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Synthesis, characterization and application of ethylenediamine functionalized chelating resin for copper preconcentration in tea samples

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HIGHLIGHTS

- ▶ A novel ethylenediamine chelating resin for adsorption has been synthesized and well characterized.
- ▶ It showed higher affinity towards Cu(II) compared to Ni(II), Cd(II), Co(II), Zn(II) or Pb(II).
- ▶ It can be regenerated effectively using 1.0 mol L^{-1} HCl solution without any adsorption capacity decrease.
- ▶ It was employed for selective separation and preconcentration of Cu(II) ions in waters and foods.

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ABSTRACT

A novel ethylenediamine functionalized chelating resin (ED resin) with simple technology, high adsorption capacity and significant selectivity was synthesized. It was characterized by elemental analysis and infrared spectra, and was applied for determination of metal ion in tea samples. The optimized synthesis conditions is molar ratio ED:Cl = 2:1, 100 °C as reaction temperature and DMF as solvent. ED resin can be used in separating Cu(II) from aqueous solutions. The adsorption processes were evaluated by Langmuir and Freundlich isotherms. Pseudo-second-order kinetics showed better accordance. Thermodynamic parameters indicated that adsorption process was spontaneous and endothermic. Thomas model was applied to determine the characteristic parameters of column useful for process design. Finally, Cu(II) can be eluted by 1.0 mol L^{-1} HCl solution. AAS method was applied for copper determination after the pre-concentration step, and the results indicated that ED resin is essentially free from interferences, which can contribute to accurate determination in waters and foods.

1. Introduction

Currently, food safety problems brought by trace heavy metal pollution are of great concern [1]. Heavy metals, especially Cu(II), Pb(II), Cd(II), Ni(II), have become prominent pollutants because of their toxic and lethal effects [2]. Trace heavy metals are ubiquitous environmental contaminants, which are mobile and easily taken up by plants in the environment. Among these, copper is the most commonly contaminant which can cause haemic heart disease, anemia bone disorders. Due to the low metal contaminated concentration in food samples, the development of new methods for quantifying copper ion is required and challenged.

Flame atomic absorption spectrometry (FAAS) is widely used for determination not only because it is available in most laboratories, but also its significant anti-interference capability over inductively-coupled plasma atomic emission spectrometry (ICP-AES) or electro thermal atomic absorption spectrometry (ETAAS). And considering its sufficiently low detection limit, a preconcentration step is required in order to reach an appropriate level of sensitivity [3–5].

Solid-phase extraction (SPE) [6–8] is preferable to co-precipitation [9], electro-deposition, liquid–liquid extraction [10] and membrane filtration in preconcentration step, mainly owing to its advantages such as selectivity, eco-friendliness, reusability and high pre-concentration factors [11,12]. Moreover, the use of chelating resin has received a great attention for analysis of the complex mixtures in diverse fields. In recent years, there is a constant demand for selective resins for the recovery of either toxic or valuable metals from liquids [13,14]. Chelating resin is basically an organic copolymer containing donor atoms which can successfully interact with the metal ions through coordinate bond whereas polymer backbone makes them more efficient by offering large surface area. It has some advantages over solvent extraction such as higher pre-concentration factor, better efficiency, greater reproducibility and greater simplicity in handling [15]. Some recent examples of resins containing functional groups with nitrogen

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atoms such as N,N′-bis(salicylidene)ethylenediamine [16], 2,3-dihydroxybenzaldehyde with an amino copolymer [17], and 3-((4-ethylphenylamino)methyl)benzene-1,2-diol [18], have affinity for copper and other heavy metal ions. However, the adsorption capacity for Cu(II) were not that satisfactory (i.e. 26.9 mg/g, 31.4 μmol/g (2.01 mg/g), 89.7 ± 8.4 μmol/g (5.74 ± 0.54 mg/g), respectively). Ethylenediamine (ED) is a well-known complexing agent which is able to bind to metal ions in solution and solid state, and the synthesis of ED functionalized polystyrene has been reported [19,20]. However, no research about ethylenediamine functionalized with chloromethyl polystyrene resin was conducted.

In this work, a new chelating resin with ethylenediamine as functional group was synthesized and it was obtained by substituted reaction induced ethylenediamine onto PS-Cl, then the adsorption characteristics of ED resin for metal ion from aqueous solutions was carried out. The influence of experimental conditions such as reaction solvent, reaction temperature, molar ratio of reagents of synthesis has been investigated. Static, dynamic adsorption and desorption process have also been examined. ED resin is expected to be a chelating resin with simple technology, high adsorption uptake and selectivity, and it was supposed to be widely applied for determination of metal ion in waters and foods.

