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Preparation of zirconium oxy ion-imprinted particle for the selective separation of trace zirconium ion from water

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A B S T R A C T

Zr(IV) oxy ion-imprinted particle (Zr-IIP) was prepared using the metal ion imprinting technique in a sol–gel process on the surface of amino-silica. The dosages of zirconium ions as imprinted target, (3-aminopropyl) triethoxysilane (APTES) as a functional monomer and teraethyl orthosilicate (TEOS) as a cross-linker were optimized. The prepared Zr-IIP and Zr(IV) oxy ion non-imprinted particle (Zr-NIP) were characterized. pH effect, binding ability and the selectivity were investigated in detail. The results showed that the Zr-IIP had an excellent binding capacity and selectivity in the water. The equilibrium data fitted well to the pseudo-second-order kinetic and the Langmuir model for Zr(IV) binding onto Zr-IIP, respectively. The saturate binding capacity of Zr-IIP was found to be 196.08 μmol g^{-1}, which was 18 times higher than that of Zr-NIP. The sequence of binding efficiency of Zr-IIP for various ions was Zr(IV) > Cu(II) > Sb(III) > Eu(III). The coordination number has an important effect on the dimensional binding capacity. The equilibrium binding capacity of Zr-IIP for Zr(IV) decreased little under various concentrations of Pb(II) ions. The analysis of relative selectivity coefficient (K_r) indicated that the Zr-IIP had an appreciable binding specificity towards Zr(IV) although the competitive ions coexisted in the water. The Zr-IIP could serve as an efficient selective material for recovering or removing zirconium from the water environment.

1. Introduction

Zirconium (Zr) is one of the abundant elements in the earth's crust, but it distributed dispersedly [1]. It is a suitable metal applied for making refractories, foundry mold, cladding nuclear fuel and controlling materials in nuclear reactors, space and metal alloys, etc. [2]. Therefore, separation and recovery of even trace amount of it from waste water can be worthwhile. Several methods such as ion exchange, solvent extraction and precipitation for the binding of this metallic ion from aqueous solution have been investigated [3]. The separation and determination processes of low levels of Zr(IV) from the water are mainly based generally on a suitable utilization of available materials and techniques [4]. However, the slow adsorption–desorption kinetics and non-ideal selective adsorption capacity are the shortcomings for the present binding materials. Therefore, it is necessary to improve the selectivity of the separated materials.

Molecular imprinted technology (MIT) is an emerging molecular recognition technique, which shapes the specific recognition sites in synthetic polymers by using templates or imprinted molecules [5]. Metal ion imprinted polymers (IIPs) are imprinting ions instead of molecules and they recognize metal ions after the imprinting. The recognition mechanism is based on MIT technique [6]. Recently, many IIPs such as Hg(II) [7], Cu(II) [8], Cr(III) [9] and Cd(II) [10] have been reported in removing some toxic heavy metal ions. But there is less selective exploration for separating the expensive rare metal of Zr(IV) in the water. Among the reported synthesis methods the metal ion imprinted polymers are prepared by different approaches including bulk, suspension and precipitation polymerization [8]. Recently, the sol–gel process is increasingly employed to synthesize the metal ion imprinted polymers. For example, Rajiv Gandhi prepared and characterized the silica gel/chitosan composite for the removal of Cu(II) and Pb(II) [11]. Arh-Hwang studied the crosslinked metal-complexed chitosans for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in the sol–gel process [12]. These experiments had the desired results and the sol–gel process showed the expected advantages including low cost and simple condition. However, it is regrettable

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that the selectivity of those IIPs is not very satisfactory. Moreover, Mo(VI) oxy ion imprinted particle (Mo-IIP) with high selectivity was prepared in a sol–gel process in our previous work [13].

In this paper, Zr(IV) ion imprinted particle (Zr-IIP) with high adsorption capacity and selectivity for Zr(IV) was synthesized in a sol–gel process. Zr(IV) was the target ion. SiO_2, TEOS and APTES were selected as the supporter, cross-linking agent and functional monomer, respectively. The optimal dosages of target and the functional monomer were investigated. The prepared samples were characterized by scanning electron microscopy (SEM), a standard Brunauer–Emett–Teller (BET) analysis, Fourier transform infrared spectrometer (FTIR) and thermogravimetric analysis (TGA) in detail. The effect of pH, the binding virtue and the selective recognition of Zr(IV) onto Zr-IIP and Zr-NIP were estimated by the static experiments. Cu(II), Sb(III) and Eu(III) were selected as the latent interferon due to their similar ionic radius. The relative selectivity coefficient (K_r) was studied in the mixture system. The effect of Pb(II) ions on Langmuir isotherm of Zr-IIP for Zr(IV) was studied in the mixture system. Zr-IIP developed in this work can serve as an efficient selective material for enriching and determining Zr(IV) from the aqueous environment. All the discussions may be beneficial to the further improvement and a theoretical direction for its potential application in practice.

2. Experimental

2.1. Materials and chemicals

Ethanol, carbinol, $ZrOCl_2{\cdot}8H_2O$, ammonia, acetic acid (AcOH), Ethylenediaminetetraacetic acid disodium salt (EDTA), Ethyl silicate (TEOS), (3-aminopropyl) triethoxysilane (APTES) and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Taijin, China). All the chemicals used were of analytical grade and obtained commercially. Distilled water used throughout the experiments was obtained from laboratory purification system.

