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THE FLOCCULATION OF PAINT WASTEWATER USING INORGANIC SALTS

Olufemi Alexander Fasemore

A MSc dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Masters of Science in Engineering (MSc Eng).

Johannesburg, 2004

DECLARATION

I solemnly declare that this dissertation is my personal work, unassisted investigation. It is being submitted for the Masters of Science in Engineering in the University of the Witwatersrand, Johannesburg. I also declare that it has never been submitted for any degree or examination in another university.

_____

Signature of Olufemi Alexander Fasemore

_____ day of _____2004.

ABSTRACT

Wastewater is generated in the production of water-based paints when vessels and filling lines are washed in between batches. This results in a dilute paint wastewater stream. This dissertation concerns the study of the treatment of wastewater, using flocculation and coagulation processes. Standard jar test were used in screening the flocculants. The inorganic flocculants used were ferric chloride ($FeCl_3$) and aluminium sulphate ($Al_2(SO_4)_3$)

A thermodynamic model is developed for understanding the coagulation and flocculation process for inorganic flocculants. Properties such as the effect of bulk concentration, pH and feed concentration of flocculant on wastewater were investigated. The impact of kinetics and other properties such as the influence of redox potential on flocculation experiments are also evaluated in order to have an understanding of the properties that influence the flocculation of wastewater. It was found that thermodynamics could be used to predict gross flocculation behaviour. However mixing and the rate of the nucleation and growth of flocs are also important and need to be controlled for efficient and reproducible flocculation.

PUBLICATIONS AND PRESENTATIONS FROM THIS RESEARCH WORK

1) Treatment of paint waste water by flocculation. Fasemore, O.A.; Glasser, D.; Hildebrandt, D.; Jewell, L.; University of the Witwatersrand. (Presented at the South African Chemical Engineering Congress, Sun City, South Africa, September 2003).

2) Jewell, L.L.; Fasemore, O.A.; Glasser, D.; Hildebrandt, D.; Heron, L.; van Wyk, N.; Cooray, B.; Towards Zero Waste Production in the Paint Industry. Water SA (2004) Vol. 30 No. 5(Special Edition) 643-647 Selected for publication from the Water Institute of South Africa Conference, Cape Town, South Africa May 2004.

Award

Second best postgraduate poster of the year 2003. School of process and material engineering, university of the Witwatersrand. Title: Treatment of paint waste water by flocculation.

DEDICATION

I dedicate this work to God almighty whom through his son Jesus Christ I found favour in South Africa and my family; my dad and mum, my brothers, Tunde and Seye, my sister Jumoke for their unflinching support and belief in my success.

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NOMENCLATURE

M^{3+}: Metallic ions (either ferric or aluminium)

(am): amorphous

(α): alpha

K_A: Equilibrium constant

$M_{1:}$ Initial mass of wastewater before dilution

$M_{2:}$ Mass of water to be added for dilution

$C_{1:}$ Amount of solid in wastewater before dilution

$C_{2:}$ Amount of solid content of waste water after dilution (constant for all dilution process at 80g of solid in 1000g of wastewater).

FTU: Formazin Turbidity Unit

β: Akaganeite

aq: Aqueous

s: solid

γ: Lepidocrocyte

CHAPTER 1

Introduction

1.1. An overview of the PLASCON wastewater problem

PLASCON is the major South African decorative coatings manufacturer. They produce different ranges of paint products that are of standard and good quality at competitive prices. Water based emulsion paints are one of the groupings which consists of different types of products. These paints are produced through a batch process in a tank or vessel and pumped through the filling lines to storage containers and distributors.

On completion of the production and filling of the containers, it is required that after every batch the tanks and filling lines be washed before the next batch of product is produced. Water is used as the cleaning solvent for the tanks and filling lines because it is the primary solvent for the water based emulsion paint. Hence the water generates wash water, which becomes a waste because it cannot be used again in the process.

The wastewater generated comprises of water and paint residues (mainly solids), which is suspended in the wastewater. The wastewater generated cannot be sent directly into the public sewage system because it does not meet the South African government effluent discharge standard. PLASCON embarked on a wastewater treatment practice in order to meet the government requirement and in turn save money and also recover paints from the wastewater. Ferric chloride ($FeCl_3$) flocculant was used for treating the wastewater but if overdosed the water and sludge recovered is toxic.

The toxic nature of water and sludge recovered leads to more expenses being incurred by PLASCON. They have to pay extra money to a waste treatment company to dispose of the toxic waste generated in their own treatment process.

Hence their waste treatment process needs to be improved. A more suitable, cheaper and safe waste treatment programme is therefore required.

The aim of the research presented in this dissertation was to evaluate the treatment of paint wastewater. After analysing various alternatives in chapter 1, it was decided to treat the wastewater using coagulation and flocculation. The experimental approach was selected in order to ensure comparable results in chapter 2. The results were interpreted within the framework of the thermodynamics of the chemistry of the flocculants in chapter 3 either (ferric or aluminium). In conclusion it was found that thermodynamics alone is insufficient to accurately predict flocculation behaviour. This kinetic factors and the composition of the wastewater were also considered. Chapter 5 is a summary of the important points of the research.

1.1.1.Source of wastewater

Wastewater can be defined as waste liquid effluent generated as a result of the use of water. The chief sources of wastewater in the environment are: domestic wastewater, run off and industrial wastewater. As explained by Metcalf and Eddy, (1979) the major sources of domestic waste water are: residential areas, commercial areas, institutional and recreational areas. Runoff is generated by natural means for example after rainfall, the earth removed as a result of erosion may be suspended in the wastewater.

The third major source is industrial wastewater and is basically produced from manufacturing and processing industries. The wastewater from PLASCON falls in this category. As described in section 1.1, the wastewater is generated when the vessel used for producing paint is washed with water. This leads to the generation of a paint wash water effluent, which cannot easily be disposed of, into the public sewerage system because of existing government legislation.

1.1.2.Existing legislation

The existing legislation from the perspective of wastewater can be divided into two standards namely: discharge standards and reuse or reclaimed water standards. In order to ensure that water disposed into the environment is not too toxic, the South Africa Bureau of Standards has a set standard in place. In this section the standard will be discussed considering some characteristics of wastewater such as: turbidity, pH, and metallic content of water.

The South African Bureau of Standard (SABS 241:1999) for turbidity for effluent disposal is not fixed for South Africa, however the reclaimed water standard is fixed at 1.0FTU this as shown by Gisclon, McCarley and McNally, (2002). The chief cause of turbidity in the PLASCON wastewater is the paint pigments, the estimated average turbidity for paint wastewater samples was around 35000FTU. However wastewater for effluent disposal is rated based on suspended solids, which is fixed at 10mg/L of, suspended solids in wastewater. (Department of water and forestry manual, 2004)

The South African Bureau of Standards for the pH of disposed effluent streams into public sewerage is between pH 6-10 as stated by Mogale municipality water works manual, (2002). The standard for the pH of reclaimed water is 6.5 to 9.5,as stated by Gisclon et al, (2000) quoting the SABS (241:1999) in a paper presented on 'The Durban water recycling project' at the Water Institute of South Africa conference, (2002). The paint wastewater pH was between 6.5 and 9.5 depending on the batch of products. Hence pH of wastewater is within the legislated limits for disposal into a public sewerage system.

The metallic content of wastewater disposal into public sewerage varies depending on the metallic compound. The toxicity level of the metallic compound is what determines the quantity in parts per million (ppm) that is permissible in a wastewater stream. The metallic elements discussed in this section are the iron and aluminium content of water. The Mogale municipality water works manual, (2002) states that the permissible level of iron that can be discharged into its

public sewerage system is less than 5ppm,while aluminium has no serious disposal limitation. The reclaimed water standard is however lower, the permissible level in reclaimed water for iron is 0.04ppm and that of aluminium is about 0.4ppm, as shown by Gisclon et al, (2002) quoting SABS (241:1999).

The electrical conductivity of a wastewater stream in line with South African Bureau of Standards requirements is about 500mS/m maximum at 20^0C as stated by Mogale municipality water works manual (2002) used in monitoring of effluent disposal by the municipal wastewater treatment department. The reclaimed water standard is however at 61mS/m as stated by Gisclon et al, (2002) quoting SABS (241:1999). The suspended solid content of wastewater should not exceed 1000mg/L, while the reclaimed water standard is about 5mg/L as shown in Gisclon et al, (2002) quoting the SABS (241:1999).

1.1.3.The waste minimisation alternatives process

In the choice of treatment processes of the waste generated different considerations were taken into account such as: physical properties of waste water generated to possible effect of the waste water on different processes proposed for the control of waste in the paint industry. In order to determine the most suitable process to use in the treatment of wastewater generated, the different methods of controlling and treatment of waste generated were analysed as shown by the organogram. Fig.1.1.

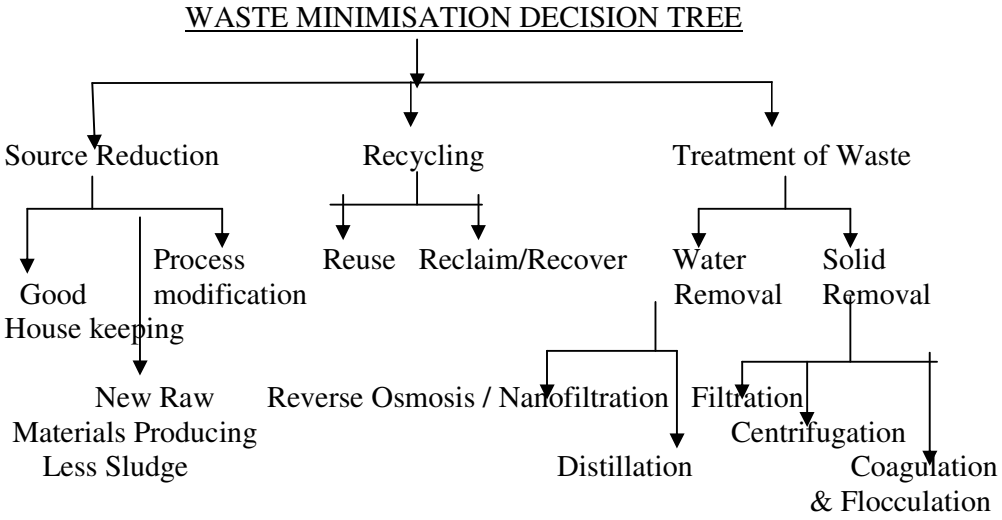


Fig 1.1 waste minimisation decision tree

The steps shown on the decision-tree in Figure 1.1 was drawn up due to the approach suggested by Perry and Green, (1997) and Chereminisinoff and Ferrante, (1989) in choosing a process for the treatment of waste. The organogram gives us a lead on how to consider each applicable step and other possible options.

The first route considered is the option of source reduction of waste generated; this is the effort to eliminate or reduce the generation of waste from source. Various options were considered as shown in Figure 1.1, in particular the alternative for source reduction by good house keeping as advocated by Chereminisinoff and Ferrante, (1989). This process requires setting up a good waste tracking and segregation system, which requires training of employees and support of the management in order to set up a good, effective, preventive spill and maintenance system. Its advantages are that it is easily applicable in the short run. In the case of occasional paint spillage in the plant, instead of using water to wash the spillage, other means of cleaning can be considered. It is cheap to put into practice, and it helps workers to make optimum use of raw materials thereby leading to reduction in running and production cost.

However another option is the introduction of new products that may produce less solids sticking to the vessels when products are being filled into cans., in order to use less solvent for cleaning the vessel. Chereminisinoff and Ferrante, (1989) refers to a case of water as the main solvent for making ink pens in place of organic solvent by Cleo wrapper. An important point is the ability to reduce cost of production of product. Another option considered is process modification, which may involve equipment change or amendment to the existing process.

Chereminisoff and Ferrante, (1989) proposed an initial use of production vessels wipers before water is used to rinse the vessels in the paint industry. An example of this is the pigging of filling lines by PLASCON for paints solids before water is used to clean the lines, this helps reduce the paint content in wastewater generated. The major disadvantage of source control assessment done on the paint production process is that after each batch of product, water is still required for a thorough cleaning of paint production vessels, and this will always lead to the generation of a wash water effluent stream.

The second major route considered is recycling, this is the direct reuse of wastewater generated, possibly as the solvent for the paint production process. There will be a problem with the quality of product being produced however, if the wash water is considered for the continuous washing of tank or vessel for paint production. Unless the quantity of wash water is controlled, a very clean tank cannot be achieved by washing with wastewater repeatedly. In the long run a stage might be reached whereby it cannot be found what to do with the wastewater again because of the mass of solid in it being too high, which makes it more difficult to reuse. Hence we have to consider other options for it. The second alternative in this section is to reclaim all the paint wash water for recycle into an entirely different process, such as using paint waste water as main solvent in a brick making industry. This idea requires a long-term study of the effects of the waste water on bricks quality. The concept of reclaiming is supported by Chereminisinoff and Ferrante, (1989), while Kirsch and Looby, (1991) suggest the idea of reuse of paint waste water in paint production process. The disadvantage of this step is that there seems to be a lot of trade offs that may lead to quality of products produced in the process of reusing and reclaiming waste being negatively affected, so it is appropriate to consider other options.

The third major route is the treatment option, which encompasses most of the other paths considered initially. It has two main paths; firstly the water removal option that helps recover water, and the solids are left behind, secondly the solid removal option in which the primary aim of the treatment process is the removal

of solid particles in wastewater. A further assessment of the water removal route shows that reverse osmosis or nanofiltration and distillation were considered. The disadvantage of the reverse osmosis and nanofiltration process is the likelihood of the blocking of the membrane by solid particles after the recovery of water, and this may lead to the membrane being damaged or involve an expensive process of cleaning it. The distillation process is however an expensive process because it involves heating that may be expensive due to utility consumption involved. The common disadvantage of these two processes is inability to make use of the existing facilities available in the plant.

On assessment of the solid removal option, it was thought that filtration and centrifugation process may not be able to effect a good separation process of solid from water because of the density of solid in the paint waste water. These two processes may come after an initial treatment programme. According to Peavy et al, (1985), filtration may be used to further remove unsedimented flocs in water recovered after the initial flocculation process. Finally the last process considered on the decision tree is coagulation and flocculation, which uses coagulating chemicals to destabilise a colloidal solution of wastewater and remove solids in the wastewater in the form of flocculated particles. Coagulation process is a cost effective, simple and easily assessable treatment process. It can be carried out using the existing plant facilities. Kirsch and Looby, (1991) made a similar assessment of coagulation and flocculation process in the choice of process for waste minimisation in coating industry. Thus after considering all the options it was decided to concentrate on coagulation and flocculation as the method of treating the wastewater. This process is further discussed later in this chapter with a breakdown of the theory and principles.

1.1.4 Choice of experimental process.

The choice of coagulation and flocculation was made after a careful study of the existing treatment processes in the plascon plant, the literature on waste water treatment, and a brief study of previous work done in treatment of paint waste water, which favours coagulation and flocculation. (Kirsch & Looby, 1991;

Chereminisinoff & Ferrante, 1989). Finally the choice of coagulation and flocculation was made based on the following: firstly the ease at which the existing facilities in the plant can be used to carry out the process (easy to get experimental data in the laboratory), secondly the cost of the process, (is cheap, easy to scale up) thirdly the modifications to an existing operational procedures can easily be executed. As suggested by Jorgensen, (1979) the removal of some solvents that are soluble in water used in the paint industry can effectively be removed by chemical precipitation and adsorption. From this it can be concluded that the choice of the coagulation and flocculation process is a justifiable decision.

1.2. Introduction to coagulation and flocculation.

Coagulation is the process in which destabilisation of particles occurs by the reduction of the repulsive potential of the electrical double layer. Hence the agglomeration of particles in suspension occurs (Faust & Aly, 1983). Flocculation on the other hand is the process in which destabilised particles are brought together to form aggregates called flocs that are of a large enough size that they are heavy enough to sediment. In this way separation of water and flocs formed is achieved. (Faust & Aly, 1983)

Sedimentation of particles in water may occur naturally, such as in situations of the large particles. However some particles will not settle because of its chemical interaction with water, for example in cases of hydrophilic compounds in water as suggested by Faust & Aly, (1983). Mechanical agitation can also be used in order to increase the momentum of large particles of colloidal solution to reduce the effect of the repulsive force electrical potential in the solution, so as to achieve coagulation of particles, which in turn aggregate and settle. However if particles are to small to be easily coagulated, chemical coagulation of particles in suspension will be used as described by Peavy et al, (1985).

1.2.1. A brief history of water coagulation technique.

The removal of particulate substances in water using coagulation process had been practised for centuries, it is recorded that chemical coagulants such as; alum ($Al_2(SO_4)_3$),ferric chloride ($FeCl_3$),ferric sulphate ($Fe(SO_4)_3$ and lime ($Ca(OH)_2$).(Faust & Aly, 1983) were used.

Romans used alum as a flocculant as far back as 200BC, Egyptians also used it as an item of trade, long before its use as a water purifier as explained by Faust and Aly, (1983). Iron coagulant was in wider use on the American continent, for example in 1884 Isaiah Smith Hyatt patented the use of ferric chloride for water treatment for the New Orleans water company (Cohen and Hannah, 1971). It is also mentioned that plants are also used as flocculants such as: almonds, beans, and nuts. The ancient Egyptians used five crushed sweet almonds to treat water after it has been fetched into a bucket. This was done by smearing crushed almonds into the vessel, the arm is dipped into the water and used to mix the water and the crushed almonds, in order to achieve clarification. Moringa oleifera seeds were also used as coagulants in the past. (Faust & Aly, 1983).

1.2.2. Colloidal stability in water solution.

A colloid can be defined as a medium in which particulates of different size interact but with the highest particulate diameter less than10µm. The particulates maximum settling velocity is less than 0.01 cm/sec, for the particles that settle due to gravity while the rest remains in suspension (Faust & Aly, 1983). A colloidal suspension contains different particulates of different sizes and nature as shown in Figure 1.2.The picture in Figure 1.2 is similar to that shown by Faust and Aly, 1983.

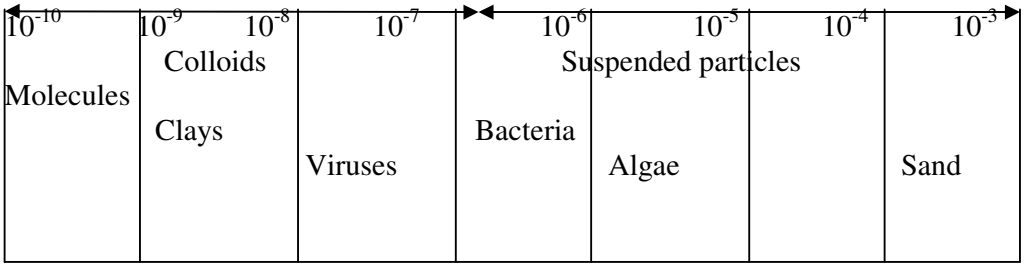


Figure 1.2. The particle size of a colloidal solution

Note: all dimensions are in μm.

The molecules and clay particles are the lowest sized particles, followed by that of the microbes in water such as; viruses, bacteria and algae, while sand particles have the largest sized particles in water.

Water from different sources contains particulate matter of different sizes and quantity. When the size of particles is above 50μm agglomeration and sedimentation of particles occurs easily, if particle size is below that size, agglomeration of suspended particles in water becomes difficult. The process of removal of particles in water, by using agglomeration and destabilisation of colloids suspended in water is used when the turbidity of the water does not meet the required turbidity standard is described as coagulation and flocculation process. However there is a clear distinction between the two terms. (Peavy et al, 1985; Faust & Aly, 1983).

1.2.3. Classification of colloids.

Colloids are classified based on the stability of its particulate in suspension. There are colloids that are eternally stable while some are temporarily stable. Reversible colloids are thermodynamically stable suspensions, such as: detergents, soap solution, proteins and starch. However irreversible colloids are thermodynamically unstable, examples are, clay, oxides of metals and microbes. The irreversible colloids can be further classified into two different types namely, diuturnal the particulate of the colloid aggregate slowly and caducous, its particulates aggregate fast. (Fair, Geyer & Okun, 1968).

1.2.4. Science of flocculation.

The primary aim of water and wastewater treatment is to make slowly aggregating suspension become a fast aggregating suspension. The major factor responsible for the unstable nature of most suspensions is the distribution of charge in colloidal suspension. In colloidal system the build up of charges on the surface of particles may lead to alteration of the arrangement of molecules in its lattice. Further at the loss of atoms due to abrasion on the surface of particles and other factors may lead to colloidal systems becoming charged and the ability to settle naturally becoming difficult (Peavy et al, 1985). In water, colloidal particles are mainly negatively charged because of the different negative functional groups on water molecules (Faust & Aly, 1983).

A negatively charged particle will have oppositely charged water ions arraigning around it, while the ions of water that are negatively charged are not attracted to the particulate of colloidal system as explained by Peavy et al, (1985). As a result of this, two colloids of the same charge find it very difficult to come together in order to settle because of the predominance of the like charges in the solution of water. Therefore an electrical potential is created and the magnitude increases as separating distance between particles decreases. The force that is required to overcome the repulsive force or the electrostatic potential is referred to as Van der Waals force of attraction. The force of attraction decreases exponentially as the distance between particles increases. It is at maximum strength when distance between colloids is at minimum. (Peavy et al, 1985; Fair et al, 1968).

The charge stabilisation effect in colloids can be summarised as the summation of the repulsive and attractive energy of the colloidal system. It may also be referred to as interaction energy. However in a medium of low ionic strength the repulsive force dominates, hence it is referred to as activation energy barrier. This forms an energy barrier that has to be overcome in other to achieve the formation of aggregates in a colloidal system. (Fair et al, 1968).

In summary the coagulation forces of stability in colloidal solution are forces of hydration. Chemical coagulation or mechanical agitation can be used to destabilise the waste water, this means to cause turbulence in order to cause particle to particle contact, this is as explained by Cohen and Hannah, (1971) and Peavy et al, (1985).

1.2.5.Types of coagulant

The two main types of coagulants used are inorganic and organic coagulants. The inorganic coagulants include: ferric chloride, aluminium sulphate and calcium chloride. The organic coagulants are polyelectrolyte coagulants, for example polyacrylamide based and are of cationic, non-ionic, and anionic category of polyacrylamide coagulants.

The effectiveness of metallic coagulants is dependent on the pH of the solution. Ferric chloride is most effective over the pH range from 4.5 to 7.5, aluminium sulphate performs best between pHs 5 and 7.5 (Peavy et al, 1985) and calcium chloride is only effective over pHs that are above 11. The colour of metallic flocculants is very important because the sludge deposited picks up the colour of the coagulant added and at times the water too. Colour is an important factor in paint industry especially if the reuse of sludge or the water is considered in the manufacture of paint. Ferric chloride colour is brownish and the hydroxide which forms the flocs and at the end the sludge picks up the brownish colour of the flocculant added. Aluminium sulphate is whitish in colour and its final sludge deposit picks up the white colour. Calcium chloride is a colourless solid and in solution its colour remains the same

Each metallic coagulant has its advantages and disadvantages, ferric chloride is cheaper, and a smaller quantity of it is used in comparison to aluminium sulphate. Ferric chloride also has the ability to consume more alkalinity in wastewater than aluminium sulphate. However this may be due to its acidity level, which is higher than that of aluminium sulphate (Crozes, White, and Marshall, 1995). However a major advantage that aluminium sulphate has in this study is that it does not

discolour the sludge deposited unlike ferric chloride that turns it brown. Reuse of sludge may be considered and hence its final colour could be an important consideration. The advantage of calcium chloride in coagulation experiments is the ability to effectively flocculate at high pH region, in wastewater that is alkaline in nature (Gehm, Bregman, and Beeland, 1976). The use of calcium chloride in the PLASCON wastewater will be difficult because it does not effectively flocculate in the pH region of wastewater samples, the pH of wastewater was between 6.5 to 9. Hence the use of calcium chloride will not be that effective as it will lead to the use of more coagulant.

The polyelectrolyte flocculants have a very high molecular weight. The lowest is the cationic polyacrylamide of around one million, and the non-ionic and anionic are between four million and thirty million respectively (Kemmer,1988). Cationic flocculants are positively charged, they perform the same way in flocculation as the metallic flocculants. They hydrolyse to yield the hydroxide ion at high pH and they become non ionic in nature. Anionic flocculants are negatively charged, they have the carboxyl group (-COOH) in their molecular structure. They ionise in water and yield hydrogen ion, hence they become non ionic at low pH. The non-ionic carry no charge (Kemmer, 1988).

In flocculation experiment as explained by Fair et al, (1968), when using polyacrylamide, the cationic polyacrylamide easily nullifies the negative charge on the colloidal particle. Hence the zeta potential, or the high net energy barrier of the colloidal solution is reduced. Agglomeration of particles is by adsorption and neutralisation, hence cationic polyacrylamide is more effective at lower pH but may function well at high pH because of its polar group (Kemmer, 1988). However, anionic polyacrylamide functions well at higher pH ranges but could as well be used in lower pH ranges when it loses hydrogen ion. The non-ionic is however not pH sensitive. (Chadik &Amy, 1983; Cohen & Hannah, 1971.).

As observed by Nozaic, et al, (2001), a major characteristic of polyelectrolytes when used in wastewater flocculation experiment is the restabilisation

characteristics. The flocs formed are redispersed back into water recovered in the process. This happens when the polyelectrolytes is overdosed into wastewater. The restabilisation makes it difficult to use the polyelectrolytes because of the narrow range they work within. Polyelectrolytes are not suitable turbidity removals because of the limited range they can work in. They only work well in low turbidity waters and in high turbidity waters they may be used as coagulant aids. (Nozaic et al, 2001)

The sludge formed by polymeric coagulants or flocculants are less voluminous in comparison to what is recovered when metallic coagulants are used. This is because they do not produce gelatinous flocs. They also do not affect the pH of water when used, neither are they as sensitive to pH as metallic flocculants as suggested by Kemmer, (1988) and investigated experimentally by Nozaic et al, (2001).

The primary experimental process for coagulation and flocculation process is the jar test experiment method. In chapter two a more descriptive explanation is given for the process. Its comparative advantage over other screening methods is the simplicity and cheapness and it can be easily controlled. Although most literature complained about its difficulty in scale up activities. (Faust and Aly, 1983; Peavy et al, 1985)

1.3.Thermodynamics of coagulation

The equilibrium reaction of metallic coagulant in waste water dictates the hydrolytic process of the two chosen metallic flocculants, parameters such as ionic strength of coagulant solution, activity coefficient of the hydrolysing cation and temperature of the medium will determine the shift of the reactions (Flynn, 1984;Stumm and Morgan, 1981). The hydrolytic reactions for ferric chloride and aluminium sulphate are similar to one another because of the +3 valency of the ferric and aluminium ions (O`Melia, 1972). They are however more effective in comparison to mono and divalent metallic compounds such as: ferrous sulphate, calcium chloride and sodium sulphate. Trivalent metallic compounds are about

1000 times more effective than monovalent and about 20 times more effective than divalent (Cohen and Hannah, 1971). In water hydrolysis reactions occur to produce hydroxides of their parent metallic compound as shown in equation [1-1] & [1-2]

$$[M(H_2O)_6]^{3+} = [M(H_2O)_5(OH)]^{2+} + H^+ \qquad [1\text{-}1]$$

$$[M(H_2O)_5(OH)]^{2+} = [M(H_2O)_4(OH)_2]^{+} + H^+ \qquad [1\text{-}2]$$

M represents either Fe^{3+} or Al^{3+} ion (Cotton, et al, 1987). These reactions mean that when aluminium sulphate or ferric chloride flocculants are added into water the pH drops because of the hydrogen ion [H^+] added into the water. Ferric chloride and aluminium sulphate have the capability of forming complex hydroxides, which its distribution in aqueous phase, and the exact composition is a function of pH and the concentration of flocculant solution. The possible hydrolytic reactions of ferric and aluminium hydroxide reactions are as shown in equations [3] to [9]. A representative M is chosen for metallic compound similar to that used by Gregory and Duan, (2001).

$$M^{3+} + H_2O = MOH^{2+} + H^+ \qquad K_A \qquad [1\text{-}3]$$

$$M^{3+} + 2H_2O = M(OH)_2^{+} + 2H^+ \qquad K_B \qquad [1\text{-}4]$$

$$M^{3+} + 3H_2O = M(OH)_{3(aq)} + 3H^+ \qquad K_C \qquad [1\text{-}5]$$

$$M^{3+} + 4H_2O = M(OH)_4^{-} + 4H^+ \qquad K_D \qquad [1\text{-}6]$$

$$M^{3+} + 2H_2O = (am)M(OH)_{3(S)} + 3H^+ \qquad K_E \qquad [1\text{-}7]$$

$$M^{3+} + 2H_2O = (\alpha)M(OH)_{3(S)} + 3H^+ \qquad K_F \qquad [1\text{-}8]$$

$$M^{3+} + 3H_2O = M(OH)_{3(S)} + 3H^+ \qquad K_G \qquad [1\text{-}9]$$

Data pattern taken from Stumm and Morgan, (1981).

The effect of temperature is not so pronounced on the equilibrium reaction of hydrolysis of ferric and aluminium hydroxide compounds as investigated by Flynn, (1984). However the equilibrium constant K is important as it helps to understand the favoured species. As further explained by Gregory and Duan, (2001) the deprotonation leads to a loss of formal charge as pH increases as described in equations [3] to [6]. Hence for the hydrolysis reactions, formation of solid hydroxide compounds takes place around the mid pH as suggested by most literature (Gregory and Duan, 2001; Jiang, and Graham, 1998). Faust and Aly,1983 suggest that whenever a super saturated metallic coagulant is used, the solubility product of the stable hydroxide solid in equation [1-8] would be exceeded. This in turn leads to the formation of metastable hydroxide solids that are amorphous in nature. From experimental analysis done by Gregory and Duan, (2001), Morel, (1983) and Faust and Aly, (1983) using data from O`Melia, (1972), it was suggested that the hydroxide solid produced is the amorphous solid hydroxide. An important point is that the final stable alpha ferric hydroxide solid (goethite) will be formed on aging after the formation of the amorphous, but this takes time, about two weeks in some cases as observed by Flynn, (1984). This is due to the metastable nature of the amorphous hydroxide solid as suggested by Gregory and Duan, (2001).