2. Materials and methods

2.1. Reagents

After introduced –CH_2Cl chelating group into the polystyrene resin (PS for short) is chloromethyl polystyrene bead (PS-Cl for short) which is an important synthesis of functional polymer materials, purchased from Chemical Factory of Nankai University of China. The parameter of PS-Cl is listed as following: degree of crosslinking 8% DVB, chlorine content 19.5%, specific surface area 43 $m^2 g^{-1}$. Ethylenediamine (ED) was from Sinopharm Chemical Reagent Lo., Ltd, China. Metal standard solutions of Cu(II), Ni(II), Zn(II), Cd(II), Co(II) and Pb(II) ions were prepared by certified reference materials stock solution (1000 μg/mL) of National standard materials research center. The buffer solution were prepared with acetic acid and sodium acetate, and all the reagents, solvents were of analytical reagent grade and were used without further purification.

2.2. Apparatus

The concentrations of metal ions were determined by atomic absorption spectroscopy (AAS), viz. Thermo Elemental Solar M6 AA. The working parameters of AAS were listed in Table 1. C, H and N elements were analyzed by Elemental Analyzer Vario EL. The surface area of the prepared resin was determined by Surface Area Analyzer, Quanta chrome Instruments Autosorb-1. Fourier transform infrared spectra of the synthesized resin samples were scanned in the region of 400–4000 cm^{-1} in KBr pellets on NICOLET 380 FT-IR spectrophotometer. The sample was shaken in the DSHZ-300A temperature constant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine. Mettler Tolledo delta 320 pH meter was used for measuring pH. The thermo-gravimetric analysis was investigated using Mettler TGA/DSC1 simultaneous thermal analyzer (with a temperature range of 50–1000 °C, heating rate of 20 °C/min, atmosphere of N_2).

Table 1
Working parameter of AAS.

Metal	Wavelength (nm)	Passband width (nm)	Lamp Current (mA)	Burner height (mm)	Propane flow (L/min)
Cd	228.8	1.0	6.0	7.0	1.2
Cu	324.8	1.0	7.5	7.0	0.9
Zn	213.9	1.0	7.5	7.0	0.9
Ni	232.0	0.5	7.5	7.0	1.2
Co	240.7	0.5	7.5	7.0	0.9
Pb	283.3	1.0	9	7.0	1.4

3. Experimental procedures

3.1. Resin pretreatment

The PS-Cl resin sample mass was crushed to 80 mesh size as needed. The resin was conditioned by alternate treatment with 2 mol L^{-1} HCl and 2 mol L^{-1} NaOH solutions. After several alternate regeneration cycles, the resin was washed until free from regenerant and finally with distilled water. The resin was air dried to remove surface moisture.

3.2. Synthesis of ED resin

A 250 mL three-neck round bottom flask was equipped with condenser, thermometer and nitrogen gas inlet tube. Thus, a certain amount of PS-Cl and 30 mL reaction solvent were added into the flask, swelling over night. Then, a certain amount of ethylenediamine and metallic sodium used as catalyst were added into the flask. Functionalization was reacted with stirring under nitrogen atmosphere at a certain temperature. After completing the reaction, the product was carefully washed several times with acetone and ether in turns to remove of an excess of diamine and amide solvent. After that the obtained resin was dried in vacuum at 50 °C.

Selected two types of solvent as the reaction system was 1,4-dioxane and DMF. The PS-Cl used in synthesis experiment was 20.0 mg. The amount of ethylenediamine depending on the different molar ratio (ED:Cl = 2:1, 3:1, 4:1, 5:1) was 13.0 mg, 19.4 mg, 25.9 mg, 32.4 mg, respectively. The range of temperature in reaction system was 40, 60, 80, 100 °C.

3.3. Batch experiment

Batch experiments were performed under kinetic and equilibrium conditions. 15 mg treated ED resin was weighed and added into a conical flask, in which a desired volume of acetic acid–sodium acetate (HAc–NaAc) buffer solution was added. After 24 h, a required amount of standard solution of Cu(II) was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Cu(II) were similarly measured.

3.4. Column experiment

Continuous packed bed studies were performed in a fixed bed mini glass column (ø 3 mm × 30 cm) with 100.0 mg resin ($D/L = 1/20$). The ED resin in the column was pre-soaked for 24 h before starting the experiment. The Cu(II) solution at a known concentration and flow rate was passed continuously through the stationary bed of sorbent in up-flow mode to avoid channeling of the effluent. The experiment was continued until a constant Cu(II) ions concentration was obtained. The column studies were performed at the optimum pH value determined from batch studies and at a constant temperature of 25 °C to be representative of environmentally relevant conditions.

3.5. Application in tea samples

3.5.1. Collection and preparation of samples

The four types of commercially tea samples were taken from the vicinity of Zhejiang province at the east part of China, viz. west Lake Longjing, Meijiawu Longjing, Jingning Hui-Ming, Suichang Longgu Beauty. With distilled water to remove sediment in tea, dry and then crushed, baked in oven 105–110 °C for 2–3 h. The 3.0000 g of crushed tea samples was taken in a PTFE beaker, added 20 mL nitric acid, sealed overnight, and then heated on a hot plate until sample completely dissolved. After cooling to room temperature, 10 mL 30% H_2O_2 was added to continue to be digestive fluid until non-brown NO_2 gas generated. The resulting solution was transferred into PTFE bottle.

