Synthesis of Zinc-Aluminum Layered Double Hydroxides and Application of Adsorption for Nitrate from Water

Hamida Edan Salman and Nahlah Jaber Hussein

*University of Karbala, College of Education for Science, Department of Chemistry.

Email: drhamida@yahoo.com or nahlagaber1992@gmail.com

Abstract. Zinc-aluminum Layered double hydroxide was synthesized by co-calcination method in molar ratio Zn/Al 3:1. The prepared layered double hydroxide were characterized by Fourier-transform infrared spectra (FTIR), X-ray diffraction (XRD) and Atomic force microscope (AFM). The synthesized layered double hydroxides were used to study the adsorption of nitrate anion (NO$_3^-$) from water. The influence of some parameters on nitrate adsorption, including pH, temperature and adsorption of kinetics. The results showed that the adsorption of nitrate anion (NO$_3^-$) on the surface of the layers (Zn/Al-LDH) increases by increasing the temperature but decreases by increasing the pH and the adsorption of isotherm is following the Freundlich equation. The adsorption of kinetics were subjected to modified first grade false the Lagergren equation. The thermodynamic parameters, such as ($\Delta H_{ad}$, $\Delta G_{ad}$, $\Delta S_{ad}$) clarified that the adsorption on the Zn/Al-LDH is endothermic and spontaneous.

Keyword: Layered double hydroxide, Adsorption, Nitrate.

1. Introduction

Layer double hydroxide these layered double hydroxides (LDHs), also called anionic clays, are solids which resemble the naturally occurring hydroxotacites Mg$_6$Al$_2$(OH)$_{16}$CO$_3$.4H$_2$O. They can be described as positively charged layers of randomly distributed M$^{++}$(OH)$_6$ and M$^{++}$(OH)$_6$, edge-sharing octahedral, similar to those in the brucite, Mg(OH)$_2$ with the interlayer space being occupied by neutralizing hydrated A$^{-n}$ anions. These materials can be represented by the general formula.

[M$_{1-x}$M$_x$(OH)$_2$]$^{2+}$[A$^{-n}$/x$n$.n$^{-}$H$_2$O]$^{-n}$. Where:- M$^{++}$=Mg$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Ni$^{2+}$,...... M$^{3+}$= Al$^{3+}$, Cr$^{3+}$, Fe$^{3+}$, ...... and A$^{-n}$ = Cl$^-$, CO$_3^{2-}$, NO$_3^-$, ...... [1,2], in which:- M$^{++}$ represents a bivalent cation, M$^{3+}$ represents a trivalent cation, and ( A$^{-n}$) represents the intercalation anions, and variable amounts of interlayer water molecules. These can be simple inorganic anions, such as (Cl$^-$, F$^-$, CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$), but also organic anions, Complex anions and heteropolyanions, with charge n$^{-}$$. These compounds present properties, high porosity surface area, and interlayer anion mobility. Due to these properties. They can be applied as catalysts or catalysis supports, in sorption and adsorption processes, and in medicinal applications, pharmaceuticals, polymer reinforcement, or environmental clean-up by ion exchange[3,4,5].
Hydrotalcite is an anionic clay consisting of sheets of octahedral Zinc/ aluminum double hydroxides, intercalated with hydrated chloride anions. The residual positive charge in the surface of the crystallites of the hydrotalcite enables this class of material to be used as an adsorbent of organic anions, or inorganic anions. The use of these materials to remove organic pollutants has been reported in the literature[6,7]. The adsorption of the anionic surfactants in the solid – liquid interface occur, firstly by electrostatic interaction with the surface charge of LDH and then, by hydrophobic interaction between the organic anions[8,9,10].

There a number of factors strongly influence the adsorption process: (1) the nature of the structural groups on the surface; (2) the molecular structure of the surfactant being adsorbed the adsorbate; (3) the environment of the aqueous phase: its pH, electrolyte content, and its temperature[11]. "Figure 1" ,Show Structure of layered hydroxides ,there are used as a material for the ion of nitrates on their layers that carry a positive charge.

