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Paint wastewater treatment using Fe3+ and Al3+ salts

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CHAPTER 1: LITERATURE REVIEW

Introduction

Water is the most important commodity world-wide because of its domestic and industrial use. Wastewater treatment is a highly recommendable practice for water recycling more especially to both economic and environmental perspective. There is a variety of technological approach in wastewater treatment, some of which are costly and seasonal whereas conventional method which is adopted in this study bears a historic positive track-record. Apart from being the first technique to be employed in wastewater treatment, research still identifies it as one of reputable and best approach mainly because of its simplicity and affordability. Since most of the countries are facing water-scarcity crisis, it is therefore economical for the industries to utilize water economically and also curtail raw water abstraction from the sources, mostly rivers and oceans. Water recycling of both process and auxiliary systems is one of the practices that are essential in water conservation. This can also eliminate contamination of the rivers by industries which discharge contaminated wastewater back into the watercourse, a phenomenon which occurs regularly around the globe. Some of the steel and mining companies paid enormous penalties in the past for environmental degradation such as underground water pollution which is caused by wastewater seepage or overflow.

Conventional wastewater treatment using inorganic coagulants is common because iron and aluminium salts are in abundance and also effective. Common inorganic coagulants include ferric chloride, ferric sulphate, and aluminium sulphate or aluminium chloride. There are various types of chemicals which are dosed during wastewater remediation using modern technological approach. Some are toxic, radioactive and hazardous such as cyanide, mercury and chlorine which are used for gold purification, radioactive elements in nuclear power utilities and chlorine gas for water disinfection. All these chemicals dissolve in drain waters and are discharged into the rivers which also flow into the rivers or oceans. They pose a danger to the ocean ecosystem and are possible causes of material degradation on ships and boats. Potable water purification complexes and hydro-power stations encounter serious operational problems when they have to abstract raw water of such poor quality from polluted rivers and oceans for their processes. Some of the reagents used for pH adjustment such as pulverized $Ca(OH)_2$ also pose a danger to the environment and human-beings. Some water treatment works use polymers for coagulants. These are very expensive coagulants and it becomes costly for the dosages to be optimized to produce treated water of good quality. Hence there are always complaints from the community about the poor quality of potable water which normally result in water-borne diseases. Apart from the type of coagulants and technique, dosages, concentration of metal ions in the coagulant, the rate and duration of mixing also play pivotal role in wastewater treatment. Electron valence, a property that determines the monoprotic, diprotic or tripotic properties of metal ions, is another factor which is an

attribute to the degree of hydrolysis during wastewater treatment. Effective hydrolysis results in a high degree of turbidity removal.

A lot of water treatment works still employ conventional techniques such as a jar test to carry out laboratory tests; which include the determination of chemical dosages each time water quality varies using pH and turbidity measurements. A lot of research has been carried out on wastewater treatment employing various treatment regimes but the production of effluent of good quality still remains a challenge. Some water treatment purification works dose varying dosing patterns, such as coagulant(s) only or combined coagulant and coagulant-aid, polyelectrolytes, but the quality of effluent is still not good. The Ministries of Water Affairs introduced Blue and Green Drop Certification, a qualification conferred to water supplying entities and water treatment training institutions for executing certain tasks in order to supply the community with water of good quality, but there is still proliferation of non-compliant cases reported.

Research Overview

A 200 mL sample of paint wastewater with coagulants dosages was used in all experiments of this study using a jar test during rapid and slow mixing at 250 and 100 rpm respectively, the supernatant was extracted to measure the pH and turbidity. The coagulants which were used include 0.043 M Fe^{3+} or Al^{3+} salts, 0.043 M Ca^{2+} and 0.043 M Mg^{2+} hydroxides, polymers consisting of 0.043 M $FeCl_3$ and 0.043 M Ca^{2+} or 0.043 M Mg^{2+} hydroxides. Another experiment includes placing 2 drops of paint

wastewater on a microscope slide for microscope observation connected to a camera to capture the area covered by flocs from a supernatant of a sample from a jar test and the drops of samples which were manually mixed with drops of coagulants. The paint wastewater samples were also taken for TGA, SEM, XRD for characterization of the metal salts and laboratory glassware. The sludge of the samples with Fe^{3+} and Al^{3+} salts dosages were heated in an oven to determine their water holding capacity.

Experiment 1

In chapter 2, paint wastewater sample was dosed with 0.043 M Fe^{3+} and Al^{3+} salts using varying dosages and dosing patterns. The samples were treated in a jar test, settled for 1 hour and measure pH and turbidity. The concentration of 0.043 M was chosen in this study as it was recommended to be used in paint wastewater treatment by Fasemore (2004). Another batch of experiment was conducted whereby wastewater was dosed with 0.043 M Fe^{3+} or Al^{3+} salts and 0.043 M Ca^{2+} or Mg^{2+} hydroxides for pH adjustment using varying dosages and dosing patterns. The samples were also treated in a jar test, settled for 1 hour and measured pH and turbidity. Another batch of experiments was conducted whereby wastewater was dosed with 0.043 M of synthetic polymers prepared by 0.043 M $FeCl_3$ and 0.043 M $Ca(OH)_2$ or $Mg(OH)_2$ to form $FeCl_2$-$Ca(OH)_2$ and $FeCl_2$-$Mg(OH)_2$ polymers. The samples were treated in a jar test, settled for 1 hour and measured pH and turbidity.

The results obtained showed that the changing pH correlates with turbidity removal in paint wastewater (alkaline) at pH range 7.11-7.73, a normal pH for wastewater

treatment (Freeze *et al*., 2001). It is also observed that the results obtained in flocculation of the paint wastewater dosed with $FeCl_2$-$Ca(OH)_2$ and $FeCl_2$-$Mg(OH)_2$ polymers do not show correlation between the pH and turbidity; when the pH is in the range of 6.58-6.62. This indicates that the pH is not a direct indicator of turbidity removal in acidic paint solutions. The results also showed that dosing sequence and dosing before or during mixing do not play a significant role in wastewater treatment.

Experiment 2

In chapter 3, the second set of experiments was carried out to investigate the possibility of replacing a jar test with a microscope slide observation. Wastewater sample was dosed with 0.043 M Fe^{3+} or Al^{3+} salts and treated in a jar test. Two drops of supernatant was placed on a microscope slide and placed on a microscope connected to a camera, Exp. A. Pictures were captured on different samples after 1, 60 and 90 minutes respectively. Separate wastewater sample and reagent of identical ratios of concentrations as above (0.043 M Fe^{3+} salt/1.6 g in 100 mL) were prepared in 100 mL glassware. Two drops of each were placed on a microscope slide with gentle manual mixing, placed under a microscope and pictures were captured using 1, 60 and 90 minutes time intervals. The visuals were printed and samples from Exp. A were compared with their corresponding visuals from Exp B. The results show that the percentage area covered by the flocs of the paint wastewater treated in a jar test correlate linearly with the percentage area covered by the flocs on the microscope slides. The results obtained using this technique also confirm that the reaction

between the drops of a sample and the drops of coagulant produces well-developed solid hydrolysis species.

Experiment 3

In chapter 4, the third set of experiments was conducted to investigate the effect of rapid and slow mixing on turbidity removal from a paint wastewater in a jar test. Wastewater samples were dosed with 0.043 M Fe^{3+} or Al^{3+} salts. The samples were treated in a jar test using rapid and slow mixing, settled for 1 hour and measured pH and turbidity. The results obtained from the jar tests (rapid mixing only and combined rapid and slow mixing) showed that turbidity in the samples with 30, 45 and 60 seconds rapid mixing showed that most of the flocs are formed within 30 seconds. There is also correlation between the pH and turbidity when paint wastewater is dosed with 0.043 M Fe^{3+} or Al^{3+} salts in their metal salts. The 0.043 M Fe^{3+} and Al^{3+} of the same concentration yielded similar pH and turbidity trend. Another observation revealed that there is correlation between pH and turbidity in samples with rapid mixing only and those with combined rapid and slow mixing.

1.1 Background and justification of wastewater treatment

Water is a commodity that is used in various human and industrial activities. It is used for drinking, bathing, cleaning, irrigation and industrial processes. Industrially, water is used in many processes such as manufacturing, irrigation, rinsing, floor

washing and cooling before it is discharged back into the source such as river or ocean. The discharge of wastewater effluent of poor quality is detrimental to the river ecosystem, groundwater, human and marine transport, hence an investigation on the best wastewater treatment is imperative to avoid undesirable consequences. The investigations conducted in this study are intended to address some of the problems encountered by the water treatment works.

The larger portion of water found in the biosphere is found in the ocean where its ability to perform some of the function is restricted to certain processes only. This restriction is due to the presence of high concentration of dissolved salts from weathering process of rocks and minerals. The supply of freshwater, especially that is not tied up in polar ice caps or flowing underground is much smaller than the quantity of water that is currently used and re-used in many parts of the world. Water which has been used in industrial processes has a high concentration of salts and impurities; hence treatment before re-use is necessary. A large amount of water is used for irrigation compared to other functions. It is also the only industry which does not discharge effluent elsewhere unless irrigation run-off into the rivers/ocean.

Water is used as a solvent and for rinsing the vessels and lines in the paint manufacturing industries. The wastewater requires extensive treatment in order to be suitable for re-use in the industrial processes or discharged back into the watercourse. Paint manufacturing occurs in batches that differ from one another, i.e. silk, matt, tex, solvent-based or water-based. The paint is produced in different batches and then

pumped through the filling lines to storage containers and distributors. After every batch, the equipment and pipelines have to be rinsed with water and discharged to the drainage system. A large amount of water is used during rinsing to avoid possible contamination between batches. Figure 1.1 is an illustration of a paint manufacturing process including treatment and effluent discharge.

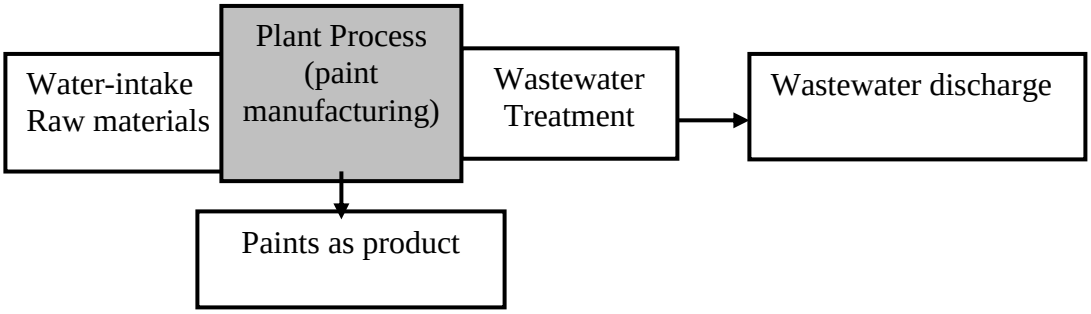


Figure 1.1: Simplified diagram of water flow in paint manufacturing.

Table 1.1 shows the levels of the salt content in discharged effluent from other sources by Gisclon *et al*. (2002) quoting from the South African Bureau of Standards (SABS) of 2002 compared to common paint wastewater.

Table 1.1: Gisclon *et al*. (2002) specifications from SABS (2002).

Parameter	**Reclaimed water**	**Paint wastewater**
pH	6.5 – 9.5	8.2 – 10.5
Iron	<0.04 mg/L	<1000 mg/L
Aluminium	<0.4 mg/L	<1.0 mg/L
Conductivity	<500 mS/cm	<640 mg/L
Suspended Solids	5 mg/L	<20 mg/L
Turbidity	1 FTU	35000 FTU

The process of wastewater treatment involves the separation of water from dissolved and suspended substances. The choice of the best treatment method depends on the physical and chemical properties of the minerals and other constituents to be separated. Since paint wastewater contains settleable organic matter, salts and suspended solids, re-use can be economical and also contribute to environmental preservation. Perry *et al*. (1997) in coordination with Chereminisinoff *et al*. (1989) established waste minimization concept to address waste handling and disposal. The choice of an effective wastewater treatment process relies on the quality and quantity of wastewater and resources to pay for the operating and capital costs of the treatment plant and equipment. The selection of the water treatment process for a specific application depends on the physical form, chemical and biological nature of the impurities. There are various treatment processes that are considerable and coagulation-flocculation is common due to its historical background, low costs and easy maintenance. Paint wastewater is a complex, multicomponent system which makes the treatment complex. This leads to complex interactions between the ingredients of the paint and reagents. The high pH contributes to complexity of treatment dynamics. Aboulhassan *et al*. (2006) discovered that the paint wastewater of poor quality requires a physic-chemical treatment rather than biological treatment due to little organic load in paint. Turbidity is removed from wastewater through a coagulation-flocculation process. This study also entails the investigation of the factors which effect optimum removal of colloidal particles in the paint wastewater using “environmentally friendly” metal hydroxide commonly used for pH adjustment and combine it with inorganic coagulants with the best hydrolysis potential. Metal

hydroxides ($Ca(OH)_2$, $Mg(OH)_2$ or NaOH) are added into wastewater for pH adjustment during treatment. Literature by Flynn (1984) and Kemmer (1988) explains their reaction in wastewater as reagents when reacting with $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$ to form $CaCO_{3(s)}$ precipitate which is removed as sludge. This study investigates the effect of these metal hydroxides in hydrolysis, which is not clearly defined in scientific literature.

There are three main methods which can be employed to economize the amount of process water, namely reduction, recycling and treatment. The two latter methods are intertwined because treatment is a common factor. Adopting such an approach will be useful more especially in the abatement of raw water abstraction from the rivers, which would reduce the risk of water shortage. Scientific research claims that climate change is in the process of endangering the environment to an extend that water scarcity will be predominant in the near future. That will be the time wastewater treatment will be necessary for re-use. The wastewater minimization decision-tree adopted by Perry *et al*. (1997) and Chereminisinoff *et al*. (1989) is shown in Figure 1.2.

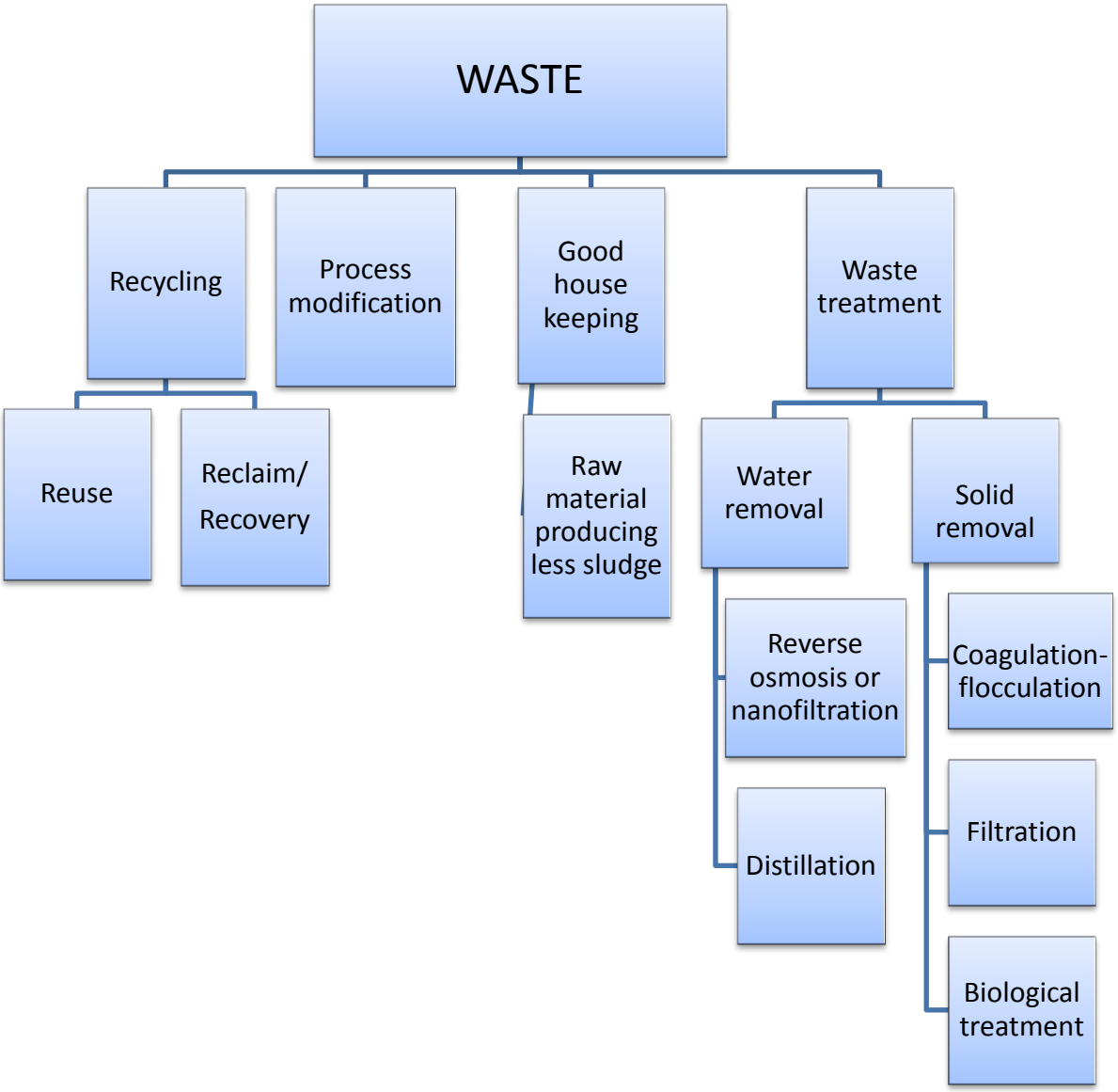


Figure 1.2: Wastewater minimization decision-tree adopted from Perry *et al.* (1997) and Chereminisinoff *et al.* (1989).

Figure 1.2 shows waste related processes, namely recycling, process modification, good house-keeping and waste minimization. It shows the steps which are followed during waste treatment and management which are divided in four main processes namely, recycling, process modification, good house-keeping and waste treatment. Paint manufacturing companies focus more on production and disregard water

recycling, a very important practice. Their wastewater effluent with uncontrolled pH and turbidity is collected by waste management companies in large volumes and are discharged into a water source in poor such conditions. The pH of paint wastewater is normally alkaline as shown in Table 1.1. This is mainly due to calcium carbonate content as it is one of the main constituents.

Re-use of wastewater in paint manufacturing is not a common practice especially for rinsing or floor washing as it is sticky and has an unacceptable odour. Wastewater of such quality can only be re-used if water is separated from chemicals through coagulation-flocculation. Other treatment techniques such as distillation, reverse osmosis, carbon nanotubes, Fenton's reagent, wet oxidation, advanced oxidation, coagulation-electro oxidation are not recommended due to their complexity and high costs. Conventional treatment using Fe^{3+} and Al^{3+} salts is therefore a recommendable option, based on its simplicity to operate and relatively cheap chemicals used. Power utilities and other industries utilize wastewater of poor quality for dust suppression and further cooling of the hot coal ash so as not to damage the conveyor belts. It is also necessary to control the pH of alkaline or acidic wastewater before it can be used in order to reduce scaling and corrosion of the pipe-work respectively (Coulson *et al*., 1999). The importance of pH adjustment is to deter solubility of metallic particles which are detrimental to aquatic life when it is discharged into the river. Another purpose of pH adjustment is to soften wastewater during treatment; where a softener metal hydroxide ($Ca(OH)_2$) reacts with bicarbonate to form calcium carbonate The pH adjustment in acidic medium can be achieved by the addition of metal hydroxide,

mostly $Ca(OH)_2$ whereas hydrochloric acid or sulphuric acid are used in an alkaline medium. The adjustment also plays a pivotal role by effecting precipitation of the dissolved heavy metal ions in the wastewater stream. Research on wastewater treatment using $Ca(OH)_2$ and $Mg(OH)_2$ has been carried out but comparison on their reaction in wastewater was never investigated, a study which is adopted in this study. They are dosed in wastewater treatment for pH adjustment whereas their ability to form polymers when reacting with metal salts to form $FeCl_2$-$Ca(OH)_2$ or $FeCl_2$-$Mg(OH)_2$ has not been noticed, the approach also adopted in this study. This study also investigates turbidity removal efficiency using Fe^{3+} and Al^{3+} salts only, Fe^{3+} and Al^{3+} salts with Ca^{2+} or Mg^{2+} hydroxide as softeners and also synthetic polymers prepared as $FeCl_2$-$Ca(OH)_2$ or $FeCl_2$-$Mg(OH)_2$.

A jar test is a technique employed to determine the effectiveness of the reagents which are used in the experiments stated above, using pH and turbidity as determinants. It is the only common conventional technique which is employed when the pH and turbidity are measured on a laboratory scale (Water Specialist Technology, 2003). It also recommended the use of a jar test to determine optimal dosages when the quality of wastewater changes in order to achieve best results. However, there are some sophisticated and costly modern techniques which have been developed such as particle size distribution (PSD) or chord length distribution (CLD) (Kempkes *et al*., 2007, Li *et al*., 2005, McCurdy *et al.*, 2004 and Li *et al*., 2006). This study investigates a more "user-friendly" technique such as the use of microscope observation of the concentration of the flocs on a microscope slide. The

advantage with microscope observation technique is that it shows representative particle count found in the samples. The study determines the effectiveness of microscope observation and compares the results with those obtained from a jar test.

The treatment of wastewater can be by physical, chemical or biological means. Chemical treatment is the most appropriate method in paint wastewater treatment. This includes the addition of a coagulant, commonly Fe^{3+} and Al^{3+} salts to destabilize the colloid (wastewater). The process is explained by the decreasing or neutralizing surface charge of the particles by adsorbing counter-ionic property of inorganic coagulants, where repulsive forces are reduced or eliminated (Gregory *et al*., 2001). The type of coagulant which are dosed and the time taken during mixing determine optimum velocity gradient (du/dy), change of velocity per change of distance, to disperse the reagents throughout the solution. Velocity gradient depends on the speed of the impellors during stirring and influences the type of destabilization. Destabilization is classified into four categories such as double layer compression, neutralization, particle bridging and entrapment in a precipitate (Sincero *et al.,* 2003). It also plays a major role on the efficiency of metal salts (coagulants) to destabilize the colloidal system. An excellent design of mixing devices requires high velocity gradient, which can be as high as 1000 s^{-1} with minimum chemical dosage. The polyelectrolytes function effectively when the velocity gradient is in a range of 400–1000 s^{-1} (Binnie *et al*., 2003). Fe^{3+} and Al^{3+} salts produce best results at velocity gradient between 20 and 70 s^{-1} (Swartz *et al*., 2004).

1.1.1 Conventional methods in wastewater treatment

$FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ are metal salts which are used in conventional wastewater treatment. They are dispersed throughout the solution during the mixing process, thereby causing colloidal destabilization and hydrolysis. Destabilization and hydrolysis form a greater part in this study, as they are used to explain the rate at which pH changes to yield better turbidity removal efficiency in a colloidal suspension during paint wastewater treatment. Effective settling of the flocs is influenced by factors such as the type of coagulant(s), mixing rate, mixing duration, structure of the clarifier and operating practice (Jiang *et al*., 1997). Wastewater treatment using inorganic coagulants has been the common process based on its easy operation and affordable operating costs. It is also preferable due to removal efficiency of organic matter, colour, odour and pathogens from paint wastewater.

pH is one of the significant parameters that determine the reduction efficiency of minerals in the wastewater (Pratt *et al*., 2007). The addition of aluminium and iron at pH of 6-8 fastens the rate of hydrolysis, leading to very rapid precipitation (Jiang *et al*., 1997). That is caused by the presence of high concentration of hydroxyl ions which increases the number of OH^- ions bound to each metal ion (M^{3+}). This reduces the charge on the hydroxo-ferric complex and the reduction of repulsive energy allows easier adsorption of hydroxo-ferric complexes (Duan *et al*., 2002). The problem encountered during hydrolysis is the inability to control the nature of coagulant species formed, as some do not play any role in adsorption. It is possible

that the hydrolysis products may be adsorbed onto the colloidal surfaces to neutralize the charge or it may interact with dissolved components in wastewater (Jiang *et al*., 1997). The rate of coagulant-colloid interaction has to be faster than the rate at which the hydroxides precipitate in order to yield maximum flocs formation. This condition is only possible with a low dosage of metal cation when the pH of the wastewater is lower than 6 and the concentration of the colloid is moderate to high (Jiang *et al*., 1997). When the dosing is restricted to a narrow range, it becomes very hard to dose the correct amount due to changing wastewater quality randomly. The ratio between the concentration of the metal ion (M^{3+}) and the mass of the colloidal particles in wastewater is important. Metal ions hydrolyse when added into wastewater, forming three types of hydrolysis species, $M(OH)^{2+}$, $M(OH)_2^{+}$ and a stable ($M(OH)_{3(s)}$) as would be shown later. The stable hydrolysis species ($M(OH)_{3(s)}$) adsorb a larger amount of colloidal particle, resulting in reduction of colloidal particles in the colloid. In this study, turbidity removal potential of Fe^{3+} and Al^{3+} salts is determined by dosing the same quantity of paint wastewater with varying dosage, dosing before or after mixing and varying rates of mixing. When the pH of the wastewater is lower than 6 and the dosage exceeds the optimal dosing point, the quality of treated water becomes poor because of re-stabilization of the colloidal particles due to charge reversal at the colloidal surface. A high chemical dosing is required when the pH is above 6 in order for wastewater treatment to produce effluent of good quality. Electrophoretic technique is used to determine the effect of pH in coagulation-flocculation. It is assumed that the resulting charge in the flocs may be caused by the

adsorption of either H^+ or OH^-. pH and buffering extent which is caused by charge neutralization play a major role in coagulation-flocculation (Juttner *et al.*, 2000).

A study was conducted by Amuda *et al*. (2006) on textile wastewater in Pakistan to determine the optimum dosage of coagulants at suitable pH to achieve maximum removal and settling characteristics of resultant flocs. Different coagulants and reagents such as ferric chloride, aluminium sulphate, lime and their combinations were dosed in the Pakistan study. Lime and polyelectrolyte magnoflocs were used as coagulant aids. The pH, dosage of coagulant aids and suitable coagulant were considered as the indicators. The results of the research found that optimum pH in textile wastewater for effective coagulation was within 5-6 (Amuda *et al*., 2006). Since the wastewater was alkaline, sulphuric and hydrochloric acids were dosed for pH adjustment. The former was recommended because bulky flocs were produced with high settling velocity. The amount and nature of suspended solids in wastewater determine the dosage required for best results, optimal flocculation. The second observation revealed that ferric chloride with or without lime/polyelectrolyte could not coagulate suspended particles in the wastewater. Aluminium sulphate produced reduction efficiency of 90 % suspended solids, 20-50 % BOD and COD within 60 minutes. Reduction efficiency of aluminium sulphate alone was less compared to when it was dosed with lime and polyelectrolyte (magnofloc) in textile wastewater (Amuda *et al*., 2006).

- **Interaction of polyelectrolytes with colloids**

Polyelectrolytes are organic coagulants that serve as alternative coagulants to Fe^{3+} and Al^{3+} salts (Droste, 1997). They are linear or branched polymers that can be used as principal coagulants or coagulant-aids in wastewater treatment. These are formed by monomers that contain an ionisable group such as carboxyl, amino or sulfonic and identified by their high molecular weight. They are cationic, anionic and the heaviest non-ionic with a molecular weight of 1, 4 and 30 million respectively. Cationic coagulants react similarly to metallic coagulants as both are positively charged and hydrolysis reactions yield hydroxide ions at high pH and become charge neutral. Anionic polyelectrolytes carry carboxyl functional group (-COOH) and ionise in water to yield hydrogen ions, turning non-ionic at low pH (Droste, 1997). The ability of the polymer to flocculate depends on the molecular weight and degree of branching. Common polyelectrolytes recommended in flocculation are cellulose compounds, polysaccharide gums, proteinaceous materials, starch and starch derivatives (Faust *et al*., 1983). The use of polyelectrolytes as coagulants is critical as coagulants overdosing can result in re-stabilization. This occurs when the flocs are re-dispersed back into the recovered water due to mutual repulsion. Polyelectrolytes are therefore suitable only for treatment of wastewater of a uniform quality and yield good results in wastewater with low turbidity (Freeze *et al*., 2001). The flocs formed by organic polymers are stronger than those formed by Fe^{3+} or Al^{3+} and can withstand higher shearing stresses. Organic polymers perform poorly when polymer segments are detached to form monomers, thus causing re-stabilization of particles (Swartz *et*

al., 2004). The disadvantage of polymers usage in wastewater treatment is that they operate effectively within a limited pH range. They also do not affect the pH of the wastewater as compared with metallic coagulants (Nozaic *et al.*, 2001). They produce less sludge in comparison to metallic coagulants, hence turbidity removal is relatively ineffective. One of the investigations in this work is to determine the effectiveness of synthetic polymers on turbidity removal in paint wastewater as replacement of commercial electrolytes. Pratt *et al*. (2007) stated that turbidity removal in wastewater treatment occurs through adsorption of colloidal particles by the flocs which have been formed during hydrolysis. Adsorption cannot be explained only in terms of increased electrical repulsion or decreased van der Waals forces. The process also involves the steric repulsive forces. When two particles collide, the outer layers interact in several possible ways as detailed by Ives (1978).

- Adsorption equilibrium is affected and causes either increase or decrease in the amount adsorbed. Increasing adsorption correlates to the increase in forces of attraction between the surfaces whereas repulsive forces lead to desorption. Adsorption and desorption are processes that are relatively slow for polymeric materials and that creates uncertainty about their role during the collision of particles.
- Adsorbed layers might be compressed and reduce the volume of the particles, hence limit the number of possible configurations for adsorbed polymer chains. A reduced number of configurations is a sign of decreased entropy, where increasing free

energy and repulsion between the particles become apparent. This phenomenon is sometimes called volume restriction or the elastic effect.

- Adsorbed layers may interpenetrate and increase the concentration of the polymer molecules bridged between the particles that are responsible for either attraction or repulsion. This process in known as mixing or the osmotic effect.

Ali *et al.,* (2002) conducted further study on the wastewater treatment focusing on electrical phenomena at surface. They stated that wastewater contains microscopically visible colloidal particles which possess high electrophoretic mobility or high zeta potential. It was also discovered that electrophoretic mobility decreases in aluminium sulphate to zero at optimum coagulation proportions where charge reversal is possible. The removal of organic colour coincides with zero electrophoretic mobility during flocculation with ferric sulphate. It was later confirmed that the complex art of water treatment should use the measurement of electrophoretic mobility or zeta potential to predict correct dosage of coagulant for best treatment results. However, the considerations for electrophoretic characteristics of colloids and their stability apply only to hydrophobic colloids. Detergents are "hydrophilic colloids" that may or may not coagulate and are also soluble at their isoelectric point and therefore may not coagulate over any range of electrophoretic mobility or zeta potential. This type of problem is common in water purification.

1.1.2 Other reagents used in wastewater treatment

Soda (Na_2CO_3) ash, caustic soda (NaOH) and lime ($Ca(OH)_2$) are other reagents that are used for pH adjustment during wastewater treatment. Liquid caustic soda is recommended in small plants and plants that require minor upward pH adjustment whereas solid caustic soda in boiler feed water pH adjustment run-ups (Amirtharajah *et al*., 1982). Caustic can be handled easily provided proper protective equipment is used whereas lime is the most economical chemical for pH adjustment. The disadvantage with lime is that it adds to the turbidity of the solution. It is therefore required to install a lime saturator, a process unit used to mix water with slurry lime from post lime system to restrict the addition of turbidity (Amirtharajah *et al*., 1982). Lime can remove heavy metal by chemical precipitation at highly alkaline state, preferably at as high as pH 11. The advantage with lime is that it is found in abundance at low costs and can also be used to effectively treat effluent containing inorganic materials with concentration of higher than 1000 mg/L. Lime wastewater treatment improves sludge settling, dewatering properties, bacterial inactivation and sludge stability (Kurniawan *et al*., 2006).

1.1.3 Properties of paint wastewater

Paint manufacturing industry is facing challenges of compliance with the legislation and by-laws which address environmental and resource preservation. Paint wastewater is characterized by a substantial amount of organic materials, high

salinity, sulphate-rich, high suspended solids and settleable organic matter. Latex paint is a complex product which consists of organic and inorganic pigments such as TiO_2 and dyestuffs, cellulosic and non-cellulosic thickeners, latexes, emulsifiers, preservatives, anti-foaming agents, solvents and coalescing agents, additives or extenders such as $CaCO_3$, aluminium silicates, iron phosphate, talc and kulu. Other additives used in manufacturing include dispersants, ammonia, AMP-95, glycols and biocides. The micro-particles consist of 30 % TiO_2 content, 10 % resin content, excellent tinting strength, chemically-inert, improved homogeneity and can be used in both water and solvent-base systems to improve the opacity and rheological behaviour of the paint. The disadvantage with micro-particles is their inability to flocculate easily during wastewater treatment for recycling (Molony, 2005). There are no by-products in the manufacturing process because all the raw materials which enter the mixers, reactors, blenders, packing machines exit as products. A varying degree of chemicals used in the manufacturing process contribute to considerable concentrations of biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxic compounds and colour. A discharge of effluent of such poor quality to the environment can cause aesthetic problems, pollutes receiving streams and impedes light penetration (Aboulhassan *et al.*, 2006). It is therefore very critical for paint industry to consider wastewater treatment before it is discharged back to the water source so that all the toxic constituents are removed, hence this study is necessary. Propylene glycol is a paint additive with preventative property against quick evaporation of the solvents and also eliminates demarcations during painting (Molony, 2005). It is a challenge because it cannot be removed from

the wastewater by both clarification and distillation. Another problem is that some of the additives used for stabilization generate odour and volatile organic compound (VOC) that are "environmentally hazardous". Some of important additives which affect paint wastewater treatment include:

- TO_2 concentrates used to provide paint with pigmentation.
- $CaCO_3$ concentrates with average particle diameter of 2.5-10 microns.
- Talc (magnesium, silicon and oxygen) used as an additive.

Table 1.2 shows properties of pigments and extenders, which are some of the additives used for pigmentation in paint.

Table 1.2: Properties of pigment and extender concentrates

	TiO_2	**$CaCO_3$ (1)**	**$CaCO_3$ (2)**	**Talc (1)**
% Pigment	77	0	0	0
% Extender	0	75	80	55
Viscosity (g/cm-sec)	95	90	94	100
FOG microns	<1	<5	<5	20
VOC (g/l)	4.95	2.9	3.7	3.05
Specific gravity	2.06	1.45	1.84	1.525

(1), (2) and (3) represent three types of pigments and extenders.

According to Table 1.2, volatile organic compounds are measured in mass per litre. The concentrations have to be accurate for the product and the environment; hence they have to be verified in each batch as required by EPA. The EPA Test method 24 below is used to calculate volatile organic compound as shown in Equation 1.1.

$$A = (V-W)(D)(10) \quad [1.1]$$

A = VOC content in g/l, V = weight of total volatile in grams, W = weight of water in grams (determined by Karl Fisher titration), D = density in g/mL.

Water and chemicals recovery is essential in paint manufacturing as the products can either be utilized to produce paint of inferior quality which can be used by low-income population or for the manufacturing of bricks, tiles, paves or other processes. Bacterial attack is another problem in paint manufacturing industry during production process. This is predominant after shutdown or holidays when emulsion was not properly rinsed from the pipeline. This is an unavoidable situation because intensive cleaning of the pipeline is impossible because of the viscosity of the paint.

Since the paint wastewater does not meet effluent standards due to high concentration of constituents, treatment is therefore inevitable before it is discharged to a source. The treatment involves physical and chemical decolourisation which includes adsorption, oxidation and chemical precipitation. Conventional chemical treatment has been recommended as the most effective process as it is able to remove organic matter with suspended solids without the interference of toxicity. Advantage of conventional chemical treatment is its ability to effectively remove dye molecules from the effluent rather than partial decomposition of dyes which can lead to the formation of harmful and toxic aromatic compounds. Another disadvantage with conventional chemical treatment is its ineffectiveness at low temperature (Eremektar *et al*., 2006).

It is important for the water catchment officials to enforce recycling of paint wastewater in order to reduce extensive abstraction of raw water as make-up to replenish wastewater loss through drainage; especially in water-scarce countries. Eremektar *et al*. (2006) conducted research at Nippon paint plant in Japan where a waste stream from a water-based paint manufacturing process was used to recover pigments and water for cleaning purpose. The average amount of paint wastewater effluent discharge from the plant was estimated at 20.9-24.5 kL/day. Their findings showed that paint wastewater contained more than 36 % of the solvent (water or thinners). Micro-organisms survive well in water-based paint because they consume available oxygen which enables anaerobic growth.