3.5.2. Pre-concentration and determination procedure

Proposed pre-concentration procedure was tested with model solutions prior to determine the trace copper in samples. An aliquot of a solution containing Cu(II) ions was placed in a column after the pH of solution was adjusted. The column was preconditioned by passing buffer solution with the same pH value through the column, and then the model solution was passed through the column at a certain flow rate. The adsorbed Cu(II) ions on the column were eluted by using 3 mL of hydrochloric acid solution. The eluent was analyzed for the determination of copper concentration by AAS. The copper content of samples was determined in accordance with atomic absorption spectrophotometry of GB/T5009.57-2003 (China) tea analytical methods.

4. Results and discussion

4.1. Synthesis and characterization of ED resin

4.1.1. Selectivity of reaction conditions

The effects of reactive solvent, the molar ratio of reagent and temperature on the yield of ED resin have been investigated and optimal reaction condition has been found according to N content (N%) and functional group conversion (FGC, %). Reaction solvent has been identified as the most important variable governing the synthesis of resin. From the results, DMF is preferable compared with 1,4-dioxane according to N content (DMF, 7.608%; 1,4-dioxane, 7.508%) under 100 °C, for 12 h. The study temperature of ethylenediamine is in the range of 40–100 °C according with its boiling point 116–117 °C. Overall the above results, the optimum conditions are as follows: DMF as reaction solvent, reaction temperature of 100 °C and molar ratio of ED to PS-Cl at 2:1 (Fig. 1). The nitrogen contents and the functional group capacity of ED resin synthesized under the optimum condition are 7.608% and 2.71 mmol FG g^{-1}, respectively (Fig. 2).

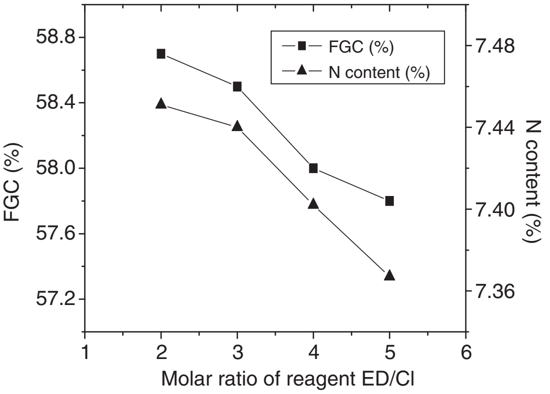


Fig. 1. Influence of molar ratio of reagent ED/Cl on N content and the percentage conversion of functional group. 12 h, DMF, 100 °C.

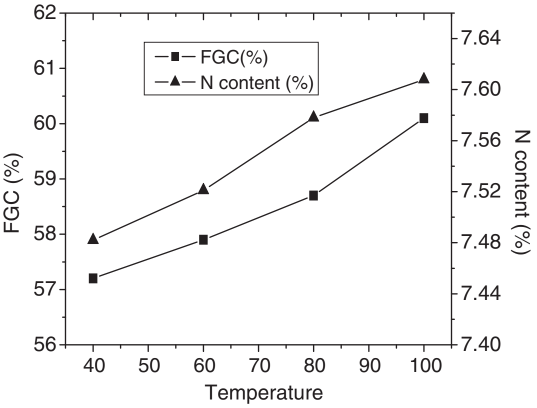


Fig. 2. Influence of reaction temperature on N content and the percentage conversion of functional group. 12 h, DMF, ED/Cl = 2.

4.1.2. FT-IR spectra

To identify the possibility of ethylenediamine bonding to PS-Cl resin, IR spectra were obtained (Fig. 3). In general, it is observed that there are significant changes in the IR spectra of PS-Cl resin and ED resin. By comparison with the curve of PS-Cl resin, the characteristic peak of 1263 and 671 cm^{-1} disappears in the curve of ED resin, and new band appears at 1684, 1550 and 853 cm^{-1}, which is the characteristic absorbance of –NH– group. The spectrum of ED resin shows that the characteristic single spectrum band of the secondary amine appears around 3400 cm^{-1}, indicating that PS-Cl resin reaction with ED are dual-link, that is, the two amines of molecular chain involved in the polymer cross-linking reaction. The dual-link will lead to additional crosslinking between macromolecule chain, enhance degree of crosslinking, simultaneity some dual-link could be formed in the same polymer chain. Therefore, the synthesis route to resins is shown schematically in Scheme 1.

