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RESEARCH ARTICLE

Modification of microcrystalline cellulose with acrylamide under microwave irradiation and its application as flocculant

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Abstract

Grafting polyacrylamide (PAM) chains onto microparticles may combine the advantages of the flocculation property of the former and the fast sedimentation of the later to realize better flocculation performance. In this work, inexpensive microcrystalline cellulose (MCC) microparticles, and monomer of acrylamide (AM) were mixed, and then irradiated under microwave. The obtained material was characterized by Fourier transform infrared spectroscopy and X-ray diffraction, and the results demonstrated successful modification of MCC with AM on the particle surface. The modification procedure has been carefully investigated to obtain an optimum preparation condition. Kaolin suspension was selected as a model to evaluate the flocculation properties of the obtained AM-MCC. Our results indicate that the AM-MCC with the highest grafting ratio of 95.5% exhibits the best flocculation performance, which is even better than that of PAM, and the turbidity can be decreased to 1.4% of the naked kaolin suspension within 2.5 min. Therefore, this work provides a low cost strategy to prepare biodegradable AM-MCC, which may have promising potential application in the water treatment and other fields.

Keywords Microcrystalline cellulose (MCC) · Polyacrylamide · Surface modification · Microwave · Flocculation

Introduction

Clean water is more and more demanding worldwide because of the increasing population and their consumption of clean water in various kinds of activities (Ali 2012; Tran et al. 2018). Treatment of wastewater to obtain clean water is still challenging because it may contain different kinds of contaminants including heavy metal ions, organic pollutants, and suspended solids (Ebeling et al. 2005; Sarika et al. 2005). Among the many methods of water treatment, flocculation is an important industrial process for solid-liquid separation during the primary purification of wastewater (Lee et al. 2014; Wei et al. 2018; Xiong et al. 2018).

Polyacrylamide (PAM), a well-known and commonly used polymeric flocculant, has the advantage of easily accessible of synthesis (Girma et al. 2005; Lee et al. 2014; Ma et al. 2017; Xiong et al. 2018) for wastewater treatment at relatively low cost. In addition, PAM has been widely applied in papermaking and fibrecements based on its flocculation properties (Cadotte et al. 2007; Negro et al. 2005). Meanwhile, various functionalities of PAM (positive, neutral, or negative charge) endow it with good settling performance in water treatment (Antunes et al. 2008; Antunes et al. 2010; Girma et al. 2005; Wong et al. 2006; Ma et al. 2017; Xiong et al. 2018). However, PAM chains are flexible, and are easily degraded under shear (Lewandowska 2006). So the re-conformation of PAM during application would affect its flocculation performances (Blanco et al. 2005; Girma et al. 2005; Negro et al. 2006; Wong et al. 2006; Rasteiro et al. 2008; Guezennec et al. 2015; Ma et al. 2017; Xiong et al. 2018). Therefore, modification of PAM with the intention to retain its flocculation performance is becoming one of the foci of the PAM flocculant (Guezennec et al. 2015). Especially, grafting PAM chains onto natural polymer to prepare environmental friendly flocculant receives more and more attention (Song et al. 2011; Wang et al. 2012; Yang et al. 2012; Das et al. 2013; Wang et al. 2013; Wu et al. 2017), based on the characteristics of the relatively low cost, rich functional groups, and biodegradation of natural polymers. For example, Song et al. (Song et al. 2011) have grafted PAM onto cellulose chains and

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subsequently hydrolyzed the grafted PAM under alkaline condition, and the obtained acrylamide-modified cellulose polyelectrolyte were used as flocculant to display up to nearly 100% removal of $Fe(OH)_3$ colloid suspension.

