Global J. Environ. Sci. Manage. 5(4): 485-500, Autumn 2019

Global Journal of Environmental Science and Management
(GJESM)

Homepage: https://www.gjesm.net/

ORIGINAL RESEARCH PAPER

Synthesis ratios of Mg-Al and Zn-Al layered double hydroxides efficiency and selectivity in nitrate removal from solution

M. Mohammadi[1], A. Mohammadi Torkashvand[1,*], P. Biparva[2], M. Esfandiari[1]

[1] *Department of Soil Science, Science and Research Branch, Islamic Azad University, Tehran, Iran*

[2] *Department of Basic Science, Sari University of Agricultural Sciences and Natural Resources, Sari, Iran*

ARTICLE INFO

Article History:
Received 28 January 2019
Revised 15 May 2019
Accepted 28 June 2019

Keywords:
Adsorption and Desorption
Contamination
Isotherm
Kinetics
Layered Double Hydroxides (LDHs)
pH
Temperature

ABSTRACT

Four diverse chlorides layered double hydroxides with diverse ratios, i.e. Mg-Al (3:1), Mg-Al (4:1), Zn-Al (4:1), and Zn-Al (3:1) LDHs, were prepared to evaluate their efficiency and selectivity towards nitrate removal from aquatic solutions. A batch experiment was done at the initial nitrate concentration of 5-1000 mg/L, pH 5 to 12, and contact time of 5-180 min. Isotherms of nitrate adsorption on LDHs, soil and soil-LDH mixtures were studied. Kinetics of adsorption, temperature effect, nitrate adsorption in nitrate adsorption, simulated soil solution and desorption on Mg-Al-LDH (4:1) were measured. At an optimum speed of 250 rpm, pH value of 7 and adsorbent dosage of 2 g/L, the amounts of nitrate adsorption on Mg-Al- LDH (3:1) and Mg-Zn-LDH (3:1) and also on Mg-Al- LDH (4:1) and Mg-Zn-LDH (4:1) were obtained after 30 and 60 min, respectively. Isotherm studies indicated that nitrate adsorption on soil, soil-LDH mixture, and LDH fitted Langmuir linear isotherm. The highest nitrate adsorption on Mg-Al-LDH (4:1) and a mixture of soil-Mg-Al-LDH (4:1) were 188.67 and 107.52 mg/g, respectively. Among the studied kinetic equations for nitrate adsorption on Mg-Al-LDH (4:1), the pseudo-second-order with R^2=0.998 had the best fitness. Negative values of ΔH in different nitrate concentrations indicated the exothermic process of nitrate adsorption on Mg-Al-LDH (4:1). In the presence of other anions, Mg-Al-LDH (4:1) removed nitrate preferentially. Moreover, Mg-Al-LDH (4:1) could exchange nitrate 20 times in different concentrations with no reduction in its adsorption capacity.

DOI: 10.22034/gjesm.2019.04.08

NUMBER OF REFERENCES	NUMBER OF FIGURES	NUMBER OF TABLES
45	5	4

*Corresponding Author:
Email: *m.torkashvand54@yahoo.com*
Phone: +982144516738
Fax: +982144516738

Note: Discussion period for this manuscript open until January 1, 2020 on GJESM website at the "Show Article.

INTRODUCTION

Nitrate contamination in water resources and nitrate fertilizers leaching from soil profile are becoming serious environmental problems worldwide. Nitrogen is one of the main nutrients for agricultural activities. Since the soil nitrogen content is not sufficient, farmers have to apply nitrogen fertilizers to supply the plants' needs. Nitrate as the main form of nitrogen easily leaches from soil to groundwater because of its very high solubility and incapability of soil to get rid of nitrate in situations of over-application, rainfall and over-irrigation. If underground drains are installed in these areas, the leached nitrate will move up into surface water sources (Kannan and Veemaraj, 2010) and then nitrate concentration will exceed the permissible contamination level which is an environmental problem. This frequently happens in an area with a high water-table level and regional advantage of agriculture. High amounts of nitrate in drinking water and/or agricultural water directly enter human life cycle and lead to methemoglobinemia, abortion, neonatal mortality and different kinds of cancer (Xu *et al*., 1992; Bidgoli *et al*., 2013). Considering the environmental aspects, the presence of nitrate in water resources causes eutrophication (algal bloom) which disturbs ecological balance (Foglar *et al*., 2005; Association A.P and Association A.W, 2012). Numerous techniques are reported to remove nitrate from water and soil. These techniques have different levels of efficacy, charge and simplicity in removing nitrate from water (Loganathan *et al*., 2013). Generally, adsorption is considered as an effective technique to remove nitrate, since it is easy to be designed and implement (Kapoor and Viraraghavan, 1997). Similar to cation adsorption by clay minerals, the adsorption process is capable of removing diverse biological and mineral contaminants, such as nitrate, from water and soil. Such anion adsorption can be seen in the soils having volcanic ash with allophane and imogolite minerals (Kleber and Jahn, 2007). Nitrogen-adsorbing clay minerals can be used in the soils lacking anion adsorption properties. Hydrotalcite has a perpetual anion exchange capability. This mineral belongs to the layered double hydroxides (LDHs) family (Rives, 2001; Khan and O'Hare, 2002). LDHs bear many similarities with clay particles such as having a layered structure, chemical composites, anion exchange properties, reactive interlayer space and volume increase when exposed to water (Berber *et al*., 2014; Murayama *et al*., 2012), using Eq. 1.

$$\left[M^{2+}_{1-x}M^{3+}_{x}(OH)^{x+}\right]\left[\left(A^{m-}\right)_{\frac{x}{m}}.n(H_2O)\right]^{x-} \quad (1)$$

Where, M^{2+} is divalent cations, M^{3+} indicates trivalent cations, A^{m-} includes anions and other organic and inorganic anions, and X is isomorphic substitution ratio of cations ($M^{3+}/M^{2+} + M^{3+}$) (Khan and O'Hare, 2002; Roy *et al*, 2001; Bernardo *et al*., 2017). These minerals give considerable properties to soils, such as significant anion exchange capacity, high buffering capacity, potential nutrient sources and colloidal properties (Park and *et al*., 2004; Benicio *et al*., 2015). In order to use LDH as a nitrate exchanger in soils to decrease nitrate leakage during farming practices, LDH should adsorb nitrate when its concentration in soil solution is high and desorb nitrate when the plant needs it. When LDHs desorb all the nitrates for plants' root needs, they can subsequently adsorb nitrates from soil (if present) (Torres-Dorante *et al*., 2008). Also, LDHs are highly eco-friendly materials and have potential abilities for increasing crop yield. Torres-Dorante *et al*. (2009) in their study on the long-term nitrate exchange properties under cropping showed that the use of LDH increased the yield of wheat, spinach and Italian ryegrass. They also reported the reasons for reduction of nitrate leaching and increase of soil buffering capacity and constructive elements. There are some factors (e.g., cation substitution degree of M^{2+} with M^{3+}, interlayer anion and cation nature, pH synthesis (potential of hydrogen) and molarity of materials) which affect capacity of nitrate adsorption by LDHs. A few studies have addressed these parameters (Bernardo *et al*., 2017). Thus, in this study, 4 types of LDHs with diverse cations and molarity ratios are investigated in terms of adsorption of synthesized nitrate, adsorptive behavior and effective factors (i.e., pH, adsorbent dosage, contact time and nitrate concentration). In order to select the adsorbent with the highest nitrate adsorption capacity, efficiencies of each LDH in adsorbing nitrate are determined. Moreover, the nitrate adsorption thermodynamics, adsorption, desorption of nitrate in aqueous solution and nitrate adsorption in simulated soil solution were investigated. The study has been conducted the in Islamic Azad University, Science and Research Branch Tehran, Iran during 2018-2019.

MATERIALS AND METHODS

Synthesis and characterization of LDHs

Magnesium chloride Hexa-hydrate (99% pure), aluminum hexa-hydrate (99% pure), Zinc chloride (99% pure) purchased from CHEM-LAB chemical industry, Belgium, salicylic acid (99% pure) and potassium nitrate (99% pure) purchased from Merk chemical industry, Germany and NaOH (purity 98%) purchased from Scharlau chemical industry, Spain were used. All of the solutions were prepared with bidi stilled water in presence of N_2 gas. All of the materials applied for preparing solutions and standards were purchased from Merck Company. To prepare Zn-Al-Cl and Mg-Al-Cl LDHs, first, 1 liter (L) of a 2M solution containing chloride solutes with M^{2+}: M^{3+} ratios of 3:1 and 4:1 were made. Then, using magnetic stirrer, this solution was added dropwise to 1 L of 4M sodium hydroxide solution and stirred in a mixer (250 rpm) for 45 m at laboratory temperature. The obtained suspension was autoclaved at 180 ℃ for 24 h. This method usually leads to highly satisfactory results, obtaining LDH with good structural organization. The suspension was washed and then oven-dried at 60 ℃ for 24 h. The X-ray diffraction (XRD) spectroscopy was employed to determine the resulted phase. XRD was obtained using a HERZOG microscope. Powder diffraction patterns of LDHs were determined using Cu anode, 40 kV (kilovolt) voltages, and 30 mA (milliampere) amperes, scan time of 5 s and 2θ range of 0-80 °. The interlayer distance was computed using Eq. 2 as of Bragg's law (Bragg, 1929).

$$\lambda n=2d\sin\theta \quad (2)$$

Where, λ is the wavelength of the experiment, n is the layer number, θ is the angle between reflecting plane of atoms and incident beam, and d is inter-planar distance. Scanning electron microscopy (SEM) was utilized to study morphology of the synthesized LDHs. SEM images were obtained using a Mira3-XMU microscope.