1.4. Kinetics of coagulation and flocculation process

Peavy et al, (1985), discuss the importance of mixing in the coagulation process, mentioning that Brownian motion in a colloidal system should exceed the electrostatic potential of the system in order to achieve destabilisation of the colloidal system. However when the distance between each particle of the colloid system is still high and the Van der Waal forces of attraction are still low, the authors propose the use of mechanical agitation to increase the collision rate so that particles could agglomerate and hence settle out of the system. It is therefore important to utilise coagulants to achieve agglomeration when mechanical means alone do not result in agglomeration of colloidal particles. On addition of

coagulants into the colloidal system quick dispersion of the coagulants to all parts of the system is important. Thus a period of rapid mixing is essential. This is usually very brief (Jiang and Graham, 1998), and it should be less than five minutes.

During the period of rapid mixing the following things do occur: hydrolysis, adsorption and precipitation (Jiang and Graham, 1998). Hahn and Stumm, (1968) give a breakdown of the following occurrences, a reduction in potential energy between particles, and an increase in Brownian motion, which leads to collisions between small sized particles. There is also a reduction in surface potential of colloid that causes the adsorption of counter ions by colloidal particles during the period of rapid mixing.

On completion of the rapid mixing period there is an onset of slow mixing, during this period orthokinetic coagulation is prevalent. Faust and Aly, (1983) describe it as a period when the particles or flocs formed are large enough that at this point the relative motion due to velocity gradient of the particles causes a high shear rate in liquid phase, in comparison to the initial period of rapid mix. It is further explained by Hahn and Stumm, (1968) that it is a period when large particles impart their own velocity to neighbouring particles. It is also a period when interparticle bridging occurs within particles in colloid. The period of slow mix may be between fifteen to thirty minutes depending on the colloidal system.

Finally the last factor that also influences the kinetics of a system is the period of sedimentation. This is the time during which the particles formed are allowed to settle. In coagulation and flocculation experiment this period is about thirty minutes. The heavy particles drop out of the fluid due to the force of gravity.

1.5. Alternative view of coagulation and flocculation

In the previous sections a review of applications of thermodynamics and kinetics has been done. Therefore this section discusses the process of coagulation and flocculation from the mechanism of the destabilisation of colloids point of view.

The ideas presented in this section require a careful study, although many authors seem to analyse coagulation and flocculation process from this perspective.
Destabilisation of colloids in coagulation and flocculation process is still being studied. However it is widely believed that the destabilisation occurs in four different ways namely: double layer compression, adsorption and charge neutralisation, entrapment and adsorption, and interparticle bridging. Any of these occurs in colloidal systems when coagulation and flocculation is utilised, and depends on the quantity of particulate content of water, the hydrolytic reactions occurring in the system, the pH of medium and lastly the impact of the destabilised particles of colloids on surrounding neighbours. (Peavy et al, 1985; Fair et al, 1968; Faust & Aly, 1983;Jiang and Graham, 1998; Jacangelo et al, 1995).

The predominant mechanism of the coagulation process may be kinetically or thermodynamically influenced in as much that there is no conclusive evidence of the occurrence of the different types of processes. As stated by Jiang and Graham, (1998) during the period of rapid mixing, the dominant mechanism for the destabilisation of the colloid may be charge neutralisation. However it is pH dependent because it is dominant at pHs below 6.5. It is also noted from various literature sources (Jiang and Graham, 1998; Vik et al, 1985; and Amirtharajah et al, 1993) that some species of metallic hydroxide also aid the neutralisation reaction at pH below 6.5. Species such as MOH^{2+}, $M(OH)_2^{+}$, are the dominant species in this region. In the neutral and upper pH region sweep coagulation is the assumed dominant mechanism. This is the process by which colloidal particles get trapped by flocs that are forming or colloidal particles become enmeshed in already formed flocs that are settling out of the colloidal system (Peavy et al, 1985). The negative monomeric species represented by $M(OH)_4^{-}$, is the dominant species in this region. A major kinetically influenced mechanism is the entrapment or enmeshment process of the sweep coagulation process.

The mechanism of flocculation process is different for polyelectrolytes the main mechanism is interparticle bridging. This is a process in which the polymer

branches become adsorbed to different particles, interlocking with one another and thereby leading to formation of a settleable mass. (Peavy et al, 1985).

1.6. A summary of our views

In summary the choice of process for treatment of wastewater is made after considering various treatment options. This is further discussed in the next chapter for the experimental process. A brief thermodynamic assessment of the hydrolytic reaction of metallic coagulants in water and the effect of kinetics in the coagulation and flocculation process are assessed. It can be highlighted that the literature does not really draw a line between the thermodynamic factors and kinetic factors. Attempts were made in some cases to interrelate thermodynamics and kinetic factors of a coagulation process but they were not well drawn out.

Assessment of the different approach to the coagulation and flocculation process shows that at present there are no easily understandable practical models to predict the effect of mixing, pH, dosage and concentration of flocculant, impact of the redox activities on metallic coagulant used in water treatment. However in order to study this an experimental investigation was carried out to investigate how these factors and other physical properties of waste water influence the coagulation and flocculation process.

The purpose of this dissertation is to look at the effects of ferric chloride and aluminium sulphate flocculants on wastewater. A thermodynamic model is developed in this perspective to study the characteristics of the two metallic flocculants in water. The main source of wastewater is known, which is the paint industry. A major problem that was encountered is the continuously varying solid content of wastewater and a varying pH for different wastewater sample. These make it difficult at times to interpret the results. However measures were put in place to check the inconsistent wastewater samples. The quality of water produced in the flocculation process was also evaluated and the conditions guiding the generation of water produced were assessed.

CHAPTER 2

Experimental Procedures and Analysis

2.1. Introduction

Based on the choice of experimental process in chapter 1 of coagulation and flocculation, an assessment of different techniques that can be used was done and the final choice of experimental process was made. This chapter explains the experimental procedure. It gives a descriptive account of the experimental verification carried out in order to confirm the consistency in the choice of the processes. The chapter is divided into two main sections namely: characterisation of the water and the flocculation tests.

2.2. Characterisation of waste water

The measured parameters in the characterisation of PLASCON wastewater are: solid content of wastewater, pH of wastewater and redox potential of wastewater. The pH of initial wastewater sample from PLASCON is measured. The pH is important because it affects the efficiency of the flocculant. The inorganic based flocculants are pH sensitive they may or may not perform well in the alkaline or acidic region, as suggested by Peavy et al, (1985). From the results obtained the pH of the wastewater samples lies between pH 6.5 and 9.

2.2.1. Total solids measurements

For the total solids measurement, the wastewater solution was thoroughly mixed under agitator at a speed of about 300rpm, for about one hour to ensure even dispersion of solid in waste water. The speed and period of agitation was chosen after observing the effect of mixing at lower speed and different durations in different experiments. Solid content test is carried out by drying a 20g mass of wastewater in a crucible placed in an oven at 130^0C for 1 hour. The representative mass of sample for drying was chosen after drying at different mass and temperature for different samples. The experimental results for various samples

show that the solid content of the different wastewater samples are different. The lowest sample was 78g of solid/1000g of wastewater. Generally the flocculent dosage required is considered to be proportional to total solids (Faust and Aly, 1983; O`Melia, 1972), hence there is a need to standardise the solid content of wastewater for the experiments. Water was used as the diluting solvent because it is the main medium of wastewater. Wastewater samples are stored in a refrigerated room at temperatures of about 10^0C.This was done to prevent the decomposition of wastewater and prevent microbial activities in wastewater.

The approach described for determination of solid content is similar to the experiment for determining solid content of paint in the industry. The only difference is that in this case there was drying wastewater, while the industry dries paint. It was important to ensure that the samples are dried out properly. Two major variables: namely temperature and quantity of waste water to be dried, were found to be factors influencing drying. If too hot an oven or if too large a quantity is dried, a skin forms trapping fluid below its surface and samples do not dry properly. Thus it was decided that 20g samples would be used for total solids measurements, based on the results for drying at different masses of samples, at 10g, 20g, 50g,and 100g of wastewater. Results obtained for drying of the different masses is shown on Appendix A.

2.2.2. Preparation of samples for flocculation experiments.

The results obtained from the solid content determination experiments for different samples of waste water show that the solid content varies between 78g of solids in 1000g of waste water and 206.8g of solids in 1000g of waste water. Therefore in order to study the process of flocculation effectively using the wastewater the solid content of the wastewater has to be taken to a standard level for all wastewater samples before use in the experiments. These will help record comparable results. Another important step to carry out is ensuring a well-mixed wastewater sample as emphasised in section 2.2.1.The speed of agitator was set at 300rpm when using a 5L vessel for the wastewater sample. The speed of 300rpm

was chosen because when wastewater in 5L vessel is mixed at this speed, spillage of wastewater is avoided and as well effecting a well mixed medium.

A solid content of 80g of solids in 1000g of wastewater was chosen for this investigation. This mass was chosen because of the need for a solid content that can be used for comparable studies of the different flocculants. Another reason is that initial flocculation experiments using 0.043 moles/Litre ferric chloride solution (a concentration obtained from the literature) yielded the widest range of results showing good flocculation at a solid content of wastewater of 80g of solids in 1000g of waste water.

For samples in which the solid content in the water is more than 80.00g of solids in 1000g of waste water, the volume of water required for the dilution of the wastewater to the required mass of solid content of 80g in 1000g of wastewater is calculated using equation [1] as defined.

$$M_1C_1 = M_1C_2 + M_2C_2 \qquad [2\text{-}1]$$

$M_{1:}$ Initial mass of waste water before dilution

$M_{2:}$ Mass of water to be added for dilution

$C_{1:}$ Amount of solid in waste water before dilution

$C_{2:}$ Amount of solid content of waste water after dilution (constant for all dilution process at 80g of solid in 1000g of waste water).

Finally after dilution has been carried out a solid content test is done for the standardised wastewater sample to check the accuracy of dilution, before the flocculation experiment.

2.3. The flocculation experiment

The aim of the flocculation experiment is to determine the optimum coagulant dosage required to dose the wastewaters and separate the wastewater into water and sludge. It is also required to determine the factors affecting the optimal dosage and if the results can be explained by thermodynamic model. Some of the

probable factors that may affect the results of flocculation could be concentration and volume of coagulants dosed. The type of coagulant and finally the solid content of wastewater.

2.3.1. Preparation and dosing of flocculant solutions

The inorganic flocculants that were screened are ferric chloride ($FeCl_3.6H_2O$) (Saarchem, 99%purity) and aluminium sulphate ($Al_2(SO_4)_3$) (Saarchem, 97%purity). The flocculant concentrations were prepared by weighing the required masses on a Mettler instrument, mode PE 160 weighing balance. The weighed sample was dissolved in the required deionised water in a calibrated volumetric flask to give the desired concentrations. The ferric chloride feed solution was 0.043moles/Litre and that of aluminium sulphate was 0.084moles/Litre solution. These concentrations were chosen so that the concentration of metal ions in the feed solution was approximately 2400 ppm in each case. The feed concentration was increased for some specific experiments such as: using higher concentrated coagulant feed concentrations of ferric chloride and aluminium sulphate at concentrations of 0.32,0.69 and 4.6moles/litre respectively.

Polyacrylamide, a polyelectrolyte flocculant, was also screened in its different forms. It is available in anionic, non-ionic and cationic (Zetachem) forms. A 1g/L solution of polyacrylamide was used, because this concentration gave favourable flocculation results. Attempts to prepare a more concentrated solution of polyacrylamide lead to the formation of a highly viscous flocculant solution. This concentration also coincides with the theoretically proposed concentration for the use of polyelectrolytes. (Nozaic et al, 2001)

The flocculants were dosed into wastewater samples of 400mL at 20, 40, 60, 80, 100, 120mL respectively, for 0.043moles/litre ferric chloride and 0.084moles/ litre aluminium sulphate solutions. The choice of 400mL of wastewater is because the volume is large enough to ensure good homogeneous mixing and reproducibility. The 5L can was used once because of the need to investigate the flocculation

process at a small scale before scale up. For higher concentrations of ferric chloride and aluminium sulphate, flocculant solutions were dosed into wastewater at the corresponding bulk concentrations of 0.043moles/litre of ferric chloride and 0.084moles/litre of aluminium sulphate flocculant solution in wastewater.

The dosing of coagulant into the wastewater was done in different ways in order to determine the best way of adding flocculant. It was found that the concentration of the flocculant affected the optimal manner of dosing. The easiest means of dosing the low concentration ferric chloride (i.e. 0.043moles/litre of $FeCl_3$), into the wastewater, was by pouring of ferric chloride solution into wastewater and it gave reproducible results. Other techniques were also tried such as: injection of solution above and below surface of wastewater in beaker, and gradual or controlled addition. The different techniques gave similar results.

However for the high concentration ferric chloride solutions, (above 0.32moles/litre), the spontaneous addition technique, and the syringe injections above and below surface of wastewater gave different results. This is because at high concentration whenever the flocculant solution touches the surface of the water, it forms lump size flocs that cannot be easily dispersed by the speed of agitation of the impellers. However a fair flocculation result was achieved with controlled gradual addition of the flocculant above the wastewater surface. The 0.32moles/litre ferric chloride solution was dosed at a rate of 4.47mL /min. It is thought that time is required for dispersion of the coagulant dose added for flocculation to take place as suggested by Faust and Aly, (1983).

The same dosing technique was used for aluminium sulphate flocculant and they also have similar results at different concentrations as that of ferric chloride.

For cationic polyacrylamide flocculant, the spontaneous addition and gradual addition gave favourable results at a concentration of 1g/L. Attempts to use higher concentrated solution of polyacrylamide would be difficult because of its highly viscous nature if prepared.

2.3.2.The Jar tests

The jar tests are carried out using a flocculator or jar test rig (BIBBY) Stuart scientific flocculator SW1 model. It is essential that the flocculant solution for the flocculation process is prepared to the required dosage before the jar test experiment. In order to ensure good mixing agitation was carried out for about 1minute for good dispersion of flocculant particles of ferric chloride, in order to prevent the particles of the flocculant from sticking to the container. The aluminium sulphate was prepared in such a way that it was left for about 1 hour so that its particles can dissolve in water because it is not as soluble as ferric chloride in water.

After a period of constant agitation by the mixer as described in section 2.1.1.The waste water is divided into six beakers with 400mL in each. The beakers are positioned in the flocculator and agitated at a speed of about 50rpm (Anonymous Retrieved March 26 2002), in order to avoid particles of wastewater from settling and to maintain uniform dispersion of particles in wastewater. The coagulant solution of required volume and concentration is dosed into the jars as discussed in section 2.3.1. After dosing the mixing speed of the flocculator was increased to 250rpm (Anonymous. Retrieved March 26 2002), immediately so as to ensure even dispersion of flocculant solution in the wastewater solution.

Rapid mix at 250rpm should not exceed 1minute so as to quickly disperse coagulant solution in wastewater. Reduce speed to 60rpm for 9 minutes (Anonymous. Retrieved March 26, 2002) in order to allow the growth of floc particles in solution. Observe each beaker at 3-minute intervals to detect floc formation. Reduce mixing to 25rpm for 4 minutes and then further to 10rpm for 2 minutes (Anonymous. Retrieved March 26, 2002) this is done in order to prevent floc particles formed from breaking up. The flocculator was turned off and allow contents in beakers to settle for about 30 minutes.

A major observation point in the jar test experiments was when the optimum coagulant dosage is achieved in the coagulation process; recovery of clear water is easily noticed and flocs formed faster at points with higher bulk concentration of coagulant in comparison to jars with inadequate coagulant concentration. However after the experiment is ended quality of water recovered was determined by measuring parameters such as turbidity, pH, redox potential, metal content and conductivity.

2.4. Measurement of properties of flocculated water

The measurement of water quality properties is important because there are government standards guiding the wastewater effluent disposal and reclaimed water reuse in South Africa in order to check environmental pollution as well as ensure quality and a safe working conditions for citizens in general.

2.4.1. pH and redox potential measurement of water

The pH meter is a CRISON micro pH 2002 model pH electrode with the inside filled with silver chloride solution and an outer glass casing with a small membrane covering at the tip. The measurement of pH is carried out by using a pH meter, the pH meter is first calibrated using pH technical buffer solutions of 4 and 7 before usage. The calibration was done according to the standard procedure. The measurement of pH of water recovered is done by decanting water recovered into a beaker and the pH probe is inserted to read off the measurement on the digital screen of the meter. The same pH meter is also used to determine the redox potential of water recovered which is a measure of the reducing or oxidising ability of water recovered. A negative reading on the digital display indicates an oxidising potential of water while a positive number display indicates a reducing potential of water recovered.

2.4.2.Atomic adsorption analysis

This is the technique that is used to determine the metallic content of water recovered. The equipment is calibrated by preparing standard solutions of the

element to be measured, and the corresponding lamp for the element to be measured is also fitted unto the equipment. A careful selection of different parameters to aid equipment in functioning properly is also selected from the analyser's memory database. Metal ion concentrations were determined using a Varian Flame Atomic Adsorption spectrometer (Model: Spectra AA 55B). In the measurement of ferric ions, acetylene is used as fuel with air as the carrier and the flame stoichiometry is oxidizing. The range of detection is between 0 μg/ml to 30 μg/mlm, values beyond this may have to be diluted to a specific level and measured. For aluminium ions, acetylene is used as the fuel and the carrier is nitrous oxide. The flame stoichiometry is reducing. The range of detection for aluminium is from 0 μg/ml to 400 μg/ml. The operation of the atomic adsorption column is in accordance with manufacturer's operating manual. In order to ensure quality control of the process samples were measured repeatedly.

2.4.3.Turbidity measurement

Turbidity was measured with an infra-red HANNA PORTABLE MICROPROCESSOR TURBIDITY METER. It functions by passing a beam of infrared ray of light through a vial inserted in the measuring cell of the turbidity meter. The vial is cleaned with a cleaning solution after use. The vial is handled with a lint free cloth so that the instrument reading will not be impaired, the calibration of the instrument is done once in a month. In other to ensure good quality reading, samples are measured repetitively.

The infrared light is from a high emission source with wavelength reaching an optimum performance at around 890nm, it contains a sensor, which is placed at an angle of 90 degrees to the direction of light rays. The sensor detects the amount of light scattered by the undissolved particles in the sample, unit of turbidity for the instrument is the formazin turbidity units (FTU), all these as explained by the Hanna turbidity meter handbook. The maximum ranges of the turbidity measurement possible are from 0 FTU to 1000FTU, values beyond 40 FTU are required to be diluted in a 100mL flask. The basic dilution factor and measured

turbidity is used to determine the actual turbidity of the sample. The formula shown is used to determine the final turbidity of sample.

$Vos = 3000/T$ [2-2]

Vos= volume of sample to be added into turbidity water free sample to make 100mL

T= turbidity reading of meter exceeding 40 FTU

Using this formula the actual turbidity of sample is known

T_n X 100mL / Vos = T_a [2-3]

When T_n = new meter reading

T_a = actual turbidity value of the original sample

2.4.4.Conductivity measurement

Conductivity is measured using a Jenway (4071) conductivity meter, which is measured in mS/cm and calibrated using a standard potassium chloride solution. This is a measure of electrical conductance of water or mineral content of water, it is important to measure conductivity of water in order to know the likelihood of the water becoming corrosive. (Kemmer, 1988).

2.4.5. Concluding remarks

In conclusion, the experimental process is a combination of standard procedures carried out such as: jar tests and solid content tests. Some of the processes were optimized in order to get a fair result. The description given for these processes enables the study of the inorganic and organic flocculants using jar tests experiment. The characteristics of different flocculants were considered in making final decisions on experimental pattern. However different wastewater sample interaction with different flocculant also plays an important role in the choice of the final process. Finally the characterization of water recovered was done in order to ensure that the measured parameters are within the existing South African environmental regulations in order to assess the viability of the treatment process.

CHAPTER 3

Thermodynamic Analysis of Flocculation

3.1 Introduction

In this chapter a model is developed to evaluate the two metallic flocculants namely, ferric chloride and aluminium sulphate, using the thermodynamics of the reactions of the hydrolysis process. Initially an assumption that flocculation occurs when wastewater is saturated with metallic salts of the coagulant was made.

The aim is to use thermodynamics to predict which factors will influence flocculation and what trends would be observed. The model looked at the types of solid that would be formed under equilibrium conditions and what factors would influence flocculation most. The model developed will be used in chapter four to compare the results obtained in the experimental process with model predictions. The model will give an indication whether thermodynamics or kinetics is the more important characteristic that dictates the flocculation process, and also if kinetics overrides thermodynamics in particular regions in the flocculation process.

3.2 An overview of thermodynamics of solution and precipitation of ferric Ions

For the equilibria of ferric ions different literature sources give varying equilibrium constants (K) for the same hydrolysis reactions but in different solutions.

These may be due to reasons such as: different ionic strength of solution, which may lead to different activity coefficients for species in the hydrolytic reactions. The Table 3.1 shows different reactions and equilibrium constant (K) values with reference to the authors. The K values of equilibrium reactions may also vary as a result of the use of a background electrolyte during experimental measurement. The temperature at which the data were measured was at 25^0C.

Equations from Faust and Aly (1983)	Faust & Aly (1983)	Stumm and Morgan (1981)	Baes and Mesmer (1976)	Dentel and Gosset (1988)	Morel (1983)	Jiang and Graham (1998)	Flynn (1984)
	K						
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	6.50E-03	6.50E-03	6.50E-03	6.50E-03	6.30E-03	6.30E-03	6.31E-03
$Fe^{3+} + 2H_2O = FeOH_2^{+} + H$	2.14E-06	2.14E-06	2.14E-06	2.14E-06	2.00E-06	1.99E-06	2.00E-06
$Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+$	1.00E-12	1.00E-12	1.00E-12	1.00E-12		1.99E-12	2.00E-12
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	2.50E-22	2.50E-22	2.50E-22	2.51E-22	2.51E-22	1.99E-22	2.00E-22
$Fe^{3+} + 2H_2O = \alpha$-Fe(OOH)s $+ 3H^+$	3.16E-01	3.16E-01	3.16E-01			5.01E-01	5.01E-01
$Fe^{3+} + 2H_2O =$ am- Fe(OOH) $+ 3H^+$	3.16E-03	3.16E-03	3.16E-03	2.82E-04	6.31E-04	5.01E-04	1.26E-05
$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$	1.00E-04						

Table 3.1 Comparison of equilibrium data for ferric hydrolytic reactions

The chemical equilibria for Fe^{3+} as given by Faust and Aly, (1983) were considered with their corresponding equilibrium constant (K). The equilibrium constant was calculated at a temperature of 25^0C from log K and zero ionic strength. The equilibrium constants used by Dentel and Gosset, (1988), were taken from Stumm and Morgan (1981) and they were calculated at ionic strength of zero, and a temperature of 25^0C.The data from Morel, (1983), were originally from Baes and Mesmer (1976) and they were also determined at an ionic strength of zero and temperature of 25^0C. The data from Jiang and Graham, (1998), was originally reported by Flynn, (1984). Flynn's data were measured at 25^0C at zero ionic strength. A critical look at Table 3.1 shows some slight variance in the equilibrium constant data, in particular the aqueous phase. Some authors did not show some equilibrium reactions perhaps because the reactions were not considered in their analysis. A major variation noticed is the large value for Flynn,

(1984) for the equilibrium constants of the third reaction, which was twice the equilibrium constant for other authors except Jiang and Graham, (1998). Although Flynn (1984) accepted that there might have been errors up to about (-0.2 to +0.2) range. Another major difference is the solid phase equilibrium reactions for Jiang and Graham, (1998), Morel, (1983) and Flynn, (1984) the equilibrium constant data for this reactions are smaller in comparison to that in the columns two to four for these authors, Stumm and Morgan (1981), Baes and Mesmer (1976) and Dentel and Gosset (1988). This is because they measured the data experimentally.

An observation noticed in the data reported by the different authors is the different values reported by different authors, which becomes more noticeable at the solid precipitate formation equilibrium reactions. The different authors have not all explicitly given the conditions of their experiments, such as: ionic strength, temperature etc. It is thought that the differences in the equilibrium data for the solid phases is due to the metastable phase of amorphous solid that is formed quickly and that then gradually transforms to alpha solid phase. The difference in data may be due to the stable phase being reached at different rates in different experiments. The time allowed by different authors for a solution to attain equilibrium with the solid varied widely.

The determination of the equilibrium data in Table 3.1 as explained by Dyer et al, (1998), is mostly measured in the neutral pH range and this coincides with the pH of the experimental process between 6.5 to 9. Baes and Mesmer, (1976) explain that the pH range at which hydrolysis of metals occurs is of significant importance because of the precipitation of solid hydroxide species but that there are limitations to the study of these. However Dyer et al, (1998) pointed out that one of the main problems is the lack of technology to measure metal species that are of very low concentration, below 10^{-5} M. He suggests that solubility data measured between 1960 – 1970 should not be relied on but viewed with caution. Therefore the reactions and data used in this dissertation were taken from Faust and Aly, (1983) and Stumm and Morgan, (1981). Firstly this data was chosen because it shows more hydrolysis reactions than the others. Secondly it gives a

comprehensive picture of the aqueous and solid phases at equilibrium. Finally because all the hydrolytic data were measured at the same media conditions such as, ionic strength and temperature, it is advisable to choose the reactions that give most information about ferric ion hydrolysis. In order to do a comprehensive basic study, however the final data that may be used in chapter 4 may be different after an understanding has been derived from this section. For example the data of Flynn, (1984) and Jiang and Graham, (1998) were experimentally measured or estimated from experimental conditions.

An important point that should be noted is the non-ideality of the medium in which the experiment was carried out. According to Stumm and Morgan, (1981) the activity coefficient of a solute in an ideal solution is unity, because the concentrations of ions in the medium tend towards zero, but in the case of waste water the ion concentration is not zero, hence the solution will not be ideal. Therefore we may infer that the activity coefficient of ions in our medium is not unity.

The ionic strength of the solution cannot easily be determined but an approximation may be reached, based on the information available about the initial concentration of ferric chloride feed added. The real ionic strength value of our medium will be difficult to determine because of the unknown concentrations of the other metallic compounds in waste water such as: titanium, calcium and others. However it can be approximated based on the concentration of ferric chloride fed into wastewater. The ionic strength of solution increases the activity coefficient of individual ions in the medium decreases, as suggested by Stumm and Morgan, (1981). Moreover as suggested by Flynn, (1984) increasing the ionic strength of a solution may decrease or increase the equilibrium constant of an equilibrium reaction.

3.2.1 Hydrolysis reactions of Fe^{3+} ions in solution

	K (equilibrium)	
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	6.50×10^{-3}	[3-1]
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	2.14×10^{-6}	[3-2]
$Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+$	1.0×10^{-12}	[3-3]
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	2.50×10^{-22}	[3-4]

Equations (3-1 - 3-4) is as given in Stumm and Morgan, (1981).

Ionic strength = 0

Temperature = 25°C

In waste water treatment when metallic compounds are used for treatment purposes, it is thought that the formation of various aquometallic compounds occurs, which may be monomeric, dimeric, polymeric metallic hydroxides and solid hydroxides, in particular this is thought to occur for the neutral aqueous species, $Fe(OH)_{3,\,aq}$. It is assumed that this equilibrium reaction occurs when ferric chloride coagulant is added into water in order to achieve the formation of a ferric hydroxide solid precipitate. (Faust and Aly, (1983); Jiang and Graham, (1998)).

On addition of ferric chloride coagulant into the wastewater different species of hydroxides of ferric are produced as mentioned in the previous paragraph. However the various species formed are pH dependent, the dominant species on addition of 0.043moles/litre of ferric chloride are shown as a function of pH in Figure 3.1. This is known as the species distribution curve. The polymeric species are not shown in equations 3-1 to 3-4, because it is thought that they do not easily exist in the pH range the flocculation experiment is carried out.

Dyer et al, (1998) suggested that they exist more in the low pH ranges and at high concentration of metallic compounds in water. However the formation reactions of polymeric species are kinetically slow and they are of low solubility, which

gives them good adsorption properties on solids (Dyer et al, 1998). The experimental working range of pH of the wastewater was between 6.5 – 9.0 and so the dominant species in this range are those considered in Figure 3.1.

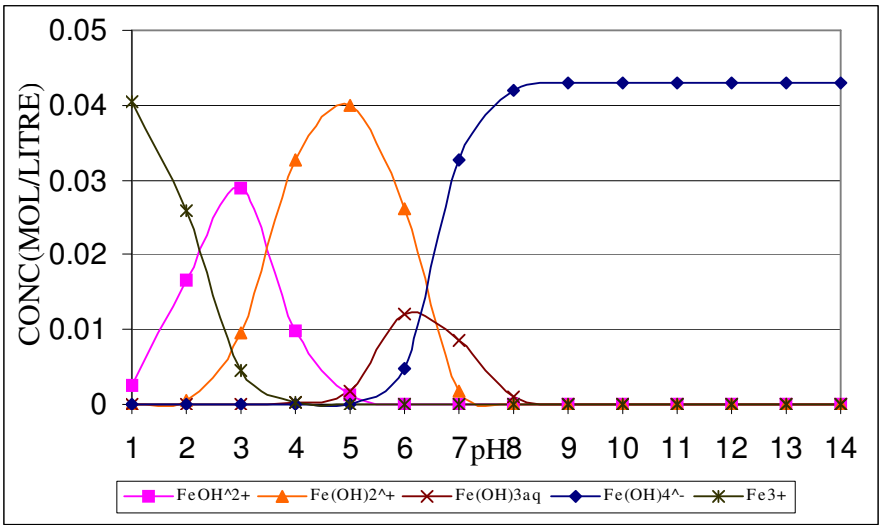


Figure 3.1 Ferric hydroxide species distribution curve

The species distribution curve shows that the $Fe(OH)_2^+$ is the dominant species from pH 6.5 till around pH 7. Above pH 7 the dominant species becomes $Fe(OH)_4^-$. From the literature the optimum performance for ferric chloride is within 4.5 to 7.5 (Peavy et al, 1985). However these two species, $Fe(OH)_2^+$ and $Fe(OH)_4^-$ are the dominant species in this pH range. The ionic strength may affect the speciation but at this stage, this is not included because we are working at fairly low concentrations of ionic species in wastewater.

