RESEARCH ARTICLE

Selective removal of Cu(II) from contaminated water using molecularly imprinted polymer

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Abstract   A synthetic molecularly imprinted polymer (MIP) was prepared by noncovalent imprinting technique for the selective removal of Cu^{2+} from aqueous solutions. In the preparation of imprinted polymer, Cu^{2+} was used as the template, oleic acid as the functional monomer and divinylbenzene as the cross-linker. The surface morphologies and characteristics of the MIP were determined by BET, scanning electron microscopy (SEM), FTIR and energy dispersive X-ray spectrometer (EDS). The proper adsorption and selective recognition ability of the MIP were studied by an equilibrium-adsorption method. In general, the removal efficiency of Cu^{2+} increased rapidly with pH from 2 to 7 and decreased at a pH 8. The removal efficiency of Cu^{2+} increased with temperature from $25°C$ to $50°C$. Competitive adsorption studies showed that the coexisting cations have no obvious influence on the adsorption of Cu^{2+}. In addition, the variation in the adsorption ability of the MIP that was repeatedly used was investigated, and it showed excellent reproducibility.

Keywords   copper, molecularly imprinted polymer, water treatment, removal

1   Introduction

Heavy metal ions are always the main and priority control pollutant in water environments, due to their toxicity and detrimental effect on living species, including humans. The origin of the heavy metal contamination of drinking water lies in the illegal disposal of industrial effluents, which eventually find their way into underground aquifers. Another source of heavy metals in tap waters is the corrosion of the metal pipes used to provide water to consumers [1]. Copper is an essential element for human health since low concentrations play an important role in enzyme-mediated systems. However, high levels of copper are non-degradable and can accumulate in living tissues. Therefore, excessive Cu^{2+} in water should be removed to a permitted level of less than 1 mg/L that makes the water safe and suitable for drinking purposes [2].

Many researchers have made efforts to remove Cu^{2+} from contaminated water using several processes, such as chemical precipitation, adsorption, ion exchange, membrane filtration, evaporation, electrodialysis and reverse osmosis [3–10]. However, these conventional technologies remove all metal ions, which make the removal process turn out to be less effective. Therefore, the search for low-cost and highly selective removal methods is still essential.

Molecular imprinting is a convenient and powerful technique for the preparation of polymeric materials as specific molecular recognition receptors [11]. The imprint is like a lock that is only compatible with the correct key, similar to biological systems, such as enzymes and substrates, antibodies and antigens, and hormones and receptors. Molecular imprinting of synthetic polymer is a process where functional and cross-linking monomers are co-polymerized in the presence of the template molecule. The concept of the molecular imprinting technique is illustrated in Fig. 1. The functional monomers initially form a complex with the imprint molecule followed by a process of polymerization, and then their functional groups are held in position by the highly cross-linked polymeric structure. Subsequent removal of the imprint
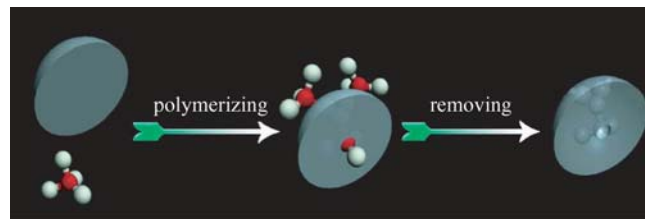
Fig. 1   Schematic illustration of the molecular imprinting technique

molecule reveals binding sites which are complementary in size and shape to the template molecule [12].

The molecularly imprinted polymer (MIP) is stable, easy to prepare, and inexpensive. Therefore, molecular imprinting offers a cheap and versatile platform for creating a polymer matrix with molecule-specific recognition properties with applications ranging from purification of racemic mixtures, to chemical sensing and catalytic control of complex chemical reactions. The field of molecular imprinting has drawn much attention in the past decade and is documented in several very comprehensive reviews [13–17].

The molecular imprinting technique offers potential for the removal of pesticides and endocrine-disrupting compounds from waste and drinking water, and it can also be used to remove heavy metals, rare metals and radioisotopes with high specificity [18–20].

In this paper, we describe a simple approach to preparing synthetic receptors for Cu^{2+} by using the molecular imprinting technique. The objective of this study is to prepare and characterize a Cu(II)-imprinted polymer that can be used for water treatment effectually. A key attribute of the Cu(II)-imprinted polymer is its specific selectivity to the target Cu^{2+} and potential regeneration.