Experiment of nitrate adsorption on LDH, soil and LDH-soil mixture

Samples of nitrate solution were made synthetically using potassium nitrate. 2 mL of chloroform was added for solution preservation. In this study, a series of preliminary tests were performed in the absence of adsorbents to investigate the impact of nitrate sorption to the plastic walls of containers. Results of nitrate concentration measuring at the end of the experiments indicated no sorption to the walls. Tests were done in a 100-mL Erlenmeyer flask holding 0.1 g LDHs and 50 ml nitrate solution with 100 mg/L nitrate. A shaker device with agitation speed of 180 rpm was used for all experiments. The samples were centrifuged at 5000 rpm for 25 min, surface of filtrate extract was collected and its nitrate concentration was measured using a spectrophotometer model UV/Vis T90 company PG (Keeney and Nelson, 1982). To reach optimal experimental conditions, first, the influence of pH was investigated in the range of 5 to 12 and its optimum value was reported. For pH adjustment of the solution, 0.5 N NaOH and HCl were applied. In the next step, the effect of contact time in the optimum pH range was determined within 5 and 140 min. After optimization of contact time and pH, the effect of various dosages of adsorbent from 0.5 to 10 g/L was investigated and the optimal dosage of each LDH was determined. Then, at optimum conditions and ambient temperature, impact of various initial concentrations (5-1000 mg/L) on nitrate adsorption on LDHs was investigated. To quantify adsorption capacity and adsorption amount of the soil-LDH mixture, 0.1 g of the soil-LDH mixture with mixture ratios of 0.1, 0.3, and 0.5% were weighted and then agitated at equilibrium time and optimum pH, and finally the nitrate concentration was analyzed. Among the mixture ratios, 0.3% had the highest adsorption and, therefore, the next experiments were done with this ratio of soil-LDH mixture using nitrate solution with concentrations of 5-1000 mg/L at optimum pH and equilibrium time. To evaluate nitrate adsorption on soil, 0.1 g soil was weighted and 50 ml nitrate solution with initial

Table 1: Soil specifications used in the study

sand	silt	clay	texture	Bulk density	Particle density	Electrical conductivity	pH	Nitrate	Total nitrogen	Lime
%	%	%	-	g/cm^3	g/cm^3	dS/m	-	mg/kg	%	%
91	2	7	Sandy	1.322	1.65	0.452	7.8	0	0.019	31

concentrations of 5-1000 mg/L was mixed with it. Afterward, the mixture was agitated for 60 min in pH 7 with agitation speed of 180 rpm in laboratory temperature and analyzed to measure its nitrate concentration. The pH, equilibrium time, agitation speed and adsorbent dosage were determined before starting the adsorption experiment. Soils were sampled from Maraveh Tappeh in Golestan Province, Iran with coordinates of 01, 82', 40" N and 77, 94', 41" E. The soils were air dried, passed through a 2 mm sieve and kept for testing. Some properties of the studied soil are presented in Table 1. Sandy soil was used for the experiment. It should be noted that the soil was poor in organic matter, and the amount of its nitrate was zero as its acidity was slightly alkaline. Adsorption efficiency and nitrate adsorption capacity were computed using Eqs. 3 and 4.

$$\%Re = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3)$$

$$qe = \frac{(C_i - C_e)}{M} \times V \quad (4)$$

Where, R_e is nitrate removal efficiency (%), C_i shows the solution initial concentration (mg/L), C_e refers to equilibrium concentration of the solution (mg/L), q_e represents quantity of the nitrate adsorbed on adsorbent (mg/g), V is suspension volume (L), and M stands for adsorbent dosage (g).

To determine adsorption parameters, the equilibrium data were fitted into Freundlich (Eq. 5), Langmuir (Eq. 6), and Temkin (Eq. 7) isotherm models as:

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \quad (5)$$

$$\frac{C_e}{q_e} \frac{1}{Q_{max} b} = + \frac{1}{Q_{max}} C_e \quad (6)$$

$$q_e = B\ln A + B\ln C_e \quad (7)$$

Where, q_e is quantity of nitrate adsorbed on adsorbent surface (mg/g), C_e denotes equilibrium concentration (mg/L), b is an equilibrium constant of the Langmuir adsorption model (1/mg), Q_{max} refers to maximum adsorption capacity, K_f and n are Freundlich constants respectively showing adsorption capability and adsorption intensity, B indicates heat of adsorption and equals RT/b, A is equilibrium binding constant (1/mg).

Study of nitrate adsorption kinetics on LDH

To study the controlling actions of the adsorption procedure, the LDH with the highest nitrate adsorption capacity (Mg-Al (4:1) was selected and used. 0.1 g Mg-Al-LDH (4:1) was mixed with 50 ml nitrate solution (in two concentrations of 50 and 100 mg/L). The obtained mixture was agitated for 5-140 min at a rate of 180 rpm in laboratory temperature. The extracts were centrifuged at 5000 rpm for 25 min, and 0.5 ml aliquots were taken from the top of the suspension and analyzed for determining the final nitrate concentration. The data were fitted with diverse kinetic models including the pseudo-first-order (Eq. 8), Elovich (Eq. 11), pseudo-second-order (Eq. 9), exponential model (Eq. 12) and intra-particle diffusion (Eq. 10).

$$\log(qe - qt) = \log qe - \frac{k_1 t}{2.303} \quad (8)$$

$$q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right) lnt \quad (9)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) \quad (10)$$

$$\log q_t = \log a + b\log t \quad (11)$$

$$q_t = x + K_p t^{0.5} \quad (12)$$

Where, Fq_e and q_t are respectively the amount of nitrate adsorbed at equilibrium time and t (mg/g), k_1 shows the rate constant of first-order adsorption (1/min), α (mg/g/min) and β (g/mg) are coefficients of Elovich equation, k_2 refers to rate constant of pseudo-second-order equation (g/mg min), a and b are the constants of the exponential equation, K_p is intra-particle constant (g/mg $min^{0.5}$), and x denotes the constant related to boundary layer thickness (mg/g).

Thermodynamics of nitrate adsorption on LDH

In order to investigate temperature effect on adsorption amount and ndothermicity/exothermicity of reaction, thermodynamic studies were carried out on 0.5 g Mg-A;-LDH (4;1) in 50 ml nitrate solution with

nitrate concentrations of 10-200 mg/L in ambient temperature of 20-60 °C. The three thermodynamic parameters to be measured in adsorption studies include standard enthalpy (ΔH), standard free energy (ΔG) and standard entropy (ΔS). Amounts of ΔH and ΔS are calculated using Eqs. 13, 14 and 15.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

$$\mathrm{Kd} = \frac{q_e}{C_e} \quad (14)$$

$$\Delta G = -\mathrm{RTlnK_d} \quad (15)$$

Where, ΔH is enthalpy of the process in kJ/mol, ΔS is entropy of the process in kJ/K mol, R shows universal gas constant (8.314 J/mol K), K_d (L/g) is the ratio of contaminant amount adsorbed on adsorbent (mg/g) to its residual amount in solution (mg/L), and T is solution temperature (K).

Nitrate adsorption on LDH in soil solution

To evaluate nitrate adsorption on Mg-Al-LDH (4:1), a solution containing HPO_4^{2-}, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- with the concentrations of 1, 10, 80, 150 and 200 mg/L, respectively, was prepared. These concentrations were selected according to the solution contents in agricultural soils under cropping and fertilizer application (Torres-Dorante *et al*., 2008). 0.1g of Mg-Al-LDH (4:1) was added to the solution and after reaching an equilibration state, it was agitated at optimum pH in laboratory temperature. The extracts were centrifuged for 25 min at 5,000 rpm. An aliquot of the surface of the solution was taken and then concentrations of sulfate, nitrate, phosphate, carbonate and chloride anions were measured. The amounts of anions adsorbed on LDH were calculated by subtracting their after-shaking concentrations from their pre-shaking concentrations.

