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# Synthesis, characterization and release of a-naphthaleneacetate from thin films containing Mg/Al-layered double hydroxide

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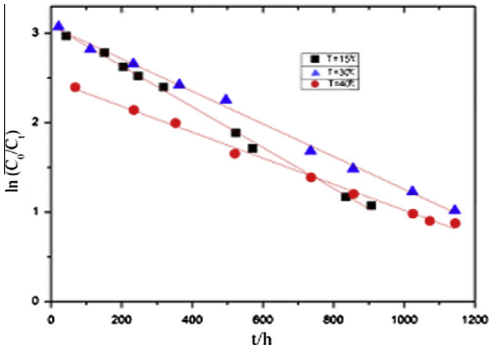
## HIGHLIGHTS

- Intercalated NAA into the Mg/Al–$NO_3$–LDH by ion-exchange method.
- Thin films were made by the LBL method with polymers and Mg/Al–NAA–LDH.
- The films were put into various solutions, and discuss the release mechanism.
- The mechanism accorded with first-order kinetics.

## GRAPHICAL ABSTRACT

The data obtained from the NAA released into the aqueous solution at different temperature and pH solutions fitted to the first-order kinetic. The kinetic indicated that the release process was controlled by the course of dissolution and ion-exchange process.

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## ABSTRACT

An active agent a-naphthaleneacetate (NAA), a plant growth regulator was intercalated into the layered double hydroxides Mg/Al–LDH by ion-exchange method. And we prepared the films by the method of layer-by-layer self-assembly with Cationic Polyacrylamide, Polyacrylic acid sodium and LDH. The obtained compounds were characterized by X-ray diffractometer (XRD), Fourier transform infrared (FT-IR) and Scanning Electron Microscopy (SEM) techniques. The XRD datas demonstrated the guest size and the orientation of anions between the layers was determined. After intercalation, it was proposed that the NAA anions were accommodated in the interlayer region as a bilayer of species with the carboxyl attaching to the upper and lower layers. The FT-IR of the powder from film shows that Mg/Al–NAA–LDH was absorbed on the quartz glass. The film was putted into various solutions, and the release of NAA from the film showed obvious release effect. The release mechanism may be based on the dissolution and ion-exchange process according to first-order kinetics.



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## 1. Introduction

Controlled release formulation for delivery of specific agents, such as drug in human, and of other active agents in environmental and industrial applications, has attracted considerable attention during the past several decades [1]. Slow/controlled release has been widely investigated in the fields of industry, agriculture and daily life productions for the release of active substances, such as nutrients, pesticides, drugs and aromatics [2]. Slow/controlled release allows a slower release, prolongs duration of active agents and reduces the loss by evaporation and divulge, so it can improve the utilization efficiency as well as reduce the environmental pollution and save resources.

Recently, intense research interests have been paid on the layered inorganic solids because of their ability to encapsulate and immobilize various organic molecules in the interlayer space [3–5]. Hydrotalcite and Hydrotalcite-like compounds (LDH) are consisted of positively charged metal hydroxide, the anionic species and water molecules, whose general formulas are $M^{II}_{1-x}M^{III}_{x}(OH)_2Y^{n-}_{x/n}\cdot m\ H_2O$·[6–9], where $M^{II}$ and $M^{III}$ are divalent and trivalent metal ions, respectively, and $Y^{n-}$ is the interlayer anion, $x$ is equal to the molar ratio of $M^{III}/(M^{II}+M^{III})$ and ranges from 0.17 to 0.33. As the $M^{II}$ is partly exchanged by $M^{III}$, it is necessary to balance the positive charge by anions, which could be inorganic or organic anions. They can be easily introduced into the interlayer of LDH by coprecipitation or ion-exchange reaction. So far, there are many reports about the intercalation of substances in the LDH, such as pesticides [10], drugs, DNA [11–15] and plant growth regulators [16]. Moreover, LDH hybrids with anti-inflammatory [17,18], antihypertensive [19] and anticancer drugs [4,20] are also studied with controlled release. Depending on its usage, preference of the anions and cations that form the intercalated LDH is the most important and thus can be chosen according to the resulting properties of the desired products [21].

1-Naphthylacetic (NAA) is one of the well known plant growth regulators, whose function is to accelerate the plant root growth and to promote cell division and tissue differentiation, allowing for even more growth, furthermore, it can enhance plant drought resistance the cold resistance and saline resistance to hot wind. Literatures showed various kinds of slow or controlled release polymers containing NAA has been synthesized which were based on both synthetic and natural polymers [22]. Although polymers are the main hosts for drugs, natural polymers often have low reactivity with the bioactive compounds due to its poor solubility in common solvents [23], therefore the use of inorganic matrixres has recently received an increasing attention [24,25], but to our knowledge it is rarely reported about the controlled release from films that formed by LDH and polymers.

