Research Article

A Modified Preparation of Cellulosic-Absorbent Resin for Cu^{2+} Removal under Microwave Irradiation

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The absorbent resin for Cu^{2+} removal was prepared under microwave irradiation through grafting acrylamide (AM) and acrylic acid (AA) to cellulose. The initiator is a kind of redox system composed of potassium persulfate/sodium thiosulfate. The crosslinking agent is *N,N'*-methylene bisacrylamide. The optimal reaction conditions are as follows: the ratio of AA to cellulose is 10 : 1, initiator to AA is 0.65 wt%, crosslinking agent to AA is 1.0 wt%, neutralization degree of AA is 75%, microwave power level is 320 W, and time is 300 s. The maximum absorption capability of the resin is $65 \text{ mg} \cdot \text{g}^{-1}$. Different from previous studies, the reaction was carried out without the protection of nitrogen and troublesome posttreatment. The product was obtained directly by one-step synthesis without purification and drying of the crude product. The pollution and cost caused by organic solvent are avoided, and the whole preparation period is shortened deeply. Moreover, the time of absorption equilibrium is shorter. In a word, the preparation in this paper has the obvious advantages, such as simple process, short time, no pollution, low-energy, and low-cost.

1. Introduction

In order to enhance the qualities of our living environment, the removal of heavy metal ions in soil and water has become urgent and important. The removal methods and technologies are imperative and have aroused environmentalists' high attention. There are various conventional technologies [1–10] to remove heavy metal ions from wastewater, such as coagulation, oxidation/filtration, chemical precipitation, reverse osmosis, absorption, electrochemistry, and ion exchange. However, there are some problems about these technologies, such as second-pollution, high-cost, and inconvenient process. Therefore, it is necessary to develop safe and highly effective new techniques. Especially, polymeric absorbents using some natural macromolecule compounds as grafted framework to prepare heavy metal ions removal absorbent resin are promising and attractive [11–17]. The natural macromolecule compounds are usually starch, cellulose, chitosan, and so on.

As one of the most abundant natural macromolecular compounds, cellulose is a promising candidate for further functionalization by attaching various functional moieties to its hydroxyl residue. In our previous studies [18–22], acrylic acid (AA) and/or acrylamide (AM) were grafted to starch or cellulose using the microwave irradiation method, and the heavy metal ions absorbing capacities of these manually modified natural products had been evaluated thoroughly. Compared to conventional heating, our previous preparation under microwave irradiation is of high efficiency and homogeneous heating. However, it is still necessary to treat the resin by conventional drying or other troublesome posttreatment, such as precipitation with organic solvent and washing [18–20]. Based on the experiments of super-absorbent preparation [21–23], we have made a further investigation on the preparation of cellulosic-absorbent resin for Cu^{2+} . We determined the correct ratio of solid reactant, liquid reactant, and other aqueous constituents. In addition, the modification of the microwave oven makes the reaction easily controllable. As a result, the polymerization

was carried out steadily and rapidly with high conversion, and the bits of low molecular by-product and water evaporated or volatilized before the completion of the reaction. Moreover, the characterization of microwave irradiation makes the resin's porous structure superior. Therefore, copolymerization and postdrying were proceeding simultaneously and completely in the microwave reactor. Compared to our previous work and other literatures [18–23], the advantages of the preparation process in this paper are shorter time, greener and simpler process, lower energy consumption, higher metal ions removal ratio, and quicker absorption equilibrium. Especially, the absorption capability for Cu^{2+} increases by 30%, and the time of absorption equilibrium shortened to two-thirds of the previous [18, 20].

2. Experimental

2.1. Materials and Methods. Cellulose used in the experiments is from the ordinary filter paper and was smashed completely. The initiator is potassium persulfate (KPS) and sodium thiosulfate, which is a kind of redox system. N,N' -Methylene bisacrylamide is a crosslinking agent. There are two kinds of grafted monomers, which are acrylic acid (AA) and acrylamide (AM). These chemicals are of analytical grade and were used directly without further purification. The solution's pH value was adjusted by 0.1 M NaOH solution.

The microwave reactor is a self-modified Galanz domestic microwave oven (Guangdong, China, 2450 MHz and 800 W). The concentrations of metal ions were determined by atomic absorption spectroscopy (AAS) (novAA400, Analytik Jena AG, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-670FTIR spectrophotometer in the range of 400–4000 cm^{-1} with KBr discs to determine the structure of the resin.

2.2. Preparation of Absorbent Resin. A typical experiment is as follows: Firstly, 0.1 g cellulose completely infiltrated by about 5 g deionized water in 100 mL beaker was irradiated under 160 W for 2 min. Secondly, the mixture with added 0.65 mL initiator solution with the concentration of 1% was irradiated under 200 W for 20 s. Successively, 1 mL crosslinking agent solution with the concentration of 1%, 1 g AA, and 3.3 g AM were added. At the same time, the neutralization degree of the system was adjusted by NaOH solution to 75%. Finally, all the reaction materials were irradiated under 320 W for 300 s. The products do not need any posttreatment, such as precipitation, drying, washing, and so on. The appearance of the products is white or pale yellow, porous, and dry.

