

COAGULATION AND FLOCCULATION TREATMENT OF WASTEWATER IN TEXTILE INDUSTRY USING CHITOSAN

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ABSTRACT

Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate were commonly used as coagulants. However, a possible link of Alzheimer's disease with conventional aluminium based coagulants has become an issue in wastewater treatment. Hence, special attention has shift towards using biodegradable polymer, chitosan in treatment, which are more environmental friendly. Moreover, chitosan is natural organic polyelectrolyte of high molecular weight and high charge density which obtained from deacetylation of chitin. Experiments were carried out on textile industry wastewater by varying the operating parameters, which are chitosan dosage, pH and mixing time in order to study their effect in flocculation process by using chitosan. The results obtained proved that chitosan had successfully flocculated the anionic suspended particles and reduce the levels of Chemical Oxygen Demand (COD) and turbidity in textile industry wastewater. The optimum conditions for this study were at 30 mg/l of chitosan, pH 4 and 20 minutes of mixing time with 250 rpm of mixing rate for 1 minute, 30rpm of mixing rate for 20 minutes and 30 minutes of settling time. Moreover, chitosan showed the highest performance under these conditions with 72.5% of COD reduction and 94.9% of turbidity reduction. In conclusion, chitosan is an effective coagulant, which can reduce the level of COD and turbidity in textile industry wastewater.

Keywords: *Chitosan; textile wastewater; coagulation; flocculation; wastewater treatment.*

1.0 INTRODUCTION

Textile dyeing processes are among the most environmentally unfriendly industrial processes, because they produce colored wastewaters that are heavily polluted with dyes, textile auxiliaries and chemicals [1]. Besides, textile finishing's wastewaters, especially dye-house effluents, contain different classes of organic dyes, chemicals and auxiliaries. Thus they are coloured and have extreme pH, COD and BOD values, and they contain different salts, surfactants, heavy metals, mineral oils and others. Therefore, dye bath effluents have to be treated before being discharged into the environment or municipal treatment plant [2].

Textile dyes are structurally different molecules themselves with low or no biodegradability. The removal of color is associated with breakup of the conjugated unsaturated bonds in molecules. For this reason, many chemical treatment processes have been used extensively to treat textile wastewaters. Most of the studies, such as chemical precipitation, adsorption by activated carbon photocatalytic oxidation, ozonation and Fenton' oxidation focusing on color removal although effective, are

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expensive or can cause further secondary pollution [3]. In most water treatment plants, the minimal coagulant concentration and the residual turbidity of the water are determined by the Jar-Test technique. Besides, physical-chemical treatment allows reducing dissolved, suspended, colloidal and non settleable matter as well as colouring from dyes. Depending on the wastewater characteristics, COD of a textile effluent can be reduced between 50% and 70% after optimizing the operating conditions such as pH, coagulant and flocculants concentrations [2].

Coagulation or flocculation process was conducted for the treatment of industrial wastewater to achieve maximum removal of COD, TP and TSS. Therefore, Amudaa and Amoob [4] investigated the effect of coagulant dose, polyelectrolyte dose, pH of solution and addition of polyelectrolyte as coagulant aid and found to be important parameters for effective treatment of beverage industrial wastewater. Colloid particles are removed from water via coagulation and flocculation processes [5]. Besides, Guibal and Roussy [6], pointed that the coagulation and the flocculation of suspended particles and colloids result from different mechanisms including electrostatic attraction, sorption (related to protonated amine groups) and bridging (related to polymer high molecular weight).

Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate were commonly used as coagulants [7]. Additionally, high COD removal capacities have been observed during the combined action of alum and lime for the treatment of stabilized leachates. However, it has been stated out recently that there may be a possibility for aluminium-based coagulants to link with Alzheimer's disease [8]. Hence, a special attention has been given to the environmental friendly coagulant or flocculent, chitosan.

Chitin is cellulose like biopolymer widely distributed in nature, especially in marine invertebrates, insects, fungi, and yeasts. Its deacetylated product, chitosan, is readily soluble in acidic solutions, which makes it more available for applications. Chitosan is a biodegradable, non-toxic, linear cationic polymer of high molecular weight. Besides, chitosan was an effective agent for coagulation of suspended solids from various food processing wastes [5]. Moreover, chitin extraction also does not cause any disturbance to the ecosystem, its embraces all advantages provided by polysaccharides, considering it as the source of chitosan, and both are biocompatible biopolymers for animal tissues with low toxicities and significant biomedical applications [9]. Chitosan coagulation produced flocs of better quality, namely larger flocs and faster settling velocity. The effectiveness of chitosan for coagulating mineral suspensions was improved due to the presence of inorganic solutes or due to addition of materials extracted from soils at high pH [5].

