Pathways of phosphate uptake from aqueous solution by ZnAl layered double hydroxides
X. Cheng, Y. Wang, Z. Sun, D. Sun and A. Wang

ABSTRACT

ZnAl layered double hydroxides (LDHs) were prepared by urea hydrolysis-based coprecipitation for removing phosphate from aqueous solutions. The chemical formula of the product was determined as Zn$_{5.54}$Al$_{3.02}$(OH)$_{8.73}$(CO$_3$)$_{0.57}$Cl$_{0.64}$·7.84H$_2$O. Chloride ion was the major interlayer anion of the ZnAl LDHs. Adsorption of phosphate onto the ZnAl sorbent over the entire study period was not in close agreement with pseudo-first-order or pseudo-second-order models. The adsorption can be divided into two steps. A fast adsorption was observed during the first 10 h with a marked increase in the concentration of Cl$^-$ in the bulk solution. This indicated that the adsorption of phosphate was largely attributed to the ion exchange between phosphate and the interlayer Cl$^-$. A second fast adsorption of phosphate occurred after 10 h. During this period, the pH increased slowly, whereas the Cl$^-$ concentration was stable. The uptake of phosphate was likely attributed to OH$^-\rightarrow$H$_2$PO$_4^-$/HPO$_4^{2-}$ ion exchange as well as surface adsorption/complexation. Acidic conditions favored adsorption of phosphate by ZnAl LDHs, which is consistent with the pH increases during the adsorption. Coexisting anions, e.g., SO$_4^{2-}$ and CO$_3^{2-}$, are competitive ions for the adsorption of phosphate. The results verify the contribution of ion exchange and surface adsorption/complexation in the removal of phosphate by ZnAl LDHs.

Key words | adsorption, layered double hydroxides, pathway, phosphate, ZnAl

INTRODUCTION

Removal of phosphate from waste streams by adsorption has attracted increasing attention in recent years (Chitrakar et al. 2006; Das et al. 2006; Karaca et al. 2006; Cheng et al. 2009). The use of an adsorptive process not only reduces consumption of chemicals and sludge production during phosphate removal, but also enables recovery of phosphate via desorption (Kuzawa et al. 2006). Materials studied for adsorptive removal of phosphate include minerals (e.g., goethite, dolomite), industrial byproducts (e.g., fly ash, blast furnace slag), and metal oxides/hydroxides (i.e., aluminium oxide, iron oxide) (Seida & Nakano 2002; Cheng et al. 2009).

Layered double hydroxides (LDHs), also called hydrotalcite-like compounds, have been shown to be efficient adsorbents for separation of phosphate from aqueous solutions (Das et al. 2006) and also real streams (Chitrakar et al. 2005; Cheng et al. 2009). The formula of these compounds can be described as [$\text{M}_2^{x+}$,$\text{M}_3^{x+}$,$\text{A}^{n-}$]$_{1/n}$,$\text{H}_2\text{O}$, where $\text{M}_2^{x+}$ and $\text{M}_3^{x+}$ denote divalent and trivalent metal cations, respectively, and $\text{A}^{n-}$ is the intercalated anion. The exchangeability of interlayer anions and the high-density positive charge of the sheets from the isomorphic substitution of $\text{M}_2^{x+}$ by $\text{M}_3^{x+}$ were generally believed to be responsible for the high capacity of LDHs for phosphate removal (Cheng et al. 2010). Since LDHs are a group of compounds with great compositional diversity, the mechanisms for phosphate removal could also vary among compounds. For example, the released metal cations and/or hydroxides were shown to play a critical role during the enhanced uptake of phosphate by LDHs containing iron (Seida & Nakano 2002). More recently, it was illustrated that removal of triphosphate by MgFe-Cl-LDHs was mainly due to surface adsorption and near-edge intercalation, while its uptake by CaFe-Cl-LDHs could be attributed to dissolution of LDHs and the subsequent precipitation of calcium phosphate (Zhou et al. 2011). Overall, the interaction between phosphate and LDHs is currently far from well understood. In addition, LDH
dissolution-phosphate precipitation would be undesirable if phosphate recovery and adsorbent reuse are anticipated. Our previous work has shown that ZnAl LDHs have a high capacity for separation and recovery of phosphorus from aqueous solutions, as well as a satisfactory stability (Cheng et al. 2009, 2010). In this study, the process of phosphate uptake by ZnAl LDHs was investigated in more detail and the possible pathways involved are discussed.

