

## Layered Double Hydroxide as a Potential Matrix for Controlled Release Formulation of Phenoxyherbicides

*Hidroksida Lapisan Berganda sebagai Matrik Berpotensi bagi Formulasi Pelepasan Terkawal terhadap Fenoksiherbisida*

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### Abstract

Phenoxyherbicides, namely 4-(2,4-dichlorophenoxy)butyrate (DPBA), 2-(2,4-dichlorophenoxy)propionate (DPPA) and 2(3-chlorophenoxy)propionate (CPPA) were intercalated separately into the interlamellae of Zn/Al layered double hydroxides (LDHs) by direct co-precipitation method for the formation of their nanohybrids, DPBA-LDH, DPPA-LDH and CPPA-LDH, respectively. Powder x-ray diffraction patterns of the sample show that the interlayer spacing expanded from 8.9 Å in LDH to 28.14, 21.44 and 20.05 Å for DPBA-LDH, DPPA-LDH and CPPA-LDH nanocomposite, respectively. Release study of the phenoxyherbicides, DPBA, DPPA and CPPA anion from their respective nanohybrids were carried out at different concentrations of sodium phosphate. The maximum percentage release of DPBA, DPPA and CPPA into 0.008 M sodium phosphate was found to be different; 51, 76 and 87 %, respectively. Rapid release of the phenoxyherbicides was observed at the beginning of the process followed by a slower one near to the equilibrium. Kinetic study shows the release behavior for all the phenoxyherbicides from their nanohybrids is governed by pseudo second order.

**Keywords** intercalation; nanohybrids; phenoxyherbicides; control release; kinetic study

### Abstrak

Fenoksiherbisida, iaitu 4-(2,4-diklorofenoksi)butirat (DPBA), 2-(2,4-diklorofenoksi) propionat (DPPA) dan 2(3-klorofenoksi)propionat (CPPA) telah berinterkelasi secara berasingan ke dalam ruang antara lapisan Zn /Al berlapis berganda hidroksida (LDHs) dengan kaedah se-pemendakan langsung bagi pembentukan masing-masing untuk nanohybrid, DPBA-LDH, DPPA-LDH dan CPPA-LDH. Corak belauan serbuk sinar-x sampel menunjukkan bahawa jarak di antara ruang telah membesar daripada 8.9 Å dalam LDH kepada 28.14, 21.44 dan 20.05 Å masing-masing untuk nanokomposit DPBA-LDH, DPPA-LDH dan CPPA-LDH. Kajian lepasan terkawal fenoksiherbisida, anion DPBA, DPPA dan CPPA daripada nanohybrid masing-masing telah dijalankan pada kepekatan natrium fosfat yang berbeza. Peratusan pelepasan maksimum DPBA, DPPA dan CPPA ke dalam 0.008 M natrium fosfat telah didapati berbeza, iaitu masing-masing 51, 76 dan 87 %. Pada awalnya

proses pelepasan pesat bagi fenoksiherbisida telah belaku dan diikuti dengan proses yang perlahan apabila hampir pada keseimbangan. Kajian kinetik menunjukkan kelakuan pelepasan bagi semua fenoksiherbisida daripada nanohybrid adalah mengikut tertib kedua pseudo.

**Kata kunci** interkelasi; nanohybrid; fenoksiherbisida; kawalan pelepasan; kajian kinetik

## Introduction

Various harmful substances have been contaminating soils and aqueous environments to threaten human health. One approach to minimize such transport losses is to use controlled release formulation in which the pesticides is incorporated in a matrix or carrier before application, thereby limiting the amount available for unwanted processes. Numerous synthetic and natural material have been proposed for use in controlled released formulation and have been shown to reduce pesticide leaching through soil to the water table. Recently there has been a new interest of the control release formulation in the use of natural soil constituents, such as clays, iron oxides, or humic acids (Gerstl *et al.*, 1998; Johnson & Pepperman, 1998; Gonza'lez-Pradas *et al.*, 1999; El-Nahhal *et al.*, 2000; Hermosı'n *et al.*, 2001).

Layered double hydroxides (LDHs) or the so-called anionic clays, are a class of materials which is simple to prepare have received increased attention due to their tailor-made properties and wide applications (Cavani, 1991). A wide range of composition can be obtained for these materials by changing the nature of the metal cations and the ratio  $M^{II}/M^{III}$  as well as the type of the intercalated anion  $X^{m-}$  in the general formula:  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [X^{m-}_{x/m} \cdot mH_2O]$  (Newman & Jones, 1998; de Roy, 1998).

These materials as are now well established as excellent anion exchanger and their extensive intercalation chemistry has widespread applications in areas such as heterogeneous catalysis (Vaccari, 1999; Boyapati *et al.*, 2002) optical materials (Corma *et al.*, 1995; Ogawa & Kurodo, 1995) biomimetic catalysis (Tagaya *et al.*, (1994); Sels *et al.*, (1999)) separation science (Ukrainczk *et al.*, 1995; Fogg *et al.*, 1999) and as DNA reservoirs (Fogg *et al.*, 1998; Choy *et al.*, 2000).

In this work, we describe the potential use of LDH as a matrix for slow release of herbicides by intercalation of this material with phenoxyherbicides anion DPBA, DPPA and CPPA (Figure 1) into the interlayer. Herbicides that have the greatest potential for groundwater contamination are characterized by their high water solubility and moderate to long half-lives. The use of controlled release formulations of herbicides may also restrict their movement through the soil profile. In addition, kinetic studies have been carried out using four models to study the release profile of anion from the nanohybrids, namely zeroth, first, pseudo-second order and parabolic diffusion. Kinetic analysis was performed to correlate the experimental data based on these models.

