

Full Length Research Paper

The effect of water hardness on paint wastewater treatment by coagulation-flocculation

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A 169.2 g of paint was diluted in 1 L potable water. A 200 ml of the sample was poured into six 500 ml glass beakers and dosed with 0.043 M FeCl₃, 0.043 M of Al₂(SO₄)₃ or AlCl₃, respectively employing varying dosing sequence and varying dosages before and after mixing in a jar test to determine turbidity removal efficiency. Samples were stirred at 250 rpm for 2 min and 100 rpm for 10 min, settled for 1 h after which the pH and turbidity were measured. In a second set of experiments, the samples were dosed with combined 0.043 M FeCl₃ and 0.043 M Ca(OH)₂ or 0.043 M Mg(OH)₂. In a third set of experiments, the samples were dosed with 0.043 M FeCl₃-Ca(OH)₂ or 0.043 M FeCl₃-Mg(OH)₂ of synthetic polymers. The results from the first and the second sets of experiments showed that pH correlates with turbidity removal, dosing before or during mixing do not play a significant role in wastewater treatment. There is no correlation between pH and turbidity from the results in the third sets of experiments. It indicates that pH is not a direct indicator of turbidity in the treatment of more alkaline solution.

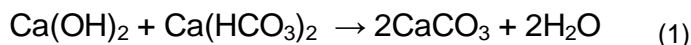
Key words: Paint, dosing, mixing, pH, turbidity, polymer.

INTRODUCTION

Wastewater can be found in an alkaline or acidic medium as characterized by the presence of hydroxyl ions (OH⁻) or hydrogen ions (H⁺) in the colloid, respectively. Fe³⁺ and Al³⁺ metal salts are the most commonly used coagulants in wastewater treatment, but research indicates that these metal salts are effective at pH range of 7 to 10 (Freeze et al., 2001; Tan et al., 2000; Binnie et al., 2003; Ghaly et al., 2006; Aysegul and Enis, 2002). Wastewater pH has been identified as one of the parameters which influence effective wastewater treatment (Juttner et al., 2000; Aboulhassan et al., 2006). The pH enables the concentration of coagulants to exceed the solubility of their metal hydroxides so that precipitates can be formed (Aguilar et al., 2005; Wang et al., 2004; Tunay, 2003; Shammas, 2004). A pH lower than 6 causes adsorption of the hydrolysis products onto

the colloidal surfaces to interact with dissolved components in the colloid, thus, resulting in restabilization which is caused by charge reversal (Jiang and Graham, 1997; Amuda and Amoo, 2006; Ghaly et al., 2006).

A high chemical dosing is required when the wastewater pH is above 6 (Jiang and Graham., 1997; Gregory and Duan, 2001; Lee, 2001; Ghaly et al., 2006; Molony, 2005; Pratt et al., 2007). Sulphuric or hydrochloric acid is dosed for pH adjustment in alkaline colloid, whereas Ca(OH)₂, NaOH or Na₂CO₃ are dosed in acidic colloid (Water Specialist Technology, 2003). Ca(OH)₂ is common in water softening because it reacts with HCO₃⁻ to form CaCO₃ as shown in Equation 1.



The problem in dosing with Ca(OH)₂ is that it adds to the turbidity of the solution, which in turn 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

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of turbidity (Kurniawan et al., 2006). Lime also has a tendency of forming clogs which block the pipeline of the hoppers where it is dosed (Lethabo Water Treatment Plant Manual, 1989).

FeCl₃ has been chosen as a coagulant in this study because of its ability to consume more alkalinity in the wastewater than Al₂(SO₄)₃ due to its acidic property and its high valence electron as stated by Duan and Gregory, (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 and Shen, 2001). The effectiveness of the coagulation depends on the change in ionic concentration and increases exponentially as the charge of the ions added (Binnie et al., 2003; Jiang and Llyod, 2002; Dey et al., 2004; Mahdavi et al., 2001).

Coagulants with multiple electrical charges such as anionic and cationic polymers are effective in wastewater treatment. These coagulants form bridges between colloidal particles and both polymers are able to coagulate negative charged colloidal particles.

A lot of wastewater treatment works prefer the use of both coagulant and coagulant aids in coagulation-flocculation to improve flocs density and strength. The high molecular mass polymers (polymeric flocculants) form bridges between particles that result in the formation of aggregates (Duan and Gregory, 2003).

In treatment where polymers are used as coagulants, the velocity gradient must be in the range of 400 to 1000 s⁻¹ (Binnie et al., 2003). The flocs formed by organic polymers are stronger than those from Fe³⁺ and Al³⁺ salts and can withstand higher shearing stresses (Swartz and Ralo, 2004).

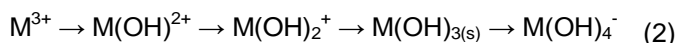
The use of FeCl₃ with coagulant aids is recommended in wastewater treatment to remove turbidity, chemical oxygen demand (COD) and sludge production. This treatment involves physical and chemical decolourisation that includes adsorption, oxidation and chemical precipitation (Aboulhassan et al., 2006).

A study conducted by Aboulhassan et al. (2006) on the effectiveness of FeCl₃ together with polyelectrolyte to remove organic and colouring matters from paint wastewater, revealed that it is effective at pH range of 8 to 9 and the dosing of 650 mg/L. It showed 82% reduction potential of COD and 94% for colour. This investigation focuses on paint wastewater due to its chemical complexity resulting from multiple components, which makes treatment a complex process. Aboulhassan et al. (2006) realized that the poor quality of paint wastewater requires a physicochemical treatment rather than biological treatment due to a high concentration of constituents.

In wastewater treatment, hydrolysis is a main process which involves the reaction of the metal ion (M³⁺) of the metal salt with the hydroxyl ion (OH⁻) to form a hydrolysis

species which are flocs and the hydrogen ions are released into the solution, causing a pH drop (Sincero and Sincero, 2003) (Equation 2).

