Release Behavior of Dichlorprop from Zn/Al-LDH-Dichlorprop Nanocomposite into Chloride, Carbonate and Phosphate Solutions

Norhayati Hashim[a,b*], Sharifah Norain Mohd Sharif[a], Zuhailimuna Muda[a], Illyas Md Isa[a,b], Suriani Abu Bakar[b,c], Noorshida Mohd Ali[a], Mohd Zobir Hussein[d], Mazidah Mamat[e]

[a]Department of Chemistry, [b]Nanotechnology Research Centre, [c]Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia
[d]Materials Synthesis and Characterization Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia 43400 UPM Serdang, Selangor, Malaysia
[e]Foundation of Science Study Centre, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

Graphical abstract
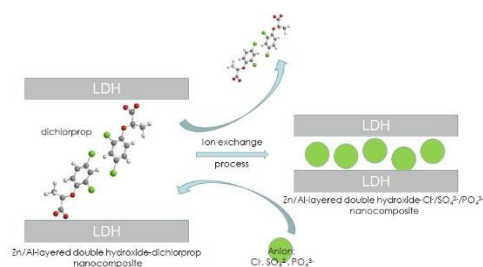
Abstract

A release study of dichlorprop phenoxyherbicides from the interlayer of a Zn/Al-layered double hydroxide-dichlorprop nanocomposite was performed with various concentrations of sodium chloride, sodium carbonate and sodium phosphate and a mixture of sodium chloride, sodium carbonate and sodium phosphate in aqueous solution. The release study of dichlorprop showed that release is dependent on the concentration of the aqueous solution. The accumulated release percentage of dichlorprop phenoxyherbicides into the solution was found to be higher in solutions containing carbonate, phosphate, and a mixture of carbonate or phosphate anions. Confirmation of the release process was confirmed by the PXRD pattern of the powder recovered from highly concentrated solutions of sodium chloride, sodium carbonate, and sodium phosphate with basal spacing of 7.8 Å, 7.6 Å and 7.4 Å, is due to chloride, carbonate, and phosphate intercalation, respectively. The kinetic study revealed that dichlorprop release into sodium carbonate and sodium phosphate solutions is governed by pseudo-second order kinetics, while release into sodium chloride solution is governed by parabolic diffusion. This study shows that a layered double hydroxide might be used as a host for the controlled release of the phenoxyherbicide dichlorprop.

Keywords: Dichlorprop, Zn/Al-LDH-dichlorprop, Nanocomposite, Release Behavior

Abstrak

Satu kajian pelepasan fenoksiherbisida diklorprop daripada ruang antara lapisan nanokomposit hidroksida Zn/Al lapisan berganda dilakukan dalam pelbagai kepekatan larutan akueus natrium klorida, natrium karbonat dan natrium fosfat dan campuran larutan akueus natrium klorida, natrium karbonat dan natrium fosfat. Kajian pelepasan diklorprop menunjukkan bahawa ia adalah bergantung kepada kepekatan larutan akueus. Peratusan pelepasan terkumpul fenoksiherbisida diklorprop ke dalam larutan campuran didapati lebih tinggi berbanding dengan dalam larutan yang mengandungi karbonat, fosfat dan campuran karbonat atau fosfat anion. Pengesahan kepada proses pelepasan disahkan dengan corak PXRD bagi serbuk hasil yang diperolehi pada kepekatan tertinggi larutan natrium klorida, natrium karbonat dan natrium fosfat menunjukkan jarak basal 7.8 Å, 7.6 Å dan 7.4 Å masing-masing yang disebabkan oleh interkalasi klorida, karbonat dan fosfat. Kajian kinetik mendedahkan bahawa pelepasan diklorprop ke dalam larutan natrium karbonat dan natrium fosfat dikawal oleh tertib kedua pseudo manakala pelepasan ke dalam larutan natrium klorida dikawal oleh peresapan parabolik. Kajian ini menunjukkan bahawa lapisan berganda hidroksida mungkin boleh digunakan sebagai tuan rumah untuk rumusan lapisan terkawal fenoksiherbisida, diklorprop.

