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A Study on the Relative Performance of Different Coagulants and the Kinetics of COD in the Treatment of a Textile Bleaching and Dyeing Industrial Wastewater

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Untreated wastewater from textile industries when discharged to nearby waterways would cause considerable health concerns to humans and animal life and to the host environment. They contain various chemicals such as dyes, detergents and surfactants, some of which are recalcitrant to biodegradation. Such wastewater can be better remediated by chemical treatment.

The treatment of a textile bleaching and dyeing industrial wastewater was done by Coagulation and Flocculation Method using a jar test apparatus. Alum, polyaluminum chloride (PAC), and ferrous sulfate were used in separate runs as coagulants, while excelfloc 264 (a polyacrylamide copolymer) was used as flocculant. Preliminary tests were first conducted to determine the appropriate coagulation and flocculation agitation rates and settling time. The initial pH of the sample effluent was varied from 5 to 8 for alum coagulation, 5 to 8.5 for PAC coagulation and 9 to 11 for ferrous sulfate coagulation. The dosages of each coagulant and the excelfloc were varied from 200 to 1000 ppm, and 0.5 to 2.5 ppm, respectively.

Experimental results showed that the optimum initial pH of the wastewater using alum, PAC, and ferrous sulfate were 7, 7.5, and 10, respectively. The optimum dosages of the coagulants were found to be 600ppm for alum and 800ppm for both PAC, and ferrous sulfate. The optimum flocculant dosages were 1.5ppm with alum, 1 ppm with PAC and 2ppm with ferrous sulfate. The highest percentage removal of COD, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), chromium, and color were found to be 58.55%, 65%, 36.51%, 76.45%, and 78.96%, respectively, using alum: 65.4%, 67.5%, 35.84%, 44.92%, and 75.49%, respectively using PAC; and, 55.72%, 34.16%, 33.95%, 19.88%, and 48.56%, respectively, using ferrous sulfate. Among the three coagulants tried, coagulation with PAC gave the highest percentage of COD removal of 65.64% and TSS removal of 67.5% while alum gave the highest removal of both chromium and color at 76.45% and 94.49%, respectively. Rapid and slow agitation rates used were 240rpm for 1 minute and 40rpm for 20 minutes, respectively; while settling time was 30 minutes.

Kinetics of the COD removal was studied at the optimum conditions. Kinetic model, determined by curve fitting with the coagulation/flocculation reaction, was observed to follow a first-order rate of reaction.

Keywords: Bleaching and dyeing industrial wastewater, performance, coagulants, flocculants, optimum conditions, kinetics

INTRODUCTION

Water pollution becomes an environmental concern when industrial effluents are discharged into the waterways without prior treatment. Wastewater from textile bleaching and dyeing industry is usually characterized by high chemical oxygen demand (COD), sizeable solids, and intense dark color, which can give adverse effects to the host aquatic environment. Such harmful characteristics are due to the dyes, detergents and surfactants the wastewater contains (Alinsafi et al. 2006; Duk Jon Joo et al. 2005; Vera, Vinder, and Simonic 2005; Banat et al. 1996; and, Museyin 2004).

The dyeing process usually gives off strong and dark colored wastewater that contains partially exhausted dyes which contribute to the high levels of COD, solids content, and pH to the host environment. This kind of wastewater is resistant to biodegradation. Such wastewater can be remediated using the chemical treatment method.

Especially in developing countries, where high treatment cost and difficulty in treating the above wastewater is quite a problem, a simple and efficient treatment process for textile wastewater is highly desired. Coagulation and flocculation have been widely used as a primary treatment prior to biological treatment (Metcalf and Eddy 2003) due to their capacity for the effective removal of solids, color, and various chemical compounds in the water (Lorimer et al. 2001).

There are two types of dyeing processes being done in the industry of concern, a plant located in Valenzuela, Bulacan (a province in the central part of Luzon, the largest island in the Philippines) namely: cotton dyeing and polyester dyeing. Reactive dyes are used for cotton dyeing, while dispersed dyes are used in polyester dyeing. Due to the complex structure of the dyes, biodegradability has been ineffective. Therefore, the chemical treatment by coagulation/flocculation is deemed essential.

Although coagulation/flocculation is the suitable chemical treatment process for the textile wastewater, a large amount of sludge can be generated and the treatment capability is dependent on pH as well as on the dosages of coagulant and flocculant (Museyin 2004). Also, since the reactive dyes are recognized as recalcitrant compounds (Vera, Vinder, and Simonic 2005) and the dispersed dyes are not soluble in water, wastewater treatment becomes difficult especially for such an effluent with fluctuating pH, color, metals such as chromium, and low biodegradable organic and inorganic components which contribute to high COD.

The objective of this study was to compare the performance of three coagulants—alum, PAC, and ferrous sulfate—and get the best combination, at the optimum conditions, of an anionic flocculant and cationic coagulant in the treatment of a bleaching-and-dyeing textile wastewater as well as to determine the kinetics of the COD removal at these optimum conditions.

