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An ion-imprinted functionalized SBA-15 adsorbent synthesized by surface imprinting technique via reversible addition–fragmentation chain transfer polymerization for selective removal of Ce(III) from aqueous solution

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HIGHLIGHTS

- Novel mesoporous surface ion-imprinted polymer was prepared by RAFT polymerization.
- High selectivity and satisfied adsorption capacity for Ce(III) were obtained.
- Ce(III)-IIP could be used as a potential adsorbent for Ce(III) removal in wastewater.
- The dynamic column performance was firstly studied to adsorb Ce(III) by Ce(III)-IIP.

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ABSTRACT

A novel Ce(III) ion-imprinted polymer (Ce(III)-IIP) has been prepared by surface imprinting technique with reversible addition–fragmentation chain transfer (RAFT) polymerization based on support matrix of SBA-15. The prepared adsorbent is characterized by FT-IR, XRD, SEM, TEM, nitrogen adsorption–desorption, GPC, and TGA. The results suggest that the surface imprinted polymer synthesized by RAFT is a thin layer. For adsorption experiments, Ce(III)-IIP is investigated to remove Ce(III) by column study at different flow rates, initial metal ion concentrations, and adsorption temperature. The dynamic kinetics analyses reveal that the overall adsorption process is successfully fitted with the pseudo-first-order kinetic model and the equilibrium time was 60 min. Meanwhile, the experimental data is in good agreement with Thomas model. Ce(III)-IIP has the excellent selectivity and regenerate property. Meanwhile, the proposed method has been successfully applied in the removal of Ce(III) in natural water samples with satisfactory results. All the results suggest that Ce(III)-IIP could be used as an excellent adsorbent for efficient removal of Ce(III) from aqueous solution.

1. Introduction

Molecular imprinting is an evolving and versatile technique for the creation of molecular recognition systems in three-dimensional cross-linked polymers, namely molecularly imprinted polymers (MIPs) [1,2]. Thanks to the remarkable recognition properties for template, MIPs have been widely applied as selective separation sorbents [3] and recognition elements in sensors [4]. Similar to MIPs, ion-imprinted polymers (IIPs), as selective sorbents for a particular chemical element, have received much attention [5,6]. However, IIP prepared by traditional technique exhibits some disadvantages such as slow mass transfer and incomplete template removal [7]. Therefore, surface imprinting technique has been proposed as a novel and more feasible alternate [8–10]. The surface ion-imprinted polymer with binding sites situated at the surface shows many advantages such as the low mass transfer resistance, good accessibility to the target species, complete removal of templates, better mechanism intensity and excellent reusability compared with the conventional imprinted materials [11–13]. The advances in this field have found that the support materials usually used include magnetic materials [14], carbon-based materials [15], silicon-based materials [16] and so on, which also achieve the excellent combination of support materials and surface imprinting technique. Recently, among various solid supports, the silicon materials selected as the support have attracted extensive research interest. However, the common

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silicon materials can often restrict the adsorption capacity of the surface imprinted polymer because of its limited surface area, which may not achieve the satisfied results.

Mesoporous silica is an excellent silicon-based material that possesses highly ordered pore structures, large surface area, tunable pore size, thick pore walls, high hydrothermal stability, and good adsorption property [17]. Therefore, several research groups have developed the surface imprinted polymer to remove cobalt [18], copper [19], lead [20] and so on, which were generally synthesized in the surface of mesoporous silica by conventional free radical polymerization. However, traditional radical polymerization processes are usually rather difficult to control with regard to chain propagation and termination and the polymers generally have a broad size distribution due to side reactions, which also normally lead to polymer networks with heterogeneous structures [21,22]. The presence of heterogeneity within the network structures of the imprinted polymer can exacerbate the broad binding site heterogeneity and loss of the template binding affinity [23].

In order to overcome these intrinsic and general limitations, controlled/living radical polymerization (CRP) techniques have drawn much attention and could be used to synthesize polymers with well defined and complex architectures in the past decades [24]. Among the CRPs developed so far, reversible addition–fragmentation chain transfer (RAFT) polymerization has proven to be one of the most versatile systems. The greatest advantage of RAFT is that no expensive agent and no undesired metal species are introduced during the polymerization process, which also are environment friendly and mild polymerization conditions [25]. Also, the processes of RAFT polymerization is thermodynamically controlled with negligible chain termination and constant slow chain growth, which remarkably improve the match in the chain growth and chain relaxation rates and thus lead to homogeneous polymer networks [26]. Moreover, the controllability of RAFT polymerization could attribute to use of reversible chain transfer agent and the resulting fast and dynamic equilibrium between active species and dormant species [27,28]. Up to now, MIPs prepared by RAFT polymerization with homogeneous structures are often used to extract toxic organic pollutants [29,30]. However, to our best knowledge, there are few reports on removal of metal elements using mesoporous material of surface ion-imprinted polymer synthesized by RAFT polymerization.

Cerium, as one of the most abundant rare earth elements and the low and medium radioactive metal elements, has attracted more attention in application. Moreover, cerium has variety of isotopes and some of them are harmful to animals and human beings because of the high chemical toxicities and radiological hazards. Therefore, in order to subsequent uses and determine the harmful cerium, selective removal of cerium from liquid and solid sources such as wastewater and soil mineral is desirable.

