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Potential Application of Biopolymer Chitosan and Cationic/Anionic Polymers in Textile Wastewater Treatment

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Abstract. Biopolymer chitosan have been investigated for color removal in textile wastewater by using coagulation process of biopolymers and synthetic polymers. After the wastewater samples were treated with 0.1% chitosan for chitosan coagulation process, coagulation process of cationic or anionic polymer were performed by using chitosan and cationic polymer (CSC) or chitosan and anionic polymer (CSA) polymer concentrations of 0.1, 0.2 and 0.4 g/l at pH 6-8, respectively. The color removal efficiency of textile wastewater samples before and after treatment with chitosan followed by cationic/anionic polymers has been evaluated. The color removal by chitosan was dependent on pH and the maximum percent removal $31.4 \pm 3.3\%$ has been observed at pH 7. The optimum parameters for polymer-biopolymer coagulation process in this study was CSC at dosage of 0.2 g/l, pH 8 and CSA at dosage of 0.1 g/l, pH 7. Besides, its chemical analyses including Chemical Oxygen Demand (COD), dissolved solid, and suspended solid were analyzed in order to consider the potential application of chitosan in textile wastewater treatment. The results showed that the COD, dissolved solid and suspended solid of pre-treated textile wastewater were 290, 3998.7 and 280.7 mg/l, respectively, however, both dissolved solid and suspended solid were higher than the regulatory standard for wastewater. As the optimum condition, the COD, dissolved solid and suspended solid of textile wastewater after treatment with CSC (0.2 g/l at pH 8) were 260.7, 1939.8 and 103.6 mg/l, respectively, while the COD, dissolved solid and suspended solid of textile wastewater after treatment with CSA (0.1 g/l at pH 7) were 190.6, 3002.2 and 106.8 mg/l, respectively. All of the results after treatments were within the regulatory standard. Therefore, the combination of chitosan and cationic/anionic polymers could be utilized in textile wastewater treatment.

1. Introduction

Nowadays, water pollution has gradually increased resulting from escalating pollution of fresh water resources either untreated or inadequately treated wastewater. The wastewater is a major environmental issue of the textile industries as textile wastewater pollutants are generally caustic soda, detergents, starch, wax, urea, ammonia, toxic dyes and heavy metal ions [1]. Because of threatened human health and ecological systems, the pollutant removal from textile wastewater is necessary. Therefore, various technologies in wastewater treatment have been studied such as adsorption, membrane filtration, chemical oxidation and coagulation [2]. The coagulation/adsorption is one of the most commonly used wastewater treatment techniques, which involved the physical adhesion of chemicals onto the surface of a solid.



Chitosan, the second most abundant biopolymer, are used for a wide range of applications i.e. agriculture, food processing, medicine, cosmetics, and biotechnology. For environmental applications, chitosan has been used as coagulant to treat a variety of wastewaters such as food processing industrial wastewaters, brewery wastewater, paper mill wastewater and olive oil wastewater [3]. As a biological cationic polymer, chitosan is being used to treat dairy wastewater at pH up to 5.25 by coagulation. Moreover, chitosan has a potential to remove pollutants containing metal ions and phenol derivatives. Chitosan with higher deacetylation degree exhibits greater efficiencies in removing pollutants either by adsorption or coagulation [4]. It was reported that the performance of chitosan in wastewater treatment vary with wastewater quality. For these reasons, this study was to investigate the potential application of chitosan for treatment of textile wastewater in the color removal, COD, DS and SS by coagulation-flocculation process.

2. Experimental

2.1. Materials

Textile wastewater was collected from Thai Towel Co. Ltd. (Nakornphatom, Thailand). The sample was stored at 4°C to minimize the changes in wastewater characteristics. Chitosan extracted from cuttlebones with a degree of deacetylation more than 80% and a moisture content of 9-10%, cationic polymer (FLOCTEX 3611) and anionic polymer (FLOCTEX 2413) were supplied by Thai Towel Co. Ltd. Glacial acetic acid, NaOH, HCl and other reagents were of analytical grade.

