

# Preparation and Adsorption Performance of a Cellulosic-Adsorbent Resin for Copper(II)

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Received 28 October 2004; accepted 7 April 2005

DOI 10.1002/app.22986

Published online 11 January 2006 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The adsorbent resin was prepared by grafting copolymerization of acrylic acid and acrylamide onto cellulose under microwave irradiation, and was applied to adsorb copper ions from wastewater. The influences of adsorption time, resin particle size, pH values, and temperature of solution on its adsorption performance were investigated. At the optimal adsorption conditions, adsorption ratio could get to 99.2% and the adsorption capability reached 49.6 mg/g. Furthermore, adsorption theory model was based and study showed that the physical adsorption was dominating and it accorded to Freundlich isotherm model. XPS of adsorbent resin complex was tested, which

ensured the chelating groups onto adsorbent surface. Adsorbent resin could be regenerated using 8%  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , which had good regeneration effect, and experiment showed that adsorption ratio could still keep over 90% when resin was regenerated seven times. So, heavy metal-ions could be reclaimed from gel resin and the circulation of resources could be realized. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2951–2956, 2006

**Key words:** cellulose; grafting copolymerization; adsorbent resin; adsorption; adsorptive isothermal model

## INTRODUCTION

With the enhancement of the quality for living environment, all kinds of pollution problems and diseases caused by heavy-metal ions have already aroused people's attention, and so how to deal with these problems has become an imperative project to environmentalists. Presently, the common ways of dealing with heavy-metal ions mainly include chemical sedimentation, superfiltration, flocculation of inorganic compounds, ion-change resin,<sup>1,2</sup> etc.

However, there exist problems using above methods, such as high running cost and the second-pollution during the course of use. Because of these demerits, researchers have already devolved themselves to prepared macromolecule metal complex (MMC) using natural macromolecule compounds, such as starch and cellulose, as grafted framework to synthesize adsorbent to adsorb heavy-metal ions. About this study, there are some international or national reports.<sup>3,4</sup>

As we all know, cellulose is the most abundant reproducible resource on the earth. Although there are some reports<sup>5,6</sup> about high additive value utilization, it is mainly used as brute feeding stuff and fuel at

present, and so its utilization ratio is poor. Then cellulose has a latency utilization and exploitation. This paper first grafted Acrylic Acid and Acrylamide onto cellulose direct using microwave irradiation instead of water-bath to prepare adsorbent to adsorb copper ion from water. This not only realizes high value of utilization for cellulose, but also widens the development of functional material. The MMC can be used many times and has good bio-degradation character, which does not cause the second-pollution in the course of use. Because of these advantages, adsorbent resin should become an application foreground water reagent.

## EXPERIMENTAL

### Materials and instruments

Acrylic Acid (AA) was purified by distillation under reduced pressure to remove the inhibitor before use. Cellulose based on filter paper was smashed before use. All the other chemicals were analytical grade products: Acrylamide (AM), *N,N*-methylene diacrylamide, Potassium persulfate (KPS), Sodium thiosulfate, bluestone, ammonia, and sodium hydroxide.

Galanz microwave stove (WD900ESL23I-3), electrothermal blast furnace and mini-vegetation disintegrator were produced by Taisite instrument corporation. 721 spectrophotometer was produced by Gaomi instrument analysis company, ShanDong. ESCA, PHI 5F00 was made in America.

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Contract grant sponsor: Harbin Institute of Technology; contract grant number: HIT MD2000–28.

### Copper uptake

A weighed amount of dry sample (0.1 g) was placed and immersed into a glass beaker, which was full of 100 mL pure water. After a period of swelling time, gel resin was filtered. Then the gel resin was added to a certain concentration solution of copper-ion. After some adsorption time, the gel resin was filtered and the adsorption ratio ( $\alpha\%$ ), the adsorption capability ( $Q$ ), and distribution coefficient ( $\beta$ ) between solution and organic part were calculated. After adsorption, the gel resin containing copper-ion was added to the ammonia solution, whose concentration was 8% to desorb copper ions and realize the regeneration of adsorption resin, calculating the desorption ratio. Respective calculation formulas were as following:

$$\alpha\% = \frac{C_0 - C}{C_0} \times 100\% \quad (1.3.1)$$

$$\beta = \frac{C_0 - C}{C} \quad (1.3.2)$$

$$Q = C_0 \times \alpha\% \quad (1.3.3)$$

$$\gamma\% = \frac{C_x \times 100\%}{C_0 - C} \quad (1.3.4)$$

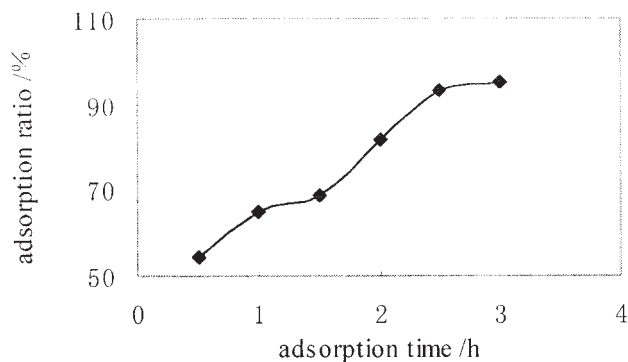
Where  $C_0$  was the initial concentration of copper ions,  $C$  was the concentration of copper ions out-water, and  $C_x$  was the copper ions concentration of regeneration solution, respectively.

## RESULTS AND DISCUSSION

### Preparation of the cellulosic-adsorbent resin with microwave irradiation

Because of the advantages of microwave irradiation,<sup>7</sup> this paper used it as a heating method to prepare cellulosic-adsorbent resin. Through a series of performance testing experiments, the synthesization factors, including the dosage of monomer, initiator, crosslinker, and neutralization degree, were optimized. Preparation process was as follows:

Water was added to a given filter paper, smashed by mini-vegetation disintegrator, and mixed round equably in a 100-mL polyfluortetraethylene beaker. Then the beaker was placed in the center of the microwave stove and heated for several minutes under 360 W microwave irradiation. Then, the beaker was taken and a certain volume of oxidation-deoxidization initiators (Potassium persulfate/Sodium thiosulfate) was added, initiating 5 min under 90 W microwave irradiation. Finally, quantitative polymer AA/AM and crosslinker *N,N*-methylene diacrylamide were added into the beaker and the system was



**Figure 1** Effect of adsorption time on adsorption performance.

adjusted to a certain neutralization degree, using sodium hydroxide solution, mixing equably. Then the beaker was put into the microwave stove of the center and was irradiated for several minutes under 3600 W. After the reaction, the product was cut into pieces and was immersed into ethanol for at least 4 h. Then the product was dried at 60°C for 12 h in the electrothermal blast furnace. All samples were triturated and dried in an oven at 60°C for at least one day before any testing. In this reaction process, it only took several minutes for the copolymerization by microwave irradiation, which is greatly shorter than water-bath requiring 10 h.

### Effect of experimental conditions on the adsorption performance of copper(II)

To ascertain the optimal adsorption conditions, this paper investigated the effect of adsorption conditions on its performance, such as the particle size of adsorbent resin, adsorption time, the pH value, and temperature of solution on copper(II) performance.<sup>8</sup>

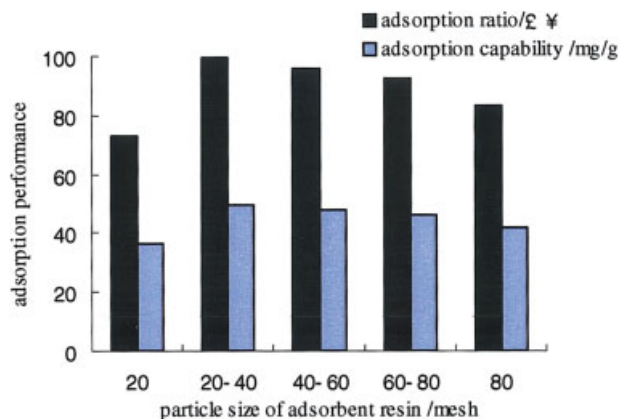
#### Effect of the adsorption time

The gel resin (0.1 g) was added into 100 mL copper ion ( $C = 50$  mg/L) solution and the concentration of copper-ion in the solution was tested periodically to ascertain the optimal adsorption time.

From Figure 1, we can see that the adsorption ratio enhanced following increased adsorption time and gradually stabilized when the adsorption time got to 2.5 h. Here, the adsorption ratio was 95.2% and adsorption capability reached 47.6 mg/g, so the optimal adsorption time was 2.5 h.

