

Phosphate removal from water using lithium intercalated gibbsite

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Abstract

In this study, lithium intercalated gibbsite (LIG) was investigated for its effectiveness at removing phosphate from water and the mechanisms involved. LIG was prepared through intercalating LiCl into gibbsite giving a structure of $[\text{LiAl}_2(\text{OH})_6]^+$ layers with interlayer Cl^- and water. The results of batch adsorption experiments showed that the adsorption isotherms at various pHs exhibited an L-shape and could be fitted well using the Langmuir model. The Langmuir adsorption maximum was determined to be 3.0 mmol g^{-1} at pH 4.5 and decreased with increasing pH. The adsorption of phosphate was mainly through the displacement of the interlayer Cl^- ions in LIG. In conjunction with the anion exchange reaction, the formation of surface complexes or precipitates could also readily occur at lower pH. The adsorption decreased with increasing pH due to decreased $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ molar ratio in solution and positive charges on the edge faces of LIG. Anion exchange is a fast reaction and can be completed within minutes; on the contrary, surface complexation is a slow process and requires days to reach equilibrium. At lower pH, the amount of adsorbed phosphate decreased significantly as the ionic strength was increased from 0.01 to 0.1 M. The adsorption at higher pH showed high selectivity toward divalent HPO_4^{2-} ions with an increase in ionic strength having no considerable effect on the phosphate adsorption. These results suggest that LIG may be an effective scavenger for removal of phosphate from water.

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1. Introduction

Phosphorus is an element most commonly associated with eutrophication in surface waters [1–3]. The over-enrichment of lakes, rivers and seas with phosphorus as a result of human activities can accelerate eutrophication that subsequently results in the deterioration of water quality and limits its usage. For example, eutrophication has been linked to shellfish poisoning of humans [4]. The bloom of toxic microalgae species as well as oxygen depletion that results from eutrophication can also have harmful effects on aquatic organisms and can reduce the benthic biomass and biodiversity [2,3,5]. These may further lead to ecological loss and a reduction in the economic values of aquatic ecosys-

tems. Meanwhile, with the growing population of the world, the global fresh water supply is already expected to be limited, so the impact of high levels of phosphorus can ultimately condemn millions of people to an avoidable premature death. Protection of water resources is an urgent task for healthy living and sustainable development. For water conservation, the removal of phosphorus from surface waters and wastewaters to control eutrophication is of great importance.

Conventional techniques for removing phosphorus from waters include physical (e.g., settling and filtration), chemical (e.g., precipitation, ion exchange, and sorption), biological processes (e.g., consumption by algae, bacteria or plants) [6–8]. Among these techniques, anion exchange and adsorption methods are more preferred because of their low cost, ease of equipment use, lower sludge production and the potential of recycling retained phosphorus.

In this study, a novel adsorbent, Li intercalated gibbsite (LIG) was investigated for its effectiveness for phosphate removal from

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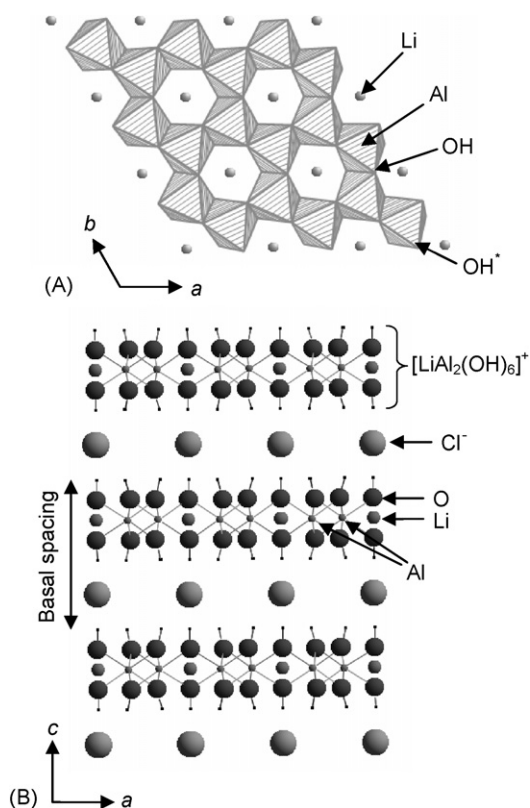


Fig. 1. Crystal structure of lithium intercalated gibbsite projected along the *c* and *b* axes, respectively.

