



Effect of incoming and outgoing exchangeable anions on the release kinetics of phenoxyherbicides nano hybrids

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ABSTRACT

The release of chlorophenoxyherbicides agrochemicals, namely 2-chloro- (2CPA), 4-chloro and 2,4,5-trichloro (TCPA) phenoxyacetates from their nano hybrids into various aqueous solutions; carbonate, sulfate and chloride was found to be controlled by pseudo-second order rate expression. The percentage saturated released was found to be anionic-dependent, in the order of carbonate > sulfate > chloride for the release media and 2CPA > 4CPA > TCPA for the anionic guests. This study demonstrates that the release of the phenoxyherbicides agrochemicals from the nano hybrid compounds can be tuned by choosing the right combination of exchangeable anions both the incoming and the outgoing anions.

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1. Introduction

Agrochemicals in particular pesticides, herbicides and plant growth regulator have been widely used in the modern agriculture to maintain the quality and high yield production of crops. Amongst these, chlorophenoxyherbicides such as 2,4-dichlorophenoxyacetic acid (24D), 2,4,5-trichlorophenoxyacetic acid (TCPA) and 4-chlorophenoxyacetic acid (4CPA) are the most commonly used. These chemicals may reach human through the food chain, drinking water or by direct contact with the chemicals. It was reported that such agrochemicals have been contaminating groundwater as well as surface water at extremely very low level [1]. The retention of pesticides by soil may prevent its short term access to the surface and groundwater and on nontarget organisms, but the persistent of the undegraded pesticide or of harmful metabolites leads to its accumulation in the environment and increase the risk to human health [2].

Nowadays, controlled release technologies have emerged as an approach to solve this problem [3] not only attaining the most effective use of the active agent, but may also preventing the environmental pollution [4]. Ideally the delivery system should be able to release the bioactive material at precisely the required

rate needed by the crops [5]. This will prevent problem of leaching, evaporation, degradation and excessive use of the harmful chemicals [6]. Various natural and synthetic materials have been proposed to be used in pesticide controlled release formulation which trapped or sorbed the pesticides in an inert support and gradually released over time [7]. The use of natural biodegradable polymer such as alginate [3] and starch [8–11] were studied for controlled release of 1-naphthalene acetic acid (NAA), atrazine, alachlor and 24D. The release of 1-naphthalene acetate (NAA) from the alginate formulation was found to be controlled by the pH of the release media [3]. Controlled release formulation using lignin [12] and chitosan [5] for atrazine was also reported. The use of natural polymer in the preparation of the controlled release formulation is of special interest due to possible biological degradation of the matrices and relatively low cost of the raw materials [9].

Sorption plays a fundamental role in the transport dynamic, persistence, transformation and bioaccumulation of pesticides [13]. Sorption of metalaxyl and cyprodinil was found to be dependent on the soil organic matter and humic acid [14,15]. Studies on the quaternary ammonium herbicides, paraquat, diquat and difenzoquat show that most of the sorption capacity in the soil was related to clay, in the order of paraquat > diquat > difenzoquat [16]. Clay minerals including organically modified clay have been used as a matrix for controlled release of herbicides such as hexazinone [17], fenuron [18], simazine [19] and picloram [17]. Similarly, anionic clay, so-called layered double hydroxides (LDHs) can be used as a layered host for anionic pesticides namely 4CPA [20], 24D [8,21–23]

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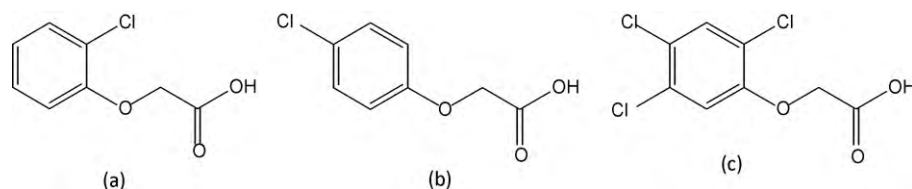


Fig. 1. Molecular structure of 2-chlorophenoxyacetic acid (a), 4-chlorophenoxyacetic acid (b) and 2,4,5-trichlorophenoxyacetic acid (c).

and 4-chloro-2-methylphenoxyacetic acid (MCPA) and picloram [7].

LDHs are a 2D layered material, commonly known as hydroxide-like materials or anionic clays. The general formula is $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}A_{x/n}^{n-}m\text{H}_2\text{O}$, where M^{2+} and M^{3+} = di-, tri-valent metal cations, A is the interlayer anion and x is the mole fraction of $M^{3+}/(M^{2+} + M^{3+})$ having a typical value of 0.25 [24]. The 2D negatively charged layered structure of LDH makes it flexible to be used as a host for many chemicals, especially herbicides of anionic type to balance the charge. By the virtue of ion-exchange property, the resulting host-guest materials can be used as a controlled release formulation of agrochemicals such as NAA [25] and 24D [21,26,27].

