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Preconcentration and Determination of Copper in Aqueous Solution with Epoxy Resin-based Monolithic Column Containing Large Interconnected Pores

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Preconcentration and Determination of Copper in Aqueous Solution with Epoxy Resin-based Monolithic Column Containing Large Interconnected Pores

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Abstract: A novel monolithic column containing large interconnected pores was simply prepared from epoxy resin and triethylenetetramine (TETA) and pore-forming reagent (polyethylene glycol, PEG-1000) by *in-situ* polymerization. PEG-1000 was both solvent at the initial stage and phase-separation reagent at the later stage of polymerization reaction. Its structure was characterized by Fourier transform-infrared spectra (FTIR) and scanning electron microscopy (SEM), respectively. The results showed that the pore characteristics of monoliths depended strongly on the amount of PEG-1000. A column method has been established for the preconcentration and determination of copper(II) combined with inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a simple glass-tipped tube. The adsorption-desorption characteristics of the monoliths for Cu(II) in aqueous solution were investigated in detail. The ion concentrations in batch adsorption experiments were determined by ICP-AES. Copper ions could form complexes with the amino groups of the monoliths, and be quantitatively retained in the pH ranges of 5.0–9.0. The uploaded column was eluted by 1.0 mol L^{-1} HNO_3 and recovery of Cu(II) was more than 97%.

Keywords: Monolithic column, porous adsorbent, epoxy resin, preconcentration, determination, copper, ICP-AES

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INTRODUCTION

With developing of industry (e.g. the electroplating and metal-finishing industry), metal ions are more and more released into the environment system and lead to serious pollutions (1). The preconcentration and determination of metal ions (e.g. copper) from aqueous samples waste have received increasing importance in environmental evaluation and protection in recent years (2). Though numerous methods have been described for preconcentration of copper, there are many disadvantages, such as the lower adsorption capacity of ion chromatography (3), ir-regenerated material of water soluble polymer adsorbent (4), and tedious syntheses of organic reagents for solvent extraction (5), plenty of organic solvents and reagents (6), mass transfer limitation of ionic imprinting technology (7, 8), lower selectivity and adsorption capacity of ion-exchange resins (9), and so on. Chelating resins are generally efficient in the removal and recovery of heavy metal ions because of their physical and chemical stabilities (10–12). There have been many reports on the concentration and separation of trace elements in sample solutions by means of different chelating moieties immobilized on various synthetic and natural polymeric networks (13).

An efficient adsorbing material should consist of a stable and insoluble porous matrix having active ligand groups that interact with heavy metal ions (14). Epoxy resin is an ideal matrix because it is inexpensive, stable under acidic and alkali conditions, non-swelling, high thermal resistance, and has a simple and rapid preparation process (15, 16). The specificity of a particular ligand toward target metal ions is the result of a conventional acid-base interaction between the ligand and the metal. Matejka (17) and Wang (18) suggested that alkaline earth-metal cations do not strongly coordinate with amine N-atoms and therefore are not taken up by the tertiary amine in adsorbent materials. Hence, epoxy resin and triethylenetetramine (TETA) were selected as basic materials of chelating adsorbent in this paper.

Meanwhile, the macroporous adsorbent possesses a higher adsorption capacity and velocity of mass transfer than the conventional solid-phase adsorbent does. The existence of macropores would provide convenient channels for metal ions into the interior of adsorbents when they were used in adsorption of metal ions in aqueous solutions. In this study, a novel macroporous resin was prepared from epoxy resin and TETA by using the microphase separation polymerization method (19, 20). In the preparation process of polymer, the polyethylene glycol (PEG-1000) was used as a solvent at the initial stage and phase-separation reagent at a later stage of polymerization reaction. After polymerization completion, PEG-1000 was completely removed from the polymer by the water-cleaning process and the macropore structure formed. Moreover, the porosity could be easily controlled by adjusting added amounts of PEG-1000.

