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Preparation of core–shell magnetic ion-imprinted polymer by sol-gel process for selective extraction of Cu(II) from herbal medicines

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Abstract

A novel magnetic surface ion-imprinted polymer (c-MMWCNTs-SiO_2-IIP) was firstly synthesized by using c-MMWCNTs as the core, 3-ammonium propyltriethoxysilane (APTES) as the functional monomer, tetraethylorthosilicate (TEOS) as the cross-linker and Cu(II) as the template. c-MMWCNTs-SiO_2-IIP was evaluated for selective extraction of Cu(II) from herbal medicines extraction by magnetic solid phase extraction (M-SPE) procedure. Factor affecting the separation and preconcentration of the target heavy metal was pH. Under the optimized experimental conditions, the adsorption kinetics and adsorption capacity of c-MMWCNTs-SiO_2-IIP toward Cu(II) were estimated. The results indicated that the adsorption mechanism was corresponding with the pseudo-second-order adsorption process with a correlation coefficient (R^2 = 0.985), and the maximum adsorption capacity is 42.2 mg/g. The relative selectivity factor (β) values of Cu(II)/Zn(II) and Cu(II)/Pb(II) were 38.5 and 34.5, respectively. c-MMWCNTs-SiO_2-IIP was applied for extracting and detecting Cu(II) in herbal medicine combined with flame atomic absorption spectrometer successfully with high recoveries ranged from 95.6% to 108.4%.

Keywords: core–shell, c-MMWCNTs-SiO_2-IIP, sol-gel, Cu(II), magnetic solid phase extraction (M-SPE)

1. Introduction

Herbal medicines have played an important role in a thousand years of Chinese history. Active pharmaceutical ingredients (API) extracted from the herbal medicines and complementary alternative medicines (CAM) have attracted extensive attention throughout the world. [1] However, contaminants, such as herbicides, pesticides, microbes and heavy metals caused by the surrounding environment have become a severe problem that makes it unsafe for disease curing and ultimately prevents the exports of API and CAM. Clinical studies show that some heavy metals are toxic, but the tolerable amount of heavy metals plays a role in assisting drug efficacy. Therefore, accurate and efficient qualitative control of heavy metals in Chinese medicinal materials is of great significance.

To screen for heavy metal contamination, several analytical methods, including AAS, ICP-MS, HPLC and NAA, have been applied to determine the suspected heavy metal toxicity. [2-4] Since traditional adsorbents, such as Fe_3O_4 particle,[5] carbon nanotubes [6] and magnetic CNTs/Fe_3O_4 composites (c-MMWCNTs) [7, 8] which bear no selectivity cannot separate analytes efficiently from the complex samples, the development of selective adsorbents is necessary to apply in the complex samples.

It is well known that molecularly imprinted polymers (MIPs) have been widely applied in selective enrichment of organic compounds in complex samples. However, MIPs is not suitable for ionic heavy metals. The preparation of ion imprinting polymers (IIPs) is similar to that of MIP, which is obtained by chelating metal ions and ligands atoms, and then polymerizing with polymer monomer. The combination and breakdown of the coordinate bond between metal ions and ligands can be controlled by changing medium conditions. Currently, the main preparation methods of IIPs are bulk polymerization, in-situ polymerization, precipitation polymerization and suspension polymerization and so on. Although these methods possess the advantages of high selectivity, some disadvantages were suffered, such as the heterogeneous distribution of the binding sites, embedding of most binding sites, and poor site accessibility for target ions. To

overcome the above shortcomings, the surface imprinting polymerization has gotten wide attention. So far, the surface imprinting polymers which take Pb^{2+}, [5] Ag^{+}, [9] Cu^{2+}, [10] Hg^{2+} [11] and other metal ions as templates have been successfully prepared, bearing the advantages of high selectivity, high adsorption capacity as well as fast combination capability.

Sol-gel method is the typical representative of the surface imprinting method. Namely, under the effect of an appropriate catalyst (acid, alkali and neutral), inorganic or metal alkoxide can capture oxides and other solid compound through hydrolysis, polymerization, aging and drying steps. In sol-gel method, the most widely used crosslinking agent is alkoxy silane, especially tetramethoxysilane (TMOS) [12-14] and tetraethoxysilane (TEOS). Templates and the functional monomer are mainly combined with non-covalent bond, including hydrogen bonds, metal-ligands conjugation, ionic bond, hydrophobic function, the van der Waals force and so on. [15]

Although copper is one of the essential trace elements in the human body, intolerable amount of copper can do great harm to human health and cause serious illness, such as nausea, vomiting, weight loss, dehydration, sluggish and anorexia. Few researches on preparing ion-imprinted materials for extraction of copper ions from complex samples have been reported.[16] In this work, a core-shell magnetic ion-imprinted polymer (c-MMWCNTs-SiO_2-IIP) based on c-MMWCNTs was synthesized for the first time with surface imprinting technique. During the preparation process, c-MMWCNTs-SiO_2-IIP was prepared by sol-gel method using c-MMWCNTs-SiO_2 as the core, copper ion as the templates, 3-ammonium propyltriethoxysilane (APTES) as the functional ligand, and tetraethylorthosilicate (TEOS) as the cross-linker. The obtained product was explored for the copper ion adsorption behavior and selectivity, and applied in the extraction and determination of copper ions in herbal medicine.

