Research paper

Comparison of adsorption and desorption of phosphate on synthesized Zn-Al LDH by two methods in a simulated soil solution

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Keywords:
Phosphate
Zn-Al LDH
Urea hydrolysis method
Uptake mechanism

1. Introduction

Phosphorus is a naturally occurring element that can be found in all living organisms, as well as in water and soils and plays an important role in plant growth. In the recent decades, layered double hydroxides (LDH) have been extremely used as an effective sorbent for inorganic anions such as arsenate (Caporale et al., 2011), molybdate (Ardau et al., 2012), selenite (Paikaray et al., 2013), fluoride (Kang et al., 2013), nitrate (Halajnia et al., 2012; Islam and Patel, 2009) and phosphate (Cheng et al., 2009, 2010; Das et al., 2006; Yu et al., 2015). LDH are represented by the general formula [M1−x2+x M3+x (OH)2]x+(An−1)x−/n·m(H2O), where M2+ and M3+ are divalent and trivalent cations, respectively. The value of x is equal to M3+/(M3+ +M2+) and An− is the intercalated anion (Goh et al., 2008). A great number of studies have been focused on the phosphate uptake from water or wastewater by LDH (Cheng et al., 2010; Das et al., 2006; Peng et al., 2009) but some studies have suggested that the phosphate containing LDH is applicable as a slow release phosphate fertilizer (Novillo et al., 2014; Woo et al., 2011). Since in the agricultural soils especially calcareous soils phosphorus availability restricts because of poor solubility and its fixation, the use of LDH as a slow release phosphate fertilizer, not only alleviates the depletion of the scarce and non-renewable natural phosphate resource (Yu et al., 2015) but also can be an important role in the phosphorus supply to the crops. Additionally, phosphorus recovery leads to the protecting and improving water quality, improving operation and performance at waste treatment facilities, and improving food security and social equity (Mayer et al., 2016).

The most commonly method for LDH preparation is co-precipitation method (Goh et al., 2008) but urea hydrolysis is another technique that can be produced LDH with larger particles (μm range) and higher crystallinity (Inayat et al., 2011; Hibino and Ohya, 2009). Due to these properties Geng et al. (2013) revealed that the thiosulfate adsorption in synthesized Mg-Al LDH by urea hydrolysis method was higher than the prepared LDH by co-precipitation method. However, the type of interlayer anion is the essential disadvantage of urea hydrolysis method because of carbonate containing LDH will usually produce by this method (Hibino and Ohya, 2009; Liu et al., 2014; Ogawa and Kaiho, 2002). Recently, a nitrate containing Zn-Al LDH with Zn/Al molar ratio of 2 was directly synthesized using modified urea hydrolysis method (Inayat et al., 2011). In their method, the addition of ammonium nitrate (NH4NO3) to the reaction mixture (zinc and aluminum nitrate salts and urea) leads to the increase of the nitrate/urea molar ratio and decrease of the final solution pH. Hence, Zn-Al LDH with nitrate as the interlayer anion will be synthesized. Since, carbonate anion reduces the anion...
exchange capacity in LDH (Parker et al., 1995), it seems that phosphate uptake capacity of synthesized Zn-Al LDH by modified urea hydrolysis method may be different with the prepared LDH by general urea hydrolysis method. Therefore, the main objective of the present study was to compare the phosphate uptake properties of synthesized Zn-Al LDH by general and modified urea hydrolysis methods in terms of time effect, pH, selectivity and initial phosphate concentration in a simulated soil solution environment. Moreover, the phosphate desorption from the LDH were investigated.

2. Materials and methods

All the chemicals used were of analytical grade and obtained from Merck manufacture. Zn-Al LDH with Zn/Al molar ratios of 2 and 3 were synthesized using general (G method) and modified (M method) urea hydrolysis methods (Costantino et al., 1998; Inayat et al., 2011). For the synthesis of each ratios in G method, zinc and aluminum nitrate (Zn + Al = 0.5 M), and urea (1.65 M) were dissolved in distilled water. Then the clear mixture maintained at 90 °C for 48 h under stirring. After cooling, white precipitate was collected by filtration (Whatman 42 filter paper) and washed with distilled water continually. Finally, solids were dried at 70 °C for 18 h. Zn2G-Al and Zn3G-Al were used for demonstration of synthesized LDH by G method with 2 and 3 molar ratios, respectively. M method was similar to the G method except that a solution of 1 M NH4NO3 was used for dissolving of salts and urea. In the both of synthesis methods, boiled distilled water was used for preparation and washing the filtered precipitates. For identification the synthesized LDH by M method at ratios of 2 and 3, Zn2M-Al and Zn3M-Al was used, respectively.