**Figure 1.** Structure of layered hydroxides

### 2. Experimental Part

#### 2.1. Preparation of Zn/Al-LDH.

Zn-Al-LDH was synthesized by coprecipitation technique these compounds were first prepared by the Preparation of (Zn/Al-LDH) by mixing (ZnCl₂/AlCl₃.6H₂O). The concentration of Zinc Chloride (ZnCl₂) salt (0.5M), at weight (6.814 g), and concentration of aluminum chloride (AlCl₃.6H₂O) is (0.16M), at weight (3.862 g), where 100 ml were preparation was (pH=8) by addition of a drops NaOH at a concentration (2M), with continuous stirring for 2h, and heating for (18h) and tuning at 70°C, the deposit was then separated by a centrifuge. The precipitate was filtered and washed with distill water, and dried at 70°C. All of the obtained products were then ground into fine powder and kept in sample bottle for further use [12].
\[
\begin{array}{l}
M^{2+} (Zn^{2+}) + M^{3+} (Al^{3+}) \\
\text{Ratio (Zn/Al) = 3:1}
\end{array}
\]

\[\text{↓} \]

Added of drops of NaOH

\[\text{↓} \]

pH=8

\[\text{↓} \]

Heating 70°C, 18h

\[\text{↓} \]

Separation + filtered washed

\[\text{↓} \]

Nano Compound

\[\text{↓} \]

Dried at 70°C

\[\text{↓} \]

Grinding + storage

\[\text{↓} \]

Diagnosis by FT-IR, X-RD, AFM

**Planned 1.** Shows how to prepare nano materials

2.2. *Calibration curve.*

A calibration curve has been identified which represents the relationship between absorption and concentration by preparing 5 sequential concentrations within the range (5-25ppm) of the NO$_3^-$ solution used in the study and then measuring the absorption of these concentration at wave length $\lambda_{\text{max}}(207.5)$nm of the ion NO$_3^-$ and then drawing the standard curve between absorption and concentration ,show is ‘**figure 2**’, Uv-Visible spectrum of sodium nitrate , and ‘**figure 3**’. show Calibration curve for sodium nitrate.
2.3. Characterization of Zn/Al-LDH.

The synthesized Zn/Al-LDH were characterized by XRD spectrophotometer to type Shimadzu PW-6000 diffractometer. The Fourier transform infrared (FTIR) spectra of the
solids were obtained, in the 400-4000 cm⁻¹ range, using KBr pellet technique and Atomic force microscope (AFM) was used for a surface scan of the prepared layered double hydroxide.

2.4. Kinetic studies.

The kinetic studies were carried out as follows: 0.15g adsorbent material (Layered double hydroxide) was added into (30ml) sodium nitrate at concentration the range (5-25 ppm) and the mixture at temperature (298K), and pH=7. The nitrate ion uptake by samples was calculated by the following Lagergren equation [13,14]:

$$\log(q_e-q_t)=\log q_e-(K_{ad}/2.303) \quad (1)$$

Was used to extract the average constant of the adsorption rate. This method depends on the difference between the amount of the adsorption equilibrium ($q_e$) and ($q_t$), quantity at time $t$.

Where:

$q_e$ = ($C_o-C_e$) unite (mg/L).

$q_t$ = ($C_o-C_t$) unite (mg/L).

$K_{ad}$: constant rate of adsorption its unite (min⁻¹).

$C_o$, $C_e$, and $C_t$ (mg/L) are initial, equilibrium and at time ($t$) of NO₃⁻ concentration respectively.

2.5. Adsorption isotherm.

The adsorption isotherm was determined using batch studies: 0.15g and (30ml) nitrate solution of various initial concentration (5-25 ppm) were poured into the volumetric flask. The time required to reach equilibrium as determined in equilibrium studies was (150 min). A series of isotherm were determined at the temperature of (298K). The adsorption amount [Qₑ(mg/g)] was obtained using the following equation [15]:

$$Q_e=[C_o-C_e]V/m \quad (2)$$

Were $V$(L) is the volume of solution, and $m$(g) is the adsorbent mass.

2.6. Effect of temperature.

For the purpose of studying the effect of temperature in adsorption studied isotherm adsorption of nitrate ions with different temperature is (298-318)K.
2.7 Effect of pH.