2.2. Instrumentations

The surface micrograph and element distribution of the prepared samples were assessed by a S4800HSD scanning electron microscope (Japan). The surface area and the pore parameters of the samples were measured by an ASAP 2020 multipoint Brunauer–Emett–Teller apparatus (USA). FTIR spectra were recorded using an AVATAR 360 FTIR spectrometer with a spectral range of 4000–400 cm^{-1} (USA). Thermogravimetric analysis was performed by a NETZSCH STA 409 PC/PG (China). The concentrations of Zr(IV) were detected by ICPS-750 (Perkin Elmer).

2.3. Preparation of particles

Firstly, the uniform silica was synthesized by TEOS hydrolysis with ammonium hydroxide according to the report by Stöber et al. [14]. Secondly, 0.400 g (dry weight) of the prepared silica was added into the carbinol and dispersed by the ultrasound for 20 min. Then 2 mL APTES, 0.677 g $ZrOCl_2{\cdot}8H_2O$, 4 mL TEOS and 1 mL acetic acid were added into the above mixture in sequence, and the suspension (pH 4.5) was stirred for 12 h at room temperature. Thus Zr(IV) oxy ion-imprinted particle performed and then dried at 80 °C for 12 h. Finally, to remove Zr(IV) template, the imprinted particles were washed for 12 h with a mixture of methanol and acetic acid (9:1, v/v) by Soxhlet extraction. The products were washed for 3 times by EDTA and then dried under vacuum at 80 °C. The dry particles were stored in a sealed bottle for use. As a reference, Zr-NIP was prepared by the same protocol without the template.

2.4. Batch binding experiments

Single batch binding experiments were conducted to test the binding kinetics, isotherms and selectivity of Zr(IV) onto the Zr-IIP. All binding experiments were carried out in 150 mL flasks with 50 mL binding solution containing. After the addition of 0.05 g of the prepared particles each, the flasks were shaken at 200 rpm and 25 ± 2 °C for 12 h (having achieved the binding equilibrium). The pH of the mixture was remained at about 4.5. For the binding kinetics experiment, the specimens were sampled at defined time intervals from 2 to 720 min with 55 $\mu mol\ L^{-1}$ Zr(IV) initial concentration. The binding isotherms were investigated over various initial concentrations ranging from 22 to 1100 $\mu mol\ L^{-1}$ of Zr(IV) solution. The selectivity binding experiments were conducted by preparing single solution of Zr(IV), Cu(II), Sb(III) and Eu(III) with each initial concentration of 165 $\mu mol\ L^{-1}$. The effect of Pb(II) ions on Langmuir isotherm of Zr(IV) onto Zr-IIP were conducted by preparing mixture solution of Zr(IV)/Pb(II). The initial concentrations of Zr(IV) were 55 $\mu mol\ L^{-1}$and that of Pb(II) ranged from 0 to 110 $\mu mol\ L^{-1}$. In order to test the reproducibility, the experiments were carried in triplicates and the reproducibility was found to be within ±5%. After binding equilibrium, the saturated samples were separated by centrifugation and determined by ICP. The binding capacity (q) and efficiency (E) were calculated by the following equations [15]:

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

where q ($\mu mol\ g^{-1}$) is the adsorbate binding capacity, C_0 and C_e ($\mu mol\ L^{-1}$) are the initial and equilibrium adsorbate concentrations in the solution, respectively, V (L) is the volume of the solution, W (g) is the amount of the samples added to the solution, E (%) is the removal rate.

3. Results and discussion

3.1. Dosages selection of imprinted Zr(IV) and functional monomer

Fig. 1 shows the possible reaction mechanism of Zr-IIP preparation. In this procedure, TEOS acting as a cross-linker reagent was easy to hydrolyze under the existence of acetic acid as catalyst. One end of APTES was cross-linked with the silica during the hydrolysis process. The other end was the amino group and it acted as the functional monomer. The memory sites were formed by the coordination key between Zr(IV) ions and the amino groups. Then the template ions of Zr(IV) were removed by elution of EDTA. Finally, the recognition sites onto the Zr-IIP were shaped. The coordination number might have an important effect on the dimensional binding capacity.

The suitable dosages of the imprinted target ion and the functional monomer were crucial factors that effected on the quantity of the imprinted sites. The binding efficiency of Zr(IV) ions onto Zr-IIP was studied at different molar ratio of Zr(IV) ions to amino groups. As seen in Fig. 2, the binding efficiency of Zr(IV) was only 33% at the molar ratio of Zr(IV) to amino groups for 1:2 under the same binding condition. Amino groups could not coordinate with enough Zr(IV) ions to form the imprinted sites. The binding efficiency of Zr(IV) reached the maximum value of 55% at the molar ratio of Zr(IV) to amino groups for 1:4. It illustrated that enough imprinted ions are supplied and the maximum quantity of Zr(IV) sites formed onto the Zr-IIP at this dosages. It seemed that four coordination compounds of Zr(IV) were the main imprinted sites in the synthetic process of Zr-IIP. However, the binding efficiency