2　Experimental

2.1　Materials

Cupric nitrate, oleic acid, ethylenediamine tetraacetic acid (EDTA), absolute ethanol, and chloroform were purchased from BODI Chemicals (Tianjin, China). Divinylbenzene and 2,2′-azobisisobutyonitrile (AIBN) were purchased from Institute of Guangfu Fine Chemical Research (Tianjin, China). All the other chemicals were of reagent grade.

2.2　Preparation of the MIP by emulsion polymerization

For the preparation of the Cu(II)-imprinted polymer, the functional monomers were purified prior to use via standard procedures in order to remove stabilizers. Then 4.0 g of Cupric nitrate (template) was mixed with 10 mL of purified oleic acid (monomer) in 20 mL of chloroform, followed by the addition of 10 mL of divinylbenzene (cross-linker) and 0.5 g of AIBN (initiator). The solution was then purged with nitrogen for 5 min to remove oxygen, sealed and then incubated at 70°C for 20 h in a water bath. The resultant polymer was washed with MeOH/acetic acid solution (9 : 1, v/v) in a Soxhlet extractor to remove the target metal ions and then filtered off. This procedure was repeated several times until copper ions could not be detected in the filtrate. The remaining particles were dried under vacuum at 60°C and used for the following studies.

As a control, a non-imprinted polymer (NIP) was also prepared in parallel with the MIP by using the same synthetic protocol in the absence of the template.

2.3　Adsorption studies of Cu(II)-imprinted polymer

Adsorption experiments for Cu^{2+} were conducted using a batch-wise method. The dry imprinted polymer (1.0 g) was immersed in 100 mL solution containing 0.5 mol/L of Cu^{2+}, and the pH value of the solution was 7.0. The mixture was shaken in thermostated water at 25°C for 2 h. The same experimental conditions were adopted to study the influence of temperature on Cu^{2+} removal.

In order to investigate the selective adsorption of the MIP, 1.0 g of the MIP and 1.0 g of the NIP were added into 100 mL solutions containing four heavy metal ions (Cu^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}, 0.1 mmol/L for each ion). The mixture was shaken in thermostated water at 25°C for 5 min.

To determine the effect of pH on the removal of Cu^{2+} from aqueous solution, 0.1 g of the MIP was dispersed in 100 mL of solutions containing 0.065 mmol/L of Cu^{2+}. The initial pH values of the solutions were adjusted from 2.0 to 8.0 using 0.5 M HCl and 0.5 M NaOH as appropriate. The mixture was shaken in thermostated water at 25°C for 5 min.

The amounts of metal ions on the polymer were evaluated by the residual concentration of metal ions in the filtrated aqueous solutions.

2.4　Analytical methods

The concentrations of Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} were determined by using an atomic absorption spectrophotometer (Model AAnalyst 100, PE Co., Ltd., USA). The scanning electron microscopic (SEM) photographs of the MIP and the NIP were taken by an FEI Sirion scanning electron microscope (Philip Co., Ltd., Holland). Surface area analysis and average pore diameter of the MIP were measured by an Autosorb-1-C chemisorption-physisorption analyzer (Quantachrome, Co., Ltd., USA). The structures of the MIP were determined by a Fourier Transform Infrared Spectrometer (AVATAR 360, Nicolet., USA). The main elements were analyzed using an energy dispersive X-ray spectrometer (EDS).

3　Results and discussion

3.1　Effect of contact time

Figure 2 shows the effect of contact time on the adsorption of Cu^{2+} onto the MIP. It is noted that the adsorption of Cu^{2+} increased quickly with time and then reached equilibrium. The average adsorption rate was 0.38 mg/min. The contact

time to reach equilibrium was 80 min. The final capacities for adsorption of Cu^{2+} onto the MIP reached 30.2 mg/g.
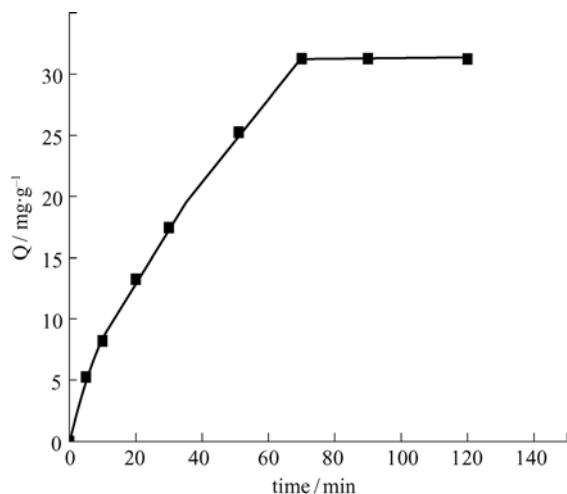

