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# Synthesis and Imprinting Efficiency Investigation of Ion Imprinted Nanoparticles for Recognizing Copper

Jin Jia<sup>a,b</sup>, Aihua Wu<sup>b,\*</sup>, Shengji Luan<sup>a,b</sup>

## Abstract

The Cu<sup>2+</sup> imprinted nanoparticles were synthesized with simple approach including imprinting and crosslinking in aqueous solution. The morphologies of imprinted polymers were alterable with changed component ratio and illustrated by field emission scanning electron microscope. The obtained nanoparticles were applied as novel polymeric adsorbents with outstanding adsorption capacity and good selectivity to recognize and remove copper ions. The component ratio of PEI, crosslinking agent and template ions were systematically studied with their influence to morphology and imprinting efficiency of sorbents. The crosslinking degree and amount of imprinted sites was investigated with different component ratio and was confirmed to be the key factor of the imprinting efficiency. The appropriate dosage ratio of PEI, ECHA and template Cu<sup>2+</sup> was 1 g : 1 g : 2.5 mmol and imprinting efficiency can be significant improved. The maximum selectivity coefficients of the nanoparticles for Cu<sup>2+</sup>/Cr<sup>3+</sup> and Cu<sup>2+</sup>/Zn<sup>2+</sup> were 5.21 and 21.00. The result could extend to other polymers with improvement of imprinting efficiency and further application.

*Keywords:* Ion imprinted nanoparticle; Polyethyleneimine; Imprinting efficiency

## 1 Introduction

Metal ion extraction and quantification in the aqueous environment remains a major issue because of their high toxicity, persistence and susceptible carcinogenic effect<sup>1-4</sup>. Selective recognition of metal ions is a real challenge for a large range of applications in the analytical field including extraction, detection and quantification. For that purpose, ion-imprinted polymers (IIPs) have been increasingly developed during the past decades<sup>5-8</sup>. The crosslinking of linear chain polymers carrying metal-binding groups is the well-developed technique used to prepare IIPs<sup>9,10</sup>. This approach has advantages of simpler steps needed than polymerization and can avoid disturbing of initiator. Moreover, the IIPs possess good chemical stability<sup>11</sup>. Chen et al. prepared chitosan imprinted microparticles with a series of template metal ions: Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> by crosslinking either with epichlorohydrin<sup>12</sup> or glutaraldehyde<sup>13</sup>. Adsorption capacity for Cu<sup>2+</sup> was 21.12 mg/g, and selectivity for Cu<sup>2+</sup>/Zn<sup>2+</sup>, Cu<sup>2+</sup>/Ni<sup>2+</sup> and Cu<sup>2+</sup>/Pb<sup>2+</sup> were 1.91, 0.97, 0.29, respectively. Nishad et al. performed a similar work with Co<sup>2+</sup> as the template and epichlorohydrin as the crosslinking agent<sup>14</sup>. Chen et al. prepared Cu<sup>2+</sup> imprinted porous film adsorbent Cu-PVA-SA and used it for adsorption Cu<sup>2+</sup> with maximum uptake of 79.30 mg/g. The film can be conveniently used without centrifugation or filtration methods. The selectivity of Cu<sup>2+</sup>/Zn<sup>2+</sup> and Cu<sup>2+</sup>/Cd<sup>2+</sup> were 2.25, 2.79<sup>15</sup>. Nguyen et al. used methacrylic acid and vinyl pyridine to prepared Cu<sup>2+</sup> imprinted porous polymethacrylate micro-particles. The selectivity coefficient of Cu<sup>2+</sup>/Zn<sup>2+</sup> and Cu<sup>2+</sup>/Ni<sup>2+</sup> were 42.38, 43.48<sup>16</sup>. Recently, polymer-based materials as fluorescent chemosensors for Cu<sup>2+</sup> in aqueous environment also developed rapidly<sup>17-19</sup>.

Branched polyethyleneimine (PEI) is a cationic polymer which has been used for a wide variety of biological applications<sup>20</sup>, can also act as a polymeric adsorbent for some heavy metals via chelation<sup>21</sup>. The amine groups exist in primary, secondary and tertiary forms with a branching site at every 3 ~ 3.5 nitrogen atom in any given chain segment, each with the potential to be protonated. Thus, it can form chelation complexes with heavy metal ions with advantage of good hydrophilicity, high adsorption capacity and rapid chelating rate<sup>22</sup>. The character of PEI has attracted wide attention of investigators, and its applications in adsorption separation fields of heavy-metal ions are developing<sup>23-25</sup>. Recently, crosslinking or grafting of PEI as novel imprinted adsorbents was widely investigated. Gao et al. grafted PEI onto SiO<sub>2</sub> and used surface imprinting technique to form IIP-PEI/SiO<sub>2</sub>. Static and dynamic adsorption process were studied and revealed imprinted material had specific recognition ability for the template ions<sup>26</sup>. Liu et al. investigated diffusion mechanism of PEI imprinted adsorbent. They found that Co<sup>2+</sup> adsorption was controlled by the intraparticle diffusion mechanism, along with a considerable film diffusion contribution<sup>27</sup>. A great amount of works have done on synthesis and applications of PEI imprinted material. However, the study on imprinting efficiency and binding activity were still big problems.