To study the effect of change in pH of solution in adsorption. The adsorption of NO$_3^-$ was studied on a surface layer double hydroxide for molecular proportions by the same method in determining the adsorption of isotherm and at values pH(2,4,7,9,12), the solution acid was modification using standard solution and using a device (pH-meter).

3. Results and Discussion

3.1. Characterization of Zn/Al-LDDH.

3.1.1 Fourier transform infrared spectra (FTIR).

The layers zinc /aluminum double hydroxide show several distinct beams certain frequencies, where the vibration range of the (O-H) set was shown at (3460) cm$^{-1}$, it is transverse package with interference from different types of hydroxyl group, such as hydroxide of layered and hydroxide of water which is physically adsorbed [16]. While the packet lies between (603)(430) cm$^{-1}$ to vibration bond (Al-O) and (Zn-O) [17] respectively. ‘Figure 4’, show is FTIR Spectrum of Zn/Al-LDH before the adsorption. The adsorption of the nitrate ions has many distinctive beams. This is evidence of the success of the adsorption process, the broad beam (3462 cm$^{-1}$) indicates the group vibration (O-H)[16], the beams (1363 cm$^{-1}$) indicate the presence of (NO$_3^-$) [18] between the layers of nano compound where packet lies between (603) (430) cm$^{-1}$ to vibration bond (Al-O), (Zn-O) [17] respectively. ‘Figure 5’, show is FTIR Spectrum after(NO$_3^-$) adsorption on Zn/Al-NO$_3$ LDH.

![FTIR Spectrum of Zn/Al-LDH](image-url)

**Figure 4.** FT-IR Spectrum of Zn/Al-LDH.
3.1.2 X-ray diffraction.

The x-ray diffraction of the layers double hydroxide was studied, ‘figure 6’. Shows the spectrum of the x-ray diffraction of layers zinc/aluminum double hydroxide, that the crystalline level (003) (006) (009), the crystal level (003) shows at the angle (11.289°), and crystalline dimension (d) (7.31 Å). While the level (009) shows at the angle (31.679°) and crystalline dimension (d) (2.822 Å). The crystal level (006) shows at the angle (22.668°), and crystalline dimension (d) (3.919 Å), but after the nitrate ion adsorption show change in the crystalline level (003), the crystal level (003) shows at the angle (12.201°), and crystalline dimension (d) (8.8 Å), was studied. ‘Figure 7’. Shows the spectrum of the x-ray diffraction of layers zinc/aluminum double hydroxide when nitrate ion adsorption.
Figure 7. X-ray Spectrum of Zn/Al-LDH after NO\textsubscript{3} adsorption.

3.1.3 Atomic Force Microscope (AFM).

The outer surface of the layers zinc/aluminum double hydroxide was studied using an atomic force microscope as shown in ‘Figure 8A’, tow-dimension image of layers double hydroxide. The tow- dimension image of layers double hydroxide showing molecular clusters of spherical shapes ‘Figure 8B’, shown a three-dimension picture of a section of the surface of the layers zinc/aluminum double hydroxide , it appears elevation of molecular of aggregation height the limit (19.26) nm and Sa (Roughness Average) is 3.6nm And Sq (Root Mean Square) is 4.31nm, Sy (Peak-Peak) is 19.1 nm and Sz (ten Point Height) is 18.8 nm. The means of particles size for layers double hydroxide there limit to (75.91nm). This indicates that compound is nano.

Figure 8. (A) Picture Tow –dimensional , (B) Picture Tree- dimensional for (Zn/Al-LDH) by atomic force microscopy
3.2. Adsorption isotherm.

The adsorption of sodium nitrate was studied on the surface of the (LDH) isotherm adsorption obtained as shown in ‘figure 9’ and table (1) show Isotherm adsorption of nitrate used on the surface (LDH) at a temperature (298K) and pH=7.

The graph shown that the general from of adsorption isotherm is the type ($S_2$) according to the Giles classification , which is based on the foundation of Frindlich for adsorption which indicating the surface is a heterogeneous surface [19].

The heat of adsorption decreases by increasing of the surface [20].The molecules are formed vertically on the surface and this confirms the increased form of isotherm by increasing the concentration of solution[21] ,it is also possible to deduce from these forms of isotherms that the overlap of the material absorbed with the surface takes place through force that include (Hydrogen bonding, dispersion force) [22]. Form (S) is often produced because the adsorption process is accompanied by the solvent molecules of dissolved molecules on the absorbent surface[23].