MATERIALS

The coagulants used were analytical grade potassium aluminum sulfate dodecahydrate (alum), industrial grade polyaluminum chloride

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(PAC), and ferrous sulfate ($FeSO_4$. $7H_2O$). Excelfloc 264, an anionic polyacrylamide copolymer was used as flocculant. Concentrated sulfuric acid and analytical grade sodium hydroxide were used for pH adjustment. Whatman glass fiber filter (1.58 μm pore size) was used for total suspended solids (TSS) determination and Gelman filter (0.45 μm pore size) was used for absorbance measurement to determine color removal (Lorimor et al. 2001).

PROCEDURE

Wastewater from a textile bleaching and dyeing industry was first characterized as to pH, COD, total suspended solids (TSS), total dissolved solids (TDS), total solids (TS), color, and chromium (Cr). Preliminary tests were done to determine the appropriate agitation rate, flocculation rate, and settling time duration after flocculation.

Four beakers, each filled with 1000 mL sample of untreated wastewater, were used for each run of jar test. After adjusting the pH of the sample, depending on the type of coagulant, a measured amount of the coagulant was added, and the solution was mixed at the agitation rate of 240 rpm for one minute. Then, a fixed amount of the flocculant was added and the solution was mixed at the slow rate of 40 rpm for 20min. The pH was recorded after coagulation and flocculation. After flocculation, the flocs were left to settle for 30min. The supernatant liquid was analyzed for COD, TSS, TDS, TS, color as well as Cr levels. Then the optimum conditions such as for pH, coagulant dosage, and flocculant dosage were determined.

COD, TSS, TDS, TS, and were determined using the Standard Methods for the Examination of Water and Wastewater Treatment (Clescerl, Greenberg, and Eaton 2003). Color removal was determined by measuring the absorbance of the sample at maximum wavelength, I_{max} = 653nm using UV–visible spectrophotometer (UV-1700).

The effects of agitation rate, agitation time, and settling time were studied due to their influence on the treatment system. The performances of the three coagulants were then compared. Finally, the reaction kinetics of the COD removal at the optimum conditions was determined.

RESULTS AND DISCUSSION

The sample wastewater under study was the effluent discharge collected at a point immediately after the production process of a textile plant in Valenzuela, Bulacan. The characteristics of the dark-blue colored sample were as given in Table 1.

Table 1. Characteristics of the Raw Wastewater

Parameter	Unit	Value
pH	-	12.58–12.14
Chemical Oxygen Demand	ppm	666.48–669.19
Total Suspended Solids	ppm	116–132
Total Dissolved Solids	ppm	3241–33256
Total Solids	ppm	3436–3451
Color ($Abs_{\lambda_{max}=653nm}$)*	cm^{-1}	0.1342–0.1336
Chromium	ppm	0.5336–0.5349

* $Abs_{ë_{max}=653nm}$ means absorbance measurement at maximum wavelength, 653nm

Figures 1 (a) and 1 (b) show the profile of COD concentration at different agitation times during the coagulation and flocculation process. As shown in the graphs, the rates of coagulation and flocculation agitation are important in the treatment process. Although high agitation rate provides kinetic energy to reduce the repulsive force between the colloids prior to charge neutralization, there is a certain limit to allow the destabilization of the colloidal particles. Beyond this limit rapid agitation may allow the restabilization of colloids. Similarly, slow agitation rate should be high enough to ensure an effective homogenization of the flocculant and the pollutants in the wastewater, but low enough not to break the aggregation of flocs. Optimum high agitation rate and slow agitation rate were found to be 240rpm and 40rpm, respectively.

The agitation time is also important (Chichcean Kan et al. 2002) to facilitate good coagulation/flocculation. It should be long enough (20mins.) to get sufficient kinetic energy for the colloidal particles in the wastewater to aggregate. If the agitation time is not sufficient for complete coagulation/flocculation, the colloids will not be able to react with the cationic coagulants such that bridging of flocs by the anionic polymer cannot take place. Figure 2(a) shows that flocculation agitation time should be 20mins. On the other hand, the reduction of COD is also dependent on the settling time as reflected in the graph of Figure 2(b). Although COD decreased significantly during the first 30 minutes of settling time, the figure shows that COD stopped decreasing beyond this time.