4.2. Batch experiments

4.2.1. Influence of pH on the sorption of six metal ions

The pH of aqueous solution has been identified as the most important variable governing the adsorption capacity of adsorbent [21]. The study is restricted up to maximum pH 6.0, due to hydrolysis of metal ions at higher pH. The influence of pH on the adsorption behavior of ED resin for Cu(II), Ni(II), Cd(II), Co(II), Zn(II), Pb(II) metal ions is illustrated in Fig. 4 that the uptake of metal ion as a function of hydrogen ion concentration is in the range of pH 3.0–6.0 for an initial concentration of metal ions 5.0 mg/30.0 mL with 15.0 mg ED resin at 25 °C, 100 rpm. It can be easily seen that the ED resin of sorption capacity for Cu(II) is far more than for other metal ions. It is deduced from the results that Cu(II) ion can be easily separated from these metal ions using ED resin. The highest adsorption capacity for Cu(II) was 237 mg g^{-1} at pH 6.0, much more than paper [16–18] reported. The ED resin shows high selectivity and adsorption capacity for copper. Therefore, the adsorption performance of ED resin for Cu(II) ion studies at pH 6.0 in the HAc–NaAc system.

4.2.2. Adsorption kinetics

The adsorption kinetics of Cu(II) ions onto ED resin has been investigated for an metal ions concentration of 5.0 mg/30.0 mL with 15.0 mg ED resin and various temperatures, i.e. 15 °C, 25 °C, 35 °C. Several kinetic models are available to examine the controlling mechanism of adsorption from a liquid phase on the ED resin

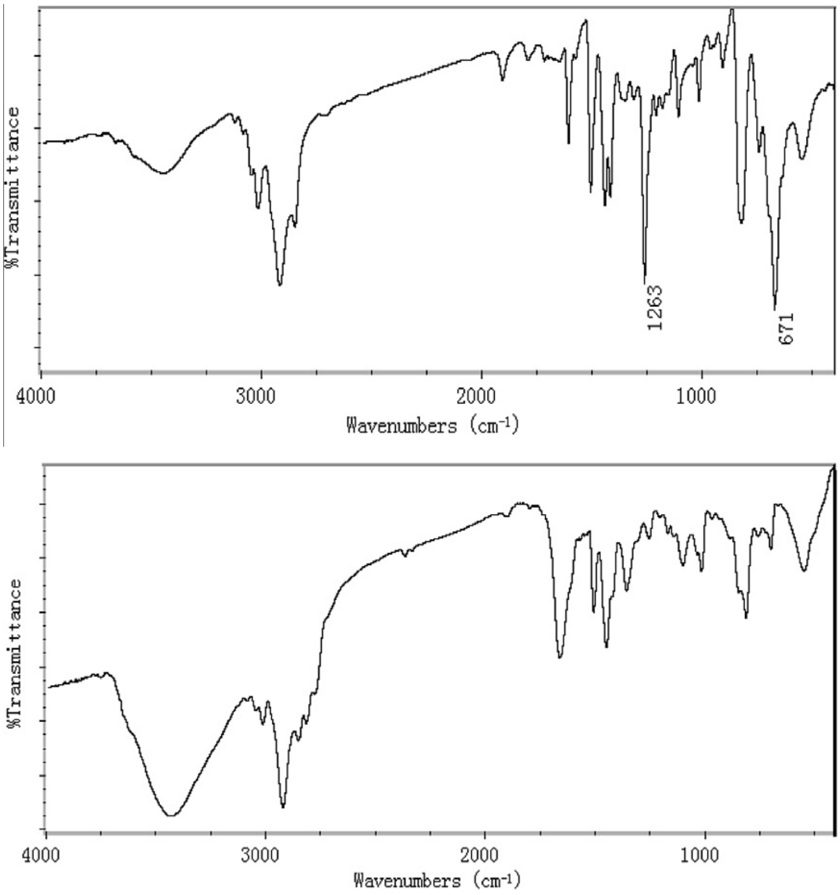
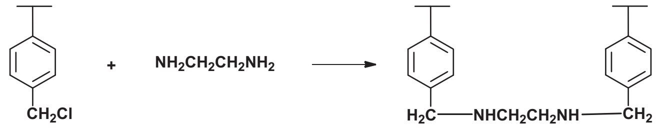


Fig. 3. The infrared spectra of PS-Cl resin and PS-ED resin.



Scheme 1. Synthesis route for ED resin.

and to interpret the experimental data obtained. The kinetics of adsorption can be described by the Lagergren-first-order rate expression [22,23] that is given by:

$$\ln(Q_e - Q_t) = \ln Q_1 - k_1 t \tag{1}$$

The pseudo-second-order kinetic model equation [24–26] is given as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_2^2} + \frac{t}{Q_2} \tag{2}$$

where Q_e and Q_t are the amounts of Cu(II) ions adsorbed on the adsorbent at equilibrium and at various times t (mg g^{-1}); Q_1 and Q_2 are the calculated adsorption capacity of the Lagergren-first-order model and the pseudo-second-order model (mg g^{-1}), respectively; k_1 and k_2 are the rate constant of the Lagergren-first-order model (h^{-1}) and the pseudo-second-order model (g mg^{-1} h^{-1}).The fitting validity of these models is traditionally checked by the linear plots of $\ln(Q_e - Q_{t)}$ vs t, and t/Q_t vs t, respectively. From the slope and intersection of the straight line obtained, the corresponding constant values for the Lagergren-first-order and pseudo-second-order kinetic models, for each temperature studied, provide the respective