Apparently, no major studies have been done to clarify the textile wastewater by using chitosan in coagulation and flocculation process. Therefore, this study was carried out to analyze the effect of chitosan in clarifying textile wastewater in flocculation process in different experimental conditions. The optimum pH, dosage and mixing time needed to achieve the best performance of chitosan in flocculation process were determined.

2.0 EXPERIMENTAL

2.1 Sample collection and materials

Sample of textile wastewater was collected from a textile company which is situated in Kulai, Johor Bahru. The sample had been stored in the refrigerator in order to

minimize the changes in the characteristics of wastewater sample since it may vary from day to day.

Chitosan was purchased in the form of white fine powder from Agros Company. The Chemical Oxygen Demand (COD) reagent vials in high range (0 to 15 000 mg/l) were purchased from Hach Company.

2.2. Coagulant preparation

Stock solution of chitosan should be prepared before starting the experiment. 3g of chitosan which purchased in form of white fine powder was used. Then, 96g of distilled water and 1g of acetic acid were added in order to dilute the chitosan powder. Pinotti et al. [3] pointed that chitosan solutions were prepared by dissolving the chitosan in 1% acetic acid solution during continuous agitation for several hours. According to Guibal and Roussy [6], chitosan dissolved in acetic acid, was used in the coagulation and flocculation processes. Besides, Pan et al. [5] pointed that chitosan is soluble in acidic solution, which makes it more available for application. Therefore, acetic acid needs to be added in order to dilute the chitosan powder.

2.3 Jar test

A conventional jar test apparatus was used in the experiments to coagulate sample of textile wastewater by using chitosan. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. Besides, the sample of wastewater was adjusted from the initial pH 12.99 to pH 4 in the experiments due to chitosan is soluble in acidic aqueous phases, but insoluble in basic aqueous phases. The pH was controlled by adding either strong acid (HCl) or strong base (NaOH). Before fractionated into the beakers containing 500mL of suspension each, the samples of textile wastewater were mixed homogeneously. Then, the samples ought to be measured for turbidity and COD for representing an initial concentration. After the desired amount of chitosan was added to the suspension, the beakers were agitated at various mixing time and speed, which consist of rapid mixing (250 rpm) for 10 minutes and slow mixing (30 rpm) for 20 minutes. After the agitation being stopped, the suspension was allowed to settle for 30 minutes. Finally, a sample was withdrawn using a pipette from the top inch of supernatant for turbidity and COD measurements which representing the final concentration. All tests were performed at an ambient temperature in the range of 26-30°C. In the experiment, the study was conducted by varying a few experimental parameters, which were chitosan dosage (12-66 mg/l), pH (2-10) and mixing time (10-30 minutes) in order to study their effect in flocculation and obtain the optimum condition for each parameter.

2.4 Analytical analysis

The COD test was performed by colorimetric method using Spectrophotometer HACH Model DR/2000. It is used to measure the oxygen demand for the oxidation of organic matters by a strong chemical oxidant which is equivalent to the amount of organic matters in sample. Moreover, turbidity was measured by using HACH Ratio/XR Turbidimeter which the sample was filled into a sample cell and put into the cell holder for measurement. While the pH of wastewater was measured by using a digital Horiba pH meter F-21. The pH meter was calibrated by using buffer solutions of pH 4.0 and pH 7.0 before starting the experiments.

3.0 RESULTS AND DISCUSSION

Studies on the effects of chitosan dosage, pH and mixing time are the experiments which were conducted in order to investigate the sorption capacity of chitosan in flocculation process. Since the Chemical Oxygen Demand (COD) level in wastewater from textile industry is considered as the most important parameter, so it has been used as the indicator on the sorption capacity of chitosan in these experiments by supporting with other parameter which is turbidity. The characteristics of the wastewater from petroleum refinery were as follow:

3.1 Effect of chitosan dosage

Dosage was one of the most important parameters that been considered to determine the optimum condition for the performance of chitosan in coagulation and flocculation. Basically, insufficient dosage or overdosing would result in the poor performance in flocculation. Therefore, it was crucial to determine the optimum dosage in order to minimize the dosing cost and obtain the optimum performance in treatment.

