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Regular Article

Removal of phosphate from water by lanthanum-modified zeolites obtained from fly ash

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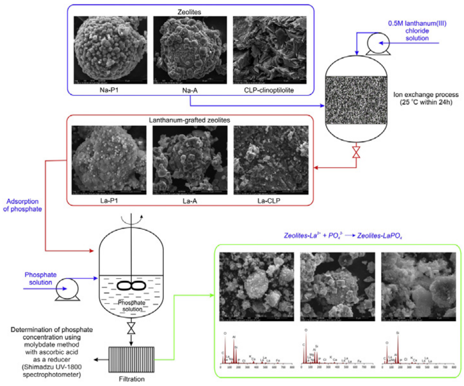
GRAPHICAL ABSTRACT



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ABSTRACT

The possibility and effectiveness of removal of phosphate from aqueous solutions with the use of new low-cost synthetic zeolites obtained from fly ash and modified with lanthanum, was studied. Physicochemical properties of the zeolites were characterized by different techniques such as X-ray diffraction, low-temperature nitrogen sorption and scanning electron microscopy. It has been established that lanthanum is preferentially located in the zeolites channels and cages, which is related to the ion-exchange method of modification. Introduction of lanthanum cations leads to a reduction in BET surface area, mainly due to a decrease in the area of micropores and reduction in the pore volume. The key element of the study was a series of tests of phosphate adsorption from aqueous solutions. The efficiency of adsorption process was found to depend on the concentration of adsorbate, pH of its solution and temperature. The sorption capacity of zeolites obtained from fly ashes (La-P1, La-A) towards phosphate was compared with that of a natural zeolite – clinoptilolite, modified with lanthanum (La-CLP). The sorption capacities of the particular samples were as follows: La-P1 – 58.2 mg/g, La-A – 44.0 mg/g and La-CLP – 24.6 mg/g. The experimental data were well fitted by the Langmuir isotherm model. The sorption capacities of all samples towards phosphate increased with temperature increasing from 25 to 60 °C. The values of the thermodynamic parameters ΔH^0 and ΔG^0 revealed that the adsorption was spontaneous and endothermic.

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1. Introduction

The presence of phosphate in water is a result of natural processes of washing out from the rocks and minerals, from the soil in which phosphorus compounds were introduced with fertilizers and from pollution with municipal or industrial waste. In groundwater and surface water the concentration of these compounds may vary in a wide range (from 10^{-3} mg to a few milligrams of PO_4^{3-} in liter). The excess of phosphate in water can contribute to eutrophication of water reservoirs [1–6], which leads to abundant development of vegetation and intensive activity of zooplankton using large amounts of oxygen which can cause death of aerobic organisms living in water. A consequence of these processes is disturbed equilibrium of the water ecosystem [1–3]. The phenomenon of water eutrophication is undesirable and dangerous. Therefore, the removal of phosphate from water is very important. Phosphorus compounds can be removed by different methods: adsorption, ion exchange, coagulation, microfiltration and precipitation [1,3,5–8]. Chemical precipitation is a costly process, requiring the purchasing, transportation, and storage of chemical precipitants, and produces vast quantities of sludge that must be properly disposed. Biological processes are quite sensitive to water parameters e.g. temperature, resulting in decreased stability and reliability. At present of greatest interest are adsorption processes because of high effectiveness, nontoxicity, simplicity, availability of a wide range of adsorbents and the possibility of use in a wide range of concentrations [1,3,6].

So far a large number of adsorbents of phosphate have been tested, including: zeolites [9], synthetic hydrotalcite [10], furnace slag [11], fly ash [12], mesoporous silicates [13], bentonite [14], alum and aluminum hydroxide [15], zirconium hydroxides [16], calcium based materials [17], aluminum oxide and ferric hydroxide [18], and red mud [19]. The use of the materials containing Fe or Ca in reservoirs to control PO_4^{3-} loading should be limited [9]. Iron-based adsorbents are sensitive to changing redox conditions and phosphate bound to iron can be released into the overlying water column when reductive conditions prevail at the sediment surface. High pH conditions may lead to reduced efficiency of phosphate removal from Fe containing materials and bound phosphorus may be desorbed by OH^-. Surface precipitation of phosphate by Ca-based materials is promoted at high pH, but low pH retards this process [9]. Moreover, this process is generally less effective when the phosphate concentration is relatively low.