The shapes of porous adsorbents are mainly particulate or fiberized. In recent years, porous monolithic stationary-phase media for high-performance separation of inorganic and organic ions has attracted increasing interests (21). Because of easy and cheaper preparation, high capacity and performance, simple and reproducible column filling, extremely high porosity, transport based on convection and better hydrodynamic properties compared to conventional packed columns, and the easy production in various shapes and dimensions in contrast to membranes, the monolithic stationary-phase have been widely applied in conventional liquid-chromatography (LC) (22, 23). The preparation of monoliths mainly utilized inorganic oxides of silica or titania or polymer matrixes (24). The polymer-based monoliths are usually prepared via the single-step *in-situ* copolymerization of monomers (e.g. methacrylates, acrylamide, styrene and their derivations), cross-linkers, initiators, inert solvents, and porogens (25). In this article, a new polymer-based monolith was simply and successfully prepared by epoxy resin and TETA and PEG-1000.

At present, more reported applications of monoliths in other fields are increasing continuously and gradually, such as molecular imprinted polymer monoliths (MIPMs), μ-HPLC, solid-phase micro-extraction (SPME), capillary electrophoresis (CE) (26), ion chromatography (IC), frontal affinity chromatography (FAC) (27), immobilized metal-chelate chromatography (IMAC) (28), micro-fluid chip devices (29), and preparative chromatography (30). While the monoliths have been already applied in many chromatographic interaction modes, there are only few reports about the application of the monoliths for conventional column chromatography. The target analytes were mainly focused on relatively large organic molecules and biomolecules (e.g. DNA, protein and viruses) (31, 32), and the inorganic ions were relatively neglected (21). So, we selected copper ion as target analyte of preconcentration and determination on prepared monolithic column.

To our knowledge, the epoxy resin-TETA monolithic column has not been employed previously for the preconcentration and determination of Cu(II) from aqueous solution. The synthesis, structure, and evaluation of the monolith for the adsorption of Cu(II) were investigated in the present article.

EXPERIMENTAL

Instruments and Apparatus

An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for all metal-determinations. The instrumental parameters were those recommended by the manufacturer. Nicolet NEXUS 460 FT-IR spectroscopy (Nicolet Instrument Corporation, USA.) was employed to recorder FT-IR spectra of the monoliths. A model pHS-3CT digital pH meter (Shanghai Dazhong Analysis Instrument Factory, China) was used to measure pH values. The flow rate of liquid through columns was controlled by a model BT00-100M peristaltic pump (Baoding Laonger Precision Pump

Limited Company). The shape and surface morphology of the monoliths were examined on a scanning electron microscope (S-570, Hitach, Japan). Super constant temperature bath vibrator (Nantong Experimental Instruments Factory, Jiangsu Province, China) was used for controlling temperature.

Reagents and Standards

Stock solutions (1000 mg L^{-1}) of the elements were prepared by dissolving appropriate amounts of nitrate salts in 1.0% HNO_3 and further diluted daily prior to use. The pH was adjusted with diluted HNO_3 and $NH_3 \cdot H_2O$. Epoxy resin, triethylenetetramine, PEG-1000 and other reagents were purchased from the Shanghai Chemistry Regent Limited Company, P. R. China. They were not purified further.

