

## Synthesis of Dichlorprop-Zn/Al-hydrotalcite Nanohybrid and its Controlled Release Property

(Sintesis Nanohibrid Diklorprop-Zn/Al-hidrotalsit dan Sifat Lepasannya)

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### ABSTRACT

*New phase-pure nanohybrids of dichlorprop[2(2,4-dichlorophenoxy)propionate]-intercalated Zn/Al-LDH were successfully prepared using either co-precipitation or ion exchange methods. The basal spacing expansion from 8.9 Å in the layered double hydroxide (LDH) to 18.7 and 21.7 Å of the nanohybrids was observed. This together with FTIR, DTG/TGA and compositional studies show that dichlorprop was successfully intercalated into the Zn/Al-layered double hydroxides interlayer. Release study of dichlorprop showed that it is dependent on the concentration of the incoming ionic species and governed by the pseudo-second order kinetic. This study suggests that the layered double hydroxide might be used as a matrix for controlled release formulation for a herbicide, dichlorprop and the release of the herbicide can be tuned using parameters such as method of synthesis and the concentration of the incoming ionic species to be ion exchange with. This is towards new generation of agrochemicals which are safer as well as user- and environmentally-friendly.*

*Keywords: Dichlorprop; layered double hydroxide; nanohybrids; pseudo-second order kinetic*

### ABSTRAK

*Fasa tulen bahan baru nanohibrid, diklorprop 2(2,4-diklorofenonoksi) propionat terinterkalasi ke dalam lapisan Zn/Al-LDH telah berjaya disediakan dengan menggunakan sama ada kaedah pemendakan atau pertukaran ion. Didapati terdapat pengembangan jarak basal daripada 8.9 Å bagi LDH kepada 18.7 dan 21.7 Å bagi nanohibrid. Ini, berserta kajian FTIR, DTG/TGA dan kajian komposisi menunjukkan bahawa diklorprop telah berjaya diinterkalasikan ke dalam lapisan hidroksida berganda Zn/Al. Kajian lepasan diklorprop menunjukkan lepasan bergantung kepada kepekatan spesies ion mendatang dan mematuhi kinetik tertib pseudo-kedua. Kajian ini menunjukkan bahawa lapisan berganda hidroksida sesuai digunakan sebagai matrik formulasi lepasan terkawal bagi racun rumpai, diklorprop dan lepasan racun rumpai ini boleh dilaraskan dengan menggunakan parameter cara mensintesis dan kepekatan spesies ion yang boleh ditukar ganti. Ini adalah ke arah penjaanaan bahan agrokimia generasi baru yang lebih selamat, mesra pengguna serta mesra alam.*

*Kata kunci: Diklorprop; kinetik tertib pseudo-kedua; lapisan berganda hidroksida; nanohibrid*

### INTRODUCTION

Inorganic materials, particularly of layered double hydroxide (LDH)-type are attracting increasing interest lately due to their versatile multifunctional applications. LDH compound consists of brucite-like sheets, in which divalent cations are partially replaced by trivalent cations. Consequently, the layers become positively charged and the counter anions,  $A^n$  are needed to balance these charges. The counter anion can subsequently be replaced by other anions through various procedures. The LDH general formula is:  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^n)_{x/n} \cdot mH_2O$ , where  $M^{2+} = Mg, Zn, Ni, Cu, Mn$ ; and  $M^{3+} = Al, Cr, Fe$ ;  $x=0.2-0.4$ .  $A^n$  is an anion, such as  $Cl^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $ClO_4^-$  (Cavani et al. 1991; Newman & Dones 1999; Vaccari 1999).

Generally, the intercalation of anion can be accomplished by various routes such as direct co-precipitation method or exchange process. In the former method, the LDH is contacted with a solution of the guest

anion to be intercalated while in the latter method addition of a mixed  $M^{2+}$  and  $M^{3+}$  solution to a basic solution of the anion have to be done. In the rehydration method, calcined LDH is contacted with a solution containing the anion followed by aging (Newman & Dones 1998). Co-precipitation method is the most widely adopted to synthesize LDHs in which a mixed alkaline solution is added to a mixed salt solution and the resultant slurry is aged at a desired temperature. For both ion-exchange and co-precipitation methods, physicochemical and structural properties of the resulting materials depend on the precipitation pH, temperature, ageing time, washing and drying conditions (Aisawa et al. 2001; Aisawa et al. 2005; Radha et al. 2005). Previous work showed that different methods of preparation produce materials with different physicochemical properties (Dupin et al. 2004).

Works on the intercalation of the various organic molecules into the hydroxide layers have been exploited

for various purposes and application in many different areas such as medicine (Tronto et al. 2004), bioactive agent (Aisawa et al. 2005), catalyst (Beaudot et al. 2001; de Acro et al. 2004), anti-inflammatory drugs (Ambrogi et al. 2001; Constantino et al. 2003), urea biosensor and supports (Vial et al. 2006) and decolorizing agents (Hussein et al. 2004).