Kata kunci: Diklorprop, Zn/Al-LDH-Diklorprop, Nanokomposit, Tingkah laku pelepasan

1.0 INTRODUCTION

Herbicides are used to kill unwanted plants in the agriculture sector. However, the heavy use of herbicides in this sector has given rise to serious underground water contamination and human health problems. To overcome this problem, it is important to develop new herbicide formulations that are safer, highly effective, and low cost. Layered materials, especially layered double hydroxides (LDH), are suitable nanomaterials for the preparation of controlled release formulation (CRF) of herbicides due to their unique host-guest type structure [1]. Research in controlled release formulations has attracted considerable attention in recent years, especially in the pharmaceutical [2] and environmental [3] industries. For example, studies on the release of different non-steroidal anti-inflammatory drugs (NSAIDs) intercalated between Mg/Al/Fe-hydrotalcite interlayers showed slow dissolution of the drug in solution [4]. Meanwhile, the simultaneous release of both 2-(3-chlorophenoxy)propionate (CPPA) and 4-(2,4-dichlorophenoxy)butyrate (DPBA) herbicides from Zn/Al-LDH into the release media was found to be fitted by a pseudo second-order equation [5]. In both of these studies, LDH demonstrated potential to be applied as a layered host material for drug and herbicide release. LDH as a CRF material in the environment may significantly reduce water contamination in the agriculture sector; for example, the use of a CRF may restrict herbicide movement through the groundwater and soil. As reported by Bruna [6], an organohydrotalcite layered material has been used as a novel host material for the slow release of terbuthylazine, a widely applied agricultural herbicide. The synthesized herbicide (with additional CRF formulation) was compared to a standard commercial formulation of the herbicide. The results showed the promising capacity of the organohydrotalcite layered material to serve as a suitable support for herbicide slow release formulations with the aim of reducing the adverse effects derived from rapid transport losses of the chemical once applied to soils.

The structure of LDH is made up of positively charged edge sharing octahedra, which forms host layers with a brucite-like structure. The combination of divalent and trivalent cations in the LDH structure produces excessive positive charges in the interlayer, which need to be balanced by the presence of the interlayer anions. LDH can be represented by a general formula, $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2][A^{n-}_{(x/n)}].zH_2O$ with M^{2+} is a metal such as Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and M^{3+} is a trivalent metal ion such as Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, Ni^{3+}, Mn^{3+} [1, 7]. A^{n-} is an interlayer anion such as CO_3^{2-}, NO_3^-, SO_4^{2-} or Cl^-, x is the charge density, that is, the molar fraction of $M^{3+}/(M^{2+} + M^{3+})$, and n represents the charge of the interlayer anion [8]. In this study, we report on the controlled release properties of a phenoxyherbicide, dichlorprop anion (2-(2,4-dichlorophenoxy)propionic acid) from DPPADI (Zn/Al-LDH-dichlorprop nanocomposites synthesized by a co-precipitation method), and DPPAEX (Zn/Al-LDH-dichlorprop nanocomposites synthesized by an ion exchange method) nanocomposites into sodium chloride, sodium carbonate, and sodium phosphate solutions. The release of dichlorprop into a mixture of chloride, carbonate, and phosphate solution was also assessed to determine the effect of single, binary and ternary anions toward the release behaviour of phenoxyherbicides.

2.0 METHODOLOGY

Synthesis and characterization of Zn/Al-LDH-dichlorprop (DPPADI and DPPAEX) has been done in a previous report [9]. The controlled release study into aqueous solution was done at salt concentrations of 0.001 M-0.008 M in solution (sodium chloride, sodium carbonate and sodium phosphate). A Perkin Elmer UV-Vis spectrophotometer equipped with Lambda 35 software was used to determine the release of the anion from the metal hydroxide layers of the nanocomposite in three different salt solutions. A 6.0 mg sample was weighed and put in contact with 3 mL of aqueous solutions of sodium chloride, sodium carbonate, and sodium phosphate in order to study the effect of the different salts toward the release of the anion. The concentration of the anion released into the solution was continuously monitored, and measured by UV-Vis spectrophotometry. The percentage of accumulated release from the nanocomposites was calculated using the equation of zeroth order ($x = t + c$, where x is the percentage release of the intercalated LP anions at time t, c is a constant). The release of DPPADI and DPPAEX were fitted into four kinetic order models: zeroth order, first order, pseudo-second order, and parabolic diffusion.

A sample of 0.5 g was put in contact with 500 mL of each of the following solutions: 0.008 M sodium chloride, sodium carbonate, and sodium phosphate. The content was vigorously stirred at room temperature for various periods of time, and the slurry was then centrifuged, dried in an oven at 70°C, ground and kept in sample bottles for powder X-ray diffraction (PXRD) characterization. The PXRD patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer in the 2θ range of 2° to 60° using filtered Cu-K$_\alpha$ radiation (λ = 0.1540562 nm) at 40 kV and 20 mA with 2˚ min^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Controlled Release Study

Figures 1, 2 and 3 show the release profile of dichlorprop from the DPPADI and DPPAEX nanocomposites into four different concentrations of sodium chloride, sodium carbonate and sodium phosphate aqueous solutions, respectively.