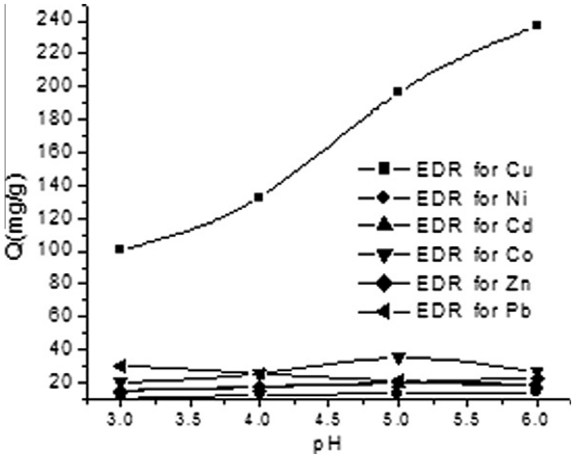


Fig. 4. The capacity of ED resin in different pH, Metal ions 5.0 mg/30.0 mL, 15.0 mg ED resin , at 25 °C, 100 r/min, in the pH ranged from 3.0 to 6.0.

kinetic constants, k_1, k_2, R_1^2, R_2^2, and Q_1, Q_2 parameters. The correlation coefficient (R_2^2) for the pseudo-second-order equation is better than the correlation coefficient (R_1^2) for the Lagergren-first-order equation, ranging from 0.9809 to 0.9851 and 0.9052 to 0.9814, respectively. Moreover, the experimental-calculated capacity of the pseudo-second-order model produces good fittings, as observed in Table 2. Thus, good linearity of the pseudo-second-order plots and a much better agreement with a comparison of Q_e values (experimental and those obtained from the slopes of the second-order plots) are indicated that the interactions would follow the

Table 2
Comparison of different kinetics models of ED resin adsorption.

T (°C)	Q_e (mg g^{-1})	Lagergren-first-order			Pseudo-second-order		
		k_1 (h^{-1})	Q_1 (mg g^{-1})	R_1^2	k_2 (g mg^{-1} h^{-1})	Q_2 (mg g^{-1})	R_2^2
15	179	0.83	376	0.9814	0.93×10^{-3}	205	0.9851
25	222	1.25	400	0.9052	1.51×10^{-3}	246	0.9809
35	257	1.65	420	0.9707	1.87×10^{-3}	302	0.9822

pseudo-second-order kinetics [27]. This means that the pseudo-second-order kinetic model can describe the Cu(II)/ED resin adsorption system studied in our work.

4.2.3. Adsorption isotherms

The Langmuir and Freundlich isotherms are studied in 30 mL solutions with the initial metal ions concentration varying in the range of 0.07–0.20 mg mL^{-1} with 15.0 mg ED resin at desired pH, 100 rpm and 15 °C, 25 °C, 35 °C.

The adsorption data are analyzed to see whether the isotherm obeyed the Langmuir [28] and Freundlich [29] isotherm models. The linear forms of the Langmuir and Freundlich isotherms are represented by the following equations:

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \tag{3}$$

Freundlich isotherm:

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \tag{4}$$

where Q_e is the equilibrium Cu(II) ions concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium Cu(II) ions concentration in solution (mg mL^{-1}), $Q_{\max}$ is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir constant and related to the free energy of adsorption; K_F is Freundlich constant and n (dimensionless) is the heterogeneity factor. The plots of C_e/Q_e versus C_e (Langmuir) for the adsorption of Cu(II) ions onto ED resin give a straight line of slope $1/Q_{\max}$ and intercept $1/Q_{\max}K_L$; by plotting lg C_e versus lg Q_e (Freundlich) to generate K_F and n from the intercept and the slope, respectively. One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent [30]. The other Freundlich constants n is a measure of the deviation from linearity of the adsorption. The numerical values of n at equilibrium lay between 1 and 10, indicating that Cu(II) ions is favorably adsorbed by ED resin at all the studied temperatures.

The Langmuir and Freundlich parameters for the adsorption of Cu(II) ions onto ED resin are being listed in Table 3. It is evident from these data that the adsorption of Cu(II) ions onto ED resin is fitted well to the Langmuir isotherm model than that of the Freundlich isotherm model, as indicated by the R^2 values and the adsorption capacity values in Table 3. The Langmuir model is the best-known isotherm for describing adsorption from aqueous solution. The Langmuir model assumes that there is no interaction between the adsorbate molecules. The adsorption is localized in a monolayer. The maximum adsorption capacity ($Q_{\max}$) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for Cu(II) ions. A comparison of the maximum capacity of ED resin with that of some other adsorbents reported in literatures is given in Table 4 [31–35], indicating that ED resin possesses a good capacity to pre-concentrate Cu(II) in aqueous solution.

