (50 – 100 µm, see Figure 5.9) is much less than that observed for blue ink (15 – 200 mm, see Figure 5.3), indicating that magenta pigment is less sensitive to pH changes and this is reflected in the overall removals, with relatively high removals achieved at pH values far from the optimum pH 6.5 – 8 (e.g. 78% at pH 5 and 84% at pH 9, see Table 5.8).

5.4.3.3 Electrophoretic Mobility

The EM after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.10.
The EM curve for the mixed pigment-hydrous Fe(II) oxide solids contained in magenta ink is similar to that found for the industrial wastewater Sample 2 (compare Figures 5.10 and 4.30), i.e. the negative EM value decreases with the decrease in pH and no charge reversal observed at low pH level.

Between pH 6.5 and 8 where the foam drainage removals are high (see Figure 5.7) and the flocs are large (see Figure 5.9), the EM values of the mixed magenta pigment-hydrous Fe(II) oxide solids were found to range between $-2.0 \times 10^{-8}$ and $-0.5 \times 10^{-8}$ m$^2$/sV (see Figure 5.10). The large flocs at high negative EM values (between pH 7 and 8) suggest that ‘bridging flocculation’ and/or heteroflocculation (see Section 2.2.3.5) may be responsible for the high degree of flocculation that is able to overcome the electrostatic repulsion between the solids contained in magenta ink.

Below pH 6, the EM values are small and negative ($< 0.5 \times 10^{-8}$ m$^2$/sV) but the resultant floc sizes are relatively small ($< 80 \mu$m, see Figure 5.9) suggesting steric stabilisation that exists between the magenta pigment particles is inhibiting the coagulation of the mixed pigment-hydrous Fe(II) oxide solids. The influence of ‘bridging flocculation’ at high pH and steric stabilisation at low pH will be addressed further in Section 5.4.7.2.

### 5.4.3.4 Effect of Surfactant Concentration

The flotation outcome for magenta ink after the additions of Fe(II) to a concentration of 5 mM and CTAB up to a concentration of 500 ppm is shown in Figure 5.11. The corresponding flotation behaviour is shown in Table 5.9.
The presence of CTAB was found to have no influence on the removal outcomes (see Figure 5.11). It is possible that the hydrophobicity of the large solids of mixed pigment-hydrous Fe(II) oxide in the absence of CTAB is adequate for both particle-bubble attachment efficiency (resulting in high liquid in cell removal) and foam stability (high foam drainage removal). The introduction of CTAB may not necessarily have any impact on the hydrophobicity of the mixed magenta pigment-hydrous Fe(II) oxide solid as the resultant hydrophobicity is dependent on the orientation of the adsorbed CTAB as previously discussed in Section 2.2.4.2.

The negligible influence of CTAB on the flotation of magenta ink indicated that the high initial foam destabilisation effect observed at low CTAB concentration (100 ppm) during the flotation of industrial wastewater samples at pH 6.5 (see Section 4.5.2.3) was not due to the presence of magenta ink.
5.4.4 Yellow Ink

5.4.4.1 Flotation in the Absence and Presence of Fe(II) Hydrous Oxide

The flotation outcomes for yellow ink in the absence and presence of 5 mM Fe(II) after the addition of CTAB to a concentration of 300 ppm are shown in Figures 5.12 and 5.13 respectively. The corresponding flotation behaviour is shown in Tables 5.10 and 5.11.

![Figure 5.12](image1)

**Figure 5.12:** Removal of contaminants for yellow ink as a function of pH with no coagulant addition and 300 ppm CTAB.
(Note: (i) There is no clear distinction between liquid and foam in the flotation cell at pH 8 and 9, and (ii) a different contaminant removal range on y-axis.)

![Figure 5.13](image2)

**Figure 5.13:** Removal of contaminants for yellow ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.
(Note: A different contaminant removal range on y-axis.)
Table 5.10: Flotation behaviour for yellow ink in the absence of coagulant with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
<td>96</td>
<td>59</td>
</tr>
<tr>
<td>6.5</td>
<td>103</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>125</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>123</td>
<td>57</td>
</tr>
<tr>
<td>9</td>
<td>72</td>
<td>108</td>
</tr>
</tbody>
</table>

In the absence of Fe(II), the removals for yellow ink were found to increase with the decrease in pH. At pH 5, the following flotation characteristics can be observed, (i) a relatively high removal of 77% achieved for liquid in cell, (ii) a high volume of liquid remaining in cell (155 mL or 86% of the initial sample volume), and (iii) the high initial foam destabilisation resulting in no foam carryover observed (see Table 5.10). Between pH 6 and 7, the increase in foam volume and the decrease in liquid in cell volume suggest high initial foam stability although the solids retention within the foam remains poor. The low foam persistence can result in the foam drainage being more concentrated with contaminants compared to that found in the initial sample, hence denoted as negative contaminant removal (see Table 5.10).

At pH 8 and 9, there was no clear distinction between the liquid layer and the bubbles above the liquid in the flotation cell during flotation. This implied that the particle-bubble attachment efficiency is poor with the solids being carried over for drainage occurring simply through entrainment and hence, the solids retention during foam drainage is poor (i.e. between −7 and 0% removal achieved, see Table 5.10).

Table 5.11: Flotation behaviour for yellow ink with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>23</td>
<td>130</td>
</tr>
<tr>
<td>6</td>
<td>36</td>
<td>125</td>
</tr>
<tr>
<td>6.5</td>
<td>34</td>
<td>130</td>
</tr>
<tr>
<td>7</td>
<td>26</td>
<td>132</td>
</tr>
<tr>
<td>8</td>
<td>17</td>
<td>138</td>
</tr>
<tr>
<td>9</td>
<td>80</td>
<td>66</td>
</tr>
</tbody>
</table>
In the presence of 5 mM Fe(II), flotation of yellow ink was found to be severely adversely affected by foam destabilisation, resulting in low foam volume (< 0.2 L) and foam drainage that are more concentrated with respect to contaminants than their initial samples (see Figure 5.13). This instability may be a result of excessive floc hydrophobicity and large floc size, thereby having a destabilising effect on the foam as soon as they are formed resulting in the redispersal of the removed solids back into the flotation cell (reflected in the relatively poor liquid in cell removals). Evidence of contact angle above 90° for diarylide yellow pigment has been shown to occur in the presence of high concentrations of Yellow Pigment 13 (up to 40% w/w) in varnish with contact angle of 95° achieved at the solid/liquid interface [158].

An alternative and complementary explanation for the low foam stability observed in this system is that the low frothing ability of the solution (i.e. in the absence of the solids) is due to the precipitation of CTAB with the anionic surfactant dispersants in the sample, depleting the concentration of surfactant at the air-liquid interface during flotation (see Section 4.5.1.3). The influence of CTAB concentration on the flotation of yellow ink at pH 6.5 was investigated further and reported in Section 5.4.4.4.

A comparison of the flotation curve for yellow ink (see Figure 5.13) and those for the industrial wastewater samples (see Figures 4.35 – 4.38) in the presence of 5 mM Fe(II) and 300 ppm CTAB showed that the pH region where optimum removals are achieved is very different (i.e. pH 6 – 7 for industrial wastewater samples and pH 8 for yellow ink). Similar to blue ink, this high removal of 85% achieved at pH 8 is not of any practical use as it is distinctly different compared to the optimum pH (6.5) found for industrial ink wastewater samples at identical process conditions (see Section 4.5.2.3).

At pH 6.5, in contrast to magenta ink (see Section 5.4.3.1), the presence of yellow ink in the industrial wastewater is expected to be detrimental towards the flotation outcome. This detrimental effect is, however, very different compared to that expected from the presence of blue ink in that foam destabilisation occurs as soon as it is formed while for blue ink, destabilisation of the foam occurs much later and this may be attributed to their differences in pigment sizes. The poor foam stability results in high volume of liquid in cell and low volume of foam. More importantly, this foam characteristics resulting from the flotation of yellow ink (in the presence of 5 mM Fe(II) and 300 ppm CTAB at pH 6.5) do not allow flotation to be conducted in HLC mode.
5.4.4.2 Floc Size

The average size of the mixed pigment-hydrous Fe(II) oxide solids after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.14.

![Figure 5.14: Average floc size for yellow ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.](image)

The flocs for the yellow ink are largest at low pH values between 5 and 7 (see Figure 5.14). The increase in pH results in the decrease in the floc sizes. Interestingly, the largest floc sizes correspond to the lowest foam drainage removals (compare Figure 5.13 and 5.14). This may be attributed to the high initial foam destabilisation by the large hydrophobic solids (diarylide yellow pigment is naturally hydrophobic, [158]) leading to a foam that is very high in solids content and readily gives up the solids upon film thinning to solids dimension, i.e. very early on the drainage stage. Alternatively, it may be due to insufficient surfactant concentration to sustain a foam.

The low foam stability in the presence of large flocs (> 100 µm, see Figure 5.14) is not consistent with the results obtained for industrial wastewater samples (e.g. Sample 2, see Figures 4.33 and 4.36), blue (see Figures 5.2 and 5.3) or magenta inks (see Figures 5.7 and 5.9) where the main factor governing foam stability is the size of the flocs. This low foam stability in the presence of large hydrophobic solids too, does not agree with the results obtained by Johansson and Pugh [153] who found that foam stability increases with hydrophobicity in the presence of large solids (quartz particles of 74 – 106 µm). Again, this may be attributed to excessive yellow pigment hydrophobicity and/or a lower surfactant coverage at pigment surface.
5.4.4.3 Electrophoretic Mobility

The EM after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.15.

*Figure 5.15:* EM for yellow ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: Between pH 5 and 6.5, the EM of the solids was slightly negative. It was not shown in the graph due to inability to conduct measurements at such low mobility.)

The EM curve for the mixed pigment-hydrous Fe(II) oxide solids contained in yellow ink is similar to those found for both the industrial wastewater Sample 2 and the magenta ink (compare Figures 5.15, 4.30 and 5.10 respectively), i.e. the negative EM value decreases with the decrease in pH value and no charge reversal was observed at low pH value.

The EM curve is similar to the floc sizes (compare Figures 5.14 and 5.15) and this is consistent with increased flocculation behaviour at low EM value. The decrease in floc sizes at low pH (5) and low EM value for both industrial wastewater Sample 2 (see Figure 4.33) and magenta ink (see Figure 5.9) is, however, not observed. It is possible that the hydrophobic attractive force between the yellow pigment solids is responsible for maintaining the large floc sizes at low pH value (i.e. overcoming the force that is responsible for inhibiting flocculation at low pH values for magenta ink and industrial wastewater Sample 2).

5.4.4.4 Effect of Surfactant Concentration

The flotation outcome for yellow ink after the additions of Fe(II) to a concentration of 5 mM and CTAB up to a concentration of 500 ppm is shown in Figure 5.16. The corresponding flotation behaviour is shown in Table 5.12.
Figure 5.16: Removal of contaminants for yellow ink as a function of CTAB concentration with 5 mM Fe(II) at pH 6.5.
(Note: A different contaminant removal range on y-axis.)

