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Enhancement of selective Cu(II) sorption through preparation of surface-imprinted mesoporous silica SBA-15 under high molar concentration ratios of chloride and copper ions

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ABSTRACT

We synthesized and characterized surface-imprinted poly (ethyleneimine) (PEI)-grafted mesoporous silica SBA-15 (Cu-imprinted PEI-SBA-15) for selective Cu(II) sorption from aqueous solutions. To enhance the Cu(II) selectivity of Cu-imprinted PEI-SBA-15, Cu(II) loading on PEI-SBA-15 was increased via Cu(II) sorption under high-molar-concentration ratios of chloride (Cl) and Cu(II) ions. Then, selective Cu(II) sorption sites were increased through imprinting processes (crosslinking and elution) on Cu-loaded PEI-SBA-15. Selective experiments were performed using Cu-imprinted PEI-SBA-15 prepared at various $[Cl^-]/[Cu(II)]$ ratios, ranging from 2 to 1000. In multinary solutions containing divalent ions, such as Cu(II), Pb(II), Zn(II), Ni(II), and Co(II), Cu(II) selectivity was highest (79.62) at a $[Cl^-]/[Cu(II)]$ ratio of 500; the relative Cu(II) selectivity for Cu-imprinted PEI-SBA-15 over PEI-SBA-15 was 29.24. In multinary solutions containing Cu(II) along with trivalent and tetravalent ions, such as Al(III), Cr(III), and Zr(IV), the Cu(II) selectivity was also highest (3.40) at a ratio of 500; the relative Cu (II) selectivity was 3.96. In this study, we demonstrated that the Cu(II) selectivity of surface-imprinted SBA-15 could be enhanced through its preparation under high $[Cl^-]/[Cu(II)]$ ratios.

1. Introduction

Ion-imprinting technology (IIT) is an advanced technology to selectively recognize target ions in aqueous media using ion-imprinted materials [1]. Polymerization imprinting techniques have been used to prepare ion-imprinted polymers via polymerization of functional monomers around template ions. After polymerization, the template ions are extracted from a polymer matrix through an elution process to generate binding cavities for target ions [2,3]. However, ion-imprinted polymers have several drawbacks, including incomplete removal of template ions, formation of diffusion barriers, low binding capacity, slow mass transfer, and slow binding kinetics [4]. Surface imprinting techniques have been advanced to overcome these problems. During the preparation of ion-imprinted materials, binding cavities are formed on or near the surface of a support matrix through an imprinting process [1,4]. In surface imprinting techniques, silica particles are preferred as a support matrix due to their physico-chemical stability, thermal resistance, and high reusability [5,6]. Organic functionalities, such as organosilanes and polyamines, are grafted on the silica particles to synthesize ion-imprinted materials [7–10].

Poly (ethyleneimine) (PEI) is a cationic polyamine containing large numbers of amine groups on the macromolecules; branched PEI has primary, secondary, and tertiary amine groups [11–13]. PEI has an excellent sorption capacity for heavy metal ions through very strong metal chelation [14–18], which should facilitate its immobilization on a matrix to be used for heavy metal removal due to its water solubility [19]. Some researchers have used PEI for the preparation of ion-imprinted materials [20–23]. An and Gao [21] grafted PEI on silica gel surfaces and crosslinked with epichlorohydrin to synthesize Cr(III)-imprinted silica for selective Cr(III) removal. Liu et al. [22] used PEI as a functional macromolecule, mesoporous silica SBA-15 as a support matrix, and epichlorohydrin as a crosslinking agent to prepare Co(II)-imprinted SBA-15. Wang et al. [23] synthesized Fe(II)-imprinted silica through functionalization of silica surfaces with PEI for the selective removal of Fe(II) from a rare earth solution.

