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Green synthesis of a novel hybrid sorbent of zeolite/lanthanum hydroxide and its application in the removal and recovery of phosphate from water

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ABSTRACT

The traditional process of zeolite synthesis from coal fly ash produces large amount of waste alkaline solution, besides zeolite product. A novel hybrid sorbent, which was composed of zeolite and lanthanum hydroxide (La-ZFA), was produced by using soluble lanthanum chloride to react with waste alkaline solution after the traditional process. This study investigated the capability of phosphate removal by La-ZFA. The sorbent has a high phosphate removal capacity, with a sorption maximum of 71.94 mg/g, according to the Langmuir model. The removal of phosphate by La-ZFA performs well at a wide pH range, reaching $> 95\%$ from pH 2.5 to pH 10.5 when initial P concentration < 100 mg/L. Release of OH^- during the interaction of phosphate with La-ZFA was observed. The formation of the monoclinic $LaPO_4$ phase was identified by XRD analysis. The uptake of phosphate by La-ZFA was explained on the basis of the adsorption mechanism of the ligand exchange process. The sorbed phosphate could be recovered by hydrothermal treatment in 3 M NaOH at 250 °C, with a simultaneous regeneration of La-ZFA. Repeated sorption–desorption tests indicated that regenerated La-ZFA could be reused for phosphate removal. Therefore, synthesis of La-ZFA could impart additional function of phosphate removal to original zeolite, with the effective utilization of waste alkaline solution.

1. Introduction

Excessive accumulation of phosphate in water bodies may cause eutrophication, which in turn lead to serious environmental problems. In last decades, (hydr)oxides of iron, aluminum and calcium or materials containing these (hydr)oxides for their use as adsorbents in reducing phosphorous levels from water/wastewater have been widely investigated [1–4]. Some limitations have however been associated with these kinds of adsorbents: the performance, in terms of reducing phosphorous concentrations, is strongly affected by pH; and the adsorbed phosphate can be re-released when the pH and/or redox conditions are changed [5,6].

Lanthanum is a rare earth element that is considered to be environmentally friendly and is relatively abundant in the earth's crust. It is thus less costly than other rare earth elements [7–9]. Lanthanum is known to have a high affinity for phosphate and it was reported that the lanthanum–phosphate complex forms, even when present in low concentrations [10,11]. Firsching and Brune [12] reported the solubility product, K_{sp} of $LaPO_4$ in aqueous solution to be -24.76, which is the least soluble among the rare-earth-phosphate complexes. La is also insensitive to changing redox conditions. Considerable attention has therefore been focused on the development of lanthanum-containing materials for the removal of phosphate in recent years. Among these, bentonite clay that has been modified by lanthanum, commercially known as Phoslock®, has been the most intensively investigated [13–22]. The use of Phoslock® to bind P in sediments, as means of controlling internal P loading in lakes, has been investigated by a number of research workers. It has been found that the product effectively prevented P release from sediment, reduced P concentrations in water [13–18], and lowered the cyanobacterial biomass and microcystin concentrations [18]. The Phoslock® product also performs well in terms of phosphate uptake from aqueous solutions [19,20], from wastewaters [19], and from lake water [21,22].

Other lanthanum-containing materials have been investigated for the retention of phosphate from water, including La-impregnated silica gel [23], La-impregnated alumina [24], La loaded mesoporous silica SBA-15 [25], La loaded activated carbon fiber (ACF) [26–28], La bound to chelex-100 resin [29], La doped vesuvianite [30], mixed lanthanum/aluminum pillared montmorillonite [31] and La treated juniper bark fiber [9].

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Coal fly ash (CFA) is a solid waste that is generated in great quantities worldwide. Since 1985, the synthesis of zeolites from CFA (ZFAs) has been extensively investigated as a means of recycling [32]. A number of zeolites have been produced from CFA, including Na-P1, philipsite, chabazite, F linde, herschelite, faujasite, analcime, zeolite A, zeolite X, zeolite Y, and hydroxysodalite [32]. In previous studies we showed that ZFA could be used for simultaneously removing cationic pollutants, such as heavy metals, ammonium and oxyanions (such as phosphate) from water/wastewater [33–37]. We found that negatively charged zeolite was responsible for cation removal, while non-zeolitic fraction such as Ca and Fe oxides, were suitable for anion (phosphate) immobilization. It should however be stressed that the content of the oxides in ZFA used for the binding of phosphate may be very limited, with the concentration levels of the oxides being dependent on the origin of the CFA. As stated previously, the binding of phosphate by these oxides is strongly affected by pH and there are problems associated with their use, due to their tendency to the re-release phosphate. Furthermore, the synthesis of ZFA by means of hydrothermal reactions produces a waste alkaline solution.

In this study we introduced a novel method for producing ZFA/$La(OH)_3$ hybrid material (hereafter denoted as La-ZFA) by adding soluble lanthanum salt to a mixture of ZFA/waste alkaline solution, following the traditional ZFA preparation process. In this way, the neutralization of the waste alkaline solution led to the formation of lanthanum hydroxide, yielding a La-ZFA hybrid material. It is hoped that the production of the hybrid material will retain its affinity to cations, but also greatly increase its performance in terms of oxyanionic pollutants removal. In our present study we focus on the sorption of phosphate by the hybrid material, with emphasis on the capacity and mechanism of sorption, as well as the recovery of sorbed phosphate.

