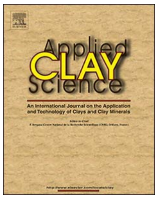
Applied Clay Science 152 (2018) 333–341

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay



Research paper

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

Hadis Hatami, Amir Fotovat*, Akram Halajnia

Department of Soil Science, Faculty of Agriculture, Ferdowsi University of Mashhad, Iran

ARTICLE INFO

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

ABSTRACT

Zinc aluminum layered double hydroxides (LDH) with Zn/Al molar ratios of 2 and 3 were synthesized by general (Zn_{2G}-Al, Zn_{3G}-Al) and modified (Zn_{2M}-Al, Zn_{3M}-Al) urea hydrolysis methods. The effects of time, pH, selectivity and initial phosphorous concentration were investigated on phosphate uptake by synthesized LDH in a simulated soil solution. Moreover, phosphate desorption from studied LDH was evaluated. Based on the results, nitrate containing Zn-Al LDH were synthesized by both methods. However, the presence of carbonate ion in the interlayer space of Zn_{3G}-Al was recorded. The kinetics experiments indicated that the pseudo-second order model well described phosphate uptake on all LDH. The lowest uptake (1.09 mmol g^{-1}) was observed for Zn_{3G}-Al likely due to Zn/Al molar ratio, the presence of carbonate in the interlayer space and incomplete phosphate intercalation mechanism. Phosphate adsorption isotherms of LDH were in agreement with Freundlich model. Although phosphate uptake decreased in the presence of other anions, the highest selectivity especially in the pure nitrate containing LDH were measured for phosphate anion. Phosphate uptake declined with increasing the pH from 6 to 8. The amounts of phosphate desorption from prepared LDH were between 23.2 and 36.3% suggesting that synthesized LDH may have potential to be used as a slow release phosphate fertilizer in soils.

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 $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}m(H_2O)$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively. The value of x is equal to $M^{3+}/(M^{3+}+M^{2+})$ and A^{n-} 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 (NH_4NO_3) 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

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* Corresponding author.
E-mail addresses: hatami.ha@mail.um.ac.ir (H. Hatami), afotovat@um.ac.ir (A. Fotovat), halajnia@ferdowsi.um.ac.ir (A. Halajnia).

https://doi.org/10.1016/j.clay.2017.11.032
Received 23 July 2017; Received in revised form 22 November 2017; Accepted 23 November 2017

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. Zn_{2G}-Al and Zn_{3G}-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 NH_4NO_3 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, Zn_{2M}-Al and Zn_{3M}-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:H_2O (Das et al., 2003). X-ray diffraction (XRD) patterns were recorded using a Unisantis XMD 300 diffractometer with CuKα radiation ($\lambda = 0.15418$ 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 1 M NH_4NO_3 solution buffered at pH 7 and then were washed with 0.1 M NH_4NO_3 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 (pH_{ZPC}) values were determined considering the difference between final and initial pH by the shaking of 0.1 g synthesized LDH in 20 mL KNO_3 solution (0.03 M) with pH previously set by 0.1 M HNO_3 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 KNO_3 at pH = 7 as a background electrolyte, containing a concentration of 10 mM KH_2PO_4 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 KH_2PO_4 at pH 6, 7 and 8 (solid-to-solution ratio of 5 g L^{-1}, $I = 0.03$ M KNO_3 and shaking time = 480 min). The adsorption isotherms were determined using an initial concentration range of 1 to 50 mM of phosphate from KH_2PO_4 and another conditions were similar to previous experiments (solid-to-solution ratio of 5 g L^{-1}, $I = 0.03$ M KNO_3, 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 KNO_3 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 HNO_3. 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 Zn_{2G}-Al, Zn_{3G}-Al and 1.79 (± 0.06) and 2.30 (± 0.04) for Zn_{2M}-Al and Zn_{3M}-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 Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-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 (003 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 $a = 2d_{110}$, $c = 3d_{003}$ (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 Zn_{3G}-Al showed a new phase with basal spacing of 7.46 Å at 11.84° 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 Zn_{3G}-Al along with nitrate anion. Inayat et al. (2011) reported that in the 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 Zn_{3G}-Al while, the final pH of this LDH was close to the Zn_{2G}-Al. This result suggested that Zn/Al molar ratio may also affect the intercalation of carbonate anions into the interlayer apace 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,

