

## Synthesis of Mg/Al layered Double Hydroxide (LDH) Nanoplates for Efficient Removal of Nitrate from Aqueous Solutions

**maryam mohammadi**

Iran, Sari University of Agricultural Sciences and Natural Resources, Sari  
mohamadimaryam99@yahoo.com

**mohammad ali bahmanyar**

Iran, Sari University of Agricultural Sciences and Natural Resources, Sari  
m.bahmanyar@sanru.ac.ir

**fardin sadegh zade**

Iran, Sari University of Agricultural Sciences and Natural Resources  
Sarifardin.upm@gmail.com

**pouria bi parva**

Iran, Sari University of Agricultural Sciences and Natural Resources, Sari  
p.biparva@sanru.ac.ir

### Abstract

Abstract With respect to nitrate loss from agricultural soils of temperate regions, nitrate leaching is an important phenomenon. Decomposition of plants and other organic residues in soil and improper disposal of wastewater and nitrogen fertilizers causes interred nitrate in surface water, groundwaters. Nano LDH-chloride was synthesized using hydrothermal technique and then characterized using scanning electron microscopy and EDS and nitrate removal from aquatic solutions by this mineral was evaluated at different pHs, times, rotation speeds, adsorbent concentrations and nitrate solution concentrations. Microscopic images of synthesized nanoplates were examined with electron microscopes EDS and SEM with two magnification. Results indicated that, dimensions of nanoplates were at nano scales so that the average thickness of nanoplates was 20 nanometers and their diameter was 250 nm. the higher magnification of the LDH indicated that the nano particles were flake- like shape. were Optimal conditions of adsorption: pH=7, 250 rpm: rotating speed, 45 min: time, and 0.1 g: adsorbent concentration. Nitrate adsorption on chloride-LDH was well explained with Longmuir model which is obvious from high values of R<sup>2</sup>. This material could adsorb nitrate from aquatic solutions efficiently.

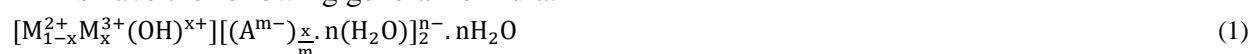
**Keywords :** nanoplates, longmuir model, nitrate, layered double hydroxide (LDH), adsorption

## 1. Introduction

From past times up to now, adverse materials are contaminating soils and aquatic environments and threatening human health. Instead of using modern knowledge of agriculture for higher yields, farmers have enhanced amount of chemical fertilizers like nitrogen fertilizers per unit of area (Singh et al, 1978; Acosman et al, 2010). Using different types of chemical and organic (livestock, human) fertilizers, decomposition of plants, and other organic residues in soil, and inappropriate disposal of wastewater, are the reasons behind the presence of nitrate in surface water, groundwater and drainage water flowing in the agricultural drainage networks (Hamilton and Helsel, 1995). Most agricultural lands are located in temperate regions with very low anion exchange capacity. Because of having negative charge, nitrate ions don't adsorb on soil colloids and they can leach under the root zone or to drainage water. Therefore, this ion not only cause to reduction of nitrogen fertilizers efficiency, but also causes exceeding of nitrate concentration over acceptable limits (Berber et al, 2014; Bengtson and Annadotter, 1989). European Union has established a limit for nitrate value in drinking water that is 50 mg nitrate per liter. Recently, EU has adopted groundwater manual which reverses uptrend of nitrate concentration when it exceeds over 37.5 mg/l in groundwater. Nitrate ion is known as soil and water pollutant and with respect to health, environment and economic, nitrate leaching is an important issue (Acosman et al, 2010). Large amounts of nitrate in drinking water causes diseases like blue baby syndrome, cancer, stomach and brain tumor, etc (Rodríguez-Maroto, 2009; Chabani et al, 2009; Jahed- Khaniki et al, 2008). Therefore, nitrate concentration is one of the most important criteria of groundwater quality and it is important to have knowledge about its concentration in soil and water resources (Jia et al, 2005; Wang, 1997; Wang et al, 2003). Common methods for reducing nitrate leaching and its removal from water, includes: ion exchange, biological denitrification, reverse osmosis and chemical reduction (Rodríguez-Maroto, 2009; Chatterjee et al, 2009). Conducting each of these methods in large scale is expensive and time-consuming. So, for reducing nitrate leaching, we need inexpensive and high efficiency adsorbents and methods (Berber et al, 2014).

