*Full Length Research Paper*

# The effect of mixing on the treatment of paint wastewater with $Fe^{3+}$ and $Al^{3+}$ salts

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A 169.2 g of paint was diluted in 1 L of potable water. A 200 ml of sample was poured into 500 ml glass beakers and dosed with 10, 20, and 30 ml of 0.043 M of all coagulants (Iron: Fe and Aluminum: Al salts), respectively in jar tests. Samples were mixed at 250 rpm for 30, 45, and 60 s, respectively. Additional set of experiments was conducted with combined rapid mixing at 250 rpm for 30, 45 and 60 s followed by slow mixing at 100 rpm for a further 10 min, pH and turbidity were measured on the samples. The turbidity in the samples with 30, 45, and 60 s rapid mixing showed that most of the flocs are formed within 30 s. The results also showed a correlation between the pH and turbidity. $Fe^{3+}$ and $Al^{3+}$ of the same concentration yield a similar pH and turbidity trend. The added slow mixing showed no appreciable benefits. This was confirmed by microscope experiments using 2 drops of the same solution from rapid mixing only (Experiment A) and placed them in microscope slides after mixing. A similar experiment was conducted with combined and slow mixing. Images were captured after 30 min of settling using a camera. The results showed that the percentage area covered by the flocs in Experiment A are not different to the corresponding percentage area covered by the flocs in Experiment B.

Key words: Paint, dosed, mixing, turbidity, correlation.

## INTRODUCTION

Effective wastewater treatment is a very critical process since the effluent has to be of good quality so that it should not be detrimental to either human health or environment. Water is abstracted from a source, used in various industrial processes and then treated with chemicals to meet effluent discharge standards before it is discharged back to the source. Most of the rivers around the globe contain highly polluted water which is caused by concentrated industrial effluent discharge. This is because some water treatment works lack technical knowledge which is related to effective wastewater treatment. The treatment process is based on thermodynamic principles which include nucleation, crystal growth and aggregation of the destabilized suspended particles in a solution (Wu and Wang, 2001;

Tan et al., 2000). It is imperative for water treatment personnel to have a clear understanding about the role which is played by coagulation, flocculation and settling on destabilization, hydrolysis and adsorption. A lot of cases have been reported globally regarding the poor quality of potable water which is supplied to the community, as well as poor quality effluent discharged into the rivers. Considerable research has been conducted on the various aspects which involve coagulation-flocculation, but it has not been possible to identify the difference between coagulation and flocculation processes. Metcalf and Eddy (2003) described coagulation as the destabilization of wastewater that occurs within seconds after addition of a coagulant, but did not specify effective time to the process. Bryun et al. (2005) conducted a study on the water treatment using an instantaneous flash mixer and reported that charge neutralization occurs within 1 s of major flocculation process, but their explanations were

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not related to the dosage, pH, turbidity and reaction time. The literature does not indicate which process between coagulation and flocculation plays a major role in high turbidity removal.
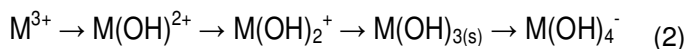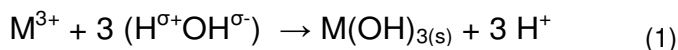
Mixing also plays a role during the process by dispersing coagulants that are added to a colloid (Binnie et al., 2003). Hamidi et al. (2007) determined the speed of rapid and slow mixing that is required for effective coagulation-flocculation but their rapid mixing differed from that determined by Tan 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 restabilization of the particles as charge reversal on the colloidal suspension occurs (Swartz and Ralo, 2004; Aboulhassan et al., 2006). Duan and Gregory (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; Ali and Sengupta, 2002; Gregory and Duan, 2001; Jiang and Lloyd, 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; Wang et al., 2004; Tunay, 2003; Shammas, 2004).

$Fe^{3+}$ 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). Literature reports that the best velocity gradient ($\Delta v/\Delta d$) with $Fe^{3+}$ and $Al^{3+}$ salts is between 20 and 70 $s^{-1}$ (Swartz and Ralo, 2004). O'Melia and Shen (2001) reported that slow mixing is important after rapid mixing since it is a stage where relative motion induces a velocity gradient of the particles which is a cause of a high shear rate in a liquid phase. There are two stages of mixing, namely rapid (flash mixing) and slow. The former disperses coagulants throughout the colloidal particles to cause destabilization and hydrolysis (Sincero and Sincero, 2003). The latter process is the stage where formation of larger aggregates occurs due to the collision of flocs through velocity gradient and differential velocity (Sincero and Sincero, 2003). The larger flocs which are formed adsorb the colloidal particles and the increasing settling velocity results in settling (Aboulhassan et al., 2006; Aguilar et al., 2002, 2005). Poor removal of suspended particles occurs when destabilization of colloidal particles is influenced by adsorption of strongly charged partially hydrolyzed metallic ions (Duan and Gregory, 2003).

Several studies confirmed that Aluminum hydroxide has minimum solubility in a pH range of 5.0 to 7.5 (Tebbutt, 1983). Lower values of pH increase the solubility rapidly whereas higher values increase solubility at a slower rate. Iron hydroxide shows a minimum solubility in a wide pH range of 7 to 10, while values outside this range increases the solubility of Iron than Aluminium hydroxide (Binnie et al., 2003). Crozes et al.

