

The synthesis and adsorption performance of polyamine Cu²⁺ imprinted polymer for selective removal of Cu²⁺

Jun-Xin Duan¹ · Xi Li² · Chao-Can Zhang¹

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Abstract In this paper, the Cu²⁺ ion-imprinted polymer (Cu²⁺-IIP) was prepared in the homogeneous phase by the ion-imprinted technology. Polyethyleneimine was used as the basic bone which was rich in amino-functionalized groups to coordinate with template Cu²⁺ and the 1,2-bibromoethane was used as a crosslinker. The chemical structure and surface morphology of the imprinted polymer were characterized by Fourier transform infrared spectroscopy (FTIR) and the scanning electron microscopy (SEM). Batch adsorption studies were performed to evaluate the adsorption capacity, the adsorption isotherm and the adsorption selectivity of Cu²⁺-IIP. The maximum adsorption capacity of Cu²⁺-IIP was 83.3 mg/g, significantly more than most of the reported adsorbents and also about 2.4 times that of non-imprinted polymer (Non-IIP) in this work. In addition, Cu²⁺-IIP performed good adsorption selectivity towards Cu²⁺ with the interference of Ni²⁺, Zn²⁺, or Pb²⁺. These results indicated that Cu²⁺-IIP is a promising adsorbent for the real wastewater treatment.

Keywords Cu²⁺ · Ion-imprinted polymer · Adsorption · Selectivity

✉ Xi Li
chemlixi@whut.edu.cn

¹ School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

² School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, China

Introduction

With the global industrialization, the water contamination caused by metal ions becomes a general problem for the human health, ecological conditions, the modern agriculture and irrigation systems [1–5]. Therefore, the effective removal of toxic heavy metals by appropriate treatment technologies is a crucial issue for a long time [6].

Among the heavy metals, Cu^{2+} is not acutely toxic to humans. But its extensive use and increasing level in the environment may cause serious health problems [7]. So it was enrolled in the 13 toxic metal species on the EPA's priority pollutant list [8]. The conventional methods of Cu^{2+} removal from the wastewater are chemical precipitation, ion exchange, electrolysis, reverse osmosis processes and adsorption on activated carbon [9]. But these methods are industrially applicable for the non-preferential separation. The inherent lack of selectivity is a major drawback [10]. To remove or separate a specific metal ion from a mixture, a selective separation method is required.

Molecular imprinting technique, as selective sorbents for a particular chemical form of the given element, has become a powerful method for the preparation of sturdy materials that have the ability to recognize a specific chemical species [11, 12]. For metal ions, the molecular imprinting can be exactly interpreted as the ionic imprinting. Metal ions used as template molecules, the selectivity of the ionic imprinted polymer (IIP) enhances because of the memory effect of the polymer on the imprinted ions from the specific interaction of ligands with the metal ions as well as the coordination geometry, the coordination number, the size and the charge of metal ions. There are a number of published papers related to the preparation of imprinted polymers for the selective adsorption of Cu^{2+} . As early as 1976, Nishide et al. [13] prepared a chelate resin through crosslinking a complex of poly(4-vinylpyridine) with a metal ion (Cu^{2+} , Fe^{3+} , Co^{2+} , Zn^{2+} , Ni^{2+} , and Hg^{2+}) as a template. The resin comparatively adsorbed the metal ion which was used as a template. Afterwards, to improve the adsorption capacity, selectivity, rapid uptake kinetics and reduce costs, various of imprinted methods were developed, such as grafting functional groups, which can coordinate with metal ion on the silica gel surface [14–16], some composite sorbents containing natural biopolymer as chitosan [17–19], Cu^{2+} imprinting polymer nanoparticles [20–22] or microspheres [23], and hydrogel [24, 25].

Among these, amino-functionalized metal ion-imprinted sorbents [26–28] were paid great attention, because amino groups easily form coordination bonds with Cu^{2+} . Liu et al. [29] found that the Cu^{2+} adsorption capacity increased obviously through injecting Congo Red rich in $-\text{NH}_2$ into the crosslinked chitosan hydrogels.

Therefore, polyethyleneimine (PEI), a kind of water-soluble polyamine with a large quantity of amino groups, naturally gathered intense interest of researchers as an ideal trapping agent for metal ions [30–32]. An and Gao [33] reported that PEI/ SiO_2 had the high adsorption amount for plumbum ions even in the presence of the high concentration of alkaline-earth metal ions. Deng et al. [34] synthesized a novel Cu^{2+} imprinted membrane by pressure-driven depositing poly(ethyleneimine) (PEI)

onto the surface of a polyacrylonitrile (PAN) ultrafiltration (UF) membrane combined with ion imprinting technique. The imprinted membrane exhibited the good specificity and recognition to the Cu^{2+} . The structure, effective equilibrium constant, stoichiometric ratio, and the reaction energy change of complex formation of Cu^{2+} and PEI were investigated by Kislenco and Oliynyk [35], and the complex formation processing within the sorbents imprinted with Cu^{2+} was investigated in ESR method by Zagorodni [36]. All these researches provided the mature conditions for using PEI as the chelating agent to prepare Cu^{2+} imprinted sorbents.

