Removal of TSS, turbidity, colour, Zn(II) and Cu(II) from synthetic wastewater using FCC and FSC, generated from Groundwater Treatment Plant Sludge (GWTPS)

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Abstract

Groundwater Treatment Plant Sludge (GWTPS) which was collected from Chicha, Kelantan, Malaysia was found to contain 30% of Fe_2O_3. Ferric Chloride Coagulant (FCC) and Ferric Sulfate Coagulant (FSC) were generated through digestion of GWTPS with HCl and H_2SO_4, respectively. The effect of various dosages of GWTPS and volume of distilled water to generate the highest concentration of FCC and FSC was studied. Coagulation and flocculation study was conducted to observe the effectiveness of FCC and FSC in removing TSS, turbidity, colour, Zn(II) and Cu(II) from synthetic wastewater. Optimum production of FCC can be achieved at ratio of 10g (GWTPS): 20 mL (HCl): 100 mL (distilled water), while for FSC the optimum production ratio was obtained at 7g (GWTPS): 4 mL (H_2SO_4): 100 mL (distilled water). Approximately 2.9% (29126 mg/L) of FCC and 1.8% (18548 mg/L) of FSC were generated from GWTPS. It was observed that FCC was effective as a coagulant as almost 100%, 99% and 98% of TSS, turbidity and colour was removed from synthetic wastewater, respectively, when 23 mg/L (0.4 mL) dosage of FCC was used. As for FSC, approximately 100%, 98% and 97% of TSS, turbidity and colour was removed from synthetic wastewater, respectively, with only 22 mg/L (0.6 mL) dosage of FSC used. The optimum pH for FCC and FSC in removing Zn(II) and Cu(II) from synthetic wastewater was found to be pH 7 and pH 8, respectively. Approximately 23 mg/L (0.4 mL) dosage of FCC and 22 mg/L (0.6 mL) dosage of FSC was needed to give remarkably high removal of Zn(II) and Cu(II).
Keywords: groundwater sludge, digestion, recycled coagulant, Zn(II), Cu(II).

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1 Introduction

Approximately 5 tonnes of sludge is generated from Chicha Groundwater Treatment Plant daily that requires offsite disposal. The produced sludge, GWTPS was found to contain Fe_2O_3, CaO, SiO_2, Al_2O_3 and other constituents. GWTPS, due to its content of potential adsorptive behaviour and easily available nature coupled with the fact that it is free of charge can be considered as potential inexpensive adsorbent. Due to their low costs, the use of natural waste product as sorbent may eliminate or reduce the need of expensive adsorbent. The valuable metals in the GWTPS such as iron (Fe), can be generated into recycled iron coagulant in treating various pollutants in water or wastewater. Numerous studies have been conducted by other researchers in recycling and reusing sludge as either adsorbent or coagulant [1, 2]. In line with the government challenge and economic drive towards waste avoidance and beneficial reuse of waste, an effort should be made in studying the potential use of the GWTPS. Therefore, rather than entombing the GWTPS to the receiving environment, it is better to recycle the sludge into another valuable added product. Therefore, an alternative solution is studied by reusing the GWTPS as generated coagulants, FCC and FSC in removing Total Suspended Solids (TSS), turbidity, colour, Zn(II) and Cu(II) from synthetic wastewater.

Coagulation and flocculation process is widely employed for TSS [3], colour [4] and turbidity [5] removal from industrial wastewater as it is efficient and simple to operate. Therefore, the idea of recovering the iron content in GWTPS to produce Ferric Chloride Coagulant (FCC) and Ferric Sulfate Coagulant (FSC) may be favourable for the treatment of wastewater. Similar studies have been made by numerous researchers in reusing sludge generated from water treatment plant for the use of dye [6], heavy metal [7] and turbidity [8] removal from industrial wastewater.

2 Methodology

2.1 Preparation of GWTPS

Approximately 1 kg of GWTPS was dried at 103°C for 24 hours in an oven and was then ground into 0.5 mm size using a grinder according to Standard Method [3]. The prepared GWTPS was stored in a closed container for use.