(1995) reported that the Aluminium ions form an acidic medium in water and exhibit less solubility than ferric ions. Ghaly et al. (2006) and Aysegul and Enis (2002) discovered that the addition of $Fe^{3+}$ and $Al^{3+}$ salts at a pH 6 to 8 causes an uncontrollable rise in the rate of hydrolysis which leads to a very rapid precipitation. Wastewater treatment can also be explained as a process where coagulants are added to a colloidal system to cause destabilization and hydrolysis, thus forming agglomerates which are adsorption substrates (Juttner et al., 2000). A choice of coagulant with high destabilizing and hydrolysis power is essential, since these two reactions determine the size and the concentration of the flocs in a solution (Chen, 2002). More ionic charge and high electron valence on the metal ions strengthen neutralization of the ionic charge of the medium (Flynn, 1984). The presence of a high concentration of hydroxyl ions combined with more $Fe^{3+}$ or $Al^{3+}$ ions reduce the charge on the hydroxoferric complex (Barnes and Wilson, 1983; Pratt et al., 2007). Physical theory states that destabilization occurs when the zeta potential of the colloidal system is reduced, thus resulting in the adsorption of the counterion and a decrease of the electrical double layer (Benefield and Morgan, 1999; US EPA, 2000). The addition of inorganic coagulants also reduces the surface potential of colloid and the potential energy between the particles, while increasing van der Waals forces of attraction (Swartz and Ralo, 2004).

A study by Ali and Sengupta, (2002) on surface electrical phenomena reported that raw water contains microscopically visible colloidal particles that possess high electrophoretic mobility or high zeta potential which have to be reduced by chemical treatment. This occurs during destabilization when the equilibrium between the electrostatic forces of repulsion and van der Waals forces of attraction are disturbed; a shift towards van der Waals forces of attraction reduces the diameter of the neighbouring particles and the distance between them. The particles collide with one another to form flocs, whereas the $M^{3+}$ ions hydrolyse by forming a bond with $OH^-$ as a result of a cleavage of the polar water molecules ($H^{\sigma+}OH^{\sigma-}$) to form metal hydroxide species as shown by Equations 1 and 2

$$M^{3+} + 3\ (H^{\sigma+}OH^{\sigma-})\ \rightarrow M(OH)_{3(s)} + 3\ H^+ \qquad (1)$$

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

Equation 1 depicts the hydrolysis reaction when metal ion reacts with hydroxyl ions, whereas Equation 2 represents the different species which are formed during hydrolysis, where the pH of a solution decreases during hydrolysis process. The first solid species formed is an unstable am~$M(OH)_{3(s)}$. It is formed due to a very low solubility product of the metal hydroxide. Ageing causes the conversion of an unstable amorphous metal hydroxide to

a stable $\alpha \sim MO(OH)_{(s)}$, which is formed at the lowest $M^{3+}$ concentration. Some other species such as beta ferric hydroxide ($\beta \sim MO(OH)_{(s)}$) are also possible depending on the compound which is used in the wastewater treatment process (O'Melia and Shen, 2001).

All of the above results are very interesting because they do not necessarily help the practitioner to devise a detailed procedure for clarifying a wastewater stream. This study is aimed at using the theory together with experiments to devise a procedure for clarifying paint wastewater. Although, the experiments are conducted on paint wastewater, the operating philosophy also covers wastewater from other sources such as industries and agriculture. We note from Equation 1 that as solid hydroxide is formed, the pH of the solution should fall and so the value of the pH should be an indicator of the degree of floc formation. The objective of this study is to determine which factors such as rapid and slow mixing, dosing amounts and nature of the coagulant affect the quality of the paint wastewater using pH and turbidity as indicators. The study also determines which chemical process between coagulation and flocculation is responsible for optimal flocs formation in order to achieve maximum adsorption.

## MATERIALS AND METHODS

### Paint wastewater sample

The solid content of the paint was determined by drying a 20 g of the water-based paint in triplicate in a crucible in an oven at 250°C for 3 h. The average mass obtained was 6.2 g showing that the ratio of solid paint to water is 1:3.2. An 80 g mass of solid paint was assumed in order to prepare 80 g solid/1000 g wastewater. As described above, this was 169.2 g aqueous paint per litre of water. The coagulant dosage required is considered to be proportional to total solids (Faust and Aly, 1983).

### Coagulants

The use of 0.043 M of $Fe^{3+}$ and $Al^{3+}$ ions during flocculation of the paint wastewater yielded a wide range of results showing effective flocculation at a solid content of 80 g solids in 1000 g of paint wastewater (Fasemore, 2004).

The calculation of the mass of metal salt of 0.043 M of $M^{3+}$ ($M^{3+}$ = Fe or Al) is shown in Table 1:

### Procedure for jar tests and microscopic observations

The equipment used for the jar tests was a BIBBY Stuart Scientific Flocculator (SW1 model), which had six adjustable paddles with rotation speeds between 0 to 250 rpm. As explained above, a paint wastewater sample was prepared by dissolving 169.2 g of water-based paint in 1 L of distilled water. The pH and turbidity of this sample solution were 8.9 and > 500 NTU, respectively. A 200 ml of the sample (16 g solid paint in 200 ml) was poured in six 500 ml glass beakers. The first three beakers were mixed at 250 rpm rapid mixing for 30, 45 and 60 s, respectively using a stop-watch, whereas the other three beakers were mixed at 250 rpm for 30, 45 and 60 s followed by slow mixing at 100 rpm for 10 min. The experimental procedure is detailed below:

The first and the fourth beakers were dosed with 10 ml of 0.043 M $Fe^{3+}$ ($FeCl_3$) during 30 s rapid mixing. The mixing in the first sample was stopped after 30 s and the pH was measured immediately. The mixing in the fourth sample was reduced to 100 rpm for 10 min. The pH was immediately measured after 10 min. The samples settled for 1 h and thereafter the pH and turbidity were measured. A similar experiment was conducted by dosing the second and the fifth samples with 10 ml of 0.043 M $Fe^{3+}$ ($FeCl_3$) but rapid mixing was for 45 s. The mixing in the second sample was stopped after 45 s and the pH was measured immediately. Mixing in the fifth sample was reduced to 100 rpm for 10 min. The pH was immediately measured after 10 min of slow mixing. The samples settled for 1 h and thereafter the pH and turbidity were measured. The third and sixth samples were dosed with 10 ml of 0.043 M $Fe^{3+}$ ($FeCl_3$) during 60 s during rapid mixing. The mixing in the third sample was stopped after 60 s and the pH was measured immediately. The mixing in the sixth sample was reduced to 100 rpm for 10 min. The samples settled for 1 h and thereafter the pH and turbidity were measured.

The second and third batches of experiments were conducted in the same manner as above except that 10 ml of 0.043 M $Fe^{3+}$ ($FeCl_3$) dosage was increased to 20 and 30 ml of 0.043 M $Fe^{3+}$ ($FeCl_3$) dosages, respectively.

The experiments above were repeated by replacing 0.043 M $Fe^{3+}$ ($FeCl_3$) dosage with 0.043 M $Fe^{3+}$ [$Fe_2(SO_4)_3$], 0.043 M $Al^{3+}$ ($AlCl_3$) and 0.043 M $Al^{3+}$ ($Al_2(SO_4)_3$) dosages, respectively.

An additional study (Experiments A and B) was conducted by placing 2 drops of the supernatant from each sample with rapid mixing only (Experiment A) and combined rapid and slow mixing (Experiment B) immediately after mixing (rapid-mixed for 30, 45 and 60 s, respectively or combined rapid and slow mixing) onto a microscope slide. Another slide was placed on top separated by 2 mm and observed at magnification of 400× under a light microscope. The samples were photographed after 30 min of settling. The images were plotted and used to determine the areas covered by the flocs.

A supplementary study was conducted by pouring the same 200 ml of paint wastewater samples used in previous experiments in five 500 ml glass beakers, dosed with 20, 30, 40, 50 and 60 ml 0.043 M $Fe^{3+}$ ($FeCl_3$). The samples where mixed at 250 rpm for 2 min and settled for 1 h, and thereafter the pH and turbidity were measured. A similar experiment was conducted with samples dosing without mixing, settled for 1 h, and thereafter the pH and turbidity were measured.

### Performance evaluation

In the experiments treated in a jar test, the pH and the turbidity of the samples were measured after 1 h of settling. The pH measurements determined the rate at which the hydrogen ions are released into the solution as illustrated in Equation 1. Turbidity was to determine the particle removal potential by each coagulant ($Fe^{3+}$ and $Al^{3+}$ salts). In Experiments A and B, the images showing the area covered by flocs produced by the microscopic observation determine the amount of solids produced during the flocculation. The work comparing the results from jar tests and those on a microscope slide gave us confidence 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).

#### *pH meter*

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

**Table 1.** Preparation of coagulant solution using 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 |
| $Fe_2(SO_4)_3.18H_2O$ | 15.0 | 0.0215 | 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 |

tip was used.

### Turbidimeter

A Hanna Microprocessor Turbidimeter was used to determine turbidity of the supernatant using NTU as a unit of measure. The instrument was calibrated every month using 0.1, 10, 100 and 1000 NTU calibration solutions.

### Camera

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.

### Electron microscope

A Wiezt Wetzlar light microscope (made in Germany) with adjustable vertical optical stage was used to obtain the images.

### Area covered by the flocs

The images produced by a light microscope were printed in order to measure the area covered by the flocs in a total area covered by the sample. 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 either in spherical or non-spherical form. The total area covered by the flocs was compared to the total area covered by the sample.

## RESULTS

Figures 1a to d illustrate measured pH after 1 h settling with 10, 20 and 30 ml dosages of 0.043 M $Fe^{3+}$ and 0.043 M $Al^{3+}$ ions in metal salts, respectively as a function of the rapid mixing (250 rpm) for 2 min compared with combined rapid (250 rpm) and slow mixing (100 rpm) for 10 min. The pH measured immediately after rapid mixing and after an hour differed by less than 0.1.

The pH in all the samples measured immediately after rapid mixing and those which were measured after 1 h of settling are below 0.1 pH units. This indicates that the hydrogen ions were released into the solution during rapid mixing and the extra hydrogen ions released after a further 1 h settling play an insignificant role.

Figures 1a, 1b, 1c and 1d show that the pH obtained in the samples which have been dosed with 10 ml of 0.043 M of $Fe^{3+}$ and $Al^{3+}$ salts is alkaline, above 7.0. The solution had an opaque colour and there was no apparent floc formation and evidence of settling. This was confirmed by the turbitity measurements where the readings all remained off-scale,

The results further show that the pH in the samples with 20 and 30 ml of 0.043 M of $Fe^{3+}$ and $Al^{3+}$ dosage during rapid mixing are not significantly different to the pH in their corresponding samples with combined 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 0.043 M $FeCl_3$ in Figure 1a shows a decreasing pH from 8.9 to a range of 6.43 to 3.50, Figure 1b shows pH reduction to a range of 6.37 to 3.30, Figure 1c shows pH reduction to a range of 6.81 to 4.80 and Figure 1d shows a pH reduction to a range of 6.36 to 3.33. The pH values in Figures 1a to d also show a decreasing trend with increasing rapid mixing time, the reduction is from 8.9 to a range of 6.5 to 3.4. The pH values yielded by monoprotic ($MCl_3$) metal salts is slightly higher than that of their corresponding diprotic [$M_2(SO_4)_3$] metal salts.

