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Characterization of adsorbent microspheres of cellulose and acrylic acid and its adsorption behaviors for metal ions

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ABSTRACT

Acrylic acid was grafted onto cellulose by graft copolymerization in [AMIM]Cl ionic liquids. Then, microspheres were prepared by an inverse suspension polymerization technique. The cellulose-graft-poly (acrylic acid) was confirmed by FTIR spectrum, thermo gravimetric analyzer, and a transmission electron microscope. The optimal conditions of synthesis was selected from orthogonal tests, the results of which show that the optimum reaction conditions were as follows: amount of monomer, 4 g/g cellulose (CE); dosage of initiator, 0.15 g/g CE; dosage of crosslinker, 0.05 g/g CE; reaction temperature, 60°C; and reaction time, 1.5 h. The adsorption behavior of the polymer microspheres for Cu^{2+} and Mn^{2+} ions was investigated showing that its adsorption capacity increased as initial concentration of metal ions, and contacting time increased. When pH value of solution was 5, it reached maximum adsorption amount as 201 and 175 mg/g for Cu^{2+} and Mn^{2+} ions, respectively.

Keywords: Cellulose; Acrylic acid; Graft copolymerization; Ionic liquid; Adsorption

1. Introduction

Heavy metals and their compounds are widely involved in industries and it is inevitable that metal-contaminated materials are released into our environment, which has posed a great threat on environmental safety and human health. Therefore, the removal of heavy metal ions from contaminated water is of great significance for public health and environment. Recent research has been focused on the application of materials for adsorption and separation of heavy metal ions through mesoporous adsorption [1], electroplating [2], ion exchange [3], membrane separation [4], and biosorbent adsorption [5–7]. Among these methods, adsorption is regarded as one of the most effective and cost-efficient approaches.

Cellulose, as one of the most abundant natural organic biopolymers on earth, is an interesting green biomaterial with the potential of replacing the fossil materials. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, and linear stiff-chain homopolymer is characterized by its hydrophilicity, chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semi-crystalline fiber morphologies [8,9]. Despite its several advantages, chemical modifications of cellulose need to be carried out for wider applications [10]. The microsphere technique by inverse suspension

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polymerization process has been extensively studied in recent years for the preparation of microspheres.

Cellulose graft copolymerization is one of the important chemical processing ways to modify cellulose into functionalized copolymer. It has become a research hotspot [11–13]. However, its large molecular weight and high degree of polymerization make its functional application to be hampered. Conventionally, vinyl monomers are grafted onto cellulose in heterogeneous system by conductive heating with an external heat source (e.g. an oil-bath or heating mantle) [14–16]. This is a comparatively slow and inefficient method for transferring energy into the system. The homogeneous reaction of the cellulose could control the degree of substitution and the chemical and physical properties of the cellulose effectively [17]. Ionic liquids, 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) [18], which are regarded as one of green solvent for chemical reactions, not only have high thermal stability, wide liquid range, and strong polarity, but also possess the property to break many hydrogen bonds of crystal structure into microcrystalline cellulose, increasing reactivity of hydroxyl functional groups.

Adsorption ability of cellulose-based material is one of the most important applications, both natural and modified cellulose could adsorb many materials. Since cellulose containing a large number of hydroxyl, the anionic group could be introduced in the cellulose by derivatization reactions to prepare the cationic adsorbent. As far as further improvement the adsorption capacity of cellulose is concerned, poly (acrylic acid) has been a choice to graft onto the backbones of cellulose. Copolymers obtained from poly (acrylic acid) and cellulose will combine the advantages of both, such as adsorption capacity and conformation stable compounds with metal ions. In this work, the graft copolymerization of acrylic acid (AA) with cellulose using [AMIM]Cl as a reaction medium was achieved in good yield for short reaction time. Moreover, the adsorption behavior of the obtained graft copolymers was also tested in Cu^{2+} and Mn^{2+} ions aqueous solutions because Cu^{2+} and Mn^{2+} ions are main contaminant in industrial effluents.

