Synthesis and performance of organic-coated magnetite particles

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Abstract

Polymeric-coated magnetite particles with an adsorbed layer of extractant have been synthesized and are being evaluated for application in the separation and recovery of low concentrations of europium from water solutions. Physical characterizations of the extractant adsorbed particles were performed by X-ray diffractometry, Scanning Electron Microscopy and FT-IR spectrometry. Metal separations have been performed at various HNO_3 concentrations. Separation efficiency of the polymeric magnetic particles and the equilibrium adsorption isotherm of europium were investigated. Moreover, the magnetic field effect in the separation using a magnet was also verified.
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1. Introduction

The increase in nuclear and industrial activities has intensified environmental pollution and the deterioration of some ecosystems, with the accumulation of pollutants such as heavy metals, synthetic compounds and toxic radioactive wastes. Growing attention is being given to the potential health hazard presented by radiotoxic and heavy metals to the environment and the need for economic and effective methods for the removal of metals has resulted in the development of new separation technologies.

The search for new technologies involving the removal of toxic metals from aqueous waste has directed attention to synthetic new materials with high capability of removal, such as magnetic particles prepared by coating iron or another ferromagnetic material with either an organic polymer or ion-exchange resin. The ion-exchange resin is attached to the particle by adsorption or by direct bonding [1,2]. Organic solvents can be adsorbed onto the polymeric surface by contacting the particles with the solvent in a volatile diluent that is subsequently removed by evaporation [3,4]. These coatings selectively separate the contaminants onto the particles due to their chemical nature. Once loaded, the particles can be recovered from the waste stream using a magnet. These magnetic particles are superparamagnetic; that is, they do not become permanently magnetized after aggregate formation. Hence the particles may be reused. Stability of the polymeric coating and the covalent attachment of molecules also contribute to use and reuse of the particles.

The magnetically assisted chemical separation (MACS) process which uses extractant-coated magnetic particles combined with magnetic field has provided a more efficient chemical separation [5,6]. These magnetic particles showed an efficiency higher than in traditional solvent extraction techniques [7]. The identification of the observed synergism has been difficult due to the chemical complexity of the microparticle support. It was verified that the presence of a relatively weak magnetic field (0.3 T) in the separation processes using magnetite-containing polyamine-epichlorohydrin resin and magnetite particles has increased the sorption capacity of these materials for metallic ions [8–11].

This work studies the magnetic particles comprising a metal oxide core surrounded by a stable silane coating to which CMPO–TBP molecules were coupled. The magnetic particles may be used for the removal of pollutant ions from an aqueous solution in which they are contained. The magnetic field effect in the metal separation was also verified.

2. Experimental

2.1. Preparation of magnetic particles and coating procedure

Magnetite particles were prepared by the usual co-precipitation method, by adding 5 mol/l NaOH solution

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into the mixed solution of 0.25 mol/l ferrous chloride and 0.5 mol/l ferric chloride (molar ratio 1:2) until the pH reached 11 at room temperature. The slurry was washed with distilled water until the pH became neutral. Three washings were sufficient to achieve neutral pH. The slurry was then washed once with 0.02 mol/l NaCl. These particles were primarily coated with 3-aminopropyltriethoxysilane. This was achieved by heating the magnetite suspension with glycerol and 40 ml of a 10% water solution of 3-aminopropyltriethoxysilane (pH 4.0; adjusted with glacial acetic acid) on a water bath at 85–90 °C for 4 h. Then the silanized magnetite was thoroughly washed with water and 0.2 mol/l NaCl solution.

2.2. CMPO/TBP coating procedure

The silanized magnetite particles were mixed with methanol to disperse the particles and to act as a volatile solvent for the coating. A CMPO–TBP mixture (0.75 mol/l CMPO) was added to particles and shaken for 15 min. The methanol was then removed by evaporation at room temperature. Under these conditions, 20 wt.% CMPO/TBP-coated magnetic particles were obtained. These magnetic particles were called magnetic resins.