Lately, work on agrochemicals, in particular pesticide is of current interest. The extensive use of pesticides in agriculture has been a serious environmental concern because of the potential run off and leaching of these compounds through the soil, thus contaminating the surface and ground water. Hence, the production and use of herbicide must be controlled to minimize the potential damage to the environment and public health. An effective way is to design smart formulations, which combines the optimum bioactivity and minimum amount of herbicide. The use of controlled release formulations of herbicides will restrict their movement through the soil profile and prevent contamination of the surface and ground water. Several synthetic cationic surfactants, organic polymers, natural plant lignin and starch materials have been proposed as supporting agents for pesticides in these formulations (Gish et al. 1991). Previous study on herbicides-intercalated Mg/Al layered double hydroxide (LDH) synthesized by direct, regeneration and ion exchange methods shows slow release property (Cardoso et al. 2006).

A compound, 2-(2,4-dichlorophenoxy) propionic acid (Figure 1(a)) commonly known as dichlorprop, is a selective, systemic, hormone-type phenoxy herbicide. It acts by simulating the action of natural hormones and produce uncoordinated plant growth which is selective as it is toxic to dicotyledonous but not monocotyledonous plants. Therefore, it can be used to control 'dicot' (broad leaved) weeds in 'monocot' crops (e.g. cereals, grass). This compound accounts for most herbicide production world wide.

In this work we attempted to intercalate a herbicide, dichlorprop into layered double hydroxide by direct co-precipitation and indirect ion exchange method. In addition, this study was also conducted to assess the potential use of layered double hydroxide as a matrix for a controlled release formulation of dichlorprop, in order to develop new generation of safer-and environmentally-friendly agrochemicals. This development would be able to avoid direct contact of herbicides with the users as well as to reduce leaching off possibility of the herbicides into soil to reduce the contamination of the ground water by harmful agrochemicals from agriculture activities.

## MATERIALS AND METHOD

All chemicals used in this synthesis were obtained from various chemical suppliers and used without further purification. Zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ , HmbG, 98%) and aluminium nitrate hydrate ( $Al(NO_3)_3 \cdot 9H_2O$ , HmbG, 98%) were used as sources of

the cations while dichlorprop ( $C_9H_8Cl_2O_3$ , Sigma-Aldrich, 95%) was used as the starting material of the guest anion. All solutions were prepared using deionized water.

The preparation of the nanohybrid was carried out using direct co-precipitation method. A mother liquor containing  $Zn^{2+}$  and  $Al^{3+}$  cations with Zn to Al initial molar ratio  $R = 3.0$  was prepared. Dichlorprop solution with concentrations of  $0.025 \text{ mol L}^{-1}$  to  $0.3 \text{ mol L}^{-1}$  was slowly added to the mother liquor with simultaneous dropwise addition of aqueous NaOH ( $2.0 \text{ mol L}^{-1}$ ) to bring the solution to  $pH 7.50 \pm 0.02$ . The reaction was carried out under nitrogen atmosphere and the resulting precipitate was aged at  $70^\circ\text{C}$  in an oil bath shaker for 18 h. The synthesized material was then centrifuged, thoroughly washed with deionized water then dried in an oven at  $70^\circ\text{C}$ . The resulting nanohybrid was then powdered and stored in a sample bottle for further use and characterizations.

In the anion exchange method, the nitrate in the interlayer gallery of the layered double hydroxides of Zn/Al prepared earlier was exchanged with dichlorprop, the herbicide for the formation of Zn/Al-dichlorprop nanohybrid. About 2.00 g Zn/Al-LDH was put in contact with 100 mL aqueous solution of dichlorprop and aged for 18 h at  $70^\circ\text{C}$ , using various concentrations of guest anions,  $0.009 - 0.2 \text{ mol L}^{-1}$ . The solution was then aged for another 18 h at  $70^\circ\text{C}$ . The resultant slurry was centrifuged, washed with deionized water and dried in an oven at  $70^\circ\text{C}$ , ground and kept in a sample bottle for further use and characterizations.

The release of dichlorprop from its interlamellae host into the release media, the aqueous solutions at various initial concentrations of sodium carbonate was done by adding about 0.20 g of the nanohybrid into a 500 mL of the aqueous solution. The accumulated amount of dichlorprop released into the solution was measured at preset time at  $\lambda_{\text{max}} = 230 \text{ nm}$  using a Perkin Elmer uv-visible Spectrophotometer, Lambda 35.

Powder X-ray diffraction patterns were recorded from  $2-60^\circ\text{C}$  on an ITAL 2000 diffractometer using  $\text{Cu K}\alpha$  radiation at 40 kV and 30 mA. FTIR spectra of the materials were recorded over the range  $400-4000 \text{ cm}^{-1}$  on a Perkin-Elmer 1752X Spectrophotometer using KBr disc method. Thermogravimetric and differential thermogravimetric analyses (TGA/DTG) was carried out using a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer with heating rate of  $10^\circ\text{C min}^{-1}$  between  $35^\circ\text{C}$  and  $1000^\circ\text{C}$ , under nitrogen flow rate of about  $50 \text{ mL min}^{-1}$ . The BET surface area of the samples was determined by a BEL Japan Belsorp mini using nitrogen gas adsorption-desorption technique at 77 K together with the BET equation.

## RESULTS AND DISCUSSION

### PHYSICO-CHEMICAL PROPERTIES

Figure 1(a) show XRD patterns for Zn/Al-LDH and the resulting nanohybrid synthesized by co-precipitation and

ion exchange method, labeled as DPPADI and DPPAEX, respectively.