1.2 Colloids and colloidal suspension

Colloidal system is divided into colloidal suspensions and emulsions. Solids are suspended in water in the former and insoluble liquids (oils) are suspended in water in emulsions. The suspended materials are in two categories, stable material which are caused by the forces of attraction between particle and water (hydrophilic) and mutually repulsive material (hydrophobic) caused by the repulsive forces between neighbouring particles. Hydrated coagulants form hydrophobic colloids in water and the stability which occurs is as a result of electrostatic repulsion whereas stability in hydrophilic colloids (proteins, starches and fats) is caused by forces of attraction between water and particles. It is more difficult to coagulate the stable suspension formed by hydrophilic colloids than hydrophobic colloids (Suzuki, 1990). The large

surface area in a given volume in a colloid allows substances to concentrate and subsequently adsorbed onto this surface or surface of substance and come in contact with water and acquires an electrical charge to give electro-kinetic properties. The surface electrical charges in the colloidal system are caused by the affinity between the colloidal materials in water, ionized atoms or groups of atoms that leave the colloids. The surface charge then attracts the ions carrying opposite charges and creates a cloud of "counter-ions". During this reaction, the adsorption decreases due to increasing repulsive forces between the particles. The colloids that carry similar charges in the medium repel one another. The presence of counter-ions in the medium complicates the repulsion between the colloidal particles and causes fall-off in repulsive forces as distance increases. When the colloidal particles come closer, they are then subjected to van der Waals forces of attraction (Swartz *et al.,* 2004).

Coagulation in a hydrophilic colloid occurs when the colloidal suspension is destabilised due to the reduction of the chemical energy in the system and electrical forces are weakened. Two approaches are used to explain the basic mechanisms of destabilization of colloidal particles. The first approach is based on the coagulant which determines the solubility constants, stability constants, equilibrium constants, heat of reaction, chemical composition and the effective charge and valence type (Ives, 1978). The second approach involves the actual determination of the electrophoretic mobility of individual particles (Faust *et al.* 1967). Electrophoretic mobility is the migration of charged colloidal particles or molecules through a solution under the influence of an applied electric field usually provided by immersed

electrodes. The Schultze-Hardy rule emphasizes that the products of hydrolysis from Al^{3+} and Fe^{3+} salts are more effective in reducing or neutralizing the zeta potential of colloidal particles than the divalent cations (Fault *et al*., 1967).

1.3 Dispersion of colloidal particles

Dispersion is classified as either lyophilic or lyophobic, where the former is characterized by a solid that shows affinity for water or other dispersion medium that forms sols during mixing. Lyophobic sols are formed by the addition of coagulants to a colloidal suspension or as a result of mechanical mixing. Lyopholic sols are sensitive to the addition of electrolytes into a bulk phase (Ives, 1978). Certain lyophobic colloids become unstable and flocculate when coagulants are added. Multivalent ions, Fe^{3+} and Al^{3+} react effective in a medium concentrated with net negative charged particles. Schulze-Hardy rule states that the valence ions with opposite charge to that of the sol determines the effectiveness of coagulation (Ives, 1978). Aluminium salt shows more effectiveness in flocs formation at concentration around 60 mg/L (Ives, 1978 and Meghzili, 2008). Treatment of the solid-liquid interface by chemical addition in the form of surface-active agents or electrolytes can alter colloidal dispersion, causing a change in particle size and interfacial area.

1.4 Theory of coagulation and flocculation

Coagulation and flocculation play a pivotal role in wastewater treatment. The former

involves the destabilisation of the colloid and the latter is the formation of larger flocs which later settle due to high settling velocity (Aboulhassan *et al*., 2006, Aguilar *et al*., 2002, Aguilar *et al*., 2005). The processes occur after coagulants are added to a colloidal suspension such as raw water from the river, industrial or sewage wastewater. Some authors use coagulation and flocculation separately while others use flocculation to refer to both processes (Kemmer, 1988). The distinction between the two processes is that coagulation is the destabilization of the colloid after the addition of the coagulants. This occur when the electrostatic forces of repulsion are reduced and van der Waals forces of attraction increase. Flocculation is a subsequent reaction which occurs when larger flocs are formed through velocity gradient and differential velocity of colloidal particles. The former is explained as the partial derivative of velocity with reference to position within a continuous medium, usually fluid (dv/dx)) whereas the latter is the formation of larger flocs due to Brownian motion of the fluid. Coagulation process depends on the dosage whereas the latter depends on the mixing effect (Dao *et al.,* 2001). Coulson *et al*. (1999) describe flocculation as the formation of large conglomerates of particles with occluded liquid and the flocs which are enlarged particles of higher density intermediate between that of constituent particles and liquid. The forces of attraction and repulsion between colloidal particles, namely van der Waals and electrostatic forces as well as forces due to adsorbed macromolecules influence flocculation (Coulson *et al*., 1999). Different authors describe coagulation-flocculation of flocculation in different forms; hence it is necessary to conduct a further investigation of the subject, an approach adopted in this study.

Coagulation-flocculation is a process which leads to nucleation, crystal growth and aggregation of the destabilised suspended particles in the solution (Kemmer, 1988). Nucleation is the formation of the first particles of precipitate capable of spontaneous growth into large crystals of a more stable solid phase in an unstable, supersaturated solution. Nucleation can be homogeneous or heterogeneous where the former is formed in a bulk solution in the absence of any other solid surface. Heterogeneous nucleation occurs at moderate supersaturation where particles of a material provide the nucleation sites for another material. Subsequent to nucleation is crystal growth that is (1) diffusion of atoms or molecules of crystallising substance through the solution or surrounding environment, (2) diffusion of atoms over the surface of crystals to special sites on the surface, (3) incorporation of atoms into crystal within special sites on the surface and (4) diffusion of heat of crystallization away from crystal surface counter-ions. Adsorption of the coagulant is the mechanism which takes place during coagulation in wastewater to effect charge neutralization, enmeshment of interparticle bridges and agglomeration which are formed in a precipitate. The amount or concentration of coagulants added into wastewater during treatment must be sufficient to exceed the solubility of their metal hydroxides so that precipitates can be formed. There are series of hydrolytic reactions that occur after the addition of coagulants, namely simple hydroxo complexes (MOH^{2+}), colloidal hydroxometal polymers and the metal hydroxide precipitates. Coagulants can be added with concentration that is high enough to rapidly precipitate the metal hydroxide [$Al(OH)_3$], [$Fe(OH)_3$], [$Mg(OH)_2$] or metal carbonate [$CaCO_3$], where colloidal particles are enmeshed in these precipitates (Moore *et al*., 1976). Adsorption

dynamics are defined in various ways by different authors. Some authors such as Kemmer (1988) and Coulson *et al*. (1991) state that the metal hydroxides (flocs) are adsorbed by colloidal particles whereas others state that colloidal particles are enmeshed in these precipitates (Moore *et al*., 1976, Ives, 1978 and Duan *et al*., 2002). This shows that more research is necessary. The colloidal charge in most wastewater coagulation requires positively charged inorganic polymers. Table 1.3 shows the pH values at which common metals precipitate (Moore *et al*., 1976)

Table 1.3: Precipitation of metal hydroxides from dilute solutions vs. pH[a]

Metal	**pH**	**Metal**	**pH**
Fe^{3+}	2.0	Ni^{2+}	6.7
Al^{3+}	4.1	Cd^{2+}	6.7
Cr^{3+}	5.3	Zn^{2+}	6.7
Cu^{2+}	5.3	Co^{2+}	6.9
Fe^{2+}	5.5	Hg^{2+}	7.3
Pb^{2+}	6.0	Mn^{2+}	8.5

Table 1.3 shows that the Hg^{2+} and Mn^{2+} precipitate in alkaline medium whereas the rest in acidic medium. The information can be used during wastewater treatment for pH control.

Flocculation process is further explained as the agglomeration of small particles which are dispersed throughout a colloidal suspension to form larger particles, namely flocs. When these larger particles grow bigger to an extent that they scatter visible light, they are called colloids. Dispersed particles carry charges and create either attractive or repulsive forces amongst the neighbouring particles. When the

attractive forces exceed repulsive forces, the particles coalesce and yield aggregates that settle under gravitational or centrifugal forces. The forces of repulsion from particles that carry the same charge prevent the settling.

Flocculation can also be explained in terms of particle and fluid dynamics. According to flocculation-rate theory, the rate of flocculation depends upon the order of mixing, the extent of adsorption of the coagulant and the character and the extent of the subsequent agitation which determines the size of the floc which has been formed (Goldberg *et al*., 2002). That occurs when the particles are completely destabilised, but there could be some suspensions not affected due to partial stabilization, hence only a fraction of collision is effective. The partial stabilization of suspended particles is caused by an energy barrier which is caused by the interaction between electrical double layer and van der Waals forces. These barriers can be reduced by the addition of electrolytes as they will destabilize the fraction that stabilized. Another factor that retards the rate of flocculation is the thinning of the films of liquid between the particles. The film flows radially under laminar conditions and exerts a viscous resistance that impedes the contact between two neighbouring particles surfaces (Ives, 1978).

Settling plays a major role during the separation of impurities from wastewater. Settling velocity is the most important parameter during wastewater treatment in this regard. The shape of the particles and viscosity of the liquid play the less significant role in determining settling velocity in the colloidal suspension. Under a laminar

flow, the settling velocity of the particles which causes turbidity is directly proportional to the square of its diameter, the shape of the particles and viscosity of the liquid (Barnes *et al*., 1981 and Thomas *et al*., 1996). Brownian motion can disrupt settling indefinitely in colloidal sized (less than 1 µm) particles under stable colloidal suspension. Minute particles have to be induced and come together to form large particles before they could settle rapidly and ready to be removed by sedimentation process (Barnes *et al*., 1981 and Thomas *et al*., 1996).

Brownian motion also plays pivotal role in flocculation by causing collision between the particles to stick together as they move randomly. The probability for collision to occur to any single particle is proportional to the concentration of the particles. At this stage, particles grow to such an extent that Brownian motion no longer plays a role due to collision frequency of the particles in the medium (Amirtharajah *et al*., 1982 and Thomas *et al*., 1996).

- **Perikinetic flocculation**

Brownian motion causes the particles to collide and stick together as they move randomly during perikinetic flocculation stage. Most of colloidal sols (colloidal suspension of very small solid particles) which deal with stability of dispersion are based on perikinetic phenomena. Those phenomena originate from Brownian translation and rotation of the dispersed particles or their aggregates. Perikinetic flocculation is influenced by the thermal condition of the colloidal system and is

induced by the addition of coagulants which reduce or eliminate repulsive barrier. Sometimes unstable sols tend to be slow in perikinetic flocculation due to low concentration of particles and that requires the introduction of large concentration of other particles to enhance flocculation kinetics (Dobias, 1993). Flocculation is classified into micro-flocculation and macro-flocculation. Micro-flocculation is significant for particles in the size range from 0,001 to 1 μm and macro-flocculation for particles of size greater than 1 or 2 μm. Micro-flocculation is also referred to as perikinetic flocculation explained as the aggregation of particles occurring due to random thermal motion of fluid molecules, (i.e. Brownian motion). Macro-flocculation is influenced by induced velocity gradient and differential settling (Metcalf *et al*., 2003).

The formation of flocs has been a subject usually explained by dividing the process in three steps such as coagulation/precipitation, flocculation and particle separation (sedimentation, filtration). Flocs are formed in all three steps but with different particle sizes. The size of particles leaving the first step is formed in seconds in the range 0.5–5 μm and they referred to as primary particles. Floc formation is the second step which occurs when primary particles collide and form bigger settleable flocs of the size range 100–5000 μm. The first step deals with the chemistry of the process while the last two with physical aspects. Coagulation or destabilization of particles/colloids and precipitation of soluble minerals are the two processes which take place when the coagulants (Fe^{3+} and Al^{3+} salts) are added into wastewater. The

former is where separation of impurities from water during wastewater treatment takes place.

- **Orthokinetic flocculation**

Orthokinetic flocculation is the second stage caused by movement of particles close together by gentle water motion. The contact occurs either by random Brownian motion or forced collision of colloidal particles due to velocity gradients that has caused by fluid mixing. The rate of flocculation depends on the particle nature, size, concentration and the velocity shear gradient of the water. Mathematical models have been constructed to determine the effectiveness of some of parameters but could not be validated (Suzuki, 1990). One of the models by Suzuki (1990) assumes that if two or more particles come close together, they collide and form a larger particle. The closeness that determines the collision of the particles to occur is defined as "zone of influence" and if the zones of two particles overlap, then the particles will agglomerate. The model also assumes that the particles are so small (below 0.001 μm) that they have negligible settling velocity and will travel with the same velocity as water. If the water moves at uniform velocity or stationery, relative motion of particles must be established in order to cause collision. This will keep the inter-particle distance unchanged for a long period without any chance of larger floc formation. Some collisions will only occur when there is a velocity shear gradient that will cause relative motion between particles (Suzuki, 1990). It is during this stage that larger particles and flocs are formed where relative motion by velocity gradient

of the particles creates a high shear rate in the liquid phase (Faust *et al*., 1983 and McCurdy *et al.*, 2004). Large particles impart their velocity to the neighbouring particles and the inter-particle bridging within particles in the colloidal system occurs during macro-flocculation stage.

Rapid mixing is more preferable in some water treatment plants operations because it causes the coagulants to disperse immediately throughout the colloid. Agitation is done in a turbulent regime and the chemicals are dosed in a most turbulent zone near the impellor. Rapid mixing causes rapid hydrolysis of coagulants which takes place within seconds. Since rapid mixing influences destabilization-hydrolysis, it is important to have ideal dosage to produce the best results (Swartz *et al*., 2004). Perikinetic and orthokinetic flocculation can occur at equal rates depending on the radius of particles. These measurements were done at various velocity gradients in water at temperature 25 ^{0}C as shown in Table 1.4:

Table 1.4: Particle radii for equal perikinetic and orthokinetic flocculation (Ives, 1978).

Velocity gradient, G (s^{-1})	Radius of particles (μm)
1	1.05
10	0.5
20	0.4
50	0.3
100	0.23

Table 1.4 shows that orthokinetic flocculation co-exists with perikinetic flocculation when particles size between 0.23 to 1.05 μm correspond to velocity gradient in a range of 1-100 s^{-1} (Ives, 1978).

- **Differential settling**

This type of flocculation occurs when particles of different sizes are found in the solution, as in sludge blanket or solid contact clarifier. Relative motion occurs between particles when large particles settle faster than smaller particles. Large particles move downwards to settle and collide with smaller particles that move randomly due to Brownian motion, thus causing flocculation. The movement of large particles can also cause a localized velocity shear gradient that can hasten orthokinetic flocculation of very small particles around that area (Suzuki, 1990)

Thomas *et al*. (1996) stated that the interactions between particles in sufficiently dilute systems are treated as binary collisions between rigid spheres in perikinetic and orthokinetic flocculation. This analysis assumes that relative motion between pairs of particles is described by superposition of isolated particle motion. Each particle behaves in an individualistic manner and the only interactions are from combined attraction and repulsion of electrostatic fields. The force field is caused by van der Waals forces and electrical double layer repulsion.

Transportation and attachment are dynamic reactions that cause flocculation (perikinetic) through collision of two particles by virtue of variation in fluid-particle velocities. Orthokinetic flocculation occurs due to imposed velocity gradients during mixing and differential sedimentation of differential settling velocities of particles (Thomas, 1996).

Sedimentation is the last process that influences kinetics of the system. This is the stage flocs are allowed to settle by gravity due to their high settling velocity. There are three important parameters considered during sedimentation process, namely, sedimentation velocity, degree of flocculation (β) and sedimentation volume (f) or height (H) of flocculated suspension as shown by Equation 1.2.

$$f = V_u / V_O \qquad [1.2]$$

V_u = final or ultimate volume of sediment, V_O = original volume of suspension before settling.

Sedimentation volume is a ratio of the final or ultimate volume of sediment (V_u) and the original volume of sediment (V_O) before settling. When a measuring cylinder is used to measure the volume, Equation 1.2 is employed:

$$f = H_u / H_O \qquad [1.3]$$

H_u= final or ultimate height of sediment, H_O = original height of suspension before settling

Sedimentation volume can have values ranging from less to greater than 1; f is normally less than 1; If f = 1, such product is said to be in flocculation equilibrium and it does not show clear supernatant on standing sedimentation volume ($f_¥$) for deflocculated suspension

$$f_¥ = V_¥ / V_O \qquad [1.4]$$

$f_¥$= deflocculated suspension, $V_¥$= deflocculated volume of suspension (Martin *et al*., 1966). Figure 1.3 shows the processes that occur during flocculation.

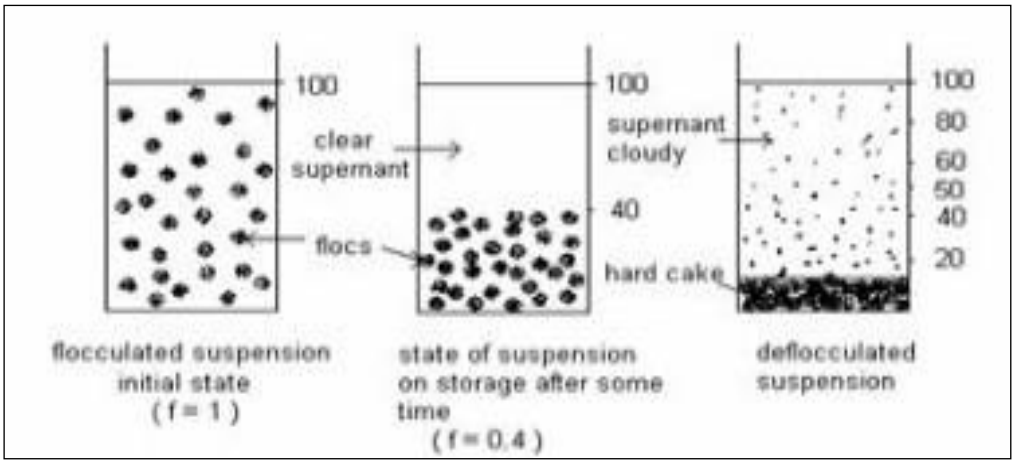


Figure 1.3: Suspensions quantified by sedimentation volume (f), Martin *et al*. 1966.

Figure 1.3 shows three glass beakers containing flocs formed before settling, after settling for a certain period and dispersed colloidal particles which did not form flocs (de-flocculation) respectively. This is one area this study investigates, i.e. direct flocs count using a microscopic observation unlike a jar test using turbidity measurement; which does not depict the visual representation of the flocs formed in the beakers.

Equation 1.5 is an equation of a very useful parameter for flocculation:

$$\beta = f/f\infty \qquad [1.5]$$

$$= V_u/V_o \qquad (\beta = V\infty/V_o = V_u/V\infty)$$

$$= \frac{\text{ultimate sedimentation of flocculated suspension}}{\text{ultimate sedimentation of deflocculated suspension}}$$

After coagulation-flocculation process, sedimentation follows based on the degree of flocculated and deflocculated suspensions. Flocculated suspensions form flocs that settle due to increasing particle size. Porosity of the flocs also plays a pivotal role in sedimentation as liquid is entrapped and the suspensions settle due to larger and heavier size. The settling rate of individual particles is slow and prevents entrapment of liquid medium which also impairs the formation of larger flocs in deflocculated suspensions. The larger flocs settle faster and smaller particles remain dispersed in the supernatant, forming a cloudy appearance whereas in flocculated suspension which are larger and smallest, particles form flocs and settle (Martin *et al*., 1966).

Brownian motion prevents sedimentation by keeping the dispersed material in random motion. The Brownian motion depends on the density of the dispersed phase, density and viscosity of the colloid. Kinetic bombardment of the colloidal particles by the molecules of the medium will keep the particles suspended provided their size is below critical radius, a radius which is below settling velocity. Brownian motion can be observed when the particle size is about 2 to 5 μm where the density of particles and viscosity of the medium allow random motion of colloidal particles. Brownian motion becomes less important and sedimentation becomes favourable when the radius of suspended material increases (Martin *et al*., 1966). Small charged particles do not settle in stationary fluid under gravity within a reasonable time-frame due to their small mass and also subjection to other forces. Figure 1.4 shows the forces acting on a particle.

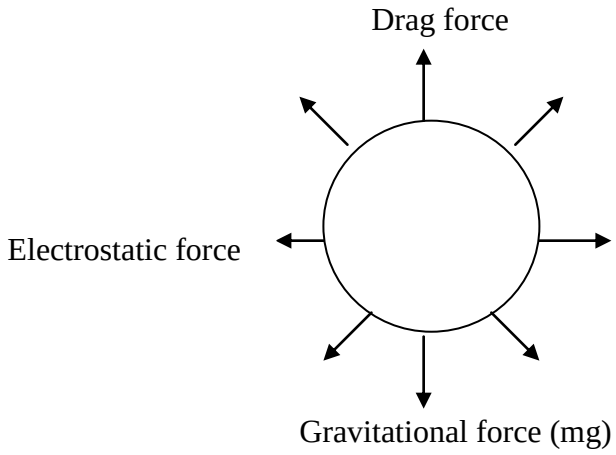


Figure 1.4 Forces acting on a particle

Increasing the mass of the particle such that gravitational force is greater than drag force and neutralizing the charge causes settling of the particles. Flocculation becomes effective when gravitational force is greater than the drag force.

When the density of the suspended particles is greater than that of the dispersion medium, they float above medium. Settling and sedimentation do not occur when the density of the dispersed phase equals to the density of dispersion medium. An increase in viscosity of the medium decreases the settling of particles because sedimentation velocity becomes inversely proportional to viscosity of the dispersed medium. The viscosity is the opposing force to fluid flow which is a characteristic of a medium (Martin *et al*., 1966). Viscosity is proportionality constant between the shear rate and shear stress for Newtonian fluid is expressed by Equation 1.7.

$$\eta = S/D \qquad [1.7]$$

Where η = viscosity, S = shear stress and D = shear rate (η has units g/cm-sec or N-sec/m^2)

Aysegul *et al.* (2002) revealed that mixing dynamics show that there is no uniformity of dispersion during mixing. The velocity of the medium decreases as the medium comes closer to the boundary wall of the vessel. The fast-moving particles overtake slow-moving particles in a velocity field, collide and stick together to form larger particles that are removed by settling or gravity separation. Particles move in a curved

path in an induced velocity gradient towards the settling point and differential settling particles move perpendicularly with different settling times (Metcalf *et al*., 2003).

1.5 Mixing

Mixing is necessary after addition of coagulants to disperse them. There are two types of dispersion processes, one consists of fragile particles with re-agglomeration and the other is process that requires both dispersion and coalescence. The average and maximum shear rates caused by mixing determine the ultimate particle size produced. When the material is kept long enough in the mixing tank, the size of the particles is determined by maximum shear rate around the impeller as they will subsequently move towards that area. The maximum shear rate includes gas-liquid and liquid-liquid dispersion where equilibrium between dispersion and coalescence is established in the mixing tank. Figure 1.5 shows fluid direction during mixing.

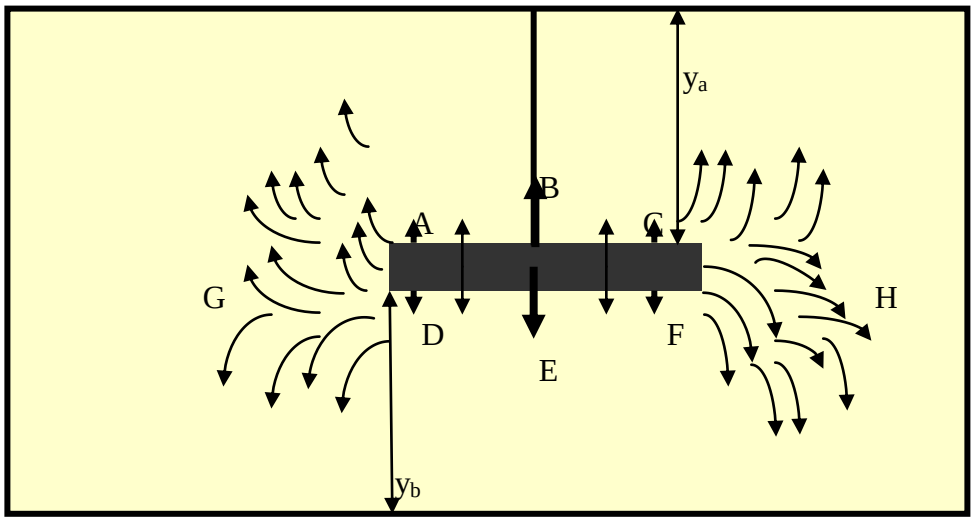


Figure 1.5: Movement of colloid during rapid mixing.

A, B, C, D, E, F, G and H = direction of flow, area inside A, B, C, D, E and F = void created by impeller during turning, y_a and y_b = area not directly affected by impeller.

Figure 1.5 shows the directions of the movement of the colloidal suspension during rapid mixing. The liquid near the impeller experiences maximum kinetic energy whereas above and below is forced upwards and downwards by shear forces respectively. The shear rate plays a pivotal role during dispersion of the metal ions (Oldshue, 1983). The speed of the impeller creates turbulent motion of the colloidal suspension, thus increasing the rate of destabilization-hydrolysis, causing increasing rate of adsorption. The shear rate at high speed breaks the flocs and reduces the surface area of the flocs (Oldshue, 1983). The time taken for mixing relates to shear work, the product of the shear rate and the duration of time taken. This is termed shear rate of strain (shear flow or distortion ratio) expressed as m/m of strain induced in the process. It is therefore essential to determine whether a lower shear rate and longer time may give equivalent results to other patterns of shear rates and the durations of time (Oldshue, 1983). According to the findings of the previous research, intensive extensive mixing for a longer period seems to be an attribute to poor effluent quality by causing rupturing of the flocs (high shear rate) at high speed. The research does not indicate the effective time frame within which maximum flocs are formed. The work in this study investigates the optimal time within which effective flocs are formed to achieve maximum adsorption.

Turbulent dissipation length, the measure of the size of the turbulent eddies is another quantity that plays a role in mixing dynamics. These turbulent eddies are responsible for the energy utilised during mixing. Shear rates are classified into macro- and micro-scale, where the former is responsible for particles size greater than 500 µm or larger and the latter far particles less than 100 µm. There are four considerable quantities in the mixing tank during wastewater treatment namely, maximum velocity at the impeller zone, average velocity gradient in the impeller zone, average velocity gradient in the entire batch zone and minimum velocity gradient in the batch volume (Oldshue, 1983).

Clark *et al*., (1993) conducted studies on the effect of mixing conditions on aluminium precipitation. The studies were based on the neutralization of $AlCl_3$ solutions in a mixing tank reactor where the kinetics of hydrolysis reactions was investigated with respect to mixing time-scale. The research showed that there is competition between formation of polynuclear hydrolysis products and precipitated solids. The findings of research on the formation of flocs by binary encounters through the perikinetic and orthokinetic mechanisms do not clearly define the cause of the flocs break-up in an agitated system. The flocs break-up poses a problem in wastewater treatment as it affects the distribution of floc sizes throughout the flocculating colloidal suspension. The break-up influences the performance of solid-liquid separation processes. Flocs break-up in dilute agitated suspensions is influenced by the interaction of individual flocs with fluid forces (Heath *et al.*, 2002).

1.6 Destabilization process

Destabilization is a process which occurs during mixing and it is as classified under double layer compression, charge neutralization, particle bridging and entrapment in a precipitate. The process occurs immediately after coagulants (metal salts) are added into a colloid and mixed together. Destabilization of the repulsive environment requires the addition of salts which contain multicharged ions that will change the ionic property of the colloidal particles and form aggregates (Kemmer, 1988).

Destabilization by particle bridging does not require rapid mixing as that can break the chain of particles bonded by polymers whereas charge neutralization is affected at lower pH. Binnie *et al.* (2003) stated that the type of destabilization common in a colloid with high velocity gradient around 1000 s^{-1} is double layer compression and charge neutralization is predominant above 5000 s^{-1}. In wastewater treatment where polymers are used as coagulants, the velocity gradient must be in the range 400–1000 s^{-1} (Binnie *et al*., 2003). The results obtained by many researchers confirm that the best treatment results are obtained when the velocity gradient in the mixer is high (Binnie *et al*., 2003). Another advantage of the higher velocity gradient is that a lower dosage is required during the treatment process. Equation 1.8 shows initial hydrated metal ion dissolving in a solution during hydrolysis.

$$Fe(H_2O)_6^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad [1.8]$$

The speciation which results in various hydrolysis species determines the rate of adsorption, a process driven by deprotonation . The speciation occurs when the hydrogen ions from water molecules surrounding the metal ion (hydration sphere) are released into the colloid, and the hydroxyl ions react with the metal ion to form hydrolysis species, Equation 1.8. The hydrolysis chain for a metal ion continues until the formation of an uncharged metal hydroxide with very low solubility, $M(OH)_{3(s)}$.

A study was carried out by Amuda *et al.* (2006) to flocculate sludge from chemical industrial wastewater in order to remove COD, TP and TSS using ferric chloride and non-ionic polyacrylamide. It was found that some municipalities prefer activated carbons for treatment of wastewater; where COD and some volatile organic compounds (chloroform, benzene and carbontetrachloride) are adsorbed onto carbon surface. Their study revealed the best COD, TP and TSS removals of 73, 95 and 97 % occurred at pH 9.0 with ferric chloride dosage of 300 mg/L respectively. The addition of 25 mg/L polyelectrolyte to 100 mg/L ferric chloride resulted in 91, 95 and 97 % COD, TP and TSS removal respectively. Sludge production was higher in the ferric chloride dosage alone compared to 60 % reduction when both ferric chloride and polyelectrolyte were added. It is concluded that coagulation-flocculation may be a useful pre-treatment process in chemical wastewater treatment prior to biological treatment (Amuda *et al*., 2006)

Ghaly *et al*., (2006) conducted experiments using river water at pH 9.5. When alum and ferrous sulphate were dosed in wastewater, pH decreases with increasing dosing

rate. An increase in the concentration of $Al_2(SO_4)_3$ at 1.0-3.0 mg/L resulted in pH drop to 6.2–3.8, whereas $Fe(SO)_4$ caused pH drop to 6.4–5.1. On the contrary, increasing the concentration of $FeCl_3$ by 1.0-3.0 mg/L caused pH drop to 2.3–3.8. The pH of treated wastewater was lower than before treatment with all chemical coagulants, namely 3.8 for $Al_2(SO_4)_3$, 4.1 for $Fe(SO)_4$ and 2.2 for $FeCl_3$.

1.7 Properties of coagulants

1.7.1 Common coagulants in wastewater treatment

In 1989 when aluminium sulphate was used as the main coagulant, water quality regulations in the United Kingdom set a limit on the aluminium concentration in potable water. The limit was as a result of the association of aluminium with Alzheimer's disease. In addition, ferric sulphate was superior to aluminium sulphate because of its effectiveness over a wide range of pH. Another advantage with the former is its use for water decolourization at low pH, removal of manganese at high pH and clarification of water with low temporary but high permanent hardness. Ferric chloride can also be used but the problem is its corrosive properties and difficulty in handling, storage and dosing (Binnie *et al*., 2003).

1.7.2 Combined coagulant and coagulant-aids dosages

Since some wastewater consists of various constituents and additives, a lot of

wastewater treatment works dose combined coagulant(s) and coagulant aids to improve turbidity removal. Coagulant aids have a tendency of forming polymeric chains (polyelectrolytes) which have opposite charge to the colloidal particles. Polyelectrolytes, which are identified by high molecular weight interact with the surface of opposite charged particles and adsorbed, resulting in charge neutralization (Ives, 1978). Polyectrolytes are cationic, anionic and the heaviest non-ionic with a molecular weight of a million, four million and thirty million respectively. Cationic coagulants react similarly to metallic coagulants due to their positive charge and hydrolysis reactions to yield hydroxide ions at high pH and become neutrally charged in nature. Anionic polyelectrolytes carry carboxyl functional group (-COOH) and ionise in water to yield hydrogen ions, turning non-ionic at low pH (Droste, 1997). Ferric chloride and coagulant aids are recommended for complex wastewater treatment due to their ability to effectively remove turbidity, COD, colour and sludge production (Eremektar *et al*., 2006). The complexity of the wastewater is attributed to the presence of compounds such as $FeHPO_4^+$, $AlSO_4^+$ and $MgSO_4$ whereas some are common in natural waters. Organic complexes of metal ions such as strong complexes formed by Fe^{3+}, Ca^{2+} and EDTA are commonly formed. There are also simple hydrated ions found in the colloid such as Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-} etc. These ions are surrounded by one or more hydration layers which depend on the charge carried by the ions and polar nature. Acids are also found in natural water in the form of humic and fulvic acid. They form complexes with ions such as Fe^{3+} and many metals in natural waters exist largely as organically-bound species. Complexation which is caused by metal ions can have a strong effect on flocculation and adsorption

behaviour of metal hydroxides, hence polyelectrolytes are necessary. In some cases $AlSO_4^+$ which consists of Al^{3+} and SO_4^{2-} complex formation occurs in ions of lower charge which decreases flocculating power. The complex compound, $AlSO_4^+$ is a much poorer coagulant than Al^{3+} because of the positive monovalence (Ives, 1978). Unlike with nitrates and perchlorate solutions, electron microscopy shows faster agglomeration of the spheres on polymer in chloride solutions and the appearance of rods in 3-4 hours. The main effect of Cl^- on ageing of the polymer is that the final species formed during precipitation is α-FeO(OH) (Flynn, 1984).

Another approach, namely pre-polymerisation of inorganic coagulants was developed on aluminium and iron salts since the 1980 (Jiang *et al*., 1997). Polymers such as polyaluminium chloride (PACl) and polyferric chloride (PFCl) are used in the process. The preparation involves partial hydrolysis of acidic aluminium chloride and ferric chloride solution in special reactor. Polymeric species formed depend on the concentration of M^{3+}, ratio of moles of the base added and moles of Al^{3+} or Fe^{3+} ions [OH]/[Al] or [OH/Fe] mole ratio, duration on hydrolysis of M^{3+} solution, anions in the solution, mixing mode of base with the M^{3+} solution and nature and strength of the base. The most predominant parameters which govern the nature of species are basic ratio, temperature and time (Jiang *et al*., 1997). PACl and PFCl have been used in wastewater treatment and their use in drinking water has been researched. The results showed that they have high treatment efficiency for heavy metals, COD, turbidity, and reflect superior performance in wastewater at low temperature. $FeCl_3$ showed superior performance in colour removal and organic matter in the surface

water than PFCl; and the advantage with PFCl is its lower sensitivity to water temperature variation (Jiang *et al*., 1997). Apart from the use of metal salts and pre-polymerisation of inorganic coagulants to remove heavy metal in wastewater, lime is also a reagent which can be added to soften the complex colloid as shown by Equation 1.9.

$$Ca(HCO_3)_2 + Mg(HCO_3)_2 + 2\ Ca(OH)_2 \rightarrow 3\ CaCO_{3(s)} + MgCO_3 + 4\ H_2O \quad [1.9]$$

Further investigations of alternative polymerised coagulants in drinking water were conducted in 1990 by Jiang *et al.* (1997). The research on polyaluminium silicate sulphate (PASS) was used in drinking water in Europe, North America and Asia. The comparison between conventional coagulants and PASS showed that the latter requires less pH adjustment and lower dose to achieve the equivalent treatment performance. It also showed a better performance at low temperature, improved natural organic matter removal and low concentration of residual coagulant in treated water (Jiang *et al*., 1997). Although there were some advantages associated with the technique, it is labour-intensive and costly to prepare the coagulants compared with conventional wastewater treatment.

