CHAPTER FOUR

RESULTS AND DISCUSSION

The results to be presented and discussed in this section are based on the averaged results of a series of experiments carried out to study the general characteristics of the wastewater and the response of the soap and detergents wastewater when subjected to variations in coagulation and flocculation process conditions. Parameters investigated in this study included type and optimum coagulant dosage, optimum pH, optimum mixing time, optimum mixing speed, and optimum settling time. The study was extended to re-evaluate the characteristics of the wastewater at optimum treatment conditions. The possibility of double treatment was also reviewed with the optimum conditions obtained. The water was initially treated with the most preferred coagulant and followed by the most preferred coagulant aid. Absorption studies were also carried out to evaluate color substance and surfactant removal.

4.1 Characterization Studies

The wastewater collected was generated from a number of activities in the soap and detergent plant. The main source of wastewater was from the washing process during the change of product, from the laundry bar line, oral care line household surface care line and the soap finishing line. The characteristics determined were temperature, pH suspended solids, zeta potential value, the chemical oxygen demand and surface tension. The values are as presented in **Table 4.1.**

Table 4.1: Wastewater Characteristics

Parameter	Values
Temperature (^{0}C)	23 to 27
pH	9 to 12.5
Suspended Solids (mg/l)	1500 to 1800
Zeta Potential (mV)	-38 to $-$ 25
Chemical Oxygen Demand (mg/l)	20 000 to 36 000
Surface Tension (dynes/cm)	32 - 35

4.2 Determination of Optimal Conditions Influencing the Coagulation and Flocculation Process During the Treatment of Wastewater.

4.2.1 Determination of Optimum Type and Coagulant Dosage

One of the main parameters that must be studied in any wastewater or effluent treatment plant is the type of coagulant suitable and its optimum dosage since the main operating cost of a treatment plant greatly depends on the type and dosage of coagulant used. In the case where the coagulant chosen is not suitable, then not only the cost escalates but the effluent will not meet the standards set by the relevant authorities.

Figures 4.1, 4.2, 4.3, 4.4 and 4.5. show the changes of zeta potential value for the respective coagulation agents and coagulant aids. **Figure 4.1** shows the dosage of alum from 0.1 mg/l until about 3.0 g/l. The zeta potential value increased from - 38 mV

to about – 1.6 mV. For additional dosage of alum from 3.0 g/l to 5.0 g/l, it shows no significant variation other than the slight drop at 3.8 g/l to -3 mV and back again to –2 mV for the dosage of 3.9g/l. The zeta potential value did not touch 0 mV or change to positive values within the limitation of the study of 5.0 g/l of alum dosage.

Figure 4.2 shows the change of zeta potential values against coagulant concentration for ferric sulfate. It shows marginal variation in zeta potential value from dosage from 0.1 mg/l up to 8.0 g/l. A sharp increase in the zeta potential value was experience for dosages between 8.0 g/l to 9.0 g/l, the change in zeta potential value was from about –24 mV to –5.1mV. Additional dosage of ferric sulfate from 9.0 g/l to 10.0 g/l did not exhibit further increase in zeta potential values. The values remained at an average of -5.0 mV.

Figures 4.3 and 4.4 represent variation in zeta potential value with dosage of polyvinyl alcohol and sodium alginate respectively. The addition of polyvinyl alcohol and sodium alginate to the wastewater displayed minimal changes in the zeta potential values even at dosages as high as 5.0 g/l. Additional dosages were not evaluated as it was not cost effective for the wastewater treatment process.

Figure 4.5 shows variation of zeta potential values of polyethylenimine. It seems to show very little variation of zeta potential readings at dosages below 1.0 g/l. A slight increase in zeta potential values was recorded for dosages between 1.0 g/l to 1.6 g/l. The maximum value recorded was –20.0 mV at 1.6 g/l dosage. Further additions of polyethylenimine showed a drop in the zeta potential values. The study was terminated at 3 g/l as the addition beyond 1.6 g/l did not give the required response.
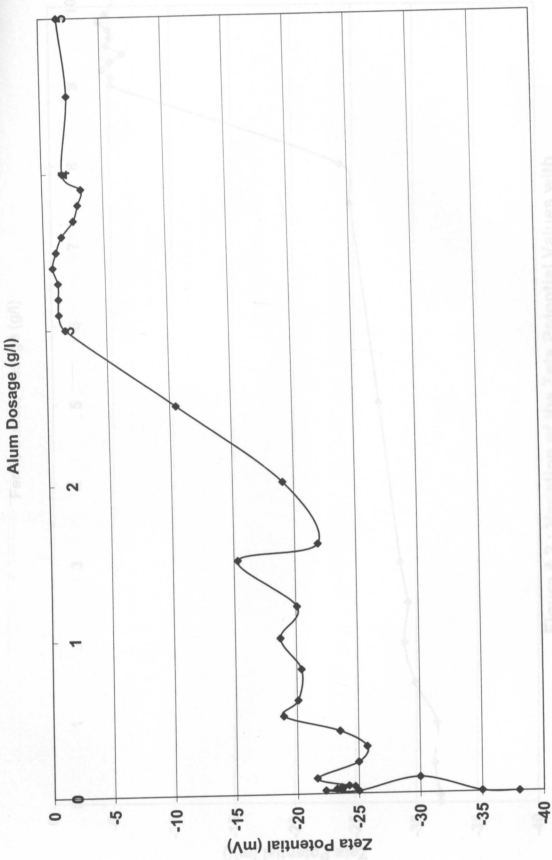
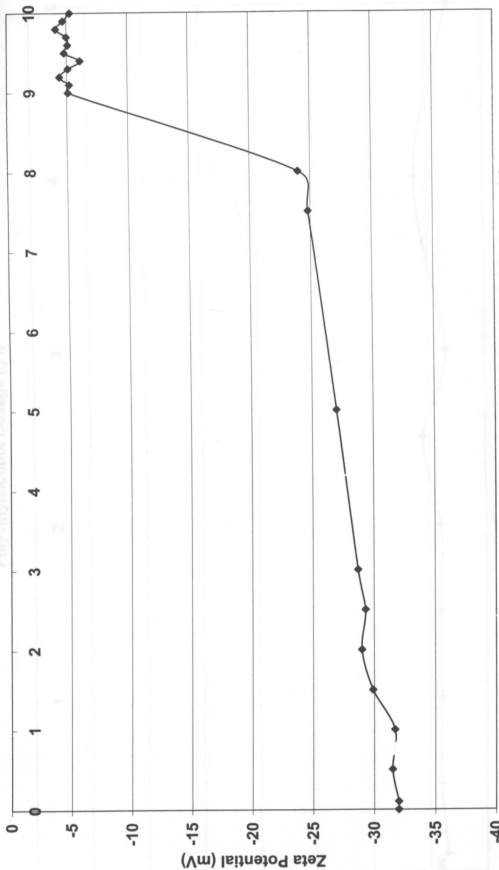Figure 4.1 : Variation of the Zeta Potential Values with Alum Dosage

Figure 4.2 : Variation of the Zeta Potential Values with Ferric Sulfate Dosage
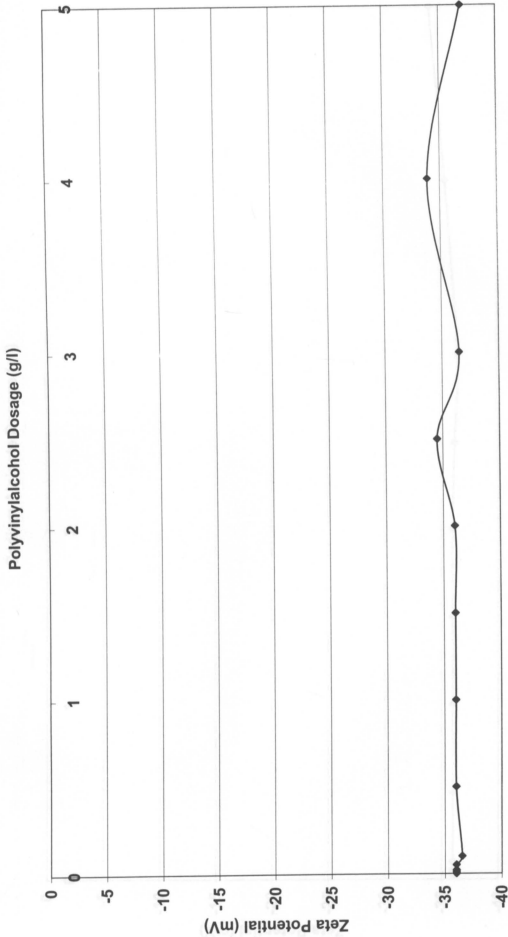
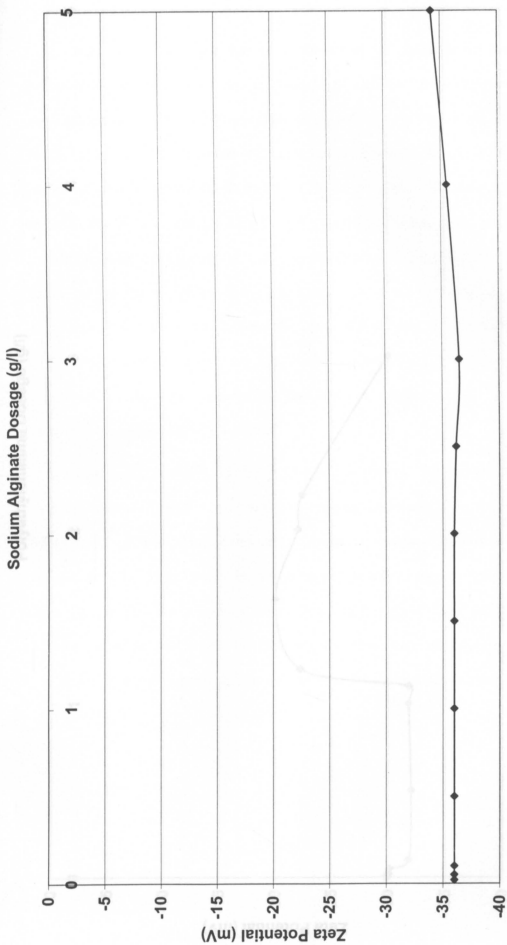Figure 4.3 : Variation of the Zeta Potential Values with Polyvinyl alcohol Dosage

Figure 4.4 : Variation of the Zeta Potential Values with Sodium Alginate Dosage

Figure 4.5 : Variation of the Zeta Potential Values with Polyethylenimine Dosage

Figures **4.6, 4.7 and 4.8** show the effect of alum, ferric sulfate and polyethylenimine respectively on the removal of turbidity. Polyvinly alcohol and sodium alginate did not exhibit any effect on the turbidity removal of the wastewater. Hence, tabulation of the reduction was not possible. **Figure 4.6** shows a steep increase in turbidity removal from the dosage of 0.2 g/l to 0.6 g/l of alum. The turbidity removal recorded was 70 %. At dosages 0.6 g/l to 1.0 g/l a steep reduction on the percentage of turbidity removal was experienced. The percentage of turbidity removal increased from below 10% at the dosage of 1.0 g/l to about 60% at the dosage of 1.6 g/l. The percentage of turbidity removal further increased to 90% from 60% as the dosage of alum was increased from 1.6 g/l to 2.5 g/l. Further addition of alum dosage was not able to completely remove the turbidity. The percentage of turbidity removal remained at 90% up to the addition of 5.0 g/l of alum.