However, effective hydrolysis only occurs when the coagulants are dispersed throughout the colloidal suspension, thereby causing destabilization during the coagulation-flocculation process (Sincero and Sincero, 2003). There are a series of hydrolytic reactions that occur after the addition of coagulants, namely: simple hydroxo complexes (MOH²⁺), colloidal hydroxometal polymers and the metal hydroxide precipitates. Moore et al. (1978) illustrated hydrolysis of a metal ion with water to form a stable metal trihydroxide and the speciation of hydrolysis species, as expressed in Equation 2. Feng and Nansheng (2000) explained hydrolysis as a time-dependent process that could be defined as hydrolysis-polymerization-precipitation.



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 in the wastewater during treatment. Conventional wastewater treatment works generally use inorganic coagulants, inorganic coagulants together with coagulant aids or synthetic organic coagulants. Coagulant aids are costly hence, this study investigates the turbidity removal efficiency of combined coagulants as an alternative method to coagulants dosed alone or together with coagulant aid. Ferric chloride and coagulant aid are recommended in the treatment of wastewater due to its ability to remove turbidity, COD, colour and sludge production (Amuda et al., 2000).

From Equation 2, we notice that as hydroxide is formed, the pH of the solution decreases and so the value of the pH could be an indicator of the degree of hydrolysis, while turbidity values indicate the efficiency of coagulant(s) to remove colloidal particles from a colloid.

The objective of this study was to determine the relationship between the pH and turbidity in paint wastewater treatment using Fe³⁺ or Al³⁺ salts, combined Fe³⁺ and Al³⁺ salts, combined FeCl₃ and calcium or magnesium hydroxide or FeCl₃-Ca(OH)₂ and FeCl₃-Mg(OH)₂ polymers to achieve optimum turbidity removal. Another objective was to compare turbidity removal when coagulants are dosed prior and during mixing.

MATERIALS AND METHODS

In this study, coagulation-flocculation treatment has been applied to a water-based paint using 0.043 M Fe³⁺ in FeCl₃, 0.043 M Al³⁺ in AlCl₃ and 0.043 M Al³⁺ in Al₂(SO₄)₃, combined 0.043 M Fe³⁺ in FeCl₃ and 0.043 M Ca²⁺ in Ca(OH)₂ or 0.043 M Mg²⁺ in Mg(OH)₂, 0.043 M FeCl₃-Ca(OH)₂ or 0.043 M FeCl₃-Mg(OH)₂ polymers using a jar test, where the pH and turbidity of the supernatant were measured after 1 h settling.

Paint wastewater sample

Solid content of paint is carried out by drying 20 g of water-based paint in triplicate in a crucible placed 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 1:3.22. 80 g mass of solid paint was weighed 0.043 M FeCl₃, 0.043 M AlCl₃ or 0.043 M Al₂(SO₄)₃ respectively during mixing at 250 rpm for 2 min and 100 rpm for 10 min. The samples settled for 1 h and thereafter the pH and turbidity were in order to prepare 80 g solid/1000 g wastewater as the coagulant dosage required is considered to be proportional to total solids (Faust and Hunter, 1983).

Potable water

Potable water used has pH, turbidity and conductivity of 8.12, 0.1 NTU and 192 mS/cm, respectively

Coagulants

Inorganic coagulants of 0.043 M of Fe³⁺ and Al³⁺ ions (a concentration obtained from the literature) are dosed, and during flocculation of the paint, wastewater yielded a wide range of results showing effective flocculation at a solid content of 80 g paint solids in 1000 g of water (Fasemore, 2004). The calculation of the mass of metal salt to obtain 0.043 M of M³⁺ (M³⁺ = Fe or Al) is as follows:

Monoprotic metal salts (MCl₃)

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6H_2O \text{ (} M^* = \text{Fe or Al)} \quad (3)$$

Diprotic metal salts [M₂(SO₄)₃]

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*_2(SO_4)_3 \cdot 18H_2O/2 \text{ (} M^* = \text{Fe or Al)} \quad (4)$$

Table 1 shows monoprotic and diprotic metal salts dosed into the paint wastewater samples.

The metal salt-metal hydroxide [FeCl₃-M(OH)₂] polymers were prepared in the following manner:

a) A preparation of 0.043 M FeCl₃-Ca(OH)₂ polymer was made by dissolving 11.4 g FeCl₃·6H₂O hexahydrated CP and 3.18 g Ca(OH)₂ to 1 L distilled water with 50 rpm slow mixing for 5 min and allowed to react for 6 h

b) A preparation of 0.043 M FeCl₃-Mg(OH)₂ polymer was made by dissolving 11.4 g FeCl₃·6H₂O hexahydrated CP and 2.49 g Mg(OH)₂ to 1 L distilled water with 50 rpm slow mixing for 5 min and allowed to react for 6 h.

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 to 250 rpm. A 169.2 g of water-based paint was dissolved in 1 L distilled water to prepare the paint wastewater sample. 200 ml of the solution was poured into six 500 ml glass beakers.

The pH and turbidity of control sample were 9.32 and > 500 NTU, respectively. Different batches of experiments were conducted by dosing the paint wastewater samples with varying quantities of 0.043 M FeCl₃, 0.043 M AlCl₃ and 0.043 M Al₂(SO₄)₃, combined 0.043 M FeCl₃ and 0.043 M Ca(OH)₂ or 0.043 M Mg(OH)₂, 0.043 M FeCl₃-Ca(OH)₂ or 0.043 M FeCl₃-Mg(OH)₂ polymers 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.

Experiment A

Experiment 1: An experiment was conducted 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 measured. A similar experiment was conducted with combined dosing of 5, 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ with 5, 10, 15, 20, 25 and 30 ml 0.043 M AlCl₃ before and after mixing at 250 rpm for 2 min and 100 rpm for 10 min, settled for 1 h and thereafter the pH and turbidity were measured. A second similar batch of experiments was conducted with combined dosing of 5, 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ with 5, 10, 15, 20, 25 and 30 ml 0.043 M Al₂(SO₄)₃ before and after mixing at 250 rpm for 2 min and 100 rpm for 10 min, settled for 1 h and thereafter the pH and turbidity were measured.