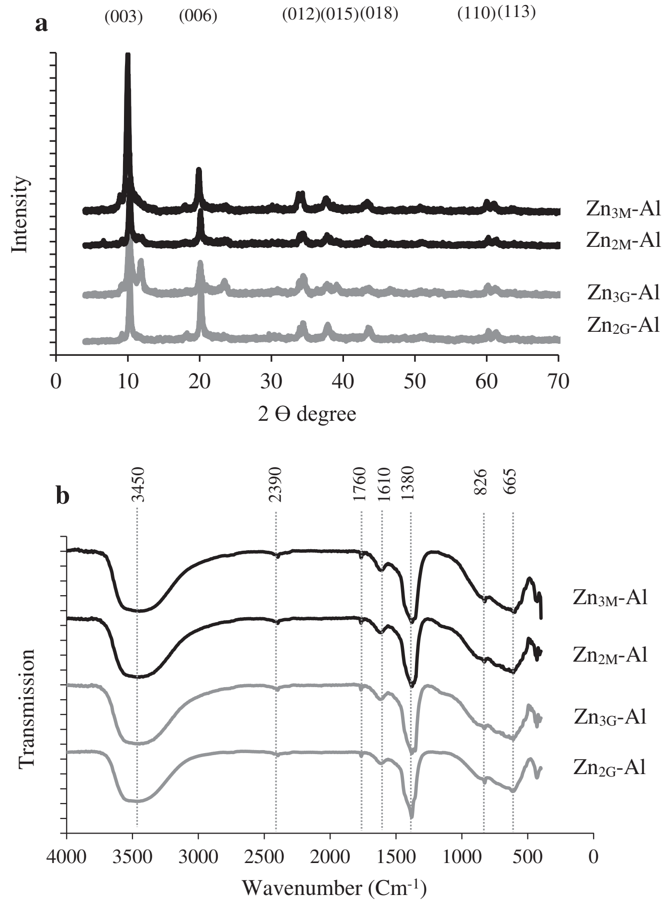

Fig. 1. XRD patterns (a) and FT-IR spectra (b) of Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-Al before phosphate uptake.

Table 1
XRD data of diffraction peaks and the lattice parameters of synthesized LDH.

Samples	d_{003} (Å)	d_{110} (Å)	Lattice parameters	
			a (Å)	c (Å)
Zn_{2G}-Al	8.582	1.535	3.070	25.746
Zn_{3G}-Al	8.682	1.537	3.074	26.046
Zn_{2M}-Al	8.601	1.536	3.072	25.803
Zn_{3M}-Al	8.861	1.542	3.084	26.583

2010; Yu et al., 2015). The absorption bands at about 1380, 826 and 665 cm^{-1} corresponded to ν_3, ν_1 and ν_4 vibrations of the nitrate groups, respectively (Legrouri et al., 1999; Woo et al., 2011). The absorption band at 1380 cm^{-1} in the Zn_{3G}-Al splits into double bands at 1350 and 1380 cm^{-1} showing the reduction of carbonate anion which probably created due to interactions between the carbonate ions and water molecules in the interlayer or cations from the layers (Mohan Rao et al., 2005). Hence, the appearance of this band refers to the presence of carbonate in the Zn_{3G}-Al which was consistent with XRD result (Fig. 1a). The bands observed for carbonyl groups at 1760 cm^{-1} (Liu et al., 2014) and 2390 cm^{-1} were related to the CO_2 background of the measurement system (Islam and Patel, 2009, 2010).

SEM images and corresponding EDS spectrum of synthesized LDH were depicted in Fig. 2. According to SEM images the well-crystallized, regular and plate-like particles of LDH with particle size ranges 1–2 μm was produced. This morphology is typical for LDH (Liang et al., 2010). The similarity of SEM images for synthesized LDH indicated that synthesis methods did not significantly influence the morphology of LDH. These results were in agreement with the finding of Inayat et al. (2011). The results from EDS spectra clearly showed the presence of Zn, Al and O indicating Zn-Al LDH have been successfully synthesized.