**METHODOLOGY**

**ZnAl preparation**

ZnAl LDHs were prepared by urea hydrolysis-based co-precipitation. A solution of ZnCl₂ (0.4 M Zn²⁺), AlCl₃ (0.2 M Al³⁺), and urea (2.4 M) was stirred at 100 °C for 24 h. The resulting slurry was washed thoroughly with deionized water. The precipitate was then dried at 45 °C overnight and was ground to, on average, 100-μm particles. X-ray diffraction (XRD) patterns of the prepared ZnAl were analyzed to determine the mineral phases and crystallinity of the samples. Chemical composition of the prepared samples was examined after dissolving a known quantity of sample in 0.5 M HCl.

**Phosphate adsorption assay**

Phosphate adsorption batch assays were conducted by adding ZnAl to phosphate solutions at pH 7 and 25 °C. The phosphated LDHs were denoted as ZnAl(C-t), where C (mg P/L) represented the starting concentration of phosphate and t (h) represented the contact time. Assays for adsorption isotherms were performed at temperatures from 25 to 50 °C. To study the effect of pH, phosphate solutions were adjusted to pH 4–10 using 1 M HCl or NaOH. The effect of coexisting ions was investigated using phosphate solutions spiked with different anions and cations.

**Analytical methods**

Zn and Al in the prepared ZnAl LDHs were measured by an inductively coupled plasma optical emission spectrometry (ICP-OES) system (Optima 5300DV, PerkinElmer). The content of C, H, and O was determined by an elemental analyzer (Vario EL III Elementar Analysensysteme GmbH, Hanau, Germany). Cl⁻ was measured by ion chromatography (ICS-3000, Dionex).

XRD patterns of the samples were obtained using a Rigaku X-ray diffractometer (D/Max-RB) with CuKα radiation (λ = 1.5418 nm) over a 2θ from 10° to 80° with a scan rate of 5° (2θ)/min. Surface area and pore property were measured by the N₂ adsorption–desorption isotherm and Barrett–Joyner–Halenda (BJH) method on an ASAP 2020 instrument (Micromeritics) after powder samples were outgassed overnight under vacuum conditions (10⁻⁵ Torr) at 80 °C. pH and PO₄³⁻ were examined according to standard methods (APHA et al. 1998).

**RESULTS AND DISCUSSION**

**ZnAl structure**

XRD patterns of the prepared and phosphated ZnAl LDH samples are illustrated in Figure 1. The intense and narrow diffraction peaks for the (003), (006), and (009) planes showed that the prepared (raw) sample had a typical LDH structure (Evans & Slade 2006). The XRD pattern also revealed the absence of impurity phases, e.g., ZnO, which is commonly seen with other synthesis methods (Cheng et al. 2010). This is probably attributed to the relatively constant pH value governed by the continuous urea hydrolysis-based coprecipitation (He et al. 2006). The Zn/Al ratio in the LDHs was close to 2, which suggests that the precipitation was complete (Table 1). Cl⁻ was the major interlayer anion as in the initial solution for ZnAl preparation. According to the XRD patterns of phosphated ZnAl LDHs (Figure 1), there were no new mineral phases, e.g., hopeite (Zn₃(PO₄)₂·2H₂O), generated during the uptake of phosphate.
phosphate by ZnAl LDHs even with a concentration of phosphate of 310 mg/L and a contact time of 72 h (for ZnAl(310-72)). This could exclude chemical precipitation as a major pathway for the phosphate removal. The result is consistent with Koilraj’s study, in which hopeite formation was only seen during the phosphate removal by a ternary LDH ZnAlZr with a Zn/(Al + Zr) ratio greater than 2 (Koilraj & Kannan 2013).