Zn/Al ratio in studied LDH was measured by atomic absorption spectrophotometer (PerkinElmer HGA 700) after digestion in 1:1 HCl:H2O (Das et al., 2003). X-ray diffraction (XRD) patterns were recorded using a Unisantis XMD 300 diffractometer with CuKα radiation (λ = 0.15418 nm) at 45 kV and 0.8 mA. A Thermo Nicolet AVATAR 370 Fourier transform infrared spectroscopy (FTIR) was used to verify the presence of functional groups in the range of 400–4000 cm−1. The morphology of LDH was observed by LEO 1450 VP scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS). Before observation, each sample was sputter-coated with a thin gold layer to prevent charging and to improve the image quality.

Halajnia et al. (2012) method was used for the measurement of anion exchange capacity (AEC) of synthesized LDH. In this method, LDH were saturated by 0.5 M NH4NO3 solution buffer at pH 7 and then washed with 0.1 M NH4NO3 for five times (after each washing, supernatant was discarded). Then, nitrate ions were displaced by five additions of chloride ions using 1 M KCl and finally nitrate concentrations in the extracts were measured by UV-spectrophotometer method (Edwards et al., 2001). The zero point charge (pHzPC) values were determined considering the difference between final and initial pH by the shaking of 0.1 g synthesized LDH in 20 mL KNO3 solution (0.03 M) with pH previously set by 0.1 M HNO3 and 0.1 M KOH solutions (shaking time = 24 h, initial pH = 4–12) (Fiol and Villaescusa, 2009). The batch techniques were carried out to determine the uptake kinetics of phosphate on the LDH. An amount of 0.1 g of synthesized LDH were mixed with 20 mL of 0.03 M KNO3 at pH = 7 as a background electrolyte, containing a concentration of 10 mM KH2PO4 and were shaken for 5, 10, 20, 30, 60, 240, 480 and 720 min. The suspensions were filtered and phosphate concentration in supernatants determined by molybdate method (Murphy and Riley, 1962). Selectivity of synthesized LDH for phosphate was studied at a solution with initial concentration of 10 mM from each of the following anions: phosphate, sulfate, bicarbonate and chloride which are the common anions in soil solutions (solid-to-solution ratio of 5 g L−1, pH = 7 and shaking time = 480 min). The amount of sulfate and chloride in the supernatants were measured by turbidimetric (EPA, 1978) and titration with silver nitrate (Chapman and Pratt, 1961) methods, respectively. Bicarbonate was calculated from the difference between the amount of nitrate exchanged and sum of adsorbed phosphate, sulfate and chloride (Torres-Dorante et al., 2008). The pH dependence of phosphate uptake in LDH were carried out using 10 mM KH2PO4 at pH 6, 7 and 8 (solid-to-solution ratio of 5 g L−1, I = 0.03 M KNO3 and shaking time = 480 min). The adsorption isotherms were determined using an initial concentration range of 1 to 50 mM of phosphate from KH2PO4 and another conditions were similar to previous experiments (solid-to-solution ratio of 5 g L−1, I = 0.03 M KNO3, pH = 7 and shaking time = 480 min). For investigation of phosphate desorption at a concentration of 50 mM, 15 mL from equilibrium solutions were substituted with 15 mL of 0.03 M KNO3 and shaken for 480 min. Substitution was repeated four times and phosphate concentrations in extracts were determined.

All experiments (LDH preparation and phosphate analysis) in this study were repeated twice and the pH adjustments were performed by 0.5 M KOH and 0.5 M HNO3. The phosphate uptakes were calculated from the difference between the initial and final (in supernatants) phosphate concentrations.