In our paper we first intercalated NAA into LDH with ion-exchange method, then used the layer-by-layer self-assembly (LBL) method, which was proposed by Decher [26]. The LBL method has been extensively used as a simple and effective method for the preparation of polyelectrolyte multilayer films. A wide range of inorganic materials has been assembled with appropriate polymers to produce multilayer films. Thus we used electrical polymers and NAA–LDH to form the controllable film. After the film was crosslinked, it was put into various solutions with different pH and temperature. At a certain period of time we tested the concentration of NAA released from film with UV–visible spectrophotometer at 282 nm.

## 2. Materials and methods

All solutions were prepared with deionized water (resistance is 18.2 MΩ), and all the chemicals utilized in the experiment were of analytical grade, and were used without further purification.

### 2.1. Synthesis of O-naphthylacetyl LDH

The precursor Mg/Al–$NO_3$–LDH was obtained by co-precipitation reaction in a $N_2$ atmosphere. In our experiment we used $Al(NO_3)_3{\cdot}9H_2O$ (0.025 mol) and $Mg(NO_3)_2{\cdot}6H_2O$ (0.05 mol), with a initial molar rations of 1:2, then added some deionized water and the solution pH was adjusted to 8 with NaOH solution. The suspension was aged at 80 °C for 12 h and stirred simultaneously, then the resultant was separated by centrifugation, washed thoroughly with deionized water until neutral pH was reached, and dried at 80 °C in a vacuum. Thus we obtained the precursor Mg/Al–$NO_3$–LDH.

The Mg/Al–NAA–LDH was obtained by the method of ion-exchange method. Mg/Al–$NO_3$–LDH (0.277 g), NAA (1.94 g), 100 mL absolute ethylalcohol and 100 mL deionized water were treated with great vigorous stirring under a $N_2$ atmosphere for 24 h at 70 °C and the product was centrifugationed and washed with deionized water to be neutral and then dried under 80 °C for 12 h.

### 2.2. Assemble of Mg/Al–NAA–LDH film

The film of Mg/Al–NAA–LDH was fabricated with the layer-by-layer self-assembly (LBL) method. Prior to the deposition of the multilayer films, substrates of quartz glass wafer were cleaned by immersion in a ultrasonic bath of $H_2SO_4$ and deionized water for 20 min, respectively. Next, substrates of quartz glass wafer were immersed in a bath of $H_2O_2/NH_3{\cdot}H_2O/H_2O$ (1/1/5, v/v/v) with ultrasonic treatment for another 20 min, and washed with deionized water. They were put into positive electricity Cationic Polyacrylamide (CPAM) and electronegative Polyacrylic acid sodium (PAAS) solutions for 20 min separately and the procedure was repeated twice. Washed them with deionized water, thus the substrates were obtained with a negatively charged surface. Then they were immersed into Mg/Al–NAA–LDH for 20 min, and subsequently in PAAS, CPAM for 20 min, respectively. The process was shown in Fig. 1. In Fig. 1a, 1 and 3 were CPAM, Mg/Al–NAA–LDH, while 2 was PASS. Thus we obtained a circulation as shown in Fig. 1b, then repeated the next deposition until got the number of the films we want.

The films were crosslinked under 80 °C for 12 h, and were immersed into solutions of different temperature and initial pH. In order to compare, 0.1 g of Mg/Al–NAA–LDH powder was put into 100 mL with various pH solutions. The amount of NAA liberated

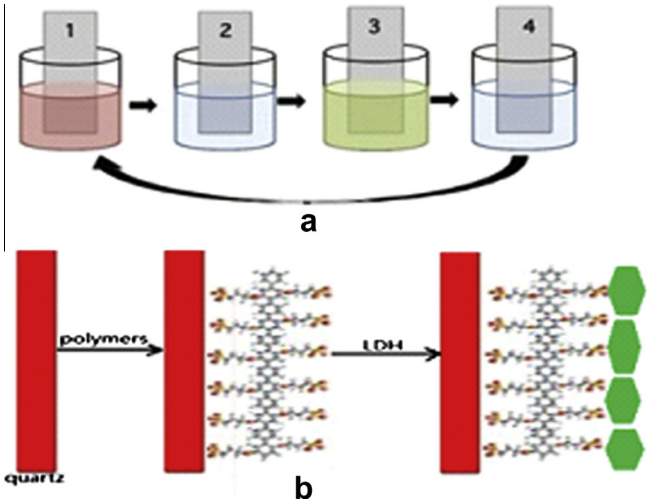


**Fig. 1.** Schematic diagram of layer-by-layer self-assembly process.