

Textile Wastewater Treatment using Hybrid Chitosan-polyacrylamide Flocculant

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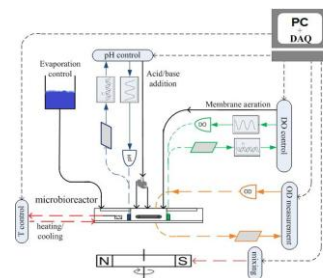
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Abstract

In this study, a natural polymer, chitosan was modified with polyacrylamide (PAM) to prepare an efficient flocculant using redox grafting method. The effectiveness of the modified chitosan (chitosan grafted polyacrylamide) was tested on treatment of industrial textile wastewater. The effect of dosage, pH and settling time on the performance of flocculation process was also investigated. The treated textile wastewater was analyzed by its color removal, COD and turbidity reductions. The results obtained showed that the modified chitosan performed better than unmodified chitosan in the reduction of COD and turbidity of textile wastewater.

Keywords: Chitosan; chitosan grafted polyacrylamide; flocculation; redox technique; textile wastewater

Abstrak

Dalam kajian ini, polimer semulajadi, kitosan telah di modifikasikan dengan poliakrilamid (PAM) untuk menghasilkan flokulan yang efektif dengan menggunakan kaedah tergabung redox. Keberkesanan kitosan termodifikasi (kitosan tergabung polyacrylamid) telah di uji ke atas rawatan air sisa industri tekstil. Kesan dos, pH dan masa pemendapan ke atas keberkesanan proses flokulasi juga telah di kaji. Air sisa yang terawat di analisa untuk penyingkiran warna, pengurangan COD dan pengurangan kekeruhan. Keputusan yang diperolehi menunjukkan bahawa kitosan termodifikasi adalah lebih baik daripada kitosan tidak termodifikasi dalam pengurangan COD dan pengurangan kekeruhan sisa air tekstil.

Kata kunci: kitosan; kitosan tergabung poliakrilamid; penggumpalan; teknik redoks; sisa tekstil

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1.0 INTRODUCTION

Flocculation is an efficient and cost-effective process for the treatment of water and wastewater. Natural and synthetic polymers, which are able to destabilize colloidal suspensions, have found wide application as flocculating agents. Natural polymers are fairly shear-stable and biodegradable, but their biodegradability reduces their shelf life. Water-soluble synthetic polymers, meanwhile, undoubtedly is very efficient and has been extensively used for wastewater treatment. However, it has disadvantages of non-biodegradability, toxicity, unstable under shearing and some is associated with high costs [Singh *et al.*, 2003]. Thus, a more efficient and environmental friendly flocculant is desirable.

In recent years, considerable attention has been paid on the synthesis of copolymers that combine the advantages of both synthetic and natural polymers. Thus, a great number of copolymers were achieved by grafting synthetic polymers, mainly, flexible chain of polyacrylamide (PAM) on some polysaccharide backbone, such as gum guar [Wan *et al.*, 2007], starch [Chang *et al.*, 2008], konjac glucomannan [Tian and Xie,

2008], chitosan [Singh *et al.*, 2006, Wang *et al.*, 2008], carboxymethylstarch [Sen, *et al.*, 2009] and tamarind kernel [Ghosh *et al.*, 2010].

There are several methods that available to synthesize grafted polymers such as conventional redox grafting [Da Silva *et al.*, 2007, Kaith *et al.*, 2007], microwave irradiation, γ -ray irradiation [Wang *et al.*, 2008, Xu *et al.*, 2008] and electron beam [Vahdat *et al.*, 2007].

In this study, it was aimed to prepare chitosan grafted polyacrylamide by using redox technique. Chitosan and polyacrylamide (PAM) has been chosen as natural and synthetic flocculant, respectively as both have been extensively used for wastewater treatment. Chitosan is an N-deacetylated derivative of chitin, the second most abundant natural organic resource only next to cellulose on the earth (Juang and Shao, 2002). It is widely distributed in arthropods, crustaceans, fungi, and yeast (Chung *et al.*, 2003). Because of the inter- and intra-molecular hydrogen bonding, chitosan can be dissolved in only acidic solution through the interaction between H^+ and $-NH_2$. On the other hand, PAM is a generic name for thousands of polymers ($-CH_2CHCONH_2-$) containing acrylamide as the major

constituent. It is a crystalline and relatively stable monomer which has different charges (anionic, cationic or neutral), charge densities and molecular weights and they are amorphous and water soluble. PAM is a high molecular weight polymer, which could adsorb onto the surface of sludge particles with its long-chains where the tails and loops are extended far beyond its surface and can interact with other particles via bridging flocculation.