3.2.2. Theory of species interaction with solid precipitate

$$Fe^{3+} + 2H_2O = \alpha\sim Fe(OOH)_{(s)} + 3H^+ \qquad 0.31623 \times 10^{0} \qquad [3\text{-}5]$$

$$Fe^{3+} + 2H_2O = (am)Fe(OOH)_{(s)} + 3H^+ \qquad 3.1623 \times 10^{-3} \qquad [3\text{-}6]$$

$$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+ \qquad 1.0 \times 10^{-4} \qquad [3\text{-}7]$$

Equations (3-5 – 3-6) is as given in Stumm and Morgan, (1981).

Equation (3-7) is from Faust and Aly, (1983)

Ionic strength = 0

Temperature = 25°C

The formation of ferric hydroxide solids is a progressive step that involves, the hydrolysis of species as discussed in the previous section. As suggested by

Gregory and Duan, (2001) it involves the gradual deprotonation of water molecules in the hydration shell, hence leading to the formation of a solid hydroxide phase as shown:

$$Fe^{3+} \longrightarrow Fe(OH)^{2+} \longrightarrow Fe(OH)_2^{+} \longrightarrow Fe(OH)_{3(s)}$$

In the reactions shown from literature, the solid precipitate that is formed at the early stages is the unstable amorphous ferric hydroxide [am~$Fe(OH)_{3(s)}$]. However Faust and Aly, (1983) proposed that this occurs when the solubility product of the ferric hydroxide solid [$Fe(OH)_{3(s)}$] is exceeded, and that this ferric hydroxide solid is formed at low feed concentration. However Stumm and Morgan, (1981) explain that due to the metastable nature of the amorphous ferric hydroxide formed it undergoes a slow aging process that leads to the formation of the stable goethite alpha ferric hydroxide [α~ $Fe(OOH)_{(s)}$]. Different types of ferric hydroxide solid may be formed depending on the compound that is being used in the waste water treatment process, as reported by Baes and Mesmer, (1976). Biedermann and Chow, (1966) observed the formation of akaganeite ferric hydroxide [β~FeO(OH)] as the active solid formed in a chloride medium. There are other possible solids that can be formed such as: lepidocrocite ferric hydroxide [γ~$Fe(OOH)_{(s)}$] that can easily be transformed into the inactive and stable alpha ferric hydroxide when heated in the presence of alkaline solution. (Baes and Mesmmer, 1976).

A noteworthy point is the conflicting literature available about the occurrence of the stable solids. Some important factors determining the type of solid precipitated are: concentration of initial ferric chloride solution, the aging of hydrolysed polymer formed in the process, the medium in which the solid is formed (Baes and Mesmer, 1976) and the ionic strength of the ferric chloride solution, as suggested by Flynn, (1984).

3.2.3 The free ferric ion in equilibrium with ferric hydroxide species

The choice of the reactions and the equilibrium constant were based on the suggestions of O`Melia,(1972), namely that at low ionic strength of colloid the electrostatic potential is greater than the Van der Waals forces of attraction, which may cause a high activation energy barrier in particles in colloidal solution. In comparison to a high ionic strength solution, which has a lower electrostatic potential although higher than the Van der Waals forces of attraction in colloidal solution. O`Melia, (1972) discussed further that it is easier for precipitates to form in solution of high ionic strength than the lower ionic strength solution. In the waste water for this study, it is assumed that the ionic strength of waste water tends towards zero and the data measured at zero ionic strength is used.

$Fe^{3+} + 2H_2O = \alpha\sim Fe(OOH)_{(s)} + 3H^+$ $0.31623 \times 10^{0\,\#}$ [3-8]

$Fe^{3+} + 2H_2O = (am)Fe(OOH)_{(s)} + 3H^+$ $3.1623 \times 10^{-3\#}$ [3-9]

$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+$ $1.0 \times 10^{-4\,*}$ [3-10]

[#] This indicates data from Stumm and Morgan, (1981).

[*] This indicates data from Faust and Aly, (1983).

Ionic strength = 0

Temperature = 25^o

The Figure 3.1 shows a plot of LogC vs. pH for the different ferric hydroxide solid species. This shows the solubility of free ferric ion in solution for the three ferric hydroxide solids shown in equations 8 to 10. The line in the uppermost region represents the ferric hydroxide. From Faust and Aly, (1983) its nature is not as well defined as it is in Stumm and Morgan, (1981). The middle line represents the amorphous ferric hydroxide solid. The lowest line represents the alpha ferric hydroxide solid. Based on discussions of Stumm and Morgan, 1981, the phase with the fastest rate of formation is the amorphous solid hydroxide, while the most stable phase is the alpha ferric hydroxide.

However from the three solid phase lines in Figure 3.2 it may be inferred that at lower pH the solubility of the three solids increases, there is more ferric ion [Fe^{3+}]

in solution at saturation. It should be noted that the solids considered in Figure 3.2 are in equilibrium with other aqueous phase ferric hydroxide species as suggested by Stumm and Morgan, (1981). Hence it does not give adequate information in order to characterise the total solubility of the ferric hydroxide complexes formed in solution and that are at equilibrium with the solid phases.

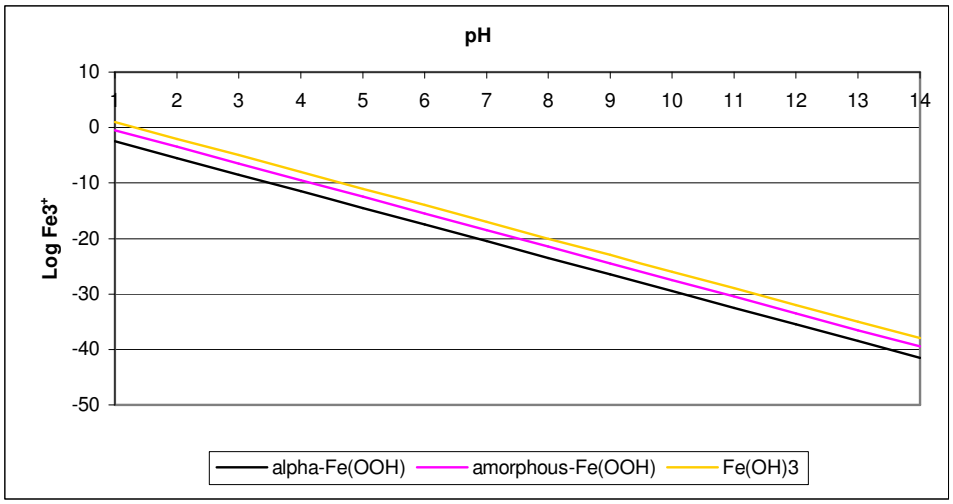


Figure 3.2 Total ferric ion lines for the solid phase

Discussing further it is known from thermodynamics that alpha ferric hydroxide [α~ $Fe(OOH)_{(s)}$] is the most stable phase and will form at lowest Fe^{3+} concentration and as shown in Figure 3.2 the ferric ion line of this solid phase is the lowest. However for some reason if its formation is slow amorphous ferric hydroxide [(am~ $Fe(OOH)_{(s)}$] could occur as shown in Figure 3.2 with the mid line representing the ferric ion formed for the amorphous ferric hydroxide phase. Again at a higher concentration of ferric ion (Fe^{3+}) if for some reason such as kinetics of the formation of amorphous ferric hydroxide being slow or its solubility product is not reached there is formation of ferric hydroxide solid [$Fe(OH)_{3(s)}$] ,which is shown by the upper most line.

The information on solubility at equilibrium in Figure 3.2 is not adequate to describe the solubility of solid hydroxides at equilibrium with all aqueous phase ferric hydroxide ion species. Hence it is essential that we should have a picture

that shows the interactions for all the species in the system, this is in line with Stumm and Morgan's (1981) suggestion.

3.2.4 The total ferric ion in aqueous phase in equilibrium with the solid phase

The Figure 3.3 shows the plot of the total ferric ion concentration in solution for the three solid hydroxide phases at equilibrium as a function of pH. In section 3.2, the ferric species given are: Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_{3(aq)}$, and $Fe(OH)_4^-$. The species listed are present for all the three solid phases.

Different authors propose different suggestions. O`Melia, (1972) suggests that for destabilisation that will lead to the precipitation of the metallic hydroxide to occur there must be an addition of oversaturated ferric chloride coagulant solution. As explained earlier the addition of ferric ion coagulant will lead to the formation of various species of ferric hydroxide species. However there are conflicting claims in the literature and according to Jiang and Graham, (1998), these species formed are the main destabilisation agents of colloids around the neutral pH range because at this pH the Fe^{3+} ion is virtually non-existent, and in contrast to this O`Melia, (1972) suggested that the destabilising species are the polymeric species of ferric ions formed on addition of the Fe^{3+} salts, while some even lay emphasis more on the kinetics of the process.

It might have been proper for some of these authors to be more directional and affirmative in their arguments. However based on the model and analysis of different references, it may be ideal to suggest that the thermodynamic properties of flocculant solution, thermodynamic conditions of waste water medium and kinetics to a lesser extent, are the principal factors determining the extent of the flocculation process. The Figure 3.3 shows the total solubility of ferric ions species in solution as it relates to the formation hydroxide solid for the three solid phases evaluated in equations [3-8] to [3-10].

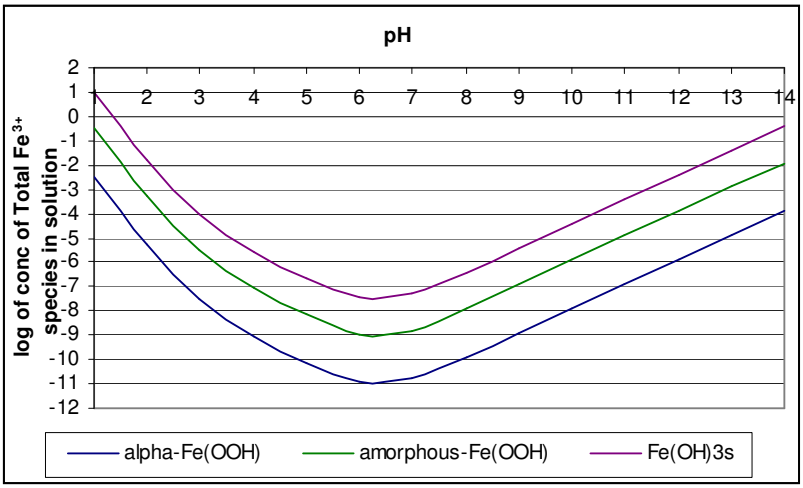


Figure 3.3 Total solubility curve of ferric ion species

In Figure 3.3 the uppermost curve represents the total ferric species in equilibrium with the ferric hydroxide solid [$Fe(OH)_{3(s)}$]. The figure shows that the total ferric species concentration is highest for all the three solid phases and perhaps this phase covers the upper region and perhaps it is be favoured by slow kinetics. The amorphous phase from most literature is the easily formed phase on feed addition and rapid mix. The middle curve represents the total ferric ion species in solution and the region where it can be formed is over the mid regions. The total concentration of soluble ferric species in solution is lower than that of ferric hydroxide. The lowest curve represents the solubility of the total ferric species for the alpha ferric hydroxide. It has the lowest concentration of ferric species in solution; this will be expected because this phase is formed, as a result of aging process of the amorphous ferric hydroxide or other ferric hydroxide solid species. By the time the alpha ferric hydroxide solid is formed it is expected that the bulk of ferric species in solution will have been precipitated out of solution.

The plot in Figure 3.3 gives an indication that the solubility of the total ferric ion species is at minimum at around pH 7 for all the solid phases considered in equations 8 to 10 in section 3.2.3. Hence to reduce the Fe content in recovered water the final pH of wastewater should be at a neutral pH. The nature of the anion may affect the solubility the of hydroxide species in the system, anions such as: chloride, sulphate and carbonate may shift the solubility of the species, by

increasing the pH range, for the precipitation of solid hydroxides to occur. (Kemmer, 1988; Gregory and Duan, 2001). Flynn, (1984) gave more explicit information about how anions affect the nature of solid phase formed for example chloride solution favours the precipitation of akagenite, while low molecular hydrolysis ions favour the production of lepidocrocite. The sulphate medium favours the precipitation of amorphous hydroxide, which on aging changes to alpha or goethite based hydroxide.

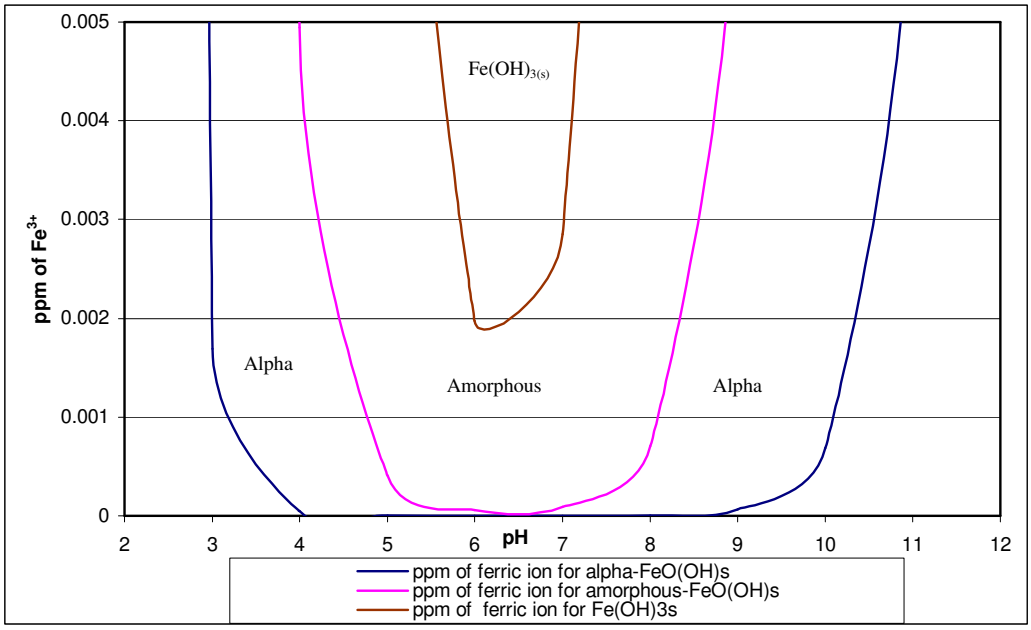


Figure 3.4 The theoretical model for Fe^{3+} content of recovered water

In Figure 3.4 we have replotted Figure 3.3 but changed the y-axis to concentration of Fe in ppm, as this is what is measured using the atomic adsorption column. The minimum concentration of Fe detectable by the atomic adsorption column is 1ppm, this may hinder the interpretation of experimental results slightly. The Fe content in recovered water is predicted using the thermodynamic equilibrium data of the hydrolytic reactions. Figure 3.4 shows the expected Fe content in solution generated using the equilibrium data for each possible solid phase, the phase with the smallest region is the ferric hydroxide [$Fe(OH)_{3(s)}$] between pH of 6 and 7.This means to produce a ferric hydroxide solid the waste water pH should be

between 6 and 7, and the Fe concentration should correspond to the value on the y-axis. The next region is the amorphous ferric hydroxide solid [α~ $Fe(OOH)_{(3s)}$], which is between pH 4.5 and 7.5, for the ferric content to be at the concentration shown the pH of waste water should be within this range. From literature this range is the optimum working range for ferric chloride flocculant. It may also be the main reason why most literature assumes the production of amorphous ferric hydroxide solid but in most cases it is presented as a kinetic based effect. The alpha hydroxide is the last and it is the most stable form. It can be produced between pH 3 and 10 and the corresponding Fe content of water recovered, should correspond to the value shown on y-axis.

A conclusion can be drawn from Figure 3.4 that the Fe content of water recovered is pH sensitive. Therefore it is important to control pH, since the Figure 3.4 shows that solid phase formed is dictated at the working pH of wastewater solution. However based on the thermodynamic analysis of the system, Figure 3.4 shows that the formation of a particular type of ferric hydroxide solid is pH dependent and perhaps different types of solid can be formed in wastewater as the pH regions are crossed. This is in contrast to most literature that are kinetics based and that suggest that the type of solid formed initially was amorphous and after a period of ageing the alpha ferric hydroxide is formed. In chapter 4 an evaluation will be done between using this model to choose the solid phase produced in the experimental process, the results obtained experimentally, and the theory, in order to determine the dominant factor of flocculation process, namely whether it is thermodynamically or kinetically initiated.

3.3 The use of aluminium sulphate as a flocculant

This section discusses the hydrolytic reactions of aluminium sulphate coagulant in water. Emphasis is laid on the hydrolysis of aluminium ion in solution, to form hydroxide species in aqueous and solid phase. The subsequent sections discuss the different equilibrium interactions of the aluminium hydroxide species in detail.

3.3.1 An overview of hydrolytic reactions of Aluminium ion (Al^{3+})

The chemical equilibria for Al^{3+} as given by Faust and Aly, (1983) were considered with their corresponding equilibrium constants (K). The equilibrium constant was calculated at a temperature of 25^0C from log K and an ionic strength of zero. The equilibrium constants given by for Dentel and Gosset, (1988),were originally from Stumm and Morgan (1981), and Baes and Mesmer (1976). Stumm and Morgan's (1981) data were calculated at ionic strength of zero, and a temperature of 25^0C.The data of Graham and Nigel, (1998), was taken from Baes and Mesmer (1976), the data were measured in a 1M KCl at 25 ^{0}C. The next paragraph discusses the problems identified in the data presented in Table 3.2.

The data shown in Table 3.2 are the same for some species, but notably different equilibrium constants are reported, in particular for some aqueous and solid phase equilibrium reactions. An example is the values of K in row 6 columns 4 and 5 (Dentel and Gosset, 1988; Jiang and Graham, 1998), in comparison to other equilibrium constant for this same reaction it was quite large. A suggested reason for these discrepancies could be the different media of measurement for the equilibrium constant or different experimental conditions under which the values were determined.

For reasons explained in section 3.2 for the selection of data for ferric aqueous equilibria the reactions and data presented by Faust and Aly, (1983) and Stumm and Morgan, (1981) will be used for aluminium aqueous equilibria as well. Finally the likelihood of the wastewater medium being of low ionic strength is considered.

Equations from Faust and Aly, (1983)	Faust and Aly (1983)	Stumm and Morgan (1981)	Baes and Mesmer (1976)	Dentel and Gosset (1988)	Jiang and Graham (1998)
	K				
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	1.0E-05	1.0E-05	1.07E-05	1.07E-05	1.07E-05
$Al^{3+} + 2H_2O = Al(OH)_2^+ + H$	5.01E-10	5.01E-10	5.01E-10	5.01E-10	5.36E-10
$Al^{3+} + 3H_2O = Al(OH)_{3(aq)} + 3H^+$	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.07E-15
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	1.0E-23	1.0E-23	1.0E-23	1.995E-22	1.07E-23
$Al^{3+} + 2H_2O = \alpha$-Al(OOH)s $+ 3H^+$	3.16E-9	3.16E-9	3.16E-09		3.1E-09
$Al^{3+} + 2H_2O$ = am- Al(OOH) $+ 3H^+$	3.16E-11	1.59E-11		7.08E-10	3.16E-10
$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$	1.00E-09				

Table 3.2 Comparison of equilibrium data for aluminium hydrolytic reactions

3.3.2 The hydrolytic reactions of Al^{3+} ions in solution

The hydrolytic reactions shown in equations (3-11 – 3-14) are for the hydrolytic reactions of aluminium ion (Al^{3+}) in water. The reactions are reversible and very rapid, the hydroxide species are stable and they easily come to equilibrium with unhydrolysed cations, water and hydrogen ion as suggested by Baes and Mesmer, (1976).

	K (equilibrium)	
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	1.0×10^{-5}	[3-11]
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	5.01×10^{-10}	[3-12]
$Al^{3+} + 3H_2O = Al(OH)_{3(aq)} + 3H^+$	1.0×10^{-15}	[3-13]
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	1.0×10^{-23}	[3-14]

Equations (3-11 - 3-14) is as given in Stumm and Morgan, (1981).

Ionic strength = 0

Temperature = 25^oC

O`Melia, (1972) suggested that the aluminium ions added into water are acidic in nature and that Al^{3+} exist in species form in aqueous media. Crozes et al, (1995)

suggest that they are less soluble in comparison to ferric ion in water. Similar data discrepancies as were noticed for the ferric ion were also identified in the data for aluminium ion. However the choice of data was made because it was measured at 25^0C, zero ionic strength, with no influence of background electrolyte. The equilibrium reactions shown in equations (3-11 – 3-14) are for the monomeric species. Some polymeric species exist such as: $Al_3(OH)_4^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$. Equilibrium reactions are not shown because it is believed that they do not exist at the pH of the wastewater used between 6.5 to 9. It is suggested by Baes and Mesmer, (1976) and Gregory and Duan, (2001) that they occur at very low pH, while Dyer et al, (2001) suggest that they are slow to form. Another reason is that there is a lot of doubt about the participation of the polymeric species in the coagulation and flocculation process, although Baes and Mesmer, (1976) reported the existence of polymeric $Al_{13}O_4(OH)_{24}^{7+}$, at pHs between 3.5 to 4.5. The dominant species in our experimental pH range (viz. between 6.5 and 9) are those considered in Figure 3.5.

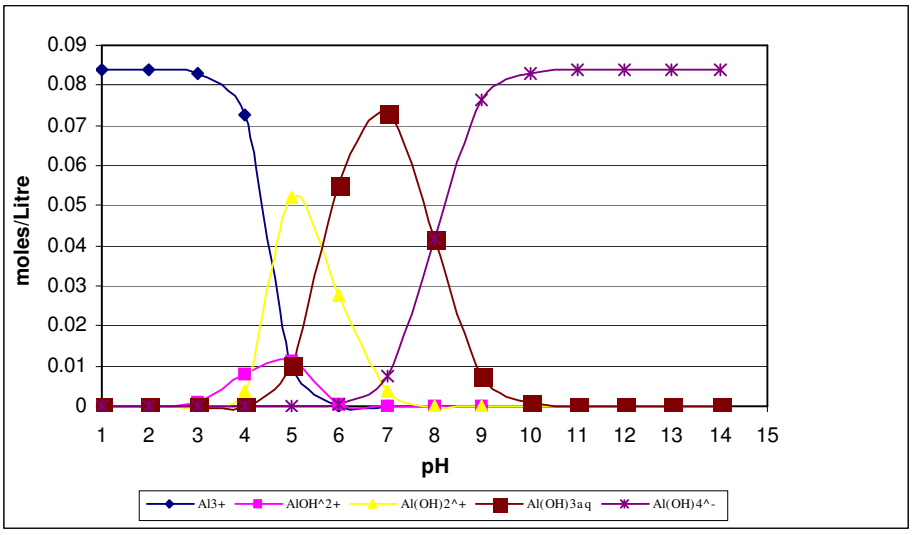


Figure 3.5 Aluminium hydroxide species distribution curve

The species of aluminium hydrolysis reactions in water on addition of 0.084moles/litre concentration of aluminium sulphate flocculant into wastewater are shown as a function of pH in Figure 3.5. The dominant species is the neutral aqueous based $Al(OH)_{3(aq)}$ in the pH ranges of 5.5 to about 8 and this is the zone

where effective coagulation actually takes place, above pH 8 the dominant species is $Al(OH)_4^-$.

The different aluminium hydroxide species occur in relatively narrow pH range of about 5 to 6 pH units in comparison to that of ferric hydroxide species shown in Figure 3.0 that covers about 8 pH units. Gregory and Duan, (2001) propose that this is due to the coordination number for Al decreasing from 6 to 4 as the reaction proceeds from hexahydrate to tetrahydrate alumina. For the ferric ion the coordination number remains at 6 for all the hydrolysed species. As discussed earlier it will be expected that as the concentration of solution is increased the shape of the speciation curve will change with some of the polymeric species becoming more prominent in the picture that will be produced.

3.3.3 The interaction of aluminium species with its hydroxide solids

The purpose of this section is to briefly evaluate if thermodynamics or kinetics is the primary factor initiating the formation of solid aluminium hydroxide solid. Equations 3-15 to 3-17 introduce different possible solid phases that can be formed during equilibrium reactions for aluminium species.

$Al^{3+} + 3H_2O = \alpha\sim Al(OH)_{3(s)} + 3H^+$ 3.163×10^{-9} [3-15]

$Al^{3+} + 3H_2O = (am)Al(OH)_{3(s)} + 3H^+$ 3.1623×10^{-11} [3-16]

$Al^{3+} + 3H_2O = Al(OH)_{3(s)} + 3H^+$ 1.10×10^{-9} [3-17]

Equations (3-15) is as given in Stumm and Morgan, (1981).

Equation (3-16- 3-17) is from Faust and Aly, (1983).

Ionic strength = 0

Temperature = 25^oC

The formation of monomeric species and solid precipitate in a colloidal medium involves different stages. It is proposed by Stumm and O`Melia, (1968) that it involves the hydrolysis of metallic ions, destabilisation of solid-liquid interface, flocculation of destabilised solid particles and an aging process for flocs formed and finally the precipitation of the metal hydroxide formed. However Johnson and Amirtharajah, (1983) proposed that these stages outlined above may be a rate

controlled process under different chemical conditions such as: different concentration of flocculant feed and different nature of waste water medium.

From the earlier discussions in this chapter, the ionic strength and activity coefficient of metallic ions in a medium will affect the equilibrium of a reaction. These factors may increase the equilibrium constant or reduce it depending on the species being measured. The non-ideality of a compound may also dictate the level of activity of a medium thereby affecting the reactions in the medium, hence influencing the precipitation of solid hydroxide in the medium. The illustration shown next gives a brief idea of how the species in the medium would dictate the precipitation of aluminium hydroxide solid in an aqueous medium, this is similar to the representation by Gregory and Duan, (2001).

$$Al^{3+} \leftrightarrow Al(OH)^{2+} \leftrightarrow Al(OH)_2^{+} \leftrightarrow Al(OH)_{3(s)}$$

Gregory and Duan, (2001) explain further that each step involves a deprotonation process, hence the equilibria are shifted to the right as pH increases .The precipitation of aluminium hydroxide solid occurs between pH 5.5 and 7.5 when aluminium hydroxide is used as suggested by Peavy et al, (1985). Gregory and Duan, (2001) propose that this zone of solid precipitation may be widened when the sulphate ions in the medium act as catalyst causing the polymeric species to cause precipitation of hydroxides at low pH.

There are different types of aluminium hydroxide solids that may be precipitated at equilibrium. Baes and Mesmer, (1976) describe them as follows: amorphous aluminium hydroxide [am~$Al(OH)_3$], this is the unstable solid phase produced initially during precipitation of solid. Secondly, the aluminium hydroxide $Al(OH)_3$, namely the solid that is produced at low concentration as described by Faust and Aly, (1983). Finally gibbsite [α~ $Al(OH)_{3(s)}$] , which is the most stable of aluminium hydroxide precipitates and it is produced as result of ageing of other aluminium hydroxide solids as explained by Stumm and Morgan, (1981). The

model that will be developed in later section will help to clarify the thinking about the system of formation of this solid hydroxide precipitate.

3.3.4 The aluminium ion in equilibrium with aluminium hydroxide species

This is determined by the development of a log of Al^{3+}/pH diagram for the solid phase equilibrium reactions of aluminium hydroxide.

$Al^{3+} + 3H_2O = \alpha\sim Al(OH)_{3(s)} + 3H^+$ $3.163 \times 10^{-11\#}$ [3-18]

$Al^{3+} + 3H_2O = (am)Al(OH)_{3(s)} + 3H^+$ $3.1623 \times 10^{-9*}$ [3-19]

$Al^{3+} + 3H_2O = Al(OH)_{3(s)} + 3H^+$ $1.10 \times 10^{-9*}$ [3-20]

[#] This indicates data from Stumm and Morgan, (1981).

[*] This indicates data from Faust and Aly, (1983).

Ionic strength = 0

Temperature = 25°C

The Figure 3.6 shows a plot of log of concentration of Al^{3+} vs. pH for the different aluminium hydroxide solid species. The uppermost line gives the solubility of aluminium ion for the amorphous aluminium hydroxide species. The middle line shows the solubility of aluminium ions when the solid phase aluminium hydroxide is produced, finally the third line is the representation of aluminium ion solubility when gibbsite, the alpha aluminium hydroxide is the solid precipitate. An important point about Figure 3.6 is that it does not give adequate information of the other aqueous based species in equilibrium with the solid hydroxide phases.

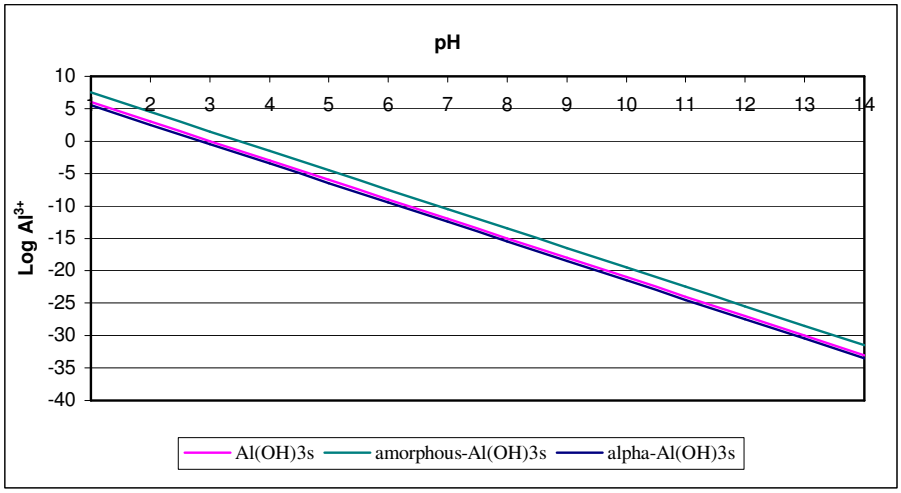


Figure 3.6 Total aluminium ion line for the aluminium hydroxide solid phase

The Figure 3.6 shows that as the pH decreases the solubility of the three solid phases increases and the aluminium ion content is highest at saturation. On consideration of thermodynamics, alpha aluminium hydroxide solid is the most stable phase and at low concentrations it forms at the lowest aluminium ion (Al^{3+}) concentration. However if formation is slow aluminium hydroxide solid may be formed in the regions between the alpha and hydroxide lines as shown in Figure 3.6; it can only be formed over a very narrow region as the equilibrium lines almost coincide for these two phases. The amorphous phase line shows that at high concentration the amorphous phase is the most likely to be formed and also with the highest concentration of aluminium remaining in solution.