Nitrate adsorption date were treated according to the linear formulas of the following logarithmic equation [24]

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{............ (3)}$$

The table1, and ‘figure 9’, clears show the nitrate adsorption is identical to the equation of Frindlich and when drawing the linear relationship between $\log Q_e$ in contrast $\log C_e$ we get a straight line as in ‘figure 10’, show Frindlich precautions for adsorption of nitrate on the surface (LDH).

Sodium nitrate adsorption data were also processed in light of the linear relationship of Langmuir equation as shown in the ‘figure 11’ .Langmuir precautions for adsorption of nitrate on the surface (LDH).

When drawing the relationship values $C_e/Q_e$ and $C_e$ we get a straight line.

as a linear a relationship[25]:

$$\frac{C_e}{Q_e} = \frac{1}{a} + \frac{b}{a} C_e \quad \text{...................... (4)}$$

The experimental parameters and correlation coefficients were calculated from the date of these rectangle ,as shown in the table 3, show the values of Frindlich a constant of the nitrate on surface (LDH) .
Table 1. Adsorption of nitrate on the surface LDH at the temperature 298K and pH=7.

| Cₒ ppm | Ce(mg/L) | Qe(mg/g) |
|--------|----------|----------|
| 5      | 3.007    | 1.328    |
| 10     | 5.872    | 2.752    |
| 15     | 6.769    | 5.487    |
| 20     | 7.517    | 8.322    |
| 25     | 9.540    | 10.306   |

Figure 9. Isotherm adsorption of nitrate used on the surface (LDH) at a temperature (298K) and pH=7.

Table 2. The logarithms of each Ce,Qe nitrate composition.

| Cₒ ppm | Log Ce | Log Qe |
|--------|--------|--------|
| 5      | 0.478  | 0.411  |
| 10     | 0.768  | 0.439  |
| 15     | 0.830  | 0.739  |
| 20     | 0.876  | 0.920  |
| 25     | 0.979  | 1.013  |
Figure 10. Frindlich precautions for adsorption of nitrate on the surface (LDH).

Figure 11. Langmuir precautions for adsorption of nitrate on the surface (LDH)
Table 3. The values of Frindilch a constant of the nitrate on surface (LDH).

| $K_f$  | $N$  | $R^2$ |
|-------|------|-------|
| 0.812 | 1.855| 0.917 |

3.3. Effect of temperature.

A study of the effect of temperature in the adsorption of the compounds used in this study according to the different molar ratios and in the experimental temperature range (298-318)K as show in the table 4, effect of temperature rang (298-319)K in the adsorption on nitrate to the surface (LDH). *Figure 10*, show Adsorption Isotherm of sodium nitrate on the surface (LDH) at different temperature.

The experimental results indicate that the adsorption of these compound increases by increasing the temperature ,ie this is a type (endothermic process) [26].This is evidence of the absorption process in addition to the process of adsorption in the sense of the sorption process. As the temperature increases ,the adsorbed particles spread inside the surface pores become more rapid [27 ].

Table 4. Effect of temperature in the adsorption of nitrate on the surface LDH within the experimental temperature range(289-318)K.

| $C_a$ Ppm | 298K Ce(mg/L) | Qe(mg/g) | 308K Ce(mg/L) | Qe(mg/g) | 318K Ce(mg/L) | Qe(mg/g) |
|-----------|--------------|----------|--------------|----------|--------------|----------|
| 5         | 1.943        | 2.038    | 1.869        | 2.087    | 1.584        | 2.277    |
| 10        | 3.850        | 4.100    | 3.534        | 4.310    | 2.954        | 4.697    |
| 15        | 4.335        | 7.110    | 3.955        | 7.363    | 3.586        | 7.709    |
| 20        | 5.546        | 9.636    | 4.556        | 10.296   | 4.124        | 10.584   |
| 25        | 6.158        | 12.561   | 5.631        | 12.912   | 5.114        | 13.257   |
3.4. Effect of pH.