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>0</td>
<td>73</td>
<td>77</td>
</tr>
<tr>
<td>100</td>
<td>47</td>
<td>113</td>
</tr>
<tr>
<td>300</td>
<td>34</td>
<td>130</td>
</tr>
<tr>
<td>500</td>
<td>70</td>
<td>103</td>
</tr>
</tbody>
</table>

The addition of CTAB is detrimental to the flotation of yellow ink (see Figure 5.16). The overall removals decrease from 95% to 38% as the CTAB concentration is increased from 0 ppm to 500 ppm. The decrease in removal can be attributed to the decrease in foam stability with the lowest foam stability occurring at system with 300 ppm CTAB. This is reflected by the corresponding decrease in both the surviving foam volume after the flotation run (from 0.2 L to 0.0 L, see Table 5.12) and the foam drainage removal (from 93% to –93%). One of the possible contributing factors to the excessive foam destabilisation is the increase in hydrophobicity resulting from CTAB adsorption onto the diarylide yellow pigment solids surface through the surfactant’s ionic head group, i.e. the electrostatic attraction between the cationic head group and the negative pigment solids surface is stronger than the hydrophobic attraction between the surfactant’s tail and the hydrophobic surface sites of the organic pigment. Another possibility is the depletion of the anionic surfactants from the pigment surfaces upon CTAB addition and exposure of the hydrophobic diarylide yellow pigment surface. The latter explanation is consistent with the decrease in foam stability at low CTAB concentration (100 ppm) for industrial wastewater samples (see Figures 4.19 and 4.20) and a higher anionic surfactant.
concentration (in yellow ink) than industrial wastewater samples, i.e. minimum foam stability (reflected by the lowest foam drainage removal) occurs at a higher CTAB concentration for yellow ink (compare Figures 4.19 and 5.16).

5.4.5 Black Ink

5.4.5.1 Flotation in the Absence and Presence of Fe(II) Hydrous Oxide

The flotation outcomes for black ink in the absence and presence of 5 mM Fe(II) after the addition of CTAB to a concentration of 300 ppm are shown in Figures 5.17 and 5.18 respectively. The corresponding flotation behaviour is shown in Tables 5.13 and 5.14.

Figure 5.17: Removal of contaminants for black ink as a function of pH with no coagulant addition and 300 ppm CTAB.
(Note: No liquid left in the flotation cell after flotation run).

Figure 5.18: Removal of contaminants for black ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.
Table 5.13: Flotation behaviour for black ink in the absence of coagulant with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>127</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>159</td>
<td>0</td>
</tr>
<tr>
<td>6.5</td>
<td>161</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>165</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>177</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>177</td>
<td>0</td>
</tr>
</tbody>
</table>

In the absence of Fe(II), low removals were achieved at all pH values tested, with an increase in removals at low pH. This result is consistent with those obtained in the flotation of blue and magenta inks (see Figures 5.1 and 5.6). Similar to blue (see Table 5.4) and magenta (see Table 5.7) inks, above pH 6.5, the absence of any liquid in cell after the flotation run and the poor foam drainage removals are indications of a high initial foam stability but low foam persistence, i.e. these particle are too small to initially destabilise the foam, or to give rise to a solids-stabilised foam on drainage (see Section 2.4.2).

Table 5.14: Flotation behaviour for black ink with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>129</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>88</td>
<td>58</td>
</tr>
<tr>
<td>6.5</td>
<td>121</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>23</td>
</tr>
<tr>
<td>8</td>
<td>79</td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>115</td>
<td>28</td>
</tr>
</tbody>
</table>

In the presence of 5 mM Fe(II), the removals increased significantly, especially between the pH 6.5 and 8 (compare Figures 5.17 and 5.18) with the highest overall removals of 88 to 93% and foam drainage removals of 79 to 92% being achieved. The contaminant removal decreases as the flotation pH deviates further from 6.5 – 8. This trend is similar to that observed for magenta ink (see Figure 5.7).

A comparison of the flotation curve for black ink (see Figure 5.18) and those for the industrial wastewater samples (see Figures 4.35 – 4.38) in the presence of 5 mM Fe(II) and 300 ppm
CTAB showed that the pH regions where optimum removals were achieved overlap at pH 6.5 – 7 (i.e. between pH 6 and 7 for industrial wastewater and between pH 6.5 and 8 for black ink). At pH 6.5, for example, the overall removal achieved is 90% (see Table 5.14), close to the range of 91 – 96% removals achieved for low to above average solids content industrial wastewater samples under identical conditions (see Table 4.12). At this pH value, the removals for foam drainage and liquid in cell were 89% and 95% respectively (see Table 5.14). With the favourable removal outcome, it is therefore likely that the presence of black ink in the industrial wastewater will aid the flotation results. The influence of black ink in the flotation of mixed component simulated wastewater samples is to be investigated further in Section 5.5.

5.4.5.2 Floc Size

The average size of the mixed pigment-hydrous Fe(II) oxide solids after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.19.

![Figure 5.19](image)

*Figure 5.19:* Average floc size for black ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

The flocs in black ink are largest (> 100 µm) between pH values 6 and 8, decreasing in size as the pH deviates further from these pH values. This floc size curve is similar to the foam drainage removal curve (compare Figures 5.18 and 5.19). This is consistent with high solids retention within foam for large hydrophobic solids. This observation is also consistent with the results observed for both the industrial wastewater Sample 2 and the simulated wastewater samples (blue and magenta inks) where the formation of large flocs were found to be necessary for high foam drainage removals.
5.4.5.3 Electrophoretic Mobility

The EM after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.20.

\[ \text{Electrophoretic mobility (10}^{-8} \text{ m}^2/\text{sV}) \]

\[ \text{Flotation pH} \]

**Figure 5.20:** EM for black ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB. (Note: Between pH 5 and 7, the EM of the solids was slightly negative. It was not shown in the graph due to inability to conduct measurements at such low mobility.)

The EM curve for the mixed pigment-hydrous Fe(II) oxide solid contained in black ink is similar to those found for both the industrial wastewater Sample 2 and the simulated wastewater samples of magenta and yellow inks (compare Figures 5.20, 4.30, 5.10 and 5.15 respectively), i.e. the negative EM value decreases with the decrease in pH value and no charge reversal was observed at low pH value.

Similar to the trend found in magenta ink system, large floc sizes (> 100 µm, see Figure 5.19) between pH 6.5 and 8 corresponds to moderate negative EM values (between $-1.3 \times 10^{-8}$ and $-0.5 \times 10^{-8}$ m$^2$/sV, see Figure 5.20). This suggests the occurrence of ‘bridging flocculation’ and/or heteroflocculation as discussed in Section 5.4.3.3. Also, the relatively smaller flocs (60 – 90 µm) found below pH 6 in spite of the small and negative EM values (< $0.5 \times 10^{-8}$ m$^2$/sV) may be due to a inhibition to flocculation as a result of steric stabilisation and/or the presence of less hydrous Fe(II) oxide surface (due to high Fe(II) solubility) for the polymers to interact with. The influence of ‘bridging flocculation’ at high pH and steric stabilisation at low pH will be addressed further in Section 5.4.7.2.
5.4.5.4 Effect of Surfactant Concentration

The flotation outcome for black ink after the additions of Fe(II) to a concentration of 5 mM and CTAB up to a concentration of 500 ppm is shown in Figure 5.21. The corresponding flotation behaviour is shown in Table 5.15.

![Figure 5.21: Removal of contaminants for black ink as a function of CTAB concentration with 5 mM Fe(II) at pH 6.5.](image)

*Figure 5.21:* Removal of contaminants for black ink as a function of CTAB concentration with 5 mM Fe(II) at pH 6.5.

*Table 5.15:* Flotation behaviour for black ink with 5 mM Fe(II) at optimum pH 6.5.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Remova ls</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>0</td>
<td>103</td>
<td>41</td>
</tr>
<tr>
<td>100</td>
<td>118</td>
<td>28</td>
</tr>
<tr>
<td>300</td>
<td>121</td>
<td>22</td>
</tr>
<tr>
<td>500</td>
<td>131</td>
<td>14</td>
</tr>
</tbody>
</table>

The removal outcome at various CTAB concentrations in the flotation of black ink (see Figure 5.21) is similar to that found for magenta ink (see Figure 5.11), i.e. the presence of CTAB was found to have minimal influence on the flotation outcome with a small differences in the removals achieved as CTAB is increased to 500 ppm (i.e. between 83 and 90% for the overall removal, between 79 and 89% for the foam drainage removal, and between 93 and 98% for the liquid in cell removal, see Table 5.15). The minimal influence of CTAB concentration on the flotation outcome of black ink showed that the high initial foam destabilisation effect observed at low CTAB concentration (100 ppm) during the flotation of industrial wastewater samples at pH 6.5 (see Section 4.5.2.3) was not due to the presence of black ink.
5.4.6 White Ink

5.4.6.1 Ink Flotation in the Absence and Presence of Fe(II) Hydrous Oxide

The flotation outcomes for white ink in the absence and presence of 5 mM Fe(II) after the addition of CTAB to a concentration of 300 ppm are shown in Figures 5.22 and 5.23 respectively. The corresponding flotation behaviour is shown in Tables 5.16 and 5.17.

Figure 5.22: Removal of contaminants for white ink as a function of pH with no coagulant addition and 300 ppm CTAB.
(Note: There is no foam carryover between pH 6.5 and 8 due to poor foam stability. Foam drainage removal at pH 6 is –94%, see Table 5.16.)

Figure 5.23: Removal of contaminants for white ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.
(Note: Foam drainage removal at pH 9 is –367%, see Table 5.17.)
### Table 5.16: Flotation behaviour for white ink in the absence of coagulant with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>5</td>
<td>76</td>
<td>92</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>153</td>
<td>0.00</td>
</tr>
<tr>
<td>6.5</td>
<td>0</td>
<td>167</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>162</td>
<td>0.00</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>169</td>
<td>0.00</td>
</tr>
<tr>
<td>9</td>
<td>19</td>
<td>112</td>
<td>2.00</td>
</tr>
</tbody>
</table>

In the absence of Fe(II), the flotation outcome for white ink is very different from that found in blue, magenta or black inks (see Figures 5.1, 5.6 and 5.12 respectively) in that, a high volume of liquid remained in the cell after the flotation run (especially between pH 6 and 8 where > 153 mL or 85% of the initial sample volume retained in the cell, see Table 5.16) suggesting high initial foam destabilisation by the white pigment solids. The high removal for liquid in cell (> 97% between pH 5 and 8, see Table 5.16) is an indication of floc hydrophobicity and high particle-bubble attachment efficiencies. A possible explanation is that the solids are large and hydrophobic enough to rupture the thin liquid film between the solids and the bubble (hence, high particle-bubble attachment efficiency) but their foam destabilising effect is greater than the frothing ability of the surfactants, resulting in the failure to establish a solids-stabilised foam.

### Table 5.17: Flotation behaviour for white ink with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>104</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>109</td>
<td>0.2</td>
</tr>
<tr>
<td>6.5</td>
<td>61</td>
<td>105</td>
<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>57</td>
<td>110</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>38</td>
<td>129</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>157</td>
<td>0.0</td>
</tr>
</tbody>
</table>

These flotation characteristics are similar to those found in the flotation of yellow ink at pH 5 in identical process conditions (see Table 5.10) but the surface chemistry of these two inks may be very different. For both inks, the addition of CTAB may deplete the anionic surfactants from solution and from the pigment surfaces (see Section 2.2.4.3) thereby decreasing the frothing ability of the solution and exposing the solids surface (coating agent such as alumina for white ink and organic yellow pigment for yellow ink). This would be expected to result in the
increase in solids hydrophobicity for yellow ink resulting in the flotation characteristics observed. In contrast, for white ink, the exposure of the positively charged alumina at pH below 9 (IEP ~ 9.2, [45]) may lead to less favourable conditions for CTAB adsorption and hence, the solids are made less hydrophobic and are less likely to lead to the establishment of a solids-stabilised foam. Even though the overall removals achieved are above 97% (for pH 6.5 – 8), the failure to establish a solids-stabilised foam results in HLC mode being unsuitable for the flotation of white pigment in the absence of any added coagulant.