2.3. Characterization

The materials thus prepared were examined by the following conventional techniques:

- powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using Cu Kα radiation (30 kV and 15 mA);
- the magnetite particles were observed under a scanning electron microscope (SEM);
- infrared (IR) spectra in KBr matrix were taken using a Bomem Fourier transform infrared (FTIR) spectrometer.

2.4. Extraction process

The extraction efficiency was evaluated using the distribution coefficient, K_d. For distribution measurements, 50 mg of the CMPO/TBP-coated microparticles and 1.150 ml of Eu(III) nitric solution containing $^{152/154}$Eu were shaken mechanically and equilibrated for 20 min at room temperature. Then the samples were placed on top of a ring magnet, 4.5 cm external diameter, 1.5 cm internal diameter and 4 cm thickness, for 20 min to settle the particles and 0.5 ml of supernatant was taken for the measurement of γ-activity with a NaI(Tl) well-type scintillation detector. The distribution coefficient, K_d, was calculated with the following equation:

$$K_d = [(C_i - C_f)/C_f]V/M \text{ (ml/g)}$$

where C_i and C_f are aqueous metal concentrations (cpm) before and after equilibrium contact, V is the volume of the aqueous phase in ml and M is the mass of microparticles in g.

2.5. Adsorption isotherms

The adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. The results are generally expressed as a plot of the concentration of chemical adsorbed (mg/g) versus the concentration remaining in solution (mg/l) at a constant temperature. Three types of adsorption isotherm are considered: linear, Freundlich and Langmuir [12,13].

2.5.1. Linear isotherm

The simplest expression of equilibrium adsorption is the linear isotherm:

$$q_{eq} = K_d C_{eq}$$

where q_{eq} is the amount of adsorbed solute per weight of adsorbent (mmol/g), K_d is the distribution coefficient and C_{eq} (mmol/ml) is the residual liquid phase concentration, after equilibrium.

2.5.2. Freundlich isotherm

If the number of adsorption sites is large relative to the number of solute molecules, it is possible to use the Freundlich isotherm. The model is based on the assumption that ions are accumulated infinitely on the sorbent surface, as described by the following equation:

$$q_{eq} = K_f C_{eq}^{1/n}$$

where K_f and $1/n$ are the Freundlich constants and are indicators of adsorption capacity and adsorption intensity, respectively. A value of $1/n$ less than one indicates favorable adsorption. If the constant n has a value of 1, the Freundlich isotherm is identical to the linear isotherm.

By taking the log of these terms, a straight line develops making it easier to obtain the slope and intercept of the line:

$$\log q_{eq} = \log K_f + 1/n \log C_{eq}$$

2.5.3. Langmuir isotherm

In the Langmuir model, adsorption increases linearly with increasing solute concentration at low C values and approaches a constant value at high concentrations because there are a limited number of adsorption sites in the adsorbent.

This model is described by the equation:

$$q_{eq} = QK_L C_{eq}/(1 + K_L C_{eq})$$

where K_L is the Langmuir constant related to the energy of adsorption and Q is the maximum adsorption capacity.

The above equation can be rearranged to a linearised form:

$$C_{eq}/q_{eq} = 1/Q\,K_L + C_{eq}/Q$$

The constants Q and K_L can be evaluated from the slope and the intercept of linear equation by plotting C_{eq}/q_{eq} against C_{eq}.

3. Results and discussion

3.1. Characterization

Fig. 1 illustrates diffractograms of the materials precipitated from solutions of Fe^{2+} and Fe^{3+} recently prepared and after 1–5 days aging time. These solutions were kept and aged in a dark place at room temperature. All samples were magnetic only in the presence of the magnetic field of a magnet. These diffractograms show that all peaks are characteristic of the magnetite and solutions of Fe^{2+} and Fe^{3+} with 5 days of aging are stable and produce magnetite particles.

