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Polyacrylamide grafted cellulose as an eco-friendly flocculant: Key factors optimization of flocculation to surfactant effluent

Hangcheng Zhu[a], Yong Zhang[a], Xiaogang Yang[a], Lan Shao[b], Xiumei Zhang[a], Juming Yao[a,*]

[a] *Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Ministry of Education, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, China*
[b] *Technique Center, Hangzhou Xinhua Group Co., Ltd., Hangzhou 310011, China*

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ABSTRACT

The discharge of effluents from surfactant manufacturers is giving rise to increasingly serious environmental problems. In order to develop the eco-friendly flocculation materials to achieve effective removal of pollutants from the surfactant effluents, the bamboo pulp cellulose from *Phyllostachys heterocycla* is employed as the skeleton material to synthesize an eco-friendly bamboo pulp cellulose-g-polyacrylamide (BPC-g-PAM) for flocculation. The BPC-g-PAM is used with the metal ions as the coagulant to treat the effluent from a surfactant manufacturer. The response surface methodology coupled with Box–behnken design is employed to optimize the key factors of coagulation–flocculation. The results show that the combination of Fe^{3+} with BPC-g-PAM achieves the best coagulation–flocculation performance like, the fast treatment time, minimum coagulant and BPC-g-PAM dosages compared with the other two combinations of Al^{3+} with BPC-g-PAM and Ca^{2+} with BPC-g-PAM. Therefore, the combination of Fe^{3+} with BPC-g-PAM is expected to promote its application for the pollution control in the surfactant manufacturers.

1. Introduction

Owing to surfactants' multiple industrial and living applications, they are being used in all aspects of people's life like cosmetic and pharmaceutical products, textile, foodstuff and so on. However, on the other hand, with environmental pollutants becoming a rising problem in real life, surfactants and their production processes are gradually emerging as a potential threat to natural environment, especially the effluent discharged from surfactant plants (Heredia, Martín, & Moreno, 2012). There are several physico-chemical methods to remove residual surfactants and other pollutants from surfactant effluent, such as chemical adsorption (Rosu, Marlina, Kaya, & Schumpe, 2007), adsorption on coagulation (Kaleta & Eletorowicz, 2013) and electrochemical removal (Panizza et al., 2013). With regard to different types of surfactant products, the method to deal with their effluents is quite different.

Coagulation–flocculation is now commonly employed for the first segment processing of surfactant effluent due to its high efficiency, low cost and simple operation (Heredia, Martín, & Martín, 2009; Jangkorn, Kuhakaew, Theantanoo, Klinla-Or, & Sriwiriyarat, 2011). Coagulation is a process of destabilizing surfactant effluent to form small agglomerates by dominant charge neutralization. Then flocculation plays the role of contact and adhesion whereby dispersed particles to form larger-size clusters by charge neutralization, bridging and sweeping. In the process of coagulation–flocculation, its performance is governed by multiple parameters, such as type and dosage of coagulant and flocculant (Desjardins, Koudjonou, & Desjardins, 2002; Liang, Sun, Li, Ong, & Chung, 2014), pH value and temperature of solution (Cai et al., 2013; Liimatainen et al., 2011; Liimatainen, Sirviö, Sundman, Hormi, & Niinimäkia, 2013; Miller, Fugate, Craver, Smith, & Zimmerman, 2008), agitation speed and time (Almubaddal, Alrumaihi, & Ajbar, 2009; Teh, Wu, & Juan, 2014), feeding order of chemicals (Almubaddal et al., 2009). The optimization of these parameters is of significance to improve coagulation–flocculation efficiency.

At present, synthetic flocculants, such as polyacrylamide and polyacrylic acid, are widely used in flocculation of industrial wastewater due to their stable monomer source, matured synthesis technology and excellent flocculation effect (Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011). However, based on their monomers from petrochemical industry, the flocculation sludge formed by synthetic flocculants is difficult to be biodegraded after

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* Corresponding author at: College of Materials and Textiles, Zhejiang Sci-Tech University, Xiasha Higher Education Park, Hangzhou 310018, China.
E-mail address: yaoj@zstu.edu.cn (J. Yao).

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Table 1
Physicochemical characteristics of the raw surfactant effluent.

Parameters	Data
Chemical oxygen demand (COD_{Cr}) (mg/L)	9460 ± 52
Biochemical oxygen demand (BOD_5) (mg/L)	1302 ± 16
Size of suspended solids (nm)	535.2 ± 15.1
Zeta potential (mV)	−42.4 ± 2.3
Turbidity (NTU)	351
pH value	6.5

it is landfilled underground in a relatively long time. Some of its decomposition products even cause potential health hazards owing to the release of toxic monomers (Bo et al., 2012). Therefore, some natural polymer-based flocculants begin to attract attention and may provide an alternative to traditional synthetic flocculants, due to the growing needs for more eco-friendly and safe products (Pal et al., 2011; Yang et al., 2014).

Cellulose is the most abundant natural polymer in the world. Due to its numerous reactive hydroxyl groups and long-chain structure, cellulose is considered as one of the most suitable skeleton materials for the synthesis of natural polymer-based flocculants (Roy, Semsarilar, Guthrie, & Perrier, 2009). *Phyllostachys heterocycla* bamboo cellulose is classified as a kind of long-fibered fibrous material whose fiber length is comparable to that of softwood. Due to its short growth period, long fiber length and similar chemical composition to softwood, *P. heterocycla* bamboo cellulose attracts much attention and is being used as raw materials for many high-value products (Zhou et al., 2014).