The presence of 5 mM Fe(II) increases the foam stability with higher foam carryover volume, lower volume of liquid in cell and higher solids retention within the foam, especially between pH 5 and 7 (compare Tables 5.16 and 5.17). The clean foam drainage at these pH values (e.g. 96% removal at pH 6.5, see Figure 5.23) suggests that the flocs are large and hydrophobic. Above pH 7, however, the increase in the amount of liquid in cell and the decrease in foam volume with the increase in pH suggests increased initial foam destabilisation and low foam persistence. The high foam destabilisation may be attributed to the increase in CTAB adsorption with head-down orientation due to the increased negative EM value of the mixed white pigment-hydrous Fe(II) oxide solids with pH, resulting in excessive solids hydrophobicity. An alternative and complementary explanation is that CTAB precipitates in the presence of anionic surfactant dispersants, leading to insufficient frothing ability to compensate for the amount of destabilisation by the solids. The influence of CTAB concentration on the flotation of white ink at pH 6.5 is to be investigated further in Section 5.4.6.4.

A comparison of the flotation curve for white ink (see Figure 5.23) and those for the industrial wastewater samples (see Figures 4.35 – 4.38) in the presence of 5 mM Fe(II) and 300 ppm CTAB showed that the pH regions where optimum removals were achieved were similar (i.e. at pH 6.5 – 7). At pH 6.5, for example, the overall removal is 97%, higher than the removals achieved for other simulated wastewater samples investigated (36, 94, 42 and 90% for blue, magenta, yellow and black ink respectively) under similar process conditions. Although the foam volume is low (0.2 L, see Table 5.17) and the volume for liquid in cell is high (105 mL) due to high initial foam destabilisation by the large and hydrophobic solids, the establishment of a solids-stabilised foam upon drainage results in good solids retention within foam (reflected in 96% foam drainage removal). The high foam carryover volume and the low foam drainage removals in the flotation of blue ink at pH 6.5 are in direct contrast to the flotation characteristics of white ink. It is therefore possible that the high initial foam destabilisation by the mixed white pigment-hydrous Fe(II) oxide solids may compensate and aid in the flotation of blue ink. The flotation of mixed inks is to be discussed further in Section 5.5.
5.4.6.2 Floc Size

The average size of the mixed pigment-hydrous Fe(II) oxide solids after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.24.

**Figure 5.24:** Average floc size for white ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

Large flocs (> 100 µm) were observed between pH 5 and 9. Similar to magenta ink system (see Figure 5.9), the size of mixed white pigment-hydrous Fe(II) oxide solid is less sensitive to pH changes. This, however, is not reflected in the foam drainage removal curve (see Figure 5.23), with the removals decreasing sharply as the pH deviates from 6.5 while the floc size showed a smaller and more moderate decrease. The low foam drainage removal can be attributed to high initial foam destabilisation by the large and very hydrophobic solids with CTAB adsorbing with head-down orientation through favourable electrostatic interaction and/or CTAB-anionic surfactants precipitation as previously discussed in Section 4.5.1.3. The differences in flotation response between white and magenta inks may be due to the resultant solid hydrophobicity which in turn depends on the orientation of the adsorbed surfactant (see Section 2.2.4.2).

5.4.6.3 Electrophoretic Mobility

The EM after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.25.
Figure 5.25: EM for white ink as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

In contrast to the EM curve for both the industrial wastewater Sample 2 (see Figure 4.39) and other simulated wastewater samples (blue, magenta, yellow and black inks, see Figures 5.4, 5.10, 5.15 and 5.20 respectively), the EM curve for the mixed white pigment-hydrous Fe(II) oxide solid showed a charge reversal to a net positive surface charge at pH values below 6.2. This charge reversal may be attributable to several factors. The depletion of anionic surfactants from the pigment surfaces (due to CTAB-anionic surfactants precipitation, see Section 2.2.4.3) can lead to the exposure of the coating agent (such as alumina), which was found to dominate the surface characteristics of white TiO₂ pigment [45, 78]. This pigment is present in white ink samples and exposure of the alumina surface (iep = 9.2, [45]) would be expected to render the surface more positive at low pH values. Charge reversal can also occur under conditions where the Fe(II) hydrous oxide solids is present in sufficient quantities and heterocoagulation with the pigment solids produce a floc that has a net positive charge. This explanation is less likely due to the high solubility of hydrous Fe(II) oxide below pH 8 (see Figure 4.31).

A comparison between the floc size (see Figure 5.24) and the EM value of the mixed white pigment-hydrous Fe(II) oxide solid showed that the large increase in the negative EM value (from 0 to −2.3 x 10⁻⁸ m²/sV) with the increase in pH (from 6 to 9) is not reflected in a decrease in floc sizes. The floc sizes remained similar (ranging between 110 and 130 µm). This may be attributed to the ‘bridging flocculation’ and/or heteroflocculation by the long chain polymers as discussed in Section 2.2.3.5. The influence of polymers on the flocculation behaviour will be discussed further in Section 5.4.7.2. Alternatively, the hydrophobic attraction between the hydrophobic solids may play an important role during flocculation.
5.4.6.4 Effect of Surfactant Concentration

The flotation outcome for white ink after the additions of Fe(II) to a concentration of 5 mM and CTAB up to a concentration of 500 ppm is shown in Figure 5.26. The corresponding flotation behaviour is shown in Table 5.18.

Figure 5.26: Removal of contaminants for white ink as a function of CTAB concentration with 5 mM Fe(II) at pH 6.5.
(Note: The foam drainage removal at 100 ppm CTAB is −389%.)

Table 5.18: Flotation behaviour for white ink with 5 mM Fe(II) at optimum pH 6.5.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Removals</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
</tr>
<tr>
<td>0</td>
<td>24</td>
<td>143</td>
<td>0.05</td>
</tr>
<tr>
<td>100</td>
<td>9</td>
<td>160</td>
<td>0.0</td>
</tr>
<tr>
<td>300</td>
<td>61</td>
<td>105</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>69</td>
<td>95</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The flotation characteristics for white ink (see Figure 5.26) include high foam destabilisation at low CTAB concentration (100 ppm) and good foam solids retention at high CTAB concentrations (300 and 500 ppm). The low foam stability at low CTAB concentration is reflected in the negligible surviving foam volume and the low foam carryover volume (see Table 5.18). A possible explanation for this instability is the exposure of the hydrophilic pigment surface (that cannot sustain a stable foam) as a result of the depletion of anionic surfactants from the surface through reaction with the added CTAB (see Section 2.2.4.3).

The increase in foam stability with further increase in CTAB concentration above 100 ppm is consistent with large hydrophobic solids stabilising the foam, with CTAB adsorbing through
head-down orientation similar to the monolayer hydrophobic structure model of CTAB adsorption on TiO$_2$ pigment surface as described in [54]. The foam stability is reflected in the increase in foam volume as CTAB concentration increases above 100 ppm (see Table 5.18).

The foam drainage removal trend for white ink is similar to that found in the flotation of industrial wastewater Samples 2 and 3 (see Figures 4.19 and 4.20). It is likely that Sample 3 contains a high concentration of white ink as its Al(III) content (a key metal found in white ink, see Tables 4.4 and 5.3) is relatively high in comparison to other common metals. The Al(III) content in Sample 2, on the other hand, is relatively low. The flotation behaviour observed in Sample 2 may have therefore been caused by the presence of, for example, yellow ink, which was found to give similar flotation outcome (see Figure 5.16).

The foam destabilisation at low CTAB concentration is not found in the flotation of other printing inks except for yellow ink. A possible explanation for this involves the inherent nature of the solids involved. Titanium dioxide and its coating agents (alumina and silica) in white ink are inorganic and hydrophilic in nature while the pigments in other printing inks investigated, i.e. blue, magenta and black inks, are organic pigments and hence, are inherently hydrophobic in the absence of additives. The depletion of the anionic surfactants from the pigment surfaces by generation of hydrous Fe(II) oxide surface (see Figure 2.8) would expose the hydrophobic surfaces in blue, magenta and black inks. The exposure of these hydrophobic surfaces is not detrimental to the formation of solids-stabilised foam as long as the solids are of appropriate sizes and hydrophobicity. The detrimental effect on foam stability of organic pigment of excessive hydrophobicity may be responsible for the poor flotation outcome in the flotation of yellow pigment as shown in Section 5.4.4.

5.4.7  Coating

5.4.7.1  Flotation in the Absence and Presence of Fe(II) Hydrous Oxide

The flotation outcomes for coating in the absence and presence of 5 mM Fe(II) after the addition of CTAB to a concentration of 300 ppm are shown in Figures 5.27 and 5.28 respectively. The corresponding flotation behaviour is shown in Tables 5.19 and 5.20.
Figure 5.27: Removal of contaminants for coating as a function of pH with no coagulant addition and 300 ppm CTAB.
(Note: There is no foam carryover between pH 7 and 9 due to poor foam stability.)

Figure 5.28: Removal of contaminants for coating as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

Table 5.19: Flotation behaviour for coating in the absence of coagulant with 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th></th>
<th>Removals</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
<td>Foam (L)</td>
<td>Foam drainage (%)</td>
</tr>
<tr>
<td>5</td>
<td>27</td>
<td>141</td>
<td>0.3</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
<td>145</td>
<td>0.2</td>
<td>95</td>
</tr>
<tr>
<td>6.5</td>
<td>0</td>
<td>177</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>174</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>175</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>176</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(Note: No foam carryover recorded between pH 6.5 and 9.)
Table 5.20: Flotation behaviour for coating with 5 mM Fe(II) and 300 ppm CTAB.

<table>
<thead>
<tr>
<th>Flotation pH</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>89</td>
<td>57</td>
</tr>
<tr>
<td>6.5</td>
<td>71</td>
<td>72</td>
</tr>
<tr>
<td>7</td>
<td>89</td>
<td>62</td>
</tr>
<tr>
<td>8</td>
<td>72</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>68</td>
<td>94</td>
</tr>
</tbody>
</table>

In the absence of Fe(II), the flotation characteristics for coating is similar to that found in the flotation of white ink, i.e. (i) a high volume of liquid remaining in cell after the flotation run (especially above pH 6 where > 174 mL or 97% of the initial sample volume was retained in the cell, see Table 5.19), suggesting high initial foam destabilisation by the coating solids, and (ii) a high removal for liquid in cell (> 91%) throughout the pH level tested except for pH 6.5 where an unusually low 80% removal is achieved, see Figure 5.27), indicating high floc hydrophobicity and high particle-bubble attachment efficiency. As previously discussed in the flotation of white ink, the above characteristics can also be a result of poor solution frothing ability due to precipitation of CTAB with the anionic surfactants (see Section 2.2.4.3). The influence of CTAB concentration on the flotation of coating at pH 6.5 is to be investigated further in Section 5.4.7.4. In summary, even though overall removals above 97% can be achieved, the failure to establish a solids-stabilised foam results in HLC mode being unsuitable for the flotation of coating in the absence of any added coagulant.

