Synthesis of a novel magnetic polyacrylamide coagulant and its application in wastewater purification
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ABSTRACT
In this study, a novel magnetic polyacrylamide (PAM) coagulant based on the core of magnetite (Fe₃O₄), with oleic acid serving as modifier and acrylamide as monomer, was synthesized to remove suspended solids in kaolin-suspended water. The composites were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermo gravimetric analysis and scanning electron microscopy. The results demonstrated that 82.8% of turbidity removal rate was obtained in 5 min of static settling in simulated kaolin-suspended water. This proved to be superior to that of PAM and poly aluminum chloride. Also confirmed in this study was the fact that zeta potential was significantly correlated with turbidity removal.

Key words | acrylamide, coagulant, Fe₃O₄, magnetic

INTRODUCTION
Turbidity is a widely accepted index used to estimate water quality, which is mainly caused by suspended substances (Khamis et al. 2015; Villota et al. 2015; Zeng et al. 2015). Due to its low capital and operational costs, coagulation has been regarded as one of the general methods for removing turbidity during wastewater treatment (Burton & Tchobanoglous 1991). The polyacrylamide (PAM) family of polymers and copolymers is the most widespread and universal coagulant due to its extreme water solubility and high molecular state (Yamamoto & Sefton 1996; Biswal & Singh 2004; Sen et al. 2011; Wang et al. 2013). In the present study, copolymers of acrylamide with cationic, anionic or amphoteric monomers were synthesized (Ho et al. 2010; Ghosh et al. 2011). Using these coagulants makes it possible for flocs to be formed efficiently and increase in size, which will benefit their settlement behaviors. However, there are still challenges in separating some flocs from water, which will lead to a reduction in the efficiency of their sedimentation. Accordingly, it has become an urgent issue to develop effective coagulants based on environmentally friendly principles for removing a large percentage of suspended solids from wastewater.

Fe₃O₄ has been widely used in magnetic separation due to its low toxicity, convenient separation and small size (Uheida et al. 2006; Tang et al. 2010; Warner et al. 2010). For example, Fe₃O₄ was taken into account when magnetic seeds were combined with ferric sulfate (PFS) to remove arsenic from wastewater through high gradient superconducting magnetic separation (Li et al. 2010). Although the insolubility of Fe₃O₄ limited its practical application in wastewater treatment (Maity & Agrawal 2007), many attempts have been made to synthesize adsorbents by grafting manifold polymers onto the surface of Fe₃O₄ particles. The objective in doing so is to enhance their stability and sorption capacity (Mak & Chen 2004; Ren et al. 2010; Zhou et al. 2010; Badruddoza et al. 2011; Li et al. 2013). Inspired by such ideas, this study puts forward a new solution: firstly, combine a traditional coagulant PAM molecule on the surface of magnetic Fe₃O₄ particles; and secondly, develop a new kind of coagulant by improving its separation efficiency. To date, little attention has been paid to using magnetic composites as a coagulant.

We need to use some type of modification agent to alter the surface properties of Fe₃O₄, as this will assist the lipophilic group of PAM to bind with magnetic particles. Moreover, it is evident that agglomeration frequently occurs between Fe₃O₄ particles (Laurent et al. 2008). To prevent this, surface modification is necessary (Lee et al. 2007). Oleic acid is one kind of modifier that performs efficiently because of its hydrophilic group and lipophilic group distribution at both ends of the molecular chain (Suslick et al. 1996), which makes it possible to combine oleic acid molecules with the surfaces of magnetic particles.

doi: 10.2166/wst.2016.500
The synthesis process of the coagulant is as follows. First, \( \text{Fe}_3\text{O}_4 \) particles were selected as magnetic matter, oleic acid as the modifier, and acrylamide as the monomer. Then, the synthesis mechanism was discussed and the properties of the magnetic polyacrylamide (MPAM) coagulant were characterized. Besides, a series of coagulation experiments with the coagulant were also executed in wastewater containing kaolin.

 **MATERIALS AND METHODS**

**Materials**

Sodium bisulfite (\( \text{NaHSO}_3 \)), potassium persulfate (\( \text{K}_2\text{S}_2\text{O}_8 \)), ethanol (\( \text{C}_2\text{H}_5\text{OH} \)), oleic acid (\( \text{OA}, \text{CH}_3(\text{CH}_2)7\text{CH} (\text{CH}_2)7\text{COOH} \)), acetone (\( \text{CH}_3\text{COCH}_3 \)), PAM (\( \text{C}_3\text{XH}_5\text{XNXOX} \)) and poly aluminum chloride (PAC, \( \text{Al}_2\text{Cl}_n(\text{OH})_{6-n} \)) were analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). \( \text{Fe}_3\text{O}_4 \) nanoparticles (98% metals basis, 20–30 nm), acrylamide (AM, analytical reagent grade) and kaolin (chemical reagent grade) were obtained from Aladdin Reagent Co., Ltd (Shanghai, China). All the other materials were acquired from several suppliers. Water used throughout was deionized.

