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Adsorption of Pb(II) from aqueous solution by silica-gel supported hyperbranched polyamidoamine dendrimers

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HIGHLIGHTS

- ► SiO_2-G0–SiO_2-G4.0 were promising adsorbents for the removal of Pb(II).
- ► The optimum pH was 5 for the adsorption of Pb(II) by all the products.
- ► The pseudo-second-order model best describe the adsorption kinetics.
- ► Langmuir model provide best correlation of the experimental data.
- ► The adsorption was controlled by film diffusion and chemical ion-exchange mechanism.

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ABSTRACT

The adsorption properties of silica-gel supported hyperbranched polyamidoamine dendrimers (SiO_2-G0–SiO_2-G4.0) have been investigated by batch method. The effect of pH of the solution, contact time, initial Pb(II) ion concentration, temperature and coexisting metal ions have been demonstrated. The results indicated that the optimum pH value was 5. Adsorption kinetics was found to follow the pseudo-second-order model and controlled by film diffusion. The adsorption isotherms were fitted by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. Langmuir isotherm model was found to be more suitable to describe the equilibrium data, suggesting the uptake of Pb(II) ions by monolayer adsorption. From D–R isotherm model, the calculated mean free energy *E* demonstrated the adsorption processes occurred by chemical ion-exchange mechanism. FTIR analysis revealed that amine groups were mainly responsible for the adsorption of Pb(II) by amino-terminated adsorbents, while C=O of ester groups also participated in the adsorption process of ester-terminated ones. The adsorbents can selectively adsorb Pb(II) from binary ion systems in the presence of Mn(II), Cu(II), Co(II), and Ni(II). Based on the results, it is concluded that SiO_2-G0–SiO_2-G4.0 had great potential for the removal of Pb(II) from aqueous solution.

1. Introduction

Water pollution of heavy metal ions has become a severe environmental problem in these few decades. Since they are persistent, non-biodegradable, toxic, and accumulative within biological systems, such metal ions pose a serious threat to human and aquatic ecosystems even if they are in low concentration [1–4]. Among these heavy metals, lead ions are significant contamination sources of water, because they are widely used in a variety of industrial processes such as electronics, battery manufacture, petroleum refining, and metal mining [5]. When absorbed or ingested by humans, their acute toxicity can cause mental retardation, kidney diseases, semi-permanent brain damage and many other symptoms [6,7]. Therefore, the removal of lead from aqueous solution is still the focus of extensive research [8–10].

A number of methods and technologies, such as chemical precipitation, ion exchange, solvent extraction, and adsorption, have been designed for the removal of lead from aqueous solution [11]. Among these methods, adsorption is considered to be one of the most efficient and promising methods [9–13]. The main advantage of adsorption is that adsorbents have strong affinity and high loading capacity for heavy metal ions [8]. Adsorbents such as activate carbon [14], zeolite [15], clay [16,17], kaolinite [18] and silica gel [19–21], have been employed extensively to the removal of metal ions from aqueous solution. As one of the promising adsorbents, silica gel has received great attention not only due to its excellent properties such as thermal and mechanical stability, large surface area, and well-modified surface, but also to be relative simple in

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comparison to polymer resin, with rapid adsorption kinetics, good swelling resistance in different solvents, and chemical stability [22,23].

In general, the adsorption of silica gel mainly depends on the functional groups covalently bond to the surface. Various functional groups, such as those containing nitrogen, sulfur, oxygen, and phosphorus atoms, have been used for the chemical modification of silica gel [20,24–26]. In recent years, polyamidoamine (PAMAM) dendrimers are widely used to the chemically modified silica gel [22,27–32]. It is well known that PAMAM dendrimers have the advantages of well-defined geometry with different terminal functional groups, high density of nitrogen and oxygen atoms, and the possibility of introducing functional groups such as hydroxyl, ester, and carboxyl. These advantages make them promising candidates as novel adsorbents [22,28,29,31].

In our previous studies [22,33], a series of amino- and ester-terminated silica-gel supported hyperbranched PAMAM dendrimers (SiO_2-G0–SiO_2-G4.0) were synthesized and adsorption properties for metal ions were investigated. Both the amino- and ester-terminated adsorbents exhibited better adsorption capabilities for Au(III) and Pd(II) than other metal ions. As a further investigation, the present study aims to investigate the feasibility of SiO_2-G0–SiO_2-G4.0 as efficient adsorbents for the removal of Pb(II) from aqueous solution. The effect of pH of solution, contact time, initial Pb(II) concentration, temperature and coexisting metal ions on Pb(II) adsorption were systematically investigated. The adsorption mechanism had been elucidated by analyzing the FTIR spectra, adsorption kinetics and isotherms data.