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Spivak et al. investigated HPLC of target imprinted adsorbate and other mixtures, the larger difference of retention time indicated more binding activity of the imprinted polymer<sup>28</sup>. Asanuma et al. put forward batchwise guest-binding experiments to measure binding activity of the imprinted polymer. The dissociation constant of complex was chosen as target of binding activity and calculated by Scatchard equation<sup>29</sup>. Molochnikov et al. used ESR method to investigate the complex formation processes within the template ions. The presence of certain copper complexes was found to be a convenient characteristic of the imprinting efficiency<sup>30</sup>. Some other methods or influence factors were investigated later, such as thermodynamic simulation<sup>31</sup>, solvent effect<sup>32</sup>, ratio of substrates<sup>33-35</sup>, imprinting group's number and relative position of the template molecule<sup>36</sup>. However, little attempt was done to characterize the factor of crosslinking degree and morphology, as well as their influence to the imprinting efficiency.

The objective of this work is to develop novel Cu<sup>2+</sup> imprinted nanoparticles with copper ions, PEI and epichlorohydrin amine (ECHA). The imprinted nanoparticles were prepared with simple synthetic approach including imprinting and crosslinking in aqueous solution. Morphology and structure were characterized by scanning electron microscopy and infrared spectroscopy. The obtained nanoparticles were applied as novel adsorbent to selectively adsorb copper ions. Cr<sup>3+</sup> and Zn<sup>2+</sup> were chosen as competing ions due to their remarkable adsorption capacities with PEI, which could improve the comparability between ion imprinted polymer (IIP) and non-imprinted polymer (NIP). Moreover, imprinting efficiency of sorbents was indicated through adsorption capacity and selectivity coefficient. The crosslinking degree and morphology were changed by dosage ratio of PEI, crosslinking agent, template ions in synthetic process and their influence to imprinting efficiency were investigated in detail. The results obtained can be extended to many other types of functional polymers and support for synthesis and further applications of IIP.

## 2 Experimental

### 2.1 Material and reagents

Branched PEI with weight average molecular weight of 25 kDa and epichlorohydrin was obtained from Aldrich. Ammonia was obtained from Guangzhou Chemical Reagent Factory. Copper nitrate trihydrate and other several kinds of metal salts were received from Sinopharm Chemical Reagent Corporation. All those chemical reagents used in this study were of analytical grade. Freshly deionized and distilled water was used as the dispersion medium.

### 2.2 Instrumentation and characterization

FAAS was purchased from Thermo (Solaar-S4). FESEM was from Tescan (MIR3 XMH). IR was from Shimadzu (Prestige-21). Laser particle size analyzer was from Malvern (Nano ZS90). Ultrasonic cleaners were from Shanghai HongYu Institute (SH3200). Mechanical stirrer was from Ika (RW28). The pH meter was from HACH Corporation (Sension156). Filtering centrifuge tube from Millipore (50 mL, MWCO 3k) and dialysis tube from Yuanye Bio-Technology Corporation (MWCO 100k) were utilized in this study.

The surface morphological image and elemental composition of the synthesized Cu<sup>2+</sup> imprinted polymer were obtained from SEM experiments. The polymer was examined after coating a dried sample with a thin layer of platinum. The cross-linking between PEI and ECHA was confirmed by performing IR study in KBr from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> for the samples of PEI and Cu<sup>2+</sup> imprinted polymer. Adsorption capacity was analyzed by FAAS.

### 2.3 Synthesis of ion imprinted nanoparticles

#### 2.3.1 Preparation of oligomer ECHA

The reaction between epichlorohydrin and ammonia was described as Molochnikov et al.<sup>30</sup>. 1 mol of NH<sub>4</sub>OH (aqueous solution) was added drop-wise to 2 mol of epichlorohydrin at 60 °C with vigorous agitation for 3h. The oligomer ECHA was obtained.

#### 2.3.2 Synthesis of Cu<sup>2+</sup> imprinted nanoparticles

The imprinted polymer was prepared from PEI and ECHA. 3.025g Copper nitrate trihydrate were dissolved in 30 mL of water and mixed with 5g PEI. The mixture was under ultrasound for 30 min to prepare the desired complexes. Then, the obtained oligomer ECHA was added drop wise with constant stirring at 80 °C. 30 min after finish adding of ECHA, 1 M NaOH was added to adjust solution pH to 10. The whole reaction mixture was stirred at 80 °C for 3 h. Afterward the copper ions were eluted repeatedly with 1 M hydrochloric acid and EDTA. The metal ions were recovered completely as confirmed by the conductivity of solution achieving stability. Finally the sorbents was washed with extensive distilled water until the washing water was neutral. The sorbents were stored at sealed bottle for further use. Also non-imprinted polymer was synthesized by adopting the same protocols as above excluding copper ions.

#### 2.4 Static adsorption experiments

The PEI, IIP and NIP adsorption studies for the  $\text{Cu}^{2+}$  were carried out in batch experiments. In order to determine the adsorption capacity, 1.25 mg sorbents were introduced into different volumetric flasks, respectively. 25 mL of  $\text{Cu}^{2+}$  solution with different initial concentration were then added into each volumetric flask. The pH of above mixture solution was adjusted to 5 by 0.1 M  $\text{HNO}_3$  or 0.1 M NaOH solution. The mixture was put in an ultrasonic bath for 30 min to finish adsorption process. After adsorption equilibrium, the mixture solution was filtered through ultrafiltration centrifuge tube (MWCO 3k, whereas average molecular weight of PEI was 25 kDa). The residue  $\text{Cu}^{2+}$  left in the filtrate were analyzed by an atomic adsorption spectrometer. The amounts of  $\text{Cu}^{2+}$  adsorbed were determined from the difference between the concentrations of initial and final filtrate solutions. The equilibrium adsorption capacity ( $q_e$ ) can be calculated by the equation 1.

$$q_e = \frac{(C_0 - C_e)V_L}{M} \quad 1$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of  $\text{Cu}^{2+}$  in solutions (mg/L), respectively.  $V_L$  is the volume of solution, and  $M$  is the weight of the adsorbent (g).