Copper (Cu) is used widely in industries, such as mining, paint manufacturing, electroplating, steel production, electronics, and finishing processing. Copper-containing industrial wastewater is discharged primarily as a form of cupric ion (Cu^{2+}) into water environments, causing serious environmental and health problems. Cu(II) is known to be a toxic, carcinogenic heavy metal ion [24]. Several researchers have synthesized Cu(II)-imprinted silica using

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diethylenetriamine [9,25], [3-(2-aminoethylamino)propyl] trimethoxysilane [26,27], N-[3-(trimethoxysilyl)propyl]ethylenediamine [28], poly (allylamine) [10], N,N′-bis(4-hydroxysalicylidene)ethylene-1,2-diamine [29], and oligomers [30], as organic functionalities for selective sorption of Cu(II) from aqueous solutions. Most of these researchers did not use a crosslinker to fix Cu(II) complex sites on the silica during the imprinting process (Table S1, Supplementary Information (SI)). Studies related to grafting PEI on silica particles and using a crosslinker during imprinting to produce Cu(II)-imprinted silica are limited. Only one study, reported by Gao et al. [20], prepared ion-imprinted silica gels through grafting of PEI onto the surfaces of silica particles and ionic imprinting with epichlorohydrin as a crosslinker. They performed batch experiments in binary solutions containing Cu(II)/Zn(II) and Cu (II)/Ni(II) to examine the selective Cu(II) removal by imprinted silica gels.

The aim of this study was to synthesize and characterize surface-imprinted PEI-SBA-15 (Cu-imprinted PEI-SBA-15) in the selective sorption of Cu(II) from aqueous solutions. This study focused on the two parts: (i) examine the influence of molar concentration ratios of chloride (Cl) and Cu(II) ions on the Cu(II) loading on PEI-SBA-15 and (ii) observe the effect of imprinting processes on the increase of selective Cu(II) sorption sites in Cu-loaded PEI-SBA-15. Selective experiments were performed in multinary solutions of divalent metal ions and of trivalent/tetravalent metal ions using PEI-SBA-15 and Cu-imprinted PEI-SBA-15. Selectivity and relative selectivity were calculated from the experiments to evaluate the enhancement of Cu(II) selectivity.

2. Materials and methods

2.1. Preparation of PEI-SBA-15

All chemicals used in the experiments were purchased from Sigma Aldrich (Saint Louis, MO, USA) unless stated otherwise. A schematic diagram of the synthesis of PEI-SBA-15 is shown in Fig. S1 (SI). Prior to the preparation of PEI-SBA-15, mesoporous silica SBA-15 was synthesized following the method from Liu et al. [31]. Based on the synthetic SBA-15 particles, PEI-SBA-15 was prepared following the method modified from Wang et al. [23]. 3-chloropropyl-SBA-15 (CP-SBA-15) was prepared through reacting 5 g of SBA-15 with 100 mL of (3-chloropropyl)trimethoxysliane (≥97%) at 80 °C for 6 h, to which 1 mL of deionized water was added intermittently. CP-SBA-15 was filtered and dried at 60 °C overnight. After cooling, CP-SBA-15 particles were obtained through fragmentation with a mortar and pestle. To prepare PEI-SBA-15, 50 mL of poly (ethyleneimine) (PEI) solution (50% in H_2O) and 1 g of CP-SBA-15 were stirred at 90 °C for 6 h. After the reaction, PEI-SBA-15 was filtered, washed with deionized water, and dried at 60 °C overnight. After cooling, PEI-SBA-15 particles were obtained through fragmentation with a mortar and pestle.

2.2. Preparation of Cu-imprinted PEI-SBA-15

Cu-imprinted PEI-SBA-15 was prepared following a method modified from Wang et al. [23]. A schematic diagram for the synthesis of Cu-PEI-SBA-15 is presented in Fig. 1. In the synthesis of Cu-imprinted PEI-SBA-15, the following procedures were used to enhance Cu(II) selectivity: (i) enhance the Cu(II) loading on PEI-SBA-15 via Cu(II) sorption under high molar concentration ratios of chloride (Cl) and Cu (II) ions and (ii) increase selective sorption sites for Cu(II) through imprinting processes (crosslinking and elution) on Cu-loaded PEI-SBA-15.

Prior to the preparation of Cu-imprinted PEI-SBA-15, Cu(II) ions were loaded onto PEI-SBA-15 at a fixed Cu(II) concentration of 1000 μM and molar $[Cl^-]/[Cu(II)]$ concentration ratios of 2, 50, 100, 200, 500, and 1000. Cu(II) loading on the PEI-SBA-15 was conducted by adding 1 g of PEI-SBA-15 into a 1-L solution of NaCl and Cu(II) ions under vigorous stirring for 6 h at 30 °C. Cu-loaded PEI-SBA-15 was filtered and dried at 60 °C overnight.

