Chemical Engineering Journal 254 (2014) 163–170

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Removal and recovery of phosphate from water by lanthanum hydroxide materials

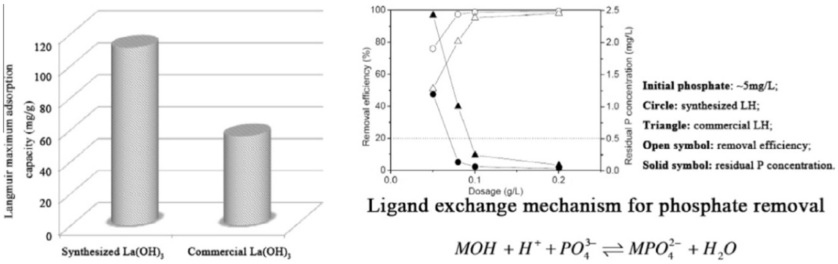
Jie Xie [a], Zhe Wang [a], Shaoyong Lu [b], Deyi Wu [a,*], Zhenjia Zhang [a], Hainan Kong [a]

[a] School of Environmental Science and Engineering, Shanghai Jiao Tong University, No. 800, Dongchuan Rd., Shanghai 200240, China
[b] Research Centre of Lake Environment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

HIGHLIGHTS

- A lanthanum hydroxide adsorbent was prepared from waste alkaline solution.
- The Langmuir adsorption maximum for phosphate reached 107.53 mg/g.
- The affinity of lanthanum hydroxide toward phosphate was high over a wide pH range.
- The adsorption mechanism was explained by the ligand exchange process.
- Phosphate removal by lanthanum hydroxide performs well in real water/wastewater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 March 2014
Received in revised form 25 May 2014
Accepted 26 May 2014
Available online 2 June 2014

Keywords:
Lanthanum hydroxide
Wastewater
Phosphate
Adsorption
Recycling

ABSTRACT

The adsorption of phosphate from water by two lanthanum hydroxides (LHs), a commercial LH and a synthesized LH from waste alkaline solution, was investigated. The amorphous synthesized LH had higher specific surface area, and showed greater performance for phosphate adsorption than the crystalline commercial LH. The phosphate adsorption data agreed well with the Langmuir model with the calculated maximum capacity of 107.53 mg/g (dry weight) for synthesized LH and 55.56 mg/g (dry weight) for commercial LH, respectively. The affinity toward phosphate was high over a wide pH value range, from about 2.5 to 9.0 for commercial LH and from about 2.5 to 12.0 for synthesized LH, respectively. Release of La was negligible when pH > 4.0. FTIR measurements showed that the monodentate surface species of $\equiv$La-OPO$_3$ was formed via ligand exchange mechanism. In the coexistence of chloride, nitrate, sulfate and hydrogen carbonate anions, phosphate removal by LHs was only slightly affected. The uptake of phosphate ($\sim$5 mg/L) from real effluent by LHs performs well at a dose of 1 kg/10m^3, with the removal efficiency exceeding 99% for synthesized LH and 90% for commercial LH, respectively. The adsorbed phosphate could be successfully recovered by hydrothermal treatment in NaOH solution, and the regenerated LHs could be reused for phosphate removal.

1. Introduction

Though a number of elements are required by organisms, just five elements (carbon, oxygen, hydrogen, nitrogen and phosphorus) make up 93–97% of the biomass of organisms, including plants, animals, fungi, and bacteria [1]. Phosphorus is not very abundant in the biosphere. Sedimentary rocks that are especially rich in phosphorus are mined for fertilizer and applied to agricultural soils since about 170 years ago [2,3]. However, phosphate rock is a non-renewable resource and it is predicted that current global reserves may be depleted in 50–100 years [2,3]. What is

---

* Corresponding author. Tel.: +86 21 54748529; fax: +86 21 54740825.
E-mail address: dywu@sjtu.edu.cn (D. Wu).

http://dx.doi.org/10.1016/j.cej.2014.05.113
1385-8947/

more, the global phosphorus cycle does not include a substantial atmospheric pool, differing from other four elements. As a result, phosphorus entering into water bodies could hardly be recycled to land for use in agriculture. It is also known that accumulation of phosphorus is a leading cause of eutrophication for relatively stagnant water bodies such as lakes and estuaries. Therefore, on one hand, phosphorus removal from wastewater before discharge has to be considered to protect natural waters from eutrophication. On the other hand, the depletion of phosphorus fertilizer urges us to investigate the recovery and reuse of phosphorus from wastewater.

Adsorption is superior to chemical treatment (such as precipitation with iron salts, alum, or lime) and biological process for phosphate removal from water/wastewater in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants, and reduced production of sludge [4–6]. More importantly, adsorbed phosphorus may be recovered provided that the adsorption amount is high and a suitable desorption method could be found. With the adsorption technique, hence, the use of a good adsorbent is crucial to guarantee the efficiency of wastewater treatment.

The utilization of industrial wastes or by-products as adsorbents for phosphate removal has been widely investigated, including fly ash based materials [7,8], biosorbent from organic residues [9], blast furnace slag [10], red mud [11,12], spent alum sludge [13], ferric sludge [14], and iron-rich residues [15], etc. The major advantage of using these kinds of adsorbents for wastewater treatment is cost-effective. However, more effective adsorbent for phosphate removal with the merit of phosphorus recovery is in urgent demand.