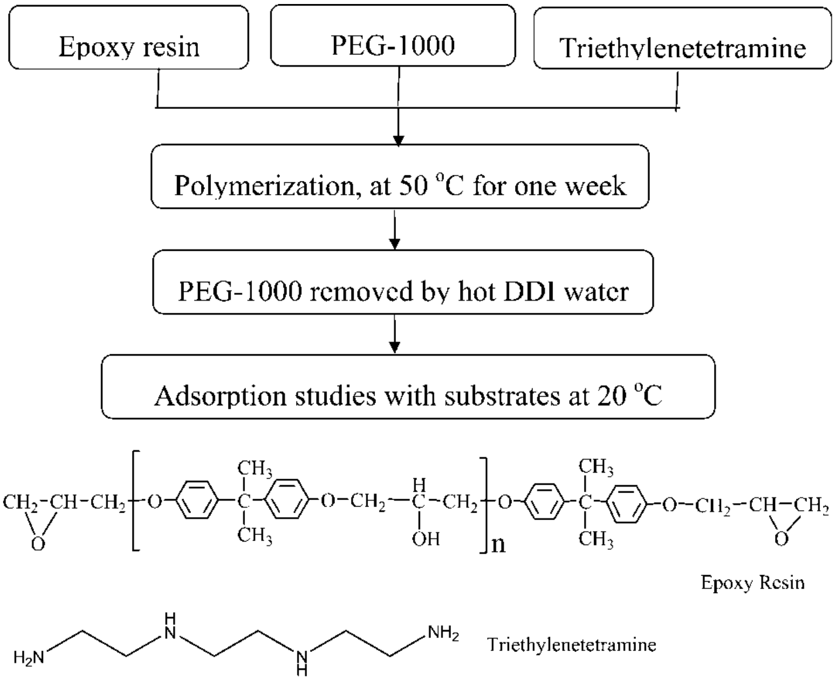
Unless otherwise stated, all water is 18 MΩ cm distilled de-ionized water (DDI) purified with a Milli-Q system (Millipore, USA) and all reagents used were of analytical grade and all solutions were prepared with DDI water. Standard lab-ware and glassware used were repeatedly cleaned with HNO_3 and rinsed with DDI water, according to a published procedure.

Preparation of Monolithic Column

3.0 g epoxy resin and 1.0 g TETA were dissolved in equal amounts of melted PEG-1000 under strong agitating. The mixture presented transparent ropy solution, and then was poured into an i.d. 1.0 × 10.0 cm glass-tube the bottom of which could be controlled by a stopcock. With polymerizing, the transparent liquid gradually turned white as a result of phase separation in the process of curing. The completion of the polymerization reaction needed one week in an oven at 50°C, and then the white monolith with the glass-tube was cut into 1.0 × 2.0 cm pieces. The 1.0 cm i.d. × 2.0 cm length columns were repeatedly treated with a large amount of hot DDI water till one could remove all of PEG-1000 and dried in a vacuum oven at room temperature for at least 48 h (Scheme 1).

General Procedure for Adsorption-Desorption of Cu(II)

The selected monolithic column was soaked in DDI water overnight. The standard solutions of metal ions were pipetted into conical flasks and were adjusted to pre-fixed pH with aqueous ammonia and dilute HNO_3. Then, the solutions were passed through the adsorbing columns at a flow rate that could be controlled with a peristaltic pump. The ion concentrations in the discharged solutions were determined by ICP-AES and the binding capacities of ions on the monolithic column could be calculated. The adsorbed monolithic