3. Results and discussion

3.1. Characterization of LDH

The measurement of Zn and Al concentrations showed that Zn/Al ratios were 1.86 (± 0.05) and 2.61 (± 0.07) for Zn2G-Al, Zn3G-Al and 1.79 (± 0.06) and 2.30 (± 0.04) for Zn2M-Al and Zn3M-Al, respectively. The measured Zn/Al ratios were smaller than theoretical values. Moreover, these values for synthesized samples by G method were greater than M method. Inayat et al. (2011) stated that time dependency of the pH of the synthesized LDH would be the main reason for this difference between two methods. In other words, increasing of pH in the G method was faster and higher than M method, therefore formation of LDH took place more quickly leading to higher Zn/Al ratios. In our study, the final pH of solutions for Zn2G-Al, Zn3G-Al, Zn2M-Al and Zn3M-Al were 6.99 (± 0.02), 7.05 (± 0.04), 6.89 (± 0.04) and 6.87 (± 0.04), respectively.

The XRD patterns of synthesized LDH in the 2θ value of 4–70° showed sharp and symmetric reflections (002 and 006 planes) at lower 2θ values and broad and asymmetric reflections (015 and 018 planes) at higher 2θ indicating a well-formed layered structure (Fig. 1a). XRD data of reflections and lattice parameters (Table 1) calculated by a = 2d110, c = 3d003 (Chitrakar et al., 2007), showed that all synthesized samples were nitrate containing Zn−Al LDH. This result was in accordance to Zhang et al. (2013). However, the XRD pattern of Zn3G-Al showed a new phase with basal spacing of 7.4 Å at 11.8° as a result of the presence of carbonate ions as guest anion (Inayat et al., 2011; Liu et al., 2014; Song et al., 2012). Accordingly, it can be concluded that carbonate exists in the interlayer space of Zn3G-Al along with nitrate anion.

Inayat et al. (2011) reported that in G method, nitrate form of Zn−Al LDH with Zn/Al ratio of 2 was produced before 30 h synthesis time, while the synthesized samples after this time showed an increase in fraction of carbonate containing LDH due to the increasing of pH solution. In other words, the presence of carbonate in the interlayer space of synthesized LDH by G method depended on the synthesis time and pH solution of LDH. In the present study, carbonate phase was observed only in Zn3G-Al while, the final pH of this LDH was close to the Zn3G-Al. This result suggested that Zn/Al molar ratio may also affect the intercalation of carbonate anions into the interlayer space as well as time and pH of the synthesis solution. Inayat et al. (2011) also showed that, independent from the synthesis time, nitrate containing LDH was synthesized by M method. This was in agreement with our finding in current study.

The FT-IR bands of synthesized LDH were shown in Fig. 1b. Two bands around 3450 and 1610 cm−1 for all samples assigned to O–H stretching vibrations and H–O–H bending vibration of the interlayer water molecule, respectively (Cheng et al., 2010; Hosni and Srasra,
The results from EDS spectra clearly showed the presence of Zn, Al and O indicating Zn-Al LDH have been successfully synthesized.

According to the chemical analysis, the empirical formulas of the Zn2G-Al, Zn3G-Al, Zn2M-Al and Zn3M-Al should be Zn0.65 Al0.35 (OH)2 (X)0.36 0.71 H2O, Zn0.72 Al0.28 (OH)2 (X)0.28 0.70 H2O, Zn0.64 Al0.36 (OH)2 (X)0.36 0.71 H2O and Zn0.70 Al0.30 (OH)2 (X)0.30 0.66 H2O, respectively. Therefore, the measured AEC of Zn2G-Al, Zn3G-Al, Zn2M-Al and Zn3M-Al (2.77 (± 0.07), 2.03 (± 0.02), 2.75 (± 0.04) and 2.53 (± 0.02) mequiv. g⁻¹, respectively) were slightly less than the theoretical AEC (2.95 (± 0.05), 2.33 (± 0.04), 2.95 (± 0.06) and 2.56 (± 0.03) mequiv. g⁻¹, respectively) which was calculated from structural formulas. It was probably due to blocking some of anion exchange sites by carbonate anions. Based on research, carbonate is an unfavorable anion for exchange reactions due to its high affinity for LDH (Halajnia et al., 2012; Ramírez-Llamas et al., 2015). Additionally, Parker et al. (1995) stated that even in the cases that carbonate ions have not been deliberately added to solution, CO2 might be absorbed from atmosphere as carbonate source reducing AEC. As expected measured AEC in Zn2G-Al and Zn2M-Al were larger than the Zn3G-Al and Zn3M-Al because of the change of Zn/Al molar ratio. Therefore, the lowest measured AEC value was obtained in Zn3G-Al due to higher Zn/Al molar ratio and the presence of carbonate in the interlayer space.