#### 2.5 Selectivity experiments

The competitive absorption experiments were conducted by preparing mixture of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{3+}$ , and each metal ion initial concentration was from 0.5 mg/L to 18 mg/L, respectively. After adsorbing with the mixed metal ions, the initial and equilibrium concentration of every kind of metal ion was detected by atomic adsorption spectrometer. In order to investigate the selectivity of the adsorbent, static adsorption experiment results were used for evaluation. Distribution coefficient was calculated as equation 2<sup>37</sup>.

$$K_d = \frac{C_p}{C_e} \quad 2$$

where  $K_d$  is the distribution coefficient.  $C_e$  is the equilibrium concentration of  $\text{Cu}^{2+}$ .  $C_p$  is the amount of  $\text{Cu}^{2+}$  adsorbed on per weight unit of sorbent after equilibrium. The selectivity coefficient for the binding of  $\text{Cu}^{2+}$  in the presence of competitor ions can be obtained from equilibrium binding data according to equation 3.

$$K = \frac{K_d(\text{Cu})}{K_d(M)} \quad 3$$

where  $K$  is the selectivity coefficient,  $M$  represents  $\text{Zn}^{2+}$  or  $\text{Cr}^{3+}$ .  $K$  represents  $\text{Cu}^{2+}$  adsorption selectivity when there are other metal ions in aqueous solution. The larger  $K$  indicates a stronger selective ability for the  $\text{Cu}^{2+}$ .

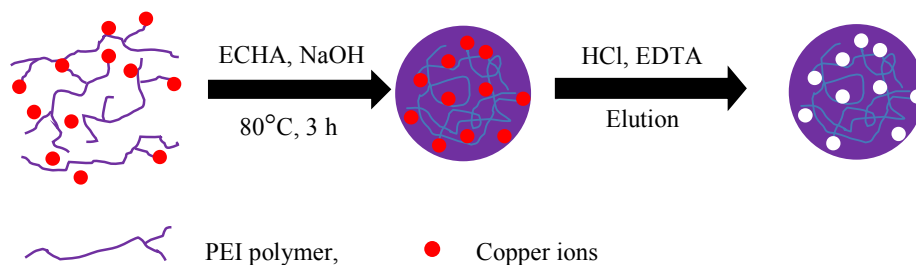
A relative selectivity coefficient,  $K'$ , can be defined by equation 4 and the larger of  $K'$  can indicate the enhancement of adsorption affinity and selectivity of imprinted sorbents for the copper ions with respect to non-imprinting sorbents.

$$K' = \frac{K_{\text{imprinted}}}{K_{\text{non-imprinted}}} \quad 4$$

### 3 Results and discussion

#### 3.1 Synthesis of $\text{Cu}^{2+}$ imprinted nanoparticles

The synthesis process of  $\text{Cu}^{2+}$  imprinted nanoparticles was illustrated in Scheme 1. PEI and  $\text{Cu}^{2+}$  were mixed in water under ultrasonic oscillations to form a coordination complex. EHCA and NaOH were added at  $80^\circ\text{C}$  with vigorous agitation. The product was purified by dialyzing (MWCO, 100k). To investigate the influence of crosslinking degree towards morphology and imprinted efficiency of sorbents, parallel experiments were proceeded including: (a) different dosage of ECHA, (b) different dosage of initial imprinting copper ions. All these sorbents were synthesized as described above. The non-imprinted polymer (NIP) was also synthesized in a similar fashion.

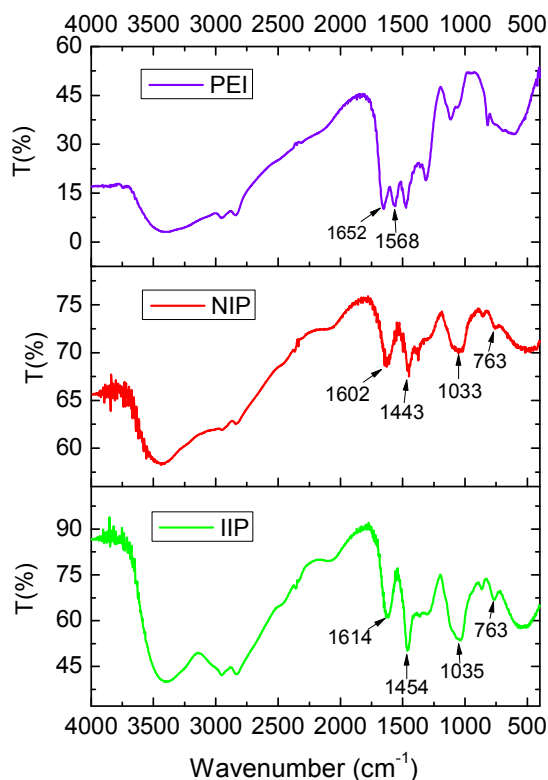


**Scheme 1** Synthesis of  $\text{Cu}^{2+}$  imprinted PEI nanoparticles

### 3.2 Characterization

#### 3.2.1 IR analysis

Infrared spectrum was recorded on a Shimadzu (Prestige-21) spectrophotometer using KBr disk. PEI, NIP and IIP were characterized as shown in Fig. 1. Similar peaks displayed including asymmetric stretching of  $\text{CH}_2$  at  $2950\text{ cm}^{-1}$ , symmetric stretching of  $\text{CH}_2$  at  $2845\text{ cm}^{-1}$  and stretching vibration at  $1652\text{ cm}^{-1}$ . The absorption peak around  $1568\text{ cm}^{-1}$  indicates bending vibration of  $\text{NH}_2$  in PEI. Disappearing of this peak in NIP and IIP is due to crosslinking reaction of  $\text{NH}_2$  or coordination effect with copper ions. The peaks at  $1035\text{ cm}^{-1}$  and  $1035\text{ cm}^{-1}$  are indicative to the presence of the C-O bond in NIP and IIP. A very weak C-Cl peak can be found at  $763\text{ cm}^{-1}$ . The results confirmed that the PEI was