Experiment 2: A similar first batch of experiments was conducted by pouring 200 ml sample in five 500 ml glass beakers. The samples were dosed with combined 20 ml of 0.043 M FeCl₃ in each beaker and 20, 30, 40, 50 and 60 ml of 0.043 M AlCl₃ or 0.043 M Al₂(SO₄)₃ during mixing at 250 rpm for 2 min and 100 rpm for 10 min, settled for 1 h and thereafter the pH and turbidity were measured. A second batch of experiments was conducted where the samples were dosed with combined 20 ml of 0.043 M AlCl₃ or 0.043 M Al₂(SO₄)₃ and 10, 20, 30, 40, 50 and 60 ml of 0.043 M FeCl₃ at 250 rpm for 2 min and 100 rpm for 10 min, settled for 1 h and thereafter the pH and turbidity were measured.

A third batch of experiments was conducted where the samples were dosed with either combined increasing (10 to 60 ml) of 0.043 M FeCl₃ and decreasing (60 to 10 ml) of 0.043 M AlCl₃ or 0.043 M Al₂(SO₄)₃ or combined increasing (10 to 60 ml) of 0.043 M AlCl₃ or 0.043 M Al₂(SO₄)₃ and decreasing (60 to 10 ml) of 0.043 M FeCl₃ during rapid mixing at 250 rpm for 2 min and 100 rpm for 10 min, settled for 1 h and thereafter the pH and turbidity were measured.

Experiment B

Experiment 3: A similar batch of experiments was conducted 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 0.043 M FeCl₃ during mixing at 250 rpm for 2 min and 100 rpm for 10 min. The samples were allowed to settle for 1 h before the pH and turbidity were measured.

A similar second batch of experiments was conducted with combined dosing of 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ and 10, 15, 20, 25 and 30 ml of 0.043 M Ca(OH)₂ during mixing at 250 rpm for 2 min and 100 rpm for 10 min. The samples settled for 1 h before the pH and turbidity were measured.

The third batch of experiments was conducted with combined dosing of 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ and 10, 15, 20, 25 and 30 ml of 0.043 M Mg(OH)₂ during mixing at 250 rpm for 2 min and 100 rpm for 10 min. The samples were settled for 1 h before the pH and turbidity were measured.

A fourth batch of experiments was conducted by dosing the samples with 0.043 M FeCl₃-Ca(OH)₂ polymers and 0.043 M FeCl₃-Mg(OH)₂ polymers, respectively during mixing at 250 rpm for 2 min and 100 rpm for 10 min. The samples settled for 1 h before the pH and turbidity were measured.

Performance evaluation

The pH was used as a determinant to assess the rate of hydrolysis and hydrolytic potential of coagulants at different mixing duration,

Table 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 ₂ O	11.4	0.0430	0.043
AlCl ₃ .6H ₂ O	10.1	0.0430	0.043
Al ₂ (SO ₄) ₃ .18H ₂ O	13.6	0.0215	0.043
Ca(OH) ₂	3.18	0.0430	0.043
Mg(OH) ₂	2.49	0.0430	0.043

whereas turbidity was to determine the removal of colloidal particles from the samples.

pH measurement

A MetterToledo Seven Multimetric (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.

Turbidity measurement

Hanna Microprocessor Turbidimeter (made in Japan) was used to determine turbidity or the suspended particles in the supernatant using NTU as a unit of measure.

RESULTS

pH and turbidity of the samples with increasing dosages of 0.043 M Fe³⁺ in FeCl₃, 0.043 M Al³⁺ in Al₂(SO₄)₃ or AlCl₃ salts

Figure 1 shows that the pH values in the samples which have been dosed with 10 ml of 0.043 M FeCl₃, 0.043 M Al₂(SO₄)₃ and AlCl₃; 20 ml 0.043 M AlCl₃ are in an alkaline state. These pH values have been reduced from 9.32 to 7.73, 7.42, 8.23 and 7.11, respectively.

The samples are opaque, which also indicates that deflocculation took place. This occurs when there is no separation between the particles and the solvent (distilled water) during coagulation and also that the flocs which were formed were not too large to remove the colloidal particles.

The pH values in the samples with combined 10 ml 0.043 M (FeCl₃) and 10 ml 0.043 M [Al₂(SO₄)₃] or 0.043 M (AlCl₃) dosages added before stirring were reduced to 5.68 and 6.43, respectively. The dosages of 20 to 60 ml of 0.043 M (FeCl₃), 0.043 M [Al₂(SO₄)₃] and 0.043 M (AlCl₃) yielded pH in a range of 5.64 to 2.9, 6.61 to 2.0 and 7.11 to 3.7, respectively.

The pH range of the combined dosages (20 to 60 ml) of the same coagulants before mixing was in the range of 6.43 to 3.51, whereas the pH of the samples with dosing, during mixing, was in the range of 6.41 to 3.33.

According to Figure 2, turbidity in the samples with 10 ml of 0.043 M FeCl₃ dosage, 10 ml of 0.043 M Al₂(SO₄)₃ and 10 to 20 ml of 0.043 M AlCl₃ is over-range. This is

also applicable to all those samples with only 10 ml added before and during mixing. The pH in these samples is above 7.0, the samples are alkaline and opaque.

This shows that deflocculation yielded poor turbidity removal because the flocs which have been formed were too small and not dense enough to remove the colloidal particles.

The turbidity in the samples with 20 to 60 ml of 0.043 M FeCl₃, 20 to 60 ml of 0.043 M Al₂(SO₄)₃ and 30 to 60 ml of 0.043 M AlCl₃ is reduced from a value above 500 NTU to a range of 115 to 62 NTU, 64 to 50 NTU and 105 to 49 NTU, respectively. Figure 2 shows that all the samples with low turbidity correspond to the samples with pH values below 7.0 in Figure 1.