Although each has its own advantages, the adsorption capacity of reported similar imprinted sorbents is still low [37–39], which could not meet the demand of the waste water treatment, especially at the high metal ion concentration. The low capacity may attribute to the limited grafting amount of chelating agents or the low compatibility between the body surface and chelating agents [40].

In this study, PEI long chain as the basic bone, Cu^{2+} as the imprinted ion, and 1,2-dibromoethane as the cross linker, a Cu^{2+} imprinted polymer, containing abundant amino groups were synthesized by the ion-imprinted technology with no any initiator condition. The whole reaction was carried out in the homogeneous phase and synthesis procedures are rather brief. Here, PEI long chain was employed as the basic bone (functional monomer) rather than being grafted to other substrates, which naturally increased the amino-group amounts largely. The synthesized imprinted sorbent had high adsorption capacity due to the specific cavities from the imprinted template and the chelation of the abundant amino groups. The imprinted sorbent was characterized by Fourier transform infrared spectroscopy (FTIR) and the scanning electron microscopy (SEM). The adsorption kinetics, isotherm, and selectivity of the Cu^{2+} imprinted polymer were also investigated.

Experimental

Materials

50.09 wt% linear PEI was purchased from Xiya Reagent-Puruidi Instrument Co., Ltd. (Chengdu, China). All other necessary chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Wuhan, China). 1,2-Dibromoethane was chemical grade and the others were analytical grade. All solutions were prepared using the distilled water.

Instruments and apparatus

An IRIS INTREPID IIXSP model inductively coupled plasma (ICP-OES, Thermo Electron Co. America) was used for the determination of all metal ions. The instrumental parameters of ICP-OES were in accordance with the manufacturer's instructions. The pH values were measured by PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded using a Magna-560 spectrometer (Thermo Nicolet Co., USA). SEM images were obtained by a scanning electron microscope (JEOL,

JSM-5610LV). All adsorption experiments were accomplished in a model SHZ-82(A) Vapour-bathing Constant Temperature Vibrator (Beijing Ke Ning Bio-Tech. Center, Beijing).

Preparation of polyamine Cu^{2+} ion-imprinted polymer

The preparation procedure includes three steps as shown in Fig. 1.

The first step is the preparation of Cu^{2+} -PEI complex. 12 g of 50.09% PEI was dissolved in 60 mL DMSO. Then, 8.4 g of stoichiometric $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into the DMSO solution under mechanical stirring. The resulting reaction mixture was stirred about 1 h at room temperature.

The second step is the cross-linking reaction. With vigorous stirring, 6 mL 1,2-dibromoethane and excessive anhydrous K_2CO_3 powder were added to the above solution at 60 °C. At this temperature, the cross-linking reaction was carried out about 4 h. Then, the reaction was continued at 120 °C for 24 h. The solid polymer was obtained by the filtration.

The third step is the elution of imprinted Cu^{2+} in the polymer. The polymer was washed by distilled water and ethanol in sequence. Then, the polymer was soaked in 0.1 M HCl solution to remove the Cu^{2+} , and followed by washed with plenty of distilled water till the solution is neutral. The polymer was dried in a vacuum oven at 60 °C about 24 h. Finally, the dried polymer was further ground. The particles of 0.1–0.3 mm size were selected as the experiment Cu^{2+} imprinted adsorbent (Cu^{2+} -IIP).

For comparison, non-imprinted polymer (Non-IIP) was prepared according to the above approach with an exception that Cu^{2+} was not added.

Adsorption experiments

Adsorption kinetics

In this experiment, nine capped conical flasks containing 50 mL 50 mg/L Cu^{2+} ion solutions (C_0) at the pH 6 and 0.015 g Cu^{2+} -IIP were shaken in a vibrator at a rotating rate of 130 rpm at 25 °C. One of the flasks was taken out at the adsorption time of 10, 20, 30, 40, 50, 60, 80, 100, and 120 min, respectively. The solid was filtered and the concentration of Cu^{2+} (C_t) in the filtrate was measured by ICP. The adsorption capacity (Q_t) was calculated by the following equation:

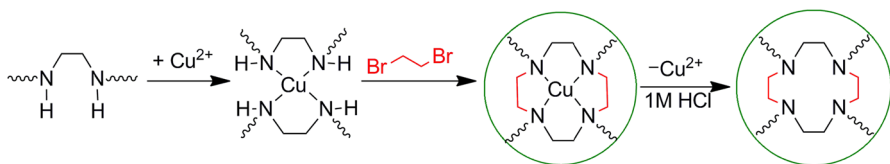


Fig. 1 Synthesis route of Cu^{2+} imprinted polymer

$$Q_t = \frac{(C_0 - C_t)V}{m}, \quad (1)$$

where V was the volume of solution and m was the weight of Cu^{2+} -IIP.