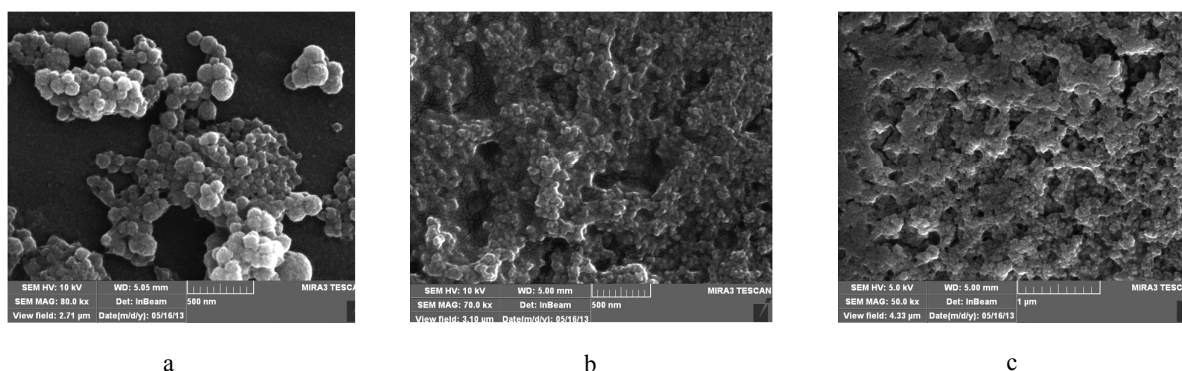


**Fig. 1** Infrared spectrum of PEI, NIP and IIP

successfully crosslinked with ECHA. Moreover, a slight of blue shifting of peaks from NIP to IIP was found around  $1602\text{ cm}^{-1}$  and  $1443\text{ cm}^{-1}$ . It can be explained by the interactions with copper ions. The coordination of amino group with copper ions would increase electronegativity of nitrogen atom and enhanced chemical bond strength of C-N and N-H.

### 3.2.2 Particle diameters and structure of IIP

Surface morphology of  $\text{Cu}^{2+}$  imprinted nanoparticles was characterized by field emission scanning electron microscope (MIR3 XMH). Fig. 2 illustrated the IIPs with different dosage ratio of PEI and ECHA as mentioned in synthesis section. Particle diameters and standard deviations were measured by laser particle size analyzer (Malvern ZS90) and the results were shown in Table 1. Increasing dosage ratio of ECHA caused larger crosslinking degree. As a consequence, the nanoparticles displayed larger particle diameters and more wide distribution. Nanoparticles could be obtained with uniformly spherical and around 100 nm of diameter when dosage ratio of PEI/ECHA was from 2 to 1. With further increasing of crosslinking agent, the nanoparticles were gradually caked and formed dense reticular structure. The result showed that the morphology and structure of sorbents were relevant to the dosage of crosslinking agent, which controlling the crosslinking degree of the reaction.



**Fig. 2** FESEM images of  $\text{Cu}^{2+}$  imprinted nanoparticles with dosage ratio of PEI and ECHA: (a) 1:0.5, (b) 1:1, (c) 1:1.5

**Table 1** Particle diameters and standard deviations of IIPs with different crosslinking degree

	Dosage ratio (PEI/ECHA)	Diameter (nm)	Standard deviations ( $\pm$ nm)
a	1:0.5	88.3	15.2
b	1:1	104.5	26.8
c	1:1.5	495.3	202.4

## 3.3 Absorption experiment

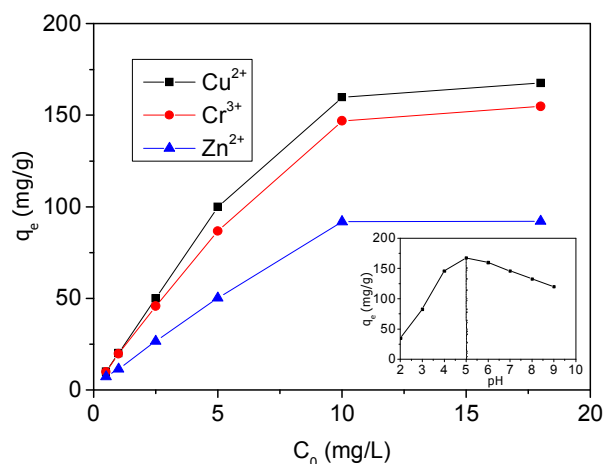
### 3.3.1 Adsorption property of PEI

Before embarking on the research of  $\text{Cu}^{2+}$  imprinted nanoparticles, the adsorption property of PEI was investigated. The adsorption experiments of PEI towards several metal ions were accomplished in previous studies.  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  were chosen as target ions due to their remarkable adsorption quantities as shown in Fig. 3. The adsorption experiments with changed pH were investigated and shown in inset of Fig. 3. At lower pH, the adsorption quantity was very low because PEI were located with positively charged protonated amine groups causing the repulsion force to the similar charged copper ions. With increasing solution pH, deprotonation degrees of amine groups were enhanced and



their chelating capacities were increased simultaneously. When solution pH reached to 5 or higher, precipitation effect of copper ions signally existed and decreased coordination effect. The changes of solution pH greatly affected the amount of copper ions adsorbed onto PEI. Thus pH of all the solution was adjusted to 5 for the maximum adsorption quantity.