Nitrate adsorption and desorption on LDH

Nitrate desorption capacity of LDH; 0.1 g Mg-Al-LDH (4:1) was placed in a filter funnel and 50 mL of nitrate solution in different concentrations (50, 100, and 300 mg/L) was added to it. At equilibrium time, optimum pH and laboratory temperature, the solution was agitated (adsorption) and the extracts were filtered by vacuum suction. Next, aliquot of the filtrated extract was analyzed to specify the nitrate concentration. To evaluate the desorption process, after filtration, 50 ml potassium chloride solution (1M) was mixed with the solution due to its high selectivity for nitrate adsorption. The extracts were re-agitated at equilibrium time, optimum pH and laboratory temperature. An aliquot of the filtrated extract was analyzed to specify nitrate concentration after filtration (Torres-Dorante *et al*., 2008). Following each adsorption and desorption step, the amount of nitrate adsorbed on LDH was determined using the discrepancy between anion concentration prior to and after shaking. Each complete cycle of adsorption-desorption was replicated 20 times.

RESULTS AND DISCUSSION

Characteristics of LDHs

The crystallinity of LDHs and the distance between baselines can be measured by XRD. XRD patterns

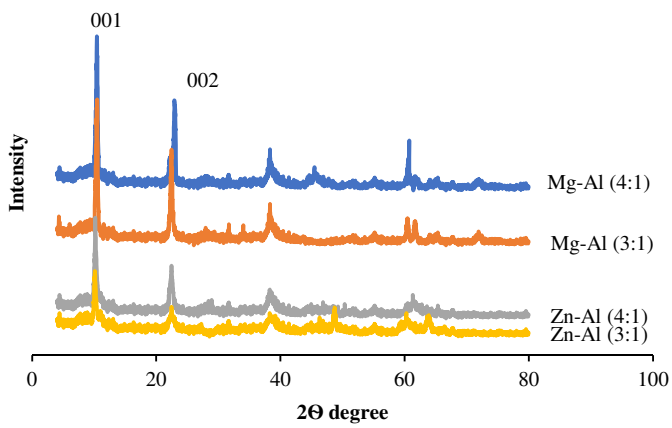


Fig. 1: XRD analysis of Mg-Al (4:1), Zn-Al (4:1), Mg-Al (3:1) and Zn-Al (3:1) synthesized LDHs

show the peaks of (001) base-line in relation to the arrangement of layers (Fig. 1). Nonbaseline peaks, which are considered as unbalanced ones, are related to the structure of the layers. XRD patterns of Mg-Al (4:1), Mg-Al (3:1), Zn-Al (4:1) and Zn-Al (3:1) LDHs in the range of 2Θ=0-80° with a sharp peak respectively in 2Θ=10.42°, 2Θ=10.5°, 2Θ=10.18° and 2Θ=10.12° indicated a crystalline structure. Furthermore, XRD patterns of LDHs indicate that LDH is the predominant mineral of the synthesized mixture. Molar ratios of M^{2+}/M^{3+} in Mg-Al (4:1), Mg-Al (3:1), Zn-Al (4:1) and Zn-Al (3:1) LDHs were measured as (4.6:1), (3.2:1), (3.9:1) and (3:1), respectively. Mg-Al LDHs had higher molar ratios compared to Zn-Al LDHs. This outcome is in line with the records of Benício *et al.* (2018). Interlayer distances of Mg-Al (4:1), Zn-Al (4:1), Mg-Al (3:1) and Zn-Al (3:1) LDHs were measured as 8.48, 8.68, 8.42 and 8.73Å, respectively. SEM analyses are important in determining the morphological characteristics of LDHs. SEM images of LDHs are presented in Fig 2. Layered crystals or overlap of the layers can be observed in these images. Shapes and sizes of crystals are different in various synthesized LDHs. Considering the preparation method and composition of the materials; some changes are seen in the shape and size of LDHs (Figueredo Benicio et al., 2015).

Nitrate adsorption on LDHs

Effects of contact time

Diagram of the effect of contact time on nitrate removal by LDHs is presented in Fig. 3A. Nitrate adsorption by LDHs increased with time and then remained steady. Therefore, in Mg-Al (4:1) and Zn-Al (4:1) LDHs, with increase of contact time from 5 to 60 min, nitrate removal efficiencies in Mg-Al (3:1) and Zn-

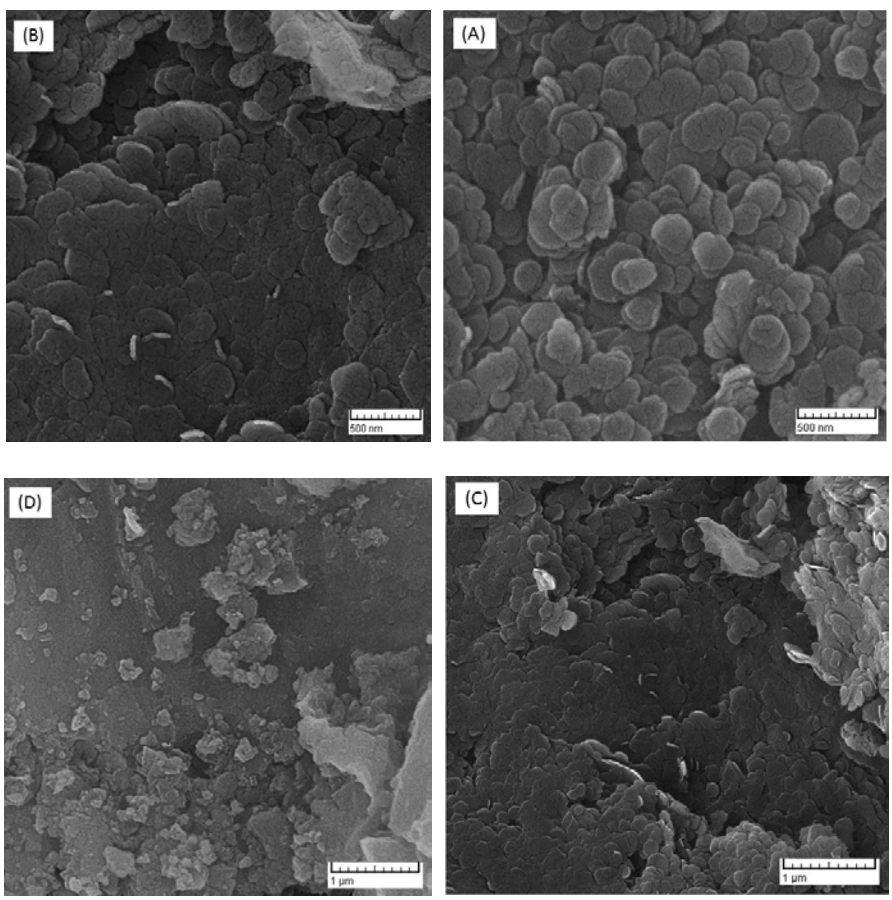


Fig. 2: SEM images of synthesized LDHs: (A) Mg-Al (4:1), (B) Mg-Al (3:1), (C) Zn-Al (4:1), and (D) Zn-Al (3:1)

