Solid State Sciences 81 (2018) 1–7

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Phosphate uptake behavior of layered rare earth hydroxides *l*-RE$(OH)_3$ (RE = Sm, Gd, Er, and Y) from water

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ARTICLE INFO

Article history:
Received 29 March 2018
Accepted 10 April 2018
Available online 13 April 2018

Keywords:
Rare earths
Layered hydroxides
Adsorption
Phosphate

ABSTRACT

The use of rare earths (REs) provides various advantages for removal and recovery of phosphate from water because they have high affinity to form stable complexes with phosphates even at low concentrations. Very low solubility of rare earth $REPO_4$ in water was expected to induce a high phosphate adsorption rate and capacity. In this study, layered rare earth hydroxides, *l*-RE$(OH)_3$ (RE = Sm, Gd, Er, and Y), have been employed to remove or recover phosphate from aqueous solution. This layered polymorph of *l*-RE$(OH)_3$, which is composed of hydroxocation layers, exhibited a high point of zero charge ($pH_{pzc} > 10$) and significantly enhanced adsorptive ability for phosphates over a wide pH range. The isotherm and kinetics of phosphate adsorption on *l*-RE$(OH)_3$ were explained dominantly by the Langmuir isotherm model and pseudo-second-order kinetic model, respectively. A strong dependence of isotherm and kinetic parameters on RE demonstrated that the adsorption of phosphate on *l*-RE$(OH)_3$ is a chemisorption dominated process involving the replacement of −OH by phosphate ion to be included into the coordination polyhedra of RE. The desorption of phosphate from *l*-RE$(OH)_3$ was slow but the desorption efficiency for all RE members was higher than 97% in a 1.0 M NaOH solution after 4 days at room temperature. Considering high capacity and stability as well as no significant interference in recovery of phosphate from waters containing common competing anions, this rare earth adsorbent series is proposed as a promising alternative for efficient and sensitive phosphate recovery from natural and wastewaters.

1. Introduction

Phosphorus, in the form of phosphates in water, is one of the essential nutrients that humans and animals need, and also a requisite of fertilizers for agricultural food production. Unfortunately, the excessive and inefficient use of phosphate causes serious eutrophication of environmental waters and the world is gradually running short of the natural phosphate rock deposits [1–4]. Hence, it is important to develop materials to recover and reuse phosphorus in environmental and industrial wastewaters.

Several advantages such as cost-effectiveness, simplicity, and flexibility in industrial operations consider the adsorption method as one of the most promising candidates in comparison with other technologies developed for removal and recovery of phosphate from wastewater [1,5,6]. As conventional adsorbents show unsatisfactory selectivity toward phosphate and undergo considerable interference by common inorganic anions such as SO_4^{2-}, NO_3^-, Cl^- and HCO_3^- [7], various types of metal oxides and metal hydroxide-based materials have been investigated for improved adsorption of phosphates [8–12]. The phosphate adsorption kinetics and equilibria of such metal oxides and hydroxides are determined mainly by the surface hydroxyl groups with amphoteric properties [13]. Unfortunately, many hydroxide-based adsorbents have weakly positive surface charge at only low pH, so that their phosphate uptake capacity is significantly lowered at neutral pH despite an efficient operation at acidic conditions [14,15]. As a consequence, it is not surprising that considerable interest has been focused on the ability of layered double hydroxides (LDHs) with positive zeta potentials over a wide pH range to remove phosphate from contaminated waters by surface adsorption in recent years [16,17]. It was proposed that the phosphate uptake process of LDHs is not due to anion exchange in the interlayers as might have been anticipated, but partially dissolved LDHs form insoluble amorphous phosphate salts at the surface [18]. However, the ion exchange

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https://doi.org/10.1016/j.solidstatesciences.2018.04.008
1293-2558/

reaction with coexisting organic (*i.e.* carboxylates, sulfonates, and sulfates, etc.) and inorganic (oxo-)anions in the interlayer space is inevitable and significantly reduce the selectivity of LDHs during phosphate adsorption [19–22].