To prepare Cu-imprinted PEI-SBA-15, 1 g of Cu-loaded PEI-SBA-15 and 0.25 g of ethylene glycol diglycidyl ether (EGDE, Tokyo Chemical Industry Co., Tokyo, Japan) as a crosslinker were added into 50 mL of absolute ethanol and reacted at 25 °C for 4 h under continuous stirring. After the reaction, particles were washed with 1 l of 0.1 M HCl solution to remove the template Cu(II) ions and unreacted EGDE and then washed with deionized water to neutralize the pH. The particles were filtered and dried at 60 °C for overnight. After cooling, Cu-imprinted PEI-SBA-15 was obtained through fragmentation with a mortar and pestle.

2.3. Characterization of PEI-SBA-15 and Cu-imprinted PEI-SBA-15

PEI-SBA-15 and Cu-imprinted PEI-SBA-15 were characterized using several techniques [32]. Field-emission scanning electron microscopy (FE-SEM, Supra 55 V P, Carl Zeiss, Oberkochen, Germany) and energy-dispersive X-ray spectroscopy (EDX, AURIGA, Carl Zeiss) were used to analyze the surface morphology and elemental composition. Fourier-transform infrared (FTIR) spectroscopy (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) was used to analyze the effect of PEI impregnation and ion imprinting on PEI-SBA-15 and Cu-imprinted PEI-SBA-15. X-ray photoelectron spectroscopy (XPS, AXIS HSi, Kratos Analytical, Shimadzu, Japan) scans with Al Kα radiation ($h\nu = 1253.6$ eV) was used to analyze the chemical bonding and elements of PEI-SBA-15 and Cu-imprinted PEI-SBA-15. N_2 adsorption-desorption isotherm analysis was performed using a surface area analyzer (BELSORP-max, BEL Japan Inc., Osaka, Japan). The zeta potentials were measured using an electrophoretic light scattering (ELS) spectrophotometer (ELS-Z1000, Otsuka Electronics, Osaka, Japan).

2.4. Cu(II) selectivity experiments

Cu(II) sorption experiments were performed under batch conditions to characterize PEI-SBA-15 and Cu-imprinted PEI-SBA-15 in Cu(II) sorption. The desired concentration of Cu(II) solution was prepared by diluting a stock solution (0.1 M), which was prepared from the copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$, EP grade, Duksan Pure Chemicals). All of the batch experiments were performed at 30 °C in triplicate.

pH experiments were performed with 50 mL polypropylene conical tubes containing 30 mL solutions of PEI-SBA-15 (adsorbent dose = 1 g/L) and Cu(II) ions (initial concentration = 1000 μM), which were shaken in a shaking incubator at 120 rpm. Then, 0.1 M NaOH and 0.1 M HCl solutions were used to adjust the initial pH of the solution from 2 to 5. After reaction for 24 h, the samples were collected and filtered through a 0.45-μm membrane filter. The Cu(II) concentration was analyzed using inductively coupled plasma optical emission spectrometry (iCAP 7200 ICP-OES Duo, Thermo Fisher Scientific, Waltham, MA, USA). The Cu(II) sorption capacity (q, μmol/g) can be calculated with the following equation:

$$q = \frac{C_i - C_f}{C_a}, \tag{1}$$

where C_i is the Cu(II) concentration in the aqueous phase before sorption reaction, C_f is the Cu(II) concentration in the aqueous phase after sorption reaction, and C_a is the adsorbent dose.

Cu(II) selectivity experiments were performed in multinary solutions containing binary metals, including Cu(II), Pb(II), Zn(II), Ni(II), and Co(II). The multinary metal solutions (each metal concentration = 200 μM) were prepared with $CuCl_2{\cdot}2H_2O$, lead (II) chloride ($PbCl_2$, ≥98%), zinc (II) chloride ($ZnCl_2$, ≥98%), nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, ≥ 96%), and cobalt (II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, ≥ 95%). The solution pH was adjusted to 5 with 0.1 M HCl and 0.1 M NaOH solutions. Cu(II) selectivity experiments were performed under batch conditions (adsorbent dose = 1 g/L). First, 30 mg of each adsorbent (PEI-SBA-15 and Cu-imprinted PEI-