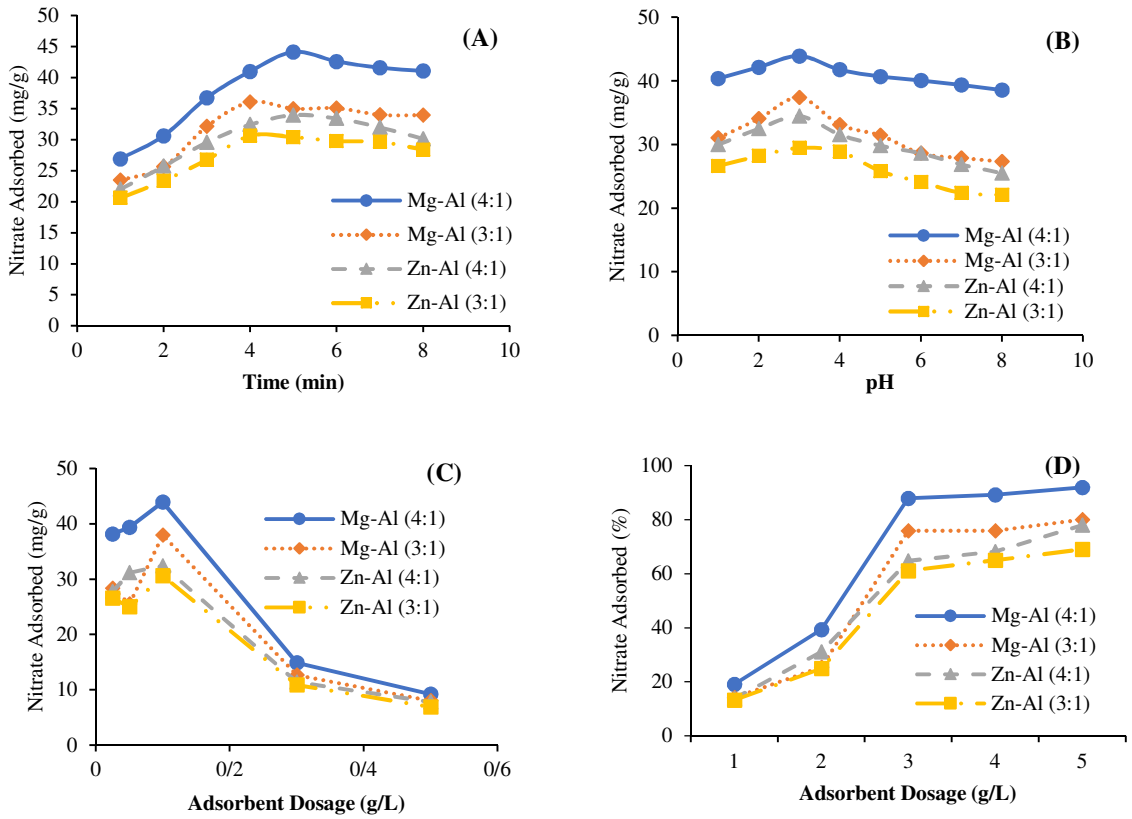


Fig. 3: (A) Impacts of contact time on the amounts of nitrate absorbed by the synthesized LDHs, (B) Impact of pH on nitrate removal by the synthesized LDHs, (C) Impacts of adsorbent dose on nitrate adsorption amount, and (D) Nitrate removal percentage by synthesized LDHs (initial concentration: 100 mg/L, agitation speed: 180 rpm)

Al (3:1) LDHs increased to 34% and 24% respectively. At higher contact times, nitrate adsorption did not have large changes and equilibration was established between nitrate ions and adsorbents, due to reduction of active sites with time. Generally, by increasing the reaction time, the contact time between contaminant ions and adsorbent increases and ions have more time to be adsorbed on sorption sites on the particles' surfaces. Therefore, 60 min and 45 min were appointed as the equilibrium times for Mg-Al (4:1) and Zn-Al (4:1) LDHs and for Mg-Al (3:1) and Zn-Al (3:1) LDHs, respectively. Percentages of nitrate removal by Mg-Al (4:1), Mg-Al (3:1), Zn-Al (4:1) and Zn-Al (3:1) LDHs at equilibrium times were 88, 72, 68, and 61%, respectively. Nitrate removal percentage at equilibrium time depends on LDH type, synthesis condition, applied method and initial concentration of nitrate. Consequently, the nitrate removal percentage can be different in different studies**.** In addition, Islam and Patel, (2010) reported 40 min as the equilibrium time for Zn-Al-LDH (3:1).

pH effect

Diffusion status of positive and negative charges on the sorbent surface, which is a function of the reaction medium pH, is among the highly significant environmental factors that can affect contaminant adsorption on solid surfaces. This factor, by changing the equilibrium status of electrical charges, can affect the adsorption of different contaminants onto various surfaces. Therefore, it is very important to specify the impact of this parameter on the adsorption of various contaminants by various adsorbents. The trend of pH impact on nitrate adsorption by LDHs (Fig. 3B) shows that the amounts of nitrate adsorption in the studied pH range (5-12) increase in pH range of 5-7 and decrease in pH range of 7-12 (6-10%). Adsorption reduction with increase of pH can be attributed to

the increased negative surface charges. However, reduction of nitrate adsorption with decrease of pH to below 4 can be attributed to the presence of chloride ion (due to adding HCl for pH adjustment) and nitrate ion for adsorption on the surfaces of LDHs. Because of high capacity of LDH in buffering solutions, reduction of adsorption due to pH increase is not significant. For all the studied LDHs of Mg-Al (4:1), Zn-Al (4:1), Mg-Al (3:1) and Zn-Al (3:1), the highest amounts of nitrate removal were detected in pH 7, at which 88%, 69%, 75%, and 59% nitrate were removed from 100 mg/L nitrate solution, respectively. For all of the adsorbents, pH 7 was considered to be optimum. Islam and Patel, (2010) reported that pH increase from 6 to 12 in nitrate concentration of 100 mg/L could decrease adsorption rate of Zn-Al-LDH (3:1) from 75.7 to 67.6%. Possibly, the LDH synthesis method, its anions and cations and optimum condition of the experiment affect the equilibrium pH, leading to different pH values in different works.

Impact of adsorbent dosage

Determining the impact of adsorbent dosage is very important since it is related to the process economy in designing large industrial-commercial systems. Considering the impact of adsorbent dosage on nitrate removal percentage (Figs. 3C and D), nitrate removal efficiency was improved with the adsorbent dosage increase, and the nitrate adsorption on LDHs decreased when the dosage exceeded 2 g/L. In this regard, the minimum nitrate removal percentages at 0.5 g/L Mg-Al (4:1), Zn-Al (4:1), Mg-Al (3:1) and Zn-Al (3:1) were 19, 13, 14 and 13%, respectively, and the maximum nitrate removal percentages at 10 g/L Mg-Al (4:1), Zn-Al (4:1), Mg-Al (3:1) and Zn-Al (3:1) were 92, 78, 80 and 69%, respectively. Although increase of adsorbent dosage enhanced nitrate removal efficiency, it decreased nitrate adsorption rate per LDH mass unit. This can be due the presence of unsaturated active sites on LDH surface, which leads to a reduction of adsorption rate. Increases in removal efficiency are due to more available surfaces in the system, whereas decrease of the contaminant adsorbed per mass unit of adsorbent is due to increase of adsorbent mass which leads to overlap of the active sorption sites. Furthermore, increase of adsorbent dosage and its accumulation leads to elongation of diffusion path in contaminant diffusion on available adsorption sites of the adsorbent surface, which results in reduction of adsorption rate. In such conditions, because of the competition among contaminant molecules for occupying empty sorption sites, some adsorption sites are non-saturated and their capacity is not used optimally and this decreases the contaminant adsorbed (nitrate) per mass unit of adsorbent. Based on Fig. 3C, 2 g/L was considered as optimal dosage for all the adsorbents. Islam and Patel, (2011) selected 0.35 g/L of Ca-Al-LDH for removing nitrate in 100 ml nitrate solution with 10 mg nitrate/L. Ivánová *et al.* (2018) showed that the nitrate concentration below the toxicity limit value was reached with removal efficiencies of 72% and 84.6% for the first stage of adsorption using 15 and 20 g/L of calcined adsorbent doses, respectively. Nitrate removal percentage at optimal dosages of adsorbent depends on LDH properties such as its type and synthesis method, types of cations used in it, its particle size, molar ratio of M^{2+}/M^{3+} and initial nitrate concentration (Das *et al*., 2006; Goh *et al.,* 2008).

Isotherms of nitrate adsorption on LDHs

The highest and lowest amounts of nitrate adsorption on Mg-Al (4:1) and Mg-Al (3:1) LDHs were respectively recorded at nitrate concentrations of 1000 and 5 mg/L. For Zn-Al (4:1) and Zn-Al (3:1) LDHs, the highest and lowest nitrate adsorption rates were obtained at 500 and 5 mg/L nitrate solutions, respectively. With increase of initial nitrate concentration, the percentage of nitrate removal by Mg-Al (4:1) and Mg-Al (3:1) LDHs increased and the percentages of nitrate removal by Zn-Al (4:1) and Zn-Al (3:1) LDHs decreased. This can be attributed to the unchanged and similar numbers of adsorption sites and more nitrate ions in the solution. Besides, with increase of initial nitrate concentration, motive force is increased, the adsorption sites are saturated with lower adsorbent energies, and finally the amount adsorbed nitrate per adsorbent mass unit is increased (Liu *et al*., 2010; Leyva-Ramos *et al*., 2008). In the studies which focus on contaminant adsorption on various adsorbents, determining the best adsorption isotherm and capacity of the used adsorbent are the most important factors for evaluating the systems functioning. To fit the data into adsorption models of Langmuir, Freundlich and Temkin, a linear form of their general equations was used and their empirical parameters were presented in Table 2. Results from regression analysis (R^2) of Freundlich, Langmuir and

Table 2: Parameters of Langmuir, Freundlich, and Temkin adsorption isotherms, and the correlation coefficients of nitrate adsorption on LDHs