## Experimental

### Method and Materials

All chemicals used in this synthesis were obtained from various chemical suppliers and used without any further purification. 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  $R = 3.0$  and  $0.025 \text{ mol L}^{-1}$  to  $0.3 \text{ mol L}^{-1}$  DPBA, DPPA and CPPA were prepared. The resulting solution was adjusted to  $pH 7.50 \pm 0.02$  by dropwise addition of an aqueous NaOH ( $2.0 \text{ mol L}^{-1}$ ). The reaction was carried out under nitrogen atmosphere. The resulting precipitate was aged at  $70 \text{ }^\circ\text{C}$  in an oil bath shaker for 18 hours. The synthesized material was then centrifuged, thoroughly washed with deionized water and dried in an oven at  $70 \text{ }^\circ\text{C}$ . The resulting nanohybrid was then powdered and stored in a sample bottle for further use and characterizations.

Powder X-ray diffraction patterns were recorded at  $2 - 60^\circ$  on an ITAL 2000 diffractometer using  $Cu K_\alpha$  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. The elemental composition of the samples molar ratio of the resulting nanohybrids and LDH were determined by using inductively couple plasma-atomic emission spectrometry (ICP-AES), using a Perkin Elmer Spectrophotometer model Optima 2000DV under standard condition and CHNS analyzer model CHNS-932 (LECO). Thermogravimetric and differential thermogravimetric analyses (TGA/DTG) were carried out using a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer with heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  between  $35-1000 \text{ }^\circ\text{C}$ , under nitrogen flow rate of about  $50 \text{ ml min}^{-1}$ .

The release of DPBA, DPPA and CPPA from its interlamellae host into the release media, the aqueous solutions at various initial concentrations of sodium phosphate was done by adding about 0.20 g of the nanohybrid into a 500 mL of the aqueous solution. The accumulated amount of DPBA, DPPA and CPPA released into the solution was measured at preset time at  $\lambda_{\text{max}} = 231, 230$  and  $217 \text{ nm}$  respectively, using a Perkin Elmer uv-visible Spectrophotometer Lambda 35.

## Results and Discussions

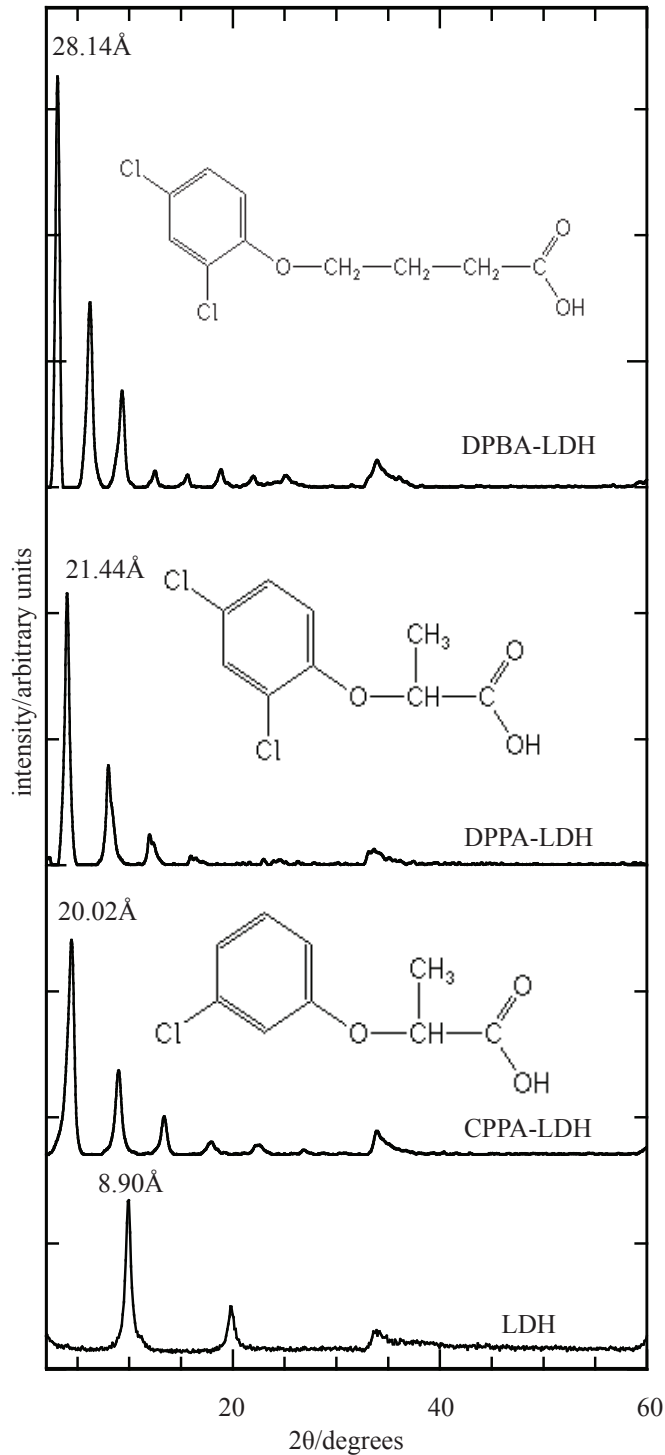
### Powder X-ray diffraction

Figure 1 illustrates the XRD patterns for pure phase Zn/Al-LDH intercalated separately with DPBA, DPPA and CPPA phenoxyherbicides at the optimized synthesis condition. The XRD patterns for Zn/Al- $\text{NO}_3$ -LDH (LDH) is also shown for comparison. LDH, DPBA-LDH, DPPA-LDH and CPPA-LDH were prepared with the same initial Zn to Al molar ratio ( $R_1=3$ ) but the optimized condition were found to be at  $0.2 \text{ mol L}^{-1}$  DPBA for DPBA-LDH and  $0.3 \text{ mol L}^{-1}$  DPPA and CPPA for DPPA-LDH and CPPA-LDH, respectively.

As shown in Figure 1, The LDH shows a well developed layered structure with the basal spacing (003) of  $8.9 \text{ \AA}$ , which is in agreement with the thickness of the anion  $\text{NO}_3^-$  and the inorganic brucite-like layer which is  $4.1$  and  $4.8 \text{ \AA}$ , respectively (Fogg *et al.*, 1998).