2 Materials and methods

2.1 Materials and instruments

Multi-walled carbon nanotubes (diameter 40-60 nm, length 5-15 μm) were purchased from

Shenzhen Nanotechnologies Port Company, Ltd., China; Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was obtained from Yufeng Chemical Reagents Company (Changsha, China); PEG-10000, ethylene glycol (EG), diethylene glycol (DEG), tetraethoxysilane and pentahydrate copper sulfate ($CuSO_4 \cdot 5H_2O$) were purchased from Aladdin; Sodium diethyl dithiocarbamate (DDTC) was obtained from Tingxin Chemical Reagents Company (Shanghai, China); 3-ammonium propyltriethoxysilane (APTES) was obtained from Diomand New Materials of Chemical Inc. (Hubei, China); Cetyl trimethyl ammonium bromide (CTAB) was obtained from Lingfeng Chemical Reagent company, Ltd. (Shanghai, China). All the reagents used in the experiments were of analytical grade. The whole process was conducted in deionized (DI) water.

The magnetic field was applied by placing a commercial NdFeB magnet (an alloy of neodymium, iron and boron; 1 cm high and 2 cm in diameter). UV-Vis absorption was characterized by UV1800 UV-Vis spectrophotometer (Shimadzu Corporation, Japan). The size and morphology of the as-synthesized materials were characterized by S-3000 scanning electron microscopy (SEM, Hitachi Corporation, Japan). The surface groups on the as-synthesized materials were measured with a 8400s FTIR spectrometer (Shimadzu Corporation, Japan). The experiments were performed by GFA-EX7i flame atomic absorption spectrometer (FAAS) (Shimadzu, Japan).

2.2 The determination of Cu(II) in aqueous solution

DDTC is selected as the chelating regent because of the second highest stability constant of Cu(II)-DDTC complex, compared with the stability constants of the other DDTC-metal complexes.[17] The theoretical stoichiometry of DDTC/Cu(II) was 2:1 and the detection wavelength was 454 nm. Since Cu(II)-DDTC complex is a kind of metal complex with low water-solubility, nonionic surfactant CTAB was added to increase the solubility of Cu(II)-DDTC complex in this work. The calibration was performed by using six Cu(II) standards at different concentrations in the range of 0 to 7.0 mg/L. The obtained linear regression equations and correlation coefficients (R^2) for Cu(II) were $A = 0.0990C + 0.0557$ and $R^2 = 0.9987$,

correspondingly, where A was the absorbance of the Cu(II) standards and C was the concentrations of Cu(II) added with the unit of mg/L. The relatively standard deviations (RSD%) of intra-day and inter-day precisions taken at the concentration of 3.0, 5.0, 7.0 mg/L were all less than 3%. The recoveries of Cu(II) in aqueous samples ranged from 98.7%±2.8% to 100.3%±2.2% (n=6). The limit of detection (LOD) of the proposed method was studied under the optimal experimental conditions. According to the experimental results the LOD of Cu(II) is 1.15 μg/L.

2.3 Synthesis of c-MMWCNTs-SiO_2

c-MMWCNTs was obtained according to the previous work reported in our lab. [18] 1.0 g c-MMWCNTs were dispersed in the mixture of 8 mL DI water, 40 mL methanol and 0.5 mL ammonia solution (30%, m/v) and sonicated for 0.5 h. Then, after 15 min continuous mechanical stirring, 0.5 mL TEOS was added into the mixture and reacted at room temperature (25 °C) for 12 h. The product can be separated by an extra magnetic field, and then dispersed in Dimethyl Formamide to remove the remaining TEOS. At last, the obtained c-MMWCNTs-SiO_2 was washed by DI water and methanol consecutively, and finally dried in vacuum at 65 °C for 12 h.

2.4 Synthesis of c-MMWCNTs-SiO_2-IIP

0.5 g c-MMWCNTs-SiO_2 was accurately weighed and sonicated in 60 ml methanol to get the mixed suspension A. 2 mmol $CuSO_4 \cdot 5H_2O$ (0.5 g) and 3.4 mmol CTAB (0.62 g) were accurately weighed, mixed with 36.0 ml DI water and then added into 50 ml conical flask to dissolve by heating. Then 2.0 ml APTES was added to form the blue flocculent precipitate which was dissolved by continuous heating. The obtained solution was named as B. Solution B and 0.7 ml TEOS were added consecutively into suspension A which was put on the mechanical stirring apparatus with the rotating speed of 1500 rpm firstly. The mixed solution was heated in the oil bath at 60°C for 6 h. The obtained copper ion imprinted polymer was washed with DMF to remove the excess of TEOS. Then DI water and methanol were used to wash three times consecutively to remove the excess DMF. Finally the washing process for the loaded polymers

was repeated with CH_3OH-0.1 M HNO_3 (volume ratio: 49:1) to remove the templates until the copper ions could not be detected anymore by DDTC. The prepared c-MMWCNTs-SiO_2-IIP was washed by DI water and methanol consecutively, and then dried in vacuum at 65°C for 12 h. The schematic preparation process of c-MMWCNTs-SiO_2-IIP was shown in Fig.1.