2. Materials and methods

Microcrystalline cellulose (MCC) and *N*-methylimidazole were provided by the J&K Chemical Reagent Co., Ltd, China. Allyl chloride was purchased from Acros Organis, USA. [AMIM]Cl was synthesized according to the literature [19–21]. AA, ammonium persulfate (APS), *N,N´*-methylenebisacrylamide (MBA), copper sulfate, and manganese sulfate were obtained by Sinophaarm Chemical Reagent Beijing Co., Ltd., while liquid paraffin and Span 80 were procured from Guangdong Guanghua Sci-Tech Co., Ltd., Guangdong, China. All other reagents and solvents used were of analytical grade.

2.1. Cellulose-graft-poly (acrylic acid) synthesis

0.6 g of MCC was dissolved in 14.4 g of [AMIM]Cl solution at 80˚C in nitrogen atmosphere for 1 h. After dissolution, 0.06 g of persulfate (APS) in DMSO was added; 2.286 mL of AA and 0.03 g of *N,N´*-MBA in DMSO, were added, respectively. The mixture was stirred under nitrogen atmosphere at 60˚C.

2.2. Microsphere preparation

The resultant dispersion was poured into light liquid paraffin containing dispersing agent (Span 80), rotated in a water bath. Then, it was cooled to ambient temperature and washed with deionized water for several times, finally with ethanol. All ended, the sample was extracted with acetone in a soxhlet apparatus for 24 h.

2.3. Sorption

Solutions of Cu^{2+} and Mn^{2+} ions were prepared. Sorption studies involved determining the amount of metal ions adsorbed as a function of pH, time, and concentration. The microsphere samples (0.1 g) were soaked in metal ion solution (50 mL) and then shook for some time at room temperature. Amount of metal ions adsorption can be calculated between initial and final concentration using an AA-220 atomic absorbance spectrophotometer (Victoria, USA). The amount of metal ion adsorption (q) was calculated using Eq. (1) [22]:

$$q = (C_0 - C_e)V/m \tag{1}$$

where C_0 and C_e are the initial and final concentrations of the metal ions (mg/L), respectively, V solution volume (L), and m the weight of the adsorbent (g).

2.4. Measurements

IR spectra were recorded from a FTIR spectrometer (Magna-IR 750, Nicolet, USA) using KBr tablet method. Thermal stability was examined on a TGA

500 thermogravimetric analyzer (Delaware, USA) in N_2 atmosphere. Transmission electron microscope (TEM) images were obtained by a JEM-100CXa, TEM at an acceleration voltage of 100 kV. An AA-220 atomic absorbance spectrophotometer (Victoria, USA) was utilized to analyze the concentration of metal ions.

3. Results and discussion

3.1. FTIR spectra

Fig. 1 shows the FTIR spectra of the graft copolymer prepared in ionic liquid. The peaks at 1,069 cm^{-1} (1,070 cm^{-1}) and the broad peak around 3,400 cm^{-1} correspond to the C–O group and the –OH group of the cellulose, respectively, which confirmed that the graft copolymer keeps the basic characteristic of cellulose. The peaks at 1,720 cm^{-1} (1,730 cm^{-1}) and 1,248 cm^{-1} (1,230 cm^{-1}) correspond to the C=O group and C–O group of the AA, respectively, which confirmed the introduction of the AA side chain into the cellulose backbone by graft copolymerization. Compared with microcrystalline cellulose, the graft copolymer for one thing, has added methylene; for another, its functional groups after reacting with AA give rise to the change of the dipole moment of C–H bond, resulting in the different transmittances at around 2,900 cm^{-1}.

3.2. Thermogravimetric analyzer

The thermal stability of the cellulose and grafted copolymer were both analyzed via Thermogravimetric analyzer (TGA). As shown in Fig. 2, the thermal decomposition of CE (b) goes through two stages. The first stage witnesses a weight loss of 4% from room temperature to 312℃, indicating the desorption of absorbed water and crystal water. The second stage begins with 312℃ and ends at 346℃ with a weight loss of 91%, indicating the degradation of cellulose. The rest of weight loss in higher temperature is carbonization process. Compared with cellulose, the thermal stability of grafted cellulose (a) decreases slightly. There is a weight loss of 10% from room temperature to 268℃ as a result of desorption of absorbed water and crystal water in the first stage. In the second stage, the break of cellulose backbone and poly acrylic acid, the degradation of cellulose backbone, and the breaking down of poly acrylic acid, all of them occur from 268 to 309℃ with a weight loss of 54.5%. And the carbonization process takes place in higher temperature.