water. This material is synthesized through LiCl intercalation of gibbsite ($\alpha\text{-Al}(\text{OH})_3$) or polymorphs and has a chemical formula $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot x\text{H}_2\text{O}$ [9–12]. Gibbsite has been recognized as an important adsorbent for phosphate in soils and sediments [13–15]. Phosphate ions are adsorbed by gibbsite through ligand exchange of surface OH groups with Al [16–21]. Formation of aluminum phosphate phases on the surface of gibbsite has been previously suggested [21–23]. The reported values for the phosphate adsorption of gibbsite was 0.2 mmol g^{-1} or less, mainly depending on the solution pH and the surface area of gibbsite [14,18,20,24]. After intercalation of lithium salt (e.g., LiCl), the structure of LIG is composed of permanent positive charged $\text{LiAl}_2(\text{OH})_6$ sheets with interlayers occupied by counter-anions and H_2O (Fig. 1) [10]. In gibbsite, each of the $\text{Al}(\text{OH})_3$ layers consists of nearly close packed OH^- ions in which the Al^{3+} occupy 2/3 of the octahedral holes in the layers [25]. Lithium cations are inserted in the vacant octahedral sites of the gibbsite-like $\text{Al}(\text{OH})_3$ layers and contribute the positive charges of the hydroxide layers (Fig. 1A) [10]. The positive charge sites in the hydroxide sheets are counterbalanced by anions intercalating between adjacent hydroxide layers (Fig. 1). Unlike gibbsite whose phosphate ions are only adsorbed on the external surface with pH dependent charges, the internal surface of each individual hydroxide sheet in LIG may additionally serve as adsorbents for phosphate and other anionic contaminants. The adsorption capacity of LIG is therefore expected to be significantly greater than that of gibbsite. Previous studies on the adsorption of some

inorganic and organic anions by LIG have demonstrated its reactivity toward these anions [26–29]. For example, a maximum adsorption of 3.81 mmol g^{-1} was previously reported for chromate [29]. To the best of our knowledge, phosphate removal of LIG has not been reported before and has been investigated in this study. The effectiveness of phosphate removal by LIG was studied as a function of pH, ionic strength and adsorbent dosage. X-ray diffraction (XRD) and ^{31}P magic angle spinning nuclear magnetic resonance spectroscopy (^{31}P MAS NMR) were used to study the structures of LIG with and without adsorbed phosphate. This aided the interpretation of the adsorption mechanism of phosphate on LIG.

2. Materials and methods

2.1. Synthesis of LIG

The adsorbent LIG was synthesized through intercalating LiCl into gibbsite ($\alpha\text{-Al}(\text{OH})_3$). Ten grams of gibbsite was added into 100 mL 10 M LiCl solution at 90°C and the temperature of the suspension was maintained at 90°C for 18 h. Subsequently, the suspension was centrifuged and the collected solids were washed with iced water until free of chloride. Iced water was used to wash the samples to inhibit the Li deintercalation reaction of LIG that would otherwise occur at higher temperatures [28]. The solid product was subsequently dried at 90°C for 24 h in an oven and stored in a glass vial prior to further use.

2.2. Phosphate adsorption kinetics

Kinetic adsorption of phosphate was observed at pH 4.5 and 9.5. Phosphate solutions were prepared by dissolving NaH_2PO_4 or Na_2HPO_4 into deionized water. The 500 mL of 100 mg L^{-1} phosphate solution at pH 4.5 or 9.5 was added into a 1 L water-jacketed reaction vessel and the temperature was adjusted to 25°C . Then, 0.25 g of the adsorbent was added into the phosphate solution. As a result, the initial phosphate concentration in the suspension was 100 mg L^{-1} while the solids concentration was 0.5 g L^{-1} . This adsorbate/adsorbent ratio was selected to ensure that residual phosphate concentrations were above detectable levels during the experiments. The pH value of the suspension was re-adjusted to a desired value, if necessary, using 10 mM NaOH and HCl solutions, and was maintained constant throughout the experiments. An aliquot of the suspension was extracted at 0, 0.25, 0.5, 0.75, 1, 2, 3, 4.5, 6, 9, 12, 24, 36 and 48 h. The withdrawn samples were filtered through a $0.45\text{-}\mu\text{m}$ cellulose acetate membrane filter to collect the filtrate and adsorbent. The phosphate concentration in the filtrates was determined using the molybdenum blue method [30]. The amount of adsorbed phosphate was calculated using the difference between the initial and final measured phosphate concentrations. The data from the duplicated experiments were then averaged. Meanwhile, the collected adsorbents were washed with deionized water until free of salt, air-dried, and grounded prior to XRD and ^{31}P MAS NMR analyses.

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