Generally, these results suggest that the synthesis method did not influence the characteristics of LDH with Zn/Al ratio of 2 while it had a considerable impact on Zn/Al ratio of 3. Therefore, it seems that M method is an appropriate technique for synthesis of nitrate containing Zn-Al LDH for both 2 and 3 ratios.

### 3.2. Effect of contact time and uptake kinetics

Phosphate uptake as a function of contact time showed a rapid increase at the first stages and then followed by a slower process until a plateau was obtained at 480 min for all LDH (Fig. 3). Phosphate uptake capacity at equilibrium time changed from 1.64 (± 0.01) to 1.67 (± 0.04) mmol g⁻¹ for all samples except Zn3G-Al which was 1.09 (± 0.02) mmol g⁻¹. According to measured AEC results, it was expected that phosphate uptake decreased with increasing of Zn/Al molar ratio but this result was not achieved for synthesized LDH by M method. Cheng et al. (2009) reported that the amounts of adsorbed phosphate were similar for both 2 and 4 molar ratios of Zn-Al LDH. Although the lower Zn/Al ratios increase the positive charge of LDH, it may lead to the formation of disordered layered structure of LDH, because of the difference between the atomic radius of zinc and aluminum (Cheng et al., 2009). On the other hand, according to XRD and FT-IR results the lower phosphate uptake by Zn3G-Al may be attributed to the presence of carbonate in the interlayer space. Triantafyllidis et al. (2010) showed that synthesized Mg-Al and Mg-Fe LDH intercalated with chloride or nitrate had higher phosphate uptake than LDH containing predominantly carbonates as interlayer anions. Furthermore, some studies have concluded that the mechanism of uptake may be another factor affecting uptake capacity. For example, Zhou et al. (2011) stated that low value of triphosphate removal by Mg-Fe LDH was mainly due to surface adsorption and near-edge intercalation mechanism.

The kinetics data of phosphate uptake by synthesized LDH were plotted against pseudo-first order, pseudo-second order (Siminon, 2016) and intraparticle diffusion (Karaca et al., 2004) models. The nonlinear form of these models can be written as follows:

\[ Q = q_e \left(1 - \exp(-k_1t)\right) \]  

\[ Q = \frac{q_e^2k_2t}{1 + q_e k_2 t} \]
Intraparticle diffusion: 
\[ q_t = (k_1 t^{0.5}) + C \]  
\[ \text{RMSE} = \left[ \frac{\sum (q_t - q_c)^2}{n - p} \right]^{0.5} \]

where \( q_e \) and \( q_t \) (both in mmol g\(^{-1}\)) were the amount of phosphate adsorbed at equilibrium and at time \( t \) (min), respectively. \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g mmol\(^{-1}\) min\(^{-1}\)) and \( k_3 \) (mmol g\(^{-1}\) min\(^{-1/2}\)) were the adsorption rate constant for pseudo-first order, pseudo-second order and intraparticle diffusion models and C was constant (Table 2). Coefficient of determination \( (R^2) \) and root mean square error \( (\text{RMSE}) \) were chosen as criteria to determine the equation of best fit (Table 2). The values of RMSE (Zhang and Selim, 2005) were obtained as follows:

The results revealed that the highest \( R^2 \) (0.967–0.989) and the lowest RMSE (0.041–0.086) values were obtained for pseudo-second order model. Moreover, the values of \( q_e \) for pseudo-second order model were closer to the experimental values, which were in accordance with other phosphate uptake kinetics studies (Cheng et al., 2009, 2010; Li

Fig. 2. SEM images and corresponding EDS spectrum of (a) Zn2G-Al, (b) Zn3G-Al, (c) Zn2M-Al and (d) Zn3M-Al.
et al., 2016; Yu et al., 2015), Yan et al. (2015) reported that chemisorption might be rate limiting step and controlling the phosphate uptake process when the data are fitted to pseudo-second order model.