Layered double hydroxides (LDHs) are anionic clay minerals belonging to a group of non-silicate compounds (Halajnia et al, 2012). LDHs have layered structure containing cationic hydroxide layers with positive charge and interlayers of anions and water. These minerals have considerable characteristics for soils such as considerable anion exchange capacity, high buffering capacity and being a potential nutrient source (Park et al, 2004). Anionic exchange capacity of these minerals shows a great potential for trapping organic and inorganic anions which makes them a nitrate exchanger in soils (Dorante et al, 2008; Halajnia et al, 2012). These minerals can be found in soils naturally but in small amounts. However, extensive ranges of these minerals can be produced both in laboratory and industrial scales and different sizes including nanosizes (Berber et al, 2014).

LDHs have the following general formula:



Where,  $M^{2+}$  indicates divalent cations (Mg, Mn, Fe, Co, Ni, Cu, Zn);  $M^{3+}$  indicates trivalent cations (Al, Fe, Mn, Cr, Co, Ni); and  $A^{m-}$  means anions including  $NO$ ,  $CO_3$ ,  $SO_4^{2-}$ , Cl, OH and other organic and inorganic anions; X is the ratio of isomorphous substitution which is usually between 0.1 and 0.7 (ohare and Khan, ۲۰۰۲; et al Roy, ۲۰۰۱). These minerals have different interesting applications in many fields that is because of their adjustability (Torres-Dorante, 2007). Several reports evaluated the effect of these clay materials in agriculture including controlled release of herbicides and phytohormones and water purification. Hosni and Srasra, (2008) examined the usage of layered double hydroxides Al- Mg and Al- Zn in removing nitrate from aquatic solutions and expressed that Mg- Al- LDH has higher nitrate adsorption capacity in comparison with Zn- Al- LDH. Tezu et al (2005) reported a 83 percent reduction of nitrate from saline water enriched with nitrates. Islam and Patel, (2011) examined nitrate adsorption on Ca- Al- LDH and indicated that in neutral condition, with using 0.35 gr of the adsorbent in 100ml of solution, nitrate with initial concentration of 10 mg/l was 84.6%. Torres-Dorante et al, (2007) and Torres-Dorante et al, (2009) explored potential applicability of an especial LDH as a nitrate fertilizer in field condition and reported its capacity to reduce nitrate leaching in greenhouse condition. Tezu et al, (2004) indicated that Ni- Fe-LDH had higher selectivity in comparison with Co- Fe- LDH and Mg- Fe- LDH for adsorbing nitrate from water that is because of the suitable basal spacing of brucite like layer.

The objectives of this study were: to synthesize nanoplates of chloride Mg- Al- LDH for removing nitrate from aquatic solutions and estimating pH, concentration, contact time, and optimal equilibrium and also applicability of adsorption isotherms for synthesized sample.

## 2. Materials and methods

### 2.1. Nano Mg-Al-LDH synthesis

NanoLDH was synthesized using hydrothermal method. By using a magnetic stirrer, 50 ml of NaOH 4M was instilled steadily to an Erlenmeyer containing a 50 ml solution made of 20.33 gr magnesium chloride hexahydrate ( $Cl_2$  Mg.6  $H_2O$ ) and 19.26 gr aluminum chloride hexahydrate ( $AlCl_3.6H_2O$ ). The solutions were prepared with double distilled water in presence of  $N_2$  gas. The resulting suspension was put in autoclave in 180 °C for 24 hours. Then, it freeze- dried in oven in 60 °C for 24 hours.

### 2.2. Investigation of LDH nanostructure

The micrographs of scanning electron microscope of model Mira 3-XMU was used for showing LDH nanoparticles.

### 2.3. Adsorption isotherms of nitrate adsorption on LDH in aquatic solutions

In all of the examinations, chloridric acid 0.1M and sodium hydroxide 0.1M was used for pH adjustment.



In order to investigate contact time, 0.3 gr LDH was added to 60 ml of 100 mg/l potassium nitrate solution. Then, this mixture was shaken on a shaker with rotating speed of 250 rpm for 5, 15, 30, 45, 60, 90, 120 and 180 minutes in laboratory temperature and analyzed for determining nitrate concentration.

In order to evaluate the effect of pH and shaker speed, 0.3 gr LDH was added to 60 ml of 100 mg/l potassium nitrate solution with pHs 5, 6, 7, 8, 9, 10, 11, and 12; the resulting mixtures were shaken at speeds (50, 100, 150, 200, 250, 300 rpm) in laboratory temperature and equilibrium time and analyzed for nitrate concentration.