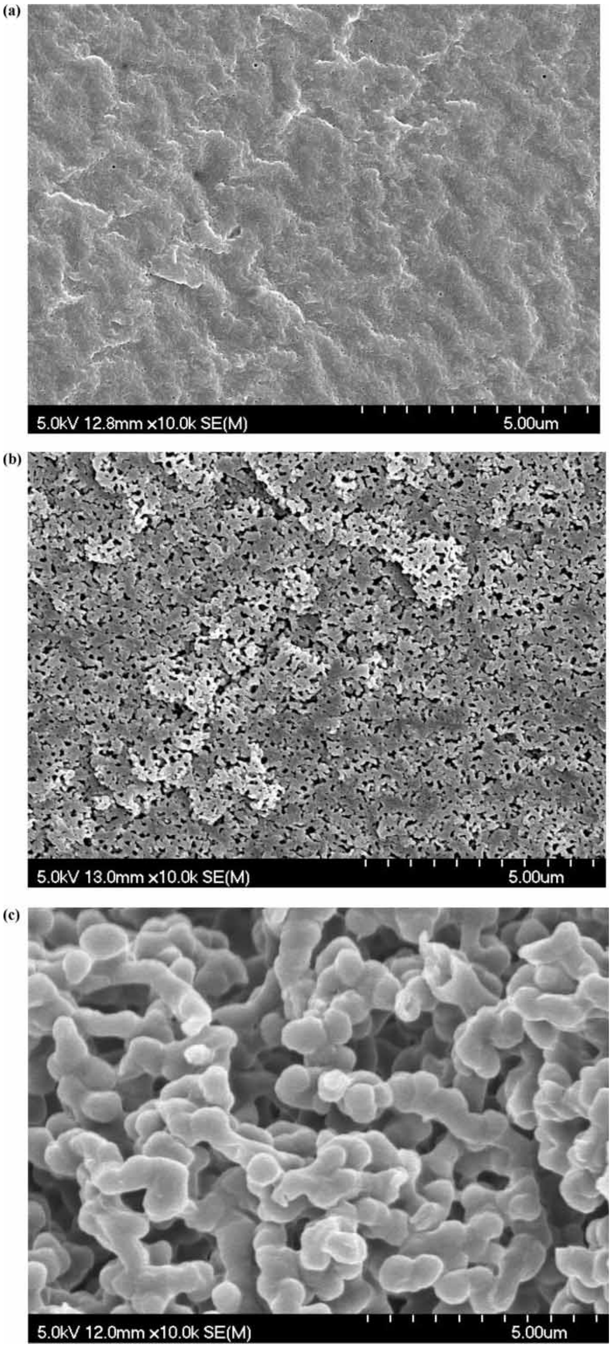
Scheme 1. Schematic representation of the monolithic column preparation.

columns were eluted with 1.0 mol L^{-1} HNO_3 and the desorbed ions were measured with complex titration or ICP-AES. All experiments were repeated three times and the average results were adopted except for a special explanation in the text.

RESULTS AND DISCUSSION

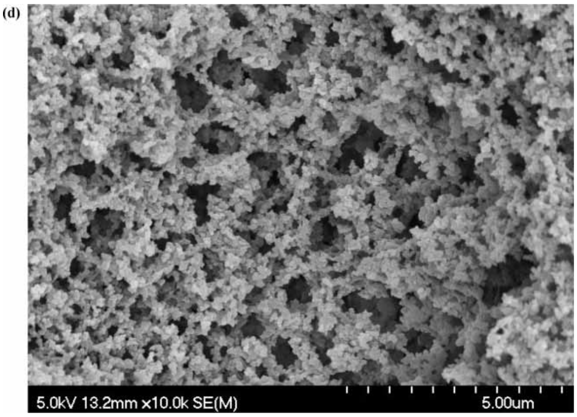
SEM Observations and Characteristics of the Monoliths

The SEM images (Scheme 2) visually showed the morphological of the monoliths. There were abundant pores distributed on the surface of the epoxy-TETA monoliths. Evidently, the pores were formed in the polymerization stage and PEG-1000 was used as pore forming agent. At the early stage of polymerization, PEG-1000 was dissolved in the mixture of epoxy resin and TETA at 50°C. With polymerizing, the solubility of PEG-1000 in the reaction system was decreased and PEG-1000 was completely separated out in the end. However, the phase separation process did not result in precipitation macroscopically. The crude product presented a white bulk polymer and PEG-1000 was not separated from epoxy-TETA bulk polymer. In other words,



Scheme 2. SEM photograph of porous epoxy-TETA monoliths. Amount of PEG-1000 (wt%): (a) 30%; (b) 45%; (c) 60%; (d) 75%.

(*Continued*)



Scheme 2. Continued.

the epoxy-TETA solid was not precipitated from PEG-1000, and micro-phase separation occurred in the polymerization process. Porous or gel resin could be differentiated by visual appearance, the former is white and opaque, the latter is ivory-white and transparent (20, 33). The epoxy-TETA monoliths were transparent and rigid absence of PEG-1000. This fact also sustained the above presumption.