In our earlier work (Liu, Yang, Zhang, Zhu, & Yao, 2014), an efficient and eco-friendly flocculant, *P. heterocycla* bamboo pulp cellulose grafted with polyacrylamide (BPC-g-PAM) was synthesized. In the present study, the BPC-g-PAM product is employed with the metal ions, Fe^{3+}, Al^{3+} or Ca^{2+} as coagulant to treat the effluent from a surfactant manufacturer. A series of coagulation and flocculation experiments are carried out to optimize process parameters. Response surface methodology coupled with Box–behnken design (RSM-BBD) is adopted to optimize key factors for the BPC-g-PAM coagulation–flocculation. It is expect that this eco-friendly BPC-g-PAM together with its optimal coagulation–flocculation process may provide potential and helpful guidelines for the efficient treatment of the effluents from surfactant manufacturers in the future.

2. Experimental

2.1. Materials

Bamboo kraft pulp, derived from *P. heterocycla*, was provided by Guizhou Chitianhua Paper Industry Co., Ltd., China. According to our previous study, the degree of polymerization of the used bamboo kraft pulp was determined as 781 (Zhu et al., 2015). Raw surfactant effluent, mainly consisting of anionic and non-ionic surfactants, was collected from Henglong Chemical Co., Ltd., China. The physicochemical characteristics of the raw surfactant effluent are listed in Table 1. Chemical oxygen demand (COD) was tested using the potassium dichromate oxidation method and biochemical oxygen demand (BOD) was determined by an iodometric method (Liu et al., 2014). Zeta potential (ZP) and Size of suspended solids were measured with the Malvern Nano ZS90 at neutral pH in 0.5 mM [NaCl] buffer (Zhu et al., 2015). Turbidity of effluent was determined using a Turb550 turbidimeter. The coagulants including aluminum chloride ($AlCl_3{\cdot}6H_2O$), ferric chloride ($FeCl_3{\cdot}6H_2O$), calcium chloride ($CaCl_2$), poly aluminum chloride (PAC), and ammonium persulfate (APS), anionic polyacrylamide (APAM) were purchased from Aladdin Chemistry Co. Ltd., China. The pH value of the surfactant effluent was adjusted to a desired value using 0.1 M HCl or 0.1 M NaOH solutions. The deionized water was used throughout the coagulation–flocculation experiments.

2.2. Synthesis of BPC-g-PAM

The BPC-g-PAM was synthesized by free-radical graft copolymerization in homogeneous aqueous solution according to our previous work (Liu et al., 2014). In brief, the polyacrylamide (PAM) was grafted onto the skeletons formed by the bamboo pulp cellulose (BPC) in the NaOH–urea homogeneous aqueous solution (7 wt% NaOH and 12 wt% urea, 4 °C) (Cai et al., 2007; Zhang, Wu, Liu, & Yao, 2013). According to the results of orthogonal experiment, the optimum synthesis conditions were presented as follows, BPC concentration at 4 wt%, APS to BPC mass ratio of 0.25 g/g, PAM to BPC mass ratio of 1 g/g, reaction temperature at 50 °C and reaction time for 1 h. The resultant suspension was washed with deionized water to neutral and extracted with 95 wt% ethanol. The product was dried at 50 °C for 6 h to obtain the target BPC-g-PAM. Its grafting ratio was measured as 43.8% and isoelectric point appeared at pH 4 (Liu et al., 2014). The flocculant concentration of 2 wt% was used for the subsequent experiments.

2.3. Coagulation–flocculation experiment

The coagulation–flocculation jar tests were carried out using 250 mL beakers and a JJ-4 six-place programmed paddle mixer at room temperature. 2 wt% $AlCl_3{\cdot}H_2O$, 1 wt% $FeCl_3{\cdot}6H_2O$ and 2 wt% BPC-g-PAM solutions were prepared for the coagulation–flocculation experiments.

2.3.1. Optimization of coagulant dosage and treatment time on coagulation

Each experiment for Al^{3+} and Fe^{3+} was carried out with the same procedure, 200 mL raw surfactant effluent at pH value of 6.5 was poured into a 250 mL beaker. The designed amount of coagulant solution was added into the beaker. The mixed solution was rapidly stirred at 200 rpm for 3 min followed by a slow stirring of 40 rpm for 7 min. After certain period of treatment time, the supernatant turbidity of the treated surfactant effluent was recorded.

2.3.2. Optimization of pH value on coagulation

In order to obtain a feasible pH condition for the combined coagulation–flocculation procedure, the effect of pH value on the coagulation with metal ions was also investigated. The pH value of the surfactant effluents was adjusted by HCl or NaOH solution. The coagulant with pre-determined dosage was then added. The turbidity was recorded with the same procedure as above.

2.3.3. Optimization of BPC-g-PAM dosage and treatment time on coagulation–flocculation

The coagulation–flocculation of the BPC-g-PAM with metal ions was determined on the conditions of the pre-determined pH value of surfactant effluent and optimum dosage of coagulant. After 3 min of vigorous stirring, the desired amount of BPC-g-PAM solution was added into the pre-coagulated surfactant effluent. A slow stirring of 40 rpm for 7 min was followed. After certain period of treatment time, the supernatant turbidity of the treated surfactant effluent was recorded.

2.4. Response surface methodology coupled with Box–Behnken design (RSM – BBD)

The RSM-BBD was employed to investigate the performance of three independent variables including coagulant dosage (X_1), pH value (X_2) and BPC-g-PAM dosage (X_3) on the response functions, which are listed in Table S1. The experimental data were analyzed