To evaluate the effect of adsorbent concentration and adsorption isotherms, (0.03, 0.05, 0.1, 0.3, 0.5, 0.7, 1 gr) of adsorbent was added to 60 ml of potassium nitrate solution with concentrations (20, 50, 100, 150, 200, 300, 500 mg nitrate per liter) in laboratory temperature, equilibrium time, shaker speed and pH and at the end of reaction, it was analyzed for nitrate concentration. These ranges of potassium nitrate concentration were defined according to field assessments reported in literature.

## 2.4. Analysis methods

For analysis, the suspensions were centrifuged with 4000 rpm for 20 minutes. Then, for determining nitrate concentrations in these suspensions, 0.5 ml of the solution was taken from upper part of it. Nitrate concentration in initial solution was determined by this method. The amount of nitrate adsorbed on LDH was calculated from the difference between nitrate concentration in solution before (initial solution) and after (equilibrium solution) shaking.

All experiments were carried out in triplicate and nitrate concentration in extracts was measured using ultraviolet spectroscopy, DPG instrument (UV/Vis + T90 spectrometer). At the end, adsorption equations of Langmuir and Freundlich were used to estimate the capacity of LDH for nitrate adsorption.

$$\text{Langmuir: } q = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (2)$$

$$\text{Freundlich: } q = K C_e^{1/n} \quad (3)$$

Where,  $q$  is the adsorbate value in mg;  $C_e$  is the equilibrium concentration in solution in (mg);  $Q_{\max}$  is maximum adsorption capacity in (mg/g);  $b$  is constant value;  $k$  is constant coefficient; and  $n$  is constant coefficient.

Equations of Freundlich and Langmuir were used for describing experimental data of the used isotherm. These equations can be expressed in linear mode:

$$\text{Freundlich: } q = K C_e^{1/n} \quad (4)$$

$$\text{Langmuir: } q = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (5)$$

Where,  $q_e$  is the amount of nitrate adsorbed per mass unit of LDH in mg/g for Langmuir equation and mg/kg for Freundlich equation;  $C_e$  is nitrate equilibrium concentration in mg per liter. In Freundlich equation,  $K_f$  and  $1/n$  are constant values. In Langmuir equation, constant of  $b$  is maximum amount of nitrate adsorbed for a monolayer cover per mass unit of LDH; and  $K_L$  is constant related to binding energy.

### 3. Results

#### 3.1. Investigation of LDH nanostructure

the scanning electron microscopy was used to investigating the nanostructure of made LDH. Microscopic images of synthesized nanoplates were examined with scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM) with two magnification. As expected, dimensions of nanoplates were at nano scales so that the average thickness of nanoplates was the 20 nm (fig. 1) and their diameter was 250 nm. their nanostructure was flake-like shape.