The effect of pH on adsorption

0.015 g of Cu^{2+} -IIP or Non-IIP was added into capped conical flasks containing 50 mL 50 mg/L Cu^{2+} solution at different pH. These flasks were shaken at 130 rpm for 4 h in the Vibrator. The temperature was set at 25 °C. Then, the adsorbents were filtered and the concentration of Cu^{2+} in the filtrate was measured by ICP. The adsorption capacity (Q) was calculated by the following equation:

$$Q = \frac{(C_0 - C_e)V}{m}, \quad (2)$$

where C_0 and C_e represented the initial and equilibrium concentration of Cu^{2+} , respectively. V was the volume of solution and m was the weight of Cu^{2+} -IIP or Non-IIP.

The effect of initial concentration of Cu^{2+} on adsorption

The effect of the initial concentration of Cu^{2+} on the adsorption was carried out by mixing 0.015 g Cu^{2+} -IIP or Non-IIP and 50 mL of the solution containing various initial concentrations of Cu^{2+} at pH 6. These mixtures were shaken in the Vibrator at 130 rpm for 4 h at 25 °C. Then, polymers were filtered and the concentration of Cu^{2+} in the filtrate was measured by ICP. The adsorption capacity (Q) was also calculated by Eq. (2).

Selectivity of Cu^{2+} imprinted polymer

To evaluate the selectivity of the synthesized Cu^{2+} -IIP, batch of static adsorption experiments was carried out. The binary mixture solutions of $\text{Cu}^{2+}/\text{Ni}^{2+}$, $\text{Cu}^{2+}/\text{Zn}^{2+}$, or $\text{Cu}^{2+}/\text{Pb}^{2+}$ were prepared. In these solutions, the concentration of each metal ion was 0.4 mmol/L. 50 mL mixture solution with pH = 6 was treated by adding 0.015 g Cu^{2+} -IIP or Non-IIP in each of 100 mL conical flasks. These flasks were shaken in the Vibrator at 130 rpm for 4 h at 25 °C. After reaching the adsorption equilibrium, the concentrations of metal ions were also measured by ICP. Distribution coefficients (K_d) for Ni^{2+} , Zn^{2+} , and Pb^{2+} with respect to Cu^{2+} were calculated by the following equation [41]:

$$K_d = \frac{(C_i - C_e)V}{C_e m}, \quad (3)$$

where K_d is the distribution coefficient (mL/g), and C_i and C_e are the initial and equilibrium concentration of metal ion, respectively. V is the total volume of the aqueous solution and m is the weight of adsorbent.

The selectivity coefficient (k) for the Cu^{2+} in the presence of competitor ions can be obtained from the following equation:

$$k = \frac{K_d(\text{Cu}^{2+})}{K_d(\text{X}^{m+})}, \quad (4)$$

where X^{m+} is the competitor ions (Ni^{2+} , Zn^{2+} , and Pb^{2+}). The larger k is, the better the selectivity of the absorbent for Cu^{2+} is.

A comparison of the k values between the imprinted and non-imprinted samples can further illustrate the imprinting effect and selectivity on the special metal ion for a given sorbent. The relative selectivity coefficient (k') can be defined by the following equation:

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{Non-imprinted}}}, \quad (5)$$

where $k_{\text{imprinted}}$ and $k_{\text{Non-imprinted}}$ represent the selectivity coefficients of the Cu^{2+} -IIP and Non-IIP, respectively. k' represents the difference of metal adsorption affinity and recognition of sites to the imprinted Cu^{2+} for the Cu^{2+} -IIP with respect to Non-IIP [42].

Results and discussion

Preparation and characterization of Cu^{2+} imprinted polymer

The homogeneous reaction is much easier to be controlled than the heterogeneous reaction. Therefore, DMSO was selected as solvent to ensure the reaction carried out in a homogeneous system. Moreover, the organic solvent can prevent the hydrolysis of Cu^{2+} resulted by the adding of anhydrous K_2CO_3 , which could increase the imprinted efficiency of Cu^{2+} .

The FTIR spectra of PEI, Non-IIP, Cu^{2+} -IIP, and Cu^{2+} -loaded IIP were shown in Fig. 2. The broad band of PEI ranging from 3300 to 3500 cm^{-1} can be assigned to the presence of $-\text{NH}$ -group. The presence of three peaks at about 2943, 2835, and 1473 cm^{-1} can be attributed to asymmetric stretching vibration, symmetric stretching vibration, and in-plane bending vibration of $-\text{C}-\text{CH}_2-\text{C}-$ group, respectively [43]. The 1643 and 1566 cm^{-1} are the bending vibration of $-\text{N}(\text{R})\text{H}$ and primary amine in PEI. Whereas the adsorption band between 3300 and 3500 cm^{-1} becomes narrow in Non-IIP, Cu^{2+} -IIP, and Cu^{2+} -loaded IIP due to $-\text{NH}_2$ and $-\text{NH}$ participating in the cross-linking reaction. Simultaneously, the peak at 1566 cm^{-1} became much lower in Non-IIP than the raw material PEI and disappeared in Cu^{2+} -IIP and Cu^{2+} -loaded IIP [44]. This result further indicated that $-\text{NH}_2$ and $-\text{NH}$ participated in the cross-linking reaction. As expected, the peak at 2943, 2835, and 1473 cm^{-1} was basically not changed. The shift from 3417 cm^{-1} of Cu^{2+} -IIP to 3409 cm^{-1} of Cu^{2+} -loaded Cu^{2+} -IIP indicated that coordination between N atom and Cu^{2+} and the similar shift from 1658 to 1655 cm^{-1} corresponding to the bending vibration of $-\text{N}(\text{R})\text{H}$ group was also observed, which