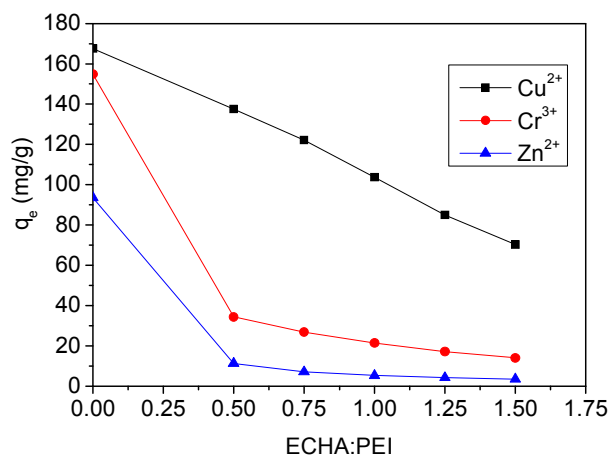
The amount of PEI was fixed in every experiment, unit adsorption quantity of PEI increased with initial concentrations of metal ions and gradually reached an equilibrium value. The equilibrium adsorption capacity for  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  were 167.6 mg/g, 154.8 mg/g and 92.1 mg/g, respectively. Thus, PEI had high adsorption capacity for these ions, but the selectively was not remarkable.



**Fig. 3** Adsorption property of PEI and effect of pH (inset)

### 3.3.2 Imprinting efficiency

$\text{Cu}^{2+}$  recognition by IIPs was proceeded as indicated in the experimental section. Parallel adsorption experiments with different crosslinking degree or imprinting ions were measured. Imprinting efficiency was investigated by adsorption capacity and selectivity coefficient of the sorbents. Fig. 4 showed equilibrium adsorption capacity of IIPs with different crosslinking agent ECHA for the mixed metal ions. The amount of template ions used for imprinting in this series of experiments was fixed. The dosage ratio of ECHA/PEI in the IIPs was from 0.5 to 1.5. In the competitive adsorption experiments, it was found that equilibrium adsorption capacities of IIPs for  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  were all lower than non-crosslinked PEI. There were three main reasons, which caused the decrease: (1) Part of coordination adsorption sites of PEI (including  $-\text{NH}_2$ ,  $-\text{NH}$  and  $-\text{N}$ ) reacted and crosslinked with ECHA in the synthesis process. (2) The embedding effect of adsorption sites due to the crosslinking process which cause difficulty of mass transfer. (3) Competitive effect of the mixed metal ions. Moreover, much significant reduction of capacities for  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  than  $\text{Cu}^{2+}$  was found. For the IIPs with maximum crosslinking degree, the adsorption capacity for  $\text{Cu}^{2+}$  was still 70.3 mg/g, however, 14.0 mg/g for  $\text{Cr}^{3+}$  and only 3.5 mg/g for  $\text{Zn}^{2+}$ .



**Fig. 4** Competitive equilibrium adsorption capacity for Cu<sup>2+</sup>, Cr<sup>3+</sup> and Zn<sup>2+</sup> with different crosslinking degree

The selectivity coefficients of Cu<sup>2+</sup> over other metal ions were calculated as mentioned in selectivity experimental section. The curve of selectivity coefficient with different crosslinking degree was shown in Fig. 5. The selectivity of non-crosslinked PEI was 1.08 and 1.80 for Cu<sup>2+</sup>/Cr<sup>3+</sup> and Cu<sup>2+</sup>/Zn<sup>2+</sup>, respectively. A significant increase of selectivity coefficient of IIPs was found. It can be explained by the memory effect of the imprinting process. The cavities with specific size and structure were formed in coordination process and immobilized by crosslinking agent ECHA. The ionic radius of Cu<sup>2+</sup> is 73 pm, which is larger than Cr<sup>3+</sup> (61.5 pm) and slightly smaller than Zn<sup>2+</sup> (74 pm). Moreover, the difference of coordination number, geometry configuration of complexes and structure of outer shell electron could also make the competitive metal ions unfit with the cavity. The curve presented that selectivity coefficient increased rapidly at first and gradually tended to stable value. With increasing amount of ECHA in synthesis process, the amount of specific cavities gradually increased. Afterwards it reached stable value when all the template ions involved into formation of imprinted sites and immobilized. Further increase of ECHA could only formed non-imprinted sites in the particles. This would reduce the adsorption capacity but invalid in enhancement of selectivity. The imprinting selectivity was improved by the crosslinking degree, however, this would cause reduction of adsorption capacity. Moreover, the IIPs with higher selectivity exhibited much compact structure as shown in Fig. 2. Thus, crosslinking degree was proved as an important influencing factor to imprinting efficiency. Taking both two factors (adsorption capacity and selectivity coefficient) into consideration, the appropriate crosslinking degree located at the inflection point of curve in Fig. 5, which indicated the dosage ratio of ECHA and PEI was 1:1.