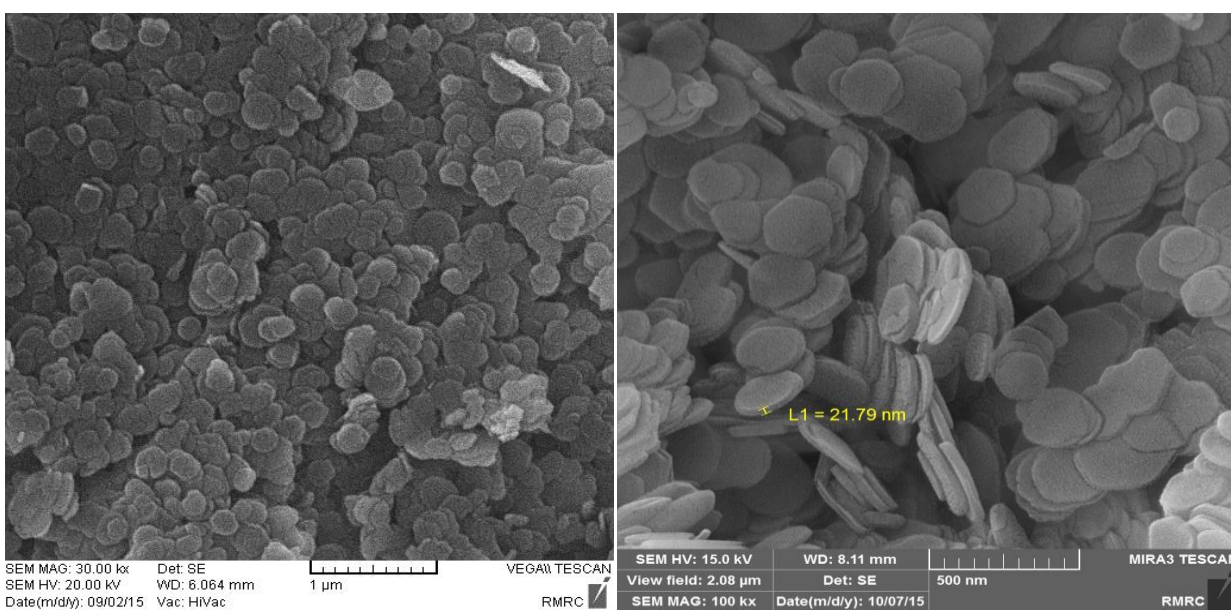


Fig 1. Image of scanning electron microscopy of LDH- chloride.

Fig. 2 shows the EDS spectrum of the LDH that indicates the presence of Mg and Al ions and the interlayer Cl anion. Na resulting from improper washing of NaOH and O from interlayer molecules were adsorbed on LDH.

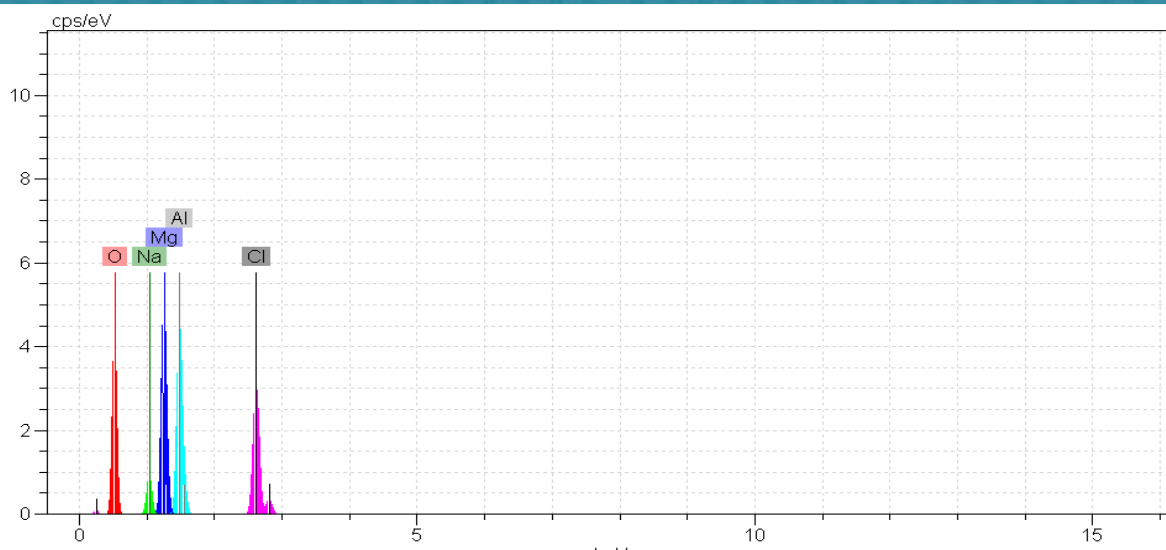


Fig 2. EDS Spectrum of the synthesised LDH

### 3.2. Nitrate adsorption isotherms

Adsorption isotherms were used to determine nitrate distribution between solid and liquid phases of LDHs. According to Fig. 3, results showed that nitrate adsorbed on LDH increased with time. In first 15 minutes, nitrate adsorption was fast and after that it increased gradually. Approximately, 40 percent of nitrate adsorption occurred at first 15 minutes. Maximum nitrate adsorption occurred at 45 minutes and after that there was a decreasing trend. Equilibrium time was considered at 45 min. According to Fig. 4, maximum nitrate adsorption on LDH recorded at 250 rpm.