All the samples with combined dosage of 0.043 M FeCl₃ and 0.043 M Al₂(SO₄)₃ added before and during mixing have low turbidity in a range of 110 to 71 NTU and 105 to 66 NTU, respectively. The pH in these samples is in a range between 5.73 to 3.51 and 5.90 to 3.63, respectively.

According to Figure 2, all the samples with combined dosage of 0.043 M FeCl₃ and 0.043 M Al₂(SO₄)₃ were below 7.0 and showed low turbidity.

pH and turbidity of the samples with constant or increasing 0.043 M Fe³⁺ in FeCl₃, and increasing or constant 0.043 M Al³⁺ in Al₂(SO₄)₃ or AlCl₃ salts, and increasing 0.043 M Fe³⁺ in FeCl₃ with decreasing 0.043 M Al³⁺ in Al₂(SO₄)₃ or AlCl₃ salts

Figure 3 shows the pH of the combined dosages with constant 20 ml of 0.043 M FeCl₃; 10, 15, 20, 25 and 30 ml of 0.043 M Al₂(SO₄)₃ decreased in a range of 4.49 to 3.51, whereas the pH of the combined dosages with constant 20 ml of 0.043 M FeCl₃; 10, 15, 20, 25 and 30 ml of 0.043 M AlCl₃ decreased in a pH range of 4.54 to 4.29.

The difference between the former combination and the latter is that Al₂(SO₄)₃ was replaced by AlCl₃, this indicates that 0.043 M Al₂(SO₄)₃ yielded a better hydrolyzing power than 0.043 M AlCl₃. The combined samples with 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ and constant 20 ml of 0.043 M Al₂(SO₄)₃ decreased in a range of 4.60 to 3.51, whereas the pH of the combined

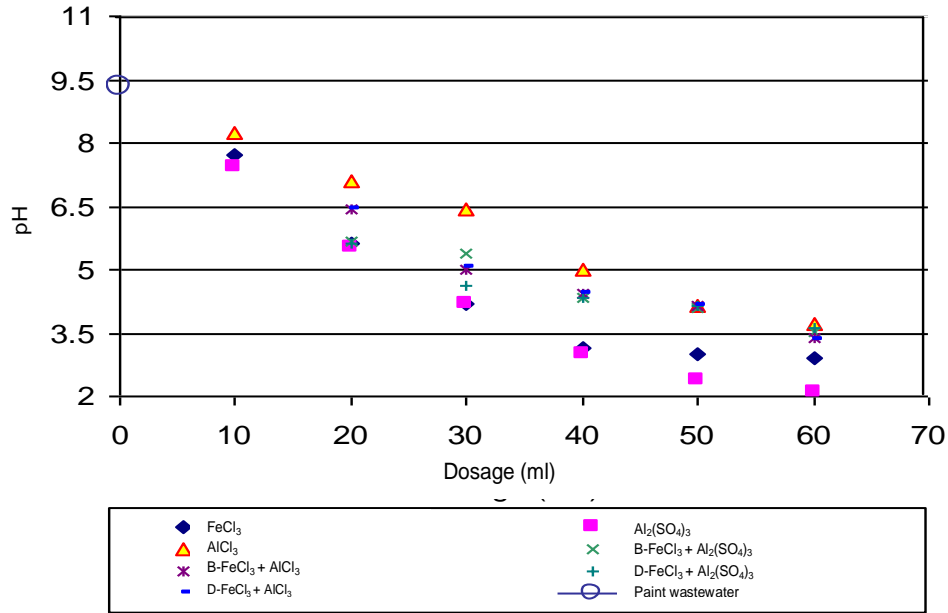


Figure 1. pH versus dosage of samples dosed with increasing Fe³⁺ and Al³⁺ salt in separate experiments. B = Coagulants were added before stirring; D = coagulants were added during stirring. \diamond = FeCl₃; \square = Al₂(SO₄)₃; Δ = AlCl₃; Υ = B-FeCl₃+Al₂(SO₄)₃; Ψ = B-FeCl₃+AlCl₃; + = D-FeCl₃+Al₂(SO₄)₃; - = D-FeCl₃+AlCl₃.

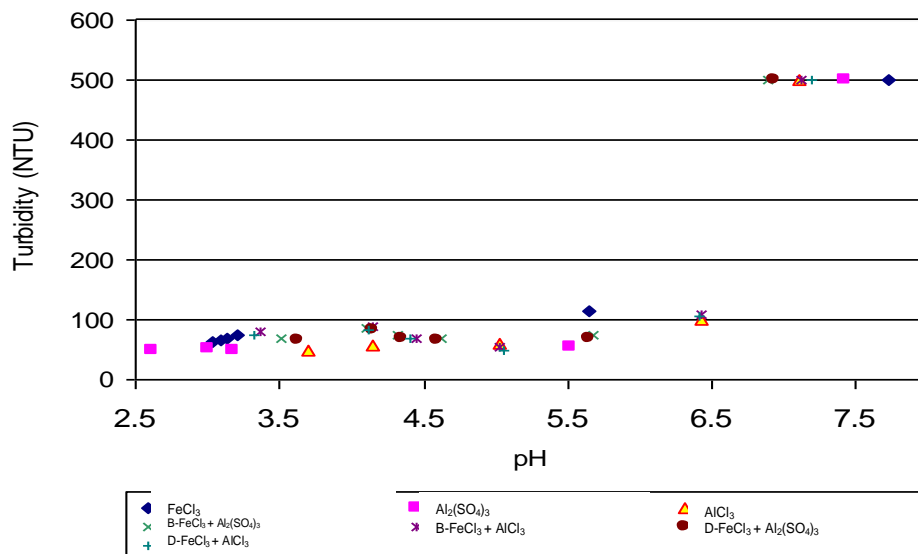


Figure 2. pH versus turbidity of samples dosed with FeCl₃ and Al₂(SO₄)₃ or AlCl₃ salts added before and during stirring. B = coagulants were added before stirring, D = coagulants were added during stirring. \diamond = FeCl₃,+Al₂(SO₄)₃; Δ = FeCl₃+AlCl₃; Υ = B-FeCl₃+Al₂(SO₄)₃; Ψ = B-FeCl₃+AlCl₃; $\sqrt{\quad}$ = D-FeCl₃+Al₂(SO₄)₃; + = D-FeCl₃+AlCl₃.

dosages with constant 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ and 20 ml of 0.043 M AlCl₃ decreased in a range of 4.70 to 3.41.

