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ORIGINAL PAPER

Synthesis of hydrophobically modified cellulose-based flocculant and its application in treatments of kaolin suspension and machining wastewater

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Abstract In this work, an efficient and hydrophobic bamboo pulp cellulose-graft-sodium silicate–polyacrylamide (BPC-g-Si–PAM) flocculant was designed and synthesized to improve its flocculation performance as well as the dewatering efficiency of coagulation sludge. The optimal synthesis process of BPC-g-Si–PAM and its optimal flocculation conditions on wastewater treatment were investigated in detail. Compared with unmodified BPC-g-PAM and commercial PAM, hydrophobic BPC-g-Si–PAM flocculant exhibited better flocculation performance with SV30 of 5.8%. Moreover, TSS, COD and turbidity reduction for machining wastewater reached upto 98.1, 86.8 and 97.6%, respectively. Compared with commercial PAM, removal rate increased by 2.69, 7.68 and 2.68%, respectively. And also BPC-g-Si–PAM exhibited higher removal efficiency for ammonia nitrogen (77.7%), total iron (99.3%), total phosphorus (93.6%) and total zinc (96.7%) than PAM. All the results demonstrated that hydrophobic BPC-g-Si–PAM has a potential application prospect in industrial wastewater treatment.

Keywords Bamboo pulp cellulose · Hydrophobic flocculant · Optimum synthesis · Wastewater treatment · Sludge dewatering

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Introduction

With high-speed development of social economy, industrial and domestic wastewater have become increasingly serious and need urgent solutions. Coagulation–flocculation process is regarded as one of the most important and widely used treatment processes of raw water (Teh and Wu 2014) and industrial wastewater (Teh et al. 2016) due to its simple apparatus required, facile operation and low cost (AlMubaddal and AlRumaihi 2009; Heredia et al. 2009; Jangkorn et al. 2011; Wang et al. 2013; Sievane et al. 2015). Until now, various inorganic and organic flocculants, such as aluminum salts, titanium salts, iron salts, and polyacrylamide (PAM) have been synthesized to treat wastewater (Amuda et al. 2006; Chang et al. 2008; Witham et al. 2012; Shi et al. 2012; Ma et al. 2017). However, there are some drawbacks for the applications of these flocculants. Inorganic flocculants usually require high dosage to be efficient and contaminate water with metal salts. For example, the effluent of iron coagulation system has corrosivity, higher color, unpleasant metallic taste and odor. In addition, the applicability of PAM as a synthesized flocculant is limited due to its non-biodegradability and toxicity of residual monomer (Witham et al. 2012; Petroudy et al. 2014; Wei et al. 2015; Ma et al. 2017).

Environmental concerns have led to research into alternative flocculants from natural and renewable sources (Choy et al. 2015). Cellulose is a promising alternative to other biodegradable flocculants because it is the most abundant biopolymer on the earth but it is also goes to waste in the form of agricultural losses in the food processing industry, forestry residues and mill residues (Zhao et al. 2007; Ahankari et al. 2011; Chandra et al. 2012; Chen et al. 2012; Nechyporchuk et al. 2016). Targeted modification of cellulose can be used to introduce the desired functional groups to prepare the most effective flocculant. Aguado et al synthesized water-soluble cationic cellulose derivatives by three different procedures, cationizing bleached hardwood kraft pulp with (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride to enhance flocculation in papermaking (Aguado et al 2017). Recently, Shak and Wu (2017) also used N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride in modifying natural seed gum for its used in treatment of agro-industrial wastewater via coagulation-flocculation process. Nanocellulose which possesses high specific surface areas and elongated, nanofibrous structures, recently has shown efficiency in flocculation of municipal wastewater (Suopajärvi et al. 2013, 2014), kaolin clay suspensions (Liimatainen et al. 2012, 2014), but also harvesting *chlorella vulgaris* (Laitinen et al. 2014). In our earlier work, an efficient flocculant, bamboo pulp cellulose (BPC) grafted with polyacrylamide was synthesized to treat kaolin suspensions, surfactant effluent (Zhu et al. 2016). In these cases, the potential problem associated with practical application is the production and disposal of the large amount of chemical sludge with high water content. It is well known that sludge dewatering is still a challenge.

