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Rapid recovery of rare earth elements in industrial wastewater by CuFe_2O_4 synthesized from Cu sludge[☆]

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ABSTRACT

This study systematically evaluates the recovery of rare earth elements (REEs) from aqueous solution and industrial wastewater using magnetic nanoparticles CuFe_2O_4 . The industrially manufactured CuFe_2O_4 displays a nonlinear isotherm for REEs adsorption, suggesting limiting binding sites on the CuFe_2O_4 surface. The recovery of REEs increases significantly from 0.1% to 99.99% with increasing pH (2.29–8.15). At room temperature, the maxima recovery rates of Nd, La, and Ce are observed to be in a high capacity of 51.02, 42.02, and 40.16 mg/g, respectively. No significant attenuation of REE adsorption is observed with increasing NaCl concentration from 0.001 to 1.0 mol/L, showing high selectivity of REEs even in such high NaCl concentration matrix. In addition, desorption efficiency increases with the increasing concentration of HNO_3 in the range of 0.005–0.05 mol/L. When HNO_3 concentration is over 0.05 mol/L, the desorption efficiency can reach almost 100% in each batch experiment. Importantly, our results show that REEs can be sorbed and recycled from liquid crystal display (LCD) polishing wastewater, suggesting that CuFe_2O_4 may be a good candidate in the efficient and rapid recovery of REEs from industrial wastewater.

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1. Introduction

Rare earth elements (REEs) consist of lanthanides (from La to Lu), together with yttrium and scandium, are chemically similar to each other^{1,2} and are essential raw materials for modern technological developments.³ Their unique physical and chemical properties result in their extensive use as exceptionally valuable components in magnetic materials, computers, clean energy, national defense, advanced transportation, health care, and catalytic applications.^{4,5} Nevertheless, due to predicted supply shortages and the limited Chinese exports, REEs has a high “supply risk” and led many countries to consider them as “critical elements”.^{1,6,7} Thus, economically viable recovery of REEs from aquatic systems will take on greater importance as their supply becomes increasingly limited.

The concentration of REEs in water spans several orders of magnitude with median concentrations of 5, 53, 71, and 170 pmol/L

for the ocean, groundwater, rivers, and lakes, respectively.⁸ However, much higher REEs (4000–80,000 pmol/L) can be found in industrial waste effluents.^{3,8–12} Hence, the effective and economically viable technology for REEs recovery from water systems has become an important issue in resolving the shortage problem of REEs.

Adsorption is considered as a fast, efficient, and inexpensive method for recovering/removing metals from aqueous solutions. Many authors have focused on the toxic elements removal.^{13–21} However, prior investigations of REEs recovery from aqueous solutions using adsorption technology are limited. Gasser and Aly pointed out that the prepared Mg–Fe–LDH–Cyanex-272 was found to be more effective for recovery of La(III) than Nd(III).²² The adsorption percent of the two metal ions was found to increase with increasing contact time, adsorbent weight and pH from 0 to 1 then it remains constant in the pH range 1–2. Additionally, the highest separation factor ($S_{\text{La/Nd}}$) value of 23.2 was obtained with 10 g/L (0.1 g/10 mL) from a mixed solution of 5 g/L of each of La(III) and Nd(III) at pH 1 and contact time 2 h. Awual et al. showed that the novel hybrid adsorbent (with functional immobilization of N-octyl-N-tolyl-1,10-phenanthroline-2-carboxamide into large and cage-pored mesoporous silica monolith) was stable and easy to

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adsorb and recover lanthanide ions by complexation mechanism.²³ They also found that the lanthanide sorption was not affected by the presence of monovalent and divalent of sodium, potassium, calcium, magnesium, chloride, sulfate and nitrate ions due to strong tendency to form stable complexation with trivalent lanthanide. Although effective these materials are cost prohibitive which may hinder their adoption when applying them at industrial plants.

Magnetic nanoparticles CuFe_2O_4 have cubic close-packed arrangement of oxygen ions with Cu^{2+} and Fe^{3+} at two different crystallographic sites²⁴ and have the potential to remove toxic ions from wastewaters.^{25,26} Nevertheless, the price of CuFe_2O_4 generated from auto-combustion, sol–gel method, or co-precipitation^{27–29} is high when the raw materials of pure chemical reagents were used for producing CuFe_2O_4 . The cost could be decreased significantly if the raw materials can be collected from industrial sludge.

Previously we reported that by combination of acid leaching, chemical exchange, and ferrite process, the magnetic nanoparticles CuFe_2O_4 can be successfully manufactured from industrial sludge.³⁰ In this study, a series of systematic experiments were designed to evaluate the feasibility of REEs recovery from aqueous solutions and real industrial wastewater using these nanoparticles under various conditions. The influences of key parameters such as pH, ionic strength (NaCl concentration), and contact time were evaluated. Additionally, the adsorption kinetics and isotherm models of REEs on magnetic nanoparticles CuFe_2O_4 were carefully examined. The information obtained here indicates great potential for designing an effective adsorbent for recovering REEs using the magnetic nanoparticles.