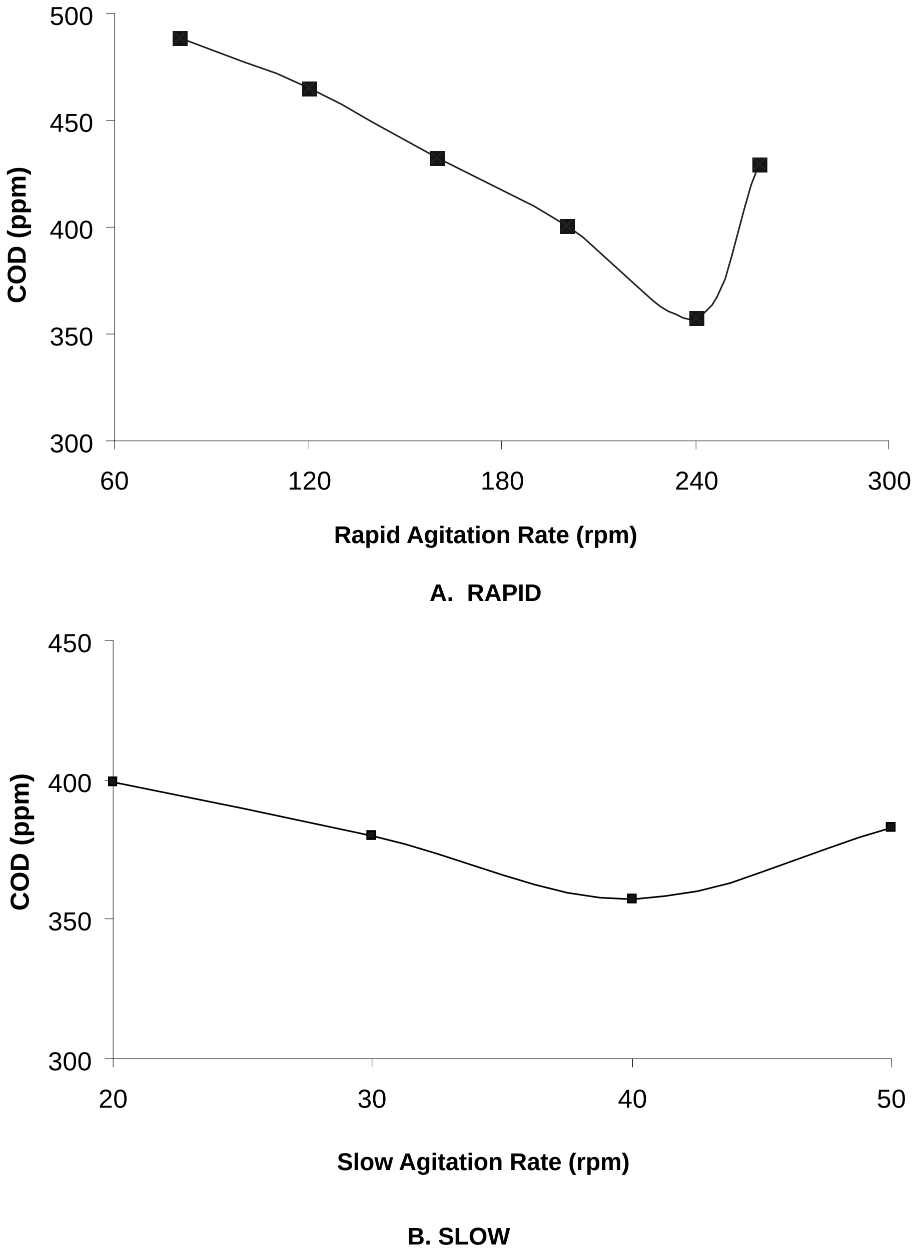
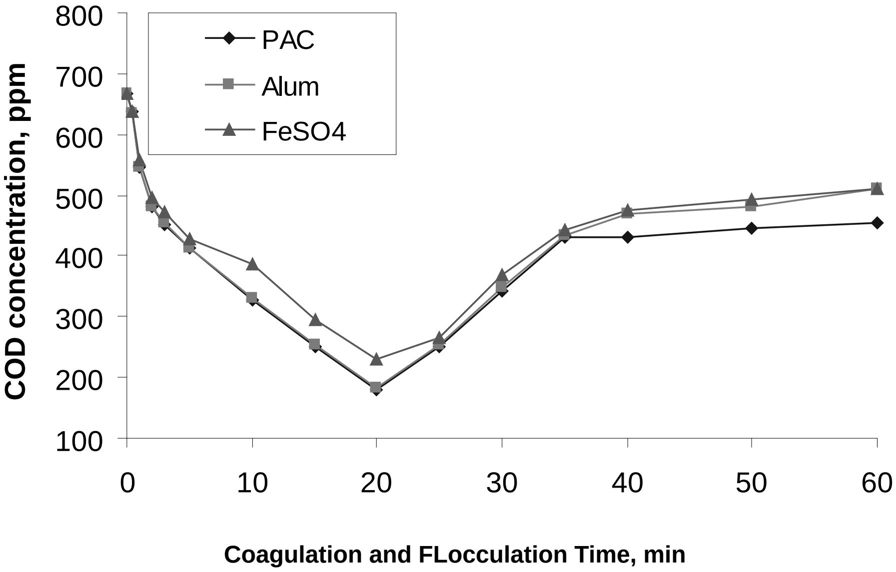


