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An application study of inorganic-organic composite polymer in flocculating reactive dye wastewater under different conditions

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Abstract. In this study, a new composite material (MCPAM), which was prepared by magnesium chloride premixed with polyacrylamide, was applied to treat simulated reactive dye (Cibacron Red FN-R) wastewater through flocculation process. Batch flocculation experiments were conducted under different conditions e.g. pH, concentration of dye, dosage and temperature to investigate their effect on dye removal (%). The maximum dye removal (%) was achieved at pH 12. The effect of temperature was investigated in the range between 20 to 50°C. The dye removal (%) decreased with the increase of temperature. An interaction was observed between temperature and concentration of dye where the dye removal (%) decreased with the increase of dye concentration from 200 to 500 mg/L at 20°C. However, at temperature beyond 30°C, an inverse behaviour was observed. Effect of dosage on the dye removal (%) was studied with respect to concentration of dye. The dye removal (%) was found to increase to a maximum value of 99 % and decrease thereafter indicates the re-suspension of destabilized flocs into the supernatant.

Keywords: Inorganic-organic composite polymer, flocculation, reactive dye, wastewater

1. Introduction

Various composite materials have been developed in recent years for coagulation-flocculation purpose in view of their better performance compared to that of conventional inorganic-based coagulants, and their lower cost compared to organic-based flocculants. There are a few terminologies used to address composite materials, such as: composite coagulant (Gao et al. 2003), composite flocculant (Gao et al. 2005), composite polymer (Liu et al. 2011), as well as hybrid polymer (Lee et al. 2010, Lee et al. 2011a). Composite materials are referred to the introduction of other effective components into the original materials to enhance the aggregating power of the materials. (Tzoupanos and Zouboulis 2011). Due to the synergetic effect of two components in one material, therefore, composite materials pose a superior performance compared to that of individual component. Generally, composite materials that used for coagulation-flocculation purpose can be classified into four primary groups: (i) inorganic-inorganic, (ii) inorganic-organic, (iii) inorganic-natural polymer, (iv) inorganic-biopolymer and (v) organic-organic composite. Inorganic-organic composite particularly have received the most attention in treating wastewater. The molecular weight and size of inorganic coagulants are much lower than that of organic flocculants, resulting the aggregating capacity remain lower than organic flocculants. To overcome this limitation, water soluble polymers e.g. polyacrylamide (PAM) has been introduced to compose with inorganic coagulants to prepare inorganic-organic composite polymers (Lee et al. 2010, Lee et al. 2011a). With this modification, the bridging mechanism of the materials hence can be enhanced. The application of these inorganic-organic composite materials required only one unit operation which is flocculation system compared to the conventional bi-operational system: coagulation-flocculation. This innovation is essential in reducing the wastewater treatment processing time especially for those industries that are dealing with large volume of wastewater, e.g. textile industry.

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Textile dyeing and printing process produce large quantities of wastewater which are often characterized with high temperature, pH, COD and colour content (Golob et al. 2005). Therefore, the effluent from the dyeing process needs to be treated before being discharged. Reactive dye particularly has been extensively used in the textile industry to colour cellulosic-based fabric. To fix the colour on the cellulosic fabric, reactive dyes are applied under alkaline condition at elevated temperature (Golob et al. 2005). The aim of the present work was to examine the ability of MCPAM composite polymer as a flocculant to treat simulated dye wastewater at different conditions considering pH, concentration of dye, dosage as well as temperature often act as important parameters in affecting the flocculation efficiency.

2. Materials and methods

2.1. Materials

Acrylamide (AM) (>99% purity, Merck) was used without further purification. Ammonium persulphate (AR, Systerm) and sodium bisulfite (GR, Acros Organics) were used as redox initiators. Magnesium chloride (≥99%, Bendosen) was used as received. Deioinized water was used in the preparation of MCPAM composite polymer.

2.2. Preparation of inorganic-organic composite polymer

As described in our previous paper (Lee et al. 2011), magnesium chloride was premixed in aqueous solution with polyacrylamide to prepare inorganic-organic composite polymer (MCPAM) with the composition of 90% $MgCl_2$: 10% PAM (w :w). The prepared aqueous solution of MCPAM composite polymer was aged for 24 hours at room temperature prior to any application. The transmission electron microscopy (TEM) image of MCPAM composite polymer is shown in Figure 1. Polyacrylamide is observed in tree-roots like structure and magnesium chloride which appears in black spots are embedded on the polyacrylamide chain.

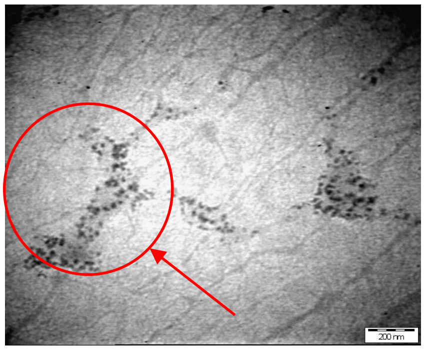

Figure 1 TEM image of MCPAM composite polymer in aqueous solution.