As shown in the figure, the resulting nanohybrid afforded well ordered nanolayered structure with expanded basal spacing from 8.9 Å in LDH to 21.7 and 18.7 Å in DPPADI and DPPAEX, respectively. The expansion is attributed to spatial orientation of dichlorprop anion inside the interlamellae of LDH together with its size which is bigger than nitrate, the LDH counter anion. Both nanohybrids produced sharp, symmetrical and intense peaks, especially for the (003) peak and relatively pure intercalated compound were obtained. Noteworthy also that the crystallinity of DPPADI is higher than DPPAEX and the latter is also shows lower crystallinity than the precursor host, LDH. The nanohybrids were prepared using 0.3 M and 0.025 M dichlorprop by direct and indirect, ion exchange method, respectively and were subsequently used for further characterizations.

The high crystallinity of DPPADI may be attributed to long range, well ordered nanolayered structure of DPPA anion in the inorganic interlamellar domain of the nanohybrid and this was taken place during the aging process. The self-organization may be attributed to better interactions between the negatively charged guest anions with the negatively charged brucite-like inorganic layers (Crepaldi et al. 2000). Compared to DPPADI, the crystallinity of DPPAEX is lower as attested by the elimination of some (hkl) reflections, the widening and the decrease of the

PXRD reflections intensity (Lakraimi et al. 2000). For DPPAEX, the crystallinity is lower than the host, LDH. The re-arrangement of the inorganic layered host to compensate the charge of the organic guest during the formation of the nanohybrid by ion exchange process is thought to be reason why the crystallinity of DPPAEX is lower than LDH. This will be subsequently plays a role in controlling the release of the intercalated guest from the inorganic host and will be discussed later.

The FTIR spectra for Zn/Al-LDH (Figure 1(b)) showed a broad and strong band in the range 3200-3600  $\text{cm}^{-1}$  centered at 3448  $\text{cm}^{-1}$  which was due to the O-H stretching vibration of the inorganic layers and interlayer water molecules. Another common wavenumber for LDH-like material is a band at 1630  $\text{cm}^{-1}$  which is assigned to the bending vibration of interlayer water molecules. For Zn/Al-LDH, a strong absorption band centered at 1384  $\text{cm}^{-1}$  is assigned to the N-O stretching vibration. A band in the lower wavenumber region corresponds to the lattice vibration mode such as the translation vibrations of Zn-OH at 611  $\text{cm}^{-1}$  and deformation vibration of OH-Zn-Al-OH at 427  $\text{cm}^{-1}$  (Feng et al. 2006; Zhang et al. 2004).

A band at 3450  $\text{cm}^{-1}$  in the FTIR spectrum of dichlorprop can be attributed to O-H stretching vibration, while a band at 1480  $\text{cm}^{-1}$  is due to an aromatic ring C=C stretching, 1713  $\text{cm}^{-1}$  to C=O stretching, 1287  $\text{cm}^{-1}$  and 1247  $\text{cm}^{-1}$  are due to the symmetric and antisymmetric stretching modes of C-O-C, respectively. A sharp band at

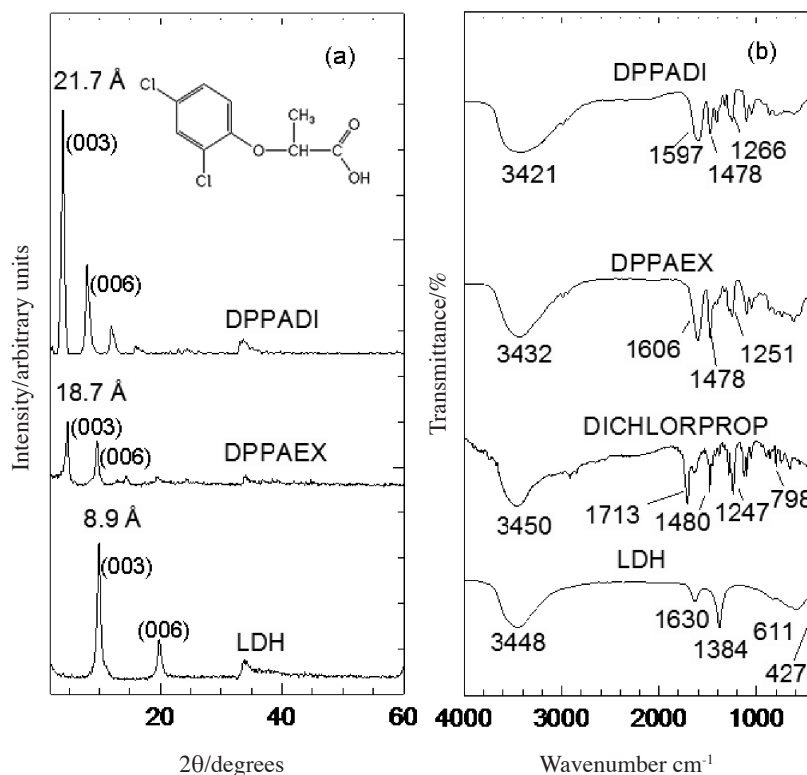


Figure 1. XRD patterns (a) and FTIR spectra (b) of LDH and its nanohybrids synthesized by direct coprecipitation method (DPPADI) and indirect ion-exchange method (DPPAEX). The FTIR spectrum of dichlorprop (DCPROP) is also given. Inset is the molecular structure of dichlorprop

798  $\text{cm}^{-1}$  is attributed to the presence of C-Cl stretching (Ragavan et al. 2006).