The fast release of the dichlorprop anion from DPPADI and DPPAEX nanocomposites were observed in the first 0-150 minutes for the sodium carbonate and sodium phosphate solutions, followed by slow release before saturated release was achieved. For sodium chloride, slower release was observed; it was concentration-dependent and the accumulated saturated maximum was achieved at around 4000 minutes for both the DPPADI and DPPAEX

nanocomposites. Ion exchange took place in the release reaction due to the higher affinity of carbonate and phosphate ion toward the dichlorprop anion. As reported by Sato and Okuwaki [10] and Ulibarri *et al.* [11], monovalent anion pesticides have low affinity toward layered materials compared to carbonate and phosphate anions for the exchange process. Therefore, intercalated dichlorprop was exchanged with carbonate and phosphate anions, and subsequently released into the solution.
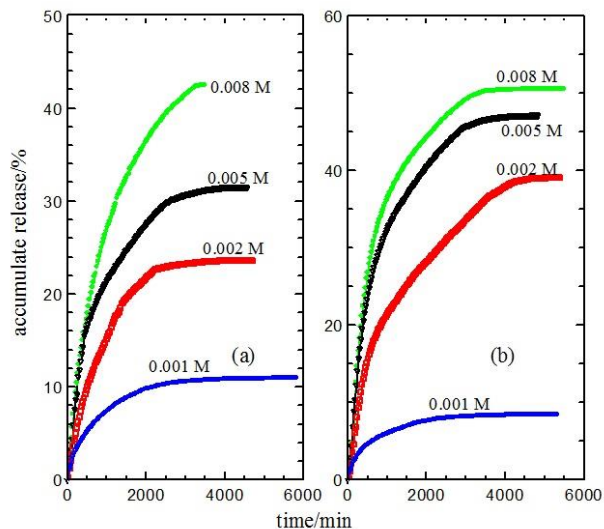

Figure 1 Release profile of DPPA from the interlamellae of the (a) DPPADI and (b) DPPAEX nanocomposites into aqueous solutions containing various concentrations of NaCl

Figure 2 Release profile of DPPA from the interlamellae of the DPPADI (a) and DPPAEX (b) nanocomposites into aqueous solutions containing various concentrations of Na2CO3 [9]

Figure 3 Release profile of DPPA from the interlamellae of the (a) DPPADI and (b) DPPAEX nanocomposites into aqueous solutions containing various concentrations of Na3PO4
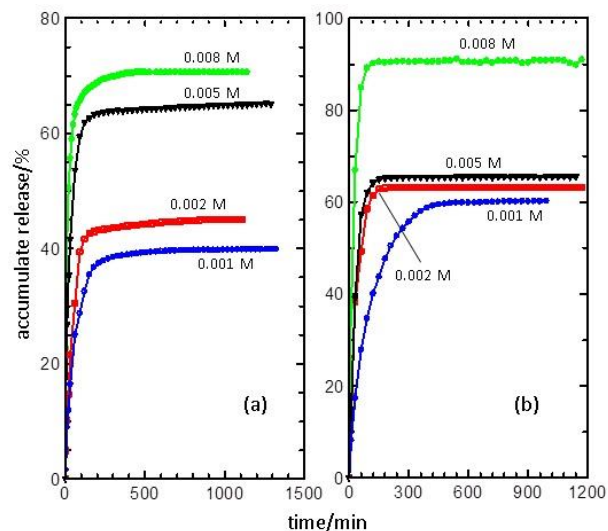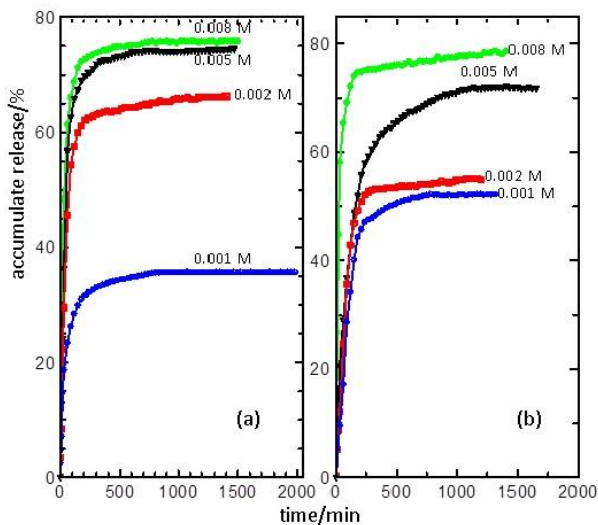
Deintercalation of dichlorprop was hindered by the new formation of layered double hydroxide at the outer layer of particle, as the release of guest was found to occur in a controlled manner. At the same time, the replacement of dichlorprop in the interlayer of LDH was mediated by carbonate, or phosphate anions from the solution. The percentage of dichlorprop anion release from both nanocomposites into the sodium chloride, sodium carbonate and sodium phosphate solutions is shown in Table 1. The slower release of dichlorprop from both DPPADI and DPPAEX into sodium chloride corresponds to the lower affinity of chloride anions toward LDH inorganic interlamellae compared to carbonate and phosphate anions. In addition, chloride anions are small monovalent anions that have less affinity than carbonate and phosphate ion for the ion exchange process in solution, as reported by Hussein [12].

For both nanocomposites, the release profiles of the dichlorprop anion from the interlayer of the nanocomposite showed higher amounts of maximum accumulated release from the DPPAEX nanocomposite compared to the DPPADI nanocomposite for all concentrations of sodium carbonate followed by sodium phosphate and sodium chloride. The orientation and arrangement of the anion within the inter gallery matrix for both nanocomposites were calculated to be the same value, 16.7 Å (Figure 4) [9]. The differences may be due to the crystallinity of the materials, which affects the amount of dichlorprop readily available to be released. The nanocomposite preparation method is the main factor that determines the physico-chemical properties of the resulting materials, thus related to surface properties and the release behaviour of the guest anion.

Table 1 Percentage release (%) of DPPA anion into various solutions

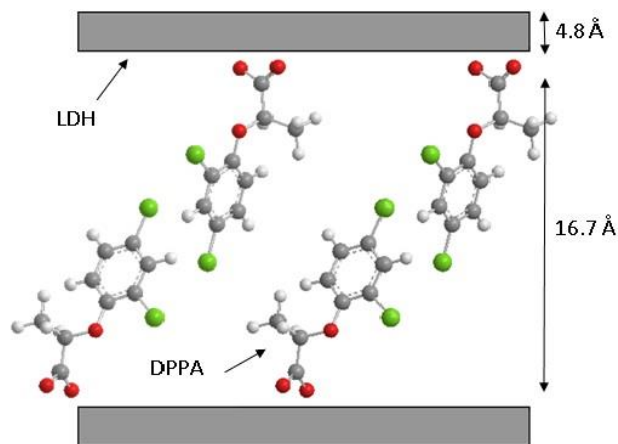|	DPPA anion					
	NaCl solution		Na$_2$CO$_3$ solution		Na$_3$PO$_4$ solution	
(M)	DPPA DI	DPPA EX	DPPA DI	DPPA EX	DPPA DI	DPPA EX
0.001	11	8	38	59	35	51
0.002	23	38	45	63	65	54
0.005	31	46	65	65	74	72
0.008	42	50	78	91	76	77

Figure 4 The proposed arrangement of DPPA intercalated into LDH inorganic interlayer for both DPPADI and DPPAEX nanocomposites [9]

In order to confirm results of the release study, solid material residues at the beginning of guest release, at 50% of accumulated release and maximum release time in the chloride, carbonate and phosphate solutions at higher concentrations were dried, and their PXRD pattern recorded for both the DPPADI and DPPAEX nanocomposites (Figure 5). At the beginning of the release time for DPPADI in all three solutions, the PXRD patterns were quite similar with basal spacing in the range of 21.3 Å to 21.8 Å corresponding to diffraction by the 003 plane of the layered system containing dichlorprop in the interlayers. A similar result was obtained from the DPPAEX nanocomposite pattern release into the chloride, carbonate and phosphate solutions. The difference in the intensity of the intercalation peak among these patterns corresponded to less crystallinity of the nanocomposite as the ion exchange process started in the solution. For the pattern at 50% accumulated release, the intensity of the intense and sharp peak of 003 reflections for the

nanocomposite decreased. At the same time, reflections corresponding to the medium anion increased, which led to an increase in the medium anion intercalated in the layers of the layered double hydroxide. This occurred as a result of the exchange of the intercalated dichlorprop with the chloride, carbonate and phosphate anions present in the medium. It may also be due to the dissolution of inorganic LDH, and the collapse of the inorganic layer [12].
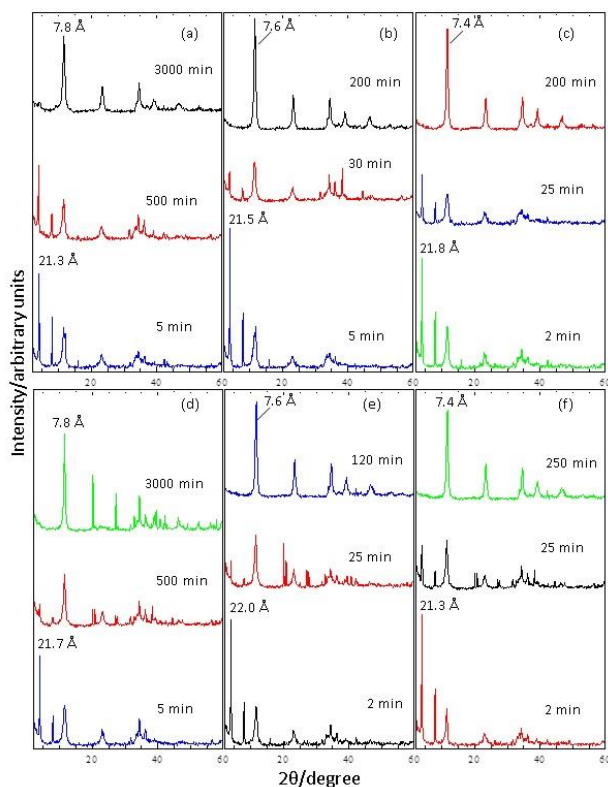

Figure 5 PXRD patterns for the samples recovered from various aqueous solutions of (a) chloride, (b) carbonate, and (c) phosphate for DPPADI and (d) chloride, (e) carbonate, and (f) phosphate for DPPAEX

The PXRD patterns for the samples dried after release achieved equilibrium show a sharp and intense peak of 003 reflections, which indicated high crystallinity of the material. The basal spacing of 7.8 Å, 7.6 Å, and 7.4 Å for that peak referred to chloride, carbonate and phosphate anions intercalated in the interlayer of LDH. The remaining intercalation peak at a lower 2θ angle was observed as an indication that not all dichlorprop in the interlayers of the nanocomposite was released into the solution via the ion exchange process. The different release times at equilibrium in different solutions was due to the differences of density anion toward the interlamellae of LDH. In the dichlorprop release study, carbonate anions showed higher density toward LDH compared to chloride and phosphate anions, which is in agreement with previous work by Hussein [12].

3.2 Kinetic Study

In order to study the release kinetics of the dichlorprop anion, data obtained from the release profile for dichlorprop from its nanocomposite into sodium chloride, sodium carbonate and sodium phosphate solutions were fitted to several kinetic models, including zeroth order (Equation (i)) [13], first order (Equation (ii)) [14], pseudo-second order (Equation (iii)) [15], and parabolic diffusion (Equation (iv)) [16]. The equation for each kinetic model is as follows:

$$x = t + c \tag{i}$$
$$\log (1 - M_i/M_f) = t + c \tag{ii}$$
$$t/M_i = 1/M_f^2 + t/M_f \tag{iii}$$
$$M_i/M_f = kt^{0.5} + c \tag{iv}$$

where x is the percentage release of the intercalated dichlorprop anions at time t, c is a constant, M_i represents the initial concentration of the dichlorprop, and M_f is the final concentration of the dichlorprop. Table 2 and Table 3 show a comparison between correlation coefficients (r^2) of the four models kinetic models.

As shown in Figure 6 (b) and (c)) and Figure 7 (b) and (c), dichlorprop release into sodium carbonate and sodium phosphate solutions from both DPPADI and DPPAEX nanocomposites was governed by pseudo-second order kinetics, while parabolic diffusion was the best fit for dichlorprop release into sodium chloride (see Figure 6 (a) and Figure 7 (a)). The correlation coefficients (r^2), under the experimental conditions described earlier, indicate that the pseudo-second order model was the best to describe the release behaviour kinetics of dichlorprop from both DPPADI and DPPAEX nanocomposites in sodium carbonate and sodium phosphate solutions. However, parabolic diffusion was found to suit the release behaviour of dichlorprop from both the DPPADI and DPPAEX nanocomposites in sodium chloride solution.

It should be stated that release of the guest anion into the carbonate and phosphate aqueous solutions from the inorganic LDH interlamellae involved the dissolution and diffusion of nanocomposite during ion exchange between the intercalated anions in the interlamellae host [17]. However, the release of the guest anion into the chloride aqueous solution was controlled by intraparticle diffusion or surface diffusion. Therefore, it could be suggested that the results indicate that external surface diffusion or intraparticle diffusion via ion exchange is the rate-determining step in the release process [18].
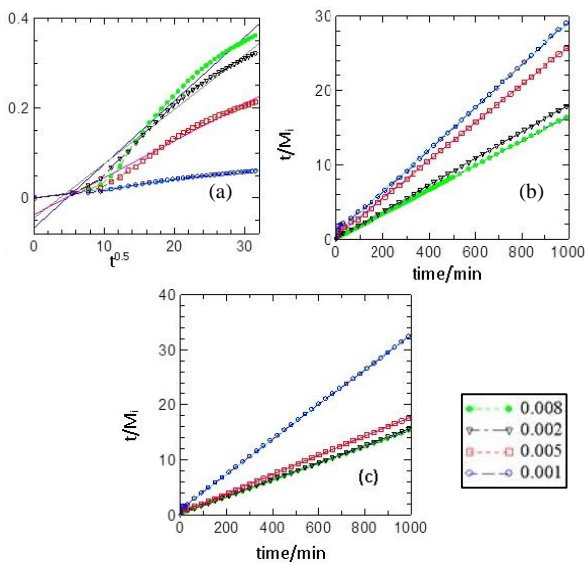
Figure 6 Fitting of the data of dichloroprop anions from DPPADI nanocomposite to the (a) parabolic diffusion in NaCl solution, (b) pseudo-second order kinetic in Na2CO3 solution, and (c) pseudo-second order kinetic in Na3PO4 solution, containing various concentration of 0.008 mol L-1, 0.002 mol L-1, 0.005 mol L-1 and 0.001 mol L-1 at t = 0-1000 min
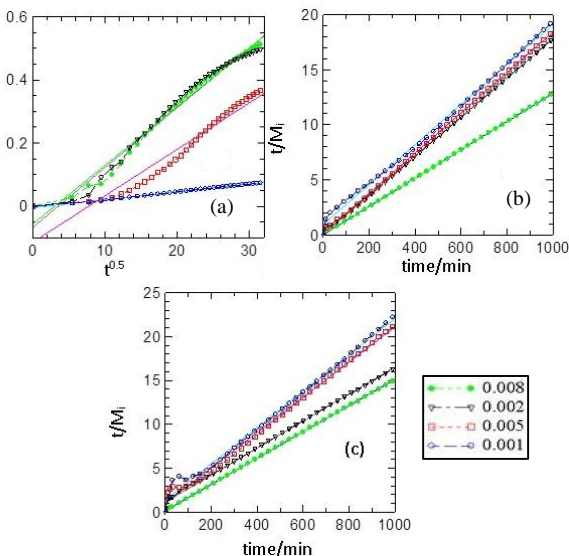

Figure 7 Fitting of the data of dichloroprop anions from DPPAEX nanocomposite to the (a)parabolic diffusion in NaCl solution, (b) pseudo-second order kinetic in Na2CO3 solution, and (c) pseudo-second order kinetic in Na3PO4 solution containing various concentration of 0.008 mol L-1, 0.002 mol L-1, 0.005 mol L-1 and 0.001 mol L-1 at t = 0-1000 min

3.3 Release Study of Dichlorprop into Mixture of Aqueous Solutions

Figure 8 (a) and (b) show the profile release of Zn/Al-LDH-dichlorprop synthesized by direct co-precipitation and indirect ion exchange methods. A solution containing chloride-carbonate-phosphate anions allowed a high level of saturated release of DPPADI with a percentage release of 88%. DPPAEX showed that the solution containing carbonate anions allowed high saturated release of dichlorprop with a value of 90%. For both nanocomposites, rapid release of dichlorprop was observed in the initial 20 minutes for all solutions except for the solutions containing chloride anions.

The percentage release of dichlorprop from the DPPADI nanocomposite in carbonate-phosphate, chloride-phosphate, chloride-carbonate, carbonate and phosphate solutions were 74, 60, 59, 71 and 76%, respectively. However, 86, 72, 50, 66 and 76% saturated release of dichlorprop from the DPPAEX nanocomposite was achieved in the solutions containing chloride-carbonate-phosphate, carbonate-phosphate, chloride-phosphate, chloride-carbonate and phosphate anions; this was mostly achieved in 150 minutes. Saturated release of dichlorprop from both nanocomposites into the chloride solution was 42% (DPPADI) and 50% (DPPAEX) with a slower initial rate compared to the other solutions. The release orders of dichlorprop into the solution are summarized and shown in Table 4.