Generally pH is considered to be an important parameter which controls the adsorption at water-adsorbent interfaces. In this view, the adsorption of NO$_3^-$ (25mg/L) by Zn/Al-LDH (0.2g) was studied at different pH values ranging from (2-12) at an ambient temperature of (298K).‘Figure 13’, show Adsorption Isotherm of Sodium nitrate on the surface (LDH) at different pH (298K).

The table 5, show effect of pH in adsorption sodium nitrate on the surface LDH at temperature 298K .

According to the results obtained an increase in the adsorption amount was shown on the surface of the(LDH) ,when pH (2,4) compared with the neutral and base mean .This is due to increases of protonation on the surface and increases of positive charge concentration of the surface which increases the amount if adsorption [28].

In the base center a decrease in the amount of the ion adsorbed occurs due to decrease of protonation on the surface [29], and the negative charge will be concentrated on the negative ion carrier ,so the adsorbed quantity will decrease as a result of the discrepancy between the negative surface charge with the negative ion and the hydroxide ion on the surface [30].

So the order :-pH=2>4>7>9>12.
Table 5. Effect of pH in adsorption sodium nitrate on the surface LDH at temperature 298K.

| C₀ ppm | pH=2  | pH=4  | pH=7  | pH=9  | pH=12 |
|--------|-------|-------|-------|-------|-------|
| Ce (mg/L) | Qe (mg/g) | Ce (mg/L) | Qe (mg/g) | Ce (mg/L) | Qe (mg/g) | Ce (mg/L) | Qe (mg/g) | Ce (mg/L) | Qe (mg/g) |
| 5      | 1.314 | 2.457 | 2.280 | 3.007 | 3.821 | 0.786 | 4.013 | 0.658 |
| 10     | 2.659 | 4.894 | 5.440 | 5.872 | 2.752 | 6.245 | 2.503 | 6.762 | 2.158 |
| 15     | 3.787 | 7.475 | 7.102 | 6.769 | 5.487 | 7.634 | 4.910 | 8.432 | 4.378 |
| 20     | 5.104 | 9.930 | 8.217 | 9.432 | 7.517 | 8.322 | 9.104 | 7.364 | 9.756 | 6.829 |
| 25     | 6.579 | 12.280 | 9.654 | 11.796 | 9.540 | 10.306 | 9.638 | 11.086 | 9.276 |

Figure 13. Adsorption Isotherm of Sodium nitrate on the surface (LDH) at different pH at temperature (298K).

3.5. Adsorption of kinetics.

Kinetic models are used to test experimental data from the adsorption of nitrate (NO₃⁻) onto Zn/Al-LDH. These Lagergern equation models include the pseudo-first-order model. The kinetic models can be linearized as shown in table 6 and ‘figure 14’, shows effect of change the primary concentration of sodium nitrate in adsorption kinetics on surface (LDH) at 298K and pH=7. The results obtained were treated according to equation (3), the value Kₐₐ was calculated from the slope of the linear relationship between Log(qₑ-𝑞ₙ) and t (time) as shown in table 6 and ‘figure 14’, the effect of the change in primary concentration at constant pH and temperature in the kinetics of adsorption of sodium nitrate is shown the smaller concentration of nitrate solution the amount of Kₐₐ increased [31].
**Table 6.** Effect of change the primary concentration of sodium nitrate in adsorption kinetics on the surface of the (LDH) at temperature 298K and pH=7.

| Time (min) | $C_o=5$ ppm |         | $C_o=10$ ppm |         |
|-----------|-------------|---------|--------------|---------|
|           | $q_t$ (mg/L) | $(q_e-q_t)$ | $Log(q_e-q_t)$ | $q_t$ (mg/L) | $(q_e-q_t)$ | $Log(q_e-q_t)$ |
| 15        | 1.534       | 0.459   | -0.338       | 3.461   | 0.667   | -0.175 |
| 30        | 1.687       | 0.306   | -0.514       | 3.632   | 0.496   | -0.304 |
| 45        | 1.795       | 0.198   | -0.703       | 3.745   | 0.383   | -0.416 |
| 60        | 1.865       | 0.128   | -0.892       | 3.876   | 0.252   | -0.598 |
| 75        | 1.900       | 0.093   | -1.031       | 3.967   | 0.161   | -0.793 |
| 90        | 1.928       | 0.065   | -1.187       | ....... | ....... | ....... |