The effect of dosage was analyzed at pH 4, 250 rpm of mixing rate for 10 minute and 30 rpm of mixing rate for 20 minutes and 30 minutes of settling time for a range of chitosan dosage which varied from 12 mg/l to 66 mg/l. Besides, the sample of wastewater was adjusted from the initial pH of 12.99 to pH 4 due to chitosan was soluble in acidic aqueous phases [5]. Moreover, Domard et al.[10] pointed out that there were 90 % of the functional group of NH_2 on chitosan surface has been protonated at pH 4. The pH was controlled by adding either strong acid (HCl) or strong base (NaOH).

The results were presented in Figure 1(a) which showed the effects of chitosan dosage on COD level and the percentage of COD levels reduction by using chitosan. While Figure 1(b) showed the effects of chitosan dosage on turbidity levels and the percentage of turbidity levels reduction by using chitosan. From the jar test experiment, the curves for the both graphs were in the U-shape form for the condition of COD level and turbidity level versus chitosan dosage. While for the condition of percentage of COD and turbidity levels reduction, the curves for the both graphs were in “N” shape [11]. Besides, it was observed that the trends for all parameters were almost identical but with different percentage of reduction for particular chitosan dosage. For the optimum chitosan dosage of 30 mg/l, chitosan recorded the highest reduction of parameters, which were the reduction of 94.90% and 72.50 % for turbidity and COD respectively. Therefore, the optimum chitosan dosage in this research was 30 mg/l.

From the dosage 12 mg/l to 30 mg/l, the percentage of reduction for COD and turbidity was increased and these were presented in Figure 1(a) and 1(b). This phenomenon could be explained based on charge density. If compared to the other coagulants, chitosan has a high charge density [12]. Moreover, the charge density of the polymer increased when polymer adsorption increased [13]. Therefore, this signifies the rapid destabilization of the particles. In other word, it can be defined as chitosan, a coagulant which has a high charge density require less amount of the coagulant to destabilize the particles.

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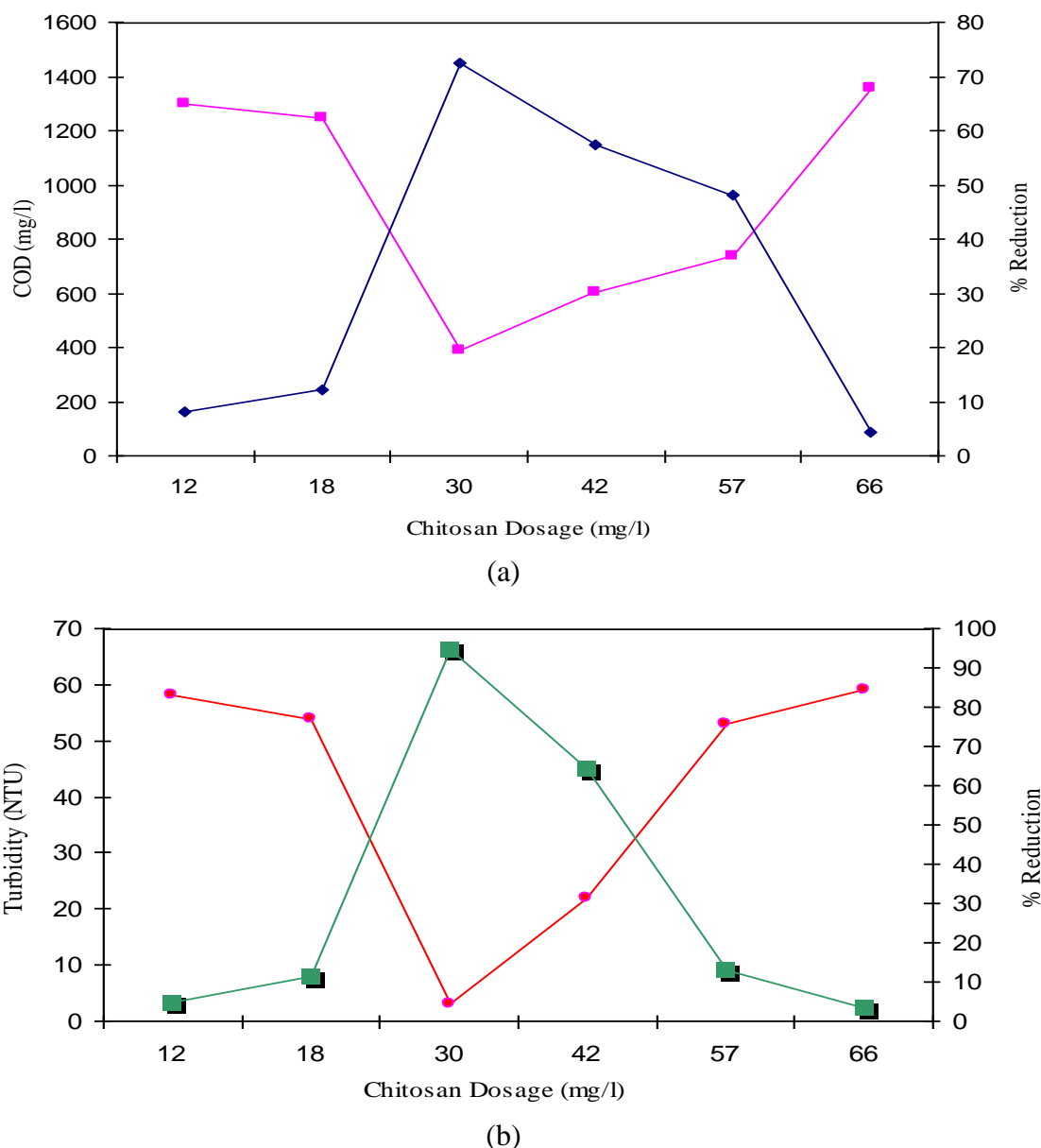