Cellulose, an easily accessible, inexpensive, biodegradable, renewable, and the most abundant natural polymer, has also been directly used as flocculant when it is at the micro (Raj et al. 2017) and nanoscale size (Balea et al. 2017; Oguzlu et al. 2017; Mohammed et al. 2018; Campano et al. 2019). However, production of nanoscaled cellulose such as cellulose nanocrystalline and cellulose nanofibril usually requires harsh condition (Blanco et al. 2018), and it often consumes large amount of mineral acid in the case of cellulose nanocrystalline while the yield is not satisfactory (Chen et al. 2016). Therefore, direct application of a nanoscaled cellulose as flocculant may still be challenging, on consideration of the relatively high cost of the nanoscaled cellulose and its large consumption in normal case of water treatment. Modification of cellulose to obtain water-soluble cellulose is another way to use it as flocculant (Song et al. 2011; Kang et al. 2015), but dissolution of cellulose in proper solvent for homogeneous modification (Xiong and Duan 2012; Kang et al. 2015) and/or harsh modification condition (Xiong and Duan 2012; Kan et al. 2013; Cai et al. 2015; Kang et al. 2015; Balea et al. 2017) are usually required for that purpose.

Another form of cellulose, i.e., microcrystalline cellulose (MCC) with particle size ranging from micrometers to hundreds of micrometers, is easily accessible and has been industrialized for decades (Trache et al. 2016). Although the relatively large particle size may restrict its scattering in water to limit its flocculation performance, the particle nature would facilitate its settling and be beneficial to separation of flocs (Das et al. 2013). For example, Machida et al. (Machida et al. 1971) have employed ceric-ion to initiate acrylamide polymerization in the presence of MCC particles, and the obtained product could be MCC surface-grafted with PAM chains or mixture of MCC and PAM, while the product could markedly accelerate the initial flocculation rate. Our previous works (Bai et al. 2018; Huang et al. 2018) suggested that surface modification of MCC with hydrophilic functional groups could improve the scattering of the MCC particles in water. In this work, MCC was surface-modified with acrylamide (AM) through a convenient way of microwave irradiation. It is expected that the AM monomers could be grafted onto MCC particles via a green strategy with low cost, so that the advantages of the flocculation property of PAM and the fast sedimentation of MCC could be combined to realize satisfactory flocculation performance. The modification procedure was carefully studied and optimized, and the obtained AM-MCC was used to flocculate kaolin suspension to evaluate its potential in water treatment.

Experiment

Materials

Microcrystalline cellulose (MCC) with particle size labeled 25 μm was purchased from Aladdin Industrial Corporation (Shanghai, China). Nonionic polyacrylamide (PAM) was supplied by Macklin (Shanghai, China). Analytical grade acrylamide (AM) and all other reagents were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China) and were used without further purification. Deionized water was used throughout. Kaolin (chemical pure) was supplied by Xilong Scientific Co., Ltd (Shantou, China).

Modification of MCC

According to our previous experience (Bai et al. 2018; Huang et al. 2018), acrylamide was firstly dissolved in water to prepare a 30 wt% solution. Then, MCC (5 g per batch) was added to be soaked in the solution with stirring for 24 h at room temperature. The solid was then filtrated, and dried in air at 60 °C. Through the above procedure, the monomer of AM was expected to diffuse onto MCC particles evenly and sufficiently. The dried mixture containing moisture content of 9.7%, which was evaluated by vacuum-drying under room temperature for over 48 h, was irradiated in a MM823LA-NS microwave oven (Midea, Fushan, China). After that, the reaction product was stirred in water for over 30 min and then centrifuged at 4000 rpm for 10 min in order to remove water-soluble components such as residual monomers and possible homopolymer of PAM. After repeating the washing process for three times, the precipitant was dried in air at 60 °C and then ground to obtain a powdery material (moisture content of 8.9%) of acrylamide-modified MCC (AM-MCC).

The modification of MCC has been optimized. First, the reaction mixture from the initial solution containing constant mass ratio of MCC to AM of 1:2 was irradiated under microwave powers of 136 W, 264 W, 440 W, 616 W, and 800 W for 5 min, respectively. Second, the reaction mixtures with the mass ratios of MCC to AM ranging from 1:1 to 1:5.5 in the initial mixture solutions were irradiated under the above obtained best powder (800 W) for 5 min, respectively. Then, the optimum irradiation time was decided by fixing the MCC to AM mass ratio of 1:4.5 in the initial mixture solution and the microwave power of 800 W.