2. Experimental

2.1. Materials and methods

SiO_2-G0–SiO_2-G4.0 were synthesized by the divergent method as described in our previous work [22]: (1) SiO_2-G0 was synthesized by the reaction of silica gel with γ-aminopropyltriethoxysilane to introduce the amino groups onto the surface of silica gel. (2) Michael addition of methylacrylate to the amino groups of SiO_2-G0 to obtain SiO_2-G0.5. (3) SiO_2-G1.0 was synthesized by the amidation of terminal ester groups of SiO_2-G0.5 with ethylenediamine. And then repeat the last two steps in sequence to obtain the following series of products SiO_2-G1.5–SiO_2-G4.0. All solutions were prepared from analytical grade chemicals and distilled water. An amount of 0.1 $\mathrm{mol\,L^{-1}}$ of Pb(II) stock solution was prepared by dissolving 3.3121 g of $Pb(NO_3)_2$ in 100 mL of distilled water. The working and standard solutions with different concentrations were prepared by diluting the stock solution. The buffer solution of pH 1.0–2.0 and pH 3.0–6.0 were obtained by adjusting of HNO_3/H_2O and acetate/acetic acid, respectively. The pH of the solution is monitored with a Seven Multi pH meter (Mettler Toledo Instruments, Co. Ltd., China). The concentrations of Pb(II) ions before and after adsorption were determined on a GBC-932 atomic adsorption spectrophotometer (AAS, GBC, made in Australia). Infrared spectra were recorded on a Nicolet MAGNA-IR 550 (series II) spectrophotometer. Test conditions: potassium bromide pellets, scanning 32 times, resolution are 4 $\mathrm{cm^{-1}}$.

2.2. Saturated adsorption

The adsorption capacities of SiO_2-G0–SiO_2-G4.0 for Pb(II) were conducted by the following procedure: about 50 mg of adsorbent was placed in a 100 mL flask and 20 mL of 0.005 $\mathrm{mol\,L^{-1}}$ Pb(II) solution was then added. The mixture was shaken in a thermostatic shaker for 12 h at room temperature, then the adsorbent was filtered off and the concentration of Pb(II) was determined via AAS. The adsorption capacity of Pb(II) was calculated according to Eq. (1):

$$q = \frac{(C0 - C)V}{W} \tag{1}$$

where q is the adsorption amount ($\mathrm{mmol\,g^{-1}}$); C_0 and C are the initial and equilibrium concentration of Pb(II), respectively ($\mathrm{mmol\,mL^{-1}}$); V is the volume of the solution (mL); and W is the weight of SiO_2-G0–SiO_2-G4.0 (g).

2.3. Effect of pH on adsorption

The effect of pH on the adsorption was conducted by adding 50 mg of adsorbent to 20 mL of 0.005 $\mathrm{mol\,L^{-1}}$ Pb(II) solution with different pH in a 100 mL flask. The following procedures were similar to Section 2.2.

2.4. Adsorption kinetics

Adsorption kinetics were performed by batch experiments as follow: a series of 100 mL flasks were charged with 20 mL of 0.0025 $\mathrm{mol\,L^{-1}}$ Pb(II) solution, then 50 mg of adsorbent was added to each flask and the mixture was shaken. At various time intervals, the adsorbent was filtrated and the concentration of Pb(II) was determined.

2.5. Adsorption isotherms

Adsorption isotherms were investigated by the following procedures: a series of 100 mL flasks were charged with 50 mg of adsorbent and 20 mL Pb(II) solution with varying initial concentration. The mixture was shaken for 12 h at different temperatures and the concentration was determined.

2.6. Adsorption selectivity

The selectivity experiments were conducted by placing 50 mg of adsorbent in a 100 mL flask, and then 1 mL of 0.1 $\mathrm{mol\,L^{-1}}$ Pb(II) solution, 1 mL of 0.1 $\mathrm{mol\,L^{-1}}$ coexisting metal ion, and 18 mL of buffer solution with pH 5.0 was added in turn. The mixture was shaken for 12 h at room temperature. Then the concentration of metal ions was determined. The adsorption capacities of Pb(II) and coexisting metal ion were calculated.

3. Results and discussion

3.1. Saturated adsorption

Saturated adsorption capacity is considered to be one of the most critical parameters to investigate the adsorption property of adsorbent for metal ions. The saturated adsorption capacities of SiO_2-G0–SiO_2-G4.0 for Pb(II) are presented in Fig. 1.

As shown in Fig. 1, the adsorption capacities of amino-terminated products for Pb(II) follow the order of SiO_2-G0 < SiO_2-G1.0 < SiO_2-G2.0 > SiO_2-G3.0 > SiO_2-G4.0, and SiO_2-G2.0 possesses the highest adsorption capacity, which exhibits the same regularity as Pt(IV) in our previous investigation [22]. As is well known, the adsorption capacity of the adsorbent basically rests with the functional groups. The increasing of generation number of PAMAM dendrimers results to the increasing number of functional groups, promoting the higher adsorption capacity when generation number was no more than 2. However, it is found that the adsorption capacity of higher generation products SiO_2-G3.0 and SiO_2-G4.0 were lower than that of SiO_2-G2.0, although they have larger number of functional groups than SiO_2-G2.0. The strong steric