**Apparatus**

The functional groups of the synthesized composites were characterized by a Fourier transform infrared spectrometer (FTIR, IS10, Thermo Scientific, USA). Thermo gravimetric analysis (TGA) was conducted on an STA 449 F3 thermal analyzer (NETZSCH, Germany) under air atmosphere at a heating rate of 20 \(^\circ\)C min \(^{-1}\) between 20 and 800 \(^\circ\)C. X-ray diffraction (XRD) analyses were executed with a D/max-2500 XRD (Rigaku, Japan) by Cu K\( \alpha \) radiation at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were created on a quanta 250 microscope (FEI, USA). Zeta potentials were measured on a Mastersizer 2000 Laser Particle Size Analyzer. Turbidity was determined by a WGZ-800 turbidimeter (Xinrui, China).

**Preparation of MPAM coagulant**

**Oleic acid-modified magnetite**

Oleic acid-modified magnetite was prepared utilizing a modified method (Maity & Agrawal 2007), as follows: \( \text{Fe}_3\text{O}_4 \) nanoparticles (2.0 g) were dispersed using 50 mL water by ultrasonication for 20 min. Oleic acid (50 mL) was then added slowly into the magnetite suspension solution, and the mixture was maintained at 60 \(^\circ\)C for 24 h in a shaking water bath. Following this, the products were collected by application of an external magnetic force and then washed several times with acetone. The reacted magnetite was continuously purified by soxhlet extraction using acetone as a solvent for 48 h (Yang et al. 2012). Finally, the oleic acid modified magnetite was dried for 24 h in a vacuum drying oven and stored in a desiccator for the ensuing experiments.

**Synthesis of MPAM coagulant**

The MPAM coagulant was prepared as follows (Chen et al. 2009, 2009a, 2009b):

(a) 0.5 g of the oleic acid modified magnetite mentioned above was dispersed into 50 mL water under mechanical stirring for 20 min to form suspension solution A. Subsequently, this solution A was transferred into a three-necked round-bottomed flask operating at 40 \(^\circ\)C in a water bath and subjected to internal stirring. Nitrogen was bubbled into the flask for 30 min after the addition of sodium bisulfite and potassium persulfate at an appropriate ratio.

(b) 25 g acrylamide was dissolved in 50 mL water to form solution B, which was then transferred into a dropping funnel fixed onto the flask in step (a). The dropping of solution B was completed in an hour, and the mixture was stirred continuously at 40 \(^\circ\)C for 6 h.

(c) Finally, MPAM was separated and washed with acetone several times, and then vacuum-dried for 24 h.

**Coagulation experiments**

Coagulation experiments of kaolin-containing wastewater were conducted in a jar test. The wastewater containing kaolin was simulated with 0.2 g kaolin dispersed in 1,000 mL water that was stabilized over 24 h. Alike was the coagulation experimental procedure, in which there was rapid stirring at 250 rpm for 2 min and then slowly at 80 rpm for 5 min after the appropriate addition of various coagulants containing PAM, PAC and MPAM. Subsequently, a series of static settling for 30 min was conducted, while that of MPAM was done for 5 min on a magnet. Then the turbidity and zeta potential of the supernatant liquid were measured.
RESULTS AND DISCUSSION

Characterization of Fe₃O₄, oleic acid modified Fe₃O₄ and MPAM

FTIR

The FTIR spectra of Fe₃O₄, oleic acid modified Fe₃O₄, and MPAM are shown in Figure 1. A characteristic peak of these three materials is at about 580 cm⁻¹ (Fe-O vibration), this being attributed to the presence of Fe-O in Fe₃O₄ (Phan & Jones 2006). In spectra b and c, the peaks at 3,440 cm⁻¹ and 3,450 cm⁻¹ could be attributed to the overlap of −OH stretching and −NH stretching vibration. The peaks at 2,970 cm⁻¹ and 2,940 cm⁻¹ may be caused by C-H stretching. For modified Fe₃O₄, the sharp peak at 1,720 cm⁻¹ may originate in the carboxyl groups of oleic acid, while the weak peak at 1,630 cm⁻¹ may be due to C = O stretching affected by the long CH₂ chain of oleic acid. These two peaks confirm the existence of oleic acid on the surface of F₃O₄ particles. For MPAM, the peaks at 1,660 cm⁻¹ and 1,400 cm⁻¹ may relate to amide C = O stretching and C-N stretching bands. The peak at 1,320 cm⁻¹ may result from the CH₂ twisting vibration (Biswal & Singh 2004). These peaks reveal that PAM has been successfully synthesized on the surface of Fe₃O₄.

