Synthesis and Characterization of Ni/Al-LDH nano hybrid with (Ascorbic acid) and Kinetic Controlled Release Study of (Ascorbic acid) From Ni/Al-LDH

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Abstract. The study include synthesis of hybrids nanocompound through a process intercalation of ascorbic acid in Ni/Al –LDHs by direct and indirect ion exchange. Nano layer, which make it has high ability to build up the useful ascorbic acdinter the layers direction on the human body. Limit the side effect of high concentration of ascorbic acidinhuman body. Characterization of this compound by X-Ray diffraction technique and FT –IR spectrophotometer before and after intercalation formation of nano compound, then cooperation to sure the form hybrid nanocompound and the two and three dimensional image of the above compound in (AFM) for the nano compound. The results showed the release of hybrids to specific liquids in different (Na2CO3, Na2SO4 ) concentration (0.5)M by direct ion exchange method. On the other hand the whole process is subject to model by pseudo-second order rate expression according to Lagregrans equation. It has been studied the percentage of rate release for both anionic (Ascorbic acid) from Ni/Al –LDHs. The results were as follows: High percentage of release in different liquid follows this arrangement: Na2CO3> Na2SO4. The result explains the ratio control release of anion from nanolayerhybrid prepare by indirect ion exchange process more hourly than release anion from nanolayershybridprepared by direct ion exchange.

Keywords. LDHs, L-ascorbic acid, nano hybridcompund

1. Introduction
Important biological of drugs and vitamins materials on the human body which has a wide using in health so to reduce the side effect of drags by using a control release of molecular as ion with nanotechnique of layers double hydroxide (LDHs) [1]. This layer are widely define as an ionic clay or hydrotalcite-like compound and often called anionic clay comparing with the more conventional cationic clay [2].is the majority often investigated anionic clay and is infrequently found in nature. The chemical composition of LDHs is represented by common formula [3].

\[ [\text{M}^{2+1-x}\text{M}^{3+ x}(\text{OH})_{2x}]+[\text{An}^{-x/n-}.Y\text{H}_{2}\text{O}]x^- \] 

divalentcation such as M\(^{2+}\) = Mg\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\) is a trivalent cation such as M\(^{3+}\) = Al\(^{3+}\), Fe\(^{3+}\), Cr\(^{3+}\), Ga\(^{3+}\), V\(^{3+}\). Mg\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), A\(^n-\) is an ion exchangeable anion such as OH\(^-\), Cl\(^-\), NO\(^3-\), CO\(^3-\), SO\(^2-\) and different organic anions [4, 5]. The x value is equal to the ratio M\(^3+/\) (M\(^2++\)M\(^3+\)),(0.2-0.33) [6, 7]. This value is ascribed to the charge density of the hydroxide basallayer, specifically, anion exchange capacity [8].LDHs layer have a positive charge diffusion on the surface of them due to the M\(^+3\) substituted forthe M\(^+2\),and the interlayer is neutralized by the intercalation of anions and water molecules. The intercalation of diverse anions into LDHs has
been classify by the following methods: calcinations-rehydration (reconstruction), ion exchange, co-precipitation, thermal reaction and hydrothermal reactions freshly, LDHs layers are play as a host substance to produce a new organic–inorganic nano hybrid material [9]. The organic-LDHs nanohybrid materials have been nanostructure and new function and expected to possess a novel The production of bimolecular-LDH nanohybrid compounds in fastidious has happen to of great important [10]. For a reality, the intercalation of the bimolecularor instancenucleotide [11] deoxyribonucleic acid [12] polypeptide [13] and amino acid [14] into LDHs was described in order to prepare the bio molecular/LDH nano hybrid compounds. LDH layer (Hydrotalcite-like) is recognized to be biocompatible materials and has originate medical applications as antacid. as well, the intercalated between drug molecules in the formanionic and various LDHs, the purpose of the study of intercalation compounds as materials then controlled release of drug [15, 16] ascorbic acid (ASA) vitamin C is most important to a body systems. Vitamin C plays a good role in the impervious system to fight unknown invaders and tumor cells and also supports the cardiovascular tissue and the free radical damage. The search is intercalation of drug anionicsuch as vitamin A, C and E by the ion exchange and co-precipitation methods, in addition, the controlled release of their vitamins from vitamin-LDH nanohybrid compounds was study by ion exchange method [17, 18].