2. Materials and methods

2.1. Materials

The CFA used in this study was obtained from the Second Power Plant of Minhang in Shanghai, China. For ZFA 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 (900 mL /150 g), NaOH concentration 2 M, and temperature 95 °C. After cooling to room temperature, ZFA was recovered by centrifugation and washed three times with double-distilled water and twice with ethanol. The ZFA products were then dried in an oven at 45 °C, ground to pass through an 80-mesh sieve, and stored in airtight containers until further use. To obtain a La-ZFA composite, a 2 N $LaCl_3$ solution was added, drop-wise (10 mL/min) with continuous stirring, into the mixture of waste alkaline solution and ZFA, after having been cooled to room temperature following the hydrothermal reaction. The volume of $LaCl_3$ solution was equal to that of NaOH used in zeolite preparation. 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 La-ZFA composite was then recovered, washed, dried, and ground in a similar manner to that used when manufacturing ZFA.

The chemical composition of materials was determined by X-ray Fluorescence Analysis (PW2404, PHILIPS Company). Moisture and loss-on-ignition were measured by the loss of weight after heating, at 105 °C for 24 h and 900 °C for 2 h. The X-ray Diffraction (XRD) patterns were recorded using D8 ADVANCE (BRUKER-AXS Company) with Cu Kα filtered radiation (30 kV, 15 mA). BET surface area was determined by NOVA1200e (Quantachrome Company) using nitrogen adsorption method. The pH value of materials was tested as following: 0.2 g of material and 40 mL of distilled water or 0.01 M $CaCl_2$ were added into centrifuge tubes and then the final pH after a 24 h equilibration period was assayed using a Hach Sension + pH meter. CEC was determined by the ammonium acetate method [38]. Zeta potential measurements as a function of medium pH were determined using a Malvern Instruments Zetasizer 2000 equipped with a microprocessor unit.

2.2. Sorption isotherms

Sorption isotherms of phosphate were performed in 50 mL centrifuge tubes. About an exact mass of 0.1 g of materials was put into centrifuge tubes containing 40 mL phosphate solution with different P concentrations, ranging from 10 to 500 mg/L. The suspensions were shaken for 24 h under 180 rpm to achieve equilibrium at 25 °C in a thermostatic chamber. After 24 h, the suspensions were centrifuged. The obtained clear supernatants were determined for phosphate by molybdenum-blue ascorbic acid method [39]. To evaluate the effect of phosphate–sorbent interaction on solution pH, the pH of phosphate solution without addition of sorbent, suspension without the addition of phosphate as well as the suspensions with the addition of phosphate were monitored (monitoring of pH for suspensions was done after being shaken for 24 h).

2.3. Influence of pH on phosphate removal

Samples of 0.10 g of material were placed in centrifuge tubes, each of which contained 40 mL of phosphate solution at P concentrations of 5, 100 and 500 mg/L. The suspensions were adjusted by additions of 0.1 M or 0.01 M HCl and NaOH, to desired pH values. After 24 h of shaking, the suspensions were centrifuged and the equilibrium phosphate concentrations were determined. The pH in the equilibrium solution was also monitored.

2.4. Lanthanum desorption

Desorption tests were conducted at different pH conditions to assess the stability of La-ZFA. La-ZFA (0.1 g) was added to each 250-mL Erlenmeyer flask containing 100 mL of doubly-distilled water, adjusted to pH levels within the range of 2.0–7.0. The method used to adjust pH was mentioned in the previous section. The mixture was continuously shaken for 24 h at 25 ± 1 °C after which the supernatant was collected and filtered prior to analysis by inductively coupled plasma-atomic emission spectroscopy (ICAP 6000 Radial, Thermo).

2.5. Phosphate desorption

La-ZFA was initially reacted, for 24 h, with the phosphate solution at a P concentration of 500 mg/L. After washing three times with doubly-distilled water, the sorbed phosphate was recovered by NaOH treatment at different conditions of temperature, NaOH concentration, and liquid/solid ratio. The percentage of desorbed phosphorus to sorbed phosphorus was calculated, so as to assess the possibility of recovering sorbed phosphate and recycling La-ZFA for further use.

It is also important for La-ZFA to be reused after the phosphate was recovered from La-ZFA. To test the performance of regenerated La-ZFA for phosphate removal, 0.5 g of sorbent was initially reacted with 200 mL of phosphate solution (200 mgP/L) for 24 h before the desorption test. The condition for phosphate desorption was 3 M NaOH at a solid/liquid ratio of 80:1 and a reaction time of 5 h, under 250 °C. The regenerated (phosphate-desorbed) La-ZFA was washed with doubly-distilled water 3 times before the next cycle of sorption and desorption. The sorption and desorption (regeneration) procedures were repeated for 5 cycles to evaluate the reus-