### 3.3. Effect of initial phosphate concentration and adsorption isotherms

To investigate the process of phosphate uptake on studied LDH, adsorption isotherm was carried out at a temperature of 25 °C. The results revealed that percentage of phosphate adsorbed by Zn2G-Al, Zn3G-Al, Zn2M-Al and Zn3M-Al decreased with increasing initial phosphate concentration from 1 to 50 mM and reached to 27.2 (± 0.61), 19.7 (± 0.07), 26.7 (± 1.13) and 26.6 (± 1.02) %, respectively. This is probably because of the saturation of adsorption sites which caused to declining of LDH affinity for phosphate anions at high concentrations. As shown in Fig. 4, the maximum phosphate adsorption for Zn2G-Al, Zn3G-Al, Zn2M-Al and Zn3M-Al were 2.72 (± 0.06), 1.97 (± 0.01), 2.67 (± 0.11) and 2.66 (± 0.10) mmol g⁻¹, respectively which were very close to measured AEC values. The isotherm data of LDH were fitted using the Langmuir (Eq. (5)) and Freundlich (Eq. (6)) models in the following nonlinear forms (Limousin et al., 2007):

\[ q_e = \frac{bq_m}{1 + \frac{1}{K_f}C_e} \]  
(5)

\[ q_e = k_1 C_e^{1/n} \]  
(6)

where \( q_m \) (mmol L⁻¹) and \( q_e \) (mmol g⁻¹) denotes the equilibrium concentration of phosphate and the amounts of phosphate adsorbed per unit mass of adsorbent, respectively. In the Langmuir equation, the \( b \) constant is the saturated adsorption capacity and \( K_f \) is a constant related to binding energy. Also, \( K_f \) and \( 1/n \) are the Freundlich constants. The values of parameters are presented in Table 3.

Of the isotherm equations tested, Freundlich model was most appropriate to represent the uptake equilibrium data, based on the \( R^2 \) and RMSE (Table 3). It seems that the uptake process of phosphate follows a multi-step pathway (Cheng et al., 2013) and several uptake mechanisms probably involved in the uptake process. 1/n constant in Freundlich model indicates the strength of adsorption and it is desirable if \( 0 < 1/n < 1 \) (Khitous et al., 2016; Yang et al., 2005). According to Table 3, the values of 1/n (0.138–0.210) indicate that the process of phosphate uptake on synthesized LDH is favorable.

### Table 2

Kinetic parameters for phosphate uptake by LDH.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_f ) (min⁻¹)</td>
<td>( q_m ) (mmol g⁻¹)</td>
<td>( q_e ) (mmol g⁻¹)</td>
</tr>
<tr>
<td>Zn2G-Al</td>
<td>0.134</td>
<td>1.094</td>
<td>0.908</td>
</tr>
<tr>
<td>Zn2M-Al</td>
<td>0.111</td>
<td>0.732</td>
<td>0.922</td>
</tr>
<tr>
<td>Zn3G-Al</td>
<td>0.093</td>
<td>1.174</td>
<td>0.951</td>
</tr>
<tr>
<td>Zn3M-Al</td>
<td>0.135</td>
<td>1.059</td>
<td>0.789</td>
</tr>
</tbody>
</table>

In order to determine the apparent energy of phosphate uptake, the Dubinin–Radushkevich (DR) equation was used. This model gives more information about the uptake process on porous sorbents (Halajnia et al., 2012). The nonlinear form of this model can be written as (Gunay et al., 2007):

\[ q_e = q_m \exp \left[ -\frac{RT \ln(1 + 1/C_e)}{2E} \right] \]  
(7)

where \( q_e \) and \( q_m \) (both mmol g⁻¹) are the amount of phosphate adsorbed per unit mass of adsorbent and the saturated sorption capacity, respectively. In the DR model, \( R \) and RMSE coefficients have been shown in Table 3.