Figure 1. Effect of Agitation Rate



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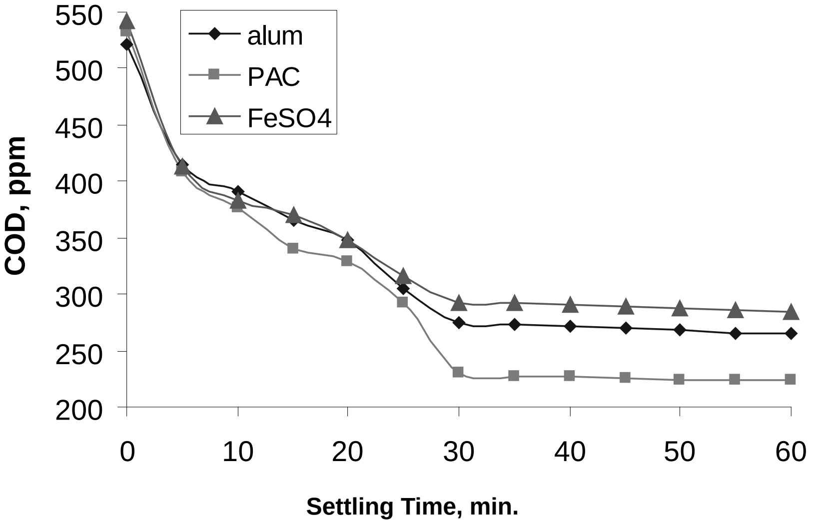

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Figure 2. Effect of Time: (a) Coagulation and Flocculation and (b) Settling

As shown in Figure 2(b), among the three different coagulants used in the study, PAC gave the greatest reduction in COD concentration. Furthermore, it was also observed that the denser flocs formed by PAC settled faster than those by alum and ferrous sulfate.

Using alum and excelfloc, the optimum pH was found at pH 7 whereas the optimum dosages of alum and excelfloc were 600 ppm and 1.5ppm, respectively, with 58.84% removal of COD, 76.45% Cr, 94.49% color removal, 65% removal of TSS, 36.51% of TDS and 37.89% removal of TS as presented in figures 3(a) and 3(b).

The effectiveness of PAC coagulation is reflected in figures 4(a) and 4(b). When PAC and excelfloc were used, good organization of coagulant (PAC) and flocculant (excelfloc) was achieved at the optimum pH of 7.5, using the optimum dosages of 800ppm PAC and 1 ppm of excelfloc with 65.64% COD removal, 44.92% Cr removal, 75.49% color removal, 67.5% TSS removal, 35.84% TDS, and 37.86% TS removal.

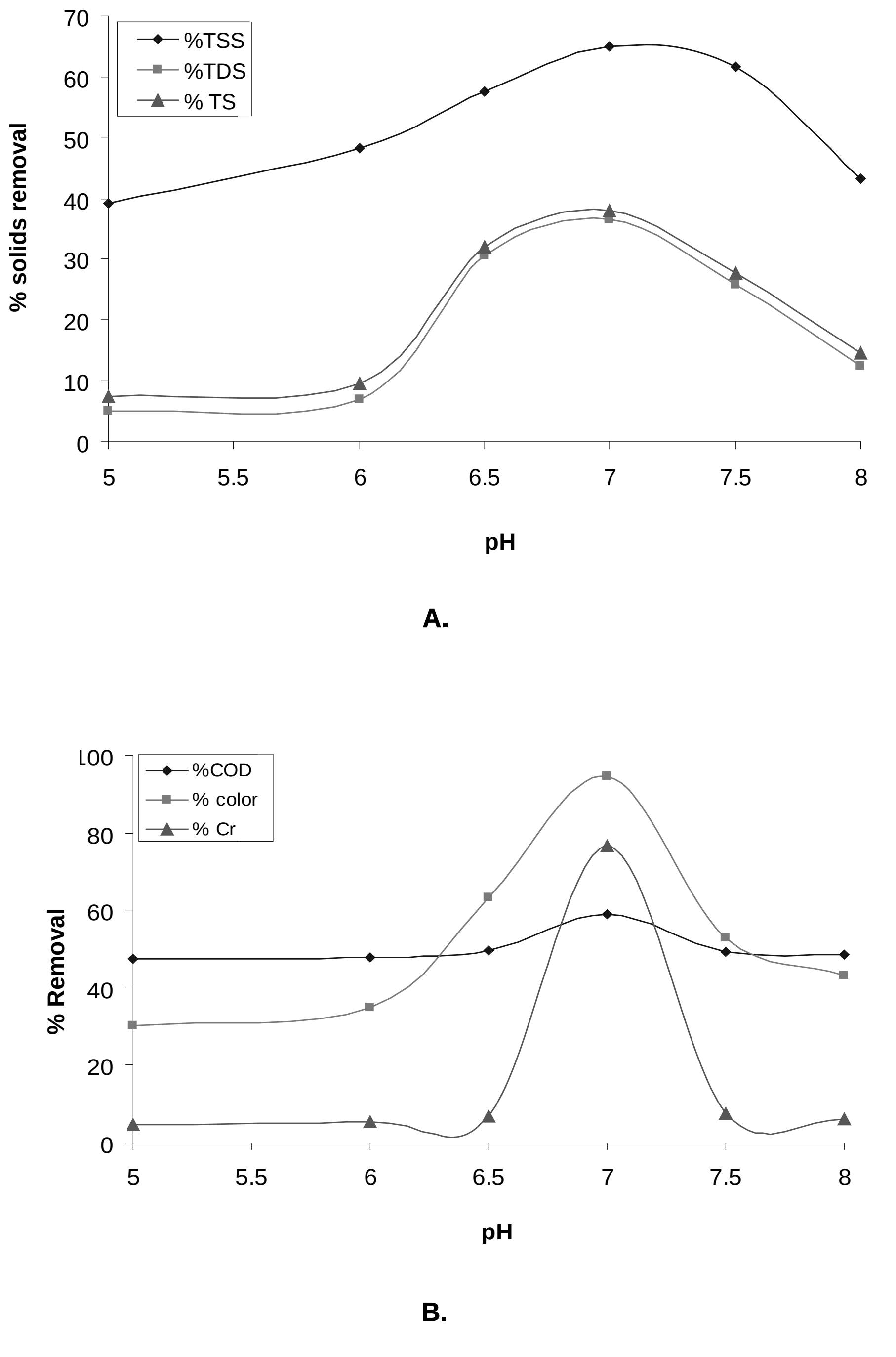
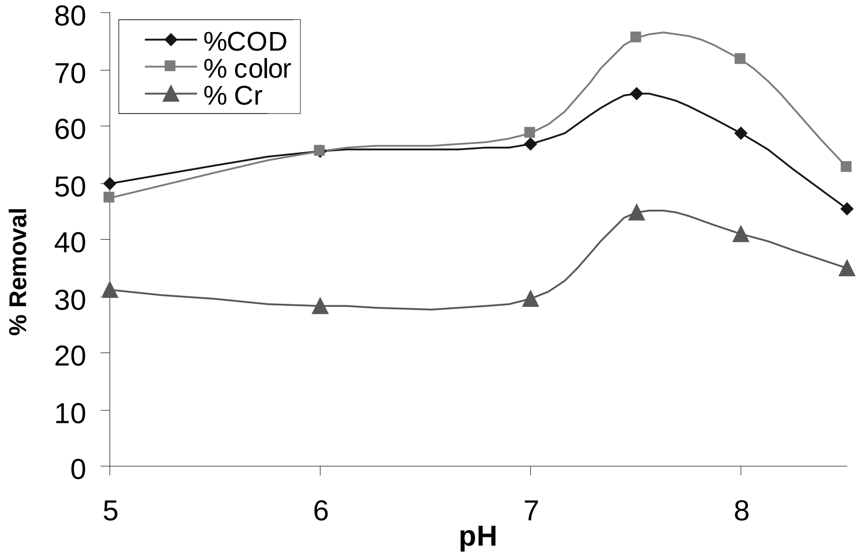