Adsorption isotherm models	Constants and coefficients of the model		
Langmuir	Q_{max} (mg/g)	b (1/mg)	R^2
Soil	1.98	0.728	0.996
Mg-Al (4:1)	188.67	0.023	0.991
Mg-Al (3:1)	161.29	0.011	0.982
Zn-Al (4:1)	133.33	0.009	0.947
Zn-Al (3:1)	119.04	0.008	0.951
Mg-Al (4:1) + Soil	107.52	0.028	0.99
Mg-Al (3:1) + Soil	86.95	0.021	0.974
Zn-Al (4:1) + Soil	76.92	0.013	0.962
Zn-Al (3:1) + Soil	58.47	0.009	0.955
Freundlich	n	K_F	R^2
Soil	8.56	1.036	0.825
Mg-Al (4:1)	1.31	3.12	0.831
Mg-Al (3:1)	1.54	3.78	0.915
Zn-Al (4:1)	1.34	1.82	0.903
Zn-Al (3:1)	1.33	1.47	0.9
Mg-Al (4:1) + Soil	1.73	4.536	0.907
Mg-Al (3:1) + Soil	1.59	2.567	0.912
Zn-Al (4:1) + Soil	1.45	1.421	0.9
Zn-Al (3:1) + Soil	1.38	1.283	0.894
Temkin	A (1/g)	B (1/mg)	R^2
Soil	2.289	0.312	0.781
Mg-Al (4:1)	1.914	0.649	0.962
Mg-Al (3:1)	3.369	1.214	0.913
Zn-Al (4:1)	4.778	1.564	0.857
Zn-Al (3:1)	4.703	1.548	0.842
Mg-Al (4:1) + Soil	1.202	0.184	0.853
Mg-Al (3:1) + Soil	2.195	0.786	0.791
Zn-Al (4:1) + Soil	3.609	1.283	0.808
Zn-Al (3:1) + Soil	4.863	1.581	0.842

Temkin models indicated that Langmuir isotherm better fitted the adsorption data. Considering Langmuir model, it is assumed that a layer deposits uniformly on adsorption sites. q_{max} (mg/g), which is one of the of the Langmuir isotherm coefficients to indicate the maximum monolayer adsorption under saturated surface adsorption sites, was estimated as 188.86, 161.29, 133.33 and 119.04 mg/g for Mg-Al (4:1), Mg-Al (3:1), Zn-Al (4:1) and Zn-Al (3:1) LDHs, respectively. Adsorption capacity depends largely on pH, ion strength, existence of other ions and adsorbent dosage (Goh *et al.*, 2008). Limited studies have proved that high nitrate adsorption capability in some LDHs depends largely on LDH properties. Some of the physical characteristics of LDHs including crystallinity, porosity, surface area, particle size and interlayer features could affect the nitrate adsorption considerably (Sasai *et al.*, 2012; Tezuka *et al.*, 2005). K_L (L/mg) is another empirical coefficient of the Langmuir model, which depends on adsorption energy. The maximum value of this coefficient was 0.023 L/mg for Mg-Al-LDH (4:1). In Freundlich model, it is assumed that adsorption surfaces are heterogeneous and adsorption energy

is not uniform. K_f and n, as the coefficients of the Freundlich model, indicate the adsorbent's adsorption capacity and the adsorbent ability to adsorb metal ions, respectively. The greater values of K_F and n suggest higher adsorption intensity and higher amounts of adsorbents (Gammoudi *et al.*, 2012; Emenike *et al.*, 2016). Among all LDHs, these values are higher for Mg-Al-LDH (3:1) (n= 1.54, K_F=3.78). The n values in the range of 1 and 10 imply a better fit of Langmuir isotherm to the data as compared to Freundlich model. According to Freundlich coefficients (Table 2), the calculated n is greater than 1 and, therefore, the data better fit the Langmuir isotherm model. Hu *et al.* (2017) stated that adsorption of Perfluorooctane sulfonate on Mg-Al-NO_3 follows the Langmuir model and the highest adsorption capability was 865 mg/g. In addition, Hosni and Seasra, (2008) recommended that the data of nitrate adsorption on Zn-Al-LDH and Mg-Al-LDH were fitted to Langmuir model. This contradicts with the results reported by Hatami *et al*. (2018) who applied Freundlich model. Isotherm of nitrate adsorption on soil was done at initial nitrate concentrations of 5-1000 mg/L. By nitrate concentration increase from 5 to 300 mg/L, its final concentration after adsorption increased from 0.44 to 2.34 mg/L. By initial nitrate concentration increase from 300 to 1000 mg/L, adsorption rate was almost stable and the final nitrate concentration decreased to 1.96 mg/L. These findings suggest that soil nitrate adsorption follows Langmuir isotherm with regression coefficient of higher than 0.996 and the maximum adsorption capacity of 1.98 mg/g (Table 2). The minimum and maximum nitrate adsorption rates by a mixture of soil and LDHs were noticed at nitrate concentrations of 5 and 500 mg/L, respectively. Results of nitrate adsorption on soil-LDH mixtures from Freundlich, Langmuir, and Temkin suggest that the data are best fitted to Langmuir model (Table 2). The highest adsorption capacities for the mixtures of soil and Mg-Al (4:1), Mg-Al (3:1), Zn-Al (4:1) and Zn-Al (3:1) LDHs were 107.52, 86.95, 76.92 and 58.47 mg/g, respectively.

The results from analysis of variances (ANOVA) revealed that the effect of treatments (i.e., soil, LDH, and a mixture of soil and LDH) on the maximum amount of nitrate adsorption was significant at the significance level of %1. Fig. 4 presents the bar chart for the impact of adsorbents on the maximum nitrate adsorption. The maximum nitrate adsorption capacities of the mixture of soil and Mg-Al (4:1), Mg-Al (3:1), Zn-Al (4:1) and Zn-Al (3:1) LDHs were 107.52, 86.95, 76.92 and 58.47 mg/g, respectively, and lower than the maximum capacity of nitrate adsorption by only LDHs. Treatments by only LDHs had higher adsorption capacities than the treatments by soil-LDH mixtures. This can be explained by a low adsorption capacity of soil (1.98 mg/g) that lowers the capacity of mixtures. According to the result, Mg-Al-LDH (4:1) is the adsorbent with the highest nitrate adsorption capacity (188.67 mg/g) and can be used in the next experimental studies.

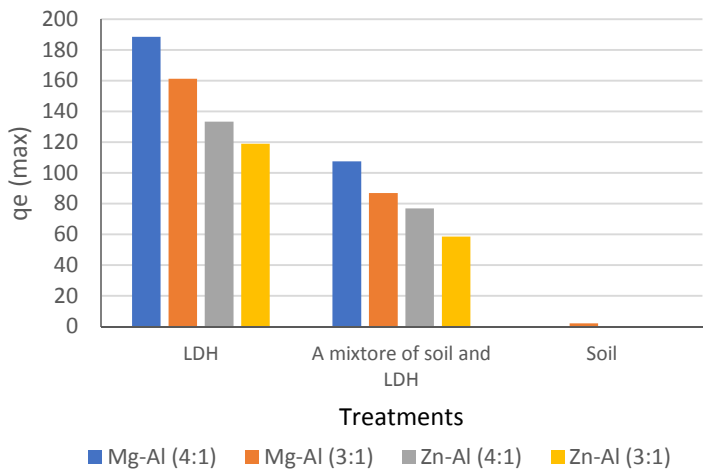


Fig. 4: Effect of adsorbents on maximum nitrate adsorption

Kinetics of nitrate adsorption on LDH

Adsorption kinetics is used as a tool for determining the controlling actions in adsorption processes. Table 3 indicates the fitness of pseudo-first-order, pseudo-second-order, intra-particle diffusion, Elovich and exponential function models to the data of nitrate adsorption on Mg-Al-LDH (4:1) in concentrations of 50 and 100 mg/L. In pseudo-first-order model, changes in adsorbate removal rate with time are related to changes of saturation concentration and amounts of adsorbent removal capacity with time. To apply pseudo-first-order model, the equilibrium time of 60 min was considered and ($q_e - q_t$) was measured at different times. Line equation of pseudo-first-order model was obtained by drawing logarithmic curve of ($q_e - q_t$) against time, and other parameters of the model were estimated using this equation. Since the coefficient of determination (R^2) in this model is low, it cannot well describe the adsorption mechanism. The predicted values of q_e for 50 and 100 mg/L concentrations using this model are 6.25 and 11.64 mg/g, respectively. Value of q_e in pseudo-first-order equation does not match the q_e values obtained from experimental data. The reason is that pseudo-first-order equation cannot fit the experimental data because of time lag due to the presence of external resistance or binding layer at the prime of adsorption process (Reddad *et al*., 2002). Line equation for pseudo-second-order model was obtained from drawing t/q_t curve against time. The R^2 values of 99.72 and 99.83 obtained for concentrations of 50 and 100 mg/L, respectively, suggested the well fit of this model to the experimental data. This is consistent with the results presented by HU *et al*. (2017) and Hatami *et al*. (2018) who used the pseudo-second-order model. In this equation, K_2 is constant of adsorption rate and shows adsorption change in relation to time. The values of this constant are 0.013 and 0.012 respectively for concentrations of 50 and 100 mg/L. In this model, the values of q_e obtained for 50 and 100 mg/L nitrate solutions (20.61 and 42.19 mg/g respectively) are closer to the experimental results. Intra-particle diffusion, Elovich and exponential equations were obtained from drawing curves of

Table 3: Results of data fitness to the kinetic models of nitrate adsorption on Mg-Al-LDH (4:1) in two initial nitrate concentrations (50 and 100 mg/L)

