SYNTHESIS OF MG/AL LAYERED DOUBLE HYDROXIDE (LDH) NANOPLATES FOR EFFICIENT REMOVAL OF NITARATE FROM AQUEOUS SOLUTIONS

M. Mohammadi¹, M. A. Bahmanyar¹, F. Sadeghzadeh¹, P. Biparva²*

¹Department of Soil Science, Sari University of Agricultural Sciences and Natural Resources, Sari, Iran
²Department of Basic Science, Sari University of Agricultural Sciences and Natural Resources, Sari, Iran

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ABSTRACT
Leaching of nitrate is an important issue on the losses of nitrate from agriculture soils in temperate zone. Decomposition of plants and other organic residues in the soil and improper discharge of sewage lead to the presence of nitrates in the sources of surface and groundwater and flowing water drainage in agricultural drainage networks and their pollution. This study aimed to study the potential use of chloride layered double hydroxide (LDH) nanoplates to remove nitrate from aqueous solutions. The nano-material of chloride-LDH was made by hydrothermal technique and then, its characteristics were specified through scanning electron micrograph and removal of nitrate from aqueous solution by the minerals was investigated in terms of pH, time, speed of shaker, different concentrations of adsorbent and surface adsorption isotherm. Microscopic images of built nanoplates were examined using FESEM and SEM electron microscope with two magnifications. The thickness of nanoplates was about 20nm and their diameter was about 250 nm. Magnified image of the synthesized nanostructures shows squamous-shape. Surface adsorption isotherm of nitrate by chloride-LDH nanoplate was explained with Langmuir model shown with the values greater than 2R. In surface adsorption of nitrate, the optimal values were measured as following: pH = 7, speed = 250 rpm, time = 45 min, concentration of adsorbent = 0.1gr.

Author Correspondence, e-mail: pb.biparva@sanru.ac.ir
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This material could adsorb nitrates from aqueous solutions efficiently and effectively.

**Key words:** pollution, nitrate, layered double hydroxide, hydrothermal, surface adsorption

1. **INTRODUCTION**

From the past to the present, different harmful substances have contaminated the soils and aquatic environments and threatened human health. Instead of taking advantage of agricultural sciences to produce more products, the farmer has increased the use of chemical fertilizers, including nitrogen fertilizers, per unit area (Singh et al., 1978). The use of chemical and organic (animal and human) fertilizers, decomposition of plants and other organic residues in the soil and improper discharge of sewage lead to the presence of nitrates in the sources of surface and groundwater and flowing water drainage in agricultural drainage networks and their pollution (Helsel and Hamilton, 1995). Most agricultural soils in temperate zones have very low anionic exchange capacity. Nitrate ion is not adsorbed to the colloids of soil due to negative charge and can be leached under root zone into groundwater and water drainage to surface water. So, not only, it reduces the efficiency of nitrogen fertilizers, but nitrate concentrations exceed the acceptable limits of pollution (berber et al, 2014; Bengtson and Annadotter, 1989). Europe Union Europe Union has imposed a limit for nitrate in drinking water which is equal to 50 mg of nitrate per liter. Recently EU has also ratified groundwater instructions that create the pilot to reverse the rising trend in the concentration of nitrate at the time that the nitrate level of groundwater is reaching to 37.5 mg of nitrate per liter. Nitrate ion has been known as water and soil pollutant that in terms of health, environmental and economic aspects, nitrate leaching is more important problem (acosman and ozdmir, 2010). High levels of nitrate in drinking water can cause the diseases such as Methemoglobinemia, cancer, stomach and brain tumors and ... (Rodriguez-Maroto et al, 2009; Chabani et al., 2009; jahed-khaniki et al, 2008) . Thus, nitrate concentration is an important measure of the quality of groundwater and knowing the concentration of this elements in soil and water resources is of particular importance (Wang et al., 2003; Wang, 1997; Jia et al., 2005). Common methods to reduce nitrate leaching and remove it from the water are ion exchange, biological de-nitrification, reverse osmosis and chemical reclamation (Rodriguez-Maroto et al, 2009; Chatterjee et al, 2009). The use of all mentioned methods on a large scale is time-consuming and costly. So, high-efficiency and low-cost methods and materials are required to reduce nitrate leaching.
LDHs have the following general formula: layered double hydroxides (LDHs) are anionic clay minerals which belong to a group of non-silicate compounds (Halajnia et al., 2012). LDHs have layered structure consisting of positively charged cationic hydroxide layers with interlayers containing anions and water. These minerals have notable features for the soil including significant anionic exchange capacity, high ability of buffering and potential food sources (Park et al., 2004). The property of anionic exchange of these minerals shows a great ability to trap organic and non-organic anions and this creates the desire to use them in the exchange of nitrate in the soil (Torres-Dorante et al., 2008; Halajnia et al., 2012). These minerals can be found naturally in soil, but small quantities of them exist. However, a wide range of these minerals can be made on both laboratory scale and industrial scale and in different size, including nano (Berber et al., 2014).