Figure 3. Effect of pH on Percentage (a) Solids Removal and (b) Removal Using Alum (600ppm) and Excelfloc (1.5ppm)



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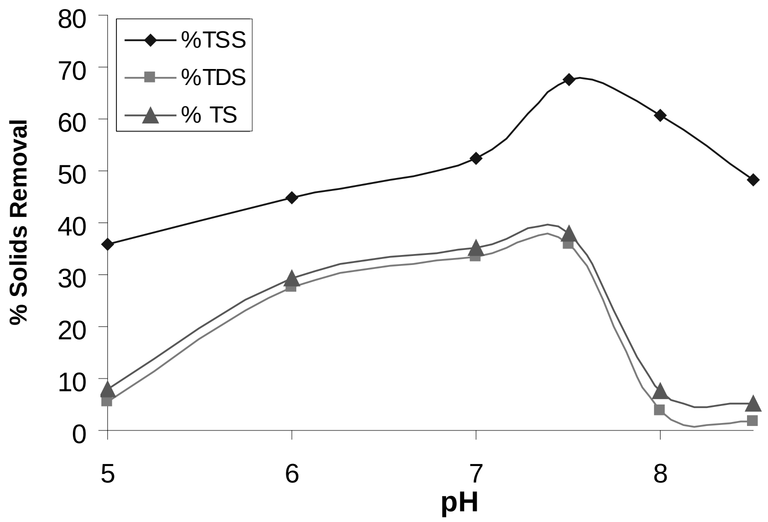

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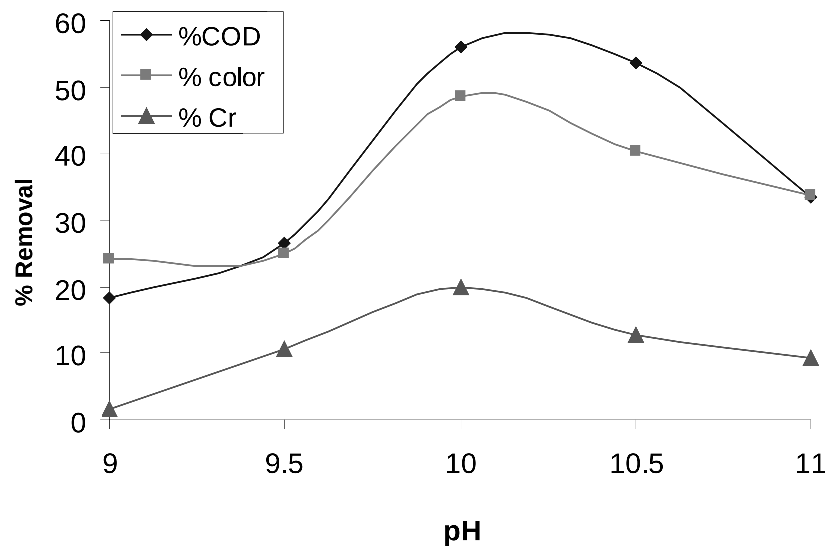
Figure 4. Effect of pH on percentage (a) Removal and (b) Solids Removal Using PAC (800 ppm) and Excelfloc (1ppm)