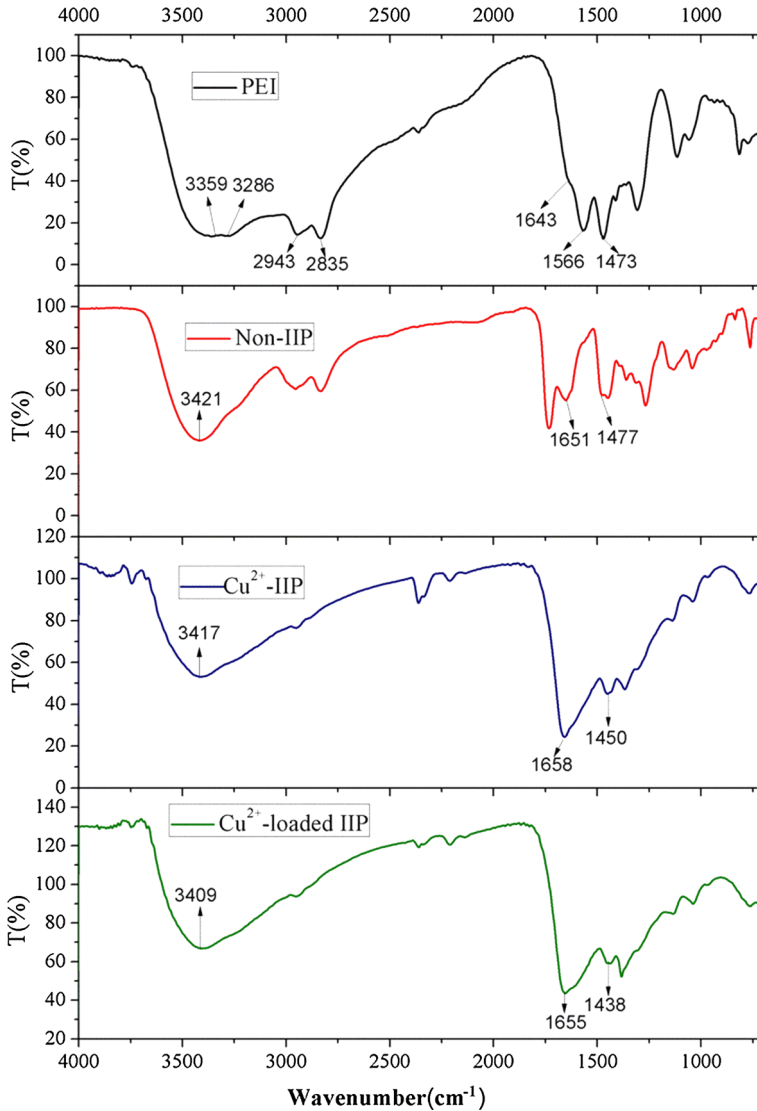


Fig. 2 FTIR spectra of PEI, Non-IIP, Cu^{2+} -IIP, and Cu^{2+} -loaded IIP

are due to the decreasing the electron density of C–N group [41, 45]. These transforms suggested that chelation action was involved and dominated in the adsorption progress, as reported by literatures [29, 46, 47].

SEM images (Fig. 3) show that the surface of Non-IIP particles is almost smooth and little porous. However, Cu^{2+} -IIP has a rough surface and a large number of porous. The porous could be attributed to the removing of Cu^{2+} after cross-linking reaction. These imprinted cavities favor to absorbing Cu^{2+} in the solution, because the mass transfer rate of metal ions towards the polymer surface was improved [48].

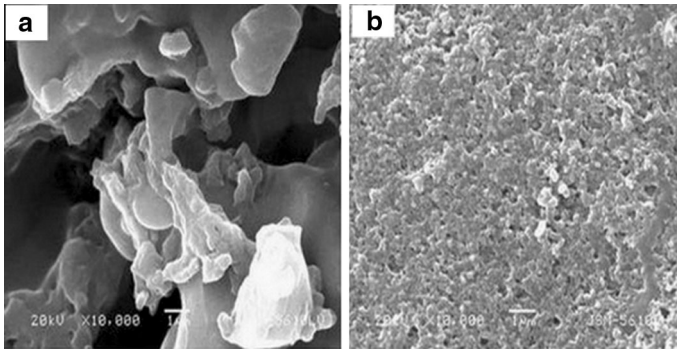


Fig. 3 SEM images of **a** Non-IIP and **b** Cu^{2+} -IIP

Adsorption of Cu^{2+} from aqueous solutions

Adsorption kinetics

The time to reach adsorption equilibrium is an important parameter for an adsorbent. Many applications, such as purification of product and deionization of waste water, require a fast absorption process. The kinetics curve of adsorption of Cu^{2+} on Cu^{2+} -IIP was illustrated in Fig. 4. The adsorption capacity was quickly up to about 40 mg/g at the first 10 min. This fast adsorption was probably due to the abundant active sites on Cu^{2+} -IIP, which could bind to Cu^{2+} by the chelation. Then with the adsorption proceeding, the adsorption sites decreased gradually. The adsorption capacity increased slowly after 10 min and nearly did not increase after