$q_e=1.993$ (mg/L) \hspace{.5cm} q_e=4.128$ (mg/L)

| Time (min) | $C_o=15$ ppm |         | $C_o=20$ ppm |         |
|-----------|-------------|---------|--------------|---------|
|           | $q_t$ (mg/L) | $(q_e-q_t)$ | $Log(q_e-q_t)$ | $q_t$ (mg/L) | $(q_e-q_t)$ | $Log(q_e-q_t)$ |
| 15        | 7.388       | 0.843   | -0.074       | 11.546  | 0.937   | -0.028 |
| 30        | 7.533       | 0.698   | -0.156       | 11.676  | 0.807   | -0.039 |
| 45        | 7.723       | 0.508   | -0.294       | 11.811  | 0.672   | -0.172 |
| 60        | 7.822       | 0.409   | -0.388       | 11.907  | 0.576   | -0.239 |
| 75        | 7.947       | 0.284   | -0.546       | 12.047  | 0.436   | -0.360 |
| 90        | 8.032       | 0.199   | -0.701       | 12.135  | 0.330   | -0.481 |

$q_e=8.231$ (mg/L) \hspace{.5cm} q_e=12.483$ (mg/L)

| Time (min) | $C_o=25$ ppm |         |
|-----------|-------------|---------|
|           | $q_t$ (mg/L) | $(q_e-q_t)$ | $Log (q_e-q_t)$ |
| 15        | 14.547      | 0.913   | -0.039 |
| 30        | 14.646      | 0.814   | -0.089 |
| 45        | 14.765      | 0.695   | -0.158 |
| 60        | 14.906      | 0.554   | -0.256 |
| 75        | 15.021      | 0.439   | -0.357 |
| 90        | 15.100      | 0.360   | -0.443 |

$q_e=15.460$ (mg/L)
Figure 14. Draw straight lines Lagergren for nitrate adsorption on the surface the LDH at different the primary concentration at its temperature 298K and pH=7.

Table 7. Values of $K_{ad}$ at the difference concentration for the sodium nitrate on the surface (LDH) at a temperature 298K and pH=7.

| $C_o$ ppm | $K_{ad}$ min$^{-1}$ $\times 10^{-2}$ |
|-----------|----------------------------------|
| 5         | 2.625                            |
| 10        | 2.349                            |
| 15        | 1.934                            |
| 20        | 1.381                            |
| 25        | 1.289                            |
3.6. Thermodynamic Study of Nitrate adsorption by Zn/Al-LDH.

The thermodynamic parameters provide information about the inherent energetic changes associated with the adsorption process.

Enthalpy ($\Delta H$) of the calculated from the slope when drawing the relationship between $[\text{Log } X_m]$ and $[1/T]$ in the rang (298-318)K as shown in table 8 and figure 15. Were calculated using the following (Vant-Hoff-Arrhenius equation) [32].

$$\text{Log } X_m = \frac{-\Delta H}{2.303RT} + \text{Con} \quad \text{(5)}$$

And the calculated free energy ($\Delta G$), ($\Delta S$) were obtained from the following equation [33-35].

$$\Delta G = -RT \ln (Q_e/C_e) \quad \text{(6)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(7)}$$

Where :

R: is the universal gas constant ($8.314 \text{ J/mol K}$).

T(K): is the temperature.

Log $X_m$: Logarithm is the greatest amount of exertion (mg/g).

Table 9, a shows the values ($\Delta H_{ad}, \Delta S_{ad}, \Delta G_{ad}$) for sodium nitrate on the surface LDH. The positive of ($\Delta H$) values indicate that adsorption on the surface of the layers Zinc/Aluminum double hydroxide is (endothermic) [36].

And negative of ($\Delta G$) values indicate that adsorption on the surface of the layers Zinc/Aluminum double hydroxide is (spontaneous) under experimental conditions [37].

The positive of ($\Delta S$) can be attributed to the fact that the adsorbed and overlapping molecules are less regularity than there from in the solution when both adsorption and absorption occur [31].
Table 8. The values (1/T) and LogXm of sodium nitrate adsorption on the surface LDH within the experimental thermal range (298-318)K.

| T(K) | 1/T (K⁻¹)×10⁻³ | LogXm |
|------|----------------|-------|
| 298  | 3.355          | 1.099 |
| 308  | 3.246          | 1.110 |
| 318  | 3.144          | 1.122 |

Figure 15. Relationship between (1/T) and Log Xm for sodium nitrate adsorption on the surface LDH.