Figure 4.7 shows the percentage of turbidity removal from wastewater treated with ferric sulfate. Turbidity removal was not evident for dosages of ferric sulfate from 0.1 g/l to 5.0 g/l. The percentage of turbidity removal increased from 0% to 40 % for dosages from 5.0 g/l to 7.8 g/l. The percentage of turbidity removal increased further from 40% to 80% for dosages between 7.9 g/l to 9.0 g/l of ferric sulfate. Further addition of ferric sulfate did not increase the percentage of turbidity removal. Percentage of turbidity removal remained at 80% for the dosages between 9.1 g/l to 10.0 g/l.
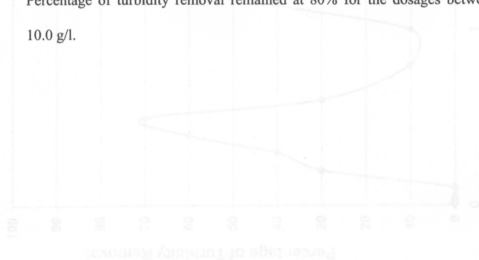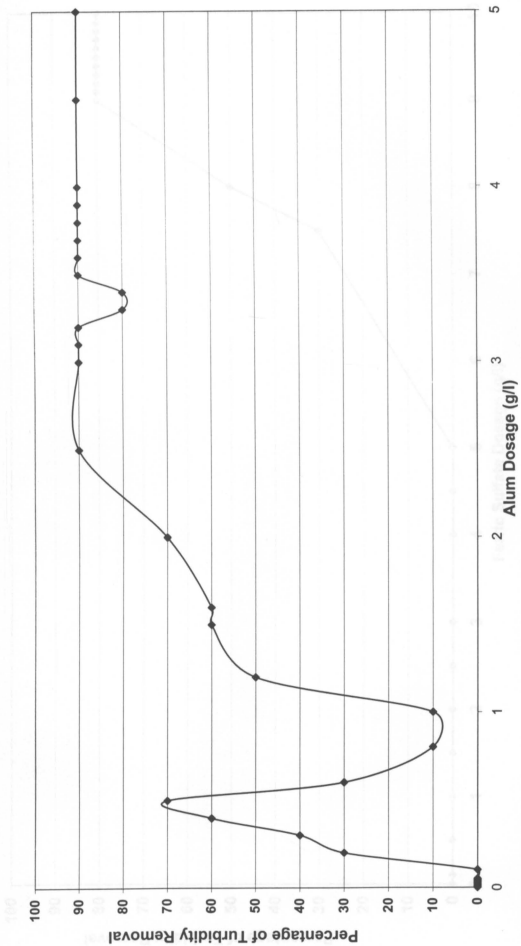
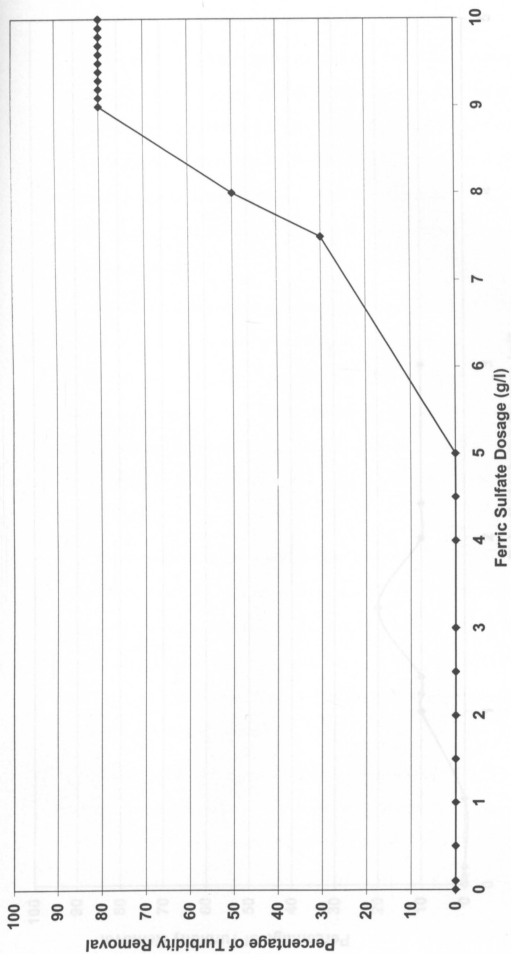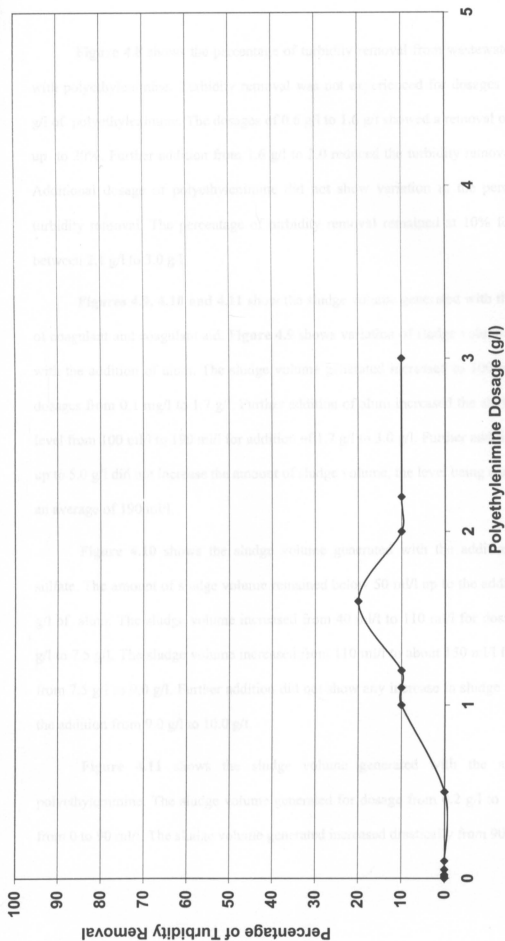Figure 4.6 : Variation of Percentage of Turbidity Removal with Alum Dosage

Figure 4.7 : Variation of Percentage of Turbidity Removal with Ferric Sulfate Dosage

Figure 4.8 shows the percentage of turbidity removal with the wastewater treated with polyethylenimine. Turbidity removal was not observed for dosage below 0.2 g/l. At only a low dosage, the dosage of 0.2 g/l to 1.4 g/l showed removal of turbidity up to 20%. Further increase from 1.4 g/l to 3.0 g/l caused the turbidity removal to 10%. Addition of a large polyethylenimine did not show significant ... percentage of turbidity removal. The percentage of turbidity removal remained at 10% for dosage between 2.0 g/l to 3.0 g/l.

Figures 4.9, 4.10 and 4.11 show the sludge volume generated with the addition of polyethylenimine and coagulant aids. Figure 4.9 shows variation of turbidity removal with the addition of alum. The sludge volume generated decreased as there was the addition from 0.1 g/l to 1.5 g/l. Further addition of alum increased the turbidity removal level from 100 ml/l to 190 ml/l by addition of 1.5 g/l to 2.5 g/l. Further increase in dosage up to 5.0 g/l did not increase the amount of sludge volume. The final sludge volume obtained at an average of 190 ml/l.

Figure 4.10 shows the sludge volume generated with the addition of aluminium sulfate. The amount of sludge volume increased from 90 ml/l to the addition of 0.1 g/l of alum. The sludge volume decreased from 40 ml/l to 10 ml/l for dosage of 0.1 g/l to 1.5 g/l. The sludge volume increased from 10 ml/l to above 40 ml/l for dosage from 1.5 g/l to 3 g/l. Further addition did not increase any more but remained for dosage from 3.0 g/l to 10.0 g/l.

Figure 4.11 shows the sludge volume generated with the addition of polyethylenimine. The sludge volume generated for dosage from 0.1 g/l to 1.1 g/l was from 0 to 90 ml/l. The sludge volume generated increased drastically from 90 ml/l to

Figure 4.8 : Variation of Percentage Of Turbidity Removal with Polyethylenimine Dosage

Figure 4.8 shows the percentage of turbidity removal from wastewater treated with polyethylenimine. Turbidity removal was not experienced for dosages below 0.5 g/l of polyethylenimine. The dosages of 0.6 g/l to 1.6 g/l showed a removal of turbidity up to 20%. Further addition from 1.6 g/l to 2.0 reduced the turbidity removal to 10%. Additional dosage of polyethylenimine did not show variation in the percentage of turbidity removal. The percentage of turbidity removal remained at 10% for dosages between 2.1 g/l to 3.0 g/l.

Figures 4.9, 4.10 and 4.11 show the sludge volume generated with the addition of coagulant and coagulant aid. Figure 4.9 shows variation of sludge volume generated with the addition of alum. The sludge volume generated increased to 100 ml/l for the dosages from 0.1 mg/l to 1.7 g/l. Further addition of alum increased the sludge volume level from 100 ml/l to 190 ml/l for addition of 1.7 g/l to 3.0 g/l. Further addition of alum up to 5.0 g/l did not increase the amount of sludge volume, the level being maintained at an average of 190 ml/l.

Figure 4.10 shows the sludge volume generated with the addition of ferric sulfate. The amount of sludge volume remained below 50 ml/l up to the addition of 5.0 g/l of alum. The sludge volume increased from 40 ml/l to 110 ml/l for dosages of 5.0 g/l to 7.5 g/l. The sludge volume increased from 110 ml/l to about 150 ml/l for addition from 7.5 g/l to 9.0 g/l. Further addition did not show any increase in sludge volume for the addition from 9.0 g/l to 10.0 g/l.

Figure 4.11 shows the sludge volume generated with the addition of polyethylenimine. The sludge volume generated for dosage from 0.2 g/l to 1.1 g/l was from 0 to 90 ml/l. The sludge volume generated increased drastically from 90 ml/l to
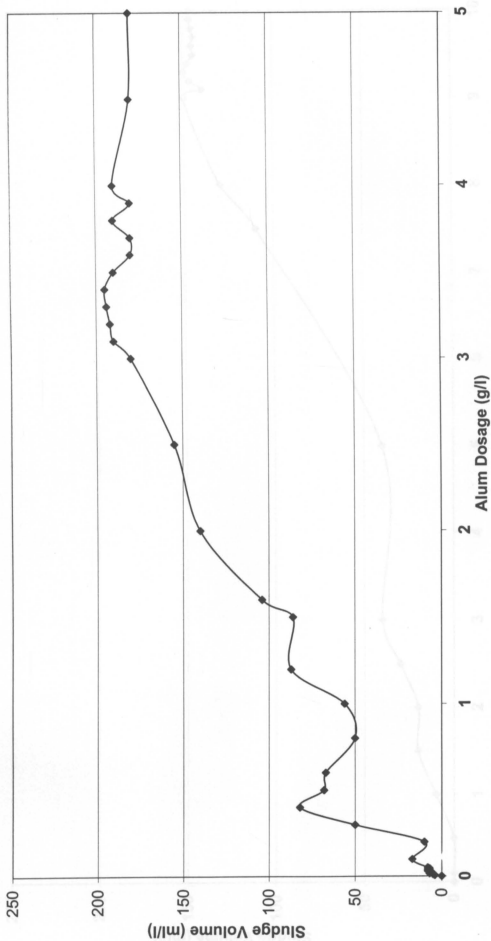
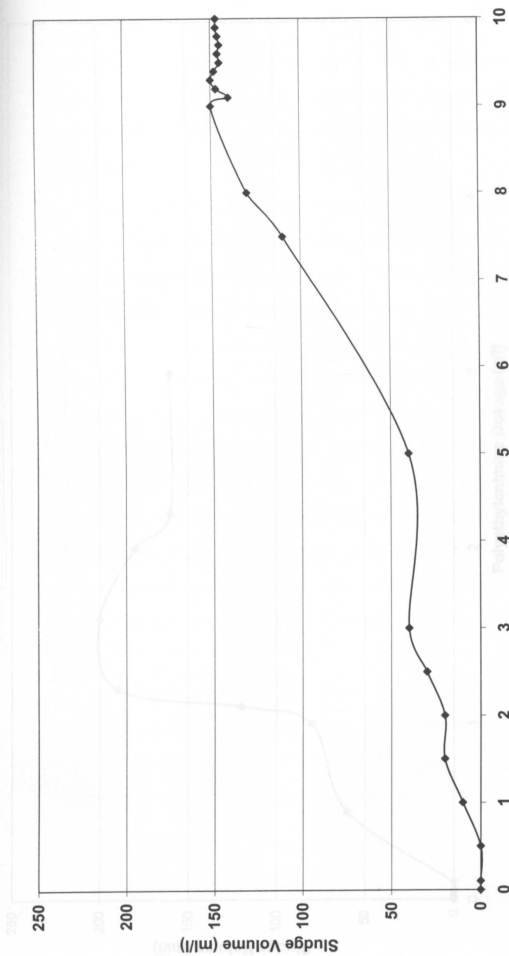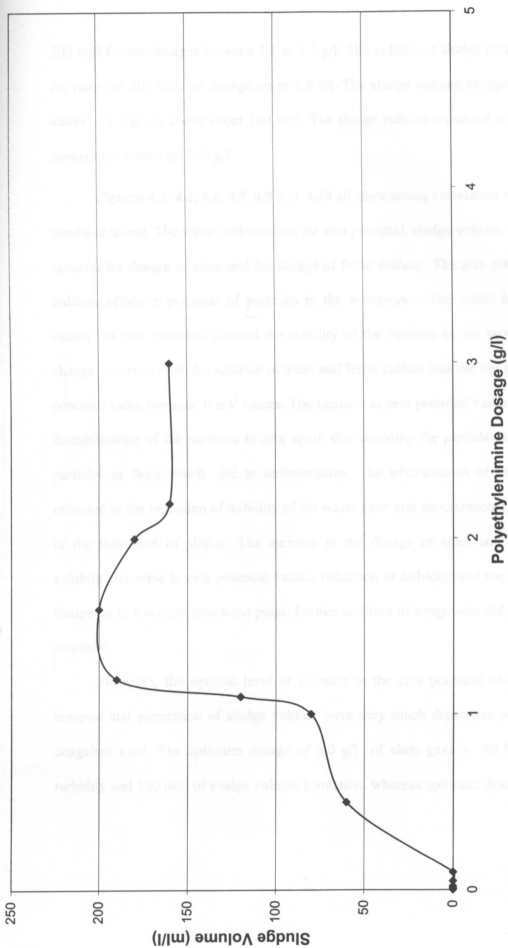**Figure 4.9 : Variation of Sludge Volume with Alum Dosage**