The intercalation of DPBA, DPPA and CPPA phenoxyherbicides into the LDH inorganic layers resulted in materials exhibiting the diffraction pattern characteristic of a pure phase nanohybrid structure with a sharp (003) diffraction peak centered at  $28.14, 21.44$  and  $20.02 \text{ \AA}$ , respectively. The interlayer spacing increases by  $19.24, 12.54$  and  $11.12 \text{ \AA}$  for DPBA-LDH, DPPA-LDH and CPPA-LDH nanohybrid in comparison with nitrate anion-pillared LDH, which shows an interlayer spacing of  $8.9 \text{ \AA}$ , indicating the successful intercalation of phenoxyherbicides anions into the interlayer region. The basal spacing of DPBA-LDH

differ to that of DPPA-LDH and CPPA-LDH, which can be related to the size of the DPBA anion which is larger than that of DPPA and CPPA anion.



**Figure 1** PXRD patterns of LDH, DPBA-LDH, DPPA-LDH and CPPA-LDH nanocomposites together with chemical structure of DPBA, DPPA and CPPA (inset)

## FTIR spectroscopy

The FTIR spectra of LDH are shown in Figure 2. Broad absorption peaks in the region 2800–3800  $\text{cm}^{-1}$  centered at 3452  $\text{cm}^{-1}$  are assigned to O–H stretching mode and deformation vibration of the LDH layer or interlayer water molecules. A band observed at 1630  $\text{cm}^{-1}$  is assigned to the bending vibration of interlayer water molecules and  $\text{NO}_3^-$  gives a very strong absorption peak at 1379  $\text{cm}^{-1}$ , and this peak has disappeared after the intercalation process, indicating that  $\text{NO}_3^-$  was fully replaced by the phenoxyherbicide anion. A band in the lower frequency 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 407  $\text{cm}^{-1}$  (Masarudin *et al.*, 2009; Zhang *et al.*, 2004) can also be observed.

The FTIR spectra of DPBA, DPPA and CPPA phenoxyherbicide anions are shown in Figure 2. A broad adsorption at 3000-3800  $\text{cm}^{-1}$  is due to the O-H stretching vibration. For all DPBA, DPPA and CPPA anions, a sharp band at 1713-1714  $\text{cm}^{-1}$  is due to the stretching band of C=O. Bands at 1466-1480  $\text{cm}^{-1}$  and 1400-1410  $\text{cm}^{-1}$  are attributed to stretching vibration of aromatic ring C=C and strong absorption bands at 1273-1287  $\text{cm}^{-1}$  and 1203-1241  $\text{cm}^{-1}$  are due to the symmetric and asymmetric stretching modes of C-O-C. A sharp band at 735-761  $\text{cm}^{-1}$  is attributed to the presence of C-Cl stretching mode (Feng *et al.*, 2006).

The observation of a broad adsorption peak at the region 3000-3800  $\text{cm}^{-1}$  for all DPBA-LDH, DPPA-LDH and CPPA-LDH nanohybrid shows the existing of O-H symmetric stretching, for all of them. The carboxylate anion gave rise to two bands, a strong asymmetrical band near 1600  $\text{cm}^{-1}$  and a weaker asymmetrical stretching band near 1400  $\text{cm}^{-1}$  (Ogawa & Kurodo, 1995). All the nanohybrid FTIR spectra (Figure 2) show the two bands of a strong symmetrical stretching and weaker asymmetrical stretching at 1590-1609  $\text{cm}^{-1}$  and 1469-1476  $\text{cm}^{-1}$ , respectively. As expected, the spectra resemble a mixture of each FTIR spectra of phenoxyherbicides anion and LDH. This indicates that the DPBA, DPPA and CPPA phenoxyherbicides anions have been intercalated into the interlayer galleries of the LDH. Some of the bands are slightly shifted in position because of the interaction between phenoxyherbicides anion and inorganic layered host.

Elemental analysis for Zn, Al and C for all the samples is given in Table 1. The molar Zn/Al ratio is in all cases reasonably close to the expected value of 3.0. The value for the DPBA-LDH, DPPA-LDH and CPPA-LDH is 2.0, 3.0 and 2.9, respectively. These show that the Zn to Al molar ratios was adjusted accordingly to compensate the anionic charge for the formation charge-neutral nanohybrids.

**Table 1** Basal spacing and chemical composition of LDH, DPBA-LDH, DPPA-LDH and CPPA-LDH nanohybrids

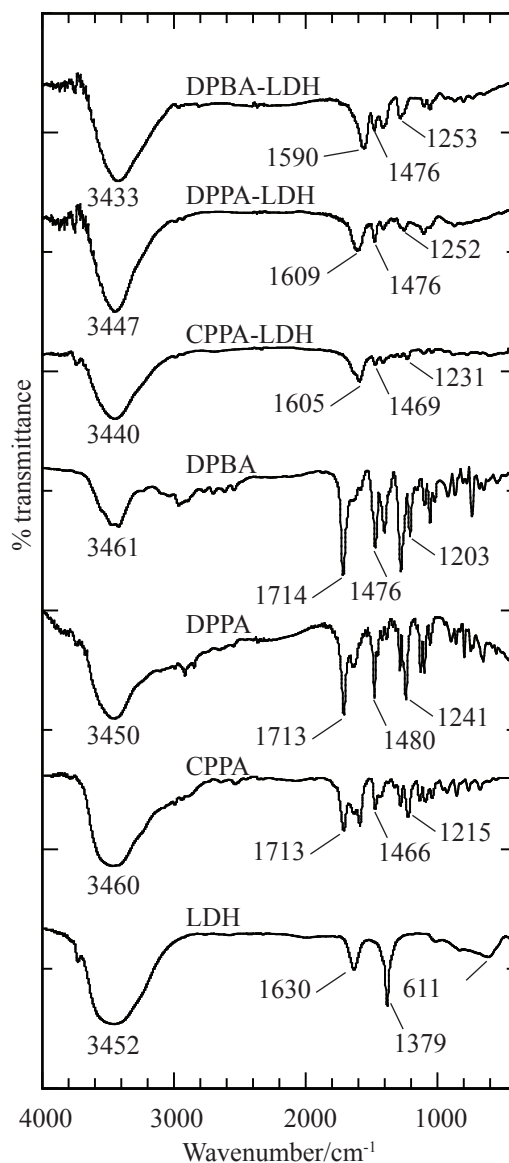
Sample/ anion	d(Å)	Zn/Al molar ratio	molecular fraction( $X_{\text{Zn}}$ )	(N)/C(%)	<sup>a</sup> anion (% w/w)
LDH	8.9	2.8	0.74	(3.0)	-
DPBA	28.7	2.0	0.67	26.4	54.72
DPPA	21.5	3.0	0.75	21.6	47.77
CPPA	20.5	2.9	0.74	20.6	38.26