3.3. Transmission electron microscope

The TEM of the polymer microspheres is displayed in Fig. 3 showing the general appearance of the microspheres. A distinguished change is detected in

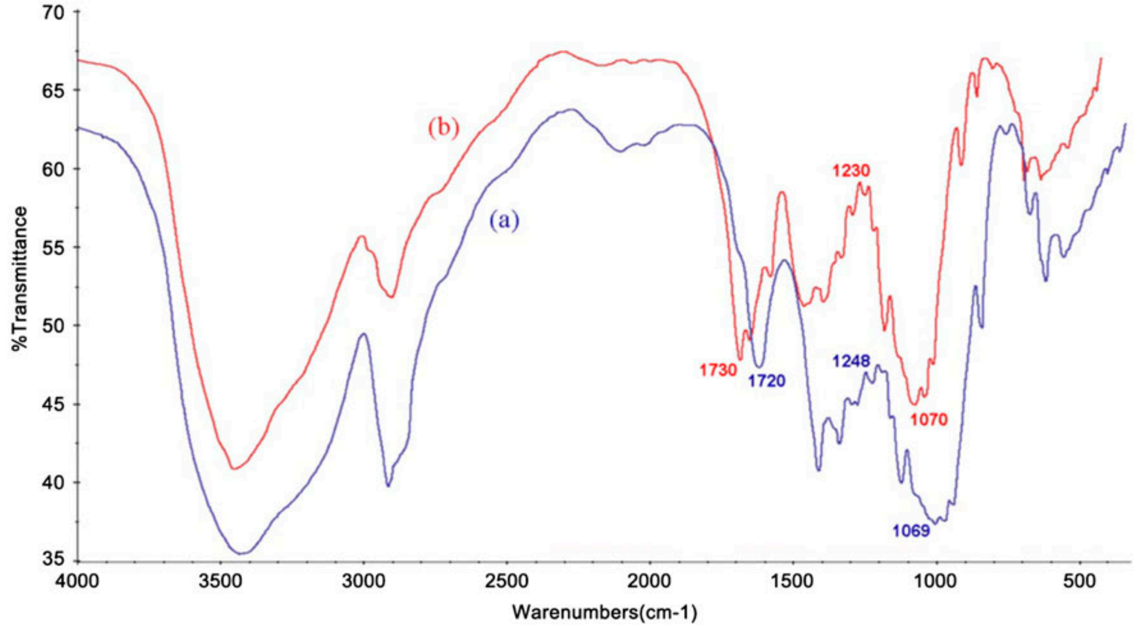

Fig. 1. FTIR spectra of the grafted cellulose (a) and cellulose (b) in ionic liquid.

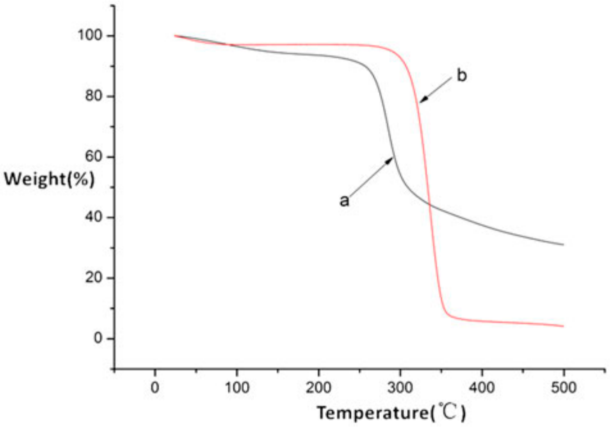

Fig. 2. TGA of native cellulose (b) and grafted cellulose (a).

the surface morphology after grafting. The smooth surface of the cellulose is lost after grafting and the fluffy morphology is clearly observed. The spherical shape is in good condition. The microspheres are found to be micron-sized around 1–3 μm.

