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Lanthanum adsorption using iron oxide loaded calcium alginate beads

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ABSTRACT

The adsorption behaviors of lanthanum (III) from an aqueous chloride medium, using iron oxide loaded calcium alginate beads were studied using equilibrium batch and column flow techniques. The effect of pH, contents of loaded iron oxide, ionic strength, adsorbent dose, contact time, and temperature on adsorption capacity of the magnetic beads was investigated. The optimum pH value was defined to be 5.0 at temperature 298 K. Kinetic and isotherm experiments were carried out at the optimum pH. It was enough to reach the adsorption equilibrium at 28 h and the maximum uptake capacity was 123.5 mg/g. Complexation, ion exchange and electrostatic interaction were all believed to play a role in lanthanum adsorption on magnetic beads. The equilibrium adsorption data were fitted to second-order kinetic equation. The Langmuir adsorption isotherm models were used for the description of the adsorption process. Furthermore, column breakthrough curves were obtained and the La (III) loaded magnetic beads were regenerated using 0.05 mol/L $CaCl_2$ solution.

1. Introduction

In recent years, rare earth elements have received considerable attention with their increasing demands in high-tech industries for their unusual spectroscopic characteristic. Lanthanum, the first rare earth element, is usually applied for advanced new materials such as super alloys, catalysts, special ceramics and organic synthesis (Kanazawa and Kamitani, 2006; Sert et al., 2008). Traditional techniques used to separate rare earth ions include precipitation, ion exchange, filtration, solvent extraction and etc. (Diniz and Volesky, 2005). Among these methods, solvent extraction has been widely used since effective extraction ability and separation selectivity (Wu et al., 2004). However, the large amount of organic solution strongly destroys the environment and harms human health.

Biosorption has increasingly received more attention because it is simple, relatively low-cost, and effective in removing metal ions from solution (Jang et al., 1991; Weltrowski et al., 1996). There is a growing interest in the development of novel non-toxic recyclable biosorbents. Alginate, a natural high molecular-weight biopolymer composed of chains of 1, 4-linked β-D-mannuronic and α-L-guluronic has attracted much attention because it is non-toxic, selective, efficient and inexpensive (Da Costa and Leite, 1991; Chen and Wang, 2001; Chong et al., 2000). It has been demonstrated that the alginates are capable of binding metal ions through carboxyl groups (Siegel and Siegel, 1973; Lim et al., 2008) and calcium alginate beads are usually prepared for their gel forming properties in the presence of multivalent cations (Martinsen et al., 1989).

Magnetic separation technique, using magnetic polymeric particles, is a quick and easy method for sensitive and reliable capture of inorganic or organic pollutants. The magnetic sorbents behave similar to or even better than various commercial adsorbents (Ngah et al., 2006). After the usage, the magnetic sorbent can be easily separated from the solution by simple magnetic force. In the literature, iron oxides have been found to be successfully used as composite materials with host materials in fabricating magnetic sorbent (Oliveira et al., 2003, 2004; Chang and Chen, 2006). Recently, Lim and Chen (2007) investigated the copper adsorption onto an alginate magnetic sorbent and the results demonstrated that the sorbent can be easily separated from the solution by an external magnet and the maximum adsorption capacity of copper ions is 60.24 mg/g, much higher than those of commercial adsorbents. Moreover, nickel and cobalt adsorptions using magnetic alginate microcapsules containing Cyanex 272 were reported by Ngomsik et al. (2006, 2009). To our knowledge, the adsorption of rare earth ions by magnetic calcium alginate beads with and without extractant has never been investigated.

The aim of present work is to prepare iron oxide loaded calcium alginate beads to determine the adsorption capacity of lanthanum from aqueous medium under batch equilibrium and column flow experimental conditions, and study in detail, the effect of various experimental parameters such as aqueous phase pH, adsorbent dose, ionic strength, temperature, contact time and initial La (III) concentration on uptake capacity, predicts the kinetic and isotherm models, deduces the adsorption mechanism and accumulates data for their potential industrial applications. Furthermore, wide-angle X-ray diffraction (WXRD) technique was used to determine the cystallographic structure and a vibrating sample magnetometer (VSM) to investigate the magnetic property of the iron oxide nanoparticle. Fourier transformer infrared spectroscopy (FT-IR) technique was chosen to confirm the

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loaded La (III) and thermogravimetric analysis (TGA) to understand the thermostability of the magnetic beads, respectively.

2. Experimental

2.1. Materials

Sodium alginate (Na-alginate), chemical grade from Shanghai of China was used as received. Stock solution of lanthanum was prepared from its oxides via dissolution in concentrated hydrochloric acid and standardized by ethylenediamine tetraacetic acid (EDTA) titration with xylenol orange as the indicator. Ferric chloride hexahydrate, ferrous chloride tetrahydrate, ammonia, calcium chloride dehydrate and other reagents were of analytical grade from China. The pH of the solutions was adjusted to the required value with 0.01 mol/L HCl and 0.01 mol/L NaOH solutions.