XRD

The XRD patterns of Fe₃O₄, oleic acid modified Fe₃O₄, and MPAM are depicted in Figure 2. The figure exhibits six characteristic peaks in Figure 2(a)–2(c) at 2θ = 30.16°, 35.52°, 43.14°, 53.56°, 57.10° and 62.66°, caused by the (220), (311), (400), (422), (511) and (440) phases of Fe₃O₄ (JCPDS No. 89–3854). This also indicates that Fe₃O₄ is coated by organic polymers and oleic acid, while its spinal structure is not destroyed. Furthermore, new peaks at 2θ < 30° in Figure 2(c) which display high intensity are possibly due to the amorphous organic polymers (e.g. PAM) (Ni et al. 2002).

TGA

The TGA curves of Fe₃O₄, oleic acid modified Fe₃O₄, and MPAM are shown in Figure 3. The mass of Fe₃O₄ rises by about 2% after 350 °C, due to ferrous ions of Fe₃O₄ being oxidized under air atmosphere. An approximately 2.5%
weight loss of oleic acid modified Fe$_3$O$_4$ is evident at 550 °C, revealing that the weight of oleic acid loaded on the surface of Fe$_3$O$_4$ particles is close to 4.5%. Furthermore, the weight loss of MPAM at 600 °C is around 70%. Combined with the results obtained in Figure 1(c), it can be estimated that about 67.5% PAM polymer is coated on the surface of Fe$_3$O$_4$ particles.

Morphology

Figure 4 shows the SEM images of unwrapped Fe$_3$O$_4$ particles (Figure 4(a)) and MPAM (Figure 4(b)), respectively. Obviously, the agglomeration phenomena do occur among Fe$_3$O$_4$ particles, but disappear in MPAM. It is also observed in the experiment that a few Fe$_3$O$_4$ particles were taken as the core and the wrapped PAM was taken as the coating layer. This structure determines the dissolubility of MPAM due to the amidogens of PAM and the ferromagnetism of MPAM attributed to the Fe$_3$O$_4$ core.

Effect of MPAM in wastewater treatment

0.4 mL of 2 g/L PAM, 2 g/L MPAM and 200 g/L PAC aqueous solutions were added into 250 mL kaolin simulated wastewater, respectively. The turbidity removal and zeta potential of the supernatant liquid after coagulation are displayed in Table 1. The highest turbidity removal percentage of 82.8% was obtained in 5 min static settling when utilizing MPAM. While the other two coagulants required more settling time to obtain a similar amount of turbidity removal, these results correlate with the absolute value of zeta potential: the lower the zeta potential value, the greater the coagulation ability, which could be explained by Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory.

CONCLUSIONS

The results obtained from FTIR, XRD, TGA and SEM indicate that PAM can be successfully coated onto Fe$_3$O$_4$ particles to form a novel MPAM coagulant. Furthermore, oleic acid as a surface modifier can help to prevent the occurrence of agglomeration among Fe$_3$O$_4$ particles. The application of MPAM in simulated kaolin wastewater reveals the highest amount of turbidity being removed. On the one hand, the PAM molecules have performed the coagulation function as expected, while on the other hand, the ferromagnetism of the core has promoted the separation of flocs from water when employing the bottom magnetic field.

It proves that MPAM as a coagulant is more effective than the traditional coagulants PAM and PAC due to its dissolubility and ferromagnetism, which may provide a
valuable research topic for exploring the synthesis of new magnetic coagulants in the future. While to make a further application of this synthetic MPAM, many specific tests should be carried out.

ACKNOWLEDGEMENTS

This study is sponsored by the following bodies: the Jiangsu Provincial Prospective Joint Research Foundation for Industry-University-Research, China (No. BY2016057-07), the National Natural Science Foundation of China (No. 20130371), and the Open Funds of Jiangsu Key Laboratory of Marine Biotechnology (No. HS14014).

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First received 20 April 2016; accepted in revised form 7 October 2016. Available online 26 October 2016