Fig. 2   Effect of contact time on the adsorption of Cu^{2+} ion onto the MIP at 25°C and pH 7.0

3.2   Effect of pH

Figure 3 shows the effect of pH on the adsorption of Cu^{2+} onto the MIP. As we can see, the pH of the solution plays an important role in affecting the adsorption characteristics of Cu^{2+} onto the MIP. As the pH value of the solution increased, the removal efficiency increased gradually and attained 84.2% at pH 7, and then decreased at pH 8. In fact, such adsorption property is favorable for Cu^{2+} removal from the drinking water because the optimal pH value approaches to its real pH values.
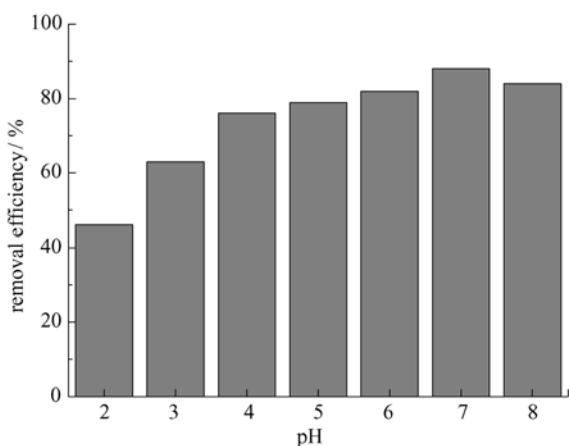

Fig. 3   Effect of pH on the adsorption of Cu^{2+} ion onto the MIP at 25°C and initial ion concentration of 0.065 mmol/L

3.3   Effect of temperature

Figure 4 shows the variation of Cu^{2+} adsorption amount with temperature. The adsorption amount of Cu^{2+} increased simultaneously with the increase in temperature from 25°C to 50°C. At 25°C, the removal efficiency was 82% and it went up to 85% and 95% as temperature increased from 30°C to 50°C. This is due to the fact that the MIP was prepared at approximately 70°C; part of the cavities was not used because the MIP cavity contracted at room-temperature. As the temperature increased, the MIP expanded and molecule motion aggravated at high temperature so that many cavities can be used and Cu(II) ion would fall off in the bonding sites aggregately.
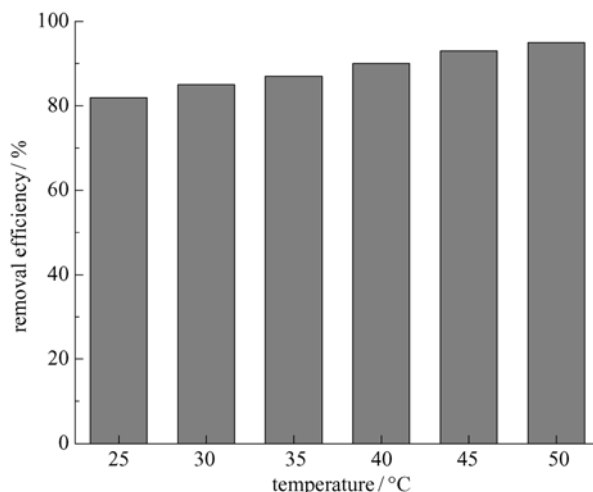

Fig. 4   Effect of temperature on the adsorption of Cu^{2+} ion onto MIP at pH 7.0 and initial ion concentration of 0.074 mmol/L