The presence of 5 mM Fe(II) increases the foam stability with higher foam carryover volume, lower volume of liquid in cell and higher solids retention within the foam (compare Tables 5.19 and 5.20). These characteristics were found in the studies of continuous mode flotation on industrial wastewater samples (see Section 4.6) to be more suitable for conducting flotation in HLC mode. The overall removals in the flotation of coating are high throughout the pH range tested with removals between 87 and 98% achieved. The removal outcomes were found to increase with the increase in pH, with removals as high as 98% achieved at pH 8 – 9 (see Figure 5.28). The highest removals coincide with conditions where the foam volume was the lowest and the volume for liquid in cell was the highest. This is consistent with destabilisation of the initial foam by larger hydrophobic solids, followed by the establishment of a solids-stabilised foam on standing.
A comparison of the flotation curve for coating (see Figure 5.28) and those for the industrial wastewater samples (see Figures 4.35 – 4.38) in the presence of 5 mM Fe(II) and 300 ppm CTAB showed that the pH regions where optimum removals were achieved were very different (pH 6 – 7 for industrial wastewater samples and pH 8 – 9 for coating). In spite of this, the achievable removals at pH region 6 – 7 for coating are still considerable (between 87 and 95%, see Table 5.20). At pH 6.5, for example, the overall removal is 91% and within the range of 91 – 96% removals achieved for low to above average solids content industrial wastewater under similar conditions (see Table 4.13). At this pH value, the removal for foam drainage is high at 97% while the removal for liquid in cell is 85%. The influence of coating in the flotation of mixed component simulated wastewater samples is to be investigated further in Section 5.5.

5.4.7.2 Floc Size

The average size of the mixed pigment-hydrorous Fe(II) oxide solids after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.29.

![Figure 5.29: Average floc size for coating as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.](image)

For coating, the floc sizes were found to increase with the increase in pH with the largest flocs observed at pH 9. A comparison of the floc size with its corresponding flotation behaviour (compare Figures 5.28 and 5.29) showed that unlike other simulated component wastewater samples, floc size is not as important in achieving good solids retention within foam and high particle-bubble attachment efficiency.

The foam drainage removals remained high (> 93%, see Figure 5.28) throughout the pH range investigated even though the average floc size is small (e.g. 30 μm at pH 5) at low pH values. The high foam drainage removal, in spite of the relatively small solids, is in contrast to that
obtained for other ink samples at similar pH values. For example, lower foam drainage removals of 68% and 55% were achieved with larger floc sizes (50 µm and 65 µm) for magenta and black inks respectively. Solids hydrophobicity may be responsible for these differences in flotation outcomes. An alternative explanation is the flocculation of the polymers through attractive lateral capillary forces (see Section 2.3.2.1) when they are brought into contact during liquid drainage from foam, effectively increasing the floc size. Polymers, such as the copolymers of carboxylic-polystyrene-polybutadiene mixture or carboxylic-polyacrylic mixture in paper or cardboard coating [49], are present in a much higher concentration in coating than polymers (as binder, non-ionic surfactant or thickener) in printing inks, as they are required to bind strongly to the paper or cardboard before any printing ink is applied.

The smaller floc sizes at low pH is in contrast to those found for industrial wastewater Sample 2 (see Figure 4.33) and the simulated wastewater samples of magenta, yellow, black and white inks (see Figures 5.9, 5.14, 5.19 and 5.24 respectively) where the floc sizes are generally larger at lower pH values. The smaller flocs at lower pH values may be due to steric stabilisation by the polymers present at the coating surface (see Section 2.2.3.5). Steric stabilisation may also be responsible for the decrease in floc size with the decrease in pH below 6 for industrial wastewater Sample 2 (see Figure 4.33), as well as simulated wastewater samples of magenta, black and white inks (see Figures 5.9, 5.19 and 5.24 respectively).

At higher pH values, in the presence of hydrous metal oxide solids (low Fe(II) solubility and high oxidation rate to Fe(III)), the increase in floc sizes may be tentatively attributed to ‘bridging flocculation’ and/or heteroflocculation (see Figures 2.9(c) and (d)) by the high molecular weight polymers. ‘Bridging flocculation’ and/or heteroflocculation may also be responsible for the large floc sizes (despite high negative EM values) observed for magenta and white inks at high pH values (9). Due to the higher polymer concentration, the effects of steric stabilisation and/or ‘bridging flocculation’ are more pronounced for coating than for the process inks or the industrial wastewater Sample 2.

Alternatively, the differences in floc size trend with pH may be attributed to their EM values and the EM values at the mixed coating-hydrous Fe(II) oxide solid surface will be investigated in the next section.

5.4.7.3 Electrophoretic Mobility

The EM after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively is shown in Figure 5.30.
Figure 5.30: EM for coating as a function of pH with 5 mM Fe(II) and 300 ppm CTAB.

The EM curve for the mixed coating-hydrous Fe(II) oxide is similar to that found for white ink (compare Figures 5.25 and 5.30), i.e. a charge reversal to a net positive surface charge was observed at low pH values with IEP at approximately pH 6.6. Similar to white ink, this may be attributed to the depletion of anionic surfactants from the coating surfaces resulting in the exposure of the coating agent such as alumina. The presence of alumina in both white ink and coating is reflected in the high concentrations of aluminium in both samples (see Table 5.3).

A comparison between the floc sizes (see Figure 5.29) and the corresponding EM values (see Figure 5.30) showed the expected increase in floc size as the IEP (approximately pH 7) is approached at pH values below the IEP. A further increase in pH values above the IEP, leading to increasingly negative surface charge, does not, however, give rise to smaller flocs. The floc size continues to increase with increasing pH, suggesting that another flocculation mechanism other than the electrostatic attraction mechanism may be dominant, e.g. ‘bridging flocculation’ and/or heteroflocculation by the high molecular weight long polymer chains functioning as flocculants as previously discussed in Section 5.4.7.2.

5.4.7.4 Effect of Surfactant Concentration

The flotation outcome for coating after the additions of Fe(II) to a concentration of 5 mM and CTAB up to a concentration of 500 ppm is shown in Figure 5.31. The corresponding flotation behaviour is shown in Table 5.21.
Figure 5.31: Removal of contaminants for coating as a function of CTAB concentration with 5 mM Fe(II) at pH 6.5.

Table 5.21: Flotation behaviour for coating with 5 mM Fe(II) at optimum pH 6.5.

<table>
<thead>
<tr>
<th>CTAB conc. (ppm)</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>100</td>
<td>36</td>
<td>133</td>
</tr>
<tr>
<td>300</td>
<td>71</td>
<td>72</td>
</tr>
<tr>
<td>500</td>
<td>116</td>
<td>31</td>
</tr>
</tbody>
</table>

From Table 5.21, in the absence of CTAB, the negligible foam carryover volume indicates that the foam produced during flotation is highly unstable while a low liquid in cell removal of 8% indicates that the particle-bubble attachment efficiency is poor. This flotation behaviour suggests that the surfactant concentration is low in the coating formulation. This result is in contrast to the higher foam stability observed in the flotation of the process inks in the absence of CTAB (see Figures 5.5, 5.11, 5.16, 5.21 and 5.26 for blue, magenta, yellow, black and white inks respectively).

The increase in CTAB concentration from 0 to 500 ppm was found to result in (i) an increase in the removal for liquid in cell from 8 to 97% (see Figure 5.31) suggesting an increased particle-bubble attachment efficiency, (ii) an increase in the foam carryover volume from 0 to 149 mL (see Table 5.21) suggesting that the foam is stabilised by the large and hydrophobic solids, and (iii) an increase in the foam volume from 0 to 1.0 L. These flotation trends indicate an increased solids hydrophobicity with increased CTAB addition, i.e. CTAB adsorbing onto the mixed coating-hydrous Fe(II) oxide solid predominantly with head-down orientation.
5.4.8 Conclusion

**Effect of Hydrous Fe(II) Oxide on Flotation of Individual Components**

The presence of 5 mM hydrous Fe(II) oxide was found to result in improvements in the flotation outcome for most of the simulated wastewater samples investigated. For example, the overall removals increased from low or negligible removals (in the absence of Fe(II)) to above 90% (in the presence of 5 mM Fe(II)) for magenta and black inks in the pH 6.5 – 7 region. For white ink and coating, the presence of hydrous Fe(II) oxide changes the surface chemistry of the solids to one that allowed flotation to be conducted in HLC mode without excessive foam destabilisation at the initial foam formation stage. The high removals achieved at pH 8 – 9 in the flotation of blue ink are less useful as these pH values are distinctly different from the optimum pH (6.5) found for industrial wastewater. There was no distinct flotation improvements by hydrous Fe(II) oxide addition in the flotation of yellow ink.

**Effect of Surfactant Concentration on Flotation of Individual Components**

The optimum surfactant concentration was found to vary significantly for the different components tested. For example, a high CTAB concentration (i.e. 500 ppm) was required to increase the foam drainage removal in the flotation of blue ink while for the flotation of yellow ink, CTAB addition was detrimental towards the foam stability and hence, the foam drainage removal. A low CTAB concentration (i.e. 100 ppm) was found to be detrimental towards the flotation of white ink while for the flotation of black or magenta inks, CTAB addition was found to have negligible effect on the flotation outcome. The optimum CTAB concentration required during the flotation of industrial wastewater would therefore be expected to depend on the concentration of each component in the wastewater. It was, however, found that a CTAB concentration of 300 ppm was effective for three of the four industrial wastewater samples investigated (see Figure 4.19 and 4.20). This CTAB concentration was found to produce a high removal outcome (relatively to other CTAB concentrations) for all the simulated single wastewater components investigated except for blue and yellow inks, and is to be used for further studies on the flotation of multiple component simulated wastewater (see Section 5.5).
**Flotation Behaviour at pH 6.5**

A summary of the flotation characteristics (in order according to floc size) after the additions of Fe(II) and CTAB to concentrations of 5 mM and 300 ppm respectively at pH 6.5 is shown in Table 5.22.

**Table 5.22:** Flotation behaviour for single component simulated wastewater samples with 5 mM Fe(II) and 300 ppm CTAB at optimum pH 6.5, in order of decreasing average floc size. The flotation behaviour for industrial wastewater Sample 2 is also shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Floc size (µm)</th>
<th>Foam drainage (mL)</th>
<th>Liquid in cell (mL)</th>
<th>Foam (L)</th>
<th>Foam drainage (%)</th>
<th>Liquid in cell (%)</th>
<th>Overall (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>120</td>
<td>121</td>
<td>22</td>
<td>0.8</td>
<td>89</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>White</td>
<td>110</td>
<td>61</td>
<td>105</td>
<td>0.2</td>
<td>96</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>Yellow</td>
<td>105</td>
<td>34</td>
<td>130</td>
<td>0.0</td>
<td>–93</td>
<td>77</td>
<td>42</td>
</tr>
<tr>
<td>Magenta</td>
<td>95</td>
<td>53</td>
<td>85</td>
<td>0.6</td>
<td>94</td>
<td>93</td>
<td>94</td>
</tr>
<tr>
<td>Coating</td>
<td>60</td>
<td>71</td>
<td>72</td>
<td>0.9</td>
<td>97</td>
<td>85</td>
<td>91</td>
</tr>
<tr>
<td>Blue</td>
<td>15</td>
<td>116</td>
<td>10</td>
<td>1.4</td>
<td>30</td>
<td>98</td>
<td>36</td>
</tr>
<tr>
<td>Sample 2</td>
<td>85</td>
<td>40</td>
<td>120</td>
<td>0.4</td>
<td>93</td>
<td>92</td>
<td>92</td>
</tr>
</tbody>
</table>

The floc sizes for magenta, yellow, black and white inks (between 95 and 120 µm), in the presence of 5 mM Fe(II) and 300 ppm CTAB, were found to be larger than those contained in the industrial wastewater Sample 2 which had an average size of 85 µm under similar process conditions. Coating is slightly smaller in size at 60 µm while the average floc size for blue ink is much smaller at 15 µm.