2.2 Preparation of generated coagulants, FCC and FSC from GWTPS

Approximately 5g of GWTPS was weighed, mixed and well stirred with 100 mL of distilled water in six 140 mL beakers. The samples were then placed on the hotplate. Various volumes of HCl, from 5 mL to 50 mL were added into each beaker and were digested at 105°C for 4 hr [10, 11]. At the end of the digestion period, the samples were allowed to cool down at room temperature, 28°C±. The samples were then filtered with 0.45 μm Whatman filter paper. Filtered samples were analyzed for final total Fe and Fe^{2+} concentration using AAS and spectrophotometer. Fe^{3+} concentration was obtained by subtracting Fe^{2+} from total Fe concentration. The same procedure was applied for different dosages of GWTPS, 7g, 10g and 15g. The generated coagulant was termed as recycled ferric chloride (FCC) in this study.

Similar experimental procedure was conducted for preparation of generated coagulant, ferric sulfate coagulant (FSC) with variation of H_2SO_4 from 1 mL to 6 mL and variation of dosage of GWTPS (5 g, 7 g, 10 g and 15 g).

2.3 Mass production of FCC and FSC

Based on procedure in Sections 2.2, the optimum dosage of GWTPS and volume of acid to generate FCC was determined. Mass production of FCC was conducted by digesting 70 g of GWTPS that had been thoroughly mixed with 700 mL of distilled water with 140 mL of HCl on a hotplate in a 1 L beaker. The mixture was allowed to evaporate to the lowest volume possible for 4 hr digested at 105°C. After cooling, the sample was then filtered with 45µm Whatman filter paper. The filtered sample was then analyzed for total Fe, Fe^{2+} and Fe^{3+} concentration.

Similar procedure was repeated for the mass production of FSC using the optimum dosage of GWTPS and sulfuric acid obtained from section 2.2. All generated coagulants were stored in a glass container for use in chemical precipitation study.

2.4 Preparation of synthetic wastewater for chemical precipitation study

In this study, the effectiveness of FCC and FSC was evaluated by conducting jar tests to remove turbidity, colour, Zn(II) and Cu(II) from synthetic wastewater. A mixture of river water (Menglembu River, Perak, Malaysia) with $ZnCl_2$ and $CuCl_2$ used as synthetic wastewater. Tables 1 and 2 show the characteristics of synthetic wastewater.

Table 1: Characteristic of synthetic wastewater.

Characteristics	Concentration
TSS	62.33 mg/L
Turbidity	54.27 NTU
Colour	416.67 PtCo

Table 2: Zn(II) and Cu(II) mixture concentration for sample A, B and C.

Water sample	Metal concentration (mg/L)
Sample A	10 mg/L of Zn(II) and 10 mg/L of Cu(II)
Sample B	25 mg/L of Zn(II) and 25 mg/L of Cu(II)
Sample C	50 mg/L of Zn(II) and 50 mg/L of Cu(II)

2.5 Chemical precipitation study using FCC and FSC

2.5.1 Effect of dosage of FCC and FSC on removal of TSS, turbidity and colour

The initial pH, TSS, turbidity and colour concentration of the synthetic wastewater was first measured prior to the experiment. A set of 12 beakers were each filled with 500 mL of synthetic wastewater. The dosage of FCC in the beakers was varied from 0 to 116 mg/L (0 to 2 mL). Samples were then rapid mixed at 120 rpm for approximately 2 min and slow mixed at 30 rpm for 20 min. The samples were then allowed to settle for 30 min. The supernatant were measured for final pH, TSS, turbidity and colour. All tests were conducted in triplicates. The same procedure was repeated for FSC with variation of dosage of coagulant from 0 to 291 mg/L (0 to 8 mL).