As shown in Figure 8 (a), the ternary system showed a high percentage of accumulated release of dichlorprop anions from the DPPADI nanocomposite compared to the other systems. This was due to the existence of a combination of carbonate and phosphate ions with strong affinity to maximize interaction with the surrounding positive charge of the interlayer of LDH. In the binary systems, as expected, the solution that combined carbonate and phosphate ions showed a higher accumulated release percentage, which corresponded to the high affinity of carbonate toward LDH, and the high density of phosphate ions in the exchange process. The other binary solutions, chloride-carbonate and chloride-phosphate, showed a low accumulated release percentage, which could be due to the low ion exchange affinity of chloride toward the interlayer of the inorganic interlamellae [19]. For the single systems, the phosphate solution showed the highest accumulated release percentage of dichlorprop compared to carbonate and chloride. This could be due to the multiple hydrolysis of phosphate, with the existence of tertiary phosphate that has a high charge density in the solution that may have increased the ion exchange process in the replacement of dichlorprop from the interlayer [20].
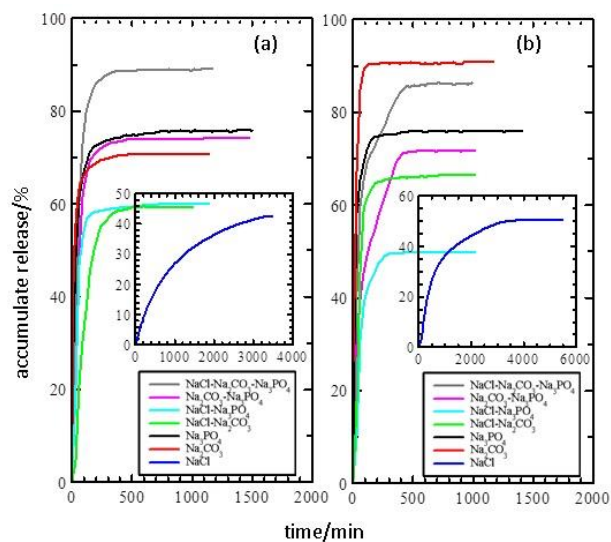
Figure 8 Release profile of DPPA from the interlamellae of the nanohybrids (a) DPPADI and (b) DPPAEX into mixture aqueous solutions

The accumulated release order of dichlorprop from the DPPAEX nanocomposite in the single system carbonate, phosphate and chloride solutions was similar to dichlorprop release from its nanocomposite, DPPAEX (Figure 8 (b)). Carbonate solution showed high percentage values due to the high affinity of carbonate anions toward the brucite-type interlayer compared to phosphate and chloride anions. The binary system containing carbonate and phosphate ions showed the highest accumulated release percentage compared to carbonate or phosphate combined with chloride, due to the low charge density of chloride that may have inhibited the ion exchange process in the solution. Carbonates and phosphates are known to have a high affinity toward LDH and a high charge density compared to chloride [21]. Therefore, carbonate and phosphate anions can be easily exchanged with the intercalated anion, i.e., dichlorprop in the ion exchange process.

For the ternary system of chloride, carbonate and phosphate, the release percentage value is lower than that of the carbonate single system, but higher than the binary, phosphate and chloride single systems. This could be due to the presence of multiple anions. Carbonate has high affinity toward LDH and phosphate has a high charge density and a maximum orientation for interaction with the positively charged layer compared to the binary, phosphate and chloride single systems. The low value of accumulated release for the ternary system compared to the carbonate single system may be due to the existence of lower affinity chloride in the system that may have inhibited the accumulated release, thus slowing down the ion exchange process. Generally, the accumulated release of dichlorprop from both DPPADI and DPPAEX

nanocomposites in various solutions is dominated by the existence of phosphate or carbonate anions in the solution. However, the existence of chloride anions in the solution decreases the percentage values of accumulated release.

4.0 CONCLUSION

A release study of the guest ion from Zn/Al-LDH-dichlorprop nanocomposites synthesized using direct co-precipitation and ion exchange methods was done in various concentrations of sodium chloride, sodium carbonate and sodium phosphate aqueous solutions. It was found that the accumulated phenoxyherbicide release into aqueous solution increases with a higher initial concentration and contact time. The accumulated release percentage of the phenoxyherbicide into solutions is in the order of: sodium carbonate > sodium phosphate > sodium chloride and a mixture of carbonate and phosphate solutions. The release profiles of the nanocomposite synthesized using the ion exchange method showed a higher maximum accumulated release of the phenoxyherbicide in all solutions compared to the nanocomposite synthesized using the co-precipitation method.

The release behaviour of dichlorprop from both the DPPADI and DPPAEX nanocomposites into sodium carbonate and sodium phosphate solutions was governed by pseudo-second order kinetics. For both the DPPADI and DPPAEX nanocomposites, the release behaviour of dichlorprop into sodium chloride solution was governed by parabolic diffusion. The effect of single, binary and ternary anions from sodium chloride, sodium carbonate and sodium phosphate during controlled release was assessed for the phenoxyherbicide nanocomposite. The solutions containing a mixture of carbonate and phosphate anions showed high initial release of phenoxyherbicide anions due to the high affinity of the incoming anions toward LDH.