\[ [M^{2+}_{1-x} M^{3+} X (OH)^{x+}] [(A^{m-})_x n(H_2O)]_2^{3-} nH_2O \]

Where \( M^{2+} \) is 2-valent cations, i.e. (Mg, Mn, Fe, Co, Ni, Cu, Zn) and \( M^{3+} \) is 3-valent cations, i.e. (Al, Fe, Mn, Cr, Co, Ni) and \( A^{m-} \) includes onions i.e. NO, CO\(_3\), Cl, OH, SO\(_4\)\(^{2-}\) and other organic and non-organic onions, \( X \) is cation substitution ratio (\( M^{3+}/ M^{2+} + M^{3+} \)) and its value is 0.1 to 0.7 (Khan and Ohare, 2002; Roy et al., 2001). These minerals have different interesting uses in a variety of fields due to their adaptive characteristics. Several studies have evaluated the effects of these clay materials in the field of agriculture, including the controlled release of herbicides and plant hormones and water purification (Torres-Dorante, 2007). Hosni and Srasra (2008) have investigated Al-Mg and Al-Zn layered double hydroxides in the removal of nitrate from aqueous solutions and stated that Al-Mg layered double hydroxides has higher nitrate adsorption capacity than Al-Zn layered double hydroxides. Tezuka et al, (2005) have reported 83% reduction of nitrates from salty water rich in nitrates. Islam and Patel, (2011) investigated the adsorption of nitrates through Al-Ca LDH and shown that adsorption of nitrates was equal to 84.6% in neutral conditions or the use of 0.35 gr adsorbent in 100 ml of nitrate solution with an initial concentration of 10 mg per liter. Torres-Dorante et al, (2009) and Torres-Dorante, (2007) discovered the potential use of one specific LDH as nitrate fertilizer in field condition and reported its ability to reduce nitrate leaching under greenhouse conditions was reported. Tezuka et al, (2004) has shown that Ni-Fe- LDH has higher selectivity for nitrate adsorption from water than Fe-Mg-LDH, Fe-Co-LDH and Al-Mg-LDH that its reason is proper foundation distance of Brucite-like layer. The aim of this study is to manufacture the chloride layered double hydroxide (LDH) nanoplates to remove nitrate from aqueous solutions and determine pH, concentration, contact time and optimal
balance. Also, the absorption isotherms for adsorption mechanism and performance of synthesized adsorbent were studied.

**Materials and methods**

Magnesium chloride hexa-hydrate (purity of 99%), aluminum hexa-hydrate (purity of 99%) produced in CHEM-LAB chemical industry, Belgium; salicylic acid (purity of 99%) and potassium nitrate (purity of 99%) produced in Merk chemical industry, Germany and NaOH (purity of 98%) of the chemical industry produced in Scharlau, Spain, were purchased and consumed. All solutions were distilled 2 times by water and degassed and prepared with N₂ gas.

**Manufacture of Al-Mg- LDH nanoplate**

LDH nanoplates were synthesized by the use of hydrothermal technique. 50ml of sodium hydroxide M4 was added to a flask of 50 ml of solution containing 20.33 gr of magnesium chloride hexa-hydrate and 19.26 gr of aluminum chloride hexa-hydrate drop by drop with magnetic stirring constantly. Obtained suspension was placed in autoclave tank at the temperature of 180 °C for 24 hours. Then, the resulting material was washed well with distilled water. Then, it was dried in oven at the temperature of 60°C for 24 hours.

**Investigation of the structure of LDH**

The micrographs of EDS, FE SEM and SEM scanning electron microscopes () with the models of Mira 3-XMU, VEGA2 and VEGA2, respectively were taken from TESCAN Company to show nanoparticles of LDH. Patterns of transmission electron microscope (TEM) with using the microscope, Zeiss-EM10C-100KV model, was taken from Daypetronic Company.