The flotation of all the simulated or industrial wastewater samples containing large flocs (> 60 µm) at pH 6.5 was found to result in good contaminant removals with the exception of yellow ink. For example, the flotation of simulated wastewater samples of magenta, black and white inks and coating, with floc size above 60 µm, achieved an overall removal of above 90% with removals for foam drainage and liquid in cell ranging from 89 – 97% and 85 – 98% respectively.

The flotation of blue ink was found to result in poor overall removal, especially in foam drainage removal where only 30% removal was achieved. The flocs were found to be too small (15 µm) to destabilise the foam at the initial stage resulting in high foam carryover volume, or
to establish a solids-stabilised foam upon liquid drainage, leading to poor solids retention within foam.

In spite of the large floc size (105 µm), the flotation of yellow ink yields a poor overall removal of 42%. This can be attributed to the excessive foam destabilisation at the initial stage resulting in high liquid volume in cell, negligible foam volume and negative foam drainage removal (foam drainage contained higher concentrations of contaminant than the influent sample).

Blue and yellow inks are therefore problematic colours in the flotation of printing ink and coating wastewater. These two inks are to be given more attention in the flotation of multiple components simulated wastewater in the next section.

5.5 Multiple Component Simulated Wastewater

5.5.1 Introduction

In the previous section, the influences of Fe(II) and CTAB concentrations on the flotation outcomes for the various components were investigated. Two problematic inks, i.e. that were difficult to remove under the conditions suitable for the flotation of industrial wastewater (5 mM Fe(II) and 300 ppm CTAB at pH 6.5), were identified – blue and yellow inks. This section investigates the flotation behaviour of mixed equal volume components in all combinations to identify the combinations that are problematic and to better define and understand the surface chemistry involved.

5.5.2 Factorial Design Experiment

A full factorial experiment comprising all the 6 simulated wastewater components investigated was designed. The flotation of samples containing two or more components is conducted at two different concentration levels (i.e. present denoted as ‘+’ and absence denoted as ‘-’). The flotation outcomes after the additions of Fe(II) and CTAB to concentrations of 5 mM and 500 ppm respectively are shown in Tables 5.23 and 5.24.
Table 5.23: Flotation behaviour for mixed components of equal volumes with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Samples</th>
<th>Volumes</th>
<th>Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B M Y Bk W C</td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>1</td>
<td>+ + + + + +</td>
<td>82</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
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<td>71</td>
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<tr>
<td>3</td>
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<td>66</td>
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</tr>
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<td>9</td>
<td>+ + - + + +</td>
<td>89</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>+ + - + + -</td>
<td>88</td>
<td>59</td>
</tr>
<tr>
<td>11</td>
<td>+ + - + + -</td>
<td>72</td>
<td>73</td>
</tr>
<tr>
<td>12</td>
<td>+ + - + - +</td>
<td>102</td>
<td>39</td>
</tr>
<tr>
<td>13</td>
<td>+ + - - + +</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>14</td>
<td>+ + - - + -</td>
<td>77</td>
<td>68</td>
</tr>
<tr>
<td>15</td>
<td>+ + - - - +</td>
<td>67</td>
<td>81</td>
</tr>
<tr>
<td>16</td>
<td>+ + - - - -</td>
<td>105</td>
<td>9</td>
</tr>
<tr>
<td>17</td>
<td>+ - + + + +</td>
<td>78</td>
<td>70</td>
</tr>
<tr>
<td>18</td>
<td>+ - + + + -</td>
<td>76</td>
<td>77</td>
</tr>
<tr>
<td>19</td>
<td>+ - + + - +</td>
<td>61</td>
<td>91</td>
</tr>
<tr>
<td>20</td>
<td>+ - + - + -</td>
<td>88</td>
<td>52</td>
</tr>
<tr>
<td>21</td>
<td>+ - + - + +</td>
<td>48</td>
<td>109</td>
</tr>
<tr>
<td>22</td>
<td>+ - + - + -</td>
<td>53</td>
<td>99</td>
</tr>
<tr>
<td>23</td>
<td>+ - + - - +</td>
<td>46</td>
<td>110</td>
</tr>
<tr>
<td>24</td>
<td>+ - + - - -</td>
<td>93</td>
<td>52</td>
</tr>
<tr>
<td>25</td>
<td>+ - - + + +</td>
<td>107</td>
<td>40</td>
</tr>
<tr>
<td>26</td>
<td>+ - - + + -</td>
<td>119</td>
<td>18</td>
</tr>
<tr>
<td>27</td>
<td>+ - - + - +</td>
<td>113</td>
<td>39</td>
</tr>
<tr>
<td>28</td>
<td>+ - - + - -</td>
<td>132</td>
<td>0</td>
</tr>
<tr>
<td>29</td>
<td>+ - - - + +</td>
<td>110</td>
<td>35</td>
</tr>
<tr>
<td>30</td>
<td>+ - - - + -</td>
<td>131</td>
<td>7</td>
</tr>
<tr>
<td>31</td>
<td>+ - - - - +</td>
<td>100</td>
<td>28</td>
</tr>
<tr>
<td>32</td>
<td>+ - - - - -</td>
<td>116</td>
<td>10</td>
</tr>
</tbody>
</table>

(Note: B – blue ink; M – magenta ink; Y – yellow ink; Bk – black ink; W – white ink; C – coating.)
Table 5.24: Flotation behaviour for mixed components of equal volumes with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Samples</th>
<th>Volumes</th>
<th>Foam Removals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B M Y Bk W C</td>
<td>Foam drainage (mL)</td>
<td>Liquid in cell (mL)</td>
</tr>
<tr>
<td>33</td>
<td>- + + + + + +</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td>34</td>
<td>- + + + + - +</td>
<td>78</td>
<td>73</td>
</tr>
<tr>
<td>35</td>
<td>- + + + - + +</td>
<td>64</td>
<td>84</td>
</tr>
<tr>
<td>36</td>
<td>- + + + - - -</td>
<td>88</td>
<td>53</td>
</tr>
<tr>
<td>37</td>
<td>- + + - + + +</td>
<td>45</td>
<td>108</td>
</tr>
<tr>
<td>38</td>
<td>- + + - + - -</td>
<td>57</td>
<td>102</td>
</tr>
<tr>
<td>39</td>
<td>- + + - - + +</td>
<td>49</td>
<td>102</td>
</tr>
<tr>
<td>40</td>
<td>- + + - - - -</td>
<td>52</td>
<td>95</td>
</tr>
<tr>
<td>41</td>
<td>- + - + + + +</td>
<td>76</td>
<td>73</td>
</tr>
<tr>
<td>42</td>
<td>- + - + + + -</td>
<td>83</td>
<td>66</td>
</tr>
<tr>
<td>43</td>
<td>- + - + - + +</td>
<td>79</td>
<td>66</td>
</tr>
<tr>
<td>44</td>
<td>- + - + - - -</td>
<td>96</td>
<td>40</td>
</tr>
<tr>
<td>45</td>
<td>- + - - + + +</td>
<td>45</td>
<td>110</td>
</tr>
<tr>
<td>46</td>
<td>- + - - + - +</td>
<td>53</td>
<td>110</td>
</tr>
<tr>
<td>47</td>
<td>- + - - - - +</td>
<td>42</td>
<td>111</td>
</tr>
<tr>
<td>48</td>
<td>- + - - - - -</td>
<td>53</td>
<td>85</td>
</tr>
<tr>
<td>49</td>
<td>- - + + + + +</td>
<td>80</td>
<td>77</td>
</tr>
<tr>
<td>50</td>
<td>- - + + + + -</td>
<td>93</td>
<td>68</td>
</tr>
<tr>
<td>51</td>
<td>- - + + + - +</td>
<td>82</td>
<td>73</td>
</tr>
<tr>
<td>52</td>
<td>- - + + + - -</td>
<td>66</td>
<td>77</td>
</tr>
<tr>
<td>53</td>
<td>- - + - + + +</td>
<td>53</td>
<td>121</td>
</tr>
<tr>
<td>54</td>
<td>- - + - + - +</td>
<td>25</td>
<td>148</td>
</tr>
<tr>
<td>55</td>
<td>- - + - - - +</td>
<td>32</td>
<td>140</td>
</tr>
<tr>
<td>56</td>
<td>- - + - - - -</td>
<td>34</td>
<td>130</td>
</tr>
<tr>
<td>57</td>
<td>- - - + + + +</td>
<td>76</td>
<td>79</td>
</tr>
<tr>
<td>58</td>
<td>- - - + + + -</td>
<td>83</td>
<td>73</td>
</tr>
<tr>
<td>59</td>
<td>- - - + + - +</td>
<td>77</td>
<td>80</td>
</tr>
<tr>
<td>60</td>
<td>- - - + + - -</td>
<td>121</td>
<td>22</td>
</tr>
<tr>
<td>61</td>
<td>- - - - + + +</td>
<td>106</td>
<td>64</td>
</tr>
<tr>
<td>62</td>
<td>- - - - - + +</td>
<td>61</td>
<td>105</td>
</tr>
<tr>
<td>63</td>
<td>- - - - - - +</td>
<td>71</td>
<td>72</td>
</tr>
</tbody>
</table>

(Note: B – blue ink; M – magenta ink; Y – yellow ink; Bk – black ink; W – white ink; C – coating.)
5.5.2.1 Identification of Favourable Flotation Characteristics

The flotation behaviour data of the various component mixtures (see Tables 5.23 and 5.24), i.e. the frequency distribution of the flotation runs according to the foam drainage and foam volumes with the level of removals, are summarised in Tables 5.25 and 5.26 respectively. The volume for liquid in cell is not used because any change in foam drainage volume usually indicates an opposite change in the volume for liquid in cell.

**Table 5.25:** Frequency distribution of flotation runs according to the foam drainage volumes and the level of removals for individual or mixed component simulated wastewater (180 mL) with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Removal (%)</th>
<th>Foam drainage volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 – 40</td>
</tr>
<tr>
<td>Above 95%</td>
<td>0</td>
</tr>
<tr>
<td>90 – 95%</td>
<td>0</td>
</tr>
<tr>
<td>80 – 90%</td>
<td>0</td>
</tr>
<tr>
<td>Below 80%</td>
<td>3</td>
</tr>
</tbody>
</table>

**Table 5.26:** Frequency distribution of flotation runs according to the foam volumes and the level of removals for individual or mixed component simulated wastewater (180 mL) with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Removal (%)</th>
<th>Foam volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 – 0.2</td>
</tr>
<tr>
<td>Above 95%</td>
<td>1</td>
</tr>
<tr>
<td>90 – 95%</td>
<td>1</td>
</tr>
<tr>
<td>80 – 90%</td>
<td>2</td>
</tr>
<tr>
<td>Below 80%</td>
<td>5</td>
</tr>
</tbody>
</table>

From Tables 5.25 and 5.26, the following observations can be made:

- out of the flotation runs that achieved removals of 95% and above, 95% (or 19 of 20 flotation runs) of these flotation runs have foam drainage volumes between 40 and 90 mL while 80% (or 16 of 20 flotation runs) of these flotation runs have foam volumes between 0.2 and 0.6 L; and
- out of the flotation runs that achieved removals of 80% and below, 83% (or 10 of 12 flotation runs) had foam drainage volumes either below 40 mL or above 90 mL, while all the flotation runs (or 12 of 12 flotation runs) have foam volumes either below 0.2 L or above 0.6 L, with 83% (or 10 of 12 flotation runs) having foam volumes outside the range of 0.2 L and 1.0 L.
High removals were achieved in flotation that produced a moderate foam volume (0.2 L to 0.6 L) and foam drainage volume (40 mL to 90 mL) suggesting that the solids in these samples (with similar suspended solids content, see Table 5.2) are of sufficient size and hydrophobicity for foam stabilisation. This is reflected in the flotation outcome for the samples that showed foam characteristic within this moderate foam volume range, i.e. all 30 flotation runs achieved overall removals of above 90% (see Table 5.26). Similarly, overall removals of above 90% were achieved for 84% (or 38 of 45 flotation runs) of the flotation runs with foam drainage volumes within the 40 mL to 90 mL range (see Table 5.25). These results indicate that flotation runs that yield moderate foam and foam drainage volumes are likely to achieve good removal results.