#### Effect of the particle size

0.1 g of adsorbent resin was fetched and crushed and the particle size was classified as follows: 20, 20–40, 40–60, 60–80, and 80 mesh. According to the above



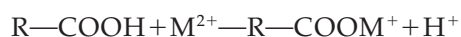
**Figure 2** Effect of resin particle size on adsorption performance [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

operation course, the adsorptive performance parameters of different samples were calculated.

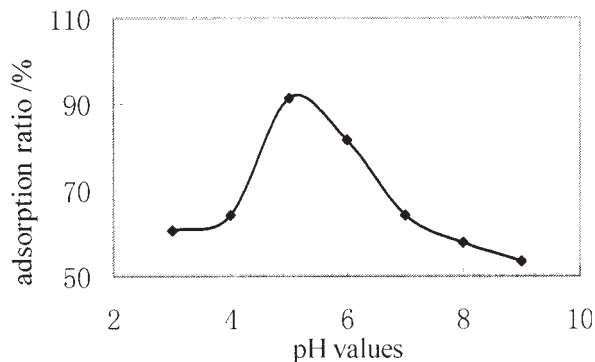
The relationship between adsorption performance and resin particle size stick out a mile, as shown in Figure 2. Adsorption ratio could reach 99.2% and the adsorption capability was 49.6 mg/g when the size was 20–40 mesh. The reason was that the concentration of chelating groups on the resin surface was so lower that decreased the adsorption ability when the particle size was bigger, and so the chelating ability enhanced with the increasing particle size. However, too small particle size caused the dissolution ratio of resin to increase, which weakened the use of adsorption and debased the times of regeneration, and the optimal resin particle size was found to be 20–40 mesh.

**Effect of pH values**

The same experiment was repeated at different pH values to test the effect of pH on adsorption performance. With the enhancement of pH values, the adsorption ratio increased formerly and decreased latterly, receiving this trend from Figure 3. The adsorption ratio could arrive at 92.04% and adsorption capability came to 46.02 mg/g when the pH value was 5. In fact, in the solution, there existed the ionization of COO<sup>-</sup>.

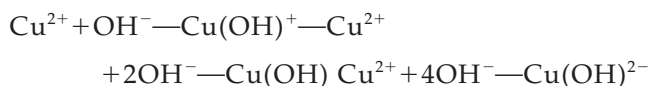


When the equilibrium removed left, which lead the degradation of the heavy-metal complex to produce R-COOH and metal ions at acidity condition, so the lower pH value held bake the forming of heavy-metal complex. However, when the pH value was too high,



**Figure 3** Effect of pH values on adsorption performance.

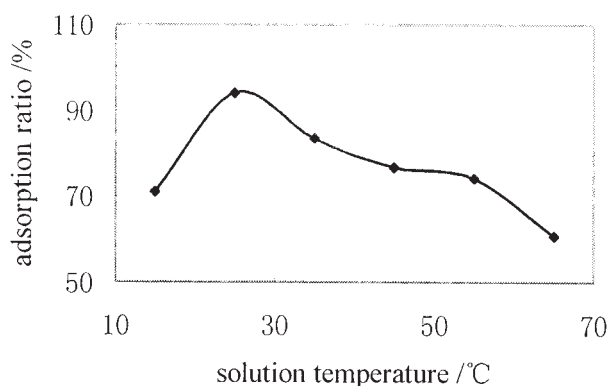
OH<sup>-</sup> had reaction priority with copper-ion forming all kinds of copper hydrate, and reaction equations were as follows:



The formation of copper hydrate would weaken the competition adsorption ability of resin, and so the optimal pH value was found to be 5.

**Effect of solution temperature**

The adsorption ratio increased formerly and then decreased latterly gradually getting across 25°C with the enhancement of solution temperature, shown by Figure 4. The reason was that the enhancement of temperature could boost reaction speed and increase collide odds between Cu<sup>2+</sup> and reaction groups, which did good to form chelate compound. On the other hand, considering that adsorption reaction was an exothermic reaction, too high temperature could accelerate decompose of chelate compound, which went against the formation of chelate compound and led to the fall of adsorption ratio. The optimal solution



