



# Synthesis of zeolite/hydrous lanthanum oxide composite from coal fly ash for efficient phosphate removal from lake water



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## ABSTRACT

We investigated the use of coal fly ash as a raw material for the production of a zeolite/hydrous lanthanum oxide hybrid material (ZHLO) and as a means of controlling internal phosphorus loading in lakes. We found that the use of ZHLO, as a method for capturing phosphate from five lake water samples, was considerably more efficient than the existing alum-treatment method. There was some variability in the performance of the ZHLO-method in different lake waters but we noted that, within the La/P molar ratio range of between 2:1 and 4:1, we were able to attain an almost-complete removal of phosphate. Correlation analysis indicated that high alkalinity reduced the performance of phosphate binding. Phosphate adsorption by ZHLO was found to decrease with increasing pH. The phosphate adsorbed at acidic pH levels was partly released with increasing pH, while phosphate that was in equilibrium solution at high pH was adsorbed when the pH declined. The extent of reversibility when using the ZHLO method was much lower than that observed when using the alum treatment method. FTIR measurements showed that the monodentate surface species of  $\equiv\text{La-OPO}_3$  was formed via a ligand exchange mechanism. Moreover, ZHLO could also function as a means of removing cationic pollutants. This has important implications in terms of preventing the release of toxic substances (such as manganese and ammonium) from sediments in eutrophic lakes.

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## 1. Introduction

The worldwide use of coal in electricity/heat generation processes produces great amounts of coal fly ash every year as a solid waste. It was estimated that 349 Mt of fly ash was produced worldwide in 2000 [1] and is over 750 Mt in 2012 [2]. China is one of the few countries in the world with coal as its main energy source, and the proportion of coal in consumption of primary energy source is 72.8% [3]. The coal-dominated energy source structure produces a large amount of coal fly ash every year. In 2011 it reached 540 Mt, increased by 5.45-fold compared with 1995 due to the rapid economic growth during this period [3]. In the world, only a part of coal fly ash is reutilized in the production of building materials such as concrete and cement, owing to its pozzolanic nature. For instance, the reutilization rate is 39% for the United States [2], 47% for Europe [2], and 68% for China [3]. In China, though the reutilization rate is currently relatively high, the total amount of coal fly ash is also extraordinarily high. As a result, a

huge amount of 173 Mt of coal fly ash is impounded or land filled, which not only occupies a lot of land, but also causes serious environmental pollution problems. Therefore, the search for new productive reuse technologies of coal fly ash is in urgent demand.

In recent years, synthesis of zeolite is one of the intensively investigated approaches for high-value reutilization of coal fly ash [4–8]. Zeolite synthesized from fly ash has not only a high cation exchange capacity (CEC), but also has been shown to be able to capture phosphate, an oxyanionic species [9–11]. Phosphorus has been identified as the leading cause of eutrophication in lakes, which is now regarded as a worldwide environmental problem. We found that the phosphate fixation capacity of synthesized zeolite was attributed to the oxides of CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, which originated from coal fly ash [9–11].

To successfully control the eutrophication of lakes, it is undoubtedly important to reduce the internal phosphorus loading from the water columns and sediments of lakes. At a global scale, a number of phosphorus-removing materials have been investigated in terms of their potential to inactivate internal P loading: iron-based compounds [12,13], aluminum-based compounds [14–21], and calcium-based materials [22] or materials containing

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components of Fe, Al or Ca [23,24]. Use of these materials in lakes to control internal P loading may have limitations because:

- (1) Iron-based materials are sensitive to changing redox conditions, and phosphorus bound to iron can be released into the overlying water column during situations when reductive conditions prevail at the sediment surface.
- (2) High pH conditions may lead to reduced efficiency of phosphorus removal from Fe and Al materials, and bound P may be desorbed by OH<sup>-</sup> [25,26].
- (3) Precipitation by Ca materials is promoted at high pH, but low pH retards the precipitation process. Precipitation is generally less effective when the phosphate concentration is relatively low, which is the case in natural lake systems.
- (4) Low pH levels (below 5.5) lead to an increase in dissolved Al<sup>3+</sup> which is toxic to aquatic organisms [27].

Therefore, there is a need to develop alternative phosphate adsorbent materials. One such alternative is Phoslock<sup>®</sup>, a bentonite clay product that has been modified by lanthanum. Lanthanum is a rare earth element that is considered to be environmentally friendly, is relatively abundant and thus less costly than other rare earth elements, and is known to have a very high affinity for phosphate [28,29]. What is the most attractive is that lanthanum is insensitive to changing redox conditions and performs well for phosphate removal at wide pH conditions. Phoslock was invented in the mid-1990s by the Commonwealth Scientific and Industrial Research organization (CSIRO) in Australia, and has recently been intensively investigated as a control for internal P loading in lakes [30–36].