FTIR spectra for DPPADI and DPPAEX (Figure 1(b)) show that dichlorprop was intercalated into the LDH interlayer space. A broad absorption band at around 3400  $\text{cm}^{-1}$  for both nanohybrid arises from the stretching mode of OH groups in the brucite-like layer and/or physisorbed water. A band at 1597  $\text{cm}^{-1}$  for DPPADI and 1606  $\text{cm}^{-1}$  for DPPAEX is attributed to carboxylate functional group of the intercalated dichlorprop anion. A band at 1478  $\text{cm}^{-1}$  for both nanohybrids can be attributed to C=C bond vibration of the aromatic group. Band observed at 1266  $\text{cm}^{-1}$  for DPPADI and 1251  $\text{cm}^{-1}$  for DPPAEX corresponds to antisymmetric and symmetric vibrations of C-O-C, respectively.

All these features together with XRD patterns lead to the indication of successful intercalation of the guest into the interlayer of the host. This indicates that the dichlorprop anions have been intercalated into the interlayer galleries of the LDH. Some of the bands are slightly shifted in position, presumably due to slightly different environment of the guests inside the layered host.

Table 1 shows the elemental composition of LDH, DPPADI and DPPAEX. The molar ratio of Zn to Al in DPPADI and DPPAEX is 2.9 and 2.7 respectively, compared to initial molar ratio of 3.0 in the mother liquor. The LDH contains about 3.1% nitrogen which agrees with the presence of strong, sharp band at 1384  $\text{cm}^{-1}$  in the FTIR spectrum. This corresponds to the nitrate group in LDH. The percentage

of dichlorprop intercalated into the interlayer of LDH is 47.8% for DPPADI and 58.5% for DPPAEX estimated from the carbon content of about 21.6 and 26.9%, respectively, indicating that intercalation has actually taken place.

The surface area and porosity of LDH, DPPADI and DPPAEX obtained by nitrogen adsorption-desorption method are given in Table 1. The intercalation of dichlorprop anion has increased the BET surface area from 1.3  $\text{m}^2\text{g}^{-1}$  for LDH to 21.6 and 2.3  $\text{m}^2\text{g}^{-1}$  for DPPADI and DPPAEX, respectively. This shows that the BET surface area of the resulting ion-exchanged materials is generally slightly higher when dichlorprop was intercalated into the LDH inorganic brucite-like interlayers but lower than its counterpart prepared by direct method. The change in pore texture with larger slit width, as a result of modification by the intercalation of dichlorprop anion into the LDH interlayer, in agreement with the expansion of basal spacing of the resulting nanohybrids (Figure 1) is thought to be the reason.

Figure 2(a) shows the nitrogen adsorption-desorption isotherms for LDH, DPPADI and DPPAEX. As shown in the figure, the nitrogen adsorption-desorption isotherm for LDH and both the nanohybrids are of Type IV indicating mesopores-type material (Sing 1998), with adsorption increasing rapidly at low relative pressure followed by a slow uptake and finally rapid near to the saturated relative pressure of >0.9. The desorption branch of hysteresis loop for DPPADI and DPPAEX are much narrower compared to LDH, indicating different pore texture of the resulting material.

TABLE 1. Basal spacing, chemical composition and surface properties of LDH and its dichlorprop nanohybrids synthesized by direct, co-precipitation and indirect, ion exchange methods

Sample	$d$ (Å)	Zn/Al molar ratio	C (%)	N (%)	<sup>a</sup> dichlorprop (% w/w)	BET surface area ( $\text{m}^2\text{g}^{-1}$ )	BJH desorption pore volume ( $\text{cm}^3\text{g}^{-1}$ )	BET average pore diameter (Å)
LDH	8.9	2.8	-	3.1	-	1.3	0.024	127
<sup>b</sup> DPPADI	21.7	2.9	21.6	-	47.8	21.6	0.022	42
<sup>c</sup> DPPAEX	18.7	2.7	26.9	-	58.5	2.3	0.028	50

a = estimated from CHNS analysis based on pure dichlorprop, b synthesized by direct method, c synthesized by indirect method.

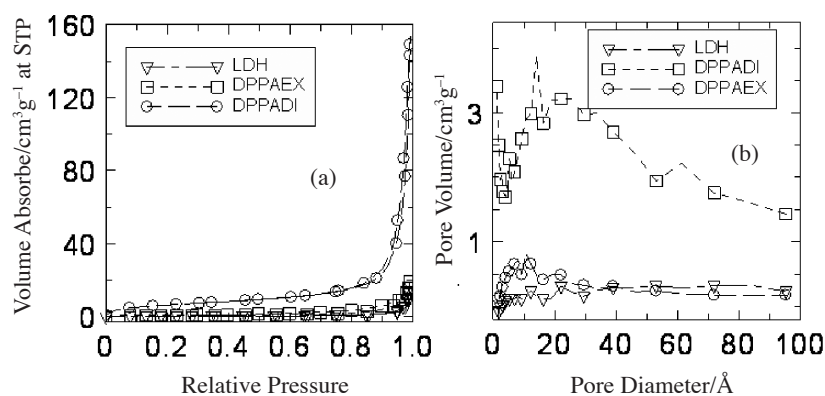


FIGURE 2. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of LDH and its nanohybrids synthesized by direct co-precipitation method (DPPADI) and indirect ion-exchange method (DPPAEX)

The BJH pore size distribution for LDH, DPPADI and DPPAEX are shown in Figure 2(b). As shown in the figure, a sharp peak pore size distribution is observed for DPPADI centered at around 15 and 60 Å. On the other hand, DPPAEX show a sharp peak with pore size distribution centered at around 8 and 11 Å, while for LDH, a broad single peak with pore distribution is centered at 22 Å is observed. The pore volume for LDH and its nanohybrids is given in Table 1. The change in pore size indicates that the pore texture was modified by the intercalation of dichlorprop anion into the LDH interlayer, in agreement with the expansion of basal spacing of the resulting nanohybrids.