Figure 4.10 : Variation of Sludge Volume with Ferric Sulfate Dosage

Figure 4.11 : Variation of Sludge Volume with Polyethylenimine Dosage

200 ml/l for the dosages between 1.1 to 1.3 g/l. The volume of sludge remained within the range of 200 ml/l for dosage up to 1.5 g/l. The sludge volume dropped for dosage above 1.7 g/l to above about 160 ml/l. The sludge volume remained at 160 ml/l for dosages between 2 g/l to 3 g/l.

Figures 4.1, 4.2, 4.6, 4.7, 4.9 and 4.10 all show strong correlation with the other results obtained. The values obtained are for zeta potential, sludge volume and turbidity removal for dosage of alum and for dosage of ferric sulfate. The zeta potential values indicate effective potential of particles in the wastewater. The initial high negative values of zeta potential showed the stability of the colloids in the wastewater. The change observed with the addition of alum and ferric sulfate was the transition of zeta potential value towards 0 mV values. The increase in zeta potential value indicated the destabilisation of the particles to stay apart, thus enabling the particles to form larger particles or flocs which led to sedimentation. The advancement of this event was reflected in the reduction of turbidity of the wastewater and simultaneously the increase in the formation of sludge. The increase in the dosage of alum and ferric sulfate exhibited increase in zeta potential values, reduction in turbidity and the generation of sludge up to a certain saturation point. Further addition of coagulants did not show any response.

However, the optimal level of increase in the zeta potential values, turbidity removal and generation of sludge volume were very much dependent on the type of coagulant used. The optimum dosage of 3.0 g/l of alum gave a 90 % removal of turbidity and 190 ml/l of sludge volume formation whereas optimum dosage of 9.0 g/l

of ferric sulfate gave a 80 % removal of turbidity and 150 ml/l of sludge volume formation. Ferric sulfate was less effective than alum even with the higher dosage.

Hashim et al. (1985) in their study of detergent wastewater treatment at a local facility recorded the optimal dosage of alum as 11 g/l at the optimal pH of 6. The amount of turbidity removal recorded was 81 % and the total suspended solid removal was 89%. Eric et al. (1998) in their study of removal of particles and trihalomethane precursors with alum dosages reported the residual turbidity decreased with the increase of alum dosage. The optimal alum concentration used was 20 mg / l. They stated at this high concentration of alum, particles were removed predominantly by sweep-floc coagulation. The precipitation of aluminum hydroxide promotes coagulation by increasing the interparticle collision rate and enmeshing suspended particles (Chowdhury, 1993 ; Montgomery, 1983).

The coagulation aids used in this study fall into the following categories: polyvinyl alcohol, a nonionic polymer; sodium alginate, an anionic polymer; polyethylenimine, a cationic polymer. **Figures 4.3** and **Figure 4.4** show that even with high concentrations, there is very little variation in zeta potential readings for wastewater treated with polyvinyl alcohol and sodium alginate respectively. It has been suggested that the main surfactant present in the wastewater is anionic in nature. Thus, anionic and nonionic coagulation aids may have caused the stabilization of colloids instead of destabilization (Dhileepan and Kumar, 1995). Coagulation aids are polymers which act by coating the particles present in the wastewater. Hence, by acting is this manner, the polymers with similar charges or non charged further stabilized the particles to remain apart from each other and suspended in the wastewater (Jesse and

Sidney, 1971). Jesse and Sidney (1971), in a similar study of treatment of wastewater with coagulant aids, reported that anionic and nonionic polymers are more suitable to be applied as flocculent aids rather than the main active flocculent themselves. Both polyvinyl alcohol and sodium alginate were discarded at this stage.

Figure 4.5, Figure 4.8 and 4.11 all yielded the same results. They showed destabilization of the colloids for the addition of 1.1 g/l of polyethylenimine. Further addition exhibited gain in stability of particles. The increase in zeta potential was marginal and the sludge obtained was "light and fluffy" which corresponds with low percentage of turbidity removal. Jesse and Sidney (1971), in a similar study of treatment of wastewater with coagulant aids, stated that cationic polymers can be used as flocculent without metal salts. However, the results obtained in this study were not satisfactory under the preset treatment conditions.

The optimum coagulant dose of alum was recommended as 3.0 g/l, ferric sulfate as 9.0 g/l and polyethylenimine as 1.6 g/l.

4.2.2 Determination of Optimum pH

Figure 4.12, 4.13 and 4.14 show variation in zeta potential values with variation in the initial pH (pH was adjusted before treatment) of wastewater treated with alum, ferric sulfate and polyethylenimine respectively.

Figures 4.12 shows variation in zeta potential values with variation in pH for wastewater treated with 3.0 g/l of alum. The zeta potential value at pH 3 was −1.0 mV.
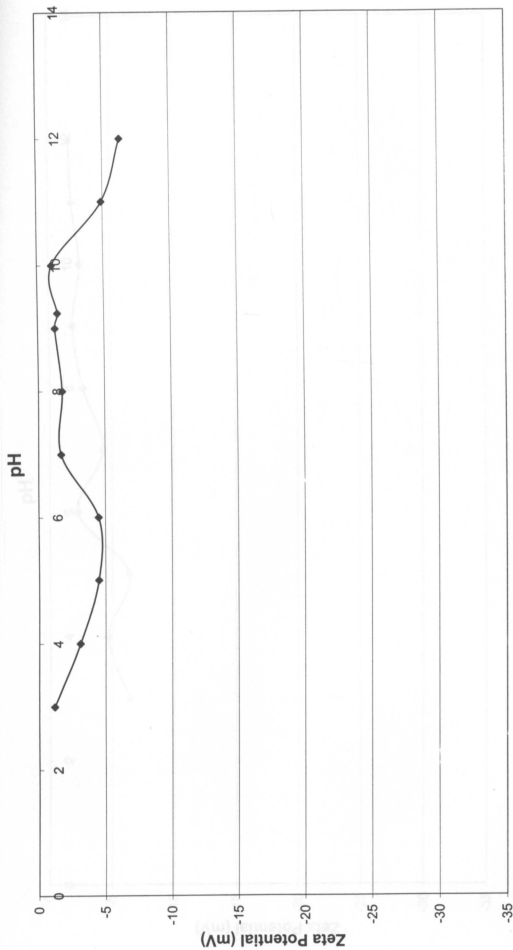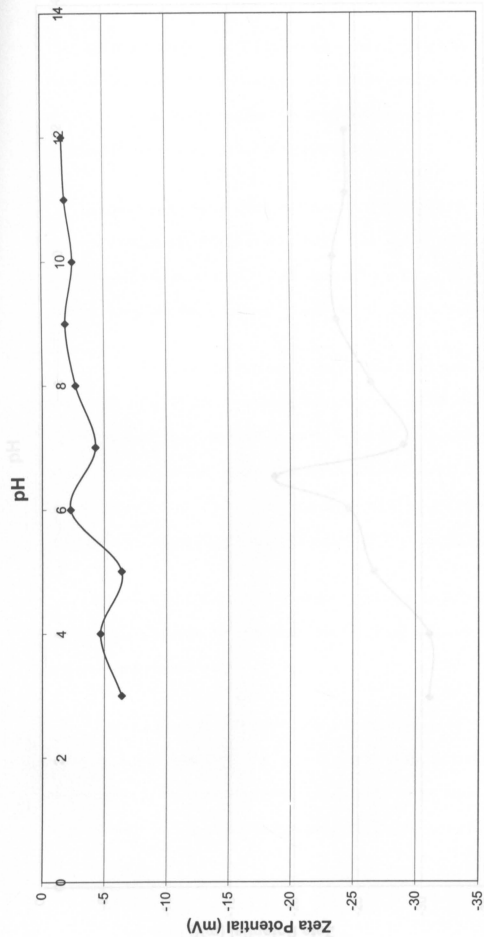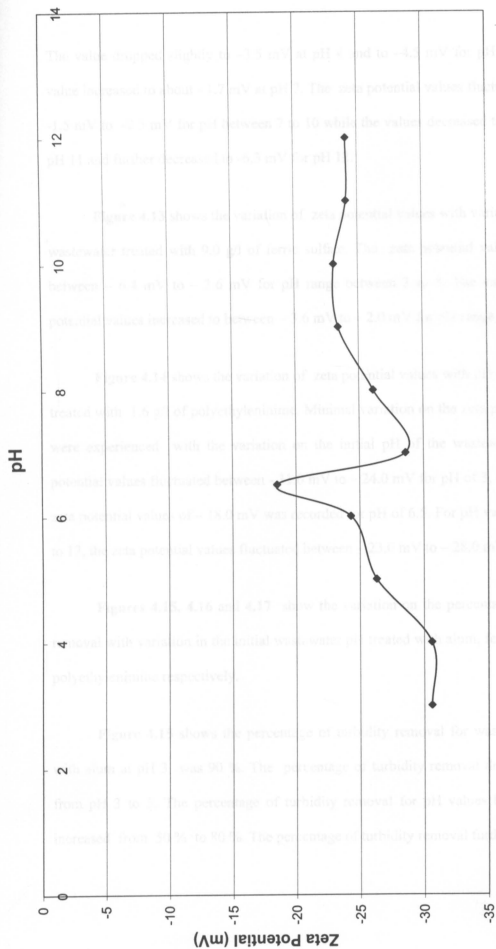
Figure 4.12 : Variation of Zeta Potential Values with pH of Wastewater Treated with Alum

Figure 4.13 : Variation of Zeta Potential Values with pH of Wastewater Treated with Ferric Sulfate

Figure 4.14 : Variation of Zeta Potential Values with pH of Wastewater Treated with Polyethylenimine

The zeta potential slightly to −31.0 mV at pH 3 and to −4.2 mV at pH 5 and 6. The value increased to about −1.5 mV at pH 7. The zeta potential values increased between −2.0 mV to −5.0 mV for pH between 8 to 10 when the value increased to −5.0 mV at pH 11 and further increase to −0.5 mV at pH 12.