At the same time, the non-ion imprinted polymer (c-MMWCNTs-SiO_2-NIP) was prepared as a control test. The schematic preparation process was just followed the above steps without adding copper ions.

According to the above method, carboxyl carbon nanotubes (c-MWCNTs) and magnetic ferroferric oxide nanoparticles (MNP) were also used as the core, and the corresponding ion imprinted polymers and non-ion imprinted polymer were prepared, respectively (c-MWCNTs-SiO_2-IIP, c-MWCNTs-SiO_2-NIP, MNP-SiO_2-IIP and MNP-SiO_2- NIP).

2.5 Batch adsorption experiments

Batch adsorption experiments of c-MMWCNTs-SiO_2-IIP and c-MMWCNTs-SiO_2-NIP were preformed in deionized water. Respective polymers (10 mg) were shaked with 10 mL of deionized water (pH= 7.5) spiked with Cu(II) at room temperature for 4 h with 1500 rpm by THZ-C Constant temperature shaker. Then the polymers were collected by an external magnetic force. The supernatant was analyzed by UV-1800 spectrophotometer (Shimadzu, Japan).

The amount of Cu(II) adsorbed by the polymers was calculated according to the following formula:

$$Q = \frac{(C_0 - C)V}{1000W} \quad (1)$$

where Q is the adsorbed amount of Cu(II) (mg/g); C_0 and C are the initial and final concentration of Cu(II) (μg/mL), respectively; V is the volume of solution (mL); W is the amount of polymer (g).

2.6 The determination of residual Cu(II) in the herbal medicine extractions

The samples analyzed consisted of different matrices (rhizome of Salvia Miltiorrhiza, herbaceous stem of Herba Ephedrae, flowers of Lonicera Japonica and root of Radix Astragali).

Four different commercial TCMs in a total of 20 samples were collected from several herbal shops in 2012. All samples were milled (particle size about 2 mm) and stored at -18°C prior to analyses for the determination of residual Cu(II). The traditional Chinese medicines (TCM) were digested by dry ashing method. The main advantages of the dry ashing method were the lower blank levels, improved (lower) background current and its ability to handle considerably larger amounts of sample. Sample preparation was carried out according to Chinese Pharmacopoeia (2010 version). Accurately weighed 0.5 g of test samples into crucible and heated with low temperature to smokeless, and then incandesced in furnace for 6 hours at 500°C. The ashes were extracted by 15 ml 8 mol/L HNO_3 for 0.5 h, then filtrated through 0.45 μm filter membrane, After acidification with HNO_3, pH of the samples were adjusted to neutral before determination by GFA-EX7i flame atomic absorption spectrometer (FAAS) (Shimadzu, Japan).

3. Results and discussion

3.1 Characteristics

Fig.2 showed the particles sizes of c-MMWCNTs-SiO_2, c-MMWCNTs-SiO_2-NIP and c-MMWCNTs-SiO_2-IIP under the same visual field. As shown in Fig. 2A, Fe_3O_4 nanoparticles were deposited onto the surfaces of the c-MWCNTs. As shown in Fig.2B and 2C, the diameters of c-MMWCNTs-SiO_2-NIP and c-MMWCNTs-SiO_2-IIP were increased, indicating that a polymer layer might have been successfully coated on the surfaces of c-MMWCNTs-SiO_2.

8400s FT-IR spectroscopy (Shimadzu, Japan) was used to study the chemical structure of c-MMWCNTs (A), c-MMWCNTs-SiO_2-NIP (B) and c-MMWCNTs-SiO_2-IIP (C). The results were shown in Fig.3. A strong peak at 3400-3500 cm^{-1} corresponding to the stretching O-H was observed in all the samples. [19] The strong peak at 620 cm^{-1} belonged to the stretching Fe-O, which indicated the Fe_3O_4 particles were encapsulated inside of c-MMWCNTs-SiO_2-IIP. The peaks at 1650 cm^{-1} and 950-980 cm^{-1} corresponded to the in-plane bending vibration of C-NH_2 and asymmetric stretching vibration of Si-OH, respectively. It was notable in Fig.3C that the asymmetric stretching vibration peaks of O-Si-O at 1000-1250 cm^{-1} and Si-O-C at 1380cm^{-1} in

c-MMWCNTs-SiO_2-IIP were stronger than that of c-MMWCNTs-SiO_2-NIP, which indicated the formation of O-Si-O polymer.

3.2 Adsorption behaviors of imprinted polymers

3.2.1 Adsorption capacity

Since c-MMWCNTs were consisted of c-MWCNTs and MNP, IIPs corresponding to c-MMWCNTs, c-MWCNTs and MNP were prepared and investigated of adsorption capacity. The adsorption capacity of IIPs toward Cu(II) was investigated by batch experiments. Fig.4A is Cu(II) isothermal adsorption behavior on c-MMWCNTs-SiO_2-IIP (c-MWCNTs-SiO_2-IIP or MNP-SiO_2-IIP). It can be seen that the adsorption capacity of c-MMWCNTs-SiO_2-IIP (or c-MWCNTs-SiO_2-IIP, MNP-SiO_2-IIP) increased with the increasing initial concentration of Cu(II) solution. When the initial concentration increased to a certain degree, the adsorption capacity tended into balance. The order of the adsorption capacity for three adsorbents was found as follows, c-MWCNTs-SiO_2-IIP > c-MMWCNTs-SiO_2-IIP > MNP-SiO_2-IIP with the amount of 42.8 mg/g, 36.6 mg/g and 18.5 mg/g respectively, which might be attributed to their specific surface area.