Lanthanum is a rare earth element that is considered to be environmentally friendly and is relatively abundant in the earth's crust [16–18]. Lanthanum is known to have a high affinity for phosphate and the lanthanum–phosphate complex forms, even when present in low concentrations of phosphate [19,20]. As a result, considerable attention has been focused on the use of lanthanum-containing materials for the removal of phosphate in recent years [18–27].

Although a great number of works have been undertaken on the synthesis of zeolite from coal fly ash as a productive measure for the reuse of the solid waste, problems related to waste alkaline solution remains unsolved [28]. Thus, it is important to search for a method to recycle the waste alkaline solution following zeolite synthesis from coal fly ash.

The aim of our present study was to develop an efficient adsorbent from the waste alkaline solution, for the removal and recovery of phosphate from wastewater. For this purpose, lanthanum hydroxide (LH) was prepared by neutralization of lanthanum chloride solution with the waste alkaline solution generated during the conversion of coal fly ash into zeolite. The synthesized LH was investigated for its potential as an adsorbent to remove and recover phosphate from wastewater. For comparison, a commercial LH was also examined.

2. Materials and methods

2.1. Materials

Coal fly ash used in this study was obtained from the Second Power Plant of Minhang in Shanghai, China. For zeolite preparation, a conventional refluxing method was used, with vigorous stirring, under the following reaction conditions: reaction time 24 h, liquid/solid ratio 6 mL/g, NaOH concentration 2 M and temperature 95 °C. After being cooled down to room temperature, waste alkaline solution was recovered by centrifugation, and a ~0.67 M $LaCl_3$ solution was added, drop-wise (10 mL/min) with continuous stirring. The volume of $LaCl_3$ solution was equal to that of waste alkaline solution (200 mL). To guarantee a sufficient reaction of $LaCl_3$ with the alkaline solution, stirring was kept for 4 h, following the addition of $LaCl_3$. The formed lanthanum hydroxide was then washed three times with double-distilled water and twice with ethanol. Finally, the product was dried in an oven at 45 °C, ground to pass through an 80-mesh (with the diameter of 180 μm) sieve, and stored in airtight containers until further use.

Besides the above synthesized lanthanum hydroxide, a pure commercial LH in its power form was purchased from Aladdin Industrial Corporation (Shanghai, China) and was used without any modification.

The chemical composition of materials was determined by X-ray fluorescence analysis (PW2404, Philips). Moisture was measured by the loss of weight after heating at 105 °C for 24 h. CEC was determined by the ammonium acetate method [29]. The X-ray diffraction (XRD) patterns were recorded using D8 ADVANCE (BRUKER-AXS) with Cu Kα filtered radiation (30 kV, 15 mA). Particle morphology was observed by SEM using a JEOL JSM-7401F microscope. The FTIR spectra were recorded with a FT-IR spectrophotometer (SHIMAZU IRPrestige-21) using the KBr method. BET surface area was determined by NOVA1200e (Quanta chrome) using the nitrogen adsorption method. To determine pH value, 0.2 g of material and 40 mL of distilled water were added to the centrifuge tubes and the final pH value was taken, using a Hach-Sension+ pH meter, after a 24 h equilibration period. The soluble components in waste alkaline solution and the effluent following the treatment of waste alkaline solution with $LaCl_3$ were acidified for analysis by using an inductively coupled plasma-atomic emission spectroscopy (ICAP 6000 Radial, Thermo Company).

The batch adsorption experiments for phosphate were performed in duplicate and the mean data are reported in this paper.

2.2. Adsorption isotherms

Adsorption isotherms of phosphate were performed in 50-mL centrifuge tubes. About 0.1 g of material was put into centrifuge tubes containing 40 mL phosphate solution with different concentrations of phosphate, ranging from 5 to 500 mg/L. The suspensions were shaken in a thermostatic chamber at 25 ± 1 °C for 24 h at 180 rpm. After 24 h, the equilibrium pH was measured and the suspensions were centrifuged. The clear supernatants were determined for phosphate, using the molybdenum-blue ascorbic acid method [30]. The amounts of phosphate adsorbed per unit mass of adsorbent were calculated from the differences between the initial and the final phosphate concentrations in solution:

$$Q_e = (c_o - c_e)V/m$$

where V is the sample volume in L, c_o is the initial phosphate concentration in mg/L, c_e is the equilibrium phosphate concentration in mg/L, and m is the dry weight of adsorbent in g.

2.3. pH Studies

The effect of solution pH on phosphate removal was measured in the same fashion with the adsorption isotherm measurements, except that the initial phosphate concentration was 100 mg/L. The suspensions were adjusted to the desired pH values with 0.1 M HCl or NaOH. After 24 h, the equilibrium pH was measured and the suspension was centrifuged for analyzing the residual phosphate concentration in supernatant.

To assess the stability of LH materials under different pH conditions, 0.1 g sample was added to each 250-mL Erlenmeyer flask containing 100 mL of doubly-distilled water (DD water). The mixtures were adjusted to pH levels within the range of 2.0–7.5 and continuously shaken for 24 h at 25 ± 1 °C. After centrifugation, the supernatant was collected and filtered prior to analysis for La