Figures 2a to 2d illustrate turbidity after 1 h settling with 10, 20, and 30 ml dosages of 0.043 M $Fe^{3+}$ and 0.043 M $Al^{3+}$ ions in metal salts, respectively as a function of the rapid mixing (250 rpm) for 2 min compared with combined rapid mixing (250 rpm) and slow mixing (100 rpm) for 10 min. Note that the values for the 10 ml dosage have not been plotted as their values were all over-range (>500 NTU).

Figures 2a to d represent the same samples in Figures 1a to d showing the comparison between turbidity and rapid mixing time. As mentioned, the turbidity in the samples which have been dosed with 10 ml of 0.043 M of $Fe^{3+}$ and $Al^{3+}$ salts are all over-range, greater than 500 NTU. The turbidity in samples with 20 and 30 ml of 0.043 of $Fe^{3+}$ and $Al^{3+}$ salt dosages decreases slightly with increasing rapid mixing time, which shows a similar changing trend to that shown by changing pH with rapid mixing time in Figures 1a to d. 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 to their corresponding samples with combined rapid and slow mixing, which is reduced from >500 NTU to a range of 92 to 117 NTU. This study considers turbidity below 120 NTU as a specification based on the nature of the
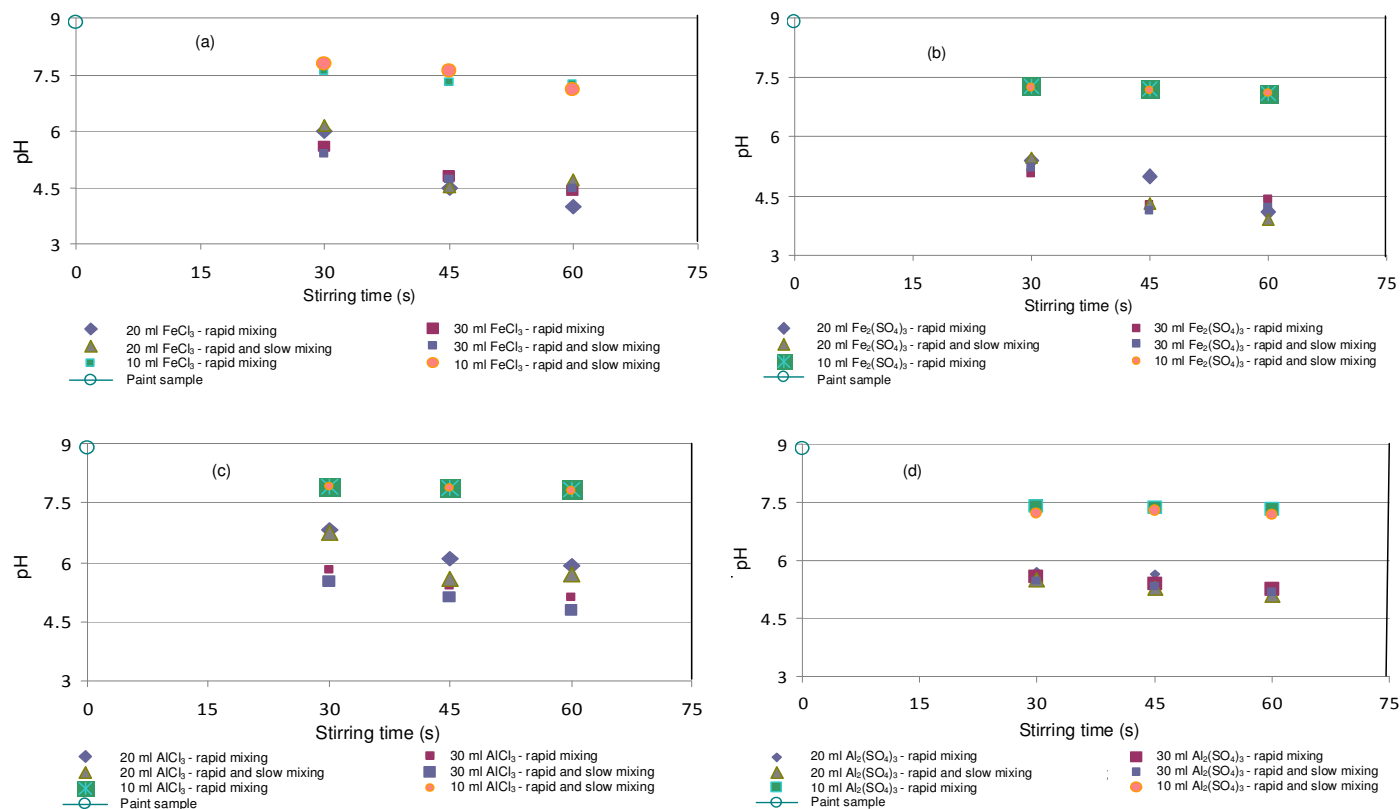
**Figure 1.** Measured pH after 1 h settling with addition of 10, 20 and 30 ml, respectively of (a) 0.043 M $Fe^{3+}$ in $FeCl_3$ (b) 0.043 M $Fe^{3+}$ in $Fe_2(SO_4)_3$, (c) 0.043 M $Al^{3+}$ in $AlCl_3$ and (d) 0.043 M $Al^{3+}$ in $Al_2(SO_4)_3$ as a function of the rapid stirring (250 rpm) time with and without the slow mixing (100 rpm) for 10 min. Note the pH immediately after rapid mixing stopped and after an hour differed by less than 0.1.