Although the adsorption capacity of c-MMWCNTs-SiO_2-IIP was slightly lower than that of c-MWCNTs-SiO_2-IIP, c-MMWCNTs-SiO_2-IIP can quickly be separated from the solution due to the magnetic performance, which bringing great convenience to the experiment. Therefore, c-MMWCNTs-SiO_2-IIP was selected as the further research object in this study. Compared the adsorption capacity of c-MMWCNTs-SiO_2-IIP with that of c-MMWCNTs-SiO_2-NIP, the result was shown in Fig.4B. The adsorption capacities of c-MMWCNTs-SiO_2-IIP was 36.6 mg/g, which was nearly three times more than that of c-MMWCNTs-SiO_2-NIP 13.1 mg/g. This can be explained that the presence of the functional group of $–CH_2–NH_2$ in the selective hole of c-MMWCNTs-SiO_2-IIP can absorb more Cu(II) by coordination effect. [20]

In this experiment, c-MMWCNTs-SiO_2-IIP was prepared by the surface imprinting method, and Langmuir equation is suitable for monolayer adsorption on a surface, thus in order to further

discuss the adsorption behavior of Cu(II) on c-MMWCNTs-SiO_2-IIP, Langmuir isotherm model was used to analyse the isothermal adsorption data obtained from Fig.4B. The Langmuir equation was expressed as follow:

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}C_e} \quad (2)$$

where q_e (mg/g) is the equilibrium adsorbed amount of Cu(II), Q_{max} (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the equilibrium concentration, and b (L/mg) is the adsorption equilibrium constant. The correlation coefficient (R^2) and the maximum adsorption capacity (Qmax) was calculated as 0.997 and 42.2 mg/g (shown in Fig.5.).

3.2.2 Adsorption kinetic

Adsorption kinetic experiments of Cu(II) on c-MMWCNTs-SiO_2-IIP and c-MMWCNTs-SiO_2-NIP were conducted in aqueous solution by a batch system. Briefly, 20.0 mg of the imprinted sorbent was added to 50 mL of 100 μg/mL Cu(II) aqueous solution at pH 7.0. It can be seen that a much higher adsorption capacity was achieved on c-MMWCNTs-SiO_2-IIP shown in Fig.6. Saturation adsorption of 40.4 mg/g can be obtained within 50 min, which can be attributed to the high coordination effect between -CH_2-NH_2 and Cu(II). However, the saturation adsorption of c-MMWCNTs-SiO_2-NIP, which was obtained within 120 min, was obviously smaller than that of c-MMWCNTs-SiO_2-IIP, indicating the good affinity to Cu(II) of c-MMWCNTs-SiO_2-IIP.

Moreover, the pseudo first-order and pseudo second-order kinetic models were used to investigate the kinetic mechanism driving Cu(II) adsorption further. [21, 22] The pseudo-first order equation is given as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (3)$$

where k_1 is the rate constant of first order sorption (min^{-1}); q_e is the amount of solute sorbed at equilibrium (mg/g); q_t is the amount of solute sorbed on the surface of the sorbent at time t (mg/g).

The pseudo-second order equation is given as follows:

$$\left(\frac{t}{q_t}\right)=\left(\frac{1}{k_2 q_e^2}\right)+\left(\frac{t}{q_e}\right) \quad (4)$$

where k_2 is the rate constant for the pseudo second-order adsorption of Cu(II) (g/mg min), and all other variables in pseudo-second order equation are the same with pseudo-first order equation as described above.

Fig.7 was the plots of the linearized form of pseudo first-order and pseudo-second order model. The calculated equilibrium adsorption capacity ($Q_{e,cal}$ = 53.2 mg/g) was obtained from pseudo-first-order with a low correlation coefficient (R^2 = 0.965). Whereas, the calculated equilibrium adsorption capacities ($Q_{e,cal}$ = 46.5 mg/g) estimated from pseudo-second-order kinetic model with a high correlation coefficient (R^2 = 0.985), is relatively close to the maximum adsorption capacity (Q_{eq} = 42.2 mg/g). Therefore, the adsorption system of c-MMWCNTs-SiO_2-IIP toward Cu(II) was better fit to pseudo-second order model. And this adsorption mechanism was predominant for the ion-imprinted adsorbent system based on the assumption that the rate-limiting step might be chemical sorption between chemical binding sites on the surface of c-MMWCNTs-SiO_2-IIP and Cu(II). [5]

3.2.3 Selectivity

The selectivity of c-MMWCNTs-SiO_2-IIP toward Cu(II) was evaluated by competitive adsorption in the presence of various competitive metal ions. A mixture of Pb(II), Cu(II) and Zn(II) was added into deionized water to obtain 25ml of 100 μg Pb(II), 100 μg Zn(II) and 100 μg Cu(II). After a competitive adsorption equilibrium reached for 4 h, the concentration of Pb(II), Zn(II) and Cu(II) in the remaining samples were detected by FAAS. The following equations were used to quantify the selectivity of c-MMWCNTs-SiO_2-IIP : [23]

Distribution ratio (mL/g),

$$K=\frac{Q}{C_e} \quad (5)$$

where Q is the adsorption capacity (mg/g).