<sup>a</sup> = estimated from CHNS analysis based on pure DPBA, DPPA and CPPA

The amount of phenoxyherbicides anion incorporated, as determined by the carbon content, depends on the anion used. The presence of nitrogen in LDH agrees with FTIR spectra (Figure 2) which shows a broad adsorption band at  $1379\text{ cm}^{-1}$  due to  $\text{NO}_3^-$  functional group. The percentages of carbon in the phenoxyherbicides nanohybrids are different due to their different carbon number in the formula weight. As a result of carbon content loading percentage of phenoxyherbicides was estimated as given in Table 1.

### Thermal analysis

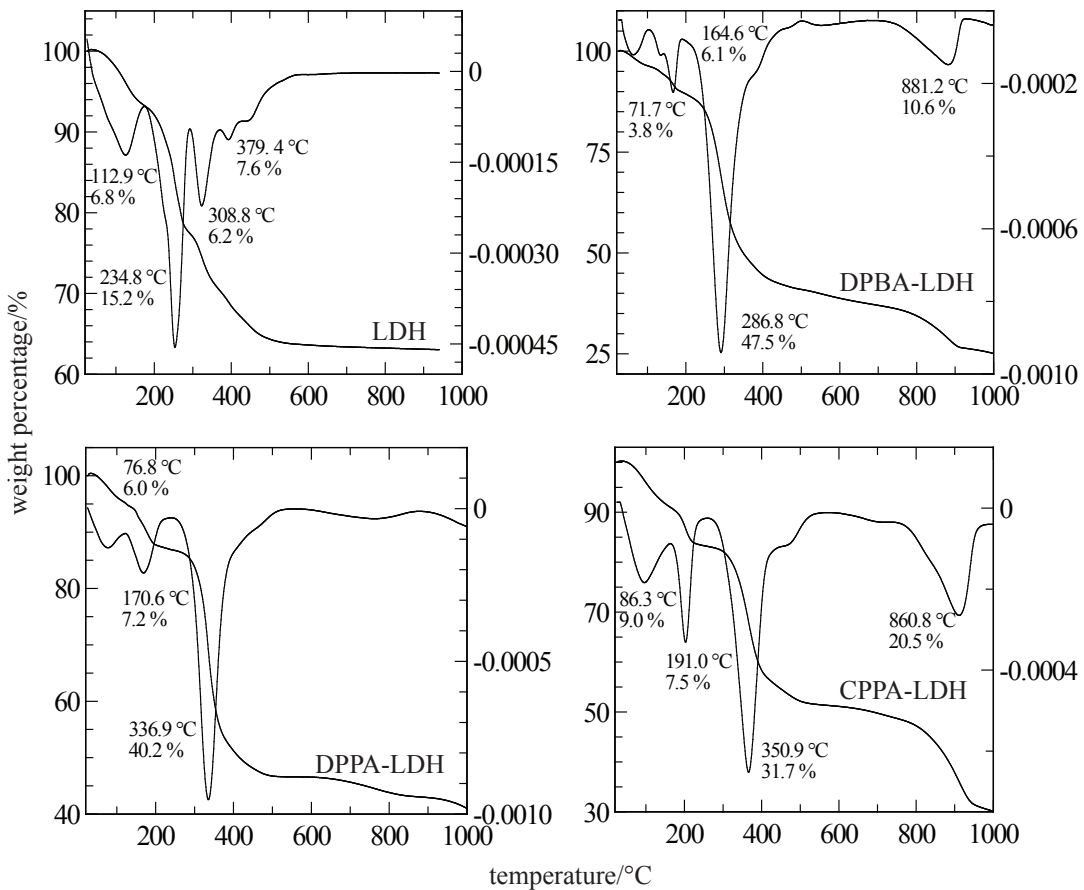
LDH and its nanohybrids were subjected to the thermal analysis by measuring the weight changes with temperature and three major stages of weight lost were observed. The first



**Figure 2** FTIR spectra of LDH, DPBA, DPPA, CPPA herbicides anion and its nanocomposites

stage was characterized by the loss of surface water or physically adsorbed water and interlayer water observed at 35 - 200 °C (Figure 3). The second stage was attributed to the removal of interlayer anions and dehydroxylation of the hydroxyl layer which can be observed at 201 - 600 °C. The third weight loss above 601 °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. For Zn/Al-layered double hydroxide, the weight loss is due to decomposition of the nitrate anions which occurred at 234.8 °C, compared to 286.8 °C – 350.9 °C in the nanohybrids.

As shown in Figure 3, the nanohybrids show high maximum temperature for anion removal, which is above 280.0 °C when compared to the DPBA, DPPA and CPPA anions in the pure form in which the maximum temperature of 231.7 °C, 271.6 °C and 204.3 °C, respectively was observed. This shows that DPBA, DPPA and CPPA intercalated between the layers of Zn/Al-LDH is thermally more stable than their counterpart, implying that Zn–Al-LDHs can be used as an alternative inorganic matrix for storing organic molecule. Summary of data is given in the Table 2.