**Figure 4** Effect of solution temperature on adsorption performance.

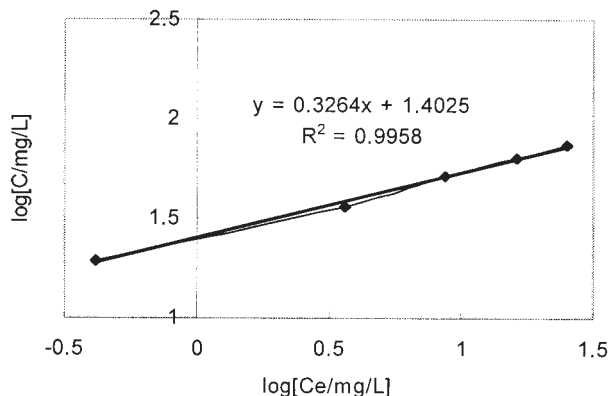


Figure 5 Freundlich adsorption isothermal equation.

temperature was 25°C. At this adsorption environment, adsorption ratio was 94.06% and adsorption capability reached 47.03 mg/g.

#### Adsorption isothermal model

Various concentrations of copper-ion solution was prepared and the adsorption performance of resin was tested to investigate the adsorption isothermal equation and the main sorption power. Experimental data were as follows:

Based on Freundlich adsorption isothermal model, namely  $\log C = \log k + 1/n \log C_e$ , adsorption isothermal equation could be concluded shown from Figure 5:  $\log C = 2.407 + 0.328 \log C_e$  ( $R^2 = 0.9958$ ). From this equation, there was a better linearity relationship between  $\log C$  and  $\log C_e$  from the correlation coefficient  $R$ . ( $R^2 = 0.9958$ ). To test the strictness of this adsorption equation, put  $C_e$  ( $C_e = 16.41$  mg/L) to the equation ( $\log C = 2.407 + 0.328 \log C_e$ ) and through calculation got  $C$  ( $C = 639.13$  mg/Lg), then compared with 635.84 mg/Lg, which was got through experiment. So, relative error was only 0.58%, which proved that the adsorption equation had good catholicness under some concentration scope. This proved that there existed physical adsorption during the course of adsorption.

where,  $C$  was the change in concentration of copper-ion caused by adsorbent resin at adsorption balance,

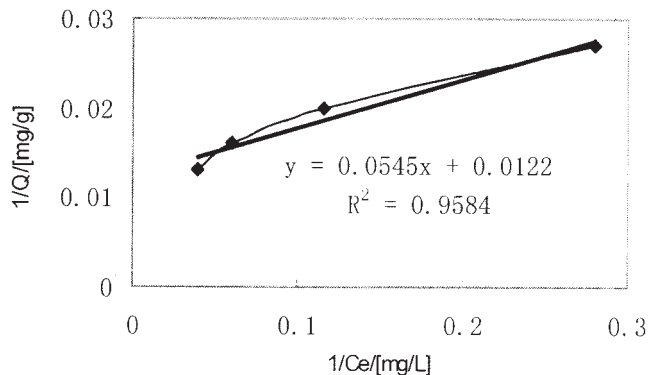


Figure 6 Langmuir adsorption isothermal equation.

which was calculated by the formula  $C_0 - C_e/m$  and its unit was mg/gL;  $C_e$  was the concentration of copper-ion at a certain time, and its unit was mg/L.  $k$  and  $n$  were constants to reaction system at a certain temperature;  $m$  was the adsorbent resin quantity, respectively.

Based on Langmuir adsorption isothermal model,  $\frac{C_e}{Q} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}$ , and its equivalence transmogrification was  $\frac{1}{Q} = \frac{1}{bQ_0C_e} + \frac{1}{Q_0}$ , adsorption isothermal equation was described by a linearity relation equation and its square of correlation coefficient was 0.9548, namely  $\frac{1}{Q} = 0.0545/C_e + 0.0122$  ( $R^2 = 0.9584$ ), which was shown clearly from Figure 6. So a conclusion was drawn that there also existed physical adsorption in the adsorbing process, while physical adsorption was more advantageous than the chemical adsorption, which is found through the linearity connection coefficient (Table I).

where  $Q$  was the adsorption capability and its unit was mg/g;  $Q_0$  was the maximum adsorption capability;  $C_e$  was defined as the above; and  $b$  was the constant under the given reaction system, respectively.

From Figures 5 and 6, a clear conclusion was made that there not only existed physical adsorption, but also existed chemical adsorption, and the copper-ion was removed by cooperation of two kinds of adsorbing; but physical adsorption was in the highest flight during the course of adsorption.