2.5.2 Effect of initial pH on Zn(II) and Cu(II) mixture removal at fixed dosage of FCC and FSC

The effect of pH needs in removing Zn(II) and Cu(II) from the synthetic wastewater was conducted. 500 mL of sample A (10 mg/L of Zn(II) and 10 mg/L of Cu(II)) was placed into 12 beakers. The pH for each sample was varied from pH 1 to pH 12 using 0.5N HCl and 0.5N NaOH. Constant dosage of FCC, 23.29 mg/L (0.4 mL) was dosed into each beaker. All samples were rapid mixed at 120 rpm for approximately 2 min and slow mixed at 30 rpm for 20 min. The samples were allowed to settle for 30 min. The supernatant of the samples were measured for final pH and residual equilibrium Zn(II) and Cu(II) concentrations. The experiment was repeated for FSC with the dosage fixed at 22.46 mg/L (0.9 mL).

2.5.3 Effect of dosage of FCC and FSC on Zn(II) and Cu(II) mixture removal at optimum pH

Twelve beakers were filled with 500 mL of sample A (refer Section 2.4) and pH for each sample was adjusted to the optimum pH obtained from Section 2.5.2. Various dosages of FCC from 0 to 116 mg/L (0 to 2 mL) were added into each beaker. The samples were then rapid mixed at 120 rpm for approximately 2 min and slow mixed at 30 rpm for 20 min. Sample were then allowed to settle for 30 min and the supernatant were measured for final pH and residual equilibrium Zn(II) and Cu(II) concentrations. The test was repeated for sample B (refer Section 2.4) and C (refer Section 2.4). The same procedure was repeated for chemical precipitation test using FSC with dosages of FSC varied from 0 to 74 mg/L (0 to 8 mL).

3 Result and discussions

3.1 Effect of dosage of GWTPS and volume of HCl in the production of FCC

The effect of dosage of GWTPS and volume of HCl in the production of FCC were investigated by measuring the concentration of Fe, Fe^{2+} and Fe^{3+} for after each digestion process. The results of the digestion of GWTPS with HCl were plotted in Figure 1 (a), (b) and (c) below and summarized in Table 3.

From Figure 1, it can be observed that the concentration of Fe, Fe^{2+} and Fe^{3+} after digestion increased when the volume of HCl was increased. However, the concentrations of Fe, Fe^{2+} and Fe^{3+} decreased as the maximum FCC was achieved. It can also be observed higher dosages of GWTPS required greater