Figure 1 Effects of chitosan dosage on (a) COD level and the percentage of COD level reduction (b) turbidity level and the percentage of turbidity level reduction by using chitosan. -■-, COD level; -◆-, % COD level reduction; -●-, turbidity level; -■-, % turbidity level reduction

There was a drastic drop for the percentage of reduction for COD and turbidity when the chitosan dosage concentration was in the range of 30 mg/l to 66 mg/l. This poor performance was due to the phenomenon of excess polymer is adsorbed on the colloidal surfaces and producing restabilized colloids. Thus, there were no sites available on the particle surfaces for the formation of interparticle bridges. The restabilized colloidal particles can become positively charged and cause the electrostatic repulsion among the suspended solids.

3.2 Effect of pH

The pH will not only affects the surface charge of coagulants, but also affects the stabilization of the suspension. Besides, the solubility of chitosan in aqueous solution is influenced by pH value. Therefore, the study of pH was essential to determine the optimum pH condition of the treatment system. The effect of pH was analyzed at optimum dosage, 30 mg/l, with 20 minutes of mixing time, 250 rpm of mixing rate for 10 minutes and 30 rpm of mixing rate for 20 minutes and 30 minutes of settling time for a range of pH which varied from pH 2 to pH 10.

The results were presented in Figure 2(a) which showed the effects of pH on COD level and the percentage of COD level reduction by using chitosan in flocculation. Figure 2(b) showed the effects of pH on turbidity level and the percentage of turbidity level reduction by using chitosan. From the jar test experiment, the curves for the both graphs were in the U-shape form for the condition of COD level and turbidity level versus pH. While for the condition of percentage of COD and turbidity levels reduction, the curves for the both graphs were in “N” shape [11]. Moreover, it was observed that the trends for all parameters were almost identical but with different percentage of reduction for particular pH.

By analyzing every curve in Figure 2(a) and 2(b) which for COD and turbidity reductions respectively; it can be stated that the pH of textile wastewater has an influence on coagulation using chitosan. Furthermore, the figures demonstrate that over 72.5 % COD reduction and 94.9 % turbidity reduction can be achieved at pH 4. Therefore, the optimum pH condition of the treatment system was pH 4. This was supported by the statement of the sorption capacity of chitosan was optimum at pH 4 – 5 when it interacts electrostatic with anions in solution [14].

Domard et al. [15] pointed out that there are 90 % of the functional group of NH_2 on chitosan surface has been protonated at pH 4, and gradually reduced to about 50% as pH increased to 6. Therefore, the positive charges on the chitosan surface will significantly decrease as solution pH increased, so the contribution by the charge neutralization of the chitosan to destabilize the particles becomes less important as pH increased. The properties of chitosan, including its cationic behavior and molecular weight, may be used both for charge neutralization (coagulating effect for anionic compounds) and for particle entrapment (flocculating effect). Moreover, based on observation, the floc produced by chitosan appears rapidly at pH 4 and form a large size, which can be easily settled.