This work aimed at studying the effect of the incoming exchangeable anions in the release media on the kinetic release behavior of the outgoing intercalated anion from their respective phase pure, well-ordered chlorophenoxyacetates-Zn-Al-layered double hydroxide nanohybrids. The release of the phenoxyherbicides; 2CPA, 4CPA and TCPA was done separately, in which each nanohybrid was kept in contact with each aqueous medium; carbonate, sulfate and chloride and their release behavior was compared. This work is performed to find the potential application of Zn-Al-LDH as the support host for the herbicides by focusing on their controlled release behavior.

2. Experimental

2.1. Synthesis of LDHs and the nanohybrids

All the chemicals for the synthesis were used as received without further purification. All solutions were prepared using deionized water. N2CPA was synthesized by self-assembly method from mixed aqueous solution of 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.05 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. 0.2 M 2CPA and 2 M NaOH was slowly added to the solution with vigorous stirring under nitrogen atmosphere until the final pH of 7.5 ± 0.2 . The precipitates were aged for 18 h in an oil bath shaker at 70°C , filtered, thoroughly washed and dried in an oven at 70°C . Similar procedure was performed to prepare N4CPA and NTCPA from mixed aqueous solution of 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.025 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the addition of 0.4 M 4CPA to form N4CPA and 0.4 M TCPA to form NTCPA. LDHR4- CO_3 was prepared by self-assembly method, similar to that described by Miyata [28], using slow addition of alkaline solution (2 M NaOH and 2 M Na_2CO_3) to a mixed aqueous solution of 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.05 M $\text{Al}(\text{NO}_3)_3$. LDHR4-Cl was prepared by slow addition of NaOH 2 M to a mixed aqueous solution of 0.1 M ZnCl_2 and 0.05 M AlCl_3 . LDHR4- SO_4 was prepared by slow addition of 2 M NaOH to a mixed aqueous solution of 0.1 M $\text{Zn}(\text{SO}_4)_2$ and 0.05 M $\text{Al}_2(\text{SO}_4)_3$. LDHR2- CO_3 , LDHR2-Cl and LDHR2- SO_4 were prepared by similar procedure except with the molar ratio of Zn to Al = 2.

2.2. Characterization

Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Shimadzu XRD-6000 powder diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.540562 \text{ \AA}$) at 40 kV and 30 mA, 2° min^{-1} . Elemental

composition of the samples and the Zn/Al molar ratio of the resulting nanohybrids and LDH were determined 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).

2.3. Release of chlorophenoxyacetates herbicide

Release of chlorophenoxyacetates herbicide from the hosts was studied using 0.0005 M aqueous solutions of Na_2CO_3 , Na_2SO_4 and NaCl. The accumulated amount of chlorophenoxyacetates released into the solution was measured *in situ* at $\lambda_{\text{max}} = 273, 216.5$ and 206.5 nm for 2CPA, 4CPA and TCPA, respectively, using a Perkin Elmer UV-vis Spectrophotometer Lambda 35. Data was collected, stored and fitted to zero-, first-, pseudo-second order kinetics and parabolic diffusion model.

3. Results and discussion

Fig. 1 shows the molecular structure of 2-chlorophenoxyacetic acid (2CPA), 4-chlorophenoxyacetic acid (4CPA) and 2,4,5-trichlorophenoxyacetic acid (TCPA). These agrochemicals are amongst the most commonly used to control weeds in fields, grasslands, lawns and recreational areas [29] as well as for the monocot crops such as cereals and sugarcane [30].

3.1. Formation and physicochemical properties of the nanohybrids

PXRD patterns for LDHs as hosts, and their respective nanohybrids with chlorophenoxyacetates prepared at the optimum condition, in which a pure phase, well-ordered nanolayered structure could be obtained are shown in Fig. 2. Hybridization of Zn-Al-LDH with 2CPA, 4CPA and TCPA for the formation of their respective nanohybrids was accomplished using direct coprecipitation method and the resulting nanohybrids were labeled as N2CPA, N4CPA and NTCPA, respectively, with basal spacing of 18.5, 20.1 and 26.2 \AA , respectively. The expansion of the basal spacing in comparison with the LDHs can be attributed to the bulkier size of the guests than nitrate together with their spatial orientation in the interlamellae space of the LDH. The carbon content of N2CPA, N4CPA and NTCPA is 17.6, 20.5 and 20.0%, which gave percentage loadings of 34.2, 39.8 and 53.3%, respectively, as listed in Table 1.