2.2. Preparation of iron oxide nanoparticles

Magnetite was prepared using the modified Massart method (Donia et al., 2008). Firstly, ferric and ferrous chloride solutions were mixed at 60 °C for 30 min. Then, ammonia solution was added dropwise to the above solution under vigorous stirring. A black precipitate was formed which was allowed to crystallize for another 30 min under stirring at 90 °C. The molar ratio of $FeCl_2$:$FeCl_3$:$NH_3 \cdot H_2O$ was 1:2:16. All the above processes were run under total N_2 protection. Last, the precipitate was filtered off and washed with deoxygenated water through magnetic decantation until the pH of the suspension became below 7.5.

2.3. Preparation of iron oxide loaded calcium alginate beads

1.5 g sodium alginate powder was dispersed in 100 mL deionized water to give a 1.5% w/v alginate solution. This solution was mixed with a mechanic stirrer at 80 °C until a transparent, viscous solution was obtained. Then 0.5 g or 1.0 g Fe_3O_4 particle was mixed with the above viscous solution and stirrer for 2 h. Magnetic calcium alginate beads were obtained by adding dropwise this aqueous solution (magnetic gel) into 2% $CaCl_2$ solution using a syringe. Magnetic beads of 1.8–2.0 mm in diameter were formed and kept in contact with $CaCl_2$ solution for 24 h, which led to the formation of stable gel beads. Finally, they were washed several times with distilled water and dried in the vacuum drying chamber at 55 °C for 24 h. After whole stripping with 36% HCl, the contents of iron and calcium were determined by measuring absorbance using an atomic adsorption spectrophotometer (Perkin Elmer 3100 model). The amount of alginate was obtained approximately by mass balance of the magnetic gel and magnetic bead.

2.4. Batch studies

Batch adsorption experiments were performed by agitating using a mechanical shaker at 200 rpm/min in 250 mL conical flasks with specified amount of dry beads in contact with 50 mL of $LaCl_3$ solution of desired concentration at varying pH for 28 h at 298 K. It was confirmed through the preliminary experiments that 28 h was sufficient to attain equilibrium between adsorbent and adsorbate. After attaining equilibrium, the sorbent was separated by an external magnet. Then the aqueous phase concentration of lanthanum was determined by measuring absorbance using a UV–vis spectrophotometer (China, Model UV-752) with three-bromine arsenazo as a chromomeric reagent at 635 nm (Jia et al., 2005). The concentration of Ca (II) was analyzed with an atomic adsorption spectrophotometer. Normally, no ionic strength was kept except for the effect of sodium chloride concentration on the adsorption. The temperature was maintained at 298 K unless otherwise stated. The adsorption capacity of the sorbent was determined by material balance of the initial and equilibrium concentrations of the solution. Each experiment was repeated at least three times and the mean values were taken. The amount adsorbed per unit mass of adsorbent at equilibrium was given as follows:

$$q_e = \frac{(C_{ini} - C_e)V}{m}. \quad (1)$$

The removal or uptake efficiency (%) of lanthanum by magnetic bead could be expressed as Eq. (2):

$$uptake(\%) = q_e / q_{ini} \times 100 \quad (2)$$

where q_e (mg/g) and q_{ini} (mg/g) were the equilibrium uptake and initial lanthanum concentrations, respectively. C_{ini} and C_e (mg/L) denoted the initial and equilibrium concentrations of La (III) ions in aqueous solution, V was the total volume of the solution in liters and m was the mass of the dry magnetic beads used in grams.

2.5. Column adsorption studies

Column flow adsorption experiments were conducted in a glass column of about 2.0 cm internal diameter and 20 cm length. The column was filled with a known weight of the adsorbent while tapping the column such that the column was filled without voids. The pH of the inlet solution was adjusted to 5.0 at the start of the experiment. The effluent solution was collected at different time intervals and the concentration of La (III) ion in the effluent solution was determined by UV–vis spectrophotometer. Breakthrough curves were obtained by plotting the volume of the solution against the ratio of the concentration of effluent at any time (C_e) to that of the inlet solution (C_o), C_e/C_o.

2.6. Desorption studies

After the column was completely exhausted, the remaining aqueous solution in the column was drained off by pumping air through the column. Desorption of solute from loaded adsorbent was carried out by 0.05 mol/L $CaCl_2$ solution as an eluent at a fixed flow rate of 1 mL/min at constant temperature. After elution the loaded adsorbent was carefully washed with distilled water to remove $CaCl_2$ from the column before the influent adsorbate solution was reintroduced for the subsequent adsorption–desorption cycles. The adsorption–desorption cycles were performed thrice for each lanthanum solution using the same bed to check the sustainability of the bed for repeated use.

2.7. Characterization of magnetic beads

X-ray diffraction (XRD) was done in a diffractometer (Model APD-10, Philips, Netherlands) equipped with Cu $K\alpha_{1,2}$ radiation source between 10° and 70° (2θ) at room temperature. Magnetization curve of the iron oxide particles was recorded with a vibrating sample magnetometer (USA, Model Lakeshore 7400) for a solid sample at room temperature with an applied magnetic field up to 5000 Oe. A FT-IR (USA, Model Nicolet Avatar 360) was used for the confirmation of the loading of La (III) to magnetic beads in a solid sample. FT-IR spectra were obtained with KBr pellets and the spectrum was taken from 4000 to 500 cm^{-1}. A thermal analyzer (Model Netzch TG 209) was used in the temperature range of 10–900 °C at a heating rate of 10 °C/min with nitrogen flushed at 200 mL/min.