Selectivity factor ,

$$\alpha = \frac{K_t}{K_c} \quad (6)$$

where K_t and K_c are the distribution ratio Cu(II) and Pb(II) or Zn(II), respectively.

Relative selectivity factor ,

$$\beta = \frac{\alpha_i}{\alpha_n} \quad (7)$$

where α_i and α_n are the selectivity factor of c-MMWCNTs-SiO_2-IIP and c-MMWCNTs-SiO_2-NIP.

Since Zn(II) and Pb(II) can be determined directly in the aqueous solution when mixed with Cu(II), in the selectivity experiment the concentration of the ions were measured by FAAS. The absorbance (A) of Cu(II), Zn(II) and Pb(II) stock solutions were determined at 324.8 nm, 213.8 nm and 283.3 nm by FAAS, respectively. Table 1 listed the distribution ratio, selectivity factor and relative selectivity factor of c-MMWCNTs-SiO_2-IIP and c-MMWCNTs-SiO_2-NIP for Cu(II). As shown in Table 1, the distribution ratio and selectivity factor of c-MMWCNTs-SiO_2-IIP were much greater than that of c-MMWCNTs-SiO_2-NIP, showing that c-MMWCNTs-SiO_2-IIP born higher selectivity for Cu(II). Moreover, the distribution ratio of c-MMWCNTs-SiO_2-IIP for Cu(II) was much higher than those for other ions. The results implied that the imprinted cavities and specific binding sites in a predetermined orientation were formed. Cu(II), Zn(II) and Pb(II) had the same charge, and Cu(II) and Zn(II) had the similar atomic radius, but higher selectivity of c-MMWCNTs-SiO_2-IIP for Cu(II) might be attributed to the different chelation forces between nitrogen atoms in APTES toward various ions. Relative selectivity factor (β) represented relative affinities of imprinting ions. β(Cu(II)/Zn(II)) and β(Cu(II)/Pb(II)) of c-MMWCNTs-SiO_2-IIP were 38.5 and 34.5, respectively. It can be referred that the affinity order of c-MMWCNTs-SiO_2-IIP toward Cu(II), Zn(II) and Pb(II) was Cu(II) > Zn(II) > Pb(II).

3.2.4 Effect of pH on the adsorption and desorption of Cu(II)

It is well known that pH plays an important role in the adsorption performance of the imprinted polymer toward different ions . [24]Since Cu(II) started precipitating when the pH of the solution was bigger than 7.0 , [25] the effect of pH on the adsorption of c-MMWCNTs-SiO_2-IIP toward Cu(II) was studied with varying pH from 1.0 to 7.0 and the results were presented in Fig.8. The results showed that the adsorption percentage of Cu(II) increased with the increasing pH of the aqueous solution from 1.0 to 7.0. At lower pH, the adsorption capacity of Cu(II) is very low due to two reasons. One is the protonation of $–CH_2–NH_2$, which might hinder the complexation between Cu(II) and the functional groups; [26]The second one is the over acidity might hydrolyze the O-Si-O-Si bond structure in the c-MMWCNTs-SiO_2-IIP polymer, thus affecting its absorption capacity.

Since the acid condition can decrease the adsorption of Cu(II) on c-MMWCNTs-SiO_2-IIP, low pH could contribute to the elution. However, the volume of the polymers decreased gradually when washed by CH_3OH-0.1 M HNO_3 (9:1, v/v) mixture solution during the elution process. It can be referred that the coating layer might be destroyed. Thus, the c-MMWCNTs-SiO_2-IIP polymer loaded with Cu(II) should be eluted with suitable eluent. To find the suitable eluent, the loaded c-MMWCNTs-SiO_2-IIP polymers were washed with CH_3OH-0.1 M HNO_3 mixture solution of different acidity (9:1 or 49:1, v/v). When washed by CH_3OH-0.1 M HNO_3 (9:1, v/v) mixture solution, the supernatant was clear with no Cu(II) after eluting for about 6 or 7 times, but the volume of the polymer decreased significantly. When washed by CH_3OH-0.1 M HNO_3 (49:1, v/v), the supernatant was clear with no Cu(II) after eluted for about 20 to 30 times, and the volume of the polymer showed no obvious change. From the apparent phenomenon, it can be speculated that CH_3OH-0.1 M HNO_3 (49:1, v/v) might be the suitable eluent. To support the above-mentioned conclusion, the polymers washed by two eluents were characterized by SEM and the results were shown in Fig.9. It was obviously that the volume of c-MMWCNTs-SiO_2-IIP eluted by CH_3OH-0.1 M HNO_3 (49:1, v/v) was bigger than that washed by CH_3OH-0.1 M HNO_3 (9:1, v/v), indicating that strong acid can destroy the structure of c-MMWCNTs-SiO_2-IIP.

Therefore, the acidity of the solutions should be strictly controlled during the process of experiment.

