

Facile and Efficient Method for the Adsorption and Separation of Lanthanum Rare Earth Metal Oxide Using Iron(II) sulfide Nanoparticles Coated on Magnetite

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Abstract

A novel iron sulphide adsorbent using magnetite embedded with nanosized Fe_3O_4 was prepared and applied to separation lanthanum (III) from aqueous solution. This adsorbent combines the advantages of magnetic nanoparticle with magnetic separability and high affinity toward rare earth metals, which provides distinctive merits including easy preparation, high adsorption capacity, easy isolation from sample solutions by the application of an external magnetic field. The adsorption behaviors of lanthanum (III) from an aqueous medium, using iron sulphide magnetite nanoparticles were studied using equilibrium batch and column flow techniques. The effect of pH, contents of loaded iron sulphide nanoparticles, ionic strength, adsorbent dose, contact time, and temperature on adsorption capacity of the magnetic beads was investigated. All of the results suggested that the $\text{FeS}/\text{Fe}_3\text{O}_4$ Nanoparticles could be excellent adsorbents for La(III) contaminated water treatment.

Keywords: *nano magnetite, Lanthanum ion; Adsorption.*

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 [1, 2]. Traditional techniques used to separate rare earth ions include precipitation, ion exchange, filtration, solvent extraction and etc[3]. Among these methods, solvent extraction has been widely used since effective extraction ability and separation selectivity [4]. However, the large amount of organic solution strongly destroys the environment and harms human health.

Magnetic separation technique, using magnetic polymeric particles, is a quick and easy method for sensitive and reliable capture of inorganic or organic solutions. The magnetic sorbents behave similar to or even better than various commercial adsorbents[5]. 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[6-8]. To our knowledge, the adsorption of rare earth ions by magnetite nanosized coated with iron(II) sulfide beads with and without extractant has never been investigated.

The aim of present work is to prepare nanoparticle of magnetite iron oxide loaded with iron(II) sulfide 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 and temperature, X-ray diffraction (XRD) technique was used to determine the

crystallographic structure and a vibrating sample magnetometer (VSM) to investigate the magnetic property of the iron oxide.

Preparation of magnetite iron oxide nanoparticles

Magnetite was prepared using the modified Massart method [9]. 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 $\text{FeCl}_2:\text{FeCl}_3:\text{NH}_3\cdot\text{H}_2\text{O}$ 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.

Preparation of magnetite iron oxide loaded iron(II) sulfide nanobeads

1.5 g iron(II) sulfide powder was dispersed in 100 mL deionized water to give a 1.5% w/v solution. This solution was mixed with a mechanic stirrer at 80 °C until a transparent, viscous solution was obtained. Then 0.5 g Fe_3O_4 nanoparticle was mixed with the above viscous solution and stirrer for 2 h. Magnetic beads were obtained by adding dropwise this aqueous solution into 2% CaCl_2 solution using a syringe. Finally, they were washed several times with distilled water and dried in the vacuum drying chamber at 55 °C for 24 h.

Batch studies

Batch adsorption experiments were performed by 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 with three-bromine arsenazo as a chromomeric reagent at 635 nm [10]. 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:

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 to that of the inlet solution.

Results and discussion

As expected, the XRD pattern of iron oxide nanoparticle (fig. 1) is characterized of the inverse spinel structure of Fe_3O_4 and the result is similar to the literature[11]. The magnetic hysteresis loop, obtained by VSM (Fig. 2), shows two coincident magnetization curves. No magnetic hysteresis phenomenon is observed, and the coercive force and remanence are close to zero. This reflects an important feature of the magnetic nano-materials, i.e. superparamagnetic, which is usually observed when the magnetic particles are less than 10 nm in diameter.

Effect of pH on adsorption

As pH is an important factor affecting the uptake of cations from aqueous solutions, the dependence of La (III) uptake on aqueous pH is studied. The uptake capacity increases from about 1.9 to 98.7 mg/g as pH increases from 2.2 to 3.5. Above pH 3.5, its effect on the uptake becomes insignificant and reaches a plateau. However, with an increase in pH, more negative sites are becoming available for the adsorption of La (III) ion, which leads to the uptake increases at higher pH. Considering the hydroxylation of La (III) at higher pH, the optimum initial pH is defined to be 5.0. In addition, the final pH is obviously higher than the initial pH. The final pH changes only 5.6 to 5.9 when initial pH ranges from 4.0 to 5.5, demonstrating a buffering ability caused by calcium alginate.