Figure 4.13 shows the variation of zeta potential values with variation in pH for wastewater treated with 7.0 g/l of polyethylenimine. The zeta potential values increased between −4.0 mV to −1.5 mV for pH range between 3 to 7. Next, the zeta potential values increased to between −3.0 mV to −2.0 mV for 7.0 mg/l.

Figure 4.14 shows the variation of zeta potential values with variation in pH for wastewater treated with 1.0 g/l of polyethylenimine. Minimal variation in the zeta potential values were experienced with the variation on the initial pH. The wastewater zeta potential values increased between −4.0 mV to −31.0 mV at pH of 4, 5 and 6. The minimal value of −1.50 mV was reached at a pH of 6.0. For pH range between 7 to 12, the zeta potential values fluctuate between −31.0 mV to −20.0 mV.

Figures 4.15, 4.16 and 4.17 show the variation of the percentage turbidity removal with variation in the initial wastewater pH treated for alum, ferric chloride and polyethylenimine respectively.

Figure 4.15 shows the percentage of turbidity removal for wastewater treated with alum at pH was 90 %. The percentage of turbidity removal drops to 50 % from pH 3 to 5. The percentage of turbidity removal for pH value between 5 to 7 increased from 50 % to 90 %. The percentage of turbidity removal further increased to

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The value dropped slightly to –3.5 mV at pH 4 and to –4.5 mV for pH 5 and 6. The value increased to about - 1.7 mV at pH 7. The zeta potential values fluctuated between -1.5 mV to -2.5 mV for pH between 7 to 10 while the values decreased to –5.0 mV for pH 11 and further decreased to -6.3 mV for pH 12.

Figure 4.13 shows the variation of zeta potential values with variation in pH for wastewater treated with 9.0 g/l of ferric sulfate. The zeta potential values fluctuated between – 6.4 mV to – 3.6 mV for pH range between 3 to 8. The variation in zeta potential values increased to between - 3.6 mV to – 2.0 mV for pH range 8 to 12.

Figure 4.14 shows the variation of zeta potential values with pH for wastewater treated with 1.6 g/l of polyethylenimine. Minimal variation on the zeta potential values were experienced with the variation on the initial pH of the wastewater. The zeta potential values fluctuated between - 31.0 mV to – 24.0 mV for pH of 3, 4, 5 and 6. The zeta potential values of – 18.0 mV was recorded for pH of 6.5. For pH values between 7 to 12, the zeta potential values fluctuated between – 23.0 mV to – 28.0 mV.

Figures 4.15, 4.16 and **4.17** show the variation on the percentage of turbidity removal with variation in the initial wastewater pH treated with alum, ferric sulfate and polyethylenimine respectively.

Figure 4.15 shows the percentage of turbidity removal for wastewater treated with alum at pH 3 was 90 %. The percentage of turbidity removal dropped to 50 % from pH 3 to 5. The percentage of turbidity removal for pH values between 5 to 7 increased from 50 % to 80 %. The percentage of turbidity removal further increased to
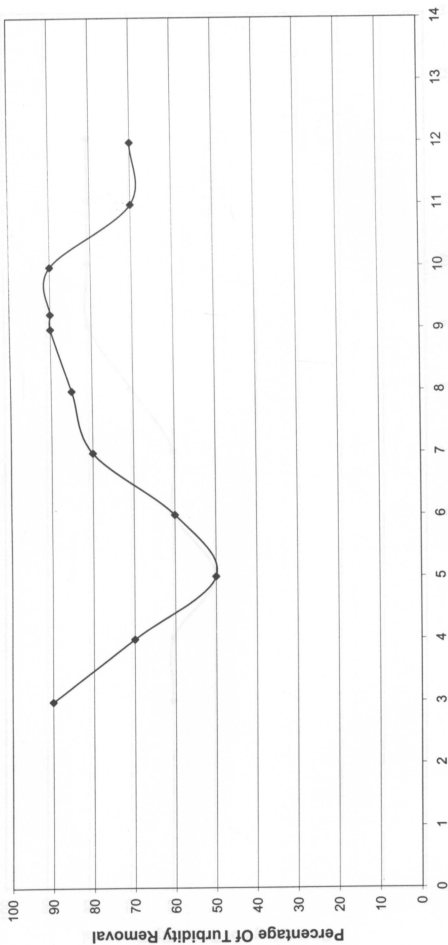
pH

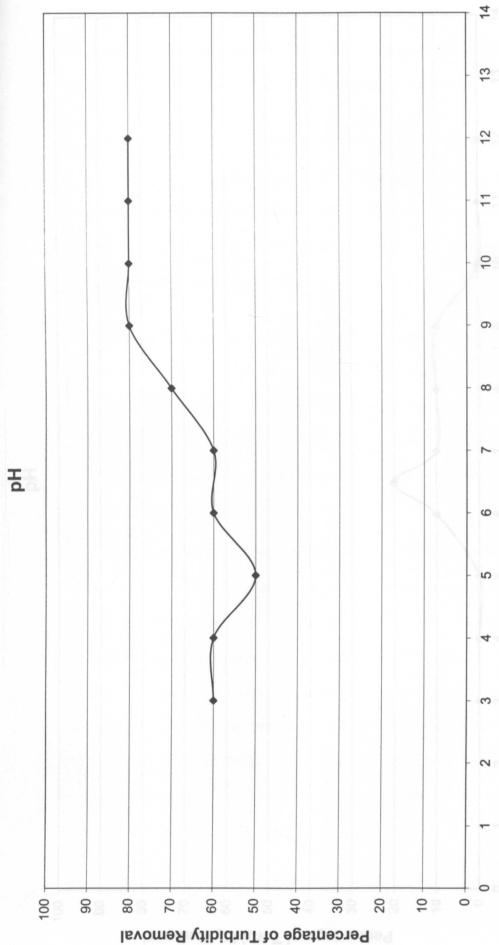Figure 4.15 : Variation of Percentage of Turbidity Removal with pH of Wastewater Treated with Alum
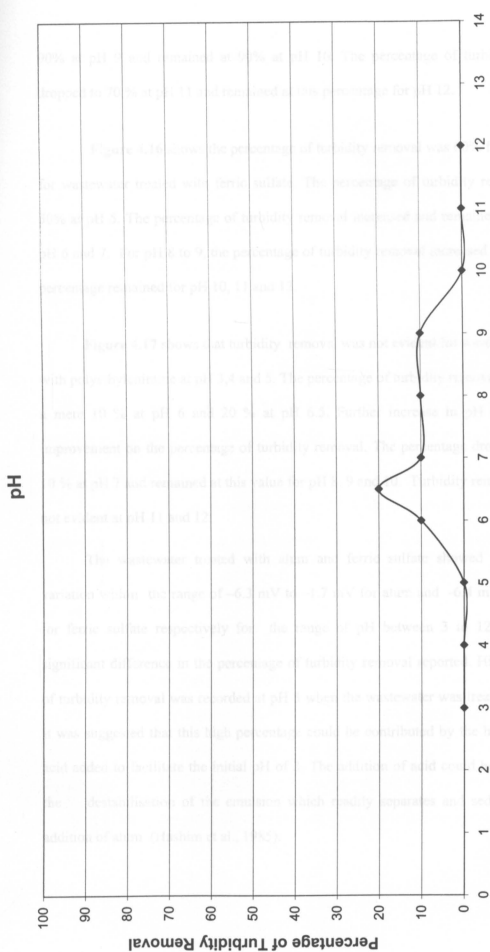
Figure 4.16 : Variation of Percentage of Turbidity Removal with pH of Wastewater Treated with Ferric Sulfate

Figure 4.17 : Variation of Percentage of Turbidity Removal with pH of Wastewater Treated with Polyethylenimine

90% at pH 9 and remained at 90% at pH 10. The percentage of turbidity removal dropped to 70 % at pH 11 and remained at this percentage for pH 12.

Figure 4.16 shows the percentage of turbidity removal was 60% for pH 3 and 4 for wastewater treated with ferric sulfate. The percentage of turbidity removal fell to 50% at pH 5. The percentage of turbidity removal increased and remained at 60 % for pH 6 and 7. For pH 8 to 9, the percentage of turbidity removal increased to 80 %. This percentage remained for pH 10, 11 and 12.

Figure 4.17 shows that turbidity removal was not evident for wastewater treated with polyethylenimine at pH 3,4 and 5. The percentage of turbidity removal increased to a mere 10 % at pH 6 and 20 % at pH 6.5. Further increase in pH did not show improvement on the percentage of turbidity removal. The percentage dropped again to 10 % at pH 7 and remained at this value for pH 8, 9 and 10. Turbidity removal was also not evident at pH 11 and 12.

The wastewater treated with alum and ferric sulfate showed zeta potential variation within the range of –6.3 mV to –1.7 mV for alum and -6.4 mV to -2.0 mV for ferric sulfate respectively for the range of pH between 3 to 12, indicating a significant difference in the percentage of turbidity removal reported. High percentage of turbidity removal was recorded at pH 3 when the wastewater was treated with alum. It was suggested that this high percentage could be contributed by the high amount of acid added to facilitate the initial pH of 3. The addition of acid could have resulted in the destabilisation of the emulsion which readily separates and sediments by the addition of alum (Hashim et al., 1985).

The percentage of turbidity removal was much higher for the wastewater with the initial pH higher than 7. The addition of alum and ferric sulfate to the wastewater during coagulation depressed the pH of the wastewater by the presence of excess hydrogen ions. The alkalinity present in the wastewater should serve as the buffer to resist the drastic pH changes. The wastewater should have a sufficient buffering capacity to resist the pH depression that occurs during coagulation with alum and ferric sulfate. Hence it can be suggested that wastewater with pH higher than 7 had the capacity to resist the depression of pH by addition of alum and ferric sulfate and effectively removed the particles coated with amorphous salt hydroxides by precipitation (Ogedengbe, 1984;   Letterman and Prasit, 1982). It is also suggested that at higher pH , bridging of particles was enhanced, such that emeshment of the colloidal particles would bring about clarification of the wastewater by the sweep floc mechanism (Hashim et al., 1985).

At pH 12, a reduction in the percentage of turbidity removal was experienced for wastewater treated with alum. It is suggested that the dosage of alum (3.0 g/l) did not generate enough hydrogen ions to depress the final pH of the wastewater to the optimum working range of alum.

Ogedengbe (1984) studied the turbidity removal characteristics of the water under varying alum and pH conditions. He reported that turbidity removal was considerably better with samples at pH 8 compared to the original sample at the initial pH of 6.7. He also remarked better flocs were formed at higher pH. Hashim et al. (1985) in a study of optimal coagulants and conditions for the treatment of detergent wastewater found that alum alone at pH 3 and 6 was not effective in removing turbidity

and suspended solids. They found the turbidity removal to be 30 %. When the experiment was repeated with alum and lime combination, the pH increased to 11.6 and turbidity removal increased to 81 % of the original value.

Jesse and Sidney (1971) stated that the pH zone of alum ranges from 5.5 to 7.8 and irons salts have a broader action range of pH 5.5-8.5. However, the pH range of alum and ferric sulfate in this study ranged between 9 to 10 for alum and 9 to 12 for ferric sulfate respectively.