The operating pH of 4.0 could influence the chitosan behavior. In acidic solution, the amino groups of chitosan were protonated. Besides, chitosan would be expected to exhibit behavior typical of a polyelectrolyte when under these conditions. Polyelectrolyte act as coagulant aids in the treatment of water and wastewater; they may also be used as primary coagulant for the same purpose. Many polyelectrolytes are advantageous over chemical coagulants because they are safer to handle and are easily biodegraded. The removal of COD and turbidity increased with increasing dose of polyelectrolyte [4]. Moreover, the protonation of amino groups of chitosan in solution makes chitosan positively charged which act as cationic polyelectrolyte. Since the particles in textile suspension was negatively charged, chitosan was very attractive as coagulant by allowing the molecule to bind to negatively charged surface via ionic or hydrogen bonding. This will further reduce or neutralize the particles surface charge. Therefore, the particles destabilization by chitosan could be explained by charge neutralization mechanism.

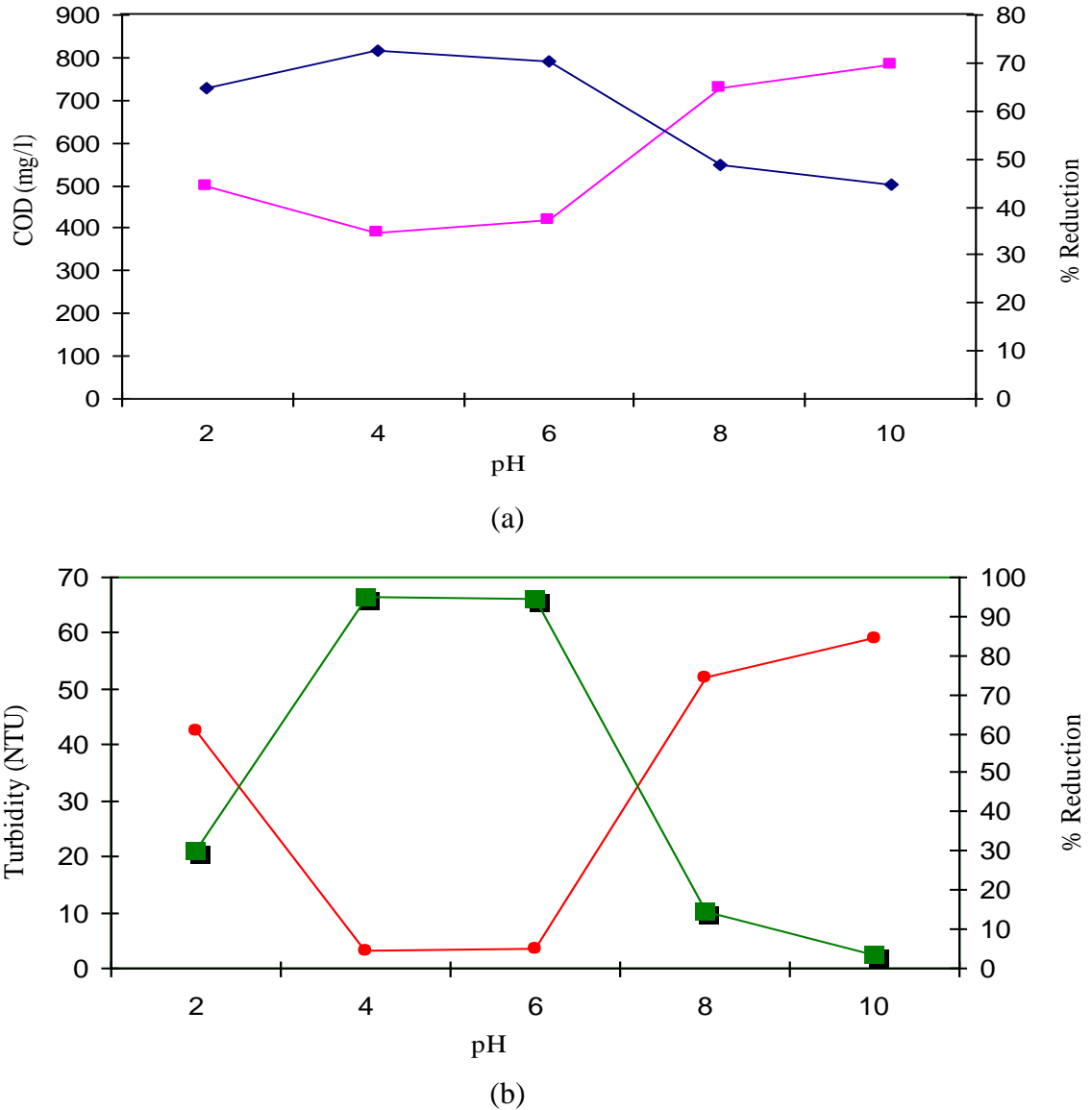


Figure 2 Effects of pH on (a) COD level and the percentage of COD level (b) turbidity level and the percentage of turbidity level reduction by using chitosan. -■-, COD level; -◆-, % COD level reduction; -●-, turbidity level; -■-, % turbidity level reduction

Takahashi et al. [16] proved that the solubility of chitosan decreases as the pH varies towards the basic condition. Chitosan dissolves in aqueous solution at pH less than 6.0. Over pH 6.0, it becomes insoluble in solution and exists as solid particles. This statement was supporting the obtained results in this experiment which the performance of chitosan in flocculation was worse in basic medium than acidic medium. Besides, Roussy et al. [1] also proved that chitosan at alkaline pH shows very low efficiency and required high concentration of chitosan to achieve the required treatment levels. This confirmed that, at least partial, protonation of chitosan amino group was required to achieve efficient coagulation of these organic suspensions.

3.3 Effect of Mixing Time

Besides the effect of chitosan dosage and pH, mixing time also play an important role on flocs formation and growth in flocculation process. Polymeric flocculent disperses throughout the medium and adsorbs on the colloidal particle surfaces for interparticle bridging or charge neutralization during the mixing period. Besides, longer mixing time will lead to an increase in flocs breakage. Hence, it decreases the flocculation rate. On the other hand, if the mixing time is too short, the collisions between the flocculants and colloids are not efficient to precipitate suspended solids in wastewater. Thus, the flocculation rate is not optimum under this condition. Therefore, a study was conducted on the effect of mixing time in flocculation.