3.4. Optimization of the reaction conditions

Orthogonal testing design, as an optimization method for evaluating multiple factors, is capable of reducing iterations as well as improving accuracy and efficiency. The optimal conditions were selected from parameters of amount of monomer, AA (g/g CE); amount of initiator, APS (g/g CE); dosage of crosslinker, MBA (g/g CE); reaction temperature; and reaction time that mainly affect the synthesis of graft copolymer. The controllable factors are shown in Table 1.

Table 1
Factors and levels

	Levels			
Factors	1	2	3	4
A Monomer amount (g/g CE)	3	4	5	6
B Initiator dosage (g/g CE)	0.05	0.1	0.15	0.2
C Crosslinker dosage (g/g CE)	0.01	0.05	0.1	0.2
D Reaction temperature (℃)	40	50	60	70
E Reaction time (h)	1.5	2	2.5	3

According to the experimental design theory, the orthogonal array L_{16} (4^5) was selected to carry out the test program. The criterion of each test is dependent on the Cu^{2+} ions adsorption of the graft copolymer samples. The test outcomes are shown in Table 2.

The reaction temperature impacts on the metal ion adsorption most, while the reaction time affects the slightest. The order of the influence of each variable turns out to be D>A>B>C>E. The optimum level of each variable is A-5, B-3, C-2, D-3, and E-1. Therefore, the optimum reaction conditions were as follows: amount of monomer, 4 g/g CE; dosage of initiator, 0.15 g/g CE; dosage of crosslinker, 0.05 g/g CE; reaction temperature, 60℃; and reaction time, 1.5 h.

3.5. Sorption studies

3.5.1. Effect of the pH value

It is well known that the pH value of metal solutions can influence the adsorption performance of metal ions as well as the protonation of the carboxylic groups in the copolymer [23]. Fig. 4 shows the adsorption behavior of metal ions on polymer microsphere

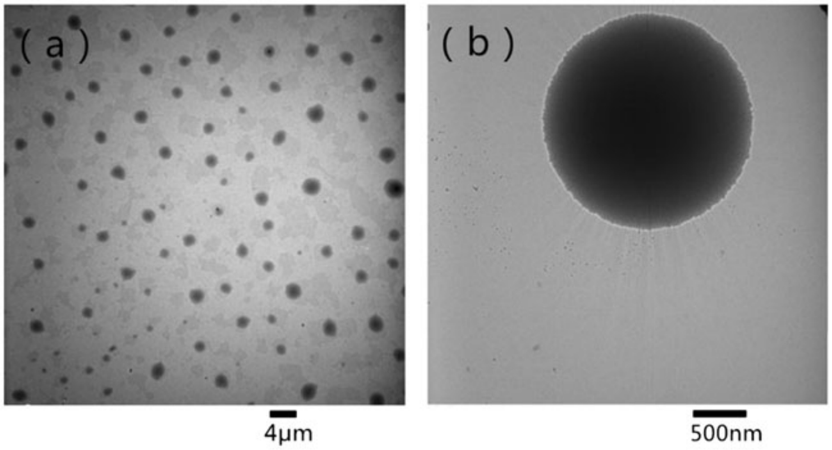

Fig. 3. TEM of the polymer microsphere prepared in ionic liquid (a,b).

Table 2
Result of orthogonal experiments

No	A (g/g CE)	B (g/g CE)	C (g/g CE)	D (℃)	E (h)	Adsorption amount (mg/g)
1	3	0.05	0.01	40	1.5	78.6
2	3	0.1	0.05	50	2	89.3
3	3	0.15	0.1	60	2.5	100.3
4	3	0.2	0.2	70	3	118.2
5	4	0.05	0.05	60	3	139.3
6	4	0.1	0.01	70	2.5	165.8
7	4	0.15	0.2	40	2	108.7
8	4	0.2	0.1	50	1.5	104.2
9	5	0.05	0.1	70	2	95.1
10	5	0.1	0.2	60	1.5	86.7
11	5	0.15	0.01	50	3	98.8
12	5	0.2	0.05	40	2.5	76.6
13	6	0.05	0.2	50	2.5	42.1
14	6	0.1	0.1	40	3	52.7
15	6	0.15	0.05	70	1.5	160.4
16	6	0.2	0.01	60	2	98.1
k_1	96.600	88.775	110.325	79.150	107.475	
k_2	129.500	98.625	116.400	83.600	97.800	
k_3	89.300	117.050	88.075	106.100	96.200	
k_4	88.325	99.275	88.925	134.875	102.250	
R	41.175	28.275	28.325	55.725	11.275	
17[a]	4	0.15	0.05	60	1.5	172.6