The turbidity removal was poor for polymer with a maximum removal of 20 % as shown in Figure 4.17. This corresponds to high negative values of zeta potential, which indicates the repulsion between particles. The zeta potential value also correlated with the fact that the flocs observed during sedimentation stage were light and fluffy. Hence, it did not settle easily and this caused increased turbidity.

The optimum pH for treatment of wastewater with alum and ferric sulfate is pH 9.

4.2.3 Determination of Optimum Mixing Time

The following experiments were only conducted for metal salts, and coagulant aids were discarded. **Figures 4.18 and 4.19** show the variation on the zeta potential values with variation in the mixing time in the flocculation stage of the wastewater treated with alum and ferric sulfate respectively.

Figure 4.18 shows the variation on the zeta potential values with variation in the mixing time for wastewater treated with 3.0 g/l of alum at pH 9. The zeta potential
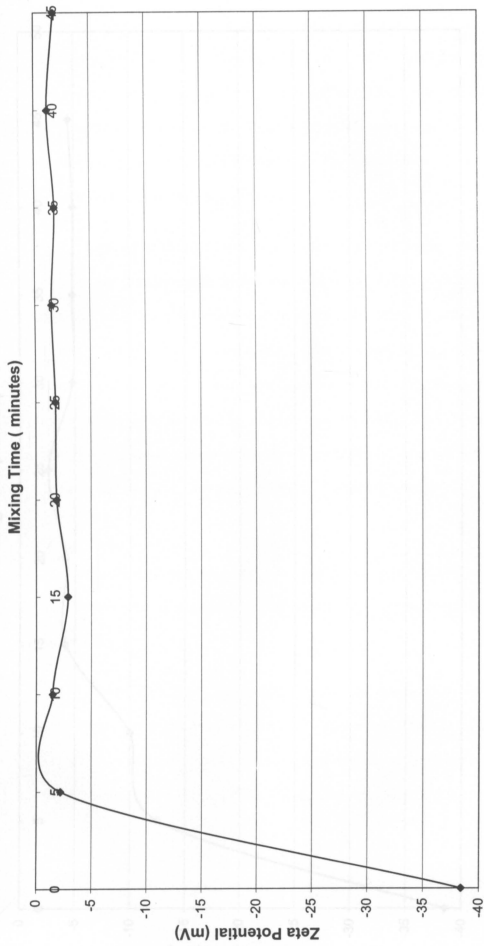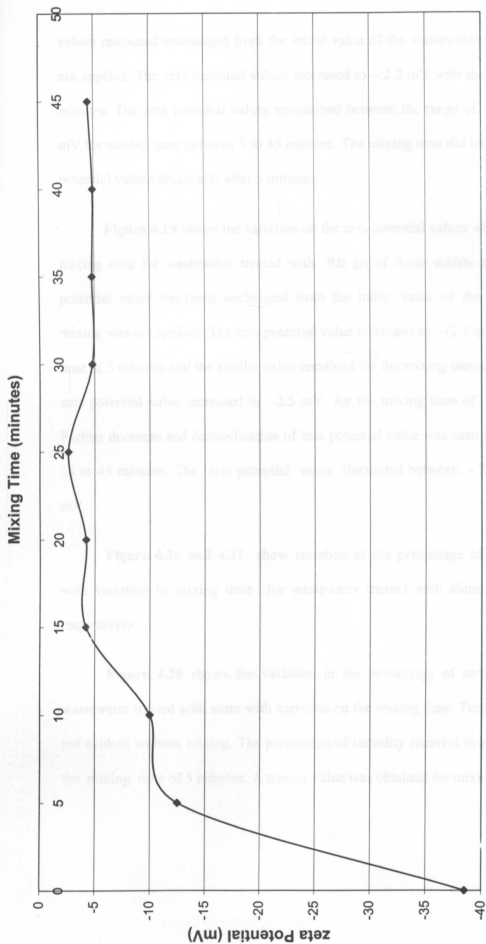
Figure 4.18 : Variation of Zeta Potential Values with Mixing Time of Wastewater Treated with Alum

value remained unchanged from the initial value of the wastewater when mixing was not applied. The zeta potential values increased to – 2.2 mV with the mixing time of 5 minutes. The zeta potential values maintained between the range of – 1.0 mV to – 0.2 mV for mixing time between 5 to 45 minutes. The mixing time did not increase the zeta potential value drastically after 5 minutes.

Figure 4.19 shows the variation on the zeta potential values with variation in the mixing time for wastewater treated with 9.0 g/l of ferric sulfate of pH 5.0. The zeta potential value remained unchanged from the initial value of the wastewater when mixing was not applied. The zeta potential value increased to – 12.5 mV with the mixing time of 5 minutes and the similar value remained for the mixing time of 10 minutes. The zeta potential value increased to – 2.5 mV for the mixing time of 12 minutes. There was a decrease and destabilization of zeta potential value was seen for mixing time of 15 to 45 minutes. The zeta potential value fluctuated between – 2.8 mV to – 5.0 mV.

Figure 4.20 and 4.21 show variation of the percentage of turbidity removal with variation in mixing time for wastewater treated with alum and ferric sulfate respectively.

Figure 4.20 shows the variation in the percentage of turbidity removal for wastewater treated with alum with variation on the mixing time. Turbidity removal was not evident without mixing. The percentage of turbidity removal increased to 70 % for the mixing time of 5 minutes. A similar value was obtained for mixing time of 10 to 15

Figure 4.19 : Variation of Zeta Potential Values with Mixing Time of Wastewater Treated with Ferric Sulfate

values remained unchanged from the initial value of the wastewater when mixing was not applied. The zeta potential values increased to – 2.2 mV with the mixing time of 5 minutes. The zeta potential values maintained between the range of – 3.0 mV to – 0.5 mV for mixing time between 5 to 45 minutes. The mixing time did not increase the zeta potential values drastically after 5 minutes.

Figure 4.19 shows the variation on the zeta potential values with variation in the mixing time for wastewater treated with 9.0 g/l of ferric sulfate at pH 9. The zeta potential value remained unchanged from the initial value of the wastewater when mixing was not applied. The zeta potential value increased to -12.5 mV with the mixing time of 5 minutes and the similar value remained for the mixing time of 10 minutes. The zeta potential value increased to -2.5 mV for the mixing time of 15 to 25 minutes. Further decrease and destabilization of zeta potential value was seen for mixing time of 25 to 45 minutes. The zeta potential value fluctuated between - 2.5 mV to - 5.0 mV.

Figure 4.20 and 4.21 show variation of the percentage of turbidity removal with variation in mixing time for wastewater treated with alum and ferric sulfate respectively.

Figure 4.20 shows the variation in the percentage of turbidity removal for wastewater treated with alum with variation on the mixing time. Turbidity removal was not evident without mixing. The percentage of turbidity removal increased to 70 % for the mixing time of 5 minutes. A similar value was obtained for mixing time of 10 to 15
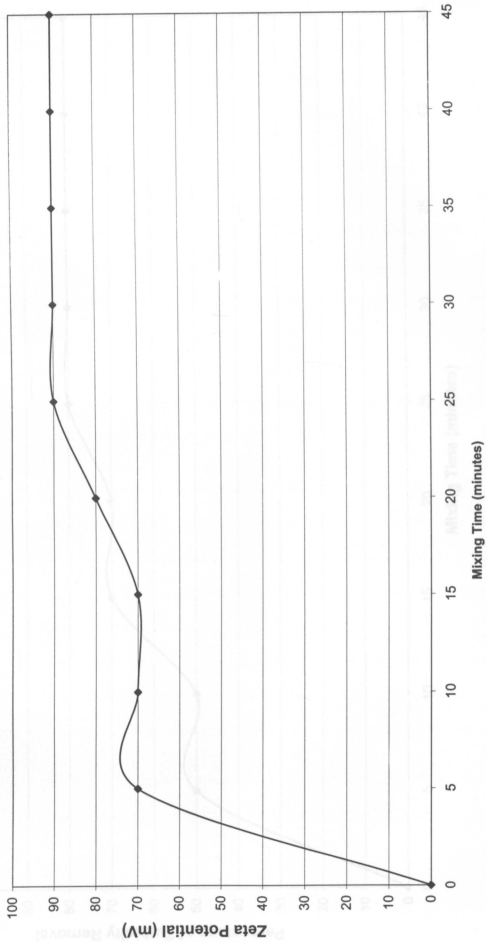
Figure 4.20 : Variation of Percentage of Turbidity Removal with Mixing Time of Wastewater Treated with Alum
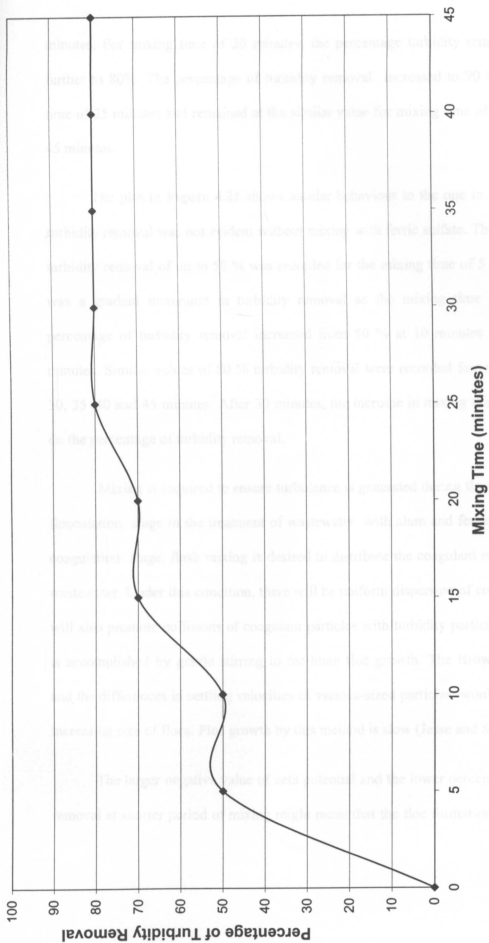
Figure 4.21 : Variation of Percentage of Turbidity Removal with Mixing Time of Wastewater Treated with Ferric Sulfate

minutes. For mixing time of 20 minutes, the percentage turbidity removal increased further to 80%. The percentage of turbidity removal increased to 90 % with mixing time of 25 minutes and remained at the similar value for mixing time of 30, 35, 40 and 45 minutes.

The plot in **Figure 4.21** shows similar behaviour to the one in **Figure 4.20** as turbidity removal was not evident without mixing with ferric sulfate. The percentage of turbidity removal of up to 50 % was recorded for the mixing time of 5 minutes. There was a gradual increment in turbidity removal as the mixing time increased. The percentage of turbidity removal increased from 50 % at 10 minutes to 80 % at 25 minutes. Similar values of 80 % turbidity removal were recorded for mixing times of 30, 35 ,40 and 45 minutes. After 30 minutes, the increase in mixing time had no effect on the percentage of turbidity removal.

Mixing is required to ensure turbulence is generated during the coagulation and flocculation stage in the treatment of wastewater with alum and ferric sulfate. In the coagulation stage, flash mixing is desired to distribute the coagulant effectively to the wastewater. Under this condition, there will be uniform dispersion of coagulant and this will also promote collisions of coagulant particles with turbidity particles. Flocculation is accomplished by gentle stirring to facilitate floc growth. The Brownian movement and the differences in settling velocities of various-sized particles would result in ever-increasing size of flocs. Floc growth by this method is slow (Jesse and Sidney, 1971).

The larger negative value of zeta potential and the lower percentage of turbidity removal at shorter period of mixing might mean that the floc formation might have not

reached optimum size. Hence, residual particles of coagulant and wastewater particles remain in the wastewater for mixing times shorter than 25 minutes for wastewater treated with alum and ferric sulfate (Treweek and Morgan , 1979).