The TGA-DTG profiles of LDH, dichlorprop, DPPAEX and DPPADI are shown in Figure 3. In the case of pure dichlorprop, there is only one main thermal event that can be observed at 271°C, attributed to the decomposition and subtle combustion of dichlorprop with weight loss of 98%. The TGA/DTG profiles of LDH shows four thermal events of weight losses which occurred at 110°C, 245°C, 304°C and 369°C with weight losses of 6.8%, 15.3%, 5.9% and 7.2%, respectively. The first weight loss in LDH corresponds to the removal of water physisorbed on the external surface of the particles. The second weight loss is attributed to strongly held water molecules. The third and fourth weight losses are almost completed at 370°C and correspond to removal of hydroxyl group from brucite-like layers and the removal of interlayer anions.

The TGA-DTG curves of DPPADI reveal three distinguishable weight loss steps occurring at 78°C, 170°C and 336°C with losses of 6.0%, 7.2% and 40.6%,

respectively. However, TGA-DTG curves of DPPAEX show four steps of weight loss which occurred at 72°C, 159°C, 338°C and 958°C with weight losses of 5.2%, 6.4%, 42.7% and 13.8%, respectively. For both DPPADI and DPPAEX, the first weight loss is due to the removal of surface physisorbed water molecules and the second stage is attributed to the removal of interlayer anion and dehydroxylation of the hydroxyl layer. The third weight loss above 300°C corresponds to the major decomposition/combustion of the organic moiety in the interlayer of the nanohybrid leaving only a relatively less volatile metal oxide. The weight loss (13.8%) occurred at around 958°C for DPPAEX was found to be less dominant in DPPADI. We attribute this observation as due to the decomposition of more stable compound of the inorganic layered composition of the nanohybrid by combustion reaction (Lakraimi et al. 2000).

Compared to the decomposition temperature of pure dichlorprop with maximum temperature of 271°C, the thermal stability of dichlorprop is greatly improved after intercalation between the LDHs layers which is 366°C for DPPADI and 338°C for DPPAEX, implying that Zn–Al-LDHs can be used as an alternative inorganic matrix for storing active organic moiety with better thermal stability.

#### RELEASE PROPERTIES

The release of dichlorprop from the DPPADI and DPPAEX nanohybrids into Na<sub>2</sub>CO<sub>3</sub> media prepared at four different concentrations of Na<sub>2</sub>CO<sub>3</sub> solution is shown in Figure 4. Fast release of dichlorprop from DPPADI and DPPAEX

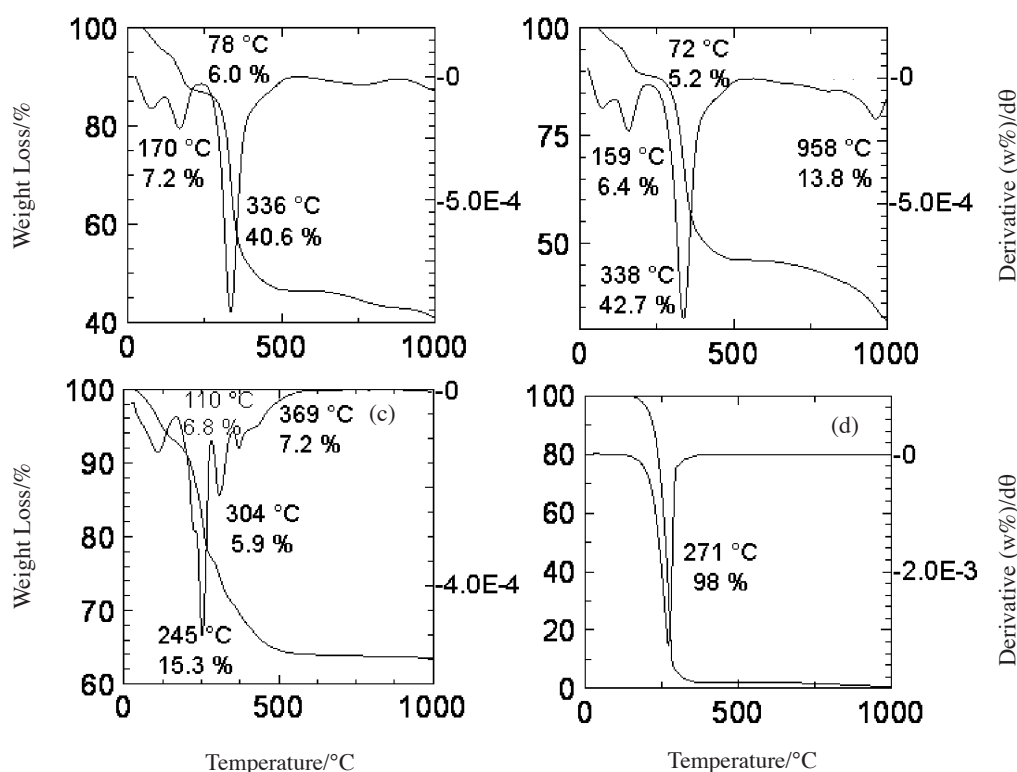


FIGURE 3. TGA/DTG thermograms of the nanohybrids synthesized by direct co-precipitation method (DPPADI) (a) and indirect ion-exchange method (DPPAEX) (b), LDH (c) and dichlorprop (d)

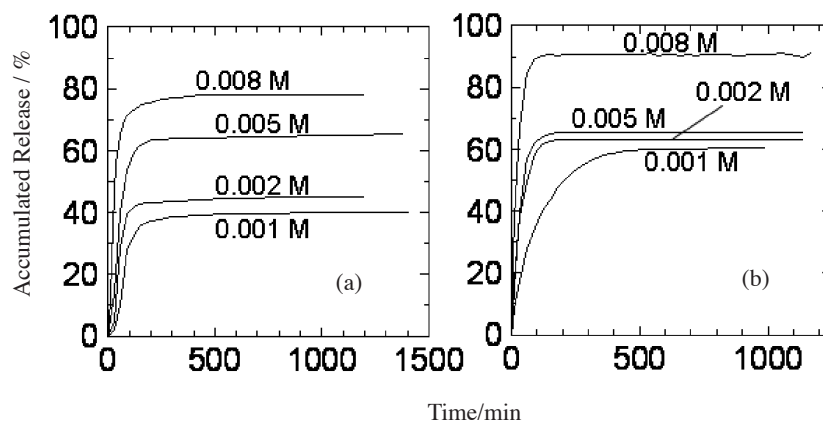


FIGURE 4. Release profiles of dichlorprop from the nanohybrids synthesised by direct co-precipitation method, DPPADI (a) and indirect, ion-exchanged method, DPPAEX (b) into various concentrations of  $\text{Na}_2\text{CO}_3$  solutions

nanohybrid can be observed in the first 0-150 min, followed by a slower one thereafter before a saturated release is achieved.

The reason for the ion exchange process to have taken place is due to the higher affinity of the smaller size and higher charge of carbonate anions compared to dichlorprop. The greater affinity of carbonate anions for the exchange sites on LDHs compared to the affinity of monovalent anionic pesticides for such sites has previously been reported by several authors (Sato et al. 1991; Ulibarri et al. 1995). As a result, the intercalated herbicides was exchanged by carbonate anions and subsequently released into the solution. The release was found to be of controlled manner as the deintercalation of the guest is hindered by the formation of the "new LDH" at the outer layer of the particles. This was attributed to the replacement of the intercalated herbicides by carbonate and hydroxyl anion from solution. The percentage release of dichlorprop from both DPPADI and DPPAEX into  $\text{Na}_2\text{CO}_3$  solution is shown in the Figure 5.

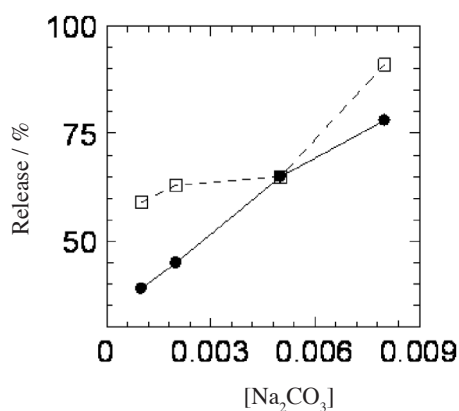


FIGURE 5. Plot of the maximum accumulated percentages release of dichlorprop against concentration of the  $\text{Na}_2\text{CO}_3$  aqueous solutions from the nanohybrids synthesised by direct co-precipitation method, DPPADI (solid line) and indirect, ion-exchanged method DPPAEX (dotted line)

The results from the release profiles of dichlorprop from both nanohybrids show that the amount of the maximum accumulated dichlorprop released from DPPAEX is higher and faster than DPPADI for all the  $\text{Na}_2\text{CO}_3$  concentrations. This is due to the difference in the amount of dichlorprop which is readily available to be released, which can be possibly tied up to the crystallinity of the materials.

The nanohybrid material that was obtained through the indirect ion exchange method possess lower crystallinity, but higher loading of the dichlorprop herbicide. In addition the resulting nanohybrid is able to release the active substances in higher percentage with greater rate. These are the properties that are desired for the controlled release formulation.

The method of preparation plays an important role in determining the physico-chemical properties of the resulting nanohybrids, in particular their surface properties and release behavior of the guest. The release of DPPA from DPPADI was found to be at a much slower rate than that of DPPAEX in carbonate solution. Such observation can be related to the orientation and arrangement of the anion within the inter-gallery matrix as well as the size of the crystallites. The anion is thought to be arranged in a well-ordered manner in the host during the intercalation process through direct self assembly route and therefore led to the formation of nanohybrid with much higher crystallinity compared to the nanohybrid synthesized using anion exchange method. Release of the intercalated guest from nanohybrid with high crystallinity and larger size particle would be slower than the ones with lower crystallinity and smaller size. This is due to the stability of the anion arrangement as discussed earlier.

Although the BET surface area of the DPPADI material is about 10 times higher than DPPAEX and it is expected that the high surface area characteristic could enhance the kinetic release, but the result seems otherwise. Although the specific surface area is high, the less accessibility of the surface of DPPADI to be ion exchanged with the incoming

anion possibly explained the lower release rates of DPPADI than DPPAEX.

Four models were used to fit the release data of dichlorprop from the nanohybrids; zeroth order (1) (Valelas et al. 1995), first order (2) (Hussein et al. 2007), pseudo-second order (3) (Lu et al. 2006) and parabolic diffusion (4) (Kodama et al. 2001) for which the equations are as shown below, in which  $x$  is the percentage release of dichlorprop at time  $t$ ,  $M_i$  and  $M_f$  are the concentration of dichlorprop in solution at time  $t$ , whereas  $M_f$  is the concentration of dichlorprop at equilibrium and  $C$  is a constant.

$$x = t + C \quad (1)$$

$$-\log(1 - M_i/M_f) = t + C \quad (2)$$

$$t/M_i = 1/kM_f^2 + t/M_f \quad (3)$$

$$M_i/M_f = kt^{0.5} + C \quad (4)$$

Figure 6 displays the experimental data fitted to the pseudo-second order kinetic models for dichlorprop released from both nanohybrids using  $\text{Na}_2\text{CO}_3$  as the release media. Parameters such as rate constants,  $k$ , correlation

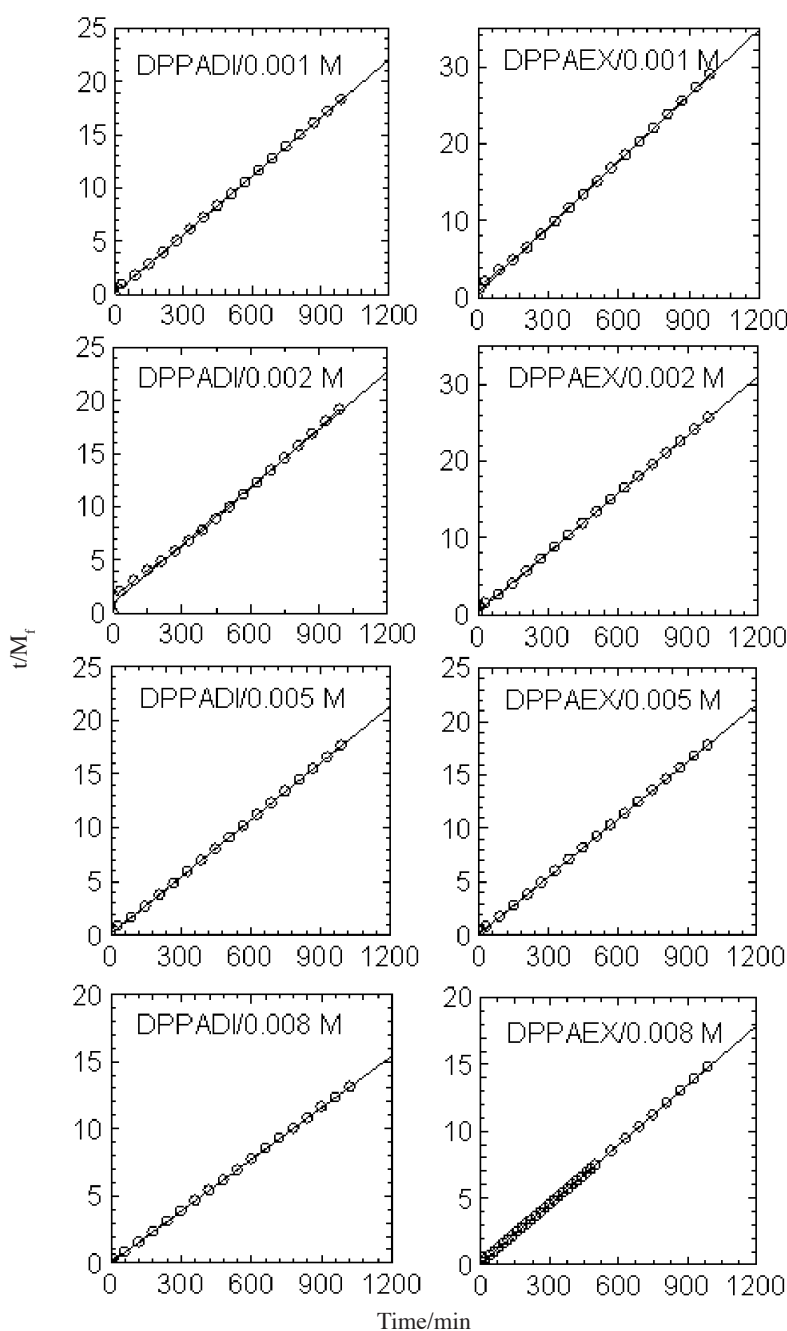


FIGURE 6. Fitting of dichlorprop release data from the nanohybrids synthesised by direct co-precipitation method, DPPADI and indirect ion exchange method, DPPAEX into  $\text{Na}_2\text{CO}_3$  solutions at various concentrations to pseudo-second order kinetics

coefficients,  $r^2$  and related constants are listed in Table 2, along with  $t_{1/2}$ , i.e. the time required for 50% of dichlorprop is released, calculated using the corresponding equations. For both DPPADI and DPPAEX, the  $k$  values increase and  $t_{1/2}$  values decrease as the concentration of the sodium carbonate increases. This is obvious because as the concentration of the carbonate increases, more carbonate species are available to replace dichlorprop, resulting in lower values of  $t_{1/2}$  and higher values of  $k$  (Figure 7(a) and (b)).

Table 2 shows that compared to other models used in this work, the pseudo-second order kinetics give the best fit for dichlorprop release from both DPPADI and DPPAEX in  $\text{Na}_2\text{CO}_3$  solutions. It can also be seen that linearization of the zeroth order, first kinetic order and parabolic diffusion model do not fit nicely to the experimental data (Table 2)

as shown by their correlation coefficients ( $r^2$ ) under the experimental conditions described earlier, which indicates that the pseudo-second order is the best to describe the release behavior kinetic of dichlorprop from the DPPADI and DPPAEX nano hybrids. This shows that the release of the dichlorprop from the inorganic LDH interlayer involved dissolution of nano hybrids as well as ion exchange between the intercalated anions in the interlayer LDH and the carbonate anions in the aqueous solution which is controlled by pseudo-second order.

## CONCLUSIONS

A herbicide compound, 2(2,4-dichlorophenoxy)propionic acid (dichlorprop) was intercalated into the interlamellae of Zn/Al layered double hydroxide (LDH) for the formation

TABLE 2. Rate constants and correlation coefficients obtained by fitting of the data of the release of dichlorprop from DPPADI and DPPAEX into  $\text{Na}_2\text{CO}_3$  solutions

$\text{Na}_2\text{CO}_3$ concentration (mol L <sup>-1</sup> )	Zeroth order	First order	Parabolic diffusion	Pseudo-second order		
				$r^2$	$k$ (10 <sup>-2</sup> )/mol <sup>-1</sup> Ls <sup>-1</sup>	$t_{1/2}$ (min)
nanohybrid synthesized by direct method (DPPADI)						
0.001	0.461	0.492	0.697	0.099	29	0.999
0.002	0.405	0.436	0.636	0.129	20	1.000
0.005	0.341	0.395	0.565	0.192	9	1.000
0.008	0.207	0.304	0.409	0.223	6	1.000
nanohybrid synthesized by ion exchange method (DPPAEX)						
0.001	0.545	0.618	0.772	0.0341	56	0.997
0.002	0.254	0.288	0.464	0.243	8	1.000
0.005	0.236	0.267	0.438	0.250	7	1.000
0.008	0.248	0.309	0.458	0.372	3	1.000

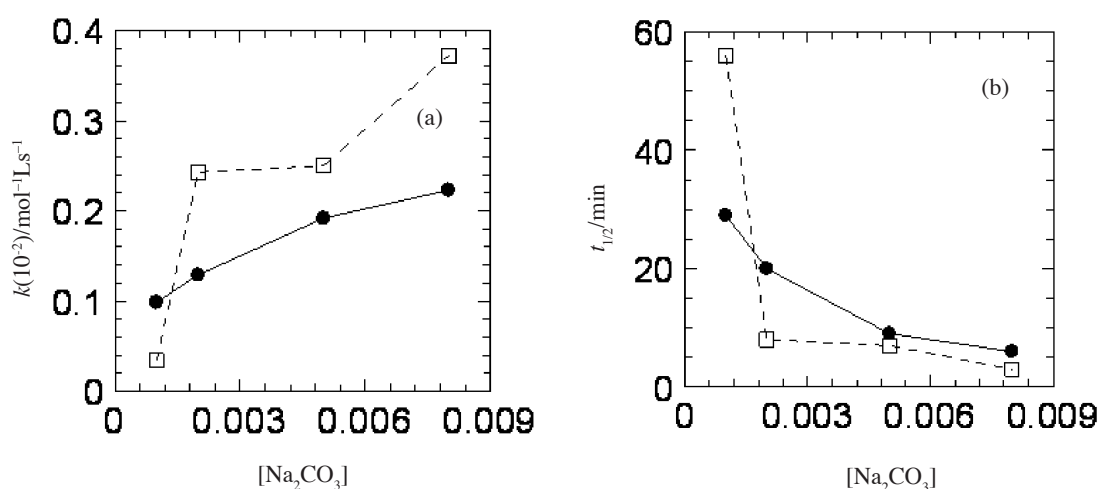


FIGURE 7. Plot of  $k$  (a) and  $t_{1/2}$  (b) values against concentration of sodium carbonate for the release of dichlorprop from the nano hybrids synthesised by direct co-precipitation method, DPPADI (solid line) and indirect, ion-exchanged method DPPAEX (dotted line)



of new organic-inorganic nanohybrids and subsequently used as a controlled release formulation. Two methods of intercalation were adopted, direct co-precipitation and indirect ion exchange methods. The interlayer spacing of LDH increased from 8.9 to 18.7 and 21.7 Å for the nanohybrid synthesized by ion exchange and by direct method, respectively. Both methods afforded well ordered nanohybrid materials when they were synthesized at the same pH and ratio but at different concentrations of dichlorprop. Release of dichlorprop into Na<sub>2</sub>CO<sub>3</sub> aqueous solutions is shown to be governed by pseudo-second order kinetics with the maximum release of 78 and 91%, from the nanohybrid synthesized by direct co-precipitation and indirect, ion exchange method, respectively. This work shows that LDH can be used as an effective medium for controlled release formulation of a herbicide, dichlorprop.

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