1.7.3 Effect of the pH in coagulation-flocculation

Fe^{3+} and Al^{3+} salts are added into wastewater and hydrolyse to form insoluble material, namely ferric hydroxide or aluminium hydroxide respectively. Acid is

produced in the reaction resulting in a decrease in the pH of the solution. Hydrolysis involves deprotonation of the metal ion surrounded by six water molecules to form a series of multivalent charged hydrous oxide species. These species may range from positive metal hydroxides at low pH to negative metal hydroxides at a more alkaline state, which subsequently form hydrous oxide species with only one metal ion. Both hydroxide and hydrogen ions are involved in coagulation, where the pH plays a significant role (Hubell *et al*., 2003). The formation of metal hydroxides depends on the solubility of metallic particles which also depends on the pH of the medium. Al^{3+} and Fe^{3+} have limited solubility around neutral pH because of precipitation of amorphous hydroxide which plays a pivotal role in coagulation and flocculation processes. The positively charged precipitates may be deposited on the impurities (hetero-coagulation) causing charge neutralization and destabilization (Duan *et al*., 2002). The precipitation of the dissolved heavy metal ions occurs effectively when the pH of a wastewater stream has been adjusted. The wastewater pH has to be adjusted to a level at which the metal salts reach their minimum solubility; normally between 7.5 and 11. Coagulants with low solubility can achieve very high removal efficiencies. When they are used as a "polishing coagulants", the dosage can be lowered depending on the quantity of metals that are precipitated as hydroxides by adjusting the pH level. The pH of 8.5 is normally recommended for the polishing effect but its value will vary depending on the presence of chelating or complexing agents in the wastewater. A jar test can always be employed to ensure that the optimum pH between 7.5 and 11 is determined. The pH is adjusted by addition of

sodium hydroxide, soda ash or lime in an acidic solution whereas hydrochloric acid or sulphuric acid in an alkaline solution (Water Specialist Technology, 2003).

The type of the material and the pH of the solution determine the charge on the colloidal surfaces. High pH (alkaline) colloids become negatively charged and positively charged at low pH (acidic). This can be interpreted as the exchange of H^+ and OH^- ions in a water medium to maintain equilibrium. The wastewater can also be at a neutral point (isoelectric point), which is when the charges of the materials present in the wastewater is neutral, depending on the nature of the colloids and the concentration of other materials. At this point, there is no charge mobility and destabilization through neutralization cannot continue.

The addition of aluminium sulphate and sodium hydroxide in wastewater changes the pH of the medium. The sulphates from aluminium sulphate ($Al_2(SO_4)_3$) undergo hydration reactions to form HSO_4^- and OH^- whereas lime ($Ca(OH)_2$) forms Ca^{2+} and OH^-. Wastewater treatment with lime yields improved sludge settling, dewatering characteristics, bacterial inactivation capability and sludge stability. Lime is commonly used internationally in inorganic effluent treatment with metal content higher than 1000 mg/L and the pH of 11. Advantages of lime include simplicity of process, inexpensive equipment requirement, convenient and safe operation. Disadvantages with lime include clogging of pipeline, excessive sludge production that requires further treatment, high cost of sludge disposal, slow metal precipitation, tendency to increase turbidity, poor settling, aggregation of metal precipitates and long-term environmental impact of sludge (Kurniawan *et al*., 2006). The optimum pH value for various water or wastewater treatments can be determined through jar tests.

Several experiments confirmed that aluminium hydroxide has minimum solubility at neutral pH of 7, where lower values increase the solubility rapidly whereas higher values increase solubility slowly (Binnie *et al*., 2003). The type of destabilization also plays an important role in the pH of the solution, e.g. for charge neutralization the pH must be 5 (acidic) so that the excess positive charges will neutralize negative charges in colloidal particles. Ferric hydroxide has minimum solubility in a wide pH range of 7–10, that gives it more flexibility during hydrolysis. Any pH outside this range increases the solubility of iron than aluminium hydroxide (Binnie *et al*., 2003).

Some other experiments which were conducted in Thailand showed that a complete Zn^{2+}, Cd^{2+}, Mn^{2+} cations removal in synthetic wastewater was achieved at pH 11. Wastewater with Ni^{2+} concentration of 51.6 mg/L was treated at pH 7.5 and 10.5; the results show 71 and 85 % Ni^{2+} removal respectively. This high percentage removal could be due to the removal of a higher concentration of Ni^{2+} in the form of insoluble hydroxide compounds at higher pH values (Kurniawan *et al*., 2006).

1.7.4 Factors which affect hydrolysis

There are two coordination complexes formed during hydrolysis of a metal ion, namely octahedral and tetrahedral. The octahedral coordination complex is acidic and the tetrahedral is basic. These reactions are given by Moore *et al*., (1978) as follows:

$$[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H_3O^+ \qquad [1.10]$$

$$[M(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [M(H_2O)_4(OH)_2]^{+} + H_3O^{+} \quad [1.11]$$

$$[M(H_2O)_4(OH)]^{+} + H_2O \rightleftharpoons [M(H_2O)_3(OH)_3] + H_3O^{+} \quad [1.12]$$

This species, $[M(H_2O)_3(OH)_3]$, the metal hydroxide starts to behave like a weak oxo acid which ionises to give oxo anions where water molecules are dismembered from the hydrated metal to form:

$$[M(H_2O)_3(OH)_3] \rightleftharpoons [M(OH)_4]^{-} + H_3O^{+} + H_2O \quad [1.13]$$

$$[M(OH)^{-}_4] \rightleftharpoons [M(O_4)]^{5-} + 4\ H^{+} \quad [1.14]$$

$$[M(O_4)]^{5-} + 2\ H^{+} \rightleftharpoons [M(O_3)]^{3-} + H_2O \quad [1.15]$$

$$[M(O_3)]^{3-} + [M(O_4)^{5-}] + 8\ H^{+} \rightleftharpoons [M_2(O_3)] + 4\ H_2O \quad [1.16]$$

Equation 1.12 is a stable metal hydroxide with maximum flocs formation. This is followed by adsorption of the colloidal particles which are suspended in the solution. Equations 1.13-1.16 show the series of anionic hydrolysis reactions which result in metal oxide.

Adsorption process often dominates flocculation and aggregation in the solution. Factors that play an important role in the process are translational and rotational motion of dispersed particles in the liquid, surface charge of particles and the interaction forces between particles. The sign and the magnitude of surface charge are

directly related to colloidal stability and influence the adsorption characteristic of particles. Molecules which are adsorbed on the surface change the surface charge and particle interaction through structural effects. Adsorbed layers of polyelectrolyte are affected by the long-range electrostatic repulsive forces between the surfaces of the particles and can adjust since they depend on the pH, salt concentration and surface charge (Sulkowski *et al*., 2005). Ferric ions readily undergo hydrolysis, complexation, polymerization and precipitation in aqueous solution. In general, the ferric ion monomers and polymers produced during hydrolysis have a stronger tendency to precipitate than aluminium. Stabilization of the iron polymers to optimal state of coagulation is always a problem when coagulant and commercial products of high quality have to be prepared. The study of Fe^{3+} hydrolysis is carried out on partially neutralized solution prepared by slow addition of a base. Despite numerous investigations, the mechanism of hydrolysis-polymerization-precipitation of Fe^{3+} and the quantitative principles have not been clearly defined (van De Woude *et al*., 1983). The nature and behaviour of hydrolysis products are controlled by the components and the concentration of the primary Fe^{3+} solution, pH, components of co-existing anions, temperature, time of ageing, traces of contaminants including dust particles which can seed the precipitation of the solid, preparation methods and other chemical transformation (van De Woude *et al*., 1983).

Hydrolysis of the metal ions can also be related to the electron configuration of the metal element. This occurs during hybridization of the metals when they start reacting

during chemical reactions (Wulfsberg, 1987). The structural formulae of Fe^{3+} and Al^{3+} metal salts which are used as coagulants in the experiments are:

Fe = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Al = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

Fe^{3+} is more hydrophilic than Al^{3+} and it therefore releases more H^+ in the solution during hydrolysis. Fe^{3+} and Al^{3+} are expressed as $M(H_2O)_6{}^{3+}$ during hydrolysis, where a metal ion is surrounded by water molecules. The proton from the metal complex is drawn towards the secondary water molecules to form hydronium ions, H_3O^+ as shown by Equation 1.8. The pH decreases as more hydrogen ions are released due to a high hydrophilicity. Hydration energy (exothermic) plays a role in the structural configuration of the compounds, hydration energy and the radii of Fe^{3+} and Al^{3+} are 4376 and 4660 kJ/mol, 78 and 67 µm respectively. Three stages of hydration occur, the first endothermic process includes a change in enthalpy (ΔH) when the water molecules overcome attractive forces in the solute particles to break chemical bonds. The second endothermic process includes the separation of the solvent molecules to accommodate the solute and the third is exothermic process which includes the formation of new attractive interactions between solute and solvent particles. Energies 1 and 2 are added and if they are greater than 3 (negative number), the process is endothermic (Wulfsberg, 1987). The precipitation rate of metal ions is determined by:

$$pH = pK_a - (1/z) \log [M^{z+}] - 5.6/Z \qquad [1.17]$$

The pK_a values for Fe^{3+} and Al^{3+} are 2.2 and 5.0 respectively. The processes that are involved in hydration energy give a number of species which are formed from $M(H_2O)_6^{3+}$, $[M(H_2O)_5.OH]^{2+}$, $[M(H_2O)_4.(OH)^{+}]_2$, $[M(H_2O)_3(OH)_3]$ $M(OH)_4^{-}$, MO_4^{5-}, M_2O_3 as shown by Equations. 1.10-1.16. Such a chain of hydrolysis species reactions starts from iron cations, hydroxo cations, precipitates, hydroxo anions, oxo anions. Table 1.6 shows a comparison of some of their properties of Fe and Al:

$$pK_a = 15.14 – 88\ 16\ (Z^2/r) \qquad [1.18]$$

Table 1.5: Comparison between the properties of Fe^{3+} and Al^{3+}.

Metal	Radius (Å)	χ_p	Z^2/r	Max oxid No.	pk_a
Fe	1.25	>1.8	0.04 - 0.1	6	1 - 6
Al	1.18	1.5	0.1–0.16	3	1 - 6

The properties of iron and aluminium can be used to determine their reactivity. χ_p=Pauling electronegativity and Z^2/r = charge per surface area. Wulfsberg (1987) discovered that the metal ions with electronegativity above 1.5 such as Fe are more acidic and have a higher hydrolysing potential than those less than 1.5. The ratio Z^2/r also determines hydrolysis reactivity of a metal ion, both Fe^{3+} and Al^{3+} have ionic charge of 3 and radii 1.25 and 1.18 (ionic radii 0.64 and 0.52) respectively. Both metal ions show high hydrolysing potential because their charge density is equal and greater than 0.1. The lower the negative logarithm of equilibrium constant (pk_a), the more acidic and higher hydrolysing potential the metal ion becomes (Wulfsberg, 1987). Table 1.5 compare the relationship between (Z^2/r) ratio and acidity of metal. It

shows that Fe^{3+} falls between 1 and 6, which is a range of cations that are moderately acidic. Table 1.5 also shows that Fe^{3+} is more acidic than Al^{3+} by using a Pauling electronegativity (χ_p) value of 1.5 as the base. The χ_p value for Fe^{3+} is greater than 1.8 whereas Al^{3+} has not been classified but can be calculated from Z^2/r, the ratio of 0.1 to 0.6 as shown in Table 1.5. The pK_a value of 1-6 falls within a range of weakly acidic cations, hence it is expected that the samples treated with Fe^{3+} should show a more acidic nature than Al^{3+}. Higher rate of hydrolysis is influenced by the lower pK values, more acidic cation and a greater Z^2/r ratio. Hydrolysis is also expressed by low electronegativity which also includes a group of very electropositive metals with Pauling electronegativity below 1.4 and cations having a standard reduction potential of 1.6 V or below (Wulfsberg, 1987).

1.7.5 Hydrolysis and formation of precipitate species

Studies have shown that hydrolysis of iron and aluminium salts is more sophisticated than the expression of the formulae as they can only be useful as approximations of reaction products and quantitative relationships. This is caused by some hydrolysis species which are formed at very low pH values. Hydrolysis of aluminium ions in solution is complicated and undefined. It forms various complex species in solution with varying pH values. It appears as Al^{3+} in pure water with low pH and forms $Al(OH)_4^-$ or $Al(OH)_5^{2-}$ in alkaline solution. It forms $Al(OH)_3$ precipitates in a dilute solution near neutral pH only when there are no any anions other than hydroxide (Hammer, 1977). Ferric and aluminium salts are widely used for the treatment of

potable water and a variety of aqueous effluents. The gelatinous metal hydroxide or flocs are also used in the treatment of wastewater which contains heavy metal cations because they are easily adsorbed by the metal hydroxide even when they are soluble at the pH suitable for coagulation-flocculation. The treatment is less successful in the presence of some coordinating ligands since they form soluble metal complexes such as hydrous metal oxide which are largely adsorbed by the floc at lower pH values below that customarily used in water treatment (Freeze *et al*., 2001). These metal salts are also used in coagulation-flocculation process together with lime to precipitate iron as shown by Equation 1.19.

$$Ca(OH)_2 + Fe^{2+} \rightleftharpoons \quad Ca^{2+} + Fe(OH)_{2(S)} \qquad [1.19]$$

Some of the heavy metals which are precipitated by lime include Zn^{2+}, Cd^{2+}, Mn^{2+}. This also hastens the speed of reaction and subsidence of the precipitate, but the problem is that too little lime allows iron to remain in solution whereas excess lime may promote growth in the sand filter. Ferric salt has advantages over aluminium salt because of manganese removal, shorter reaction time, wider pH range and insolubility of flocs at higher pH values. However, the use of iron is critical since ferric carbonate that normally occurs has no coagulant value. The advantage with iron compounds is that they produce heavy flocs that settle easily under favourable conditions at low costs. Another disadvantage is the tendency of iron floc to pass the filter or settlement tank and stimulate bacterial growth (Eremektar, 1971).

Dyer *et al*., (1998) conducted experiments to determine the behaviour of the iron in aqueous solution forming different species. Various ferric hydroxide solids were formed at varying pH values of the medium. The concentration of the iron in the solution was below 0.05 mol/L. The results of their work revealed that $Fe(OH)_3$ is dominant at pH 6.5- 7.0 whereas $Fe(OH)_4^-$ at pH above 7.0. Figure 1.6 shows ferric hydroxide species formed during coagulation process at different pH of the solution.

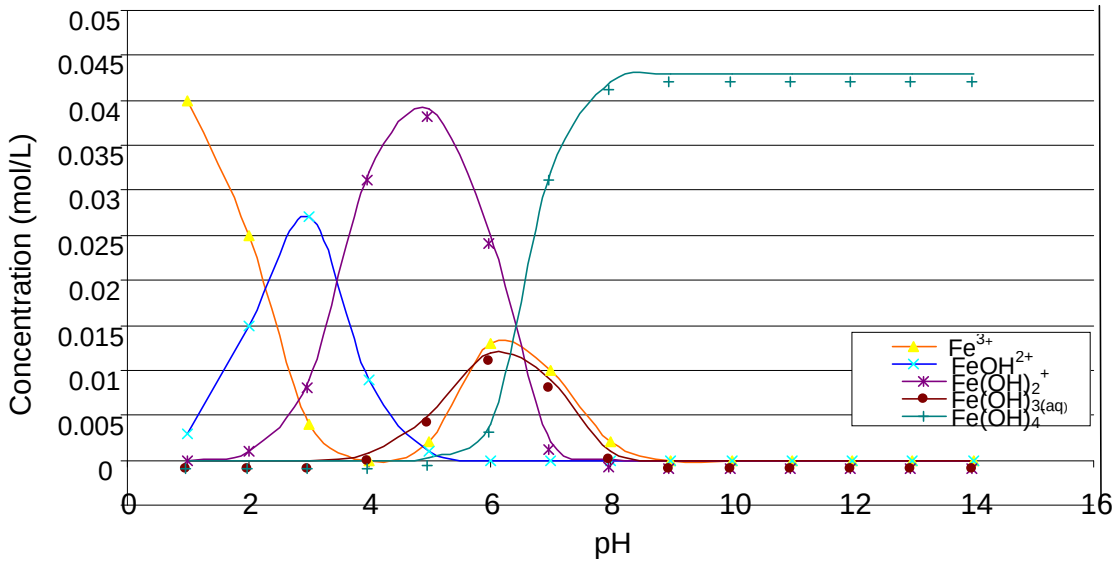


Figure 1.6: Ferric hydroxide species distribution curve (Flynn, 1984).

Figure 1.6 shows that there are at least four species that co-exist in aqueous solution in the pH range less than 5, namely Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and a very small fraction of dimer $Fe_2(OH)_2^{4+}$. According to the study from the potentiometry, it is evident that hydrolysis of ferric ion in perchlorate solution results primarily in the dimer. It was also revealed that a dimer is diamagnetic, indicating strong electronic

interactions between ferric ions. Fe^{3+} is a dominant photo-reactive species in a solution with pH less than 2.5, $Fe(OH)^{2+}$ is at pH 2.5-5.0. The species distribution is controlled by equilibrium equations of the low molecular weight hydrolysis species (Flynn, 1984, Faust *et al*., 1983) shown as:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad (K_1 = 2.7 \times 10^{-3}\ M) \qquad [1.20]$$

$$Fe^{3+} + 2\ H_2O \rightleftharpoons Fe(OH)_2^{+} + 2\ H^+ \qquad (K_2 = 1.3 \times 10^{-8}\ M) \qquad [1.21]$$

$$2\ Fe^{3+} + 2\ H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2\ H^+ \qquad (K_3 = 6 \times 10^{-4}\ M) \qquad [1.22]$$

Each species has an area of dominance with some overlap as explained by Peavy (1985). $Fe(OH)^{2+}$ is the first species to form due to decreasing concentration of Fe^{3+}. It covers an area in the pH range 1 to 5. It is followed by $Fe(OH)_2^{+}$ which falls within pH range 2 to 7, and follows $Fe(OH)_{3(aq)}$ which covers pH of 4 to 8. The last species is $Fe(OH)_4^{-}$ which covers pH range 4 to 14. The degree of hydrolysis process is determined by equilibrium state between coagulants and colloidal suspension. The shift in equilibrium reaction depends on factors such as activity coefficient of metal ion (M^{n+}), ionic potential of metal salts and the temperature of the medium. The more ionic charge on the metal ion, the more effective it becomes (Flynn, 1984). Temperature does not show any significant effect on hydrolytic reactions of metallic coagulants. Most of the studies show that metal hydroxides are formed between pH 4 and 10 (Jiang *et al*., 1997; Flynn, 1984).

Apart from the metal hydroxides which are formed during hydrolysis ranging from cationic to anionic species, there are solid species which are derived from the stable metal hydroxide species (($M(OH)_{3(aq)}$). The first solid species to be formed are unstable amorphous ferric hydroxides ($am\sim Fe(OH)_{3(s)}$). These species are formed due to very low solubility of ferric hydroxide. Ageing converts unstable amorphous ferric hydroxide to a stable alpha ferric hydroxide ($\alpha\sim FeO(OH)_{(s)}$), which is formed at the lowest Fe^{3+} concentration. Some other species such as beta ferric hydroxide ($\beta\sim FeO(OH)_{(s)}$) are also possible depending on the compound used in the wastewater treatment process (Faust *et al*., 1983). Faust *et al*. (1983), O'Melia *et al.* (2001) and Casas *et al*. (2000) discovered further formation of other hydroxide species such as gama hydroxide (γ-$Fe(OOH)_{(s)}$) which can be converted to stable alpha ferric hydroxide when heated in the presence of alkaline solution.

Polasek *et al*. (2002) discovered that crystal growth from hydrolysis of $FeCl_3$ is directed to particular minerals, mainly a $\beta\sim FeOOH$ because of a lack of suitable nuclei for the growth to other more stable mineral species. This species is formed from aqueous $FeCl_3$ solutions under a wide range of hydrolysis including dilute or concentrated solution with base of up to 2.8 OH/Fe mole ratio even at elevated temperatures (Polasek *et al.*, 2002).

Flynn (1984) discovered that deposition of precipitates in hydrolysed Fe^{3+} solutions begins in days to weeks and continues for months. All ferric species appear

octahedrally coordinated to O^{2-}, OH^- and H_2O. X-rays and infrared spectroscopy reveals that precipitates formed by nitrate and perchlorate solutions consist of α-$FeO(OH)_{(s)}$ whereas some of γ-$FeO(OH)_{(s)}$ are formed by solutions with low concentration of Fe^{3+} and OH/Fe ratios. The quantities and the formation rate of α-$FeO(OH)_{(s)}$ indicate that it is a product of the ageing of the polymer and γ-$FeO(OH)_{(s)}$; which is formed by the low molecular weight species. An increase in ionic strength accelerates the precipitation rate of goethite and inhibits lepidocrocite. Ruf *et al*. (2000) discovered that the precipitation rate is faster in solutions of polymer separated by gel filtration than solutions which are not separated. The pH change during ageing is accelerated by Cl^- (Flynn, 1984). The X-ray diffraction and infrared spectroscopy revealed that precipitates formed by hydrolysed Fe^{3+} in nitrates and perchlorate solutions consist of goethite and lepidocrocite formed by solutions with low concentration of Fe^{3+} and OH/Fe mole ratios. Increasing ionic strength accelerates the precipitation rate of β-$FeO(OH)_{(s)}$ and inhibits the formation of lepidocrocite. This indicates that goethite is the product of ageing polymer whereas lepidocrocite is derived from low molecular weight species (Ruf *et al*., 2000). Flynn (1984) also identified ferric oxides and hydrous oxides, Fe_2O_3 and $FeO(OH)_{(s)}$ as polymorphic. The phases that are important during hydrolysis of Fe^{3+} and Al^{3+} are α-Fe_2O_3 (hematite), α-$FeO(OH)_{(s)}$ (goethite), β-$FeO(OH)_{(s)}$ (akaganeite) and γ-$FeO(OH)_{(s)}$ (lepidocrocite). Aluminium metal ion yields α-Al_2O_3 (corundum), α-AlO(OH) (diaspore), M'_xMnO_2 (hollandite) and γ-$AlO(OH)_{(s)}$ (boehmite) (Flynn, 1984). The structures of α-, β- and γ-$FeO(OH)_{(s)}$ are composed of double chains of edge-shared $Fe(O,OH)_6$ octahedral. Feng *et al*. (2000) explains the formation of these

hydroxide species as a complicated time dependent process defined as hydrolysis-polymerization-precipitation. Three classes of products are formed during hydrolysis from different species such as low molecular weight complexes, $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe_2(OH)_2^{4+}$, hydrolytic polymer ($Fe_n(OH)_m$ $(HO_2)_x^{(3n-m)+}$), precipitated hydroxides, am-$Fe(OH)_3$, precipitated oxides, FeOOH and Fe_2O_3 are produced (Flynn, 1984). Electron microscopy showed faster agglomeration of the spheres on polymer in chloride solutions with appearance of rods at 3-4 hours unlike in nitrates and perchlorate solutions. The main effect of Cl^- on ageing of the polymer is that the final species formed during precipitation is α-$FeO(OH)_{(s)}$.

Ionic strength of the solution also plays a major role in the rate of precipitation. Higher ionic strength leads to higher rate of precipitation and vice versa. This is because a solution with high ionic strength has lower electrostatic potential and higher van der Waals forces of attraction, thus causing higher rate of precipitation (O'Melia, 1972). The solubility products of iron precipitates are as follows:

$$Fe^{3+} + 2\ H_2O \rightleftharpoons \alpha\sim Fe(OOH)_{(s)} + 3\ H^+ \qquad k_s = 3.16 \text{ X } 10^{-1} \qquad [1.23]$$

$$Fe^{3+} + 2\ H_2O \rightleftharpoons am\sim Fe(OOH)_{(s)} + 3\ H^+ \qquad k_s = 3.16 \text{ X } 10^{-3} \qquad [1.24]$$

$$Fe^{3+} + 3\ H_2O \rightleftharpoons Fe(OH)_{3(s)} + 3\ H^+ \qquad k_s = 1.0 \text{ X } 10^{-4} \qquad [1.25]$$

Equations 1.23 and 1.24 show that amorphous ferric hydroxide is formed at a lower solubility product than alpha ferric and ferric hydroxide species. Matijevic *et al*. (1966) conducted further studies on the hydrolysis of ferric ions in aqueous solution.

They focused on the instability of partially hydrolysed Fe^{3+} solutions that are manifested during increasing and decreasing intensity of coloration of the solution. The novel techniques enabled them to distinguish four steps which lead to hydrolysis-precipitation process. These steps include the hydrolysis of monomer and dimers, reversible rapid growth to small polymers, the formation of slowly reacting large polymers and precipitation of solid phase. The process consists of (1) the formation of the low molecular weight species; (2) the formation of red cationic polymer; (3) ageing of polymer to form oxide phases and (4) precipitation of oxide phases directly from low molecular weight precursors. The reaction rate of Fe^{3+} has been conducted on ferric chloride, ferric nitrate or ferric perchlorate at room temperature and 0.001–0.1 M. The results showed that Fe^{3+} solutions depend on the nature and mode of the basic reagents such as alkali hydroxide or ammonia. The reaction of Fe^{3+} solution with these basic reagents forms precipitates, and re-dissolves only if the amount of the base is equal or less than 2.5 mol of base per mole of iron.

The addition of aluminium sulphate to water with bicarbonates compounds produces hydrated aluminium hydroxide which carries down organic substances. Eremektar (1971) reported the effectiveness of alumino-ferric in water treatment. Water was free from carbondioxide by running it over lime to form calcium carbonates which precipitate. Coagulant also precipitated after the addition of caustic soda or soda ash prior to alumino-ferric dosage. Aluminium sulphate showed a strong coagulating power by attaining maximum precipitation at pH 5.5 compare to aluminium chloride which was at pH 8. Unlike ferric flocs, aluminium sulphate flocs dissolve at pH 10 to

11 (Eremektar, 1971). Hydrolysis of aluminium ions tends to form stable aluminium hydroxide species. Aluminium ions form an acidic medium in water and exhibits less solubility than ferric ions (Crozes *et al*., 1995). Coagulants with low solubility can achieve very high turbidity removal efficiencies. The species behave identical to ferric hydroxide species, which dominates at different pH values shown as:

- $Al(OH)_{3(aq)}$ dominates at pH 5.5 – 8.0
- $Al(OH)_4^-{}_{(aq)}$ dominates at pH above 8.0

Aluminium hydroxide species which are formed during coagulation process of aluminium salts with a concentration less than 0.09 mol/L are shown in Figure 1.7.

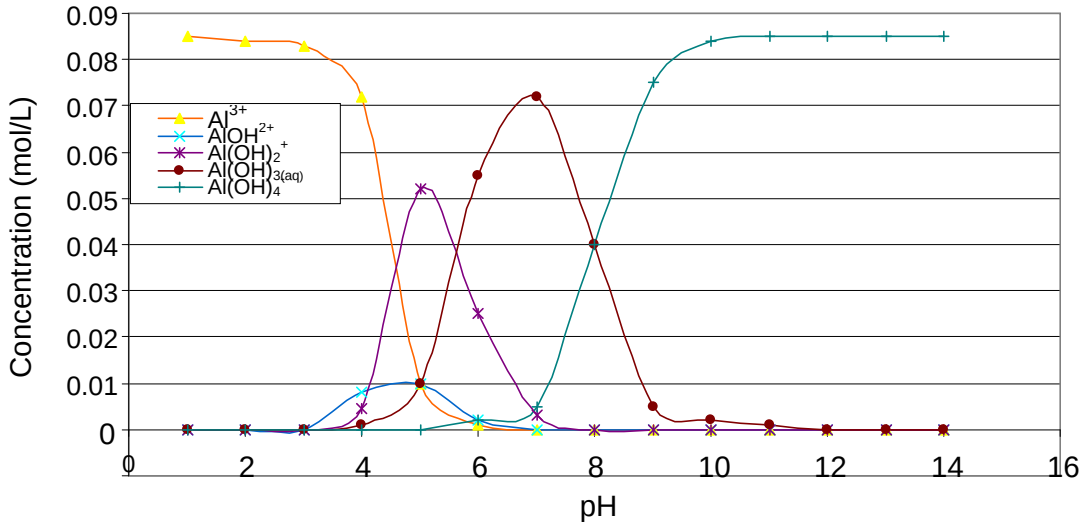


Figure 1.7: Aluminium hydroxide species distribution curve (Flynn, 1984).

Since their formation depends on the pH of the solution, the first species, a small fraction of $Al(OH)^{2+}$ is formed at pH range 3 to 6; then $Al(OH)_2^+$ that dominates within pH 4 to 7 followed by the most dominant species, $Al(OH)_3$ in a pH range 4 to 9 and $Al(OH)_4^-$ formed at pH above 8.

Aluminium hydroxide also form different species that involve hydrolysis of ions such as destabilization before solid-liquid interface, flocculation, ageing process of floc and the formation of aluminium hydroxide (O'Melia, 1998). Equations 1.26–1.28 show solubility products of the species.

$$Al^{3+} + 3\ H_2O \rightleftharpoons \alpha\sim Al(OH)_{3(s)} + 3\ H^+ \qquad k_s = 3.16\ X\ 10^{-9} \qquad [1.26]$$

$$Al^{3+} + 3\ H_2O \rightleftharpoons am\sim Al(OH)_{3(s)} + 3\ H^+ \qquad k_s = 3.11\ X\ 10^{-11} \qquad [1.27]$$

$$Al^{3+} + 3\ H_2O \rightleftharpoons Al(OH)_{3(s)} + 3\ H^+ \qquad k_s = 1.10\ X\ 10^{-9} \qquad [1.28]$$

Equations 1.26–1.28 show that amorphous aluminium hydroxide is formed at a lower solubility product than alpha aluminium and aluminium hydroxide species. It shows that amorphous aluminium hydroxide is formed at a lower solubility product than alpha, amorphous and ferric hydroxide species as shown by Equations 1.26–1.29. Aluminium sulphate is commonly used in most wastewater treatment works to avoid Alzheimer disease by forming complex reactions as follows (Binnie *et al*., 2003).

$$H_2SO_4 + Ca(HCO_3)_2 \rightleftharpoons CaSO_4 + 2\ H_2CO_3 \qquad [1.29]$$

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O \qquad [1.30]$$

$$Al_2(SO_4)_3 + 3\ Ca(HCO_3)_2 \rightleftharpoons 2Al(OH)_{3(s)} + 3\ CaSO_4 + 6CO_2 \qquad [1.30=1]$$

In the reaction where 1 mg/L of aluminium sulphate is dosed, 0.5 mg/L of alkalinity is destroyed with the production of 0.44 mg/L of carbon dioxide. Aluminium sulphate has low solubility at pH range of 5.0–7.5 and any water or wastewater pH outside this range yields unsuccessful coagulation (Tebbutt, 1983).

1.8 Comparison of aluminium sulphate and ferric chloride

Ghaly *et al*. (2006) conducted an experiment on wastewater with a pH of 9.2. The ions which form alkalinity in wastewater are OH^-, CO_3^{2-} and HCO_3^-. The addition of either 100 mg/L of ferric chloride or aluminium sulphate reduced the pH to 8.9. A tremendous pH reduction occurred when 500–600 mg/L of ferric chloride and aluminium sulphate were added, reducing the wastewater pH to 5.7 and 6.6 respectively. A further addition of 3 mg/L of ferric chloride and aluminium sulphate in wastewater decreased the pH to 3.8 and 3.9 respectively. A decrease in wastewater pH was caused by the consumption of alkalinity by ferric chloride and aluminium sulphate (Ghaly *et al*., 2006). Although ferric chloride and aluminium sulphate are both metal salts, their effect on pH drop during hydrolysis differs. The reaction of chloride from ferric chloride forms HCl, which dissociates completely to form H^+ and Cl^-. In the case of aluminium sulphate, the protons combine with sulphates from aluminium sulphate to form H_2SO_4 which dissociates to form H^+ and HSO_4^-. A further dissociation occurs to form H^+ and SO_4^{2-} which can also shift backwards to H^+

and HSO_4^-, thus behaving as a buffer (Ghaly *et al*,. 2006). A study conducted by Fault *et al*. (1967) revealed that $AlCl_3$ is more effective than $Al_2(SO_4)_3$ during hydrolysis due to the repressive effect of the bivalent sulphate ion. The presence of basic compounds in water depends on the pH of wastewater and reacts to neutralize acids as flows:

$0.5\ CO_3^{2-} + HCO_3^-$: neutralize acids at pH range 4.5–8.3 (p-alkalinity)

$0.5\ CO_3^{2-} + OH^-$: neutralize acids at pH range 8.3–12.8 (m-alkalinity)

A study by Byrne *et al.* (2000) states that there is poor understanding of inorganic complex behaviour of Fe^{3+} even after extensive studies were conducted for many years. The poor or incomplete characterization of Fe^{3+} hydrolysis is attributed to the inherent complexity of its chemistry present at high concentrations and analytical challenges at low concentrations. Their results and discussion were based on the evaluation of consecutive hydrolysis constants which is expressed by Equation 1.32:

$$\beta_n = [Fe(OH)_n^{3-1}][H_6^+][Fe^{3+}]^{-1} \qquad [1.32]$$

The equilibrium state of Fe hydrolysis is expressed by Equation 1.33.

$$Fe^{3+} + nH_2O \rightleftharpoons Fe(OH)_n^{(3-n)+} + H^+ \qquad [1.33]$$

Where $n \leq 3$, the solubility behaviour of $Fe(OH)_3$ is expressed as K_{so} which describes the relationship between the concentrations of Fe^{3+} and H^+ in equilibrium with hydrous ferric oxides expressed as:

$$K_{so} = [Fe^{3+}][H^+]^3 \qquad [1.34]$$

Metal ions such as Al^{3+} and Fe^{3+} are strongly hydrated by six water molecules in an octahedral configuration as represented by $M(H_2O)_6^{3+}$. According to Equations 1.32–1.34, simple unhydrolyzed ions such as Fe^{3+} and Al^{3+} are found in aqueous solution at low pH. As the pH of the solution increases, the equilibrium starts shifting to the right until uncharged species ($M(OH)_{3(aq)}$) are produced. Their low solubility in water forms precipitate such as gelatinous $M(OH)_3$ and increasing pH may re-dissolve the precipitate when $M(OH)_4^-$ ions are formed. The advantage of using iron and aluminium salts in wastewater treatment is their high electron valence which enables them to adsorb soluble species and cause particles-charge reduction. These metal salts form hydroxide precipitates as fine colloidal dispersion during the initial stage. The particles aggregate to form hydroxides which enmesh the colloidal particles present in wastewater during "sweep flocculation" (Ives, 1978). Hydroxide precipitation can also lead to sweep flocculation when the colloidal particles are enmeshed in the growing precipitate and removed (Duan *et al*., 2002). Duan *et al*. (2002) stated that although results on the research about flocculation were well explained in terms of established ideas, a clear understanding of the 'sweep flocculation" mechanism did not supplement the work.

1.9 Physical and chemical factors in colloidal suspensions

1.9.1 Hydrodynamic interaction between particles

Hydrodynamic forces also play a role in the collision of particles and occur when the fluid in the decreasing space between them is squeezed out. Hydrodynamic interactions arise mainly from the distortion of the fluid flow when the particles are present. Such distorted fluid flow causes the particles to deviate from their linear path and start rotating relative to one another and subsequently collide. The prevailing inter-particle colloidal forces in an unstable suspension become attractive and then enhance the colloidal efficiency, defined as the ratio of actual coagulation frequency and collision frequency. Table 1.6 compares particle size and settling velocity of particles with specific gravity of 2.8 in water at 10 ^{0}C (Tebbutt, 1983).

Table 1.6: Comparison between particle size and settling velocity, Smoluchowski (1917).

Particle size (μm)	Settling velocity (m/s)
1000	6×10^{2}
100	2×10
10	3×10^{-1}
1	3×10^{-3}
0.1	1×10^{-5}
0.01	2×10^{-7}

Smoluchowski's (1917) postulated that the most rapid coagulation occurs when every contact of particles in a colloidal system causes the adherence of one particle to

another. There is an assumption from Smoluchowski's (1917) research which states that all collisions lead to attachment irrespective of other forces such as electrostatic repulsion, van der Waals or hydrodynamic forces. (Flynn, 1984)

Adler (1981) conducted an investigation relating to the theory of hydrodynamic interactions in hetero-dispersed systems using equations for laminar flow conditions. The findings show that collision frequencies were the highest when colliding particles subjected to hydrodynamic, electrostatic and van der Waals forces were of the same size. Thomas *et al*. (1996) calculated the collision efficiencies of hydrodynamic forces for various size ratios of particles which collide. Predicted results showing comparison on curvilinear and rectilinear models follow:

- Collision frequencies are $\leq 0.5\ s^{-1}$ in perikinetic flocculation.
- Collision frequencies are $\leq 5\ s^{-1}$ in orthokinetic flocculation.
- Collision frequencies are $2 - 3\ s^{-1}$ or less for differential sedimentation.