Characterizations

Fourier transform infrared (FTIR) spectroscopies of the samples were recorded with a Nicolet Avatar 360 instrument (Nicolet, Madison, WI, USA). The samples were vacuum-dried at 40 °C for 48 h before mixing with KBr to produce disks for the measurements. X-ray diffraction (XRD) patterns

of pure PAM, the unmodified MCC, and the AM-MCC were recorded using a Bruker D8 ADVANCE X-Ray Diffractometer (Bruker, Germany) with Cu-Kα radiation. The samples were continuously scanned from 5° to 50° (2θ) at a speed of 0.0167° s^{-1}. The N element content (W_N, %) in the obtained AM-MCC product was analyzed by a VarioEL III Element Analyzer (Elementary Analysen System GmbH, Germany).

Flocculation application

A 0.25% (wt/vol) kaolin aqueous suspension was prepared to test the flocculation performance of the AM-MCC, and desired pH of the kaolin suspension was adjusted using 0.1 M HCl or 0.1 M NaOH aqueous solution. The AM-MCC or the pristine MCC or PAM was added into the above prepared kaolin suspension with a volume of 1 L, and then immediately stirred at 225 rpm for 30 min. After predetermined time to settle, a syringe equipped with a 2-cm-long needle was used to take 15 mL solution below the liquid level, and its turbidity was determined using an AQ3010 turbidity meter (Orion AQUAfast, Thermo Scientific, USA). Each of the given turbidity value was averaged from three parallel measurements in Nephelometric Turbidity Unit (NTU).

Results and discussion

Modification of MCC with AM

The modification of MCC with AM was checked by FTIR (Bai et al. 2018). Figure 1 compares the spectra of the pristine MCC, the surface-modified MCC (AM-MCC), and the PAM. The peaks at around 897 and 1161 cm^{-1} in the spectrum of MCC can be assigned to the $\beta(1 \rightarrow 4)$ linked D-glucose units of cellulose, and the C–O–C functional groups are located at 1033 and 1056 cm^{-1}, and the O–H bending vibration of absorbed water is found to peak at 1639 cm^{-1}, while the –OH stretching vibration band is at around 3350 cm^{-1} (Bai et al. 2018). The PAM exhibits two typical bands of amide respectively peaked at 1648 cm^{-1} and 1617 cm^{-1} in the spectrum. In the spectrum of the AM-MCC, the bands at 1677 cm^{-1} and 1619 cm^{-1} are attributed to C=O and N–H stretching of amide of the grafted AM molecules (Liu et al. 2016; Bai et al. 2018), respectively. It is worth mentioning that the N element content was determined to be almost zero for the mixture filtrated from the initial mixture solution and dried under 60 °C, which was carefully washed with water to remove water-soluble components such as AM monomers or thermally polymerized PAM before element analysis. Those results suggest successful modification of MCC with AM through the microwave irradiation.

Figure 2 shows the XRD patterns of pure PAM, the pristine MCC, and the AM-MCC. The XRD spectrum of the pure PAM shows a wide absorption band, indicating the amorphous structure (Cao et al. 2019). The diffraction peaks at 14.8°, 16.5°, 22.7°, and 34.6° observed in the MCC pattern can be indexed to the diffraction planes of $1\bar{1}0$, 110, 200, and 040 for cellulose I crystal, respectively (Klemm et al. 2005; Huang et al. 2018; French 2014). The diffraction peaks for the AM-modified MCC are located at the same 2θs as those of the MCC, while slightly decrease in intensity can be observed. This result indicates retaining of the crystalline structure after the modification procedure, while a small decrease in crystallinity of the AM-MCC. In addition, those results suggest that the modification would have taken place only on the surface of the MCC particles.

According to the modification, the microwave radiation would provide heat with high efficiency (Thakur et al. 2013) to generate free radicals on the molecular backbone of MCC.