Table 1

Basal spacing and chemical composition of LDH and its chlorophenoxyacetates nanocomposites.

sample	d (Å)	R _i	M _i	Zn/Al ratio	X _{Al}	% C/N (w/w)	% CPA (w/w)
N2CPA	18.5	2	0.2	1.9	0.36	17.6 (C)	34.2
N4CPA	20.1	4	0.4	3.68	0.22	20.5 (C)	39.8
NTCPA	26.5	4	0.4	3.93	0.20	20.0 (C)	53.3

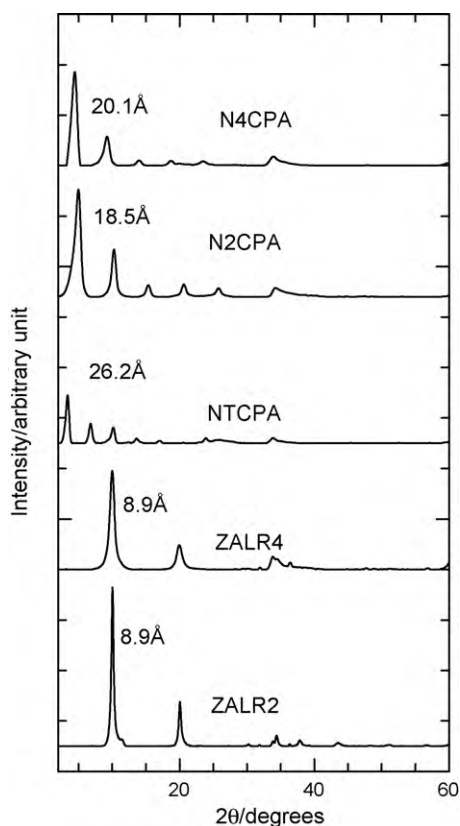


Fig. 2. PXRD patterns of Zn-Al-LDH and its resulting nanocomposites with various chlorophenoxyacetates moieties, 2CPA (N2CPA), 4CPA (N4CPA) and TCPA (NTCPA).

3.2. Release profile of the guest anions

The release profiles of 2CPA, 4CPA and TCPA from their respective nanohybrids interlamellae into the aqueous solutions containing various incoming or 'sacrificial' anions, namely carbon-

ate, sulfate and chloride are shown in Fig. 3(a–c). The release of the herbicides from their respective nanohybrids was fast for the first 300 min followed by a slower one thereafter before reaching the saturated release at about 500 min for 2CPA and 4CPA. However, the saturated release for TCPA extended to around 2000 min in all the studied media (Fig. 3(d–f)). Generally, the release rate of the herbicides in all the media is in the order of 2CPA > 4CPA > TCPA.

3.3. The effect of incoming exchangeable anion in the aqueous media

As shown in Fig. 3, for all the guest herbicides, percentage saturated release of the anions is in the order of carbonate > sulfate > chloride with percentages saturated release of 91, 82 and 68% for 2CPA; 72, 63 and 48% for 4CPA compared to 66, 57 and 32% for TCPA, respectively. This shows that the affinity of carbonate, sulfate and chloride towards the inorganic interlamellae for all the nanohybrids is in the given order, in agreement with previous work by Miyata [28]. This works demonstrate that the affinity of the incoming anion plays an important role in determining the percentage amount of saturated release of the anion from the nanohybrid into the aqueous solution. In another word, ion-exchange process is controlled by the affinity of the anions to be ion exchanged and subsequently determined the amount of the guest to be released.

Kinetic release rates for all the anions into the release media is also in the order of carbonate > sulfate > chloride, as reflected by the k values. The $t_{1/2}$ value, i.e. the time taken for the herbicides concentrations to be at half of their accumulated saturated release are shown in Table 2. The $t_{1/2}$ of the accumulated saturated release was 71, 79 and 210 min for 2CPA, 4CPA and TCPA, respectively in Na_2CO_3 . A slightly higher $t_{1/2}$ was observed for all herbicides in Na_2SO_4 amounted of 77, 97 and 282 min, respectively, for 2CPA, 4CPA and TCPA. Release of herbicides into the NaCl aqueous solution gave the highest $t_{1/2}$ values, amounted of 103, 146 and 442 min for 2CPA, 4CPA and TCPA, respectively. The $t_{1/2}$ values is in the order of carbonate < sulfate < chloride agrees with the release rate of the herbicides in the respective aqueous solution, as $t_{1/2}$ is inversely

