Ion-imprinted carboxymethyl chitosan–silica hybrid sorbent for extraction of cadmium from water samples

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ABSTRACT

A new ion-imprinted carboxymethyl chitosan-functionalized silica gel sorbent was synthesized by surface imprinting technique using Cd(II) as the template, carboxymethyl chitosan (CMCS) as the functional monomer and glutaraldehyde as the cross-linking agent for the selective adsorption of Cd(II) from aqueous solution. The optimum batch experimental conditions (pH, amount of adsorbent, contact time) and column experimental conditions (concentration and volume of elution solution) were evaluated. The maximum static adsorption capacity of the ion-imprinted sorbent for Cd(II) was 20.7 mg/g. The enrichment factor of Cd(II)-imprinted polymer for Cd(II) was 257. The relative selectivity factor values of Cd(II)/Pb(II), Cd(II)/Co(II) were 5.3 and 1.5, respectively. The recoveries of water samples were about 98.0–104.0% (R.S.D. $\leq$ 0.8). The proposed method was successfully applied to determination of Cd(II) in water samples with satisfactory.

1. Introduction

With the industrial development, a large variety of cadmium is discharged into the environment, causing serious environmental pollution and threatening people's health, even at low concentrations. According to the standards for drinking water quality, the concentration limit of cadmium ions is 0.005 mg/L. Because of low concentration of Cd(II) and complex matrix interferences in environmental samples, various separation and preconcentration methods had been used prior to determination [1–3]. Solid-phase extraction (SPE) is one of the most used techniques for separation of selected analytes due to its simplicity, rapidity, minimal cost, and low consumption of reagents [4,5]. However, the basic disadvantage of traditional SPE adsorbents is lack of selectivity for metal ions [6], which leads to the interference of other species for the determination of the target metal ions. Recently, it was extensively reported that the selectivity of SPE can be enhanced by using molecularly imprinted polymer (MIP), which had synthetic recognition sites with high selectivity and affinity for the template [7]. Ion imprinted polymer (IIP) is similar to MIP, but they can recognize metal ions after imprinted and retain all of virtue of MIP [8]. Different kinds of imprinted polymers have been reported for recognition of cadmium ion [9–11].

Chitosan (CS) is the N-deacetylated products of chitin that is the second most abundant natural biopolymer after cellulose. As an abundantly available low-cost adsorbent, this natural polymer and the derivatives have received great attention in the application of metal adsorption due to the high ratio of hydroxyl groups and amine groups [12–15]. However, the poor mechanical and chemical stability of pure CS limits the application [16]. Many chemical modifications have been applied to improve the physical and chemical properties of CS. Coating CS on preformed microparticle, e.g., silica gel with chemical cross-linking process has shown a successful method [17,18]. The essence lies in the combination of the functionality of CS and advantages of silica gel, e.g., large surface area and excellent mechanical resistance. To the best of our knowledge, the analysis of real water samples has not been well documented with Cd(II)-imprinted CS-functionalized silica gel sorbent.

In this study, we synthesized a Cd(II)-IIP using carboxymethyl chitosan (CMCS) as functional monomer and glutaraldehyde as the cross-linker on support matrix of silica gel by surface imprinted technology. This adsorbent was packed in a column and used for the separation and preconcentration of Cd(II) prior to their determination by flame atomic absorption spectrometry (FAAS). The effects of pH, amount of adsorbent, contact time, concentration and volume of elution solution and coexisting ions on the preconcentration and determination of cadmium ions were investigated. The proposed method was applied to determine cadmium in tap and lake water in Fuzhou University.

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2. Experimental

2.1. Reagents and apparatus

Carboxymethyl chitosan (CMCS, average molecular mass ca. 300,000, degree of deacetylation 85%, and degree of substitution is 80%) was purchased from Dalin Xindie Chitin Company (Dalin, China). Glutaraldehyde (25% water solution) was purchased from Shanghai Chemical Reagents Company (Shanghai, China). Silica gel (60–100 mesh) was purchased from Qingdao Ocean University Chemical Company (Qingdao, China) and 3-aminopropyltrimethoxysilane was purchased from Nanjing Yudeheng Fine Chemical Company (Nanjing, China).

A flame atomic absorption spectrometer (TAS-986) purchased from Beijing Pgeneral Company (Beijing, China) was used for the determinations of metal ion. FT-IR spectra in KBr were recorded using a TENSOR 27 FT-IR (Bruker, Germany) and scanning electron microscopy (Nova NanoSEM 230, FEI, USA) were used for the characterization of the prepared materials. ASAP 2020 surface analyser (Micromeritics, USA) was used for the research of surface area. A pHS-10C digital pH meter purchased from Xiaoshan Instrument Factory (Hangzhou, China) was used for the pH adjustments. A self-made glass microcolumn (45 mm × 1.6 mm i.d.) was used in this study.