**Measurement of the concentration of nitrate**

To produce the solutions and standard nitrate ion, the composition of potassium nitrate (KNO₃) was used. 1000mg/l stock solution of nitrate was prepared. Then, the standard solutions were prepared from 0 to 10 mg/l with the use of stock solution. For analysis, the solutions were centrifuged for 20 min at 4000 rpm. Then, 1 ml of the upper part of solution was removed to determine the nitrate concentration of the solutions. To read the nitrate concentration of the solutions, the spectrophotometry method of Keeney and Nelson (1982) was used. 0.5 ml of solutions and also, the standard solution were transferred into a 50 ml Erlenmeyer flask and 0.5 ml of the salicylic acid-sulfuric acid mixture (5 g salicylic acid in 95 ml of concentrated sulfuric acid) was added to it and after shaking for 30 min, 10 ml of 4-normal NaOH was added and it was set aside for 30 min to complete the formation of yellow
color. Then, their absorptions were read at the wavelength of 410 nm using a spectrophotometer. Plotting calibration curve for standard solution, the concentrations of the solutions were obtained. The surface absorption of nitrate was calculated by the difference between the initial concentration of nitrate before (initial solution) and after shaking (equilibrium solution). All experiment were repeated 3 times.

2. RESULTS

Nano structure of LDH

Scanning electron micrography (microscopic) was used to investigate the nano structure of LDH. Figure 1 showed the manufactured chloride-LDH picture. The microscopic images of manufactures nanoplates were investigated by the use of SEM and SEM FE electron microscope with two magnifications. As predicted, the dimensions of nanoplates are at the scale of nanometer so that the thickness of nanoplates was about 20nm (Figure 1-a). Smaller magnification of synthesized nanostructures shows scale-shape (Figure 1-b). Figure 2 shows the synthesized sample of EDS that given it, the presence of the ions of Al and Mg and interlayer ion of Cl were observed. Na is the result of incomplete washing of NaOH and O is of interlayer and adsorbed molecules on the LDH. Figure 3 shows TEM related to synthesized LDH.

![Fig.1. Scanning electron microscopic image for manufactured chloride-LDH](image-url)
The effect of contact time on the nitrate adsorption by LDH

To investigate the effect of contact time, 0.3 gr of LDH was added to 60ml of potassium nitrate solution with the concentration of 100mg/l and obtained mixture was stirred for 5, 15, 30, 45, 60, 90, 120 and 180 min at a speed of 250 rpm and ambient temperature with shaker and finally, it was analyzed to determine its concentration. Given Figure4, the results showed that the surface adsorption of nitrate has increased on LDH over time. In first 15 min, the surface adsorption of nitrate was fast and after that it has increased gradually. About 40% of surface adsorption of nitrate occurred in first 15 min. in 45 min, the surface adsorption of
nitrate reached its maximum value, then, it showed decreasing trend. The balanced time was considered at the point of 45 min.

![Graph showing effect of contact time on nitrate adsorption on LDH](image)

**Fig.4.** Effect of contact time on the surface adsorption of nitrate on LDH

**The effect of pH and the speed of shaker on the adsorption of nitrate with LDH**

To investigate the effect of pH and the speed of shaker, 0.3 gr of LDH was added to 60ml of potassium nitrate solution with the concentration of 100mg/l at the pH of 5, 6, 7, 8, 9, 10, 11 and 12 was added and obtained mixture was stirred at the speeds of 50, 100, 150, 200, 250 and 300 rpm at the time of balance and ambient temperature and then it was analyzed to determine its concentration. The speed of stirring is an important parameter in surface adsorption, because the speed of stirring reduces the boundary layer around the particles, as a result, the transfer coefficient of outer layer increases and of course, stirring at very high speeds prevents the particles to reach the active point and reduces the efficiency (dogan et al, 2009 and mittal et al 2009). Given Figure5, increasing the speed of stirring to 250 rpm, the adsorption of nitrate increased and at the speed of 300 rpm, it decreased. The maximum surface adsorption of nitrate occurred at 250 rpm. The value of pH was nearly constant at primary values (5 to 12) and a little reduction in surface adsorption of nitrate was observed (Figure6). This is associated to the high buffering capacity of LDH in the range of high pH. The optimal pH was considered 7. The pH was not constant during the adsorption, as a result, the tests were done with the use of buffered nitrate solutions.
The effect of the dosage of adsorbent on the adsorption of nitrate with LDH

To investigate the effect of the dosage of adsorbent, 0.03, 0.05, 0.1, 0.3, 0.5, 0.7 and 1 gr of LDH was added to 60ml of potassium nitrate solution with the concentration of 100mg/l was added and obtained mixture was stirred at the optimal speed, time and with optimal pH at the ambient temperature and finally it was analyzed to determine its concentration. Given figure7, the maximum surface adsorption of nitrate occurred in the solution with 0.1 gr of adsorption. In 0.1 gr of LDH, 80.97% of nitrate was removed from the 100 ppm solution of potassium nitrate at optimal time, speed and with optimal pH.