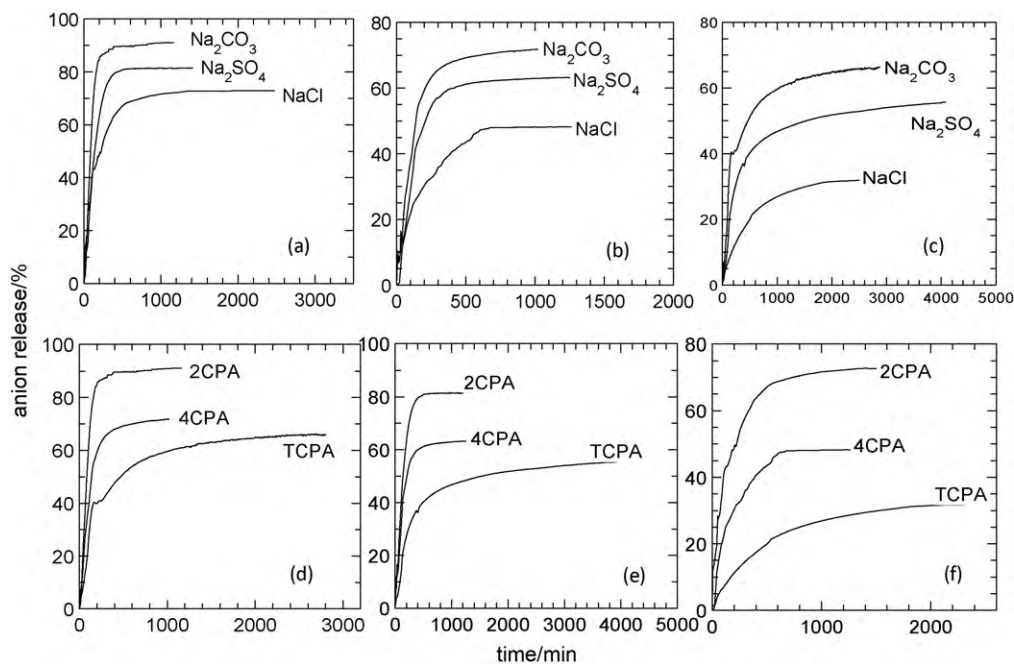


Fig. 3. Release profile of 2CPA (a), 4CPA (b) and TCPA (c) into 0.0005 M aqueous solutions containing various anions, CO_3^{2-} , SO_4^{2-} and Cl^- from their respective nanohybrids, N2CPA, N4CPA and NTCPA and comparison of release of 2CPA, 4CPA and TCPA into Na_2CO_3 (d), Na_2SO_4 (e) and NaCl (f).

Table 2
Fitting the release data of 2CPA, 4CPA and TCPA from N2CPA, N4CPA and NTCPA, respectively into various media using zeroth, first, parabolic diffusion and pseudo-second order kinetic models for 0–1000 min. Only $t_{1/2}$ and k values for pseudo-second order are given in the table. The regression, r^2 values and the equations used for each model are also given in the table.

Equation	Zero order $C_t = kt + c$			First order $-\log(1 - C) = kt + c$ Regression, r^2			Parabolic diffusion $C_t/C_{eq} = c + kt^{0.5}$			pseudo-second order $t/C_t = 1/k_2 C_{eq}^2 + (1/q_e) \cdot t$		
	2CPA	4CPA	TCPA	2CPA	4CPA	TCPA	2CPA	4CPA	TCPA	2CPA	4CPA	TCPA
Media												
Na ₂ CO ₃	0.87	0.53	0.75	0.98	0.65	0.85	0.54	0.49	0.52	0.98	0.99	0.98
Na ₂ SO ₄	0.55	0.57	0.79	0.67	0.65	0.85	0.62	0.60	0.49	0.99	0.99	0.96
NaCl	0.69	0.74	0.93	0.80	0.79	0.95	0.66	0.59	0.56	0.99	0.99	0.95
Pseudo-second order												
	$t_{1/2}$ (min)			$k (\times 10^{-4}) (\text{Lmg}^{-1} \text{min}^{-1})$								
Media							2CPA		4CPA		TCPA	
Na ₂ CO ₃	71			79			2.48		2.35		0.92	
Na ₂ SO ₄	77			97			2.20		2.10		0.79	
NaCl	103			146			1.80		1.70		0.62	

c = a constant, C_{eq} = concentration of anion at equilibrium, C_t = concentration of anion at time t , C_o = initial concentration of the anions.