In this study, the optimum floc growth time to produce optimum settleable floc was 25 minutes for alum and ferric sulfate. The percentage of turbidity removal neither improved nor reduced with flocculation time of more than 25 minutes.

The optimum mixing time for the treatment of wastewater with alum and feric sulfate was 25 minutes. Detention time of 30 to 60 minutes is generally adequate to produce flocs that will settle in a reasonable time (Jesse and Sidney, 1971).

4.2.4 Determination of Optimum Mixing Intensity

Figure 4.22 and Figure 4.23 show the variation of the zeta potential values with mixing intensity at the flocculation stage of the wastewater treated with alum and ferric sulfate respectively.

Figure 4.22 shows the variation of the zeta potential values with mixing intensity for wastewater treated with 3.0 g/l of alum at pH 9 and employing a mixing time of 25 minutes. The zeta potential values remained unchanged when mixing was not applied. When mixing was employed at 10 rpm, there was an increase in the zeta potential from -38 mV to –2.9 mV. At 20 rpm, the value further increased to -1.7 mV. The zeta potential values fluctuated between –1.7 mV to – 1.0 mV for mixing intensities of 30, 40, 50 and 60 rpm.
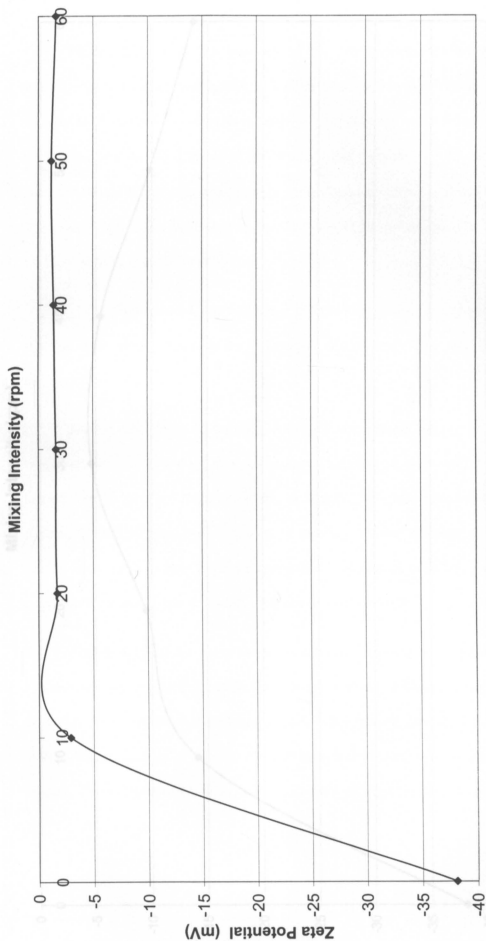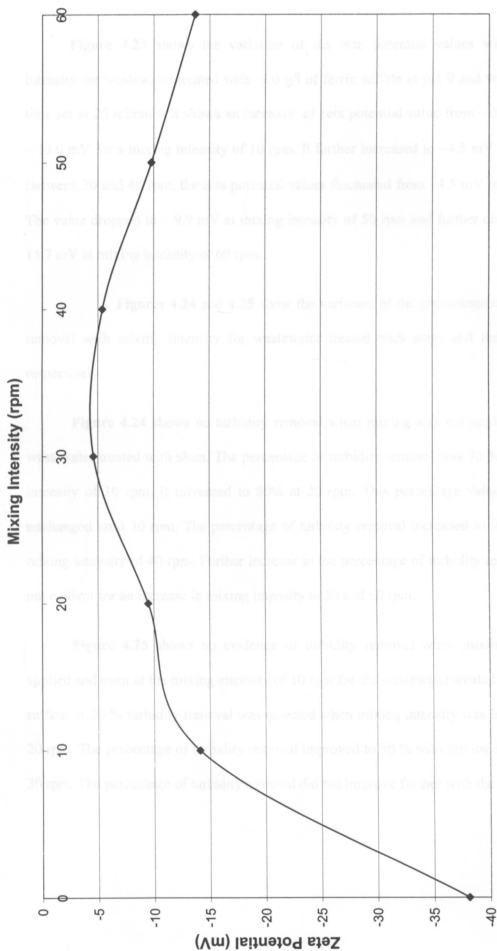
Figure 4.22 : Variation of Zeta Potential Values with Mixing Intensity of Wastewater Treated with Alum

Figure 4.23 : Variation of Zeta Potential Values with Mixing Intensity of Wastewater Treated with Ferric Sulfate

Figure 4.23 shows the variation of the zeta potential values with mixing intensity for wastewater treated with 9.0 g/l of ferric sulfate at pH 9 and with mixing time set at 25 minutes. It shows an increase of zeta potential value from – 38.0 mV to – 13.0 mV for a mixing intensity of 10 rpm. It further increased to –4.5 mV at 30 rpm. Between 30 and 40 rpm, the zeta potential values fluctuated from –4.5 mV to –5.5 mV. The value dropped to – 9.9 mV at mixing intensity of 50 rpm and further dropped to – 13.7 mV at mixing intensity of 60 rpm.

Figures 4.24 and **4.25** show the variation of the percentage of turbidity removal with mixing intensity for wastewater treated with alum and ferric sulfate respectively.

Figure 4.24 shows no turbidity removal when mixing was not applied for the wastewater treated with alum. The percentage of turbidity removal was 70 % at mixing intensity of 10 rpm. It increased to 80% at 20 rpm. This percentage value remained unchanged until 30 rpm. The percentage of turbidity removal increased to 90 % at the mixing intensity of 40 rpm. Further increase in the percentage of turbidity removal was not evident for an increase in mixing intensity to 50 and 60 rpm.

Figure 4.25 shows no evidence of turbidity removal when mixing was not applied and even at the mixing intensity of 10 rpm for the wastewater treated with ferric sulfate. A 20 % turbidity removal was detected when mixing intensity was increased to 20 rpm. The percentage of turbidity removal improved to 80 % with mixing intensity of 30 rpm. The percentage of turbidity removal did not improve further with the increase in
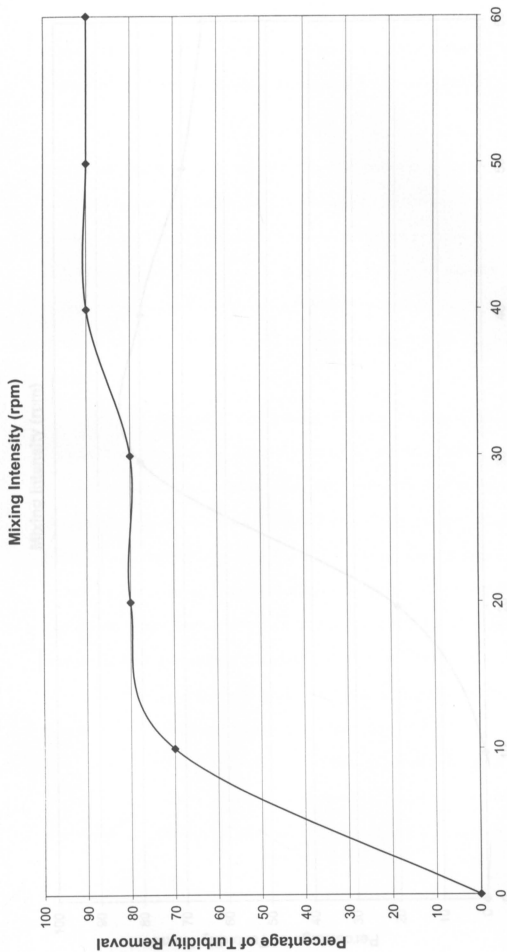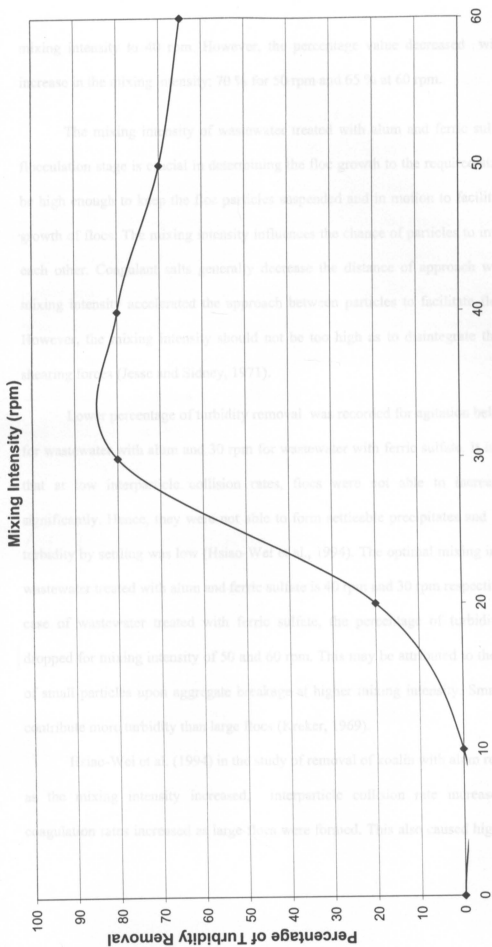
Figure 4.24: Variation of Percentage of Turbidity Removal with Mixing Intensity of Wastewater Treated with Alum

mixing intensity to 30 rpm. However, the percentage value increased with further increase in the mixing intensity; 70 % for 50 rpm and 65 % at 60 rpm.

The mixing intensity of wastewater treated with alum and ferric sulfate at the flocculation stage is crucial in determining the floc growth to the required size. It must be high enough to keep the fine particles suspended and in motion to facilitate further growth of flocs. The mixing intensity influences the chance of particles to interact with each other. Coagulant with intensity decrease the distance of approach while high mixing intensity accelerated the approach between particles to facilitate collision. However, the mixing intensity should not be too high as to disintegrate the flocs after the formation (Jiao and Snoeyink, 1971).

Lower percentage of turbidity removal was recorded for turbidity below 30 rpm for the wastewater with alum and 30 rpm for wastewater with ferric sulfate. This is at low mixing intensity. At low mixing intensity, flocs were not able to increase in size significantly. Flocs may not be able to form sizeable precipitates and were not able to be removed by settling was low (Hsiao-Wen et al., 1999). The optimal mixing intensity for wastewater treated with alum and ferric sulfate is at 30 rpm and 30 rpm respectively. In the case of wastewater treated with ferric sulfate, the percentage of turbidity removal dropped the mixing intensity of 50 and 60 rpm. This may be attributed to the breakage of small particles upon aggregate breakage at higher mixing intensity. Small particles contribute more turbidity than large flocs (Hendler, 1999).

Hsiao-Wen et al. (1999) in the study of removal of kaolin with alum reported that as the mixing intensity increased, interparticle collision rate increased. Hence, coagulation rate increased as large flocs were formed. This also caused higher settling

Figure 4.25 : Variation of Percentage of Turbidity Removal with Mixing Intensity of Wastewater Treated with Ferric Sulfate

mixing intensity to 40 rpm. However, the percentage value decreased with further increase in the mixing intensity; 70 % for 50 rpm and 65 % at 60 rpm.

The mixing intensity of wastewater treated with alum and ferric sulfate at the flocculation stage is crucial in determining the floc growth to the required size. It must be high enough to keep the floc particles suspended and in motion to facilitate further growth of flocs. The mixing intensity influences the chance of particles to interact with each other. Coagulant salts generally decrease the distance of approach whereas the mixing intensity accelerated the approach between particles to facilitate floc growth. However, the mixing intensity should not be too high as to disintegrate the flocs by shearing forces (Jesse and Sidney, 1971).