While Figure 3.6 shows when solid phase and aqueous phase are in equilibrium with one another, it does not give adequate information on the solubility of other aqueous hydroxide species in equilibrium with these solid phases. Therefore it is necessary to give a picture that provides adequate information on the aqueous species, this is shown in Figure 3.7 in the next section.

3.3.5. The total aluminium ion in aqueous phase in equilibrium with the solid phase

Figure 3.7 shows the plot of the total aluminium ion concentration in solution for the three solid hydroxide phases at equilibrium. In section 3.3, the aluminium species given are: Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$,$Al(OH)_{3(aq)}$,and $Al(OH)_4^{-}$. These species are present for the equilibrium reactions for all the three solids.

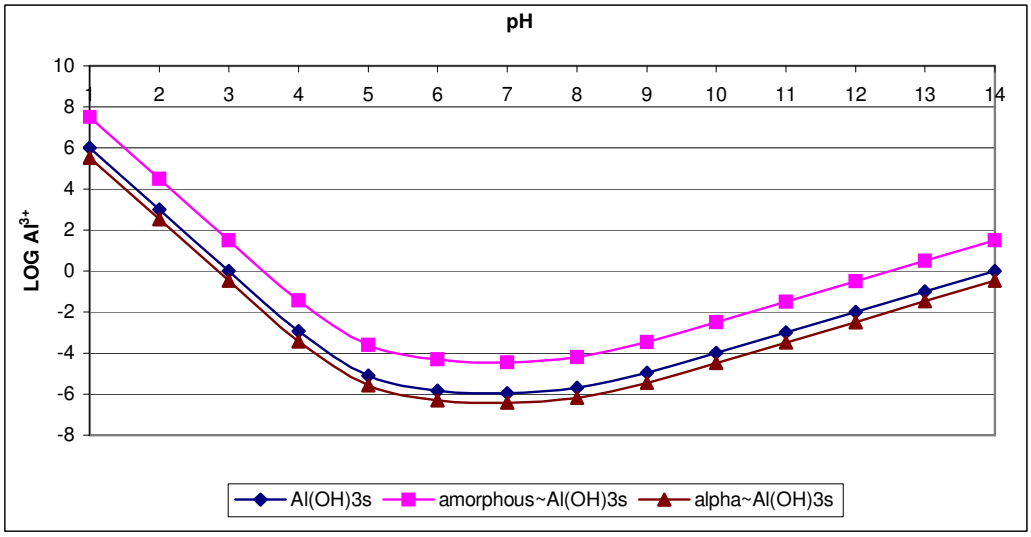


Figure 3.7 Total solubility curve for aluminium ion species

The three curves in Figure 3.7 show the total solubility of the aluminium hydroxide species, the point of minimum solubility is between pH 6 and pH 7,this implies that to recover water with the lowest concentration of aluminium ions the pH range for flocculation of waste water should be kept between 6 and 7. From the literature, the most likely solid to be produced is the amorphous hydroxide solid, but in Figure 3.7 the uppermost curve represents the total aluminium ion species solubility for amorphous aluminium hydroxide phase. It is seen to have the highest concentration of aluminium ion in solution when formed. The middle line shows that aluminium hydroxide is formed in the intermediate concentration range and the aluminium ion content of water recovered will not be as high as that of amorphous. The last curve is the thermodynamically most stable solid, its

concentration of aluminium ion in recovered water is the lowest. Many authors describe it as the final phase formed due to a gradual ageing process of the amorphous phase formed initially (Stumm and Morgan, 1981; Baes and Mesmmer, 1976)

There are possibilities of producing other types of aluminium hydroxide solids. These are dependent on the nature of the initial solution of aluminium compound used (Baes and Mesmmer, 1976). Anions have a profound effect on the solubility of aluminium species and nature of solid hydroxide formed, anions such as: sulphate, fluoride and phosphate are known to shift the solubility of aluminium species. According to Gregory and Duan,(2001) and De Hek et al,(1978) sulphate increases the zone of precipitation of aluminium hydroxide solids. While Reiber et al, (1995) suggest that fluoride ions compete with hydroxo complexes to bind to available spaces on metal ions and Jiang and Graham, (1998) state that phosphate ions increase the rate of hydrolysis of aluminium hydroxide species.

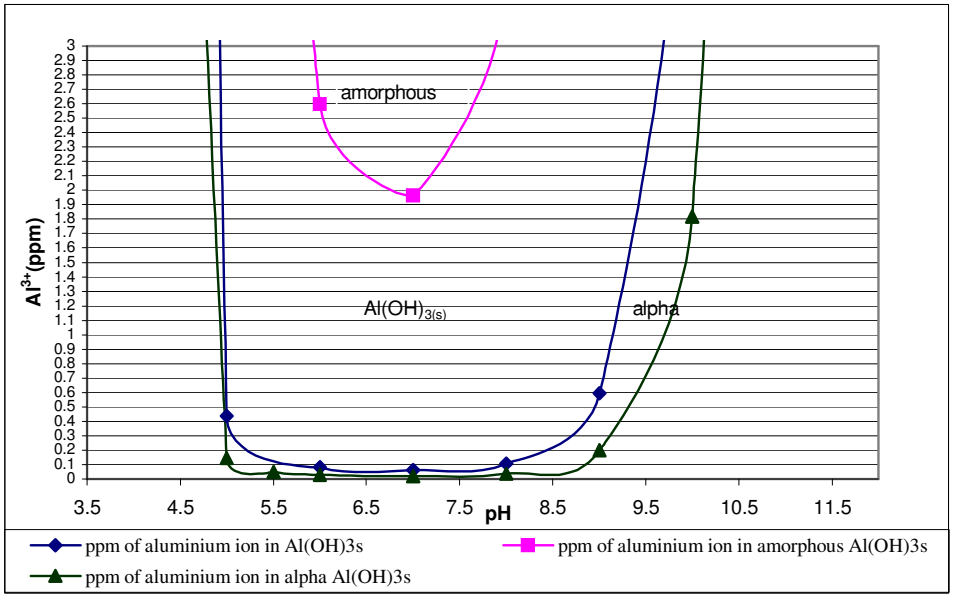


Figure 3.8. Theoretical model for aluminium content of recovered water

In Figure 3.8 we have replotted Figure 3.7 but changed the y-axis to concentration of Al^{3+} in ppm as this is what is measured using atomic adsorption spectroscopy.

The minimum concentration that can be measured using the atomic adsorption spectroscopy is 0.03ppm of Al^{3+} ion in water recovered. The aluminium content of water recovered is determined theoretically using the thermodynamic equilibrium data for the hydrolytic reactions. Figure 3.8 shows the expected aluminium content in solution. The solid phase in equilibrium with the highest concentration of aluminium species in solution is the amorphous hydroxide. Therefore in order to produce an amorphous based solid hydroxide the working range of the waste water should be between pH 6 and 7.5, this a very narrow range hence pH of waste water may need to be controlled. The aluminium hydroxide solid is the next region it covers a wide pH range from pH 5 to about pH 9, while the most stable phase, the alpha hydroxide solid (gibbsite), is stable over the biggest range between pH 5 and 10. The aluminium hydroxide and the alpha hydroxide phases overlap with one another so it may be difficult to differentiate which of the phases is produced. However an important point is that the concentration of aluminium ions in water recovered is lowest for these two solids, in comparison to that of amorphous solid hydroxide.

The aluminium ion is highly sensitive to changes in pH. The amorphous phase only forms in a narrow region at neutral pH . Since this is the region were solid hydroxide is formed the waste water pH should be maintained in this zone so as to achieve optimum flocculation. The sensitivity of the aluminium ions to pH is more pronounced at pH's less than 5 and above 8.5.This may be the reason why the precipitation of solids is not favourable at pH's lower than 5 and higher than 7.5. From literature the optimum performance of aluminium sulphate flocculant is between pH 5.5 and 7.5 (Peavy et al.1985).

3.4. Concluding remarks

The theoretical models developed for the ferric and aluminium ion will help develop a better understanding of the coagulation and flocculation process. The theoretical model for the solid phase will be used in the next chapter to evaluate the experimental results. This will help to identify the region of coagulation and flocculation where thermodynamics and kinetics are important respectively.

CHAPTER 4

Experimental Results and Discussions

4.1. Introduction

The results of flocculation experiments using ferric chloride and aluminium sulphate are evaluated using the measured properties of the recovered water such as the pH, turbidity and metal concentration. The results are presented and discussed in this chapter; the tables of experimental results are given in Appendix C. In particular we wish to compare the thermodynamic predictions from chapter 3 with experimental results.

As an aid to understanding this chapter some terminology and conventions are introduced below.

Bulk concentration: The concentration of inorganic flocculant added in the waste water medium. It is different for each jar in the same set of experiment.

Feed concentration: The initial concentration of inorganic flocculant before addition into wastewater medium.

Graphs – Same colour and symbol set refers to a single set of experiments where bulk concentration of flocculant changes.

The symbol O represent good flocculation, turbidity < 100FTU,while

● represent poor flocculation, turbidity > 100FTU (this could be of any colour)

The error bar is used to indicate percentage error at 5% for experimental points to plotted value in Figure 4.1 and Figure 4.3.

4.2. Ferric chloride coagulation and flocculation experiments.

4.2.1. Turbidity of recovered water - a measure of coagulation efficiency

It is sometimes difficult to decide when flocculation occurs or compare flocculation efficiency. Initially visual inspection was used to decide on flocculation efficiency however this gives no basis for comparison of various experiments that at least by visual inspection seemed efficient. A comparison of the turbidity of various samples that visually seemed to be similar gave very different turbidity readings. Thus a more quantitative measurement was required to determine the onset of flocculation. It was decided that a turbidity measurement of 100FTU or less corresponds to successful flocculation, since the turbidity measurement is less than 100FTU based on our experimental results for the recovered water from the preliminary tests that yielded good flocculation. Figure 4.1 shows the results of turbidity measured when various amounts of a ferric chloride feed of 0.043mol/L is added to wastewater.

Note that it was later observed that samples that are clear by visual inspection have turbidity of 500FTU or less. This has been indicated as the zone of visual clarity on Figure 4.1.

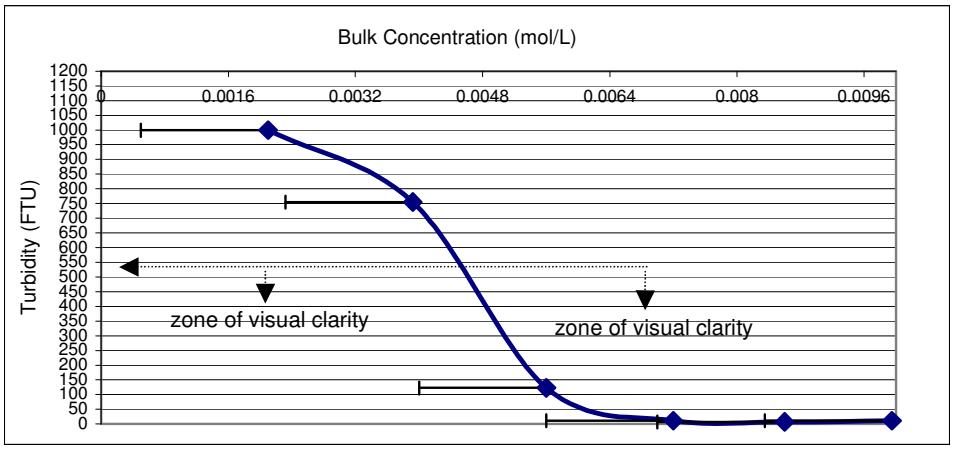


Figure 4.1 Zone of effective turbidity when varying quantities of 0.043mol/L ferric chloride are added to wastewater

Figure 4.1 above shows the plot of turbidity measured when various amounts of ferric chloride flocculant at a concentration of 0.043mol/L are added to

wastewater. A table of the results is given in Appendix C. The turbidity instrument does not measure turbidity above 1000FTU. Thus the reading that is above 1000FTU is indicated in Figure 4.1 as an approximate reading of 1000FTU.

From Figure 4.1 the tests for which the bulk concentrations were 0.002mol/L and 0.004mol/L have high turbidity readings that are between 750FTU and 1000 FTU. From the results of the experiment most of the recovered water samples at these low bulk concentrations are not of good clarity on visual inspection.

Beyond the bulk concentration of 0.004mol/L, there was a sharp drop in the turbidity curve to low values below 100FTU. The bulk concentration where the turbidity was around 100FTU was 0.006mol/L bulk.

Increasing amounts of flocculant solution did not further reduce the turbidity noticeably. At bulk concentrations from 0.008mol/L to 0.01mol/L the turbidity becomes constant. This occurs at these bulk concentrations due to adequate ferric chloride coagulant dosages to effect nucleation and the growth of flocs resulting in settling after the retention period. The lowest turbidity measurement was 6 FTU. It can be concluded that once there is sufficient ferric chloride for flocculation to occur, further increases in ferric chloride dosage lower the turbidity only marginally.

In conclusion we can suggest that visual clarity of water does not necessarily correspond to water of low turbidity as shown in Figure 4.1. Hence based on this, we defined successful flocculation as the points where turbidity of water recovered was lower than 100FTU. It should be noted that the turbidity measurements are carried out about 10 hours after the jar test experiments are stopped. It should also be mentioned that the flocculation process is termed good flocculation when the formation of sludge becomes more distinct and sludge is well formed. In regions where bulk concentrations are low, namely at about 0.002mol/L it may be difficult to have a well-formed sludge which can be

separated from the recovered water. These are thus also samples where the turbidity of the water recovered is very high.

4.2.2 Comparing thermodynamic predictions with experimental results.

From the results presented in Figure 4.1, it is expected that flocculation will depend on the quantity of flocculant added to the wastewater and not the initial concentration of the flocculant. Moreover since flocculation depends on the formation of amorphous ferric hydroxide (am~$Fe(OH)_3$), thermodynamics predicts, as shown on Figure 4.2 that flocculation will not occur either at very low or very high pH`s.

In this section an investigation of each of these predictions and a comparison of experimental results with thermodynamic predictions is discussed.

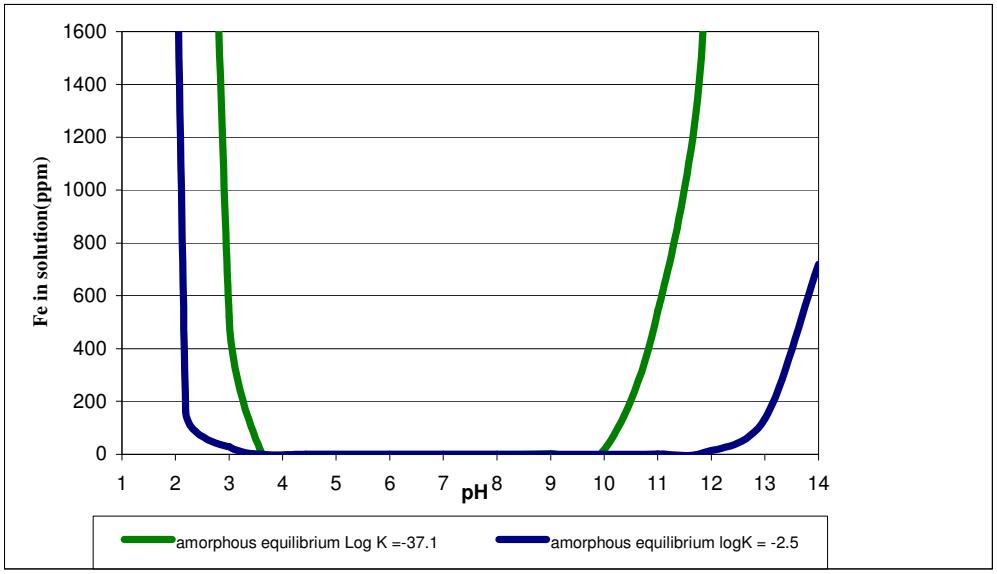


Figure 4.2 The plot of amorphous solid phase equilibrium constant

The active solid phase for which the equilibrium is considered to be relevant to flocculation is the amorphous phase. This phase is metastable and there is some

difficulty in measuring its equilibrium constant accurately because the solid phase undergoes rearrangement to form alpha ferric hydroxide (α~$Fe(OH)_3$) over time. From the literature, the amorphous phase is formed quickly. This corresponds to the period of measured parameters in our experiment (Flynn, 1983; Stumm and Morgan, 1981). For amorphous ferric hydroxide the log K reported in the literature varies between –37.1 (Flynn, 1983) and –2.5 (Faust and Aly, 1983). The log K value of –37.1 was chosen because the conditions of measurement were similar to that of our experiments as it was determined about 48 hours after solid hydroxide formation.

Figure 4.2 suggests, as discussed in Chapter 3, that flocculation depends on the bulk concentration and not on the initial feed concentration. To test the repeatability of the experimental technique, the same quantity of 0.043mol/L ferric chloride were added to 3 different wastewater samples. The results are shown in Figure 4.3. Although the initial pH`s of the samples varied slightly, all three samples flocculated efficiently at roughly the same bulk concentration. Thus we can deduce that experimental repeatability is high.

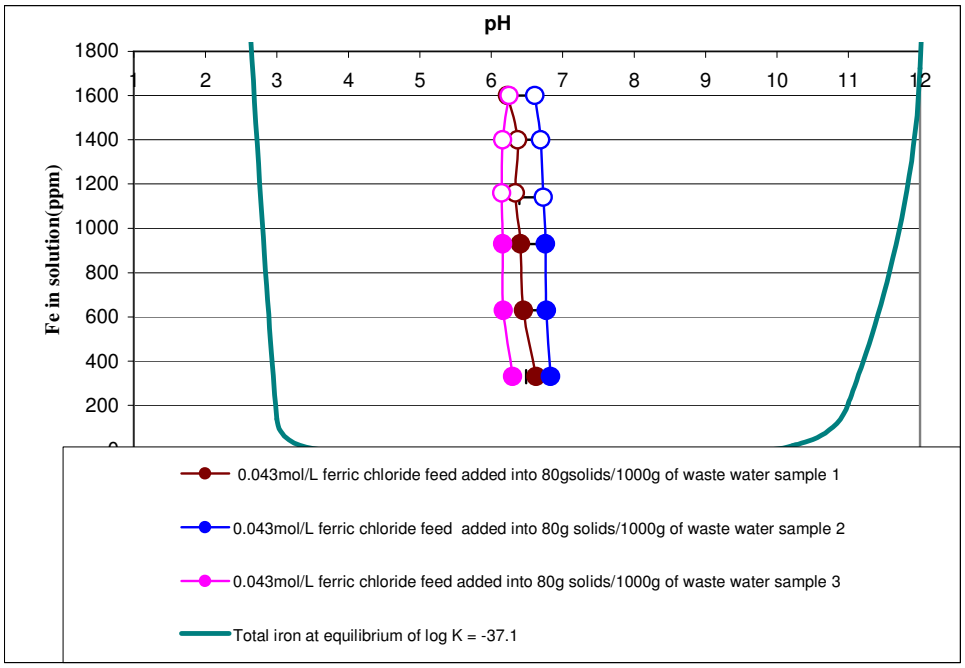


Figure 4.3 The effect of bulk concentration on flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Repeatability of results

In spite of all points lying within the region where amorphous ferric hydroxide (am~$Fe(OH)_3$) precipitates not all tests exhibited successful flocculation.

An important result is that although there appears to be a well defined boundary demarcating efficient flocculation from no or poor flocculation the boundary does not coincide with that predicted by thermodynamics. The experimental boundary occurs at a much higher concentration of ferric chloride than predicted by thermodynamics, as can be seen in Figure 4.3. A major reason for the difference is the difference in equilibrium conditions of the theoretical value and that of the experiment. Another point is that the properties of the medium in which the equilibrium conditions of the theoretical value were measured is different from that of the experiment. The medium for the experiment was paint wastewater. In conclusion, the bulk concentration for the ferric chloride necessary for flocculation to occur in the experiments is higher than that predicted by the model.

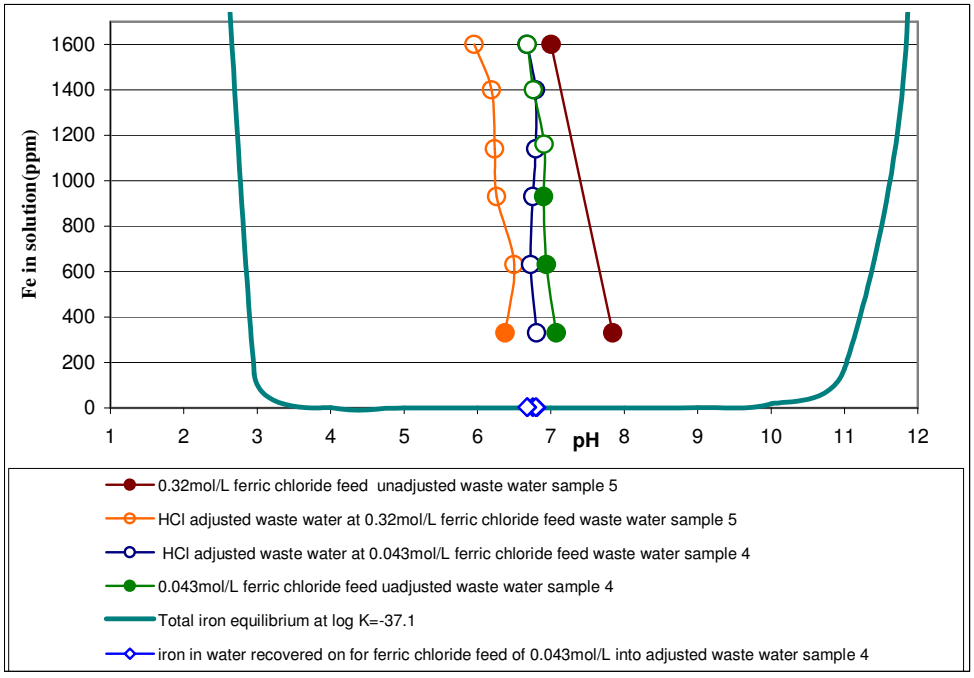


Figure 4.4 The effect of pH on flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Effect of pH on flocculation:

According to thermodynamics, because of the U-shape of the curve, flocculation occurs only within a particular pH range: namely 4 to 10. Outside this range flocculation will not occur. Peavy et al, (1985) suggest that the ferric chloride flocculant is most effective between 5.5 and 7.5. This raises the question of whether there are optimal pH`s for achieving flocculation within the pH 4 – 10 region where flocculation can occur. This was tested by flocculating two different wastewater samples. For each of these we did flocculation tests at the original pH and at an adjusted pH. The results are shown in Figure 4.4 for unadjusted and HCl adjusted wastewater when 0.043mol/L and 0.32mol/L ferric chloride solution is dosed into wastewater. The pH adjusted wastewater is adjusted using about 50mL of a 3 M HCl acid solution.

The results show that for unadjusted waste water (i.e. higher pH), at a feed concentration of 0.043mol/L, the onset of good flocculation occurs from a bulk concentration of 1150ppm. In comparison, when HCl is used to adjust the pH of the initial wastewater sample, all samples tested flocculated. This clearly shows that lowering the pH of wastewater samples increases the efficiency of flocculant added.

Since the entire points lie within the region in which precipitation is predicted by thermodynamics, flocculation is much more sensitive to pH than expected from thermodynamics. Thermodynamics does predict that flocculation is pH dependent at much lower pHs and much higher, namely pH of less than 3 and greater than 11. Furthermore we can see that the efficiency of flocculation is very sensitive to pH and as seen from the experimental results even relatively small changes in pH can have a large effect.

Figure 4.4 also shows the results of experiments for a ferric chloride feed concentration of 0.32mol/L when wastewater is adjusted using HCL and when unadjusted wastewater is used. The points for unadjusted wastewater lie on the right hand side of the chart. Good flocculation was not observed for any of these points, while for the HCl adjusted wastewater the onset of good flocculation occurs at a bulk concentration of 600ppm ferric chloride.

In conclusion, a comparison can be drawn for the different experiments. It shows that a better flocculation result is achievable by adjusting the pH to lower values, into a range of about 5.5 to 6.

However, according to Stumm and Morgan, 1981, it is advisable to adjust wastewater to a pH such that the carboxylic compounds and chains in wastewater are not broken and phenols are not easily formed. Thus care should be taken in dropping the pH of the wastewater as the formation of phenols occurs at a pH of about 5.5.

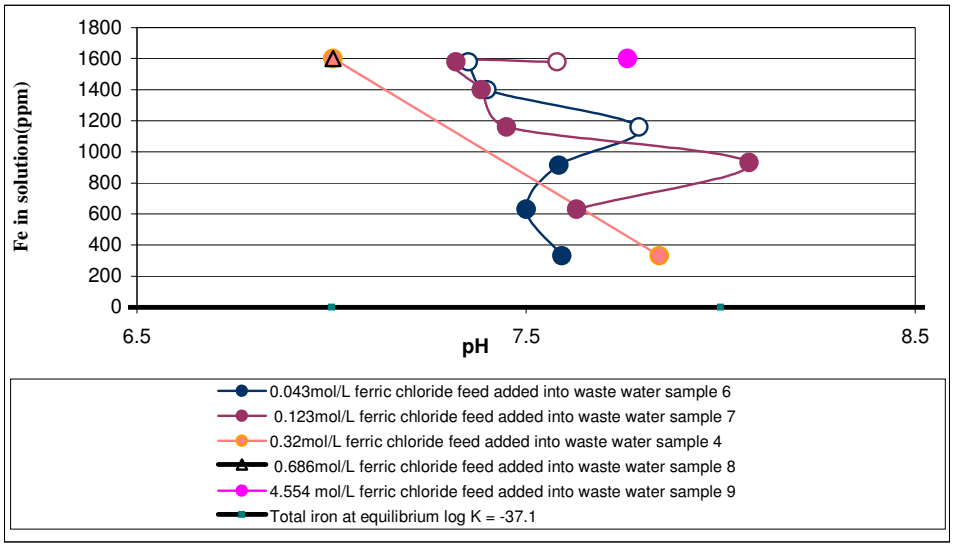


Figure 4.5 the effect of different feed concentration

O, △ = Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Effect of feed concentration of ferric chloride on flocculation

According to thermodynamics the important factor in precipitation formation is the bulk ferric chloride concentration. This prediction was tested by using different ferric chloride feed concentrations and adding specific amounts of these solutions to attain the same bulk concentration. The results of these experiments are shown on Figure 4.5. The experiments were carried out at ferric chloride feed concentration of 0.123, 0.32, 0.686 and 4.55mol/L (the bulk concentrations of ferric chloride in wastewater were the same as in the experiments with feed concentration of 0.043mol/L ferric chloride flocculant). The results for the higher concentration feeds were not as favourable as that of 0.043mol/L feed ferric chloride concentration. Furthermore the higher feed concentrations all gave similar results.

At low concentrations where flocculation does not occur for example for the 0.043mol/L feed it is proposed, nucleation occurs at the expense of growth resulting in a very fine precipitate that is too fine to settle in a reasonable time. This adds solid particles to the colloidal suspension and results in recovered water that is milky. At high feed concentrations, nucleation and growth occur very fast not allowing time for the paint solids and the precipitate to interact, resulting in large precipitate particles that form a coarse sludge, and are unable to remove the stable colloidal suspension, resulting in unflocculated paint material remaining behind in the recovered water

In Figure 4.5 it was found that at the lowest concentration of ferric chloride tested, namely 0.043mol/L ferric chloride, the wastewater flocculates above a bulk concentration of 1160ppm. However at higher concentrations, flocculation only occurred at 1600ppm ferric chloride bulk concentration (0.123mol/L) or not at all (0.32mol/L, 0.686mol/L, 4.554mol/L). Although the thermodynamics predicts that the formation of the precipitate, is independent of feed concentration, flocculation is dependent not only on the amount of ferric chloride added but also the initial concentration.

It was observed that on dosing high concentrations of flocculant into wastewater very fast nucleation occurs, which leads to the formation of lumpy flocs that float on the recovered water. Moreover, despite agitation at very high speeds, even dispersion of the flocculant into the wastewater could not be achieved and so the recovered water was not clear and good flocculation did not occur. From this we conclude that optimising the mixing process is essential in order to achieve good flocculation when flocculating at very high concentration.

The most dilute concentration of ferric chloride feed gave favourable results. We postulate that at this concentration nucleation and gradual floc growth in the wastewater is favoured. In comparison to the more concentrated ferric chloride flocculants the onset of good flocculation occurred from 1160ppm. This result was verified for different 80g solids/1000g of wastewater samples. In contrast, at high concentrations of ferric chloride feed, mixing is postulated to be slow relative to the addition rate of ferric chloride.

In summary, the addition of more concentrated ferric chloride flocculant does not produce very good flocculation results at the same bulk concentration of ferric chloride in wastewater. This does not follow what has been predicted by thermodynamics. In the next section we will discuss how kinetics limits thermodynamic predictions for ferric chloride feeds of different concentrations.