Kinetic model	Model's constants	Nitrate concentration of 50 mg/L	Nitrate concentration of 100 mg/L
Pseudo-first order	q_e (mg/g)	6.257	11.649
	K_1 (1/min)	-0.019	-0.012
	R^2	0.647	0.437
Pseudo-Second order	q_e (mg/g)	20.618	42.194
	K_2 (mg/g min^{-1})	0.013	0.012
	R^2	0.997	0.998
Intra-particle diffusion	X (mg/g)	6.114	17.104
	K_p (g/mg $min^{0.5}$)	1.47	2.441
	R^2	0.763	0.63
Elovich	α (mg/g min)	7.117	22.626
	β (g/mg)	0.247	0.133
	R^2	0.936	0.859
Fractional power	a	7.498	22.771
	b	0.22	0.131
	R^2	0.869	0.817

q_t against $t^{0.5}$, q_t against lnt and log qt against log t, respectively. These models could not well describe the adsorption process as they had low R^2 values (Table 3). Values of x in intraparticle diffusion model were determined from intercept of the obtained line. The amount of x refers to the thickness of film layer, and it was 6.11 and 17.10 mg/g for 50 and 100 mg/L nitrate solutions, respectively. K_p in an intra-particle diffusion model is constant of intercellular diffusion rate, and it was 1.47 and 2.44 (g/mg $min^{0.5}$) respectively for 50 and 100 mg/L solutions. Notably, these values were close to the results reported by Islam and Patel (2010) and Shafigh *et al.* (2019). Their results showed that Elovich order equations were the best-fit equations used. According to Table 3, among the explored models, pseudo-second-order model better fits the kinetic data of nitrate adsorption.

Effect of temperature on the rate of nitrate adsorption by LDH

Thermodynamic data of nitrate adsorption by Mg-Al-LDH (4:1) are shown in Table 4. Positive values of ΔH suggest that nitrate adsorption process by adsorbents is endothermic while the negative values suggest that the process is exothermic. Negative values of ΔH at different nitrate contents suggest that nitrate adsorption on Mg-Al-LDH (4:1) is an exothermic process. It means that lower temperatures lead to higher nitrate adsorption rates. In this regard, LDH can reduce leaching risks in the cold seasons without plant growth, as an advantage of nitrate adsorption on LDH. This result is similar to the results reported by Chabani *et al.* (2006); Chatterjee and Woo, (2009); and Khataee and Khani, (2009) about nitrate adsorption on anion exchange resin, chitosan, and granular activated carbon respectively. In all the studied concentrations, ΔH value was below 40 kJ mol. According to Table 4, similar to ΔH, ΔS has a negative value. Negative ΔH and ΔS imply that at low temperatures the process is a spontaneous reaction. Moreover, when both ΔH and ΔS have the same signs (i.e. both are positive or negative) the reaction is reversible and, in certain cases, is of an equilibrium type. ΔG increases with the increase of temperature in constant concentrations. At 20 ℃, in all concentrations, ΔG has a negative value, suggesting a spontaneous adsorption process, but it becomes positive with an increase from 20 to 60 ℃ (20, 30, 40, 50 and 60 ℃), suggesting a non-spontaneous reaction in higher temperatures. Amount of nitrate adsorption is reduced with temperature increase from 20 to 60 ℃. At a constant temperature of 20 ℃, amounts of nitrate adsorption in concentrations of 10, 50, 100, 150 and 200 mg/L were 4.34, 20.28, 44.95, 62.54 and 76.33 mg/g, respectively, while at a constant temperature of 60 ℃, those of nitrate adsorption in the same concentrations were 0.465, 9.66, 28.01, 43.01 and 43.77 mg/L, respectively. Therefore, it can be inferred that at constant temperatures, increase of nitrate concentration can increase adsorption. However, when the temperature starts to increase, the amount of adsorption decreases with the nitrate concentration. LDH particles tend to become aggregated at high temperatures probably due to the lower adsorption at higher temperatures. Kataee and Khani, (2009) reported that increase of temperature leads to the decrease of nitrate adsorption on activated carbon. Physical differences, cations used in LDH, molar ratio of M^{2+}/M^{3+} and investigational conditions can have significant effects on sorption process.

Mechanisms of nitrate adsorption on LDH in soil solution

Fig. 5A indicates the adsorption process of nitrate, carbonate, phosphate, sulfate and chloride ions

Table 4: Values of the thermodynamic parameters of nitrate adsorption by Mg-Al-LDH (4:1) in the concentration of 10, 50, 100, 150 and 200 mg/L

Nitrate concentration (mg/L)	ΔH (kJ/mol)	ΔS (J/mol/k)	ΔG (kJ/mol)				
			20℃	30℃	40℃	50℃	60℃
10	-83.5	-275.33	-2.9	0.15	2.7	5.4	8.22
50	-39.36	-129.47	-1.86	0.07	1.8	2.65	3.19
100	-38.97	-121.96	-3.63	-1.79	-0.17	0.43	1.24
150	-24.39	-77.48	-2.24	-0.26	0.13	0.6	1.09
200	-27.38	-90.51	-1.16	0.27	1.26	1.66	2.61

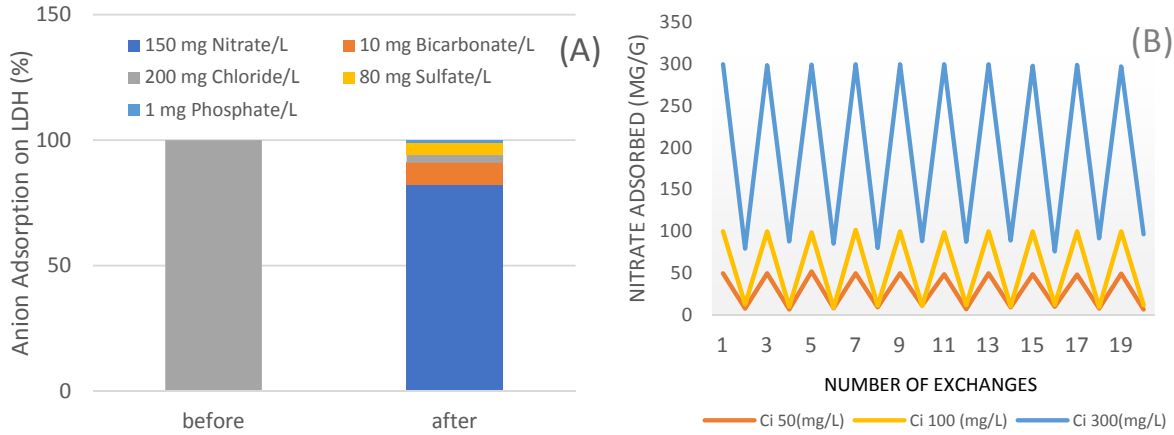


Fig. 5: (A) Mechanisms of anion adsorption on Mg-Al-LDH (4:1) in the stimulated soil solution (B) Nitrate adsorption and desorption on Mg-Al-LDH (4:1) in concentrations of 50, 100, and 300 mg/L

at certain concentrations in the simulated soil solution. In the presence of other anions, efficiency of nitrate removal by Mg-Al-LDH (4:1) was 75.44%, indicating the preferential adsorption of nitrate on LDH. As can be seen in Fig. 5, when LDH was exposed to simulated soil solution, its whole surface interacted with anions so that only 9.83% of AEC was covered with chloride. In this study, the anion selectivity of LDH from high to low levels is as the following order: nitrate, carbonate, sulfate, and phosphate. This order is in accordance with the results obtained by Torres-Dorante *et al*. (2008) and Xue *et al*. (2016). Also the results obtained by Tong et al. (2017) showed that the co-existing anions had an inhibitory effect on nitrate adsorption, which was in the order of $PO_4^{3-} > SO_4^{2-} > Cl^- > ClO^{4-}$. However, it is in contrast with the results obtained by Bull (2001), who reported the following order: carbonate, nitrate, chloride, and sulfate. Higher adsorption of nitrate rather than carbonate on Mg-Al-LDH (4:1) can be defined by low carbonate content of the solution. Low concentration of the carbon selected in the simulated solution is similar to the carbonate content in the soil solution. According to the results of nitrate adsorption isotherms, amounts nitrate adsorption on Mg-Al-LDH (4:1) decreased from 82.73 to 75.44% (7.3% reduction) in the presence of other anions in the simulated soil solution. This result is in line with the results of nitrate adsorption isotherms for soil-Mg-Al-LDH (4:1) mixture exposed to real soil solution (Table 2). In the Mg-Al-LDH (4:1)-soil mixture, the nitrate removal percentage was 73.64%, showing a little difference (approximately 2%) with the simulated soil solution (75.44%).