3.4   Effect of Cu^{2+} initial concentration

Figure 5 shows the effect of the initial concentration of Cu^{2+} on the adsorption capacities of Cu^{2+} by the MIP. The adsorption capacities of Cu^{2+} increase with the increase of Cu^{2+} initial concentration. An increasing Cu^{2+} initial concentration above the range 0.1–100 mmol/L led to an increase in the equilibrium adsorption capacity of Cu^{2+} ions adsorbed on the MIP from 6×10^{-4} mmol/g to
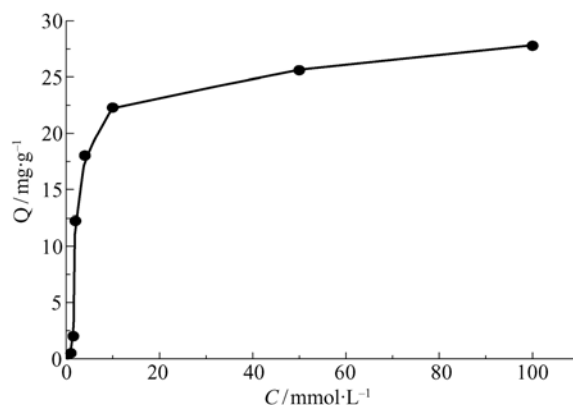

Fig. 5   Effect of Cu^{2+} initial concentration on the adsorption of Cu^{2+} ion onto MIP at 25°C and pH 7.0

0.44 mmol/g. A sharp increase in the equilibrium adsorption capacity occurred at a Cu^{2+} initial concentration of below 2 mmol/L, and attained a value of 0.2 mmol/g at a Cu^{2+} initial concentration of 2 mmol/L.

3.5 Competitive adsorption

In order to demonstrate the specific selectivity to the target Cu^{2+}, the effects of common coexisting ions on the adsorption of Cu^{2+} on the MIP were investigated. Cations such as Mn^{2+}, Co^{2+}, and Ni^{2+} ions were selected as competing cations towards Cu^{2+}, because they have similar ionic radius and particle size. Figure 6 shows the competitive adsorption of Cu^{2+} on the Cu(II)-imprinted polymer and non-imprinted polymer.
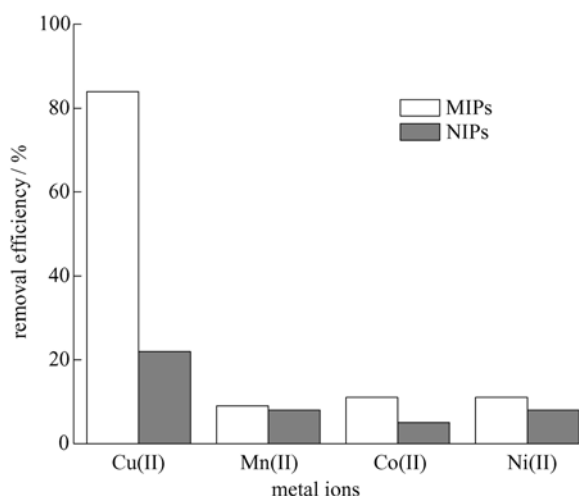

Fig. 6 Competitive adsorption for four ions of Cu^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} onto the MIP at 25°C and pH 7.0

It can be concluded that the Cu(II)-imprinted polymer shows a higher selectivity towards Cu^{2+} than other competing cations. On the other hand, the non-imprinted polymer shows a much lower selectivity to Cu^{2+}.

3.6 Reproducibility of MIP

The stability and potential regeneration of the MIP were investigated. Adsorption results of repeated uses of the MIP are shown in Fig. 7. The MIP can be reused after regeneration with 0.1 mol/L of EDTA for 2 h, and is stable for up to 10 adsorption cycles without obvious decrease in the adsorption capacity for Cu^{2+}. The demonstrated reusability of the MIP over several adsorption-desorption cycles is an advantage compared with single-use activated carbon.