[a] Experiment conducted under the optimal conditions select from orthogonal experiments.

with the increase of pH value. As shown in Fig. 4, for both metal ions, their adsorption were minimal when pH < 4. And when the pH is 5, both metal ions reached significant adsorption. The amount of adsorption increases as pH value increases from 2 to 5, and then decreases from 5 to 7. When the pH is 5, the amount of adsorption reaches 172 and 195 mg/g for Mn^{2+} ion and Cu^{2+} ion, respectively.

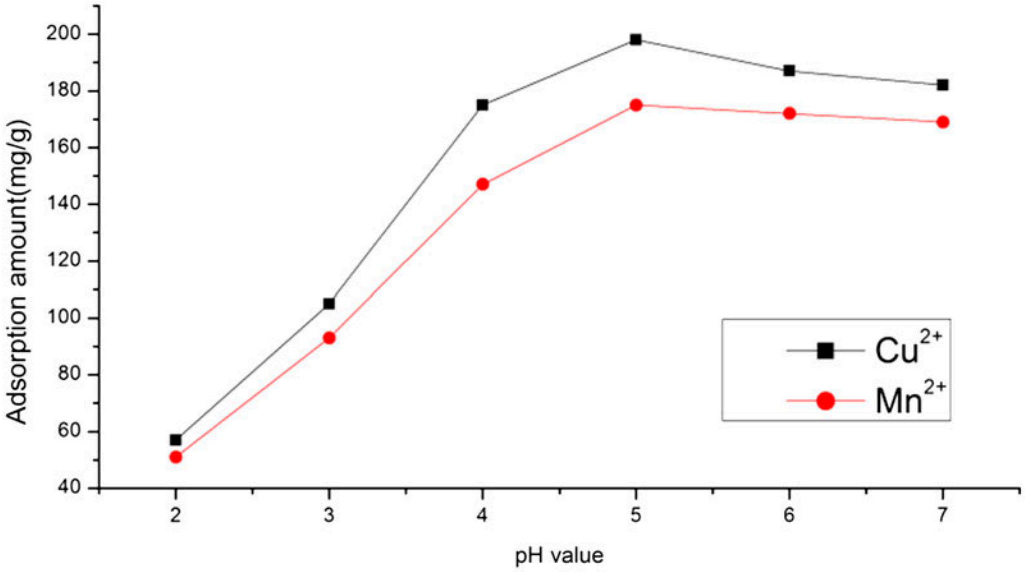

Fig. 4. Effect of pH on the metal ion adsorption amount.

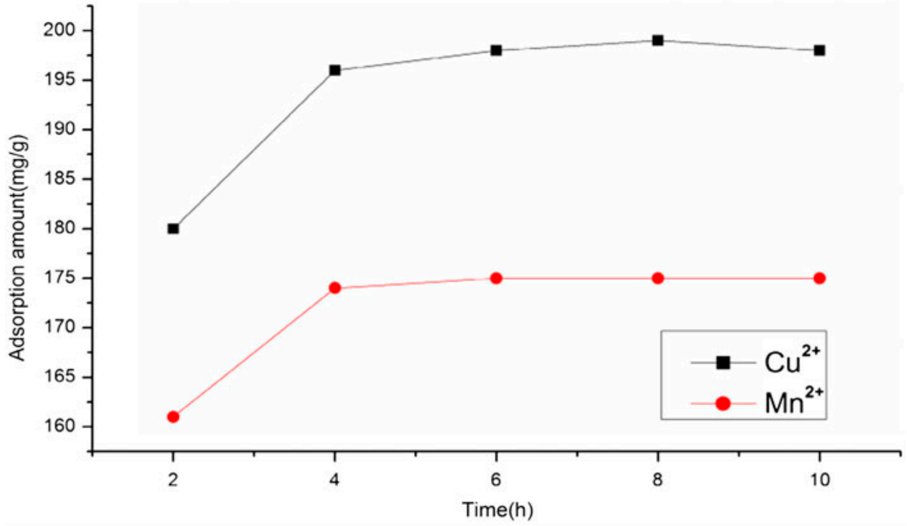

Fig. 5. Effect of contacting time on the metal ion adsorption amount.