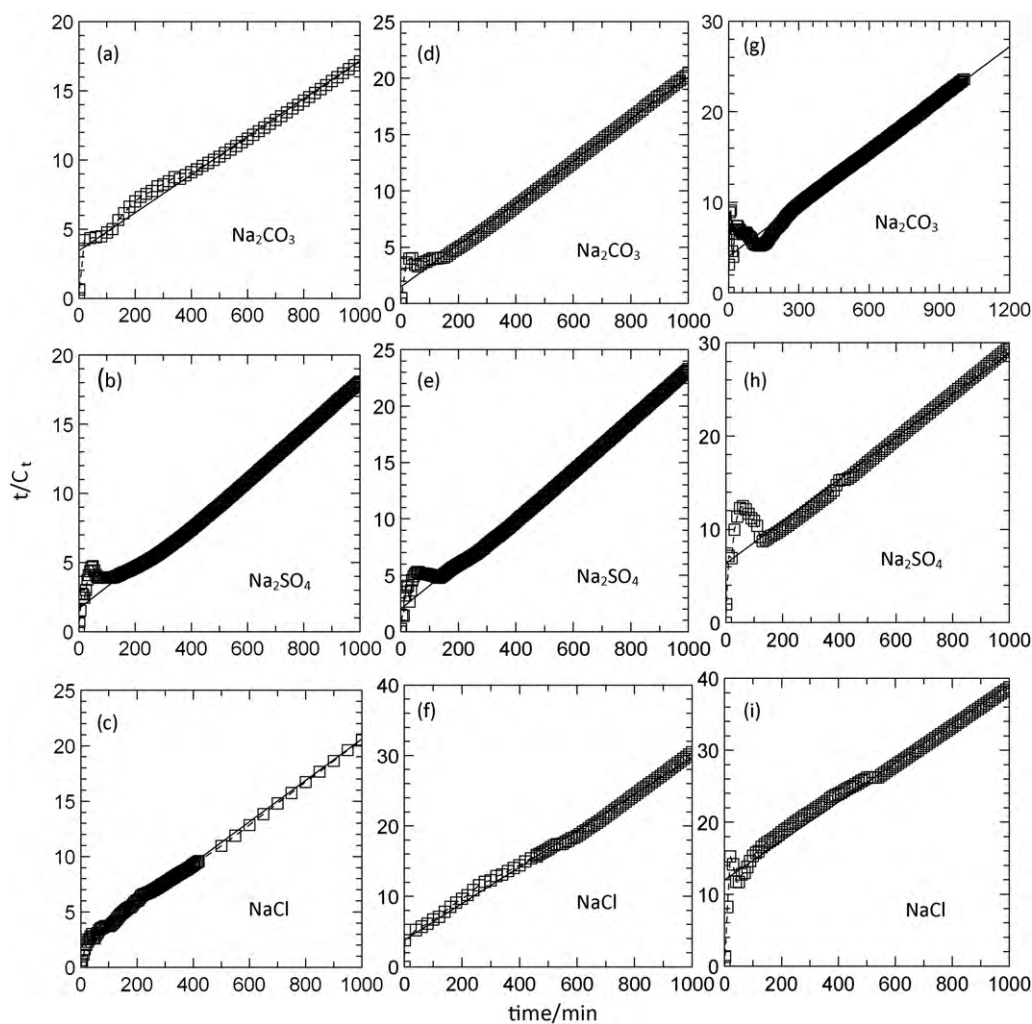


Fig. 4. Fitting the release data of phenoxyherbicides from their nanohybrids into various media (Na₂CO₃, Na₂SO₄ and NaCl) using pseudo-second order kinetics for N2CPA (a–c), N4CPA (d–f) and NTCPA (g–i).