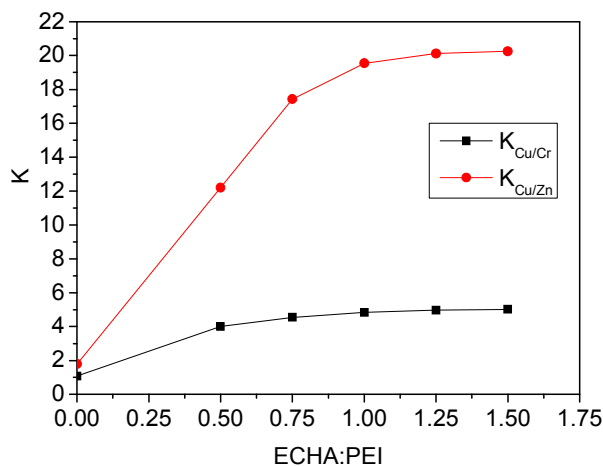
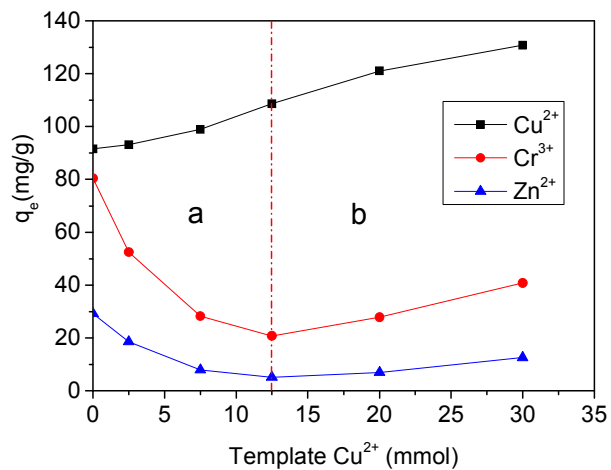
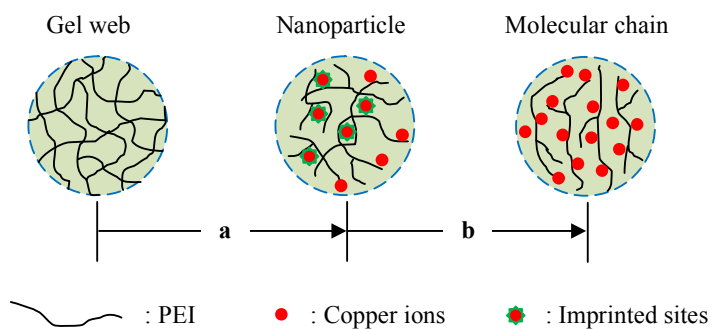


Fig. 5 Selectivity coefficient of IIPs with different crosslinking degree

To further investigate the influence towards imprinting efficiency, sorbents with different amount of template ions (from 0 to 30 mmol) in imprinting process were measured. The dosage ratio of ECHA and PEI was 1:1 in this experimental series. Equilibrium adsorption capacity of IIPs with different dosage of template ions was shown in Fig. 6. The crosslinked PEI without imprinting of  $\text{Cu}^{2+}$  (NIP) was chosen as blank. The adsorption capacity of blank for  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  were 91.6 mg/g, 80.4 mg/g and 29.3 mg/g, respectively. The decrease of capacity comparing with non-crosslinked PEI (refer Table 2) could be similarly explained by the crosslinking and embedding effect as mentioned above. With increasing amount of template ions used in imprinting process, adsorption capacity curve of  $\text{Cu}^{2+}$  kept growth and presented S-shaped, whereas curves of  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  rose after an initial decline and presented U-shaped in Fig. 6. The adsorption capacities for mixed metal ions were mainly influenced by amount of specific cavities and mass transfer efficiency. Moreover, the amino groups of PEI (including  $-\text{NH}_2$ ,  $-\text{NH}$  and  $-\text{N}$ ) were competed by coordination and crosslinking reaction. The amount of specific cavities firstly increased with template  $\text{Cu}^{2+}$  and then reached maximum value. Afterwards, excessive copper ions resulted in vast majority of crosslinking sites were occupied by copper ions to form coordination complex. Lacking of crosslinking sites, accompanied with reduction of immobilization would cause decrease of specific cavities. Moreover, the morphology of the sorbents was changed from gel web to small particles and eventually became molecular chains with gradually reduced crosslinking degree. The mass transfer efficiency of metal ions was improved in this process. Fig. 6 could divide into part **a** and **b** according to the curve shape. The decrease of adsorption capacities for  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  in part **a** could explained by increased amount of specific cavities as well as the selectivity. Then the increase of  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  in part **b** was due to decrease of specific cavities and improvement of mass transfer efficiency. The rise of curve for  $\text{Cu}^{2+}$  could be similarly explained by increased amount of specific cavities in part **a** and improvement of mass transfer efficiency in part **b**. The relatively more rapid growth in connection part of **a** and **b** in S-shaped curve of  $\text{Cu}^{2+}$  also indicated the significant morphology changes of sorbents, from dense gel web to nanoparticles. To easy understanding this process, the changes of amount of imprinted sites and morphology were illustrated in Scheme 2. The part **a** and **b** represented different stage with gradually increased copper ions and respectively corresponded to the Fig. 6. Lack of template ions would cause inefficient imprinting and over crosslinking. On the contrary, the imprinted sites could hardly be immobilized with excessive template ions. A proper amount of template ions was proved to be vital in controlling morphology and imprinting efficiency of sorbents.



**Fig. 6** Competitive equilibrium adsorption capacity for  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$  with different dosage of template  $\text{Cu}^{2+}$



**Scheme 2** Morphology and amount of imprinted sites dependence on template ions  
 (a) The amount of imprinted sites increases with increasing ions; (b) The amount of imprinted sites decreases with excessive ions

The curve of selectivity coefficient with different dosage of template ions was shown in Fig. 7. The selectivity coefficient of NIP (blank) for  $\text{Cu}^{2+}/\text{Cr}^{3+}$  and  $\text{Cu}^{2+}/\text{Zn}^{2+}$  were 1.14 and 3.13, respectively. With increasing dosage of template  $\text{Cu}^{2+}$ , the selectivity coefficient significant increased, following by the decrease. The maximum value of selectivity coefficient located at 12.5 mmol of  $\text{Cu}^{2+}$ , which was in concert with Fig. 6. It confirmed that selectivity coefficient was determined by amount of imprinted sites. To achieve optimal imprinting efficiency (including maximum selectivity coefficient and minimum adsorption quantities for competitive metal ions), the proper amount of template  $\text{Cu}^{2+}$  was 12.5 mmol. The maximum selectivity coefficient in this experimental series for  $\text{Cu}^{2+}/\text{Cr}^{3+}$  and  $\text{Cu}^{2+}/\text{Zn}^{2+}$  were 5.21 and 21.00, respectively.