In this work the layer able to intercalation the active molecule as ascorbic acid or any other drugs as anion in two layers, where layers are host and an ions are agents, because of high concentration of ascorbicacid may causes cancer and breaking down (DNA) so we most using control release by application the nanotechnique.

2. Materials and Methods

2.1. synthesis of Ni/Al-LDHs by co-precipitation method

The natural NO3 -LDHs were prepared by a usualCo-precipitation method. A mixed solution of(0.1M) of (Ni(NO3)2 . 6H2O) and(0.05M) of (Al(NO3)3.9H2O) when molar ratio (R=2/1), was drop and drop to (0.1 M)Na2NO3 solution at 298 K with stirring and it reduces at its temperature250C for 12 h. The solution pH was adjusted at (6.5) for the Ni/Al-LDHs bydrop wise addition of (2M ) NaOH solution through the step by step of the mixed solution separate the precipitate the washing by D.W and drying at room temperature figure 1 [19].

Figure 1. Schematic representation of the LDH structure [1].

2.2. Kinetic Controlled Release of (Ascorbic acid)

Using direct ion exchange to release V.C from honest (Ni/Al-LDHs) to dilute solution (0.5M) from Na2SO4, Na2CO3, then measure the release concentration of ionion by U.V ray at the λmax.

2.3. Study of percentage to release ascorbic acid from nanohybrid compound
Using U.V ray to study percentage to release inion, by taking solution (0.001g) nano compound dissolve in (3.5mL) from HCl (2M) then measure the absorbance at \( \lambda_{\text{max}} \) to determine the total concentration of inion in layer CT as the following equation

\[
\% = \frac{C_t}{C_T} \times 100 \quad \text{.....(1)}
\]

3. Result and Discussion

Figure (2) explains the spectra of X-Ray diffraction through the different in the value of thin layer before and after intercalation the inion ion inter the layer by using the Bragg low \[20\] \((2\sin\theta=n\lambda)\) while \((\lambda=1.540562\text{Å})\), \(n=1\) is the different in value of the thin layer causes by the effect of volume and the chemical structure for the organic molecular in the layer double hydroxide, and figure show the crystal level is \((hkl)\) from \((003)\) until \((0012)\), the before the intercalation \(d=8.5\text{Å}\) of \((003)\) is angle \(5^\circ\), after the intercalation of ascorbic acid \(d=10.8\text{Å}\) at the same of the crystal level the angle is deflection \(4.2^\circ\), this result show the succeed intercalation of ascorbic acid between Ni/Al LDHs.

![Figure 2. Powder X-ray diffraction patterns for: (a) Ni/Al NO3–LDHand (b) Ni/Al – VC](image)

Figures (3, 4, 5) explains FT-IR spectrum of ascorbic acid (VC), (Ni/Al – NO3–LDH) and (Ni/Al – VC-LDH). The ascorbic acid (VC) shows the assimilation peaks of alkyl \(\nu\text{C–H}\) stretch in the \((2964\text{cm}^{-1})\), The assimilation peaks of cycle \(\nu\text{C–H}\) stretch in the \(2900\text{cm}^{-1}\), wide absorption peak in the \((3344–3416\text{ cm}^{-1})\) area is assigned to \(\nu\text{O–H}\) group stretches and weak absorption peak of \(\delta\text{-OH}\) at \(1323\text{cm}^{-1}\) of absorption peaks of \(\nu\text{C–C}\) stretch at \((2025 \text{ cm}^{-1})\) hydroxide, absorption peaks of alcohol \(\nu\text{C–O}\) stretch at \(1093\text{cm}^{-1}\), absorption of \(\nu\text{(C=O)}\) \((1753\text{cm}^{-1})\), absorption peaks of \(\nu\text{(C=C)}\) in \((1402-1456 \text{ cm}^{-1})\) area, absorption two peaks of \(\nu\text{(C-O-C)}\) at \((1141 \text{ cm}^{-1})\) and \((1224 \text{ cm}^{-1})\) \[21\]. 