Lower percentage of turbidity removal was recorded for agitation below 40 rpm for wastewater with alum and 30 rpm for wastewater with ferric sulfate. It is suggested that at low interparticle collision rates, flocs were not able to increase in size significantly. Hence, they were not able to form settleable precipitates and removal of turbidity by settling was low (Hsiao-Wei et al., 1994). The optimal mixing intensity for wastewater treated with alum and ferric sulfate is 40 rpm and 30 rpm respectively. In the case of wastewater treated with ferric sulfate, the percentage of turbidity removal dropped for mixing intensity of 50 and 60 rpm. This may be attributed to the formation of small particles upon aggregate breakage at higher mixing intensity. Small particles contribute more turbidity than large flocs (Kreker, 1969).

Hsiao-Wei et al. (1994) in the study of removal of koalin with alum reported that as the mixing intensity increased, interparticle collision rate increased. Hence, coagulation rates increased as large flocs were formed. This also caused higher settling

rates and lower residual turbidity. However, they also observed that mixing intensity had a constrained working range. At values above this range, an increase in turbidity caused breakage or destabilization of flocs. They also reported that the working range of mixing intensity can be correlated to the dosage of coagulant used. The limitation of mixing intensity for kaolin treated with 72 μm and 96 μm alum was 57 s^{-1} and 26 s^{-1}, respectively. The koalin treated with lower dosage of alum had a higher limitation range of mixing intensity values. The findings were similar to the results obtained from the present study. The wastewater treated with 3.0 g/l of alum did not show destabilization of flocs at mixing intensities of 50 rpm or 60 rpm. However, the wastewater treated with 9.0 g/l of ferric sulfate showed destabilization of flocs at 50 rpm and 60 rpm. Hence, it is concluded that the dosage of coagulant used has an influence on the effective working range of mixing intensity.

The optimum mixing intensity can be taken as 30 rpm for both alum and ferric sulfate.

4.2.5 Determination of Optimum Settling Time.

Figures 4.26 and 4.27 show the variation on the zeta potential values with settling time for the wastewater treated with alum and ferric sulfate respectively.

Figure 4.26 shows the variation of the zeta potential values with settling time for wastewater treated with 3.0 g/l of alum at pH 9 and with mixing time of 25 minutes at 30 rpm. The zeta potential value was –24.0 mV at 10 minutes of settling time. The zeta potential value improved to -15.0 mV at 20 minutes. It showed further increase
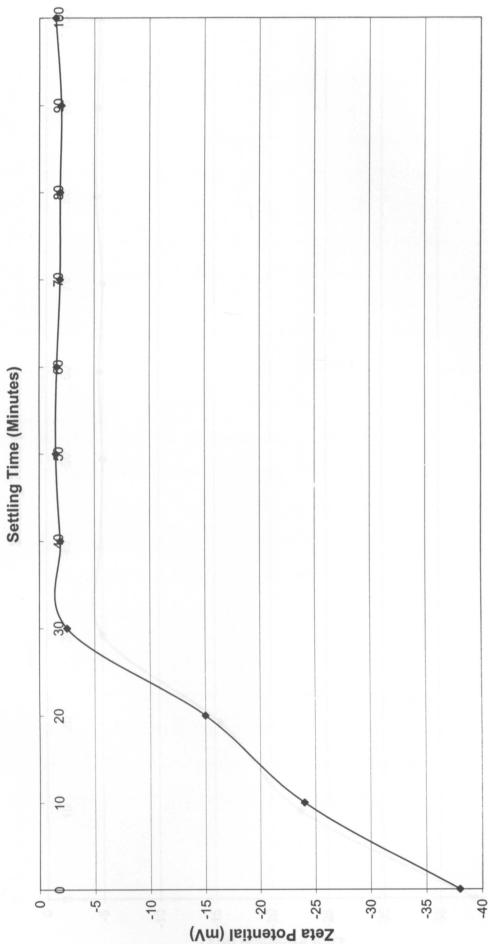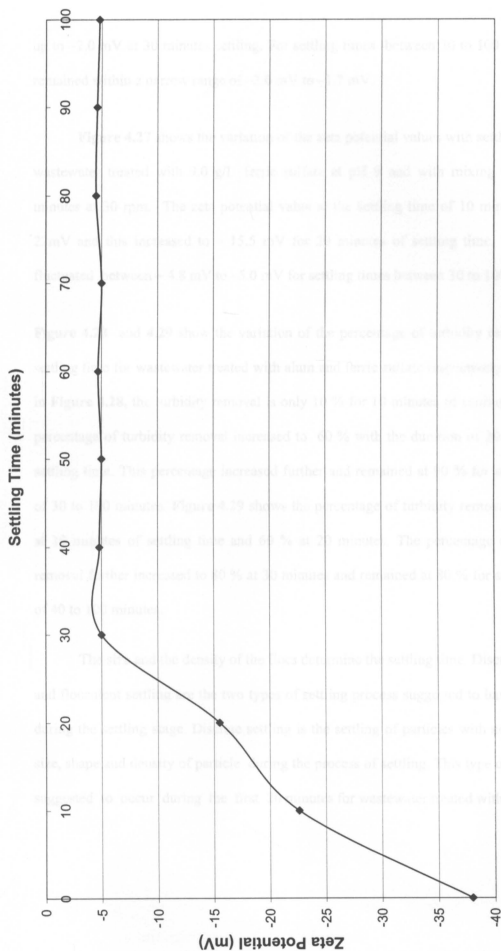
Figure 4.26 : Variation of The Zeta Potential Values with Settling Time of Wastewater Treated with Alum

Figure 4.27 : Variation of Zeta Potential Values with The Settling Time of Wastewater Treated with Ferric Sulfate

up to –2.0 mV at 30 minutes settling. For settling times between 30 to 100 minutes, it remained within a narrow range of –2.0 mV to –1.7 mV.

Figure 4.27 shows the variation of the zeta potential values with settling time of wastewater treated with 9.0 g/l ferric sulfate at pH 9 and with mixing time of 25 minutes at 30 rpm. The zeta potential value at the settling time of 10 minutes was – 22mV and this increased to – 15.5 mV for 20 minutes of settling time. The values fluctuated between – 4.8 mV to –5.0 mV for settling times between 30 to 100 minutes.

Figure 4.28 and **4.29** show the variation of the percentage of turbidity removal with settling time for wastewater treated with alum and ferric sulfate respectively. As shown in **Figure 4.28,** the turbidity removal is only 10 % for 10 minutes of settling time. The percentage of turbidity removal increased to 60 % with the duration of 20 minutes of settling time. This percentage increased further and remained at 90 % for settling time of 30 to 100 minutes. **Figure 4.29** shows the percentage of turbidity removal was 10% at 10 minutes of settling time and 60 % at 20 minutes. The percentage of turbidity removal further increased to 80 % at 30 minutes and remained at 80 % for settling time of 40 to 100 minutes.

The size and the density of the flocs determine the settling time. Discrete settling and flocculent settling are the two types of settling process suggested to have occurred during the settling stage. Discrete settling is the settling of particles with no change in size, shape and density of particle during the process of settling. This type of settling is suggested to occur during the first 20 minutes for wastewater treated with alum and
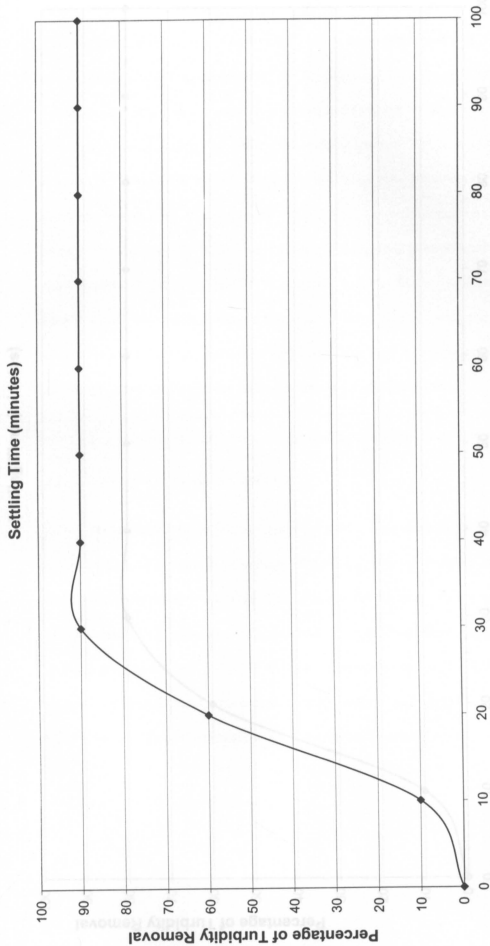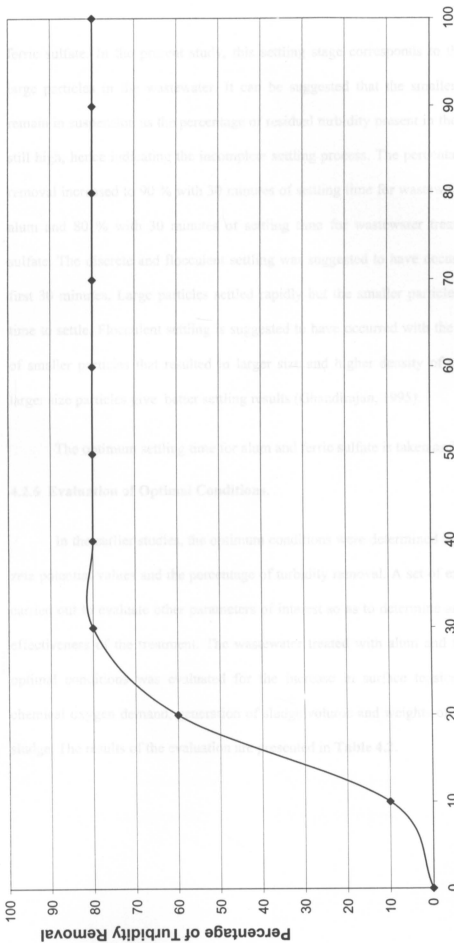
Figure 4.28 : Variation of Percentage of Turbidity Removal with Settling Time of Wastewater Treated with Alum

Figure 4.29 : Variation of Percentage of Turbidity Removal with Settling Time of Wastewater Treated with Ferric Sulfate

ferric sulfate. In the present study, this settling stage corresponds to the presence of large particles in the wastewater. It can be suggested that the smaller particles still remain in suspension as the percentage of residual turbidity present in the wastewater is still high, hence indicating the incomplete settling process. The percentage of turbidity removal increased to 90 % with 30 minutes of settling time for wastewater treated with alum and 80 % with 30 minutes of settling time for wastewater treated with ferric sulfate. The discrete and flocculent settling was suggested to have occurred during the first 30 minutes. Large particles settled rapidly but the smaller particles needed more time to settle. Flocculent settling is suggested to have occurred with the agglomeration of smaller particles that resulted in larger size and higher density of particles. These larger size particles give better settling results (Ghandirajan, 1995).

The optimum settling time for alum and ferric sulfate is taken as 30 minutes.

4.2.6 Evaluation of Optimal Conditions.

In the earlier studies, the optimum conditions were determined by evaluating the zeta potential values and the percentage of turbidity removal. A set of experiments was carried out to evaluate other parameters of interest so as to determine and compare the effectiveness of the treatment. The wastewater treated with alum and ferric sulfate at optimal conditions was evaluated for the increase in surface tension, reduction of chemical oxygen demand, generation of sludge volume and weights of solid present in sludge. The results of the evaluation are presented in **Table 4.2.**

Table 4.2: Evaluation of Results of Wastewater Treated with Alum and Ferric Sulfate at Optimal Conditions.