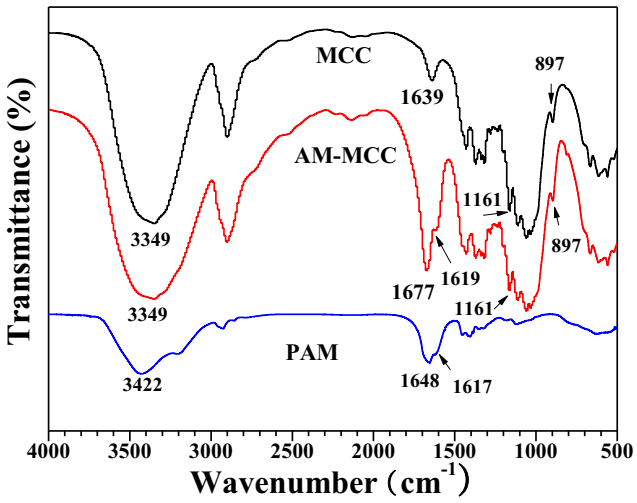


Fig. 1 FTIR spectra of the unmodified MCC, the AM-MCC, and PAM

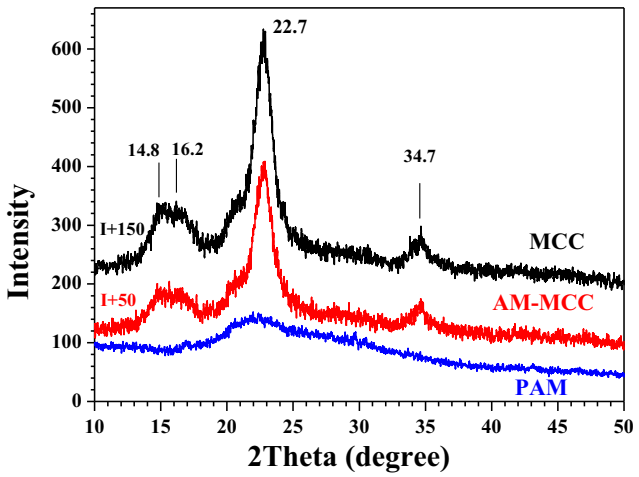


Fig. 2 XRD patterns of pure PAM, the pristine MCC, and the AM-MCC

Then the free radicals would initiate the grafting polymerization of the neighboring AM molecules (Roy et al. 2009; Thakur et al. 2013; Liu et al. 2015a, b), similar as the grafting of AM onto chitosan (Singh et al. 2006). The possible mechanism of modification of MCC with AM is suggested in Scheme 1.

Optimization of modification of MCC

Modifying MCC with AM introduces nitrogen element into the material, so that the content of N (W_N, %) in the material will reflect the degree of modification. The content of AM (W_{AM}, %) grafted onto MCC can be calculated by Eq. (1)

$$W_{AM} = (W_N/0.1971) \times 100\% \quad (1)$$

where the numerical value 0.1971 is the nitrogen content in the molecule of AM. The grafting rate (*GR*, %) can then be calculated through

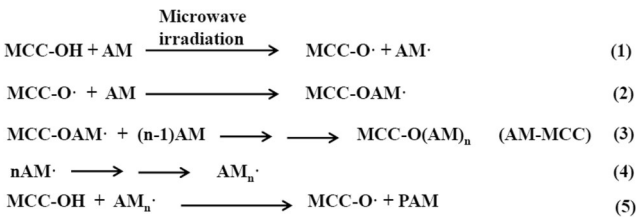
$$GR = [W_{AM}/(1-W_{AM})] \times 100\% \quad (2)$$

A higher *GR* suggests better modification of MCC.

Figure 3 displays the dependence of the *GR* of the obtained AM-MCC on the microwave power, where the mass ratio of MCC to AM was kept constant to be 1:2 and the irradiation time to be 5 min. It is clear that the grafting rate of AM-MCC increases with improving of the microwave power. This is understood that higher microwave power would provide more heat to activate the reactants, so that more free radicals might be produced to obtain AM-MCC with higher grafting rate.

Figure 4 displays the effect of the mass ratio of MCC to AM on the grafting rate. It can be seen that the *GR* increases gradually with increasing AM content in the reaction. When the mass ratio of MCC to AM was 1:4.5, the *GR* of the AM-MCC reached the highest of 45.6%, while it decreased when the mass ratio was 1:5.

