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Nano-hematite prepared by activation of natural siderite and its performance on immobilization of Eu(III)

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Nano-hematite was synthesized by calcining siderite ($FeCO_3$) and characterized using TEM, XRD, FT-IR, XPS, specific surface area and potentiometric titration. The characterization results showed that nano-hematite was synthesized by calcining $FeCO_3$ under atmospheric conditions. The batch experiments indicated the adsorption of Eu(III) on nano-hematite significantly increased with increasing pH 2.0–6.0 while the Eu(III) adsorption was independent of ionic strength. The presence of CO_3^{2-} promoted the adsorption of Eu(III) on nano-hematite over a wide range of pH conditions. The adsorption kinetics and isotherms of Eu(III) on nano-hematite were fitted well by pseudo-second kinetic model and Langmuir model, respectively. The maximum adsorption capacity of Eu(III) on nano-hematite calculated by Langmuir equations was 13.02 mg/g at pH 5.5 and $T = 293$ K. The desorption experiments revealed that the adsorption of Eu(III) on nano-hematite was an irreversible process. According to the XPS analysis, the oxygen-containing functional groups of nano-hematite (i.e., Fe-OH) played a crucial role in the Eu(III) adsorption. These findings demonstrated that the nano-hematite could be used as a valuable adsorbent for preconcentration and immobilization of Eu(III) from aqueous solutions in the environmental cleanup.

1. Introduction

Treatment of underground water containing radionuclides has become a momentous tasking virtue of its long term threat to humans and animals (Chen et al., 2013; Sun et al., 2012b; Wang et al., 2015a). The removal of radionuclides from aqueous solutions (e.g., Eu(III), U(VI)) has been universally studied using a wide variety of adsorbents in the late years (Ding et al., 2014, 2015; Shao et al., 2015; Sun et al., 2015). As a trivalent lanthanides, Eu(III) has been extensively investigated on various adsorbents such as clay minerals (Fan et al., 2009; Hu et al., 2010; Tertre et al., 2006; Wang et al., 2015b), metal oxides (Chen et al., 2009a; Tan et al., 2009), and carbon materials (Chen et al., 2008; Sheng et al., 2010; Sun et al., 2013; Tan et al., 2008). Wang et al. (2006b). reported the desorption of Eu(III) from humic acid–Al_2O_3 colloid surfaces. Sun et al. (Sun et al., 2012a) found that the adsorption capacity of Eu(III) on mesoporous Al_2O_3/expanded graphite composites at pH 6.0 and $T = 293$ K was 5.14 mg/g. However, the so low adsorption capacity of the natural adsorbents limited its actual application in environmental cleanup. To improve the adsorption capacity, numerous studies on the adsorption of Eu(III) on nano-materials were carried out in recent years such as graphene oxides (Ding et al., 2014; Ren et al., 2014; Sun et al., 2012b), nano-alumina oxides (Montavon et al., 2006, 2007; Wang et al., 2006a) and nano-iron oxides (Chen et al., 2009b; Yang et al., 2012).

Shanna L. Estes et al. (2013). studied the thermodynamics of Eu(III) adsorption onto hematite. Adsorption behaviors of Eu(III) on micro-meter size hematite have already been published previously by different authors (E.M. El Afifi et al., 2016; Thomas et al., 1998). Furthermore, to reduce the cost, various natural materials were also utilized to remove Eu(III) from aqueous solution. El Afifi et al (E.M. El Afifi et al., 2016). reported the adsorption capacity of Eu(III) on natural hematite(0.25–0.425 mm) at pH 4.7 and $T = 298$ K was 12.30 mg/g. As the particle size decreased to lower than 0.25 mm, the adsorption capacity increased to 20.81 mg/g. The capacity was relatively high and meanwhile the material was interesting. To the best of our knowledge, siderite can be transformed into hematite by calcination. Meanwhile, report on that hematite from annealing of siderite was utilized as adsorbent was rarely observed (Guo et al., 2008), although siderite was utilized to remove AsO_4^{3-}, F^-, Cu^{2+}, Pb^{2+} from aqueous solution (Danková et al., 2015; Erdem and Özverdi, 2005; Guo et al., 2010, 2011).

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Therefore, in this study, the investigation of Eu(III) adsorption onto nano-hematite obtained from calcining the nature siderite was carried out. The aims of this article were to (1) synthesize nano-hematite and characterize it using TEM, XRD, FT-IR, XPS, potentiometric titration and specific surface area; (2) investigate the effect of environmental factors (reaction time, pH, ionic strength, temperature and initial concentration) on the adsorption capacity of Eu(III) on nano-hematite by batch techniques; (3) determine the adsorption mechanism between nano-hematite and Eu(III) by using XPS analysis. The highlight of this study is to utilize nano-particles in the remediation of radioactive pollution.

2. Experimental

2.1. Preparation of nano-hematite

The nano-hematite was synthesized by calcining natural siderite (66.3% of siderite, 22.4% of clay minerals and quartz, 11.3 wt% of goethite) under atmospheric conditions. Briefly, the high purity of natural siderite was obtained by crushing, grinding and screening to less than 200 mesh(<0.10 mm). Afterwards, the screened powder of natural siderite was heated up to 600 °C for 30 min under atmospheric conditions. Subsequently, the powder was cooled to room temperature naturally for further used. Eu(III) stock solution of 0.1 mol/L was prepared from Eu_2O_3 (purity 99.99%) after dissolution and dilution within 0.01 mo/L $HClO_4$ solution. All chemicals used in this study were analytical-grade, and all the solutions were prepared with Milli-Q water.