2.2. Coagulant Preparation

A conventional jar test was used in this study to coagulate wastewater using chitosan. 1 g/l chitosan dose was prepared by dissolving chitosan in 1% acetic acid. The experiment was carried out as a batch test, 600 ml of wastewater sample was treated with 15 ml chitosan solution under different operating pH (pH 6-8). The pH was controlled by adding either HCl or NaOH. After that, the wastewater suspension was agitated at various mixing time and speed, which consist of rapid mixing (100 rpm) for 1 min and slow mixing (30 rpm) for 30 min. After the agitation being stopped, the suspension was allowed to settle for 1 hour and the supernatant was collected for further analysis. After treated with chitosan, the parallel batch studies were performed using anionic or cationic polymer at dose of 0.1-0.4 g/l and pH 6-8 under the same agitation conditions to study the optimum condition for each parameter and their effect in coagulation and flocculation.

2.3. Analytical methods

The wastewater parameters such as pH, %transmittance at 550 nm, Chemical Oxygen Demand (COD), dissolved solid (DS) and suspended solid (SS) were analyzed according to the procedures described by the American Public Health Association (APHA). For color removal, the absorbance of the untreated and treated samples was measured at 550 nm using UV-VIS spectrophotometer. The optimum wavelength was obtained by scanning the untreated sample. The statistic analysis was performed by SigmaPlot using One Way ANOVA with Duncan's test.

3. Results and Discussion

The characteristics of the wastewater, such as an initial pH, %transmittance, COD, DS and SS were investigated as shown in Table 1 indicating the presence of high amounts of organic and inorganic matters in the textile wastewater. It can be noted that textile wastewater is generally alkaline and contains high pigment contents. Moreover, COD, DS and SS level in wastewater were used as the indicator on the sorption capacity to determine the optimum condition for the performance of chitosan in treatment.

Parameter	Value
pH	9
%transmittance	50.4 ± 0.5
COD, mg/l	290 ± 10
DS, mg/l	$3,999 \pm 101$
SS, mg/l	281 ± 28

Table 1. Characteristics of the textile wastewater sample.

Many polyelectrolytes such as ionic polymers were widely used as chemical coagulants because they have high dye binding capacity, however, they are not easily biodegraded [5]. Chitosan are advantageous over chemical coagulants as it is non-toxic and biodegradable materials.

The percentage of color removal was investigated under different pH (6–8) using chitosan as a coagulant to treat textile wastewater shown in Figure 1. It can be seen that the color removal by chitosan was dependent on pH and the maximum percent removal $31.4 \pm 3.3\%$ has been observed at pH 7. As chitosan was used in the coagulation and flocculation processes, the particles destabilization by chitosan was resulted from charge neutralization and particle entrapment [6]. Due to its cationic behavior, the negatively charged particles in textile suspension are allowed to bind to chitosan *via* ionic or hydrogen bonding [5].

In this study, the adsorption capacity of the dye by chitosan can be improved in the further treatment with either anionic or cationic polymer. After the wastewater samples were treated with 0.1% chitosan for primary coagulation process, the coagulation process of cationic/anionic polymer were performed by using polymer concentrations of 0.1, 0.2 and 0.4 g/l at pH 6-8, respectively. The color removal efficiency of textile wastewater samples before and after treatment with chitosan followed by cationic polymers (CSC) or chitosan followed by anionic polymers (CSA) has been evaluated. Figure 2 indicates the effectiveness of chitosan followed by anionic or cationic polymer to observe the optimal dosage and pH in color removal. It was observed that the color removal efficiency was highest at pH 8 and 7 for CSC and CSA, showing 44.1% and 41.8% removal, respectively. However, there was a statistically significant difference between CSC and CSA as shown in the Figure ($p < 0.05$). %Color removal also related to concentration of ionic polymers as shown in Figure 3. Under the optimum pH (CSC at pH 8 and CSA at pH 7), CSC and CSA indicated the highest color removal at concentration of 0.2 g/l and 0.1 g/l showing 46.5% and 41.8% removal, respectively. Consequently, the optimum parameters for polymer-biopolymer coagulation process in this study was CSC at dosage of 0.2 g/l, pH 8 and CSA at dosage of 0.1 g/l, pH 7. There was a statistically significant difference between CSC and CSA at different concentration as shown. Yadav *et al.* reported that the performance of the coagulation process declines when the pH increases. An increase in alkalinity can alter the nature of hydrolysis products which may influence the destabilization of the colloidal particles. Generally, colloidal particles in water are negatively charged [7]. A change in a coagulant dose may be attributed to the reversal of charge. At higher coagulant concentration, the development of positive charge on the surface of colloidal particles caused by adsorption of excess positively charged ions can promote repulsive interaction and hinder settling.