The pH_{ZPC} of Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-Al were 8.6 (± 0.25), 8.4 (± 0.20), 8.75 (± 0.15) and 8.4 (± 0.30), respectively which were close to that reported by Yan et al. (2015) for Zn-Al LDH (8.69).

According to the chemical analysis, the empirical formulas of the Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-Al should be $Zn_{0.65}$ $Al_{0.35}$ $(OH)_2$ $(X)_{0.35}$ 0.61 H_2O, $Zn_{0.72}$ $Al_{0.28}$ $(OH)_2$ $(X)_{0.28}$ 0.70 H_2O, $Zn_{0.64}$ $Al_{0.36}$ $(OH)_2$ $(X)_{0.36}$ 0.71 H_2O and $Zn_{0.70}$ $Al_{0.30}$ $(OH)_2$ $(X)_{0.30}$ 0.66 H_2O, respectively. Therefore, the measured AEC of Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-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, CO_2 might be absorbed from atmosphere as carbonate source reducing AEC. As expected measured AEC in Zn_{2gG}-Al and Zn_{2M}-Al were larger than the Zn_{3G}-Al and Zn_{3M}-Al because of the change of Zn/Al molar ratio. Therefore, the lowest measured AEC value was obtained in Zn_{3G}-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 Zn_{3G}-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 Zn_{3G}-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 (Simonin, 2016) and intraparticle diffusion (Karaca et al., 2004) models. The nonlinear form of these models can be written as follows:

$$\text{Pseudo} - \text{first order: } q_t = q_e(1 - \exp(-k_1 t)) \qquad (1)$$

$$\text{Pseudo} - \text{second order: } q_t = q_e{}^2 k_2 t/1 + q_e\, k_2\, t \qquad (2)$$