Han *et al*. (1992) presented the numerical expressions which relate the correction factors for the conversion of the rectilinear model to the curvilinear model. The expressions showed a direct relation as the functions of the size ratio of colliding particles and the ratio of the hydrodynamic shear forces to van der Waals forces between colliding particles. Han *et al*. (1992) compared curvilinear collisions between particles of all sizes in the range 1-1000 μm and developed the following:

- Orthokinetic flocculation not important in the curvilinear than rectilinear model.
- The curvilinear model predicts a lower collision frequency than in the rectilinear model and the reduction in collision frequency becomes less when the particles are of same size.
- Orthokinetic flocculation is no longer directly proportional to local velocity gradient (G), as predicted by Camp *et al*. (1943) as shown by Equation 1.35.

$$G = (\varepsilon/\nu)^{1/2} \qquad [1.35]$$

ε = energy dissipation

ν = kinetic viscosity

1.9.2 Intermolecular forces in a colloid

Zeta and electrical potential are the forces which are involved in colloidal stability and exist at the edge of the agglomerate and play a major role in stabilization. Colloidal particles are always charged and the repulsive and attractive forces of particle-particle or particle-fluid influence stability of colloids. Zeta potential has a lower value in heterogeneous suspensions because of complicating factors involved (Tebbutt, 1983). Zeta potential is based upon the diffuse-layer thickness (δ) and is a qualitative useful expression because of its measurability. The stability of a colloidal suspension decreases when the zeta potential decreases and it is expressed as:

$$Z = 4\ \pi\delta q/D^* \qquad [1.36]$$

δ = diffuse layer thickness, q = net (apparent) particle charge, D* = dielectric constant of water

The addition of metal salts disturbs the stability of the colloid in two ways such as their effect in the extent of the diffuse layer around the particles and by specific effect on the electric potential controlling colloid stability (Ives, 1978). The depth of the diffuse layer determines the predominance of attractive forces irrespective of whether particles of like charges are brought close to one another or not. When the ionic strength of the solution increases, the distance of effective repulsive forces decreases toward the particle surface and causes the net-charge curve between attractive and repulsive forces to drop entirely towards attraction force region as shown in Figure 1.8.

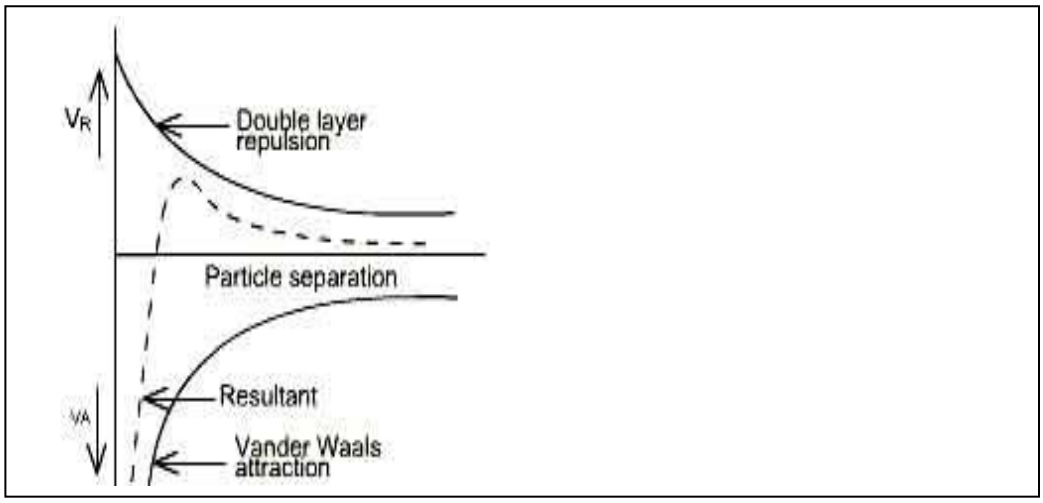


Figure 1.8: Forces exerted between the colloidal particles.

The particles are attracted to one another by van der Waals forces and the addition of electrolytes increases ionic strength of the solution which results in double-layer compression (Lee, 2001).

1.10 Challenges in paint wastewater treatment

A lot of paint manufacturing organizations do not treat their paint wastewater. Their wastewater is collected by waste disposal companies some of which do not comply with the rules and regulations pertaining to waste disposal. The river ecosystem is vulnerable to foreign materials ingress more especially the type of ingredients which are used during paint manufacturing. It cannot be guaranteed where the paint wastewater is disposed because of ongoing complaints which are related to illicit waste disposal practices. Some of the cases such as river algal bloom which normally takes place in the Vaal River; a situation caused by phosphate, one of the paint constituents can be associated with paint wastewater discharge into the river.

A study by Ntwampe (2005) showed that Vaal river water has low mineral content with biofouling rate of 1.6 $mg/dm^2.d$ than 6.6 $mg/dm^2.d$ from the power stations in the neighbourhood. The finding of this study shows that the algal bloom and any disturbance within the Vaal river is as a result of effluent discharge of poor quality. The main challenge with the paint manufacturing industry is that it will be costly to treat wastewater due to its complexity. That will require the construction of the treatment plant, operating and labour cost as well as other related costs. Another reason which is an attribute to the lack of wastewater treatment facilities is that paint

wastewater was never considered to be hazardous to the environment. This is because of the fact that the ingredients are not stated on the paint containers for public knowledge. The quantity of wastewater generated in an average paint manufacturing company is approximately 25-38 kL/day as mentioned in sub-section 1.1.3.

Paint is in a high demand due to high industrial and residential development where is paint is used extensively around the globe, mainly due to escalating population and economic growth. This would trigger the necessity to implement stringent rules pertaining to the handling of paint wastewater; thereby causing EPA to implement law which protect the environment. As a lot of research has been conducted on flocculation from civil perspective, most of the available information is more on the design of the water/wastewater clarification systems. Although a lot of research has been conducted on coagulation-flocculation, the information about hydrolysis and adsorption is not clear. Some of the researchers stated that the hydrolysis species (flocs) are adsorbed onto the colloidal particles whereas others stated that the colloidal particles are embedded in the agglomerates (Ives, *et al*., 1978, Jiang *et al*., 1997, Peavy *et al.,* 1995). These concepts are not definite and therefore make it difficult for wastewater treatment operators to employ the best water treatment practice in order to produce effluent of good quality.

Research and development must put more emphasis on coagulation-flocculation dynamics since it is the most simple and easily maintainable technique compared to modern sophisticated techniques. Another problem encountered in paint wastewater

treatment is its high pH values of 8-10; which then makes it difficult to be treated under normal treatment regime as stated by Jiang *et al*. (1997). Other challenges facing paint wastewater treatment is the limited understanding of the factors which play pivotal role in effective treatment such as the minimum retention time required during mixing, the effect of rapid and slow mixing on the formation of well-developed flocs, cost effective metal hydroxides (softeners) to be dosed, the optimal pH in the treatment of alkaline wastewater, the hydrolyzing power between ferric and aluminium salts as well as between monoprotic and diprotic metal salts, the role of chemical and physical properties of the coagulants.

1.11 Benefits of the study

The findings in this study will encourage paint manufacturing industry to focus on wastewater recycling; which will incur long-term cost savings. Although the capital costs to erect a wastewater treatment could be high, there is a return-on-investment to purchase raw water from the water source in future as well as to avert envisaged penalties to be instituted to polluters of rivers and waste dumping sites. The study in this work focuses on very crucial factors which play a pivotal role in wastewater treatment such as alternative polymers to replace expensive commercial polyelectrolytes, the correlation between pH and hydrolysis during coagulation-flocculation, determine the most effective metal salt(s) and ideal concentration of metal ion that can adsorb a considerable amount of colloidal particles (turbidity removal), determine optimal dosages, mixing dynamics to produce water effluent of

good quality without re-stabilization or flocs rupture, identify proper retention time during treatment to achieve a better sedimentation, determine metal hydroxide which can be used for pH adjustment without any harm, identify a convenient and fast laboratory testing technique for the production of good quality effluent, effect of rapid and slow mixing in flocs formation, effect of monoprotic and diprotic reagents in wastewater treatment.

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CHAPTER 2: The effect of metal salts and metal hydroxides on the pH-turbidity in hard paint wastewater treatment.

Abstract

A 169.2 g of paint was diluted in 1 litre of potable water. A 200 mL of the sample was poured into six 500 mL glass beakers and dosed with 0.043 M $FeCl_3$, 0.043 M of $Al_2(SO_4)_3$ or $AlCl_3$ respectively, employing varying dosing sequence and varying dosages before and after mixing in a jar test to determine their turbidity removal efficiency. Samples were stirred at 250 rpm for 2 minutes and 100 rpm for 10 minutes, settled for 1 hour after which the pH and turbidity were measured. In a second set of experiments the dosages were a combination of $FeCl_3$ and 0.043 M $Ca(OH)_2$ or 0.043 M $Mg(OH)_2$ was employed and measurements were done as before. In a third set of experiments, 0.043 M $FeCl_3$–$Ca(OH)_2$ or 0.043 M $FeCl_3$–$Mg(OH)_2$ of synthetic polymers, were employed as reagents using similar measurements . The results from the first and the second sets of experiments showed that pH can be correlated with turbidity removal and the rate of hydrolysis does not depend on whether it is done before or during mixing. There is no correlation observed between pH and turbidity from the results of the third sets of experiments and thus pH cannot be used as a direct indicator of turbidity in the treatment of more alkaline solution.

2.1 Introduction

Wastewater can be found in an alkaline or an acidic medium. The pH of wastewater has been identified as one of the parameters which influence effective wastewater treatment (Juttner *et al.,* 2000, Aboulhassan *et al*., 2006). Adjustment of the pH to an optimal range enables the concentration of coagulants to exceed the solubility of their metal hydroxides so that precipitates can be formed (Aguilar *et al*., 2002 and Wang *et al*., 2004). It is therefore important to adjust pH before treatment in order to achieve pH range which is recommended for effective hydrolysis. pH adjustment in an alkaline colloidal suspension requires sulphuric or hydrochloric acid whereas in acidic colloid, metal hydroxide such as $Ca(OH)_2$, NaOH or Na_2CO_3 are used (Sarkar *et al.,* 2005 and Water Specialist Technology, 2003). Paint wastewater has a relatively high hardness due to high Ca^{2+} and Mg^{2+} content. The treatment is therefore different from other operations because pH adjustment requires acid dosage. Water hardness can also be caused by aluminium, iron, and other divalent and trivalent cations (Water Specialist Technology, 2003). Metal hydroxide dosage is common practice in water softening to remove bicarbonates from the colloidal suspension. $Ca(OH)_2$ and Na_2CO_3 are typically used to remove dissolved minerals which cause scaling on a metal surface. $Ca(OH)_2$ reacts with HCO_3^- to form $CaCO_3$ as shown in Equation 2.1.

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2\ CaCO_3 + 2\ H_2O \qquad [2.1]$$

Further addition of $Ca(OH)_2$ reacts according to Equation 2.2.

$$Mg(HCO)_3 + Ca(OH)_2 \rightarrow CaCO_{3(s)} + MgCO_3 + 2\ H_2O \qquad [2.2]$$

$Ca(OH)_2$ also reacts with orthophosphate in wastewater to form hydroxyapatite ($Ca_5OH(PO_4)_3$) precipitates and magnesium to form magnesium hydroxide, $Mg(OH)_2$ (Culp *et al*., 1971). However, $Ca(OH)_2$ has a problem of increasing turbidity of the solution, which requires a lime saturator. This is a process unit used to mix water with slurry lime from a post-lime system to restrict the addition of turbidity (Amirtharajah *et al*., 1982, Kurniawan *et al*., 2006). Since $Ca(OH)_2$ increases turbidity in a solution, an investigation of an alternative metal hydroxide which will replace $Ca(OH)_2$ for pH adjustment or softening is necessary. The study should investigate the reactions which occur when metal hydroxide reacts with metal salts to form metal hydroxide species (flocs) as shown by Equation 2.3.

$$2\ FeCl_3 + 3\ M(OH)_2 \rightarrow 2\ Fe(OH)_3 + 3\ MCl_2\ (M = Ca \text{ or } Mg) \qquad [2.3]$$

This study investigates turbidity removal efficiencies of various reagents such as Fe^{3+} and Al^{3+} salts, a combination of Fe^{3+} or Al^{3+} salt with either Ca^{2+} or Mg^{2+} hydroxide, synthetic polymers formed by Fe^{3+} or Al^{3+} salt with either Ca^{2+} or Mg^{2+} hydroxides at varying dosages and dosing sequences. The rationale is to determine whether synthetic polymer can replace commercial polymers which are relatively costly. Dosage is one of the factors which play a pivotal role during wastewater treatment so that best turbidity removal can be achieved. Accurate dosages seem to be a main challenge, hence investigation of this nature is considered in this study. Inorganic coagulants are in the form of monoprotic (MCl_3) and diprotic ($M(SO_4)_3$). Although

research has shown the comparison in turbidity removal between these two classes, it has not been indicated how they relate to destabilization-hydrolysis. Their hydrolyzing potential, measured by the rate at which pH decreases with increasing or decreasing dosages has also been investigated in this study. The turbidity removal efficiencies of all the reagents used in the experiments are compared by using the correlation between the pH and turbidity. Such information is imperative in wastewater treatment complexes in order to be able to choose ideal metal salts which will produce effluent of good quality. Varying dosages which are investigated in this study can also enable the Water Chemist(s) to calculate the mass of the colloidal particles which can be removed by a mass of metal ions (Fe^{3+} or Al^{3+}) to improve wastewater treatment. This is calculated by applying concentration of metal ions in varying dosages added to 200 mL of paint wastewater sample.

It has been recommended that a pH of 6–8 is ideal for wastewater treatment; this is because the metal salts are more effective in destabilization-hydrolysis, thus leading to very rapid precipitation (Freeze *et al*., 2001). When the pH of wastewater is lower than 6, adsorption of the hydrolysis products onto the colloidal surfaces for neutralizing the charge is possible. It may also interact with dissolved components in the colloid, thus resulting in re-stabilization which is caused by charge reversal at the colloidal surface (Jiang *et al*., 1997, Amuda *et al*., 2006, Ghaly *et al*. (2006). A high chemical dosing is required when the wastewater pH is above 6 to produce effluent of good quality (Jiang *et al*., 1997; Gregory *et al*., 2001, Lee, 2001, Ghaly *et al*., 2006, Molony, 2005, Pratt *et al*., 2007).

A study conducted by Aboulhassan *et al*. (2006) on the effectiveness of $FeCl_3$ together with polyelectrolyte in paint wastewater to remove organic and coloring matters revealed that it is effective at pH range 8-9 and a dosing of 650 mg/L. It showed 82 % reduction potential of COD and 94 % for colour. The investigations in this study focus on paint wastewater due to its chemical complexity which is caused by multiple components, which makes treatment a complex. Aboulhassan *et al*. (2006) realized that the poor quality of paint wastewater requires a physico-chemical treatment rather than biological treatment due to a high concentration of constituents.

Ntwampe *et al.* (2013) stated from their study that Fe^{3+} and Al^{3+} salts dosage in paint wastewater form large flocs which condense to form dense cake-like, spongy polymers that settle spontaneously due to high settling velocity. These polymers act as a filter and trap the residual colloidal particles, causing further turbidity reduction.

In this study, more focus is based on $FeCl_3$ as a coagulant because of its ability to consume more alkalinity in the wastewater than $Al_2(SO_4)_3$. This is attributed to its acidic property and its high valence electron (3+) as stated by Duan *et al.* (2002). Ferric ions readily undergo hydrolysis, complexation or polymerization and precipitation in aqueous solution; and also ferric ion monomers and polymers produced during hydrolysis have a stronger tendency towards precipitation than aluminium ions (O'Melia *et al.,* 2001). Fe^{3+} is more hydrophilic and results in the release of more H^+ to the solution during hydrolysis. $FeCl_3$ can also be used for water decolourization at low pH and can also remove manganese at high pH; and it is also effective in water with low temporary and high permanent hardness. The concentration of the coagulants must be sufficient to rapidly precipitate the metal

hydroxide [$Al(OH)_3$], [$Fe(OH)_3$], [$Mg(OH)_2$] or metal carbonate [$CaCO_3$] so that the colloidal particles can be enmeshed in these precipitates. The colloidal charge in most wastewater coagulation requires positively charged inorganic polymers (Moore *et al*., 1976). The effectiveness of coagulation depends on the change in ionic concentration and increases exponentially as the charge of the ions increases (Binnie *et al*., 2003, Jiang *et al*., 2002, Dey *et al*., 2004, Mahdavi *et al*., 2001). Coagulants with multiple electrical charges such as anionic and cationic polymers are more effective in wastewater treatment. These coagulants form bridges between colloidal particles and both polymers are able to coagulate negative charged colloidal particles. The high molecular mass polymers (polymeric flocculants) form bridges between particles that result in the formation of aggregates (Duan *et al*., 2003). The flocs formed by organic polymers are stronger than those of Fe^{3+} and Al^{3+} salts and can withstand higher shearing stresses. (Swartz *et al.*, 2004).

In wastewater treatment, hydrolysis is a main process which involves the reaction of the metal ion (M^{3+}) in a metal salt with the hydroxyl ion (OH^-) to form a hydrolysis species (flocs) and the hydrogen ions are released into the solution, causing a pH drop (Sincero *et al.*, 2003), see Equation 2.4. However, effective hydrolysis only occurs when the coagulants are dispersed throughout the colloidal suspension, thereby causing destabilization during the coagulation-flocculation process (Sincero *et al.*, 2003 and Sarti *et al*., 2004). There are series of hydrolytic reactions that occur after addition of coagulants, namely simple hydroxo complexes (MOH^{2+}), colloidal hydroxometal polymers and the metal hydroxide precipitates. Moore *et al*. (1978) illustrate hydrolysis of a metal ion with water to form a stable metal trihydroxide and the speciation of hydrolysis species, as expressed in Equation 2.4. Feng *et al*. (2000)

explained hydrolysis as a time-dependent process that could be defined as hydrolysis–polymerization–precipitation.

$$M^{3+} \rightarrow M(OH)^{2+} \rightarrow M(OH)_2{}^{+} \rightarrow M(OH)_{3(s)} \rightarrow M(OH)_4{}^{-} \qquad [2.4]$$

These hydrolysis species are the adsorbents that reduce the turbidity in the wastewater. The concentration of the residual colloidal particles determines the turbidity reduction potential of the coagulants dosed into wastewater during treatment. Amuda *et al*. (2007) described wastewater treatment as a process whereby coagulants are added to a colloidal system to cause destabilization and hydrolysis, thus forming agglomerates. Conventional wastewater treatment works generally use inorganic coagulants or a combination of inorganic coagulants with coagulant-aid (polymers) or synthetic organic coagulants. A lot of wastewater treatment works prefers the use of both coagulant and coagulant aids to improve flocs density and strength. The use of $FeCl_3$ with coagulant aids is recommended in wastewater treatment for the removal of turbidity, COD and more sludge production (Amuda *et al*., 2006). This treatment involves physical and chemical decolourisation that includes adsorption, oxidation and chemical precipitation (Aboulhassan *et al*., 2006 and Goldberg, 2002). Coagulant-aids are expensive; hence this study investigates the turbidity removal efficiency synthetic polymers to replace coagulant aids.

From Equation 2.4 above, it can be noticed that as hydroxide is formed, the pH of the solution decreases when hydrolysis continue to the right side. This is when I decided

that pH can be considered as an indicator of the degree of hydrolysis whereas turbidity indicates the adsorption potential of the reagents. The objective of this study is to the determine the effect of $Mg(OH)_2$ as pH adjustment reagent or polymer with Fe^{3+} salt ($FeCl_3$–$Mg(OH)_2$ polymers) on turbidity removal in paint wastewater with hardness to replace $Ca(OH)_2$. Other reagents such as Fe^{3+} or Al^{3+} salts, combination of Fe^{3+} and Al^{3+} salts were also dosed. The rationale is to determine the dosing method which can yield the best turbidity removal at specific pH ranges.

2.2 Materials and methods

In this study, coagulation-flocculation treatment has been applied to a water-based paint by dosing with Fe^{3+} and Al^{3+} ions. The ionizing salts being $FeCl_3$,$AlCl_3$ and$Al_2(SO_4)_3$. These were all prepared as 0.043Molar solutions. A 0.043 M solution combining $FeCl_3$ with $Ca(OH)_2$ or $Mg(OH)_2$, and another of $FeCl_3$–$Ca(OH)_2$ or 0.043 M $FeCl_3$–$Mg(OH)_2$ polymers were also prepared. The jar test was used to monitor the progress of the flocculation.

2.2.1 Paint wastewater sample

Solid content of paint was determined by drying 20 g of water-based paint in a crucible placed in an oven at 250 ^{0}C for three hours. These tests were triplicates and the average mass obtained was 6.2 g showing that the ratio of solid paint to water is

about 4:9. To prepare synthetic paint wastewater sample 80 g mass of solid paint was weighed and added to 1 litre of water. It should be noted that the coagulant dosage required is expected to be proportional to total solids (Sincero *et al.,* 2003).

2.2.2 Coagulants

The recommendation to use of 0.043 M of $Fe^{3+}$and Al^{3+} ions concentration came from literature (Fasemore, 2004). During flocculation of the paint wastewater, a wide range of results showing effective flocculation at a solid content of 80 g paint solids in 1000 g of water were obtained.

The calculation of the mass of metal salt to obtain *0.043 M of* M^{3+} (M^{3+} *= Fe or Al*) is as follows:

Monoprotic metal salts (MCl_3)

$$0.043\ M \text{ of } M^{3+} \text{ x mass of } M^*Cl_3 6H_2O\ (M^* = Fe \text{ or } Al) \qquad [2.5]$$

Diprotic metal salts ($M_2(SO_4)_3$)

$$0.043\ M \text{ of } M^{3+} \text{ x mass of } M^*_2(SO_4)_3 18H_2O/2 (M^* = Fe \text{ or } Al) \qquad [2.6]$$

Table 2.1: Preparation of coagulant solution using 1 L distilled water.

Salt	Mass of salt (g)	Salt concentration (mol/L)	M^{3+} concentration (M)
$FeCl_3.6H_2O$	11.4	0.0430	0.043
$AlCl_3.6H_2O$	10.1	0.0430	0.043
$Al_2(SO_4)_3.18H_2O$	13.6	0.0215	0.043
$Ca(OH)_2$	3.18	0.0430	0.043
$Mg(OH)_2$	2.49	0.0430	0.043

The metal salt-metal hydroxide ($FeCl_3$-$M(OH)_2$) polymers were prepared in the following manner:

a) Preparation of 0.043 M $FeCl_3$-$Ca(OH)_2$ polymer was made by dissolving 11.4 g $FeCl_3.6H_2O$ CP and 3.18 g Ca(OH) to 1 litre of distilled water with impeller set at 50 rpm for a slow mixing duration of 5 minutes and then was allowed to react for 6 hours to allow enough for reaction.

b) Preparation of 0.043 M $FeCl_3$-$Mg(OH)_2$ polymer was made by dissolving 11.4 g $FeCl_3.6H_2O$ CP and 2.49 g $Mg(OH)_2$ to 1 litre distilled water with 50 rpm slow mixing time of 5 minutes and reaction time of 6 hours as described above **.**

2.3 Procedure in jar tests.

The equipment used for the jar tests was a *BIBBY Stuart Scientific Flocculator (SW1 model)*, which has six adjustable paddles with rotating speeds between 0–250 rpm.

169.2 g of water-based paint was dissolved in 1 litre of distilled water to prepare the paint wastewater sample. 200 mL of the solution was poured in each of the six 500 mL glass beakers for the test. The pH and turbidity of control sample were 9.32 and > 500 NTU (over-range) respectively. To each of these beakers different dosages of 0.043 M solutions that provided Fe^{3+} and Al^{3+} ions were added. The experiment was conducted by employing varying rates of dosages (dosing single coagulant in increasing order or combined coagulants in increasing order or one coagulant increasing and the other decreasing or one coagulant constant and the other varying), varying mixing rates (rapid mixing or slow mixing) and dosing before or during mixing. The rationale to carry out these experiments was to determine correlation between the pH changing trend and turbidity removal. The experiments were conducted in the following order:

In the first set of experiments, each sample was dosed with $FeCl_3$ and treated in a jar test. Two separate similar sets of experiments were carried out replacing $FeCl_3$ with $AlCl_3$ and $Al_2(SO_4)_3$ respectively. Two other separate similar sets of experiments were carried out replacing $FeCl_3$ with the combination of $FeCl_3$ with $Ca(OH)_2$ and $FeCl_3$ with $Ca(OH)_2$ respectively. The last two separate sets of experiments were carried out replacing $FeCl_3$ with $FeCl_3$-$Ca(OH)_2$ and $FeCl_3$-$Mg(OH)_2$ polymers respectively

$FeCl_3$, $AlCl_3$ and $Al_2(SO_4)_3$, a combination of $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ dosage, $FeCl_3$–$Ca(OH)_2$ or $FeCl_3$–$Mg(OH)_2$ polymers were dosed using varying rates of dosages, varying mixing rates and dosing before or during mixing in order to establish the pH values that yielded highest potential for turbidity removal.

2.3.1 Experiment A-dosages with Fe^{3+} and Al^{3+} salts only.

Experiment 1-samples run in a jar test with Fe^{3+} and Al^{3+} salts dosage only.

A set of experiments was carried out in a jar test by pouring 200 mL of synthetic paint wastewater into six 500 mL beakers. Samples were dosed with 10, 20, 30, 40, 50 and 60 mL of $FeCl_3$ when combined with $AlCl_3$ or $Al_2(SO_4)_3$). The volume ratios were 1:1. These were mixed at a speed of 250 rpm for first 2 minutes and then reduced to 100 rpm for the next 10 minutes. The samples were left to settle for 1 hour before pH and turbidity were measured.

A similar set of experiments was carried out with a combination of 5, 10, 15, 20, 25 and 30 mL $FeCl_3$ with 5, 10, 15, 20, 25 and 30 mL $AlCl_3$ dosage before and after mixing and run through a jar test similarly to the first set of experiments.

The experiment above was repeated but this time $Al_2(SO_4)_3$ replaced $AlCl_3$.

Experiment 2- samples run in a jar test with Fe^{3+} and Al^{3+} salts dosage only using varying dosing patterns.

The experiments were conducted as described for set 1 experiments, however in this particular case, the dosage of $FeCl_3$ was fixed at 20ml, while that of $AlCl_3$ was varied from 20 to 60 ml. The initial impeller speeder for the mixer was 250rpm for a 2

minute duration followed by a 10 minute run at 100 rpm. One hour settling time was allowed before pH and turbidity measurements.

Part 2 of these set of experiments was also similar to Part 2 of set 1 experiments described above.

A second set of experiments was carried out where the samples were dosed with a combination of 20 mL of 0.043 M Al^{3+} in $AlCl_3$ or $Al_2(SO_4)_3$ and 10, 20, 30, 40, 50 and 60 mL of 0.043 M Fe^{3+} in $FeCl_3$ and run through a jar test similarly to the first set of experiments. A third batch of experiments was carried out where the samples were dosed with either a combination of increasing (10–60 mL) of $FeCl_3$ and decreasing (60–10 mL) of $AlCl_3$ or $Al_2(SO_4)_3$ or a combination of increasing (10–60 mL) of $AlCl_3$ or $Al_2(SO_4)_3$ and decreasing (60–10 mL) of 3 M Fe^{3+} in $FeCl_3$ during rapid mixing and run through a jar test similarly to the first set of experiments.

2.3.2 Experiment B- dosages with Fe^{3+} salt and metal hydroxides and polymers.

Experiment 3- samples run in a jar test with Fe^{3+} salts dosage with Ca^{2+} and Mg^{2+} hydroxide or $FeCl_3$-Ca^{2+} or Mg^{2+} polymers.

A similar set of experiments was carried out by pouring 200 mL paint wastewater samples into five 500 mL glass beakers. The samples were dosed with 20, 30, 40, 50 and 60 mL of $FeCl_3$ during mixing at 250 rpm for 2 minutes and then reduced to 100 rpm for 10 minutes. The samples were allowed to settle for 1 hour before the pH and turbidity were measured.

A similar second set of experiments was carried out with a combination of 10, 15, 20, 25 and 30 mL of $FeCl_3$ and 10, 15, 20, 25 and 30 mL of $Ca(OH)_2$ dosage during mixing and run through a jar test as done in the first set of experiments. The third set of experiments was carried out with a combination of 10, 15, 20, 25 and 30 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL $Mg(OH)_2$ dosage during mixing and run through a jar test as done in the first set of experiments. A fourth batch of experiments was carried out by dosing the samples with $FeCl_3$-$Ca(OH)_2$ polymers and $FeCl_3$-$Mg(OH)_2$ polymers respectively during mixing and run through a jar test similarly to the first set of experiments.

2.3.2 Experiment B- dosages with Fe^{3+} salt and metal hydroxides and polymers.

Experiment 3- samples run in a jar test with Fe^{3+} salts dosage with Ca^{2+} and Mg^{2+} hydroxide or $FeCl_3$-Ca^{2+} or Mg^{2+} polymers.

A similar set of experiments was carried out by pouring 200 mL paint wastewater samples into five 500 mL glass beakers. The samples were dosed with 20, 30, 40, 50 and 60 mL of $FeCl_3$ during mixing at 250 rpm for 2 minutes and then reduced to 100 rpm for 10 minutes. The samples were allowed to settle for 1 hour before the pH and turbidity were measured.

A similar second set of experiments was carried out with a combination of 10, 15, 20, 25 and 30 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL of $Ca(OH)_2$ dosage during mixing and run through a jar test as done in the first set of experiments. The third set of

experiments was carried out with a combination of 10, 15, 20, 25 and 30 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL $Mg(OH)_2$ dosage during mixing and run through a jar test similarly to the first set of experiments. A fourth batch of experiments was carried out by dosing the samples with $FeCl_3$-$Ca(OH)_2$ polymers and $FeCl_3$-$Mg(OH)_2$ polymers respectively during mixing and run through a jar test similarly to the first set of experiments.

2.4 Performance evaluation

The pH readings that were taken while coagulated and flocculated samples settled were the basis for comparing rate of hydrolysis.

2.4.1 pH measurement

A MetterToledo Seven Multimeter (made in Germany) pH meter with an electrode filled with silver chloride solution and the outer glass casing with a small membrane covering at the tip was used. The pH meter was calibrated daily before analysis with pH technical buffer solution 4 and 7. A 50 mL supernatant was poured into 100 mL glass beakers and inserted under the probe with gentle shaking for 1 minute and left to stabilize before the readings for calibration were taken.

2.4.2 Turbidity

Hanna Microprocessor Turbidimeter (made in England) was used to determine turbidity using NTU as a unit of measure. The instrument was calibrated every month using 0.1, 10, 100 and 1000 NTU calibration solutions. The supernatant was poured into a vial and inserted in a measuring cell. The cover was closed and the infrared light beam was automatically passed through the vial from emission source with a wavelength of around 890 nm. A sensor was placed at 90^0 to the direction of light beam. The sensor detected the amount of light scattered by suspended particles.

2.5 Results

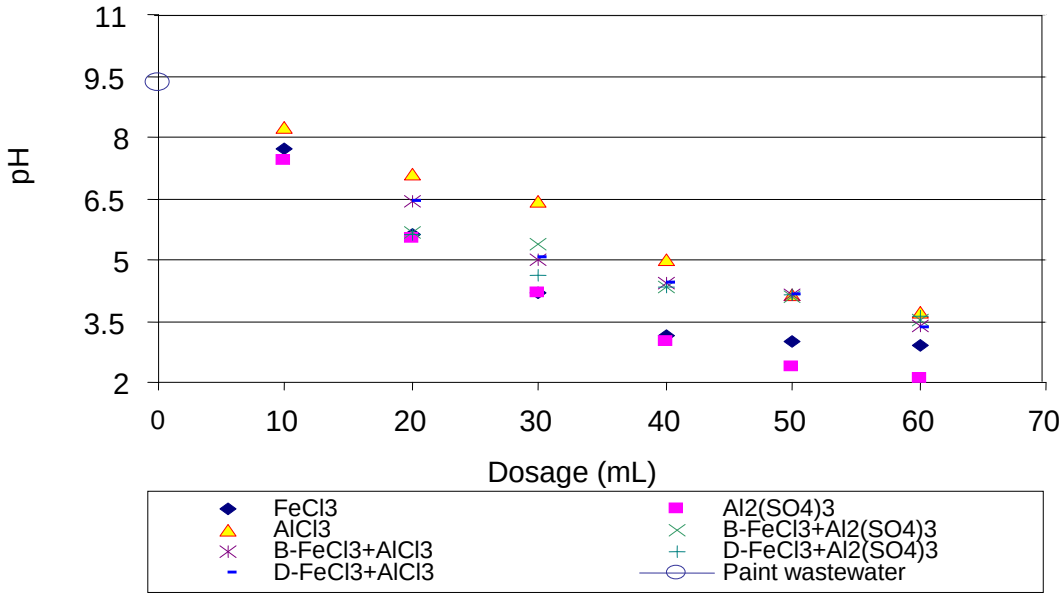


Figure 2.1: pH vs dosage with increasing Fe^{3+} and Al^{3+} salt in separate experiments.
B=coagulants were added before stirring, D=coagulants were added during stirring.

Figure 2.1 shows that the pH in samples with 10 mL of all three metal salts and 20 mL $AlCl_3$ are in an alkaline state and have been reduced from 9.32 to 7.73, 7.42, 8.23 and 7.11 respectively. The samples are opaque, which indicates that de-flocculation occurred. This occurs when de-flocculation takes place and the flocs are tiny structures which cannot agglomerate and promote adsorption. The pH values in the samples with a combination of 10 mL $FeCl_3$ and 10 mL $Al_2(SO_4)_3$) dosages before mixing is 5.68 whereas it is 6.43 in a combination of 10 mL $FeCl_3$ and $AlCl_3$. It is found that 20–60 mL of $FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$ dosages yielded pH range of 5.64–2.9, 6.61–2.0 and 7.11–3.7 respectively. The pH range obtained in the same combined dosages before mixing is in the range of 6.43–3.51, whereas the pH of the samples with dosing during mixing is in the range between 6.41–3.33.

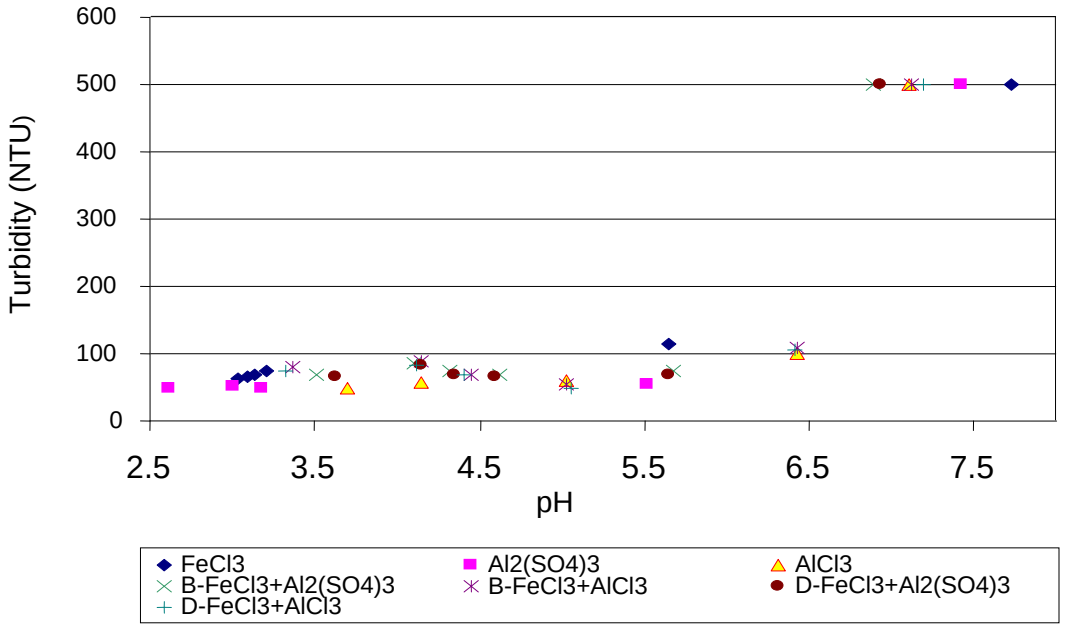


Figure 2.2: pH vs turbidity for samples dosed with $FeCl_3$ and $Al_2(SO_4)_3$ or $AlCl_3$ salts added before and during stirring.
B=coagulants were added before stirring, D=coagulants were added during stirring.