From Scheme 2, the porosity was gradually increased with increasing amount of PEG-1000. Similar to the membranes, they are characterized by very large and highly interconnected pore-channels that can reach over 1 μm in diameter. They could be applied in different fields of chromatography ranging from very small scale (micro- and nanoscale), through analytical to preparative scale (34). Considering the mechanical strength of materials, the **(c)** monolith was selected as experimental adsorbents. The monoliths have large interconnected pores of 0.1–3.0 μm size with a mean pore size of 1 μm. The porosity was determined and calculated to 72%, which was larger than the ratio of PEG-1000 to the monolith. It probably comes from two aspects: micro-pores in the inner of resin micro-particles and cavity formed by micro-particles stacking in curing process.

Analysis of FT-IR Spectra

The existence of the functional groups in epoxy-TETA monolith was verified and analyzed by the FT-IR (KBr) spectrum (35, 36). Figure 1 shows the FT-IR spectra of pure epoxy resin (curve **a**), epoxy-TETA monolith absence of Cu(II) (curve **b**) and that of epoxy-TETA monolith saturated with copper ion (curve **c**). The characteristic absorption peak at 913.07 cm^{-1} of epoxy group (curve **a**) has been disappearing in the epoxy-TETA monolith (curve

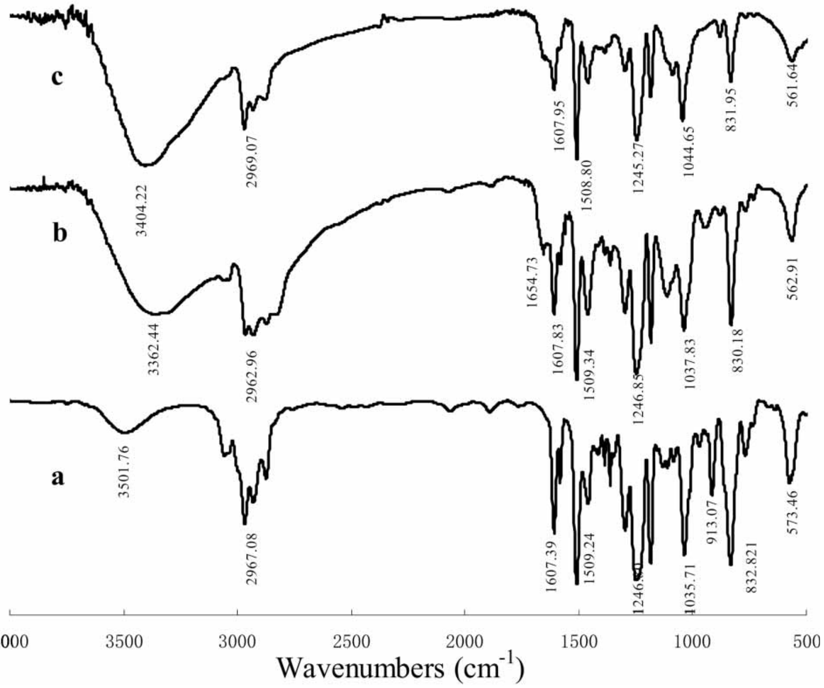


Figure 1. FT-IR spectra: **a** pure epoxy resin, **b** epoxy-TETA monolith absence of Cu(II), **c** epoxy- TETA monolith saturated with copper ions.

b). The peaks at 3362.44 cm^{-1} (-N-H) and 1654.73 cm^{-1} (-C-N-) have been present in curve **b**. It means that epoxy groups have completely reacted with triethylenetetramine. Comparing curve **b** with curve **c**, the absorption peak position of -N-H has changes from 3362.44 cm^{-1} (curve **b**) to 3404.22 cm^{-1} (curve **c**). It means that the coordination interaction of the Cu(II) ion and amidogen has strongly changed the stretching vibration of N-H. In other words, the Cu(II) ion has effectively coordinated with amidogen.