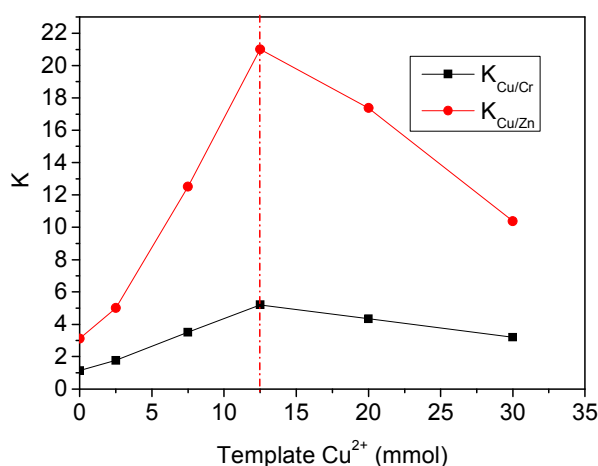


Fig. 7 Selectivity coefficient of IIPs with different dosage of template  $\text{Cu}^{2+}$

Thus, successful imprinting could be achieved through equilibrating dosage ratio of PEI, ECHA and template ions. Taking the factors of adsorption capacity and selectivity coefficient into consideration, the optimal imprinting efficiency was found with dosage ratio of 1 g : 1 g : 2.5 mmol for PEI, ECHA and template  $\text{Cu}^{2+}$ . The adsorption properties and selectivity of PEI, NIP and IIP were summarized in Table 2. The adsorption capacity of IIP for  $\text{Cu}^{2+}$  was higher than NIP, whereas lower for competitive ions. The relative selectivity coefficient of IIP for  $\text{Cu}^{2+}/\text{Cr}^{3+}$  and  $\text{Cu}^{2+}/\text{Zn}^{2+}$  were 4.57 and 6.71 times higher than NIP, respectively. It proved  $\text{Cu}^{2+}$  imprinted PEI had more adsorption affinity and binding abilities for  $\text{Cu}^{2+}$  with the specific cavities. The imprinting efficiency can be significant improved with appropriate dosage ratio of raw material, which also determines the amount of imprinted sites and morphology of sorbents.

Table 2 Adsorption property of PEI, non-imprinted PEI and  $\text{Cu}^{2+}$  imprinted PEI

Morphology	PEI		NIP		IIP		$K'_{\text{I/P}}$	$K'_{\text{I/N}}$
	Polymer		Gel web		Nanoparticle			
Metal ions	Q (mg/g)	K	Q (mg/g)	K	Q (mg/g)	K		
$\text{Cu}^{2+}$	167.6		91.6		108.6			
$\text{Cr}^{3+}$	154.8	1.08	80.4	1.14	20.8	5.21	4.82	4.57
$\text{Zn}^{2+}$	92.1	1.82	29.3	3.13	5.2	21.00	11.54	6.71

Table 3 listed properties of some similar systems based on  $\text{Cu}^{2+}$  imprinted polymers. Adsorption and selectivity coefficient were chosen for comparison. PEI reveals good selectivity and outstanding capacity for copper ions with comparison to the other imprinted sorbents. It is also worth mentioning that non-imprinted PEI already has quite good selectivity for  $\text{Cu}^{2+}/\text{Ni}^{2+}$  and  $\text{Cu}^{2+}/\text{Cd}^{2+}$  according to our previous study. The effect of imprinting is more significant and convinced through comparison of  $\text{Cu}^{2+}/\text{Zn}^{2+}$  and  $\text{Cu}^{2+}/\text{Cr}^{3+}$ . The selectivity of  $\text{Cu}^{2+}/\text{Zn}^{2+}$  and  $\text{Cu}^{2+}/\text{Cr}^{3+}$  really has an obvious improvement comparing with NIP.

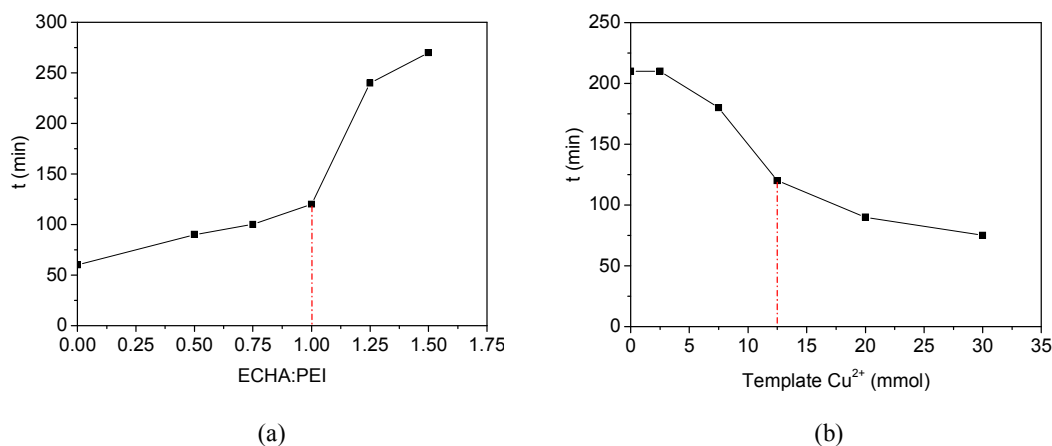
**Table 3** Comparison of similar systems based on  $\text{Cu}^{2+}$  imprinted polymers