In Figure 2.2, turbidity in the samples with 10 mL of all three metal salts ($FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$) added before or during mixing is over-range (>500 NTU). The pH in these samples is above 7.0, which are alkaline and opaque. This shows that de-flocculation yielded poor turbidity removal because the flocs which have been formed were small to remove colloidal particles through adsorption. The turbidity in the samples with both 20–60 mL of $FeCl_3$ and $Al_2(SO_4)_3$ as well as 30–60 mL of $AlCl_3$ is reduced from a value above 500 NTU to a range of 115–62 NTU, 64–50 NTU and 105–49 NTU respectively. Samples with low turbidity have pH below 7.0 as shown in Figure 2.1. All the samples with a combination of $FeCl_3$ and $Al_2(SO_4)_3$ dosages added before and during mixing have low turbidity in a range of 110–71 NTU and 105–66 NTU respectively; and correspond to pH range of 5.73–3.51 and 5.90–3.63 respectively. According to Figure 2.2, all the samples with a combination of $FeCl_3$ and $Al_2(SO_4)_3$ dosages were below 7.0 and showed low turbidity.

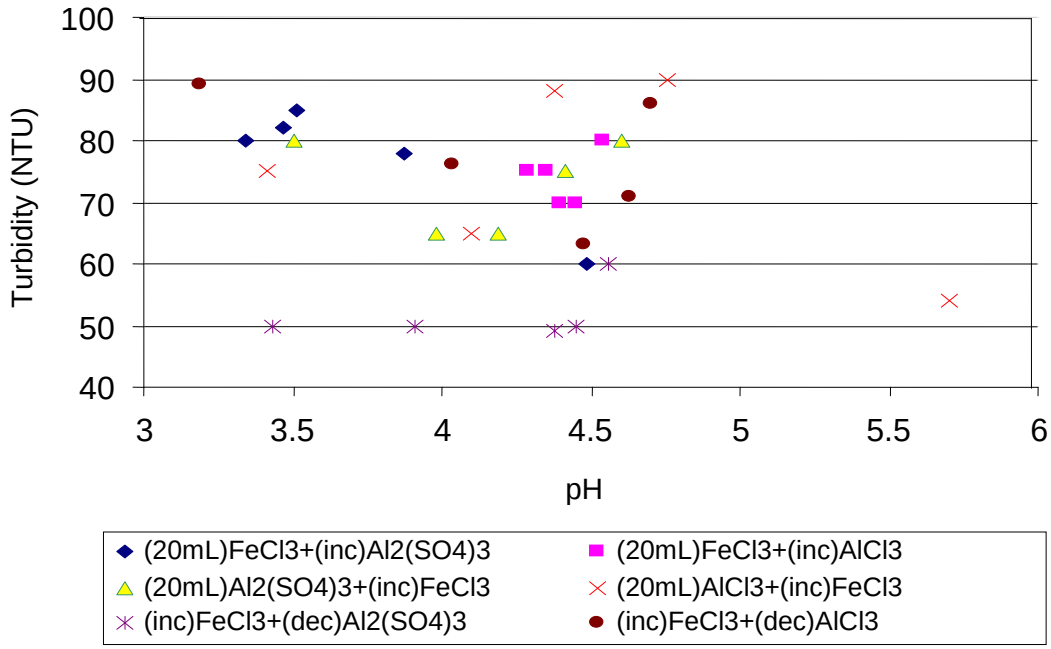


Figure 2.3: pH vs turbidity for samples dosed with either constant (20 mL) $FeCl_3$ or increasing $Al_2(SO_4)_3$ or $AlCl_3$ salts or constant $Al_2(SO_4)_3$ or $AlCl_3$ and increasing $FeCl_3$, $FeCl_3$ is added in increasing order whereas $Al_2(SO_4)_3$ or $AlCl_3$ salt in decreasing and vice versa.
20 mL = constant dosage, inc = increasing order, dec = decreasing order.

Figure 2.3 shows that the pH in the samples with a combination of constant 20 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL $Al_2(SO_4)_3$ dosage decreased to a range of 4.49–3.51. The pH in the samples with a combination of constant 20 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL $AlCl_3$ dosage decreased in a pH range between 4.54–4.29. In the former combination, the pH difference between samples is lower than the latter; this indicates that $Al_2(SO_4)_3$ yielded a better hydrolyzing power than $AlCl_3$.

Samples with a combination of constant 20 mL $Al_2(SO_4)_3$ and 10, 15, 20, 25 and 30 mL $FeCl_3$ dosage showed a decreasing pH range of 4.60–3.51, whereas the pH in the

samples with a combination of constant 20 mL $AlCl_3$ and 10, 15, 20, 25 and 30 mL $FeCl_3$ dosage decreased in a range of 4.70–3.41.

Samples with a combination of 10, 15, 20, 25 and 30 mL $FeCl_3$ and 30, 25, 20, 15 and 10 mL $Al_2(SO_4)_3$ dosage showed decreasing pH range of 4.56–3.43 whereas the pH trend in a combination of 10, 15, 20, 25 and 30 mL $FeCl_3$ and 30, 25, 20, 15 and 10 mL $AlCl_3$ dosage, it is in a range of 4.70–3.19. NB: Equation 2.4 shows the rate of hydrolysis of a metal salt with decreasing pH between hydrolysis species. The pH decreasing trend above indicates the rate of hydrolysis of each metal (M^{3+}) salt.

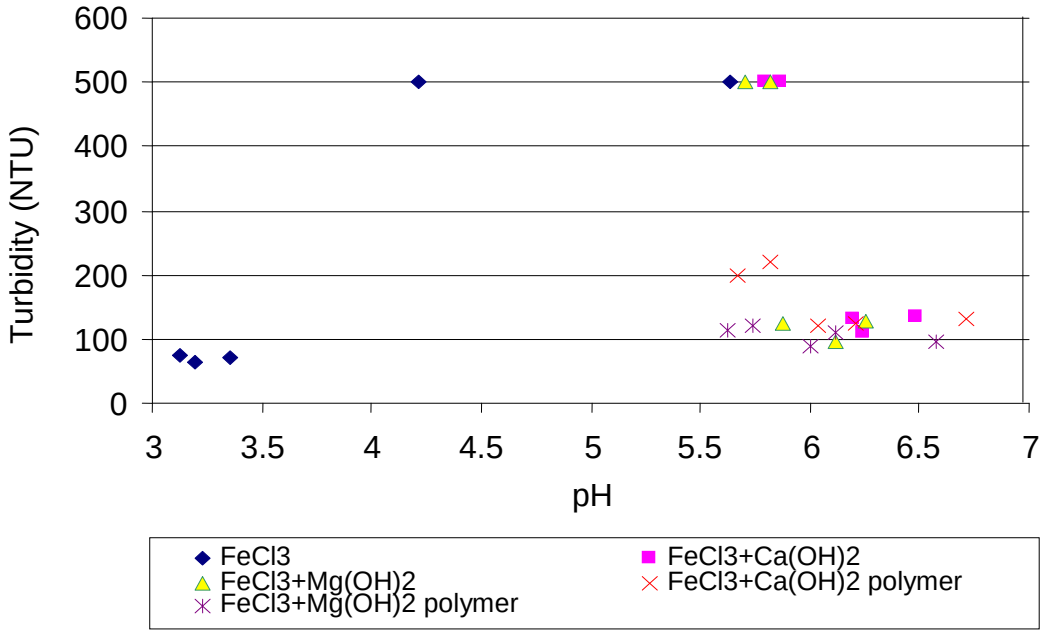


Figure 2.4: pH vs turbidity of the samples dosed with increasing $FeCl_3$ only, $FeCl_3$ and $Mg(OH)_2$ or $Ca(OH)_2$, $FeCl_3$+$Ca(OH)_2$ or $Mg(OH)_2$ polymers.

The results in Figure 2.4 show that the pH in samples which have been dosed with $FeCl_3$ only decreases (with increasing dosage) in a pH range 3.20–5.66. Turbidity in

the first two samples (20 and 30 mL dosage) with pH values 5.66 and 4.21 was over-range (greater than 500 NTU) and the rest of the samples with 40–60 mL dosage show turbidity in a range of 65–70 NTU. The pH in the samples which had been dosed with a combination of 10, 15, 20, 25 and 30 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL $Ca(OH)_2$ dosage decreased from 9.32 to 5.8, 5.88, 6.2, 6.24 and 6.48 respectively. The pH changing trend in the samples increased with increasing dosages differs from that shown by the samples dosed with $FeCl_3$ only, as well as the samples shown in Figure 2.1. This could be attributed to the hydroxyl ions released by the metal hydroxide of Ca^{2+} and Mg^{2+} when they increased the alkalinity in the solutions, thus changing the treatability of the more alkaline paint wastewater. The pH in the samples which had been dosed with a combination of 10, 15, 20, 25, 30 mL $FeCl_3$ and 10, 15, 20, 25 and 30 mL $Mg(OH)_2$ dosage decreased from 9.32 to 5.7, 5.82, 5.88, 6.12 and 6.26 respectively. Turbidity of the first two samples (20 and 30 mL) with a combination of $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ corresponds to the pH range of 5.80–5.86, which is greater than 500 NTU; whereas the pH and the turbidity in the rest of the samples dosed with 40–60 mL was in a range of 5.88–6.48 and 97–136 NTU respectively. The pH in the samples which had been dosed with $FeCl_3$-$Ca(OH)_2$ decreased to 6.71, 6.21, 6.04, 5.82 and 5.67; and the pH in the samples with $FeCl_3$-$Mg(OH)_2$ polymers decreased to a range of 6.58–5.62. This shows a similar changing trend to that in the samples which had been dosed with 20, 30, 40, 50 and 60 mL of $FeCl_3$ only. This means that the pH decreases with increasing dosages, thereby yielding turbidity in a range of 90–120 NTU.

Further two identical batches of experiments were carried out on paint wastewater samples with $FeCl_3$, $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ dosages respectively. The samples in the first batch were treated in a jar test with rapid mixing at 250 rpm for 4

minutes, 100 rpm for 10 minutes and settled for 1 hour whereas the samples in the second batch settled without prior mixing to plot Figures 2.5 and 2.6.

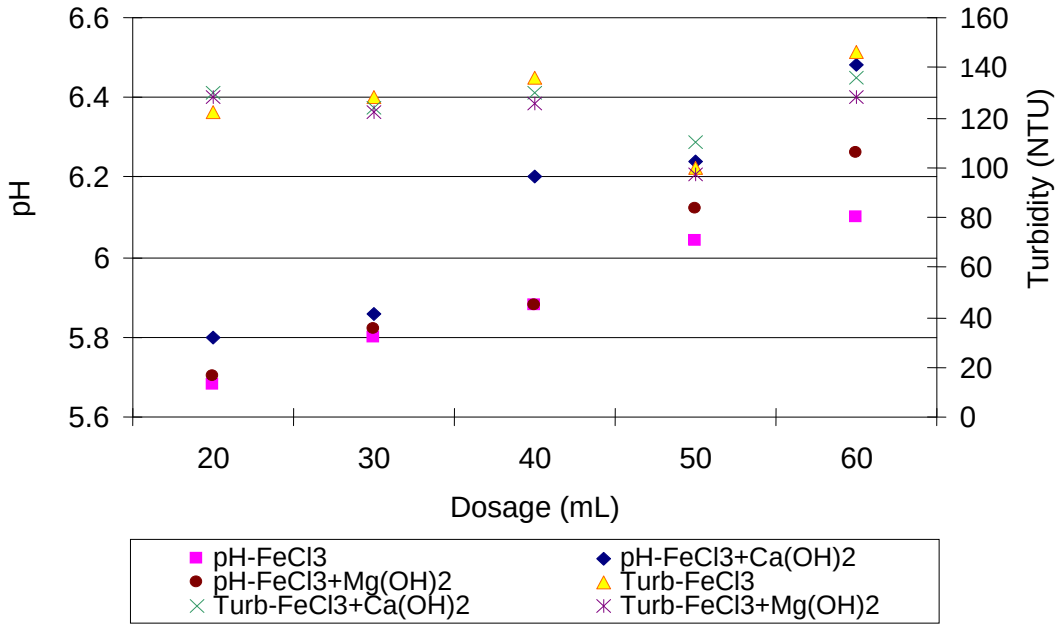


Figure 2.5: pH, turbidity and dosage for samples with increasing $FeCl_3$, $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ during rapid mixing.

The pH yielded by $FeCl_3$ dosage in Figure 2.4 with 250 rpm rapid mixing for 2 minutes is in a range of 3.0-3.6 whereas the corresponding pH in Figure 2.5 is almost double at a range of 5.6-6.1. Mixing in the latter experiment was doubled to determine the impact of mixing time on floc formation; which can affect turbidity removal. Turbidity in the samples in Figure 2.4 is slightly lower than in Figure 2.5, in a range of 100-120 NTU and 120-142 NTU respectively. I suggest that the discrepancy is caused by rupturing of the flocs during prolonged time of 4 minutes during rapid mixing, thus causing re-stabilization (Swartz *et a*l., 2004). Probably that

might have been caused by the reversal of hydrolysis reaction as shown by Equation 2.3, thereby re-stabilizing the colloidal suspension. This postulate can be linked to the findings of the study conducted by Ntwampe *et al* (2013) stating that effective flocs formation occurs within 30-60 seconds during rapid mixing.

Figure 2.6 represents the pH, turbidity and dosage of paint wastewater samples with $FeCl_3$, $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ dosages respectively measured after 1 hour settling without mixing.

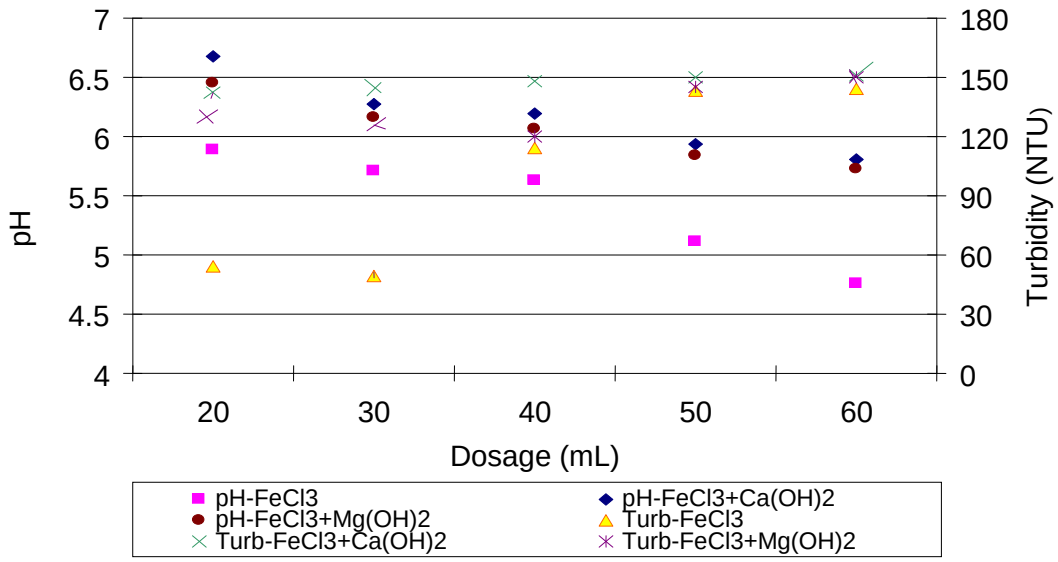


Figure 2.6: pH, turbidity and dosage for samples with increasing $FeCl_3$, $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ without mixing.

The pH in the samples with $FeCl_3$, $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ dosages without mixing in Figure 2.6 is identical to the pH of their corresponding samples with mixing in Figure 2.5. The pH values confirm the results obtained in Figure 2.4, which shows that the pH in samples which have been dosed with metal salts during mixing

do not differ significantly from the pH in the same samples without mixing. Turbidity shown in Figure 2.6 is in the range of 122-154 NTU. This turbidity changing trend is slightly higher than the sample with rapid mixing in Figure 2.5.

2.6 Discussion

Part 1-samples with Fe^{3+} and Al^{3+} salt dosage only.

This part of the study discusses the pH and turbidity changing trend with increasing combination of $FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$ dosage added before or during mixing respectively. After addition of metal salts to a paint wastewater sample, hydrolysis takes place and the pH of hydrolysis species decreases (Equation. 2.4). The pH changing trend reflects the ability of the metal ions of the metal salt to hydrolyze the sample. Turbidity readings indicate the ability of each metal ion (Fe^{3+} and Al^{3+}) destabilizes to form flocs which adsorb colloidal particles in the paint wastewater. The comparison of the pH values of treated wastewater with Fe^{3+} and Al^{3+} has demonstrated their hydrolyzing power. Figure 2.1 showed the decreasing pH trend of 7.73–2.90, 7.42–2.0 and 8.23–3.70 with $FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$ dosages respectively; indicating that $Al_2(SO_4)_3$ yielded a higher hydrolyzing power than $FeCl_3$ and $AlCl_3$. This shows that at low pH, $Al_2(SO_4)_3$ has the ability to attract a large number of hydroxyl ions (OH^-) from the cleavage of water molecules with the release of hydrogen ions, which also caused a decrease in pH of the colloid. The low pH with $Al_2(SO_4)_3$ dosages also shows that $Al_2(SO_4)_3$ has relatively more ability to

cause destabilization of the colloidal suspension, resulting in effective hydrolysis. The latter is a process where adsorption substrates, namely hydrolysis species or metal hydroxides are formed. The pH obtained in Figure 2.1 fall below 6.5, a region mostly dominated by charge neutralization as well as MOH^{2+} and $M(OH)_2^{+}$species (Jiang *et al.*, 1997). The pH range also shows that "sweep flocculation", a process by which colloidal particles are trapped by flocs or enmeshed in the flocs which have already been formed and settle out of the colloidal system (Peavy *et al*., 1995).

Equation 2.4 shows that the formation of stable flocs ($Fe(OH)_3$) occurs during hydrolysis; hence hydrolyzing power is used to describe the rate of flocs formation. The decreasing rate of pH with 0.043 M Al^{3+} ions in $Al_2(SO_4)_3$ is from 9.32 to a range of 7.42–2.0. The low pH changing trend to a pH value of 2.0 indicates that $Al_2(SO_4)_3$ has a relatively higher hydrolyzing power. According to Figure 2.1, the samples which had been dosed with 10 mL of all three metal salts and 20 mL $AlCl_3$ are alkaline with a pH above 7.0. These samples are opaque and the tiny particles that are dispersed throughout the solution indicate that de-flocculation occurred. This shows that the degree at which the hydrogen ions (H^+) were released into the solution during hydrolysis is low, hence there was a low concentration of hydroxyl ions (OH^-) to react with metal ions to form flocs (hydrolysis species) as shown in Equation 2.4. This also reveals that the pH of the solution is an indication of the rate at which hydrolysis occurs. Electron valence also forms part in the rate of hydrolysis because it enhances the force of attraction on the hydroxyl ions. Since the OH^- is formed from the cleavage of water molecules, protons (H^+) are released into the solution and cause a pH drop. The opaque colour shown by alkaline solutions indicates that the flocs are very small to form agglomerates, hence adsorption is impossible. It is suggested that

the tiny particles in the opaque paint wastewater samples which have been dosed with 10 and 20 mL of the coagulants indicate that nucleation occurred but no further reactions such as crystallization and aggregation (larger flocs). The concentration of metal ions (Fe^{3+} and Al^{3+}) added to paint wastewater was not sufficient to exceed the solubility of their metal hydroxides to form precipitates (Moore *et al.*, 1978). It was observed that the higher pH decreasing rate of the samples with 0.043 M Al^{3+} in $Al_2(SO_4)_3$ dosage in Figure 2.1 showed a higher concentration of OH^- ions bonding to Al^{3+} ions compared to Fe^{3+} and Al^{3+} in $FeCl_3$ and $AlCl_3$ respectively. This is explained in Equation 2.4 when high concentration of metal ions (M^{3+}) react with hydroxyl ions (OH^-) from the water molecules and more hydrogen ions (H^+) are released into the solution due to high hydrophilicity (Wulfsberg, 1987). The pH in all the samples decreases in a uniform trend with increasing dosages from 10 to 60 mL. The results also showed that the pH in the samples with a combination of $FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$ dosage before mixing is identical to the pH of their corresponding samples which have been dosed during mixing. This indicates that dosing before and during mixing is insignificant; which also show that trivalence property of metal ions influences the rate of hydrolysis.

Figure 2.2 shows the turbidity of the same samples which were used to plot pH-dosage in Figure 2.1. This study considers turbidity below 100 NTU as the best removal efficiency, 100–120 NTU as moderate removal efficiency and above 120 NTU as poor removal efficiency. This specification seems to be conservative as it is below a normal specification of 150 NTU, a value stipulated by different water treatment works. According to Figure 2.2, the samples with 10 mL of all three metal salts dosage have pH above 6.5 and turbidity above 500 NTU. This indicates that 10 mL of $FeCl_3$, $Al_2(SO_4)_3$ or $AlCl_3$ cannot flocculate 16 g of colloidal particles in paint

wastewater. Turbidity in the samples with a combination of 20–60 mL $FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$ dosage before and during mixing shown in Figure 2.2 is also low as in Figure 2.1. A low turbidity between the samples with 20–60 mL of 0.043 M Fe^{3+} or Al^{3+} ions dosages separately or combined in Figure 2.2 confirms that equal number of moles of metal ions (Fe^{3+} or Al^{3+}) in a solution react homogeneously on the same concentration of the colloidal particles. The changing trend between the pH and turbidity in Figures 2.1 and 2.2 indicates that there is a correlation between the two parameters. The results also shows that a combination of a monoprotic salt ($FeCl_3$) and a diprotic salt ($Al_2(SO_4)_3$) dosages yield a better hydrolyzing power and better turbidity removal compared to their corresponding a combination of monoprotic salts ($FeCl_3$ and $AlCl_3$) dosage. I postulate that a double dissociation which occurs with diprotic H_2SO_4 of a metal salt ($M_2(SO_4)_3$) which behaves as a buffer during hydrolysis, thus enhancing further hydrolysis unlike in monoprotic metal salts. It is suggested that dissociation of HCl with monoprotic metal salts ($FeCl_3$ and $AlCl_3$) occurs completely in a single reaction; allowing no further reaction (Casas *et al*., 2000). I suggest that a better turbidity removal with diprotic metal salts occurs when primary hydrolytic species precipitate together and adsorb residual particles onto the particles during the second dissociation (Chang *et al.* 2004). Such a finding has been confirmed in a study by Ntwampe *et al*. (2013) to investigate the effect of mixing rates on optimal flocs formation.

Since Fe^{3+} and Al^{3+} salts show effectiveness in removing a broad range of impurities from wastewater, I also suggest that two mechanisms, namely charge neutralization of negatively charged colloids by cationic products and incorporation of impurities in an amorphous hydroxide precipitate are predominant in my experiments as stated by Duan *et al.* (2002). They also indicated that the importance of the two mechanisms

depends on the pH and coagulant dosage, which are the parameters I focused on. This also suggests that destabilization is mainly achieved by adding smaller quantities of cations such as Fe^{3+} and Al^{3+} rather than large amounts of salts.

The results in Figure 2.3 show that a combination which includes increasing $FeCl_3$ and decreasing $Al_2(SO_4)_3$ or $AlCl_3$ dosage yields the best turbidity removal in a range of 49–90 NTU. This also happens in a combination which includes decreasing $FeCl_3$ and increasing $Al_2(SO_4)_3$ or $AlCl_3$ dosage. Figure 2.3 also shows that the pH values in all the samples are less than 6.0. The observations from samples where one metal salt is increased and the other is decreased indicate that the rate of hydrolysis in paint wastewater is identical with volume ratios of Fe^{3+} and Al^{3+} ions. This also shows that volume ratio of either metal ion (M^{3+}) is insignificant, i.e. 3.0 or 0.33 Al/Fe volume ratios exhibit identical reactivity in a colloid.

Part 2-samples with a combination of $FeCl_3$ and Ca^{2+} or Mg^{2+} hydroxide, polymers of $FeCl_3$ and Ca^{2+} or Mg^{2+} dosage.

The experiments in Part 2 were carried out to determine the changing behaviour of the pH with turbidity when the paint wastewater was dosed with 0.043 M Ca^{2+} in $Ca(OH)_2$ and 0.043 M Mg^{2+} in $Mg(OH)_2$ respectively as observed in Figure 2.4. Since the paint wastewater was more alkaline, pH of 9.32, the addition of coagulants increased the concentration of OH^- ions in the samples, thus causing further hydrolysis of the Fe^{3+} ions. According to Metcalf *et al.* (2003), the advantage of dosing $Mg(OH)_2$ in the solution of such pH is its ability to cause maximum pH of 9.0

in wastewater, giving a buffered pH control compared to $Ca(OH)_2$ which can reach pH of 12.0. Magnesium salts form $Mg(OH)_2$ precipitates when the pH is raised above 9.5, which is the pH range in our experiments, and precipitates are not complete until the pH reaches 11 (Metcalf *et al.*, 2003). $Mg(OH)_2$ has a low solubility and can rise to a maximum of pH 9.0 in a case where it is overdosed.

Unlike Figures 2.2 and 2.3, the results in Figure 2.4 showed that the changing pH does not correlate with the turbidity removal. This behaviour is not strange because there is addition of Ca^{2+} and Ma^{2+} hydroxide to the samples. Turbidity values do not change consistently with decreasing pH and increasing dosages. This behaviour is shown by the pH and turbidity changing trend in the samples with a combination of $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$ dosage; when compared to the their corresponding samples with equal dosages of $FeCl_3$-$Ca(OH)_2$ or $FeCl_3$-$Mg(OH)_2$ polymers. The branches of the polymers are adsorbed onto different colloidal particles, interlocking with one another and thereby leading to the formation of a settleable mass (Peavy *et al.*, 1995). It is inevitable to have varying pH-turbidity changing behaviour between Fe^{3+} and Al^{3+} dosages alone, a combination of $FeCl_3$ with Ca^{2+} or Mg^{2+} hydroxides or polymers of $FeCl_3$ and Ca^{2+} or Mg^{2+} hydroxides dosage. The pH value in the samples with $FeCl_3$-$Ca(OH)_2$ polymer is slightly lower than the pH in $FeCl_3$-$Mg(OH)_2$ polymers whereas turbidity of the former is slightly higher than their corresponding samples of the latter. The turbidity values also fluctuate with decreasing pH during hydrolysis and also show that $FeCl_3$-$Mg(OH)_2$ polymers form larger and dense (sponge-like) flocs which enable them to achieve maximum mass transfer of the colloidal particles during adsorption. My experimental findings show that synthetic $FeCl_3$-$Mg(OH)_2$ polymers have a high turbidity removal potential in paint

wastewater. Under experimental conditions, the reaction of $FeCl_3$ with $Ca(OH)_2$ before dosing form polymers that yielded the best turbidity removal as shown by Figure 2.5. There is an improved turbidity removal in paint wastewater dosed with $FeCl_3$–$Ca(OH)_2$ or $FeCl_3$–$Mg(OH)_2$ polymers compared to the turbidity obtained when they are added as separate reagents, $FeCl_3$ and $Ca(OH)_2$ or $Mg(OH)_2$. This suggests that the polymeric compounds which are formed by reacting $FeCl_3$ with $Ca(OH)_2$ or $Mg(OH)_2$ form a similar filter-cake structure; which is perceived to cause improvement in turbidity removal. The alkalinity of these polymers shows that there is additional discharge of OH^- into the colloidal suspension, which reacted with residual Fe^{3+} ions and form more hydrolysis species which condense and form more filter-cake structures; where extra mass transfer of the colloidal particles occurs. Based on the identical turbidity removal of $FeCl_3$-$Ca(OH)_2$ or $FeCl_3$-$Mg(OH)_2$ polymers, this shows that the two compounds have similar characteristics. I therefore conclude that these reactions which lead to turbidity removal in the paint wastewater are of a physical nature. A further postulate is that the turbidity removal in the samples which have been dosed with 0.043 M $FeCl_3$-$Ca(OH)_2$ or $FeCl_3$-$Mg(OH)_2$ polymers occurs by filtration process through the filter-cake structure. According to Equation 2.4, the hydrolysis species ($Fe(OH)_3$) is formed by Fe^{3+} ion and OH^- ion the metal hydroxide. This reaction differs from Equation 2.1, whereby the Fe^{3+} ions reacts with OH^- from the water molecules to form $Fe(OH)_{3(s)}$ and the metal salts ($Ca(OH)_2$ or $Mg(OH)_2$) dissolve in the solution. This indicates that the metal hydroxides added into paint wastewater in Equation. 2.1 adjust the pH of the solution whereas the metal hydroxides in Equation. 2.4 form polymers with $FeCl_3$. The comparison between the pH and turbidity in Figures 2.1, 2.2 and 2.3 shows that the changing trend is uniform, which shows that there is correlation between the pH and

turbidity; which is not the case with the pH and turbidity changing trend in Figure 2.4. The results in Figure 2.5 show that the pH in the samples which have been stirred (mixing) is identical to those without stirring (mixing) whereas turbidity in the former is slightly lower than the latter.

2.7 Conclusions

The results obtained in this study indicate that there is a correlation between the pH and turbidity in paint wastewater when metal salts (Fe^{3+} or Al^{3+} salt) are added separately or combined. $Al_2(SO_4)_3$ showed a higher hydrolyzing power in paint wastewater than $FeCl_3$ and $AlCl_3$. A combination of monoprotic metal salts, $FeCl_3$ and $AlCl_3$ shows a better hydrolyzing power than monoprotic with diprotic, $FeCl_3$ and $Al_2(SO_4)_3$. Effective turbidity removal occurred at pH values below 6.0 in paint wastewater containing 16 g of solid paint with $FeCl_3$, $Al_2(SO_4)_3$ and $AlCl_3$ dosages. The dosing sequence and dosing before or during mixing do not play any significant role in turbidity removal in paint wastewater. Consistent turbidity results show that equal moles (0.043 M) of Fe^{3+} in $FeCl_3$, Al^{3+} in $AlCl_3$ or $Al_2(SO_4)_3$ dosages respectively, flocculate the same mass of solid paint (16 g) in a solution. The homogeneity in turbidity removal potential indicates that Fe^{3+} and Al^3 salts with identical concentration and volume react similarly in equal volume of wastewater containing 16 g of solid paint. Since the entire process focuses on turbidity removal, a process which involves a physical phenomenon (adsorption), I suggest that adsorption in coagulation-flocculation process is physical. The findings reveal that $Al_2(SO_4)_3$ shows the best turbidity adsorption, $AlCl_3$ a bit lower but better than $FeCl_3$;

I conclude that $Al_2(SO_4)_3$ has a better destabilization-hydrolysis potential compared to $AlCl_3$ and $FeCl_3$.

The samples which have been dosed with Fe^{3+} salt together with either $Ca(OH)_2$ or $Mg(OH)_2$ show that the pH is not a direct indicator of turbidity removal in a more alkaline colloidal suspension such as paint wastewater. The best turbidity removal was obtained from a combination of Fe^{3+} salt and $FeCl_3$–$Ca(OH)_2$ or $FeCl_3$–$Mg(OH)_2$ dosage at pH values below 3.5. In addition, the pH and turbidity in paint wastewater with $FeCl_3$–$Ca(OH)_2$ or $FeCl_3$–$Mg(OH)_2$ polymers do not correlate, this showed that the pH is not an ideal indicator of turbidity removal during treatment of more alkaline paint wastewater; the behavior shown when paint wastewater was dosed with Fe^{3+} salt together with either $Ca(OH)_2$ or $Mg(OH)_2$ for pH adjustment. The results show that the sample with more acidic pH of 3.5 yields the best turbidity. However, the effluent of such low pH has to be neutralized with a basic reagent before it is discharged to a water-course. A further test was carried out on characterization of the sludge of the paint wastewater on SEM micrographs as shown in Figure S1 under appendix to show crystal morphology of the FeCl3–$Ca(OH)_2$ or $FeCl_3$–$Mg(OH)_2$ polymers. The micrographs show that $FeCl_3$–$Mg(OH)_2$ polymers is a longitudinal fibre-like structure whereas $FeCl_3$–$Ca(OH)_2$ polymers are solid structures with pebble-like structures on top.

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CHAPTER 3 Comparison of jar tests and microscope slide experiments for flocculation of paint wastewater

Abstract

A 169.2 g of paint diluted in 1 L potable water sample was prepared. 200 mL per beaker of this sample was poured into six 500 mL glass beakers and dosed with 0.043 molar solution of $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ or $Al_2(SO_4)_3$ and were treated in a jar test. Two drops of the supernatant were placed under a light microscope which had been fitted with a camera. The images were captured after 1, 30, 60 and 90 minutes in order to determine the area covered by the flocs on a microscope slide. A further experiment was carried out using the same sample before a jar test and same ratio (1:10) of paint wastewater sample-coagulant and placed on a microscope slide with gentle mixing. The samples were also observed under the microscope. The images of the samples were also captured after 1, 30, 60 and 90 minutes to compare the area covered by the flocs with those of the first set of experiments. The observations from both set of experiments showed that area covered by the flocs in the jar test correlates linearly with the area covered by flocs in the microscope slide experiment. An equivalent means of testing can be conducted using microscope observation, which may be preferable to a jar test on the grounds of simplicity and lower cost.

1. Introduction

In the previous experiments I investigated flocculation of paint wastewater focusing

on the physico-chemical treatment dynamics, yet analytical investigation is necessary to advance changing technology. A jar test was identified as an area to be investigated in this study to reveal a technique which can measure the concentration of colloidal particles in a more accurate and representative manner. I assume that a jar test consumes relatively more time from the preparation of the standards, conducting experiment, waiting for the samples to settle before taking measurements and calibration of equipment. A jar test is a laboratory technique which is used by water treatment analysts to determine the effectiveness of coagulants on the wastewater during coagulation/flocculation. Parameters which are important include pH, turbidity and mixing rates and retention time. The tests are conducted frequently based on the frequency at which feed raw water quality changes due to anthropogenic, meteorological and climatic conditions. The objective is to keep treated water in good quality as stipulated by the operating manual and plant specifications in order not to damage plant and equipment. Hoadley *et al*. (1977) recommended a jar test for determining parameters such as pH, coagulant dosage, alkalinity and flocculation time. The pH tests measure the acidity or alkalinity of the water prior and after treatment whereas turbidity tests measure the concentration of the colloidal particles. However, in wastewater treatment, turbidity is the parameter of the highest priority as indicated that it can cause damage to pipe-work and has detrimental effect on humans where wastewater is treated for potable water supply. Turbidity plays a critical part in industries because treated wastewater (effluent) is recycled to various processes such as product process plants, cooling systems, auxiliary systems, dust suppression, horticultural activities, where a high concentration of colloidal particles may damage the plant and equipment or spoil the quality of the end-products. Although turbidity measurement is commonly employed by water treatment works, this technique is not

ideal for tackling wastewater-related problems such as precise amount of dissolved salts and turbidity in treated water (Duan *et al*., 2006).

If process water is discharged to a water source untreated, it may affect the equipment (pipes, pumps and valves) which are used for transfer and the river ecosystem negatively. Thus the removal of turbidity, which relies on the pH of the treated water, is essential. Appropriate and effective dosages are shown by a high adsorption capacity of the flocs and high turbidity removal (O'Melia *et al*., 2001, Goldberg *et al*., 2002, Meghzili, 2008, Ghaly *et al*., 2006 and Metcalf *et al.,* 2003). A pH in the range 8–9 has been recommended for the flocculation of paint wastewater (Aboulhassan *et al*., 2006). A pH, which can be measured either on-line or manually in the laboratory, is considered as a fundamental operating parameter.

The quality of feed wastewater also plays a vital role in wastewater treatment (Amuda *et al*., 2006, Amuda *et al*., 2007 and Gregory *et al*., 2001). The varying quality of feed raw water in the treatment works can be caused by various plant operating factors such as the concentration of the mineral content, temperature, dosages, dosing and mixing rates. Some wastewater treatment works use reservoirs that are situated 'upstream' from the wastewater purification plant to allow the heavy material to settle out. This also allows mixing of the feed and attenuates variations in feed composition. However, changes in the feed properties can still occur at any time and require that laboratory tests are carried out frequently in order to adjust the dosages and achieve optimal turbidity removal efficiency.