**Figure 3** DTA-DTG thermograms of LDH, DPBA-LDH, DPBA, DPPA-LDH, DPPA, CPPA-LDH and CPPA. The analysis is given in Table 2.



**Table 2** TGA-DTG results for LDH, DPBA, DPPA, CPPA and its nanohybrids

Temperature (°C)	Weight loss			Total weight loss (%)
	35-200	201-600	601-1000	
LDH	6.8 (T <sub>max</sub> =112.9 °C)	29.0 (T <sub>max</sub> =234.8 °C)	-	35.8
DPBA-LDH	9.9 (T <sub>max</sub> =114.6 °C)	47.5 (T <sub>max</sub> =286.8 °C)	10.6 (T <sub>max</sub> =881.2 °C)	68.0
DPPA-LDH	13.2 (T <sub>max</sub> =170.6 °C)	40.2 (T <sub>max</sub> =336.9 °C)	-	53.4
CPPA-LDH	14.5 (T <sub>max</sub> =191.0 °C)	31.7 (T <sub>max</sub> =350.9 °C)	20.5 (T <sub>max</sub> =860.8 °C)	66.7

### Controlled release

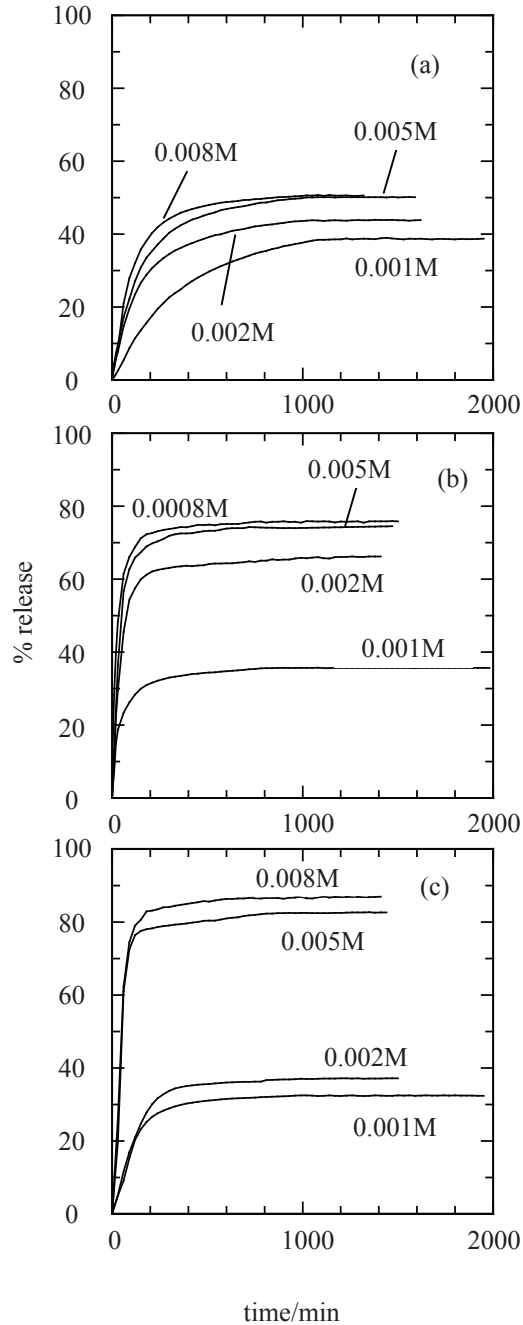
Figure 4 shows the release profile of DPBA, DPPA and CPPA herbicides from their respective nanohybrids into four different concentrations of sodium phosphate solutions, 0.001, 0.002, 0.005 and 0.008 mol L<sup>-1</sup>. Generally, herbicides release increases with the increase concentration of Na<sub>3</sub>PO<sub>4</sub> solution, due to the higher ion exchange capability of the herbicides anion which was intercalated between the LDH interlayers with PO<sub>4</sub><sup>3-</sup> in the solution. The reason that the ion exchange process could take place is due to the higher affinity of the smaller size and higher charge density of phosphate anions compared to DPBA, DPPA and CPPA. Previous studies reported that the greater affinity of carbonate anions for the exchange sites on LDHs compared to the affinity of monovalent anionic pesticides for such sites (Ragavan *et al.*, 2006; Cardoso *et al.*, 2006; Sato & Okuwaki, 1991) resulted in ion exchange process to occur.

The release profiles of DPBA, DPPA and CPPA herbicides from their respective nanohybrid show a similar release pattern with slow release at the beginning followed by a faster one thereafter, until it reach to an equilibrium, in the range of 0 to 200 minutes. The maximum release of herbicides anion at 0.008 mol L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub> shows that CPPA give the highest percentage release with 87 %, compared to DPPA and DPBA with values of 76 % and 51 %, respectively (Figure 4). This is due to the different ability of the herbicides anion to be deintercalated from the layered double hydroxide into the medium by ion exchange process. CPPA anion with smaller relative molecular mass than DPPA and DPBA anions will be replaced easily by phosphate anion and subsequently release into the solution. This observation was supported by PXRD study which shows that the basal spacing of CPPA-LDH is 20.02 Å while DPPA-LDH and DPBA-LDH is 21.44 Å and 28.14 Å, respectively, where the size intercalated CPPA anion into the interlayer lamellae is smaller than DPPA and DPBA anions.