Effect of pH and Flow Rate on Cu(II) Adsorption

Equal concentrations of Cu(II) standards were diluted to equal volumes and adsorbed on monolithic column in the pH range 1–9 as described above. Considering hydrolysis of metal ion in strong alkali solution, pH above 9.0 was not tested. The results show that the sorption quantity of Cu(II) increases with the pH value increases. The sorption quantity is very low below pH 4.0 owing to the protonation of resin. Cu(II) ions can be quantitatively enriched with recovery >95% at pH 5.0–9.0, and pH 5.0 is chosen as enrichment pH for further experiments.

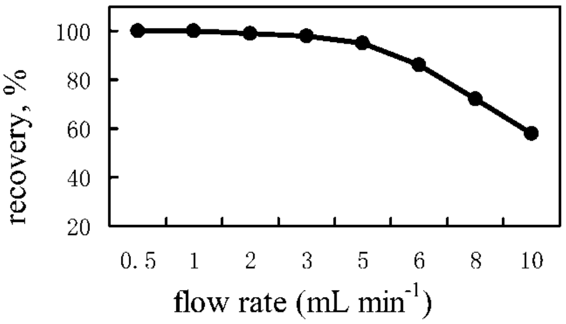


Figure 2. Effect of flow rate (mL min^{-1}) on recovery. 1.0 μg mL^{-1} Cu(II), 20°C.

When using the recommended procedure, the flow rate for adsorption of the analytes on monolithic columns was varied from 0.5 to 10.0 mL min^{-1}. The results (Fig. 2) show that Cu(II) ions can be quantitatively adsorbed at flow rates below 5.0 mL min^{-1} and 4.0 mL min^{-1} flow rate was selected for further study. The pores in the monoliths are open and highly interconnected, forming a network of channels. The mobile phase is forced to flow through them, transporting the sample molecules to the active (binding) sites by convection. This results in an extremely fast mass exchange between the mobile phase and the stationary phase than the more traditional sized particle-packed columns (34).

Adsorption Capacity of the Monolith

The maximum adsorption capacity of the monolith was determined by static experiments. The dried monolith was taken out, cut into small pieces, and weighed accurately. They were placed in each of the eight conical flasks. A stock solution of Cu(II) ion was added to each flask and diluted to an equal volume. The acidity of each solution was adjusted to pH 5. The vessels were shaken for 12 h at 20°C in a mechanical vibrator. The concentrations of Cu(II) in solution were measured by ICP-AES until equilibrium was reached and adsorption capacity of Cu(II) ions on the monoliths could be calculated. As can be seen in Fig. 3, the amount of Cu(II) adsorbed per unit mass of small monolith pieces increased with the initial concentration of Cu(II). In order to reach the "saturation", the initial Cu(II) concentrations were increased till the plateau values (maximum adsorption capacity values) were obtained. The average maximum adsorption capacity was 92 mg g^{-1} for three replicate measurements.

Effect of Foreign Ions on Copper Adsorption

Different foreign ions, NaCl, KBr, KI, $NaNO_3$, Na_3PO_4, Na_2SO_4, $Ca(NO_3)_2$, and $Mg(NO_3)_2$, respectively were added to each equal quantity of the metal

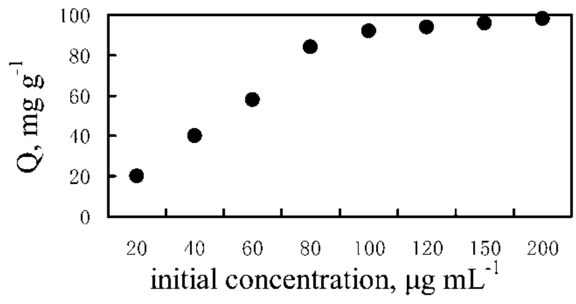


Figure 3. The effect of Cu(II) initial concentration on the maximum adsorption quantity of epoxy resin-TETA monolith. pH 5.0, 20°C.

ion standard solution, then adsorbed and determined according to the general procedure. The results show that the tolerance limits of the investigated electrolytes of the monolithic column are 20–100-fold of copper ions, indicating that the monolithic column can be suitably used as adsorbent for Cu(II) in high electrolytes. The reported tolerance limit is defined as the ion concentration causing a relative error $< \pm 5\%$.