In the case of coagulation/flocculation by ferrous sulfate and excelfloc, the optimum pH was 10 and the optimum dosages were 800ppm ferrous sulfate and 2ppm excelfloc with 55.72% COD removal, 34.16% TSS removal, 19.88% Cr removal, and 48.56% color removal. As presented in figures 5(a) and 5(b), due to the appearance of brownish yellow color when ferrous sulfate was added to the sample wastewater, the color removal was relatively lower than that with alum and PAC coagulation.



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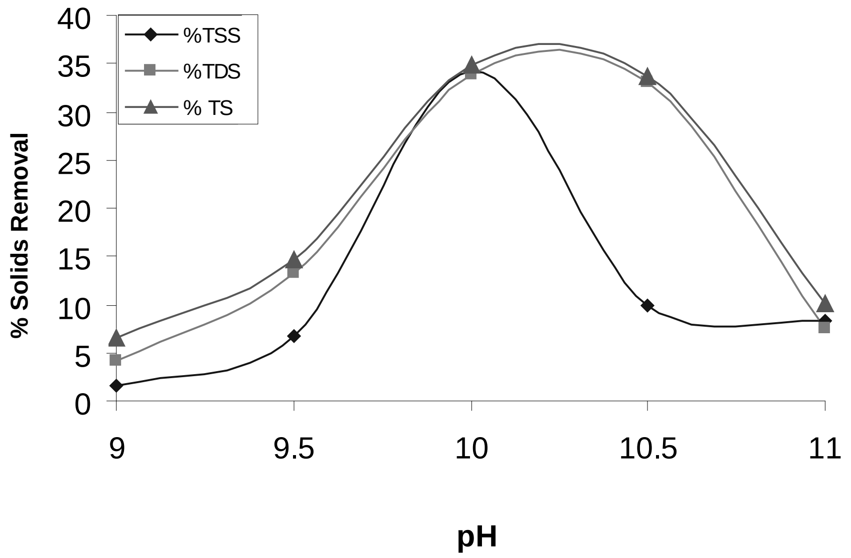

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Figure 5. Effect of pH on Percentage (a) Removal and (b) Solids Removal Using Ferrous Sulfate (800ppm) and excelfloc (2ppm)

The influence of the coagulant and flocculant dosages were investigated in the range of 200 to 1000 ppm (at optimum pH using optimum excelfloc dosage) and 0.5 to 2.5 ppm (at optimum pH using optimum coagulant dosage) respectively, as shown in figures 6(a) and 6(b).