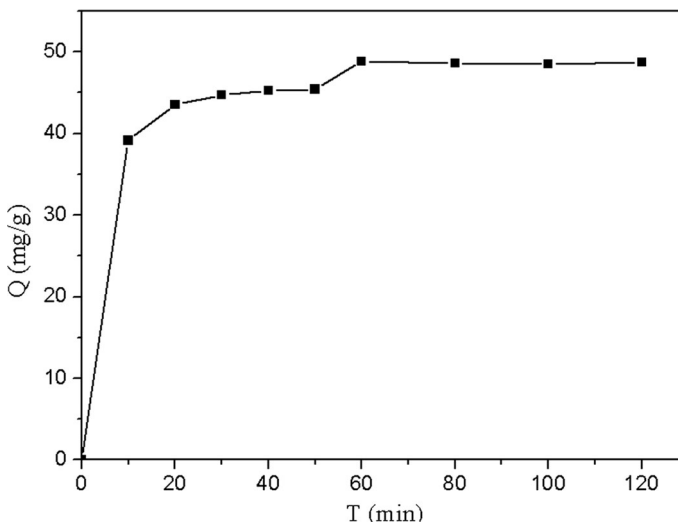


Fig. 4 Kinetics of Cu^{2+} adsorption on Cu^{2+} -IIP. Cu^{2+} -IIP: 0.015 g; pH = 6; Cu^{2+} : 50 mg/L; temperature: 25 °C

adsorption time of 60 min. This indicated the adsorption nearly reached equilibrium. This sorption rate was higher than some other imprinted sorbents [5, 18, 49]. To ensure complete adsorption, a long enough adsorption time (4 h) was applied in all following adsorption experiments.

Effect of pH

The adsorption capacity of Cu^{2+} -IIP and Non-IIP at different pH was given in Fig. 5. The adsorption capacity increased with the increase of pH, in according with results reported by Gao et al. [14] and Sgawky [50]. The low uptake of Cu^{2+} at pH 2–3 is because the amino groups (NH_2) on the PEI chains were protonated to NH_3^+ , which induced an electrostatic repulsion for Cu^{2+} [18]. With increasing of pH, the functional groups (NH_2) deprotonated, benefiting to Cu^{2+} binding. Hence, the sorption enhanced. At pH range of 5–6, the adsorption capacity increased slowly. The adsorption experiments were also carried out at pH 6.5 and 7.0, respectively. However, blue precipitate was found in the solution of Cu^{2+} , because copper oxides or hydroxides formed at $\text{pH} > 6$ [19, 28]. That means that both adsorption and precipitation are responsible for the removal of Cu^{2+} , and the solution above pH 6 is not suitable for adsorption experiments. To avoid the formation of precipitation, the pH 6 was chosen for the total adsorption experiments.

Identical experiments with Non-IIP were run for comparison. Obviously, the sorption capacity of Cu^{2+} -IIP is much greater than that of Non-IIP.

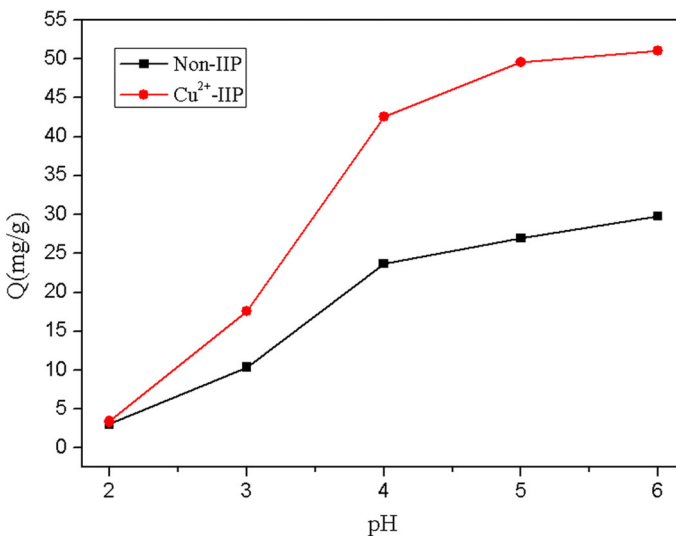


Fig. 5 Effect of pH on uptake of Cu^{2+} onto the prepared Cu^{2+} -IIP and Non-IIP. Sorbents: 0.015 g; Cu^{2+} : 50 mg/L; shaking time: 4 h; temperature: 25 °C

Adsorption isotherms

Cu^{2+} adsorption isotherm of Cu^{2+} -IIP and Non-IIP was presented in Fig. 6. As the increase of the initial concentrations of Cu^{2+} from 30 to 90 mg/L, the equilibrium adsorption capacity of Cu^{2+} -IIP and Non-IIP all increased. When concentrations of Cu^{2+} were up to 70 mg/L, the adsorption become very slowly. However, a direct comparison showed that Cu^{2+} -IIP adsorbed more Cu^{2+} from the solution than Non-IIP due to the high affinity of the imprinted polymer to template ion led by a mass of cavities whose shape, size, and spatial arrangement of functional groups are complementary to the template Cu^{2+} after leaching.