The concept presented in this paper is to synthesize a hydrophobically modified cellulose-based flocculant to improve its flocculation performance as well as the dewatering efficiency of coagulation sludge. We take into account to use bamboo pulp cellulose as the molecular backbone, introduce acrylamide as cationic group, sodium silicate as hydrophobic group to synthesize hydrophobic bamboo pulp cellulose-graft-sodium silicate-polyacrylamide (denoted as BPC-g-Si–PAM) flocculant through radical copolymerization. The flocculation performance of BPC-g-Si–PAM with $AlCl_3$ as coagulant aid for simulated kaolin wastewater was investigated. Residual turbidity of kaolin suspension and settling volume percentage (SV30) of sludge as indexes were used to optimize process parameters. Furthermore, the practical effect of BPC-g-Si–PAM for treating machining wastewater was also assessed in terms of SV30, residual turbidity, solution pH, chemical oxygen femand (COD), ammonia nitrogen content, total iron, total phosphorus and total zinc.

Experimental

Materials

Bamboo pulp with cellulose content of 91.3% and DP of 781, derived from *P. heterocycla*, was provided by the Guizhou Chitianhua Paper Industry Co., Ltd.,China. Anionic polyacrylamide (PAM, Mw=1 200 000), acrylamide (AM), ammonium persulphate (APS), aluminum chloride ($AlCl_3{\cdot}6H_2O$), Kaolin clay (superfine size of 11 μm) were purchased from Aladdin Chemistry Co. Ltd., China. Machining wastewater was obtained from Zhejiang XX Auto Parts Co, Ltd.. Main physicochemical characteristics of machining wastewater were listed in Table 7.

Synthesis of BPC-g-Si–PAM flocculant

BPC-g-Si–PAM flocculants were synthesized according to our previous report with a modification (Zhang et al. 2013; Liu et al. 2014; Zhu et al. 2016). In brief, 4 g of BPC was dissolved in 100 mL of 7 wt% NaOH/12 wt% urea solution, and then transferred into a 250 mL four-neck flask for 30 min stirring under nitrogen atmosphere. 1 g of APS was then added into the above solution. After 15 min for stirring, desired amounts of acrylamide and sodium silicate were added into the mixture. The polymerization reaction was performed according to the orthogonal experiment listed in Table 1. After reaction, the products were

Table 1 Factor and level design of the orthogonal $L_9(3)^4$ experiment for BPC-g-Si–PAM synthesis

Factor/level	Temperture (°C)	Acrylamide (g)	Sodium silicate (g)	Time (h)
1	50	1.2	0.3	2
2	55	1.5	0.6	4
3	60	1.8	0.9	6

extracted with dehydrating ethanol at room temperature, then dried at 50 °C to obtain the bamboo pulp cellulose-graft-sodium silicate-polyacrylamide (BPC-g-Si–PAM) flocculants. Meanwhile, bamboo pulp cellulose-graft-polyacrylamide (BPC-g-PAM) as a control was synthesized under optimal synthesis conditions without sodium silicate.

Characterization of BPC-g-Si–PAM

The features of the samples were recorded by Field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) after sputtering with gold. The chemical structures of the samples were determined by Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, Thermo Electron Corp., USA) ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The contact angle of samples was measured using JY-B2C Contact angle analizer.

Flocculation to kaolin suspension

Kaolin suspension with a concentration of 500 mg/L as simulated wastewater was used to assess the flocculation performance of BPC-g-Si–PAM. The pH value of kaolin suspension was adjusted to 4.0, 7.0 and 10.0 before flocculation. After adding desired amount of $AlCl_3$ as coagulant aid, the mixture was stirred at 200 rpm for 3 min, followed by adding BPC-g-Si–PAM under 80 rpm stirring for 3–7 min at room temperature. Herein, an orthogonal experiment presented in Table 2 was designed to achieve an optimal flocculation condition. After settling for 30 min, the residual turbidity of the supernatant was determined using a Turb550 turbiditor. And also the settling volume percentage (SV30, %) of sludge was calculated according to the following equation (Agridiotis et al. 2007):

$$SV30(\%) = {}^{V_{\text{sludge}}}\!/_{V_{\text{mix}}} \times 100 \quad (1)$$

where V_{sludge} is the volume of sludge after 30 min standing, V_{mix} is the total volume of the mixture.