constituents found in paint wastewater. The turbidity values in the samples with 20 and 30 ml of 0.043 M $AlCl_3$ are higher than the turbidity in the samples with 20 and 30 ml of 0.043 M $FeCl_3$ or $Fe_2(SO_4)_3$ and 0.043 M $Al_2(SO_4)_3$ dosages in Figures 2a, b and d, respectively. These results showed that $AlCl_3$ is less effective in the removal of colloidal particles from the paint wastewater than $FeCl_3$, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ of the same dosages and concentrations.

Figure 3 reveals that percentage turbidity removal obtained in the samples in Experiment A is virtually the same as that in their corresponding samples in Experiment B, that is, turbidity in the samples with rapid mixing for 30, 45 and 60 s in Experiment A, is within experimental error and the same as that in the corresponding samples with combined rapid and slow mixing. Figure 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 $FeCl_3$ dosage covered area in the ranges of 16 to 19 and 17 to 19%, respectively; whereas the samples with 0.043 M $Fe_2(SO_4)_3$ covered areas in ranges of 14 to 15 and 12 to 14% respectively. Figure 3 also shows that the flocs which are formed in the supernatant of the samples in both experiments with 0.043 M $AlCl_3$ dosage covered

area in the ranges of 18 to 20 and 20 to 21% respectively; whereas the samples with 0.043 M $Al_2(SO_4)_3$ dosage covered areas of 11 to 15 and 12 to 14% respectively.

## DISCUSSION

Lee (2001) stated that the addition of electrolytes, which 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 rapid mixing time 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 to form hydroxide species which are setlleable (Equation 1). The equation also depicts that the rate of hydrogen ions ($H^+$) release into the solution is directly proportional to the rate of the formation of metal hydroxide species.

This study revealed the physicochemical dynamics of the changing pH to the wastewater, which is not apparent in a lot of research that has been conducted. The study
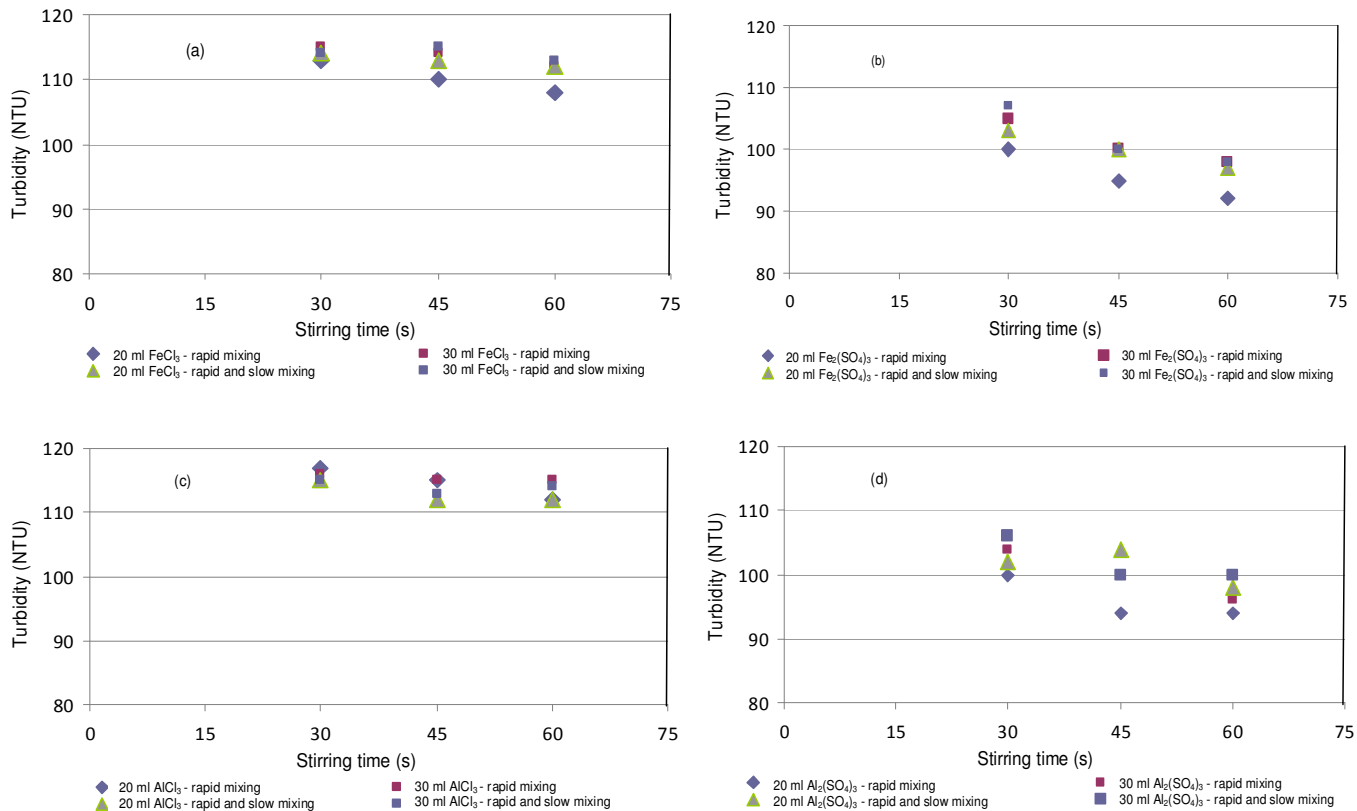
**Figure 2.** Measured turbidity after one hour settling with addition of 10, 20 and 30 ml, respectively of (a) 0.043 M $Fe^{3+}$ in FeCl$_3$, (b) 0.043 M $Fe^{3+}$ in $Fe_2(SO_4)_3$, (c) 0.043 M $Al^{3+}$ in AlCl$_3$ and (d) 0.043 M $Al^{3+}$ in $Al_2(SO_4)_3$ as a function of the rapid stirring (250 rpm) time with and without the slow mixing (100 rpm) for 10 min. Note the values for the 10 ml addition have not been plotted as their values were all over-range (>500 NTU).
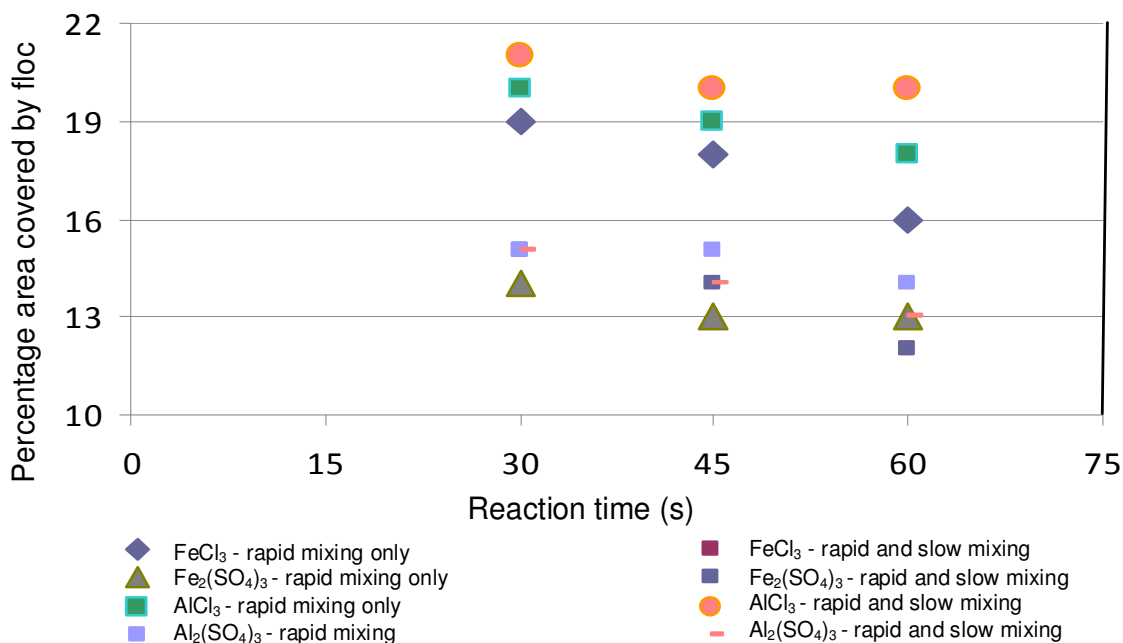