### Phosphate adsorption kinetics and isotherms

Phosphate adsorption onto ZnAl LDHs over the duration of the study period did not agree well with pseudo-first-order or pseudo-second-order models as shown by the inset in Figure 2. The adsorption can apparently be divided into two steps (Figure 2). During the first 10 h, a fast adsorption of phosphate was observed with a marked increase in the concentration of Cl\(^{-}\) in the bulk solution (Figure 3). The adsorption kinetics can be satisfactorily described by a reversible first-order model \( (R^2 = 0.95) \) especially in the first 4 h when the majority of Cl\(^{-}\) release was seen (Rengaraj et al. 2005). The results indicated that the uptake of phosphate was largely attributed to the ion exchange between phosphate ions and the interlayer Cl\(^{-}\). The molar ratio of released Cl\(^{-}\):phosphate uptake (as P) was around 2 during the initial time (inset in Figure 3). This agrees with the replacement of Cl\(^{-}\) by HPO\(_4^{2-}\), which has a high affinity to LDHs. The ratio decreased and ended up at approximately 1.6 after 10 h of contact, revealing the contribution of H\(_2\)PO\(_4^{+}\) and HPO\(_4^{2-}\) in exchange for Cl\(^{-}\). A small increase in pH from 7.0 to 7.2 was seen in this period in spite of the removal of HPO\(_4^{2-}\) as an alkaline form. This suggests that phosphate was able to replace alkaline ions, e.g., OH\(^{-}\), in the interlayer space or on the LDH surface.

The second fast adsorption of phosphate occurred after 10 h, and was in close agreement with pseudo-first-order \( (R^2 = 0.98) \) and pseudo-second-order \( (R^2 = 0.96) \) kinetic models (Figure 2). The concentration of Cl\(^{-}\) remained stable during the period, indicating that phosphate-chloride ion exchange was not responsible for the removal of phosphate by ZnAl LDHs at this stage (Figure 3). The level of pH had a small increase, especially between 10 and 24 h when the majority of phosphate uptake was observed. This result suggests that phosphate could have been partially removed via ion exchange with OH\(^{-}\) in addition to surface adsorption and complexation (Yao & Millero 1996).

The isotherms of phosphate uptake are shown in Figure 4. The uptake of phosphate decreased with temperature increasing. Although the observed effect of temperature was minor, it indicates that adsorption was in general an exothermic process. Freundlich models described the

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<th>Table 1</th>
<th>Physicochemical properties of ZnAl LDHs</th>
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<tr>
<td>ZnAl</td>
<td>Chemical formula (estimated)</td>
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<td>Zn(<em>{15.54})Al(</em>{3.02})(OH)(<em>{8.73})(CO(<em>3))(</em>{0.57}) Cl(</em>{5.66})·7.84H(_2)O(^{a})</td>
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<td>Specific surface area (BET) (m(^2)/g)</td>
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<td><strong>BET</strong>: Brunauer-Emmett-Teller.</td>
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<td><strong>a</strong>Small amounts of S and N detected in the sample were not listed and could be the result of chemical impurities.</td>
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*Figure 2| Kinetics of phosphate adsorption by ZnAl LDHs and data fitting (LDH dosage: 0.25 g/250 mL of phosphate solution, initial concentration of phosphate: 31 mg-P/L, temperature: 25 ± 1°C).*

*Figure 3| Variation of Cl\(^{-}\) and pH during phosphate adsorption by ZnAl LDHs.*

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*Figure 4| Variation of Cl\(^{-}\) and pH during phosphate adsorption by ZnAl LDHs.*
phosphate uptake by ZnAl LDHs better than Langmuir models, though the agreements with the two types of models were not perfect (Figures 4(a) and 4(b)). This also suggests that the uptake of phosphate was a multi-pathway process.