Imprinted sorbents	Adsorption capacity for $\text{Cu}^{2+}$ (mg/g)	Selectivity coefficient				Ref.
		$\text{Cu}^{2+}/\text{Zn}^{2+}$	$\text{Cu}^{2+}/\text{Cr}^{3+}$	$\text{Cu}^{2+}/\text{Ni}^{2+}$	$\text{Cu}^{2+}/\text{Cd}^{2+}$	
Chitosan	21.12	1.91	-	0.97	-	12
PVA-SA	79.30	2.25	-	-	2.79	15
Methacrylic acid	15.90	17.50	-	4.30	25.20	38
Chitosan, polystyrene	46.25	2.47	-	5.67	-	39
Thiozylmethacrylamide	76.30	24.50	26.70	20.1	4.91	40
Methacrylic acid, vinyl pyridine	46.12	42.38	-	43.48	-	16
PEI	108.59	21.00	5.21	-	-	This work

- represents do not measured or investigated in references.

### 3.3.3 Adsorption rate

In order to investigate the adsorption efficiency of imprinted nanoparticles, the adsorption time was taken into account. Time allowed to reach equilibrium adsorption of every sorbent was measured and shown in Fig. 8. The concentration of metal ions in solution were detected every 15 min and calculated adsorption capacity. The adsorption time was recorded when the results kept constant. The equilibrium time increased with crosslinking degree, or with decreasing of template ions. The adsorption rate was mainly influenced by mass transfer process. As the morphology changes in Fig. 2, greater crosslinking degree caused more difficult for metal ions transferring from solution to inner sorbents. It was worth mentioning that the rapid changes of curves indicated by dotted lines once again proved significant change of sorbent morphology. The sorbent with optimal imprinting efficiency required about 2 h to reach equilibrium.



**Fig. 8** Equilibrium adsorption time of sorbents. (a) different crosslinking degree. (b) different dosage of template  $\text{Cu}^{2+}$ .

### 3.4 Desorption and reuse

The regeneration of the sorbents was key factor of their availability in economical water pollution control. The previous study presented that adsorption capacity was greatly affected by pH. The adsorbed sorbents were eluted by 0.1 M hydrochloric acid with 5 times and then detected by atomic absorption spectrophotometer to indicate removal efficiency of metal ions. In order to obtain the reusability of  $\text{Cu}^{2+}$  imprinted nanoparticles, adsorption-desorption cycles were repeated 5 times by using the same sorbent for single  $\text{Cu}^{2+}$  solution. The adsorption capacity for  $\text{Cu}^{2+}$  of reused sorbents was shown in Fig. 9. After 5 cycles reused, the adsorption capacity for  $\text{Cu}^{2+}$  was just 12.2% of decrease. The loss of adsorption capacity was mainly determined by amount of residual copper ions in elution process. The results suggested that the  $\text{Cu}^{2+}$  imprinted nanoparticles had certain regeneration adsorption efficiency, and could be used repeatedly.

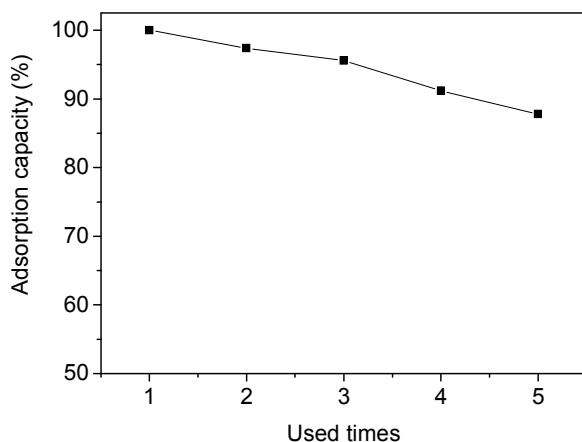


Fig. 9 Adsorption capacities of IIPs for  $\text{Cu}^{2+}$  after regeneration.

## 4 Conclusion

In this study, the  $\text{Cu}^{2+}$  imprinted PEI nanoparticles were successfully synthesized through crosslinking of PEI with ECHA in an aqueous medium. The infrared spectrometer and scanning electron microscope were used for characterization. The imprinted nanoparticles with particle diameters of around 100 nm in diameter had high chemical stability, outstanding adsorption capacity and good selectivity. Morphologies and particle diameters of imprinted sorbents were alterable with changed component ratio. This will have a great influence to mass transfer efficiency, as well as adsorption capacity. Moreover, the imprinting efficiency of sorbents was investigated through adsorption capacity and selectivity. It revealed the amount of imprinted sites (or specific cavities) was determined by crosslinking degree and was the key factor of imprinting efficiency. The optimal dosage ratio of PEI, ECHA and template  $\text{Cu}^{2+}$  was 1 g : 1 g : 2.5 mmol. The imprinted nanoparticles exhibited a great improvement of selectivity towards  $\text{Cu}^{2+}$ . Selectivity coefficient of obtained nanoparticles for  $\text{Cu}^{2+}/\text{Cr}^{3+}$  and  $\text{Cu}^{2+}/\text{Zn}^{2+}$  were 5.21 and 21.00, respectively. This work could be extended to many other types of functional polymers in investigating and improving imprinting efficiency. It also provided an novel adsorbent to effectively recognition, recover and utilize  $\text{Cu}^{2+}$  from waste water.

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