The effect of microwave irradiation time on the grafting rate of AM-MCC is shown in Fig. 5. The diagram displays that the *GR* increases with irradiation time, and the highest grafting rate of 95.5% can be reached for 3 min of microwave irradiation. Too long time of irradiation resulted in decrease in *GR*, possibly due to degradation of the formed product (Kopperud et al. 1998). Even longer times of microwave irradiation such as 6 min and 8 min have been tried, while only



Scheme 1 Mechanism of modification of MCC with AM under microwave radiation

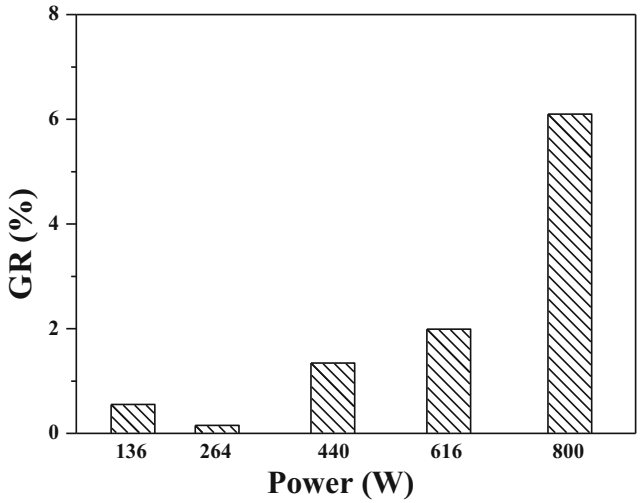


Fig. 3 Dependence of *GR* (%) on the microwave power, where the mass ratio of MCC to AM was kept constant to be 1:2 and the irradiation time to be 5 min

dark brown or charred products were obtained. According to the above results, an optimum condition for modification of MCC with AM has been established to be the mass ratio of MCC to AM should be 1:4.5 in the initial mixture solution, and the resultant dried mixture could be irradiated for 3 min under a microwave power of 800 W.

Flocculation performance

The obtained AM-MMC has been successfully applied to reinforce hydrogels, where PAM chains have been confirmed to graft onto the surface of the MCC particles (Bai et al. 2018). Meanwhile, PAM is a well-known flocculant to assist solid/liquid separation in water containing suspension (Girma et al. 2005; Wong et al. 2006; Cadotte et al. 2007; Antunes et al.

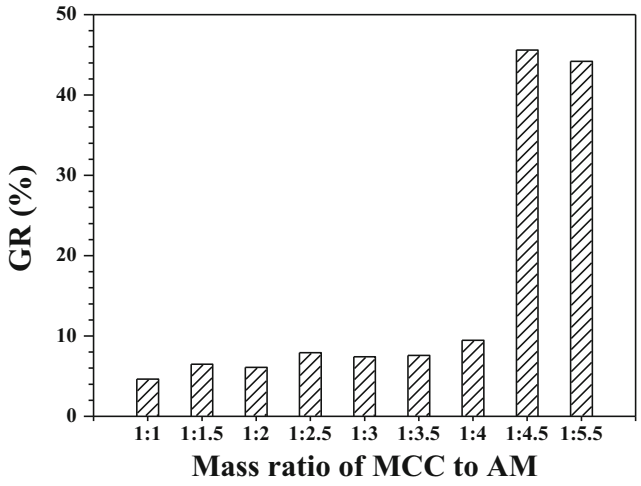


Fig. 4 Effect of the mass ratio of MCC to AM on the modification, where the microwave power and irradiation time were kept constant to be 800 W and 5 min

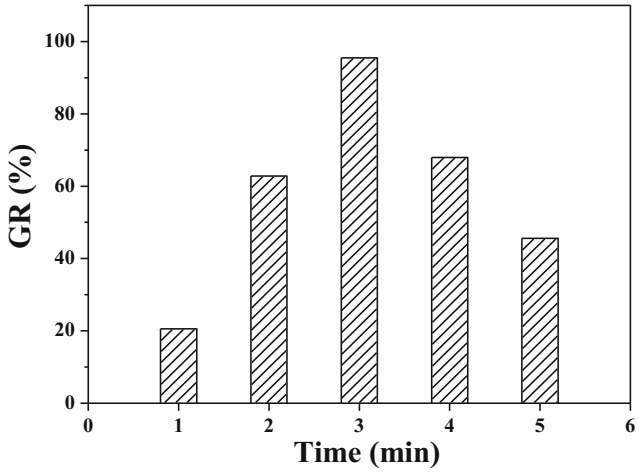


Fig. 5 Effect of microwave irradiation time on the grafting modification of MCC, where the microwave power was 800 W and the mass ratio of MCC to AM was 1:4.5