**Fig.5.** Effect of speed of shaker on the surface adsorption of nitrate on LDH

**Fig.6.** Effect of pH on the surface adsorption of nitrate on LDH
The effect of adsorption isotherms on the adsorption of nitrate with LDH

To investigate the effect of adsorption isotherms, 0.1 gr of LDH was added to 60ml of potassium nitrate solution with the concentrations of 20, 50, 100, 150, 200, 300 and 500 mg/l and stirred at optimal speed and pH at balance time and ambient temperature and finally, it was analyzed to determine the concentration of nitrate. This range of potassium nitrate concentration was defined based on field measurement reported in the literature. The adsorption equations of Langmuir and Ferendlich were used to investigate the capacity of LDH in terms of the adsorption of nitrate. Langmuir model is one of the most important models of one-layer adsorption models which is based on the constant number of adsorption places and every place has the ability to receive one molecule of adsorbent. The conditions are the same for all places and there are no collisions between the molecules of adsorbent (Bazargan Lari, 2011). Another isotherm adsorption model is Ferendlich model. These two models are stated as following (Chen et al., 2011).

Langmuir: \[ q = \frac{Q_{\text{max}} b C_e}{1 + b C_e} \]

Ferendlich: \[ q = K C_e^{1/n} \]

Where, \( Q \) is the amount of adsorbent (mg), \( C_e \) is the equilibrium concentration of the adsorbent in solution (mg), \( Q_{\text{max}} \) is the maximum capacity of adsorption (mg/g), \( b \) is constant, \( k \) is constant coefficient, \( n \) is constant coefficient.

Surface adsorption of nitrate on LDH increased by increasing the external concentration of nitrate. Figure 8 shows the isotherm of nitrate adsorption on LDH.
Langmuir and Ferendlich equations were used to explain the experimental data of isotherm. These equations can be expressed in a linear fashion.

Ferendlich equation
\[ \log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \]

Langmuir equation
\[ \frac{C_e}{q_e} = \frac{C_e}{b} + \frac{1}{L_K}b \]

Where \( q_e \) is the values of adsorbed nitrate per unit mass of LDH in mg/g for Langmuir and mg/kg for Ferendlich and \( C_e \) is an equilibrium concentration of nitrate in mg/l. in Ferendlich equation, \( 1/n \) and \( F_K \) are constant. In Langmuir equation, \( b \) is constant and maximum adsorbed nitrate per unit mass of LDH for one-layer cover and \( L_K \) is a constant related to bond energy. Table 1 shows their values. Ferendlich and Langmuir linear isotherm models were shown in figures 9 and 10. The high value of \( R^2 \) showed that the data was more consistent with Langmuir equation than Ferendlich equation. It shows the one-layer surface adsorption on nitrate on LDH.

**Table 1.** Parameters of Ferendlich and Langmuir isotherm models

<table>
<thead>
<tr>
<th>Catchy</th>
<th>Temperature ( ^\circ\text{C} )</th>
<th>Ferendlich isotherm</th>
<th>Langmuir isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( K_r )</td>
<td>( N )</td>
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<tr>
<td>LDH</td>
<td>23±2</td>
<td>2.576</td>
<td>1.2642</td>
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</table>
3. CONCLUSION

LDH synthesized by hydrothermal technique, as an artificial adsorbent manufactured at nano scale in the laboratory, could adsorb nitrate from aqueous solutions well. The thickness of nanoplates is about 20nm and their diameter is about 250nm. Balance time and optimal speed of stirring were considered at the point of 45 min and 250 rpm, respectively. The adsorption of nitrate almost remained stable with the changes of pH from 5 to 7 and it showed a slight decreasing trend. The optimal pH was considered 7. The maximum surface adsorption of nitrate on LDH was considered in the amount of 0.1 gr of LDH. 0.1 gr of LDH removed 80.97% of nitrate from 100ppm solution of potassium nitrate at optimal time, pH and stirring speed. The high value of R² showed that the data was more consistent with Langmuir equation than Ferendlich equation. Given the results, chloride-layered double hydroxide...
(LDH) nano-mineral manufactured in this study can be used as effective and efficient adsorbent for removal of nitrate from aqueous solutions. To prevent the pollution of surface and ground water which is an important problem of most soils in temperate zones, the use of this low-cost and environment-friendly clay mineral is sufficient for effective removal of nitrate.

4. REFERENCES