Fig. 2 shows the IR spectra of the silanized magnetite (a) and CMPO/TBP-coated magnetite particles (b). As it can be seen in Fig. 2a, the adsorption of silane polymer onto the surface of magnetite particles was observed with broad bands at 3409 and 1033 cm^{-1} assigned to Si–OH and Si–O–Si groups, respectively, and a band at around 1099 cm^{-1} assigned to (C–Si) bond.

In Fig. 2b, the appearance of bands at 2959 and 2872 cm^{-1} is noted. They represent (C–H) stretching modes bonding to surface. The characteristic bands of C=O and P–ϕ groups of CMPO are observed at around 1632 and 1465 cm^{-1} in CMPO/TBP-coated particles, respectively. The band at 1028 cm^{-1} corresponding to P–O–C group

Fig. 2. IR of the (a) silanized magnetite and (b) CMPO/TBP-coated particles.

indicates the presence of TBP. Furthermore, the P=O group of CMPO and TBP can be observed at 1264 cm^{-1}.

Fig. 3 represents the SEM micrographs of the magnetite particles and CMPO/TBP-coated particles. SEM observation revealed coarser precipitates composed of agglomerates of nanoparticles forming microparticles.

3.2. Removal efficiency of CMPO/TBP-coated particles

In this study, the removal of Eu(III) ions of 10^{-6} to 10^{-4} mmol/ml concentration using the CMPO/TBP-coated particles was analysed as a function of nitric acid concentration by varying the concentration from 0.01 to 3 mol/l. In the experiments with nitric acid solutions of 0.01 and 0.1 mol/l concentrations, the particles of magnetic resin not settling in 20 min, because peptization occurred, were discarded. As shown in Fig. 4, the distribution coefficient of Eu(III) decreases with increasing HNO_3 concentration, independent of metal ion concentration. Therefore, the equilibrium sorption capacity of the mag-
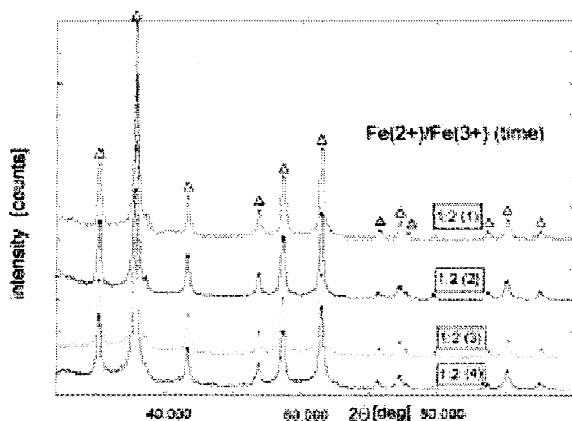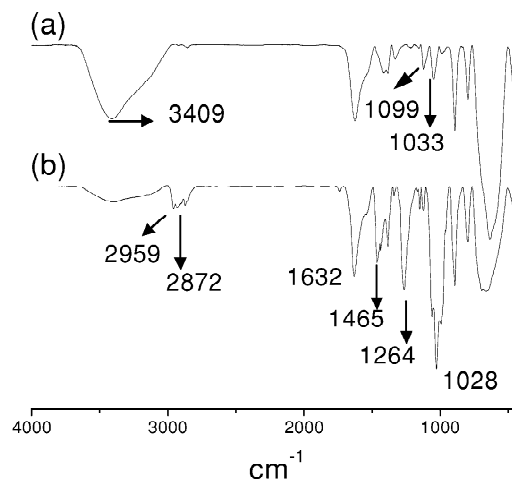

