

## **Kinetics Study and controlled release of Synthesized Phenoxy herbicides-Based Nanocomposites from; 2, 4 -dichloro- and 2, 4, 5-trichlorophenoxy acetates with Zn/Al Layered double hydroxide interlamellae**

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### **Abstract**

The synthesis of phenolxy herbicides- Zn/Al-layered double hydroxides nanohybrids by reacting 2, 4-di chloro- (24D) and 2, 4, 5-trichlorophenoxy acetic acid (TCPA) nanocomposites were accomplished using direct method of ion exchange. The release of nanohybrids into various aqueous salutions; carbonate and phosphate was found to be controlled by parabolic diffusion at the beginning of the process. On the other hand, the whole process is governed by pseudo-second order rate expression. The percentage saturated released was found to be anionic-dependent, in the order of carbonate > phosphate for the release media and 24D > TCPA for the anionic guest. This study suggests that the release of the phenoxyherbicides agrochemicals from the nanohybrid compounds can be tuned by choosing the right combination exchangeable anions both in the incoming and the out coming anions.

**Keywords:** *Phenoxyherbicides, 2,4-dichlorophenoxy acetate, 2,4,5-trichlorophenoxy acetate, layered double hydroxide, hydrotalcite, nanohybrids.*

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## Introduction

Agrochemicals in particular pesticides, herbicides and plant growth regulator have been widely used in modern agriculture to maintain the high yield production of crops both in term of quality and quantity. Chlorinated phenoxyacetic acid herbicides such as 2, 4-dichlorophenoxy acetic acid (2,4D), 2, 4, 5-trichlorophenoxy acetic acid (TCPA) and 4-chlorophenoxy acetic acid (4CPA) are among the most widely 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].

Controlled release technologies have emerged as an approach to solve this problem [2] not only attaining the most effective use of the active agent, but also prevention of the environmental pollution [3]. Ideally the delivery system should be able to release the bioactive material at precisely the required rate needed by the crops [4]. This will prevent the problem of

leaching, evaporation, degradation and excessive use of the chemicals which are harmful to the environment [5]. Various natural and synthetic materials have been proposed to be used in pesticide controlled release formulation which trap or sorb the pesticides in an inert support or matrix, then gradually release over time [6]. The natural biodegradable polymer such as alginate [2] and starch [7- 10] were used for control release of 1-naphtalene acetic acid, atrazine, alachlor and 24D. The release of 1-naphtalene acetic acid from the alginate formulation was very much influence by the pH of the release media [2]. Controlled release formulation using lignin [11] and chitosan [4] for atrazine were also reported. The use of natural polymer in the preparation of the controlled release system is of special interest due to the possible biological degradation of the matrices and a relatively low cost of the raw materials [8].

Clay minerals including organically modified clay have been used as a matrix for controlled release of herbicides such as hexazinone [12], fenuron [13], simazine [14] and picloram [12]. Similarly, anionic clay or the so-

called layered double hydroxide (LDH) can be used as a layered host for anionic pesticides of 4CPA [15], 2, 4-D [6, 16-18] and MCPA, and picloram [6].

LDHs are a 2D layered material, commonly also known as hydrotalcite-like materials or anionic clays. The general formula is  $[M_x^{2+}M_y^{3+}(\text{OH})_2]^{x+}A_{x/n}^{n-} \cdot y\text{H}_2\text{O}$ , where  $M^{2+}$  are divalent cations,  $M^{3+}$  are trivalent cations,  $A^{n-}$  is the interlayer anion and  $x$  is the mole fraction of  $M^{3+}/(M^{2+} + M^{3+})$  having a typical value of 0.25 [19]. The two dimensions negatively charged layered structure of LDH makes it flexible to be used as a host for many molecules, 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 [20] and 24D [21-23].

This work aimed studying the effect of exchangeable anions in the release media as well as the one to be released on the kinetic release behavior from their respective phase pure, well-ordered Chlorophenoxyacetates-Zn-Al-layered double hydroxide nanohybrids. The release of the phenoxyherbicides; 24D and TCPA were done separately, in which each nanohybrid was kept in

contact with each aqueous medium; carbonate and sulphate and their release behavior was compared. This work is performed to assess the applicability of Zn-Al-LDH as a matrix for the herbicides by focusing on their controlled release behavior.

## Experimental

### *Synthesis of nanohybrids material*

The formation of the nanohybrids by separately intercalation of 24D and TCPA into the Zn-Al-LDH interlamellae was done using direct co-precipitation method from mixed aqueous solutions of  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  with the initial molar ratio, Zn/Al ( $R_i$ ) in the mother liquor of 2 and 4 for the formation of nanocomposit (N24D) and (NTCPA), respectively. The chemicals for the synthesis were used as received and the solutions were prepared using deionized distilled water. The pH was adjusted to 7.5 by slow addition of 2 M sodium hydroxide under nitrogen atmosphere. The concentration of 24D and TCPA was fixed at 0.16 and 0.4 M, respectively. The slurry obtained was aged for 18 h in an oil bath shaker at 70 °C. The resulting precipitate was centrifuged, thoroughly washed and dried overnight in an oven at 70 °C,

and kept in a sample bottle for further use and characterizations.

### 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,  $2^\circ \text{ min}^{-1}$ . Fourier transform infrared (FTIR) spectra were recorded by using a Perkin-Elmer 1725X Spectrophotometer in the range of 400 - 4000  $\text{cm}^{-1}$ . The elemental composition of the samples and the Zn/Al 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). The BET surface area of the solids was determined by a Micromeritics surface area and pore size analyzer (ASAP 2000) using

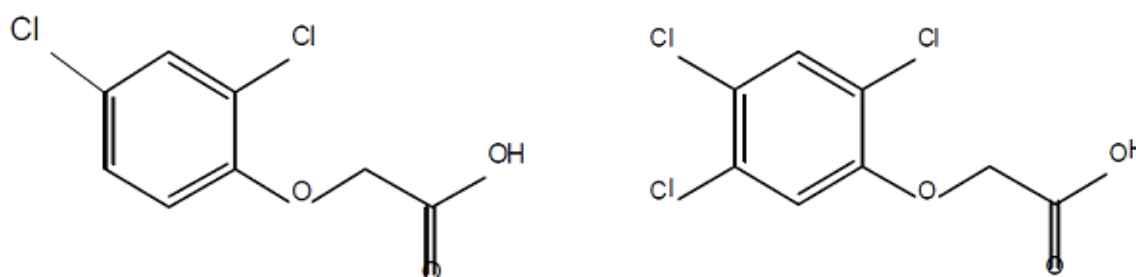
nitrogen gas adsorption-desorption technique at 77 K together with the BET equation.

### Release study of chlorophenoxyacetates

Release of chlorophenoxyacetates from the hosts was studied in various solutions; 0.0005M  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_3\text{PO}_4$ . The accumulated amount of chlorophenoxyacetates released into the solution was measured *insitu* at  $\lambda_{\text{max}}=284.6$  and 206.5 nm for 24D and TCPA respectively using a Perkin Elmer UV-Vis Spectrophotometer Lambda 35.

### Results and Discussion

Fig. 1 show the molecular structure of chlorophenoxyacetates; 2,4-dichlorophenoxyacetic and 2,4,5-trichlorophenoxyacetic acid (TCPA). These agrochemicals are the most widely used herbicides, to control weeds in fields, grasslands, lawns and recreational areas <sup>[24]</sup> as well as for the monocot crops such as cereals and sugarcane <sup>[25]</sup>.

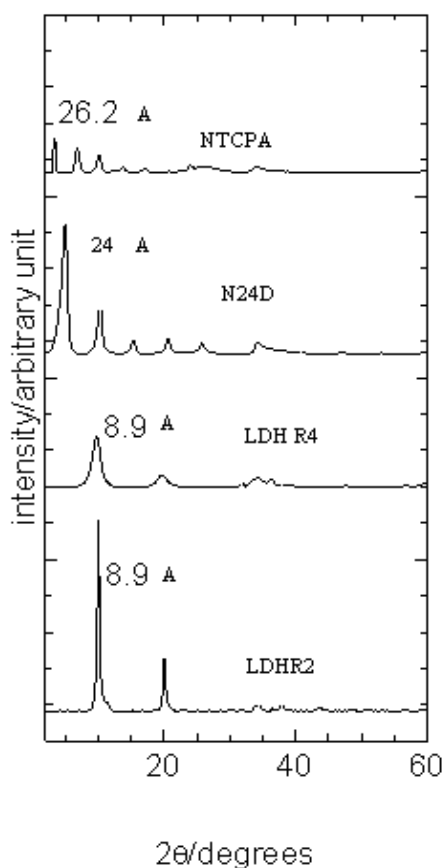


**Fig. 1. Molecular structure of 2,4-di chlorophenoxy acetic acid(a) and 2,4,5 Tri chlorophenoxy acetic acid(b).**

### *Formation and physico-chemical 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.



**Figure 2. PXRD patterns of LDH and its phenoxyherbicides nanocomposites of LDHR2, LDHR4, N2CPA and NTCPA.**

Hybridization of Zn-Al-LDH with 2,4D and TCPA separately for the formation of their respective nanohybrids was accomplished using direct co-precipitation method and the resulting nanohybrids, labeled as N24D and NTCPA, respectively, have a basal spacing of 24 and 26.5 Å,

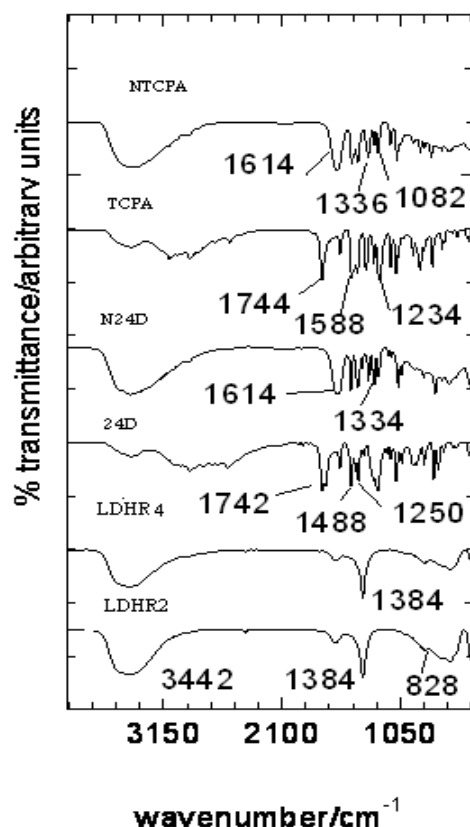
respectively. The expansion relative to the LDHs can be attributed to the bulkier size of guest molecule, which replaces nitrate, together with the spatial orientation of the anions in the interlamellae space of the LDH. The

carbon content of N24D and NTCPA is 17.6 and 20.0 %, respectively with percentage loading of the anion of 34.2 and 53.3 %, respectively and resulting BET surface area is 2.5 and 51.4 m<sup>2</sup>/g,

respectively. The  $x_{Al}$  value is 0.36 and 0.20, respectively.

### *Infrared Study*

The intercalation reactions were also supported by FTIR results (Fig. 3).



**Fig. 3 FTIR spectra of LDH and its phenoxyherbicides nanocomposites of N24D and NTCPA together with 24D, TCPA, LDHR2 and LDHR4.**

The IR spectrum presented common features of LDH-like materials with the characteristic frequencies associated with the presence of 24D and TCPA respectively. For LDH, a large band is observed around 3450 cm<sup>-1</sup>, which corresponds to the -OH stretching molecules, at lower frequency in LDHs compared to OH stretching vibrations in

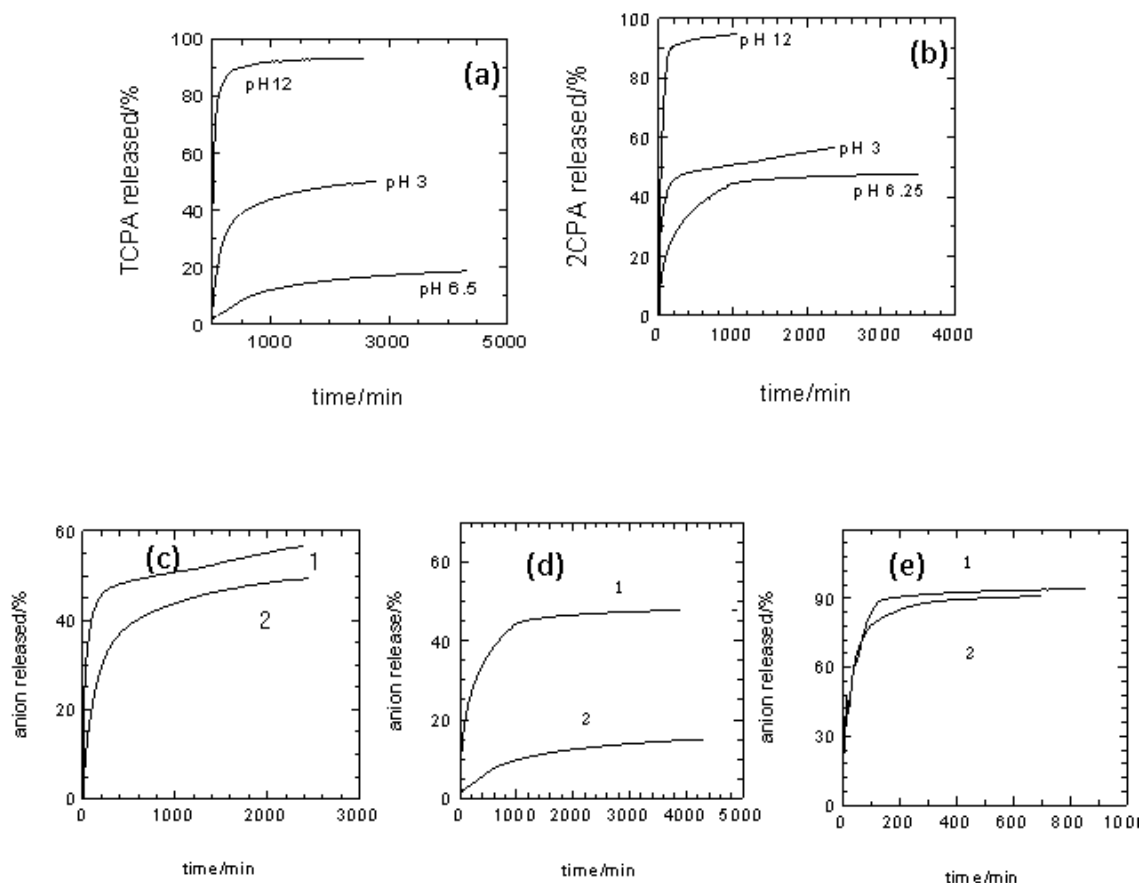
free water at 3600cm<sup>-1</sup>. This was related to the formation of hydrogen bonding of the interlayer water with guest anions as well as with hydroxide groups of the layers. Appearance of a weak band at 828 cm<sup>-1</sup> and a strong absorption band at 1384cm<sup>-1</sup> are attributed to the presence of nitrate in the interlamella as an anion present in LDH). Another common frequency for

LDH-like material was the bending vibration of water at  $1625\text{ cm}^{-1}$ . The absorption bands observed in the low-frequency region of the spectra can be interpreted as lattice vibrations modes which can be attributed to M-O from  $850$  to  $600\text{ cm}^{-1}$  and O-M-O near  $400\text{ cm}^{-1}$ . The presence of 24D and TCPA resulted from their characteristic vibration, including asymmetric and symmetric stretching vibration of  $\text{-C=O}$  in carbonyl group represented each by two intense bands near  $1614\text{ cm}^{-1}$  and around  $1336\text{ cm}^{-1}$ , resulted from the formation of carboxylate anion prior to the intercalation process. Disappearance of bands around  $1744\text{ cm}^{-1}$  and  $1234\text{ cm}^{-1}$  may also be observed as the chlorophenoxyacetic acid structurally transform to chlorophenoxyacetates. Fine bands around  $770\text{ cm}^{-1}$  and  $840\text{ cm}^{-1}$  can be attributed to the C-H deformation vibration out of the plane of the aromatic cycle. The C=C valence vibrations were

present at  $1488$  and  $1400\text{ cm}^{-1}$  in the form of a shoulder to the bending vibration band of water. Bands around  $785\text{-}540\text{ cm}^{-1}$  are due to C-Cl vibration mode. Absorption band for nitrate were observed at  $1384\text{ cm}^{-1}$  for N2,4D and NTCPA synthesized with  $0.05 - 0.16\text{ M}$  N2CPA indicated that nitrate and guest anion are co-existing in the LDH interlayer. The  $\text{NO}_3^-$  absorption band disappeared as the concentration of the 2,4D went higher, showed a complete elimination of nitrate anion and the inclusion of the new guest anion into the LDH interlayer.

***The effect of exchangeable anion in aqueous media on the release of phenoxyherbicides***

The release profiles of 24D and TCPA from their respective nanohybrids interlamellae into aqueous solutions containing various sacrificial anions, namely carbonate and phosphate are shown in Figs.4.



**Fig.4 Release profile of phenoxyherbicides nanocomposites of 24D and 3,4,5 TCPA into distilled water at pH 3, 6.5 and the release from nanocomposite (a) N24D, (b) NTCPA and the comparison of release profile of 24D and 3,4,5TCPA at pH 3 (c), 6.5 (d) and 12 (e) .**

As shown in the figures, for all the phenoxyherbicides, percentage saturated release of the anions is in the order; carbonate > phosphate; with percentages saturated release of 85 %, for 24D compared to 32 %, for TCPA, respectively.

This shows that the affinity of the carbonate and phosphate is in the same order, in agreement with previous work by Miyata <sup>[26]</sup>. This means that the affinity of the sacrificial anion plays a role in determining the

percentage amount of saturated release of the anion from the nanohybrid into the aqueous solution. In another words, ion exchange process is governed by affinity of the anions to be exchanged. Kinetic release rates for all anion into the release media was also in the order of carbonate > phosphate.

In general, several factors such as the affinity of the anion towards the Zn-Al-LDH inorganic interlamellae, the method of preparation of the nanohybrid, the extent of the



dissolution of the inorganic LDH with the collapse of the nanolayered structure and the actual composition of the nanohybrid are important and may contribute to the amount of 24D and TCPA to be released into the aqueous solution. If all the factors were set the same, yet the release property is different, then the nature of the anion intercalated is also an important factor that governs the released amount of 24D and TCPA from its host.

***The effect of exchangeable anion in the nanohybrids on the release of phenoxyherbicides***

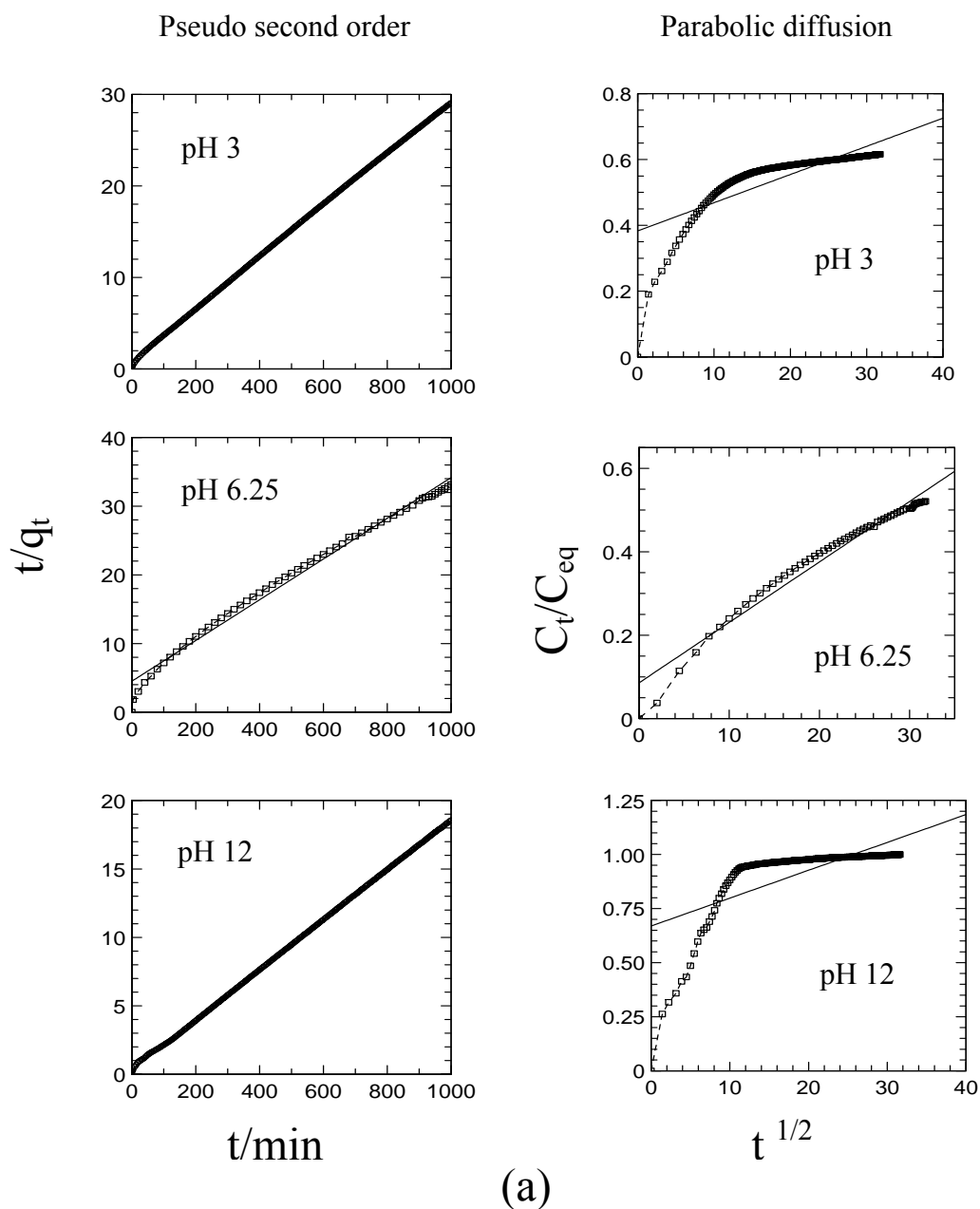
For a given release medium, carbonate, phosphate, the release profiles of 24D and TCPA from their respective nanohybrids are compared (Figs. 4).

For all media, order of the percentage saturated release of the phenoxyherbicides can be given as; 24D > TCPA. This shows that 24D is easily released from the nanohybrid compared to TCPA 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

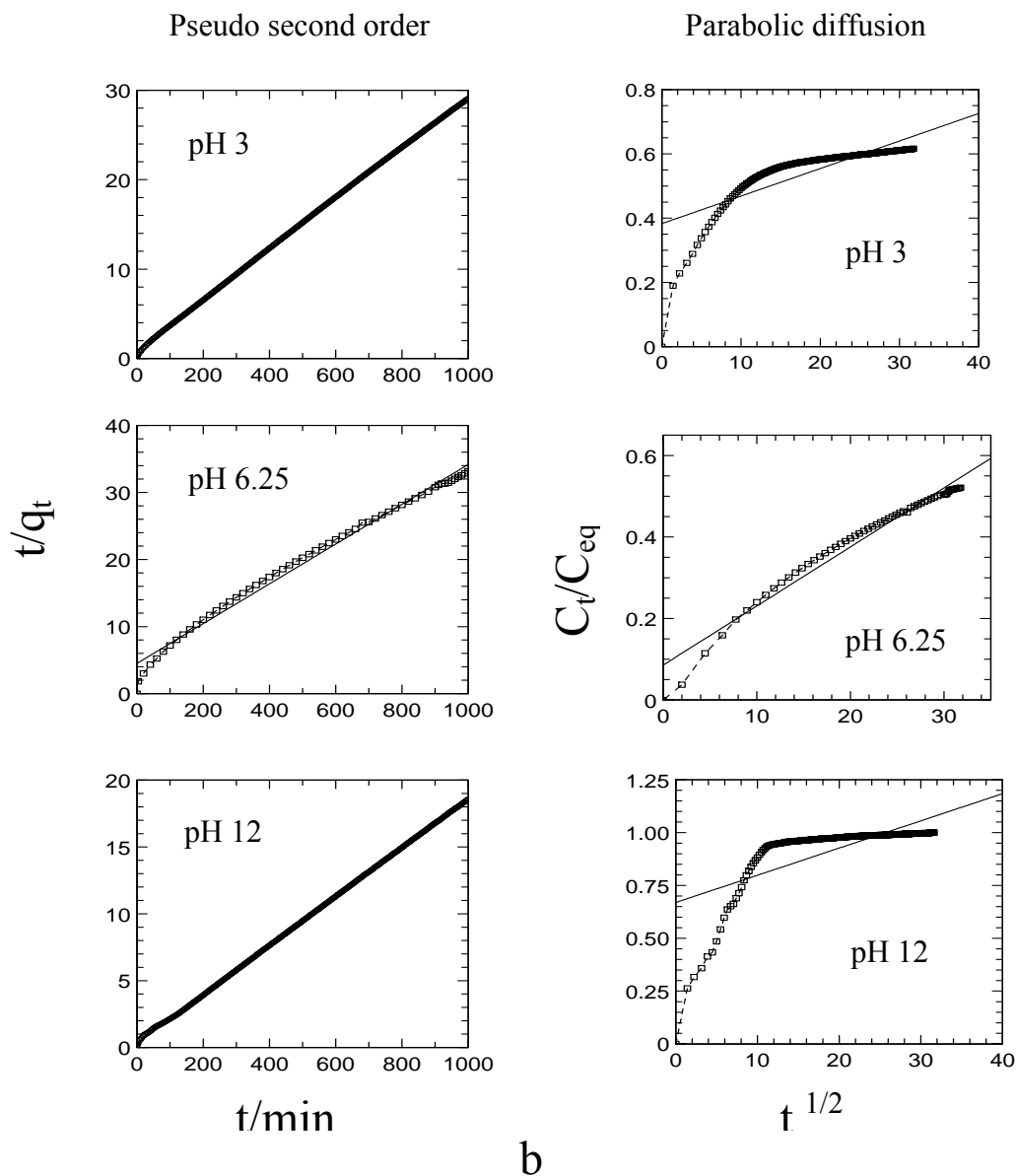
3 chlorine atoms attached to the aromatic ring, and therefore a stronger electrostatic forces as well as coordination bonds between the an ion and the host is expected and therefore less easily to be released compared to 2,4D.

***Kinetic release of exchangeable anion into the media***

In order to get some insight into the kinetics of release of the anions from their respective nanohybrids, quantitative analyses of the data obtained from the release study were fitted to zero-, first-, pseudo second-order kinetics as well as parabolic diffusion models Fig. 5.



**Figure 5 a: Fitting the release of phenoxyherbicides from their nanohybrids into distilled water pseudo-second order kinetics and parabolic diffusion at pHs = 3, 6.25 and 12 for N24D.**



**Figure 5 b: Fitting the release of phenoxyherbicides from their nano hybrids into distilled water pseudo-second order kinetics and parabolic diffusion at pHs = 3, 6.25 and 12 for NTCPA.**

The resulting the parameters obtained from the fitting for pseudo second-

order kinetics and parabolic diffusion are listed in Table 1.

**Table 1: Basal spacing, chemical composition, surface and thermal properties of LDH and its phenoxyherbicides nanocomposites of N24D and NTCPA.**

BET average pore diameter (Å)	BJH desorption pore volume (cm <sup>3</sup> g <sup>-1</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	loading percentage % (w/w)	Nitrogen/Carbon content % (w/w)	x <sub>Al</sub>	Zn/Al ratio	d (Å)	sample
	0.01	1.05	-	2.8	0.32	2	8.9	LDH R2
	0.025	7.4	-	2.5	0.22	3.64	8.9	LDH R4
	0.005	2.54	34.2	17.6	0.36	1.9	24	N24D
	0.3	61.6	53.3	20	0.2	3.93	26.2	NTCPA

N24D		NTCPA		LDH R2		LDH R4		24D		TCPA	
T°C	Δm°C	T°C	Δm°C	T°C	Δm°C	T°C	Δm°C	T°C	Δm°C	T°C	Δm°C
110	8.7	178.5	11.0	122.7	7.3	118.0	7.6				
205	7.7	297.5	41.6	260.4	28.0	241.2	25.0	248.5	98.4	281.5	98.6
367	24.6										
CHNS		17.6		20.0							
		34.2		53.3		28.0		25.0		16.0	
Total Δm/%		41		52		35.3		32.6		98.4	
		904		36.8		910		25.2			
Total Δm/%		77.8		77.8		35.3		32.6		98.4	
										98.6	

As a result of the fitting, the  $t_{1/2}$  values i.e. the time taken for the phenoxyherbicides concentrations to be at half of the accumulated saturated release were calculated and found to be 71 and 103 minutes for carbonate and phosphate, respectively for 24D. Similar trend was observed for TCPA with the  $t_{1/2}$  values of 97 and 442 min

for TCPA for carbonate and phosphate, respectively.

The  $t_{1/2}$  values of the release of the phenoxyacetates can be summarized as:

24D < TCPA.

The highest release of phenoxyherbicides is in the order of: carbonate > phosphate 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. However, weaker host-guest interaction will also help, resulted in higher percentage of saturated release. The results of 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.

### Conclusion

Layered materials of organic-inorganic nanohybrids type, in which the organic moieties namely phenoxyherbicide agrochemicals were successfully interleaved separately into the Zn-Al-LDH inorganic interlamellae. This new generation of agrochemicals of phenoxyherbicides can be prepared by using 24D and TCPA as a guest anion into the Zn-Al layered double hydroxide, as an inorganic host. The physicochemical properties of the three resulting nanohybrids are found to be different, indicating that their release property is also different.

The release of the phenoxyherbicides depends on the guest anion intercalated into the inorganic layered host as well as the sacrificial anion available in the media to be exchanged with them. The release of 24D and TCPA from their interlamellae of organic-inorganic nanohybrids into the

carbonate, phosphate aqueous solutions can be better expressed by parabolic diffusion at the beginning of the process. However, pseudo-second-order rate expression is better than the other models to express the whole process. For a given nanohybrids, the percentage saturated amount of 24D and TCPA released was found to be in the order of carbonate > phosphate. For a given release media, the order is 24D > TCPA. This study suggests that zinc-aluminium-layered double hydroxide can be used as a carrier with controlled release capability for herbicides. This is towards the generation of new safer agrochemicals; for users- and environmentally-friendly agrochemicals.

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