	Initial Values	Treatment with alum	Treatment with Ferric Sulfate
Zeta Potential (mV)	- 37.5	-1.7	-4.8
Percentage of Turbidity Removal (%)	0	90	80
Surface Tension (dynes/cm)	31.0	67.3	65.1
Chemical Oxygen Demand (mg/l)	27000	5800	6700
Sludge Volume (ml/l)	0	190	150
Weights of Solids in Sludge (mg/l)	0	66.5	55.6

The surface tension values recorded suggested that the removal of surfactant by treatment with alum was better than the treatment using ferric sulfate. The percentage of reduction of chemical oxygen demand recorded for wastewater treated with alum and ferric sulfate was 78.5 % and 74.8 %, respectively. The sludge volume and the weight of solids generated from the treatment of wastewater with alum was higher than the values recorded for ferric sulfate. Hence, it can be concluded that the wastewater treated with alum gave better results than that treated with ferric sulfate.

In addition, the use of alum had a further advantage because the dosage is only 3.0 g/l which was approximately three times less than the amount for ferric sulfate. This

means, there will be lesser requirements for inventory, storage and sludge disposal in the process of the running of the plant.

4.2.7 Double Chemical Treatment

The experiments for the treatment of wastewater with coagulant and coagulant aids were carried out with alum as the preferred coagulant and polyethyeleninime was selected as the coagulant aid. Optimal conditions as determined for the experiments using alum (refer to Sections 4.2.1, 4.2.2.,4.2.3., 4.2.4. and 4.2.5) were used. The results are as tabulated in **Table 4.3** and these are compared with the results for wastewater treatment with alum in **Section 4.2.6.**

In comparing the results obtained from single chemical treatment with alum and double chemical treatment with alum and polyethylenimine, it can be concluded that the double chemical treatment was more effective. The zeta potential value improved to – 0.9 mV, moving even closer to zero value. The percentage of turbidity removal further increased from 90 % from single chemical treatment to 94 % for double chemical treatment. The removal of surfactant exhibited improvement as the value of the surface tension increased from 67.3 to 68.2 dynes / cm with double chemical treatment. The percentage of reduction of chemical oxygen demand showed improvement as the percentage increased from 78.2% to 87 %. The sludge volume and the weight of solids generated from the treatment of wastewater with double chemical treatment was higher than the values recorded with single chemical treatment.

Table 4.3 : Results after Double Chemical Treatment of Wastewater

Parameter	Initial Values	Treatment with Alum	Treatment with Alum and Polyethylenimine
Zeta Potential (mV)	-36.2	-1.7	-0.9
Percentage of Turbidity Removal	0	90	94
Surface Tension (dynes/cm)	31.0	67.3	68.2
Chemical Oxygen Demand (mg/l)	27000	5800	3500
Sludge Volume (ml/l)	0	90	94
Weight of solids in sludge (mg/l)	0	66.3	75.2
Suspended Solids (mg/l)	15000	4300	2000

The improvement in the treatment with double chemical treatment suggest that alum is essential for flocculation process as it promotes formation of micro-flocs on which the coagulant aid such as polyethylenimine is able to absorb on; hence increasing the floc size to facilitate better settlement. This suggestion is complemented by the results of Kruize (1981) and Chin et al. (1997). Kruize (1981) stated that polyelectrolytes were used to increase the radius of the flocs and to make the flocs more compact and readily settable. Chin et al. (1997) in the study of sludge dewatering with polymer dosage added that the polymer toughened the flocs and increased the density of

the flocs. The other consideration was the high molecular weight of polymers. The increased efficiency obtained with treatment with polyelectrolytes may be due, at least in part, to the generation of the high density particles and therefore increased settling agglomerates (Letterman and Prasit, 1982). It was also suggested that the possibility of formation of a salt-bridge between polymer and clay, accelerated floc formation (Kruize, 1981).
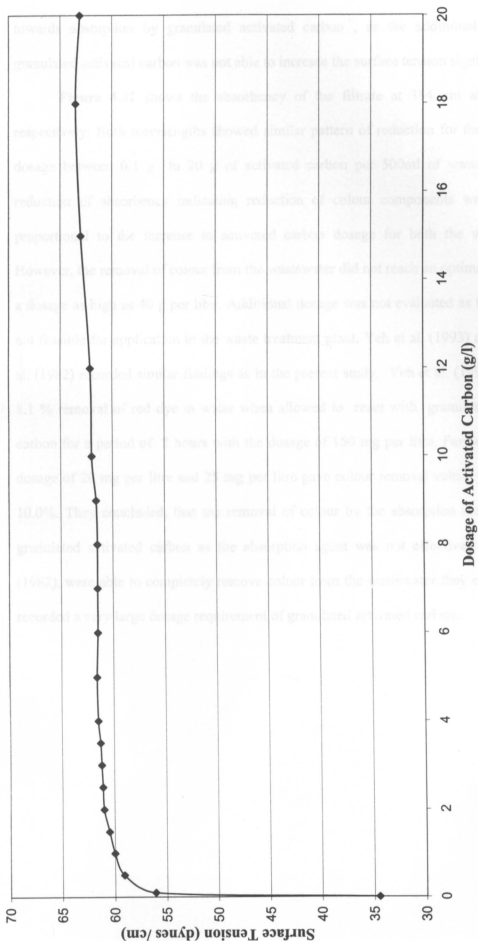
Charge neutralization is also a dominant factor that should be taken into consideration. Polyethylenimine is a cationic polymer and the wastewater was negatively charged. The addition of polyethylenimine shifted the zeta potential values from -1.7 mV to -0.9 mV, moving even closer to zero value. This suggests further reduction of the double layer repulsion, hence enhancing aggregation of particles to form flocs and facilitated settlement (Letterman and Prasit, 1982).

Treatment with alum and polyethyelenimine is more effective than treatment with alum without coagulant aids.

4.3 Adsorption Studies

Activated carbon has been reported by several researchers as an effective absorption agent with respect to the reduction of chemical oxygen demand, color component and surfactants in the process of treating wastewater.(Nabil, 1998; Srimurali et al., 1998; Gharaibeh et al., 1998). This study was conducted to determine the performance of granulated activated carbon in the wastewater with respect to the removal of color and reduction of surfactant, indicated by the reduction of surface tension value.

The surface tension reading is an indicator of the presence of surfactants, as surfactants reduce the surface tension of water. Yamaguchi and Hoffman (1997), reported that increased concentration of various surfactants, such as Zwitterionic surfactant (tetradecldimethlamine oxide), cationic surfantant (tetradecyltrimethylamine ammonium bromide) and nonionic surfactants reduced the surface tension of water. The surface tension reading of distilled water was determined as 72.5 dynes/cm and the initial wastewater surface tension value was 34.5 dynes/cm. **Figure 4.30** shows the changes in surface tension values with the concentration of granulated activated carbon dose. The surface tension values showed a drastic increase for absorbent dosage of 0.1g per 500 ml of wastewater, that is from 34.5 dynes/cm to 56.1 dynes/cm. Further increase in absorbent did not show significant changes in the surface tension values. The values maintained from 60 dynes/cm to 63.1 dynes/cm for the range of dosage of 0.2 to 20 g. A minimal dosage of 0.1 g/l of activated carbon was the effective dosage for the removal of surfactants from the wastewater in the present study. Additional increase in dosage did not show significant results. Atsuko et al. (1990) stated activated carbon showed variation in absorption efficiency for different surfactants. They recorded findings of reduction of anionic and nonionic surfactants when allowed to react with activated carbon for absorption. They stated that the anionic and nonionic surfactant removal efficiency by activated carbon absorption was 67.45% and 31.7%, respectively , with a dosage of 150 mg of activated carbon per litre of wastewater. The optimal dosage in the present study was 200 mg (0.2 g) of activated carbon per litre of wastewater. However, the surface tension readings indicated the presence of surfactants in the wastewater. It can be suggested that the remaining surfactants exhibited resistance

towards adsorption by granulated activated carbon , as the increased dosage of granulated activated carbon was not able to increase the surface tension significantly.

Figure 4.30 shows the absorbency of the filtrate at ...., ... and ... nm respectively. three samples give toward similar pattern of reduction for the absorption dosage between 0.1 g/l to 20 g of activated carbon per 500ml of wastewater. The reduction of absorbance, indicating reduction of colour component was generally proportional to the increase in activated carbon dosage for both the wavelengths. However the removal of colour from the wastewater did not reach a minimal residual with a dosage as high as 20 g per litre. Additional dosage was not evaluated as the trial was not feasible in application to the waste treatment plant. Yeh et al. (1993) and Yeh et al. (1985) reported similar findings in the present study. Yeh et al. (1993) reported 6.1 % removal of red dye in water when allowed to react with granulated activated carbon for a period of 48 hours with the dosage of 150 mg per litre. At the lower dosage of 75 mg per litre and 20 mg per litre gave colour removal of 5.50% and 10.0%. They concluded that the removal of colour by the absorption process with granulated activated carbon as the absorption agent was not a viable solution. Yeh et al. (1985) were able to completely remove colour from the wastewater, they reached but recorded a very large dosage requirement of granulated activated carbon.

Figure 4.30 : Variation of Surface Tension of Wastewater with Dosage of Granulated Activated Carbon

towards absorption by granulated activated carbon , as the additional dosage of granulated activated carbon was not able to increase the surface tension significantly.

Figure 4.31 shows the absorbency of the filtrate at 384 nm and 392 nm respectively. Both wavelengths showed similar pattern of reduction for the evaluation dosage between 0.1 g to 20 g of activated carbon per 500ml of wastewater. The reduction of absorbency indicating reduction of colour components was generally proportional to the increase in activated carbon dosage for both the wavelengths. However, the removal of colour from the wastewater did not reach an optimal level with a dosage as high as 40 g per litre. Additional dosage was not evaluated as the cost was not feasible for application in the waste treatment plant. Yeh et al. (1993) and Davis et al. (1982) recorded similar findings as in the present study. Yeh et al. (1993) recorded 8.1 % removal of red dye in water when allowed to react with granulated activated carbon for a period of 2 hours with the dosage of 150 mg per litre. Further additional dosage of 20 mg per litre and 25 mg per litre gave colour removal values of 9.8% and 10.0%. They concluded, that the removal of colour by the absorption technique with granulated activated carbon as the absorption agent was not effective. Davis et al. (1982), were able to completely remove colour from the wastewater they evaluated but recorded a very large dosage requirement of granulated activated carbon.
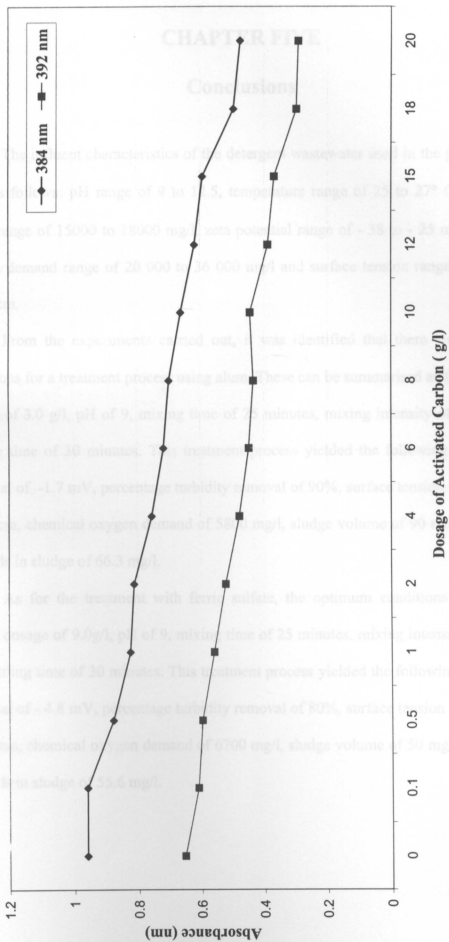
Figure 4.31 : Variation of Absorbance at 384 nm and 392 nm of Wastewater with Dosage of Granulated Activated Carbon