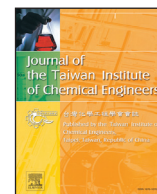




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Preparation of dual-function chelating resin with high capacity and adjustable adsorption selectivity to variety of heavy metal ions

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ABSTRACT

To simultaneously remove various heavy metals from wastewater, a novel two-step approach, which involves grafting of monomers and subsequent derivation with mixed ligands, was proposed to develop dual-function chelating resin with high capacity. Specifically, glycidyl methacrylate (GMA) was grafted onto polystyrene resin via surface-initiated atom transfer radical polymerization and followed by derivation with 5-aminosalicylic acid (ASA) as hard base and 2-(4-imidazolyl)ethylamine (IMEA) as soft base to obtain the polymeric brush-type ASA/IMEA-PGMA@PS. The adsorption property was investigated by Cu(II) and Pb(II), Cd(II) and Ag(I), as well as Fe(III) and Cr(III), which are junctional, soft and hard acids, respectively. The adsorption amounts depend largely on the ratio of two ligands. At 1:1 of ASA to IMEA, the adsorption capacities of the obtained resin are 0.87, 1.57, 0.70, 1.47, 1.90 and 1.19 mmol/g for Cu(II), Pb(II), Cd(II), Ag(I), Fe(III) and Cr(III), respectively. Moreover, the adsorbent displays strong salt tolerance and excellent reusability. Furthermore, the adsorption obeys Langmuir model and the pseudo second-order kinetics model, and is mechanically dominated by chelation interaction. These findings demonstrate that the prepared resin can be applied in the treatment of complicated saline effluent, and the proposed approach has potential to develop variety of dual-function chelating resins.

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1. Introduction

The effective removal of heavy metals from industrial wastewater has attracted much attention because of the hazardous impacts of them on organisms. Adsorption based on chelation interaction is regarded as an effective method in terms of simplicity of design and ease of operation. Consequently, there are many works on the development of chelating adsorbents during past few decades [1–4]. In general, the preparation of chelating adsorbent includes two aspects, matrix and functionalization. Because the functional groups largely dominate the selectivity and adsorption capacity, the surface functionalization of adsorbent becomes one of the important research aspects [4,5].

Adsorption selectivity essentially depends on the types of modified ligands on adsorbent. So far, a variety of chelating adsorbents have been developed and they are approximately sorted into three categories according to the hard-soft-acid-base (HSAB) theory [6]. One is the adsorbent preferring hard acids as well as junctional acids, e.g., Cr(III) [7] and Fe(III)/Al(III) [8], which employs hard bases as ligands, such as salicylic acid [8] and tannin [7]. Another

is the adsorbent better adsorbing soft acids as well as junctional acids, e.g., Hg(II)/Cu(II) [11], Cd(II)/Pb(II) [10], etc. The bonded ligands are soft bases, e.g., polyamine [9], thiol [3], heterocyclic compounds [4,11], thiourea-contained compounds [10,12], and other compounds containing N and S [2], etc. The two types can achieve better efficiency in wastewater containing hard- or soft-metals, respectively. However, in case of complex wastewater, these adsorbents cannot simultaneously remove both hard- and soft-metals effectively. To resolve this problem, the third adsorbent is developed, which enables simultaneously remove various heavy metals. The used ligands are composed of hard O and soft N or S, e.g., azo-salicylic-acid-linked compounds [13], aminated maleic anhydride [14], resacetophenone [15], anthranilic acid [16], vinylamidoxime [17], etc. Most of them require either special treatment or complex synthesis [13,17], or is materials-consuming [14,16], limiting their wide application.

In this work, our aim is to prepare a dual-function chelating resin suitable for simultaneous removal of hard and soft metals from wastewater. Instead of the third ligands, the mixture of the first and second ligands is employed to achieve this purpose. Considering that polystyrene resin (PS) is a versatile platform to prepare various adsorbents and the surface modification via surface-initiated atom transfer radical polymerization (SI-ATRP) can enhance the capacity of adsorbents [18], we

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proposed a two-step strategy to prepare the dual-function chelating resin with high capacity. Firstly, glycidyl methacrylate (GMA) was grafted via SI-ATRP onto PS to endow the surface of PS with abundant epoxy. Subsequently, the mixed ligands were immobilized onto the surface of PS. Herein, 5-aminosalicylic acid (ASA) and 2-(4-imidazolyl)ethylamine (IMEA) are easily available and are representative hard and soft bases, respectively. The application of the modified resin was tested using harmful metals, for instances, Cu(II) and Pb(II), Fe(III) and Cr(III), as well as Cd(II) and Ag(I), which are of junctional, hard and soft acids, respectively. In addition, the controllability in selectivity of the prepared resins was indicated by adjusting the ratios of two ligands on resins.

2. Materials and methods

2.1. Preparation of the ASA/IMEA-PGMA@PS

Total amount of 40 mmol with different ratios (1:0, 0:1, 1:1, 1:3, 3:1) of ASA to IMEA was dissolved into water, the solution was adjusted to pH 11.0 with NaOH, into which THF was added. The mixture was poured into 5.0 g of PGMA@PS (PGMA@PS was prepared according to our previous work [19]). The reaction was proceeded at 80 °C for 12 h. The resulting ASA/IMEA-PGMA@PS was filtered out, washed with THF, water and methanol, and dried under vacuum.