### Kinetic study

Kinetic studies of release of DPBA, DPPA and CPPA from its nanohybrid were analyzed by applying four different kinetic models so that the behavior of the release process can be





**Figure 4** Release profile of (a) DPBA, (b) DPPA and (c) CPPA from the interlamellae of the nanocomposite into the aqueous solutions containing various concentrations of  $\text{Na}_3\text{PO}_4$ .

studied. The methods used are zeroth order (Ulibarri *et al.*, 1995), first order (Valelas *et al.*, 1995), pseudo-second order (Hussein *et al.*, 2007; Lu *et al.*, 2006) and parabolic diffusion (Kodama *et al.*, 2001), for which the equations are given below, in which  $x$  is the percentage

release of herbicides anion at time  $t$ ,  $M_i$  and  $M_f$  are the initial and final concentrations of herbicides anions, respectively and  $C$  is a constant. The parameter correlation coefficients,  $r^2$  rate constants,  $k$  are given in Table 3 along with  $t_{1/2}$  values i.e. the time required for 50 % of DPBA, DPPA and CPPA to be released, calculated from the corresponding equations.

$$x = t + C \tag{1}$$

$$-\log(1 - M_i / M_f) = t + C \tag{2}$$

$$t / M = 1 / kM^2 + t / M_f \tag{3}$$

$$M_i / M_f = kt^{0.5} + C \tag{4}$$

**Table 3** Rate constants and correlation coefficients obtained from fitting of the release data of DPBA, DPPA and CPPA from DPBA-LDH, DPPA-LDH and CPPA-LDH into  $\text{Na}_3\text{PO}_4$  solutions.

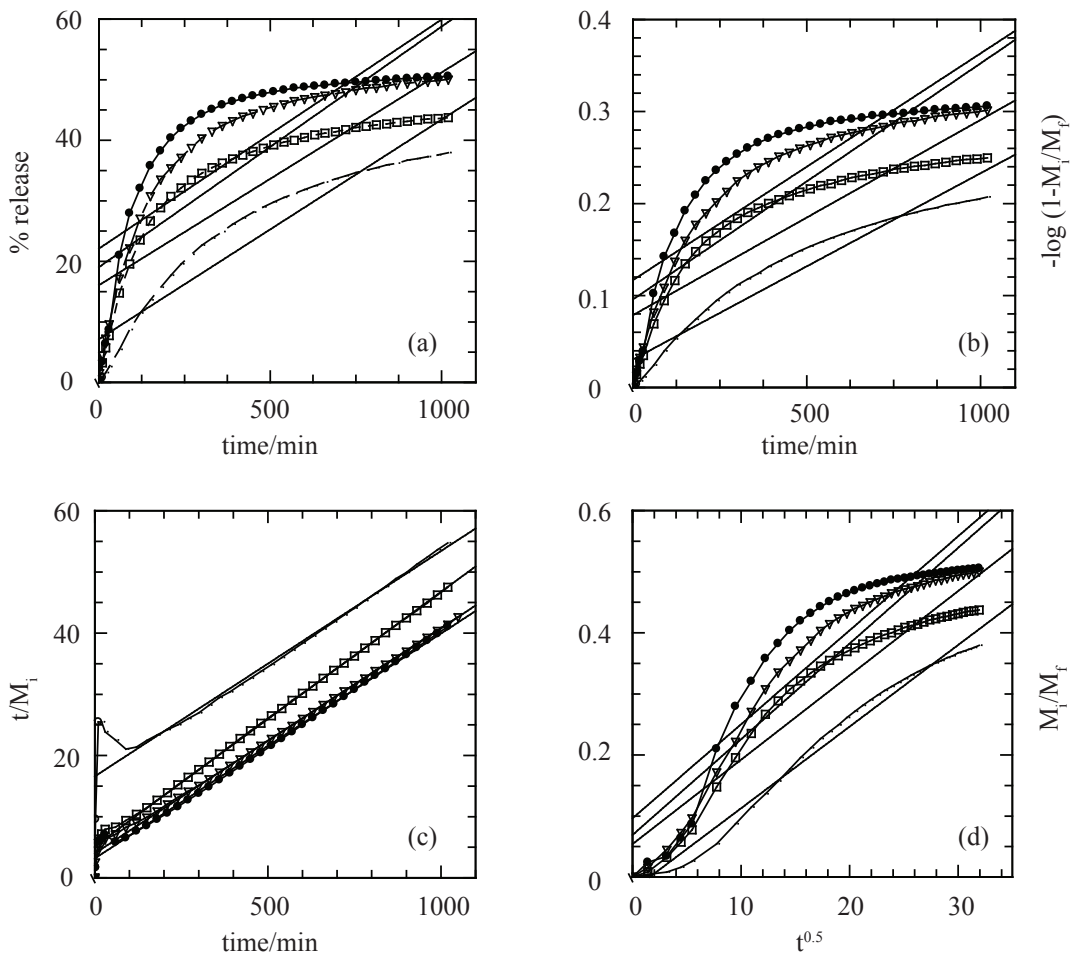
DPBA-LDH						
$\text{Na}_3\text{PO}_4$ Concentration (mol L <sup>-1</sup> )	Zeroth Order	First Order	Parabolic Diffusion	Pseudo-second Order		
				$r^2$	$k (\times 10^{-3})(\text{mg}^{-1}\text{Ls}^{-1})$	$t_{1/2}$ (min)
0.008	0.893	0.927	0.984	0.910	0.042	94
0.005	0.726	0.783	0.909	0.995	0.033	119
0.002	0.715	0.780	0.902	0.996	0.033	138
0.001	0.621	0.648	0.833	0.993	0.008	644
DPPA-LDH						
0.008	0.505	0.546	0.734	1.000	0.044	31
0.005	0.424	0.494	0.655	0.999	0.080	126
0.002	0.413	0.506	0.645	0.999	0.140	194
0.001	0.376	0.476	0.030	1.000	1.035	345
CPPA-LDH						
0.008	0.552	0.588	0.765	0.990	0.292	19
0.005	0.552	0.590	0.765	0.989	0.237	25
0.002	0.290	0.439	0.492	0.998	0.138	95
0.001	0.291	0.454	0.501	0.999	0.159	96

Figures 5, 6 and 7 show the fitting of the data to various models for DPBA, DPPA and CPPA. The released was done into sodium phosphate solutions at difference concentrations. The extent of time of DPBA, DPPA and CPPA release in which the values are fitted to the equation and the regression are given in Table 3 for time intervals of 0-1000 minutes.