The pH decreasing trend in combined dosage with 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ and 30, 25, 20, 15

and 10 ml of 0.043 M Al₂(SO₄)₃ is in a range of 4.56 to 3.43, whereas the pH trend in the combined samples with 10, 15, 20, 26 and 30 ml of 0.043 M FeCl₃ and 30, 25, 20, 15 and 10 ml of 0.043 M AlCl₃ is in a range of 4.70 to 3.19.

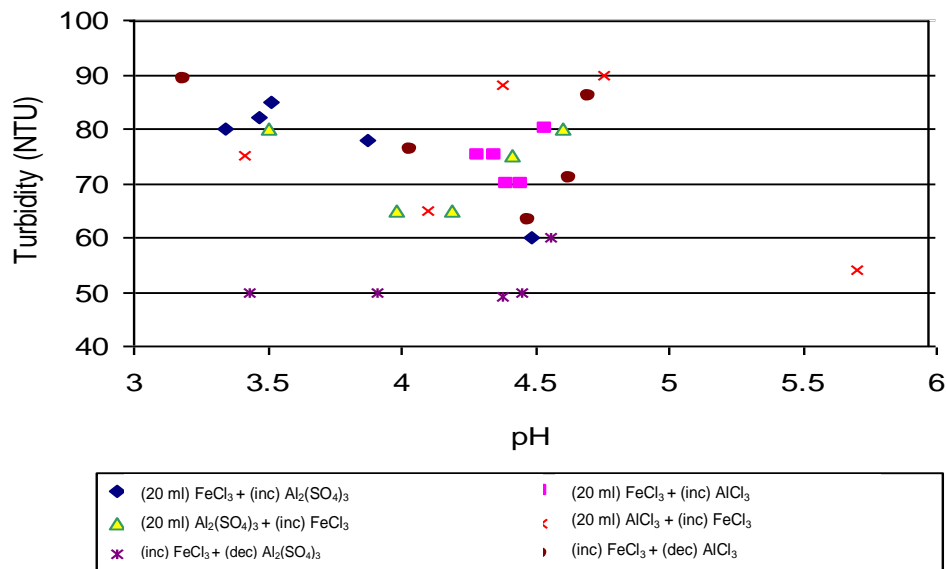


Figure 3. pH versus turbidity of the samples dosed with either constant (20 ml) FeCl₃ or increasing Al₂(SO₄)₃ or AlCl₃ salts or constant Al₂(SO₄)₃ or AlCl₃ and increasing FeCl₃, and in the other samples FeCl₃, is added in increasing order whereas Al₂(SO₄)₃ or AlCl₃ salt in decreasing order and vice versa. 20 ml = constant dosage; inc = increasing order; dec = decreasing order. \diamond = (20 ml) FeCl₃ + (inc) Al₂(SO₄)₃; \square = (20 ml) FeCl₃ + (inc) AlCl₃; Δ = (20 ml) Al₂(SO₄)₃ + (inc) FeCl₃ and X = (20 ml) AlCl₃ + (inc) FeCl₃; ∇ = (inc) FeCl₃ + (dec) Al₂(SO₄)₃, ω = (inc) FeCl₃ + (dec) AlCl₃.

pH and turbidity on the samples with 0.043 M Fe³⁺ in FeCl₃ and 0.043 M Ca²⁺ and Mg²⁺ in Ca(OH)₂ and Mg(OH)₂ metal hydroxide, and FeCl₃-Ca(OH)₂ or FeCl₃-Mg(OH)₂ polymers

The results in Figure 4 show that the pH in samples which have been dosed with 0.043 M FeCl₃ only decreases (with increasing dosage) in a pH range of 3.20 to 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 samples dosed with 40 to 60 ml show turbidity in a range of 65 to 70 NTU. The pH in the samples which had been dosed with combined 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ and 10, 15, 20, 25 and 30 ml of 0.043 M Ca(OH)₂ 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, which is a different changing trend compared to that shown by the samples dosed with 0.043 M FeCl₃ only, as well as the samples illustrated in Figure 1. This could be because the hydroxyl ions released by the metal hydroxide (MOH)₂ 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 combined 10, 15, 20, 25 and 30 ml of 0.043 M FeCl₃ together with 10, 15, 20, 25 and 30 ml of 0.043 M Mg(OH)₂ 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

combined dosage of 0.043 M FeCl₃ and 0.043 M Ca(OH)₂ or 0.043 M Mg(OH)₂ corresponds to the pH range of 5.80 to 5.86 which is greater than 500 NTU. The pH and the turbidity in the rest of the samples dosed with 40 to 60 ml were in a range of 5.88 to 6.48 and 97 to 136 NTU, respectively.

The pH in the samples which had been dosed with 0.043 M FeCl₃-Ca(OH)₂ polymers decreased to 6.71, 6.21, 6.04, 5.82 and 5.67, and the pH in the samples with 0.043 M FeCl₃-Mg(OH)₂ polymers decreased to a range of 6.58 to 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 0.043 M FeCl₃ only. This means that the pH decreases with increasing dosages, thereby yielding turbidity in a range of 90 to 120 NTU. Figure 5 represents scanning electron microscopy (SEM) diagrams of the ferric chloride and magnesium or calcium polymers. FeCl₃-Mg(OH)₂ polymer consists of interconnected longitudinal structures lying on top of one another, whereas FeCl₃-Ca(OH)₂ polymer consists of non-spherical interconnected structures also lying on top of one another.