The E parameter is used for assessing the type of sorption mechanism. The E values between 8 and 16 kJ mol⁻¹ indicate the chemical adsorption and the values lower than 8 kJ mol⁻¹ demonstrate the physical adsorption of adsorbents (Köse and Kvanc, 2011). According to Table 3, the values of E between 12.025 and 13.534 kJmol⁻¹, indicate the phosphate uptake process on studied LDH follows chemical adsorption. Halajnia et al. (2013) and Khitous et al. (2016) reported chemical adsorption of phosphate for Mg-Al LDH. The amount of adsorption energy in their studies were 15.811 and 14.87 kJmol⁻¹, respectively.

### 3.4. Mechanism of phosphate uptake

Generally, two possible mechanisms are suggested for phosphate uptake by LDH: a) surface adsorption on LDH which can be occurred in several forms including, anionic exchange between phosphate anions and OH⁻ groups on LDH surface (Cheng et al., 2013), surface complexations (Li et al., 2016) and surface precipitation (Kollraj and Kannan, 2010; Zhou et al., 2011). b) Anionic exchange between interlayer (e.g., nitrate, carbonate, etc.) and phosphate anions that is called phosphate intercalation (Hosni and Srasra, 2010; Tsjirimura et al., 2007).

In order to investigate the phosphate uptake mechanism, the XRD and FT-IR techniques were used after phosphate uptake by LDH at the concentration of 50 mM and drying of samples at 70 °C for 18 h (Fig. 5). The XRD results of Zn2G-Al, Zn3G-Al, Zn2M-Al and Zn3M-Al indicated that the intensity of 003 reflection has been strongly reduced and a new reflection has been appeared at 11.32 Å with basal spacing of 11.05 Å. They also indicated that the XRD pattern of Zn-Al-CO3 LDH did not change significantly even after the dihydroxylation of carbonate (was discussed in Section 3.1) remained without any changes.
not change after phosphate uptake revealing that ion exchange did not occur. Also, this basal spacing was similar to that reported by Costantino et al. (1997) for synthesized Zn-Al-H₂PO₄ at acidic and neutral pH and dried over P₄O₁₀. Badreddine et al. (1999) showed that not only the interlayer distance was not constant after phosphate uptake by Zn-Al-Cl LDH, but also depending on the phosphate species it increased to 11.87, 10.63 and 9.30 Å for Zn-Al-H₂PO₄, Zn-Al-HPO₄ and Zn-Al-PO₄, respectively. Likewise, some studies reported the basal spacing of 10.7 and 10.6 Å for Mg-Al-HPO₄ LDH (Shimamura et al., 2010, 2012). Hence, firstly it appears that H₂PO₄⁻ was probably predominant species in the interlayer space of LDH due to the obtained basal spacing (11.05–11.32 Å) and studied initial pH (7) (Costantino et al., 1997). However, as the pH of final solutions was about 8.2–8.8 therefore it is expected that HPO₄²⁻ should be the prevalent form in solution. As stated by Chitrakar et al. (2007), from their findings, Dutta and Puri (1989) has concluded that the adsorbed species of phosphate ions did not necessarily correspond to dissolved states in solution. Further research is required to clarify this observation. Secondly, the exchange of nitrate by the phosphate ion in Zn₂G-Al, Zn₂M-Al and Zn₃M-Al led to an increase of basal spacing of 003 peaks and shifted them towards lower 2θ values. In other words, phosphate intercalation mechanism has possibly occurred in these LDH. Furthermore, it seems that due to the presence of carbonate in parent Zn₃G-Al (Fig. 1a), phosphate intercalation did not completely take place in phosphate treated Zn₃G-Al; therefore, both of reflections at 7.89° and 11.66° were observed in this sample. Likewise, Costantino et al. (1997) stated that grafting reaction of phosphate anions with structural OH group occurred during the exchange process or by mild thermal treatment which led to the producing of layered Zn and Al hydroxyphosphate. Therefore, in the present study, it is possible that phosphate ions have been attached to the hydrotalcite sheet due to the drying condition of LDH (70 °C) and obtained basal spacing (11.05–11.32 Å).

