Highly efficient and selective phosphate removal from wastewater by magnetically recoverable La(OH)$_3$/Fe$_3$O$_4$ nanocomposites

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ABSTRACT

The use of lanthanum (La)-based materials for phosphate removal from water and wastewater has received increasing attention. However, challenges remain to enhance phosphate sorption capacities and recover La-based sorbents. In this study, magnetic La(OH)$_3$/Fe$_3$O$_4$ nanocomposites with varied La-to-Fe mass ratios were synthesized through a precipitation and hydrothermal method. Based upon preliminary screening of synthesized La(OH)$_3$/Fe$_3$O$_4$ nanocomposites in terms of phosphate sorption capacity and La content, La(OH)$_3$/Fe$_3$O$_4$ nanocomposite with a La-to-Fe mass ratio of 4:1 was chosen for further characterization and evaluation. Specifically, for these materials, magnetic separation efficiency, phosphate sorption kinetics and isotherm behavior, and solution matrix effects (e.g., coexisting ions, solution pH, and ionic strength) are reported. The developed La(OH)$_3$/Fe$_3$O$_4$ (4:1) nanocomposite has an excellent magnetic separation efficiency of >98%, fast sorption kinetics of 30 min, high sorption capacity of 83.5 mg P/g, and strong selectivity for phosphate in presence of competing ions. Phosphate uptake by La(OH)$_3$/Fe$_3$O$_4$ (4:1) was pH-dependent with the highest sorption capacities observed over a pH range of 4–6. The ionic strength of the solution had little interference with phosphate sorption. Sorption-desorption cyclic experiments demonstrated the good reusability of the La(OH)$_3$/Fe$_3$O$_4$ (4:1) nanocomposite. In a real treated wastewater effluent with phosphate concentration of 1.1 mg P/L, 0.1 g/L of La(OH)$_3$/Fe$_3$O$_4$ (4:1) efficiently reduced the phosphate concentration to below 0.05 mg P/L. Electrostatic attraction and inner-sphere complexation between La(OH)$_3$ and P via ligand exchange were identified as the sorption mechanisms of phosphate by La(OH)$_3$/Fe$_3$O$_4$ (4:1).

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1. Introduction

Excess phosphorus (P) released into water bodies can trigger eutrophication, affecting water quality and aquatic ecosystem health (Correll, 1998). Studies show that a P concentration above 0.02 mg P/L generally accelerates eutrophication in lakes (Heathwaite and Sharpley, 1999), leading many places to make recommendations on concentration limits for P in water bodies. For example, the United States Environmental Protection Agency (US EPA) recommends that any streams entering a lake or reservoir should have total P concentrations not exceeding 0.05 mg P/L (Loganathan et al., 2014), and the European Union (EU) defines the cut-off total P concentrations in lakes as non-risk and risk conditions of eutrophication to be < 0.01 mg P/L and > 0.1 mg P/L, respectively (Loganathan et al., 2014). For discharges from wastewater treatment plants, the permissible concentration of P will be lowered from 1–2 mg P/L to 0.1 mg P/L in the EU under the Water Framework Directive (Shepherd et al., 2016). However, these are stringent P discharge standards; traditional techniques such as chemical precipitation and biological treatment are unable to reduce phosphate concentrations to below 0.1 mg P/L (Sengupta and Pandit, 2011). Hence, other techniques are needed to meet stringent discharge requirements.

Sorption is a preferable approach for phosphate removal due to its simplicity of design, effectiveness even at low P concentrations (Loganathan et al., 2014), and potential for recovery. Many sorbents such as activated carbon, resins, industrial byproducts, and waste biomass have been explored for removing phosphate from water

(Rittmann et al., 2011), yet low sorption capacity and poor selectivity are inherent limitations for most of these materials. Due to lanthanum's strong affinity with phosphate, a number of studies have developed La-modified sorbents such as La-modified bentonite clay (Phoslock®) (Haghseresht et al., 2009), La-doped silica spheres (Huang et al., 2014b), and La-treated lignocellulosic sorbents (Shin et al., 2005) for the removal of phosphate. These sorbents have exhibited marginally enhanced phosphate sorption capacities — for example the maximum sorption capacity of Phoslock® is only 9.5—10.5 mg P/g (Haghseresht et al., 2009). Further, these sorbents are difficult to separate from wastewater after treatment. Traditional methods to recover sorbents include centrifugation and filtration; however, centrifugation is energy-intensive and filtration is prone to filter blockages (Chen et al., 2009).

Magnetic separation is faster and more effective in separating nanoparticles from wastewater compared to centrifugation and filtration (Tang and Lo, 2013). In addition, the incorporation of magnetic nanoparticles (e.g., Fe_3O_4) with La facilitates the separation and recovery of sorbents. The La acts as active sites for the removal of phosphate in water; while Fe_3O_4 allows for the magnetic separation. To date, only a few studies have reported on the use of magnetic La-based sorbents for phosphate removal (Lai et al., 2016; Rashidi Nodeh et al., 2017), and these studies have typically been restricted by complicated synthesis procedures, the use of graphene as substrate, which is relatively expensive, or low sorption capacities (i.e., 27.8 mg P/g for $Fe_3O_4@SiO_2@La_2O_3$). Additionally, the sorption mechanisms of phosphate by La-based materials have not been characterized in detail. Therefore, the objectives of this work are to: (1) develop magnetic La-based nanocomposite (i.e., $La(OH)_3/Fe_3O_4$) through a facile precipitation and hydrothermal method; (2) demonstrate selective removal of phosphate by $La(OH)_3/Fe_3O_4$ with a higher sorption capacity than other sorbents; and (3) elucidate sorption mechanisms through batch experiments (e.g., effects of pH and ionic strength), zeta potential, and spectroscopic investigations (Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS)).