**Figure 3.** Percentage area covered by flocs with FeCl$_3$, $Fe_2(SO_4)_3$, AlCl$_3$ and $Al_2(SO_4)_3$ dosage in a jar test. Microscope images of 2 drops of the supernatant from jar tests captured after 30 min of settling.

also shows the distinctive roles which are played by rapid mixing only compared with combined rapid and slow mixing using metal salts. The difference in pH of the samples measured immediately after rapid mixing or combined rapid and slow mixing and that measured after 1 h of settling ($\Delta$pH) is insignificant, and falls within the range of 0.04 to 0.1. It is therefore not necessary to plot the values as they would distort Figures 1a, b, c, and d. These low $\Delta$pH values indicate that most of the hydrogen ions were released to the solution during rapid mixing stage, resulting in the maximum formation of flocs (rate of hydrogen release is directly proportional to the rate of the formation of metal hydroxide species). The opaque solution in the samples which have been dosed with 10 ml of coagulants in Figures 1a, b, c, and d indicates that deflocculation occurred (Comas et al., 2003). This is caused by a low concentration of metal ions in the solution to form larger flocs which reduce turbidity of the treated wastewater when they settle. However, the presence of the metal ions in the solution indicates that nucleation took place but there was no further reaction which could lead to agglomeration. The pH in the samples which have been dosed with 20 and 30 ml coagulants in Figures 1a to d is identical in each reaction time, which is below 6.8. It can be concluded that a 20 ml of 0.043 M $Fe^{3+}$ or $Al^{3+}$ ions can remove 16 g of colloidal particles in paint wastewater. This also shows that 20 ml is an optimum dosage to achieve high rate of hydrolysis as explained by O'Melia and Shen (2001). Figures 1a to d show that pH in the samples with 20 and 30 ml of 0.043 M $FeCl_3$, 0.043 $Fe_2(SO_4)_3$, 0.043 M $AlCl_3$ and 0.043 M $Al_2(SO_4)_3$ dosages during rapid mixing is identical to the pH in their corresponding samples with combined rapid and slow mixing. This depicts that nucleation occurs during rapid mixing and slow mixing does not play a pivotal role in that reaction. Secondly, Figures 1a to d also show that the pH decreases with increasing reaction times, that is, pH in the samples with 30 s mixing is slightly higher than 45 s, whereas both 30 and 45 s mixing are higher than 60 s. This suggests that rapid mixing for at least 30 s is sufficient to disperse coagulants throughout the solution, thus causing nucleation, and further rapid mixing to 60 s allows further nucleation which increases the concentration of the flocs. The observations obtained from the decreasing pH with varying reaction time during hydrolysis explain the uncertainty about the effect of varying reaction times on flocs formation in water treatment operations to achieve high turbidity removal. Another problem encountered during coagulation is that Freeze et al. (2001) stated that rapid mixing for a short period may cause poor destabilization-hydrolysis, whereas rapid mixing for a prolong period may cause rupturing of the flocs, both of which result in poor adsorption. The results show that the pH values in the samples which are dosed with monoprotic metal salts in Figures 1a and c is higher than the pH values in their corresponding samples with