Table 3
Isotherm models constants for phosphate uptake by LDH.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>DR model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b (mmol g⁻¹)</td>
<td>K_L (L mmol⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td>Zn₂G-Al</td>
<td>2.502</td>
<td>1.273</td>
<td>0.542</td>
</tr>
<tr>
<td>Zn₃G-Al</td>
<td>1.662</td>
<td>1.439</td>
<td>0.302</td>
</tr>
<tr>
<td>Zn₂M-Al</td>
<td>2.471</td>
<td>1.387</td>
<td>0.529</td>
</tr>
<tr>
<td>Zn₃M-Al</td>
<td>2.467</td>
<td>1.224</td>
<td>0.529</td>
</tr>
</tbody>
</table>

Fig. 4. Phosphate adsorption (●) and desorption isotherms (■) of (a) Zn₂G-Al, (b) Zn₃G-Al, (c) Zn₂M-Al and (d) Zn₃M-Al (pH = 7, solid-to-solution = 5 q L⁻¹, I = 0.03 M KNO₃, temperature = 25 °C).

Fig. 5. XRD patterns (a) and FT-IR spectra (b) of Zn₂G-Al, Zn₃G-Al, Zn₂M-Al and Zn₃M-Al after phosphate uptake at the concentration of 50 mM.
were in following order: chloride $0 <$ bicarbonate $<$ sulfate $<$ phosphate. Therefore, among competing anions, the divalent anions indicated higher affinity for LDH compared with monovalent anions. Same results reported by Halajnia et al. (2012) for Mg-Al LDH with Mg/Al ratio of 3. Although the highest selectivity was found for phosphate anion, uptake of phosphate decreased in the presence of other anions due to competition with phosphate for adsorption sites. Other studies have also shown the decrease of phosphate uptake by Mg-Al LDH in the presence of nitrate, chloride, sulfate and selenite (Das et al., 2006) and fluoride (Cai et al., 2012). Additionally, among the studied LDH, Zn$^{2+}$G-Al, Zn$^{2+}$M-Al and Zn$^{3+}$M-Al showed higher capacity of phosphate uptake. This result suggested that the highest phosphate uptake in simulated soil solution system achieved by pure nitrate containing LDH.

3.6. Effect of pH

The results showed that phosphate uptake decreased with increasing pH from 6 to 8 (Fig. 7a) probably due to changes in phosphate species and LDH surface charge alteration (Cheng et al., 2013; Chitrakar et al., 2005; Yan et al., 2015). Such a change in LDH surface charge was depicted in Reactions (8) and (9). According to these reactions, phosphate uptake increases and decreases in acidic and alkaline condition, respectively, due to the electrostatic attraction and repulsion between the adsorbent and the adsorbate.

Acidic pH: LDH – OH + H$^+$ → LDH – OH$_2^+$

(8)

Alkaline pH: LDH – OH + H$^+$ → LDH – O$^-$ + H$_2$O

(9)

In addition, at pH $> 7$, HPO$_4^{2-}$ is the dominant species with higher adsorption free energy than H$_2$PO$_4^-$, hence phosphate uptake will be reduced (Yan et al., 2015). Moreover, competition between OH$^-$ groups and phosphate anions for sorption sites on LDH at high pH is another reason which can diminish uptake capacity (Das et al., 2006). Furthermore, as shown in Fig. 7b, the equilibrium pH of each LDH increased after phosphate uptake from to 8.2 (± 0.03) to 8.8 (± 0.02). This is in agreement with the results obtained by Cheng et al. (2009) for Zn-Al LDH with initial pH range 5–10. They reported that final pH of solutions was about 8–8.5 and this can be attributed to the amphoteric character of aluminum hydroxide. Seida and Nakano (2002) has concluded that increase of pH during the phosphate uptake might be due to the replacement of OH$^-$ groups on the surface of LDH and/or by partial dissolution of the LDH compound.