Table 9. Shows values (ΔH_{ad}, ΔS_{ad}, ΔG_{ad}) for the sodium nitrate on the surface LDH.

| T(K) | ΔH_{ad} (J/mol) | ΔG_{ad} (J/mol) | ΔS_{ad} (J/mol.k) |
|------|-----------------|-----------------|-------------------|
| 298  | -1766.6         | 12.953          |
| 308  | 2094.1          | -2124.8         | 13.697            |
| 318  | -2518.2         | 14.504          |
Conclusion

Prepared of layers double hydroxide Zn/Al-LDH and it was used as adsorbent material for adsorption of nitrate ions (NO$_3^-$). The results showed that the amount of adsorption increases with increases temperature, the adsorption process (endothermic process) and spontaneous. The type of adsorption is physical. But when increases of pH decreases the amount of adsorption, and kinetic of adsorption tracking the first order rank of laguerren. The $K_{ad}$ increases when the concentration of smaller.

Reference.

[1] Chiron N., Cuilet R., Deydier E., 2003, Adsorption of Cu(II) and Pb(II) onto a grafted Silica isotherm and kinetic models, Water Research, (17), P 3079-3086.

[2] Rives V., Ulibarr M.A., 1999, Layered double hydroxide (LDH) intercalated with metal coordination compounds and oxometalates, Coordination Chemistry Reviews, (181), P101-120.

[3] Chang Z., Evans D.G., Duan X., Vail C., Chanbaja J., Prevote V., 2005, Synthesis of [Zn/Al-CO$_3$]$_n$ Layered double hydroxide by a co-precipitation method under steady state condition, Journal of solid stat. Chemistry, (178), P 2766-2777.

[4] Wang Z., Wang E., Gao L., L. Xu, 2005, Synthesis and properties of Mg$_2$Al Layered double hydroxide containing 5-Fluorouracil, Journal of solid state chemistry, 178, P 736-741.

[5] Nalawade P., Aware B., Kadam V.J., Hirlekar R.S., 2009, Layered double hydroxide: A review, Journal of Scientific and Industrial Research, 68, P 267-272.

[6] Pavan P.C., Crepaldi E.L., Valim J.B., 2000, Sorption of anionic surfactants on layered double hydroxides, Journal of Colloidal Interface Science, 229, P 346-352.

[7] Cardoso L.P., Tronto J., Crepaldi E.L., Valim J.B., 2003, Removal of benzoate anions from aqueous solution using Mg – Al layered double hydroxides, Molecular Crystals and Liquid Crystals, 390, P 49 – 56.

[8] Scamehorn J.F., Schechter R.S., Wade W.H., 1982, Adsorption of surfactants on mineral oxide surfaces from aqueous solutions, Journal of Colloidal Interface Science, 85, P463 – 478.

[9] Huang L., Somasundaran P., 1996, The change in structure of surfactant aggregates during adsorption/desorption processes and its effect on the stability of alumina suspension, Colloids Surface, A 117, P235-244.

[10] Lopata J.J., Harwell J.H., Scamehorn J.F., 1998, Adsorption of binary anionic surfactant mixtures on a-alumina, ACS Series on Surfactant Based Mobility Control, American Chemical Society, Washington, DC, (chapter 10), p. 205.
[11] Reis M.J.D., Silverio F., Tronto J., Valim J.B., 2004, Effect of PH, Temperature, Ionic Strength on Adsorption of Sodium Dodecylbenzen Sulfate into Mg-Al-CO₃ Layered Double Hydroxide, Journal of physics and chemistry of solids, 65, P487-492.

[12] Ishilkawa T., Matsumoto K., Kandori K., and Nakayama T., 2006, Synthesis of Layered Zinc Hydroxide Chlorides in the Presence of Al(III), Journal of solid state chemistry, 179, P110.

[13] Lagergren S., (1990) Bilik. Svenska Vetenskap Han 1.24 as cited by G.S. Gnpta, G. Prason and V.N. Singh. Water Res., 24, P45-50.