Effect of ionic strength on adsorption

In this study, the effect of initial ionic strength on La (III) sorption is achieved by varying the concentrations of additive sodium chloride from zero to 0.2 mol/L. As shown in [Fig. 3](#), the low ionic strength, corresponding to the concentration of sodium chloride less than 0.03 mol/L, has little influence on the La (III) sorption, and above it, the uptake of La (III) obviously decreases with increasing concentrations of sodium chloride. The uptake capacity changes from 119.3 mg/g to 90.4 mg/g when the concentration ranges of sodium chloride are from 0.03 mol/L to 0.2 mol/L, respectively. A reasonable explanation is there is a competitive sorption between La (III) and Na^+ . At a lower ionic strength, more function groups are available for La (III) uptake, the effect of Na^+ is insignificant, when the ionic strength is high, the competition between La (III) and Na^+ for the available sites becomes important, resulting in the low La (III) uptake. **Effect of temperature on adsorption**

The effect of temperature on adsorption of La (III) on to magnetic beads can be found that the uptake capacity of La (III) increases, as the temperature in solution decreases, suggesting that the adsorption process is exothermic[12, 13].

Elution and regeneration cycles

Sorption/desorption cycles are carried out for La (III) columns using 0.05 mol/L CaCl_2 as an eluent. The break through curves for recovery of La (III) show no obvious changes during cycles. This indicates that magnetic beads have a good durability as well as good efficiency for repeated use.

Conclusions

In this study, magnetite iron oxide coated with iron(II) sulfide nanobeads were prepared to study adsorption capacity of lanthanum by batch and column flow techniques. VSM indicated that iron oxide has a good superparamagnetic property with the MS of 63.2 emu/g and prepared magnetic beads can be easily separated by an external magnet. TGA suggested that magnetic bead has an excellent thermostability and can be used at wide temperature ranges. The equilibrium batch experiment data demonstrated that the magnetic beads are effective adsorbents for the uptake of La (III) from aqueous chloride medium with the maximum uptake capacity of 123.5 mg/g. The magnetic beads could be regenerated effectively using 0.05 mol/L CaCl₂.

References

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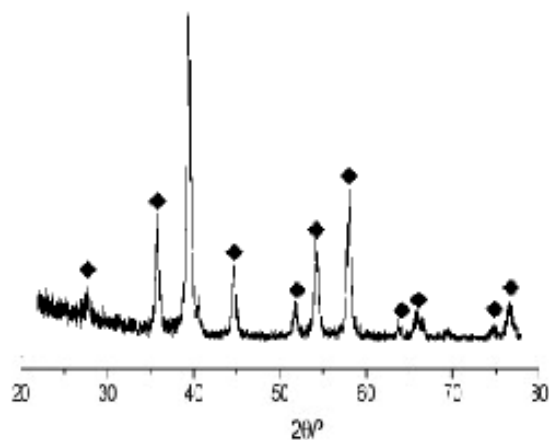


Fig 1. XRD patterns of Fe₃O₄ nano-particles

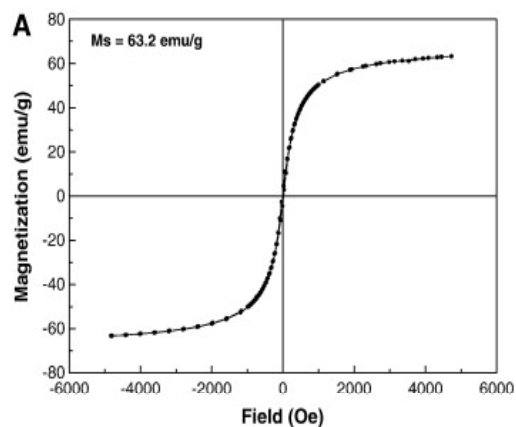


Fig. 2. (A) The specific saturation magnetization of iron oxide nanoparticles.

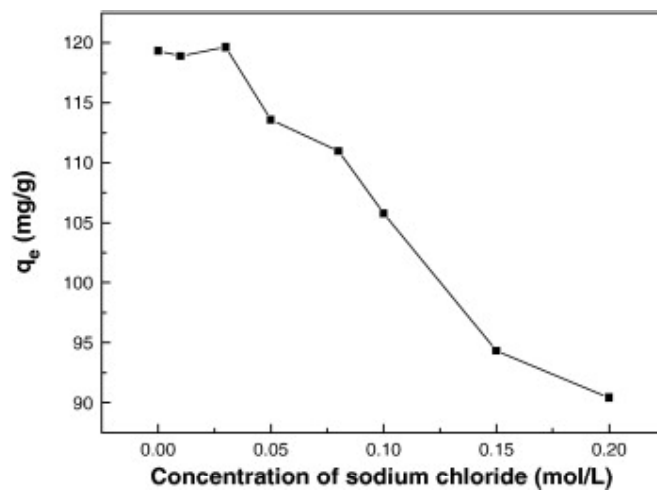


Fig. 2. The effect of ionic strength on uptake capacity of La (III) using magnetic beads. ([La]_{added} = 1×10^{-3} mol/L, m = 0.05 g dry magnetic bead, equilibrium time = 28 h, pH = 5.0 ± 0.02 , T = 298 K).