2.2. Preparation of ASA/IMEA-PS

Total amount of 10 mmol with different ratios of ASA to IMEA was dissolved in water, the solution was tuned to neutral with Na₂CO₃. The resulting solution and 64 μL of pyridine were added into the flask, in which PS (2.0 g) had been swollen in DMF for 3 h. The flask was maintained at 80 °C for 12 h. The obtained ASA/IMEA-PS was filtered, washed and dried.

2.3. Batch adsorption experiments

2.3.1. Effect of pH and salt concentration

0.100 g of various ASA/IMEA-PGMA@PS was added parallelly into 25 mL solutions of metal ion (4.0 mmol/L) with different pH or concentrations of NaCl or NaNO₃ (pH 4.5), then the mixtures were shaken under 200 rpm at 30 °C for 12 h. The supernatant was analyzed by AAS. The adsorption amount was calculated according to Eq. (1),

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is the adsorption amount (mmol/g) at equilibrium, C_0 and C_e are the initial and equilibrium concentrations (mmol/L), respectively; V is the solution volume (L), and m is the mass of the resin (g). The point of zero charge (pH_{pZC}) of ASA/IMEA/PGMA@PS was determined by solid addition method, which is presented in Supplementary material.

2.3.2. Adsorption isotherms and adsorption selectivity under competition

0.100 g of various resin was placed into a series of 100 mL of solution (pH 4.5) containing either one type of metal ion with different concentrations, or six types with each concentration of 6.0 mmol/L. The procedure for adsorption and analysis was the same as that in Section 2.3.1.

2.3.3. Adsorption kinetics and reutilization

The methods of adsorption kinetics and reutilization for ASA/IMEA-PGMA@PS were presented in Supplementary material.

3. Results and discussion

3.1. Preparation and characterization of ASA/IMEA-PGMA@PS

The preparation of ASA/IMEA-PGMA@PS includes simple two-step reaction (Fig. 1). Firstly, SI-ATRP with GMA can graft abundant epoxy onto PS, which provides higher density of ligands in post modification. The grafting degree of GMA mainly depends on initiator density, monomer concentration and polymerization time, which can be easily controlled [18,20]. Secondly, PGMA@PS was derived with ASA and IMEA under mild condition due to the high reaction activity of epoxy with amino groups. As amino-type molecule, both ASA and IMEA possess similar reactivity, so they could react with epoxy at approximately similar reaction rate. To confirm this speculation, the bonding amount of ASA and IMEA in ASA/IMEA-PGMA@PS was determined by HPLC (the method was presented in Supplementary material). As shown in Table S1, the determined ratios of ASA to IMEA are 2.86:1, 0.93:1 and 1:3.19, being close to the experimentally added molar ratios of 3:1, 1:1 and 1:3, respectively. Therefore, the derived ratios of ASA to IMEA on the surface of resin eventually depend on the molar ratios of two ligands in reaction system.

The FT-IR spectrums are shown in Fig. 2A. Compared with PS, the peaks at 1723 cm⁻¹, 901 cm⁻¹ and 831 cm⁻¹ appear belonging to C=O and epoxy in PGMA@PS, indicating PGMA was grafted onto PS [19]. After derivation, peaks of epoxy almost disappear, whereas new peaks at 1385 cm⁻¹ and 1458 cm⁻¹ appear, ascribed to phenolic hydroxyl and C–N bond, certifying ASA reacted with epoxy [21]. In addition, the peak at 1509 cm⁻¹ appears belonging to C–C/C–N stretching vibration of IMEA [22]. The imidazole ring vibrations are over-lapped with the adsorption peaks in PS skeleton and the bonded ASA.

XPS was employed to analyze surface composition (Fig. 2B and Table S2). The peak at 531.9 eV is ascribed to O1s, and the content of O on PGMA@PS dramatically goes up compared with PS, suggesting PGMA rich in O element has been grafted onto PS. After derivation, the N1s peak at 400.3 eV appears, and the content of O is further raised, owing to the presence of ASA rich in O and IMEA rich in N, respectively. On the other hand, the significant reduction of Cl for ASA/IMEA-PGMA@PS suggests that ASA and IMEA experienced nucleophilic substitution with -CH₂-Cl in the terminal, which can additionally improve the adsorption capacity according to our previous work [23]. As for ASA/IMEA-PS, the strong peaks of N1s and O1s appear, while the peak of Cl2p disappears due to the nucleophilic substitution reaction. Overall, all the results indicate that PGMA brushes have been grafted onto PS via SI-ATRP, and ASA and IMEA have been successfully immobilized onto the brushes.

The morphology of the resin was observed by SEM. After SI-ATRP, the pores still exist meanwhile the surface became more rough due to the formation of the polymer brushes (Fig. S1b). Compared with the PGMA-modified particle, no obvious change can be found on the surface of ASA/IMEA-PGMA@PS [24] (Fig. S1c). In addition, the resin was not broken during SI-ATRP and derivation reactions (Fig. S1d). The BET experiments indicate that the modified resin possesses porous structure (Fig. S2 and Table S3), and the pores are not destroyed after derivation (the discussions are shown in Supplementary material).

3.2. Effect of pH

pH is an important factor in the adsorption of metal ions. Given that relatively high pH may lead to the precipitation of metal ions, pH was controlled below 6 in this work. As shown in Fig. S3, almost no adsorption happens at pH 0.5. With pH raising, Q_e increase gradually until reach the maximum at pH 4.5. The change in Q_e is related with the surface charge because the metal ion

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