Flocculation to machining wastewater

To evaluate the potential of practical application of BPC-g-Si–PAM, machining wastewater was used to perform the flocculation experiments based on the optimized results in "Flocculation to kaolin suspension" section. The changes of SV30, turbidity, solution pH, chemical oxygen demand (COD), total suspended solids (TSS), ammonia nitrogen content, total iron, total phosphorus and total zinc were measured in detail. Under the same conditions, the commercial anionic PAM was used as control.

Results and discussion

Optimized synthesis of BPC-g-Si–PAM

Hydrophobic BPC-g-Si–PAM flocculant was synthesized through radical copolymerization. The effects of reaction temperature, time, dosages of sodium silicate and acrylamide on the flocculation performance of BPC-g-Si–PAM for kaolin suspension were

Table 2 Factor and level design of the orthogonal $L_9(3)^4$ experiment for flocculation conditions of BPC-g-Si–PAM

Factor/level	$AlCl_3$ dosage (mg/L)	Flocculant dosage (mg/L)	Stirring time (min)	pH
1	2	5	3	4
2	6	10	5	7
3	10	15	7	10

Table 3 The orthogonal $L_9(3)^4$ matrix and range analysis for BPC-g-Si–PAM synthesis

Test number	Temperature (°C)	Acrylamide (g)	Sodium silicate (g)	Time (h)	Turbidity (NTU)
1	50	1.2	0.3	2	29.2
2	50	1.5	0.6	4	26.3
3	50	1.8	0.9	6	22.5
4	55	1.2	0.6	6	14.3
5	55	1.5	0.9	2	11.7
6	55	1.8	0.3	4	9.67
7	60	1.2	0.9	4	7.76
8	60	1.5	0.3	6	10.8
9	60	1.8	0.6	2	8.48
K_1	26.00	17.09	16.56	16.46	
K_2	11.89	16.27	16.36	16.46	
K_3	9.01	13.55	13.99	15.87	
R	16.99	3.54	2.57	1.88	
Influencing order	Temperature >	Acrylamide >	Soudium silicate>	Time	
Optimum parameters	60	1.8	0.9	6	

investigated *via* $L_9(3)^4$ orthogonal experiment, and the results were presented in Table 3. The turbidity of kaolin suspension decreased from original 1302 NTU to 7.76–29.2 NTU according to the varied synthesis parameters in which corresponding turbidity removal efficiencies reached up 97.8–99.4%. Moreover, the reaction temperature played a key role during the preparation process. And the influencing order of each factor on the turbidity of kaolin suspension follows the sequence: Temperature > Acrylamide > Soudium silicate > Reaction time. Therefore, the optimal synthesis conditions of BPC-g-Si–PAM were obtained, i.e. reaction temperature at 60 °C, reaction time at 6 h, acrylamide of 1.8 g and sodium silicate of 0.9 g.

Characterization of BPC-g-Si–PAM

Under aforementioned optimal synthesis conditions, BPC-g-Si–PAM was synthesized by grafting acrylamide and sodium silicate onto cellulose molecular backbone, which was confirmed by FTIR spectra shown in Fig. 1. Compared with the spectrum of BPC, two new peaks at 1666 and 1565 cm^{-1} were found in the BPC-g-Si–PAM, which are assigned to the stretching vibrations of C=O, and the bending vibration of N–H, respectively. The shifting of band from 3385 cm^{-1} in the spectra of BPC to 3422 cm^{-1} in BPC-g-Si–PAM could be due to the overlapping of O–H and N–H stretching (Dash et al. 2012; Teotia et al. 2012). The typical peak of Si–O bond at 1045 cm^{-1} overlapped with the C–O bond (1059 cm^{-1}) present in cellulose (Shang et al. 2009). Moreover, the peak at 1427 cm^{-1} in the spectra of BPC assigning to the stretching vibrations of CH_2–OH disappeared or splited into 1451 and 1404 cm^{-1} in BPC-g-Si–PAM. All these results revealed that acrylamide and sodium silicate were grafted onto cellulose molecular backbone, and the active primary hydroxyl group at C_6 position preferentially participated in the grafting reaction (Ho et al. 2010; Ma et al. 2017).