Table 2 Rate constants, half-life ($t_{1/2}$) and correlation coefficients obtained from the fitting of the data of DPPA release from DPPADI into NaCl, Na_2CO_3 and Na_3PO_4 solutions [9]

DPPADI							
NaCl Concentration (mol L^{-1})	Zeroth Order	First Order	Pseudo-second Order	Parabolic Diffusion			
		r^2		r^2	k ($s^{-0.5}$)	$t_{1/2}$ (min)	
0.001	0.905	0.910	0.955	0.989	0.00200	62656	
0.002	0.936	0.950	0.429	0.975	0.00833	4202	
0.005	0.926	0.949	0.716	0.981	0.0121	2028	
0.008	0.924	0.950	0.00198	0.969	0.0143	1587	
Na_2CO_3 Concentration (mol L^{-1})	Zeroth Order	First Order	Parabolic Diffusion	Pseudo second Order			
		r^2		r^2	k ($mg^{-1}Ls^{-1}$)	$t_{1/2}$ (min)	
0.001	0.461	0.492	0.697	0.999	0.00099	29	
0.002	0.405	0.436	0.636	1.000	0.00129	20	
0.005	0.341	0.395	0.565	1.000	0.00192	9	
0.008	0.207	0.304	0.409	1.000	0.00223	6	
Na_3PO_4 Concentration (mol L^{-1})	Zeroth Order	First Order	Parabolic Diffusion	Pseudo second Order			
		r^2		r^2	k ($mg^{-1}Ls^{-1}$)	$t_{1/2}$ (min)	
0.001	0.505	0.546	0.734	1.000	0.044	345	
0.002	0.424	0.494	0.655	0.999	0.080	194	
0.005	0.413	0.506	0.645	0.999	0.140	126	
0.008	0.376	0.476	0.03	1.000	1.035	31	

Table 3 Rate constants, half-life ($t_{1/2}$) and correlation coefficients obtained from-fitting of the data of DPPA release from DPPAEX into NaCl, Na_2CO_3 and Na_3PO_4 solutions [9]

DPPAEX							
NaCl Concentration (mol L^{-1})	Zeroth Order	First Order	Pseudo-second Order	Parabolic Diffusion			
		r^2		r^2	k ($s^{-0.5}$)	$t_{1/2}$ (min)	
0.001	0.943	0.948	0.922	0.997	0.00251	40426	
0.002	0.990	0.994	0.148	0.938	0.0148	1732	
0.005	0.905	0.950	0.498	0.978	0.0186	895	
0.008	0.934	0.973	0.793	0.984	0.0190	891	
Na_2CO_3 Concentration (mol L^{-1})	Zeroth Order	First Order	Parabolic Diffusion	Pseudo second Order			
		r^2		r^2	k ($mg^{-1}Ls^{-1}$)	$t_{1/2}$ (min)	
0.001	0.545	0.618	0.772	0.997	0.000341	56	
0.002	0.254	0.288	0.464	1.000	0.00253	8	
0.005	0.236	0.267	0.438	1.000	0.00250	7	
0.008	0.248	0.309	0.458	1.000	0.00372	3	
Na_3PO_4 Concentration (mol L^{-1})	Zeroth Order	First Order	Parabolic Diffusion	Pseudo second Order			
		r^2		r^2	k ($mg^{-1}Ls^{-1}$)	$t_{1/2}$ (min)	
0.001	0.498	0.564	0.718	0.994	0.000585	99	
0.002	0.482	0.531	0.718	0.951	0.000213	78	
0.005	0.654	0.780	0.865	0.997	0.000206	38	
0.008	0.338	0.442	0.555	1.000	0.000122	12	

Table 4 Release order of DPPA from DPPADI and DPPAEX into various solutions

Nanocomposites	Solution
DPPADI	$Cl^- - CO_3^{2-} - PO_4^{3-} > PO_4^{3-} > CO_3^{2-} - PO_4^{3-} > CO_3^{2-} > Cl^- - PO_4^{3-} > Cl^- - CO_3^{2-} > Cl^-$
DPPAEX	$CO_3^{2-} > Cl^- - CO_3^{2-} - PO_4^{3-} > PO_4^{3-} > CO_3^{2-} - PO_4^{3-} > Cl^- - CO_3^{2-} > Cl^- - PO_4^{3-} > Cl^-$

Acknowledgement

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