The capacity comparison with the other reported adsorbents is shown in Table 1. The adsorption capacity of Cu^{2+} -IIP in this work is about 83.3 mg/g, which is obviously superior to those of other similar adsorbents reported by literature [15, 18, 19, 21, 28, 51–53]. In addition, the adsorption capacity of Non-IIP is nearly reach the same or even higher capacity of imprinted adsorbents in Table 1. That is contributed to the specific cavities from the imprinted template and the chelation of the abundant amino groups.

In general, it is important to study the adsorption isotherm for the design of an adsorbent. Isotherm curves could describe a relationship between the ion concentration in the solution and the amount of ion adsorbed on adsorbent when the adsorption system is at equilibrium. The equilibrium is usually described by Langmuir isotherm or Freundlich isotherm.

Langmuir isotherm is based on the assumption that surface active sites existing on the solid material are equivalent and distant to each other, so that there are no interactions between molecules adsorbed to adjacent sites. The ions are adsorbed on

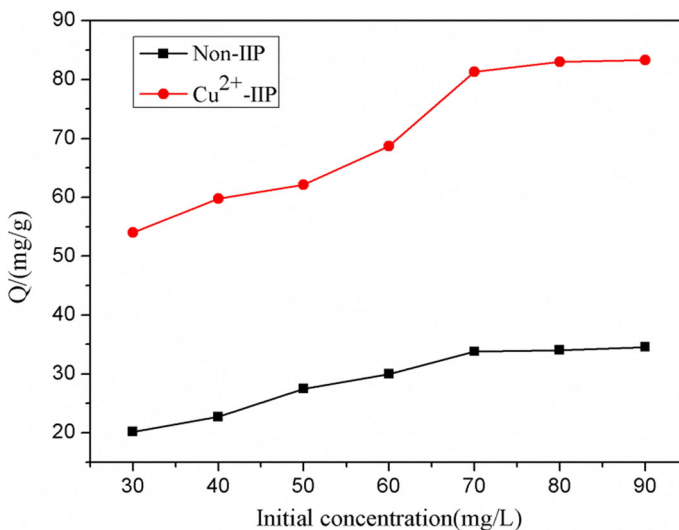


Fig. 6 Cu^{2+} adsorption isotherms of Cu^{2+} -IIP and Non-IIP. pH = 6; shaking time: 4 h; temperature: 25 °C

Table 1 Comparison of Cu²⁺ adsorption capacity and selectivity of similar imprinted sorbents in the references

Cu ²⁺ imprinted sorbents	Adsorption capacity (mg/g)	Adsorption selectivity (selectivity coefficient)			References
		Cu ²⁺ /Zn ²⁺	Cu ²⁺ /Ni ²⁺	Cu ²⁺ /Pb ²⁺	
Cu(II)-imprinted silica gel sorbent	33.33	12.3	–	–	[15]
Chitosan/Sargassum sp. composite sorbent	5.2	29.16	38.15	–	[18]
Cu(II)-imprinted chitosan/attapulgitite polymer	35.2	–	–	78.45	[19]
Ion-imprinted polymer nanoparticles	38.8	32.4	14.1	32.4	[21]
Amino-functionalized adsorbent	33.33	36.07	38.64	–	[28]
Cu(II) magnetic ion-imprinted materials	24.2	91.84	133.92	–	[51]
New copper(II) ion-imprinted polymer	14.8	6.57	126	–	[52]
Imprinted chitosans with epichlorohydrin	21.12	1.91	0.97	–	[53]
Cu ²⁺ -IIP	83.3	22.38	15.16	0.96	This work
Non-IIP	34.55	10.59	13.12	0.28	This work

a monolayer on the solid surface. Langmuir model could be expressed by the following equations:

$$Q = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$\frac{C_e}{Q} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}, \quad (7)$$

where Q is the amount of adsorbed Cu²⁺ on the ion-imprinted polymers (IIP) particles at equilibrium (mg/g), C_e is the equilibrium concentration in solution (mg/L), and Q_{\max} and K_L represent the maximum sorption capacity of adsorbent (mg/g) and affinity constant.

Freundlich isotherm could be expressed by the following equations [45].

$$Q = K_F C_e^{1/n} \quad (8)$$

$$\log Q = \left(\frac{1}{n}\right) \log C_e + \log K_F, \quad (9)$$

where Q is the amount of adsorbed Cu²⁺ on the IIP particles at equilibrium (mg/g), K_F is the Freundlich constant, and n is the Freundlich exponent. Freundlich model is empirically highly applicable for adsorbents having heterogeneous surfaces.