The use of turbidity measurement in jar tests has been reported to be somehow unrepresentative compared to advanced measurements such as particle size distribution (PSD) or chord length distribution (CLD) (Kempkes *et al*., 2007, Li *et al*., 2006, McCurdy *et al.,* 2004, Li *et al*., 2005, Langston *et al*., 2001 and Heath *et al.,* 2002). PSD which use light scattering cannot be employed for paint wastewater because the paint is likely to deposit a film on the lenses of the Malvern analyzer which may affect the accuracy of the results in cases of human error. CLD and PSD are complicated techniques and require specialized and expensive equipment. The size and shape of the flocs (spherical or non-spherical) are the most rapid means of testing the efficiency of the dose (Wu *et al*., 2001, Yu *et al*., 2008 and Li *et al.,* 2006).

Apart from all sophisticated techniques used to measure particle size distribution, more research is necessary to investigate a cheaper and simple technique to measure water quality. The jar test is a conventional technique and can also be unreliable at times, more especially when the particles are too small to flocculate and be picked up by scattered lights of the turbidity meter. A more representative and modern technique such as floc size counting is recommended; hence this study investigates the feasibility of employing this technique to measure turbidity. The study also investigates how to achieve best turbidity removal using varying mixing times using the most effective coagulant, Fe^{3+} and Al^{3+} salts. The experiments will also establish an optimal dosage required by a specific metal salt to yield the best turbidity removal.

The objective of this study is to compare the results obtained from the jar tests and microscope slide experiments and check if there is a correlation between the two so that the latter can be a replacement for a jar test, a conventional technique which uses

turbidity measurement for colloidal particles removal. Advantage of the microscope slide test is that it shows the exact concentration of flocs remaining in the colloidal suspension and does not require use of vast quantities of reagents.

3.2 Material and methods

3.2.1 Preparation of synthetic paint wastewater and coagulant solutions

A synthetic paint wastewater sample was prepared by diluting 169.2 g of paint in 1 litre of distilled water to give total solids concentration of 80 g/L as explained in Section 2.2.1.

A 0.043 M of $Fe^{3+}$and Al^{3+} ions (a concentration obtained from the literature) of monoprotic and diprotic standard solutions were prepared as stated in section 2.2.2.

3.2.2 Experiment A: Jar test

Sample of synthetic paint wastewater with the pH 8.09 were poured into four 200 mL glass beakers. The samples were dosed with 20 mL of the $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ or $Al_2(SO_4)_3$ solutions respectively (concentrations are as given in Table 2.1). The samples were treated in the jar test mixing equipment, a *BIBBY Stuart Scientific Flocculator (SW1 mode).* Each beaker was stirred at 250 rpm for 60 seconds; the mixing speed was then reduced to 100 rpm for 10 minutes. Immediately after the 10

minutes of mixing at 100 rpm, a 40 mL supernatant from the first sample was poured into a 100 mL beaker and the pH and turbidity were measured. The rest of the samples in 200 mL beakers settled for 90 minutes. Two drops of a sample from 100 mL beaker were placed between two microscopic slides held 2 mm apart using spacers, and placed on the stage of a light microscope fitted with a camera (description of the equipment used is given in section 2.3). The images of the sample were captured after 1 minute. The remaining three samples were treated in a similar manner but the images were captured after 30, 60 and 90 minutes respectively.

The pH meter and turbidity meter are similar to those described under sub-sections 2.4.1 and 2.4.2.

3.2.3 Experiment B: Microscope slide

Microscope slide experiments were carried out (Experiment B) by diluting 10 mL of each coagulant solution (used in Experiment A) in a 100 mL volumetric flask using distilled water. Then 2 drops of diluted coagulant and 2 drops of the paint wastewater (which was used in Experiment A) with the same coagulant-paint wastewater ratio (i.e. 1:10) were placed on a microscope slide and mixed manually for about 5 seconds. Another slide was placed on top and the slides were held 2 mm apart by spacers. Images of the samples were captured after 1 minute so that they could be compared with the first sample in experiment A. Further photographs of the drops of

the paint wastewater sample and coagulant were captured after 30, 60 and 90 minutes. A *Wiezt Wetzlar* light microscope (made in Germany) was used to obtain the images. The microscope slides were placed on the optical stage and image for each slide was captured at 400 times magnification. A digital *Moticam 1000, 1.3MP Live Solution Macintosh OSX Compatible* microscopy camera (made in China) was used to capture the images. It was connected to both the light microscope and a PC. The visuals were automatically saved as scf.doc file and stored in a folder. The images produced by the light microscope were printed in order to measure the fraction of the area covered by the flocs. This was accomplished by placing a 2 mm square-meshed transparency over the printed copy of the images; dark squares in the grid were counted. The total area covered by the dark flocs was compared to the total area covered by the sample. The photographs of the corresponding samples from Experiments A and B were compared to determine the size of the flocs over time.

3.2.4 Sludge drying and characterization

The water from the sludge of the samples from a jar test was drained by placing the whole cake of sludge on filter paper and was thereafter put in an oven at 250 $^{\circ}$C for three days. The cake was then ground to a fine powder and analyzed using XRD, TGA and SEM, the techniques which measure the concentrations of the metals in the sludge, the moisture content and the crystal morphological pattern of the sludge respectively. In addition, a dry paint sample was prepared for XRD analysis in the

same way. A XRD (Model Rigaku) diffractometer with CuK radiation at 150 mA and 50 kV were used in this study. Approximately 1 g of a sample was placed in the diffractometer.

For TGA analysis, the dried sludge samples that had been ground to a fine powder were sieved through a 100 mesh screen. A Stanton thermogravimetric balance (Model HT-M) was used to measure weight changes as a function of temperature under flowing nitrogen gas (99.9 % pure) at an increasing heat rate of 3 $^{\circ}$C/min and going up to 1000 $^{\circ}$C. Buoyancy correction was applied in each case. The differential weight loss was recorded as a function of time.

The instrument used in this study was a scanning electron microscope SEM (Model JEOL). A few grains of a dry sludge sample were placed on a cylindrical stub and carbon coated to prevent ionization.

3.3 Results and discussion

Figure 3.1 gives a comparison between the area covered by flocs on the microscope images for samples which have been treated in Experiments A and B using all four coagulants after 1, 30, 60 and 90 minutes. The images taken after 30 and 60 minutes do not differ significantly from those after 1 and 90 minutes, it was thus decided to plot the latter (1 and 90 minutes). The percentages covered by flocs shown for the experimental results are plotted in Figure 3.1 and it is seen that clear water constituted 80–93 % of the total area.

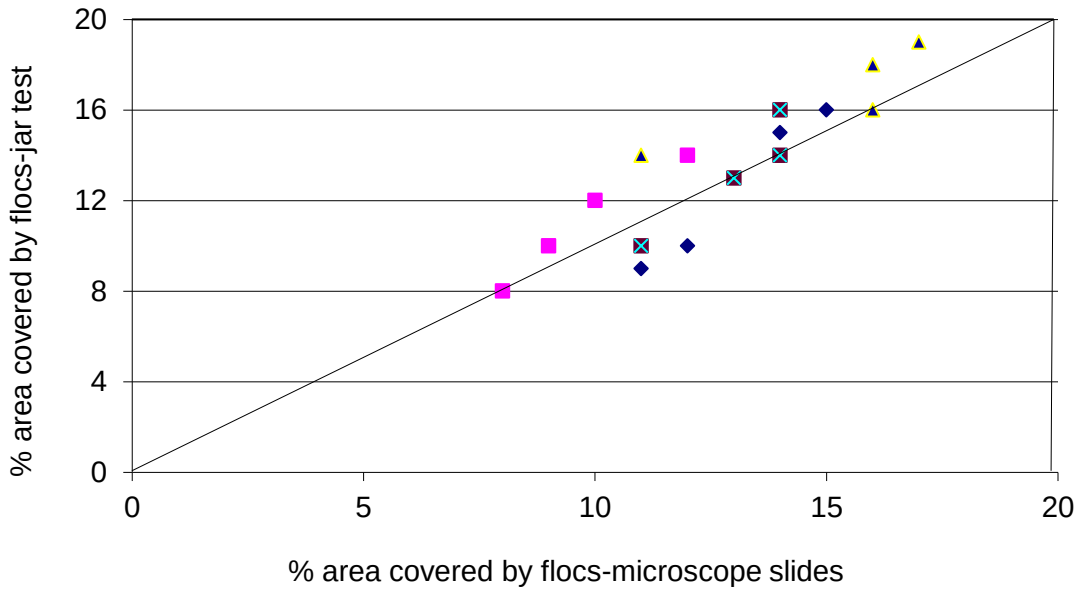


Figure 3.1: Microscopic observation using 0.043 M Fe^{3+} in $FeCl_3$ and $Fe_2(SO_4)_3$ dosing.
♦ = flocs-$FeCl_3$, ■ = flocs-$Fe_2(SO_4)_3$, Δ = flocs-$AlCl_3$, ⊗ = flocs-$Al_2(SO_4)_3$.
pH_{aver}-$FeCl_3$=4.1, pH_{aver}-$Fe_2(SO_4)_3$=3.3, pH_{aver}-$AlCl_3$=4.5, pH_{aver}-$Al_2(SO_4)_3$ = 4.6.
pH_{aver} = average pH of the samples which were photographed after 1, 30, 60 and 90 minutes measured after jar tests.

There were a slightly more colloidal particles on the microscope slide for the samples which were dosed with $AlCl_3$ and $Al_2(SO_4)_3$ compared to the corresponding those dosed with $FeCl_3$ and $Fe_2(SO_4)_3$. In addition, there is a linear relationship between the two different types of experiments; all the different coagulants lie on the same line. The comparison between the microscope images of jar tests and the microscope slides, Experiments A and B, shows that a microscope slide technique can be a suitable replacement for the jar test. The average pH of each coagulant has been included in the figure title, i.e. 4.1, 3.3, 4.5 and 4.6 for $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ respectively. These averages were taken for the samples removed from the

jar test beaker after 1, 30, 60 and 90 minutes. The average range of the pH values was between 0.12 and 0.29.

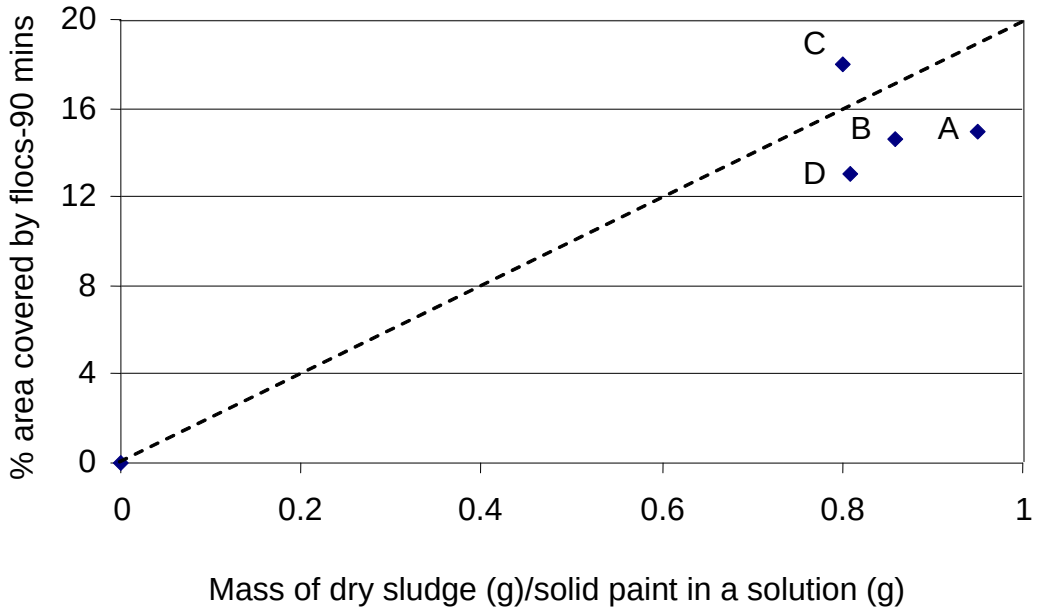


Figure 3.2: Percentage area covered by flocs vs. mass ratio of sludge/solid paint in a solution using 0.043 M Al^{3+} and 0.043 M Fe^{3+} salts.
A=$FeCl_3$, B=$Fe_2(SO_4)_3$, C=$AlCl_3$ and D=$Al_2(SO_4)_3$

Figure 3.2 illustrates that the area covered by the flocs and the fraction of solids removed are very similar in all four coagulants. These results indicate that $FeCl_3$ and $Fe_2(SO_4)_3$ removed 85.0 and 86.1 % of the total solids in the wastewater whereas $AlCl_3$ and $Al_2(SO_4)_3$ removed 82.0 and 87.7 % of the paint solids respectively. According to the area covered by flocs in Figure 3.2, $Al_2(SO_4)_3$ yielded better solids removal compared to $AlCl_3$ after 90 minutes whereas $Fe_2(SO_4)_3$ yielded almost the same solids removal as $FeCl_3$ after 90 minutes. $Al_2(SO_4)_3$ and $AlCl_3$ yielded the same mass of dry sludge whereas $FeCl_3$ yielded less dry sludge than $Fe_2(SO_4)_3$

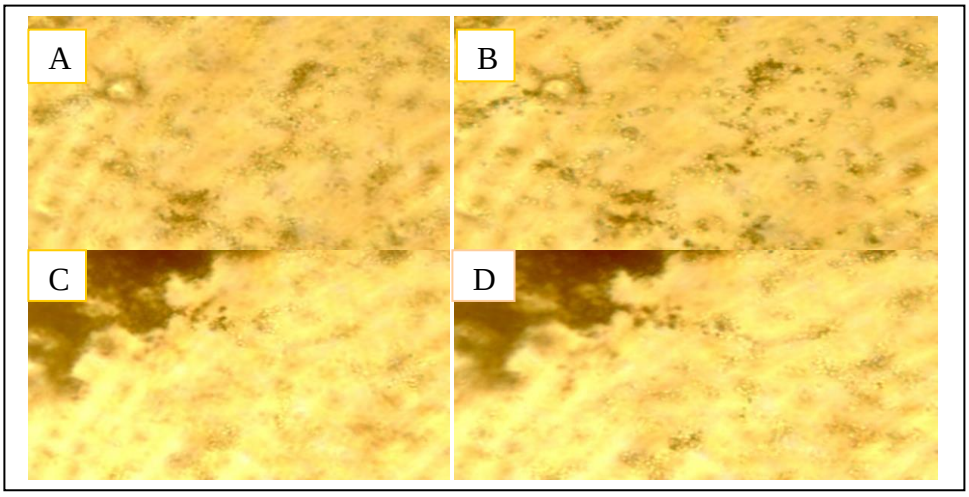


Figure 3.3a: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M ferric sulphate dosage.
A=$Fe(SO_4)_3$ - jar test for 1 min, B= $Fe(SO_4)_3$ - jar test for 90 mins, C= $Fe(SO_4)_3$ - slide for 1 min and D= $Fe(SO_4)_3$ - slide for 90 mins

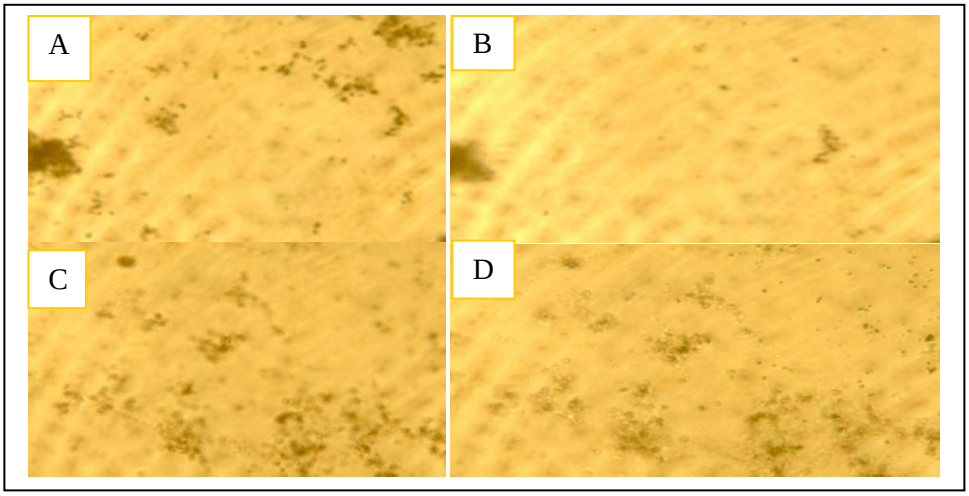


Figure 3.3b: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M ferric chloride dosage.
A=$FeCl_3$ - jar test for 1 min, B= $FeCl_3$ - jar test for 90 mins, C= $FeCl_3$ - slide for 1 min and D= $FeCl_3$ - slide for 90 mins.

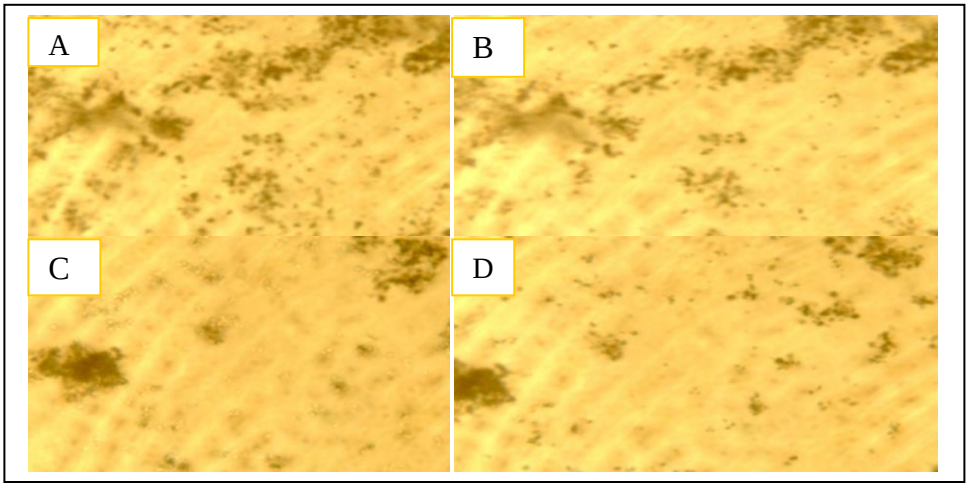


Figure 3.3c: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M aluminium sulphate dosage.
A= $Al(SO_4)_3$ - jar test for 1 min, B= $Al(SO_4)_3$ - jar test for 90 mins, C= $Al(SO_4)_3$ - slide for 1 min and D= $Al(SO_4)_3$ - slide for 90 mins

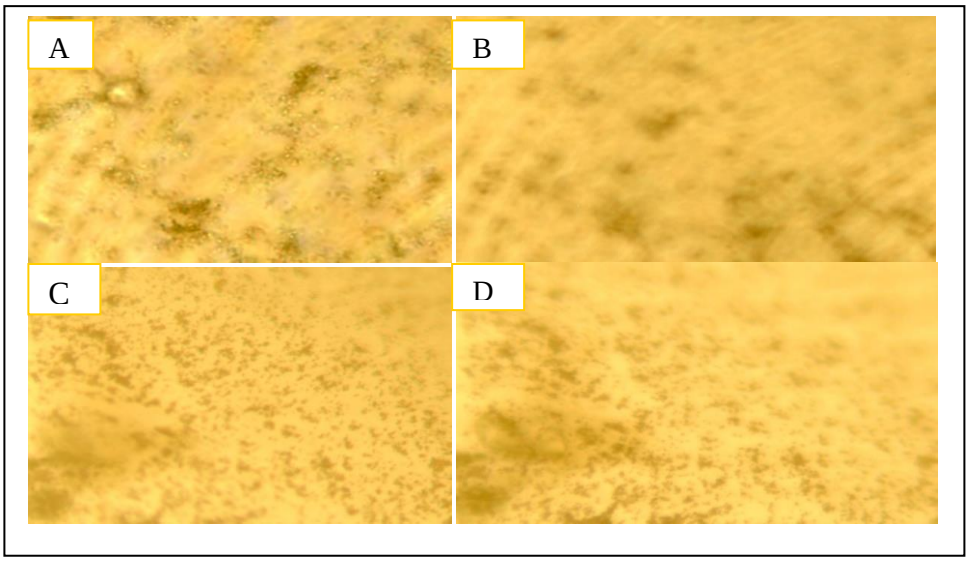


Figure 3.3d: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M aluminium chloride dosage.
A=$AlCl_3$ - jar test for 1 min, B= $AlCl_3$ - jar test for 90 mins, C= $AlCl_3$ - slide for 1 min and D= $AlCl_3$ - slide for 90 mines.

Figures 3.3a–3.3d show representative microscope images of flocs from the jar tests and microscope slide experiments after 1 and 90 minutes. The comparison of the area covered by the flocs after 30 and 60 minutes between the two tests, jar test and microscope slides, do not show significant differences; which also do not differ much from that for 1 and 90 minutes. The 30 and 60 minutes are omitted on this basis as they offer no additional information. Figures 3.3a and 3.3c show that the flocs which are formed in the microscope slide experiment ($FeCl_3$ and $AlCl_3$) after 1 and 90 minutes show localized dense structures whereas the flocs formed in a jar test are dispersed throughout the whole area. This indicates that there were more forces of attraction between the flocs formed on a microscope slide to form dense structures. Further, the method of the measurement of the percentage area covered by flocs confirmed that the flocs in experiments A and B are formed in the same way. Further test on characterization of the dry sludge of the paint wastewater samples was carried out on XRD, SEM and TGA as shown in Figures S2, S3, S4 and S5 in the Appendix.

Figures S2 and S3 show the XRD spectra of the paint sludge from the paint wastewater which has been dosed with $AlCl_3$ and $Al_2(SO_4)_3$ in a jar test and the spectrum for the dry paint itself. The samples which were dosed with $FeCl_3$ and $Fe_2(SO_4)_3$ were also run on the XRD but their spectrum has not been plotted because it was almost identical to the curve of $AlCl_3$ and $Al_2(SO_4)$. The purpose of this analysis was to determine whether the different coagulants result in different crystal morphologies in the sludge. From that data, one can see that the samples are essentially the same as the dried paint sample.

In Figure S4, the derivative of mass loss (from the TGA analysis) has been plotted against temperature. The paint consists of the pigments (clay, calcium carbonate, mica, silica, titanium oxide, talc), fillers (diatomaceous earth, lime, baryte) and binders (polyethanes, polyesters, melamine resins, epoxy). These ingredients decomposed as the temperature is increased. Paint sludge also consists of Fe^{3+} and Al^{3+} hydroxide species. The thermal curves of the samples of all four coagulants are identical. The results indicate that the samples dosed with Al^{3+} salts show a slightly bigger weight loss between 200 and 300 ^{0}C than the samples dosed with Fe^{3+} salts. This is seen as a negative peak on the derivative curves. Aluminium oxide hydroxide, boehmite (AlO(OH)), is formed at temperature around 200 ^{0}C from the decomposition of aluminium trihydroxide $Al(OH)_3$ (Aguilar *et al*., 2002). A study conducted by Thiery *et al*. (2007) revealed that well-crystallized $CaCO_3$ decomposes between 780 and 990 ^{0}C. It is only through the crystalline defects that calcite becomes thermally less stable and decomposes at a lower temperature range, where a small mass decrease which is less than 0.6% as recorded between ambient temperature and 200 ^{0}C because of the removal of physically bound water. There is a very small peak at about 900 °C which can be attributed to $CaCO_3$ decomposition. The biggest mass loss occurs between 200 and 400 °C. This has been attributed to the oxidation of the organic matter by Pansu *et al*. (2006).

Table 3.1 shows the properties of the paint wastewater sample and the sludge.

Table 3.1: pH, turbidity, mass and moles of M^{3+} in the sludge, mass and volume of sludge.

Coagulants	**$FeCl_3$**	**$Fe_2(SO_4)$**	**$AlCl_3$**	**$Al_2(SO_4)_3$**
pH-before settling	4.19	3.42	4.53	4.61
pH-after 90 mins (jar test)	3.9	3.21	4.41	4.38
Turbidity (NTU) (jar test)	100	65	84	76
Calculated mass of M^{3+} (g)	0.22	0.30	0.20	0.27
Calculated moles of M^{3+} in sludge	0.016	0.017	0.019	0.017
Sludge volume (mL)	90	106	90	95
Sludge mass (g)	12.9	15.7	15.6	14.8

Table 3.1 shows the pH, turbidity, volume and mass of sludge, number of moles and mass of Fe^{3+} and Al^{3+} in the sludge. The pH of the original wastewater sample was pH_i = 8.1. The pH values in Table 3.2 were 4.19, 3.42, 4.53 and 4.61 before settling for $FeCl_3$, $Fe_2(SO_4)_3$) $AlCl_3$ and $Al_2(SO_4)_3$ respectively, whereas the pH values after 90 minutes of settling were lower in each case, i.e. 3.90, 3.21, 4.41 and 4.38 for $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ respectively. As the cations hydrolyze, the pH drops and rapid precipitation occurs (Lee, 2001; Pratt *et al*., 2007, Baylis *et al*.,1971 and Chang *et al*., 2004). Table 3.1 shows that the pH of the sample treated with $Fe_2(SO_4)_3$ is 3.21, which is lower than 3.90 which resulted with $FeCl_3$ whereas the pH values of the samples treated with $Al_2(SO_4)_3$ and $AlCl_3$ do not differ significantly, i.e. 4.38 and 4.41 respectively. The observations show that the amount of acid with $Fe_2(SO_4)_3$ is higher than with $FeCl_3$, which also shows that the amount of hydrolysis with $Al_2(SO_4)_3$ and $AlCl_3$ is similar. Another observation is that Fe^{3+} salts give lower pH than Al^{3+} salts. Binnie *et al*. (2003) found that $Fe_2(SO_4)_3$ was superior to $Al_2(SO_4)_3$ in colloid removal in wastewater at a low pH, which confirms our results.

Table 3.1 shows that $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ result in a marginally lower turbidity (from > 500 NTU to 65 and 76 NTU respectively) than $FeCl_3$ (from > 500 to 100 NTU) $AlCl_3$ (from a value greater than 500 to 84 NTU). This indicates that sulphate salts reduce turbidity more than the corresponding chloride salt.

The results in Table 3.1 showed that $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ yield a higher sludge volume, 106 and 95 mL respectively, than the corresponding metal chlorides ($FeCl_3$ and $AlCl_3$), which is 90 mL in each case. Since more sludge is associated with colloidal particle removal, it can be concluded that diprotic coagulants have higher colloidal particles removal efficiency than their corresponding monoprotic coagulants.

3.4 Conclusions

The area covered by flocs in the microscope slide experiment correlates linearly with the area covered by the flocs in the jar test. Although a jar test might seem to be cheaper and simple to operate, it must be considered that turbidity measurement employs a complicated technique of passing the infrared light beam from emission source through the vial with a wavelength of around 890 nm. Any interference can cause faulty readings by the sensor whereas a microscope slide uses simple representative technique which employs flocs size distribution measurement. The microscope slide technique is simpler and faster than the other techniques proposed in the literature under section 3.1. The results obtained using this technique also confirm

that the reaction between the drops of a sample and the drops of coagulant produces well-developed solid hydrolysis species. A microscope observation, unlike a jar test can be used for other observations which involve matrix and crystal morphology. A further characterization test was carried out using XRD, TGA and SEM to check if there are any traces of metals from metal salt, residual moisture and the crystal morphology. The results obtained from the XRD, TGA and SEM show that the various techniques used to investigate the characteristics of sludge produced from the different coagulants yielded no significant differences as shown in S2, S3 and S4.

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CHAPTER 4: The effect of mixing on the treatment of paint wastewater with Fe^{3+} and Al^{3+} salts

Abstract

A 169.2 g of paint diluted in 1 L potable water. A 200 mL sample was poured into 500 mL glass beakers and dosed with 10, 20 and 30 mL of 0.043 M of Fe and Al salts respectively. Samples were mixed at 250 rpm for 30, 45 and 60 seconds in a jar test respectively. The samples settled for 1 hour and thereafter pH and turbidity were measured. Another set of experiments was carried out and mixed at 250 rpm for 30, 45 and 60 seconds followed by slow mixing at 100 rpm for 10 minutes, settled for 1 hour and thereafter pH and turbidity were measured. The turbidity in the samples with 30, 45 and 60 seconds rapid mixing (250 rpm) showed that most of the flocs are formed within 30 seconds. The results of Fe^{3+} and Al^{3+} salts showed a correlation between the pH and turbidity. This was confirmed by microscope experiments using 2 drops of the same solution from rapid mixing only (experiment A), placed in microscope slides connected to a camera. Images were captured after 30 minutes of settling. Similar experiment was carried out with combined rapid (250 rpm) and slow mixing (100 rpm). Images were captured after 30 minutes of settling using a camera. The results showed that the percentage area covered by the flocs in experiment A is not different to the corresponding percentage area covered by the flocs in experiment B.

4.1 Introduction

Mixing is one of the phenomena which play a vital role in wastewater treatment; mainly to disperse the coagulants throughout the colloidal suspension evenly. It induces Brownian motion in the colloidal system such that it should exceed the electrostatic potential of the system in order to achieve destabilization (Peavy *et al.*, 1995). When the distance between each particle in the colloidal system is greater than van der Waals forces of attraction, destabilization is deterred and no reaction will take place. Mechanical agitation is employed when destabilization fails after addition of metal salts into the colloidal system, which is estimated to be completed in less than five minutes (Jiang *et al.,* 1997). Three main processes, namely hydrolysis, adsorption and precipitation occur immediately after the addition of a metal salt. Gregory *et al*. (2001 and Pratt *et al.,* 2007) issued a breakdown of some reactions which form part of coagulation-flocculation process, namely reduction of potential energy between particles, an increase in Brownian motion to effect collisions between small particles and reduction in surface potential of the colloid which causes the adsorption of counter-ions by colloidal particles during rapid mixing.

The treatment process is mainly based on thermodynamic principles which include nucleation, crystal growth and aggregation of the destabilized suspended particles in a solution (Wu *et al*., 2001, Tan *et al*., 2000). Kinetics also plays a part during coagulation and flocculation processes. It is imperative for water treatment personnel to have a clear understanding about the role played by coagulation, flocculation and

settling on destabilization, hydrolysis and adsorption. A lot of cases have been reported around the globe regarding the poor quality of potable water supplied to the community, as well as poor quality effluent discharged into the rivers. Considerable research has been conducted on the various aspects regarding coagulation-flocculation, but it has not been possible to identify the difference between them. Metcalf *et al.* (2003) described coagulation as the destabilization of wastewater that occurs within seconds after addition of a coagulant, but did not specify the effective time-frame. Bryun *et al.* (2005) conducted a study on the water treatment using an instantaneous flash mixer and reported that charge neutralization occurs within one second of major flocculation process, but their explanations were not related to the dosage, pH, turbidity and reaction time. Literature does not indicate which of the process between coagulation and flocculation plays a major role in high turbidity removal. Duan *et al.* (2002) stated that flocculation has been well explained but information about the thermodynamics of the process is still not available. Literature states that coagulation process depends on the dosage whereas the flocculation depends on the mixing (Kemmer, 1988 and Jiang *et al*., 2002). The concentration of coagulants which are added to wastewater must be sufficient to exceed the solubility of their metal hydroxides so that precipitates can be formed (Aguilar *et al*., 2002)

Mixing also plays a role during wastewater treatment process by dispersing coagulants that are added throughout a colloidal suspension (Binnie et al, 2003). Hamidi *et al*. (2007) determined the speed of rapid and slow mixing that is required

for effective coagulation-flocculation but their rapid mixing differed from those determined by Tan *et al* (2000). Their optimal values for slow mixing relate to those determined by Tatsi *et al*. (2003). Prolonged rapid mixing and overdosing are the two factors which result in poor effluent due to re-stabilization of the particles as charge reversal on the colloidal suspension occurs (Swartz *et al*., 2004, Aboulhassan *et al*., 2006). Literature states that coagulation process depends on the dosage whereas the flocculation depends on the mixing (Kemmer, 1988, Ali *et al.*, 2002, Gregory *et al*., 2001 and Jiang *et al*., 2002). The concentration of coagulants which are added to wastewater must be sufficient to exceed the solubility of their metal hydroxides so that precipitates can be formed (Aguilar *et al*., 2002 and Wang *et al*., 2004). Peavy *et al*. (1985) stated the importance of mixing in coagulation, indicating that destabilization can be achieved when Brownian motion in a colloidal suspension exceeds electrostatic potential of the system. They mentioned that mechanical agitation becomes necessary when the distance between each particle is high and the van der Waals forces of attraction are low. The mechanical agitation increases collision rate of the particles to form agglomerates; which settle out of the system. This shows that a choice of more effective coagulants is very significant as mechanical means alone does not achieve envisaged results. This also shows that the effective metal salts disperse spontaneously throughout the colloidal suspension to cause destabilization and hydrolysis in the colloidal system (Peavy *et al*., 1995). Jiang *et al*. (1997) stated that adsorption and precipitation occur during the period of rapid hydrolysis. A series of reactions such as the reduction in potential energy between the particles and increase in Brownian motion, which leads to collisions between small

particles occurs. In addition, reduction in surface potential of a colloid that causes the adsorption of counter ions by colloidal particles during rapid mixing occurs.

According to Peavy *et al*. (1995), the role of mechanical agitation (mixing) in coagulation-flocculation is unclear. It is also important to have knowledge about the impact of both rapid and slow mixing as well as impellor speed and retention time using a jar test. The results will indicate the type of mixing (rapid and slow) which plays a pivotal role in wastewater treatment. The information will further indicate optimal mixing dynamics so that re-stabilization process, which is caused by rupturing of the flocs by shear forces as stated by Freeze *et al*. (2001), can be avoided. Prolonged rapid mixing and overdosing result in the effluent of poor quality as re-stabilization of the particles occurs due to charge reversal on the colloidal suspension (Swartz *et al*., 2004), (Aboulhassan *et al*., 2006). Research shows that investigation relating to the impact of chemical dosing, either prior or during mixing; on turbidity removal has not been extensively conducted. Since mixing induces kinetic energy, a knowledge of such nature is essential in order to understand the correlation between kinetic energy, rate of mixing and destabilization at zero and initial velocities. Such an investigation, as well as the turbidity removal efficiency between monoprotic and diprotic metal salts dosages is necessary. The benefit of the findings is to know about mixing dynamics, dosing, effective metal ion in a metal salt, correlation between pH-turbidity and destabilization-hydrolysis.

Fe^{3+} and Al^{3+} salts are commonly used in wastewater treatment because of their high valence electrons, high electronegativity and charge per surface area (Z^2/r) (Spellman 2009). O'Melia (2001**)** has reported that slow mixing is important after rapid mixing since it is a stage in which relative motion induces a velocity gradient of the particles, which are prone high shear rate in a liquid phase. Sincero *et al*. (2003) and Ghaly *et al*. (2006) explained rapid mixing as the stage where coagulants are dispersed throughout the colloidal particles in order to cause destabilization and hydrolysis whereas the formation of larger aggregates occurs during slow mixing due to the collision of flocs through the velocity gradient and differential velocity. The larger flocs which are formed adsorb the colloidal particles and the increasing settling velocity causes settling (Aboulhassan *et al*., 2006).

4.2 Material and methods

4.2.1 Paint wastewater sample

A synthetic paint wastewater sample was prepared by diluting 169.2 g of paint to a volume of 1 litre with distilled water to give total solids concentration of 80 g/L as explained in Section 2.2.1.

4.2.2 Coagulants

A 0.043 M of $Fe^{3+}$and Al^{3+} ions (a concentration obtained from the literature) of monoprotic and diprotic standard solutions were prepared as discussed in Section 2.2.2.

4.2.3 Procedure for jar tests and microscopic observations

The equipment used for the jar tests is the same *BIBBY Stuart Scientific Flocculator (SW1 model)* which is explained in section 2.3. A 169.2 g of water-based paint in 1 litre of distilled as done in previous experiments. The pH and turbidity of this sample solution were 8.9 and > 500 NTU respectively. The experiments were carried out by pouring 200 mL of the sample (16 g solid paint in 200 mL) into six 500 mL glass beakers. The first three beakers were treated with 30, 45 and 60 seconds rapid mixing (250 rpm) only respectively using a stop-watch, whereas the other three beakers were treated with combined mixing, 30, 45 and 60 seconds rapid (250 rpm) followed by slow (100 rpm) mixing for 10 minutes.