[14] Singh A.K., Singh D.S., Pandey K.K., and Singh V.N., 1988, Wollastonite as Adsorbent for Removal Fe(II) from Water, J. Chem. Technol. Biotechnol., 42, 39.

[15] Murrel J.N., and Buchrt E. A., 1974, Properties of Liquide and Solution, Jhon Wiley and sons, 47(3).

[16] Cardoso L.P., Celis R., Cornejo J., and Valim J., 2006, Layered Double Hydroxides as Supports for the Slow Release of Aside Herbicides, J. Agric. Food Chemistry, 54, P 5968.

[17] Bin M.Z., Hussein, Bahar F.A., and Yahaya A.Hj., 2010, Synthesis and Characterization of Hippurate- Layered double hydroxide Nanohybrid and Investigation of its Release Property, J. Iran Chemistry society, Vol. 7, P45.

[18] Comejo J., Celis R., Avlovic L.P., Ulibarri M.A., and Hermosin M.C., 2000, Structural Changes in Phenol-intercalated hydrotalcite caused by heating, J. Material Chemistry, 35, P 771.

[19] Charles H.G., Anthong P.O., and Eston L., 1974, J.of colloid and interface science, 47(3).

[20] Al-Banis T.A., Hela D.J., Sakellarid T. M., and Danis T.G., 2002, J. Chem., Vol(2), No.3, PP.237-244.

[21] Kipling J. J., 1965, Adsorption from Solution of Non, Electrolytes Academic press.

[22] Giles C.I., and Smith D., 1974, J. Colld. Interface. sci., 47, 111.

[23] Giles C.H., and Anthouy P., 1974, J. Colld. Interface. sci, 47, 766.

[24] Metcalf and Eddy, 1991, Waste water Engineering, 3rd ed, 317.

[25] Langmuir L., 1918, J. Amer. Chem. Soc., 40, 1361.

[26] Khawla Kani Jassim, 2003, A clay Alkawelin in the adsorption toluene and Aniline and some of its deriatives, Master thesis, University of Kufa.

[27] Rovi V.P., Jasra R.V. and Bhat T.S.G., 1998, J. Chem. Technol Biotechnol., 71, 173-179.
[28] Grommena R., Hauteghem I.V., Ambeke M.V.W and Erstraete W.V.V., 2002, An improved Nitrifying Enrichment to Remove Ammonium and Nitrate from freshwater Aquaria systems, Aquaculture, 211, 115-124.

[29] Aoki T., Munemori M., 1982, Water Rose, 16, 793.

[30] Amsiveayam C.N., Angeetha D., 2005, Removal and Recovery Nitrate from Water by ZnCl₂ Activated Carbon from Coconut Core Pith, an agriculture solid Waste, India. Journal Chemical Technology, Vol. 12, pp 513, 521.

[31] Panday K.K., Prased G., Singh V.N., 1984, Removal of Cr(VI) from Aqueous Solution by Adsorption on Fly ash Wollastonite, J. Chem. Technol. Biotechnol. A-Chemical Technology, 34, p. 367-74.

[32] Weber J.Jr., and Morris J.C., 1968, Kinetics of Adsorption on Carbon from Solution, J. Sant. Engng Div. Am. Soc. Cir. Engrs, Vol. 89, p. 31.

[33] Panday K.K., Gup Prasad and Singh V.N., 1985, Water Res., 19 (7), pp. 869-973.

[34] Jalal Mohammed Saleh, 1980, Surface Chemistry and, First Edition, University of Baghdad, p36, 13, 68.

[35] Shaw J.D., BSC, 1980, Introduction to Colloid and Surface Chem. 3rd.

[36] Al-Hajimi, S. Abdul-mahdi, 2006, Preparation and Study of adsorption Kinetics for 2-[(3-hydroxy phenyl) iso]-4,5-di phenyl imidazole, Master thesis, college of Education for girls, University of Kufa.

[37] Mahdi Naji Zakum, 1982, Introduction to Analytical and Physical Chemistry, Faculty of Science, University of Basrah, 127-Second edition, p285.

[38] Al-Khudhiry, Abed Z.M., M.Sc. Tesis, 2002, University of Baghdad.