2.3. Absorption Study. The absorption studies in Cu^{2+} removal experiments were operated in 250 mL conical flasks. There was the mixture of 100 mL Cu^{2+} solution with the concentration of 250 mg/L and 0.2 g absorbent resin in the flasks. These flasks were agitated in a thermostatic water bath for 100 min at a speed of 120 rpm. At the end of the period, the resins were immediately removed from the absorbate

FIGURE 1: Effects of absorption time on Cu^{2+} absorption capability.

solution and the concentration of residual metal ions in solutions was determined by AAS.

The absorption capability for Cu^{2+} of the resin was calculated according to the difference of the metal ions concentration in the aqueous solution before and after absorption, using Equation (1) [24]. In order to desorb Cu^{2+} from the resin and make the resin regenerate, the absorbed resin with Cu^{2+} was soaked in ammonia solution with the concentration of 8%:

$$Q = \frac{(C_0 - C) \times V}{W}, \quad (1)$$

where Q (mg/g) is the absorption capability, which means the amount absorbed per unit mass of absorbent resin at equilibrium, C_0 and C (mg/L) are, respectively, the initial and equilibrium metal concentrations, V is the volume of the Cu^{2+} solution (L), and W is the weight of the dry absorbent resin (g). The value of Q denotes the heavy metal removal capacity of the resin.

3. Results and Discussion

3.1. Effects of Absorption Time on Cu^{2+} Absorption Capability (Q). The resin was added into Cu^{2+} solution, and the concentration of Cu^{2+} in the solution was tested periodically to determine the optimal absorption time. From Figure 1, it can be found that the absorption capability enhanced with the increase of absorption time and gradually stabilized when the absorption time reached 100 min. Therefore, the optimal absorption time was 100 min. Compared to the previous study [18], the time of absorption equilibrium obviously shortened, which is only two-thirds of the previous. Considering the differences of the resins' appearances, it is deduced that the microwave irradiation makes the pore size and porous structure of resin more homogeneous and proper that are helpful to absorb and keep solution.

3.2. Effects of Initiator on Cu^{2+} Absorption Capability (Q). The redox system composed of potassium persulfate and sodium thiosulfate was used as an initiator. Potassium persulfate is the oxidant, and sodium thiosulfate is the reducer. Since oxygen is a kind of inhibitor in copolymerization, sodium thiosulfate can efficiently avoid its inhibition. Therefore, the induction period time can be shortened, and

FIGURE 2: Effects of the initiator on Cu^{2+} absorption capability. FIGURE 3: Effects of the crosslinking agent on Cu^{2+} absorption capability.

the polymerization rate can be improved. Moreover, the homopolymerization of AA or AM can be prevented efficiently.

Figure 2 indicates the effects of the initiator on Q . It is obvious that the absorption capability first increases to a certain value and then remains without obvious change with the increase of the initiator concentration. The maximum of Q is about 62 mg g^{-1} at the initiator's concentration of 0.65 wt% to AA. In the preliminary period of polymerization, both the concentration of free radical on the surface of cellulose and the decomposition rate of oxidant increase with the enhancement of the initiator concentration. When the initiator concentration reaches a certain degree, the homopolymerization and chain termination induced by free radical will accelerate markedly, and equilibrium is formed. Therefore, the metal removal capability of the resin is almost not changed.

3.3. Effects of Crosslinking Agent on Cu^{2+} Absorption Capability (Q). The changes of Q with the concentration of the crosslinking agent are indicated in Figure 3. During the period that the concentration of the crosslinking agent is from 0.2% to 1.0%, the value of Q increases and reaches the maximum at 1.0%. However, if the concentration of the crosslinking agent continuously increases, the value of Q begins to decrease. It is considered that the lower the concentration of the crosslinking agent, the lower the crosslinking density. If the density is low to an extent, the network of the resin is so incomplete and imperfect that it

FIGURE 4: Effects of monomer on Cu^{2+} absorption capability. FIGURE 5: Effects of the neutralization degree on Cu^{2+} absorption capability.

has obvious water solubility at the macroscopic level. As a result, the absorption capability is low in the early period. With the crosslinking agent's concentration increasing, it becomes easier to make the resin form a perfect three-dimensional network. So, the absorption capability increases. However, if the concentration of the crosslinking agent is too much, it will make the resin's crosslinking density too high to make metal ions enter the resin's interior. Therefore, if the concentration of crosslinking agent is more than 1.0%, the value of Q decreases.

3.4. Effects of Monomer on Cu^{2+} Absorption Capability (Q). If the absorbent resin has a variety of hydrophilic groups, it will be much more excellent than that having only a single group. The resin with diversified and multiple hydrophilic groups can be obtained by grafting multicomponent monomers to cellulose. Then, the resin's absorption ability can be improved considerably. In this paper, AM and AA were considered as the grafted monomers.