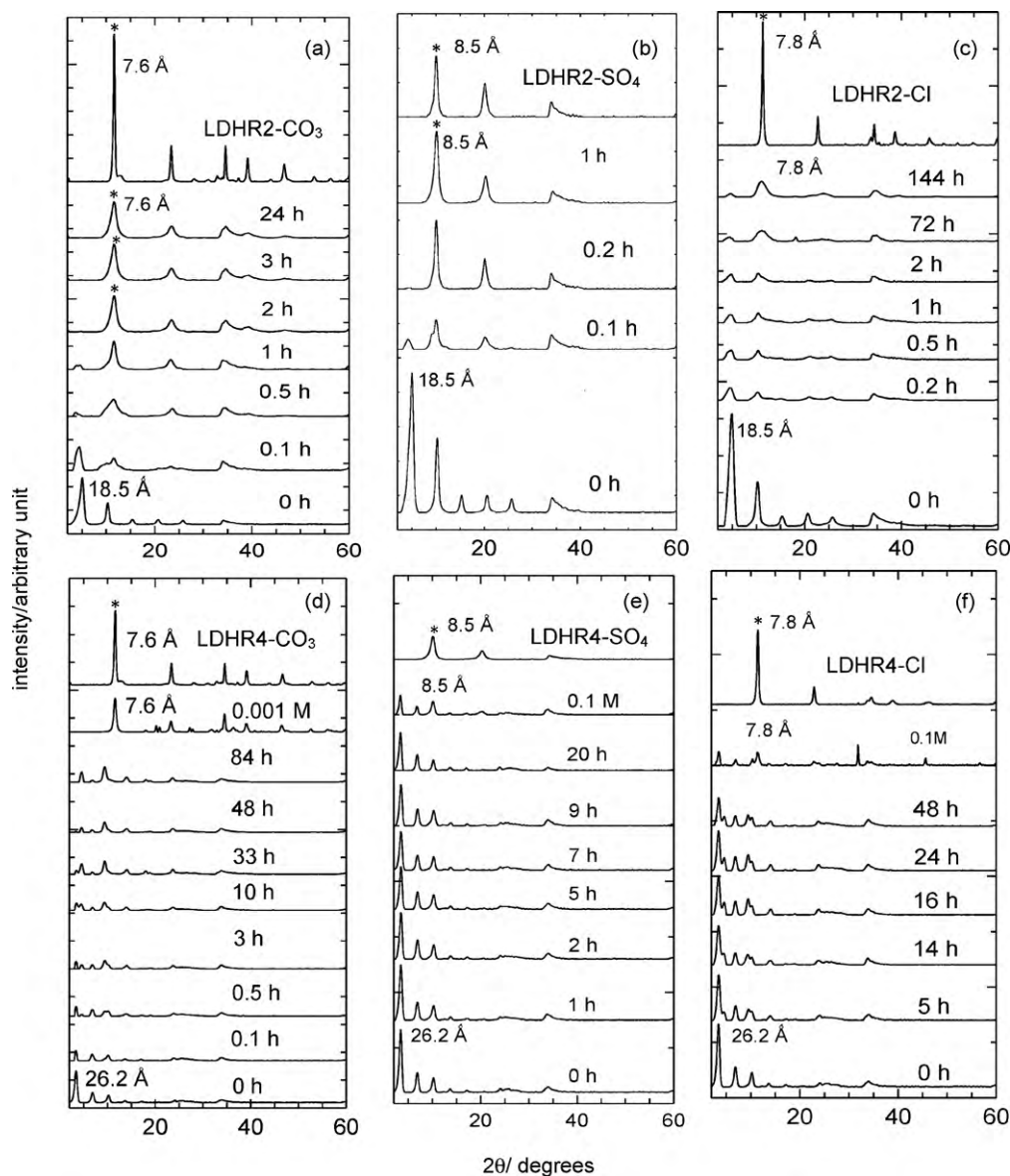


Fig. 5. PXRD patterns of the N2CPA (a–c) and N4CPA (d–f) reclaimed from the aqueous solutions of 0.0005 M Na₂CO₃, Na₂SO₄, NaCl at various release times.

proportional to the release rate. This will be further discussed in the kinetic release.

3.4. The effect of the outgoing intercalated anion

For a given release medium, carbonate, sulfate or chloride, the release profiles of 2CPA, 4CPA and TCPA from their respective nanohybrids are compared (Fig. 3(d–f)). For all the media, the order of the percentage saturated release of the chlorophenoxyherbicides can be given as; 2CPA > 4CPA > TCPA. This shows that 2CPA and 4CPA are easily released from the nanohybrid compared to TCPA which is the most difficult to be released. Such behavior can be related to their different electrostatic interaction between the host and the guest, in which TCPA has 3 chlorine atoms attached to the benzene ring, forming a stronger electrostatic forces with the host, resulting in the most difficult to be released compared to 2CPA and 4CPA. The bulkier structural compound of TCPA may also affect the release from the interlayer of the inorganic host. For 2CPA and 4CPA, the para position of the latter makes its electron donating, hence the chloride ion becomes more negatively charged and therefore

held stronger in the interlayer and not easily released compared to 2CPA.

3.5. Kinetic release

In order to get some insight into the kinetics release of the phenoxyherbicides anions from their respective nanohybrids, quantitative analysis of the data obtained from the release study were fitted to zeroth (Eq. (1)) [31], first order (Eq. (2)) [32], parabolic diffusion (Eq. (3)) [33] and pseudo-second order kinetic models (Eq. (4)) [34], as given below, in which C_{eq} and C_t are the percentage release of the herbicides at equilibrium and time, t , respectively, and c is a constant.