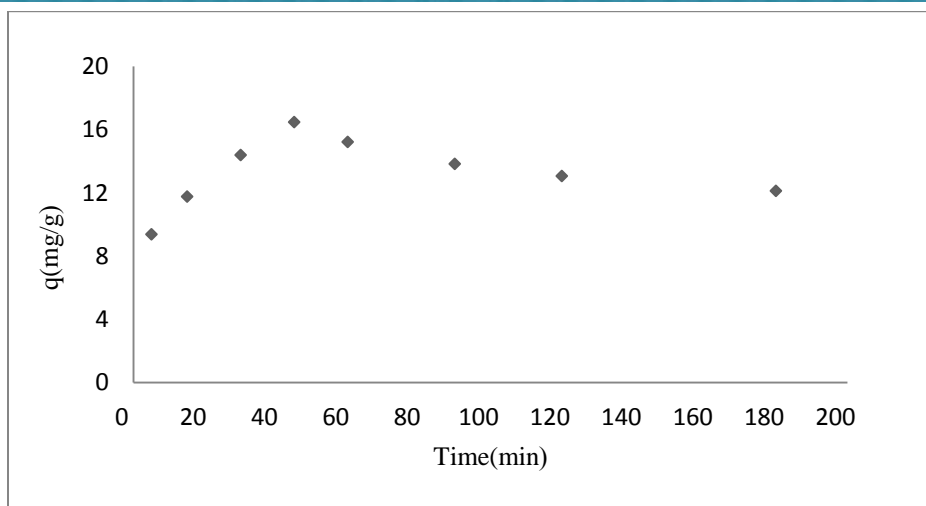


Fig 3. Effect of contact time on amount of nitrate adsorbed on LDH.

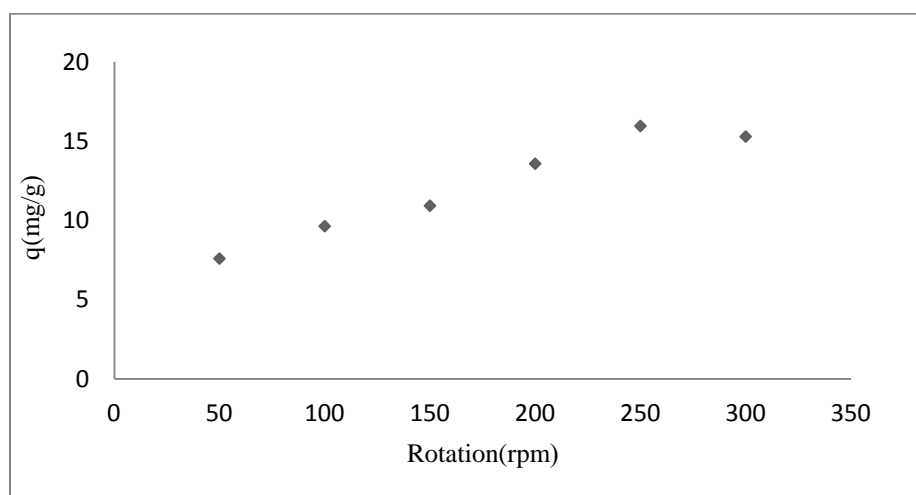


Fig 4. Effect of shaker speed on amount of nitrate adsorbed on LDH.

pH values were nearly constant at initial values (5–12) and a small reduction in nitrate adsorption was observed (Fig. 5). This was assigned to buffering capacity of LDHs at high pH ranges. pH 7 was considered as optimum pH. pH wasn't constant during adsorption, so experiment was conducted with buffered nitrate solutions.



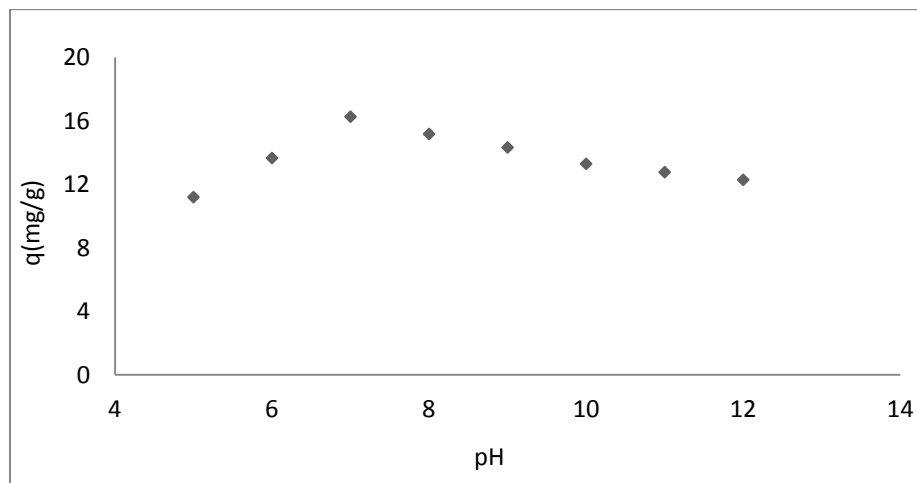


Fig 5. Effect of pH on amount of nitrate adsorbed on LDH.