The effect of mixing time was analyzed at optimum dosage, 30 mg/L and optimum pH, pH 4, 250 rpm of mixing rate for 10 minutes and 30 rpm for 20 minutes and 30 minutes of settling time for a range of mixing time which varied from 10 minutes to 30 minutes. The results are presented in Figure 3(a) and 3(b) which shows the effects of dosage on the percentage of COD and turbidity levels reduction by using chitosan in flocculation respectively. Besides, the curves for the both graphs are in the U-shape form for the condition of COD and turbidity versus mixing time. Moreover, it was observed that the trends for all parameters are almost identical but with different percentage of reduction for particular mixing time [17].

By analyzing every curve in the Figure 3 (a) and 3 (b) which for COD and turbidity reductions respectively; it can be stated that the mixing time of textile wastewater has an influence on coagulation using chitosan. Furthermore, the figure demonstrates that over 70.9 % COD reduction and 93.3 % turbidity reduction can be achieved at pH 4. Therefore, the optimum mixing time condition of the treatment system is 20 minutes [11].

Mixing period is very crucial for polymeric flocculent on their performance in flocculation. The trends that had been illustrated at Figure 3 showed that the longer or shorter agitation time would result in the poor performance of chitosan for binding and bridging [11]. At lower agitation time (i.e. 10 minutes), the collisions between the flocculants and suspended particles are low and lead to the lower flocculation rate. On the other hand, if the mixing time is too long, the flocculate chains tend to break and limiting the size of the flocs formed. The small size flocs are not dense to settle down in wastewater and thus, indirectly cause the sample to be turbid again. This phenomenon was observed in the Figure 3 which showed the lower percentage of reductions at longer mixing time (i.e. 30 minutes).

4.0 CONCLUSIONS

The characteristic of wastewater discharged from textile industrial activities was strictly controlled by Department of Environment. This was basically due to the wastewater from textile industry was contaminated with a complex set of oxygen demanding materials and poses a great problem to natural environment. Besides, the conventional aluminium-based coagulants have a possible link to Alzheimer's disease while chitosan was more favourable in wastewater treatment due to its environment friendly characteristic. As a result, the wastewater from textile industry was treated by using chitosan via coagulation and flocculation processes.