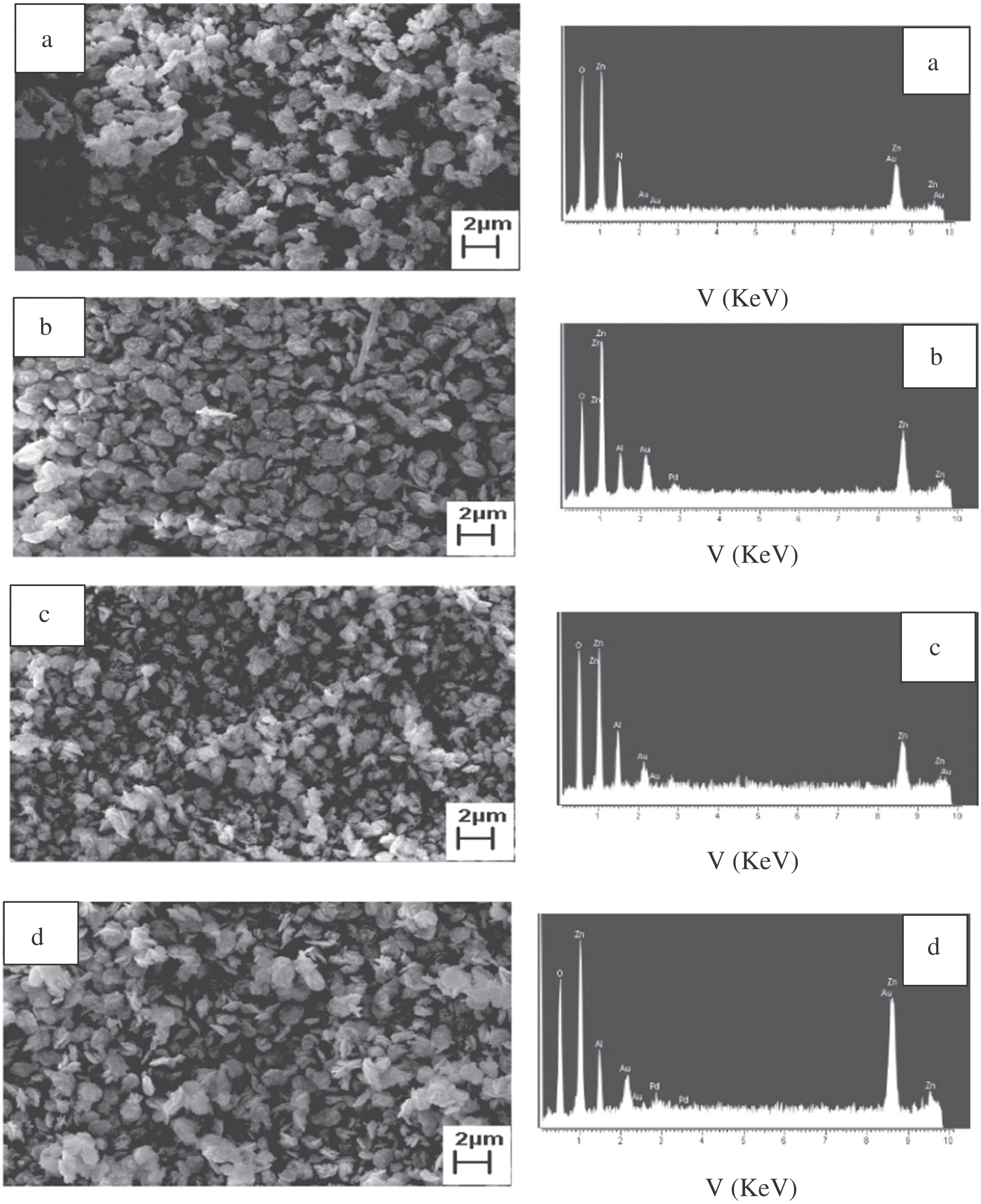

Fig. 2. SEM images and corresponding EDS spectrum of (a) Zn_{2G}-Al, (b) Zn_{3G}-Al, (c) Zn_{2M}-Al and (d) Zn_{3M}-Al.

$$\text{Intraparticle diffusion:} q_t = (k_3 t^{0.5}) + C \quad (3)$$

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 (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:

$$\text{RMSE} = [(\Sigma(q_t - q_t^*))^2/(n - p)]^{0.5} \quad (4)$$

where q_t and q_t^* (both in mmol g^{-1}) were the amount of observed and simulated phosphate adsorbed at time t, respectively. n was the number of experimental data points and p was the number of fitted parameters.

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

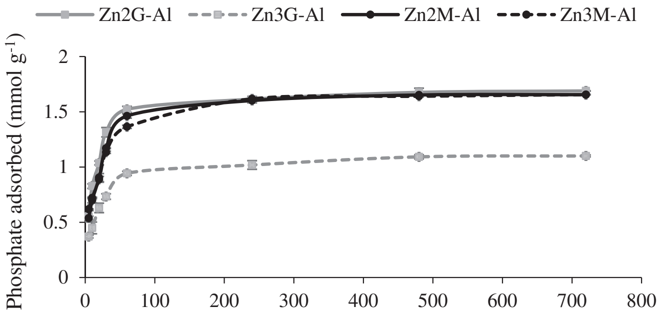

Fig. 3. Effect of contact time on phosphate uptake from solution containing 10 mM phosphate in 20 mL of solution volume for 100 mg LDH (pH = 7, I = 0.03 M KNO_3).

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 Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-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 uptake for Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-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):

$$q_e = bk_LC_e/1 + k_LC_e \tag{5}$$

$$q_e = k_FC_e{}^{1/n} \tag{6}$$

where C_e (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_L 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. This result is consistent with the findings of Cheng et al. (2013); Chitrakar et al. (2005, 2007); and Novillo et al. (2014).