According to Fig. 6, maximum nitrate adsorption occurred when the adsorbent amount was 0.1 gr.

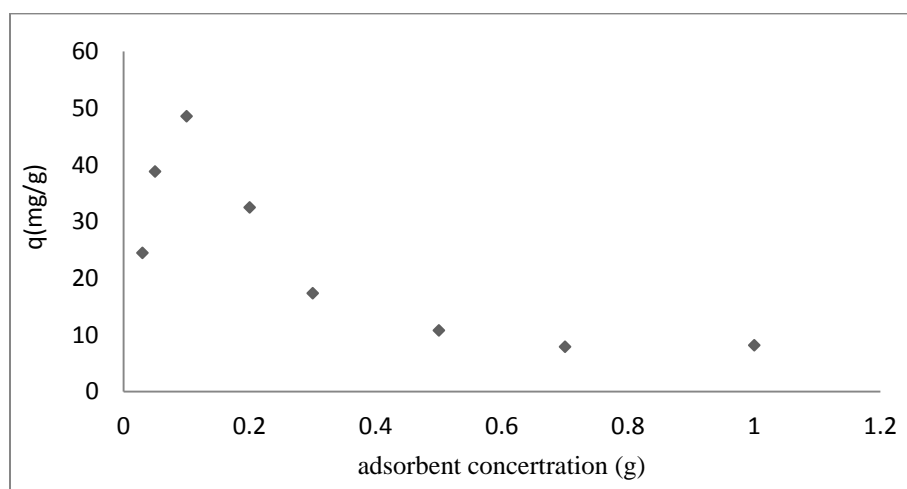


Fig 6. Effect of adsorbent concentration on amount of nitrate adsorbed on LDH.

Nitrate adsorption on LDH enhanced with increasing the external concentration of nitrate (graph. 5).



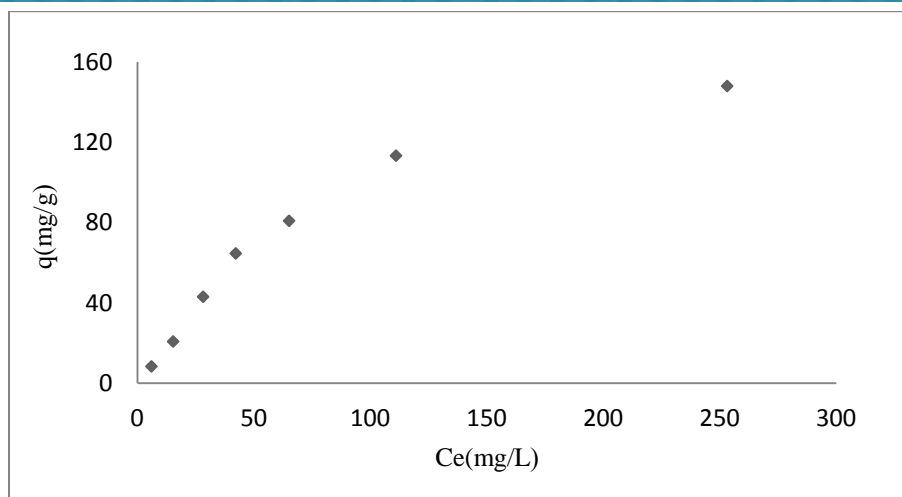


fig. 7 isotherm of nitrate adsorption on LDH

Parameters of Langmuir and Ferendlich values are presented in table. 1.

Table 1. Parameters of Langmuir and Ferendlich adsorption isotherms.

isotherms Langmuir			isotherms Ferendlich			Temperature	Catchy
b	R <sup>2</sup>	Q <sub>m</sub>	R <sup>2</sup>	n	K <sub>f</sub>	(°C)	
۰,۰۰۱۴	۰,۹۹۷	۱۰۰۰	۰,۹۰۲	۱,۲۶۴۲	۲,۵۷۶۳	۲۳±۲	LDH

High R<sup>2</sup> indicated that the data better adjusted with Langmuir equation, suggesting monolayer adsorption of nitrate on LDH (Fig. 8).