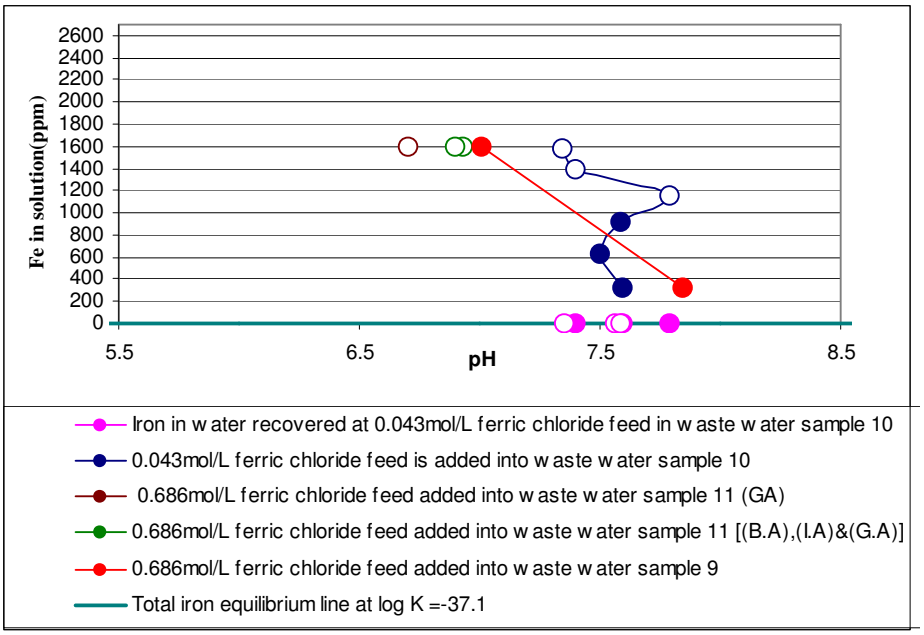


Figure 4.6.The effect of mixing and dosing techniques on flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

[G.A] Gradual Addition

[B.A] Baffled Vessel

[I. A] Inserted Agitator (Subsurface addition)

Effect of mixing on flocculation efficiency

Thermodynamics does not predict the importance of mixing but from experimental results, the rate and type of mixing was found to be important. Thus flocculation is determined not only by thermodynamics but also by kinetics. Therefore it was postulated that the mixing and addition technique is very important in order to obtain good flocculation results. The effect of gradual addition for the initial rapid mix period of flocculant was studied using highly concentrated flocculant. The feed concentration of flocculant used was 0.686mol/L ferric chloride. It was initially dosed by decanting feed ferric chloride at once into the wastewater, this experiment is represented on Figure 4.6 by the red line. It was visually noted that poor flocculation occurred with some particles

floating in the milky water recovered. The solid that floats on the wastewater was found by analysis to contain undispersed ferric chloride flocculant. It was postulated that with the rapid addition of concentrated ferric chloride solution, a localized high concentration of iron (Fe^{3+}) occurred in the wastewater. This caused the iron to precipitate out rapidly as localised pockets were super saturated at the pHs of the waste water. Hence the ferric chloride was not available for flocculation of the colloidal particles in the wastewater and so flocculation efficiency was low.

To test this hypothesis the concentrated ferric chloride feed solution was slowly added. It was fed in at a feed flow rate of 1.2mL per minute. Although some tiny particles were later observed to be floating on the water after flocculent addition, after 2 hours the particles started to settle and after 24 hours the particles had settled out completely (including the tiny particles that floated initially). The water recovered turned brown and the pH of water dropped to about 5.8 from 6.7. The changing of the colour of water recovered after 24 hours may be as result of the ferric chloride content of the particles floating on the water and possibly the reduction of ferric ions into the ferrous ion oxidation state. This will lead to an increase in the hydrogen ion content of water hence a pH shift as observed.

In the next experiment ferric chloride solution was added gradually into a baffled agitated vessel. This gave very good flocculation with no particles floating on the water recovered. The larger the vessel the more favourable the results of flocculation: a 1L test gave better results than a 250mL test because of larger operating volume of vessel which gives room for improved mixing, this is discussed in Appendix C in Table C25.3.

Good flocculation resulted when gradual dosing was used because the slow addition of flocculant allowed good mixing and an even dispersion of flocculant solution into the wastewater, and thus gradual growth of flocs in the wastewater.

Lastly, for the 0.043mol/L ferric chloride feed, the method of addition was quick addition of flocculant solution into wastewater. It was observed that good flocculation results are obtained with this technique at this concentration, the onset of good flocculation is from a bulk concentration of 1160ppm and above. At bulk concentrations where flocculation was favourable this was due to the gradual growth of flocs at these concentrations, the areas where flocculation was unfavourable indicates that only nucleation occurs. The points that lie directly on the x axis show the points for the quantity of iron measured in the recovered water namely 2ppm or less.

As before the equilibrium line shown is that for the precipitation of amorphous ferric hydroxide. It can be seen from the graph that this line accommodates all the experimental points of the flocculation process. In conclusion it can be assumed that regions beyond the line are areas where flocculation will not take place effectively, while for regions inside the equilibrium curve flocculation is governed by kinetic factors such as mixing rate, concentration of flocculant added, design of vessels and impeller type.

It was shown that efficient mixing is critical for reproducible good flocculation results, we will next compare results from standard jar tests with mechanical stirring and data from the literature, bench scale tests with a beaker and cylinder tests using a hand stirred mixing process.

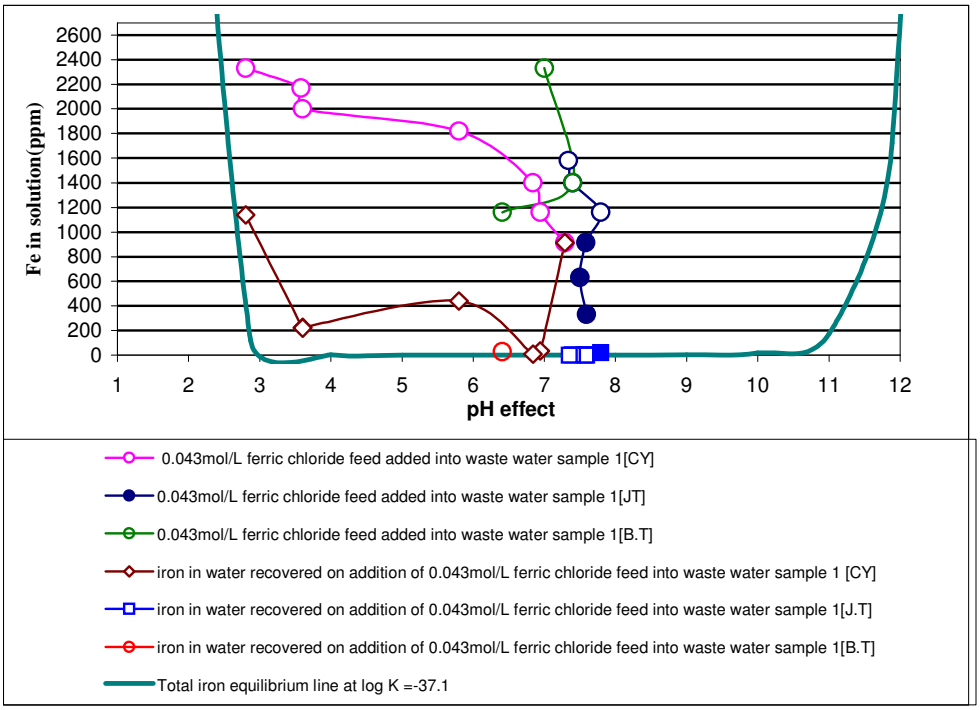


Figure 4.7 Mixing as a factor in the choice of experimental process

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

[J.T] This shows that the method of flocculation was jar test experimental process

[C.Y] This indicates that the method of flocculation was cylinder test experimental process.

[B.T] This indicates that the method of flocculation was beaker test experimental process.

Comparison of results from effect of mixing and different experimental apparatus

The previous results suggest that mixing is important. The three different experimental methods with different mixing efficiencies were considered to determine the choice of process and effect of mixing, namely: jar test, cylinder test and beaker test. The results obtained in the three different apparati were used as criteria to confirm the conclusion about mixing. For the beaker and the cylinder method the flocculant feed concentration of 0.043mol/L is added into wastewater

at different bulk concentrations mixed for about one minute and then left to settle for 12 hours. The jar test is mixed at different speeds as described in Chapter 2. Comparing the results obtained effective flocculation is achieved for the jar test at a higher bulk concentration (1160ppm) but the measured quantity of Fe in recovered water is very much lower, namely between 1ppm to 2ppm. As shown in Figure 4.7 the results of Fe content in water recovered for cylinder and beaker tests were quite high at above 20ppm although this could not be shown properly for beaker test because of the scale of the chart. The high content of Fe could be due to poor mixing technique used.

In conclusion, it was seen that for the same bulk concentration of ferric in waste water for cylinder and beaker tests, the Fe^{3+} in water recovered is always higher than that of the corresponding bulk concentration for the jar test experiment. This gives us insight into how ineffective mixing may affect flocculation. This is especially important to bear in mind when designing an operating plant.

The effect of solid content

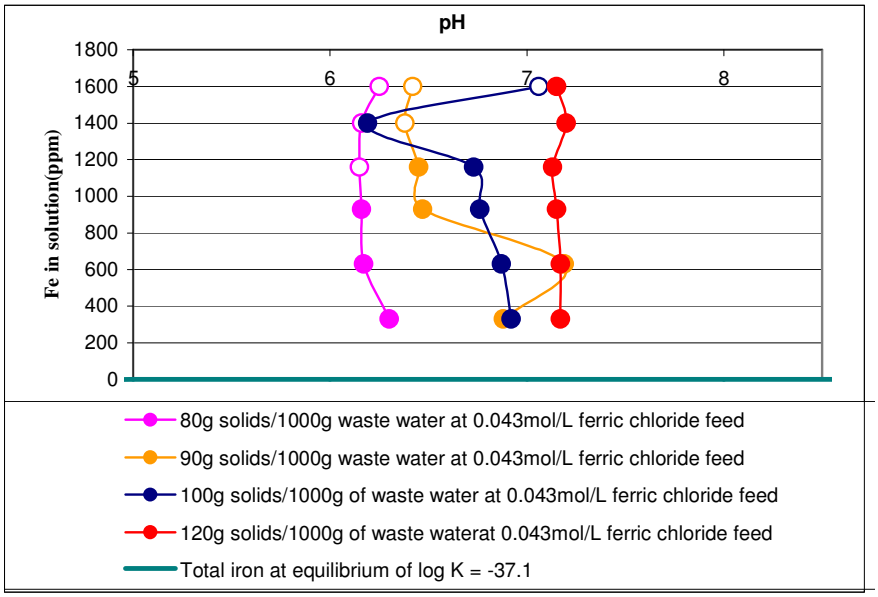


Figure 4.8 The effect of solid content on flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Thermodynamics predicts that flocculation will not be affected by the solid content of the wastewater. Experiments shown in Figure 4.8, were carried out to investigate the effect of solid content on flocculation. The graph shows the bulk concentration of ferric chloride flocculant added to waste water samples as a function of the pH of water recovered. The experiments were all carried out at a ferric chloride feed of 0.043mol/L. This feed concentration of ferric chloride was chosen because it gives the most repeatable flocculation results of the different feed concentration experiments. The legend indicates the solid content at which each experiment is carried out.

For 80g of solids in 1000g of waste water, the onset of good flocculation occurs from a bulk concentration of 1160ppm of ferric ion in wastewater, while the pH of water recovered was about pH 6,2. At 90g of solids in 1000g of wastewater the onset of good flocculation occurs at a bulk ferric ion concentration of 1400ppm For 100g of solids in 1000g of wastewater, the onset of good flocculation was also at a 1400ppm bulk concentration of ferric ion in wastewater. At 120g of solids in 1000g of waste water, no good flocculation were found.

From these results we may conclude that the solid content of the water may be an important variable to consider for use in the wastewater treatment program. It is found that as the solid content of wastewater samples increases, good flocculation occurs at higher concentrations of ferric chloride. It is postulated that nucleation occurs preferentially to growth of solid particles as the solid concentration increases. Thus more flocculant solution is required to be added to the wastewater in order to achieve both growth and the formation of flocs in water.

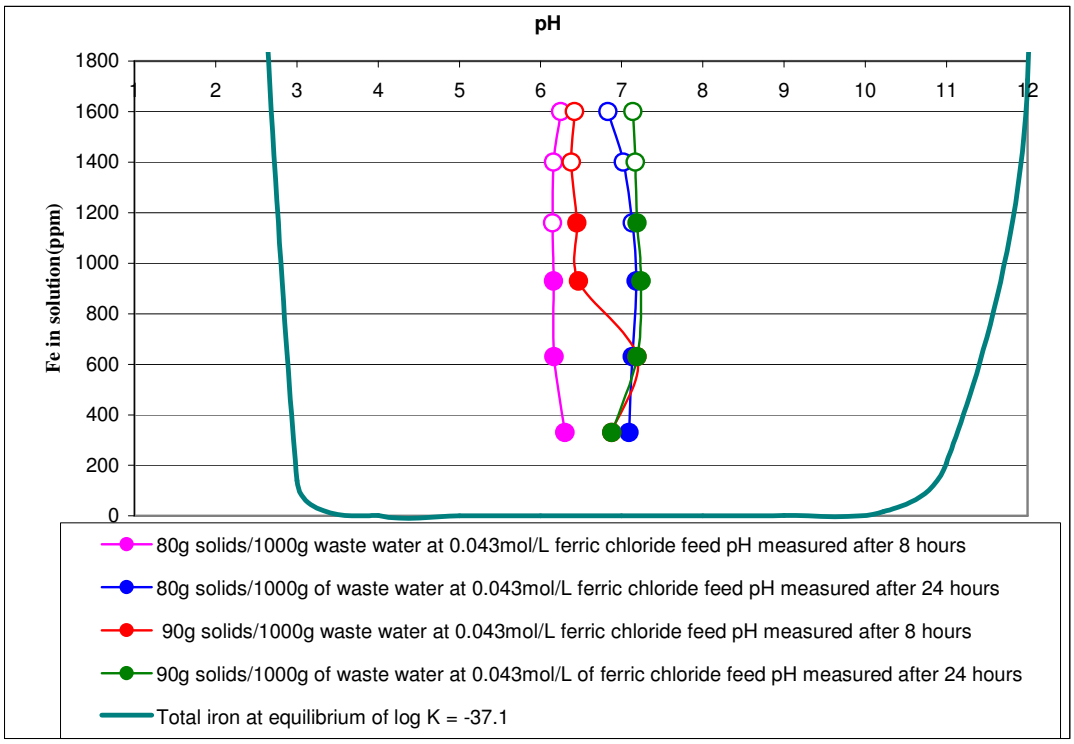


Figure 4.9 The effect of time on water recovered during flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Effect of time on pH of recovered water

Figure 4.9 shows the effect of time on the measured pH of water recovered as a function of bulk concentration of ferric chloride in wastewater. pH was measured after 8 hours and after 24 hours. It was found that the pH of the water increases with time. It is postulated that during flocculation, certain components, which play a role in the buffering equilibrium, are removed with the ferric chloride precipitate. Once this has happened the buffer re-establishes the equilibrium by reacting to consume H^+ or release OH^- and raise the pH back to the initial value. It can be seen that there are processes occurring at very different time scales. There is firstly a very fast nucleation process occurring, growth of flocs happens at a slightly longer time scale while the establishment of the aqueous equilibrium happens at a time scale of hours or days.

4.2.3. Measured Redox potential of recovered water

An interesting phenomenon was observed during flocculation. The redox potential of the waste water changed during the process. Thermodynamics predicts that flocculation occurs because of solubility conditions being exceeded. No electron transfer occurs and hence from thermodynamics no change in redox potential would be expected. However as mentioned, a change in redox potential was measured. This indicates that a reaction with an electron transfer or change in oxidation state is occurring. The extent of this reaction does not need to be large for the change in redox potential to be noticeable

Variation in redox potential during flocculation process.

Figure 4.10 shows the results of measured potential of recovered water as a function of initial pH of recovered water. It is found that there is a linear relationship between pH and redox potential. The measured potential in the experiment could be as a result of one of the following two process namely: the reduction of ferric ions to ferrous ions in the presence of organic compounds such as carboxylic acids, phenols and vinyl compounds or it may be due to hydrolysis that could lead to a release of hydrogen ions in the water recovered. From theory it is expected that as the hydrogen ion increases the potential measured also increases, while as the hydroxyl ion increases there would be a drop in measured potential value.

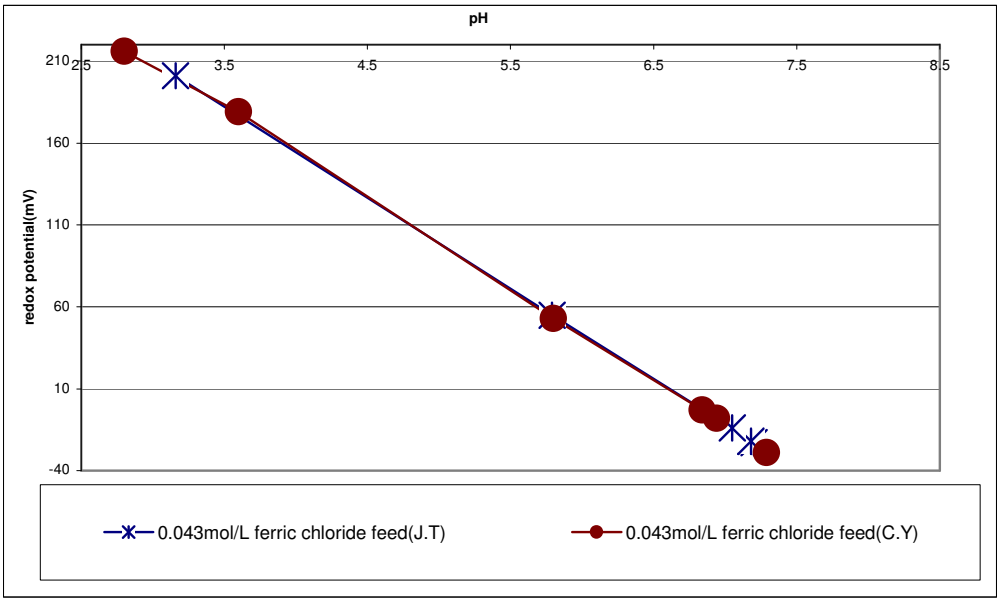


Figure 4.10 Measured redox potential

[J.T] This shows that the method of flocculation was jar test experimental process

[C.Y] This indicates that the method of flocculation was cylinder test experimental process.

The linear relationship shown in Figure 4.10 holds for almost all of the samples tested. The slope of the lines was found to be same for all wastewater samples but the batch of wastewater, i.e. batch of paint caused the line to move up or down as shown in Figure 4.11. From analysis of the process of production, it is suggested that it may be due to differences in the constituents of the paint from one batch to another.

The plots show an increase in pH and redox potential as the bulk concentration of ferric chloride in the wastewater increases. This is most likely due to the process mentioned earlier of ferric reduction to ferrous as discussed by Theis and Singer, (1974). The reduction of ferric compounds to ferrous is instantaneous in an organic environment. Therefore as the ferric bulk concentration is increased the reduction reactions are favoured which will lead to an increasing depletion of ferric ion and formation of ferrous compounds in the waste water system. Another

possible explanation stated earlier is the hydrolysis reaction, which favours hydrogen ions being released into the water. As the bulk concentration of ferric chloride is increased the hydrogen ion concentration in water recovered increases because the ferric ion with the available hydroxyl ions in solution hydrolyses to form $Fe(OH)_x^{3-x}$ species. It is also of note that the ferrous ion (Fe^{2+}) compound is also used as a flocculant.

In regions where there is high flocculant bulk concentration, there is bound to be good flocculation and high turbidity removal. Initial experimental results at low pH and very high redox potential were observed. This may be attributed to the addition of biocide into the wastewater sample on the plant in order to preserve the wastewater in storage. In subsequent experiments higher pH and lower redox potential were measured. Factors that affect the experimental process such as: dosing of biocide into wastewater in order to preserve it in storage and improper mixing techniques were studied and eliminated.

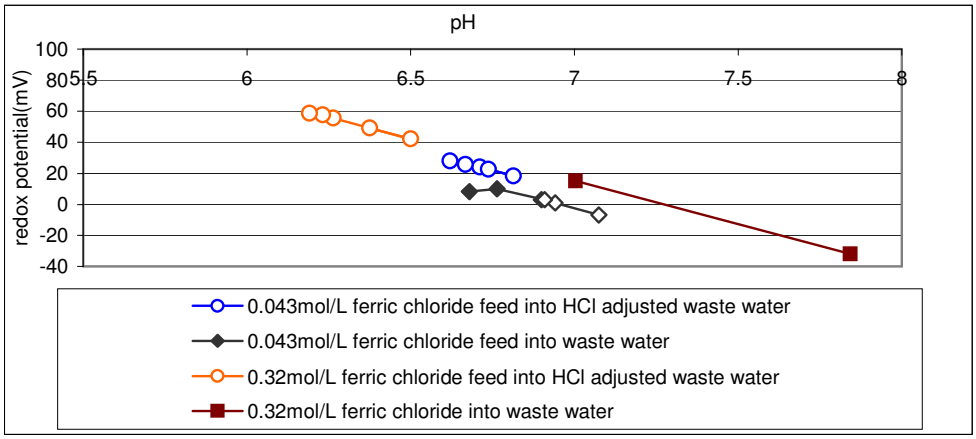


Figure 4.11 The effect of adjusted pH on measured redox potential

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

The pH of wastewater for flocculation was adjusted to a pH of about 5.5 in order to study the effect of pH on the ferric chloride flocculant. These results were compared to results obtained with no acid addition into wastewater. The unadjusted wastewater used does not contain biocide, its pH was between 7.5 and 9.2, this was out of the range where the ferric chloride flocculant performs best.

The detailed results for this particular experiment are available in Appendix C in Tables C18.1,C19.1,C20.1,and C21.1 respectively.

Flocculant concentrations of 0.043mol/L and 0.32mol/L were used for both acid adjusted and unadjusted wastewater. Figure 4.11 shows that the redox potential and pH measured for recovered water of unadjusted wastewater for the experiments at 0.043mol/L and 0.32mol/L, had lower redox potential and higher pH respectively. This is due to the following reasons: firstly since there are fewer hydrogen ions in the water recovered the potential will be lower, secondly the pH of the initial wastewater lay outside the region of optimum performance of the ferric chloride flocculant.

For the acid adjusted wastewater, the redox potential of recovered water was higher than that of unadjusted wastewater for water recovered, while the pH was lower in comparison to that of water recovered from the unadjusted wastewater. The main reason for this is that the adjusted wastewater contains more hydrogen ions because of the addition of HCl acid, hence this cause a pH shift. As mentioned earlier an increase in hydrogen ions leads to a higher redox potential measurement for the water recovered. It is of note that the clarity of water recovered when acid is used to adjust the pH is better than that of unadjusted pH. The turbidity measurement was not taken because the turbidity meter was not available at the time when the experiment was carried out.

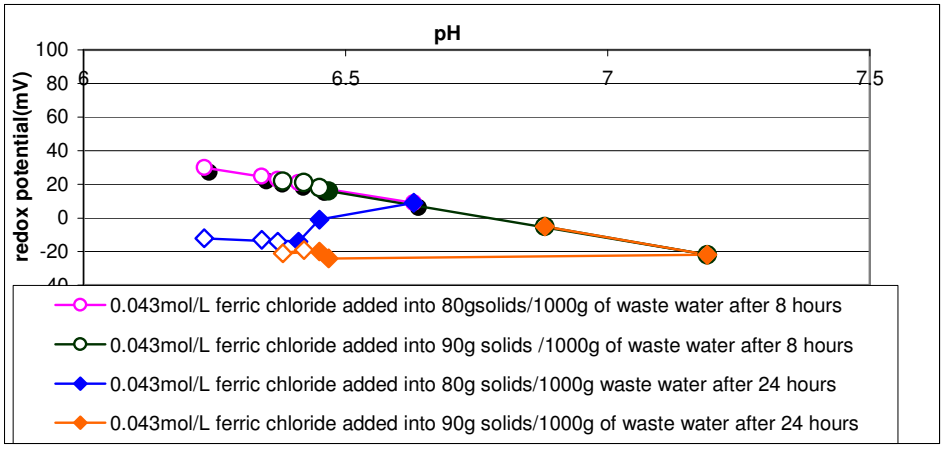


Figure 4.12 The change in measured redox potential with time

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

It was found that the linear relationship between pH – redox potential holds for measurement done after eight hours. 24 hours after completion of the experiment, the initial redox potential and pH shifted as shown in Figure 4.12. The trend observed over this period of time was increasing pH and a more negative redox potential. This can be supported by Theis and Singer, (1974) who suggested that it is a process of oxidation of the ferrous ion back to a ferric compound by the organic compounds present in the water. Another possible path is the oxidation of the ferrous compound to the ferric ion followed by complexation with hydroxyl ions to form a ferric hydroxide precipitate. An in-depth study of this phenomenon is beyond the scope of this work.

4.2.4.Turbidity evaluation as a measure of redox potential

Turbidity measurements are important in order to determine the efficiency of the flocculant used in the flocculation process. As earlier discussed in Section 4.2.1 the higher the bulk concentration of ferric chloride flocculant in the wastewater the lower the turbidity. It is however important to evaluate the redox potential of recovered water in terms of turbidity. Figure 4.13 should provide the answer.

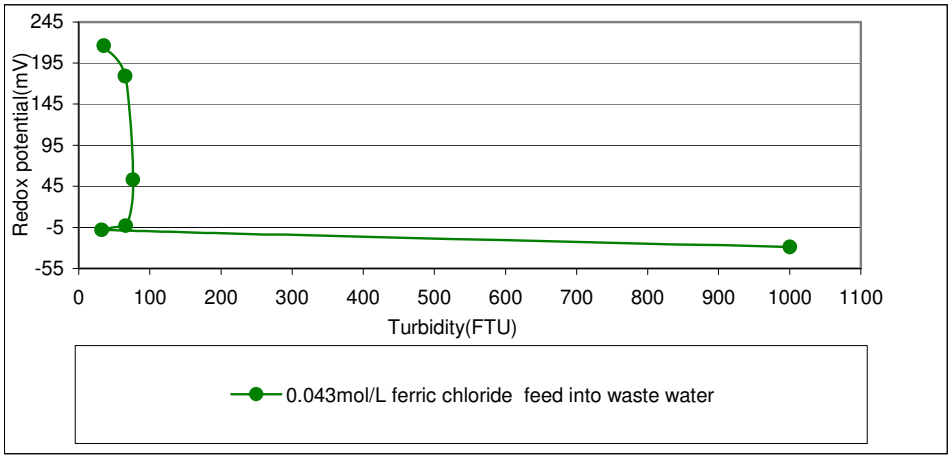


Figure 4.13 The turbidity of water recovered as a function of redox potential

Figure 4.13 shows the redox potential of water recovered plotted against the turbidity. It shows that the lower bulk concentration point from 0.006mol/l gives a low redox potential. The turbidity measurements decrease moving from right to left on the chart and as the bulk concentration of ferric chloride increases in wastewater. There is also a corresponding increase in redox potential of water recovered, this increase in redox potential can be attributed to two factors namely: increasing hydrogen ions in water recovered as pH decreases and the reduction of ferric ion in waste water to ferrous which occurs perhaps at a pH in the low region due to the presence of carboxylic compounds such as phenols. (Stumm and Morgan, 1981).

4.3. Aluminium sulphate coagulation and flocculation experiment.

This section discusses the results obtained using aluminium sulphate as a flocculant. It should be noted that ferric chloride was used to study the characteristics of flocculation. The experiments done with aluminium sulphate were used to ascertain effectiveness of other flocculants for the flocculation of the wastewater. Thus relatively few experiments were performed.

4.3.1 Turbidity of recovered water - a measure of coagulation efficiency

This section discusses the turbidity results for recovered water when aluminium sulphate is used as the flocculant. As mentioned earlier in Section 2.1, it is sometimes difficult to decide when flocculation occurs. A comparison of the turbidity of various samples leads the conclusion that the water is visually clear at about 500FTU and below. The same criterion for the onset of flocculation as for ferric chloride was chosen, namely a turbidity measurement of 100FTU or less. Figure 4.14 shows the results of turbidity measured when various amounts of aluminium sulphate feed at a concentration of 0.084mol/L is added to waste water.

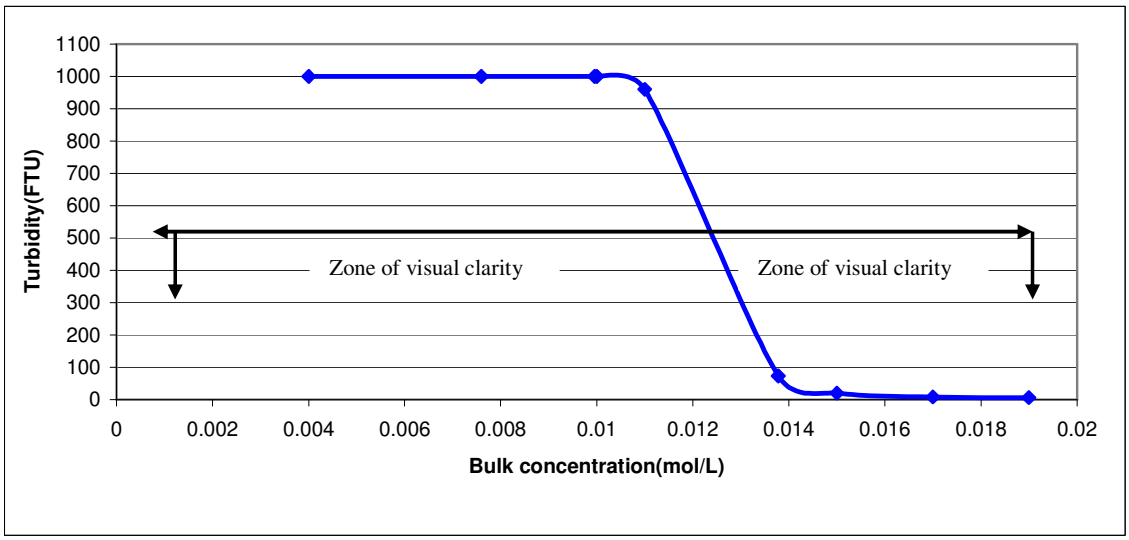


Figure 4.14 Zone of effective turbidity when varying quantities of 0.084mol/L aluminium sulphate added to wastewater

For this chart the turbidity measurements above 1000FTU for which no reading could be obtained have been assigned values of 1000FTU in order to indicate the range of concentrations tested. (The result displayed is experiment 29, Table 29.3 in Appendix C).