The equilibrium data in Fig. 6 were fitted by Langmuir isotherm and Freundlich isotherm, respectively. The plots were corresponding to be displayed in Figs. 7 and 8 and the parameters along with the regression coefficients were presented in Table 2. It can be seen that Langmuir isotherm fitted the experimental data better than Freundlich adsorption, because the correlation coefficient (R^2) was high (0.9727) and the value of Q_m (101.6 mg/g) for Cu^{2+} -IIP is close to the experimental value (83.3 mg/g). Therefore, it could be concluded that the adsorbed Cu^{2+} ions onto the Cu^{2+} -IIP showed a monolayer adsorption behavior.

The maximum adsorption capacity (Q_m) corresponds to the maximum quantity of Cu^{2+} that the adsorbent can adsorb at monolayer coverage. At this point, all the active sites had been occupied by ions, and the polymer could not adsorb any further Cu^{2+} even if the Cu^{2+} concentration in the solution was increased. This further explained the adsorption isotherms results that the adsorption capacity was no longer increased when Cu^{2+} concentration reached a certain value.

By comparing the adsorption capacity of the Cu^{2+} -IIP and Non-IIP, the maximum adsorption capacity of Cu^{2+} -IIP was obviously much higher than Non-IIP. Higher adsorption capacity can be explained by affinity constant (K_L). K_L is related to the energy of adsorption, which represents the affinity between the solute and the adsorbent. The higher value of K_L for Cu^{2+} -IIP (0.0700 L/mg) indicates that it has better affinity to adsorb Cu^{2+} than Non-IIP (0.0277 L/mg). Furthermore, the affinity between Cu^{2+} and Cu^{2+} -IIP can also be expressed by dimensionless separation factor R_L defined as follows:

$$R_L = \frac{1}{(1 + C_e K_L)}. \quad (10)$$

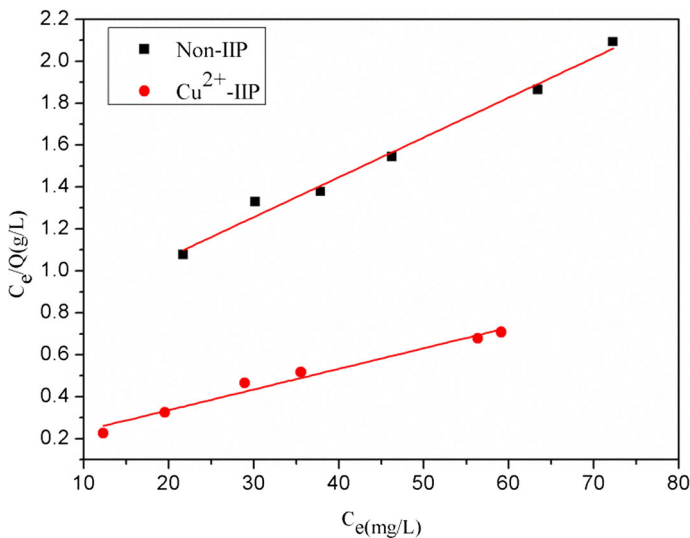


Fig. 7 Langmuir plot for the adsorption of Cu^{2+} on Cu^{2+} -IIP and Non-IIP

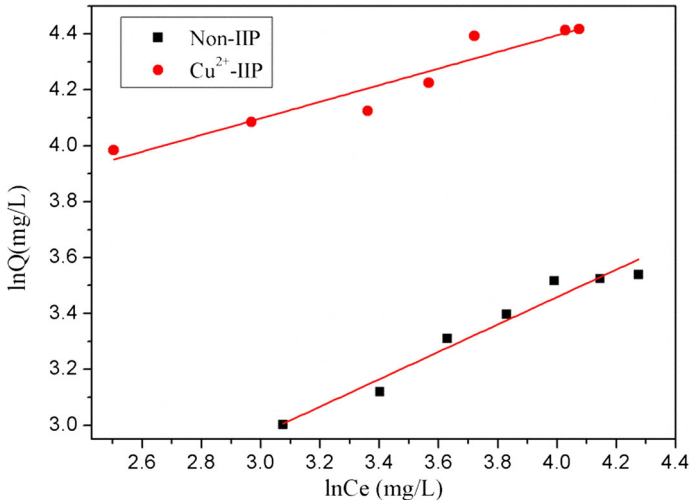


Fig. 8 Freundlich plot for the adsorption of Cu²⁺ on Cu²⁺-IIP and Non-IIP

Table 2 Isotherm model constants and regression coefficients for sorption of Cu²⁺

Sample	Experimental, Q _{max} (mg/g)	Langmuir constant			Freundlich constant		
		Q _{max} (mg/g)	K _L	R ²	K _F	n	R ²
Cu ²⁺ -IIP	83.3	101.6	0.0700	0.9727	24.6944	3.3653	0.8980
Non-IIP	34.55	52.6	0.0277	0.9847	4.4702	2.04	0.9529

Here, R_L indicates the favorability and the capacity of the adsorption system. The value of R_L between 0 and 1 represents favorable adsorption. The values of R_L were shown Table 3. All R_L were within 0 and 1, indicating that this adsorption system was favorable [54]. In general, this is a favorable adsorption system, having high affinity to template Cu²⁺ for Cu²⁺-IIP than Non-IIP.