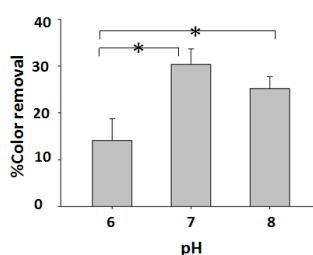
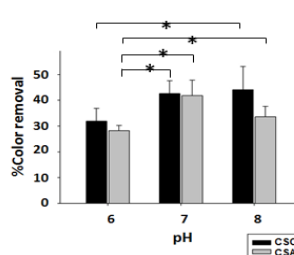
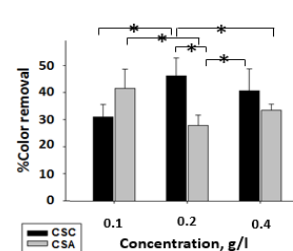
**Figure 1.** Color removal efficiency after coagulation by 0.1% chitosan at pH 6-8 (*, $p < 0.05$).**Figure 2.** Color removal efficiency after coagulation by CSC and CSA (0.1 g/l ionic polymers) at pH 6-8 (*, $p < 0.05$).**Figure 3.** Color removal efficiency after coagulation by CSC at pH 8 and CSA at pH 7 using 0.1-0.4 g/l ionic polymers (*, $p < 0.05$).

Figure 4(A-C) shows the results for COD, DS and SS of the pre-treated wastewater, wastewater after treatment with CSC and wastewater after treatment with CSA. Also, Figure 4D shows the physical characteristics of wastewater before and after treatment at pH 7. It can be seen that the treated water was obtained with the better quality after treatment with either CSC or CSA in primary coagulation step.

The results indicated that the COD, DS and SS of pre-treated wastewater were 290, 3998.7 and 280.7 mg/l, respectively, however, both DS and SS were higher than the regulatory standard for wastewater. After treatments, all parameters were within the regulatory standard. As the optimum condition, the COD, DS and SS of wastewater after treatment with CSC (0.2 g/l at pH 8) were 260.7, 1939.8 and 103.6 mg/l, respectively, while the COD, DS and SS of wastewater after treatment with CSA (0.1 g/l at pH 7) were 190.6, 3002.2 and 106.8 mg/l, respectively. Interestingly, there was a statistically significant difference between pre-treated and all treated samples (CSC and CSA) at dose of 0.1, 0.2, 0.4 g/l at pH 6-8 ($p < 0.05$). The lower COD, DS and SS is attributed to the higher removal efficiency of coagulants. CSA was effective as coagulant that CSC for COD reduction while CSC was more effective coagulant with respect to the removal performance for DS and SS. Therefore, the combination of chitosan and cationic/anionic polymers could have potential application in textile wastewater treatment.

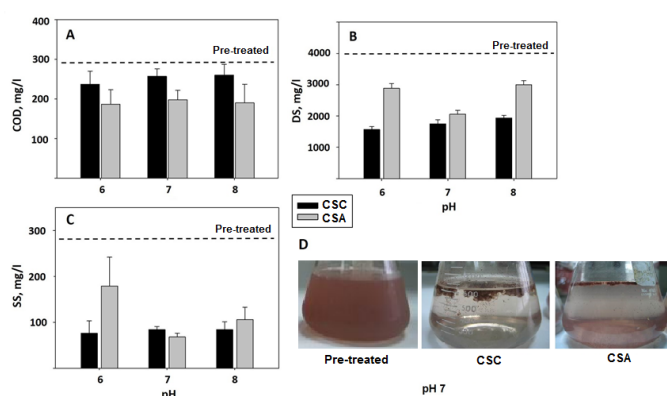


Figure 4. COD, DS, SS and color of wastewater before and after treatment with CSC and CSA. (A) COD of pre-treated wastewater and wastewater after coagulation by CSC and CSA at pH 6-8. (B) DS of pre-treated wastewater and wastewater after coagulation by CSC and CSA at pH 6-8. (C) SS of pre-treated wastewater and wastewater after coagulation by CSC and CSA at pH 6-8. (D) Color of wastewater before and after treatment with CSC and CSA at pH 7.

4. Conclusion

In this study, the wastewater from textile industry can be treated using chitosan together with cationic/anionic polymer via coagulation and flocculation process. CSC exhibited higher efficient COD removal while CSA could achieve higher efficiencies in decreasing DS and SS. Both CSC and CSA were effective for removal of turbidity with value for color removal of 30-47%. The optimum parameters for polymer-biopolymer coagulation process in this study was CSC at dosage of 0.2 g/l, pH 8 and CSA at dosage of 0.1 g/l, pH 7.

5. References

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