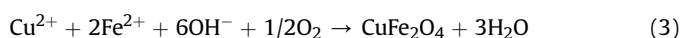
2. Materials and methods

2.1. Chemicals

The REEs stock solutions were supplied by SPEXCP CertiPrep (multi elements: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y) and of high purity (single element: La, Ce, Nd). The sodium hydroxide (NaOH) used in this study was bought from Merck (Germany). All reagents used in this study were at least of analytical grade and prepared in Milli-Q water.

2.2. Manufacturing of magnetic nanoparticles CuFe_2O_4

The magnetic nanoparticles were synthesized according to our former study which showed the technology by combination of acid leaching, chemical exchange, and ferrite process.³⁰ Evidently, the sludge collected from printed circuit board (PCB) industry shows a very high concentration of Cu (158,000 mg/kg in dry base), thus it was used as the raw material for synthesis of CuFe_2O_4 . Fig. 1 illustrates the schematic reaction system for converting Cu sludge to magnetic nanoparticles CuFe_2O_4 and then applied CuFe_2O_4 for recovery of REE from solutions. Acid leaching was conducted for extracting Cu ion from the sludge. Fe^0 was used to substitute solution Cu ion during chemical exchange. In order to ensure the supernatant meet the criterion, ferrite process was employed after chemical exchange. The magnetic nanoparticles CuFe_2O_4 were thus manufactured after the ferrite process. The main corresponding reaction of acid leaching, chemical exchange, and ferrite process can be described as Eqs. (1)–(3), respectively.



The manufactured product was collected using a Nd–Fe–B magnet by taking advantage of its magnetism. The CuFe_2O_4 was then washed with Milli-Q water several times until the solution pH reached near 7. The solids were then dried at 323 K for 24 h and stored for further investigation.

2.3. Adsorbent characterization

The detailed physical/chemical characteristics of the adsorbent are displayed in the previous work.²⁵ Briefly, XRD spectra indicate that the main diffraction peaks of these nanoparticles are at d-spacing of 0.4790, 0.2960, 0.2517, 0.2100, 0.1613, 0.1479, 0.1272, 0.1087, and 0.0964 nm. It matched well with the CuFe_2O_4 crystals (JCPDS file number 00-025-0283), confirming that these nanoparticles are in the phase of CuFe_2O_4 . TEM image displays that the primary particle sizes of the synthesized sample are on the scale of tens nanometers. Zeta potential measurements display that under acidic conditions the adsorbent has a positive surface charge up to approximately pH of 7.3, the point of zero charge (PZC). In contrast, the surface charge reverses to negative at higher pH values. Additionally, the synthesized nanoparticles not only display their high BET surface area (48.3 m^2/g), but also present the high saturation magnetization (62.52 emu/g). With the advantage of the unique magnetism, these products could be easily separated from water in 20 s by using a magnet.

2.4. Batch adsorption

The batch experiments were carried out to evaluate the adsorption processes and the equilibrium states of REEs mobilization. The multi-REEs solution including 17 REEs (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y) was used to study the effect of pH. La, Ce, and Nd solutions were employed individually for the experiments of ionic strength, kinetics, isotherms, and desorption. The desired multi-REEs and single-REE solutions were prepared by dilution of the stock standard solution (multi-REEs: 10 mg/L, single-REE: 1000 mg/L). All equilibrium adsorption experiments were individually performed at room temperature by shaking 2 mg magnetic nanoparticles using a thermostated shaker at a speed of 30 r/min for 2 h. Adsorption kinetics for REEs were also conducted by taking 10 mg/L REEs solution with 2 mg of the magnetic nanoparticles and shaking the mixture at pH 8.15. The element uptake rate of q_t (mg/g) was determined by Eq. (4):

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (4)$$

where C_0 and C_t are the REEs concentration in liquid phase at the initial and at time t (mg/L), respectively; m is the adsorbent amount (g); V is the volume used in the adsorption process (L).

To evaluate the effects of the solution pH and the NaCl concentration on the REEs adsorption, various experiments were performed by adding 2 mg of the adsorbent into a 15 mL centrifuge tube at 298 ± 1 K. The solution pH was adjusted using 0.1 mol/L HNO_3 or NaOH solution to the designated values (2.29 ± 0.01 , 4.03 ± 0.01 , 7.12 ± 0.01 , and 8.15 ± 0.01) and the NaCl concentration of the solutions was set at 0.001, 0.01, 0.1, 0.2, 0.5, and 1.0 mol/L individually by dilution of 2.0 mol/L NaCl solution. Subsequently, the nanoparticles were magnetically separated using a 4000 G magnet. The REEs concentrations in the filtrate were determined by ICP–OES (iCAP 6300, Thermo Scientific) or ICP–MS (Element II, Thermo Scientific). Prior to analysis, the supernatant was acidified with concentrated HNO_3 and stored in acid-washed bottles. Finally, the exhausted adsorbents were taken out for further desorption investigation.

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