The experimental procedure is detailed below. The first and the fourth beakers were dosed with 10 mL $FeCl_3$ during 30 seconds rapid mixing. The mixing in the first sample was stopped after 30 seconds and the pH was measured immediately whereas the rapid mixing in the fourth sample was reduced to 100 rpm for 10 minutes. The pH was immediately measured after 10 minutes of slow mixing. The samples settled for 1 hour before the pH and turbidity were measured. A similar experiment was carried

out by dosing the second and the fifth samples with 10 mL $FeCl_3$ during 45 seconds rapid mixing. The mixing in the second sample was stopped after 45 seconds and the pH was measured immediately, whereas the rapid mixing in the fifth sample was reduced to 100 rpm for 10 minutes. The pH was immediately measured after 10 minutes of slow mixing. The samples settled for 1 hour and thereafter the pH and turbidity were measured. The third and sixth samples were dosed with 10 mL of $FeCl_3$ during 60 seconds rapid mixing. The mixing in the third sample was stopped after 60 seconds and the pH was measured immediately whereas the rapid mixing in the sixth sample was reduced to 100 rpm for 10 minutes. The samples settled for 1 hour and thereafter the pH and turbidity were measured. The second and third batches of experiments were carried out in the same manner as above except that 10 mL of $FeCl_3$ dosage was increased to 20 and 30 mL of $FeCl_3$ dosages respectively. The experiments above were repeated by replacing $FeCl_3$ dosage with $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ dosages.

An additional study which consists of Experiment A and B, was carried out by placing 2 drops of the supernatant from each sample with rapid mixing only (Experiment A) and a combination of rapid and slow mixing (Experiment B) immediately after either rapid mixing only or a combination of rapid and slow mixing onto a microscope slide. Another slide was placed on top separated by 2 mm and observed at a magnification of 400 times under a light microscope. The sample drops on the microscope slides were photographed after 30 minutes of settling. The images of the microscope slides were then plotted at 30, 45 and 60 seconds time intervals and used to determine the areas covered by the spherical and non-spherical agglomerates.

A supplementary study was carried out by pouring the same 200 mL of paint wastewater samples used in previous experiments into five 500 mL glass beakers, dosed with 20, 30, 40, 50 and 60 mL $FeCl_3$. The samples were mixed at 250 rpm for 2 minutes and settled for 1 hour, and thereafter the pH and turbidity were measured. A similar experiment was carried out with samples dosed without mixing, settled for 1 hour, and thereafter the pH and turbidity were measured.

4.3 Performance evaluation

In the experiments where the samples were treated in a jar test, the pH and the turbidity was measured after 1 hour of settling after rapid mixing only or a combination of rapid and slow mixing. The pH measurements were intended to determine the rate at which hydrogen ions are released into the solution as defined in Equation 4.1, and the turbidity was to determine the particle removal potential by each coagulant (Fe^{3+} and Al^{3+} salts). In Experiments A and B, the area covered by flocs was measured on the images obtained from the microscopic to determine the amount of flocs formed from the two drop sample during the flocculation. Earlier work comparing the results from jar tests and those on a microscope slide confirmed that these results were significant. The work includes the comparison of the crystal morphology in paint wastewater samples from flocculation jar tests and microscope slide experiments as a research project by Ntwampe *et al*. (2011).

4.3.1 pH

A pH meter sourced from MetterToledo Seven Multimeter (Germany) having a pH electrode filled with silver chloride solution and an outer glass casing with a small membrane covering at the tip was utilised in this study. Preparation of the equipment was done as discussed under Section 2.4.1.

4.3.2 Turbidity

A Hanna Microprocessor Turbidimeter was used to determine turbidity of the supernatant using NTU as a unit of measure. Preparation of the equipment was done as discussed under section 2.4.2.

4.3.3 Area covered by the flocs

The images produced by a light microscope were printed in order to measure the fraction of the area covered by the flocs. This was accomplished by superimposing a 2 mm square-meshed transparency over the printed copies of the images, followed by a particle count of all the dark images which were either spherical or non-spherical in shape. The total area covered by the flocs was compared to the total area covered by the sample.

4.4 Results

Figures 4.1a–4.1d show results of pH measured after one hour of settling with 10, 20, and 30 mL dosages of 0.043 M Fe^{3+} and 0.043 M Al^{3+} ions in their respective metal salts as a function of the rapid mixing (250 rpm) for 2 minutes compared with a combination of rapid (250 rpm) and slow mixing (100 rpm) for 10 minutes.

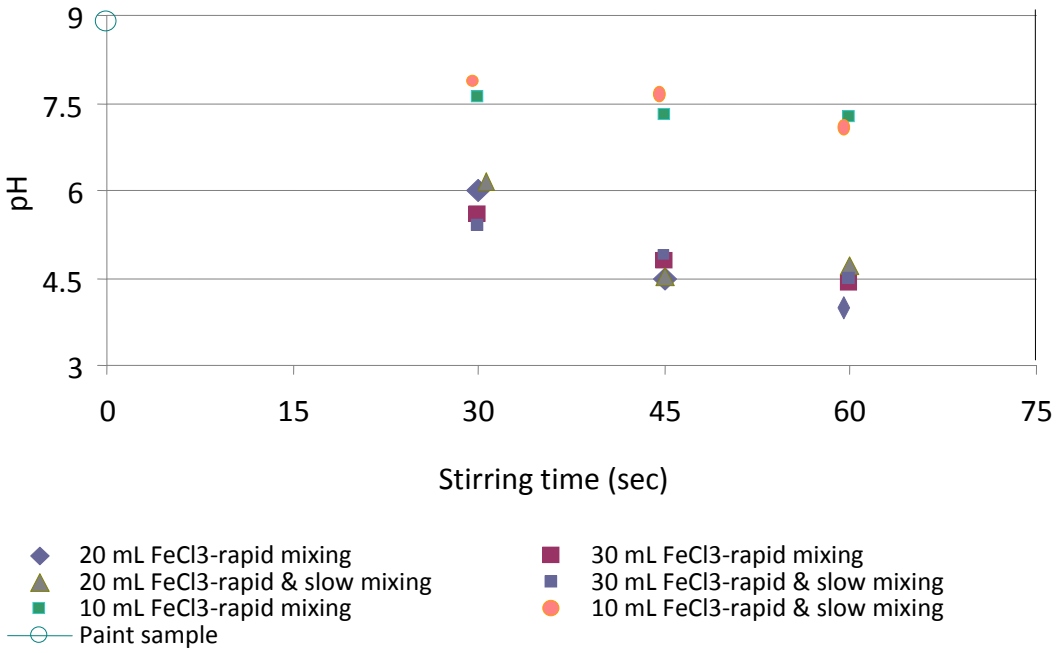


Figure 4.1a: Measured pH after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Fe^{3+} $FeCl_3$.

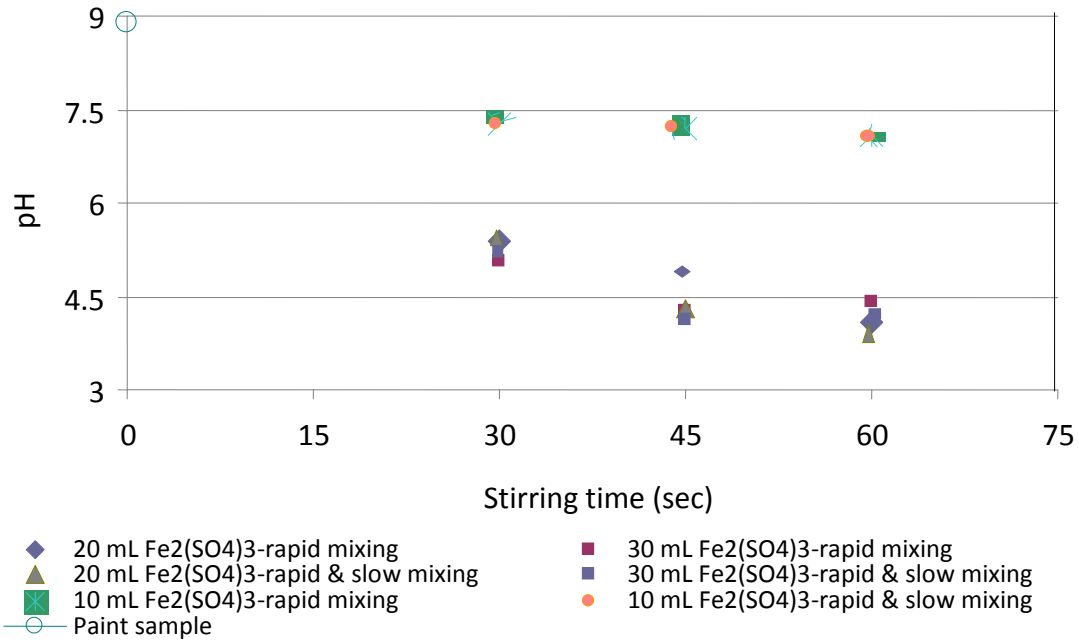


Figure 4.1b: Measured pH after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Fe^{3+} $Fe_2(SO_4)_3$.

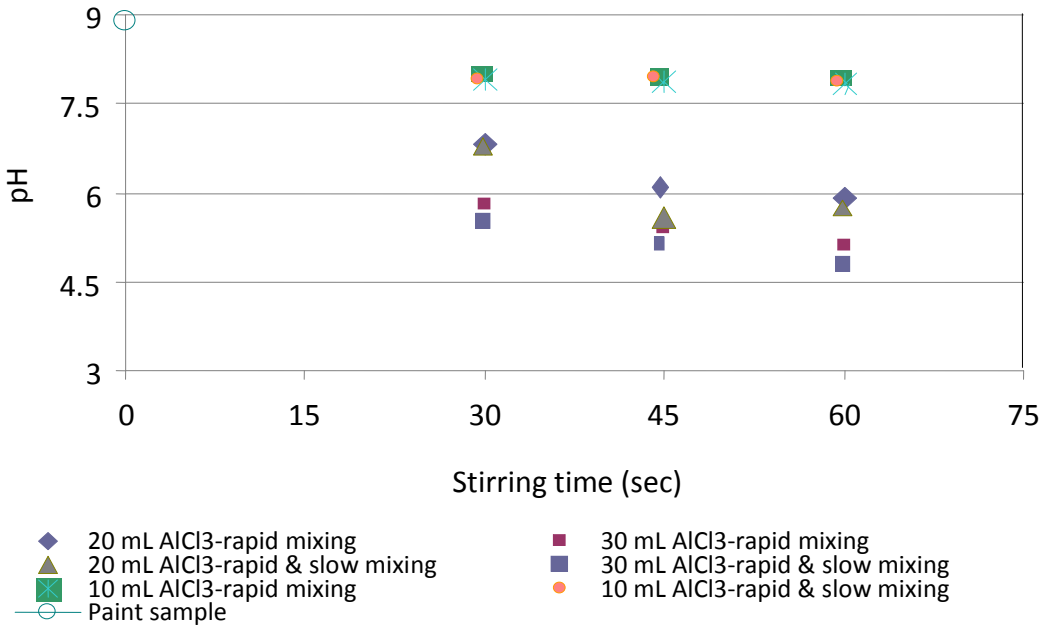


Figure 4.1c: Measured pH after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al^{3+} $AlCl_3$.

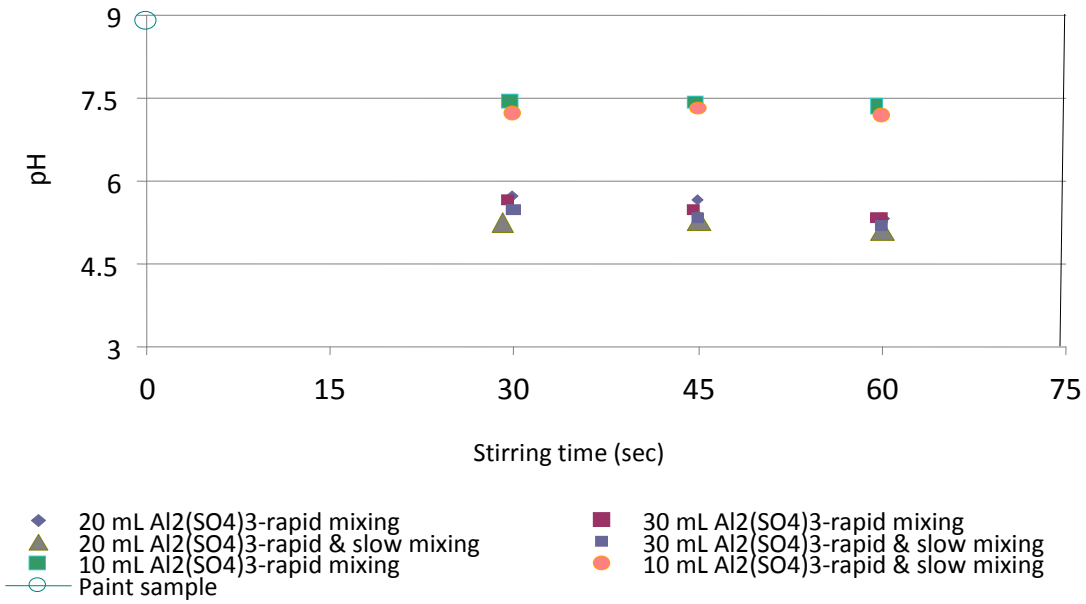


Figure 4.1d: Measured pH after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al^{3+} $Al_2(SO_4)_3$.

The pH in all the samples measured immediately after rapid mixing and those which were measured after 1 hour of settling were below 0.1 pH units. Figures 4.1a, 4.1b, 41c and 4.1d show that the pH obtained in the samples which were dosed with 10 mL of $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ were all alkaline, above 7.0. These solutions have an opaque colour with tiny white particles.

The results further show that the pH in the samples with 20 and 30 mL $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ dosages during rapid mixing are not significantly different to the pH in their corresponding samples with a combination of rapid (250 rpm) and slow (100 rpm) mixing, showing that the slow mixing has a negligible effect on the pH of the solution. The samples which have been dosed with 20 and 30 mL of $FeCl_3$ in Figure 3.1a show a decrease in pH from 8.9 to a range between 6.43

and 3.50 depending on the rapid mixing time, Figure 4.1b shows a pH reduction to 6.37–3.30, Figure 4.1c shows pH reduction to 6.81–4.80 and Figure 4.1d a pH reduction to 6.36–3.33. The pH values in Figures 4.1a–4.1d also show a decreasing trend with increasing rapid mixing time; the reduction is from 8.9 to a range of 6.5–3.4. The pH values yielded by monoprotic metal salts are slightly higher than their corresponding diprotic metal salts.

Figures 4.2a–4.2d show results of turbidity measured after 1 hour settling with 10, 20 and 30 mL of 0.043 M Fe^{3+} and 0.043 M Al^{3+} ions respectively as a function of the rapid mixing (250 rpm) for 2 minutes compared with a combination of rapid mixing (250 rpm) and slow mixing (100 rpm) for 10 minutes. Note the values for the 10 mL addition have not been plotted as their values were all over-range (>500 NTU).

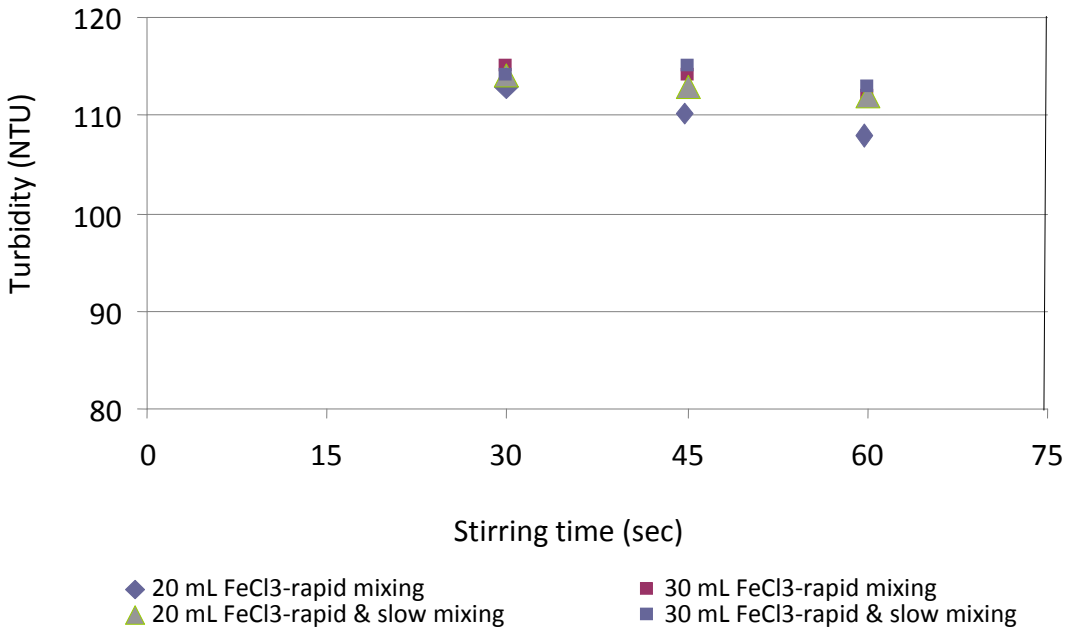


Figure 4.2a: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Fe^{3+} $FeCl_3$.

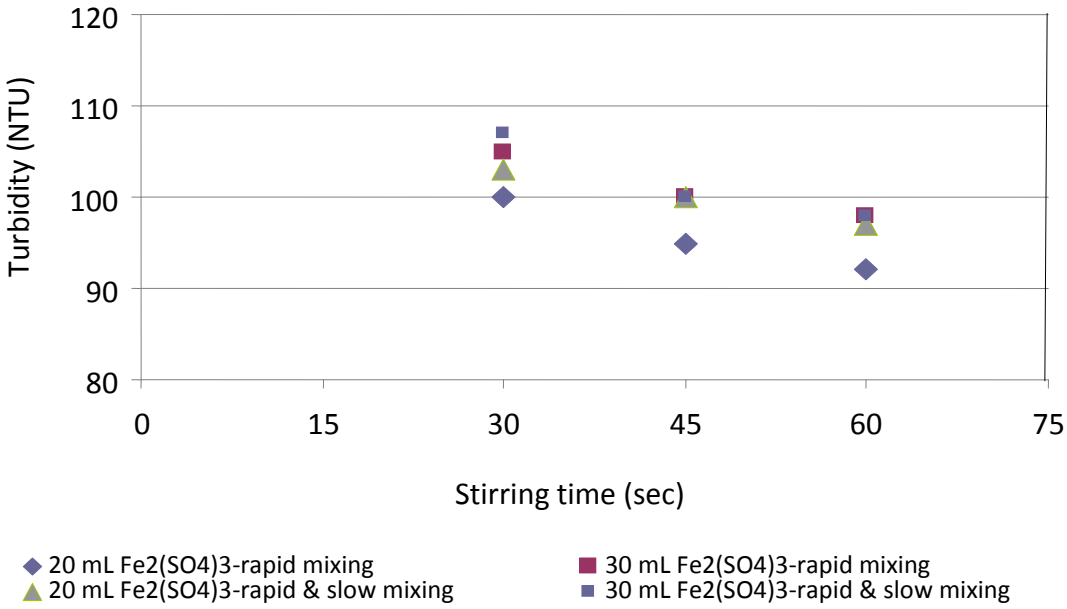


Figure 4.2b: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Fe^{3+} $Fe_2(SO_4)_3$.

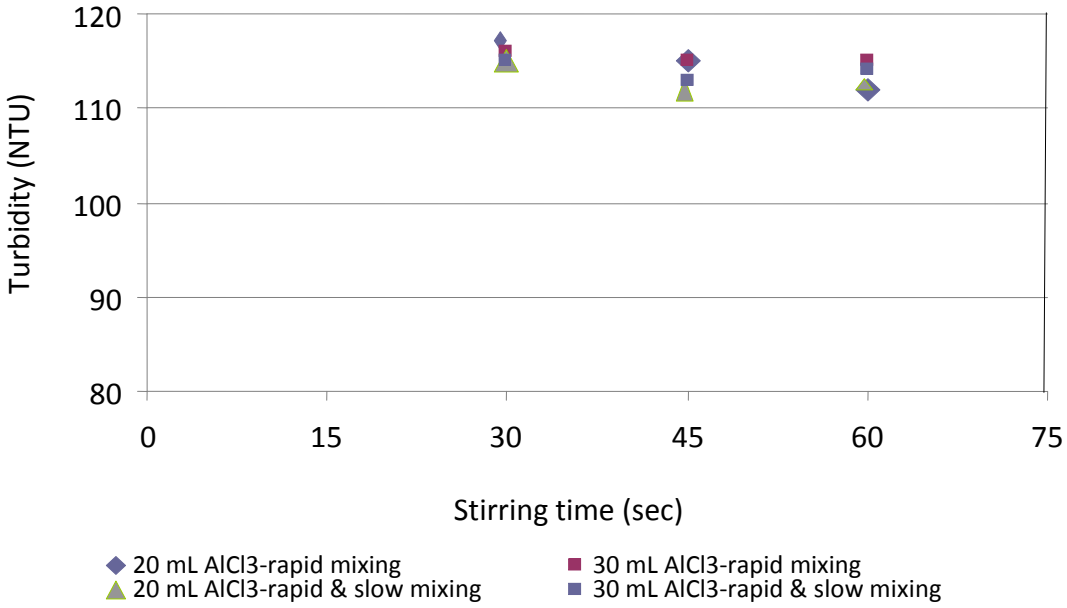


Figure 4.2c: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al^{3+} $AlCl_3$.

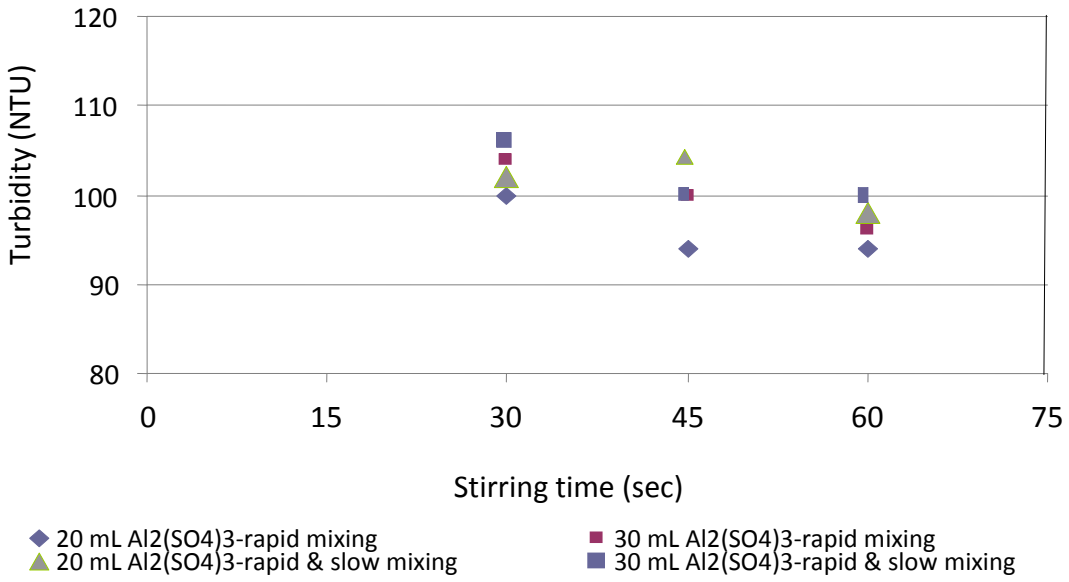


Figure 4.2d: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al^{3+} $Al_2(SO_4)_3$.

Figures 4.2a–4.2d represent the same samples as those in Figures 4.1a–4.1d but showing the comparison between the turbidity and rapid mixing time. The turbidity in the samples which have been dosed with 10 mL of $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ are all over-range, greater than 500 NTU. The turbidity in samples with 20 and 30 mL of $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ dosages decreases slightly with increasing rapid mixing time, showing a similar changing trend to their corresponding samples in Figures 4.1a–4.1d. The results show that 20 and 30 mL of 0.043 M Fe^{3+} and Al^{3+} salts in samples with rapid mixing only yield insignificantly different turbidity compared to their corresponding samples with a combination of rapid and slow mixing, reduced from >500 NTU to a range of 92–117 NTU. This study considers turbidity below 120 NTU as a specification based on the nature of the ingredients found in paint wastewater. The turbidity values in the samples with 20

and 30 mL of $AlCl_3$ are higher than the turbidity in the samples with 20 and 30 mL of $FeCl_3$ or $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ dosages in Figures 4.2a, 4.2b and 4.2d respectively. These results showed that $AlCl_3$ is less efficient in removing turbidity in the paint than $FeCl_3$, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ with the same concentrations and dosages. Figure 4.3 shows percentage area covered by flocs against reaction time.

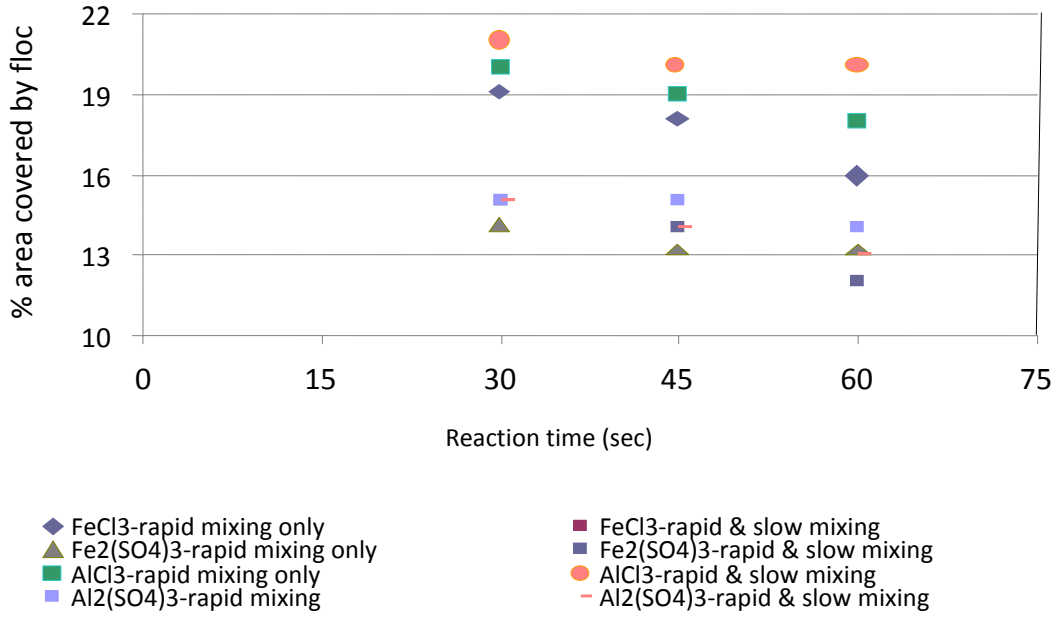


Figure 4.3: Percentage area covered by flocs with $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ dosages in a jar test.
Microscope images of 2 drops of the supernatant from jar tests captured after 30 minutes of settling.

Figure 4.3 reveals that the percentage turbidity removal obtained in the samples in Experiment A is virtually the same as that in their corresponding samples in Experiment B, i.e. turbidity in the samples with rapid mixing for 30, 45 and 60 seconds in Experiment A, is within experimental error in the same as that in the

corresponding samples with a combination of rapid and slow mixing. Figure 4.3 also shows that the flocs which are formed in the supernatant of the samples in both experiments A and B with 0.043 M Fe^{3+} in $FeCl_3$ dosage covered an area in the ranges of 16–19 and 17–19 % respectively whereas the samples with $Fe_2(SO_4)_3$ covered areas of 14–15 and 12–14 % respectively. Figure 4.3 also shows that the flocs which are formed in the supernatant of the samples in both experiments with $AlCl_3$ covered an area in the ranges of 18–20 and 20–21 % respectively whereas the samples with $Al_2(SO_4)_3$ covered areas of 11–15 and 12–14 % respectively.

Figures 4.4 and 4.5 illustrate the changing trend of the pH and turbidity between the samples with $FeCl_3$ or $Fe_2(SO_4)_3$ and $AlCl_3$ or $Al_2(SO_4)_3$ dosages during and without mixing. The experiments were intended to determine the impact of mixing in destabilization-hydrolysis process.

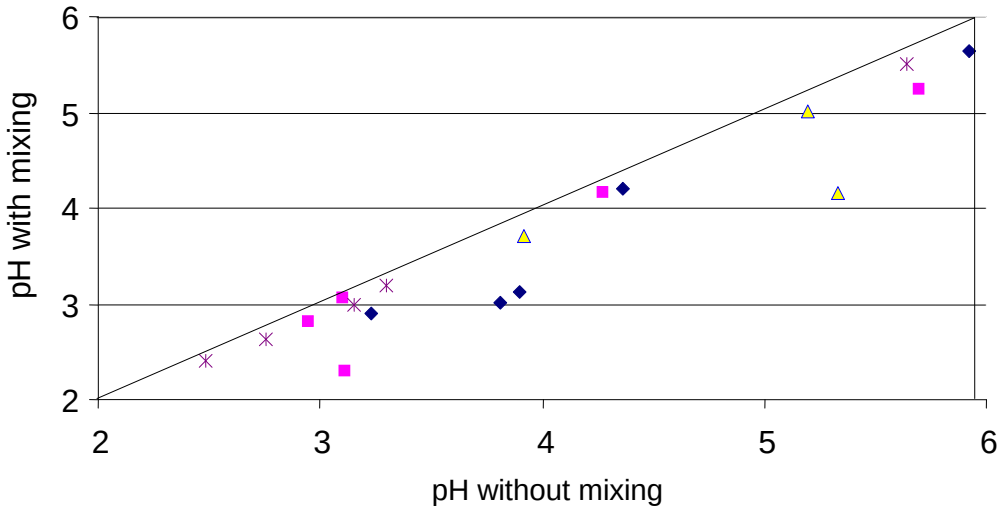


Figure 4.4: pH of the samples using $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$) and $Al_2(SO_4)_3$ with and without mixing.

♦ = $FeCl_3$, ■ = $Fe_2(SO_4)_3$, Δ = $AlCl_3$, X = $Al_2(SO_4)_3$ ×

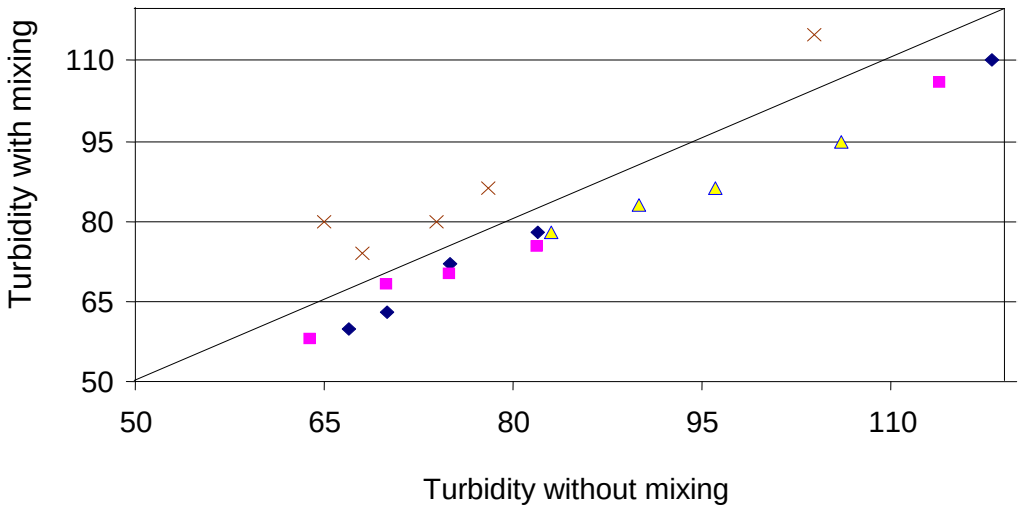


Figure 4.5: Turbidity of samples using $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$) and $Al_2(SO_4)_3$ with and without mixing.

♦ = $FeCl_3$, ■ = $Fe_2(SO_4)_3$, Δ = $AlCl_3$, × = $Al_2(SO_4)_3$

Figure 4.4 shows the pH changing trend in paint wastewater samples with $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$) and $Al_2(SO_4)_3$ dosages with and without mixing. The difference in pH of the samples with mixing and those of their corresponding sample without mixing is less than 1.0 in all the samples.

Figure 4.5 shows turbidity changing trend in paint wastewater samples with $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$) and $Al_2(SO_4)_3$ dosages with and without mixing. The difference in turbidity between the samples which have been mixed and those of their corresponding samples which have not been mixed shows is insignificant; all falls below 120 NTU.

4.5 Discussion

The difference of 0.1 in pH obtained after rapid mixing and 1 hour settling in Figures 4.1a-4.1d shows that hydrolysis is completed during the rapid mixing stage. This indicates that hydrolysis is completed during coagulation process; which also indicates that the release of hydrogen ions into the solution is affected by rapid mixing during coagulation and no further reaction (destabilization-hydrolysis) occurs during settling. Opaque colour in all the samples with 10 mL of 0.043 M metal ions dosages (Fe^{3+} and Al^{3+} salts) indicates that there is poor destabilization, hydrolysis, which resulted in de-flocculation. This is confirmed by the turbidity measurements where all the readings remained off-scale, above 500 NTU.

As Lee (2001) stated that the addition of electrolytes to increase the ionic strength of the solution (double-layer compression) is not the sole factor that causes coagulation in wastewater treatment. Our experimental results confirmed that the concentration of metal ions (M^{3+}), rate of mixing and duration of rapid mixing play a pivotal role in achieving the best turbidity removal. The pH of the colloidal suspension decreases with increasing dosages of the metal salts due to increasing concentration of metal ions in the solution, see Equation 4.1. The equation also depicts that the rate of hydrogen ions (H^{+}) released into the solution is directly proportional to the rate of the formation of metal hydroxide species. This study successfully investigated the physico-chemical dynamics of changing pH in the wastewater, which has not been thoroughly investigated before. The study also shows the distinctive roles played by rapid mixing only, compared with a combination of rapid and slow mixing using inorganic metal salts; including the pH changing dynamics immediately after both rapid mixing only, and a combination of rapid and slow mixing. The difference between pH of the samples measured immediately after rapid mixing, combination of rapid and slow mixing and that measured after 1 hour of settling (ΔpH) is insignificant, falling within the range of 0.04–0.1. Since these pH values are so small, it is therefore not necessary to plot them as they would distort the arrangement of Figures 4.1a-4.1d. These low ΔpH values indicate that most of the flocs were formed during rapid mixing, resulting in the maximum floc formation (rate of deprotonation is directly proportional to the rate of metal hydroxide species formation). The opaque colour shown in the samples with 10 mL dosage indicates that the concentration of metal ions is relatively low to destabilize equilibrium between the electrostatic forces of repulsion and van der Waals forces of attraction in the colloidal; with the formation of hydrolysis species as shown by Equation. 1.12-1.14. The tiny white

particles move haphazardly throughout the colloid, indicating that repulsive and attractive forces in the colloidal system are in equilibrium. Electrophoretic mobility of the particles in the colloid is still high and the metal ions of the coagulants are unable to disturb electrical force of repulsion and electrokinetic potential in the solution to form hydrolysis species. The molar concentration of M^{3+} is ineffective to destabilise 16 g solid paint in 200 mL paint wastewater as mentioned in sub-section 4.2.3.

The pH in the samples which have been dosed with 20 and 30 mL of coagulants in Figures 4.1a–4.1d is identical in each reaction time, below 6.8. It can be concluded that 20 mL of 0.043 M Fe^{3+} or Al^{3+} ions is able to remove 16 g of colloidal particles in paint wastewater, which also shows that 20 mL is an optimum dosage able to achieve high rate of destabilization-hydrolysis. The rate at which the pH decreases shows that it is a direct indicator of the rate of hydrolysis, see Equations 4.1 and 4.2. Figures 4.1a–4.1d show that the pH in the samples with 20 and 30 mL of $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ dosages during rapid mixing is identical to the pH in their corresponding samples with a combination of rapid and slow mixing. This indicates that nucleation occurs during rapid mixing and slow mixing does not play a pivotal role during this reaction. Secondly, Figures 4.1a–4.1d also show that the pH decreases with increasing reaction times, i.e. pH in the samples with 30 seconds rapid mixing is slightly higher than 45 seconds; whereas both 30 and 45 seconds rapid mixing are slightly higher than 60 seconds. This suggests that rapid mixing is able to disperse coagulant(s) throughout the solution within 30 seconds, and a slight further nucleation occurs in less than 60 seconds. It must also be noted that destabilization and hydrolysis are simultaneous processes which occur on the colloidal suspension and metal salt respectively. My postulate states that there are two vital processes

taking place during flocculation namely, destabilization and hydrolysis during 30 seconds of rapid mixing. Adsorption of colloidal particles occurs through velocity gradient and differential velocity during settling period induced by Brownian motion. This occurs when particles of varying sizes collide together and form larger particles which settle due to gravity.