$$C_t = kt + c \quad (1)$$

$$-\log(1 - C_t) = kt + c \quad (2)$$

$$C_t/C_{eq} = c + kt^{0.5} \quad (3)$$

$$t/C_t = 1/k_2 C_{eq}^2 + (1/q_e) \cdot t \quad (4)$$

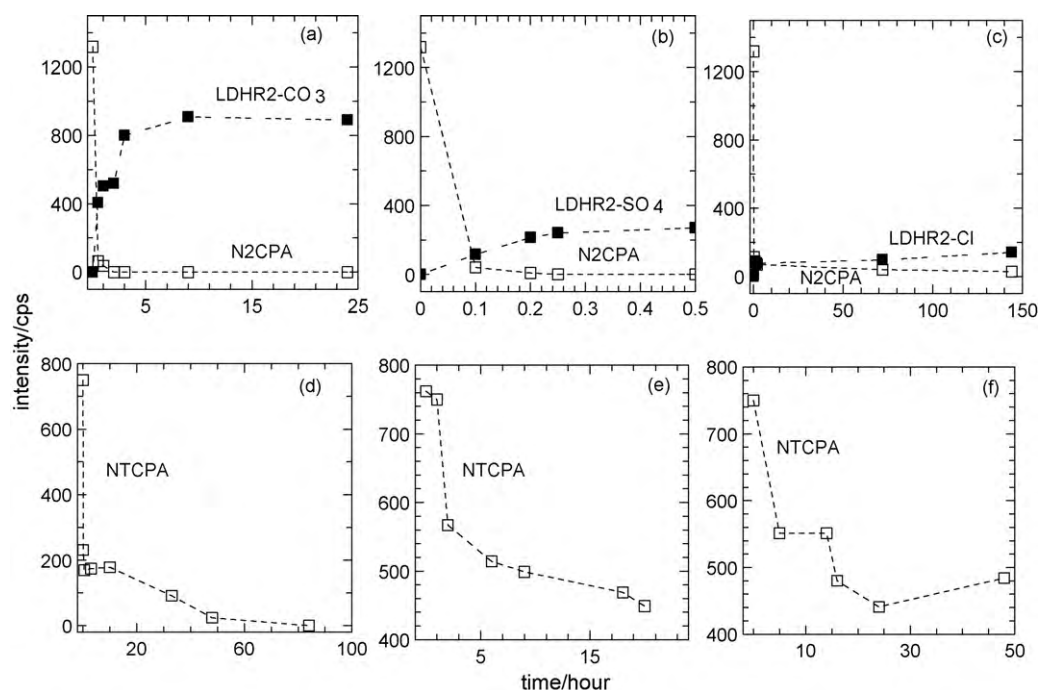


Fig. 6. Intensity comparison of the (003) reflections for the nanocomposites (opened square) and LDHs formed (closed square) as a result of ion-exchange process for the samples reclaimed after the release process of N2CPA and NTCPA in Na_2CO_3 , Na_2SO_4 and NaCl at various release times.

The resulting r^2 values and the parameters obtained from the fitting are listed in Table 2. The plots are given in Fig. 4(a–i). Most of the correlation coefficients, r^2 for the linear plots obtained are good with the best fit showed by pseudo-second order expression. This may suggest that the release of herbicides; 2CPA, 4CPA and TCPA from their hosts can be described by pseudo-second order kinetics, as reflected by the comparison of the r^2 values (Table 2). As a result of the fitting, the $t_{1/2}$ values were calculated to be 71, 77 and 103 min in carbonate, sulfate and chloride aqueous solution, respectively, for 2CPA. Similar order was observed for 4CPA and TCPA with $t_{1/2}$ values of 79, 97 and 146; and 210, 282 and 442 min for carbonate, sulfate and chloride, respectively. Therefore the order of $t_{1/2}$ values for the release of the herbicides can be summarized as, 2CPA < 4CPA < TCPA. The release of phenoxyherbicides into the aqueous solution is in the order of carbonate > sulfate > chloride aqueous solution. This indicates that the phenoxyherbicides are more easily released into the media if the available anion in the media has higher affinity towards the LDH inorganic interlayers. This shows that the exchangeable anions, either they are in the release media or in the nanohybrid can be exploited as a means to tune the release properties.

3.6. PXRD studies of the ion-exchanged products

In order to understand the ion-exchange process and the related phenomena, we subsequently recovered the resulting samples from the aqueous solution after the release experiment. N2CPA and NTCPA selected from various contact times were reclaimed, thoroughly washed, dried and characterized by PXRD. The PXRD patterns for the recovered samples from solutions are shown in Fig. 6. The PXRD of LDH- CO_3 , LDH- SO_4 and LDH-Cl, with carbonate, sulfate and chloride as the counter anion, was also given at the top of the figure for comparison. As shown in Fig. 5 the 003 reflection for N2CPA nanohybrids phase reduced in intensity after it was contacted with the aqueous solutions for 0.1–1 h contact time. On the other hand, a slower intensity reduction was observed for NTCPA for all the solutions.