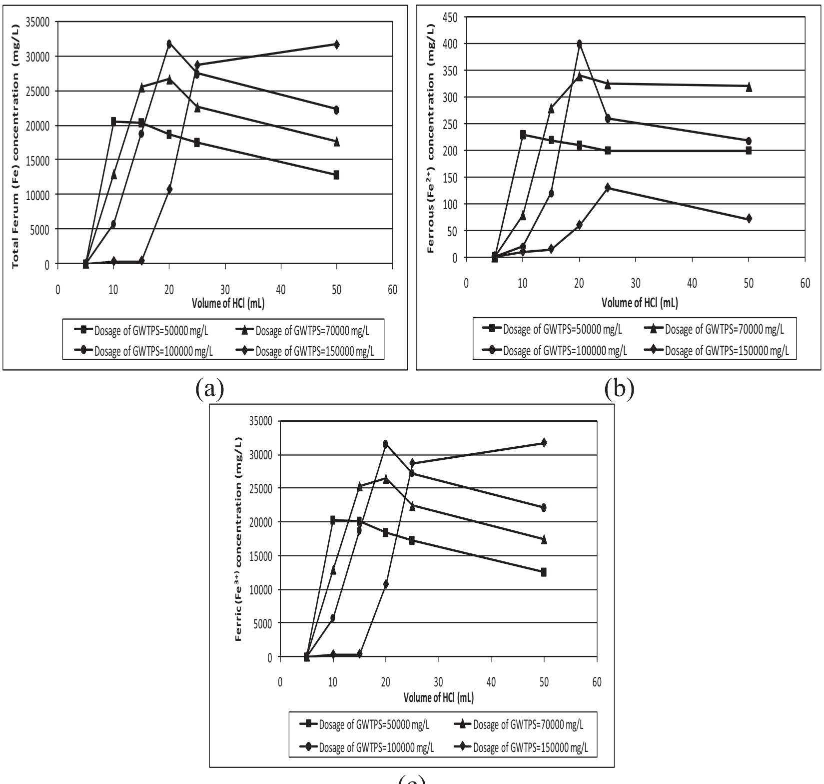


Figure 1: Concentration of (a) Fe (b) Fe^{2+} and (c) Fe^{3+} after digestion at various dosages of GWTPS and volumes of HCl.

Table 3: Summary of results of maximum point of digestion with HCl for the production of FCC.

Dosage of GWTPS (mg/L)	Volume of DW (mL)	Volume of HCl (mL)	Total Fe conc. (mg/L)	Fe^{3+} conc. (mg/L)	Fe^{2+} conc. (mg/L)
50000	100	10	20529	230	20299
70000	100	20	26763	340	26423
100000	**100**	**20**	**31872**	**400**	**31472**
150000	100	50	28807	130	28677

volume of HCI to maximise the digestion process. Additional volumes of HCl after the maximum point of FCC production lessened the concentration of Fe, Fe^{2+} and Fe^{3+} which indicate that all Fe_2O_3 composition were already used up.

By referring to the concentration of Fe^{3+} obtained in , it was found that the optimum ratio to produce FCC was achieved at ratio of 10g (GWTPS): 20 mL (HCl): 100 mL (distilled water). At this ratio, approximately 3.1% (31 472 mg/L) of FCC was generated from GWTPS.

3.2 Effect of dosage of GWTPS and volume of H_2SO_4 in the production of FSC

FSC was produced by digesting GWTPS with H_2SO_4 for 4 hr [10, 11] on a hot plate at various dosages of GWTPS and volume of H_2SO_4 while keeping the volume of distilled water constant at 100 mL. The concentrations of total Fe, Fe^{2+} and Fe^{3+} at various dosages of GWTPS and volume of H_2SO_4 are shown in Figure 2 (a), (b) and (c), respectively. The results of digestion were summarized in Table 4 below.

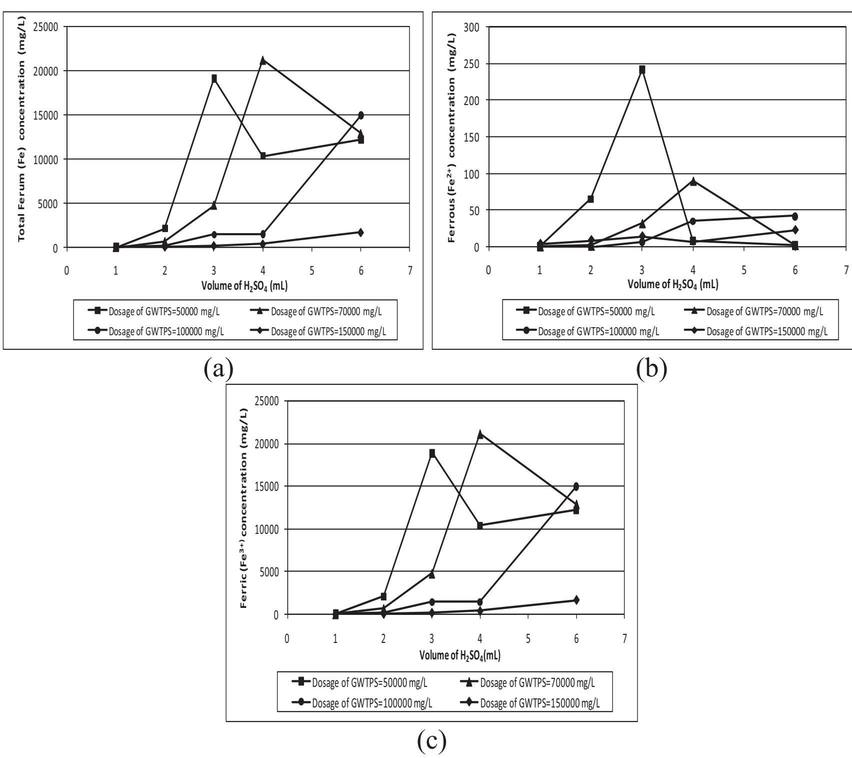


Figure 2: Concentration of (a) Fe (b) Fe^{2+} and (c) Fe^{3+} at various dosages of GWTPS and volumes of H_2SO_4.