To direct observe the feature of the BPC-g-Si–PAM, FESEM images have been taken and shown in Fig. 2. Obvious differences can be seen between BPC and BPC-g-Si–PAM. Original BPC exhibited its own fibrils. The fibrils were separated from each other. After grafting reaction, the fibrils began to stick together due to the presence of polyacrylamide and silicate. In addition, the contact angle of the modified BPC-g-Si–PAM increased to 87.2° from original 65.4° of BPC-g-PAM, which reconfirmed the presence of silicate (Fig. 3).

Flocculation performance for kaolin suspension

To optimize the flocculation process, the effects of the dosages of $AlCl_3$ and BPC-g-Si–PAM as well as stirring time, original pH on flocculation capability

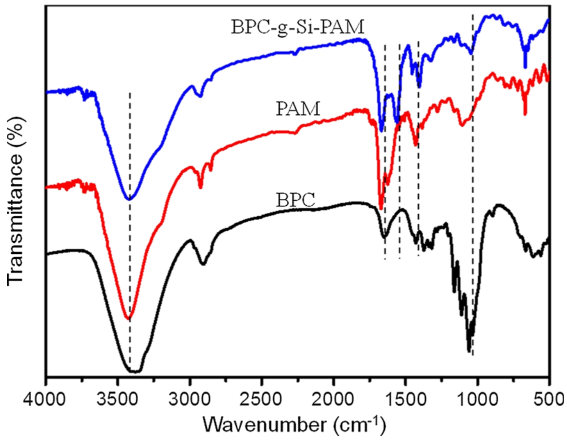

Fig. 1 FTIR spectra of BPC, PAM and BPC-g-Si–PAM

were investigated via a $L_9(3)^4$ orthogonal experiment. The turbidity of kaolin supernatant and the SV30 of sludge both changed with the varied flocculation conditions (Table 4). Turbidity as the index, the results of range analysis showed that the pH played the most important role during the flocculation process because of the fact that environmental pH has impact on the surface charge of flocculants and kaolin particles. The influence of the four factors on the turbidity of kaolin supernatant follows the sequence: pH > BPC-g-Si–PAM dosage > stirring time > $AlCl_3$ dosage (Table 5). Therefore, the optimal flocculation conditions for turbidity removal were achieved, i.e. pH at 7.0, BPC-g-Si–PAM of 5 mg/L, stirring time at 7 min and $AlCl_3$ of 6 mg/L. Under this condition, the turbidity of kaolin supernatant decreased from original 1302–25.7 NTU. SV30 as the index, the influence of the four factors follows the sequence: pH > BPC-g-Si–PAM > $AlCl_3$ dosage > stirring time (Table 6). The optimal flocculation conditions for SV30 were: pH at 10.0, BPC-g-Si–PAM of 10 mg/L, $AlCl_3$ of 2 mg/L and stirring time at 5 min. Under the optimal