2008; Guezennec et al. 2015; Ma et al. 2017; Xiong et al. 2018). So the present AM-MCC would combine the excellent flocculation performance of PAM and the advantages of MCC particle (Machida et al. 1971). Moreover, the particle nature of MCC would facilitate sedimentation after adsorbing targeted matter to enhance the flocculation performance. Therefore, the AM-MCC with the highest *GR* of 95.5% was dispersed in 0.25 wt% kaolin aqueous suspension to test its flocculation performance.

Figure 6 reveals the comparison of the flocculation performance of the AM-MCC and those of MCC and PAM, and the self-sedimentation of kaolin is also displayed in the graph.

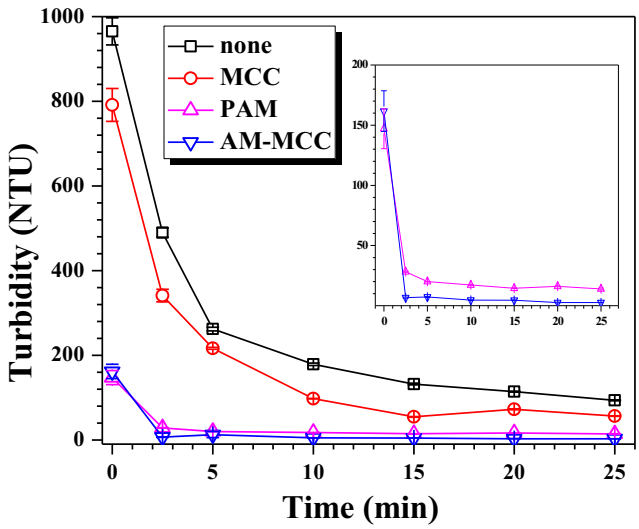


Fig. 6 Flocculation performances of the AM-MCC, the pristine MCC, and PAM. The flocculant dosage was 8 mg/L and the pH of the kaolin suspension was 7.0. The sedimentation of kaolin is also shown in the graph. Insert is the turbidity change at the scale of 0 to 200 NTU to indicate the flocculation performances of the AM-MCC and PAM. Error bars represent one standard deviation of three parallel measurements

When MCC was added, the turbidity after any time of settling was lower than that of the kaolin suspension without any flocculant, suggesting flocculation property of MCC itself to some extent (Swerin et al. 1997; Raj et al. 2017). The turbidity decreased to be almost constant level of about 55 NTU after 15 min when the pristine MCC particles were added. The flocculation performance of PAM was obvious, and the turbidity decreased to 28 NTU within 2.5 min and to 20 NTU after 5 min settling. In comparison, the turbidity decreased to 6.7 NTU after 2.5 min and to 2.6 NTU after 20 min when the AM-MCC was employed. The better flocculation performance of the AM-MCC may be attributed to the surface-grafted PAM chains and to the accelerated sedimentation resulted from the particle nature of the AM-MCC.

Figure 6 shows the influence of the AM-MCC dosage on the turbidity of the kaolin suspension. The result suggests that too low dosage of AM-MCC such as 2 mg/L and 4 mg/L results in relatively high turbidity, which might be due to inadequate PAM chains on the AM-MCC for bridging the suspended kaolin particles (Fig. 7). When the dosage was 8 mg/L, the turbidity was significantly reduced because of the bridging of more kaolin particles to form larger flocs (Antunes et al. 2010; Das et al. 2013). However, when more AM-MCC was added such as the dosage of 10 mg/L, the turbidity increased greatly, which is similar as those reported (Das et al. 2013; Zhu et al. 2016). This is possibly due to steric stabilization and electrostatic repulsion of the formed flocs (Antunes et al. 2010; Yang et al. 2012; Das et al. 2013) and to the suspension of over-loaded AM-MCC in water (Bai et al. 2018).