Large foam volumes (> 0.6 L) are usually accompanied by the corresponding large foam drainage volumes (> 90 mL) as shown in the positive correlation ($R^2 = 0.46$) between the two volumes in Figure 5.32. These flotation characteristics can be tentatively attributed to small floc size with high initial foam stability but low foam persistence, i.e. films rupture when they are thinned down to less than the solids own dimensions or when the critical film thickness is reached. Even though the foam persistence is low, a large surviving foam volume is usually recorded as this foam volume is taken at the end of the flotation run and the metastable foam, in the presence of surfactants, can persist for much longer. Examples include blue (run no. 32, see Table 5.23) and mixtures of blue and coating (run no. 31) as well as blue and magenta (run no. 16).

![Figure 5.32: The positive correlation between the volumes of foam and foam drainage for individual and mixed components of equal volumes with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.](image)

Small foam volumes (< 0.2 L) are usually accompanied by the corresponding small foam drainage volumes (see Figure 5.32). Examples include yellow (run no. 56, see Table 5.24) and
mixtures of yellow and white (run no. 54) as well as yellow and coating (run no. 55). These flotation characteristics can be a result of the flotation of moderate to large flocs with excessive hydrophobicity leading to high initial foam destabilization, with low foam volumes in the cell surviving long enough to be carried over for drainage. Alternatively, it is also possible that the foam destabilisation is a result of a decrease in surfactant concentration at the foam interfaces as CTAB reacts with the anionic surfactants to form insoluble surfactant salts.

5.5.2.2 Two-Component Combination

The flotation of individual component simulated wastewater and their removal outcomes gave an indication of their capability to be removed under conditions where good removals can be achieved for industrial printing ink wastewater (i.e. 5 mM Fe(II) and 300 ppm CTAB at flotation pH 6.5). A summary of the individual flotation behaviour under these process conditions was shown in Table 5.22, with the flotation of blue or yellow inks found to yield low removals (36% and 42% respectively). This section involves the flotation of mixtures of two components in equal volumes, focusing in particular on the mixtures involving blue and/or yellow inks.

**Flotation of Blue Ink in the Presence of One Other Component**

As previously shown in Section 5.4.3.1, the flotation of blue ink in the presence of 5 mM Fe(II) and 300 ppm CTAB at pH 6.5 yields a poor removal, with only 36% removals achieved (run no. 32, see Table 5.23). The volumes for both the foam (1.4 L) and the foam drainage (116 mL) are distinctly outside the volume ranges found to demonstrate favourable flotation outcomes (see Section 5.5.2.1). This section involved the investigation into the flotation outcomes of blue ink in the presence of one other component. The removals from the flotation of these individual components as well as that of the equal volume sample mixtures of blue ink with these components are shown in Table 5.27.

The presence of magenta ink, white ink or coating were found to increase the overall removals from 36% to 43%, 58% and 49% respectively, while the presence of black ink was found to be detrimental to the flotation of blue ink with only 19% removals achieved. The individual overall removals for the flotation of magenta, white and black inks and coating were above 90% at similar flotation conditions. The removals achieved for the mixed 50:50 with blue ink component systems are closer to those for blue ink (36%) than those achieved for other individual ink components (> 90%) suggesting that the surface characteristics of the mixed component solids are dominated by the blue pigment. This suggestion is supported by the
flotation characteristics of these mixtures (run no. 16, 28, 30 and 31 for mixtures of blue with magenta, black, white or coating respectively, see Table 5.23) resembling that of the individual blue ink (run no. 32, see Table 5.23), i.e. high volumes of foam drainage (between 100 and 132 mL) and foam (between 1.3 and 1.9 L).

Table 5.27: Flotation behaviour for individual simulated wastewater samples and blue ink mixtures (with 50% vol/vol blue ink), using 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Individual samples</th>
<th>Mixed (50:50 with blue ink) samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td>Liquid in cell</td>
</tr>
<tr>
<td>Blue</td>
<td>31</td>
<td>98</td>
</tr>
<tr>
<td>Yellow</td>
<td>–93</td>
<td>77</td>
</tr>
<tr>
<td>Magenta</td>
<td>94</td>
<td>93</td>
</tr>
<tr>
<td>Black</td>
<td>89</td>
<td>95</td>
</tr>
<tr>
<td>White</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Coating</td>
<td>97</td>
<td>85</td>
</tr>
</tbody>
</table>

It is interesting to note that the presence of yellow ink was found to increase the removals for the flotation of blue ink to 95% (see Table 5.27). This high removal achieved for the mixed component system as opposed to their individual component removals (36% and 42% for blue and yellow inks respectively) demonstrates that the surface characteristics of yellow pigment complements those of blue pigment leading to a mixed surface that exhibits a favourable flotation outcome. The foam (0.7 L, run no. 24, see Table 5.23) and foam drainage (93 mL) volumes for the mixed blue-yellow system are much closer to the typical volume range found to achieve high removals in flotation (between 0.2 and 0.6 L for foam volume, and between 40 and 90 mL for foam drainage volume, see Tables 5.25 and 5.26) compared to the volumes achieved in the flotation of blue ink (1.4 L of foam and 116 mL of foam drainage volumes, run no. 32, see Table 5.23) or yellow ink (~ 0.0 L of foam and 34 mL of foam drainage volumes, run no. 56, see Table 5.24).

There results are difficult to explain in terms of the surface charge, floc size, hydrophobicity and CTAB precipitation characteristics of the individual components, and warrant further future investigation. From a practical point of view, however, they confirm that blue ink can be problematic when mixed with other inks, particularly when mixed with black ink. They also show that mixture with yellow ink, itself a problematic ink on its own, can overcome the negative effects of both blue and yellow inks individually.
Flotation of Yellow Ink in the Presence of One Other Component

As previously shown in Section 5.4.3.3, the flotation of yellow ink in the presence of 5 mM Fe(II) and 300 ppm CTAB at pH 6.5 yields a poor removal, with only 42% removals achieved (run no. 56, see Table 5.24). The foam produced is too unstable, with no foam surviving long enough for effective separation of the foam and foam drainage effluent. This foam and foam drainage (34 mL) volumes are also distinctly outside the volume ranges found to be favourable (see Section 5.5.2.1). This section involves the investigation into the effect of yellow ink in the presence of one other component sample. The removals from the flotation of these individual components as well as that of the equal volume sample mixtures of yellow ink with these components are shown in Table 5.28.

Table 5.28: Flotation behaviour for individual simulated wastewater samples and yellow ink mixtures (with 50% vol/vol yellow ink), using 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Individual samples</th>
<th>Mixed (50:50 with yellow ink) samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td>Liquid in cell</td>
</tr>
<tr>
<td>Yellow</td>
<td>-93</td>
<td>77</td>
</tr>
<tr>
<td>Blue</td>
<td>31</td>
<td>98</td>
</tr>
<tr>
<td>Magenta</td>
<td>94</td>
<td>93</td>
</tr>
<tr>
<td>Black</td>
<td>89</td>
<td>95</td>
</tr>
<tr>
<td>White</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Coating</td>
<td>97</td>
<td>85</td>
</tr>
</tbody>
</table>

The presence of magenta ink, black ink, white ink or coating were found to increase the removals from 42% (flotation of yellow ink alone) to 84%, 76%, 66% and 54% respectively (see Table 5.28). The flotation characteristics for the mixed component systems of yellow ink with magenta ink (run no. 40, see Table 5.24) or with black ink (run no. 52) are closer to those found in the flotation of magenta ink (run no. 48) or black ink (run no. 60) individually than those found in the flotation of yellow ink (run no. 56), resulting in higher overall removals (84% and 76%). In contrast, the flotation characteristics for the mixed component systems of yellow ink with white ink (run no. 54) or with coating (run no. 55) are closer to those found in the flotation of yellow ink (run no. 56) than those found in the flotation of white ink (run no. 62) or coating (run no. 63) individually, resulting in lower overall removal outcomes (66% and 54% respectively).

In the previous section, the presence of yellow ink was found to have the highest benefit in the flotation of blue ink with the increase in the contaminant removal from 36% to 95% (see Table
Similarly, among the mixed 50:50 yellow ink component systems investigated, the presence of blue ink was found to be most beneficial in aiding the flotation of yellow ink (see Table 5.28).

**Flotation of Other Two-Component Combinations**

Although the focus in this section is on the problematic inks such as blue and yellow inks, it is important not to neglect the flotation results of other component mixtures that were found earlier to achieve good removal levels individually. This is because it is always possible that the flotation of a mixture of two components (that can be removed well individually) can result in a poor removal outcome.

Mixed component combinations containing magenta ink were found to give poorer removals compared to the flotation of their individual components. The poorer overall removal is a result of the decrease in the foam drainage removals. The foam drainage removals for magenta-black inks (70%, run no. 44, see Table 5.24), magenta-white inks (–23%, run no. 46) and magenta ink-coating (84%, run no.47) were found to be lower than for magenta ink (94%), black ink (89%), white ink (96%) or coating (97%) individually (see Table 5.22). It is difficult to generalise on the reason for these poorer removals, as the resultant systems in each combinations are different in their physical and surface chemistry.

In contrast, the flotation combinations containing black ink, white ink and/or coating were found to achieve removals above 90%, with overall removals of between 93 and 97%, foam drainage removals of between 91 and 95% and removals for liquid in cell of between 94 and 98%, being achieved.

Again, this complex behaviour is difficult to explain without further experimentation. From a practical point of view, however, the results show that magenta ink can be problematic when mixed with white ink. Further investigation of these interesting phenomena is warranted.

**5.5.2.3 Three-Component Combination**

**Flotation of Three-Component Combination including Blue Ink**

As previously discussed in Section 5.5.2.2, the flotation of blue ink can be improved significantly in the presence of yellow ink with an overall removal of 95% achieved (see Table 5.27). The presence of magenta ink, white ink or coating only increases the removals from 36%
to between 43 and 59% while black ink decreases the removal to 19%. This section involves the investigation into (i) whether the presence of another component is detrimental to the high removal outcome that can be achieved in the flotation combination of blue and yellow inks (95%), and (ii) whether the increase in the proportion of inks that were found to result in good removals individually (i.e. > 90%) can increase the achievable overall removal. The flotation outcome for three-component combination samples (including blue ink) is summarised in Table 5.29.

Table 5.29: Flotation behaviour for three-component combination (including blue ink) with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Samples containing yellow ink</th>
<th>Average removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>Yes</td>
<td>92 ± 5</td>
</tr>
<tr>
<td>No</td>
<td>87 ± 8</td>
</tr>
</tbody>
</table>

The presence of one other component in the three-component combination (including blue and yellow inks) was found not to be detrimental towards the flotation outcome, with an average overall removal of 95% ± 3%. This removal average is similar to that found for the flotation of blue and yellow inks mixture sample (95% overall removal, run no. 24, see Table 5.23).