However, the similar metal ions (such as Ni^{2+}, Zn^{2+}, Co^{2+}) have intensive influence of Cu(II) ion adsorption on epoxy-TETA monolithic column. This mainly comes from similar chemistry properties of these metal ions, especially, the chelating abilities with amidogen-N atoms. In order to improve ion-selectivity of epoxy-TETA monoliths, chemistry modification or ion-imprinted technology could be adopted in the future research works (7).

Elution Characteristic and Repeated Use

Under strong acid conditions, the coordination interaction of uploaded Cu(II) ions could be easily disrupted and subsequently Cu(II) ions are released from the monolithic column into the desorption medium. Hence, elution of Cu(II) ions from the monolithic column is possibly made by passing of HNO_3 solution as a desorption reagent. It can be observed that, in the experimental conditions used, Cu(II) ions could be quantitatively eluted with 1.0 mol L^{-1} H NO_3 with recovery >95%.

When using the recommended procedure, the flow rate for desorption of the analytes on monolithic columns was varied from 0.5 to 5.0 mL min^{-1}. The results (Fig. 4) show that Cu(II) ions can be quantitatively eluted at flow rates below 2.0 mL min^{-1} and 1.0 mL min^{-1} flow rate was selected for further study.

To test the stability, it was subjected to several loading and elution batch operations. The sorption-desorption conditions are referenced according to the above experiments. Then the monolithic column was treated with DDI water

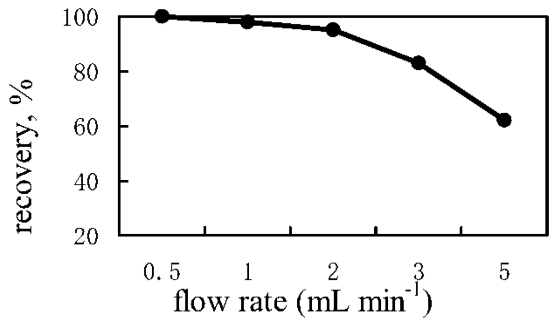


Figure 4. Effect of elution reagent flow rate (mL min^{-1}) on recovery. 1.0 mol mL^{-1} HNO_3, 20°C.

till neutral equilibration. The operating capacity was calculated from the loading and elution tests. The results from three tests agreed within <5% error up to 20 cycles of repeated experiments. The monolith shows better reusability and stability towards Cu(II). Therefore, the monoliths are suitable for repeated use without decreasing their adsorption capacities significantly. The stability of porous monolithic column comes from not only the chemical and mechanical stability of epoxy resin (15, 16), but also from the structure characteristic of monoliths. In more traditional sized particle-packed columns, the inter-particle porosity can reach values up to 40%, above this value the columns would become unstable and collapses. For monoliths this value can be up to 90% or more. This is possible because the whole column consists of a single, mechanically stable skeleton (37).

CONCLUSION

The monolithic columns find broad applications as a special class of chromatography supports. Silica and polymer-based monoliths have been produced with either bonded or coated ionic sites for anion and cation separations. However, the development of new stationary phase adsorption materials should be more concerned (38). In the present work, a new epoxy resin-based monolith containing large interconnected pores as an ion SPE adsorbent was prepared first, and the porosity could be easily controlled by adjusting added amount of PEG-1000.

Although monoliths are widely used due to the advantages described above, there are only a few applications of monolithic columns in the field of preparative chromatography. This may be mainly attributed to difficulties in preparing them for industrial applications (39, 40). And the initial work in this area focused mainly on the application of porous monolithic matrix for purification of large molecules. The future of porous monolithic media in preconcentration and determination of ions looks very promising and interesting. In this paper, a column preconcentration procedure for Cu(II) in aqueous solution was successfully established. The monolithic column exhibits good characteristics for adsorption-desorption of Cu(II). Moreover, the epoxy resin-triethylenetetramine monolith has a superior reusability and stability, which can be repeated to use 20 cycles with recoveries not less than 95%.

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