A Novel Magnetic Separation Agent Prepared by Inverse Emulsion Polymerization and Magnetic Separation Performance for Dye in Solution

Z Q Yu, C Wang*, C Tian and S P Li
School of Environmental Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China.
Key Laboratory of Cleaner Production and Industrial Wastes Resourcization in Universities of Shandong, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China.
Corresponding E-mail: shanqing123@126.com

Abstract. The discharge of industrial wastewater containing dyes is a matter of concern because dyes have harmful effects on the environment and human health. In this work, a novel magnetic separation agent of Fe₃O₄/poly (acrylamide-acryloyloxyethyl trimethylammonium chloride) [MCPAM] was designed for high-performance removal dyes by taking advantage of magnetic separation property of Fe₃O₄ nanoparticles. MCPAM was synthesized through inverse emulsion polymerization and the optimal reaction conditions were obtained by orthogonal experiments. The shape and size of MCPAM was detected by transmission electron microscopy (TEM). The chemical bonds and functional groups of MCPAM were measured by fourier transform infrared spectroscopy (FT-IR). The magnetic properties of MCPAM was surveyed by Superconducting Quantum Interference Device (SQUID MPMSXL). The magnetic separation performance of MCPAM was studied through detecting the removal efficiency of reactive red dye X-3B. The results showed that the MCPAM had core-shell structures and good magnetic properties. And the MCPAM has great potential in accelerating solid-liquid separation and improving removal efficiency of pollutants such as dye colloid in wastewater.

1. Introduction
Dyes have been widely used in textiles, rubber, paper, plastics and cosmetics industries[1]. In these industries, the release of dyes can adversely affect public health, since most dyes have harmful effects on humans and other lives[2-3]. And some of dyes can lead to cancer and genetic mutations. Due to complex chemical structure and high molecular weight, many dyes are difficult to degrade in environment [4-5]. Therefore, removing dyes from wastewater before discharging them into the natural environment is important.

Several treatment processes have been developed for removing dyes from wastewater such as adsorption[6], coagulation-flocculation[7], advanced oxidative processes[8], biological treatment[9], membrane filtration[10]. Coagulation-flocculation was one of the most commonly used methods to treat dyes. Up to now, coagulation-flocculation depends on gravity deposition to achieve solid-liquid separation in treatment process. For dealing with dyeing wastewater, the separation of traditional flocculants has some disadvantages such as long solid-liquid separation time, high production costs and
low removal efficiency\textsuperscript{[11]}. Therefore, improving removal efficiency and shortening solid-liquid separation time are urgently needed in dyeing wastewater treatment process.

Fe\textsubscript{3}O\textsubscript{4} nanoparticles are a kind of magnetic materials with great application prospects in the environmental area, because of their chemical stability and environmental friendliness\textsuperscript{[12-13]}. CPAM with high molecular weight is frequently used to treat anionic wastewater through electrostatic attraction\textsuperscript{[14]}. Therefore, a new magnetic separation agent (MCPAM) was synthetized by Fe\textsubscript{3}O\textsubscript{4} nanoparticles and CPAM through inverse emulsion method. With the action of the external magnetic field assisted gravity field, using the MCPAM could shorten solid-liquid separation time and improve the removal rate.

In this study, we reported the preparation and characterization of a new type of magnetic separation agent which was composed by Fe\textsubscript{3}O\textsubscript{4} nanoparticles and CPAM by inverse emulsion. In order to explore the effect of the dosage of gelatin, citric acid and Fe\textsubscript{3}O\textsubscript{4} nanoparticles on synthetic MCPAM, orthogonal experiments were designed.

2. Experimental

2.1. Materials

Acrylamide (AM), N, N-dimethyl aminoethyl acrylatemthyl chloride quarternary (DAC, 80%), tween20, Span80, disobutyl imidazoline hydrochloride (AIBI), reactive red dye X-3B, liquid paraffin, gelatin, citric acid and potassium chromate (KBr) were obtained from China National Medicines Co., Ltd. Deionized water was used in the entire experimental process. All chemicals used for preparation of MCPAM were used without further purification.