The changes of Q with the concentration of monomers are indicated in Figure 4. Firstly, the value of Q increases with the enhancement of the mass ratio of AA to cellulose. The maximum value of 65 mg g^{-1} is obtained at the ratio of 10 : 1. Because the more the monomer content is, the longer the branched chain is and the more the grafting yield is. Such structures are useful to configure the three-dimensional net structure of the resin, which is in favor of increasing the absorption to a certain degree. But if the monomer content is too much, the resin's net structure will be too compact to make it difficult for the metal ions to enter. Therefore, in

FIGURE 6: Effects of microwave power and irradiated time on Cu^{2+} absorption capability.

FIGURE 7: FTIR spectra of (a) cellulose and (b) resin.

Figure 4, it can be found that if the ratio of AA to cellulose is more than 10:1, the value of Q will decrease.

3.5. Effects of Neutralization Degree on Cu^{2+} Absorption Capability (Q). Our previous studies [18–23] indicate that the neutralization degree of AA is another key factor in the absorption capability (Q) of resin. The changes of Q with the change of the neutralization degree are indicated in Figure 5. AA is a kind of active monomer, which means that the reactivity and polymerization rate of it is high. When the neutralization degree of AA is low, the self-cross-linked reaction of AA is drastic and the crosslinking degree of homopolymer is of high. Moreover, the chain structure of cellulose will be destroyed by strong acidity. The result is that the low neutralization degree induces the low value of Q . However, with the increase of neutralization degree, the repellency among charges increases. It is not good to increase the absorption capability. If the neutralization degree is too high, the reactivity and polymerization rate will reduce obviously. In order to get suitable polymerization rate and hydrophilic groups, the neutralization degree should not be too low or too high. Only when the degree is proper, the network of the resin has a considerable internal osmotic pressure, which is helpful to increase and retain the absorption capacity. Therefore, with the increase of the

neutralization degree, the value of Q first increases and then decreases. And the maximum is obtained at the degree of 75%.

3.6. Effects of Microwave Power and Irradiated Time on Cu^{2+} Absorption Capability (Q). Microwave power levels and irradiation time are two important factors to influence the polymerization rate and the absorption capacity of resin. Different microwave power levels (160, 320, 480, and 600 W) were studied. The change curves of Q with the change of irradiated time under the first three power levels are indicated in Figure 6. When the level is 600 W, the reaction is too rapid to control and decomposition of resin is serious in very short time. So the curve cannot be drawn efficiently. Under the other three power levels, the changes of Q -time curves are similar. With the time prolonging, the value of Q increases first and decreases then. The maximum values of Q are, respectively, 56, 65, and 58 mg g^{-1} according to the time 600, 300, and 150 s and the power level 160 and 480 W. It is deduced that the lower the power level, the slower the rate of grafted copolymerization and the more remarkable the inhibition of oxygen, which prolong both the induction period and the polymerization time. For example, when the power level is 160 W, the polymerization rate is slow. On the other hand, when the level is more than 480 W, the strong

microwave energy advances the monomers' activity. The results are that the reactions become difficult to control and degradation of the resin is easy to occur. Moreover, because of the high activity, the monomers are easy to self-polymerize before arriving at the reactive scope of cellulose. The dual effects of degradation and self-polymerization make the high absorption capability of the resin become impossible and the polymerization process difficult to control. Considering all these factors, the optimal conditions are 320 W and 300 s.

3.7. Structural Analysis of Resin. The FTIR spectra of the cellulose and resin are shown in Figure 7. Comparing the spectra of -O=C-NH- at 1675 cm^{-1} , -CH_2 at 2930 cm^{-1} and 2850 cm^{-1} , C=O at cm^{-1} , 1452=C-N- at 1455 cm^{-1} , C-OH at $1200\text{--}950\text{ cm}^{-1}$, and O-C-O at 1017 cm^{-1} and 1167 cm^{-1} indicated that the resin is a kind of a grafted copolymer with AA and AM to cellulose.

4. Conclusions

In this paper, the preparation conditions of the absorbent resin for Cu^{2+} removal through grafting AA and AM to cellulose under microwave irradiation were studied. The optimal reaction conditions are the mass ratio of AA to cellulose of 10:1, initiator to AA of 0.65 wt%, crosslinking agent of 1.0 wt%, 75% neutralization degree, 320 W, and 300 s. Under these conditions, the maximum absorption capability is obtained, that is, $65\text{ mg}\cdot\text{g}^{-1}$ (25°C).

Compared to the conventional heating and previous studies, obvious advantages can be found in this paper, such as no protection of nitrogen, no posttreatment, short time, and high absorption capability.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

This research was performed at the Northeast Petroleum University.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Jing Shu organized the research and wrote the manuscript, and Dabiao Zhao checked the manuscript. Lili Li provided the laboratory and apparatus and revised the manuscript according to the reviews' comments.

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