**pH effect**

ZnAl LDHs was highly stable in phosphate solutions with pHs between 4 and 10 (Figure 5). The concentrations of Zn\(^{2+}\) and Al\(^{3+}\) in the bulk solution were all below 1.5 mg/L, indicating that the dissolution of ZnAl was negligible. A pH buffer effect was observed (inset in Figure 5) and can be explained by the reactions on the surface of LDHs as shown by Equations (1) and (2):

\[
\text{LDHs} - \text{OH}^+ + \text{H}^+ \rightarrow \text{LDHs} - \text{OH}_2^+ \text{(acidic solution)} \quad (1)
\]
\[
\text{LDHs} - \text{OH}^+ + \text{OH}^- \rightarrow \text{LDHs} - \text{O}^- + \text{H}_2\text{O} \text{(alkaline solution)} \quad (2)
\]

The stability of ZnAl LDHs could be due to its high crystallinity which suggests that the prepared LDHs had a highly ordered structure (Seida & Nakano 2001).

As can be seen in Figure 6, the capacity of phosphate uptake by ZnAl LDHs was markedly lower in alkaline environments than with low pHs. The result agrees with the fact that pH increased during the adsorption of phosphate (Figure 3). The phosphate adsorption did not vary significantly as pH varied within either the alkaline or acidic region. Further, the uptake of phosphate under alkaline conditions approximated the amount of phosphate uptake during the first step (Figure 2). This indicates that ion exchange-caused phosphate removal was not affected by pH, whereas the uptake of phosphate during the second step (after 24 h) was pH-dependent.

**Coexisting ions**

Coexisting anions adversely affected the adsorption of phosphate onto ZnAl LDHs (Figure 7(a)). The strength of influence was: carbonate > sulphate > nitrate ≈ chloride. Compared with monovalent anions, greater affinity of divalent anions for ZnAl was attributed to greater electrostatic interaction with positively charged LDH sheets. Since the
concentration of phosphate for the assays was 1 mM, Figure 7(a) also illustrates that the affinity of phosphate towards ZnAl LDHs is even competitive to carbonate.

In terms of cations, the influence of NH₄⁺ and Ca²⁺ was negligible (Figure 7(b)). The result verifies the contribution of ion exchange to the phosphate uptake by the ZnAl LDHs. At high concentrations, Mg²⁺ improved the removal of phosphate. This could be due to the Mg²⁺-stimulated phosphate adsorption as shown by Equations (3) and (4):

\[
\text{LDHs}-(\text{OH})_2+\text{H}_2\text{PO}_4^- \rightarrow \text{LDHs} - \text{PO}_4^- + 2\text{H}_2\text{O} \quad (3)
\]

\[
\text{LDHs} - \text{PO}_4^- + \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{LDHs} - \text{PO}_4^- - \text{Mg} - \text{H}_2\text{PO}_4^- \quad (4)
\]

First, phosphate was removed from the bulk solution via surface adsorption/complexation; second, the adsorbed phosphate provided active site for Mg²⁺ adsorption. As a result, secondary/multi-layer adsorption of phosphate occurred via electrostatic attraction between phosphate and metal ions.