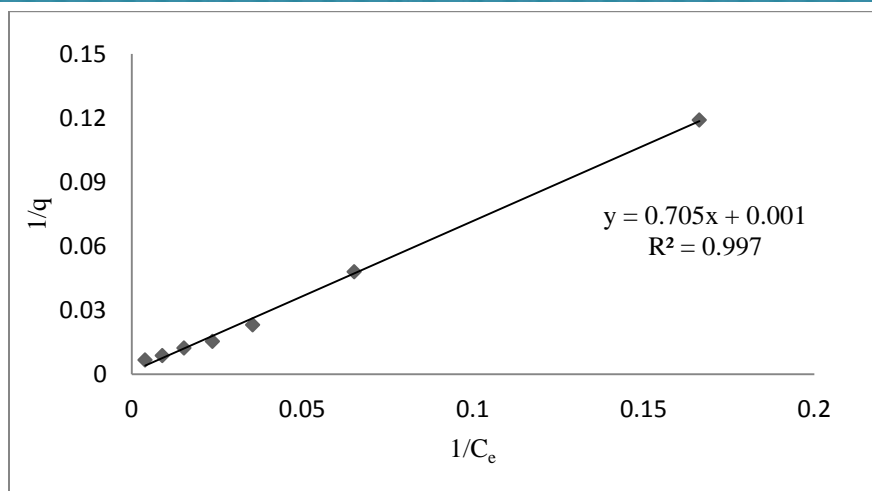


Fig. 8. fig Model isotherms Langmuir

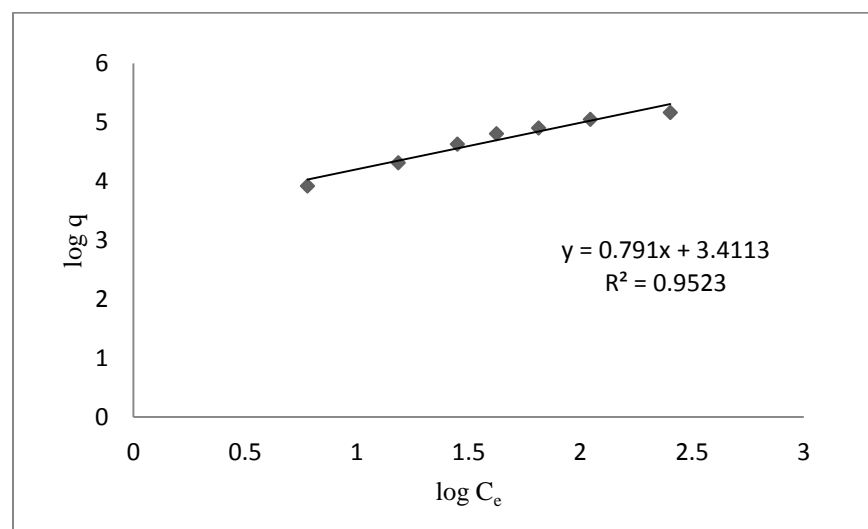


Fig. 9. fig Model isotherms Ferendlich

#### 4. Discussion and conclusions

The synthesized LDH was recorded at nano scale. 45 min was considered as equilibrium time. This is consistent with Islam and Patel (2009) who defined equilibrium time at 45 min. the pH 5 to 10, nitrate adsorption on LDH was nearly constant with a slightly decreasing trend. This was consistent with results of [You et al. \(2001\)](#) and [Ferreira et al. \(2006\)](#). Islam and Patel. (2011) reported that increasing pH from 8 to 12, reduced nitrate adsorption by Mg- Al- LDH. Tezuka et al, (2005) reported a nearly constant nitrate adsorption capacity for Ni- Fe- LDH at pH ranging 5.4–10. Maximum nitrate adsorption on LDH was 1.0 g. This observation was consistent with

reports of Torres-Dorante et al. (2008). The results were consistent with Islam and Patel (2009, 2010, 2011) and Hosni and Srasra. (2008) but were not consistent with Tezuka et al. (2005).

According to above mentioned results, the synthesized chloride nano layered double hydroxide mineral (LDH) can be used as an efficient adsorbent for removing nitrate from aquatic solutions.

In order to prevent surface and ground water from pollution which is an important problem of temperate climate agricultural soils, we propose this cheap and environment friendly clay material for efficient removing of nitrate.

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