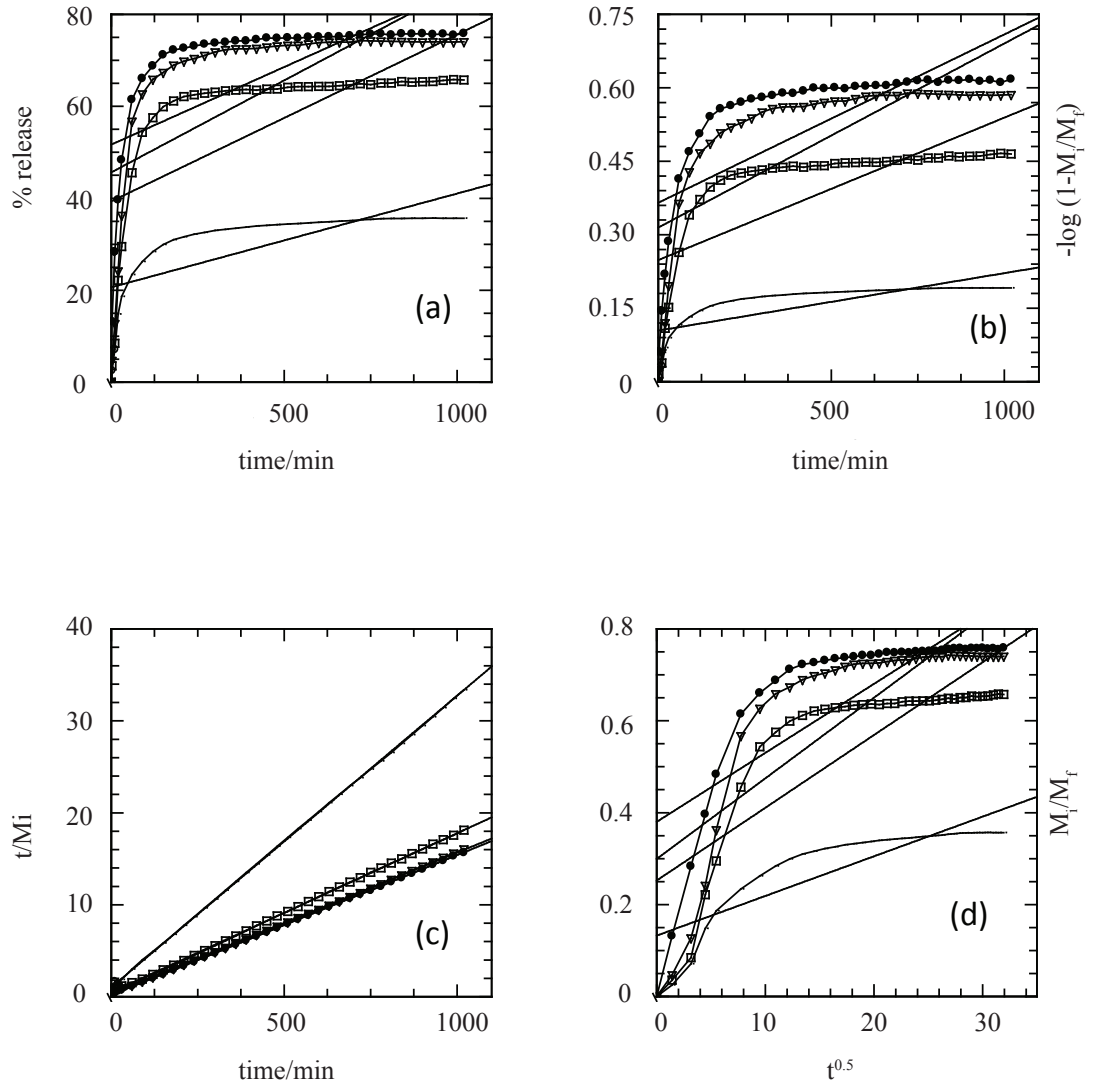
It can be seen from the figures that the best fit is for the plot of  $t/M_i$  against time, showing a good agreement with the pseudo-second order kinetics model, for all DPBA-LDH, DPPA-LDH and CPPA-LDH, in all the  $\text{Na}_3\text{PO}_4$  solutions. It can also be seen that

linearization of the zeroth order, first kinetic order and parabolic diffusion model do not fit nicely to the experimental data. It can also be seen from Figures 5, 6, 7 and Table 3, that the correlation coefficients ( $r^2$ ) is small for the first, zeroth order and parabolic diffusion model compared to the pseudo-second order. This indicated that under our experimental conditions, the pseudo-second order is better to describe the release behavior kinetic of DPBA, DPPA and CPPA from the DPBA-LDH, DPPA-LDH and CPPA-LDH nanohybrids, respectively. This shows that the release of the organic moiety from the inorganic LDH interlayer involved dissolution of nanohybrids as well as ion exchange between the intercalated anions in the interlayer LDH and the phosphate anions in the aqueous solution which controlled by pseudo-second order.