From this picture the bulk concentrations from 0.0040mol/L to 0.011mol/L have recovered water of very high turbidity of 1000FTU or higher. The water recovered at these bulk concentrations was very milky. At a bulk concentration of greater than 0.012mol/L as shown on the chart, there was a sharp drop in turbidity of water to a value below 100FTU, at a bulk concentration of about 0.014mol/L. The turbidity curve flattens off gradually to about 6 FTU at the bulk concentration of 0.019mol/L. This zone is indicated as that of good visual clarity in Figure 4.14. Based on this result we may conclude that as the bulk concentration of aluminium sulphate increases, turbidity of water was slightly lowered. This result is similar to that for ferric chloride.

The turbidity measurements were taken about ten hours after the completion of the jar test experiments, in order to ensure that the floc particles formed are well

settled. The tests, for which turbidity readings of 100FTU and above are recorded, are termed poor flocculation, and the sludge is not well-formed. Points where turbidity measurements are below 100FTU are termed good flocculation. In these tests the sludge is a finely textured compact cake and is said to be

well-formed. These terms will be used recurrently in the following sections to describe different experiments.

4.3.4 Comparing of thermodynamic predictions for amorphous aluminium hydroxide equilibrium phase with experimental results.

From thermodynamics the prediction is that flocculation will depend on the quantity of flocculant added to the wastewater and not the initial concentration of flocculant. Figure 4.15 shows that thermodynamics predicts that flocculation will not occur at pH`s below 4 or above 10. In this section we will compare the experimental results of aluminium sulphate with the thermodynamic predictions of Figure 4.15.

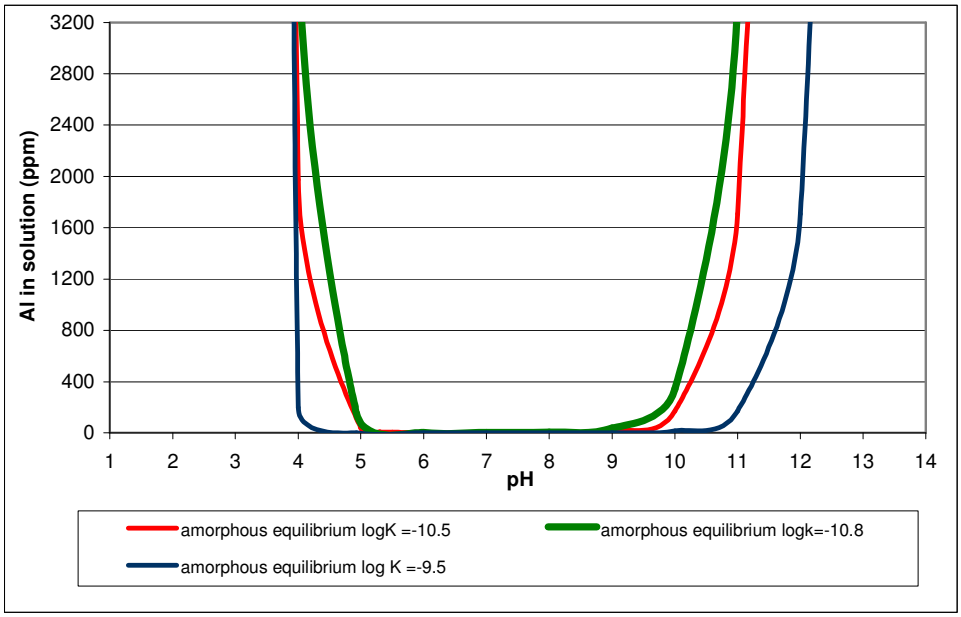


Figure 4.15. The equilibrium curve for different amorphous equilibria

Figure 4.15 shows the plot for different values of the log of the equilibrium constant (K) for amorphous aluminium hydroxide [am~ $Al(OH)_{3s}$].The log K values were obtained from different literature sources: the values range from the

smallest at –10.8 (Stumm and Morgan,1981) to the largest log K at –9.5 (Jiang and Graham, 1998). The intermediate log K of –10.5 is from Faust and Aly, (1983). The Faust and Aly (1983) data is attributed to Stumm and Morgan, (1981), but the values used are different. The largest log K from Jiang and Graham (1998) was an estimated value. The reason the value for log K was estimated is because of the metastable nature of the amorphous phase making it is difficult to measure. The equilibrium constant chosen for the analysis of the results of the experiments presented in this section is the Stumm and Morgan (1981) data because it was experimentally determined. The data from Stumm and Morgan (1981) was measured experimentally as confirmed by Baes and Mesmmer, (1976). Baes and Mesmmer (1976) acknowledge the fact that amorphous solid is formed immediately due to hydrolytic reactions of aluminium ion, this matches the time frame of flocculation, which is also a fast process.

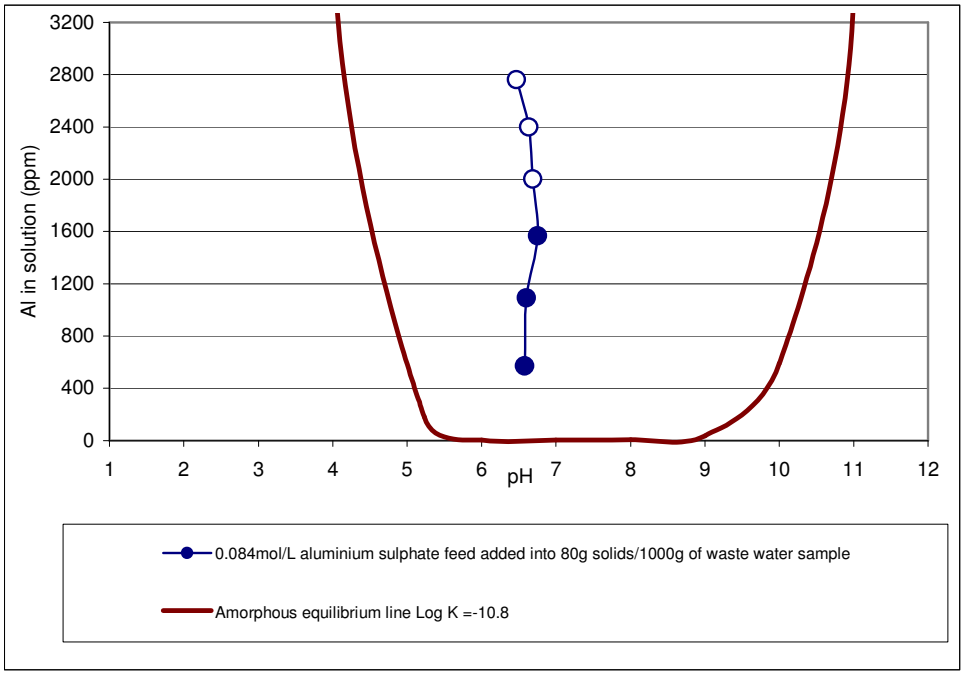


Figure 4.16. The effect of bulk concentration on flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Figure 4.16 shows the impact of bulk concentration on flocculation experiments. From thermodynamics it is predicted that flocculation will depend on the quantity of flocculant added to the wastewater. The result agrees with this with better flocculation being produced as the bulk concentration of aluminium sulphate flocculant increases in wastewater. Good flocculation is observed between aluminium bulk concentrations of 2000ppm and 2800ppm. At bulk concentrations below 2000ppm poor flocculation results are observed.

Another important observation is the well-defined boundary for points where good flocculation occurs and the points where we have poor flocculation. Looking at the flocculation boundary for our experiments it appears it does not agree with the boundary predicted by thermodynamics for the formation of aluminium hydroxide (Al $(OH)_{3S}$). The flocculation boundary occurs at a higher concentration of aluminium (Al^{3+}) bulk concentration than predicted by thermodynamics.

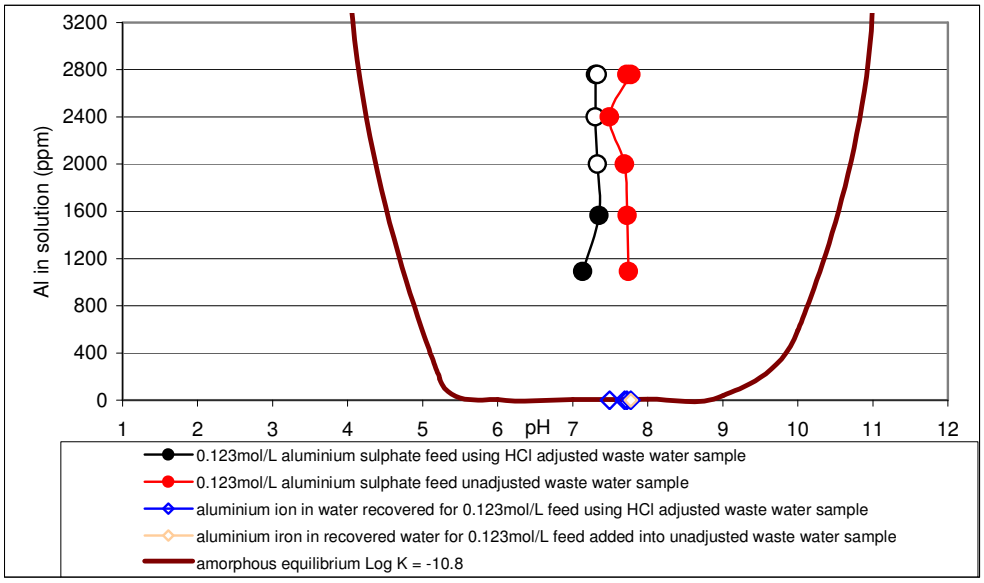


Figure 4.17. The effect of pH on flocculation

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Effect of pH on flocculation:

If all that is required for flocculation to occur is the formation of $Al(OH)_3$ precipitate, all tests lying within the region should flocculate. Since the formation of the $Al(OH)_3$ precipitate is a necessary condition for flocculation to occur, flocculation will not occur at pH`s where the precipitate does not form, that is pH`s below 5.5 and above 9. We tested this by flocculating two different waste water samples, one at its own pH and another at a lower pH.

The experimental results shown on Figure 4.17 are results of unadjusted and HCl adjusted wastewater, when 0.123mol/L aluminium sulphate solution feed is added into wastewater. A 3 molar HCl solution is used to adjust the pH of the wastewater. The results show that for the HCl adjusted wastewater the onset of good flocculation occurs from 2000ppm. However that of the unadjusted wastewater has poor flocculation points. The table of these results is in Appendix C.

Comparing these two experimental results shows that lowering the pH of wastewater increases the efficiency of the flocculant added. As for $FeCl_3$, it is likely that the efficiency of flocculation is very sensitive to pH in the region between 5.5 and 9. As is seen from the experimental results, a small change in the pH can have a large effect on flocculation.

An observation is that the pH of water recovered for both samples is in the neutral range between 7 and 8. As expected the pH of water recovered for the HCl adjusted sample is lower than that of the unadjusted sample, due to the high hydrogen ion content of the acid adjusted sample. According to the literature the aluminium sulphate flocculant performs best between pH 5.5 to 7.5 (Peavy et al, 1985). The pH of wastewater to which HCl was added was 7 and it gives a more favourable result than unadjusted wastewater, at a pH of 8.5. For the unadjusted wastewater the control of the experiment was at a concentration of 0.084mol/L

and this did not give a good flocculation result. This may be due to nature of the unadjusted wastewater or kinetic factors.

The points lying horizontally on the x-axis are the points for the amount of aluminium ion in the water recovered, these points lie in the same pH range as the test i.e. between 7 and 8. The quantity of aluminium measured in the water recovered was low between 0.1 to 0.5ppm. Therefore the bulk of the aluminium ions dosed into the wastewater end up in the aluminium hydroxide solid. Figure 4.18 shows that the results of flocculation when different feed concentrations are used. It can be seen that the concentration of Al in water recovered obeys the thermodynamic predictions.

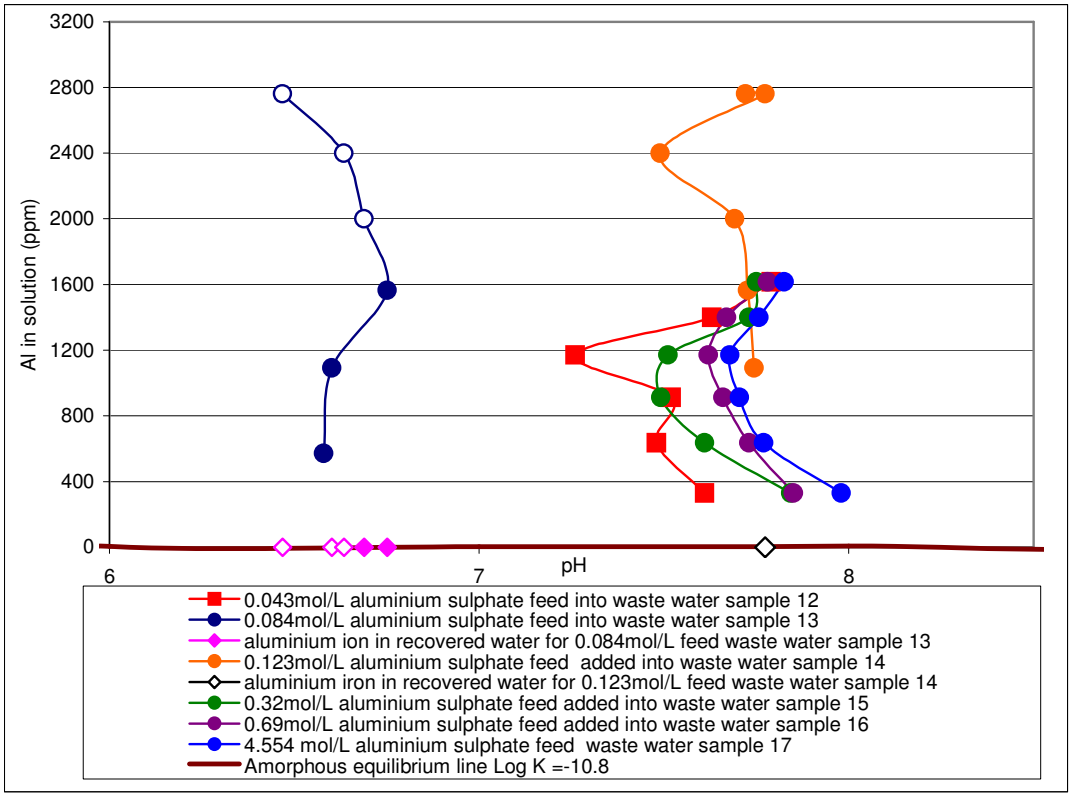


Figure 4.18 The effect of different flocculant feed concentrations

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

In Figure 4.18 the results of flocculation for different feed concentrations of aluminium sulphate are given. It was found that 0.084mol/L feed concentration gives the best flocculation results, with the onset of good flocculation at 2000ppm. For comparison 0.123 mol/L aluminium sulphate feed, was added into wastewater at the same bulk concentration as that of 0.084 mol/L aluminium sulphate feed. The result for 0.123mol/L aluminium feed was poor flocculation at all bulk concentration. A possible reason for the poor flocculation result of the 0.123mol/L feed may be the initial high pH of that part waste water sample at about 8.15.

Other experiments were carried out at 0.32, 0.69 and 4.554 mol/L feed concentrations. They had bulk concentrations between 330ppm to 1600ppm in wastewater. The aluminium sulphate feed solutions were dosed into wastewater at the same feed concentration as that of 0.043mol/L ferric chloride feed. It was seen that dosing aluminium into wastewater at the same molar feed concentration and bulk concentrations as that of ferric ion will not produce good flocculation results for the aluminium ion. For aluminium it is necessary to add flocculant at a higher dosage to give a higher bulk concentration of aluminium.

Another point worth noting is that using highly concentrated aluminium sulphate flocculants does not produce floating particles or lumpy sludge as observed for ferric chloride. It was also observed that the pH window for optimum operation for aluminium sulphate is narrower compared to ferric chloride.

The points shown in Figure 4.18 lying directly on the x-axis are the measured concentrations for the aluminium ions in recovered water. The quantity was quite low for the points that could be measured. The solutions of some of the tests could not be measured due to the high turbidity of the samples and a concern that the particles in the water would block the nebuliser of the atomic adsorption spectrometer used for the analysis. The measured aluminium content of recovered water was in the range of 0.1ppm to 0.5ppm. This is an indication that the bulk of

aluminium added does not remain in water after flocculation, it ends up in the sludge formed. One of the components of the sludge formed is amorphous aluminium hydroxide solid.

4.3.2 Results of Measured Redox Potential.

As discussed earlier for ferric chloride when considering the thermodynamics of the flocculation process, the transfer of electrons should not occur. Nonetheless, in the case of our experiments a change in redox potential is measured for aluminium sulphate flocculation experiments similar to what occurred when the ferric chloride flocculant is used. Thus it seems likely that a reaction is occurring in our flocculation process, this may be electron transfer or a change in oxidation state. Al^{3+} is unlikely to be reduced, but other cations present may have undergone reduction. The extent of the reaction may not be large as small amounts of reaction will lead to an observable change in potential, but it is of importance to mention it. Figure 4.19 shows the measured redox potential for recovered water for different samples.

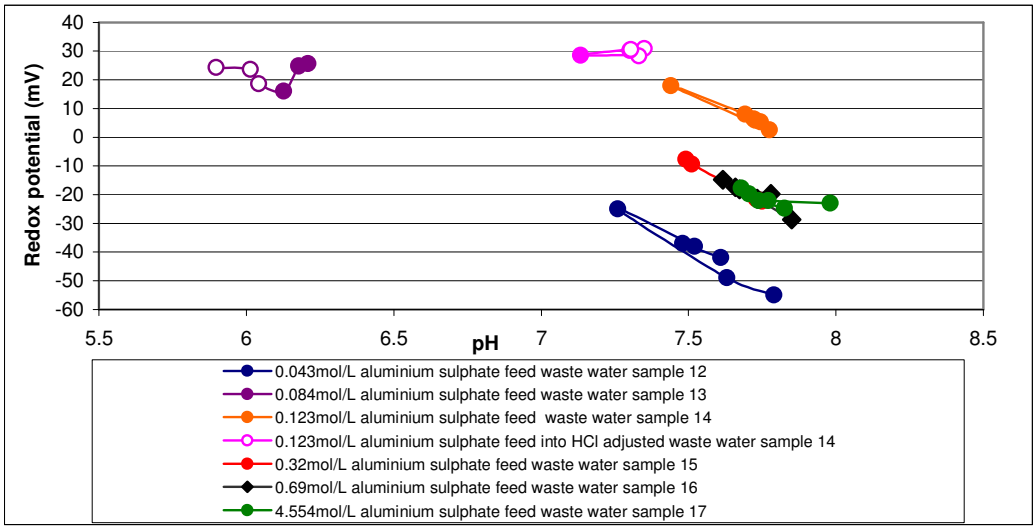


Figure 4.19 The measured potential

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Figure 4.19 shows the results of measured redox potential of water recovered against pH for different feed concentrations of aluminium sulphate. For cases where poor flocculation is observed, it was found that the result displayed some form of linearity, but not as pronounced as that displayed by ferric chloride. For each experiment the redox potential rises gradually, reaches a peak and then starts to drop. The similarity in shape for these experiments may be due to the wastewater source for which the samples used in these experiments were all the same.

The other two experimental lines in the upper region of the chart have a similar V or U shape. These experiments gave good flocculation results for most of the points. The points on the left represent a feed concentration of 0.084mol/L and the experimental points to the right represent the 3molar HCl adjusted wastewater at a feed concentration of 0.123mol/L. It is of interest to see that the points at which good flocculation starts are the lowest point on the lines for these two experiments. However as flocculation improves the redox potential increases and the pH of water recovered also increases.

Another important reason why the experiments where good flocculation occurs have a higher potential is due to the bulk concentration of the aluminium feed. However for the HCl adjusted wastewater at 0.123mol/L aluminium sulphate solution feed, increased hydrogen ion content will be a factor that will make the potential of water recovered higher. Comparing this particular result with that of unadjusted wastewater it can be seen that the measured potential at the same aluminium sulphate feed concentration of 0.123mol/L concentration has a lower value in the recovered water.

4.3.3 Turbidity evaluation as a measure of redox potential for aluminium sulphate feed

This analysis was done in order to check if the postulate being proposed in Section 4.2.4 for ferric chloride holds for aluminium sulphate. An important issue is that the number of experiments conducted using aluminium sulphate as a

flocculant, in which turbidity was measured, is small in comparison to when ferric chloride was used. However we may be able to check if there are similar characteristics to that of the ferric chloride turbidity.

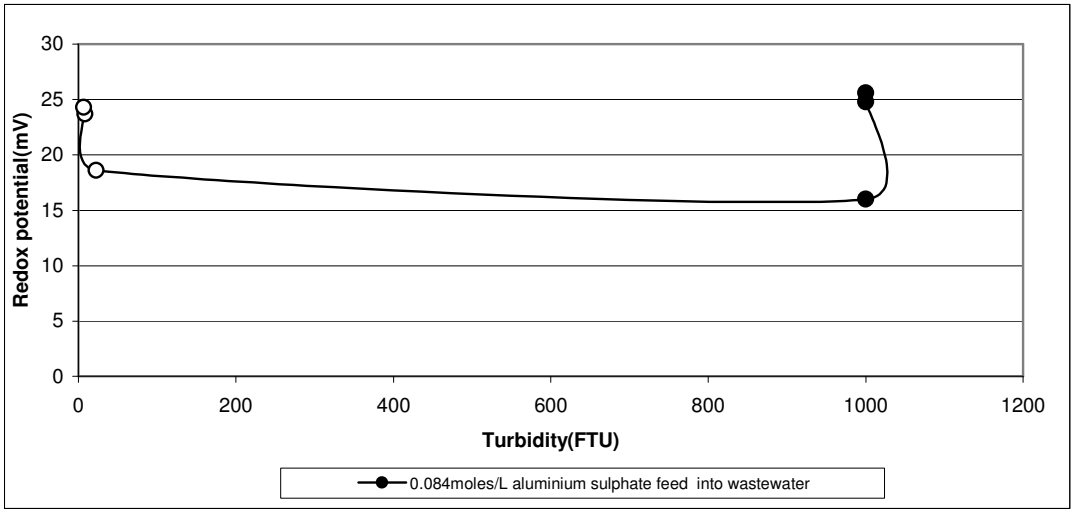


Figure 4.20 The turbidity of recovered water for aluminium sulphate feed

O Good flocculation, Turbidity < 100FTU

● Poor flocculation, Turbidity > 100FTU (this could be of any colour)

Figure 4.20 shows the measured redox potential of water recovered plotted against the turbidity measured for recovered water. The plot has different characteristics to that of turbidity measured for ferric chloride flocculation (Figure 4.13), it is U shaped in appearance. The points where poor flocculation occurs has a plot that appears to be a mirror image to that of points where good flocculation occurs. This is an artefact of having assigned values of 1000FTU`s to the poor flocculation points.

4.4 Concluding remarks on the results and discussions

The coagulation and flocculation of wastewater using ferric chloride and aluminium sulphate flocculant has been evaluated. The turbidity measurements below 100FTU were described as good flocculation and readings above that were described as poor flocculation.

The dominating factors in flocculation of wastewater are assessed using the amorphous hydroxide equilibrium data in order to determine the nature of the solids formed when both ferric chloride and aluminium sulphate are used. It can be concluded that we are able to understand the limitations in using thermodynamics to assess the process. An advantage of using the equilibrium line is to be able to predict the range in which flocculation will occur. Insight has been gained into some other dominating factors in the flocculation process, such as the importance of good mixing, adequate dosing concentration, the effect of solid content and the effect of pH. The latter is more pronounced for aluminium sulphate than ferric chloride.

The redox potential measurements were analysed and give an indication that the ferric ions may be reduced to ferrous ions. This is accompanied by the liberation of hydrogen ions into the water, which leads to a pH shift towards the acidic region. Although in the case of aluminium, the reduction of aluminium is not favoured, hydrolysis reactions favour the release of the hydrogen ion that will also cause the pH of water recovered to shift towards the acidic region. It can be said that for ferric chloride the higher the acidity the more likely the ferric ion is to be reduced to the ferrous ion. An increase in bulk concentration also indicates an increase in the redox potential of the water recovered. For aluminium sulphate, redox potential decreases until the onset of flocculation for points where good flocculation results were obtained.

Finally we are able to see that the quantity of aluminium required to achieve good flocculation is twice the quantity of ferric ion required in terms of moles.

CHAPTER 5

5.1 Conclusions and Recommendations

Flocculation experiments were carried out and the following conclusions can be made about the findings and results of these experiments.

The turbidity of water recovered improves with an increasing bulk concentration of coagulant solution added into wastewater for both ferric chloride and aluminium sulphate flocculants. Good flocculation was defined to have occurred when the turbidity of water recovered was lower than 100FTU.

Many different values for the equilibrium constants for the precipitation of amorphous solid hydroxide have been published. This is due to its metastable nature. The data used for the analysis was taken from studies based on similar measurement conditions for the equilibrium constant.

A conclusion can be drawn on what the thermodynamic equilibrium is able to predict, namely the zones where flocculation may occur and the areas where flocculation will not occur. Another important observation is that the formation of the hydroxide precipitate is a necessary but not sufficient condition for good flocculation to occur. A major limitation is the inability of thermodynamics to predict what happens within the flocculation zone.

Thermodynamics does predict that flocculation is pH dependent (in a certain range) but this degree of sensitivity to pH is predicted at much lower pHs such as 3. However for wastewater adjusted to pH between 5.5 to 7, a very good flocculation result is obtained in comparison to the result of unadjusted wastewater.

Thermodynamics predicts that flocculation should be independent of the initial feed concentration. In our experiments this cannot be said to hold because it was

found that different results were obtained for different feed concentration of flocculant at the same bulk concentrations in wastewater.

The coagulant performance in the regions where coagulation will occur is affected mostly by kinetics factor such as: mixing, design of vessels, and solid content of waste water this is postulated to be related to insufficient nucleation sites, dosing technique and time. These were all found to be very important factors in determining the effectiveness of coagulation.

From thermodynamics redox potential was assumed to be an important factor in flocculation. In our experiments the measured redox potential of the water recovered was found to change. This may be an indication of electron transfer. It is likely to be dependent on the following: the reduction and oxidation reactions in the wastewater system, (in particular when ferric ions are present) the hydrolysis reactions which lead to the release of hydrogen ions into the waste water system. This factor is more dominant when aluminium sulphate is used. The measured redox potential is pH dependent and it can be influenced by the concentration of flocculant feed added into the wastewater. This was seen in the use of ferric chloride flocculants.

The redox potential can be used as an important control parameter in flocculation processes to indicate the point at which good flocculation is achievable for a particular flocculation process.

Lastly the molar concentration of aluminium sulphate required to effect favourable coagulation is about twice the ferric chloride concentration. However aluminium sulphate produced white sludge that could potentially be reused in the paint production process. On the other hand ferric chloride is a cheaper flocculant, so that if discolouration of the sludge is immaterial, ferric chloride is the recommended flocculant.

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Appendix A

A1 Results of drying at different mass for waste water sample.

Crucible	A	B	C
Mass of crucible	85.03g	88.37g	542.96g
Mass of waste water	20.00g	50.00g	100.00g
Mass of dried sample + Mass of crucible	88.70g	98.10g	562.07g
Mass of solid content/ Mass of waste water dried	3.67g/20.00g	9.24g/50.00g	19.11g/100g
Mass of solid content/1000g of waste water	183.5g/1000g	184.8g/1000g	191.1g/1000g
Time spent on drying	1hr	2hrs	2hrs.30mins
Oven temperature	130^0C	130^0C	130^0C

Table A1.0 Table of results of drying waste water samples at different mass

A2 Checking the rate of evaporation in the drying process for waste water

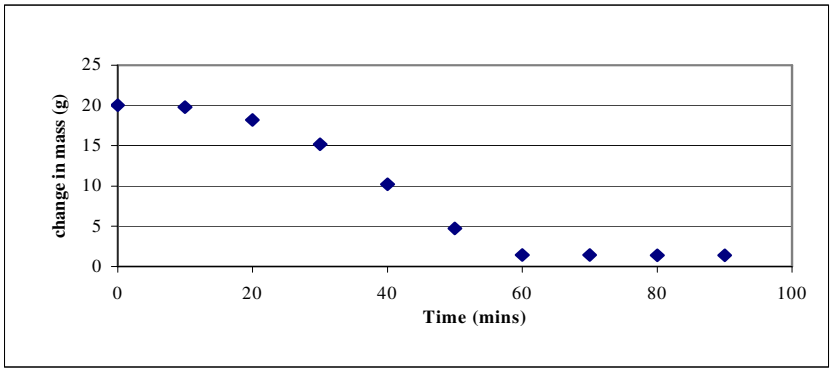


Figure A2 Rate of evaporation of water

A3 Mass of water required for dilution in different solid quantity of waste water.