The performance of prepared grafted / hybrid flocculants was tested in treating industrial textile wastewater. Textile wastewater is known as difficult-to-treat pollutants due to the contents contained in the wastewater that hard to be characterized. It is characterized by its high color, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solid (TSS). The textile industry produces large quantities of highly colored effluents that commonly toxic and resistant to destruction by biological treatment method. Besides that, textiles wastewater is a mostly non-biodegradable under both natural and sewage treatment plant conditions that is potentially nuisance to the environment (Ledakowicz *et al.*, 2001).

The effects of flocculant dosage, settling time, and pH on the performance of grafted flocculant towards removal of color, COD and turbidity of the textile wastewater were also been investigated in this study. To distinguish the superiority of the grafted flocculant towards treatment of textile wastewater, the test was also performed using solely chitosan.

2.0 MATERIALS AND METHODOLOGY

2.1 Materials

The textiles wastewater was obtained from the American and Efird (Malaysia) Sdn. Bhd. which is situated in Kulai, Johor Bahru. The wastewater was obtained for the same batch to ensure the consistency in the composition. The wastewater obtained was stored in the refrigerator to maintain the characteristic of wastewater sample under 0°C. Table 1 shows the raw characteristic of textile wastewater.

Table 1 Initial characteristic of textile wastewater

Parameter	Value
pH	12.15
COD	1245 mg/L
Turbidity	231 NTU
Color	Dark red (>3)

Chitosan was purchased from Sigma Aldrich in the form of white fine powder. The acrylamide (AM), ammonium persulfate and sodium thiosulfate also was purchased from Sigma Aldrich in the form of powder. The acetone, hydroquinone, anhydrous alcohol, hydrochloric acid (HCl) and acetic acid were purchased from Fluka. The chitosan was purified by dissolving in acetic acid solution and was washed by anhydrous alcohol for 3 times and dried at 65°C in vacuum for 48 hours before used. The ammonium persulfate and sodium thiosulfate used had the purity of 98%. 3 g of chitosan was dissolved in 1% acetic acid solution. Then, it was added with 1 M HCl until the pH reached 4.

2.2 Redox Technique

Chitosan-grafted-polyacrylamide was synthesized using the redox technique with the presence of redox ion initiators. Firstly, 3 g chitosan was dissolved in 1% acetic acid solution of 80 mL at 60 °C in flask. As the chitosan fully dissolved, the temperature was controlled at 33°C. Then, the redox initiator was added which was ammonium persulfate powder into the solution followed by the sodium thiosulfate after 5 minutes. Subsequently, the acrylamide was added by drop wise (5mL) for the next 5 minutes. The ratio of chitosan to acrylamide used was 1:1.

The mixture then was stirred for 15 minutes and then the reaction was left for 24 hours. Then, the aqueous solution of hydroquinone was added to terminate the reaction. The mixture then was poured into the distilled water to obtain slurry. The slurry then was poured in excess acetone to precipitate the product. The product then was filtered and washed with acetone and dried at 55°C until the constant weight is obtained. The final product obtained was referred as chitosan-grafted-polyacrylamide.

2.3 Flocculation Process

Flocculation ability of chitosan, and the graft copolymer was evaluated using jar test with textile waste sample. The flocculants were added into each of six 500 ml beakers with textile waste suspension. The suspensions were immediately stirred at 200 rpm for 3 min, followed by a slow stirring at 40 rpm for 15 min. Thereafter, the solution was settled for 15 min. Finally, the supernatant solution was withdrawn and analyzed for its COD, color and turbidity using COD meter (HACH DRB200 model), ASTM D1550 199 and turbidity meter (HACH model), respectively. The experiment was repeated for different flocculant dosage (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g), different pH (3,4,5,7,9 and 11) and different settling time (15, 30, 45, 60, 90 min).

3.0 RESULTS AND DISCUSSION

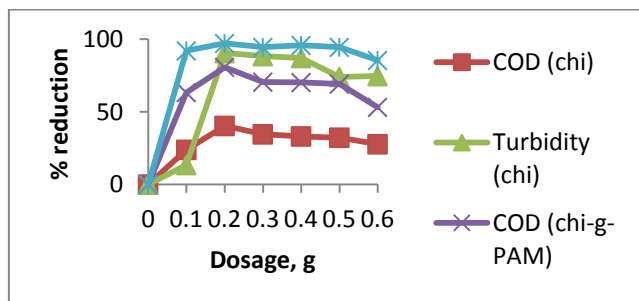
3.1 Effect of Dosage on Color, COD and Turbidity Reduction

Table 2 shows the effect of chitosan and chitosan-grafted-polyacrylamide dosage on color of textile wastewater. The settling time and pH of the sample was kept constant at 30 minutes and pH 4, respectively. As can be seen, the colors of the treated wastewater showed scale less than 0.5 when treated with chitosan regardless of dosage. Scale less than 0.5 refers to sample with clear condition (i.e. the lower the scale the clear the sample and vice versa). This indicated that chitosan is able to remove the dye color very well even at low dosage. The effectiveness of chitosan is believed due to its amine and hydroxyl functional groups, which has an extremely high affinity for many classes of dyes. On the other hand, chitosan-grafted-polyacrylamide was not as good as chitosan in removing the color as shown by the scale which is generally higher than 1.5. Nevertheless, both flocculants were able to remove the color of the waste as they were able to down the scale of raw waster from larger than 3 to less than 1.5.