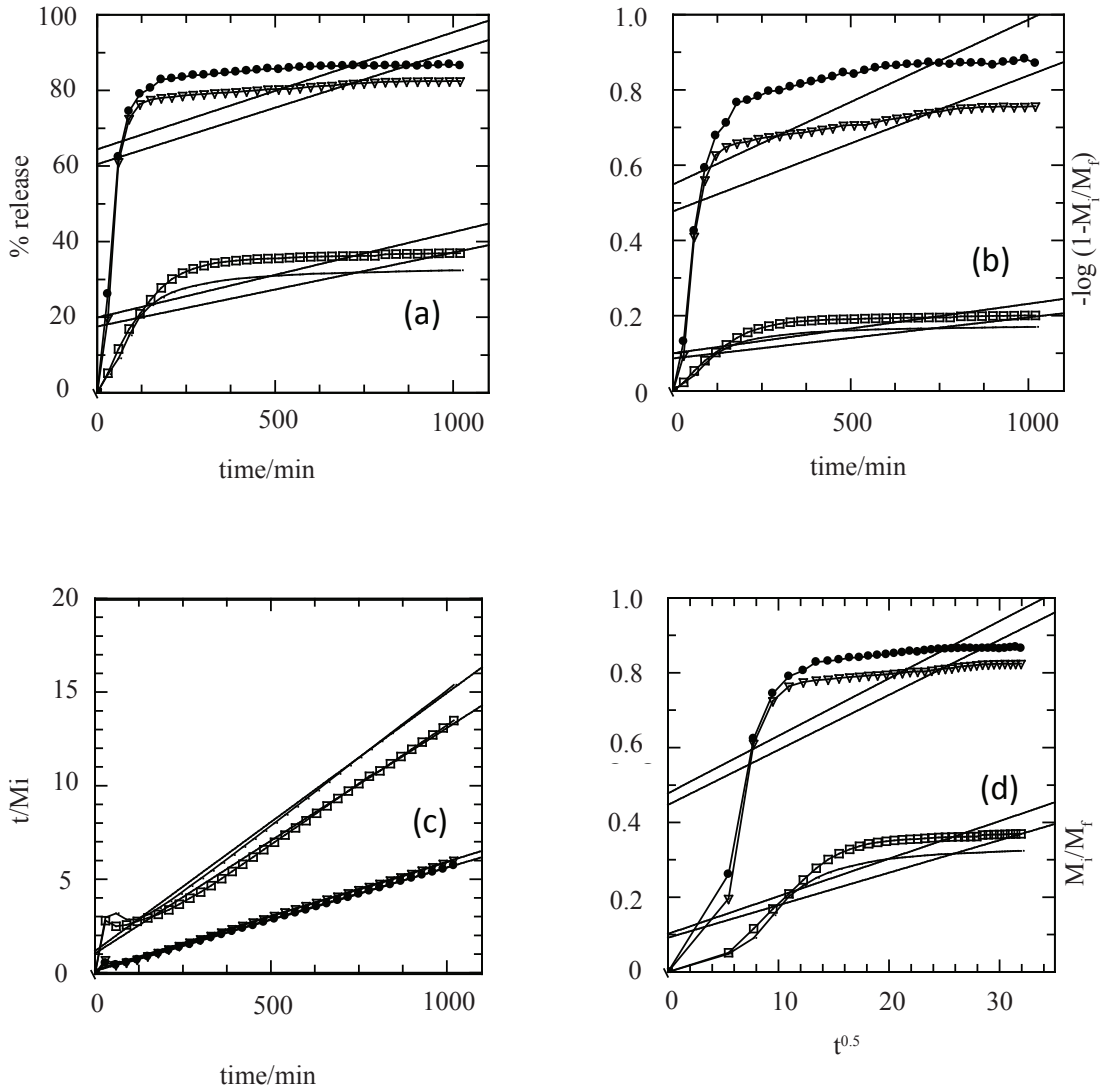
In order to compare the release behavior of DPBA, DPPA and CPPA from its DPBA-LDH, DPPA-LDH and CPPA-LDH nanohybrid, the  $t_{1/2}$  values, i.e. the time taken for



**Figure 5** Fitting of the DPBA data released into the aqueous solutions containing various concentrations of  $\text{Na}_3\text{PO}_4$ : 0.001 M (circles), 0.002 M (squares), 0.005 M (triangles) and 0.008 M (dot) to the zeroth (a), first (b) and pseudo-second order (c) kinetics, and Parabolic Diffusion (d) for DPBA-LDH ( $t = 0$ -1000 min)



**Figure 6** Fitting of the DPPA data released into the aqueous solutions containing various concentrations of Na<sub>3</sub>PO<sub>4</sub>; 0.001 M (circles), 0.002 M (squares), 0.005 M (triangles) and 0.008 M (dot) to the zeroth (a), first (b) and pseudo-second order (c) kinetics, and Parabolic Diffusion (d) for DPPA-LDH (t = 0-1000 min)



**Figure 7** Fitting of the CPPA data released into the aqueous solutions containing various concentrations of  $\text{Na}_3\text{PO}_4$ ; 0.001 M (circles), 0.002 M (squares), 0.005 M (triangles) and 0.008 M (dot) to the zeroth (a), first (b) and pseudo-second order (c) kinetics, and Parabolic Diffusion (d) for CPPA-LDH ( $t = 0-1000$  min)

the herbicides anion concentration to increase to one-half of its initial values were used (Table 3). For all the nanohybrids, the  $t_{1/2}$  values decreases as the concentration of the sodium phosphate increases. This is obvious because as the concentration of the phosphate increases, more phosphate anions are available to be ion exchanged with DPBA, DPPA and CPPA, resulting in lower values of  $t_{1/2}$ . In addition, this can also be used as a means to control the kinetics of the release of the herbicides.

## Conclusion

The intercalation of the phenoxyherbicides, DPBA, DPPA and CPPA into a layered inorganic host, LDH was carried out using the co-precipitation method. Basal spacing of the nanohybrid depends on the size of phenoxyherbicides anion. The intercalation of the phenoxyherbicides into the interlayer of LDH was proved by FTIR spectra. Thermal analysis shows that decomposition temperature of nanohybrid is higher than pure phenoxyherbicides anions which indicate that LDH host enhances the thermal stability of DPBA, DPPA and CPPA. Release of phenoxyherbicides anions from pillared materials with different concentrations of phosphate solution shows that the DPBA, DPPA and CPPA release gave the same release profile. Kinetic study of the phenoxyherbicides shows that the release is governed by pseudo-second order.

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