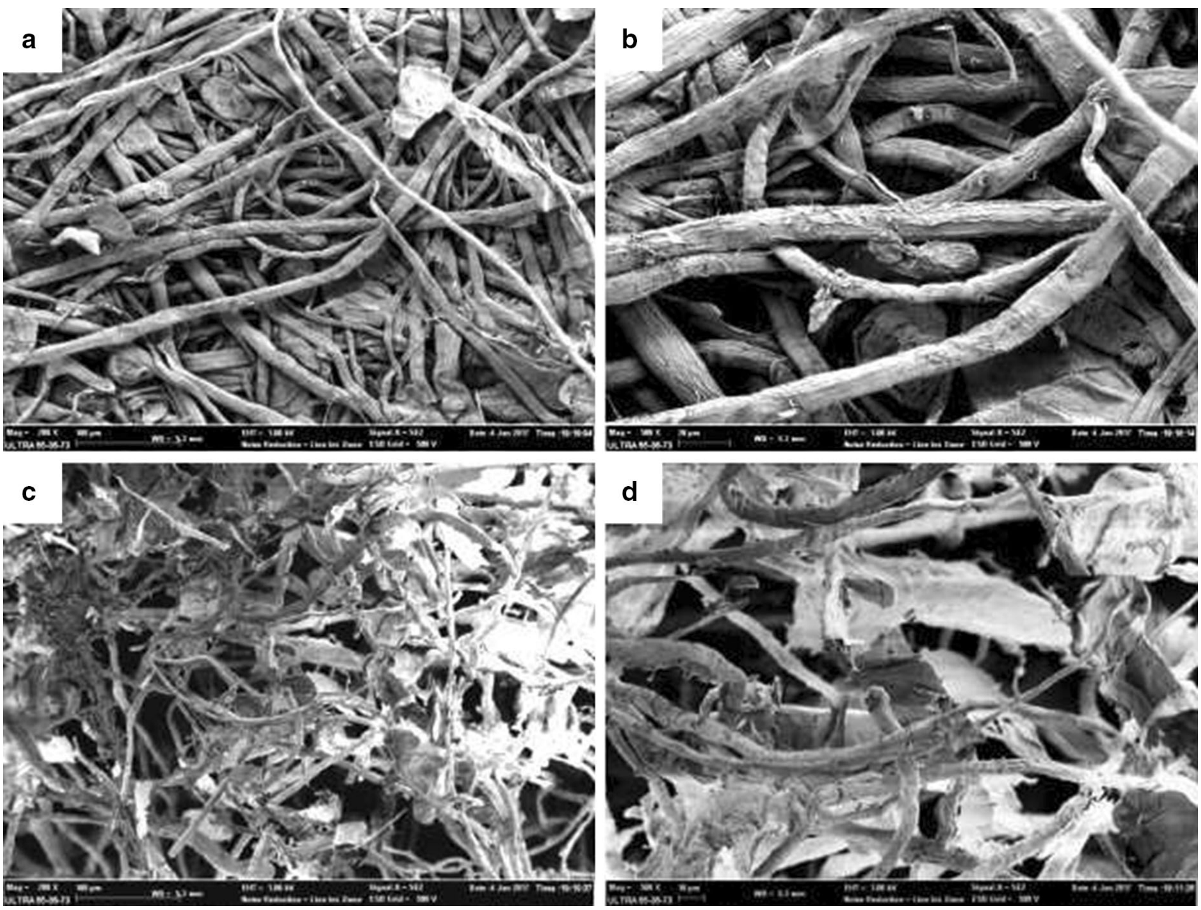

Fig. 2 Surface morphologies of **a** and **b** BPC, **c** and **d** BPC-g-Si–PAM

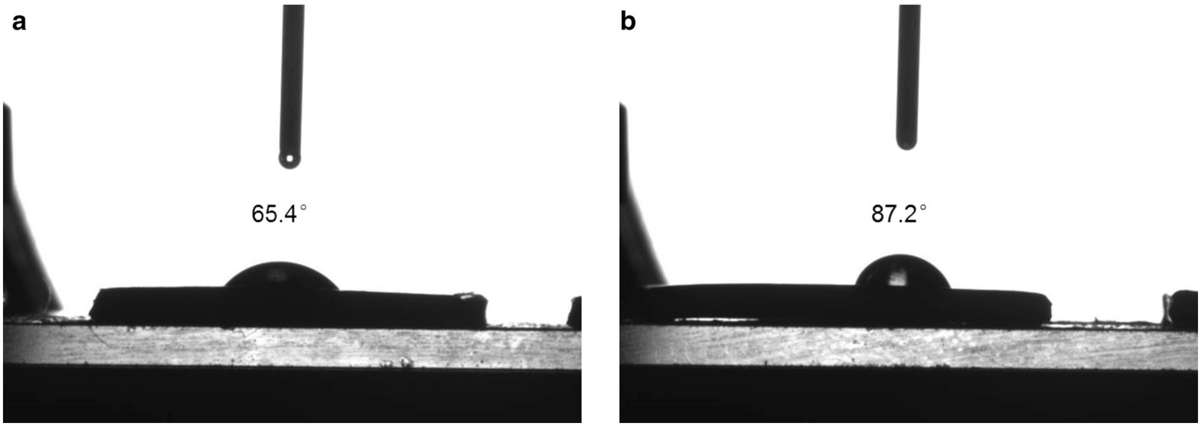

Fig. 3 Contact angles of **a** BPC-g-PAM and **b** BPC-g-Si–PAM

Table 4 The orthogonal $L_9(3)^4$ matrix for flocculation conditions of BPC-g-Si–PAM