TABLE I  
The Data of Adsorbing Copper Ions

| Initial concentration (mg/L) | Ultimate concentration (mg/L) | Adsorption ratio (%) | Contribution coefficient | Adsorption capability (mg/g) |
|------------------------------|-------------------------------|----------------------|--------------------------|------------------------------|
| 20                           | 0.416                         | 97.92                | 47.08                    | 19.58                        |
| 40                           | 3.593                         | 91.02                | 10.13                    | 36.41                        |
| 60                           | 8.635                         | 85.61                | 5.95                     | 51.37                        |
| 80                           | 16.416                        | 79.48                | 3.87                     | 63.58                        |
| 100                          | 25.075                        | 74.925               | 2.99                     | 74.925                       |

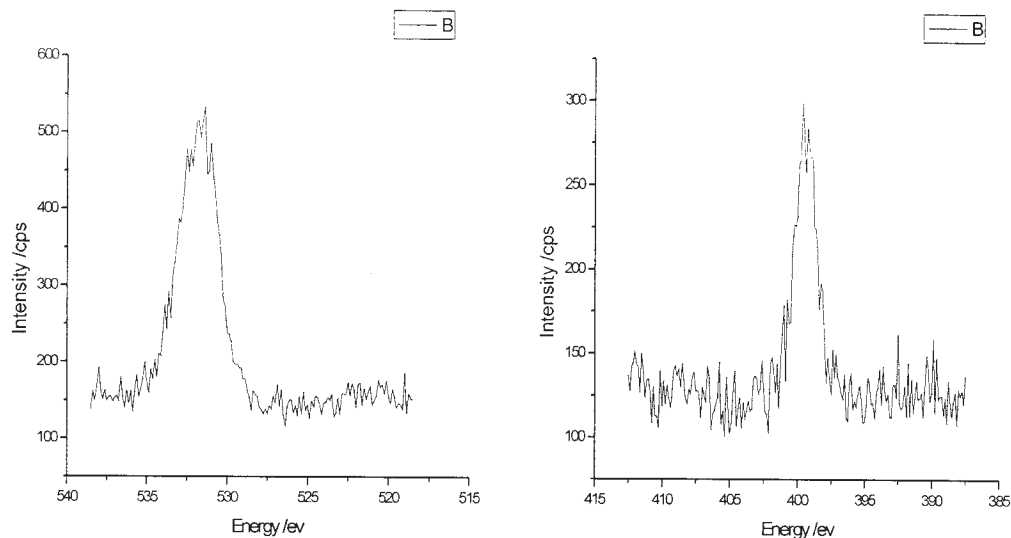


Fig.7 (a) XPS of <sup>15</sup>O

(b) XPS of <sup>15</sup>N (b)

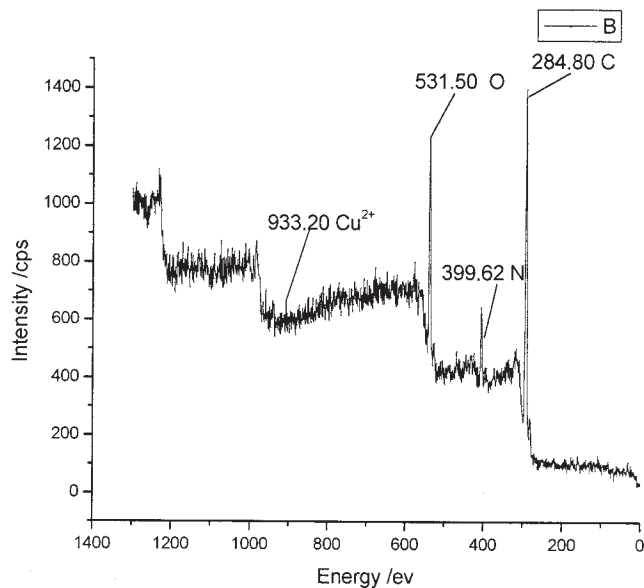


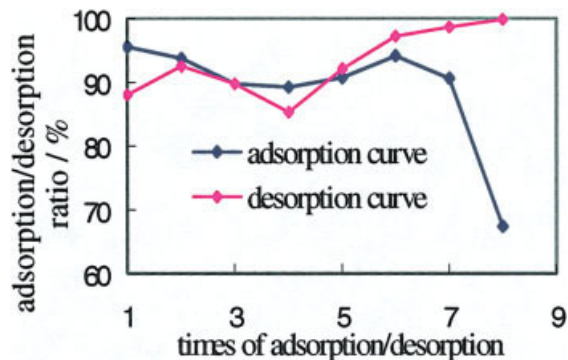
Fig. 7 (c) XPS of adsorbent resin complex

Figure 7 XPS of <sup>15</sup>O (a), XPS of <sup>15</sup>N (b), and XPS of adsorbent resin complex (c).