The ‘new’ LDH phase, which was believed to be Zn–Al-LDH with carbonate, sulfate and chloride as the counter anion were formed as a result of the anion-exchange process between the outgoing anion (2CPA) intercalated into the nanohybrids with the incoming anion from the studied media, Na_2CO_3 , Na_2SO_4 and NaCl . These ‘new’ LDH phases can be clearly observed and the formation of this phase increased as the contact time increased (Fig. 5). The PXRD result shows that this is the case in which the basal spacing of the as-synthesized LDH with carbonate, sulfate and chloride as the counter anion synthesized in this work show similar characteristics.

In order to get some insight into intercalation and de-intercalation processes that possibly occurred at the same time, the intensity of the 003 reflection for the N2CPA as well as the 003 reflection of the ‘new’ LDH formed was plotted against contact time. This is to follow the progress of the ion-exchange process (Fig. 6). When N2CPA was contacted with carbonate and sulfate aqueous solutions, the plots generally show the 003 PXRD reflections for the ‘new’ LDH increases as the 003 reflections for the nanohybrids decreased. This indicates that the intercalation of the carbonate and sulfate species into the Zn–Al-LDH and the release of 2CPA occurs at the same time. As a result, the interlayer distance decreases from 18.5 Å to 7.6 Å and 8.5 Å for the N2CPA samples reclaimed from carbonate and sulfate aqueous solution, respectively. Similar trend was also observed for chloride medium to some extent but the phase changes was very slow in which the N2CPA phase can still be observed even after 6 days. This suggests that the affinity of chloride towards LDH interlayer is lower than sulfate and carbonate, in agreement with results previously described by Miyata [28].

The decrease in the intensity of 003 diffraction peak for NTCPA was also observed for all the media, but the ‘new’ LDH phase was not easily observed (Fig. 5). In order to confirm that the ‘new’ LDH phase was actually formed, the concentration of Na_2CO_3 was increased to 0.001 M and subsequently put in contact with the nanohybrid. As a result, the LDH-carbonate can be observed as a strong diffraction peak at $2\theta = 11.5^\circ$ with basal spacing of 7.6 Å. The same was done for Na_2SO_4 and NaCl but the ‘new’ LDHs can only be observed when the concentration of both aqueous media were increased to 0.1 M, with

basal spacing of 8.5 Å and 7.8 Å, respectively, similar to the basal spacing of the as-synthesized LDH-SO₄ and LDH-Cl (Fig. 5). This shows that the 'new' LDHs phase was actually formed as expected, but the formation was too slow at lower concentration.

This study confirms that the release of the anion into the aqueous solution is followed by slow dissolution of the nanocomposite phase together with gradual collapse of the nanolayered structure. At the same time, the 'new' LDHs phase with carbonate, sulfate and chloride as the counter anion builds up. This is due to the higher affinity of carbonate and sulfate compared to 4CPA towards the Zn–Al-LDH inorganic interlayers resulted in the ion-exchange of carbonate and sulfate with both organic anions. In addition, the electrostatic interactions between the positively charged hydroxide layer and the anion became stronger as the charge on the anion increases, promoting a more stable interlayer [35].

4. Conclusion

Layered materials of organic–inorganic nanohybrid type were formed in which the organic moieties of chlorophenoxyherbicide agrochemicals were interleaved separately into the Zn–Al-LDH inorganic interlamellae. This new generation of agrochemicals can be prepared by separately encapsulating 2CPA, 4CPA and TCPA as guest anions into the Zn–Al-layered double hydroxide, the inorganic host. The physicochemical properties of the resulting nanohybrids were found to be different, suggesting that their physicochemical properties, especially their release property is also different and this study shows that this is the case. The release of the phenoxyherbicides depends on the molecular structure of the anion intercalated into the inorganic layered host as well as the anion available in the media to be ion exchanged. The release of 2CPA, 4CPA and TCPA from their interlamellae of organic–inorganic nanohybrids into carbonate, sulfate and chloride aqueous solutions can be expressed by pseudo-second order rate expression. For a given nanohybrid, the percentage saturated amount of 4CPA and TCPA released was found to be in the order of carbonate > sulfate > chloride. On the other hand, for a given release medium, the order is 2CPA > 4CPA > TCPA. This study suggests that zinc–aluminium-layered double hydroxide is a good candidate to be used as a carrier for herbicides with controlled release capability. The incoming and the outgoing exchangeable anions can be exploited to tune the release of the beneficial anion, in this case, herbicides. This is towards generation of new safer agrochemicals which are users- and environmentally-friendly as well as more efficient and economical due to its tunable release property.

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