An increase in the proportion of easily removed individual inks (i.e. magenta, black, white and coating with > 90% overall removals individually) was found to result in an average removal of 90% ± 6% (see Table 5.29). This average removal is significantly higher than the maximum removal for the flotation of two-component systems involving blue ink (i.e. 58%, see Table 5.27). This suggests that high removals (i.e. > 90%) can be achieved in the absence of yellow ink as long as the proportion of blue ink in the sample is low (i.e. < 33% vol/vol).

Flotation of Three-Component Combination including Yellow Ink

As previously discussed in Section 5.5.2.2, the flotation of yellow ink containing simulated wastewater sample can be improved significantly by the presence of blue ink (see Table 5.28). The presence of magenta ink, black ink, white or coating only increases the removals to between 54 and 84%, i.e. an average removal of 70% ± 13%. The flotation outcome for three-component combination samples (including yellow ink) is summarised in Table 5.30.
Table 5.30: Flotation behaviour for three-component combination (including yellow ink) with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Samples containing blue ink</th>
<th>Average removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
</tr>
<tr>
<td>Yes</td>
<td>92 ± 5</td>
</tr>
<tr>
<td>No</td>
<td>66 ± 25</td>
</tr>
</tbody>
</table>

As discussed on p.228, the presence of one other component in the three-component combination (including blue and yellow inks) was found not to be detrimental towards the flotation outcome with an average overall removal of 95% ± 3% (see Table 5.29).

An increase in the proportion of easily removed individual inks (i.e. magenta, black, white and coating) was found to result in an average removal of 83% ± 14% (see Table 5.30). This average removal is comparable to the maximum removal for the flotation of two-component systems involving yellow ink (84%, see Table 5.28) but significantly higher than the two-component systems’ average removal (70% ± 13%). In spite of the increase in the achievable removal (as the proportion of yellow ink decreases to 33% vol/vol), the average removal of 83% with a large standard deviation of 14% is still unsatisfactory, i.e., the presence of blue ink in the flotation of yellow ink is more important than the presence of yellow ink in the flotation of blue ink.

**Flotation of Other Three-Component Combinations**

As previously discussed in Section 5.5.2.2, the flotation involving two-component combination of magenta ink with black ink, white ink or coating resulted in poorer removals compared to the flotation of their corresponding individual component, in particular the combinations of magenta-black inks (run no. 44, see Table 5.24) and magenta-white inks (run no. 46) with removals of 77% and 56% achieved respectively. The addition of coating to these mixtures was found to increase the removals to 89% (run no. 43) and 93% (run no. 45) respectively. It is also interesting to note that the combination of magenta-black-white inks yields a removal of 94%, significantly higher compared to the two-component mixture involving magenta ink with white or black inks (77% and 56% respectively, run no. 44 and 46). The higher removals achieved with three-component systems compared to two-component systems involving magenta ink is summarised in Table 5.31.
Table 5.31: Flotation behaviour for mixed component systems involving black ink, white ink and/or coating in the presence of magenta ink with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Samples containing magenta ink</th>
<th>Foam drainage (%)</th>
<th>Liquid in cell (%)</th>
<th>Overall (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magenta</td>
<td>94</td>
<td>93</td>
<td>94</td>
</tr>
<tr>
<td>2-component mixture</td>
<td>44 ± 58</td>
<td>94 ± 2</td>
<td>75 ± 19</td>
</tr>
<tr>
<td>3-component mixture</td>
<td>86 ± 5</td>
<td>97 ± 1</td>
<td>92 ± 3</td>
</tr>
</tbody>
</table>

* standard deviation is only a guide to the variability in the results and not the range of results.

The low foam drainage average removal (44%) and large standard deviation (±58%) for the two-component mixture are due to the low removal achieved for magenta-white ink mixture (–23%). In the absence of magenta-white ink mixture, the average foam drainage removal is 77% ± 7%.

From Table 5.31, the overall removal increases from an average of 75% to an average of 92% with the increase in the proportion of black ink, white ink and/or coating. The increase is mainly a result of the improved foam drainage quality from an average of 44% to an average of 86%. This suggests that the detrimental effect in the flotation outcome when magenta ink (itself an easily removed ink with an overall removal of 94%) is mixed with one other component (black ink, white ink or coating) can be overcome by increasing the proportion of this other component within the mixed sample.

5.5.2.4 Four and Above Component Combinations

For four or more component samples, the presence or absence of yellow ink in the flotation containing blue ink does not affect the removal outcomes as shown in Table 5.32, with the average overall removals of 95% and 96% achieved respectively. The effect of magenta ink on the flotation outcome will not be considered here as it is shown to achieve removals above 90% when the proportion of magenta ink is decreased to 33% vol/vol in the presence of easily removed ink such as black, white and/or coating (see Table 5.31).

For the flotation containing yellow ink, the presence of blue ink yields a higher average foam drainage removal (94%) compared to its absence (87%). The average overall removal, however, is similar (95% in presence of blue ink and 93% in its absence). This result, along with the results achieved for two- and three-component wastewater containing yellow ink (see Tables 5.28 and 5.30), show that an overall removal of above 90% can be achieved for the
flotation of wastewater containing yellow ink in the absence blue ink provided the proportion of yellow ink does not exceed 25% vol/vol.

**Table 5.32:** Flotation behaviour for four and above component combination (in the presence or absence of blue and/or yellow inks) with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Samples containing Blue ink</th>
<th>Yellow ink</th>
<th>Foam drainage</th>
<th>Liquid in cell</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Yes</td>
<td>94 ± 3</td>
<td>97 ± 3</td>
<td>95 ± 2</td>
</tr>
<tr>
<td>Yes</td>
<td>No</td>
<td>95 ± 1</td>
<td>98 ± 2</td>
<td>96 ± 1</td>
</tr>
<tr>
<td>No</td>
<td>Yes</td>
<td>87 ± 4</td>
<td>97 ± 1</td>
<td>93 ± 1</td>
</tr>
<tr>
<td>No</td>
<td>No</td>
<td>96</td>
<td>98</td>
<td>97</td>
</tr>
</tbody>
</table>

(Note: standard deviation is only a guide to the variability in the results and not the range of results.)

The flotation of all the samples containing four or more components resulted in overall removals of above 91% (see Tables 5.23 and 5.24). The advantage of having diverse combinations in wastewater samples where no one component dominates is clearly shown in the summary of the removal results in Table 5.33.

**Table 5.33:** Flotation behaviour for individual or mixed component samples with 5 mM Fe(II) and 300 ppm CTAB at pH 6.5.

<table>
<thead>
<tr>
<th>Number of combinations</th>
<th>Average removal (%)</th>
<th>Proportion samples with removals above 90% (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Foam drainage</td>
<td>Liquid in cell</td>
</tr>
<tr>
<td>6</td>
<td>91</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>93 ± 2</td>
<td>98 ± 1</td>
</tr>
<tr>
<td>4</td>
<td>93 ± 5</td>
<td>96 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>82 ± 17</td>
<td>97 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>36 ± 71</td>
<td>96 ± 3</td>
</tr>
<tr>
<td>1</td>
<td>52 ± 76</td>
<td>91 ± 8</td>
</tr>
</tbody>
</table>

(Note: standard deviation is only a guide to the variability in the results and not the range of results.)

One of the advantages of having a diverse component combination is the decrease in the variability in the removal results achieved (including the removals for overall, foam drainage and liquid in cell), shown as small standard deviation values in Table 5.33. The standard deviation for a few of the removal results can be misleading, for example, 36 ± 71% (foam drainage removal for two-component combination) indicates that a removal of above 100% is possible. The standard deviation value is taken as a guide to the variability in removal results rather than the range that can be achieved.
The results summarised in Table 5.33 indicate that in the industrial wastewater treatment application, a larger withholding tank should be used to store the wastewater before any wastewater pre-treatment and flotation is conducted. This is to minimise the possibility of large volumes of similar problematic ink component, such as blue or yellow ink, being introduced into the treatment system. Alternatively, the plant operator can minimise this occurrence by ensuring that the amount of yellow ink disposed coincide with similar amount of blue ink unless the proportion of yellow ink in the wastewater does not exceed 25% vol/vol.

5.6 Summary

The key findings on the HLC mode flotation studies on individual simulated wastewater samples are:

- the EM of the mixed pigment-hydrous Fe(II) oxide becomes less negative with decreasing pH for all samples (with the exception of blue ink where the solids became more negative below pH 6). Two distinct patterns were observed:
  - no charge reversal with decreasing pH found for magenta, yellow and black inks. This is consistent with the EM of the solids contained in industrial wastewater Sample 2; and
  - for white ink and coating, a net positive surface charge was observed at low pH values, with iep of 6.2 and 6.6 respectively;

- low EM values do not necessary result in large flocs and/or high contaminant removals. Instead, floc size is found to be a major determinant in the extent of solids retention within the foam. In general, with the exception of yellow and white (at high pH values) inks, the foam drainage removal curve is similar in trend with the floc size curve (as a function of pH). This result is consistent with the findings for industrial wastewater Sample 2. The poor correlation between the floc sizes and foam drainage removals for yellow and white inks showed that other contributing factors such as hydrophobicity or insufficient surfactant coverage may lead to poor removals in spite of large floc formation; and

- the flotation of simulated printing wastewater at pH 6.5, i.e. the optimum pH found for industrial wastewater samples, yields the maximum (or close to maximum) removals when treating magenta, black, white inks or coating. For the flotation of blue or yellow
inks, removals achieved were far lower than the maximum removals achieved at other pH values.

The key findings of the HLC mode flotation studies on multi component simulated wastewater under the conditions chosen for industrial wastewater flotation, i.e. in the presence of 5 mM Fe(II) and 300 ppm CTAB at pH 6.5, are:

- among the samples tested, the flotation of blue and yellow inks individually were found to achieve low removals;
  - for blue ink, the mixed pigment-hydrous Fe(II) oxide solids is too small to achieve foam stabilisation. The resultant foam carryover volume is large as a result of high initial foam stability but low foam persistence (hence, low foam drainage removal). Higher CTAB concentration was found to increase the foam drainage removal but the amount required is high (e.g. > 500 ppm);
  - for yellow ink, the surface characteristics of the mixed pigment-hydrous Fe(II) oxide solids, in contrast, destabilises the foam leading to low foam carryover volume, low surviving foam volume and poor solids retention within the foam;

- the flotation of magenta, black, white and coating individually or in any number of combinations, were found to generally achieve high removals (i.e. > 90%). The only exception is the flotation of two-component combination samples in which one component is magenta ink, where they were found to produce poorer removals than their respective individual results;

- the flotation outcome for blue ink is significantly increased in the presence of yellow ink and vice-versa. It is likely that the surface characteristics of these inks complement each other leading to a mixed surface that exhibits a favourable flotation outcome. The presence of other components in the flotation of blue and yellow inks was found not to be detrimental towards the flotation outcome;

- a diverse component combination where no individual component dominates was found to be crucial in obtaining high overall removals of above 90%. This can be achieved by having a large withholding tank before any wastewater treatment is conducted; and

- samples, in particular blue and yellow inks, must not be allowed to be present in high concentrations (e.g. < 25% vol/vol) to ensure that these pigment solids do not dominate the surface characteristics of the wastewater solids.
The results presented in this chapter have shown the variability in flotation characteristics as the wastewater composition is varied. Even though it is highly unlikely that process inks such as blue or yellow will be present at high quantities at any one time (reflected by the high removals for industrial wastewater samples with low to above average suspended solids content at optimised conditions), it is always possible that this may occur, thereby resulting in flotation treatment failure. Further investigations on why flotation is inhibited in the presence of high concentrations of blue or yellow inks are warranted.
Chapter 6: Thesis Conclusion

The variability in concentration and composition of pigments contained in the wastewater over time poses a major challenge to the flotation treatment process and one of the main aims of this research was to develop a wastewater treatment process that can accommodate the changing wastewater characteristics without loss of performance.