Rare earths (RE) have high affinity to form stable complexes with phosphate even at low concentrations. Very low solubility of rare earth orthophosphate in water could be also advantageous to increase the selectivity in phosphate recovery [23,24].] Actually, the rare earth-modified adsorbents provide several promising advantages such as high adsorption capacity, wide operating pH range, and high uptake rate in a low phosphate concentration [25–28]. Layered rare earth hydroxides (LRHs) are another class of lamellar anionic clay with a general formula $RE_2(OH)_5X^{m-}{}_{1/m}\cdot nH_2O$ (RE = rare earths, X = interlayer anions) [29]. Their structure is composed of rare earth hydroxocation layers and exchangeable interlayer inorganic or organic anions. Due to the unique structure and properties, LRHs have been investigated for applications as adsorbents, catalysts, drug carriers, additives, and bioactive nanocomposites [30–33]. Nevertheless, the existence of exchangeable X^{m-} anions in the interlayer gallery is unfavorable for effective phosphate uptake of LRHs. They could be released by the intercalation of phosphate anions and the exchange reaction with coexisting organic and inorganic anions in the interlayer could occur at the same time as phosphate adsorption at the surface. In this respect, the layered polymorph (*l*-$RE(OH)_3$) of rare earth hydroxides could be an alternative for the selective and sensitive recovery of phosphate from water because the interlayer space of this derivatives is inert to intercalations of organic and inorganic anions [34].

Recently, we demonstrated that layered yttrium hydroxide, *l*-$Y(OH)_3$, has a great potential for a new adsorbent with high capacity, selectivity, and reusability to recover phosphate from natural waters containing various common anions [35]. In particular, Ce^{3+} and Tb^{3+} co-doped form, (*l*-$Y(OH)_3$:Ce,Tb), exhibited an attractive performance as a luminescent adsorbent to selectively detect phosphate in aqueous solution. The change in photoluminescence by phosphate adsorption, coupled with an increase in the solution pH, suggested the inner-sphere complexing mechanism involving a release of OH^- ions accompanied by the formation of Y–O–P bonds. This previous result indicated that the phosphate uptake characteristic is significantly improved by the interaction between phosphate ion and RE^{3+} in coordination polyhedra of *l*-$RE(OH)_3$, which is much stronger than the electrostatic interaction caused by simple ion exchange in the interlayer gallery. Therefore, our interest for phosphate adsorption of *l*-$RE(OH)_3$ was extended to RE = Sm, Gd, and Er members in the present work. High adsorption capacity reaching ~130 mg-P/g at pH = 7 as well as no significant interference by common competing anions proposed that *l*-$RE(OH)_3$ adsorbent series is promising for efficient and sensitive phosphate recovery from natural and wastewaters.

2. Experimental

Well-crystallized layered rare earth hydroxynitrates $RE_2(OH)_5NO_3\cdot nH_2O$ (LRHs; RE = Sm, Gd, Er, and Y) precursor powders were prepared for the synthesis of phosphate adsorbents in aqueous solutions at room temperature. Typically, $Sm(NO_3)\cdot 6H_2O$, $Gd(NO_3)\cdot 6H_2O$, $Er(NO_3)\cdot 5H_2O$, and $Y(NO_3)\cdot 6H_2O$ (5 mmol) were dissolved in deionized water (30 mL). A 20 mL of KOH (10 mmol) solution was then added drop-wise to the prepared mixture with vigorous stirring at room temperature. The resulting aqueous solution was aged at room temperature without stirring for 12 h. After the reaction was complete, the precipitate was collected by several repeated centrifugations and washing steps with distilled water several times to completely remove Na^+ and NO_3^- ions. The solid was then dried at 60 °C for 6 h.