Table 2 Effect of chitosan dosage on color of textile waste water

Dosage,g	Chitosan	Chitosan-grafted-PAM
0.1	< 0.5	< 1.5
0.2	< 0.5	< 0.5
0.3	< 0.5	<0.5
0.4	< 0.5	< 1.5
0.5	< 0.5	< 1.5
0.6	< 0.5	< 1.5

Figure 1 illustrates the effect of chitosan and chitosan-grafted PAM dosage on percentage reduction of COD and turbidity. As can be seen, the percentage of COD reduction was high at low dosage (0.1 to 0.2 g) which is about 80 and 40 % for chitosan-grafted-PAM and chitosan, respectively. Further adding the dosage to up 0.6 g resulted to decrement in percentage of COD reduction to about 55 and 30 % for chitosan-grafted-PAM and chitosan, respectively. The same trend was observed for turbidity with respect to dosage. With the increasing dose of the flocculants, the COD and turbidity reduction will be expected to be increased. This is because the flocculants allow neutralization of the anionic charges of the dyes that could bind together and settle with the aid of polymer bridging. However, as more flocculants were further added into the solution, the excess quaternary induced re-stabilization of the suspension and thus decreases the efficiency of the process (Anuradha Mishra *et al.*, 2000). Wang *et al.*, (2009) claimed that as the flocculant dosage increased, the zeta potential of the particle gradually increased and the compression of electrical double layer was enhanced. When the zeta potential was increased up to zero, the optimal flocculation was achieved. After the flocculant dosage was further increased, the presence of the excessive flocculant will make the suspended particles positively charged, and thus cause mutual repulsion. In this case, a further increase in flocculant dosage would result in the re-dispersal of flocs and the reduction in COD and turbidity removal. It shows that 0.1 to 0.2 g was sufficiently enough in this study. Generally, chitosan-grafted-polyacrylamide shows the higher percentage reduction for COD and turbidity compared to that of chitosan. It is believed due to longer polymer chain length owned by chitosan-grafted-polyacrylamide. Its long chain adsorbed on the surface of one colloid particle may be adsorbed onto the surfaces of the other ones, and thus two or more particles aggregated together, resulting in flocculation through “bridging”. Thus, resulting to more particles attachment to grafted polymer compared to chitosan itself.

**Figure 1** Effect of chitosan and chitosan-grafted-polyacrylamide flocculants dosages on percentage reduction of COD and turbidity

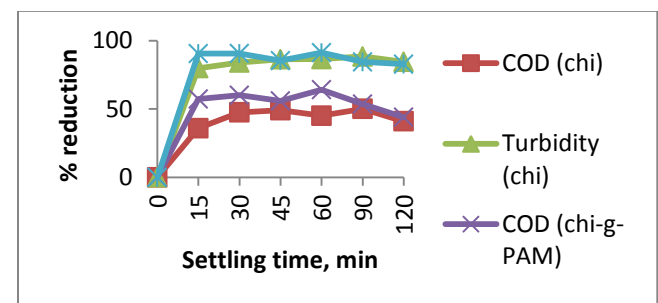
3.2 Effect of settling Time on Color, COD and Turbidity Reduction

Table 3 shows the effect of settling / sedimentation time on color removal of textile wastewater. The dosages of chitosan and chitosan-grafted-polyacrylamide were kept constant at 0.2 g. The dosage of 0.2 was chosen as it appeared to be the best dosage in reducing color, COD and turbidity of the sample as discussed early in section 3.1. The other parameters of the flocculation process were the same as in section 3.1 except the settling time. As can be seen, chitosan performed better in color removal as compared to chitosan-grafted-polyacrylamide regardless of the settling time. The results showed that the range of settling time used in this study (15 to 120 minutes) for the flocculation process seems did not give impact on the color removal. Most probably, 30 minutes were sufficiently enough to settle all the flocs formed.