Fig. 1. Diffractograms of magnetite precipitated from solutions of Fe^{2+} and Fe^{3+} with molar ratio 1:2. Time 1 = solutions of Fe with less than 1 day of aging; time 2 = solutions of Fe with 1 day of aging; time 3 = solutions of Fe with 2 days of aging; time 4 = solutions of Fe with 5 days of aging. Δ magnetite peaks.
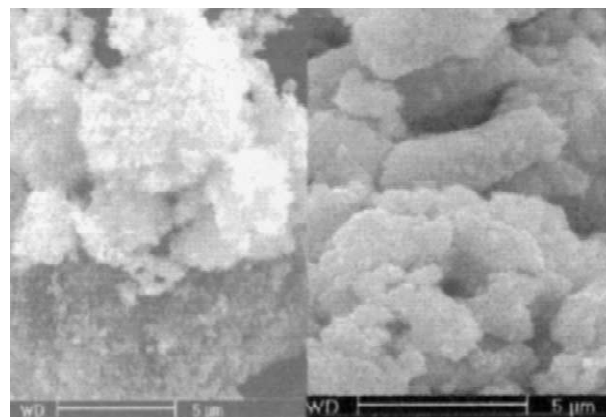

Fig. 3. SEM micrographs of the magnetite particles (a) and CMPO/TBP-coated particles (b).
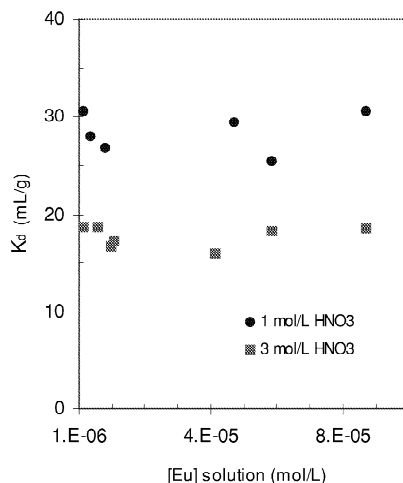
Fig. 4. Distribution coefficient of Eu(III) in HNO_3 using CMPO/TBP-coated magnetic particles.

netic resin is greater in 1 mol/l than in 3 mol/l HNO_3. At the studied concentration range of the Eu, the values of K_d can be considered practically constant in the same nitric acid concentration and it is possible to fit the linear equilibrium isotherms as can be seen in Fig. 5. In a batch system when the maximum sorption capacity is reached, the amount of metal ion sorbed will be constant and therefore the K_d values will decrease with increasing initial Eu concentration. In this study, the concentration range of Eu is sufficiently below saturation levels. The average values obtained for K_d were 29 and 18 ml/g in 1 and 3 mol/l HNO_3, respectively.

3.3. Adsorption isotherms

The linear and Freundlich isotherms were determined for the Eu(III) solutions varying the concentration from 10^{-6} to 10^{-4} mmol/ml in 1 and 3 mol/l nitric acid and are graphically represented in Figs. 5 and 6.

In Fig. 5 and in Table 1, each linear isotherm shows a high degree of correlation (r^2) and assumes that the sorbed concentration is directly proportional to the initial concentration. The slope of the linear equation is the K_d value.
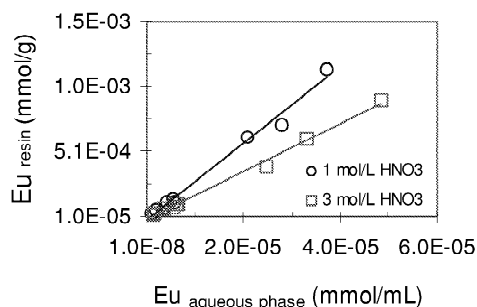

Fig. 5. Linear isotherms for Eu(III) in 1 mol/l and 3 mol/l HNO_3 on magnetic resin.
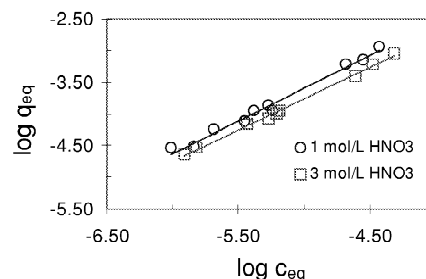

Fig. 6. Freundlich isotherms for Eu(III) in 1 mol/l and 3 mol/l HNO_3 on magnetic resin.

The linear sorption isotherm indicates a partitioning sorption throughout the whole concentration range of the Eu in nitric solution in the present study. The highest value of sorption capacity reached was 1.2×10^{-3} mmol/g. It was not possible to determine the maximum sorption capacity because the concentration range of Eu was below saturation levels.

