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Synthesis and controlled release properties of β -naphthoxyacetic acid intercalated Mg–Al layered double hydroxides nanohybrids

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Abstract Controlled release formulations have been proven to have potential in overcoming the drawbacks of conventional plant growth regulators. Novel controlled-release formulation of β -naphthoxyacetic acid (BNOA) intercalated MgAl-layered double hydroxides (LDHs) was prepared by co-precipitation method. The effects of temperature, pH value, and release medium on BNOA release were studied and the releasing mechanisms were discussed. The results of release show that the increase of temperature induces the increase of BNOA release extent. The release rate and accumulated release amount of BNOA are found to be dependent to the anion in the aqueous solution in the order of $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$. Moreover, the pH is the key controlling factor for the BNOA release processes, and with strong acid medium, the release character of BNOA is different from those at pH 7 and 12, which accompanies with fast collapse of LDHs nanolayered structure. The nanohybrid of BNOA intercalated LDHs possessed good controlled release properties and the BNOA release character from the nanohybrid fitted pseudo-second-order model in neutral medium. © 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In recent years, plant growth regulators (PGRs) have attracted significant attention because of their widespread applications in modern agriculture and turf management (Atta et al., 2012). PRGs can be categorized as auxins, gibberellins, cytokinins, abscisic acid, etc. Among auxins, β -naphthoxyacetic acid (BNOA) is more effective than natural plant hormone-indole-3-acetic acid (IAA) and widely used to promote early fruit, to control the growth of stems, roots, flowers and fruits, and to improve fruit size and color (Karadeniz et al., 2011).

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However, the deleterious effects of BNOA, such as mutagenesis, cancer and environmental problems have been demonstrated, which have attracted the attention of regulatory agencies of food safety (Celik and Tuluce, 2007). The World Health Organization (WHO) regards BNOA as slightly hazardous agrochemicals according to its acute toxicity, but there is no recommendation for the maximum permitted concentration (MPC) of BNOA in foods (Gökmen and Acar, 2000). Controlled release formulations (CRFs) have been shown to have potential in overcoming the drawbacks of conventional PGRs formulations, since they allow usage of minimum amount of PGRs for the same activity. Many research efforts have been devoted to developing controlled release formulations for PGRs, mainly using microencapsulation and inorganic material technology (Ao et al., 2013; Dubey et al., 2011; Hussin et al., 2002a; Qin et al., 2013; Qiu and Hou, 2009). Among CRFs, layered double hydroxides (LDHs) have attracted intensive attention because of their many advantages, including good biocompatibility, nontoxicity, and adjustable controlled-release properties (Atta et al., 2012; Rodrigues et al., 2013; Rives et al., 2013, 2014).

LDHs also known as hydrotalcite-like compounds are a class of anionic clays whose structures are based on brucite-like layers. LDHs have the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{n+}(A^{n-})_{x/n} \cdot mH_2O$, whereby M^{II} are divalent, M^{III} are trivalent metal cations and A represents the intercalated anion (Duan and Evans, 2006). Recently, LDHs have attracted intensive attentions because of their potential application in catalysts, adsorbents, and controlled release formulations (Barahuaie et al., 2013; Bashi et al., 2012; Kerchiche et al., 2012; Hussein et al., 2012a,b; Hussein et al., 2005; Shen et al., 2013). A variety of anionic organics, including drugs, pesticides, and herbicide have been inserted as guests into the LDHs interlayer (Wilkins, 1982; Liu et al., 2013; Atta et al., 2012; Li et al., 2013; Khan et al., 2001; Choi et al., 2014; Cardoso et al., 2006). However, only few CRFs of PGRs, such as β -naphthaleneacetate, indole-3-acetic acid, and indole-3-butyric acid have been reported and the factors affecting release and release kinetics are not yet fully understood (Hussein et al., 2002a,b; Yang et al., 2007; Qiu and Hou, 2009; Hussein et al., 2007).

In the present work, to improve the utilization of the BNOA effectively and reduce the side effect of BNOA on environment, we synthesized a novel layered composite by intercalation of BNOA anions into magnesium aluminum layered double hydroxides (MgAl-LDHs) using co-precipitation method. The surface, structural, thermal properties of BNOA anions intercalation LDHs (MgAl-BNOA-LDHs) were characterized. The BNOA anions release profiles from MgAl-BNOA-LDHs nanocomposite were measured and release mechanism was also studied.

2. Materials and methods

2.1. Materials

$Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, and Na_2CO_3 were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). BNOA was obtained from Aladdin Reagent Co., Ltd. (China). All reagents were used as raw materials without further purification. CO_2 -free deionized water was used throughout the experimental processes.

2.2. Synthesis of MgAl-BNOA-LDHs

The MgAl-BNOA-LDHs were prepared by co-precipitation method as follows. Firstly, 0.04 mol BNOA was dissolved in 100 mL decarbonated water and the pH was adjusted to about 7 using 1 Mol NaOH. A 50 mL mixture solution containing 0.6 Mol $Mg(NO_3)_2 \cdot 6H_2O$ and 0.3 Mol $Al(NO_3)_3 \cdot 9H_2O$ (Mg/Al molar ratio = 2:1) was slowly added to above mentioned BNOA solution at room temperature with vigorously stirring under N_2 atmosphere to prevent the formation of MgAl- CO_3 -LDHs. The pH of the reaction mixture was adjusted 10.0 ± 0.2 by dropwise addition of 1 Mol NaOH solution. Then the resulting slurry was crystallized at 70 °C for 48 h. The white precipitate was isolated by filtration, washed several times with hot decarbonated water and acetone successively, and dried at 80 °C for 24 h. The MgAl- CO_3 -LDHs was also prepared by a standard co-precipitation method with Na_2CO_3 in substitution for BNOA.

2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were collected using a Bruker D8 Advance XRD diffractometer at Cu K α radiation and a fixed power source (40 kV and 40 mA, = 1.5406 Å). Fourier-transform Infrared (FT-IR) spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet NEXUS 470 Fourier-transform infrared spectrophotometer using KBr pellet technique. Thermogravimetry and differential thermal analysis (TG-DTA) curves were obtained on a NETZSCH STA 449C instrument in the temperature range of 30–680 °C with a heating rate of 10 °C min^{-1} in N_2 . The specific surface area and pore-size distribution were evaluated using the nitrogen adsorption (Quantachrome Autosorb 1-C). A transmission electron microscope (TEM) (FEI Tecnai G200 S-Twin) was used to study the surface morphology of sample. The compositions of MgAl-BNOA-LDHs were determined from elemental CHO analysis with Vario EL III analyzer (Elementar) and Mg, Al elemental analysis with inductively coupled plasma atomic emission spectrometer (ICP-AES) (PerkinElmer, OPTIMA 8000DV), respectively.

2.4. Measurements of loading amounts of BNOA in MgAl-BNOA-LDHs

The loading amounts of BNOA in MgAl-BNOA-LDHs were measured by Shimadzu UV-2550 model UV-vis spectroscopy using the following method Li et al. (2013b): 0.01 g of the sample and 3 mL of 6 Mol/L HNO_3 solution were added into a 10 mL volumetric flask, and the balance was filled with water/ethanol solution with volume ratio 9:1 ethanol (Qiu and Hou, 2009). The concentration of BNOA in the resulting solution was determined by monitoring the absorbance at $\lambda_{max} = 280$ nm with UV-vis spectroscopy. The concentration was calculated by regression analysis according to the standard curve obtained from a series of standard solution of BNOA.

2.5. Measurements of release amount of BNOA in MgAl-BNOA-LDHs

To measure the release performances of BNOA from MgAl-BNOA-LDHs, 0.05 g of MgAl-BNOA-LDHs powder was

dispersed in 500 mL water/ethanol solution with volume ratio 9:1 under magnetic stirring. At specified time intervals, 2 mL of solution was removed and filtered through a 0.45 μ m micro-filtration membrane and their BNOA contents were determined by monitoring the absorbance at 280 nm with UV-vis spectroscopy to obtain the release amounts (q_t) of BNOA from MgAl-BNOA-LDHs, in turn to calculate the accumulated percent releases (X_t) of BNOA from the MgAl-BNOA-LDHs. Release tests were performed in triplicate and the results were recorded as an average.

2.6. Release kinetics equations

Release kinetics of BNOA can be evaluated with pseudo-first-order and pseudo-second-order models. According to the literature (Qiu and Hou, 2009), pseudo-first-order kinetic equation may be represented in the following linear form:

$$-\ln(1 - X_t) = k_1 t \quad (1)$$

where k_1 is the rate constant of pseudo-first-order release kinetics. If the pseudo-first-order kinetics is applicable, the plot of $-\ln(1 - X_t)$ vs. t will give a linear, and the k_1 value can be obtained from the slope of the linear plot.

Pseudo-second-order kinetic equation may be represented in the following linear form:

$$t/X_t = 1/k_2 q_e + t \quad (2)$$

where q_e is equilibrium release amount, and k_2 is the rate constant of pseudo-second-order release kinetics. If the pseudo-second-order kinetics is applicable, the plot of t/X_t vs. t will give a linear, which allows computation of k_2 .

3. Results and discussion

The molecular structure of β -naphthoxyacetic acid and its carboxylate anion are given in Fig. 1a and b, respectively. The formation of carboxylate anion was done by dissolving the acid in NaOH solution and the anion was intercalated between inorganic lamellae of the MgAl-LDHs as evidence from powder X-ray and FT-IR studies, and will be discussed later.

3.1. X-ray diffraction

XRD patterns of the MgAl-CO₃-LDHs and MgAl-BNOA-LDHs are shown in Fig. 2. The XRD pattern of the contrast MgAl-CO₃-LDHs (Fig. 1b) exhibits typical characteristics of the LDHs phase corresponding to the basal spacing of 0.75 nm, which agrees well with the literature data (Feng et al., 2006). After intercalation, the d -spacing of MgAl-BNOA-LDHs is expanded to 2.03 nm, which clearly

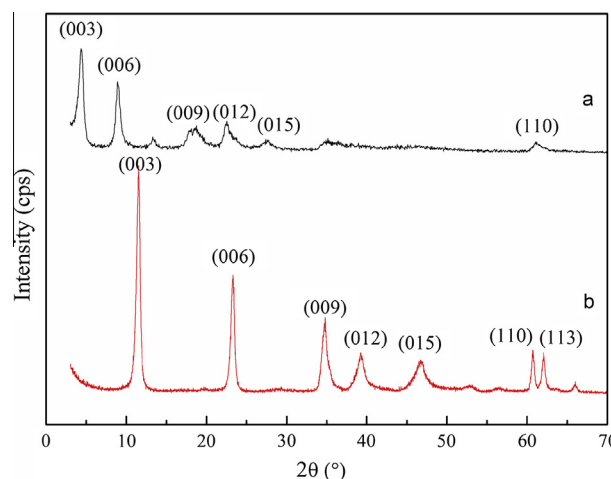


Figure 2 XRD patterns of (a) MgAl-BNOA-LDHs, and (b) MgAl-CO₃-LDHs.

demonstrates the successful incorporation of BNOA anions into the LDHs layer.

Based on the basal spacing d_{003} of 2.03 nm for MgAl-BNOA-LDHs observed by XRD, and subtracting the thickness of brucite layer (0.48 nm), the gallery height is calculated to be 1.55 nm, which is higher than that of BNOA anions (1.11 nm). However, the gallery height of MgAl-BNOA-LDHs is much smaller than the double sizes of the BNOA anions. So, as shown in Fig. 3, it was suspected that BNOA anions are located in the form of bilayer arrangement.

3.2. Fourier transform infrared spectroscopy

Fig. 4 shows the FT-IR spectra of MgAl-CO₃-LDHs, BNOA, and MgAl-BNOA-LDHs. In the spectrum of the MgAl-CO₃-LDHs precursor, shown in Fig. 4a, the absorption band around 3450 and 1360 cm^{-1} can be ascribed to the characteristic peaks of the MgAl-CO₃-LDHs (Li et al., 2013b). As shown in Fig. 4b, the FT-IR spectrum of BNOA shows two bands at 1739 cm^{-1} and 1629 cm^{-1} are due to the C=O and C=C aromatic rings stretching vibration, respectively (Jubri et al., 2009). The strong bands near 1283–1251 cm^{-1} are due to the C–O–C stretching vibrations, and the band at 1430 cm^{-1} indicated the presence of CH₂ scissoring vibration. The strong bands at 749–909 cm^{-1} are due to the presence of phenyl ring (Jubri et al., 2009). The bands at 1072 cm^{-1} are attributed to OH stretching vibrations (Feng et al., 2014). The FT-IR spectrum of MgAl-BNOA-LDHs shown in Fig. 3c contains the characteristic peaks of BNOA at 3442, 2912, 1062, 1426, 1211–1258, and 757 cm^{-1} , indicating that

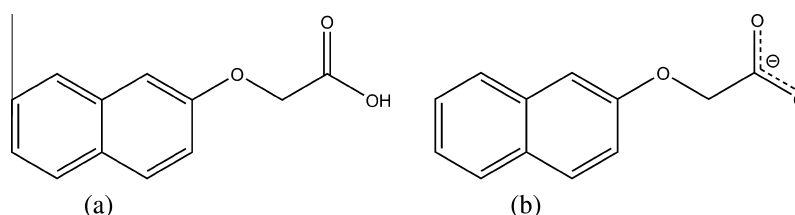


Figure 1 Molecular structure of β -naphthoxyacetic acid (a) and its anion (b).

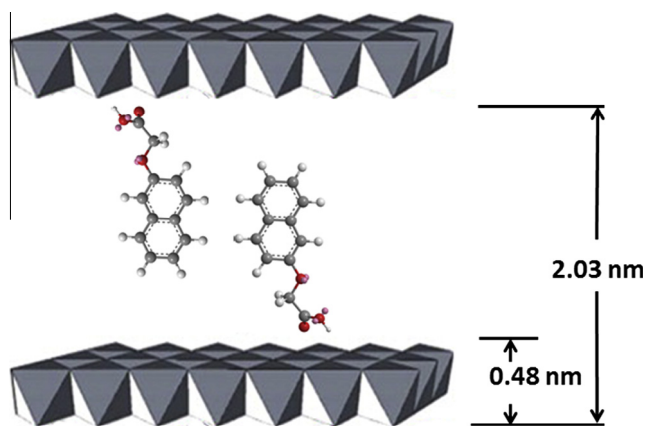


Figure 3 The probable orientation of BNOA intercalated in MgAl-LDHs interlayer.

BNOA molecules were loaded on LHDs. On the contrary, an asymmetric stretching band of —COOH in the BNOA at 1739 cm^{-1} moves markedly toward low wave number (1602 cm^{-1}) in the nanohybrids, which can be ascribed to the ionization of BNOA.

3.3. Surface property

The isotherms of nitrogen adsorption and desorption at 77 K for the MgAl–BNOA-LDHs are plotted in Fig. 5. The adsorption–desorption isotherms can be categorized as type II, indicating the presence of the character of nonporous (Fig. 5). The BET surface area and average pore diameter of MgAl–BNOA-LDHs are $52.98\text{ m}^2\text{ g}^{-1}$ and 3.4 nm, respectively. Fig. 6 shows plots of BJH desorption pore size distribution for MgAl–BNOA-LDHs. The BJH desorption pore size distribution analysis of the sample shows most pore diameters are around 3.4, 4.3 and 17.4 nm (Fig. 6), which are attributed to the interparticle spaces (Hu et al., 2005).

The TEM images of BNOA-LDHs nanohybrid samples are shown in Fig. 7. As can be seen, the BNOA-LDHs particles are of typical plate-like shape with the lateral size of 50–100 nm.

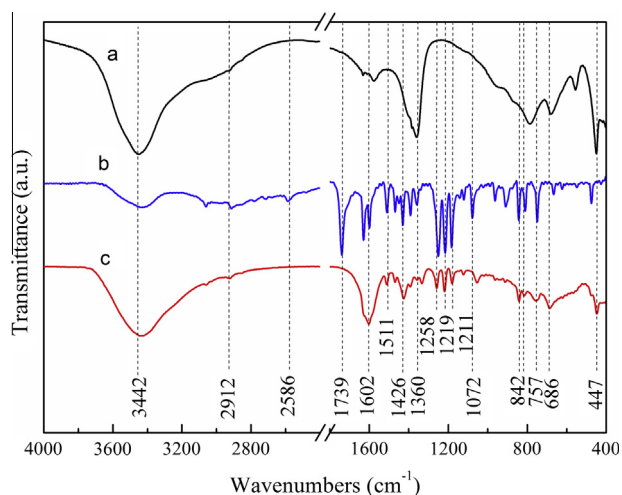


Figure 4 FT-IR spectra of (a) MgAl- CO_3 -LDHs, (b) BNOA, and (c) MgAl-BNOA-LDHs.

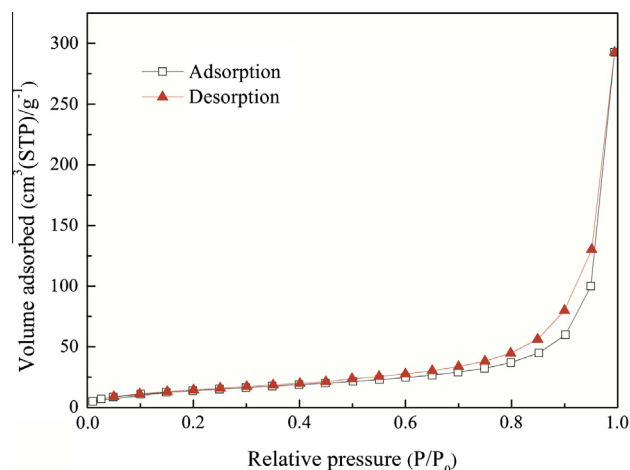


Figure 5 Adsorption–desorption isotherms of nitrogen gas for MgAl–BNOA-LDHs.

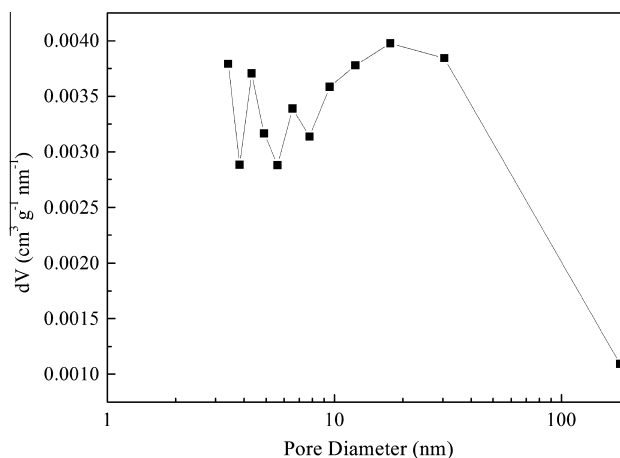


Figure 6 Pore size distribution for MgAl–BNOA-LDHs.

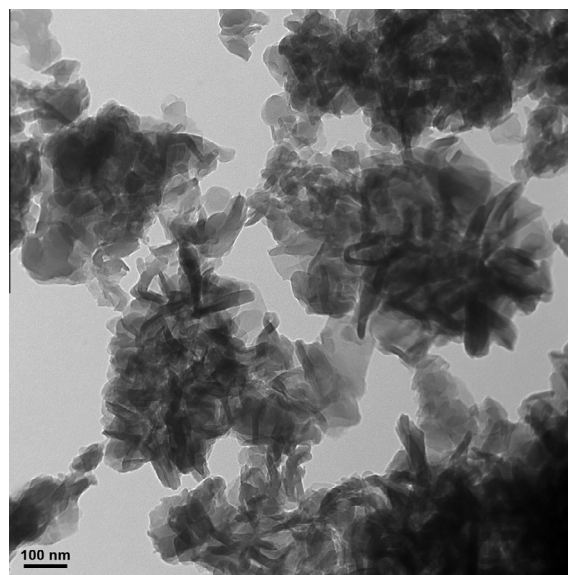


Figure 7 Transmission electron micrograph for MgAl–BNOA-LDHs.

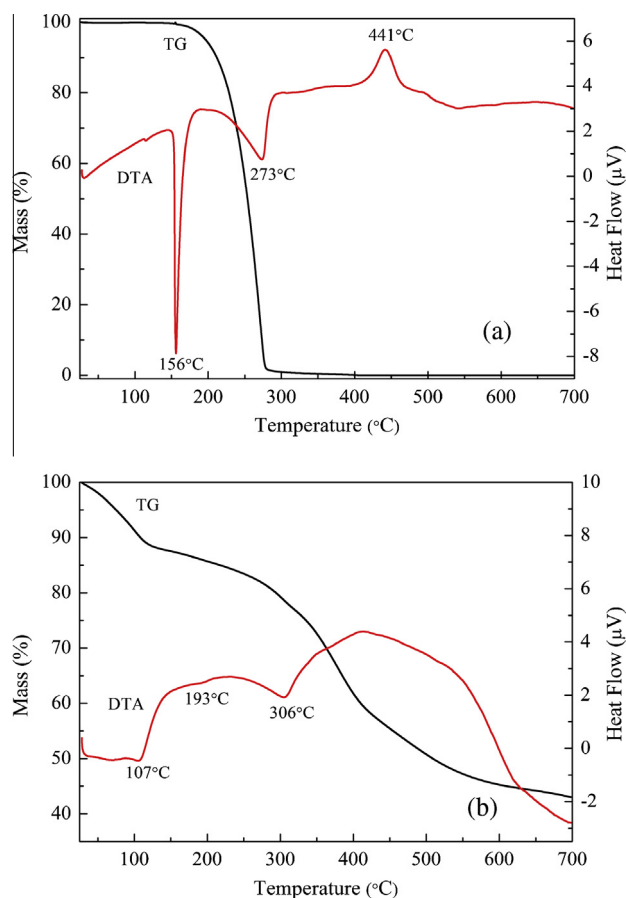


Figure 8 TG-DTA curves of (a) BNOA, and (b) MgAl-BNOA-LDHs.

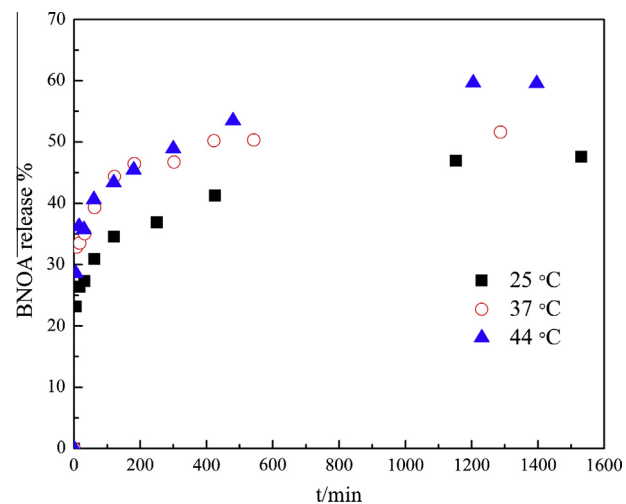


Figure 9 Release curves of MgAl-BNOA-LDHs nanohybrid at pH 7 and different temperatures 25 °C, 37 °C and 44 °C.

3.4. Elemental analysis

The composition and general formula of MgAl-BNOA-LDHs were determined from the ICP-AES, CHO elemental analysis and TG-DTA analysis. The molar ratio of Mg to

Al is close to the expected value (theoretical of 2.0), indicating that the reaction was complete during the reaction of co-precipitation. The loading amount of BNOA in MgAl-BNOA-LDHs is 48.2 wt%, and the calculated structural formula of MgAl-BNOA-LDHs is $Mg_{0.66}Al_{0.34}(OH)_2(C_{12}H_{10}O_3)_{0.34} \cdot 0.83H_2O$.

3.5. Thermal stability of nanohybrids

Fig. 8 demonstrates TG-DTA curves of BNOA and MgAl-BNOA-LDHs nanohybrids. For BNOA (Fig. 8a), the strong endothermic peaks at 156 °C in the DTA curve correspond to the phase transition of BNOA. With an increase of temperature, the main mass-loss stage in the range of 160–370 °C in TG curve can be attributed to the decomposition of BNOA and the weak exothermic peak at 441 °C corresponds to complete decomposition of BNOA. The TG-DTA curves of MgAl-BNOA-LDHs are shown in Fig. 8b. The first and second weak endothermic peaks marked at 107 and 193 °C in the DTA curve correspond to the removal of adsorbed water and

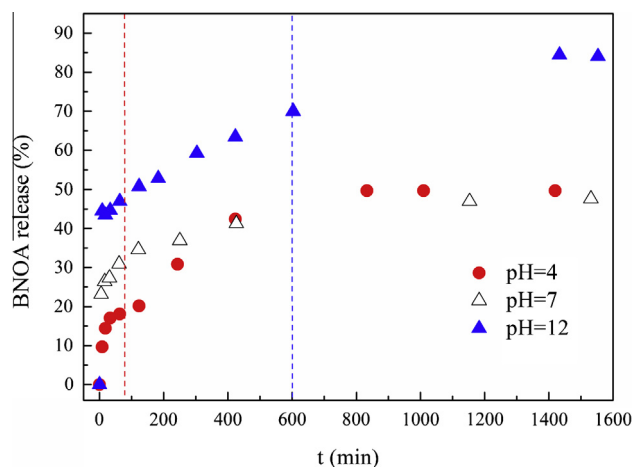


Figure 10 Release curves of MgAl-BNOA-LDHs nanohybrid at 25 °C and various pH 4, 7 and 12.

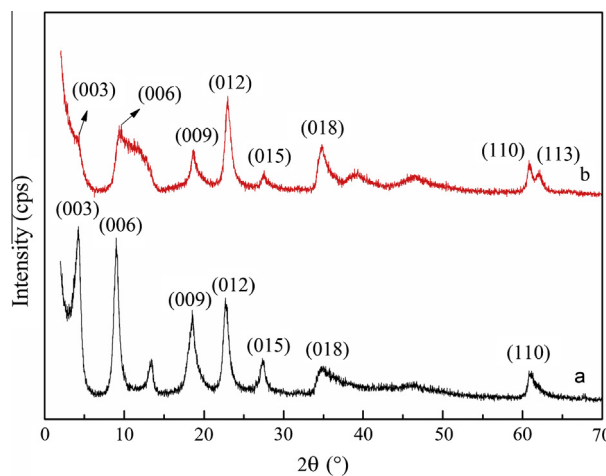


Figure 11 XRD patterns of MgAl-BNOA-LDHs after BNOA release at pH 12 (a) and 4 (b).

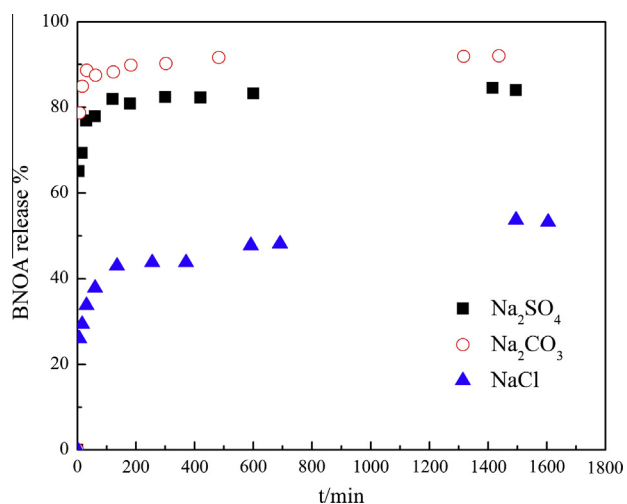


Figure 12 Release properties of MgAl-BNOA-LDHs nano hybrid at different salt solutions (0.05 M, pH 7, 25 °C).

interlayer water, respectively. The endothermic peak at 306 °C in TG curve can be assigned to simultaneous dehydroxylation and the elimination of BNOA. With the temperature increasing, a large mass loss that occurred above 400 °C can be attributed to complete decomposition. The starting decomposition temperature of BNOA shifts from 160 to 250 °C, suggesting that the intercalation of BNOA into the interlayer galleries of the LDHs markedly enhances the thermal stability of the BONA. The TG-DTA data are consistent with the result of

FT-IR analysis, which all suggest that MgAl-BNOA-LDHs is a complex system of strong supramolecular interactions between host layers and guest. This improvement of thermal stability is attributed to the interactions between the host brucite-like sheets and the guest intercalated anions, involving electrostatic attraction between opposite charges, hydrogen bonding, and the van der Waals force (Zhu et al., 2011).

3.6. Release of BNOA from BNOA-LDHs nano hybrids

3.6.1. Effect of temperature on BNOA release

Three different temperatures at 25, 37 and 44 °C were selected to observe the effect on the release of BNOA from MgAl-BNOA-LDHs nano hybrid. As shown in Fig. 9, the release of BNOA was initially rapid during the first 30 min, which can be attributed to the higher BNOA concentration difference (release driving force) between LDHs and release medium and then followed by a more gradual release. At temperature 25 °C, the release of BNOA was persistent and gradual, with release percentages of 34.5%, 47.0%, and 47.6% after 120, 1150, and 1530 min, respectively. In addition, an increase of temperature induces the increase of BNOA release extent, indicating that the release process was an endothermic reaction (Qiu and Hou, 2009).

3.6.2. Effect of pH value the solution on BNOA release

Fig. 10 shows the release profiles of BNOA from MgAl-BNOA-LDHs at various initial pH values. It is worth noting that the release profiles differ greatly for the three pH values. It can be seen that a release rate at the beginning was faster,

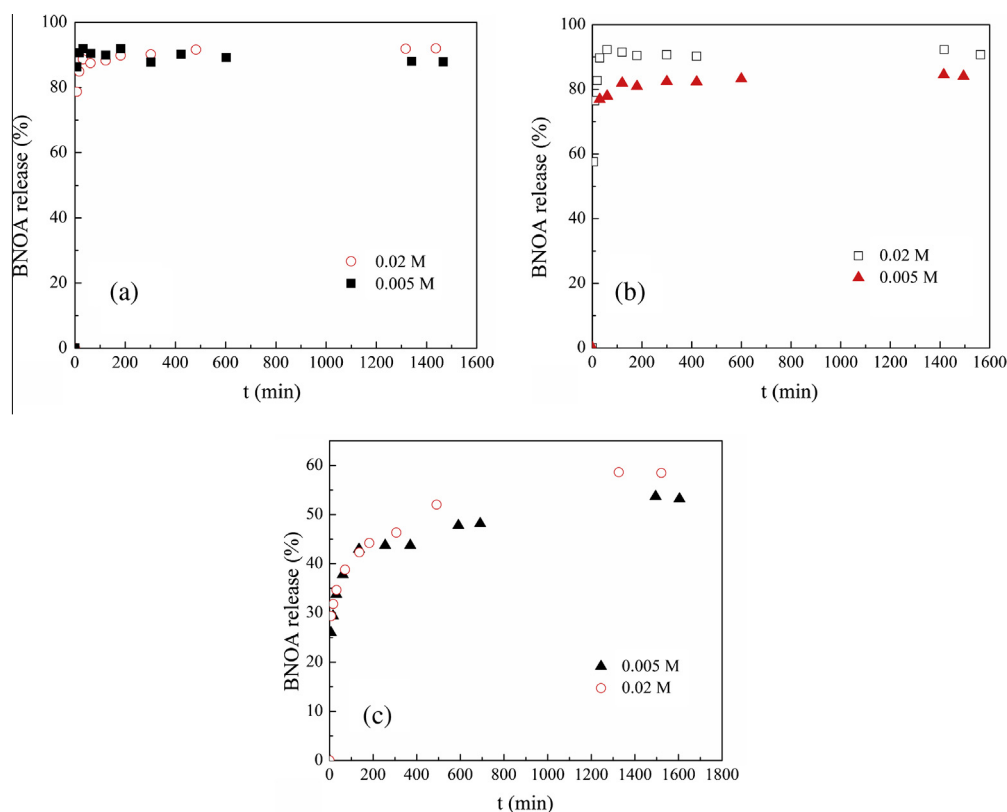


Figure 13 Release properties of MgAl-BNOA-LDHs nano hybrid at different salt concentrations (pH 7, 25 °C): (a) Na₂CO₃, (b) Na₂SO₄, (c) NaCl.

followed by a slower one until the equilibrium was attained at pH 7. However, for pH 4 the release rate of BNOA at first 60 min was faster than that of subsequent release. Moreover, at pH 12, until to 600 min the release rate of BNOA remained nearly constant. According to results of Hussein and Long (2004), several factors such as the extent of the dissolution of inorganic LDHs with the collapse of the nanolayered structure

and actual composition of the controlled release formulation are important and these will contribute to drug released into the aqueous solution. Under the strong acid condition (for example pH 4), the part of nanolayered structure of MgAl-BNOA-LDHs would collapse, which brought about faster release rate of BNOA at first 60 min, and the subsequent release profile was nearly similar to that at pH 7. However,

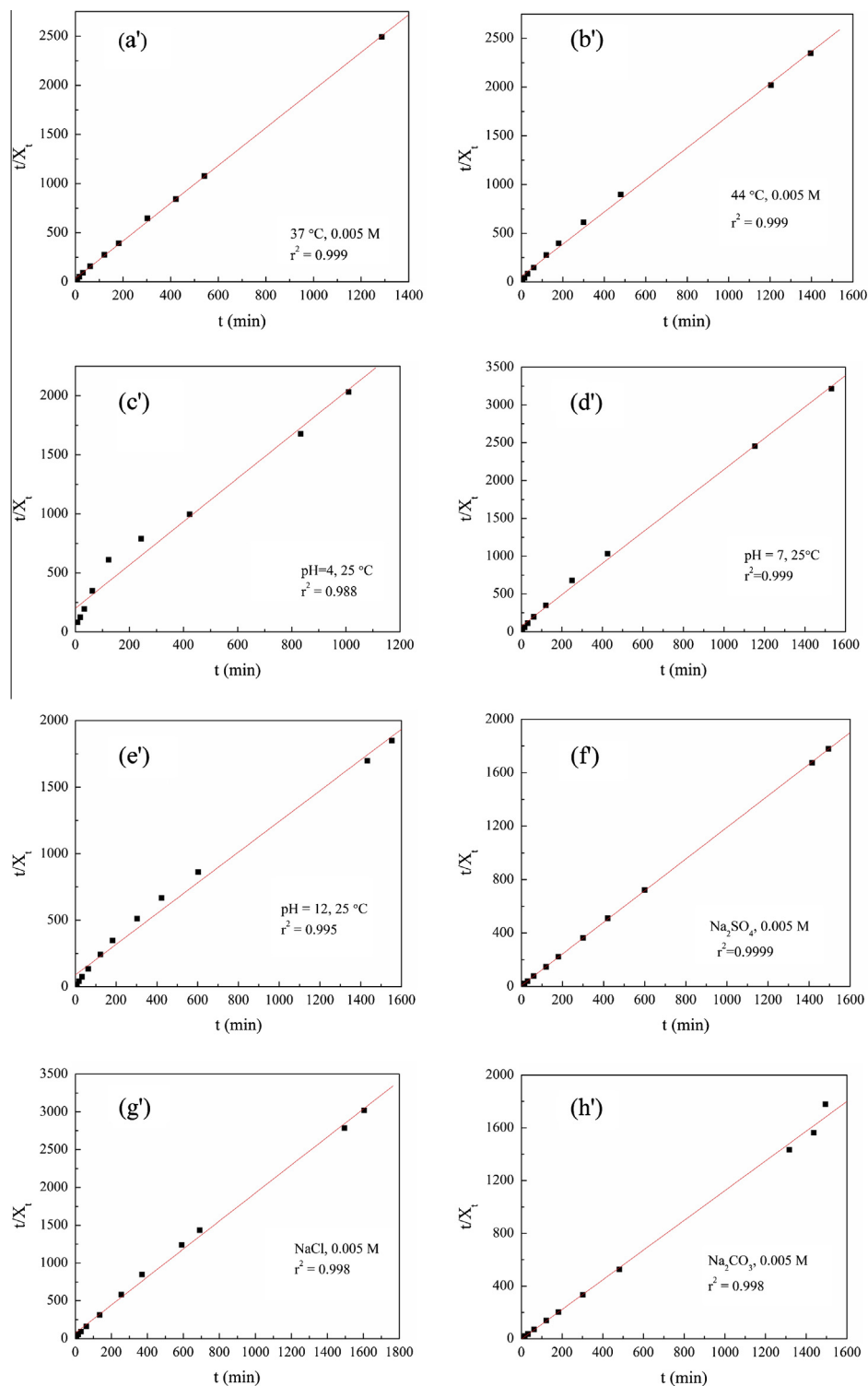


Figure 14 Linear regression curves of BNOA release data fitting with pseudo-second-order (a'–f') kinetic model for MgAl-BNOA-LDHs nanohybrids.

in aqueous solution at high pH (for example pH 12), the high concentration of OH^- ions in the solutions resulted in being ion-exchanged continuously with BNOA anions, which caused the nearly constant release rate until to 600 min and the highest BNOA release extent was obtained. To demonstrate the above-mentioned hypothesis, the MgAl-BNOA-LDHs powder was collected for XRD patterns test. As shown in Fig. 6(a), the (003) and (006) diffraction peaks of MgAl-BNOA-LDHs nearly disappear or intensity is decreased at release medium pH of 4. However, there is no obvious change in the XRD pattern of MgAl-BNOA-LDHs after BNOA release at pH 12 (Fig. 11(b)). Therefore, it can be seen that the pH is the key controlling factor for the release processes of BNOA from the MgAl-BNOA-LDHs.

3.6.3. Effect of salt anion on BNOA release

The release profiles of BNOA from MgAl-BNOA-LDHs into the aqueous solutions of Na_2CO_3 , Na_2SO_4 , and NaCl (0.005 M) are shown in Fig. 12. The release of BNOA should involve dissolution of MgAl-BNOA-LDHs as well as ion-exchange between the intercalated BNOA anions and salt anions. As shown in Fig. 12, the release of BNOA into above-mentioned salt aqueous solution is found to be dependent to the anion in the aqueous solution in the order of $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$ with the percentage release of 52%, 83%, and 92%. Compared to the release extent of without salt solution (Fig. 9 and 25 °C), it can be seen that the presence of salt may increase the release rate and accumulated release amount of BNOA, which may be due to ion-exchange processes between the BNOA anions in the interlayer and salt anions. In addition, the release amount of BNOA exposed to Na_2CO_3 is higher than that in Na_2SO_4 , and NaCl solutions, which is because the exchange ability of CO_3^{2-} for BNOA is higher than that of SO_4^{2-} and Cl^- (Cavani et al., 1991).

3.6.4. Effect of salt concentration on BNOA release

A series of salt solutions with various concentrations were used to observe the effect of salt concentration on the release of BNOA from nanohybrids. Fig. 13 shows the release profile of BNOA from nanohybrid into aqueous solution at various initial salt concentrations. It can be seen that the amount of accumulated BNOA release was generally increased with concentration of the salt anion in the aqueous solution, which was because at higher concentrations of the salt anions in the aqueous media, more ion exchange processes could be accomplished.

3.6.5. Release kinetics of BNOA from BNOA-LDHs nanohybrids

As shown in Fig. 14, the r^2 values of release data fitting with pseudo-second order model are in the range of 0.988–0.9999, while those with pseudo-first-order model are in the range of 0.666–0.914 (Fig. S1). It can be seen that the pseudo-second-order model is better satisfactory for describing the release kinetic processes of BNOA from the MgAl-BNOA-LDHs nanohybrids.

4. Conclusion

We have developed β -naphthoxyacetic acid (BNOA) anions intercalated MgAl-layered double hydroxides (LDHs) by coprecipitation method and investigated its controlled release

properties. Based on XRD result, the interlayer distance of the MgAl-BNOA-LDHs is 1.55 nm and BNOA anions are located in the gallery of MgAl-LDHs with bilayer arrangement. TEM result shows the MgAl-BNOA-LDHs particles were of typical plate-like shape with the lateral size of 50–100 nm. The results of release show that the increase of temperature induces the increase of BNOA release extent. The presence of salt may increase the release rate and accumulated release amount of BNOA and the release is found to be dependent to the anion in the aqueous solution in the order of $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$. At pH 4, it brought about faster release rate of BNOA at first 60 min, and at pH 12, until to 600 min the release rate of BNOA remained nearly constant, which can be interpreted with layered structure collapse caused by strong acid or ion-change with OH^- . These results showed that the MgAl-BNOA-LDHs possessed good controlled-release properties and the release of intercalated BNOA from the MgAl-BNOA-LDHs fitted pseudo-second-order model in neutral medium.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2015.04.034>.

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