Table 4: Summary of results of maximum point of digestion with H_2SO_4 for the production of FSC.

Dosage of GWTPS (mg/L)	Volume of DW (mL)	Volume of H_2SO_4(mL)	Total Fe conc. (mg/L)	Fe^{2+} conc. (mg/L)	Fe^{3+} conc. (mg/L)
50000	100	3	19142	242	18900
70000	**100**	**4**	**21223**	**90**	**21133**
100000	100	4	14943	42	14901
150000	100	6	1676	23	1653

From Figure 2 (a), it can also be observed higher dosages of GWTPS required greater volume of H_2SO_4 to maximise the digestion process. It is observed that higher dosages of GWTPS require greater volume of H_2SO_4 in order to reach maximum production of FSC. Additional volumes of H_2SO_4 after the maximum point of FSC production lessened the concentration of Fe, Fe^{2+} and Fe^{3+} which indicate that all Fe_2O_3 composition were already used up.

Based on the results obtained for the concentration of Fe^{3+} (Figure 2 (c)), it was found that the optimum production of FSC was obtained at a ratio of 7g (GWTPS):4 mL (H_2SO_4):100 mL (distilled water). At this ratio, approximately 2.1% (21 133 mg/L) of FSC was generated from GWTPS.

3.3 Mass production of FCC and FSC

Using the optimum ratio of FCC and FSC production obtained from Section 3.1 and Section 3.2, production of FCC and FSC was mass produced at 4 hr digestion time. Table 5 below shows the concentration of total Fe, Fe^{2+} and Fe^{3+} after mass production of FCC and FSC. The concentration of Fe was measured using AAS while Fe^{2+} concentration by Spectrophotometer. The concentration of Fe^{3+} was obtained by subtracting Fe^{2+} from Fe concentration.

Table 5: Concentration of Fe, Fe^{2+} and Fe^{3+} for FCC and FSC.

Recycled coagulant	Total Fe conc. (mg/L)	Ferrous (Fe^{2+}) conc. (mg/L)	Ferric (Fe^{3+}) conc. (mg/L)	Conc. of generated coagulants (%)
FCC	29126	212	28914	2.9%
FSC	18548	150	18398	1.8%

From Table 5, it was observed that approximately 2.9% (28 914 mg/L) of FCC was generated from GWTPS using production ratio of 100 000 mg/L (GWTPS): 140 mL (HCl): 700 mL (distilled water). Whilst approximately 1.8% (18 398 mg/L) was generated from GWTPS using production ratio of 70 000 mg/L (GWTPS): 28 mL (HCl): 700 mL (distilled water). Lower volume of H_2SO_4 was needed for the maximum production of FSC as compared to the production of FCC as H_2SO_4 used is more concentrated (98%) than HCl (37%). The concentration of FCC produced was found to be higher than FSC.

3.4 Results on effect of dosage of FCC and FSC on removal of TSS, turbidity and colour from synthetic wastewater by chemical precipitation

The effect of dosage of FCC and FSC in removing TSS, turbidity and colour from synthetic wastewater were conducted by varying dosage of FCC from 0 to 116 mg/L and dosage of FSC from 0 to 291 mg/L. Figure 3 (a), (b) and (c) shows the final concentration of TSS, turbidity and colour at various dosages of FCC and FSC, respectively.