Table 3
Isotherm constants for the adsorption of Cu(II) on ED resin at various temperatures.

T (°C)	Langmuir			Freundlich		
	$Q_{\max}$ (mg g^{-1})	K_L (mL mg^{-1})	R_L	n	K_F	R_F
15	344	3.23	0.9991	1.39	465	0.9869
25	435	3.83	0.9951	1.63	511	0.9778
35	555	3.60	0.9969	1.57	174	0.9654

4.2.4. Thermodynamic parameters

In any adsorption procedure, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amounts of Cu(II) ions adsorbed at equilibrium at different temperatures, which were 15, 25 and 35 °C, have been examined to obtain thermodynamic parameters for the adsorption system.

The changes in the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated to the adsorption process and were determined by using following equations [36]:

$$\Delta S = (\Delta H - \Delta G)/T \tag{5}$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

where R is the gas constant and T is the absolute temperature as mentioned in Arrhenius equation. K_d is the distribution coefficient of the adsorbate (Q_e/C_e).

The plot of $\ln K$ versus $1/T$ gives the straight line from which ΔH and ΔS is calculated from the slope and intercept of the linear form. Result shows the values of thermodynamic parameters of Cu(II) ions adsorption on ED resin. The negative value of ΔG (-19.4 to -15.4 kJ mol^{-1}) confirms the spontaneity of the adsorption process with increasing temperature and the positive value of ΔH (42.8 kJ mol^{-1}) suggests that the adsorption is endothermic in nature. Although there are no certain criteria related to the ΔH values that define the adsorption type, the heat of adsorption values between 5.0 and 100 kcal mol^{-1}, which are heats of chemical reactions, are frequently assumed as the comparable values for the chemical adsorption process. In addition, the values of ΔS (202 J K^{-1} mol^{-1}) are found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process [37].

Table 4
Comparison of the maximum adsorption capacities of Cu(II).

Various adsorbents	Maximum adsorption capacity of Cu(II)/(mg/g)
Collagen-tannin resin	16.64
MA-DTPA chelating resin	40.0
Modified silica aerogels	51.02
Mesoporous silica material	62
Cross-linked magnetic chitosan–isatin Schiff's base resin	103.16
ED resin (present study)	237

4.2.5. Elution

To find out the optimum eluent and the optimum concentration of the eluent, 15.0 mg ED resin adsorbed Cu(II) ions was separated and shaken with eluent until to equilibrium. The concentration of Cu(II) ions in aqueous phase was determined and then the percentage of elution was obtained. In our work, 12 mL HCl solution with different concentrations (0.5–3.0 mol L^{-1}) were employed and good results were obtained. The elution percentage is 98.1% with 0.5 mol L^{-1} HCl while it is all 100% with 1.0, 2.0, 3.0 mol L^{-1} HCl. It shows that the percentages of elution could reach 100% for Cu(II) with 1.0 mol L^{-1} HCl.

4.3. TG analysis

The thermo-gravimetric analysis (TGA) curves for the ED resin before and after the adsorption of Cu(II) ions are showed in Fig 5. When the temperature is lower than 400 °C, EDR presents an outstanding thermal stability. However, at the temperature range of 100–500 °C, EDR-Cu demonstrate two decomposition steps: one is at 200 °C and the other one is at 450 °C. These results mentioned above indicate that the ED resin within the adsorption of Cu(II) ions can lower the thermal stability and accelerate the decomposition rate.

4.4. Column experiments

4.4.1. Dynamic adsorption and desorption

4.4.1.1. Dynamic adsorption. Batch experimental data are often difficult to apply directly to the fixed bed sorption column because isotherms are unable to give accurate data. The fixed bed column operation allows more efficient utilization of the adsorptive capacity than the batch process. One of the main tools used in the investigation of the efficiency in adsorption columns is the breakthrough analysis. The volume of the treated wastewater was determined by multiplying the breakthrough time with the volumetric flow rate (θ).

The column sorption performance of ED resin for Cu(II) ions was tested at various inlet Cu(II) concentrations and flow rate under 298 K. The effect of flow rate on the sorption characteristics of ED resin in the continuous flow fixed column was examined by varying the flow rate in the range of 0.4–0.8 mL min^{-1} while the inlet Cu(II) concentration was 0.05 mg mL^{-1}, 0.10 mg mL^{-1}, 0.15 mg mL^{-1}, respectively.

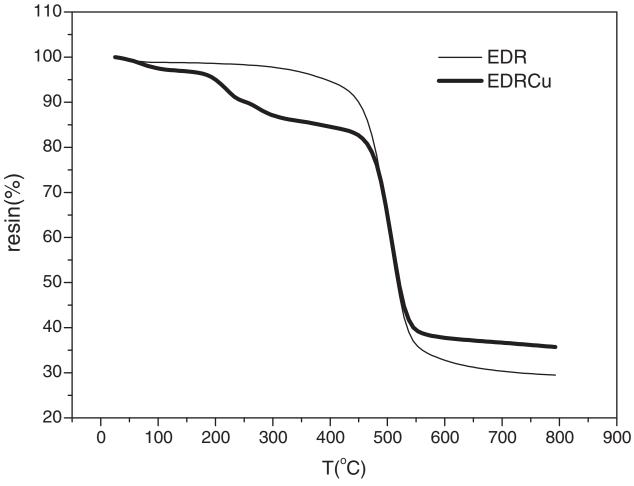


Fig. 5. The thermo-gravimetric analysis (TGA) curves for the ED resin before and after the adsorption of Cu(II) ions.