3.7. Phosphate desorption

Phosphate desorption was investigated by five successive desorption steps in the 0.03 M KNO$_3$ as background electrolyte. The results showed that the percentages of phosphate desorption were 36.3 (± 3.29), 23.2 (± 1.93), 34.5 (± 0.62) and 33.5 (± 1.25)% for Zn$^{2+}$G-Al, Zn$^{2+}$C-Al, Zn$^{2+}$M-Al and Zn$^{3+}$M-Al, respectively (Fig. 4). This observation suggested that the uptake of phosphate was partially reversible process likely due

3.5. Selectivity of the LDH for phosphate

The selectivity of Zn$^{2+}$G-Al, Zn$^{2+}$C-Al, Zn$^{2+}$M-Al and Zn$^{3+}$M-Al towards phosphate in the presence of common anions in soil solution were shown in Fig. 6. The percentage of adsorbed anions on LDH were in following order: chloride $0 <$ bicarbonate $<$ sulfate $<$ phosphate. Therefore, among competing anions, the divalent anions indicated higher affinity for LDH compared with monovalent anions. Same results reported by Halajnia et al. (2012) for Mg-Al LDH with Mg/Al ratio of 3. Although the highest selectivity was found for phosphate anion, uptake of phosphate decreased in the presence of other anions due to competition with phosphate for adsorption sites. Other studies have also shown the decrease of phosphate uptake by Mg-Al LDH in the presence of nitrate, chloride, sulfate and selenite (Das et al., 2006) and fluoride (Cai et al., 2012). Additionally, among the studied LDH, Zn$^{2+}$C-Al, Zn$^{2+}$M-Al and Zn$^{3+}$M-Al showed higher capacity of phosphate uptake. This result suggested that the highest phosphate uptake in simulated soil solution system achieved by pure nitrate containing LDH.
to chemisorption adsorption. Chitrakar et al. (2007) and Koirilaj and Kannan (2010) reported that 75% and <10% of adsorbed phosphate by Mg-Al-Zr LDH and Zn-Al-Zr LDH were desorbed into 0.1 M NaOH and 1 M NaCl solutions, respectively. Cheng et al. (2009) indicated that the amounts of phosphate desorption from Zn-Al LDH enhanced by increasing the concentrations of solutions and finally received to 21% using NaCl (20 wt%) and > 80% by NaOH (5 wt%) or NaCO3 (10 wt%). Halajnia et al. (2013) also showed that 15.7% of the phosphate on the Mg–Al LDH can be desorbed by KCl solution with concentration of 0.03 M. Therefore, it seems that the phosphate desorption from LDH can be strongly influenced by the concentration and kind of electrolyte solution as well as the type of LDH. Furthermore, the pH of solution would be another factor that affects the phosphate desorption. Novillo et al. (2014) and Li et al. (2016) reported that phosphate desorption at alkaline pH was higher than neutral pH due to the competition between hydroxyl and phosphate ions. Since the electrolyte concentration in this experiment was similar to ionic strength of soil solutions (Meers et al., 2014) and Li et al. (2016) reported that phosphate desorption at 0.03 M. Therefore, it seems that the phosphate desorption from LDH can be utilized as slow release fertilizer.

4. Conclusion

The findings in this study demonstrated that the type of synthesis method and Zn/Al molar ratio affect the balancing ion in the synthesized Zn-Al LDH. Modified method (M) was convenient for synthesis of pure nitrate containing Zn-Al LDH with molar ratios of 2 and 3. However, general method (G) led to the production of pure nitrate and nitrate-carbonate containing LDH with molar ratios of 2 and 3, respectively. Uptake kinetics for all LDH followed a pseudo-second order model. Pure nitrate containing LDH adsorbed maximum phosphate among the studied LDH, probably due to the complete intercalation, surface complexations, exchanging with surface OH groups and grafting reaction with structural OH group mechanisms. It seems that these LDH could be a suitable choice for phosphate uptake in multi-anionic environments such as soil solutions and wastewaters because of their high selectivity for phosphorous. The low amounts of phosphate desorption from synthesized LDH were observed. This may have implications for use of these compounds as a slow release phosphate fertilizer in soil. On the other hand, as the synthesized LDH contain Zn element, further research on their application in zinc deficient calcareous soils is recommended.

Acknowledgments

The authors are immensely grateful to Dr. A. Salimi, assistant professor of Ferdowsi University of Mashhad for his valuable comments.

References