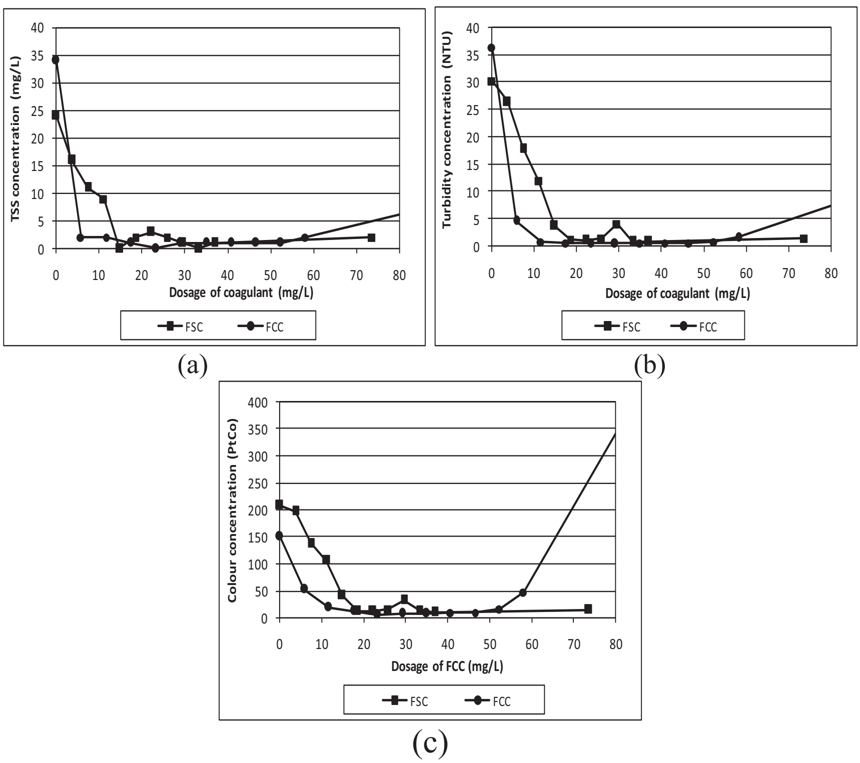


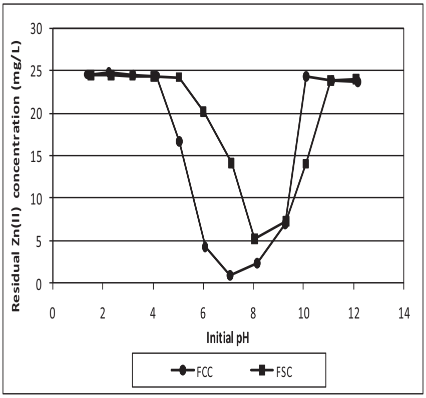
Figure 3: Concentration of (a) TSS, (b) turbidity and (c) colour at various dosages of FCC and FSC.

Figure 3 (a), (b) and (c) indicates that 23.3 mg/L dosage of FCC and 33.2 mg/L dosage of FSC was required to give the highest TSS, turbidity and colour removal from synthetic wastewater. At optimum dosage of 23.3 mg/L of FCC, approximately 100%, 99% and 98% of TSS, turbidity and colour was removed from synthetic wastewater, respectively. While approximately 100%, 98% and 96% of TSS, turbidity and colour was removed from synthetic wastewater at optimum dosage of 33.2 mg/L.

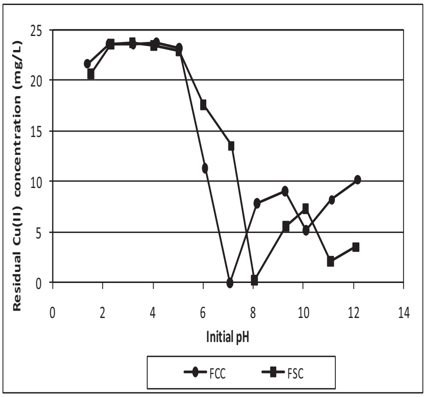
Despite the low concentration of FSC (1.8%) than FCC (2.9%), it proved to be effective in removing TSS, turbidity and colour. However, higher dosage of FSC was required to give the same removal efficiency as obtained by FCC. This suggests that both FCC and FSC were superior in removing pollutants from synthetic wastewater.