| Table 1. Peaks of the Ascorbic acid (VC) |
|-----------------------------------------|
| Frequency | \(\nu\text{C-H}\) | \(\nu\text{C=H}\) | \(\nu\text{C-O}\) | \(\delta\text{C-H}\) | \(\delta\text{C-O}\) | \(\nu\text{C-O-C}\) |
| Aliphatic | Cycle | Achole | Achole | cycle | Achole | cycle | Achole |
| Peaks | 2964 | 2900 | \(3416-3344\) | 1323 | 829 | 1093 | 1753 | 1402, 1456 | 2025 | 1141, 1224 |
Figure 3. FT-IR of ascorbic acid (VC)

The double hydroxide layers, (Ni/Al – NO₃-LDH) indicate that the saturation spikes to υO–H group stretches at (3443 cm⁻¹) and low saturation points of δ-OH at (1639 cm⁻¹) [22], the NO₃ saturation spike at(1386 cm⁻¹) in the LDHs [23], consumption spike to υ(Ni–O) at (408 cm⁻¹) in layers and, absorption peaks to υ(Al–O) at (621 cm⁻¹) in layers [24], see the table (2) and figure (4).

Figure 4. FT-IR of (Ni/Al – NO₃-LDH)

Table 2. Peaks of the (Ni/Al–NO₃-LDH) and the nano compound (Ni/Al–VC-LDH)

| Frequency | Hybrid compound | LDH |
|-----------|-----------------|-----|
| υ_Ο–Η     | 3497            | 3443|
| O–Η δ     | 1635            | 1639|
| υ_С–Η     | 2854            | -----|
| Aliphatic | 2766            | -----|
| υ_С–Η     | 2766            | -----|
| Cycle     | 2088            | -----|
| C=O       | 1790 , 1763     | -----|
| υ_NO₃     | 1386            | 1386|
| υ_С=О−С   | 1082            | -----|
| υ_С=О−С   | 1051            | -----|
| C–H δcycle| 835             | -----|
| υ_Ni–O    | 414             | 408 |
| Al–Ο υ    | 599             | 621 |
| C–H δ     | 682             | -----|

Figure 5 explains the study was characterized by using atomic Force Microscope (AFM) for the two and three-dimensional image in nano compound the figure (6A) were show the two-dimensional image molecular assemblies is a related spherical shapes, while figure (6B) were show the three-dimensional image high molecular assemblies which has limits range (50-320 nm) indicating the manufacture of the nano compound.
3.1. The kinetic of ion exchange

To study the kinetic for ion exchange (Ho and Mckay) [26] used Lagergran [27] equation to zero order, first order and second order as the following:

\[ C_t = K_0 \cdot t \] ……..(2)

\[ -\log \left( \frac{C_t}{C_t^0} \right) = \frac{K_1 \cdot t}{2.303} \] ……..(3)

\[ \frac{C_t}{C_t^0} = \frac{1}{K_2 \cdot t} + \frac{C_t^0}{C_t} \] ……..(4)

- \( C_t \) = concentration at each time by (mg. L⁻¹)
- \( C_t^0 \) = concentration at equilibrium by (mg. L⁻¹)
- \( K_0 \) = constant rate ion exchange zero model by (mg. L⁻¹. min⁻¹)
- \( K_1 \) = constant rate ion exchange first model by (min⁻¹)
- \( K_2 \) = constant rate ion exchange second model by (mg⁻¹. L. min⁻¹)
- \( t \) = reaction time by (min)

Through the note of table (3) and the kinetic figures for (VC) release from the nano compound prepare by (direct ion exchange and in direct ion exchange) ((7A,B,C,D,E,F) in sodium carbonate and sodium sulfate medial and the value (r²) we note that the kinetic of ion exchange is model second order.

**Figure 5.** AFM image of nano compound (Ni/Al – VC-LDH), (6A) two-dimensional image, (6B) three-dimensional image.

**Figure 6.** Lagergran equation model zero order (A) ion exchange in sodium carbonate (B) ion exchange in sodium sulfate.
Figure 6. Lagergian equation model first order (D) ion exchange in sodium carbonate (C) ion exchange in sodium sulfate.

Figure 6. Lagergian equation model second order (E) ion exchange in sodium carbonate (F) ion exchange in sodium sulfate.

Table 3. value for \( (r^2, k_0, k_1, k_2) \) to equation zero, first and second order for release ion exchange from the nano compound layer prepare in ethanol by direct and in direct ion exchange in (0.5M) sodium carbonate and sodium sulfate.

| Nano compound prepare by direct ion exchange | Second order | First order | Zero order |
|---------------------------------------------|--------------|-------------|------------|
| R^2 | K_2 | L / mg. min | R^2 | K_1 | l/min | R^2 | K_0 | Mg/min.L | Sample |
| 0.9878 | 1.219 | -2.49 | 0.018 | 0.861 | 0.009 | Na_2CO_3 |
| 0.9919 | 0.965 | 0.731 | 0.108 | -0.743 | 0.006 | Na_2SO_4 |

When we note the value for the constant rate second \( (k_2) \) at figure (1) result the rate kinetic release in different medial is as the following:

Na_2CO_3 => Na_2SO_4. The causes is that carbonate ion more electro file compare with sulfate ion and the figure of carbonate is triangular so is easily intercalation with LDH than sulfate ion which is tetragonal pyramid [28].
3.2. Study percentage release for ascorbic acid
The percentage release of Ascorbic acid (VC) from the hybrid nano compound prepare in ethanol by direct and in direct ion exchange at (0.5M) from sodium carbonate and sodium sulfate medial used the linear equation % Release = Ct/Cf *100.

Figure 7. Percentage of release (VC) between the nanohybrid compound in equas model from sodium carbonate (0.5M), ((A) prepare nano compound by direct ion exchange method), ((B) prepare nano compound by indirect ion exchange method).

Figure 7. Percentage of release (VC) between the nanohybrid compound in aquas model from sodium sulfate (0.5M), ((C) prepare nano compound by direct ion exchange method), ((D) prepare nano compound by indirect ion exchange method).

Table 4. Value for (percentage for release anion (VC)) by ion exchange method from the nano compound layer prepare in ethanol by direct and in direct ion exchange in (0.5M) sodium carbonate and sodium sulfate.

| t (min) | % Ascorbic acid | Concentration Mol. L⁻¹ | Sample | Sample |
|---------|-----------------|------------------------|--------|--------|
| 30      | %95             | 0.5                    | Na₂CO₃  | 2      |
| 30      | %69             |                        | Na₂SO₄  |        |

Nano compound prepare by indirect ion exchange

| 70      | 23 %            | Na₂CO₃                  | 2      |
| 70      | 5 %             | Na₂SO₄                  |        |
See the figure (8) and the table (4) from the results we note the high value for percentage is the following Na₂CO₃ > Na₂SO₄. The percentage for in ion is high value in direct method than in direct method [28].

4. Conclusion

The result appeared can be prepare nanocompound hybrid by intercalation of drugs compound Ascorbic acid as anion between nickel /aluminum double layer hydroxide by two method direct ion exchange and indirect ion exchange. And study control release by direct ion exchange process to limited the adverse effect of ascorbic acid or other drugs on human safety. Where the kinetic control release is second order at (0.5M) from sodium carbonate and sodium sulfate. The high value kinetic and percentage release at sodium carbonate. The study suggested ability use nickel/aluminum double layer hydroxide as drugs chemicalmaterial that control release of the drugs that enter human body to limited the dangerous and the adverse effect may be happen. This method is unexpensive, economic, high concentration of ascorbic acid with less or no adverse effect can occur.

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