The purposes of our present study were to develop a novel hybrid adsorbent composed of zeolite and hydrous lanthanum oxide (hereafter denoted as ZHLO), using solid waste coal fly ash as a raw material and to investigate the performance of ZHLO in terms of its capacity to take up phosphate from lake water.

## 2. Materials and methods

### 2.1. Materials

Coal fly ash was obtained from the Second Power Plant of Minhang in Shanghai, China. The coal fly ash was first treated by 2.0 M NaOH solution for 24 h, at the liquid/solid ratio of 900 mL/150 g and the temperature of 95 °C, to obtain zeolite and waste alkaline solution. The slurry was then neutralized with 900 ml of a 2 N LaCl<sub>3</sub> solution, drop-wise (10 mL/min) with continuous stirring, to produce ZHLO. The solid phase of ZHLO was then recovered by centrifugation and washed three times with doubly-distilled water and twice with ethanol. The ZHLO was finally dried in an oven at 45 °C and ground to pass through an 80-mesh sieve.

The performance of ZHLO for phosphate removal from lake water was compared with aluminum hydroxide floc (AHF), an extensively-used in-lake treatment material. The method of Berkowitz et al. [19] was used to produce AHF, which involved the addition of alum to a water sample from Lake Siyuan, Shanghai,

China. Approximately 90 L of lake water was treated with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O to yield a 25 mg/L dose of Al<sup>3+</sup>. AHF floc was collected after four days of aging, followed by air-drying and grinding to pass through 80 mesh sieves.

The X-ray Diffraction (XRD) patterns were recorded using D8 ADVANCE (BRUKER-AXS Company) with Cu K $\alpha$  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 (Shimadzu IRPrestige-21) using the KBr method. The BET (Brunauer–Emmett–Teller) specific surface area and pore size distribution were measured using the nitrogen adsorption method (equipment model: ASAP 2010 M+C, Micromeritics Inc., USA). The pore size distribution curve was obtained by the BJH (Barett–Joyner–Halenda) method.

### 2.2. Phosphate binding experiments

Lake water samples were taken from five different lakes in China from 16th to 21st of October, 2013. The lakes are located in different places, far away from each other. The aim of this sampling activity was to obtain lake water samples with different chemical properties to study their effect on phosphate removal by ZHLO and AHF. To avoid possible chemical changes, the sampling in all lakes was finished in a short time and brought back to our laboratory for experiments as soon as possible. Chemical characteristics of these lake waters are listed in Table 1. Prior to experiments, water samples were filtered through 0.45  $\mu$ m membrane filters, to remove suspended particles and organisms such as algae, and spiked with KH<sub>2</sub>PO<sub>4</sub> to attain a phosphate concentration of 680  $\mu$ g/L. Stock suspensions of ZHLO and AHF were prepared by continuous mixing of 55 mg of the materials with 100 mL filtered lake water. Subsamples of 1, 2 and 4 ml were taken from these suspensions with the concentration of 0.55 g/L and were transferred to centrifuge tubes containing 40 ml of phosphate-enriched lake water samples, to obtain the desired adsorbent doses. The final volume of each solution (for particular adsorbent doses) was maintained at 44 ml by supplementation with appropriate amounts of lake water, if necessary. The initial phosphate concentration before adsorption was ~620  $\mu$ g/L, which is representative of pore water concentrations in eutrophic lakes [36]. After being shaken for 24 h in the thermostatic chamber (model TS-2102C) at 200 rpm at 20  $\pm$  0.1 °C, the suspensions were filtered and the phosphate concentrations of filtrates were determined. Blank tests, which did not contain stock suspensions, were also carried out. All experiments were carried out in triplicate.

### 2.3. Effect of pH on phosphate removal

To assess the effect of pH on the binding of phosphate, the dosages used for ZHLO and AHF were set at 0.0125 g/L for ZHLO and 0.025 g/L for AHF. One ml of ZHLO stock suspension and 2 ml of AHF stock suspension were transferred to 50 ml centrifuge tubes so as to obtain the given dosages. The volumes of water samples were adjusted to 44 ml and the adopted initial phosphate concentration was ~620  $\mu$ g/L. The suspensions were adjusted by additions of 0.1 M or 0.01 M HCl and NaOH, to attain the desired pH values. All

**Table 1**  
Characteristics of water samples used in the tests.

Name	Location	Alkalinity (CaCO <sub>3</sub> , mg/L)	Na <sup>+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Conductivity (mS/cm)	pH	Phosphate ( $\mu$ g/L)
Lake Taihu	Jiangsu province	91.2	48.57	34.56	0.494	8.75	36.29
Lake Guanting	Beijing	233.0	168.3	35.16	1.335	7.60	8.06
Lake Dianchi	Yunnan province	135.0	53.15	38.09	0.59	8.01	10.08
Lake Erhai	Yunnan province	146.8	16.34	28.26	0.296	7.66	26.21
Lake Siyuan	Shanghai	93.6	50.16	29.51	0.472	7.76	35.25

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