3.7 Characterization of MIP

The specific surface area and pore structure of the MIP were measured, and the result can be seen in Table 1. The
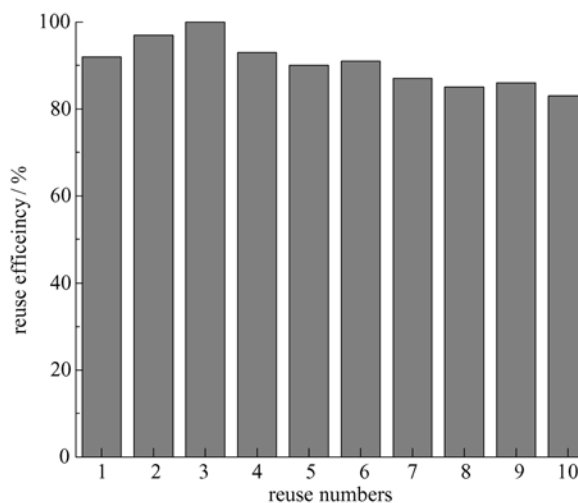

Fig. 7 Adsorption results of repeated use of MIP

Table 1 Pore characteristics of MIP

type	BET surface area/$m^2 \cdot g^{-1}$	total pore volume/$cm^3 \cdot g^{-1}$	average pore diameter/Å
non-imprinted MIP	69.7	0.93	531
imprinted MIP	24.3	0.40	656

BET surface area of MIP was decreased from 69.7 to 24.3 m^2/g, and the total pore volume of the MIP was decreased from 0.93 to 0.40 cm^3/g. It can be deduced that the MIP possesses a higher adsorption capacity toward Cu^{2+}.

Figure 8 A and B show the SEM images of the NIP and MIP, respectively. There are obvious differences between them. It is evident that the MIP exhibits an irregular, rough surface, which is more beneficial to the homogeneous binding of template ions. Moreover, there are many micro-pores which can facilitate the fast binding of template ions on the surface of the MIP. The cavities in the MIP were probably caused by the structure of the target molecule (Cu^{2+}).

Figure 9 shows the Fourier-transformed infrared spectra of NIP, MIP with loaded Cu^{2+} (imprinted MIP) and MIP without loaded Cu^{2+} (non-imprinted MIP), respectively. For all the samples, a characteristic peak at around 2926 cm^{-1} (O−H stretching vibration of oleic acid) was observed. In the preparation of imprinted polymer with oleic acid as a functional monomer, it is possible that some oleic acids form dimmers during the imprinting reaction. This means that both the final imprinted and non-imprinted reference polymer may contain the same level of functional groups. Furthermore, the IR features of the imprinted MIP showed very similar location and appearance of the major bands with those of the non-imprinted MIP except for the obvious variety at 1710 cm^{-1} and at around 1200–1320 cm^{-1}. This phenomenon might be attributed to the presence of Cu^{2+} ions in the MIP.
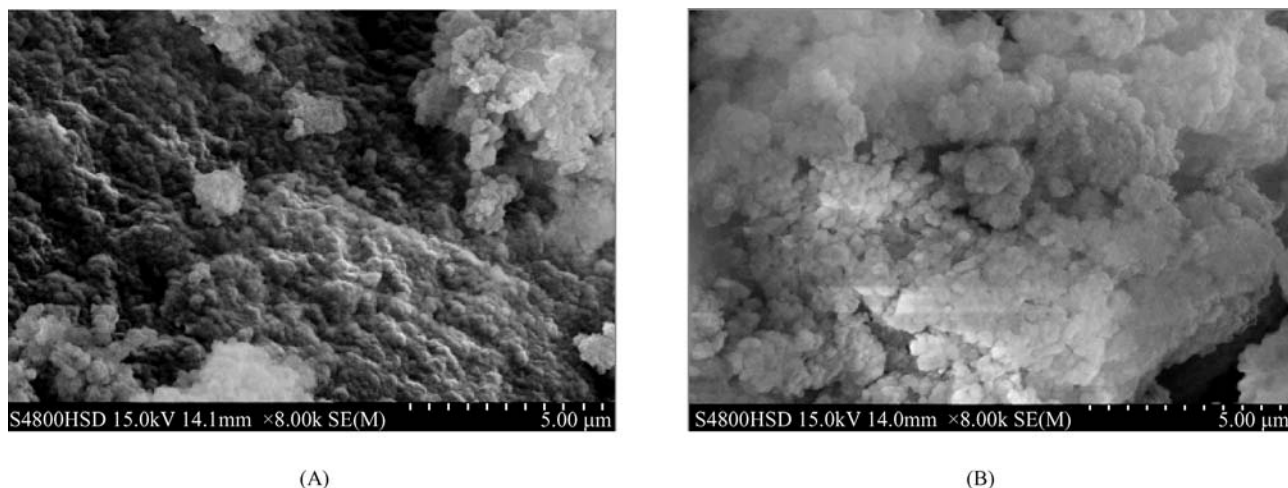
(A)