diprotic metal salts; this indicate that the former yield a lower rate of hydrolysis than the latter in Figures 1b and d. The pH changing trend in Figures 1a to d also reveal that 0.043 M $AlCl_3$ yields lower rate of hydrolysis than 0.043 M $Al_2(SO_4)_3$ and 0.043 M $Fe^{3+}$ in $FeCl_3$ or $Fe_2(SO_4)_3$.

Literature states that the hydrolytic species which are formed during hydrolysis determine the adsorption potential of the colloidal particles (Jiang and Lloyd, 2002). At present, none of the published research explains the degree of flocs formation in rapid mixing only compared to combine rapid and slow mixing, and also validate with the percentage area formed by the flocs under a light microscope, an explanation we have adopted to interpret our experimental findings. Turbidity in all the samples which have been dosed with 10 ml of 0.043 M $Fe^{3+}$ or $Al^{3+}$ in Figures 2a, b, c and d is over-range, above 500 NTU, hence, it has not been plotted as it would distort the diagrams. Figures 2a, b, c and d show that turbidity in the samples which have been dosed with 20 and 30 ml of 0.043 M $Fe^{3+}$ or $Al^{3+}$ dosage during rapid mixing only for 30, 45 and 60 s, respectively is identical to the turbidity in their corresponding samples with combined rapid and slow mixing with 20 and 30 ml of 0.043 M $Fe^{3+}$ or $Al^{3+}$ dosage. The turbidity in all the samples which have been dosed with 20 and 30 ml of 0.043 M $Fe^{3+}$ or $Al^{3+}$ dosage is in a range of 88 to 118 NTU. The identical turbidity values shown between the samples with rapid mixing and their corresponding samples with combined rapid and slow mixing indicate that nucleation is predominant; hence, high adsorption of the colloidal particles is prevalent in both mixing patterns. We suggest that rapid mixing is a process where nucleation occurs, whereas settling for 1 h allowed the formation of larger flocs which condense to form dense cake-like, spongy polymers that settle spontaneously due to high settling velocity. These polymers then act as a filter and trap the residual colloidal particles. This assumption is based on the uniform behaviour of the four coagulants ($Fe^{3+}$ and $Al^{3+}$ salts) which were dosed in the samples, thus showing that the removal of the turbidity from the colloidal suspension was a physical phenomenon. This occurred when the particles settled due to gravitational force as they collide and form larger particles (Metcalf and Eddy, 2003).

The observations from 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 reaction time. The changing trend of the pH and turbidity shown in Figures 1a to 2d indicates that there is a correlation between the both parameters (pH and turbidity). The correlation from the results of the experiments suggest that hydrolysis during coagulation can be explained by changing pH and turbidity trend. The pH and turbidity values in Figures 1a to d show that $Fe^{3+}$ and $Al^{3+}$ salts react in the same way when dosed in paint wastewater; this confirms that their chemical properties are homologous. This also shows
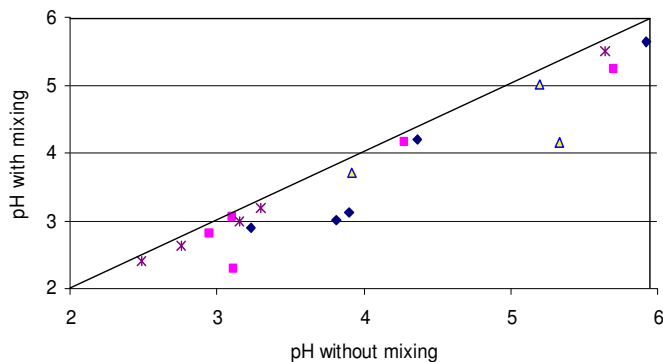
**Figure 4.** pH of the samples using 0.043 M $Fe^{3+}$ (FeCl$_3$) with and without mixing. ♦, FeCl$_3$; ■, Fe$_2$(SO$_4$)$_3$; Δ, AlCl$_3$; x, Al$_2$(SO$_4$)$_3$.
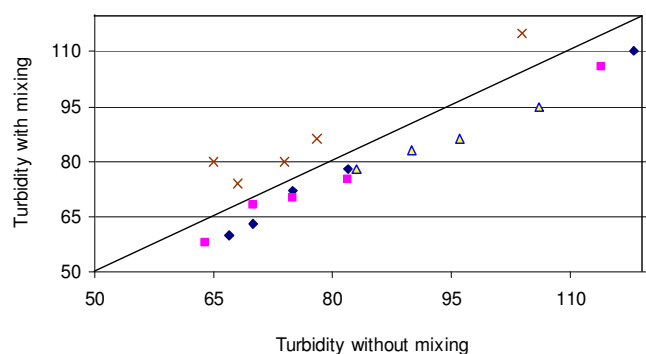


**Figure 5.** Turbidity of the samples using 0.043 M $Fe^{3+}$(FeCl$_3$) with and without mixing. ♦, FeCl$_3$; ■, Fe$_2$(SO$_4$)$_3$; Δ, AlCl$_3$; x, Al$_2$(SO$_4$)$_3$.

that the reactions which take place during rapid mixing produce flocs which are large enough to achieve optimum adsorption of colloidal particles. Since Freeze et al. (2001) stated that prolonged retention during wastewater treatment can cause restabilization process due to rupturing of the flocs by shear forces, our experimental results show that rapid mixing for at most 60 s is effective in turbidity removal based on metal ion-solid paint mass ratios (mass $M^{3+}$ ion/mass of solid paint).