Mass of water (g)	Solid content (g/g)
0	80
535	122.8
943.7	155.5
1200	176
1206	176.5
1312.5	185
1447.5	195.8
1580	206.4

Table A3 Water required for dilution

A4 Rate of water recovery from waste water

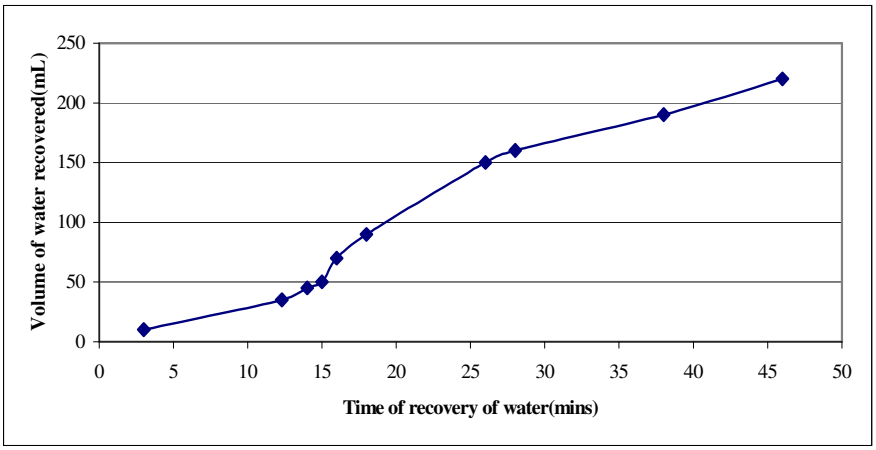


Figure A4 Rate of water recovery in jar test

A5 Solid content results for different waste water samples

Date	Solid content (mass of solid g in 1000g of waste water)
10/4/2002	123.4g of solid in 1000g of waste water
30/4/2002	109.7g of solid in 1000g of waste water
31/5/2002	120.82g of solid in 1000g of waste water
10/6/2002	206.40g of solid in 1000g of waste water
10/6/2002	179.30g of solid in 1000g of waste water
23/7/2002	142.26g of solid in 1000g of waste water
30/7/2002	174.00g of solid in 1000g of waste water
27/8/2002	152.00g of solid in 1000g of waste water
25/6/2002	184.80g of solid in 1000g of waste water

Table A5 Results of solid content of waste water

Appendix B

B1.1 Determination of concentration of ferric chloride in each jar after addition of flocculant.

This can be determined by calculating the concentration of ferric chloride in the solution where we have flocculant added into each 400mL of waste water. The flocculant solution is added in respective volumes of 20, 40, 60, 80,100 and 120mL respectively.

The mass concentration of ferric in solution is 0.695%m/m, however a basis is chosen for the calculation.

Basis : 0.695%m/m = 7g/L(0.04313 moles/Litre) concentration of ferric chloride in water

Deduce: 2.94g of ferric chloride in water of volume 0.42L = 7g/L concentration

Concentration = 2.94g/ 0.42L = 7g/L = 0.04313 moles/Litre

Therefore to find concentration of ferric chloride in the new solutions of flocculant and waste water.

Parameters.

C_1 = Actual concentration of ferric chloride flocculant solution =7g/L (0.04313moles/L)

C_2 = New concentration of ferric chloride flocculant in wastewater. = X

V_1 = Volume of actual ferric chloride solution = 420mL

V_2 = Volume of ferric chloride flocculant solution added into waste water.

V_3 = Volume of waste water used in flocculation experiment = 400mL

Calculations:

For 20mL of flocculant added.

V_2 = 20mL

$C_1 * V_2 = C_2 * V_3$

$C_2 = C_1 * V_2 / (V_2 + V_3)$

C_2 = 7g/L * 0.02L / (0.02L + 0.40L) = 0.333 g/L(0.021moles/Litre)

For 40mL of flocculant added

V_2 = 40mL

$C_1 * V_2 = C_2 * V_3$

$C_2 = C_1 * V_2 / (V_2 + V_3)$

C_2 = 7g/L * 0.04L / (0.04L + 0.40) = 0.6364g/L (0.003921 moles/Litre)

For 60mL of flocculant added

V_2 = 60mL

$C_1 * V_2 = C_2 * V_3$

$C_2 = C_1 * V_2 / (V_2 + V_3)$

$C_2 = 7g/L * 0.06L / (0.06L + 0.40) = 0.913g/L$ (0.00563moles/Litre)

For 80mL of flocculant added.

$V_2 = 80mL$

$C_1 * V_2 = C_2 * V_3$

$C_2 = C_1 * V_2 / (V_2 + V_3)$

$C_2 = 7g/L * 0.08L / (0.08L + 0.40) = 1.167g/L$ (0.00719 moles/Litre)

For 100mL of flocculant added

$V_2 = 100mL$

$C_1 * V_2 = C_2 * V_3$

$C_2 = C_1 * V_2 / (V_2 + V_3)$

$C_2 = 7g/L * 0.10L / (0.10L + 0.40) = 1.40g/L$ (0.008626moles/Litre)

For 120mL of flocculant added

$V_2 = 120mL$

$C_1 * V_2 = C_2 * V_3$

$C_2 = C_1 * V_2 / (V_2 + V_3)$

$C_2 = 7g/L * 0.12L / (0.12L + 0.40) = 1.6154g/L$ (0.009953moles/Litre)

B1.2 Calculations of aluminium sulphate concentration required from jar 1 to jar 6.

C_1 = concentration of aluminium sulphate solution =12g/L
C_2 = concentration of aluminium sulphate in each jar = A
V_1 = volume of aluminium sulphate flocculant added to each jar.
V_2 = volume of waste water = 400mL.

Therefore,

Basis: 80g of solid in 1000g of waste water.

$C_1 * V_1 = C_2 (V_1 + V_2)$

FOR 20mL

$12g/L * 0.02L = A (0.02L + 0.4L)$
$A = 0.5714 g/L$

FOR 40mL

$12g/L * 0.04 = A (0.04L + 0.4L)$
$A = 1.091gL$

FOR 60mL

$12g/L * 0.06 = A (0.06L + 0.4L)$

A =1.565g/L

FOR 80mL

12g/L * 0.08L = A(0.08L + 0.4L)

A = 2g/L

FOR 100mL

12g/L * 0.10L = A (0.10L + 0.4L)

A = 2.40g/L

FOR 120mL

12g/L* 0.12L = A (0.12L + 0.4L)

A= 2.76g/L.

B2.1 Calculation for the predictive method for ferric chloride.

CALCULATIONS

$C_1 * V_1 = C_2(V_1+V_2)$ (1)

C_1 = Actual concentration of ferric chloride flocculant

V_1 = Volume of ferric chloride flocculant solution added in waste water

C_2 = The value of concentration from graph

V_2 = The volume of waste water.

For varying solid content of solids

C_2 for 80g/1000mL of waste water of solid from plot

Firstly determine the number of solids in 400ml of waste water

32g of solid in 400mL of waste water

Now determine the corresponding C_2 from the graph use the uppermost line in Figure to determine the ratio. Then read off the C_2 value corresponding to the point for the Ratio ® value on the line on y axis of the chart to know C_2

C_2 = 1.615g/L substitute into equation 1

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

Jar1

$7 * V_1 = 1.615*(V_1 + 0.4)$

V_1 = 120mL the volume of ferric chloride flocculant required for addition at 80g /solid in waste water.

Jar 2

Solid content of waste water =111g of solid in 1000mL

Solid content in 400mL = 44.4g of solid

Now read of the ratios ® and the C_2 values on the Figure at the lowest line because of the need to test a range of results.

C_2 = 1.606g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$7 * V_1 = 1.606*(V_1 + 0.4)$

V_1= 121mL

Jar 3

Solid content of waste water =111g of solid in 1000mL

Solid content in 400mL = 44.4g of solid

Now read of the ratios ® and the C_2 values on the Figure at the middle line because of the need to test a range of results.

C_2 = 1.925g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$7 * V_1 = 1.925*(V_1 + 0.4)$

V_1= 154mL

Jar 4

Solid content of waste water =111g of solid in 1000mL

Solid content in 400mL = 44.4g of solid

Now read of the ratios ® and the C_2 values on the Figure at the uppermost line because of the need to test a range of results.

C_2 = 2.2112g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$7 * V_1 = 2.2112*(V_1 + 0.4)$

V_1= 188mL

Jar 5

Solid content of waste water =38g of solid in 1000mL

Solid content in 400mL = 15.2g of solid

Now read of the ratios ® and the C_2 values on the Figure at the uppermost line because of the need to test a range of results.

C_2 = 0.77g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

7* V_1 = 0.77*(V_1 + 0.4)

V_1= 51mL

Jar 6

Solid content of waste water =50g of solid in 1000mL

Solid content in 400mL = 20g of solid

Now read of the ratios ® and the C_2 values on the Figure at the uppermost line because of the need to test a range of results.

C_2 = 1.0096g/L

C_1*V_1 = C_2(V_1+V_2)

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

7* V_1 = 1.0096*(V_1 + 0.4)

V_1= 69mL

B2.2 Calculation for the predictive method for aluminium sulphate

CALCULATIONS

C_1*V_1 = C_2(V_1+V_2) (2)

C_1 = Actual concentration of aluminium sulphate flocculant

V_1 = Volume of ferric chloride flocculant solution added in waste water

C_2 = The value of concentration from graph

V_2 = The volume of waste water.

For varying solid content of solids

C_2 for 80g/1000mL of waste water of solid from plot

Firstly determine the number of solids in 400ml of waste water

32g of solid in 400mL of waste water

Now determine the corresponding C_2 from the graph use the uppermost line in Figure to determine the ratio. Then read off the C_2 value corresponding to the point for the Ratio ® value on the line on y axis of the chart to know C_2

C_2 = 2.762g/L substitute into equation 1

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 12g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

Jar1

$12 * V_1 = 2.762*(V_1 + 0.4)$

V_1 = 120mL the volume of aluminium sulphate flocculant required for addition at 80g /solid in waste water.

Jar 2

Solid content of waste water =111g of solid in 1000mL

Solid content in 400mL = 44.4g of solid

Now read of the ratios ® and the C_2 values on the Figure at the lowest line because of the need to test a range of results.

C_2 = 2.78g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 12g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$12 * V_1 = 2.78*(V_1 + 0.4)$

V_1= 120mL

Jar 3

Solid content of waste water =111g of solid in 1000mL

Solid content in 400mL = 44.4g of solid

Now read of the ratios ® and the C_2 values on the Figure at the middle line because of the need to test a range of results.

C_2 = 3.33g/L

$C_1*V_1 = C_2(V_1+V_2)$

C_1= is fixed at 12g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$12* V_1 = 3.33*(V_1 + 0.4)$

V_1= 154mL

Jar 4

Solid content of waste water =111g of solid in 1000mL

Solid content in 400mL = 44.4g of solid

Now read of the ratios ® and the C_2 values on the Figure at the uppermost line because of the need to test a range of results.

C_2 = 3.832g/L

$C_1*V_1 = C_2(V_1+V_2)$

C_1= is fixed at 12g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$12* V_1 = 3.832*(V_1 + 0.4)$

V_1= 188mL

Jar 5

Solid content of waste water =38g of solid in 1000mL

Solid content in 400mL = 15.2g of solid

Now read of the ratios ® and the C_2 values on the Figure at the uppermost line because of the need to test a range of results.

C_2 = 1.312g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$7 * V_1 = 1.312*(V_1 + 0.4)$

V_1= 49mL

Jar 6

Solid content of waste water =50g of solid in 1000mL

Solid content in 400mL = 20g of solid

Now read of the ratios ® and the C_2 values on the Figure at the uppermost line because of the need to test a range of results.

C_2 = 1.726g/L

$C_1 * V_1 = C_2(V_1+V_2)$

C_1= is fixed at 7g/L for the experiment

V_2= is fixed at 0.4L of waste water

V_1= is unknown

$7 * V_1 = 1.726*(V_1 + 0.4)$

V_1= 68mL

B3.1 The approach used to determine percentage metallic concentration in sludge.

The feed concentration for aluminium ion and ferric ion was 0.084moles/Litre

The measured ferric in water ranges between 1ppm to 2.08ppm for all samples

The measured aluminium content of water recovered was between 0.1ppm to 0.5ppm

Ferric ion bulk conc.	Aluminium ion conc	Jar No
0.0021moles/Litre	0.004moles/Litre	1
0.0039moles/Litre	0.0076moles/Litre	2
0.0056moles/Litre	0.011moles/Litre	3
0.0076moles/Litre	0.014moles/Litre	4
0.0086moles/Litre	0.017moles/Litre	5
0.00995moles/Litre	0.019moles/Litre	6

Table B1 Results of bulk concentration of metallic flocculant in waste water samples

A mass balance can be done over any of the jar based on the bulk concentration in any of the jar when the quantity of metal content in water recovered is known.
The volume of waste water for all jars is the same at 400mL.
An example for the mass balance calculation is done using data from optimum flocculant dosage points for ferric chloride and aluminium sulphate in chapter four.

Ferric chloride

Jar 6
Volume of water recovered = 265mL= V_2
Bulk concentration = 0.00995mol/L= C_1
Volume of waste water = 400mL = V_1
Concentration of ferric ion in water recovered =$5.38X10^{-6}$ = C_2
Therefore,
$C_1 * V_1 = C_2 * V_2$ + summation of sludge content

$C_1 * V_1 - C_2 * V_2$ = summation of sludge content

0.00995mol/L*0.4L- $5.38X10^{-6}$ mol/L*0.265L= summation of sludge content

0.00398- $1.43X10^{-6}$=summation of sludge content

0.00397857mol= summation of sludge content

percentage of ferric ion in water = [$1.43X10^{-6}$/ 0.00398]mol= 0.0003593mol

0.00036mol X 100% =0.036% of ferric ion is in water recovered

Therefore 99.964% of ferric ion feed ends up in sludge.

The step shown above is used to solve for all experiment in order to determine the percentage of feed that ends up in water recovered and sludge respectively.

Aluminium sulphate

Jar 6

Volume of water recovered = 250mL= V_2

Bulk concentration = 0.019mol/L= C_1

Volume of waste water = 400mL = V_1

Concentration of aluminium ion in water recovered =$5.59X10^{-6}$ = C_2

Therefore,

$C_1 * V_1 = C_2 * V_2$ + summation of sludge content

$C_1 * V_1 - C_2 * V_2$ = summation of sludge content

0.019mol/L*0.4L- $5.59X10^{-6}$ mol/L*0.250L= summation of sludge content

0.0076- $1.4X10^{-6}$=summation of sludge content

0.0075986mol= summation of sludge content

percentage of aluminium ion in water = [$1.4X10^{-6}$/ 0.0075986]mol= 0.0001842mol

0.0001842mol X 100% =0.018% of aluminium ion is in water recovered

Therefore 99.982% of aluminium ion feed ends up in sludge.

The step shown above is used to solve for all experiment in order to determine the percentage of feed that ends up in water recovered and sludge respectively.

Appendix C

$= There was no sludge formed

$1=There was no sludge recovered

#1=The colour of water recovered after flocculation remains the same with that of the initial waste water colour.

#=The colour of water recovered was brownish or dull in physical appearance.

#2= There was no sludge recovered.

N.M = The parameters were not measured because of the unclear nature of water recovered which can hinder instrument performances.

Experiment C 1.No flocculant is added into waste water

JAR	1	2	3	4	5	6
Volume of W.water (mL)	1000	1000	1000	1000	1000	1000
Volume of flocculant	Nil	Nil	Nil	Nil	Nil	Nil
Water recovered (mL)	Nil	Nil	Nil	Nil	Nil	Nil
Sludge formed (mL)	Nil	Nil	Nil	Nil	Nil	Nil
Mass of sludge (g)	Nil	Nil	Nil	Nil	Nil	Nil
pH of water recovered	8.20	8.20	8.20	8.20	8.20	8.20
pH of sludge	Nil	Nil	Nil	Nil	Nil	Nil

Table C1. Results for jar test experiment when no flocculant is added

Experiment C2. when ferric chloride solution of 0.006moles/Litre is added

Mass of flocculant/mass of water= 0.4g of $Fecl_3$/ 420g of water

pH of waste water	8.20
Redox potential of waste water	-79mV
Temperature of waste water	18.5^0C
Solid content of waste water	123.40g solid/1000g of waste water

TableC2.1.Analysis of waste water when ferric chloride solution of 0.006moles/Litre is added

JAR	1	2	3	4	5	6
Volume of W.water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	20	40	60	80	100	120
Bulk concentration in moles/Litre	0.00028	0.00054	0.00078	0.00099	0.0012	0.0014
New volume of solution (mL)	420	440	460	480	500	520
Water recovered(mL)	$	$	$	$	$	$
Sludge recovered	$	$	$	$	$	$
pH of water recovered	N.M	N.M	N.M	N.M	N.M	N.M
pH of sludge	$	$	$	$	$	$
Redox .P of water recovered	N.M	N.M	N.M	N.M	N.M	N.M

TableC2.2. Result of flocculation using ferric chloride solution of 0.006moles/Litre concentration.

Experiment C3. When ferric chloride of 0.022moles/Litre is dosed

Mass of flocculant/Mass of Water = 1.5g of $FeCl_3$/ 420g of water

pH of waste water	7.12
Redox potential of waste water	-18mV
Temperature of waste water	20^0C
Solid content of waste water	123.4g of solid in 1000g of waste water

Table C3.1. Analysis on waste water of waste water when ferric chloride of 0.022moles/Litre is dosed

JAR	1	2	3	4	5	6
Volume of W.water (mL)	400	400	400	400	400	400
Volume of flocculant(mL)	20	40	60	80	100	120
New volume of solution(mL)	420	440	460	480	500	520
Bulk concentration in moles/Litre	0.0011	0.002	0.0029	0.0037	0.0044	0.0051
Water recovered (mL)	$	$	$	40	60	100
Sludge recovered (mL)	Nil	Nil	Nil	200	80	200
Physical colour of water.	$	$	$	Dull	Dull	Dull
Physical colour of Sludge	N.M	N.M	N.M	Brown	Brown	Brown
pH of water Recovered	N.M	N.M	N.M	N.M	N.M	7.47
pH of sludge	N.M	N.M	N.M	N.M	N.M	7.01
Redox.P of water	N.M	N.M	N.M	N.M	N.M	-17mV

Table C3.2. Result of flocculation experiment when ferric chloride of 0.022moles/litre is used

Experiment C4. Using 0.0307moles/Litre ferric chloride flocculant.

pH of waste water	7.12
Redox potential(mV)	-18
Temperature	20^{o}C
Solid content	123g of solid in1000g of waste water

Table C4.1.Analysis of waste water for experiment using 0.0307moles/Litre ferric chloride flocculant.

pH of flocculant solution	2.27
Redox potential of flocculant solution	254mV
Temperature of flocculant solution	20^{o}C
mass of flocculant in water(g/L)	1.5g/0.42L

TableC4.2 Analysis of ferric chloride flocculant solution.

Jar	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of $FeCl_3$ added (mL)	20	40	60	80	100	120
Bulk concentration (mol/Litre)						
Volume of water recovered (mL)	$	$	$	40	60	100
Volume of sludge recovered (mL)	$1	$1	$1	400	380	380
Colour of water recovered	#1	#1	#1	#	#	#
Colour of sludge recovered	#2	#2	#2	Brown	Brown	Brown
pH of water recovered	N.M	N.M	N.M	N.M	N.M	7.47
pH of sludge recovered	N.M	N.M	N.M	N.M	N.M	7.01
Redox.P of recovered water (mV)	N.M	N.M	N.M	N.M	N.M	-17

Table C4.3 Result of jar test experiment using flocculant solution of 0.0307 moles /Litre

Experiment C5. Result of screening experiment using 0.043moles/Litre ferric chloride solution

pH of waste water	7.77
Redox potential(mV)	-53
Temperature	18^{o}C
Solid content	109.7g of solid in1000g of waste water

Table C5.1.Analysis of waste water using 0.043moles/Litre ferric chloride

pH of flocculant solution	2.02
Redox potential of flocculant solution	259mV
Temperature of flocculant solution	21.1^{o}C
mass of flocculant in water(g/L)	2.94g/0.42L

Table C5.2. Analysis of 0.043moles/Litre ferric chloride solution.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
New volume of solution (mL)	420	440	460	480	500	520
Volume of water recovered (mL)	340	330	280	240	240	200
Volume of sludge recovered (mL)	80	110	180	240	250	320
Mass of sludge recovered (g)	117.67	163.19	164.52	202.59	259.44	293.51

Physical colour of water	Milky	Milky	Brown	Brown	Clear	Slight yellow
Physical colour of sludge	White	Dull	Brown	Brown	Brown	Brown
pH of water	7.20	7.18	7.18	7.05	5.79	3.16
pH of sludge	7.10	6.80	6.42	6.31	5.47	3.60
Solid content in water recovered	28.8g/ 1000g	6.2g/ 1000g	3.8g/ 1000g	2.8g/ 1000g	2.5g/ 1000g	2.3g/ 1000g
Redox.P of water	-23mV	-22mV	-22mV	-14mV	55mV	201mV
Turbidity of water	N.M	N.M	N.M	N.M	15FTU	20FTU
Conductivity (mS/m)	198	244	276	300	336	395
Iron content in recovered water (ppm)	N.M	N.M	N.M	N.M	2.08	2.08

Table C5.3 Result of jar test screening experiment-using 0.043moles/Litre ferric chloride solution

Experiment C6 Cylinder test using 0.043moles/Litre ferric chloride solution

pH of waste water	7.77
Redox potential(mV)	-53
Temperature	18^{o}C
Solid content	109.7g of solid in1000g of waste water

Table C6.1.Analysis of waste water using 0.043moles/Litre ferric chloride

pH of flocculant solution	2.02
Redox potential of flocculant solution	259mV
Temperature of flocculant solution	21.1^{o}C
mass of flocculant in water(g/L)	2.94g/0.42L

Table C6.2. Analysis of 0.043moles/Litre ferric chloride solution.

Cyinder	1	2	3	4	5	6	7	8
Volume of waste water (ml)	400	400	400	400	400	400	400	400
Volume of $FeCl_3$ added (mL)	60	80	100	120	140	160	180	200
Volume of recovered water (mL)	250	230	215	220	280	81	175	236
Volume of recovered sludge (mL)	150	250	285	300	310	479	405	364
Bulk concentration (mol/L)	0.0056	0.0072	0.0082	0.00995	0.0116	0.0133	0.01493	0.0165
Colour of recovered water	clear	clear	clear	clear	clear	clear	clear	clear
Colour of recovered sludge	brown	brown	brown	brown	brown	brown	brown	brown
pH of water recovered	7.29	6.94	6.84	6.05	5.8	3.6	3.58	2.8
Turbidity of water recovered (FTU)	H.T	32	66	N.M	76	65		35
Iron in water recovered (ppm)	#	33	70	#	440	226	236	1138
Redox.P. in recovered water (mv)	-29	-8	-3	41	53	179	174	216
Conductivity of water mS/cm	2.75	3.22	3.68	N.M	3.94	4.3	4.14	5.48

Table C6.3.Results of cylinder test using 0.043moles/Litre ferric chloride solution

Experiment C7 Results of beaker test experiment using 0.043moles/litre of $FeCl_3$ solution

pH of waste water	7.77
Redox potential(mV)	-53
Temperature	18^oC
Solid content	109.7g of solid in1000g of waste water

Table C7.1.Analysis of waste water using 0.043moles/Litre ferric chloride

pH of flocculant solution	2.02
Redox potential of flocculant solution	259mV
Temperature of flocculant solution	21.1^oC
mass of flocculant in water(g/L)	2.94g/0.42L

Table C7.2. Analysis of 0.043moles/Litre ferric chloride solution.

Cyinder	1	2	3
Volume of waste water (ml)	400	400	400
Volume of $FeCl_3$ added (mL)	80	100	200
Volume of recovered water (mL)	230	200	200
Volume of recovered sludge (mL)	270	300	340
Bulk concentration (mol/L)	0.0072	0.0082	0.0165
Colour of recovered water	clear	clear	clear
Colour of recovered sludge	brown	brown	brown
pH of water recovered	7	7.4	6.41
Turbidity of water recovered (FTU)	45	20	13
Iron in water recovered (ppm)	N.M	N.M	27
Redox.P. in recovered water (mv)	-12	-31	21
Conductivity of water mS/cm	3.02	3.46	5.18

Table C7.3 Flocculation results for beaker test using 0.043moles/litre of $FeCl_3$ solution

Experiment C8 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	2.607
Redox potential of ferric chloride solution	280mV
Temperature of solution	26.8^0C

Table C8.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

pH of waste water	7.380
Redox potential of waste water	26mV
Temperature of waste water	25^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C8.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	300	222	240	250	250	265
Volume of recovered sludge (mL)	100	198	200	210	220	220
Physical colour of recovered water	#	#	Clear	Clear	Clear	Clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown

pH of recovered water	7.592	7.560	7.585	7.747	7.471	7.352
pH of sludge	7.161	6.877	6.784	6.682	6.871	6.512
Redox potential of recovered water	14mV	15.3mV	14.9mV	5.3mV	19.8mV	26.8mV
Turbidity of water recovered (FTU)	15866.7	754.59	123	11.06	6.78	11.52
Conductivity of water recovered (mS/m)	341	406	448	480	516	558
Iron in recovered water (ppm)	1.46	1.33	1.21	1.46	1.46	1.2
Mass of dry sludge recovered (g)	31.35	32.75	33.94	35.37	35.54	36.10

Table C8.3 Result of jar test experiment when0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C9 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 120.08g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	1.999
Redox potential of ferric chloride solution	264mV
Temperature of solution	17.1^0C

Table C9.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 120.08g of solids in 1000g of waste water

pH of waste water	7.24
Redox potential of waste water	-24mV
Temperature of waste water	15.5^0C
Solid content of waste water	120.08g of solid in 1000g of waste water

Table C9.2. Characteristics of waste water at 120.08g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400

Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	300	222	240	260	280	220
Volume of recovered sludge (mL)	140	150	240	260	280	300
Physical colour of recovered water	#	#	#	#	#	#
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	7.17	7.17	7.15	7.13	7.20	7.15
pH of sludge	6.93	6.84	6.70	6.57	6.52	6.36
Redox potential of recovered water	-21mV	-21mV	-19mV	-18mV	-23mV	-20mV

Table C9.3 Result of jar test experiment when0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 120.08g of solid in 1000g of waste water

Experiment C10 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 100g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	3.92g of $Fecl_3$ /560g of water
pH of ferric chloride flocculant	2.18
Redox potential of ferric chloride solution	255mV
Temperature of solution	20.6^0C

Table C10.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 100g of solids in 1000g of waste water

pH of waste water	6.92
Redox potential of waste water	-7mV
Temperature of waste water	20.4^0C
Solid content of waste water	100g of solid in 1000g of waste water

Table C10.2. Characteristics of waste water at 100g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	60	80	90	100	110	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0056	0.0072	0.0081	0.0086	0.0091	0.00995
Volume of recovered water (mL)	250	250	260	250	250	280
Volume of recovered sludge (mL)	210	230	230	250	260	240
Physical colour of recovered water	#	#	#	#	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.92	6.87	6.76	6.73	6.19	7.06
pH of sludge	6.13	6.12	6.07	6.09	6.08	6.05
Redox potential of recovered water	-7mV	-5mV	2mV	4mV	6mV	15mV

Table C10.3 Result of jar test experiment when0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 100g of solid in 1000g of waste water

Experiment C11 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 90g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	2.28
Redox potential of ferric chloride solution	244mV
Temperature of solution	13.1^0C

Table C11.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 90g of solids in 1000g of waste water

pH of waste water	6.99
Redox potential of waste water	-11mV
Temperature of waste water	12.1^0C
Solid content of waste water	90g of solid in 1000g of waste water

Table C11.2. Characteristics of waste water at 90g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	300	310	290	260	260	270
Volume of recovered sludge (mL)	210	230	230	220	240	250
Physical colour of recovered water	#	#	#	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.88	7.19	6.47/7.24*	6.45/7.10*	6.38/7.17*	6.17/7.14*
pH of sludge	6.13	6.12	6.07	6.09	6.08	6.05
Redox potential of recovered water (mV)	-5	-22	17/-24*	18/-20*	22/-21*	21/-19*

Table C11.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 90g of solid in 1000g of waste water

[*]= parameters measured after 24 hours

Experiment C12 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	2.04
Redox potential of ferric chloride solution	257mV
Temperature of solution	14.7^0C

Table C12.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

pH of waste water	6.92
Redox potential of waste water	-7mV
Temperature of waste water	13.2^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C12.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	320	270	250	260	260	260
Volume of recovered sludge (mL)	100	170	190	220	240	260
Physical colour of recovered water	#	#	#	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown

pH of recovered water	6.63	6.45/6.87*	6.41/7.04*	6.34/7.03*	6.37/7.06*	6.23/7.02*
pH of sludge	6.13	6.12	6.07	6.09	6.08	6.05
Redox potential of recovered water (mV)	9	18/-1	21/-14*	25/-13*	23/-14*	30/-12*

Table C12.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

[*]= Parameters measured after 24 hours

Experiment C13 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	2.00
Redox potential of ferric chloride solution	261mV
Temperature of solution	18.3^0C

Table C13.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

pH of waste water	6.68
Redox potential of waste water	6mV
Temperature of waste water	17.7^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C13.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	320	260	260	270	260	240

Volume of recovered sludge (mL)	100	180	200	210	240	280
Physical colour of recovered water	#	#	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.81	6.86	6.90	6.86	6.77	6.70
Redox potential of recovered water (mV)	-1	-4	-5	-4	1	5

Table C13.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C14 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 84.5g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	2.00
Redox potential of ferric chloride solution	204mV
Temperature of solution	19^0C

Table C14.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 84.5g of solids in 1000g of waste water

pH of waste water	6.83
Redox potential of waste water	-2mV
Temperature of waste water	17.7^0C
Solid content of waste water	84.5g of solid in 1000g of waste water

Table C14.2. Characteristics of waste water at 84.5g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120

Bulk concentration of $Fecl_3$ in moles/Litre	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	320	260	260	270	260	240
Volume of recovered sludge (mL)	100	180	200	210	240	280
Physical colour of recovered water	#	#	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.83	6.77	6.76	6.73	6.69	6.61
Redox potential of recovered water (mV)	N.M	1	2	4	5	10

Table 14.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 84.5g of solid in 1000g of waste water

Experiment C15 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	3.92g of $Fecl_3$ /560g of water
pH of ferric chloride flocculant	2.16
Redox potential of ferric chloride solution	249mV
Temperature of solution	14.8^0C

Table C15.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

pH of waste water	6.82
Redox potential of waste water	-2mV
Temperature of waste water	13.2^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C15.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	60	80	90	100	110	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0056	0.0072	0.0081	0.0086	0.0091	0.00995
Volume of recovered water (mL)	262	280	270	260	270	265
Volume of recovered sludge (mL)	198	200	220	220	240	255
Physical colour of recovered water	#	clear	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.30/7.09*	6.17/7.13*	6.16/7.18*	6.16/7.18*	6.16/7.02*	6.25/6.93*
pH of sludge	N.M	6.28	6.19	6.13	6.05	6.07
Redox potential of recovered water (mV)	27/-27*	33/-29	40/-29*	38/-32*	34/-22*	24/-11*

Table C15.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

[*]= Parameters measured after 24 hours

Experiment C16 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	3.92g of $Fecl_3$ /560g of water
pH of ferric chloride flocculant	2.16
Redox potential of ferric chloride solution	254mV
Temperature of solution	14.8^0C

Table C16.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

pH of waste water	6.82
Redox potential of waste water	-2mV
Temperature of waste water	13.2^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C16.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	60	80	90	100	110	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0056	0.0072	0.0081	0.0086	0.0091	0.00995
Volume of recovered water (mL)	265	250	250	270	270	250
Volume of recovered sludge (mL)	195	230	240	230	240	270
Physical colour of recovered water	#	clear	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	7.18	7.21	7.27	7.13	7.17	7.24
pH of sludge	N.M	6.37	6.27	6.15	6.12	6.08
Redox potential of recovered water (mV)	-31	-33	-35	-28	-31	-35

Table C16.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C17 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

Mass of flocculant $Fecl_3$ /Mass of water	3.92g of $Fecl_3$ /560g of water
pH of ferric chloride flocculant	2.20
Redox potential of ferric chloride solution	252mV
Temperature of solution	13.8^0C

Table C17.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water

pH of waste water	6.64
Redox potential of waste water	-9mV
Temperature of waste water	12.8^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C17.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	60	80	90	100	110	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0056	0.0072	0.0081	0.0086	0.0091	0.00995
Volume of recovered water (mL)	270	280	285	290	270	290
Volume of recovered sludge (mL)	190	200	205	210	240	230
Physical colour of recovered water	#	clear	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	7.06	7.04	7.08	7.03	7.02	7.14
Redox potential of recovered water (mV)	-33	-33	-36	-32	-32	-39

Table C17.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C18 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water when pH is adjusted with HCl acid.