DISCUSSION

Part 1

This part of the study explains the pH and turbidity

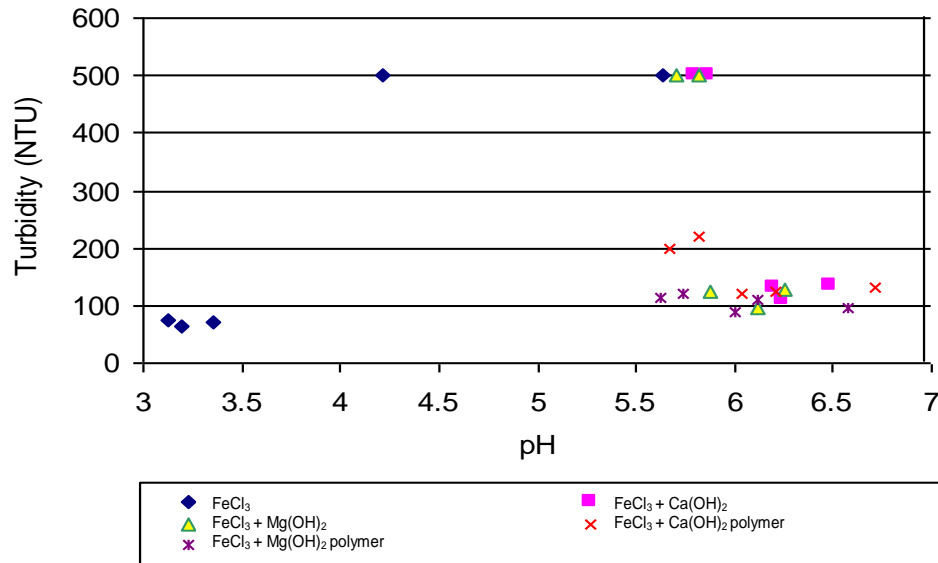


Figure 4. pH versus turbidity of the samples dosed with increasing FeCl₃ only, FeCl₃ and Mg(OH)₂ or Ca(OH)₂, FeCl₃+Ca(OH)₂ or Mg(OH)₂ polymers. \diamond = FeCl₃; \square = FeCl₃ + Ca(OH)₂; Δ = FeCl₃ +Mg; X = FeCl₃ + Ca(OH)₂ polymer; Υ = FeCl₃ + Mg(OH)₂ polymer.

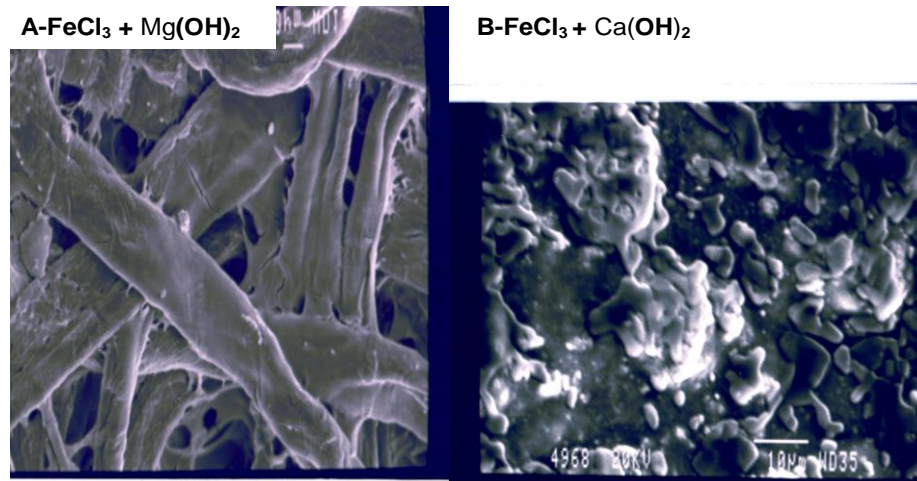


Figure 5. SEM diagrams of 0.043 M FeCl₃-Ca(OH)₂ and 0.043 M FeCl₃-Mg(OH)₂ polymers.

changing trend with increasing dosages of 0.043 M FeCl₃, 0.043 M Al₂(SO₄)₃, 0.043 M AlCl₃, respectively when added combined before or during mixing. The pH level indicated the rate of hydrolysis, as shown in Equation 2, whereas turbidity indicated the ability of each metal (Fe³⁺ and Al³⁺) ions in the metal salts (FeCl₃, Al₂(SO₄)₃ and AlCl₃) to remove colloidal particles from the paint wastewater.

The comparison between the pH of the treated wastewater with Fe³⁺ and Al³⁺ established the respective hydrolyzing power in each metal salt. Figure 1 shows the decreasing pH trend of 7.73 to 2.90, 7.42 to 2.0 and 8.23

to 3.70, respectively as shown by the samples which have been dosed with 0.043 M FeCl₃, 0.043 M Al₂(SO₄)₃ and 0.043 M AlCl₃. The observations indicate that 0.043 M Al₂(SO₄)₃ yielded a higher hydrolyzing power than 0.043 M FeCl₃ and AlCl₃.

A low pH indicates that 0.043 M Al₂(SO₄)₃ have the ability to attract a large number of hydroxyl ions from the cleavage of water molecules with the release of hydrogen ions, which in turn caused a decrease in pH of the colloid. A low pH with 0.043 M Al₂(SO₄)₃ from 9.32 to a range of 7.42 to 2.0 indicates that the metal ions had a relatively higher hydrolyzing power.

According to Figure 1, the samples which have been dosed with 10 ml 0.043 M FeCl_3 , 0.043 M $\text{Al}_2(\text{SO}_4)_3$, 0.043 M AlCl_3 and 20 ml 0.043 M AlCl_3 are alkaline, with a pH above 7.0. These samples are opaque which showed some tiny unflocculated colloidal particles throughout the solution.