Test numbers	$AlCl_3$ dosage (mg/L)	Flocculant dosage (mg/L)	Stirring time (min)	pH	Turbidity (NTU)	SV30 (%)
1	2	5	3	4	491	0.15
2	2	10	5	7	223	0.25
3	2	15	7	10	718	0.10
4	6	5	5	10	355	0.13
5	6	10	7	4	679	0.11
6	6	15	3	7	77.9	0.69
7	10	5	7	7	40.6	0.79
8	10	10	3	10	490	0.12
9	10	15	5	4	587	0.12

Table 5 Analysis of the orthogonal $L_9(3)^4$ matrix for flocculation conditions of BPC-g-Si–PAM based on residual turbidity

	pH	Flocculant dosage (mg/L)	Stirring time (min)	$AlCl_3$ dosage (mg/L)
K_1	585.667	295.533	352.967	477.333
K_2	113.833	464.000	388.333	370.633
K_3	521.000	460.967	126.233	372.533
R	471.834	168.467	126.233	106.700
Influencing order	pH > Flocculant > Stirring time > $AlCl_3$			
Optimum parameters	7	5	7	6

conditions, the SV30 can reach to 10%. These results indicated that the introduction of the hydrophobic groups enhance the flocculation performance of flocculants. The flocculation of BPC-g-Si–PAM mainly depended on charge neturalization, sweeping and adsorption/bridging coagulation by $AlCl_3$, followed by formation of larger flocs through flocculation, in which $AlCl_3$ provided cationic parches on the surface of kaolin particles, subsequently the BPC-g-Si–PAM connected the kaolin particles through these cationic patches, then precipitated together (Zhu et al. 2015).

Flocculation performance for machining wastewater

Machining wastewater are used to assess the potential of practical application of BPC-g-Si–PAM. Considering the formation of metal hydroxide precipitates

Table 6 Analysis of the orthogonal $L_9(3)^4$ matrix for flocculation conditions of BPC-g-Si–PAM based on SV30

	pH	Flocculant dosage (mg/L)	$AlCl_3$ dosage (mg/L)	Stirring time (min)
K_1	0.127	0.357	0.167	0.320
K_2	0.577	0.160	0.310	0.167
K_3	0.117	0.303	0.343	0.333
R	0.460	0.197	0.176	0.166
Influencing order	pH > Flocculant > $AlCl_3$ > Stirring time			
Optimum parameters	10	10	2	5

under alkaline environment, the flocculation conditions were determined with BPC-g-Si–PAM dosage of 5 mg/L, pH 7.0 and stirring time at 7 min. While the dosage of $AlCl_3$ was controlled with 6 mg/L or 0 mg/L according to the electropositive machining wastewater. Under the same conditions, the unmodified BPC-g-PAM and commercial anionic PAM was used as control.

As shown in Fig. 4, the turbidity of machining wastewater all dramaticlly reduced in four flocculation systems. The highest turbidity removal was found using BPC-g-PAM and BPC-g-Si–PAM with the participation of $AlCl_3$. For PAM, PAM+$AlCl_3$, BPC-g-PAM, BPC-g-PAM + $AlCl_3$, BPC-g-Si–PAM and BPC-g-Si–PAM+$AlCl_3$, the turbidity removal ratio reached to 92.9, 94.9, 97.2, 97.6, 97.2 and 97.6%, respectively. Meanwhile, the SV30 reached to 26.5, 23.0, 17.7, 14.8, 9.0 and 5.8%. In addition, the good flocculation performance of BPC-g-PAM as well as BPC-g-Si–PAM for machining wastewater was also found without the help of $AlCl_3$. All these results indicated that the hydrophobically modified BPC-g-Si–PAM flocculant have improved flocculation performance as well as the dewatering efficiency of coagulation sludge in comparison to unmodified BPC-g-PAM and commercial PAM.