2. Materials and methods

2.1. Materials and chemicals

All chemicals used in this study were analytical reagents of high purity. The $FeCl_3 \cdot 6H_2O$ (98%), $FeCl_2 \cdot 4H_2O$ (99%), trisodium citrate dihydrate, lanthanum (III) nitrate hydrate ($La(NO_3)_3 \cdot xH_2O$, x = 3—5, 99.9%), and KH_2PO_4 (99%) were purchased from Sigma-Aldrich in the US. The deionized (DI) water with a specific conductivity of 18 MΩ cm was used to prepare all solutions unless otherwise specified. A 1000 mg P/L stock solution of phosphate was prepared by dissolving 2.2171 g of KH_2PO_4 in 500 mL DI water. All phosphate in this study refers to orthophosphate unless otherwise specified.

2.2. Synthesis of Fe_3O_4 nanoparticles and $La(OH)_3/Fe_3O_4$ nanocomposites

2.2.1. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared through a modified coprecipitation method (Hu et al., 2005). First, 100 mL of DI water was bubbled by nitrogen gas for 30 min. Then 2.164 g of $FeCl_3 \cdot 6H_2O$ and 0.796 g of $FeCl_2 \cdot 4H_2O$ were dissolved in the above 100 mL deoxygenated DI water with nitrogen gas purging. $NH_3 \cdot H_2O$ (28% in H_2O) was added dropwise into the above mixture until the pH reached 11. The solution was mixed for 10 min, and then a 2-mL solution that contained 0.6 g of trisodium citrate dihydrate was injected rapidly into the mixture. The mixture was then stirred for another 1 h with nitrogen gas purging. Finally, the black products were

separated from the mixture by a magnet, and rinsed with deoxygenated DI water three times.

2.2.2. Synthesis of $La(OH)_3/Fe_3O_4$ nanocomposites

$La(OH)_3/Fe_3O_4$ nanocomposites were prepared by a precipitation and hydrothermal method. The precipitation method was adopted because of its simplicity, high efficiency, and low cost. The subsequent hydrothermal treatment could benefit the crystallinity of the products (Xiao et al., 2014). The as-prepared Fe_3O_4 nanoparticles (0.45 g) were dispersed in 60 mL of DI water under ultrasonication for 10 min. Then 0.45 g of $La(NO_3)_3 \cdot xH_2O$ in 10 mL DI water was added into the Fe_3O_4 suspension. The resulting mixture was stirred for 10 min before adding 0.45 g of NaOH dissolved in a 10 mL DI water. After being stirred for another 5 h, the mixture was transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity) and heated at 180 °C for 10 h. Finally, the autoclave was cooled down to room temperature and the products were washed with water three times. To synthesize $La(OH)_3/Fe_3O_4$ nanocomposites with different La contents, the mass ratios of $La(NO_3)_3 \cdot xH_2O$ and Fe_3O_4 (La-to-Fe) were varied from 1:1, 2:1, 4:1, to 5:1 by adjusting the amount of $La(NO_3)_3 \cdot xH_2O$ in the initial synthetic solution. The same amount of $La(NO_3)_3 \cdot xH_2O$ and NaOH was used in each synthesis. $La(OH)_3/Fe_3O_4$ nanocomposites with four La-to-Fe mass ratios of 1:1, 2:1, 4:1, and 5:1 were obtained using the above method.

2.3. Characterization of magnetic sorbents

The crystal structure of the magnetic sorbents was analyzed using an X-ray diffraction spectrometer (PW-1830, Philips, France) with Cu Kα radiation (λ = 1.5406 Å) over the 2θ range of 5-90°. The morphology of the sorbents was studied using a transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) at an accelerating voltage of 20 kV. The magnetic properties of the materials were analyzed by a vibrating sample magnetometer (VSM, Lake Shore 7037, USA) at room temperature. Nitrogen adsorption-desorption isotherms were measured at 77 K using a surface area analyzer (NOVA-3200e, Quantachrome, USA). Prior to the surface area analysis, the samples were degassed at 80 °C for 24 h. The specific surface area was determined from the adsorption branch of isotherm using the Brunauer—Emmett—Teller (BET) method in a relative pressure range of 0.05—0.30. The total pore volume was calculated from the adsorbed nitrogen amount at a relative pressure of 0.98. The La content in each $La(OH)_3/Fe_3O_4$ nanocomposite was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300 DV, Perkin-Elmer, USA). The surface charge of each sorbent was analyzed on a zeta potential analyzer (Zetaplus, LaborScience S.A., Greece) using 1 mM KCl as background electrolyte. The zeta potential values obtained were averaged over ten measurements. The functional groups of the materials were determined on an FTIR spectrometer (Vertex 70, Bruker, USA). FTIR spectra were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and were averaged over 128 scans. KBr powder was used as a background material. The chemical compositions of the materials were analyzed using an XPS (PHI 5600, Physical Electronics Inc., USA) with Al Kα radiation (1486.6 eV). All binding energies were referenced to the C1s peak at 285.0 eV.

2.4. Batch experiments

To determine the time needed to reach sorption equilibrium, the sorption kinetics of phosphate on the as-prepared $La(OH)_3/Fe_3O_4$ (4:1) nanocomposite were conducted by mixing 0.025 g of sorbents with 50 mL of 5.0 mg P/L phosphate solutions at 23 °C. Samples were drawn periodically for phosphate concentration analysis. Sorption