According to Equation 2, the degree at which the hydrogen ions (H^+) were released into the solution to achieve high rate of hydrolysis is low, hence there was a low concentration of hydroxyl ions (OH^-) to react with metal ions and form flocs (hydrolysis species). This also reveals that the pH of the solution is an indicator of the rate of hydrolysis in Equation 2.

The opacity shown by these alkaline solutions indicates that the flocs which have been formed during hydrolysis were not large and dense enough to remove the colloidal particles from the solution. In other words, the reaction rate of Equation 2 was slow and insufficient to achieve optimum adsorption. 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 there was no further reactions such as crystallization and aggregation to develop larger flocs.

The amount or concentration of coagulants added to paint wastewater during treatment was not sufficient to exceed the solubility of their (Fe^{3+} and Al^{3+} salts) metal hydroxides to form precipitates (Moore et al., 1978). It was observed that the pH of the samples that had been dosed with 0.043 M Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ in Figure 1 showed a decreasing trend that is lower than the pH trend in the corresponding samples which were dosed with 0.043 M FeCl_3 and 0.043 M AlCl_3 . This shows that 0.043 $\text{Al}_2(\text{SO}_4)_3$ has a higher hydrolyzing potential than 0.043 M FeCl_3 and 0.043 M AlCl_3 .

A higher hydrolyzing power is exhibited by increasing acidity in a solution, which indicates more release hydrogen ions (H^+) from water molecules into the solution when the hydroxyl ions (OH^-) to form a hydrolysis species as represented by Equation 2.

The higher pH changing trend with 0.043 M Al^{3+} in AlCl_3 in paint wastewater in Figure 1 show that AlCl_3 has a lower hydrolyzing power than FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$. 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 combined dosages of 0.043 M FeCl_3 , 0.043 M $\text{Al}_2(\text{SO}_4)_3$ and 0.043 M AlCl_3 before mixing is identical to the pH of their corresponding samples dosed during mixing. This indicates that dosing before and during mixing is insignificant.

Figure 2 shows the turbidity of the same samples which were used to plot pH-dosage in Figure 1. This study considers turbidity below 100 NTU as the best removal efficiency, 100 to 120 NTU as moderate removal efficiency and above 120 NTU as poor removal efficiency. This specification is conservative as it is below

150 NTU, which is a normal specification stipulated by different water treatment works. This was used to restrict the values as the experiments were conducted in a small laboratory.

According to Figure 2, the samples with 10 ml of 0.043 M FeCl_3 , 0.043 M $\text{Al}_2(\text{SO}_4)_3$ and 0.043 M AlCl_3 dosage, have pH above 6.5 and yielded high turbidity, above 500 NTU. This indicates that 10 ml of 0.043 M FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$ and AlCl_3 cannot flocculate 16 g of colloidal particles in paint wastewater.

The low turbidity in the samples with combined dosage of 20 to 60 ml 0.043 M FeCl_3 , 0.043 M $\text{Al}_2(\text{SO}_4)_3$ and 0.043 M AlCl_3 in Figure 2 added before and during mixing indicates that dosing prior or during mixing is insignificant in turbidity removal.

A low turbidity between the samples with 20 to 60 ml dosage of Fe^{3+} or Al^{3+} ions in their metal salts added separately or combined in a solution in Figure 2 confirms that equal number of moles of metal ions (Fe^{3+} or Al^{3+}) in a solution react identically to the same concentration of the colloidal particles.

The changing trend between the pH and turbidity in Figures 1 and 2 indicate that there is a correlation between the two parameters. The results also show that combined dosages of a monoprotic salt (FeCl_3) and a diprotic salt [$\text{Al}_2(\text{SO}_4)_3$] yield a better hydrolyzing power and better turbidity removal compared to their corresponding combined monoprotic salts (FeCl_3 and AlCl_3) dosages.

It is postulated here that there is a double dissociation which occurs with diprotic H_2SO_4 of a metal salt [$\text{M}_2(\text{SO}_4)_3$] which behaves as a buffer during hydrolysis, thus enhances further hydrolysis than the hydrolysis in monoprotic metal salts (FeCl_3 and AlCl_3); which involves a single stage dissociation of HCl reaction (Casas et al., 2000).

We suggest that turbidity removal with diprotic metal salts occurs when the hydrolytic species which have been formed during hydrolysis flocculate colloidal particles and precipitate together and the residual particles are flocculated onto the particles during the second dissociation reaction (Chang and Yu, 2004).

The results also show that the combined dosage with increasing of 0.043 M FeCl_3 and decreasing 0.043 M $\text{Al}_2(\text{SO}_4)_3$ or AlCl_3 , or combined dosage with decreasing 0.043 M FeCl_3 and increasing (0.043 M $\text{Al}_2(\text{SO}_4)_3$ or AlCl_3), yield the best turbidity removal in a range of 49 to 90 NTU.

Figure 3 shows that the pH values in all the samples are also less than 6.0. The observations from the samples with combined dosages, where one metal salt is increased and the other is decreased indicate that volume ratios of Fe^{3+} and Al^{3+} ions exhibit identical rate of hydrolysis in paint wastewater.

This also shows that volume ratio in either metal ions (M^{3+}) is insignificant, that is, 3.0 and 0.33 Al/Fe volume ratios exhibit identical reactivity in paint wastewater.

Part 2

The experiments in Part 2 were conducted to determine the changing behavior of the pH with turbidity when the paint wastewater was dosed with 0.043 M Ca(OH)_2 and 0.043 M Mg(OH)_2 respectively as observed in Figures 1 and 2. Since the paint wastewater was alkaline, pH of 9.32, the addition of these metal hydroxides increased the concentration of OH^- ions in the samples, thus, contributing to further hydrolysis of the Fe^{3+} ions. According to Metcalf and Eddy (2003), the advantage of dosing Mg(OH)_2 in the solution of this pH is that, it has the ability to develop 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 and precipitates are not complete until the pH reaches 11 (Metcalf and Eddy, 2003). The low solubility of Mg(OH)_2 plays a pivotal role when it is overdosed as it rises to a maximum pH of 9.0.