**Mechanisms**

The observed two-step uptake of phosphate illustrated that phosphate adsorption by the prepared ZnAl LDHs involved multiple pathways. Marked increases in Cl⁻ in the bulk solution during the first step of phosphate removal revealed that ion exchange between phosphate and chloride ions played a critical role during this period (~10 h). In terms of the phosphate removal afterwards (second step), there was no comparable release of Cl⁻ seen with phosphate being adsorbed, indicating that phosphate uptake could not be attributed to Cl⁻–H₂PO₄⁻/HPO₄²⁻ ion exchange. From scanning electron microscope (SEM) images of the raw and phosphated ZnAl, phosphate adsorption onto ZnAl LDHs did not generate additional phosphate-containing mineral phases (data not shown). Phosphate precipitation was, therefore, not responsible for phosphate removal over the entire duration of the study. Phosphate removal resulting from precipitation/coagulation has been addressed by researchers, especially for iron-containing LDHs (Seida & Nakano 2002). However, separation of phosphate in this manner is often undesirable. On the one hand, precipitation causes a continuous loss of functional components, i.e. metal ions, and consequently a sharp degradation of the capacity of phosphate adsorbents over operational cycles. On the other hand, it greatly increases the difficulty of phosphate desorption from the LDH surface for phosphate recovery. A small increase in pH during the second step of phosphate uptake suggested that OH⁻–H₂PO₄⁻/HPO₄²⁻ ion exchange could be an important pathway in addition to surface adsorption and complexation.

ZnAl had a good stability in the range of pH 4–10, which enables its repeated use in real works. The high crystallinity of the prepared ZnAl was believed to offer resistance to cation dissolution owing to high order of atomic arrangement (Koilraj & Kannan 2010). The result also excluded LDH dissolution – reprecipitation as a pathway for the P adsorption on ZnAl LDHs. However, high crystallinity reduces materials’ specific surface area, leading to a considerable decrease in their adsorption capacity. Co-precipitation using urea as a precipitant resulted in large-sized LDHs with greater crystallinity than other methods because the slow hydrolysis of urea allowed a low degree of supersaturation during precipitation (He et al. 2006).
Efforts should be made to modify methods for reducing the particle size of LDHs while still retaining their crystallinity for a good stability. Separating nucleation and aging steps during the preparation of LDHs would be one way to obtain particles with small size as well as high crystallinity.

Common coexisting anions, except carbonate, did not significantly affect phosphate uptake onto ZnAl LDHs. Recovery of phosphate by ZnAl LDHs is therefore a promising method for use in real phosphate-containing waters. However, carbonate exhibited a high affinity for ZnAl LDHs. At a comparable concentration, it showed severe interference in phosphate uptake by the LDHs. Since carbonate/bicarbonate are common anions in natural waters and industrial streams, adsorbent development for separation/recovery of phosphate must take into account the material’s selectivity for phosphate. Although some researchers have reported improvements in phosphate uptake by different LDHs, the problem of adsorptive selectivity has not been well resolved. High concentrations of Mg$^{2+}$ increased the phosphate uptake onto ZnAl LDHs by adding positive charge to the solid surface. This may show a way to further improve the capacity of phosphate adsorption on LDHs. Pathway identification is obviously helpful to address the reason for phosphate adsorption capacity and selectivity of LDHs, and more study is warranted (e.g., by research on molecular levels) for a better understanding of the relationship between LDH structure and their behavior in phosphate removal.

CONCLUSIONS

This paper investigated the behavior of phosphate during uptake onto ZnAl LDHs that were prepared by urea hydrolysis-based co-precipitation. It was observed that the adsorption was a two-step process. The first fast adsorption of phosphate occurring in the initial 10 h was largely attributed to ion exchange between phosphate and the interlayer Cl$^-$, whereas the second adsorption was possibly due to surface adsorption/complexation. ZnAl LDHs showed a good stability at pH from 4 to 10, in which acidic conditions favored the adsorption of phosphate. Coexisting anions influenced phosphate uptake by ZnAl in the order of carbonate > sulphate > nitrate ≈ chloride. Common cations, however, did not significantly affect the adsorption, except for a small stimulation by Mg$^{2+}$ at high concentrations. These results verify the contribution of ion exchange and surface adsorption/complexation in the removal of phosphate by ZnAl LDHs.

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