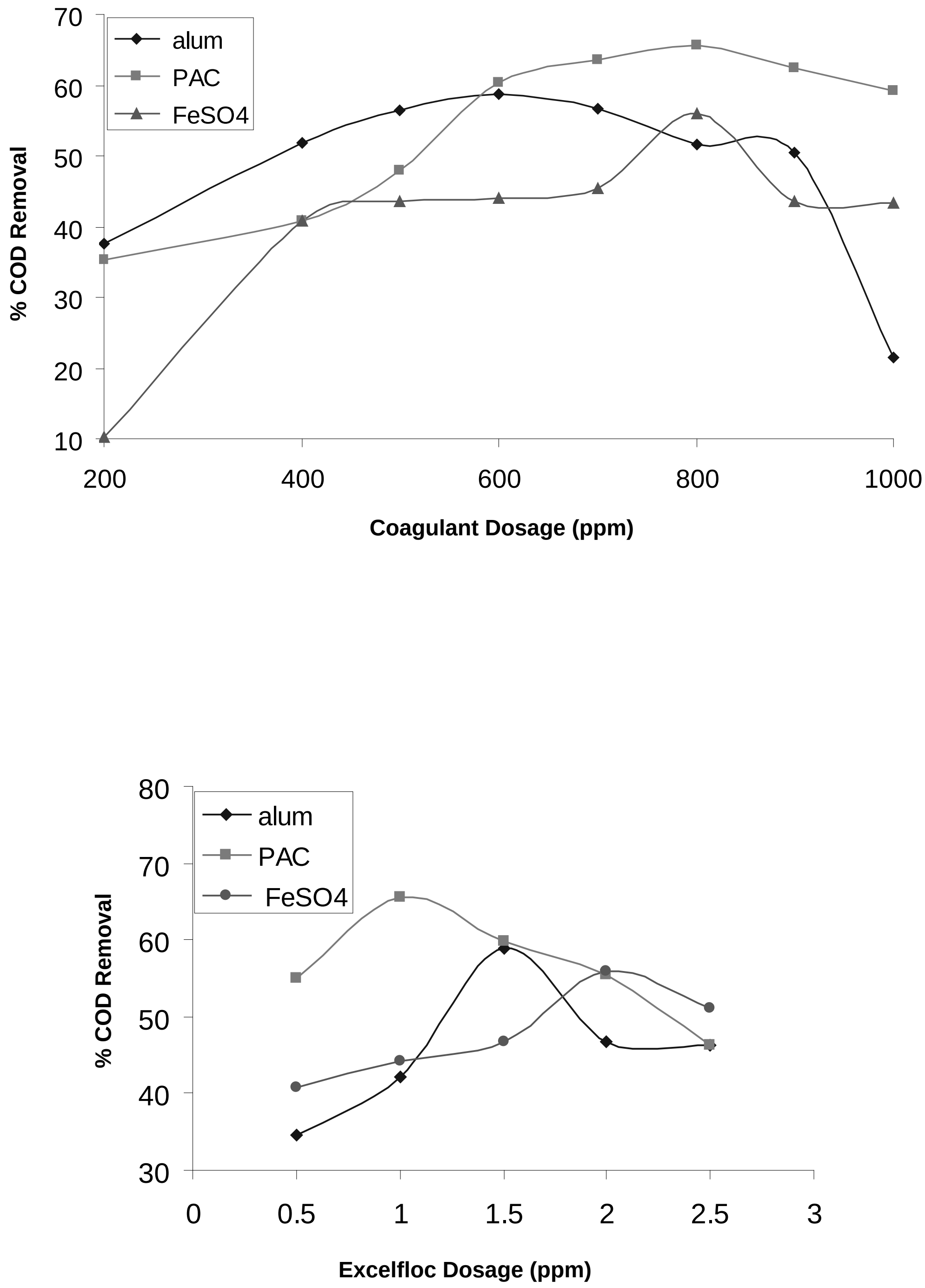
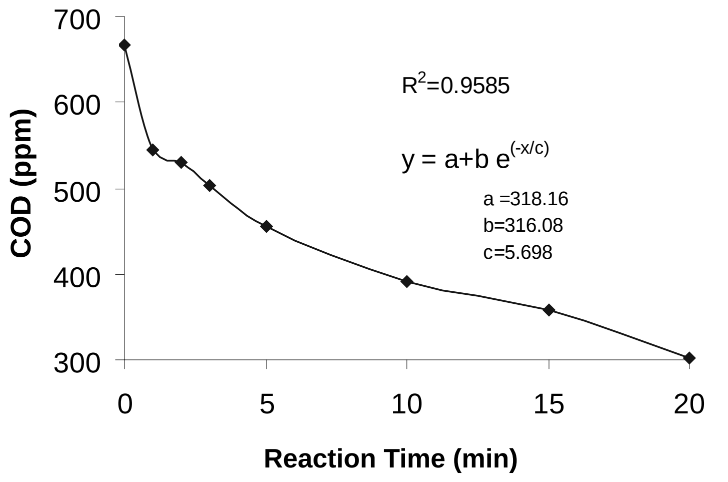


Figure 6. Effect of (a) Coagulant and (b) Flocculant Dosages

The results showed that the dosage of the coagulant should be adjusted carefully for the coagulation/flocculation process since COD removal also depends on the chemical dosages. The flocculant dosage also influences the good aggregation of flocs. It was found that an overdose of the flocculant resulted in floc floatation while an underdose led to poor aggregation of flocs, resulting in poor COD removal. When excelfloc 264 was used in excess of the appropriate dosage, the polymer may have coated the entire floc surface loosening bridging between the flocs and resulting in the formation of fragile flocs and in slow settling.

Figures 7(a), 7(b) and 7(c) show the concentration profiles of COD during the whole coagulation/flocculation time using PAC alone, flocculant alone, and both coagulant and flocculant, respectively. It was observed that there was COD removal throughout the coagulation and flocculation runs conducted at 240rpm of rapid agitation for 1min and 40rpm of slow agitation for 20min, respectively, without



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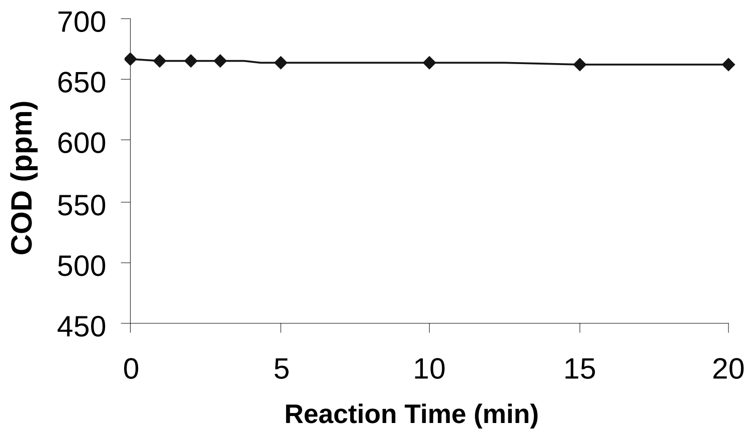

B.