2.3. Flocculation procedure

MCPAM composite polymer was used in flocculating different concentrations of Cibacron Red FN-R (CI Reactive Red 238, $C_{29}H_{15}O_{13}S_4ClFN_7Na_4$, molecular weight: 944.2 g mol^{-1}) simulated reactive dye wastewater. The pH was adjusted using acid and alkaline. Flocculation was carried out using a high torque stirrer (IKA LABORTECHNIK RW20DZM.n). The temperature of dye wastewater was controlled using thermostatic water bath (KBLee 2010). MCPAM composite polymer was introduced into the simulated reactive dye wastewater and an agitation speed of 100rpm was applied for 5 minutes. Flocs formed were allowed to settle for 30 minutes. The dye residual that remained in the supernatant was measured with spectrophotometer (HACH DR2800) at λ_{max} = 540 nm.

3. Results and discussion

3.1. Effect of pH

One of the reasons in selecting magnesium chloride to be composed with polyacrylamide to prepare MCPAM composite polymer is magnesium chloride works well in the alkaline region (Gao et al. 2007). It is well known that the working pH of the reactive dyeing process is usually high (pH > 11) (Golob et al. 2005). Therefore, no drastic pH adjustment is needed for the flocculation of reactive dye wastewater using MCPAM composite polymer. The pH range of 11.25 to 12.50 was taken into account to determine the best working pH in flocculating 500 mg/L reactive dye wastewater using a dosage of 1000 mg/L MCPAM composite polymer. Figure 2 shows that the dye removal (%) increases from pH 11.25 and achieves the highest efficiency at pH 12; however, it decreases thereafter. This is attributed to the decrease of Mg^{2+} ion content when the pH increases beyond 12 whereby almost all Mg^{2+} ions from MCPAM composite polymer have been converted to precipitable hydroxide by the excess OH^- ion. The mechanism has been proposed in Equation 1 where MCPAM composite polymer is dissociated into $[Mg^{2+}\bullet 2Cl^-]$-PAM when it is introduced into the reactive dye wastewater. Sufficient amount of OH^- ions are needed to bind with $[Mg^{2+}\bullet 2Cl^-]$-PAM to form Dye-$Mg(OH)_2$-PAM (flocs) and release Cl^- into the supernatant. Excess of OH^- ions (beyond pH 12) induces the forming of $Mg(OH)_2$-PAM precipitable species that without binding any dye molecule which in turn results in the decrease of dye removal (%)

$$\text{Dye} + 2OH^- + [Mg^{2+}\bullet 2Cl^-]\text{-PAM} \rightleftharpoons \text{Dye-}Mg(OH)_2\text{-PAM (flocs)} + Cl^- \quad (1)$$

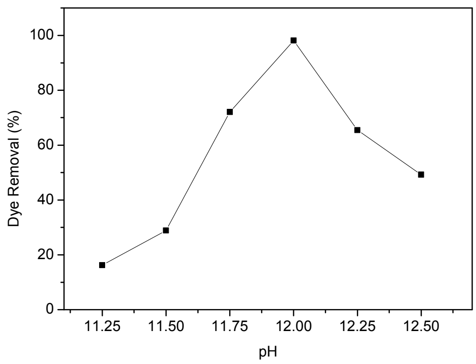

Figure 2 Effect of pH on the dye removal (%).

3.2. Effect of temperature

The effect of temperature on the flocculation of reactive dye has been investigated in the range of 20 to 50°C. The experiments were carried out for different dye concentrations (200-500 mg/L) at pH 12 using a dosage of 500 mg/L MCPAM composite polymer. As show in Figure 3, an increase in the temperature limits the efficiency of flocculation. This is due to the dye molecules with electrostatic bonding onto the MCPAM composite polymer chains are released into the supernatant at elevated temperature which somewhat it reduces the dye removal (%) (Tian et al. 2010). At 20°C, the dye removal (%) decreases from 87 to 61% with the increase of dye concentration from 200 to 500 mg/L. However, at temperature beyond 30°C, an inverse behaviour is observed. The unparallel effect implies that there is an interaction effect between the temperature and dye concentration. The results indicate that the suitable temperature to flocculate reactive dye wastewater is 30°C where it is near to the room temperature. Therefore, it is recommended cooling down the reactive dye wastewater to room temperature prior to any flocculation process take place.

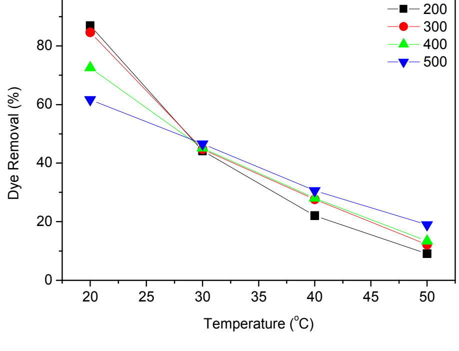

Figure 3 Effects of temperature and initial dye concentration on the dye removal.