2.2. Preparation of new sorbent

2.2.1. Preparation of aminopropyl silica gel

In order to remove any adsorbed metal ions and increase the content of −OH, silica gel was activated according to the previous report [19]. Activated silica gel (10 g) was suspended in 100 mL of 10% (v/v) 3-aminopropyltriethoxysilane in dry toluene. The mixture was refluxed with stirring at 110 °C for 12 h. The resulting aminopropyl silica gel (APSG) was filtered, washed successively with toluene, ethanol and acetone, and then dried for 12 h at 60 °C under vacuum.

2.2.2. Preparation of aminopropyl silica gel-bound glutaraldehyde

The APSG was added into a solution of 90 mL buffer solution (pH 8.0) and 10 mL glutaraldehyde. The mixture was stirred for 1.5 h at room temperature. The resulting product was filtered, washed with deionized water, and then dried under vacuum.

2.2.3. Preparation of carboxymethyl chitosan functionalized silica gel (IIP-CMCS/SiO₂)

1 g of CdCl₂·2.5H₂O was dissolved in 100 mL of 2% CMCS solution under stirring for 2 h at room temperature, and then the silica gel was added to this solution, followed that the solution was stirred

and refluxed for 2 h at 60 °C. The product was filtered, washed with deionized water, and dried under vacuum. In order to remove the Cd(II) confinement in the selective cavity of the polymer, successive washing with 2 mol/L HCl were performed. The final product was washed with deionized water and dried under vacuum. The same procedure was performed, however, without adding CdCl₂·2.5H₂O, which was designed as non-imprinted polymer (NIP).

2.3. Batch experiments

The imprinted polymer was stirred in a solution with suitable amount of metal ion for a fixed period of time at room temperature. The unextracted heavy metal ion in the solution phase was measured by FAAS.

The amount of metal ion adsorbed per unit mass of the imprinted polymer was calculated from the following equation:

$$Q = \frac{(C_o - C_e)V}{W}$$

where C_o and C_e are the initial and equilibrium concentrations of metal ion, respectively, V is the volume of metal ion solution, and W is the weight of the adsorbent.

The distribution and selectivity coefficients of Pb(II) and Co(II) with respect to Cd(II) can be obtained from the following equation:

$$D = \left[\frac{C_o - C_e}{C_e} \right] \left(\frac{V}{W} \right)$$

D represents the distribution coefficient.

A selectivity coefficient α can be defined as

$$\alpha = \frac{D_{Cd}}{D_M}$$

M represents Pb(II) and Co(II) ions.

2.4. Column experiments

In the column experiments, the imprinted polymer was packed in a glass tube and a solution containing metal ions was adjusted to a suitable pH and percolated at a certain flow rate. The heavy metal retained on the column was eluted with a suitable eluant and determined by FAAS.

3. Results and discussion

3.1. Characteristics of the prepared sorbent

Fig. 1 represented the surface morphology of IIP-CMCS/SiO₂ sorbent and NIP sorbent. The NIP sorbent exhibited a slightly rough
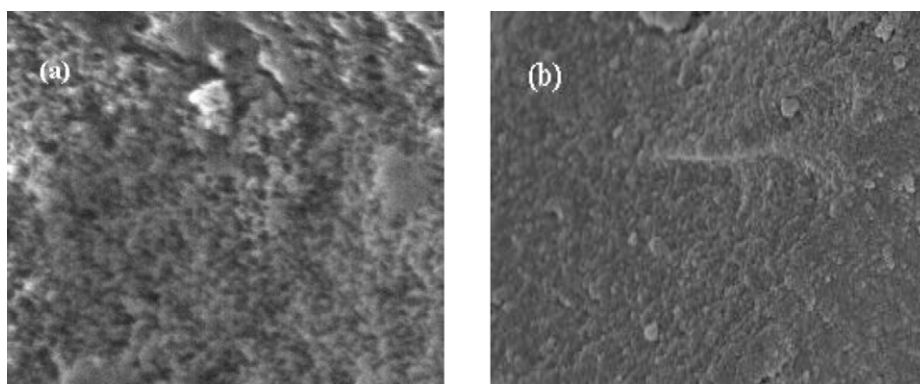

Fig. 1. SEM of IIP-CMCS/SiO₂ (a) and NIP (b) sorbents.