2.2. Instruments

Fourier Transform infrared (FTIR) was used to record the functional group of CPAM and MCPAM with potassium bromide (KBr) pellets. Transmission electron microscopy (TEM) was used to characterized the shape and size of Fe\textsubscript{3}O\textsubscript{4} nanoparticles and MCPAM. Superconducting Quantum Interference Device was used to analysis the magnetic of the MCPAM at room temperature.

2.3. Synthesis of MCPAM

According to the optimal conditions determined by CPAM synthesis, 32 ml of liquid paraffin, 3.831 g of Span 80, 0.21 ml of Tween 20, 3.282 g of AM, 1.64 g of DAC, 0.045 g of AIBI and 20ml of deionized water were added into three-necked flask. Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles, citric acid and gelatin were added into flask. After 30 minutes, initiator solution was added into flask. The reaction temperature was 60 °C. The reaction time was 6 hours and the product was purified 5 times by acetone and anhydrous ethanol. Finally the product was dried in an oven at 40 °C for 6 hours.

In order to identify the optimal preparation conditions, the dosage of gelatin, citric acid and Fe\textsubscript{3}O\textsubscript{4} nanoparticles was chosed as variable in this experiment, and their effects on the removal rate for reactive red dye X-3B was investigated. The experimental conditions were optimized by orthogonal experiment according to the factor and level table shown in Table 1.

| Factors | Levels |
|---------|--------|
| A (Gelatin) | 1 | 0.6 g |
| | 2 | 0.8 g |
| | 3 | 1.0 g |
| B (Fe\textsubscript{3}O\textsubscript{4}) | 1 | 0.2 g |
| | 2 | 1.0 g |
| | 3 | 1.8 g |
| C (Citric acid) | 1 | 0.3 g |
| | 2 | 0.4 g |
| | 3 | 0.5 g |
2.4. Magnetic separation performance test
Separation behavior of MCPAM was studied through detecting the removal efficiency of reactive red dye X-3B solution. The concentration of dye solution was 30 mg·L⁻¹. The concentration of MCPAM was 1 g·L⁻¹. 5 ml of MCPAM was added into the beaker containing 200 ml of dye solution. Then the beaker containing the mixture was placed on the motor stirrer. The motor stirrer was rotated at 200 rpm for 2 minutes, and then reduced to a low rate of 50 rpm for 10 minutes. After mixing, the treated dye solution was placed on the magnet for 5 minutes. The removal rate of reactive red dye X-3B was obtained by calculating the concentration of dye in the supernatant.

3. Results and discussion

3.1. Factors affecting synthetic MCPAM
The effects of the dosage of Fe₃O₄ nanoparticles, citric acid and gelatin on the synthesis of MCPAM were explored (Table 2). The reaction conditions and the dye removal rate of each group were listed in Table 2. It could be deduced from Table 2: RB>RA>RC. It meant that the dosage of Fe₃O₄ nanoparticles had the greatest effect on the removal rate in experiment, then followed by the dosage of gelatin but the dosage of citric acid had the less effect. The removal rate varied between 71.21% and 87.13%. Therefore, the K value revealed that the optimal parameter level is A₂B³C². When the dosage of Fe₃O₄ nanoparticles was 1.8 g, the dosage of gelatin was 0.6 g, the dosage of citric acid was 0.4 g, the MCPAM with the maximum removal rate of 90.31% of reactive red dye X-3B was obtained.

Table 2. Orthogonal experimental design and results for removal of anionic dyes.

| No. | A  | B  | C  | Removal Rate (%) |
|-----|----|----|----|------------------|
| 1   | 1  | 1  | 1  | 71.21            |
| 2   | 1  | 2  | 3  | 77.78            |
| 3   | 1  | 3  | 2  | 84.56            |
| 4   | 2  | 1  | 3  | 74.32            |
| 5   | 2  | 2  | 2  | 83.71            |
| 6   | 2  | 3  | 1  | 87.13            |
| 7   | 3  | 1  | 2  | 74.51            |
| 8   | 3  | 2  | 1  | 82.16            |
| 9   | 3  | 3  | 3  | 84.66            |
| k1  | 77.85 | 73.35 | 80.17 |
| k2  | 81.72 | 81.22 | 80.93 |
| k3  | 80.11 | 85.45 | 78.92 |
| R   | 3.87 | 12.1 | 2.01 |