In the present work, a novel Ce(III)-IIP has been prepared by surface imprinting technique via RAFT polymerization based on the support matrix of SBA-15 for the first time. Ce(III)-IIP is applied to remove Ce(III) from aqueous solution by static and dynamic adsorption tests. The effects on the static adsorption behavior of the removal process parameters are studied and the equilibrium data were fitted by the Langmuir and Freundlich models. In contrast with Ce(III)-imprinted polymers prepared by cross-linked polymerization method in our previous work [31], the adsorption capacity and adsorption equilibrium time are improved dramatically due to ultra-thin thickness and homogenous coating structure. Furthermore, the removal of Ce(III) from aqueous solution by Ce(III)-IIP as adsorbent in the fixed-bed is investigated and the parameters on the column dynamics are also discussed and optimized. The breakthrough curves for the adsorption of Ce(III) are analyzed by using Adams–Bohart and Thomas models.

2. 2 Experimental

All the chemicals and apparatus can be seen in supporting information.

2.1. Preparation of Ce(III)-IIP

2.1.1. Preparation and activation of mesoporous silica (SBA-15)

The mesoporous silica SBA-15 was synthesized according to the procedure described by Zhao et al. [32]. It was then activated with HCl (3 mol/L) by refluxing.

2.1.2. Preparation of SBA-15-Cl

To prepare SBA-15-Cl, 250 mg of activated SBA-15, 4-(chloromethyl)phenyltrimethoxysilane, and 10 mL of absolutely dry toluene were introduced into a 100 mL round-bottomed flask under the atmosphere of nitrogen. Keeping under constant temperature of 90 °C, the reaction was allowed to proceed for 24 h with continuous stirring. Then, the particles were separated from the mixture by filtration. In order to remove excess 4-(chloromethyl)phenyltrimethoxysilane, the products were washed with toluene and methanol for several times, respectively. Finally, the obtained SBA-15-Cl was dried under vacuum at room temperature.

2.1.3. Preparation of SBA-15-RAFT agent

SBA-15-RAFT agent was synthesized as follows. Briefly, a certain amount of phenylmagnesium bromide solution (1 mol/L in dry tetrahydrofuran) was warmed in oil bath to 40 °C, and then carbon disulfide was added dropwise over 10 min. The reaction was kept at 40 °C for 1 h. 500 mg of SBA-15-Cl was added to the resultant brown mixture solution and the reaction was kept at 70 °C for 60 h under the atmosphere of nitrogen. Ice hydrochloric acid (1 mol/L, 25 mL) was then added. After polymerization was complete, the product was washed several times with tetrahydrofuran, methanol, and acetone. Then, RAFT agent functionalized SBA-15 (SBA-15-RAFT) was dried in vacuum at 40 °C for 24 h. At last, the pink power could be obtained.

2.1.4. Preparation of Ce(III)-IIP

In a 100 mL round-bottomed flask, 0.1 mmol of $Ce(NO_3)_3{\cdot}6H_2O$, 0.4 mmol of 4-VP, 2 mmol of EGDMA, and 100 mg of SBA-15-RAFT were dispersed into 20 mL of methanol and 5 mL of distilled water under heating and magnetic stirring. After mixing and purging the mixture with nitrogen, 5 mg of AIBN (initiator) was added into this suspension. The resultant mixture was stirred in oil bath at 60 °C for 24 h under nitrogen protection. After polymerization, the contents were cooled to room temperature, recovered by centrifugation. In order to remove unreacted ingredients, the imprinted particles were washed with methanol/distilled water (4:1, v/v) for several times. Then, the solid was treated with 2 mol/L HCl to completely leach the coordinated and non-coordinated Ce(III). At last, the polymer was centrifuged with distilled water to neutralization, dried at 60 °C under vacuum. Then, Ce(III)-IIP could be obtained. By comparison, non-imprinted polymer (NIP) was also prepared as a blank in parallel but without the addition of $Ce(NO_3)_3{\cdot}6H_2O$.

2.2. Static and dynamic adsorption experiments

Adsorption of Ce(III) from aqueous solutions was investigated in batch and dynamic experiments. The specific operating process and all of the equations used to analyze static and dynamic adsorption data were shown in Supplementary Data.

2.3. Selectivity studies

In order to measure the selectivity of Ce(III)-IIP, the binary competitive binding ability of Co(II), Pb(II), Sr(II), Cu(II), Ca(II) and Fe(III) with respect to Ce(III) was investigated by using Ce(III)-IIP and NIP, respectively. 0.02 g of Ce(III)-IIP or NIP was added into 25 mL of 5 mg/L binary metal (Ce(III)/Co(II), Ce(III)/Pb(II), Ce(III)/Sr(II), Ce(III)/Cu(II), Ce(III)/Ca(II), and Ce(III)/Fe(III)) mixed solutions at pH 5.0. Finally, the concentration of metal ions was determined by ICP-AES. The distribution coefficient K_d (mL/g), selectivity coefficient k, and the relative selectivity coefficient k' [33] were given in Supplementary Data.

2.4. Desorption and reusability experiments

Desorption and reusability experiments were also investigated in the present study, which was exhibited in Supplementary Data.