2.2. Characterization

As-prepared nano-hematite was characterized by TEM, XRD, FT-IR, XPS, specific surface area and potentiometric titration. The TEM images were provided with a Philips JSM-6490LV transmission electron microscope. The XRD patterns were conducted on a Dandonghaoyuan 2700 diffractometer using Cu Kα radiation. FT-IR measurements were conducted by using a VERTEX-70 Fourier *trans*-form infrared spectrometer. The XPS values were conducted with a Thermo Escalab 250 electron spectrometer. The BET-nitrogen isotherms were applied in a Novawin 3000e Surface Area and Pore size Analyzer to determine the specific surface area of catalysts (SSA, m^2g^{-1}). The potentiometric acid-base titration was performed by a computer-controlled titration system (DL50 automatic titrator, Mettler Toledo).

2.3. Batch adsorption-desorption experiments

The batch adsorption experiments were conducted with 2 g/L nano-hematite and 10 mg/L Eu(III) solutions in the presence of 0.01 mol/L $NaClO_4$. The pH of the suspension was adjusted from 2.0 to 11.0 by adding negligible volume of 0.001–1.0 mol/L HNO_3 and/or NaOH solution. The adsorption isotherms were examined at pH = 5.5 ± 0.1 with the initial concentration of Eu(III) ranging from 1 to 30 mg/L. The suspensions were shaken for 24 h to achieve reaction equilibrium.

The desorption kinetics of Eu(III) on nano-hematite were examined after adsorption equilibrium by using 0.1 mol/L NaCl solution. In short, 3.0 mL of supernatant (the initial volume was 6.0 mL) after adsorption equilibrium was displayed by 3.0 mL of 0.1 mol/L of NaCl solution with the pH = 5.5 ± 0.1 adjusted with 0.001–1.0 mol/L HNO_3 solution(Ding et al., 2014; Ma et al., 2015; Sun et al., 2015). Afterwards, the aforementioned suspension was reacted for different time ranging from 5min to 24 h with continuous stirring conditions. The solid phase was separated from liquid phase by centrifugating at 9000 rpm for 15 min. The blank experiments were carried out under the same conditions. The concentration of Eu(III) was determined by a kinetic phosphorescence analyzer(KPA-11, Richland, USA) (Sun et al., 2015).

The removal percentage of Eu(III) (adsorption (%)) and adsorption capacity (Qs, mg.g^{-1}) can be formulated as Eq. (1) (Cheng et al., 2015a) and (2) (Cheng et al., 2015b), respectively:

$$\text{Adsorption (\%)} = (C_0 - C_{eq})/C_0 \times 100\% \quad (1)$$

$$Q_s = V \times (C_0 - C_{eq})/m \quad (2)$$

where C_0 (mg•L^{-1}) and C_{eq} (mg•L^{-1}) are initial concentration and concentration after adsorption, respectively. The m (g) and V (mL) are the mass of the nano-hematite and the volume of the suspension, respectively. All the experimental data were the average of triplicate determinations and the relative errors were within ±5%.

2.4. Kinetic models

The pseudo-first-order and pseudo-second-order kinetic models were used for fitting the adsorption kinetics of Eu(III) on nano-hematite in order to confirm the underlying mechanisms during the entire adsorption process(Danková et al., 2015). The linear forms were given in Eqns. (3) and (4), respectively:

$$\ln(Q_e - Q_t) = \ln(Q_e) - K_1 \times t \quad (3)$$

$$t/q_t = 1\Big/\left(K_2 \times {Q_e}^2\right) + t/Q_e \quad (4)$$

where Q_e (mg/g) and Q_t(mg/g) are the adsorption concentration of Eu(III) at equilibrium and time t, respectively. K_1 and K_2 are the pseudo-first order and pseudo-second order kinetic rate constants, respectively.

In order to have a further understanding of Eu(III) adsorption on nano-hematite, the kinetic behavior of the adsorption process was analyzed by using the intra-particle diffusion model. It was used to realize the steps involved in adsorption process and the transport of adsorbate from the exterior surface to the pores of adsorbent(Zeng et al., 2014). The model was described as Eqn. (5).

$$Q_t = k_i t^{1/2} + C \quad (5)$$

where k_i is the intra-particle diffusion rate constant and C is a constant. The intra-particle-diffusion plot gave multi-linearity, indicating that the whole adsorption process was composed of several stages.

2.5. Isotherms models

The adsorption isotherms of Eu(III) on nano-hematite can be fitted by Langmuir or Freundlich models, the linear forms are given in Eqn. (6)(Chen et al., 2009a) and(7) (Guo et al., 2011), respectively:

$$C_e/Q_e = 1/(K_L \cdot Q_m) + C_e/Q_m \quad (6)$$

$$\lg Q_e = (1/n)\lg C_e + \lg K_F \quad (7)$$

where Q_m (mg·g^{-1}) is the maximum adsorption capacity of adsorbent at complete monolayer coverage. K_L (L·mg^{-1}) is a Langmuir constant which is related to the free energy of sorption. 1/n is the heterogeneity of the adsorption sites. K_F represents equilibrium coefficient which represented the partitioning of the adsorbate between the solid and liquid phases over the concentration range studied.