Nitrate adsorption and desorption by LDH

LDHs as adsorbents can adsorb the contaminant anions such as nitrate, phosphate, sulfate and agricultural chemicals from water and soil and maintain them on their surfaces. Therefore, they can prevent nutrients leaching from the soil. Furthermore, LDH can release the anionic species once adsorbed on their surfaces and make them ready for plant use (Figueredo Benicio *et al*., 2015; Hosni and Srasra, 2009). Some quantitative studies have explored the capability of LDH for nutrient retention in water and soil (Figueredo Benicio *et al*., 2015). Fig 5(B) presents the mechanisms of nitrate adsorption and desorption by Mg-Al-LDH (4:1) at 50, 100 and 300 mg/L concentrations. Mg-Al-LDH (4:1) exchanged nitrate 20 times in different concentrations, with no reduction in its adsorption capacity. In order to evaluate the permanent exchange capacity, number of 20 processes were considered to be sufficient, because completing 20 exchange processes in soil condition lasts for more than 10 years, even in extensive crop rotations. According to the results, LDH can be considered as a long-standing nitrate exchanger to be used for controlling nitrate movement in soil and can effectively reduce nitrate leaching and fertilizer costs for farmers.

CONCLUSION

In this study, 4 types of LDHs with diverse cations and molarity ratios were synthesized and used for the removal of nitrate from aqueous media. Formation of layered crystals or overlapped layers is witnessed in the images of the scanning electron microscopy (SEM). Increase of initial concentration of nitrate led to corresponding rise in the amount of nitrate adsorbed on Mg-Al (4:1) and Mg-Al (3:1) LDHs and decrease in the content of nitrate adsorbed on Zn-Al (4:1) and Zn-Al (3:1) LDHs. Moreover, a reduction in the nitrate adsorption capability of the soil-LDH mixtures was observed with the increase of nitrate concentration. Isotherms of nitrate adsorption by LDH, soil and LDH-soil mixture demonstrated that Langmuir isotherm as the best model to fit the experimental data. In all tests performed on LDHs and LDH-soil mixtures, Mg-Al-LDH (4:1) had the highest nitrate adsorption capacity (188.67 and 107.52 mg/g) and was selected as the best LDH to continue the studies. The maximum amount of nitrate adsorption on LDH-soil mixture was reduced due to the competition of nitrate ion with other anions present in the soil for sorption sites. Negative values of ΔH at different nitrate concentrations refer to the increase of nitrate adsorption with the decrease of temperature. Therefore, LDH can mitigate the nitrate-leaching risks in cold seasons with no crops, representing the advantages of nitrate adsorption by LDHs. Additionally; efficiency of nitrate removal by Mg-Al-LDH (4:1) in the presence of sulfate, carbonate, phosphate and chloride anions in the simulated soil solution was 75.44%, which demonstrated the preferential adsorption of nitrate by LDH. Mg-Al-LDH (4:1) could exchange nitrate for 20 times in different concentrations without notable reduction of adsorption capacity. According to the results, it can be concluded that nitrate works as a long-standing nitrate exchanger for controlling nitrate motion in soil. Therefore, it can reduce nitrate-leaching, associated threats and costs of fertilizer for farmers.

ABBREVIATIONS

%	Percent
1/g	1 per gram
1/L	1 per liter
1/min	1 per minute
A°	Angstrom
C	Carbon
CO_3^{2-}	Carbonate ion
^{o}C	Centigrade
Cl^{-}	Chloride ion
dS/m	Decisiemens per meter
C_e	Concentration equilibrium
C_i	Concentration initial
G	Gram
g/cm3	Gram per cubic Centimeter
g/L	Gram per liter
g/mg	Gram per milligram
g/mg min	Gram per gram minute
H	Hours
HCO_3^{-}	Bicarbonate ion
J	Joule
K	Kelvin
kg	Kilogram
kJ/mol	Kilojoule per mole
kV	Kilo voltage
L	Liter
L/g	Liter per gram
L/kg	Liter per kilogram
L/mg	Liter per milligram
LDH	Layered Double Hydroxide
M	Molar
mA	Milli Ampere
Mg	Milligram
mg/g	Milligram per gram
mg/g min	Milligram per gram minute
mg/kg	Milligram per kilogram
mg/L	milligram per liter
min	Minute
mmol/g	Mill mole per gram
N	Nitrogen
NH_4^{+}	Ammonium ion
NO_3^{-}	Nitrate ion
pH	Potential of hydrogen
PO_4^{2-}	Phosphate ion
R_e	Removal efficiency
rpm	Revolutions per minute

S	Second
SEM	Scanning Electron Microscopy
ΔG	Standard enthalpy
ΔH	Standard entropy
ΔS	Standard free energy
SO_4^{2-}	Sulfate ion
T	Temperature
USEPA	United States Environmental Protection Agency
V	Volume
WHO	World Health Organization
XRD	X-ray diffraction

REFERENCES

Association, A.P.H.; Association, A.W.W. (1989). Standard methods for the examination of water and wastewater, American Public Health Association.

Berber, M.R.; Hafez, I.H.; Minagawa, K.; Mori, T., (2014). A sustained controlled release formulation of soil nitrogen based on nitrate-layered double hydroxide nanoparticle material. J. Soils Sediments, 14(1): 60-66 **(7 pages)**.

Bernardo, M.P.; Moreira, F.K.; Ribeiro, C., (2017). Synthesis and characterization of eco-friendly Ca-Al-LDH loaded with phosphate for agricultural applications. Appl Clay Sci., 137: 143-150 **(8 pages)**.

Benício, L.P.F.; Eulálio, D.; Guimarães, L.d.M.; Pinto, F.G.; Costa, L.M.d.; Tronto, J., (2018). Layered Double Hydroxides as Hosting Matrices for Storage and Slow Release of Phosphate Analyzed by Stirred-Flow Method. Mater. Res., 21(6): 509-525 **(16 pages).**

Benício, L.P.F.; Silva, R.A.; Lopes, J.A.; Eulálio, D.; Santos, R.M.M.d.; Aquino, L.A.d.; Vergütz, L.; Novais, R.F.; Costa, L.M.d.; Pinto, F.G., (2015). Layered double hydroxides: nanomaterials for applications in agriculture. Rev. Bras. Apl. Vacuo., 39(1): 1-13 **(13 pages)**.

Bidgoli, M.S.; Ahmadi, E.; Yari, A.R.; Hashemi, S.; Majidi, G.; Nazari, S.; Jadidiyan, M.; Azari, A., (2013). Concentration of nitrate in bottled drinking water in Qom, Iran. Arch. Hygiene Sci., 2(4): 121-125 **(5 pages).**

Bragg, W.L., (1929). The diffraction of short electromagnetic waves by a crystal. Center for Digital Philosophy., 23(45): 153 **(153 pages)**.

Bull, C. (2001). Development and evaluation of layered double hydroxides (LDHs) for nitrate exchange in soil, Cuvillier.

Chabani, M.; Amrane, A.; Bensmaili, A., (2006). Kinetic modelling of the adsorption of nitrates by ion exchange resin. Chem. Eng. J., 125(2): 111-117 **(7 pages)**.

Chatterjee, S.; Woo, S.H., (2009). The removal of nitrate from aqueous solutions by chitosan hydrogel beads. J. Hazard. Mater., 164(2-3): 1012-1018 **(7 pages)**.

Das, J.; Patra, B.; Baliarsingh, N.; Parida, K., (2006). Adsorption of phosphate by layered double hydroxides in aqueous solutions. Appl. Clay Sci., 32(3-4): 252-260 **(8 pages).**

Emenike, P.C.; Omole, D.O.; Ngene, B.U.; Tenebe, I.T., (2016). Potentiality of agricultural adsorbent for the sequestering of metal ions from wastewater. Global J. Environ. Sci. Manage., 2(4): 411-442 **(32 pages).**

Foglar, L.; Briški, F.; Sipos, L.; Vuković, M., (2005). High nitrate removal from synthetic wastewater with the mixed bacterial culture. Bioresour. Technol., 96(8): 879-888 **(9 pages)**.

Gammoudi, S.; Frini-Srasra, N.; Srasra, E., (2012). Nitrate sorption by organosmectites. Eng. Geol., 124(3): 119-129 **(10 pages)**.

Goh, K.-H.; Lim, T.-T.; Dong, Z., (2008). Application of layered double hydroxides for removal of oxyanions: a review. Water Res., 42(6-7): 1343-1368 **(25 pages)**.

Halajnia, A.; Oustan, S.; Najafi, N.; Khataee, A.; Lakzian, A., (2013). Adsorption–desorption characteristics of nitrate, phosphate and sulfate on Mg–Al layered double hydroxide. Appl. Clay Sci., 80: 305-312 **(7 pages)**.

Halajnia, A.; Oustan, S.; Najafi, N.; Khataee, A.; Lakzian, A., (2012). The adsorption characteristics of nitrate on Mg–Fe and Mg–Al layered double hydroxides in a simulated soil solution. Appl. Clay Sci., 70: 28-36 **(8 pages)**.