3.5 Results on effect of initial pH on Zn(II) and Cu(II) mixture removal from synthetic wastewater at fixed dosage of FCC and FSC

The effect of initial pH on Zn(II) and Cu(II) removal from synthetic wastewater was investigated by varying the initial pH from pH 1 to pH 12 and adding a fixed dosage of generated coagulant. Figure 4 (a) show the effect of initial pH on Zn(II) removal using FCC and FSC. It was observed that Zn(II) removal are most effective at a pH range between pH 6 and pH 8 for FCC and pH range between pH 8 to pH 9 for FSC. The optimum pH for FCC on Zn(II) removal was found to be pH 7 of which 100% Zn(II) was removed from synthetic wastewater. The optimum pH for FSC on Zn(II) removal is pH 8 of which approximately 79% of Zn(II) was removed from synthetic wastewater.



(a)



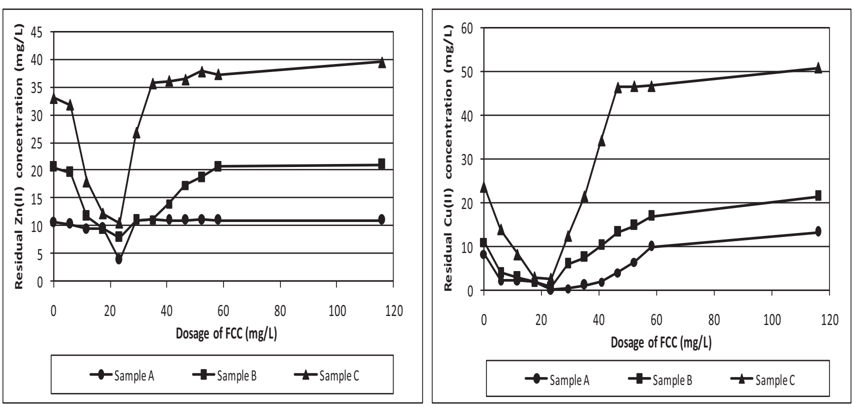
(b)

Figure 4: Concentration of residual (a) Zn(II) and (b) Cu(II) at various initial pH at fixed dosage of FCC (23.3 mg/L) and FSC (22.5 mg/L) for Sample B.

For Cu(II) removal using both FCC and FSC, the optimum pH was found to be pH 7 and pH 8 of which 100% and 99% of Cu(II) was removed synthetic wastewater, respectively (Figure 4 (b)). According to Tillman [12], the commercial ferric chloride has an effective pH range between pH 4 to 10, while commercial ferric sulfate has an effective pH range from pH 4 to 6 and from pH 8.8 to 9.2. The effective pH range for both FCC and FSC lies between the same pH ranges as commercial coagulants.

3.6 Results on effect of dosage of FCC on Zn(II) and Cu(II) mixture removal from synthetic wastewater at optimum pH

Figure 5 (a) and (b) show the effect of dosage of FCC on various initial Zn(II) and Cu(II) mixture concentration at optimum pH 7. From Figure 5 (a), it was observed that the optimum dosage of FCC is 23.3 mg/L for Zn(II) and Cu(II) removal. Using this dosage of FCC, approximately 68%, 69% and 79% of Zn(II) was removed from Sample A, B and C, respectively. While, 100%, 97% and 95% of Cu(II) was removed from initial Cu(II) concentration of Sample A, B and C, respectively (Figure 5 (b)). Cu(II) removal was found to be higher than Zn(II) removal due to the smaller size of Cu(II) ions as compared to Zn(II) ions. It was also observed that the removal of metal increased as dosage of coagulants increased until it reached optimum removal but once it reached optimum point, the removal of metal started to decrease.