3.2. Characterization of synthesized materials
The shape and particle diameter size of the Fe₃O₄ nanoparticles and MCPAM synthesized under the optimal conditions are shown in Figure 1. The particle diameter size of the Fe₃O₄ nanoparticles was about 10 nm, and both MCPAM particles and Fe₃O₄ nanoparticles had spherical shape and cubic shape.
As seen in Figure 1b, the Fe₃O₄ nanoparticles were surrounded by CPAM, and the external gray area and the internal black area were CPAM and Fe₃O₄ nanoparticles, respectively.

Figure 1. TEM images of Fe₃O₄ nanoparticles(a) and MCPAM(b).

The FT-IR spectrums of CPAM and MCPAM are shown in Figure 2. In the spectrum of CPAM, the peak at about 1210 cm⁻¹ was assigned to the C-N group, the two peaks at 1415 cm⁻¹ and 1454 cm⁻¹ were attributed to the C-O groups, the peak at about 1685 cm⁻¹ was assigned to the C=O group, the flexing vibration peak of the O-H group could be observed at 3100-3500 cm⁻¹. Comparing these two lines, the biggest difference was that the line of MCPAM had a peak at 607 cm⁻¹ which was attributed to Fe-O group[15-16]. The results showed that Fe₃O₄ nanoparticles was successfully coated with CPAM.

Figure 2. FT-IR spectrum of CPAM and MCPAM.

Magnetic hysteresis loops of MCPAM with different dosage of Fe₃O₄ nanoparticles are shown in Figure 3a recorded at room temperature. The curve of S1 indicated that magnetic response was absent in CPAM. Compared with S2, S3, S4, when the dosage of Fe₃O₄ nanoparticles was 1.8 g, the maximum Ms and the best magnetic properties were obtained. The magnetic response of the MCPAM was explored with the action of an external magnetic field in Figure 3b. According to the results presented in Figure 3b, the MCPAM moved to the side of the magnet under the external magnetic field. This phenomenon indicated that the MCPAM had a good magnetic response.
3.3. The performance of magnetic separation agent

The dye removal rate of MCPAM and CPAM is shown in Figure 4. The maximum removal rate of the reactive red dye X-3B treated with CPAM was 68.10% at 5 minutes. The removal rate of reactive red dye X-3B treated with MCPAM was 77.03% at 1 minutes, and the removal rate was increased to 90.31% in 5 minutes with the action of the external magnetic field assisted the gravity field. According to the results presented in Figure 4, the dye removal rate of MCPAM was higher than that of the CPAM, which means that MCPAM could accelerate the processing efficiency, shorten solid-liquid separation time and improve dye removal rate with the action of the external magnetic field assisted the gravity field.

MCPAM is a new type of magnetic separation agent that could remove dyes effectively through electrostatic attraction, with the action of the external magnetic field assisted the gravity field. In this study, we found the removal efficiency was improved to 90.31% with a flocculation time of 5 minutes by using MCPAM. It indicates that the magnetic separation agent could significantly shorten solid-liquid separation time, improve removal efficiency and reduce cost. The magnetic separation agent also gives a hint for treating this kind of wastewater, such as surfactant, organic pollutants, algal pollutants and pulp mill wastewater. However, the regeneration and reuse of magnetic separation agent are still unclear, and these problems need more research to extend its applications. It is expected that the magnetic separation agent can be more researched and widely used in wastewater treatment in the future.
4. Conclusions

This paper explored the preparation, characterization and the dye removal of MCPAM. The optimal conditions for the synthesis of MCPAM by inverse emulsion polymerization were obtained through orthogonal experiment. The FT-IR spectrum and TEM determined that the Fe$_3$O$_4$ nanoparticles were successfully combined with CPAM and the MCPAM particles had spherical shape and cubic shape. The hysteresis loop showed that the MCPAM particles had good magnetic properties. With the action of the external magnetic field assisted the gravity field, the MCPAM had obvious effect in accelerating separation, improving removal efficiency and shortening solid-liquid separation time.

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