**XPS of adsorbent complex**

Figure 7 was the XPS of <sup>15</sup>O (a), <sup>15</sup>N (b), and adsorbent resin complex (c). There appeared chelation that chelated heavy-metal ion with nitrogen–oxygen functional groups on the surface of adsorbent resin through the analysis of XPS shown by Figure 7. At the 399.50 electron volt, there appeared characteristic en-

ergy peak value, which approved that this was the nitrogen of CH<sub>3</sub>CONH<sub>2</sub> and only had 0.02 electron volt wrap with the standard value compared with Figure 7(a). And at the 531.50 electron volt of XPS, appeared the energy peak value, which was approved oxygen characteristic energy peak shown by Figure 7(b). At the 933.30 electron volt, appeared copper char-



**Figure 8** The regeneration of adsorbent resin [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

acteristic energy peak that debase 0.05 electron volt compared in solution. The reason was probably that the single pair electrons of nitrogen and oxygen transferred to the hollow orbit of heavy-metal ion. At the same time, this showed that  $-\text{NH}_2$  and  $-\text{COO}-$  functional groups on the adsorbent resin surface took part in the chelation and formed macromolecule metal complex.

### Regeneration of adsorbent resin

Considering the effective recycle of resource and environment protection, adsorbent resin should be regenerated with a kind of cheap and avirulent to surroundings reagent to attain the regeneration of resin and the recycling of heavy-metal ion. Adsorbent resin had the optimal adsorption performance in the acidic solution (pH = 5) gained from the adsorption performance experiment. Because adsorption/desorption was a reversible reaction, alkaline reagent, which could replace chelate groups of adsorbent resin and form compound with heavy-metal ion at the condition of being unable to destroy the organic macromolecule framework, should be selected as regeneration reagent to increase the regeneration ratio based on theory. So, this experiment used ammonia as regeneration reagent, whose volume concentration was 8%. The adsorbent complex was added and immersed in ammonia for 2 h. The solution was filtrated and the copper concentration in the filtrate was tested by calculating the regeneration ratio according to the formula of 1.3.4.

The adsorption ratio still reached over 90% even though the adsorbent resin was regenerated seven times and desorption ratio all exceeded 85% shown by Figure 8. This was because that copper ions chelated reaction groups of resin with chemical bond form in the adsorptive initial stages, and so  $\text{NH}_3 \cdot \text{H}_2\text{O}$  could not wash completely copper ions from the chelate active points of resin, which would reduce the resin adsorptive performance. However, when the regeneration over-

stepped four times, resin structure turned compact<sup>9</sup> and presented a state of flocculation, which did good to adsorption. Nevertheless, when the regeneration times overstepped seven times, the dissolution and structure destroyed of the resin would reduce the adsorptive performance, but this physical change of structure would increase the regeneration ratio.

### CONCLUSIONS

- (1) The adsorbent resin was prepared using microwave irradiation and oxidation-reduction initiator system to adsorb copper ions of waste water, which technique could shorten reaction time, simplify experiment reactor, optimize technique and stabilize the resin performance.
- (2) The effects of adsorption conditions on adsorptive performance were investigated. Under the optimal adsorption conditions, the adsorption ratio could reach 99.2% and adsorption capability was 49.6 mg/g. The 8% ammonia was used as regeneration solution to regenerate adsorption resin, at this conditions, regeneration ratio could arrived at 85% every time and adsorbent resin could be used seven times and adsorption ratio still kept 90% every time.
- (3) Based on the static adsorption, established the adsorption theory model and simulated adsorption isotherm. Experiment found that there not only existed chemical adsorption reaction, but also existed physical adsorption reaction, which two types adsorption reaction were together favorable, only physical adsorption was dominant and the adsorption theory model mainly accorded to Freundlich adsorption isothermal model.
- (4) The chelate groups on the adsorption resin surface was show through XPS of adsorption resin complex after adsorbing copper ions, which proved farther that there existed chemical bond power in all adsorption reaction powers.

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