Total adsorbed Cu(II) quantity (Q; mg g^{-1}) in the column for a given feed concentration and flow rate is calculated from the following equation:

$$Q = \int_0^v \frac{(C_o - C_e)}{m} dV \qquad (7)$$

where m (g) is the mass of the adsorbent, C_o (mg mL^{-1}) and C_e (mg mL^{-1}) are inlet Cu(II) concentration and outlet Cu(II) concentration, respectively. Successful design of a column adsorption process requires prediction of the concentration vs time profile or breakthrough curve for the effluent. The maximum sorption capacity of ED resin is also in design. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form [38]:

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp[K_T(Qm - C_oV)/\theta]} \qquad (8)$$

where K_T is the Thomas rate constant (mL min^{-1} mg^{-1}) and θ is the volumetric flow rate (mL min^{-1}), m is the mass of the resin (g), C_o and C_e are inlet Cu(II) concentration (mg mL^{-1}) and outlet Cu(II) concentration (mg mL^{-1}), separately. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_T Q m}{\theta} - \frac{K_T C_o}{\theta} V \qquad (9)$$

The kinetic coefficient K_T and the adsorption capacity of the bed Q can be determined from a plot of $\ln[(C_o/C_e) - 1]$ vs $1/\theta$ at a certain flow rate.

The adsorption data were evaluated from the Thomas model and the uptakes (Q) with respect to the initial concentration passed at different flow rates are presented, at the initial concentration of 0.1 mg mL^{-1}, the breakthrough curve follows the typical S-shape curve for column operation. Although the flow rate increases from 0.6 mL min^{-1} to 0.8 mL min^{-1}, the breakthrough curves almost overlaps (Fig. 6). Compared with lower flow rate, breakthrough volume of higher flow rate is little discrepancy and the peak shape of that is still steep, consequently, 0.6 mL min^{-1} is employed. The dynamic sorption capacity of ED resin for Cu(II) ions calculated from Eq. (7) in optimal condition is 245 mg g^{-1}, which approximates to that from Thomas model. It is more than the static sorption capacity because the contact time of the ion concentration with resins is transitory in the dynamic adsorption process. A high concentration accompanied with ED resin all along provides a high driving force for the adsorption process and this may explain why higher adsorption capacities were achieved in the column [39,40].

4.4.1.2. Dynamic desorption. Efficient elution of adsorbed solute from ED resin in column is essential to ensure the reuse of resin for repeated adsorption/desorption cycles. Desorption curve plot the effluent percentage versus elution volume from the column at a flow rate of 0.3 mL min^{-1}, less that the sorption flow rate so that volume of elution is less which helps in easy handling the

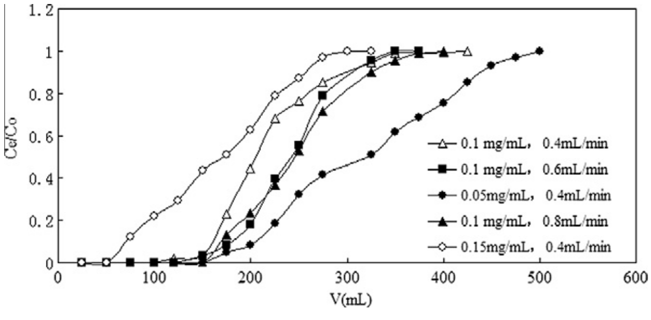


Fig. 6. Dynamic desorption curves.

metal ions. Therefore, economical metal recovery is possible. It is observed that the total volume of eluent is 50 mL and desorption process takes 2.5 h, after which further desorption is negligible. Therefore, the 1.0 mol L^{-1} HCl eluant could help in easy handling and removing of Cu(II).

4.4.2. Resin stability

The resin stability was checked by subjecting the resin to several loading and elution experiments. The capacity of ED resin is found to be practically constant (variation 2–3%) after its repeated use for more than 10 times, thus indicating the multiple use of resin column is feasible.