The adsorption selectivity

The above experiments' results clearly illustrate that imprinted polymer Cu²⁺-IIP can enhance the recognition for Cu²⁺. However, the most applications require ion-

Table 3 Separation factor R_L for Cu²⁺ adsorption onto Cu²⁺-IIP and Non-IIP

C ₀ (mg/L)	30	40	50	60	70	80	90
R _L (Cu ²⁺ -IIP)	0.5382	0.4225	0.3305	0.2867	0.2562	0.2022	0.1947
R _L (Non-IIP)	0.6243	0.5447	0.4881	0.4383	0.3991	0.3627	0.3331

Table 4 Selectivity of imprinted and non-imprinted polymer

Sample	Adsorption capacity (mg/g)						<i>k</i>						<i>k'</i>					
	$\text{Cu}^{2+}/\text{Ni}^{2+}$		$\text{Cu}^{2+}/\text{Zn}^{2+}$		$\text{Cu}^{2+}/\text{Pb}^{2+}$		$\text{Cu}^{2+}/\text{Ni}^{2+}$		$\text{Cu}^{2+}/\text{Zn}^{2+}$		$\text{Cu}^{2+}/\text{Pb}^{2+}$		$\text{Cu}^{2+}/\text{Ni}^{2+}$		$\text{Cu}^{2+}/\text{Zn}^{2+}$		$\text{Cu}^{2+}/\text{Pb}^{2+}$	
	Cu^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Pb^{2+}
Imprinted polymer	53.08	7.72	40.23	3.37	38.46	128.14	15.16	22.38	0.96	1.16	2.11	3.43						
Non-imprinted polymer	21.24	1.97	16.24	1.91	7.45	71.27	13.12	10.59	0.28									

imprinted polymer to be able to selectively bind the specific metal ion from a mixture that contains various competitors. To evaluate the selectivity of Cu^{2+} -IIP, Ni^{2+} and Zn^{2+} were chosen as competitors because of their same positive charge (+2) and similar ionic radius (Cu^{2+} : 73 pm; Ni^{2+} : 69 pm; Zn^{2+} : 74 pm) [42]. Since Pb^{2+} was a typical poisonous ion, it was also chosen as competitive metal ion. Table 4 summarized the data of the adsorption capacity (Q_m), the selectivity coefficient (k), and the relative selectivity coefficient (k'). The adsorption capacity showed that Cu^{2+} -IIP absorbed more Cu^{2+} than Non-IIP in all mixture. This is an expected result due to template effect. Random distribution of ligands in Non-IIP leads to no specificity in rebinding affinity for metal ions. However, chelation of ligands with template ions could create activated sites and cavities formed after removal of template ions which could match the imprint ion well in size and coordination geometries [20]. A comparison of adsorption capacity (Q_m) and k values showed that the adsorption ability of Cu^{2+} -IIP and Non-IIP for Cu^{2+} is stronger than that for Ni^{2+} or Zn^{2+} . This may be due to the larger stability constants of Cu^{2+} coordinating with N atom than that of Ni^{2+} or Zn^{2+} [55]. It is noted that the adsorption capacity of Pb^{2+} was much higher than that of Cu^{2+} for imprinted polymer, which is because the unit of the adsorption capacity is mg/g and the atomic mass of plumbum is heavier than that of copper. If the unit of the adsorption capacity is mmol/g, the adsorption capacity of Cu^{2+} would become higher, indicating that Cu^{2+} -IIP had more superior selectivity for Cu^{2+} than Pb^{2+} . This could be further verified by the value of the relative selectivity coefficient k' . The relative selectivity coefficient is an indicator to express metal binding affinity of recognition sites to the imprinted Cu^{2+} ions. Obviously, k' is the largest for $\text{Cu}^{2+}/\text{Pb}^{2+}$ in three binary metal systems. The reason for this is the cavities imprinted by Cu^{2+} did not fit Pb^{2+} in size. The values of k' for $\text{Cu}^{2+}/\text{Ni}^{2+}$ and $\text{Cu}^{2+}/\text{Zn}^{2+}$ are also higher than the literatures [37, 53] reported. From the above results, it can be concluded that the imprinting cavity for Cu^{2+} has good recognition memory effect and high binding selectivity.

Conclusion

The new Cu^{2+} imprinted polymer for selective removal of Cu^{2+} was synthesized in the homogeneous phase by ion-imprinted technology. The adsorption kinetics revealed that this sorption is a fast dynamic behavior. Compared with Non-IIP, the relative selectivity of Cu^{2+} -IIP is higher, suitable for the selective removal of Cu^{2+} from the mixture system. This proved that the template ion played an imprinted role in the synthesis. This imprinted polymer exhibits not only a better selectivity but also a higher capacity (83.3 mg/g) for the metal ion templates than the non-imprinted analogues. This is markedly superior as an absorbing material for absorbing Cu^{2+} . In addition, the best Cu^{2+} uptake was found at $\text{pH} = 6$, which is promising for real wastewater treatment.

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