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Adsorption of erbium(III) on D113-III resin from aqueous solutions: batch and column studies

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Abstract: The adsorption and desorption behaviors of Er(III) ion on D113-III resin were investigated. Batch adsorption studies were carried out with various Er(III) ion concentrations, pH, contact time and temperature, indicating that D113-III resin could adsorb Er(III) ion effectively from aqueous solution. The loading of Er(III) ion onto D113-III resin increased with increasing the initial concentration. The adsorption was strongly dependent on pH of the medium with enhanced adsorption as the pH turned from 3.45 to 6.75. In the batch system, the D113-III resin exhibited the highest Er(III) ion uptake as 250 mg/g at 298 K, at an initial pH value of 6.04, calculated from the Langmuir isotherm model. The adsorption kinetics was in agreement with Lagergren-first-order kinetics among the Lagergren-first-order model, pseudo-second-order model, liquid film diffusion model and intraparticle diffusion model. The adsorption data gave good fits with Langmuir isotherms. The thermodynamic parameters such as ΔG, which were all negative, indicated that the adsorption of Er(III) ion onto D113-III resin was spontaneous and the positive value of ΔH showed that the adsorption was endothermic in nature. Thomas model was applied to experimental column data to determine the characteristic parameters of column useful for process design. Er(III) ion could be eluted by using the 4.0 mol/L HCl solution. The characterization of both before and after adsorption of Er(III) ion on D113-III resin was undertaken with IR spectroscopic technique. Moreover, the surface characterization of D113-III resin was described by scanning electron micrographs (SEM).

Keywords: D113-III resin; erbium(III); kinetics; thermodynamic; equilibrium; rare earths

Rare earth elements (REEs) have been regarded as the vitamin of metals, which means that a minute amount of REEs may greatly enhance the properties of metals. REEs are the surface-active element, which plays an important role in metallurgy of materials, such as refinement of microstructure, alloying and purification of materials and metamorphosis of inclusions. For example, adding small amount of erbium can evidently improve the wettability, mechanical strength and creep rupture life of the Sn3.8Ag0.7Cu solder alloy[1]. Li et al.[2] found that the catalytic activity and magnetic susceptibility of Pt-Er/γ-Al_2O_3 catalyst had the maximum values when the erbium content was equal to 0.64%. Li et al.[3] reported that when the REEs and their alloys can be prepared in organic solvent at room temperature by electrodeposition, and it will greatly develop their application in functional materials. What's more, the adsorption of erbium ions is important from the point of view of its pre-concentration, because of its thermal neutron absorption capability (thermal neutron absorption cross section: 169 b) and high melting point (1529 °C), erbium along with other materials is used to make nuclear reactor control rods[4].

Many works is related to the separation and enrichment of rare ions (including erbium) using methods such as co-precipitation, solvent extraction, ion-exchange and solid phase extraction[5–7]. Solvent extraction and ion-exchange[8–11] are the two most common methodologies for the preconcentration and separation of trace elements from various matrices. Solvent extraction is inefficient due to the requirement of large volume of solvent, which may create health problem. In addition, solvent extraction procedures are usually time-consuming and labor-intensive.

Various adsorbents including chelating resins[12] and ion exchange resins[13–15] were used in extraction of erbium ions from various media. Chelating resins as adsorbent is with good features of easy-functional and chemical stability, shortcomings in the performance of its poor hydrophilicity, slow adsorption rate and bad elution. Ion exchange resins have been used in the chemical analysis for over 50 years. They are solid and suitably insolubilized high molecular weight polyelectrolytes which can exchange their mobile ions

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for ions of equal charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchanger. D113-III resin is a polymeric material containing a functional group (–COOH). It has not only proton that can exchange with cation, but also oxygen atom that can coordinate directly with metal ions. As a result, D113-III resin is widely used in the adsorption of metal ions from aqueous solutions.

In this work, the adsorption and desorption of Er(III) ion by D113-III resin using batch and column methods was investigated. Some factors affecting adsorption, such as contact time, initial pH of solution, initial concentration of Er(III) ion and temperature were examined. Kinetics and isotherm adsorption experiments were carried out. Thermodynamic parameters of adsorption for Er(III) ion were calculated. The Thomas model was applied to experimental data obtained from column experiments. The sample was characterized with IR spectroscopy and scanning electron micrographs (SEM).

1 Materials and methods

1.1 Apparatus

The Er(III) ion was determined with Shimadzu UV-2550 UV-VIS spectrophotometer. Mettler toledo delta 320 pH meter was used for measuring pH of solutions. The sample was shaken in the DSHZ-300A and the THZ-C-1 temperature constant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine. The IR spectra and scanning electron micrographs (SEM) was recorded on a Nicolet 380 FT-IR spectrometer and a HITACHI S-3000N electron microscope, respectively.

1.2 Materials

D113-III resin was supplied by Jiangsu Suqing Co., Ltd. and the properties are shown in Table 1. The stock solutions of Er(III) ion was prepared from erbium nitrate (A.R.). HAc-NaAc buffer solution with pH=3.45–6.75 and $C_6H_{15}O_3N$-HNO_3 buffer solutions with pH=7.20 were prepared from the NaAc, HAc, $C_6H_{15}O_3N$ and HNO_3 solutions.

Table 1 General description and properties of resin

Items	Properties
Resin	Macroporous weak acid resin
Functional group	–COOH
Structure	Macroporous
Containing moisture/%	45–50
Capacity/(mmol/g)	11.0
Wet superficial density/(g/ml)	0.74–0.80
True wet density/(g/ml)	1.14–1.20

The chromophoric reagent of 0.1% arsenazo-I solution was obtained by dissolving 0.1000 g arsenazo-I powder into 100 ml deionized water. All other chemicals were of analytical grade and purified water was used.

1.3 Adsorption experiments

Experiments were run in a certain range of pH, temperature, initial Er(III) ion concentrations, contact time as well as adsorption isotherms. The operation for the adsorption and desorption of Er(III) ion is usually carried out in batch vessels and glass columns.

Batch experiments were performed under kinetic and equilibrium conditions. A desired amount of treated D113-III resin was weighed and added into a conical flask, in which a desired volume of buffer solution with pH 6.04 was added. After 24 h, a required amount of standard solution of Er(III) ion was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium is reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Er(III) ion were similarly measured.

Continuous flow adsorption experiments were conducted in a vertical glass column of 0.45 cm inner diameter and 23.5 cm height filled with Er(III) ion solution. At the bottom of the column, a stainless sieve was attached followed by a layer of cotton wool. The particles were dropped in from the top of the column. Time taken by the particles to travel a distance of 7.4 cm in vertical direction was noted. The Er(III) ion solution was fed from the top at a fixed flow rate. The Er(III) ion solutions at the outlet of the column were collected periodically and analyzed for the Er(III) ion concentration using a UV-visible spectrophotometer at 575 nm. The flow through the column was continued till the outlet and inlet concentrations were equal. All the experiments were carried out at room temperature.

1.4 Analytical method

A solution containing lower than 75 μg of Er(III) ion was added into a 25 ml colorimetric tube, and then 2.0 ml of 0.1% arsenazo-I solution and 10 ml pH 7.20 $C_6H_{15}O_3N$-HNO_3 buffer solution were added, after the addition of deionized water to the mark of colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 575 nm and compared with blank test. The adsorption capacity (Q) and adsorption rate (E) of Er(III) ion on D113-III resin were calculated with the following formula: