Chapter 4
Integration and Analysis of Zinc-Aluminium-Layer Double hydroxide-2-oxo-L-threo-hexono-1,4- lactone-2,3-enediol and Its Controlled Released Properties With Various Types of Aqueous Media.

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Abstract

2-oxo-L-threo-hexono-1,4- lactone-2,3-enediol or also known as Ascorbic acid (ASA), vitamin C was successfully intercalated between Zn-Al layered double hydroxide, Zn-Al-LDH inorganic host is synthesis by co-precipitation method at pH 7.0 ±0.5 and Zn and Al molar ratio of 4. Both PXRD and FTIR result conform that the ASA was successfully intercalated into the Zn-Al-LDH interlayer. The X-Ray diffraction pattern showed that the expansion of basal spacing from 8.9 Å in the Zn-Al-LDH change to 11.7 Å is because of intercalation of ASA occur into the Zn-Al-LDH (intercalation of ASA into Zn-Al-LDH). The most importance feature in FTIR spectrum for Zn-Al-ASA is the disappearance of nitrate absorption band (at 1351cm⁻¹) and the presence new band at 1613cm⁻¹, due to the presence of C=C alkene, which conforms the intercalation of ASA in the ionic form in the interlayer of the LDH. The percentage saturated released of the ASA is in order of phosphate > carbonate > chloride with percentage saturated released 92 %, 64 % and 42 % respectively. This study shows that the Zn-Al-layered double hydroxide can use used as a host for controlled released formulation.

Introduction

Nano-composites are multiphase materials with one of their element existing in the dimension less than 100 nanometer because of their low toxicity, good biocompatibility and excellent biodegradability. Natural polymers have important in pharmaceutical applications (Pathania et al., 2015). In the past, studies have been focused more widely on polymer/layered silicate nano-composites due to their good and often unique combination of remarkable improved properties, e.g. thermal stability, protective properties against corrosion, mechanical, flame retardancy (Hajibeygi et al., 2015) wound dressing, biosensors, food packaging and air refining (Yadollahi et al., 2015).

The structures of LDH are as shown in Figure 1.1.

![Figure 1.1 Schematic representation of the structure of LDH](image)

Vitamin C also known as ascorbic acid is existing in many concentrations in all fresh vegetables and fruits. The molecular structures of ascorbic acid. Ascorbic acid is a water soluble vitamin that have contains a variety of biological, dermatological and pharmaceutical functions (Liu et al., 2015) and anti-oxidant properties. Human and other mammals need the ascorbic acid because it is an essential component in the diet of them (Singh et al., 2015). Humans and other mammals cannot produce their own ascorbic acid because of a lack of L-gulonolactone oxidase (Liu et al., 2015).
However, only a very small quantity of vitamin C is needed for human body for physiological functions. Both lacking and too much supply of vitamins cause risky on human body. Thus, a more sophisticated drug administration method is drug delivery and controlled release system designed to reduce such problems. The materials to store drugs and then slowly release them in order to sustain drug concentrations at the desired levels for a longer period of time by using LDH. It is very unstable to air, base, heat, light, moisture, metal ions, and effecting in decomposition to biologically in active compounds (Gao et al., 2014).

Methodology

A. Synthesis of layered double hydroxides.

250 mL of deionized water were added into the volumetric flask containing 0.1M Zn(NO$_3$)$_2$·6H$_2$O and 0.025M Al(NO$_3$)$_3$·9H$_2$O. The solution were stirred well under purging of nitrogen gas. Next, drops by drops of 2 M of NaOH were added until the pH reached pH 7 ± 0.5. Then, placed the solution in the oil bath shaker for 18 hours for aging. After aging process, the solution was centrifuge and dried under 70°C vacuum oven for 74 hours. The samples were than kept for further characterization purpose.

B. Co-precipitation method

250 mL of deionized water were added into the volumetric flask containing 0.1M Zn(NO$_3$)$_2$·6H$_2$O and 0.025M Al(NO$_3$)$_3$·9H$_2$O. The solutions were stirred well under purging of nitrogen gas. Next, 0.1M to 1.0M of ascorbic acid were added into the solution and stirred vigorously. The pH of the solutions was adjusted by addition of drops by drops of 2 M of NaOH until the pH reached pH 7 ± 0.5. Then, placed the solution in the oil bath shaker for 18 hours for aging. After aging process, the solution was centrifuge and dried under 70°C vacuum oven for 74 hours. The samples were than kept for further characterization purpose.

C. Controlled Release

3mg of nanocomposites were put on top of the sodium phosphate (Na$_3$PO$_4$), sodium sulphate (Na$_2$CO$_3$), and sodium chloride (NaCl) with 0.5 M respectively. By using Kinetic types of UV-Vis, the sample were run for 8 hours until it reach equilibrium.
Results

A. FTIR (Fourier Transform Infrared Spectroscopy)

![FTIR spectra](image)

Figure 4.2 FTIR spectra of pure ASA (a), Zn-Al-ASA (b) and Zn-Al-LDH (c).

<table>
<thead>
<tr>
<th>Absorption band cm⁻¹</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1351</td>
<td>NO₃ group</td>
</tr>
<tr>
<td>1613</td>
<td>C=O</td>
</tr>
<tr>
<td>3200-3600 cm⁻¹</td>
<td>O-H stretching</td>
</tr>
</tbody>
</table>

B. PXRD (Powder X-Ray Diffraction Analysis)

![PXRD pattern](image)

Figure 4.3 PXRD pattern of solid product (co-precipitation). (a) Zn-Al-LDH, (b) Zn-AL-ASA with 0.1 M, (c) Zn-Al-ASA with 0.95 M.

C. UV-Vis Analysis (Controlled Release)

![Release profile](image)

Figure 4.4 Release profile of ASA from Zn-Al-ASA into 0.5M aqueous solution containing various anions, PO₄³⁻, CO₃²⁻, Cl⁻.
Discussions

The FTIR spectra for Zn-Al-LDH and Zn-Al-Ascobic Acid are shown in the Figure 4.2. The intense absorption band around 1351 cm\(^{-1}\) indicates the presence of NO\(_3\) groups, which are observed in Zn-Al-LDH. This is means, NO\(_3\) group is successfully intercalated into the layer during the preparation of LDH. The absorption peaks in the 1613 and 3200-3600 cm\(^{-1}\) regions are assigned to O-H group stretching and deformation vibration of the hydroxide basal layer and interlayer water molecules (Aisawa et al., 2007). Figure 4.3 shows PXRD pattern for Zn-Al-LDH and its nanocomposites, Zn-Al-ASA at a different concentrations of ASA ranging from 0.1 M to 0.95 M. The PXRD pattern for Zn-Al-NO\(_3\) (LDH) also include in the figure for comparison. A well-crytallize nanocomposites was obtained at increase the concentration of ASA from 0.1 M to 0.95 M, where the LDH peak nitrate at 2\(\theta\)=10\(^{\circ}\) is totally diminished. The basal spacing for Zn-AL-ASA at concentration 0.95 M is 11.1 Å. The expansion of basal spacing from 9.8 Å in the Zn-Al-LDH quick change to 11.1 Å is because of intercalation of ASA occur into the Zn-Al-LDH (intercalation of ASA into Zn-Al-LDH). The Zn-Al-ASA and Zn-Al-NO\(_3\) posses an expanding LDH structure, indicating that ASA successful intercalated into LDH (Aisawa et al., 2007). As shown in Figure 4.4, the accumulated released of ASA into various aqueous solutions containing phosphate, carbonate, and chloride anion increased with contact time. The released of the ASA from the nanocomposite was fast for the first 150 minutes. The equilibrium was achieved at about 250-400 minutes. The percentage saturated release of the guest anions, phosphate, carbonate, and chloride shows that the percentage saturated release of the anion is in the order of phosphate > carbonate > chlorides saturated released of 92 %, 64 % and 42 % respectively. The highest percentage of ASA released was achieved by higher charge density anions (PO\(_4^{3-}\)), whereas the lowest percentage release was achieved in lower density anion (Cl\(^-\)). The amount of the ASA released at the equilibrium is higher for PO\(_4^{3-}\) due to higher affinity of the PO\(_4^{3-}\) anions toward LDH.

Conclusion

Zn-Al-ASA was successful synthesized via co-precipitation method using 0.98 M ASA and molar ratio of Zn to Al, R = 2. The PXRD result shows that the intercalation of ASA into Zn-Al-LDH is optimum at concentration 0.95 M, the basal spacing of Zn-Al-LDH change from 8.9 Å to 11.7 Å by means the ASA was successful inserted into the interlamellae of Zn-Al. the peak of nitrate at 1351 cm\(^{-1}\) diminished and presence a new peak of C=C (ASA) at 1613 cm\(^{-1}\), conform that all the interlayer nitrate anion have been fully replaced by ASA. The released of the ASA anion from the interlamellae of Zn-Al-ASA is controlled by the affinity of the incoming anion in the different aqueous media. The percentage saturated released of the ASA is in order of phosphate > carbonate > chloride with percentage saturated released 92 %, 64 % and 42 %.

References