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$ /420g of water
pH of ferric chloride flocculant	1.852
Redox potential of ferric chloride solution	280.2mV
Temperature of solution	13.8^0C

Table C18.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water when pH is adjusted with HCl acid.

pH of waste water	6.64
Redox potential of waste water	-9mV
Temperature of waste water	12.8^0C
Solid content of waste water	80g of solid in 1000g of waste water
pH of waste water when HCl is added	5.481
Redox potential of waste water when HCl is added	65.4mV

Table C18.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

pH of acid used=0.455
HCl concentration = 3Molar

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in moles/Litre	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	250	260	270	290	300	320
Volume of recovered sludge (mL)	170	180	190	190	200	200

Physical colour of recovered water	#	clear	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.711	6.813	6.737	6.667	6.67	6.826
Redox potential of recovered water (mV)	24.11	18.3	22.6	25.7	28	N.M

Table C18.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C19 Results for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water when pH is not adjusted with HCl acid.

Mass of flocculant $Fecl_3$ /Mass of water	2.94g of $Fecl_3$/420g of water
pH of ferric chloride flocculant	2.061
Redox potential of ferric chloride solution	280.2mV
Temperature of solution	13.8^0C

Table C19.1. Analysis for ferric chloride flocculant of 0.043mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water when pH is not adjusted with HCl acid.

pH of waste water	7.464
Redox potential of waste water	19.4mV
Temperature of waste water	12.8^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C18.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.043mol/L of ferric chloride flocculant is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	20	40	60	80	100	120
Bulk concentration of $Fecl_3$ in	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995

moles/Litre						
Volume of recovered water (mL)	320	220	250	280	280	300
Volume of recovered sludge (mL)	100	120	200	200	220	220
Physical colour of recovered water	#	#	#	#	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	7.075	6.941	6.899	6.909	6.764	6.679
Redox potential of recovered water (mV)	-6.9	1.0	3.0	3.1	10	8.3

Table C19.3 Result of jar test experiment when 0.043 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C20 Results for ferric chloride flocculant of 0.32mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water when pH is adjusted with HCl acid.

Mass of flocculant $Fecl_3$ /Mass of water	5.00g of $Fecl_3$ / 95.00g of water
pH of ferric chloride flocculant	1.809
Redox potential of ferric chloride solution	327.6mV
Temperature of solution	20.0^0C

Table C20.1. Analysis for ferric chloride flocculant of 0.32mol/L concentration when solid content of waste water was 80g of solids in 1000g of waste water when pH is adjusted with HCl acid.

pH of waste water	6.64
Redox potential of waste water	-9mV
Temperature of waste water	12.8^0C
Solid content of waste water	80g of solid in 1000g of waste water
pH of waste water when HCl is added	5.481

Table C20.2. Characteristics of waste water at 80g of solids in 1000g of waste water when 0.32mol/L of ferric chloride flocculant is used.

pH of acid used=0.319
HCl concentration = 3Molar
Volume of acid added =50mL

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	2.7	5.1	7.44	9.50	11.52	13.4
Bulk concentration of $Fecl_3$ in moles/Litre	0.0020	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of recovered water (mL)	212.7	225	227.44	219.5	221.52	213.4
Volume of recovered sludge (mL)	190	180	180	190	190	200
Physical colour of recovered water	#	clear	clear	clear	clear	clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	6.375	6.50	6.264	6.232	6.191	5.956
Redox potential of recovered water (mV)	49.1	42.2	55.6	57.7	58.7	N.M

Table C20.3 Result of jar test experiment when 0.32 mol/L of ferric chloride flocculant is dosed into waste water of solid content of 80g of solid in 1000g of waste water

Experiment C21 Results of flocculation with 0.32moles/Litre of ferric chloride solution at a solid content of waste water 80g of solids in 1000g of waste water.

pH of $Fecl_3$ flocculant	1.809
Redox potential of $Fecl_3$ solution	327.6mV
Concentration of $Fecl_3$ in solution	0.3243moles/Litre
Temperature of $Fecl_3$ solution	20^0C

Table C21.1 Analysis of 0.32moles/Litre of ferric chloride solution at a solid content of waste water 80g of solids in 1000g of waste water.

pH of waste water before dilution	9.012
pH of waste water after dilution	8.754
Redox potential of diluted waste water	-80.6mV
Solid content of waste water	80g of solid in 1000g of waste water
Temperature of waste water	13.2^0C

Table C21.2 Analysis of waste water for flocculation with 0.0326moles/Litre ferric chloride solution when no HCl acid is used.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	2.7	5.1	7.44	9.50	11.52	13.40
Bulk concentration in moles/Litre	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of water recovered (mL)	322.7	295	267	219.5	211.52	193.4
Volume of sludge (mL)	80	110	140	190	200	220
Physical colour of water	#	#	#	#	#	#
pH of water	7.843	N.M	N.M	N.M	N.M	7.004
Redox potential of water recovered	-31.8mv	N.M	N.M	N.M	N.M	15.0mV
$Fecl_3$ concentration (g/L)	0.333	0.6364	0.913	1.167	1.40	1.6154
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown

Table C21.3 Results of jar test flocculation using 0.326moles/litre of ferric chloride

Experiment C22 Flocculation experiment using 0.123moles/Litre concentration of ferric chloride solution as feed

pH of $Fecl_3$ flocculant	2.31
Redox potential of $Fecl_3$ solution	310.5mV
Mass concentration of $Fecl_3$	2%m/m
Temperature of solution	17^0C
Concentration of $Fecl_3$ (moles/Litre)	0.123moles/Litre

Table C22.1 Analysis for ferric chloride flocculant of 0.123moles/litre solution

pH of waste water	8.55
Redox potential of waste water	26mV
Temperature of waste water	20^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C22.2 Characteristics of waste water for flocculation experiment using 0.123moles/Litre

JAR	1(control)	2	3	4	5	6
Volume of flocculant added (mL)	0.043mol/L 120	13.15	19.13	24.80	30.11	35
Bulk concentration in moles/Litre	0.00995	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of water recovered (mL)	270	313	309	274	290	275
Volume of sludge (mL)	250	100	110	150	140	160
Physical colour of water recovered	#	#	#	#	#	#
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of water recovered	7.57	7.560	8.073	7.45	7.385	7.32
pH of sludge	7.19	6.877	7.76	7.13	7.233	7.034
Redox potential of water recovered	22.2mV	10mV	-6.1mV	25.6mV	31.9mV	32mV
Turbidity of water recovered (FTU)	24.80	>>1000	>>1000	>>1000	>>1000	576.5
Atomic adsorption test (ppm)	1.2	N.M	N.M	N.M	N.M	1.3
Time of floc formation	1min 20cs	1min 57secs	1min 35secs	1min 35secs	1min 23secs	1min 20secs
Redox P of sludge recovered (mV)	44.6	8.0	11.7	48.2	42.0	52.1

Table C22.3 Result of jar test experiment using 0.123moles/Litre ferric chloride solution

Experiment C23 Results of using 3M HCl for adjusting the pH of waste water when 0.123moles/Litre of ferric chloride solution is used.

Mass of $Fecl_3$ /Mass of water	5.0g of $Fecl_3$ /250g of water
pH of $Fecl_3$ flocculant	2.14
Redox potential of $Fecl_3$ solution	220mV
Temperature of solution of $Fecl_3$	20^0C
Concentration of $Fecl_3$ (moles/Litre)	0.12324moles/Litre of $Fecl_3$ solution

Table C23.1 Analysis for ferric chloride flocculant at a concentration of 0.123mol/L

pH of waste water + HCl solution	7.0
pH of waste water	8.624
Redox potential of waste water	10mV
Temperature of waste water	20^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C23.2 Characteristics of waste water for the experiment for 0.123mol/L ferric chloride flocculation experiment

JAR	1(control)	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	0.043 mol/L 120	13.15	19.13	24.80	30.11	35
Bulk concentration in moles/Litre	0.00995	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of water recovered (mL)	250	240	230	240	280	220
Volume of recovered sludge (mL)	250	160	130	150	150	210
Physical colour of water recovered	Clear	#	#	#	#	Clear
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of water recovered	7.569	7.29	7.3	7.375	7.309	7.498
pH of sludge	6.807	7.048	6.969	7.050	6.870	6.731
Redox potential of water recovered	76.3mV	38.2mV	36.1mV	33.2mV	35.8mV	24.9mV
Turbidity of water recovered (FTU)	18.24	>1000	>1000	>1000	>1000	11.64
Atomic adsorption test (ppm)	1.4	N.M	N.M	N.M	N.M	1.36
Time of floc formation	1min	1min	1min	1min	1min	1min
Redox P of sludge recovered (mV)	68.3	53.1	57.6	52.8	62.9	71.5

Table C23.3 Result of jar test experiment flocculation using 0.123mol/L ferric choride

Experiment C24 Results of flocculation at 0.686 mol/L ferric chloride flocculant solution

Mass of $Fecl_3$ /Mass of water	24.0g of $Fecl_3$ /216g of water
pH of $Fecl_3$ flocculant	0.871
Redox potential of $Fecl_3$ solution	332.8mV
Temperature of solution of $Fecl_3$	20^0C
Concentration of $Fecl_3$ (moles/Litre)	0.686moles/Litre of $Fecl_3$ solution

Table C24.1 Analysis for ferric chloride flocculant concentration of 0.686mol/L

pH of waste water	8.4
Redox potential of waste water	-69mV
Temperature of waste water	20^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C24.2 Characteristics of waste water for 0.686mol/L ferric chloride flocculant

Volume of waste water (mL)	400
Volume of flocculant added (mL)	5.9
Volume of recovered water (mL)	205
Volume of recovered sludge (mL	200
Colour of recovered water	clear after 2 hours it turned brow
Colour of recovered sludge	brown
pH of recovered water	6.7/ 5.8*

Table C24.3 Result of jar test flocculation experiment at 0.686mol/L ferric chloride feed solution

Experiment C25 Result of flocculation experiment using baffles and inserted addition while gradually dosing

Mass of $Fecl_3$ /Mass of water	24.0g of $Fecl_3$ /216g of water
pH of $Fecl_3$ flocculant	0.871
Redox potential of $Fecl_3$ solution	332.8mV
Temperature of solution of $Fecl_3$	20^0C
Concentration of $Fecl_3$ (moles/Litre)	0.686moles/Litre of $Fecl_3$ solution

Table C25.1 Analysis for ferric chloride flocculant at 0.686mol/L concentration

pH of waste water	8.4
Redox potential of waste water	-69mV
Temperature of waste water	20^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C25.2 Characteristics of waste water used at 0.686 mol/L ferric chloride feed when baffles and inserted addition while dosing gradually

JAR	1	2
size of jar (mL)	600	1000
volume of waste water used (mL)	400	400
volume of flocculant added(mL)	5.9	5.9
volume of water recovered (mL)	180	200
volume of sludge recovered(mL)	2220	200
pH of water recovered	6.926	6.896
colour of water recovered	#	clear
colour of sludge recovered	brown	brown

Table C25.3 Result of jar test flocculation experiment using baffles and inserted addition while gradually dosing

Experiment C26 Result of flocculation using 0.686 mole/Litre of ferric chloride solution.

Mass of $Fecl_3$ flocculant /Mass of water=24.00g of $Fecl_3$/ 216.00g of water

pH of $Fecl_3$ flocculant	0.871
Redox potential of $Fecl_3$ solution	332.8mV
Mass concentration of $Fecl_3$	10%m/m
Concentration in grams/Litre	109g/L
Concentration of $Fecl_3$ solution	0.686mole/Litre
Temperature of $Fecl_3$ solution	30^0C

Table C26.1Analysis of 0.686moles/Litre of ferric chloride flocculant solution

pH of waste water before dilution	9.369
pH of waste water after dilution	7.384
Redox potential of diluted waste water	-69mV
Solid content of waste water	80g of solid in 1000g of waste water
Temperature of waste water	13.2^0C

Table C26.2. Analysis of waste water for flocculation experiment using 0.686moles/Litre of ferric chloride flocculant solution.

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	1.19	2.28	3.31	4.22	5.1	5.9
Concentration in moles/Litre	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of water recovered (mL)	320.7	299	279	249.5	221.50	213.40
Volume of sludge (mL)	60	80	100	100	120	120
Physical colour of water	#	#	#	#	#	#
pH of recovered water	N.M	N.M	N.M	N.M	N.M	7.004
Redox potential of water recovered (ml)	N.M	N.M	N.M	N.M	N.M	N.M
$Fecl_3$ concentration (g/L)	0.333	0.6364	0.913	1.167	1.40	1.6154
Colour of sludge	Brown	Brown	Brown	Brown	Brown	Brown

Table C26.3. Results of jar test experiment using 0.686moles/Litre ferric chloride solution

Experiment C27 Result of flocculation using 4.554 moles/Litre ferric chloride solution

Mass of $Fecl_3$ flocculant /Mass of water= 42.5g of $Fecl_3$ /57.5g of water

pH of $Fecl_3$ flocculant	0.319
Redox potential of $Fecl_3$ solution	419.8mV
Concentration of $Fecl_3$ solution	4.554moles/Litre
Concentration of $Fecl_3$ in grams/Litre	607g/L
Temperature of $Fecl_3$ solution	45^0C

TableC27.1Analysis of 4.554moles/Litre ferric chloride flocculant solution

pH of waste water before dilution	9.369
pH of waste water after dilution	8.159
Redox potential of diluted waste water	-66mV
Solid content of waste water	80g of solid in 1000g of waste water
Temperature	13.2^0C

Table C27.2.Analysis of waste water for flocculation using 4.554mol/L $FeCl_3$

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	0.5	0.6	0.7	0.8	0.9	1.0
Bulk concentration in mol/L	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of water recovered (mL)	320.7	299	279	249.5	221.50	213.40
Volume of sludge recovered (mL)	60	80	100	100	120	120
Physical colour of recovered water	#	#	#	#	#	#
Physical colour of recovered sludge	Brown	Brown	Brown	Brown	Brown	Brown
pH of recovered water	N.M	N.M	N.M	N.M	N.M	7.761
Redox potential of water recovered (mL)	N.M	N.M	N.M	N.M	N.M	N.M
$Fecl_3$ concentration (g/L)	0.333	0.6364	0.913	1.167	1.40	1.6154

Table C27.3. Results of jar test experiment using 4.554moles/Litre ferric chloride solution

Experiment C28 Result of screening for 0.043moles/Litre aluminium sulphate solution

pH of waste water	7.89
Redox potential of waste water	-59mV
Temperature of waste water	16^0C
Solid content of waste water	80g of solid/1000g of waste water

Table C28.1 Analysis of waste water for 0.043moles/Litre of aluminium sulphate

Mass of aluminium sulphate/mass of water	2.94g of $Al_2(SO_4)_3$/420g of water
pH of Flocculant solution	4.03
Redox potential of flocculant	155mV
Temperature	14.02^0C

Table C28.2 Result of analysis for 0.043moles/Litre of aluminium sulphate

JAR	1	2	3	4	5	6
Concentration in moles/Litre	0.0021	0.00392	0.0056	0.0072	0.0086	0.00995
Volume of water recovered (mL)	360	340	360	380	280	260
Volume of sludge (mL)	60	80	100	100	220	260
Physical colour of water recovered	#	#	#	#	#	#
Colour of sludge	White	White	White	White	White	White
pH of water recovered	7.61	7.48	7.52	7.26	7.63	7.79
pH of sludge	6.209	6.178	6.127	6.042	6.013	5.897
Redox potential of water recovered	-42mV	-37mV	-38mV	-25mV	-49mV	-55mV

Table C28.3 Result of experiment for jar test for 0.043moles/Litre of aluminium sulphate solution

Experiment C29 Result of screening using 0.084moles/Litre of aluminium sulphate

Mass of aluminium sulphate/mass of water = 5.04g of $Al_2(SO_4)_3$/420g of water

pH of waste water	7.70
Redox potential of waste water	-56mV
Temperature of waste water	25^0C
Solid content of water	80g of solid in 1000g of waste water

Table C29.1.Analysis of waste water for 0.084moles/litre of aluminium sulphate

JAR	1	2	3	4	5	6
Concentration in moles/Litre	0.0040	0.0076	0,011	0.014	0.017	0.019
Volume of water recovered (mL)	270	250	240	250	235	250
Volume of sludge (mL)	150	190	220	230	265	270
Physical colour of water recovered	#	Clear	Clear	Clear	Clear	Clear
Colour of sludge	White	White	White	White	White	White

pH of water recovered	6.580	6.602	6.751	6.689	6.634	6.468
pH of sludge	6.209	6.178	6.127	6.042	6.013	5.897
Redox potential of water recovered	25.6mV	24.8mV	16.0mV	18.6mV	23.7mV	24.3mV
Turbidity of water recovered (FTU)	12666.7	11300	3600	22.53	8.00	6.48
Conductivity of water recovered (mS/m)	348	372	392	406	412	427
Atomic adsorption test (ppm)	N. M	0.1	0.5	0.2	0.4	0.3
Time of floc formation	4min 37secs	3mins 47secs	2mins 50secs	1min 45secs	1min 32secs	1min 30secs
Mass of dry sludge recovered (g)	37.35	36.12	33.94	35.37	41.54	47.23

Table C29.2 Results of jar test experiment for 0.084moles/litre of aluminium sulphate solution

Experiment C30 Result of flocculation for 0.32moles/Litre (55.5g/L) of aluminium sulphate

Mass of $Al_2(SO_4)_3$ flocculant /Mass of water=10.54g of $Al_2(SO_4)_3$ / 190g of water

pH of $Al_2(SO_4)_3$ flocculant	3.51
Redox potential of $Al_2(SO_4)_3$ solution	234.8mV
Concentration in of $Al_2(SO_4)_3$ grams/Litre	55.5g/L
Concentration of $Al_2(SO_4)_3$	0.32moles/Litre
Temperature of $Al_2(SO_4)_3$ solution	17^0C

Table C30.1 Analysis for aluminium sulphate flocculant of 0.32moles/Litre solution

pH of waste water	8.201
Redox potential of diluted waste water	-12.8mV
Solid content of waste water	80g of solid in 1000g of waste water
Temperature of waste water	15^0C

Table C30.2 Analysis for waste water for 0.325moles/Litre flocculant concentration

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	2.7	5.1	7.44	9.50	11.52	13.40
Concentration in moles/Litre	0.0021	0.00392	0.00563	0.00719	0.00863	0.00995
New volume of solution (mL)	402.7	405.1	407.44	409.5	411.52	413.40
Volume of water recovered (mL)	322.7	320	300	300	205	220
Volume of sludge (mL)	50	60	70	80	120	120
Physical colour of water	#	#	#	#	#	#
pH of water	7.843	7.61	7.491	7.511	7.73	7.75
R. potential of water recovered	-11.8mv	-10mV	-7.7mV	-9.4mV	-21mV	-22.mV
$Al_2(SO_4)_3$ concentration	0.333g/L	0.6364g/L	0.913g/L	1.167g/L	1.40g/L	1.62g/L
Colour of sludge	White	White	White	White	White	White
pH of sludge	7.001	6.99	6.967	6.863	6.969	7.104
Redox potential of sludge	20.5mV	21.3mV	22mV	26.7mV	20.7mV	12.5mV

Table C30.3 Result of flocculation experiment using 0.32moles/litre $Al_2(SO_4)_3$ solution

Experiment C31 Flocculation experiment using aluminium sulphate flocculant of 0.69moles/Litre solution

Mass of $Al_2(SO_4)_3$ flocculant /Mass of water= 12.66g of $Al_2(SO_4)_3$/ 108g of water

pH of $Al_2(SO_4)_3$ flocculant	3.463
Redox potential of $Al_2(SO_4)_3$ solution	237.7mV
Concentration of $Al_2(SO_4)_3$ in grams/Litre	117.2g/L
Molarity of $Al_2(SO_4)_3$ solution	0.69mole/Litre
Temperature of $Al_2(SO_4)_3$ solution	17^0C

Table C31.1 Analysis for aluminium sulphate flocculant of 0.69moles/Litre solution

pH of waste water	8.201
Redox potential of diluted waste water	-12.8mV
Solid content of waste water	80g of solid in 1000g of waste water
Temperature of waste water	15^0C

Table C31.2 Analysis for waste water for 0.69moles/Litre flocculant concentration

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	1.19	2.28	3.31	4.22	5.10	5.90
Concentration in moles/Litre	0.0021	0.00392	0.00563	0.00719	0.0086	0.00995
New volume of solution (mL)	401.19	402.28	403.31	404.22	405.10	405.90
Volume of water recovered (mL)	310	310	320	270	280	260
Volume of sludge (mL)	50	50	70	80	90	90
Physical colour of water	#	#	#	#	#	#
pH of water recovered	7.85	7.73	7.66	7.62	7.67	7.78
Redox potential of water recovered (mV)	-28.7	-21.4	-17.4	-14.8	-18.2	-19.8
$Al_2(SO_4)_3$ concentration	0.33g/L	0.636g/L	0.913g/L	1.17g/L	1.40g/L	1.615g/L
Colour of sludge	White	White	White	White	White	White
pH of sludge	7.74	7.36	7.18	7.00	7.13	7.06
Redox potential of sludge (mV)	-22.9	-1.30	8.70	19.30	12.70	15.70

TableC31.3 Result of flocculation experiment using 0.69moles/litre $Al_2(SO_4)_3$ solution

Experiment C32 Result of flocculation for 4.554 moles/Litre of aluminium sulphate solution.

Mass of $Al_2(SO_4)_3$ flocculant /Mass of water=44.8g of $Al_2(SO_4)_3$ /57.5g of water

pH of flocculant	2.79
Redox potential of $Al_2(SO_4)_3$ solution	272.9mV
Molarity of $Al_2(SO_4)_3$	4.55moles/Litre
Concentration of $Al_2(SO_4)_3$ in grams/Litre	785.96g/L
Temperature of $Al_2(SO_4)_3$ solution	26^0C

Table C32.1 Analysis for aluminium sulphate flocculant of 4.554moles/Litre solution

pH of waste water after dilution	8.201
Redox potential of diluted waste water	-12.8mV
Solid content of waste water	80g of solid in 1000g of waste water
Temperature	15^0C

Table C32.2 Analysis for waste water for 4.554moles/Litre flocculant concentration

JAR	1	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant (mL)	0.5	0.6	0.7	0.8	0.9	1.0
Concentration in moles/Litre	0.0021	0.00392	0.00563	0.00719	0.00863	0.00995
New volume of solution (mL)	400.5	400.6	400.7	400.8	400.9	401
Volume of water recovered (mL)	320	299	280	300	230	250
Volume of sludge (mL)	50	50	80	90	100	100
Physical colour of water	#	#	#	#	#	#
pH of water	7.98	7.77	7.705	7.679	7.737	7.825
Redox potential of water recovered (mV)	-23.0	-22.10	-19.70	-17.80	-22.1	-24.8
Aluminium sulphate concentration	0.333	0.6364	0.913	1.167	1.40	1.6154
pH of sludge	7.50	7.42	7.293	7.089	7.053	7.125
Redox potential of sludge (mV)	1.0	1.98	2.5	13.7	15.81	11.4
Colour of sludge	White	White	White	White	White	White

Table C32.3 Result of flocculation experiment using 4.554moles/litre $Al_2(SO_4)_3$ solution

Experiment C33 Flocculation experiment adjusted pH of waste water using 0.123moles/Litre of aluminium sulphate solution.

HCl concentration= 3Molar.

Mass of $Al_2(SO_4)_3$ flocculant /Mass of water	21g of $Al_2(SO_4)_3$/1000g water
pH of $Al_2(SO_4)_3$ flocculant	3.560
Redox potential of $Al_2(SO_4)_3$ solution	226.7mV
Temperature of $Al_2(SO_4)_3$ solution	20^0C
Molarity of $Al_2(SO_4)_3$	0.12324 moles/Litre of $Al_2(SO_4)_3$

Table C33.1 Analysis for aluminium sulphate flocculant for pH adjusted waste water.

pH of adjusted waste water	7.00
pH of waste water	8.145
Redox potential of waste water	-24.5mV
Temperature of waste water	20^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C33.2 Characteristics of waste water on adjusting pH for 0.123moles/Litre aluminium sulphate flocculant

JAR	1(control)	2	3	4	5	6
Volume of waste water (mL)	400	400	400	400	400	400
Volume of flocculant added (mL)	0.084mol/L 120(mL)	24.5	39.04	51.3	63.2	74.7
Concentration in moles/Litre	0.019	0.0071	0.010	0.014	0.0168	0.0194
Volume of water recovered (mL)	230	300	260	230	200	230
Volume of sludge (mL)	230	120	150	205	210	200
Physical colour of water recovered	Clear	#	#	Clear	Clear	Clear

Colour of sludge	White	White	White	White	White	White
pH of water recovered	7.330	7.134	7.350	7.331	7.302	7.305
pH of sludge	6.575	7.027	7.008	6.634	6.63	6.550
Redox potential of water recovered	28.7mV	29.4mV	30.9mV	28.4mV	30.3mV	30.6mV
Turbidity of water recovered (FTU)	24.11	380.1	250.2	60.8	29.21	21
Atomic adsorption test (ppm)	0.2	N.M	N.M	0.3	0.1	0.2
Time of floc formation	1min	1min	1min	1min	1min	1min
Redox potential of sludge recovered(mV)	73	54.0	63.7	69.4	69.6	74.1

Table C33.3 Result of jar test experiment for adjusted waste water pH for 0.123moles/Litre aluminium sulphate solution

Experiment C34 Flocculation experiment adjusted pH of waste water using 0.123moles/Litre of aluminium sulphate solution.

pH of $Al_2(SO_4)_3$ flocculant	3.56
Redox potential of $Al_2(SO_4)_3$ solution	226.7mV
Temperature of solution	20^0C
Concentration of $Al_2(SO_4)_3$	0.123 moles/Litre

Table C34.1 Analysis for aluminium sulphate flocculant of 0.123mol/L concentration

pH of waste water	8.15
Redox potential of waste water	-24.5mV
Temperature of waste water	20^0C
Solid content of waste water	80g of solid in 1000g of waste water

Table C34.2 Characteristics of waste water used for the flocculation experiment with 0.123mol/L aluminium sulphate solution

JAR	1(control)	2	3	4	5	6
Volume of flocculant added(mL)	0.084mol/L 120	24.5	39.04	51.3	63.2	74.7
Concentration in moles/Litre	0.019	0.0071	0.010	0.014	0.0168	0.0194
Volume of water recovered (mL)	280	300	250	210	220	260
Volume of sludge (mL)	200	120	150	200	200	200
Physical colour of water recovered	#	#	#	#	#	#
Colour of sludge	White	White	White	White	White	White
pH of water recovered	7.721	7.744	7.727	7.692	7.49	7.774
pH of sludge	7.516	7.427	7.258	7.415	7.008	7.384
Redox potential of water recovered	6.3mV	5.3mV	5.9mV	8.0mV	18mV	2.6mV
Turbidity of water recovered (FTU)	2066.7	>>1000	>>1000	>>1000	>>1000	387.5
Atomic adsorption test (ppm)	N.M	N.M	N.M	N.M	N.M	0.3
Time of floc formation	1min 20cs	1min 57secs	1min 35secs	1min 35secs	1min 23secs	1min 20secs
Redox P of sludge recovered (mV)	18.5	24.0	33.7	24.5	47.4	26.8

Table C34.3 Result of jar test experiment when 0.123mol/L aluminium sulphate is added