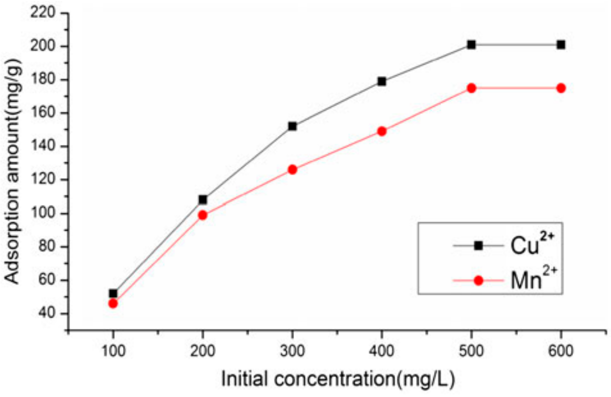

Fig. 6. Effect of initial concentration on the metal ion adsorption amount.

The adsorption process is that the oxygen atom of the carboxyl group in the grafted copolymer coordinates to metal ions, ultimately forming chelation. And also, it may be the electrostatic force between adsorbent microspheres and metal ions that plays a synergistic effect. Since the major functional group responsible for the adsorption is the carboxylic groups, at low pH value, the protonation of the carboxylic groups hinders the interaction of polymer microsphere with metal ions. The deprotonation of the carboxylic groups is occurred with increasing of pH value; then more carboxylic groups are ionized. In addition, the increasing of pH value enhances the hydrolysis of metal ions to form chelation.

3.5.2. *Effect of contacting time*

Fig. 5 shows the effect of contacting time on the adsorption capacity of polymer microsphere. The amount of metal ion adsorption increased rapidly in the first 4 h and then leveled off. In order to ensure complete adsorption, 8 h of contacting time was set throughout the investigation. There are a good number of negatively charged carboxyl groups in the grafted copolymer that possess a stronger attraction to metal ions. After 4 h, the adsorption capacity reaches balanced and consequently, the metal ion concentration maintains unchanged. The amount of adsorption increases with the increasing of contacting time and approaches to a constant value around 174 and 199 mg/g for Mn^{2+} ion and Cu^{2+} ion, respectively.

3.5.3. *Effect of initial concentration*

The adsorption capacity of polymer microsphere was significantly affected by the initial concentration of metal ions while other reaction variables maintained constant. As seen in Fig. 6, the adsorption capacity increased linearly with the rise of initial concentration of metal ion, which could be explained that the carboxyl groups in the polymer microsphere have a stronger attraction to metal ions. It is the action of acidic group molecules by cellulose materials that entirely determines the sorption of metal ions from solutions [24]. The maximum amount of metal ion adsorbed reaches 175 and 201 mg/g for Mn^{2+} ion Cu^{2+} ion, respectively.

4. Conclusion

The graft copolymerization of AA onto MCC was successfully carried out in [AMIM]Cl, whose copolymer was then confirmed by the characterization of FTIR, TGA, and TEM. The factors of grafting reaction were optimized through orthogonal experiment, whose outcomes were as follows: amount of monomer, 4 g/g CE; dosage of initiator, 0.15 g/g CE; dosage of crosslinker, 0.05 g/g CE; reaction temperature, 60℃; and reaction time, 1.5 h. The polymer microsphere showed good adsorption performance for Cu^{2+} and Mn^{2+} ions. When pH value was 5, it reached the maximum adsorption amount of 201 and 175 mg/g for Cu^{2+} and Mn^{2+} ions, respectively. The studies of adsorption demonstrated that the copolymer is promised in removing metal ions from aqueous solutions.

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Symbols

C_0	—	initial metal ion concentration
C_e	—	final metal ion concentration
m	—	the weight of the adsorbent
V	—	total volume of the solution
q	—	the amount of metal ion adsorption

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