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):

$$q_e = q_m \exp[RT\ \ln(1 + 1/C_e)^2/{-2E^2}] \tag{7}$$

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, C_e (mmol L^{-1}) is the equilibrium concentration of phosphate and E (kJ mol^{-1}) is adsorption energy. R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}) and T (°K) is temperature. The DR model constants, R^2 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 Kıvanc, 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 (Koilraj 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; Tsujimura 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 Zn_{2G}-Al, Zn_{2M}-Al and Zn_{3M}-Al indicated that the intensity of 003 reflection has been strongly reduced and a new reflection with basal spacing of 11.05–11.32 Å has appeared at 7.80–7.97°. However in the case of Zn_{3G}-Al, the reflection related to carbonate (was discussed in Section 3.1) remained without any changes at 11.66° despite the appearance of the new reflection with basal spacing of 11.19 Å at 7.89°. These results were in disagreement with the studies indicating no or small change in the basal spacing of LDH after phosphate uptake (Du et al., 2009; Khitous et al., 2016; Woo et al., 2011). However, He et al. (2010) reported the same results for Zn-Al-NO_3 LDH synthesized by urea hydrolysis method (in 4 mM of phosphate concentration). They stated that the presence of $H_2PO_4{}^-$ in the interlayer space caused to creating of a new reflection with basal spacing of 11.05 Å. They also indicated that the XRD pattern of Zn-Al-CO_3 LDH did

Table 2
Kinetic parameters for phosphate uptake by LDH.

Samples	Pseudo-first order				Pseudo-second order				Intraparticle diffusion			
	K_1 (min^{-1})	q_e (mmol g^{-1})	R^2	RMSE	K_2 (g $mmol^{-1}$ min^{-1})	q_e (mmol g^{-1})	R^2	RMSE	K_3 (mmol g^{-1} $min^{-1/2}$)	C	R^2	RMSE
Zn_{2G}-Al	0.134	1.094	0.908	0.091	0.050	1.722	0.967	0.086	0.037	0.872	0.661	0.269
Zn_{3G}-Al	0.111	0.732	0.922	0.056	0.066	1.108	0.982	0.041	0.027	0.498	0.757	0.154
Zn_{2M}-Al	0.093	1.174	0.951	0.077	0.042	1.705	0.989	0.052	0.041	0.757	0.707	0.268
Zn_{3M}-Al	0.135	1.059	0.789	0.127	0.045	1.675	0.968	0.083	0.040	0.765	0.778	0.217

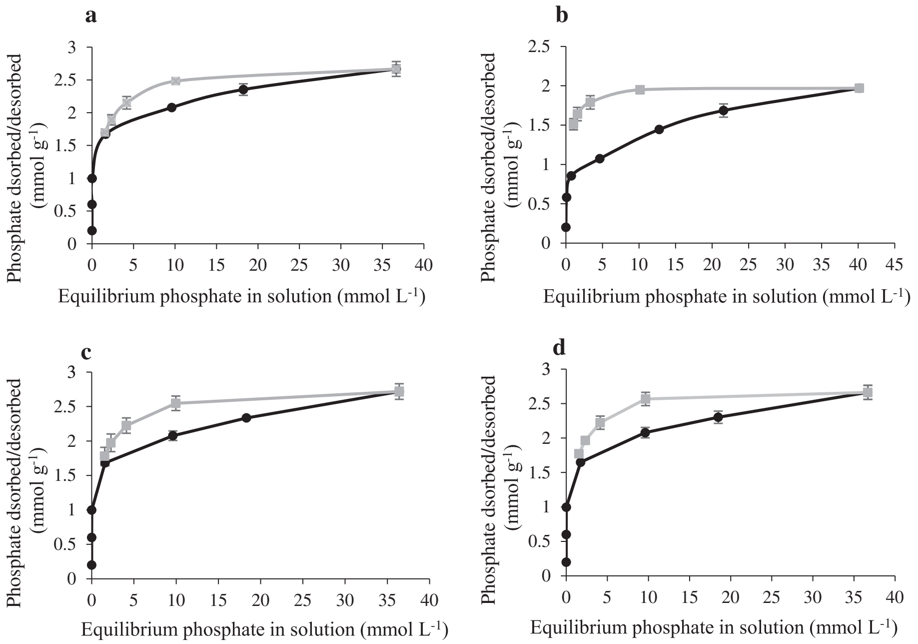

Fig. 4. Phosphate adsorption (●) and desorption isotherms (■) of (a) Zn_{2G}-Al, (b) Zn_{3G}-Al, (c) Zn_{2M}-Al and (d) Zn_{3M}-Al (pH = 7, solid-to-solution = 5 q L^{-1}, I = 0.03 M KNO_3, temperature = 25 °C).