3.3 Application

Under the optimum conditions, the imprinted polymers were used for the extraction of Cu(II) from herbal medicines spiked with various amounts of Cu(II). After incubation with herbal medicines extractions, IIP were eluted with CH_3OH-0.1 M HNO_3 (49:1, v/v) mixture solution, the concentration of Cu(II) in the elution was detected using FAAS. The linear range of the magnetic solid phase extraction coupled with FAAS method was established to be 0.70-100.00 μg/g. The correlation coefficient of the calibration graphs is 0.9974. The relatively standard deviations (RSD%) of intra-day and inter-day precisions taken at the concentration of 20.00 and 50.00 μg/g were all less than 3%. The detection limit (LOD) of the presented solid phase extraction study was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The detection limits, defined as the concentration equivalent to three times the standard deviation (N = 12) of the reagent blank were found as 0.21 μg/g.

As shown in Table 2, high recoveries ranged from 95.6% to 108.4% in the all tested concentration of Cu(II), which indicated that IIP showed a high effectivity for extracting Cu(II) from herbal medicine extractions. According to green trade standards of importing medicinal plants and the preparations, the total amount of heavy metals should be less than 20.0 μg/g, and Cu(II) less than 20.0 μg/g. Experimental results showed that Cu(II) in the herbal medicines extraction was less than 20.0 μg/g, which is according with the regulation. Reusability of c-MMWCNTs-SiO2-IIP is one of key factors in evaluating the performance of the adsorption materials. In order to investigate the reusability and stability of c-MMWCNTs-SiO_2-IIP adsorption–desorption cycle was repeated five times by using the same imprinted materials. The results showed that c-MMWCNTs-SiO_2-IIP was stable in operation process, which could be used for five cycles with lost of less than 7.2% of Cu(II) recoveries on average.

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4. Conclusions

In our work, a magnetic surface ion-imprinted polymer based on c-MMWCNTs was prepared successfully by a sol-gel process. The obtained c-MMWCNTs-SiO_2-IIP exhibited high selectivity toward Cu(II) with the relative selectivity factor over 34.5 in the presence of Cu(II), Zn(II) and Pb(II). When the magnetic adsorbent was used in herbal medicine extractions, good recoveries (>95.0%) for Cu(II) were obtained under the optimized conditions. The magnetic imprinted adsorbent can be applied to rapid extraction of Cu(II) from herbal medicine extractions, which can lower the influence of the interference matrix, thereby optimize the detection limit of detection methods. Also, the magnetic performance of c-MMWCNTs-SiO_2-IIP did not need column packing when used in the M-SPE, thereby lessening the column pressure and increasing the effective contact area which can improve the extraction efficiency. Moreover, the reusability and stability of c-MMWCNTs-SiO_2-IIP for five circles make it a promising adsorbent in selecting heavy metal ions from complex samples.

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Figure Captions

Fig. 1 Schematic expression of synthesis of c-MMWCNTs-SiO_2-IIP

Fig. 2 SEM images of c-MMWCNTs -SiO_2 (A), c-MMWCNTs -SiO_2-NIP (B) and c-MMWCNTs -SiO_2-IIP (C).

Fig.3 FT-IR spectra of c-MMWCNTs (A), c-MMWCNTs-SiO_2-NIP (B) and c-MMWCNTs-SiO_2-IIP (C).

Fig.4 The adsorption isotherms of Cu(II) on three kinds of IIPs (A) and c-MMWCNTs-SiO_2-IIP (c-MMWCNTs-SiO_2-NIP) (B)

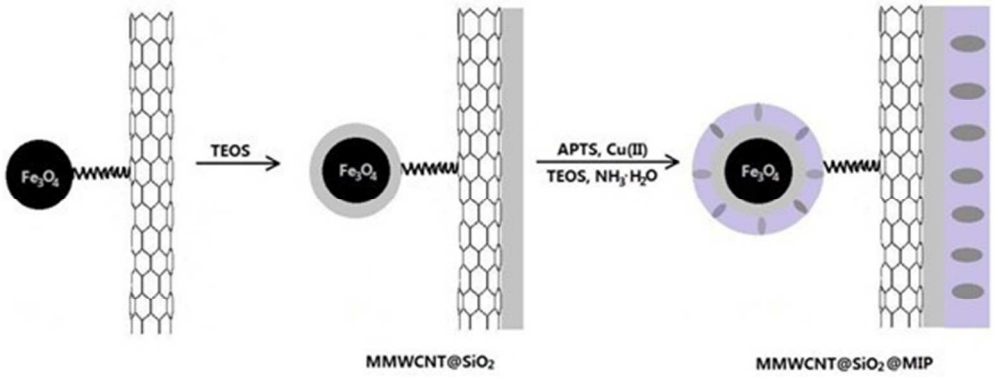
Fig.5 Langmuir isothermal model for Cu^{2+} adsorption on c-MMWCNTs-SiO_2-IIP.