6.1 Batch Mode Industrial Wastewater Flotation Studies

Coagulant requirement

The susceptibility to variability in wastewater composition was a major determinant of the choice of coagulant. The optimum flotation pH in Fe(II) system (6.5) was found to be similar for all the industrial wastewater samples tested regardless of the differences in the samples’ characteristics (e.g. suspended solids concentration and ionic strength) at fixed coagulant concentration (5 mM). The optimum pH for Al(III) or Fe(III) systems, however, decreases for higher suspended solids content and higher ionic strength samples. A constant optimum flotation pH (and dosed with a fixed amount of coagulant) presents a distinct advantage in wastewater treatment where optimised process conditions are usually governed by the wastewater characteristics, which changes over time.

The use of Fe(II) was also found to have an advantage with respect to the dosing requirements. The presence of Fe(II) in excess of the minimum requirement was found to have a much lower detrimental effect on the flotation outcome compared to those found in Al(III) or Fe(III) systems. The marked decrease in liquid in cell removal for the Al(III) or Fe(III) systems showed the decrease in particle-bubble attachment efficiency, reflecting the lower hydrophobicity of the solids contained in these systems and potentially requiring higher surfactant dosage in order to restore hydrophobicity to facilitate flotation. Fe(II) is therefore more suited for industrial use where a constant coagulant dose is desirable to simplify the process control for ease of process operation and trouble shooting.

Surfactant requirement

The type of surfactant to be used (i.e. cationic, anionic or non-ionic) was largely dictated by the surface charge of the solid to be removed. The wastewater solids were found to have a net negative charge and thus favoured the use of a cationic surfactant. Good removal of solids was
found to be possible using an anionic or a non-ionic surfactant, but this required the addition of
large quantities of hydrous metal oxide at pH values below its IEP in order to reduce the
negative surface charge of the mixed pigment-hydrous metal oxide floc, facilitating surfactant
adsorption and/or flocculation. The use of cationic surfactant was favoured as good
contaminant removals were achieved at a lower coagulant dosage. The mechanisms and
orientations of surfactant adsorption onto the solid surface, in each of these systems, however,
were not clearly understood due to the complexity of the wastewater systems studied.

The susceptibility to variability in wastewater composition was also a major determinant of the
surfactant concentration requirement. For two of the industrial wastewater samples
investigated, the presence of low CTAB concentration (100 ppm) was found to lead to worse
removal than in the absence of CTAB. Flotation at these low CTAB concentrations was found
to be characterised by high foam instability at the initial foaming stages, resulting in a low
volume of foam carryover, a high volume of liquid in cell, dirty foam drainage and low (< 50%)
contaminant removals. These foam characteristics did not allow effective flotation to be
conducted in HLC mode. This foam destabilisation effect was found to decrease with
increasing Fe(II) concentration. It was also found that in order to overcome the destabilisation
effect, increasing the CTAB dosage to 300 ppm (with respect to the sample) was necessary. At
this CTAB concentration, the solid’s surface characteristics are such that the foam can be
sustained for a prolonged period to allow solid (contained in foam)/liquid separation. Further
increases in CTAB (to 500 ppm) were found to produce ‘drier’ solids-stabilised foam due to
greater extent of liquid drainage, leading to higher volumes of treated effluent (or lower
volumes of the concentrated foam sludge contaminant).

**Optimum batch mode process conditions**

The optimum batch mode process conditions found for HLC mode flotation of industrial
printing ink wastewater samples were pH 6.5 with Fe(II) as coagulant (at 5 mM) and CTAB as
surfactant (at 300 ppm). At these optimised process conditions, above 90% solid contaminants
were removed, and between 79 and 89% of the initial wastewater volumes were recovered as
treated effluent, with the remaining 11 to 21% to be disposed in the form of concentrated foam
sludge.
6.2 Continuous Mode Industrial Wastewater Flotation Studies

In the continuous mode flotation studies on industrial wastewater, the best flotation outcomes were achieved when all the wastewater entering the flotation cell leaves the cell with the foam, i.e. the source of treated effluent is mainly from the liquid that drained from the foam rather than the liquid taken directly from the cell. It was also found that the proportion of liquid leaving the cell with the foam could be increased by (i) increasing the air throughput, (ii) decreasing the wastewater throughput and/or (iii) increasing the CTAB concentration. The increase in CTAB dosage was found to improve the removals for both the cell exit liquid and the foam drainage (increased solids retention within the foam) as well as increase the rate of liquid volume leaving the cell with the foam. High CTAB concentrations were therefore necessary to increase the wastewater throughput without loss of performance.

No optimum air or wastewater throughputs were found in the experiments conducted. In general:
- the optimum air throughput increases with the increase in wastewater throughput; and
- operation at low air and wastewater throughputs yields the best removal outcomes with a small compromise in removal outcomes when flotation is conducted at higher wastewater throughputs.

Typical results achieved at optimum process conditions are (i) > 96% of the solid contaminants were removed for flotation runs at low wastewater (30 mL/min) and air (150 mL/min) throughputs with cell residence times of 6 minutes, (ii) > 93% of the solid contaminants were removed at moderate wastewater (45 – 72 mL/min) and air (250 mL/min) throughputs with cell residence times between 2.5 and 4.0 minutes, and (iii) > 88% of the solid contaminants were removed at high wastewater (120 mL/min) and air (400 mL/min) throughputs with cell residence times of 1.5 minute. In addition, more than 87% of the initial wastewater volumes were recovered as treated effluent, with less than 13% disposed as foam sludge concentrate.

6.3 Batch Mode Simulated Wastewater Flotation Studies

Flotation studies on simulated wastewater were conducted to better understand how the various wastewater components contribute to the flotation behaviour observed during the flotation of industrial wastewater samples. The simulated wastewater samples comprised of individual or mixtures of equal volumes of the major ink components contained in the industrial wastewater. In the flotation of simulated printing wastewater under optimum process conditions for treatment of industrial wastewater samples (i.e. 5 mM Fe(II) as coagulant, 300 ppm CTAB at
flotation pH 6.5), removals greater than 90% were achieved for magenta, black, and white inks and coating. This corresponds to their small EM values and relatively large flocs under these conditions. The flotation of blue or yellow inks under these conditions, however, achieved poor results. For blue ink, the poor removal was attributed to their small size – too small for prolonged foam stabilisation. For yellow ink, excessively high hydrophobicity or poor surfactant coverage were cited as probable sources of the excessive foam destabilisation exhibited, leading to poor removal.

For flotation of mixed simulated wastewater at optimised process conditions, the results and flotation characteristics were, generally, in between those of their individual outcomes. A notable exception, however, is the high removal results achieved for samples with mixtures of equal quantities of blue and yellow inks, which individually yielded poor removal. It was also found that regardless of whether blue or yellow inks were present, samples consisting of four or more inks of equal quantities yield good removal outcomes. For three or less ink component mixtures, the presence of either blue or yellow inks was found to be detrimental towards the flotation outcome.

A comparison of the flotation characteristics and the corresponding contaminant removals revealed that floc size may be an important determinant on the foam drainage removal achieved. The foam drainage removal curves (as a function of pH) for industrial wastewater Sample 2, simulated wastewater samples of blue, magenta, black and coating, were found to be similar in trend with the floc size curves. The poor correlation between the floc sizes and foam drainage removals for yellow and white inks may be due to other contributing factors such as hydrophobicity or insufficient surfactant coverage.

A summary of the flotation behaviour data of various simulated wastewater component mixtures revealed that flotation characteristics such as volumes of foam, foam drainage and liquid in cell are good indicators of flotation outcomes. For batch mode flotation of a 180 mL wastewater sample, it was found that contaminant removals above 90% are more likely to be achieved when the final foam drainage volume is in the range of between 40 and 90 mL while the final foam volume is in the range of between 0.2 and 0.6 L. Flotation runs with foam and foam drainage volumes lower than these desirable volumes were likely to lead to dirty foam drainage and inadequate foam volume for solids attachment. Flotation runs with volumes higher than these desirable values were likely to lead to foam with high initial stability but low foam persistence, potentially leading to foam management issues (especially during scale-up operation) and dirty foam drainage (solids are too small to stabilise the foam).
6.4 Future Research Needs

The results of this research have highlighted further laboratory-based investigations that may aid in control of the flotation process.

An important area that requires further investigation before Fe(II) can be used as a coagulant at pH 6.5 is the reduction of the high Fe concentration in the treated effluent to a level that complies with the 30 ppm discharge limit. It was found in Section 4.5.3 that the flotation outcomes and characteristics can be altered by replacing half of Fe(II) with an equal concentration of Al(III) or Fe(III). The understanding of how the presence of Al(III) or Fe(III) influence the flotation outcome in a Fe(II) system can potentially lead to a reduction in Fe(II) usage without compromising on the effectiveness of contaminant removal and other favourable flotation characteristics associated with the use of Fe(II) as coagulant.

One of the areas of interest is the investigation into the fundamentals behind the advantages Fe(II) system had over Al(III) or Fe(III) systems, i.e. constant optimum flotation pH (6.5) regardless of concentration and composition of ink components in the wastewater samples and less detrimental effect when present in excess. This includes the understanding of how the solubility of these metal ions (and their hydrous oxides), their degree of hydrolysis (before precipitation) and the extent of oxidation (for Fe(II) system) affect the adsorption, precipitation and/or heterocoagulation with the pigment solid and the resultant surface characteristics of the mixed pigment-hydrous metal oxide solid. The understanding of how surface chemical properties can be changed with the introduction of these Fe(II), Al(III) or Fe(III) ions can potentially lead to utilisation of mixed hydrous metal oxide coagulants to achieve the desired flotation characteristics, especially in conditions where Fe(II) was found to be ineffective (e.g. in the flotation of blue or yellow inks).

Another area of interest is the investigation into how floc hydrophobicity is affected by the presence of CTAB. This include understanding the mechanism of surfactant adsorption, its adsorption orientation onto the mixed pigment-hydrous Fe(II) oxide solid and the extent of reaction with anionic surfactants at various CTAB concentration. This investigation would determine the cause of excessive initial foam instability found at low CTAB concentration (100 ppm) during the flotation of two of the industrial wastewater samples and whether this foam instability can occur at the optimised CTAB concentration (i.e. 300 ppm) given a different wastewater composition and concentration.
It was found in this research that floc size is an important determinant of the foam effluent quality and extent of solids retention within the foam. However, this was not always true as shown in the flotation of yellow or white inks. Other factors such as excessive hydrophobicity or surfactant deficient solid surface may lead to failure in the establishment of a solids-stabilised foam. Therefore a better understanding of the optimum range required in floc size, floc hydrophobicity and surfactant coverage to achieve a solids-stabilised foam is necessary to ensure sufficient control over the extent of solids retention within the foam.

The studies outlined in this thesis were performed using a small flotation cell (180 mL capacity) run in batch and continuous mode. Larger scale studies are required to determine how the larger cell and column dimensions affect the flotation process as well as to investigate a means of handling and dewatering the large volumes of foam produced, and determine the capacity of equipments (e.g. withholding tank, flotation column, pumps) required to treat the daily wastewater output of the printing and coating plant.

In conclusion, this research had shown that HLC mode flotation is a potential alternative treatment option to current wastewater treatment technology for treating printing ink wastewater.
REFERENCE