Table 3
Isotherm models constants for phosphate uptake by LDH.

Samples	Langmuir model				Freundlich model				DR model			
	b (mmol g^{-1})	K_L (Lmmol^{-1})	R^2	RMSE	K_F (mmol$^{(1-1/n)}$ g^{-1} $L^{1/n}$)	1/n	R^2	RMSE	q_m (mmol g^{-1})	E (KJ mol^{-1})	R^2	RMSE
Zn_{2G}-Al	2.502	1.273	0.722	0.542	1.594	0.138	0.988	0.113	2.295	13.534	0.925	0.281
Zn_{3G}-Al	1.662	1.439	0.806	0.302	0.874	0.210	0.981	0.094	1.628	12.025	0.834	0.279
Zn_{2M}-Al	2.471	1.387	0.731	0.529	1.569	0.141	0.993	0.084	2.286	13.428	0.932	0.265
Zn_{3M}-Al	2.467	1.224	0.725	0.529	1.558	0.140	0.992	0.088	2.260	13.465	0.928	0.272

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-H_2PO_4 at acidic and neutral pH and dried over P_4O_{10}. 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-H_2PO_4, Zn-Al-HPO_4 and Zn-Al-PO_4, respectively. Likewise, some studies reported the basal spacing of 10.7 and 10.6 Å for Mg-Al-HPO_4 LDH (Shimamura et al., 2010, 2012). Hence, firstly it appears that $H_2PO_4^-$ 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 HPO_4^{2-} 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 Zn_{2G}-Al, Zn_{2M}-Al and Zn_{3M}-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 Zn_{3G}-Al (Fig. 1a), phosphate intercalation did not completely take place in phosphate treated Zn_{3G}-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).

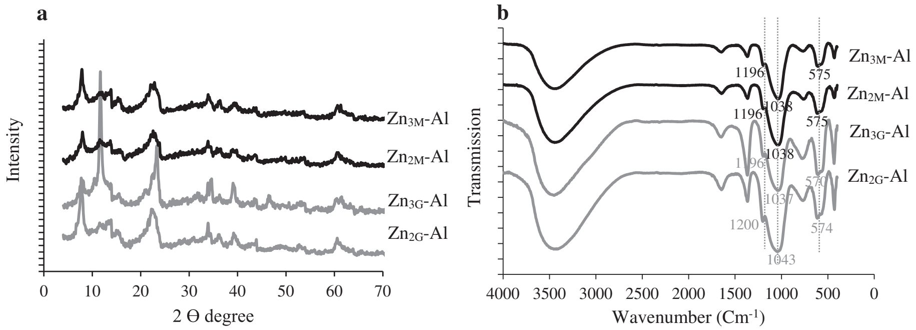

Fig. 5. XRD patterns (a) and FT-IR spectra (b) of Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-Al after phosphate uptake at the concentration of 50 mM.

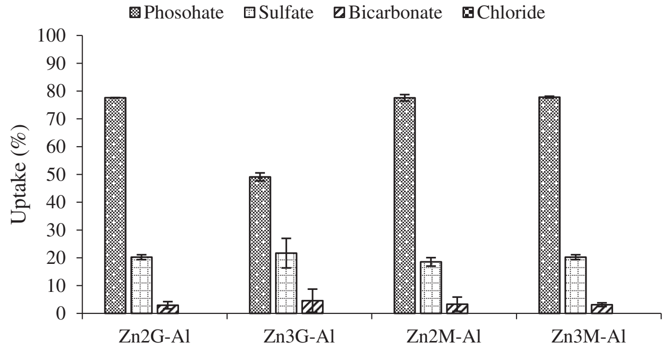

Fig. 6. Percentage of adsorbed phosphate, sulfate, bicarbonate and chloride by the LDH from 10 mM solution of each anion (pH = 7, solid-to-solution = 5 q L^{-1}).