Figure VII (b) COD concentration profile using exelfloc alone

adding excelfloc. It can be seen in Figure 7(a) that coagulation occurred at a very fast rate during the first minute and COD concentration decreased spontaneously from 667.53 to 545.21 ppm. But the reaction did not stop during coagulation time; COD removal still occurred during flocculation time until the end of the optimum slow agitation time of 20min. The clearest solution formed at that point.

No reduction of COD was observed when excelfloc alone was used as can be seen in Figure 7(b). However, when the flocculant was applied together with each of the coagulants, COD removal was enhanced quickly as shown in Figure 7(c). This makes clear the role of the coagulant and flocculant in the chemical treatment process. The overall reaction of coagulation and flocculation strongly depends on the coagulant and the role of the flocculant is mainly in the formation of the aggregation of flocs to support a faster settling rate and enhancement of COD removal as well as the decolorization of the dyeing effluent.

Similar trends were observed for both alum and ferrous sulfate coagulation and flocculation as seen in Figure 8.

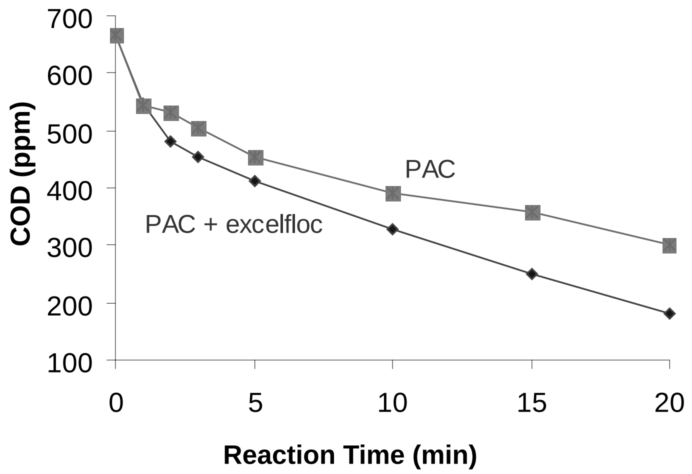

Figure VII(c) COD concentration profile using PAC with and without excelfloc

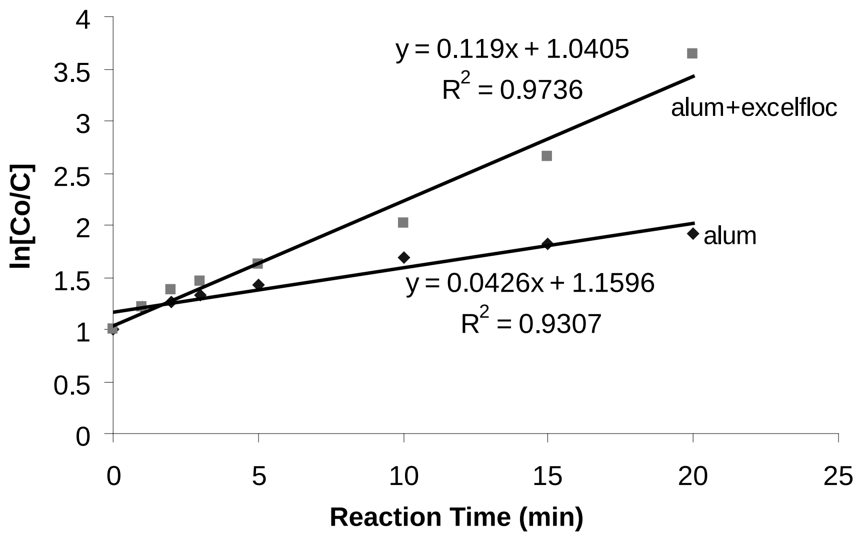

Figure 8. ln [Co/C] Versus Reaction Time Using Alum with and without Excelfloc

CONCLUSION

Jar testing proved to be an appropriate procedure in the determination of optimum pH, chemical dosage, agitation rate, and settling time for the coagulation and flocculation method. pH is an important parameter which strongly influences the efficiency of the chemical treatment. As dyes contain various organic compounds the COD removal efficiency depends upon the solubility of the organic contaminants. Overdose and underdose of the coagulant and flocculant can lead to unsatisfactory removal of waste materials. Since the best COD removal (65.64%) was achieved using PAC as coagulant and excelfloc as a flocculant, therefore, the various compounds in the textile bleaching and dyeing industry could react well with PAC. Aluminum salts are more effective than ferrous sulfate. Alum performed best in the removal of chromium content and of color.

Although COD removal was mainly achieved by using a coagulant, the enhancement of COD removal is achieved in the presence of a flocculant. The overall reaction rate was influenced largely by the coagulant. The kinetics of COD removal at the optimum conditions in the treatment of textile bleaching and dyeing industrial wastewater showed a first-order reaction.

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