The effect of pH of the kaolin suspension on the flocculation performance of AM-MCC is demonstrated in Fig. 8. The pH of

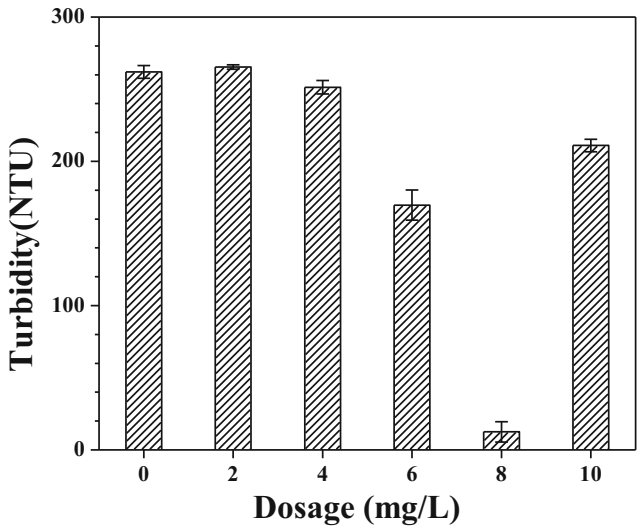


Fig. 7 Effect of dosage on the flocculation performance of AM-MCC. The pH of the kaolin suspension was 7.0 and the settling time was kept to be 5 min. Error bars represent one standard deviation of three parallel measurements

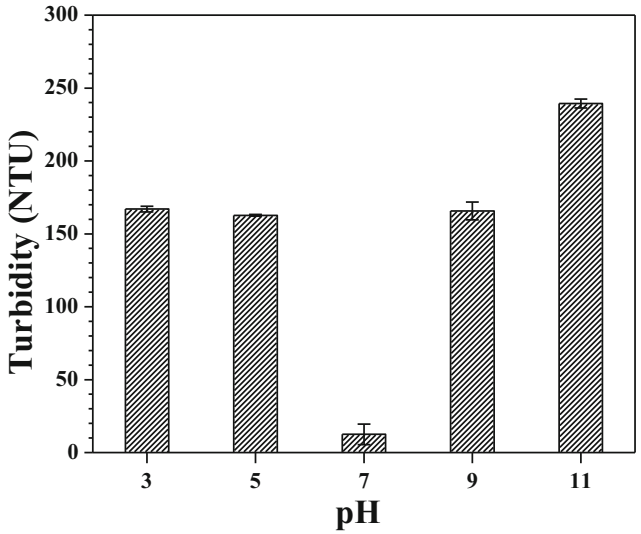


Fig. 8 Effect of pH on flocculation performance of AM-MCC. AM-MCC dosage was 8 mg/L and the settling time was kept to be 5 min. Error bars represent one standard deviation of three parallel measurements

the system will result in changes of the Zeta potential of kaolin particles (Shaikh et al. 2017) and the charge of PAM chains (Djibrine et al. 2018; Hasan and Fatehi 2018) grafted onto the MCC, leading to different flocculation behaviors. In the present case, the optimum flocculation performance of AM-MCC can be realized under neutral condition, implying the major mechanism of bridging flocculation for the present system (Das et al. 2013).

Conclusion

In summary, microcrystalline cellulose and monomer of acrylamide were mixed and then irradiated under microwave. The results of the FTIR and XRD characterizations evidence the grafting polymerization of acrylamide monomers on the MCC particle surface. The highest grafting ratio of 95.5% of the obtained AM-MCC indicates the optimum condition of modification: reactants of MCC and AM with the mass ratio of 1:4.5 in the initial solution, irradiation for 3 min under a microwave power of 800 W. Based on the advantages of the PAM chains on the particle surface and the particle nature of AM-MCC, the obtained product exhibits even better flocculation performance than that of pure PAM. The best flocculation performance can be reached with AM-MCC dosage of 8 mg/L under pH of 7.0 within 5 min, suggesting promising potential of the AM-MCC in water treatment.

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