Hatami, H.; Fotovat, A.; Halajnia, A., (2018). Comparison of adsorption and desorption of phosphate on synthesized Zn-Al LDH by two methods in a simulated soil solution. Appl. Clay Sci., 152: 333-341 **(8 pages).**

Hosni, K.; Srasra, E., (2008). Nitrate adsorption from aqueous solution by M II-Al-CO 3 layered double hydroxide. Inorg. Mater., 44(7): 742-749 **(7 pages)**.

Hu, Z.; Song, X.; Wei, C.; Liu, J., (2017). Behavior and mechanisms for sorptive removal of perfluorooctane sulfonate by layered double hydroxides. Chemosphere, 187: 196-205 **(9 pages)**.

Islam, M.; Patel, R., (2010). Synthesis and physicochemical characterization of Zn/Al chloride layered double hydroxide and evaluation of its nitrate removal efficiency. Desalin. Water Treat., 256(1-3): 120-128 **(8 pages)**.

Islam, M.; Patel, R., (2011). Physicochemical characterization and adsorption behavior of Ca/Al chloride hydrotalcite-like compound towards removal of nitrate. J. Hazard. Mater., 190(1-3): 659-668 **(9 pages)**.

Ivánová, D.; Albert, P.; Kavuličová, J., (2018). Nitrate removal from model aqueous solutions and real water by calcined Mg/Al layered double hydroxides. Appl. Clay Sci., 152: 65-72 **(7 pages)**.

Kannan, N.; Veemaraj, T., (2010). Detoxification of toxic metal ions by sorption onto activated carbon from Hevea brasiliensis bark—a comparative study. Global J. Geol. Sci., 12(2): 197-205 **(8 pages)**.

Kapoor, A.; Viraraghavan, T., (1997). Nitrate removal from drinking water. J. Environ. Eng., 123(4): 371-380 **(9 pages)**.

Khan, A.I.; O'Hare, D., (2002). Intercalation chemistry of layered double hydroxides: recent developments and applications. J. Mater. Chem., 12(11): 3191-3198 **(7 pages)**.

Khataee, A.; Khani, A., (2009). Modeling of nitrate adsorption on granular activated carbon (GAC) using artificial neural network (ANN). Int. J. Chem. Reactor Eng., 7(1): 1-15 **(15 pages)**.

Kleber, M.; Jahn, R., (2007). Andosols and soils with andic properties in the German soil taxonomy. J. Plant Nutr. Soil Sci., 170(3): 317-328 **(11 pages)**.

Leyva-Ramos, R.; Jacobo-Azuara, A.; Diaz-Flores, P.; Guerrero-Coronado, R.; Mendoza-Barron, J.; Berber-Mendoza, M., (2008). Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. Colloids Surf., A., 330(1): 35-41 **(6 pages)**.

Liu, Q.; Guo, H.; Shan, Y., (2010). Adsorption of fluoride on synthetic siderite from aqueous solution. J. Fluorine Chem., 131(5): 635-641 **(6 pages)**.

Loganathan, P.; Vigneswaran, S.; Kandasamy, J., (2013). Enhanced removal of nitrate from water using surface modification of adsorbents–a review. J. Environ. Manage., 131: **363-374 (11 pages).**

Murayama, N.; Maekawa, I.; Ushiro, H.; Miyoshi, T.; Shibata, J.; Valix, M., (2012). Synthesis of various layered double hydroxides using aluminum dross generated in aluminum recycling process. Int. J. Miner. Process., 110: 46-52 **(6 pages)**.

Nelson, D.; Sommers, L.E., (1982). Total carbon, organic carbon, and organic matter 1. Methods of soil analysis. Part 2. Chemical and microbiological properties, Method. Soil Anal., 2: 539-579 **(41 pages)**.

Park, M.; Lee, C.-I.; Lee, E.-J.; Choy, J.-H.; Kim, J.-E.; Choi, J., (2004). Layered double hydroxides as potential solid base for beneficial remediation of endosulfan-contaminated soils. J. Phys. Chem. Solids, 65(2-3): 513-516 **(4 pages)**.

Reddad, Z.; Gerente, C.; Andres, Y.; Le Cloirec, P., (2002). Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. Environ. Sci. Technol., 36(9): 2067-2073 **(6 pages)**.

Rives, V. (2001). Layered double hydroxides: present and future, Nova Publishers.

Rodríguez-Maroto, J.; García-Herruzo, F.; García-Rubio, A.; Gómez-Lahoz, C.; Vereda-Alonso, C., (2009). Kinetics of the chemical reduction of nitrate by zero-valent iron. Chemosphere, 74(6): 804-809 **(6 pages)**.

Roy, N.; Gray, S.D.; Simon, M.; Dove, H.; Corbin-Lewis, K.; Stemple, J.C., (2001). An evaluation of the effects of two treatment approaches for teachers with voice disorders: a prospective randomized clinical trial. Int. J. Speech Technol., 44(2): 286-296 **(10 pages)**.

Sasai, R.; Norimatsu, W.; Matsumoto, Y., (2012). Nitrate-ion-selective exchange ability of layered double hydroxide consisting of MgII and FeIII. J. Hazard. Mater., 215: 311-314 **(4 pages)**.

Shafigh, M.; Hamidpour, M.; Furrer, G., (2019). Zinc release from Zn-Mg-Fe (III)-LDH intercalated with nitrate, phosphate and carbonate: The effects of low molecular weight organic acids. Appl. Clay Sci., 170: 135-142 **(7 pages).**

Tezuka, S.; Chitrakar, R.; Sonoda, A.; Ooi, K.; Hirotsu, T., (2007). Studies on Selective Adsorbents for Oxo-anions. NO3-Adsorptive Properties of Mg-Fe Layered Double Hydroxides. J. Ion Exch., 18(4): 276-281 **(6 pages)**.

Tezuka, S.; Chitrakar, R.; Sonoda, A.; Ooi, K.; Tomida, T., (2005). Studies on Selective Adsorbents for Oxo-Anions. No. 3– Adsorptive Properties of Ni-Fe Layered Double Hydroxide in Seawater. Adsorpt, 11(1): 751-755 **(5 pages)**.

Torres-Dorante, L.O.; Lammel, J.; Kuhlmann, H.; Witzke, T.; Olfs, H.W., (2008). Capacity, selectivity, and reversibility for nitrate exchange of a layered double-hydroxide (LDH) mineral in simulated soil solutions and in soil. J. Plant Nutr. Soil Sci., 171(5): 777-784 **(7 pages)**.

Torres-Dorante, L.O.; Lammel, J.; Kuhlmann, H., (2009). Use of a layered double hydroxide (LDH) to buffer nitrate in soil: long-term nitrate exchange properties under cropping and fallow conditions. Plant Soil, 315(1-2): 257-272 **(16 pages).**

Tong, X.; Yang, Z.; Xu, P.; Li, Y.; Niu, X., (2017). Nitrate adsorption from aqueous solutions by calcined ternary Mg-Al-Fe hydrotalcite. Water Sci. Technol., 75(9): 2194-2203 **(9 pages)**.

Xu, G.; Song, P.; Reed, P., (1992). The relationship between gastric mucosal changes and nitrate intake via drinking water in a high-risk population for gastric cancer in Moping county, China. Eur. J. Cancer: J. ECP., 1(6): 437-443 **(7 pages)**.

Xue, L.; Gao, B.; Wan, Y.; Fang, J.; Wang, S.; Li, Y.; Muñoz-Carpena, R.; Yang, L., (2016). High efficiency and selectivity of MgFe-LDH modified wheat-straw biochar in the removal of nitrate from aqueous solutions. J. Taiwan Inst. Chem. Eng., 63: 312-317 **(6 pages)**.

AUTHOR (S) BIOSKETCHES

Mohammadi, M., PhD. Candidate, Department of Soil Science, Science and Research Branch, Islamic Azad University, Tehran, Iran. Email: *mohamadimaryam99@yahoo.com*

Mohammadi Torkashvand, M.A., PhD., Associate Professor, Department of Soil Science, Science and Research Branch, Islamic Azad University, Tehran, Iran. Email: *m.torkashvand54@yahoo.com*

Biparva, P., PhD., Assistant Professor, Department of Basic Science, Sari University of Agricultural Sciences and Natural Resources, Sari, Iran. Email: *pb.biparva@sanru.ac.ir*

Esfandiari, M., PhD., Assistant Professor, Department of Soil Science, Science and Research Branch, Islamic Azad University, Tehran, Iran. Email: *mesfandiari@ut.ac.ir*

COPYRIGHTS

Copyright for this article is retained by the author(s), with publication rights granted to the GJESM Journal. This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/).

HOW TO CITE THIS ARTICLE

Mohammadi, M.; Mohammadi Torkashvand, A.; Biparva, P.; Esfandiari, M., (2019). Synthesis ratios of Mg-Al and Zn-Al layered double hydroxides efficiency and selectivity in nitrate removal from solution. Global J. Environ. Sci. Manage., 5(4): 485-500.

DOI: 10.22034/gjesm.2019.04.08

url: https://www.gjesm.net/article_35751.html