Unlike Figures 2 and 3, the results in Figure 4 showed that the changing pH does not correlate with the turbidity removal. The turbidity values do not show a consistent change as these fluctuated with decreasing pH and increasing dosages. This behavior is shown by the pH and turbidity changing trend in the samples dosed with combined 0.043 M FeCl_3 and 0.043 M Ca(OH)_2 or 0.043 M Mg(OH)_2 compared to the pH and turbidity in their corresponding samples dosed with the same quantity of 0.043 M $\text{FeCl}_3\text{-Ca(OH)}_2$ or 0.043 M $\text{FeCl}_3\text{-Mg(OH)}_2$ polymers.

The pH value in the samples with 0.043 M $\text{FeCl}_3\text{-Ca(OH)}_2$ polymer is slightly lower than the pH with 0.043 M $\text{FeCl}_3\text{-Mg(OH)}_2$ polymers, whereas the turbidity in the former is higher than the turbidity in the latter. The turbidity values also fluctuate with decreasing pH during hydrolysis and also show that 0.043 M $\text{FeCl}_3\text{-Mg(OH)}_2$ polymers have ability to form larger and denser flocs to achieve maximum mass transfer of the colloidal particles during flocculation.

Under experimental conditions, the reaction of 0.043 M FeCl_3 with 0.043 M Ca(OH)_2 before dosing form polymers which yielded the best turbidity removal as shown by Figure 5. Improved turbidity removal from paint wastewater with 0.043 M $\text{FeCl}_3\text{-Ca(OH)}_2$ or 0.043 M $\text{FeCl}_3\text{-Mg(OH)}_2$ polymers compared to the turbidity obtained when 0.043 M FeCl_3 and 0.043 M Ca(OH)_2 or 0.043 M Mg(OH)_2 were added as separate reagents shows that the polymeric compounds (0.043 M FeCl_3 reacts with 0.043 M Ca(OH)_2 or 0.043 M Mg(OH)_2 form a filter cake. This filter-cake was able to remove a large quantity of colloidal particles from the wastewater.

The alkalinity of these polymers shows that there is additional discharge of OH^- into the colloidal suspension, which reacted with residual Fe^{3+} ions to form additional hydrolysis species. These hydrolysis species condense and form the filter-cake which results in the large mass

transfer of the colloidal particles. Based on the turbidity removal potential of the samples which have been dosed with $\text{FeCl}_3\text{-Ca(OH)}_2$ or $\text{FeCl}_3\text{-Mg(OH)}_2$ polymers, which shows that the two compounds reacted identically, therefore we conclude that these reactions which lead to turbidity removal from the paint wastewater are of a physical nature.

A further postulation is that the turbidity removal from the samples which have been dosed with polymers occurs by filtration process through the filter-cake. According to Equation 3, the hydrolysis species $[\text{Fe(OH)}_3]$ is formed by Fe^{3+} ion and OH^- ion the metal hydroxide, M(OH)_2 . This reaction differs from Equation 1, whereby the Fe ions reacts with OH^- from the water molecules to form Fe(OH)_3 and the metal hydroxides [Ca(OH)_2 or Mg(OH)_2] dissolve in the solution. This indicates that the metal hydroxides added to paint wastewater in Equation 1 adjust the pH of the solution whereas the metal hydroxides in Equation 3 form polymers with FeCl_3 . Part of our findings indicate that $\text{FeCl}_3\text{-Ca(OH)}_2$ and $\text{FeCl}_3\text{-Mg(OH)}_2$ polymers yield identical turbidity removal.

Based on the environmental impact assessment, it is advisable to replace Ca(OH)_2 with Mg(OH)_2 ; because the former poses operational and health hazard and the latter is easy to handle and dose. Another disadvantage with Ca(OH)_2 is that, it is dosed in a lime bunker which incurs costs in maintenance whereas Mg(OH)_2 is dosed directly into the wastewater. The comparison between the pH and turbidity in Figures 1, 2 and 3 show 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 4.

Conclusion

The results obtained in this study indicate that there was a correlation between the pH and turbidity in paint wastewater when metal salts (Fe^{3+} or Al^{3+} salt) are added separately or in combination. The Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ showed a higher hydrolyzing power in paint wastewater than Fe^{3+} in FeCl_3 and Al^{3+} in AlCl_3 .

Effective turbidity removal occurred at pH values below 6.0 in paint wastewater containing 16 g of solid paint when it has been dosed with 0.043 M Fe^{3+} (FeCl_3), 0.043 M Al^{3+} [$\text{Al}_2(\text{SO}_4)_3$] and 0.043 M Al^{3+} (AlCl_3). The dosing sequence and dosing before or during mixing do not play a pivotal role in turbidity removal in paint wastewater. Equal moles of Fe^{3+} in FeCl_3 and Al^{3+} in AlCl_3 or $\text{Al}_2(\text{SO}_4)_3$ flocculate the same mass of solid paint in a solution; this indicates that adsorption in that coagulation flocculation process is physical.

The samples which have been dosed with Fe^{3+} salt together with Ca(OH)_2 and Mg(OH)_2 show that the pH is not a determinant of turbidity removal efficiency. The best turbidity removal was obtained from combined Fe^{3+} salt and $\text{FeCl}_3\text{-Ca(OH)}_2$ or $\text{FeCl}_3\text{-Mg(OH)}_2$ at pH values below

3.5. In addition, the pH and turbidity in paint wastewater with FeCl_3 and $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$, $\text{FeCl}_3\text{-Ca}(\text{OH})_2$ or $\text{FeCl}_3\text{-Mg}(\text{OH})_2$ polymers do not correlate, this showed that the pH does correlate with turbidity during the treatment of a more alkaline paint wastewater.

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