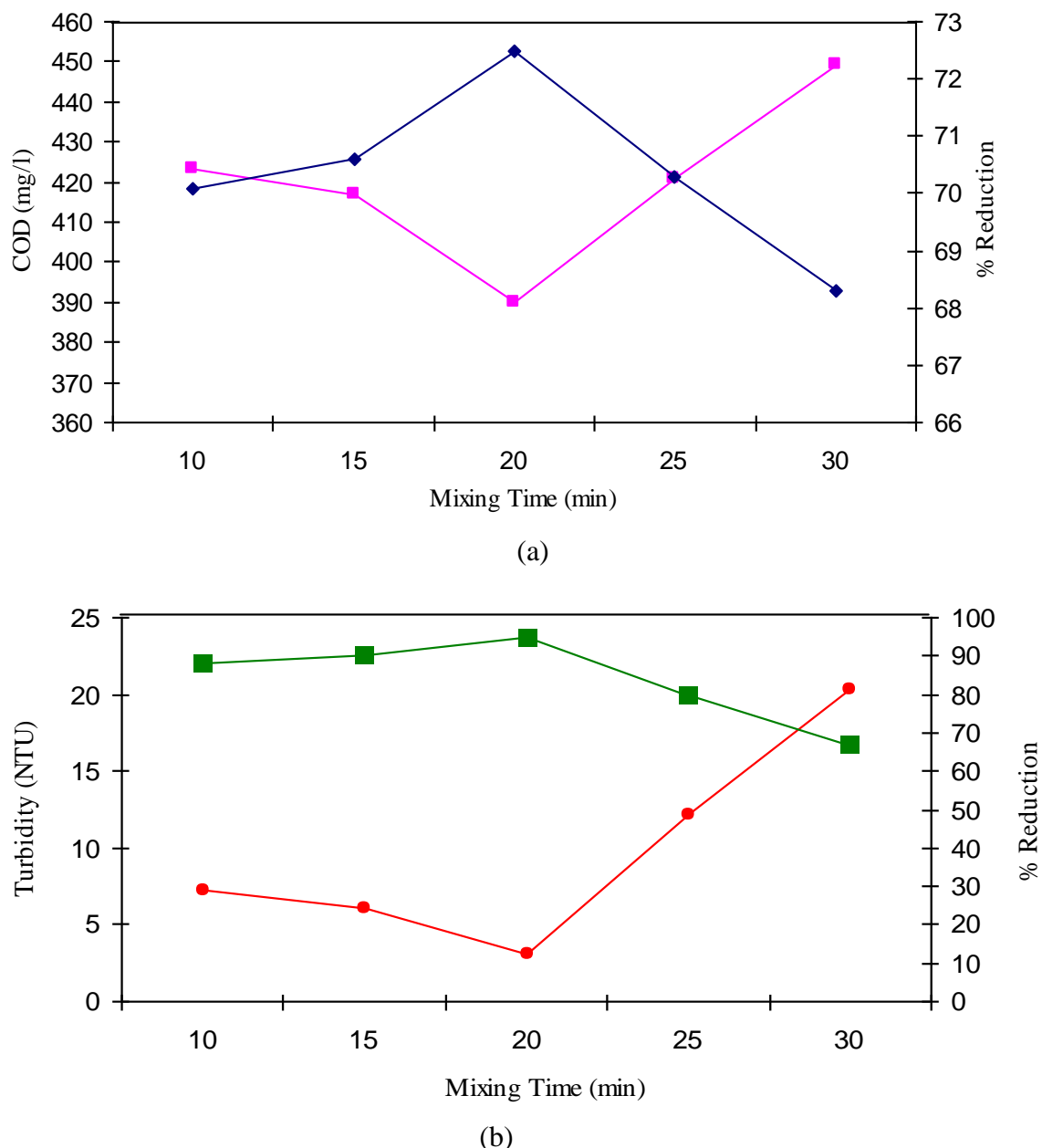


Figure 3: Effects of mixing time on (a) COD level and the percentage of COD level reduction (b) turbidity level and the percentage of turbidity level reduction by using chitosan. -■-, COD level; -◆-, % COD level reduction; -●-, turbidity level; -■-, % turbidity level reduction

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