(B)

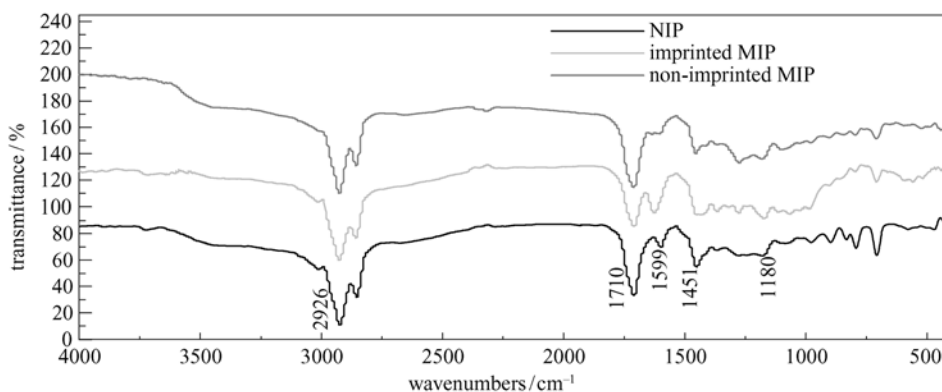**Fig. 8** SEM micrographs of NIP (A) and MIP (B)

Fig. 9 FTIR spectra of NIP, imprinted MIP and non-imprinted MIP

In order to get more structural information and understand the adsorption mechanism of the Cu(II)-imprinted polymer, an energy dispersive X-ray spectrometer (EDS) was developed for our experiments. The EDS detects X-rays from the sample excited by the highly focused, high-energy primary electron beam penetrating into the sample. The EDS provided useful information about the elemental distribution on the MIP as shown in Fig. 10 by the elemental mapping of each component. Comparing EDS images of non-imprinted MIP and imprinted MIP confirmed that only the copper element was present in the MIP. This implies that a number of cavities in the MIP facilitate diffusion of the target metal ions (Cu^{2+}) into the activity sites which are formed in the cavities, and the results further proved that the MIP has a high selectivity for target metal ions.
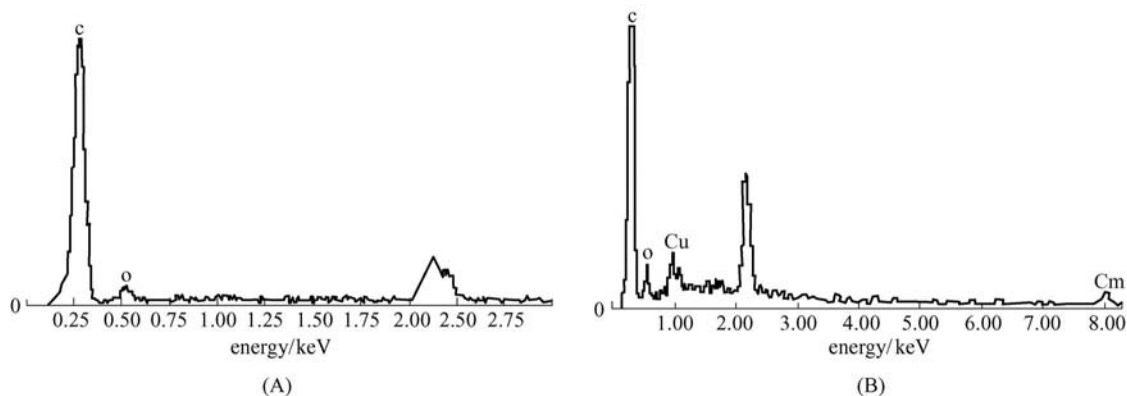

(A)

(B)

Fig. 10 EDS of non-imprinted MIP (A) and imprinted MIP (B)

4   Conclusions

Our work demonstrated the potential of the molecular imprinting technique for the removal of heavy metal from contaminated water. A Cu(II)-imprinted polymer was successfully synthesized by the emulsion polymerization approach using oleic acid as the functional monomer and divinylbenzene as the cross-linker. The obtained MIP exhibited a very high degree of selectivity and adsorption ability toward the template, namely Cu^{2+}.

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