Table 3 Effect of settling time on color removal of textile wastewater. The dosage was kept constant at 0.2 g

Settling time, min	Chitosan	Chitosan-grafted-PAM
15	< 0.5	< 1.5
30	< 0.5	< 0.5
45	< 0.5	<1.5
60	< 0.5	< 1.5
90	< 0.5	< 1.5
120	< 0.5	< 1.5

Figure 2 illustrates the effect of settling time on percentage reduction of COD and turbidity. As can be seen, the percentage of COD and turbidity reduction increased with settling time from 15-30 minutes. It seems that settling time longer than 30 minutes was not able to increase the percentage reduction of COD and turbidity more. In fact, too longer the settling time leads to decrement in percentage reduction of COD and turbidity. This probably because of flocs formed were break apart which re-stabilizes the suspension of the particles. By contrast to color removal, chitosan-grafted-polyacrylamide was better compared to single chitosan in reducing COD and turbidity of the waste. Higher molecular weight polymers is expected to settle quickly and better compared to the lower molecular weight. The high molecular weight polymer causes destabilization by bridging when segments of the polymer chain adsorb more than one particle, thereby, linking the particles together (Akbar Ali *et al.*, 2009).

**Figure 2** Effect of settling time on percentage reduction of COD and turbidity. The dosage was kept constant at 0.2 g

3.3 Effect of pH on Color, COD and Turbidity Reduction

The effect of pH on color removal of textile waste water is shown in Table 4. The dosages of flocculant and settling time were kept constant at 0.2 g and 30 minutes, respectively. The other parameters of the flocculation process were the same as in section 3.1. From the result obtained, it showed that chitosan and chitosan-grafted-polyacrylamide performed better in acidic medium with pH range 3 to 5 compared in alkaline medium as shown by scale less than 0.5.

Table 4 Effect of pH on color removal of textile wastewater. The dosage and settling time was kept constant at 0.2 g and 30 minutes, respectively

pH	Chitosan	Chitosan-grafted-PAM
3	< 0.5	< 0.5
4	< 0.5	< 0.5
5	< 1.5	< 0.5
7	< 1.5	< 1.5
9	< 1.5	< 1.5
11	< 1.5	< 1.5

Figure 3 illustrates the effect of pH of the sample on the percentage reduction of COD and turbidity. At low pH (pH 3 to 4) the percentage reduction of COD after being treated with chitosan was about 60%. Increasing the pH to 11 resulted to tremendous decrement in COD removal to about 20%. Similar trend was observed for turbidity. By increasing the pH from 3 to 11, resulted to decrement in turbidity reduction from about 85 to 78%. Chitosan-grafted-polyacrylamide also exhibits the same trend as shown by chitosan. Nevertheless, chitosan-grafted-polyacrylamide was more effective than chitosan in reducing COD and turbidity of the waste especially under alkaline medium. From the results obtained, it showed that generally chitosan had better flocculation ability under acidic condition than under alkaline medium especially in color removal and COD reduction. Under acidic condition, chitosan was positively charged as the amino groups bonded with hydrogen ions. Positive charge of chitosan neutralized the negative charges on dye molecules. This is the reason why chitosan had better flocculation ability under acidic condition. Therefore, the most likely mechanism involved with removal color of waste by chitosan seems to be charge neutralization. Under alkaline condition, there were few free hydrogen ions on chitosan and thus protonation could hardly be realized (Wang *et al.*, 2008). Consequently, chitosan was less effective under alkaline medium. However, Ch-g-PAM was able to reduce COD and turbidity excellently even under alkaline medium. This is one of the advantages of the graft copolymer. The flexible polyacrylamide chain grafted onto the rigid chitosan backbone increased the flocculant flexibility, which was in favor of the binding intensity between flocculants and colloids. In other words, grafting of acrylamide increased the flocculant bridging ability, and thus enhanced the flocculation ability. Therefore, the re-dispersion resulting from the competition of bridging could be avoided to some extent (Brastkaya *et al.*, 2005). It can be postulated that chitosan-grafted-polyacrylamide follows bridging and charge neutralization mechanisms.

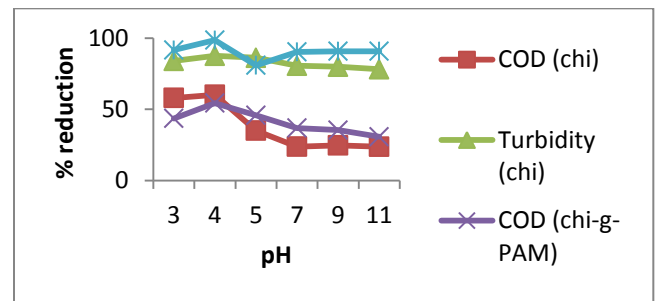


Figure 3 Effect of pH on percentage reduction of COD and turbidity. The dosage and settling time was kept constant at 0.2 g and 30 minutes, respectively

4.0 CONCLUSION

The performance of flocculation process was affected by dosage, settling time and pH. Under the range of the study, the best performance of flocculation process was achieved at acidic condition, settling time of 60 minutes and dosage of 0.2 g. Overall, chitosan-grafted-polyacrylamides was better than chitosan in the removal of COD and turbidity. However, chitosan was more superior than chitosan-grafted-flocculant in color removal.

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