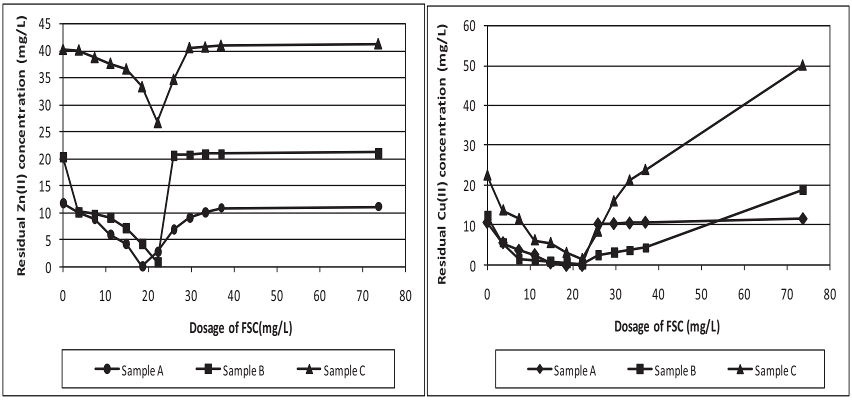


(a) (b)

Figure 5: Concentration of (a) Zn(II) and (b) Cu(II) at various dosages of FCC at optimum pH 7 for various initial concentrations of Zn(II) and Cu(II).

3.7 Results on effect of dosage of FSC on Zn(II) and Cu(II) mixture removal from synthetic wastewater at optimum pH

The result on effect of FSC dosage on Zn(II) and Cu(II) mixture removal at optimum pH 8.3 is shown in Figure 6. Figure 6 (a) and (b) indicates that the optimum dosage of FSC on Zn(II) and Cu(II) removal was found to be 18.48 mg/L, 22.2 mg/L and 22.2 mg/L for initial Cu(II) concentration of Sample A, B and C, respectively. When initial pH of Sample A was adjusted to pH 8.3, the optimum dosage was only 18.48 mg/L of which 100% efficiency can be achieved for both Zn(II) and Cu(II) removal. When initial pH of Sample B was adjusted to pH 8.3, the optimum dosage was only 22.2 mg/L of which 96% and 99% efficiency can be achieved for both Zn(II) and Cu(II) removal, respectively. When initial pH of Sample A was adjusted to pH 8.3, the optimum dosage was



(a) (b)

Figure 6: Concentration of (a) Zn(II) and (b) Cu(II) at various dosages of FSC at optimum pH 8 for various initial concentrations of Zn(II) and Cu(II).

only 22.2 mg/L of which 47% and 97% efficiency can be achieved for both Zn(II) and Cu(II) removal, respectively.

It was observed that, at higher initial Zn(II) and Cu(II) concentration, greater dosage of FSC was needed to give better metals removal efficiencies. FSC is considered superior in removing Zn(II) and Cu(II) for Sample A and B. However removal of Zn(II) for Sample C is lower than the other samples. It was also observed that lower removal of Zn(II) as compared to Cu(II) removal shows that the presence of other metal ions in solution suppressed the removal capacity.

4 Conclusions

GWTPS which contains 29.7% of Fe_2O_3 IN weight was extracted by acid digestion to produce coagulants, FCC and FSC. Approximately 2.9% of FCC and 1.8% of FSC was generated from GWTPS. The optimum ratio for maximum production of FCC (2.9%) was found to be 10g (GWTPS): 20 mL (HCl): 100 mL (distilled water). The optimum ratio for the production of FSC (1.8%) was found to be 7g (GWTPS):4 mL (H_2SO_4):100 mL (distilled water). Both generated coagulants, FCC and FSC proved to be effective in removing TSS, turbidity, colour, Zn(II) and Cu(II) from synthetic wastewater. Approximately 23.3 mg/L (0.4 mL) of FCC and 22.2 mg/L (0.6 mL) of FSC were required to give a relatively well removal of TSS, turbidity, colour, Zn(II) and Cu(II).

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