3.3. Effect of dosage

Effect of dosage on the dye removal (%) was studied with respect to concentration of dye. Figure 4 shows the effect of dosage on the dye removal (%). The maximum dye removals (%) are 99% for all dye concentrations (200-500 mg/L). Generally, a similar trend is observed for all dye concentrations where the dye removal (%) increases to a maximum value and decrease thereafter. This is because reactive dye needs certain dosage of MCPAM composite polymer in flocculation process to destabilize the molecule of reactive dye; further addition of dosage results the re-suspension of destabilized flocs into the supernatant. A ratio of dye concentration/dosage of MCPAM composite polymer at the maximum dye removal (%) is used to estimate the number of composite polymer needed to flocculate one dye molecule. It is noted that the concentration of dye decreases from 500 to 200 mg/L, the ratio of dye concentration/dosage of MCPAM composite polymer increase from 3 to 6. This implies that the probability for dye molecule and MCPAM composite polymer to collide and capture each other to form flocs is getting lower with the decrease of concentration of dye. Therefore, a dosage as high as 1200 mg/L is needed to flocculate reactive dye even at a low concentration of dye (200 mg/L) due to the low probability of molecular collision.

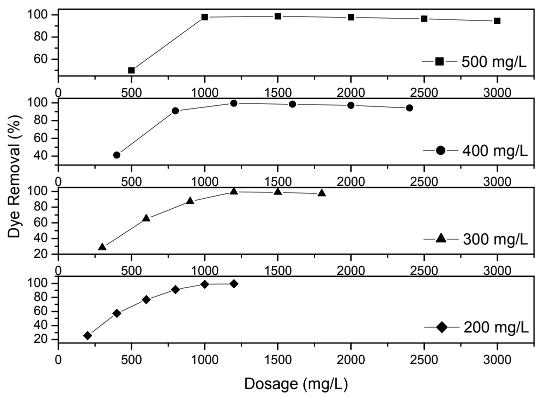

Figure 4 Effect of dosage of MCPAM composite polymer at different dye concentration.

Figure 5 (a) and (b) show the qualitative comparison of reactive dye wastewater before and after flocculation. It is noted in Figure 5(a) that flocs settled and form sludge at the bottom of the beaker. The filtered supernatant is observed to be transparent in colour. The results show that MCPAM composite polymer performs well in flocculating reactive dye wastewater.

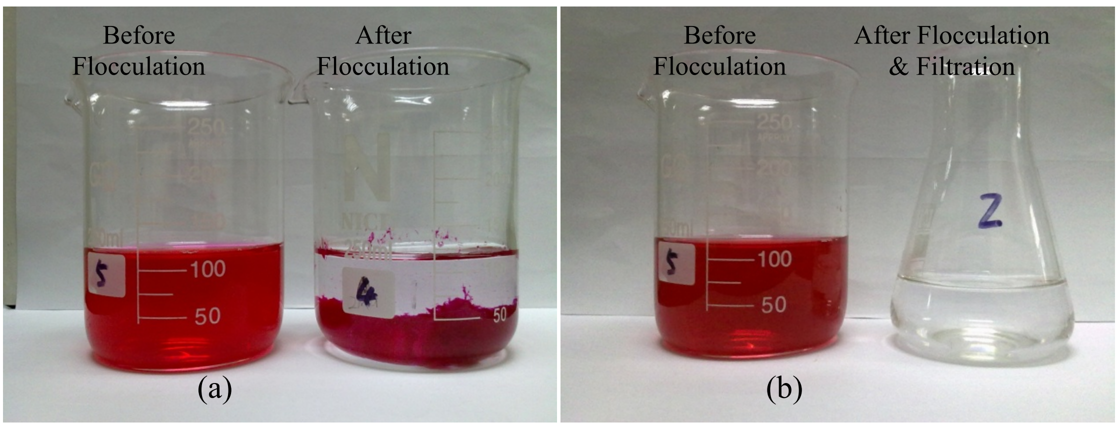

Figure 5 Comparison of reactive dye wastewater (a) before and after flocculation (b) before flocculation and after flocculation & filtration.

4. Conclusions

MCPAM composite polymer was applied to flocculate simulated reactive dye wastewater. The effects of pH, concentration of dye, dosage of MCPAM composite polymer and temperature have been taken into account to investigate the dye removal (%).The result showed that pH 12 was the best working pH in flocculating dye from wastewater. Temperature has a remarkable effect on the flocculation of reactive dye where temperature limits the efficiency of dye removal (%) when temperature increased from 20 to 50^{o}C. Thus, it is recommended that flocculation of reactive dye wastewater to be conducted near room temperature (30^{o}C). Effect of dosage on the dye removal (%) was studied with respect to concentration of dye. MCPAM composite showed a good dye removal (%) where it was able to remove 99% of dye from all dye concentrations (200 – 500 mg/L). However, the dye removal (%) decreased after it achieved the maximum efficiency. This indicates the re-suspension of destabilized flocs into the supernatant.

5. Acknowledgements

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