To prepare layered rare earth hydroxides *l*-$RE(OH)_3$, the obtained LRH crude powders were dispersed in aqueous 0.1 M NaOH solutions at pH ~ 13 to proceed the ion-exchange reaction between interlayer NO_3^- ions and OH^- ions. After stirring (750 rpm) these mixtures for 24 h at room temperature, the resulting layered hydroxide precipitates, $RE(OH)_3\cdot H_2O$ were collected by filtration, washed with copious amounts of water to remove residual salts, and then dried at 60 °C for one day. The formation of single-phased layered hydroxynitrates and layered hydroxides was confirmed by X-ray diffraction (XRD) patterns recorded with a Bruker D8 Advance diffractometer. Thermogravimetric (TG) curves to confirm complete transformation from corresponding hydroxynitrate to layered hydroxide forms and to determine the amount of interlayer water were recorded in air at a heating rate of 5 °C/min using a Seiko Instruments TG/DTA320.

A 20 mL of 100 mg/L suspension was prepared to measure the point of zero charge (pH_{pzc}) of *l*-$RE(OH)_3$ powders. Every suspension was adjusted to various pH values by adding NaOH or HCl solution with stirring (600 rpm). Then, 1.0 mL of the resulting solution was placed into a disposable folded capillary cell (DTS1070, Malvern), and the zeta (ζ) potentials were measured using a Zetasizer Nano ZS90 (Malvern).

Phosphate solution (200 mg-P/L) for adsorption reactions was prepared by dissolving AR grade KH_2PO_4 in deionized water. The adsorption isotherms on *l*-$RE(OH)_3$ were determined at 23 ± 2 °C. To investigate the pH dependence of adsorption, the initial solution pH was varied from 5 to 7 and 9 by adding 0.1 M HCl or 0.1 M KOH solution. The initial concentration of the phosphate solution was varied from 1.0 to 100.0 mg-P/L. Then, 0.1 g *l*-$RE(OH)_3$ was mixed into 200 mL of phosphate solutions of different initial concentrations and stirred (750 rpm) for 24 h. After the adsorption reaction, the supernatant was collected through filtration using a syringe filter (0.45 μm Whatman filter disc). The phosphate concentration remaining in solution was measured using the molybdenum blue-ascorbic acid method [36]. The absorbance of the intense blue phosphate-molybdate complex was measured at a wavelength of 880 nm. The amount of phosphate adsorbed on the adsorbents was calculated from the difference between the initial concentration and the equilibrium concentration in the solutions. The mean values of analysis data were adopted after 3 times repeated adsorption experiments. The absorption spectra of phosphate solutions were measured by employing UV-vis spectrophotometers (Shimadzu Multispec-1501 and a LAMBDA 35).

Adsorption kinetic experiments were also performed by similar procedure with 200 mL of aqueous solution at an initial phosphate concentration of 200 mg-P/L. After adding 0.1 g of *l*-$RE(OH)_3$ adsorbent to the phosphate solutions at initial solution pH = 5, 7, and 9, the resulting suspensions were constantly stirred for 3 min to 24 h. The supernatant was collected using a syringe filter and was analyzed to determine the residual phosphate concentration.

A set of adsorption experiments was performed to evaluate the interference of common anions on phosphate recovery by *l*-$RE(OH)_3$ in aqueous solutions containing Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^- anions. The initial phosphate concentration was 0.065 mM (2.0 mg-P/L) and the concentrations of coexisting anions were 0.065, 0.325, and 0.65 mM, respectively. The adsorption reaction was performed for 1 h with stirring at room temperature. The adsorbent dosage was fixed at 0.5 g/L. After adsorption for 1 h, the corresponding filtrates were analyzed to determine the residual phosphate concentration in solutions.

To assess phosphate desorption efficiency, 0.1 g of *l*-$RE(OH)_3$ adsorbent was reacted in a 200 mg-P/L phosphate solution at pH = 7 with constant stirring for 24 h at room temperature. The