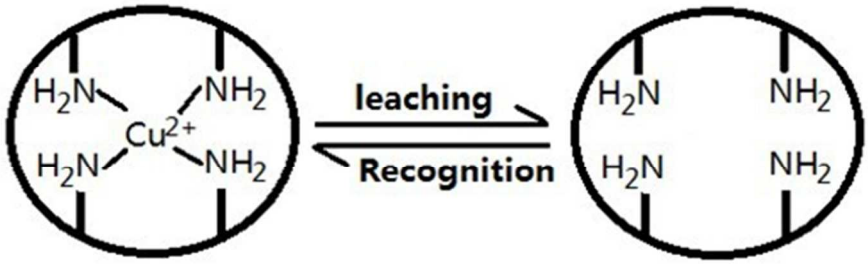
Fig.6 Adsorption kinetic curves of c-MMWCNTs-SiO_2-IIP and c-MMWCNTs-SiO_2@NIP.

Fig.7 Pseudo-first-order (A) and pseudo-second-order (B) kinetic models for adsorption of Cu(II) onto H_2-MNP.

Fig.8 Effect of pH on adsorption capacity of c-MMWCNTs-SiO_2-IIP.

Fig.9 The SEM images of c-MMWCNTs-SiO_2-IIP washed by different proportions of CH_3OH-0.1 M HNO_3: 49:1 (A) and 9:1 (B).





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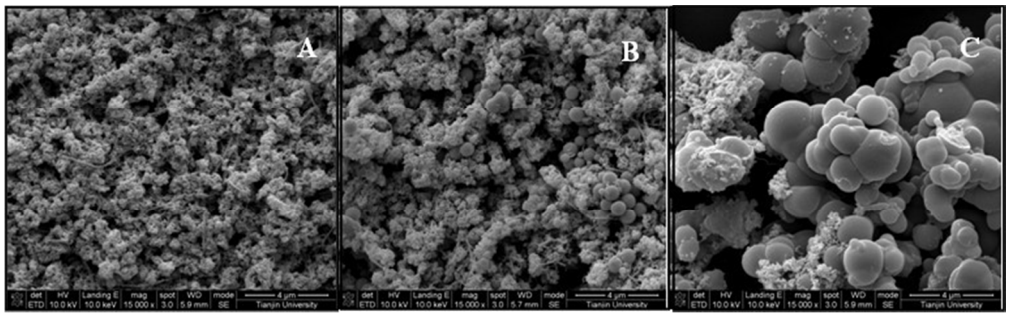

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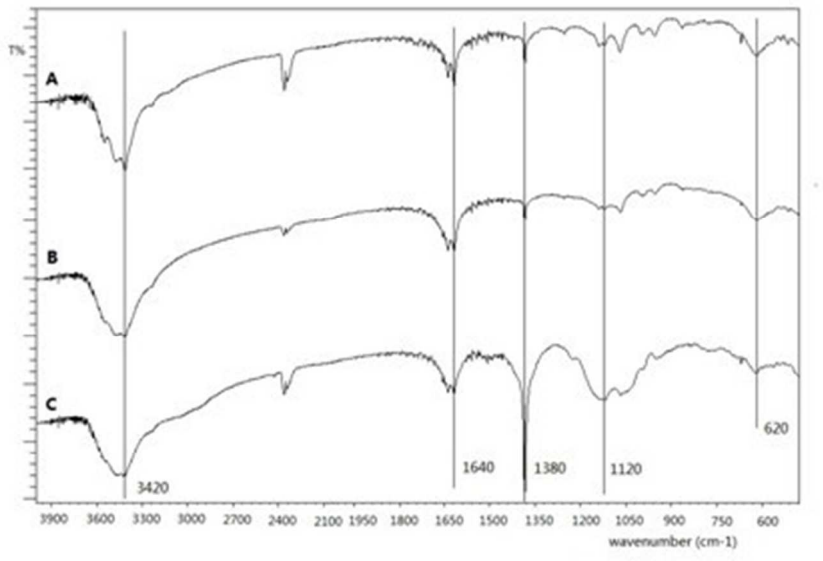

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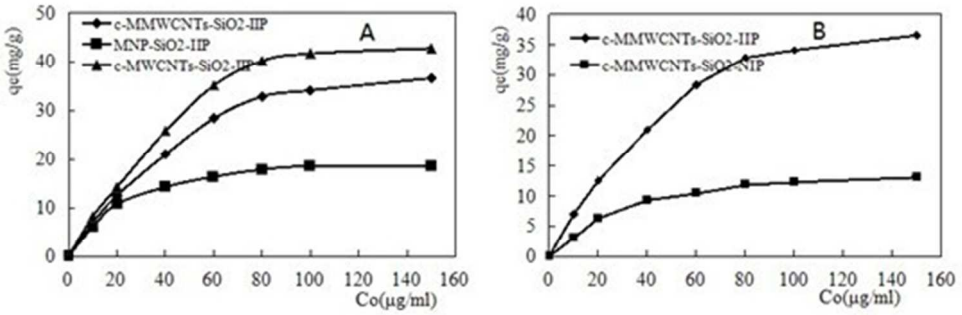

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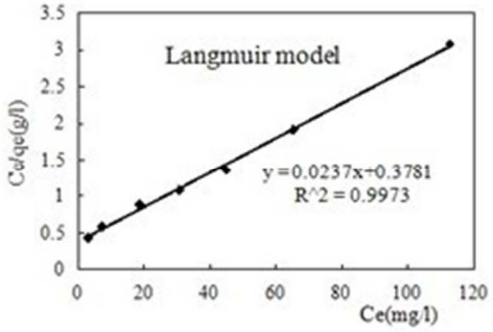