The linearised forms of the Freundlich isotherm model are given in Fig. 6 and the values of constants were calculated by the least-squares method and are shown in Table 1. The values for $1/n$ are very close to unity indicating a strong tendency to linear sorption isotherm and the K_f values are close to K_d values. The high value of correlation indicates that the data conforms well to the Freundlich model.

In this study, the Langmuir model was not applied which assumes that the number of binding sites are finite and therefore K_d decreases with increasing metal ion concentration and a nonlinear isotherm must be observed.

3.4. Effect of magnetic field

The magnetic resins will be used in the metal separation from waste solution and these resins will be recovered from liquid waste by application of a magnetic field. Hence, the effect of a magnetic field in the metal separation by CMPO/TBP-coated magnetite particles was verified.

In order to observe the effect of enhancement of sorption capacity, the experiments were performed in 3 mol/l HNO_3 concentration that presented lower K_d values of Eu.

Fig. 7 shows the isotherms of Eu(III) when varying the concentration from 10^{-6} to 3×10^{-5} mmol/ml in 3 mol/l nitric acid without a magnetic field and with a magnetic

Table 1
Parameters of the isotherm models for extraction data

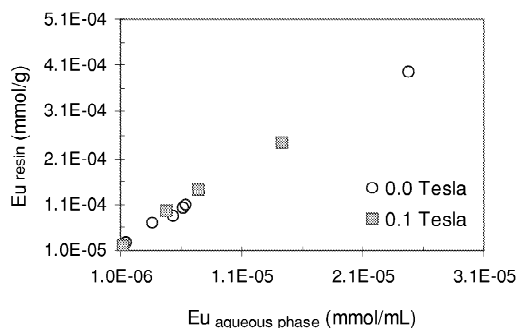| HNO_3 (mol/l)	Linear		Freundlich		
	K_d	r^2	K_f	$1/n$	r^2
1	29.5	0.989	36.3	1.03	0.986
3	18.2	0.995	14.4	0.98	0.997

Fig. 7. Linear isotherms of Eu(III) in 3 mol/l HNO_3 without and with magnetic field.

field of 0.1 T. No influence was observed in the extraction of Eu(III) with this magnetic field strength. The linear isotherms in the presence and absence of magnetic field exhibit the same slope and intercept.

4. Conclusion

The studies showed that the sorption capacity of magnetic resin for Eu ions increases with decreasing nitric acid concentration. K_d is greater in 1 mol/l than in 3 mol/l HNO_3. In order to investigate the sorption of Eu in nitric acid solution of low concentration (≤ 0.1 mol/l), the addition of an electrolyte, e.g. NaCl, is necessary to impede the peptization of the magnetic resin.

The isotherm models for magnetic resin showed excellent correlation to the linear and Freundlich isotherms because they were measured in a concentration range sufficiently below saturation levels. At the measured concentration range of Eu, the sorption is dominated by partition mechanism and the linear isotherm as well as the constant distribution coefficient (K_d) were observed. Certainly, the isotherm must deviate from linearity as the saturation point is approached.

We verified that there is no influence of the magnetic field of 0.1 T in sorption capacity of magnetic resin for the Eu in 3 mol/l HNO_3. More studies are necessary to verify the enhanced removal by magnetic field. Future experiments will focus on the influence of various magnetic field strengths in europium removal by magnetic resin, varying Eu and HNO_3 concentration.

An important aspect for applications of magnetic resin is the adsorption or binding strengths existing between: (1) the magnetite core and the polymeric coating and (2) the polymeric coating and the adsorbed extractants. Loss of chemical and physical integrity of magnetic resin during the separation process is undesirable. The loss of extractant is of prime importance in determining the economic viability of the use of magnetic resin. In our studied system, a small loss of extractants in aqueous phase was verified. Therefore, further studies are planned to investigate the chemical and physical stability of the magnetic resin.

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