4.4.3. Effect of concomitant ions

Metal ions in tea are mainly potassium, calcium, magnesium, strontium, barium, iron, manganese, zinc, copper, cobalt, nickel, cadmium and lead. The effect of few metal ions is monitored in order to calculate interference on the adsorption of Cu(II) ions. The concentration ratio of 1:2000 was used for Ca, K, Mg, 1:100 for Fe, Mn, 1:50 for Zn, Co, Ni, Cd and 1:25 for Pb. The cations were added as their nitrates or chlorides and the pH of solution was adjusted. The test does not show any significant effect on the sorption of Cu(II) ions. It concludes that sorption of calcium, magnesium, potassium ions is entirely ignored because of the sorption rate 100% for Cu(II) ions after adjusting the pH of solution. Moreover, among anions only zinc, cobalt and lead reduce the sorption in the range of 2–6% for Cu(II) ions (Fig. 7). Therefore, potassium, calcium and magnesium have no effect on the determination.

4.5. Applications

Since it is found that the preconcentration method is useful for the preconcentration of trace copper, the method is applied to the determination of copper (total copper) in tea samples under optimal experimental conditions. Depending on the concentrations of Cu(II) ions in the studied samples, a 200 mL of tea sample solutions were passed through the column under the optimum conditions determined experimentally. In order to determine the accuracy of the method, the proposed procedure has been applied to the analysis of copper in the standard materials. Under selected conditions, the recoveries of Cu(II) ions in 200 mL solutions, enriched and determined 10 times simultaneously, are in 95–100%. The precision of the method for a standard, evaluated as the relative standard deviation (R.S.D., $n = 11$), was 3.5%. The limit of detection (3σ), defined as the concentration of analyte giving signals equivalent to three times, the standard deviation of the blank plus the net blank intensity for 200 mL of sample volume, were 8.6 μg L^{-1}.

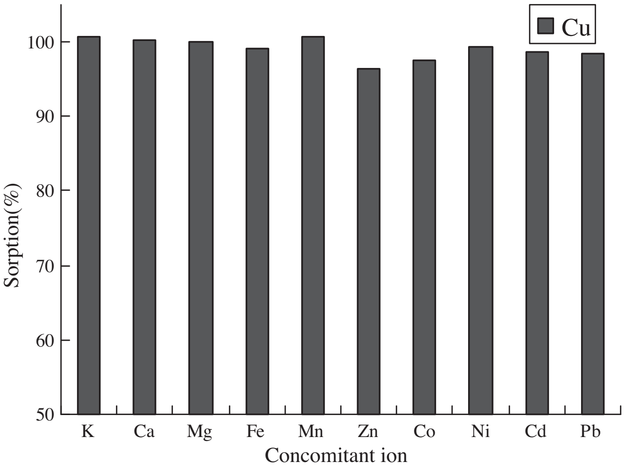


Fig. 7. Effect of concomitant ions on the sorption of Cu(II) ions.

Table 5
Analysis of Cu(II) ions in tea samples using atomic adsorption spectrometry.

Ion	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
West Lake Longjing			
Cu	0	14.43 ± 0.12	–
	5.0	19.51 ± 0.10	101.6
Meijiawu Longjing			
Cu	0	21.81 ± 0.15	–
	5.0	26.75 ± 0.09	98.8
Jingning Hui-Ming			
Cu	0	15.97 ± 0.09	–
	5.0	20.93 ± 0.13	99.2
Suichang Longgu Beauty			
Cu	0	24.05 ± 0.11	–
	5.0	29.09 ± 0.17	100.8

In order to determine the accuracy of the method, the proposed procedure has been applied to the analysis of copper in the standard reference materials of 1000 μg mL^{-1} Cu(II) (GBW(E)080534, water). The solution contained 5 μg L^{-1} of Cu(II) was added to the tea samples. The treated sample solutions and standard solutions were introduced into the column system in the same way as described previously. The working solutions were treated and the concentrations of Cu(II) were determined according to the proposed procedure. The analytical results (Table 5) for the standard materials are in good agreement with the determined values. The Cu(II) concentrations were found to be in the range of 14.43–24.05 μg L^{-1}, which were not higher than the maximum allowable levels restricted by international regulations on tea samples quality including WHO and other authorities. The results demonstrated the applicability of the AAS method and indicated that the ED resin is essentially free from interferences when applied to the pre-concentration of tea samples.

5. Conclusion

In the research, a new composite chelating resin which has N donor atoms has been synthesized. FTIR and elemental results indicate that the immobilization of ED onto PS-Cl is accomplished. The material offers the versatility to complex different metal ions due to the presence of the [$H_2N–CH_2–CH_2–NH_2$] ligand. Furthermore, the results of the present investigation shows that ED resin is a potentially useful adsorbent for the separation of Cu(II) ions from mixed solution. The kinetics of adsorption of Cu(II) on ED resin are complex and while the results are tested with models based on the Lagergren-first-order and pseudo-second-order, close conformity could be obtained with pseudo-second-order mechanism. It is evident from the experimental data that the adsorption of Cu(II) ions onto ED resin fitted well with Langmuir isotherm model than Freundlich isotherm models. The adsorption process is endothermic and spontaneous at ambient higher temperatures. Meanwhile, Thomas model is applied to experimental data obtained from dynamic studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. In conclusion, ED resin can satisfactorily be considered as an alternative application for separation and pre-concentration of Cu(II) from tea samples before determination.

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