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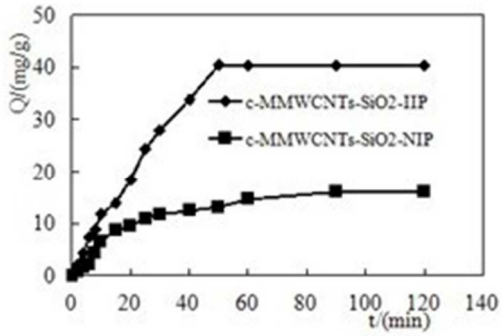

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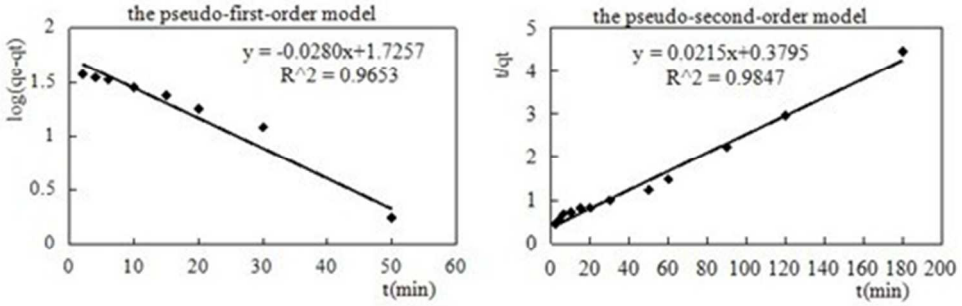

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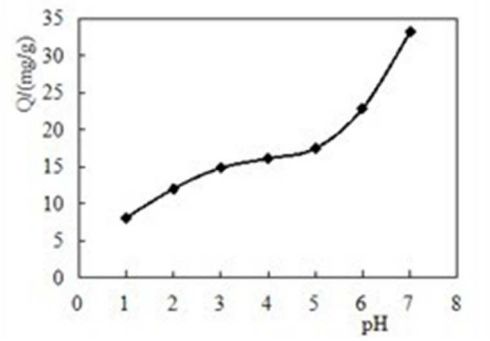

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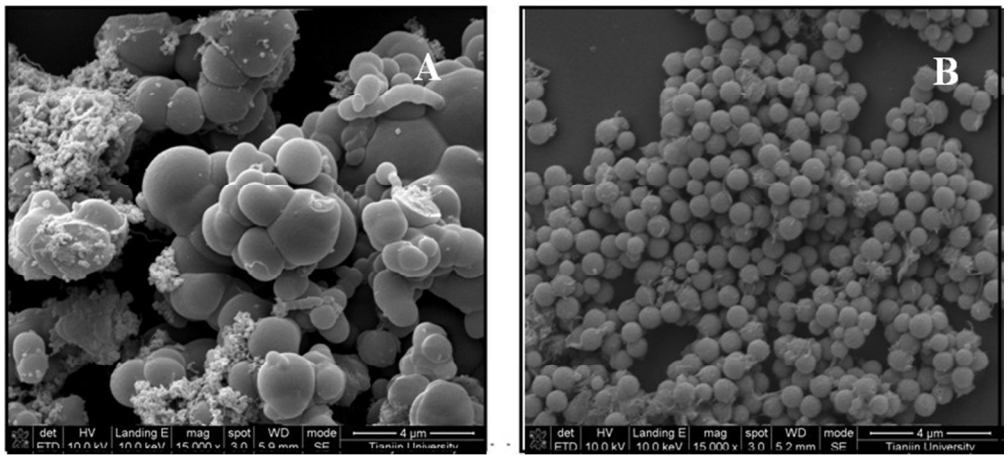

227x102mm (96 x 96 DPI)

Table 1 Distribution ratio, selectivity coefficient and relative selectivity coefficient of c-MMWCNTs-SiO_2-IIP and c-MMWCNTs-SiO_2-NIP

Metal ions	Ionic charge	Ionic radii (Å)	K(ml/g)		α		β
			IIP	NIP	IIP	NIP	-
Cu	2	0.73	2.17×10^4	5.57×10^2	-	-	
Zn	2	0.74	5.05×10^2	4.99×10^2	43.0	1.12	38.5
Pb	2	1.19	2.16×10^2	1.91×10^2	100.6	2.92	34.5

Table 2 Recoveries of Cu(II) in traditional Chinese medicine samples.

Samples	Added (μg)	Found (μg/g, n=4)	Recovery (%)
Salvia Miltiorrhiza	0	0.81±0.17[a]	--
	20	22.50±0.75[a]	108.4
	50	53.12±1.70[a]	104.5
Herba Ephedrae	0	0.77±0.18[a]	--
	20	21.33±0.85[a]	103.7
	50	52.89±1.58[a]	104.7
Lonicera japonica	0	BDL	--
	20	19.09±0.40[a]	95.6
	50	49.32±1.49[a]	98.6
Radix Astragali	0	BDL	--
	20	20.54±0. 62[a]	102.4
	50	50.28±2.53[a]	100.6

[a] Uncertainty is the standard deviation for four replicate runs.

BDL：below the detection limit