In addition to XRD patterns, FT-IR spectroscopy also confirmed the uptake of phosphate by the synthesized LDH (Fig. 5b). The FT-IR spectra of all samples showed the bands characteristic of nitrate were disappeared and new absorption bands at 1196–1200, 1037–1043 and 570–575 cm^{-1} were appeared which was assigned to δ(P-OH), ν_3(P-O) and ν_4(P-O), respectively (Badreddine et al., 1998, 1999; Legrouri et al., 1999). Li et al. (2016) stated the absorption band at 1037–1043 cm^{-1} along with a shoulder at 1197–1200 cm^{-1} revealing that phosphate was adsorbed by inner and outer-sphere surface complex mechanisms, respectively. Due to the electrostatic attraction between negative phosphate ions and the positively charged LDH surfaces at pH < pH_{ZPC} (Khitous et al., 2016; Li et al., 2016; Yang et al., 2014) outer-sphere surface complexation mechanism might be possibly involved as the values obtained for pH_{ZPC} showed (see Section 3.1). Additionally, the FT-IR spectra of LDH contained bands at 1364–1367 cm^{-1} which were due to ν_3 stretching mode of carbonate ion that might have been formed due to absorption of atmospheric CO_2 gas (Islam and Patel, 2010). However, in the case of Zn_{3G}-Al, the peak was sharper probably due to the presence of carbonate ion in the parent Zn_{3G}-Al hindering exchange of carbonate by phosphate ions. These results were in agreement with XRD data (Fig. 5a). Moreover, according to Fig. 7b, increase of the solutions pH indicated that the exchange of phosphate with OH^- groups was probably another mechanism in phosphate uptake by studied LDH. Li et al. (2016) emphasized an increase of pH as a result of the inner-sphere surface complex formation. Generally, these results suggested that the incomplete phosphate intercalation in the Zn_{3G}-Al might be another reason for low phosphate uptake in this compound.

3.5. Selectivity of the LDH for phosphate

The selectivity of Zn_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-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_{2G}-Al, Zn_{2M}-Al and Zn_{3M}-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.

$$\text{Acidic pH: LDH} - \text{OH} + H^+ \rightarrow \text{LDH} - OH_2{}^+ \qquad (8)$$

$$\text{Alkaline pH: LDH} - \text{OH} + H^- \rightarrow \text{LDH} - O^- + H_2O \qquad (9)$$

In addition, at pH > 7, $HPO_4{}^{2-}$ is the dominant species with higher adsorption free energy than $H_2PO_4{}^-$, 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_{2G}-Al, Zn_{3G}-Al, Zn_{2M}-Al and Zn_{3M}-Al, respectively (Fig. 4). This observation suggested that the uptake of phosphate was partially reversible process likely due

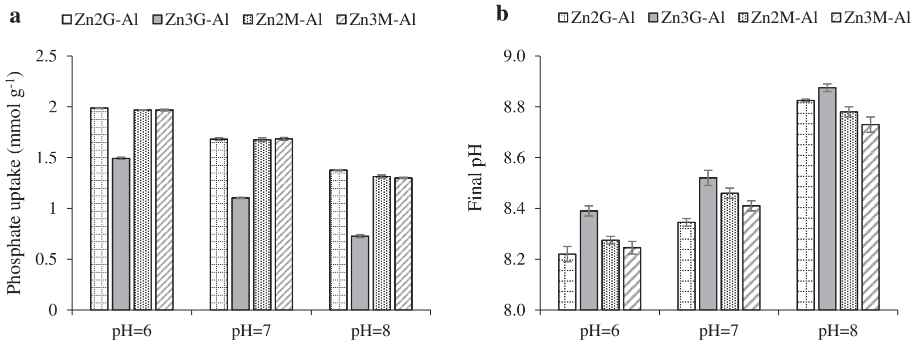

Fig. 7. Effect of pH in solutions containing 10 mM phosphate on (a) phosphate uptake by LDH and (b) final solution pH (solid-to-solution = 5 q L^{-1}, I = 0.03 M KNO_3).

to chemisorption adsorption. Chitrakar et al. (2007) and Koilraj 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 $NaCO_3$ (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., 2009) therefore, it appears that synthesized LDH can be utilized as slow release phosphate fertilizer.

4. Conclusion

The findings in this study demonstrated that the type of synthesis method and Zn/Al molar ratio affect the balancing anion 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.

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