Therefore, there is a need to develop alternative phosphate adsorbents. Considerable attention has been paid to the synthesis of lanthanum containing materials. Among them, zeolites modified by lanthanum have been the most intensively investigated [9]. Zeolites synthesized from fly ash not only show a high cation exchange capacity, but also have been found to be able to capture phosphate, as the oxyanionic species. The major advantage of using these kind of adsorbent for wastewater treatment is cost-effectiveness [20,21]. Modification of zeolites with lanthanum improves their sorption capacities towards phosphate. Lanthanum is a rare earth element that is considered to be environmentally friendly [22–24]. It is less costly than other rare earth elements. Lanthanum is known to have a high affinity to phosphate. Even at low concentrations of PO_4^{3-} ions in solution, lanthanum makes with them complex compounds. Firsching and Brune [25] have defined the solubility product, log 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.

The aim of our study was development of low-cost and effective zeolite adsorbents modified with lanthanum for removal of phosphate from aqueous solutions. The adsorption equilibria were investigated to find out which isotherm model gives the best fit to the experimental data. The effects of the adsorbate concentration, pH and temperature were examined in order to determine the optimal adsorption conditions.

2. Materials and methods

2.1. Sample preparation

The zeolites used in the study were obtained as products of hydrothermal conversion of fly ashes with water solution of NaOH, according to the scheme:

$$fly\ ash + x\ mol/L\ NaOH \xrightarrow[temperature]{time} zeolite + residuum$$

The fly ash used as a substrate for the conversion was obtained from the Power Plant Kozienice. According to the chemical composition it belongs to class F (in the ASTM C 618–08 classification). The main components (%) of this fly ash are: SiO_2: 52.12, Al_2O_3: 32.19, Fe_2O_3: 5.17, MgO: 1.29, CaO: 1.16, Na_2O: 0.49, K_2O: 2.87, TiO_2: 1.38, P_2O_5: 0.43.

The zeolites of Na-P1 and Na-A type were produced using the prototype of technological line in the following conditions [26]:

- 20 kg of fly ash, 12 kg NaOH, 90 L of technical water, 80 °C, 36 h (Na-P1),
- 15 kg of fly ash, 10 kg NaOH, 90 L, 0.2 kg of aluminum dust, 90 °C, 16 h (Na-A).

The contents of these synthetic zeolites in the material studied was 80% for Na-P1 and 83% for Na-A. The other mineral components were: mullite, quartz and residues of unreacted aluminosilicate glaze.

For comparison, the natural zeolite supported on clinoptilolite tuff excavated in the mine Sokyrnytsya (Ukraine) was also used as adsorbent of phosphate. The quantitative content of clinoptilolite (CLP) in this rock was 75%. The other supplementing mineral components were: opal CT, quartz and feldspars.

2.2. Sample modification

Lanthanum was incorporated into zeolites by ion exchange carried out at 25 °C for 24 h using 0.5 mol/L lanthanum(III) chloride solution (Aldrich). This procedure was performed twice. After washing, the resulting zeolites were dried at 150 °C.

2.3. Sample characterization

The mineral composition of zeolite materials was determined by the powder diffractometry XRD, on an X-ray diffractometer Panalytical X'pert APD with a goniometer PW 3020, Cu lamp and graphite monochromator. Analysis was performed in the angular range 5–65 (2θ), while data interpretation was made with the help of HighScore software.

Morphology of the main mineral components of the zeolites studied was characterized by scanning electron microscope (SEM) FEI Quanta 250 FEG.

The content of lanthanum was determined with the use of EDX-7000 energy dispersive X-ray fluorescence spectrometer (Shimadzu).

Textural properties of the adsorbents were characterized by nitrogen adsorption/desorption isotherms at −194,85 °C, after preliminary degassing of the samples at strictly controlled temperature (250 °C for 24 h) and under reduced pressure (10^{-3} hPa). Their surface area was determined according to the Brunauer,