The observations obtained from the decreasing pH with varying stirring time during hydrolysis explain the uncertainty about the effect of varying stirring times on flocs formation in water treatment operations to achieve high turbidity removal. Another problem stated by Freeze *et al*. (2001) during coagulation is that rapid mixing for a short period may cause poor destabilization-hydrolysis whereas rapid mixing for a prolonged period may give rise to rupturing of the flocs, both resulting in poor adsorption. The results show that the pH values in the samples which are dosed with monoprotic metal salts in Figures 4.1a and 4.1c are higher than the pH values in their corresponding samples with diprotic metal salts; indicating that the former yields a lower rate of hydrolysis than the latter, Figures 4.1b and 4.1d. The pH trends in Figures 4.1a–4.1d also reveal that $AlCl_3$ yields lower rate of hydrolysis than $Al_2(SO_4)_3$ and $FeCl_3$ or $Fe_2(SO_4)_3$. Literature suggests that the hydrolytic species which are formed during hydrolysis determine the adsorption potential of the colloidal particles (Jiang *et al*., 2002). Our experimental findings revealed the role played by both rapid mixing alone and a combination of rapid and slow mixing on the degree of flocs formation; and also validated the percentage area formed by the flocs under a light microscope, an explanation which was not available before.

Turbidity in all the samples which have been dosed with 10 mL of 0.043 M Fe^{3+} or Al^{3+} dosage in Figures 4.2a-4.2d is over-range, above 500 NTU, hence it has not been plotted as it would distort the figures which have been plotted. Figures 4.2-4.2d show that turbidity in the samples which have been dosed with 20 and 30 mL of 0.043 M Fe^{3+} or Al^{3+} dosages during rapid mixing only for 30, 45 and 60 seconds is identical to the turbidity in their corresponding samples with a combination of rapid and slow mixing with 20 and 30 mL of 0.043 M Fe^{3+} or Al^{3+} dosages. The turbidity in all the samples which have been dosed with 20 and 30 mL of 0.043 M Fe^{3+} or Al^{3+} dosages is in the range 88–118 NTU. Identical turbidity values shown by both the samples with rapid mixing and their corresponding samples with a combination of rapid and slow mixing indicate that nucleation is predominant; hence high adsorption of the colloidal particles in both mixing patterns. I suggest that rapid mixing is a process where nucleation occurs to its maximum, whereas settling for 1 hour allowed the formation of larger flocs to condense and form dense cake-like, spongy polymers that adsorbed residual colloidal particles during settling. The same finding is confirmed in the study carried out by Ntwampe *et al*. (2013) on paint wastewater treatment with synthetic $FeCl_3$-$Ca(OH)_2$ and $FeCl_3$-$Mg(OH)_2$ polymers dosages as coagulants respectively. These polymers act as filters and trap the residual colloidal particles which are moving randomly under Brownian motion. The assumption is based on the uniform behaviour of the four coagulants (Fe^{3+} and Al^{3+} salts) dosed to the samples, thus showing that the removal of the turbidity in the colloidal suspension was a physical phenomenon. This occurred when the particles settled due to gravitational force as they collide and form larger particles as mentioned by Metcalf *et al*. (2003).

The observations regarding the pH and turbidity results reveal that effective destabilization-hydrolysis, which are interpreted by the changing pH and turbidity is influenced by the dosage, rate of mixing and stirring time. The changing trend of the pH and turbidity shown in Figures 4.1a–4.2d indicates that there is a correlation between the both parameters (pH and turbidity). This correlation of the experimental results suggests that hydrolysis which occurs during coagulation can be explained by changing pH and turbidity. The pH and turbidity values in Figures 4.1a–4.2d show that Fe^{3+} and Al^{3+} salts react similarly when dosed in paint wastewater, which means that the reactions which occur during rapid mixing produce flocs which are well developed to achieve optimum adsorption. Since Freeze *et al*. (2001) stated that prolonged retention time during wastewater treatment can cause re-stabilization process due to rupturing of the flocs by shear forces, my experimental results show that rapid mixing for at most 60 seconds is effective for turbidity removal based on metal ion-solid paint mass ratios (mass of M^{3+} ion/mass of solid paint).

Another observation in Figures 4.2a and 4.2c is that the turbidity in the samples which have been dosed with monoprotic metal salts (MCl_3) is slightly higher than their corresponding samples dosed with diprotic metal salts ($M_2(SO_4)_3$) in Figures 4.2b and 4.2d. This indicates that diprotic metal salts possess a higher destabilization-hydrolytic potential than monoprotic salts. This indicates that the former have more ability to disturb colloidal equilibrium due to van der Waals forces and electrostatic forces, thus causing the formation of hydrolysis species. Although there is not much literature to explain monoprotic and diprotic dynamics regarding their ionic strength, it can be postulated from the Equations 4.5, 4.6 and 4.7 that there is 100 % dissociation in hydrochloric acid in a single stage (Equation 4.7) compared to

sulphuric acid which dissociates in a double stage (Equations 4.5 and 4.6) as stated by Casas *et al*. (2000). I suggest that double deprotonation which occurs during the speciation of (H_2SO_4) improves hydrolysis potential of diprotic metal salts.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \; k > 10 \qquad [4.5]$$

$$HSO_2^- \rightleftharpoons H^+ + SO_4^{2-} \; k = 1.3 \times 10^{-2} \qquad [4.6]$$

$$HCl \rightleftharpoons H^+ + Cl^- k = 10^7 \qquad [4.7]$$

Hypothesis by Sienko *et al*. (1961) used oxidation state of Cl^- and S^{8+} to explain the hydrolysis potential between monoprotic and diprotic metal salts. They employed a thermodynamic approach stating that more energy is required to dissociate $Al_2(SO_4)_3$ than $AlCl_3$. In SO_4^{2-}, the sulphur has oxidation of +6. Hypothetically, the electrons in octahedral water molecules of hydration experience a strong force of attraction from S^{6+} ion, hence the rate of hydrolysis increases with the release of 8 protons. The reaction is expressed as follows:

$$S^{8+} + 4\,H_2O \rightleftharpoons SO_4^{2-} + 8\,H^+ \qquad [4.8]$$

Another approach explains the varying pH values between monoprotic and diprotic metal salts using the degree of dissociation between Cl^- and SO_4^{2-} ions. It is suggested

that a double dissociation which occurs during hydrolysis with diprotic H_2SO_4 of a metal salt ($Fe_2(SO_4)_3$ or $Al_2(SO_4)_3$) occurs in a similar way as explained above; which is also applicable to monoprotic metal salts ($FeCl_3$ or $AlCl_3$). Although Kurniawan *et al*. (2006) stated that the efficiency of $Al_2(SO_4)_3$ on organic matter removal in a colloid is hindered by SO^{2-}_4 ions embedded in the precipitate; our experimental results showed that it is unlikely for that to occur to non-organic compounds. The pH values shown by the samples with rapid mixing and those with a combination of rapid and slow mixing indicate that velocity gradient plays a main role. Equation 4.9 is the calculation of the Reynolds number to determine fluid dynamics. Sarti *et al*. (2004) used 1.13 g/cm and 1 g/cm.s for density and viscosity of the wastewater respectively to calculate the Reynolds number. Diameter of a beaker = 8.5 cm, impellor speed = 250 rpm:

$$\text{Re} = \rho VD / \mu \qquad [4.9]$$

` V = (250 rpm x 2π rad)/60 sec) x 4.25 cm = 111.3 cm/s

$$\text{Re} = 1.13 g/cm\text{^}3 * 111.3 cm/s * 8.5 cm / 1 g/cm/s^{s-1}$$

= 1069.03

The Reynolds number indicates that the flow of the fluid during mixing is turbulent, which indicates that the degree of destabilization-hydrolysis that occurs during the experiments is influenced by the intensity of mixing, i.e. turbulent. Since the speed of an impellor in a jar test is set at 250 rpm, this suggests that this is an ideal speed to disperse the metal salt throughout the colloidal suspension in order to flocculate. This

shows that optimal mixing plays pivotal role by dispersing the reagent throughout the solution without the rupturing of the flocs or re-stabilization.

The results shown by Figure 4.3 indicate that the percentage area covered by the flocs in the samples with 0.043 M Fe^{3+} or Al^{3+} salts dosage during rapid mixing for 30, 45 and 60 seconds in Experiment A is identical to the percentage area covered by flocs in their corresponding samples with a combination of rapid and slow mixing in Experiment B. The difference in the percentage area covered by flocs between 30, 45 and 60 seconds intervals is insignificant. Figure 4.3 shows the results obtained in both Experiments A and B on the samples with rapid mixing only and those with a combination of rapid and slow mixing confirms that most of the flocs occur during rapid mixing for 30 seconds.

According to Figure 4.4, the pH values obtained in the samples with dosing during mixing do not differ significantly from their corresponding samples dosed without mixing. However, the pH in samples which have been dosed with $Al_2(SO_4)_3$ during mixing and without mixing show a close match than the rest.

Gregory *et al*. (2001) stated that when a chemical or coagulant is added to a solution, its chemical potential drives it to react spontaneously with the colloid. The immediate reaction is the destabilization process which is caused by the decreasing or neutralizing surface charge of the particles. This is when counter-ionic property of inorganic coagulants is adsorbed and repulsive forces are reduced or eliminated. Although they do not state that stirring must be disregarded, our experimental results confirm that chemical potential plays a pivotal role during destabilization process.

Based on the fact that destabilization-hydrolysis process is a preliminary process after coagulant(s) are added to the colloidal suspension, we postulate that the process is influenced by physico-chemical properties of a metal ion (M^{3+}) in a metal salt. The identical pH between the two experiments (samples with mixing and without mixing) in Figures 4.4 and 4.5 shows that high electron valence (Pauli electronegativity) plays a pivotal role in destabilization-hydrolysis (Peavy, 1985). The spontaneous destabilization-hydrolysis of the colloid is attributed to high electron valence of Fe^{3+} and Al^{3+} salts added to neutralize ionic charge of the colloid, thus reducing surface potential of the colloid (Peavy, 1985). Research by Barnes *et al*. (1983) revealed that the most effective flocculation occurs when Fe^{3+} and Al^{3+} are added at pH 6.5-9.0 when the concentration of hydroxyl ions is high enough to increase the number of OH^- ions bound to each Fe^{3+}. This reduces the charge on the hydroxo-ferric complex and decreases repulsive energy allows easier adsorption of hydroxo-ferric complexes. The decreasing pH from 8.9 to a range 7.33–2.40 in the samples without mixing shows that destabilization-hydrolysis is a spontaneous reaction; where mixing mainly disperses the coagulant throughout the colloidal suspension. Our finding is supported DLVO theory which explains destabilization to be caused by the spontaneous reaction between positively charged metal ions and negatively charged colloidal particles. Ionic strength is increased where it effectively screens electrical repulsion and reduces the distance between the particles, resulting in increasing effect of van der Waals forces of attraction (Gregory *et al*., 2001).

Turbidity in the samples which have been stirred (mixed) and those which have not been stirred in Figures 4.4 and 4.5 shows that optimal adsorption takes place during settling of the samples when differential velocity is predominant. Although all Fe^{3+}

and Al^{3+} salts show low turbidity, Figure 4.5 shows that Fe^{3+} salts and $Al_2(SO_4)_3$ yield turbidity lower than 110 NTU at pH lower than 4.5 compared to $AlCl_3$.

4.6 Conclusion

Most of the flocs are formed during rapid mixing between 30–60 seconds using proportional mass ratio of metal ion-solid particles (0.043 M M^{3+} in 16 g solid paint). Mixing is a mechanical phenomenon which disperses the reagent throughout the colloidal suspension and does not contribute towards destabilization-hydrolysis. The factors which play a pivotal role during destabilization-hydrolysis are chemical and physical properties of the coagulants (e.g. electronegativity, electron valence and radius) added into the colloidal suspension.

The observation obtained on turbidity results during rapid-slow mixing indicates that optimal hydrolysis, which gives rise to maximum flocs formation occurs within 30 and 60 seconds of rapid mixing. There is a high concentration of metal hydroxide formed through settling and differential velocities to form larger flocs that are able to yield maximum turbidity removal. The pH and turbidity values change during destabilization-hydrolysis process, as shown by Equation 4.1. The results show that there is a correlation between the pH and turbidity in an alkaline paint wastewater dosed with Fe^{3+} and Al^{3+} salts (specific concentration of metal ion per mass of solid paint).

Results show that 20 and 30 mL of 0.043 M of Fe^{3+} or Al^{3+} ions dosages yield identical pH values and turbidity removal in a paint wastewater. This indicates that

Fe^{3+} in $FeCl_3$ or $Fe_2(SO_4)_3$ and Al^{3+} in $AlCl_3$ or $Al_2(SO_4)_3$ have identical alkaline neutralizing potential and turbidity removal potential in paint wastewater. This suggests that destabilization-hydrolysis process is influenced by the physical phenomenon, where nucleation is a predominant process. This physical adsorption phenomenon also occur in the samples with high valence metal ions (Fe^{3+} or Al^{3+}) dosages without mixing provided that the samples are allowed to settle for at least 1 hour.

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CHAPTER 5: General conclusions

Experiments which were carried out in this study cover coagulation-flocculation dynamics and the following findings and results have been observed:

A 200 mL sample of paint wastewater (containing 16 g of solid paint) which has been dosed with 0.043 M Fe^{3+} in $FeCl_3$ or $Fe_2(SO_4)_3$ and Al^{3+} in $AlCl_3$ or $Al_2(SO_4)_3$ in increasing order respectively or combined dosages shows a consistent pH drop which correlate with decreasing turbidity. $Al_2(SO_4)_3$ showed a relatively lower pH decreasing trend with increasing turbidity removal compared to other metal salts using identical dosages and quantity of wastewater samples. This shows that $Al_2(SO_4)_3$ has a higher hydrolyzing power in paint wastewater than $FeCl_3$ and $AlCl_3$.

My experimental results show that there is a relationship between destabilization, hydrolysis, pH and turbidity. It is observed that pH decreasing trend correlates with decreasing turbidity removal (excluding $Ca(OH)_2$ and $Mg(OH)_2$ dosages). It is also observed that the rate of hydrolysis is inversely proportional to pH changing trend, based on experimental results. I therefore suggest that pH is a direct indicator of the rate of hydrolysis, which is not the case with highly alkaline colloids. In addition, hydrolysis is a process which reacts "hand-in-glove" with destabilization; I suggest that pH is also a direct indicator of the rate of destabilization based on the pH changing trend.

My results showed that the addition of metal hydroxides such as $Ca(OH)_2$ and $Mg(OH)_2$ to wastewater does not only soften wastewater "hardness' but also influences the hydrolysis process. The hydroxyl ions (OH^-) which are released by metal hydroxides react with unhydrolyzed Fe^{3+} to form hydrolysis species, thus increasing the concentration of flocs as shown by Figs. 2.3 and 2.4. This is also observed in another batch of experiments were the same quantity of paint wastewater was dosed with synthetic polymers consisting of 0.043 M $FeCl_3$ and 0.043 M $Ca(OH)_2$ or 0.043 M $Mg(OH)_2$ respectively to form 0.043 M $FeCl_3$–$Ca(OH)_2$ or 0.043 M $FeCl_3$–$Mg(OH)_2$ polymers.

$FeCl_3$ and $FeCl_3$–$Ca(OH)_2$ or $FeCl_3$–$Mg(OH)_2$ dosages yielded the best turbidity removal in wastewater with pH 3.5. $FeCl_3$–$Mg(OH)_2$ polymer yielded a better turbidity removal compared with the $FeCl_3$–$Ca(OH)_2$ polymers. It shows that the former is a better replacement for $Ca(OH)_2$, a metal hydroxide with negative environmental impact. $FeCl_3$–$Ca(OH)_2$ and $FeCl_3$–$Mg(OH)_2$ polymers have a better turbidity removal efficiency than when $FeCl_3$ is added with either $Ca(OH)_2$ or $Mg(OH)_2$. This suggests that turbidity removal occurs through adsorption of the colloidal particles onto the polymeric structures as shown in Fig. 2.5. This investigation revealed that synthetic polymers can be produced by reacting metal salt ($FeCl_3$) with metal hydroxides, a relatively cheaper polyelectrolyte compared with commercial polymeric coagulants.

The dosing sequence, dosing prior or during mixing does not play a pivotal role in turbidity removal in paint wastewater. The experimental findings show that equal number of moles of Fe^{3+}, Al^{3+} in their respective metal salts ($FeCl_3$, $AlCl_3$ and $Al_2(SO_4)_3$) respectively flocculate the same mass of solid paint (16 g) in a solution. Since the observations show that adsorption is a physical phenomenon, this indicates that the flocs form a cake-like structure which is an adsorption substrate. This finding is contrary to literature by Ives *et al*. (1978), Peavy *et al*. (1995) and Jiang *et al*. (1997) when they stated that turbidity removal occurs when hydrolysis species are adsorbed onto the colloidal particle; whereas other authors stated that colloidal particles are embedded in the agglomerates. Stumm *et al*. (1968) stated that amorphous precipitates enmesh colloidal particles through sweep floc in 'sweep coagulation' zone. They also mentioned that re-stabilization commonly occurs with positively charged precipitate at pH less than 7. At 7<pH <8, the positively charged precipitates, $[M(OH)_{3(s)}]$ collide with negatively charged particles through enmeshment. My experimental results show that the hydrolysis potential of the metal salts added to the colloidal suspension affect the pH changing trend during deprotonation, thus forming hydrolysis species resulting in adsorption.

A jar test is a common technique used to investigate ideal dosage in the wastewater in a laboratory in order to adjust the operating regime in conditions where there are changes in water/wastewater quality, strength of reagents or addition of other reagents. pH and turbidity are the main parameters used to measure water quality. A jar test technique is prone to inaccurate readings if there are foreign metals in the

samples or de-flocculated solution. Turbidity test cannot be carried out in a de-flocculated sample (over-range) as shown in the samples which were dosed with 10 mL of metal salts; which is easily determined when percentage area covered by the flocs using microscope slide technique is employed. Since the microscope test shows almost identical results compared to a jar test, I therefore recommend that the latter method should be considered as it is more representative. Advantage with the microscope test is that it employs a visual test which is more accurate, representative and reliable. Another advantage of the microscope slide test is that the standard solutions are prepared in lesser quantities and the test is faster because it does not include 1 hour settling time as in the case of a jar test. A jar test is also prone to faulty readings because the analyzing equipment requires regular calibration before use, which is a practice that is normally not fully accomplished by laboratory technicians.

The findings from the effect of mixing on the treatment of paint wastewater with 0.043 M Fe^{3+} and 0.043 M Al^{3+} salts show that effective hydrolysis occurs within 30-60 seconds at 250 rpm. This does not mean the colloidal particles are removed during this time-frame, but it is a duration in which the formation of primary adsorption substrates (hydrolysis species) occurs, nucleation stage. This observation also shows that prolonged rapid mixing is unnecessary as it can cause rupturing of the flocs; which results in re-stabilization that will affect the quality of effluent. This study managed to investigate that slow mixing is unnecessary because optimal adsorption occurs during settling; when existing flocs moves randomly through Brownian motion due to differential and settling velocities and collide with other flocs to form

larger agglomerates. These agglomerates are able to undergo spontaneous growth which results in large crystals of a more stable solid phase during settling stage.

Thermodynamics predict that flocculation process is influenced by the specific wastewater pH range, but my experimental results show that its effectiveness relies on destabilizing power of a metal ion to fasten the rate of hydrolysis with decreasing pH trend. My prediction is that the concentration of the metal ions in a metal salts (0.043 M M^{3+} in metal salt) plays a pivotal role in wastewater treatment because it is able to adjust the pH of the solution to effect destabilization-hydrolysis.

Apart from the fact that molar concentration of 0.043 M Al^{3+} in $Al_2(SO_4)_3$ has shown ability to remove a larger mass of solid paint in the wastewater than other three inorganic metal salts (high destabilising-hydrolyzing efficiency), SO_4^{2-} also showed that it plays a vital role in hydrolysis. $Al_2(SO_4)_3$ and $AlCl_3$ produce white sludge that can be recycled into the paint manufacturing processes and also utilize chemicals they contain for other processes. The former is therefore recommended to be used as coagulant. Although $FeCl_3$ is a relatively cheap product, it has corrosive property and therefore it is not recommendable more especially when the wastewater is recycled.

The observation from the XRD and TGA indicates that there is a small concentration of chemicals and moisture in the sludge, which also confirms that Fe^{3+} and Al^{3+} salts reacts effectively in hydrolysis during wastewater treatment.

Further study on the correlation between pH, ionic potential, zeta potential, electrophoretic mobility, monoprotic and diprotic properties in wastewater treatment

is necessary. The information which explains speciation of hydrolysis species is not satisfactory; hence an investigation about their formation and relation with ionic potential, pH and turbidity is necessary.

Furthermore, my results are promising but require detailed experimental follow-up (with qualitative error analysis, repeatability studies, etc)

Appendix A

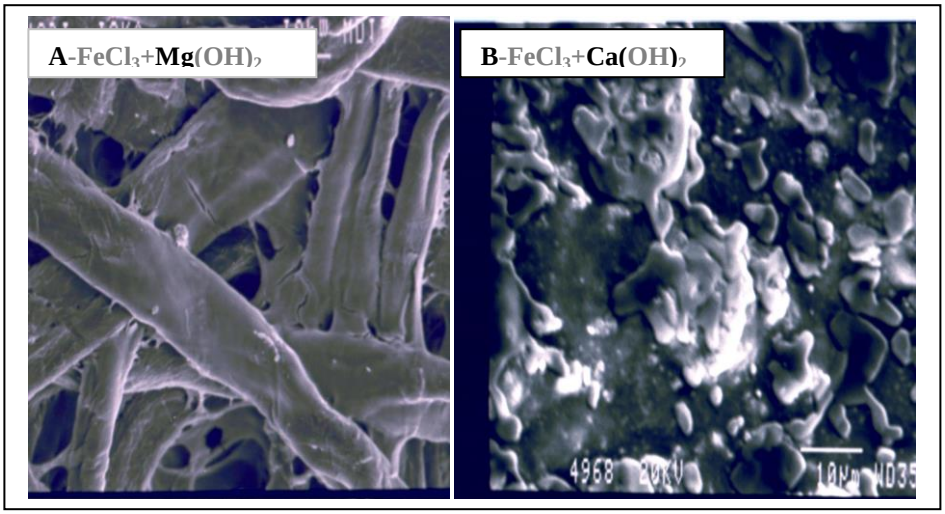


Figure S1: SEM micrographs of 0.043 M $FeCl_3$-$Ca(OH)_2$ and 0.043 M $FeCl_3$-$Mg(OH)_2$ polymers.

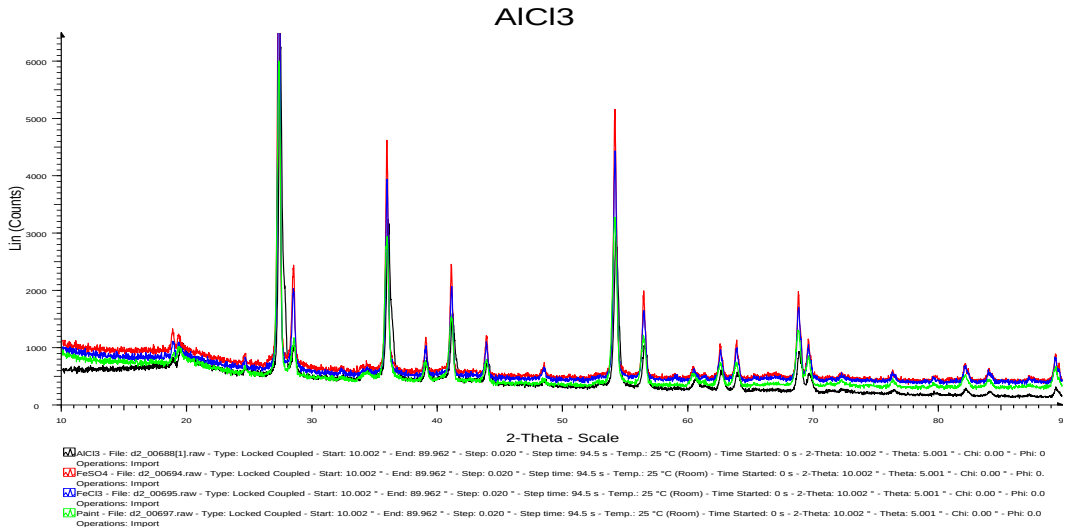


Figure S2: **XRD images of the dry sludge using 0.043 M Al^{3+} ($AlCl_3$) and 0.043 M Fe^{3+} salts.**
First sample = $AlCl_3$, second sample = $Fe_2(SO_4)_3$, third sample = $FeCl_3$, forth sample = paint
X-axis range = 500-6000 Lin (counts), Y-axis = 10-90 2-Theta.

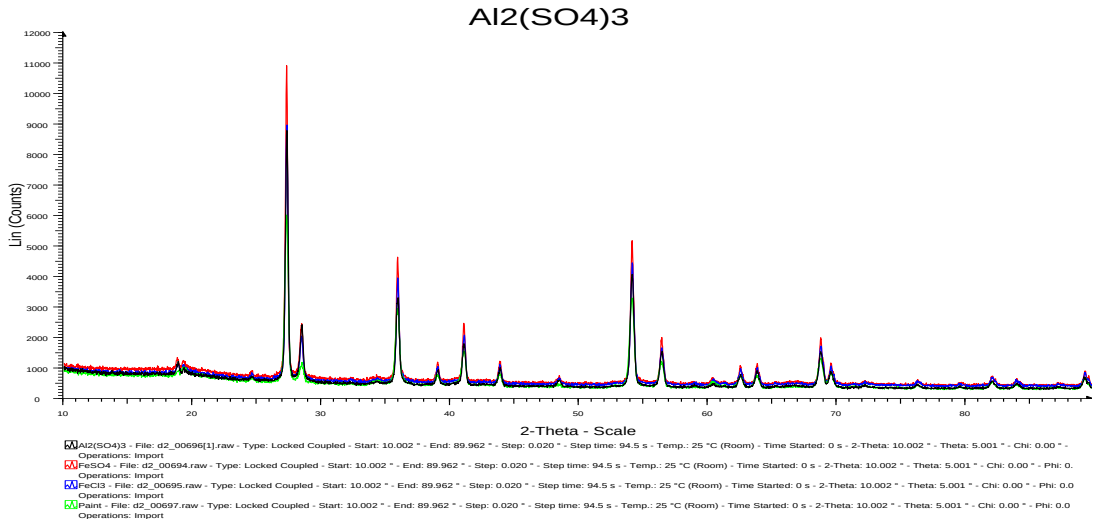


Figure S3: XRD images of the dry sludge using 0.043 M Al^{3+} ($Al_2(SO_4)_3$) and 0.043 M Fe^{3+} salts.
First sample = $Al_2(SO_4)_3$, second sample = $Fe_2(SO_4)_3$, third sample = $FeCl_3$, forth sample = paint.
X-axis range = 500-11000 Lin (counts), Y-axis = 10-100 2-Theta.

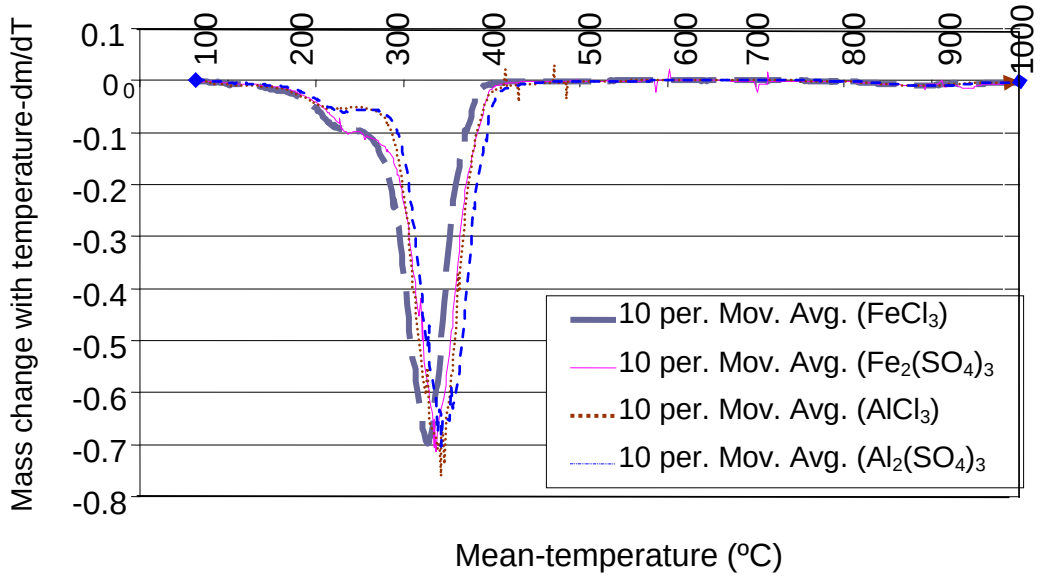


Figure S4: TGA graph of dry paint sludge dosed with 0.043 M Al^{3+} and 0.043 M Fe^{3+} salts.

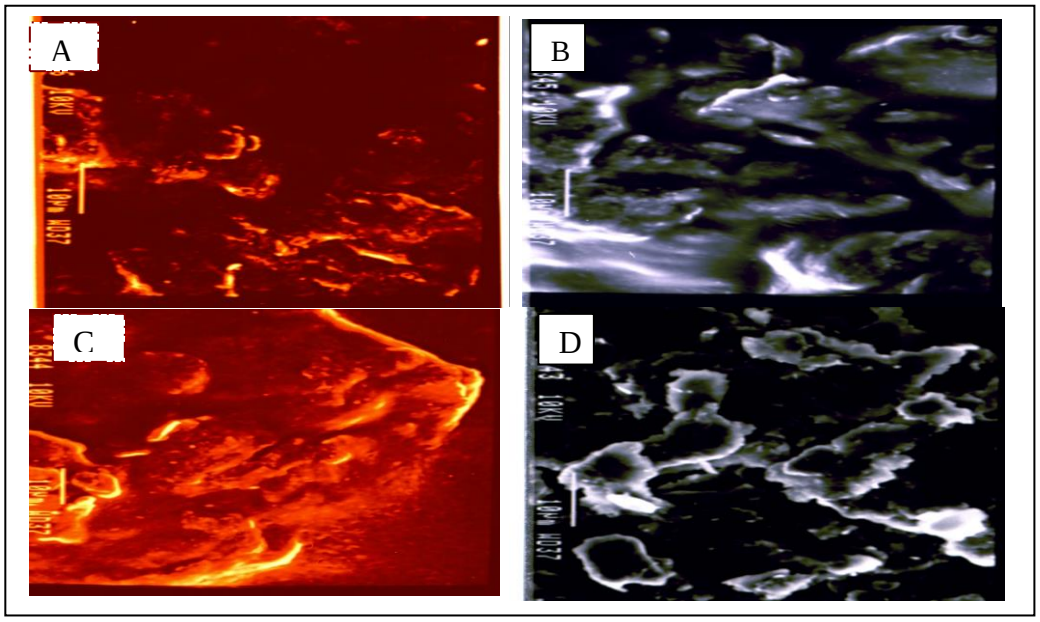


Figure S5: SEM images of dry paint sludge dosed with 0.043 M Al^{3+} and 0.043 M Fe^{3+} salts magnified 40 times.
A = $FeCl_3$, B = $Fe_2(SO_4)_3$, C = $AlCl_3$ and D = $Al_2(SO_4)_3$.

Figure S6 shows the velocity and differential velocities which influence settling as discussed under the results in Figures 2.5 and 2.6.

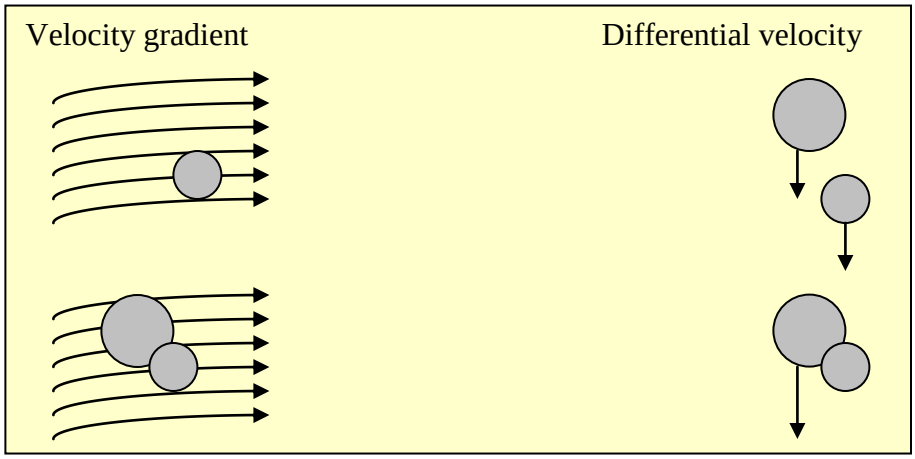


Figure S6: Flocs formation in a colloidal system due to Brownian motion.

Figure S6 shows velocity and differential velocities which are induced by energy that have been generated during rapid mixing as stated under the explanation of the results shown in Figs. 2.5 and 2.6; the graphs which show identical turbidity removal in the samples which have been mixed compared to those without mixing. This energy is used to increase the speed of particles to collide with slow moving particles which cause the formation of larger particles that will settle.

Appendix B

Jar test data tables

All tests involved use of synthetically prepared wastewater paint (169.2g per litre of water). For every test 200ml of this paint were to each of the six beakers that were

used. The dosages of the hydrolysing salts are tabulated for the sets of experiments that were conducted.

SET 1 Experiments

Run 1a

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	10	10					
2	20	20					
3	30	30					
4	40	40					
5	50	50					
6	60	60					

Run 2a

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	5	5					
2	10	10					
3	15	15					
4	20	20					
5	25	25					
6	30	30					

Run 3a

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	10		10				
2	20		20				
3	30		30				
4	40		40				
5	50		50				
6	60		60				

Run 4a

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	5		5				
2	10		10				
3	15		15				
4	20		20				
5	25		25				
6	30		30				

SET 2 Experiments

Run 1b

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	20						
2	20	20					
3	20	30					
4	20	40					
5	20	50					
6	20	60					

Run 2b

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	20	5					
2	20	10					
3	20	15					
4	20	20					
5	20	25					
6	20	30					

Run 3b

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	20		10				
2	20		20				
3	20		30				
4	20		40				
5	20		50				
6	20		60				

Run 4b

Beaker	$FeCl_3$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	Combined $FeCl_3$ and $Ca(OH)_2$ ml added	Combined $FeCl_3$ and $Mg(OH)_2$ ml added	$FeCl_3$-$Ca(OH)_2$ polymer ml added	$FeCl_3$-$Mg(OH)_2$ polymer ml added
1	20		5				
2	20		10				
3	20		15				
4	20		20				
5	20		25				
6	20		30				

SET 3 Experiments

Run 1c

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$FeCl_3$ rapid mixing	$FeCl_3$ slow mixing
1	10					
2	20					
3	30					

Run 2c

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$Fe_2(SO_4)_2$ rapid mixing	$Fe_2(SO_4)_2$slow mixing
1		10				
2		20				
3		30				

Run 3c

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$AlCl_3$ rapid mixing	$AlCl_3$ slow mixing
1			10			
2			20			
3			30			

Run 4c

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$Al_2(SO_4)_2$ rapid mixing	$Al_2(SO_4)_2$slow mixing
1				10		
2				20		
3				30		

Run 1d

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$FeCl_3$ rapid mixing	$FeCl_3$ Rapid and slow mixing
1	20					
2	30					

Run 2d

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$Fe_2(SO_4)_2$ rapid mixing	$Fe_2(SO_4)_2$ rapid and slow mixing
1		20				
2		30				

Run 3d

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$AlCl_3$ rapid mixing	$AlCl_3$ rapid and slow mixing
1			20			
2			30			

Run 4d

Beaker	$FeCl_3$ ml added	$Fe_2(SO_4)_2$ ml added	$AlCl_3$ ml added	$Al_2(SO_4)_2$ ml added	$Al_2(SO_4)_2$ rapid mixing	$Al_2(SO_4)_2$ rapid and slow mixing
1				20		
2				30		