In general, trials using BPC-g-Si–PAM as flocculants presented good flocculation performance for treating machining waster in terms of turbidity and SV30 when adding 5 mg/L of BPC-g-Si–PAM. Therefore, a global analysis of flocculation experiment for machining waster was also performed when the dosage of flocculant was 5 mg/L and $AlCl_3$ of 6 mg/L at pH 7.0 and stirring time at 7 min. The main characteristics of machining wastewater before and after flocculation test were shown in Table 7. For

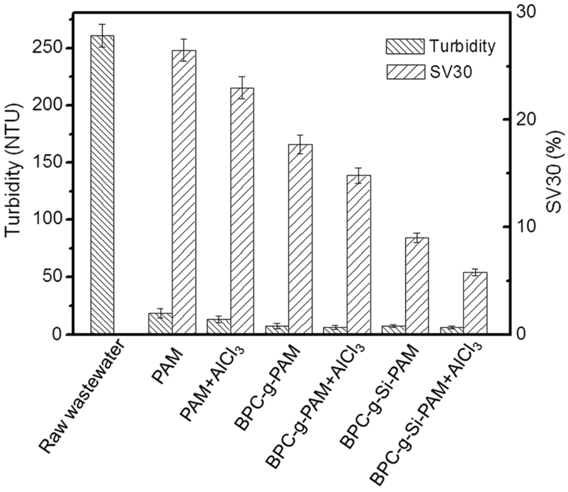

Fig. 4 Effects of different flocculants on turbidity and SV30 for machining wastewater

commercial PAM, TSS and COD removal efficiencies reached up 95.4 and 79.1%, respectively. The ammonia nitrogen removal efficiencies was 67.8%. Total iron, total phosphorus and total zinc removal efficiencies reached up 98.2, 47.3 and 95.9%, respectively. In case of BPC-g-Si–PAM, TSS, COD, ammonia nitrogen, total iron, total phosphorus and total zinc removal efficiencies reached up 98.1, 86.8, 77.7, 99.3, 93.6 and 96.7%, respectively. Obviously, the BPC-g-Si–PAM has more excellent flocculation capacity than commercial PAM in machining wastewater treatment. And these results confirmed that hydrophobic modification improved the property of sludge, while did not reduce the flocculation capacity of the cellulose-based flocculant.

It is well known that the features of flocculant play an important role during the flocculation process. The introduction of silicate as hydrophobic group make the hydrophilic of BPC-g-Si–PAM decrease,

Table 7 Main physicochemical characteristics of machining wastewater before and after flocculation test

	pH	TSS (mg/L)	COD_{Cr} (mg/L)	Ammonia nitrogen content (mg/L)	Total Fe (mg/L)	Total P (mg/L)	Total Zn (mg/L)
Raw wastewater	3.40	550	182	121	74.20	1.10	12.3
BPC-g-PAM treatment	7.25	11.0	25	24	0.51	0.07	0.39
BPC-g-Si–PAM treatment	7.30	10.6	24	27	0.53	0.07	0.40
PAM treatment	7.10	25.4	38	39	1.34	0.58	0.51

consequently enhancing the adsorption ability to suspended particle in wastewater. At the same time, the hydrophobic groups in BPC-g-Si–PAM associate each other in aqueous solution, which can improve the interaction between the flocculants, as well as promote the sedimentation rate and dewatering ability of flocs (Klucker and Schosseler 1997;Furo et al. 2000; Zou et al. 2001). All these effects can improve the flocculation performance of flocculant and dewatering efficiency of coagulation sludge, and further work will be done in the future.

Conclusions

An novel and efficient hydrophobic BPC-g-Si–PAM flocculant was successfully synthesized by grafting acrylamide and sodium silicate onto cellulose molecular backbone. The obtained BPC-g-Si–PAM exhibited better flocculation performance for simulated kaolin suspension and machining wastewater compared with BPC-g-PAM and commercial PAM. TSS, COD, ammonia nitrogen, total iron, total phosphorus and total zinc removal efficiencies for machining wastewater reached up 98.1, 86.8, 77.7, 99.3, 93.6 and 96.7%, respectively. The introduction of silicate make the hydrophilic of BPC-g-Si–PAM decrease, consequently improving the flocculation performance of the flocculant and dewatering efficiency of coagulation sludge. In brief, this novel BPC-g-Si–PAM flocculant has a great application potential for treatment of machining wastewater.

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