Another observation from Figures 2a and c is that the turbidity in the samples which have been dosed with monoprotic metal salts (MCl$_3$) is slightly higher than the turbidity in their corresponding samples dosed with diprotic metal salts [M$_2$(SO$_4$)$_3$] in Figures 2b and d. This indicates that diprotic metal salts yield a better turbidity removal potential than the monoprotic metal salts. Since both metal salts contain the same concentration of metal ions, the varying pH values may be due to their degree of dissociation. Monoprotic acids dissociate completely in a single step, whereas diprotic acids dissociate in two steps due to two hydrogen atoms. It is suggested that a double dissociation which occurs during hydrolysis of diprotic H$_2$SO$_4$ from a metal salt [Fe$_2$(SO$_4$)$_3$ or Al$_2$(SO$_4$)$_3$] behaves

as a buffer, thus enhancing further hydrolysis compared to hydrolysis which takes place in monoprotic metal salts [FeCl$_3$ or AlCl$_3$], where dissociation of HCl occurs completely in a single reaction (Casas et al., 2000). Although, Kurniawan et al. (2006) stated that the efficiency of Al$_2$(SO$_4$)$_3$ on organic matter removal from a colloidal suspension is hindered by SO$_4$ ions embedded in the precipitate, our experimental results showed that it is unlikely to occur to non-organic compounds. The pH values shown by the samples with rapid mixing and those with combined rapid and slow mixing indicate that the velocity gradient $du/dy$ does not play an essential role during the collision between the metal ions and the colloidal particles.

The results shown by Figure 3 reveal 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 s, respectively in Experiment A is identical to the percentage area covered by flocs in their corresponding samples with combined rapid and slow mixing with 0.043 M $Fe^{3+}$ or $Al^{3+}$ salts dosage in Experiment B. The difference in the percentage area covered by flocs between 30, 45 and 60 s, respectively is insignificant. The results shown in Figure 3 (Experiments A and B) from the samples with rapid mixing only and the samples with combined rapid and slow mixing, confirms that most of the flocs occurs during rapid mixing for 30 s.

Although Figure 4 shows a slightly higher pH in the samples which have not been mixed compared to the samples which were mixed, the difference is less than 1.0 in all the samples. Similarly, Figure 5 shows an insignificant change in turbidity between the samples which have been mixed with those which have not been mixed. This shows that the role which is played by stirring is to disperse the coagulant throughout the sample solution and does not play pivotal role in the rate of destabilization-hydrolysis. This also shows that chemical properties, mainly high electron valence (Pauli electronegativity) plays a major role in the destabilization-hydrolysis process.

**Conclusion**

The study shows that most of the flocs are formed during rapid mixing between 30 and 60 s using 0.043 M of $Fe^{3+}$ and $Al^{3+}$ salts-16 g solid-paint ratios, which assists with the calculation of a direct mass transfer. Destabilization-hydrolysis process, which determines the effect of a metal salt to form the flocs during wastewater treatment, can be interpreted by the changing rate of the pH and turbidity. There is a correlation between the pH and turbidity in paint wastewater which is dosed with $Fe^{3+}$ and $Al^{3+}$ salts. The pH measurement in a laboratory during wastewater treatment must not only use to determine the acidity-alkalinity for pH adjustment, but also to determine the effectiveness of the concentration

of the metal salt(s) added for better turbidity removal using pH decreasing trend. The Water Chemist can produce their in-house pH-turbidity graphs to check if their processes operate within optimum parameters. Monoprotic metal salts have a lower rate of hydrolysis than their counterpart diprotic metal salts, and $AlCl_3$ has the lowest hydrolyzing potential/power than other metal salts. The removal of turbidity from paint wastewater with $Fe^{3+}$ and $Al^{3+}$ salt dosages of the same concentration is a physical phenomenon

A 10 ml of 0.043 M of $Fe^{3+}$ or $Al^{3+}$ ions exhibits a low destabilizing-hydrolyzing potential on a 16 g solid paint in 200 ml paint wastewater. A 20 and 30 ml of 0.043 M of $Fe^{3+}$ or $Al^{3+}$ ions are optimum dosages to remove 16 g of solid paint in 200 ml of paint wastewater. Equal amounts of coagulants with the same concentration of $Fe^{3+}$ and $Al^{3+}$ ions yield identical pH 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 power and turbidity removal efficiency in paint wastewater. This suggests that destabilization-hydrolysis process is influenced by the physical phenomenon, where nucleation is a predominant process.

Our observation shows that the rate of destabilization of the solution to form hydroxide species is influenced by the chemical properties of the metal ions. Stirring of the solution is a mechanical reaction which disperses the metal ions throughout the solution with insignificant impact in the rate of hydrolysis.

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