Nanocomposite-based controlled release formulation of an herbicide, 2,4-dichlorophenoxyacetate (24D) incapsulated in zinc–aluminium-layered double hydroxide

Mohd Zobir bin Hussein *, Asmah Hj Yahaya, Zulkarnain Zainal, Loo Hee Kian

Nanomaterials Program, Advanced Materials Laboratory, Institute of Advanced Technology (ITMA), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

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Abstract

Controlled release formulation of an herbicide, 2,4-dichlorophenoxyacetate (24D) was developed by the virtue of the formation of organic–inorganic nanohybrid material and its ion exchange property. The inorganic Zn–Al layered double hydroxide (ZAL) was used as a matrix, hosting an active agent or a guest, 24D by self-assembly technique. The resulting material (ZAD) was subsequently used to study the release property of 24D into aqueous solutions containing chloride, carbonate as well as distilled water. The release of the guest 24D was found to be rapid initially followed by a more sustained release thereafter and this behavior was dependent on the type of anions and their concentrations in the release medium, the aqueous solution. The mechanism of release has been interpreted on the basis of the ion exchange process between the 24D anion intercalated into the interlamellae host and carbonate or chloride and/or hydroxyl anions in the aqueous solution.

Keywords: Hydrotalcite; Layered double hydroxide; 2,4-Dichlorophenoxyacetic acid; Nanocomposite; Herbicide; Controlled release

1. Introduction

Layered materials, especially hydrotalcite-like materials or layered double hydroxide (LDH) are amongst attractive materials for the preparation of a controlled release (CR) formulation. This material is of a two-dimensional type layered structure consisting of thin crystalline inorganic layers with a thickness of a few nanometers, which can be used as an ideal matrix for an active agent, or guest. A variety of anionic species can be inserted as guests into the interlamellae of the LDH, especially beneficial organic anions such as drugs [1], pesticides [2–4], plant growth regulators [5] and fertilizer [6]. The guest species will be interleaved between the sheets and therefore, the formation of host-guest materials for controlled release formulation can be achieved. Intercalation of an anti-inflammatory drug such as ibuprofen [1] between LDHs is aimed to give a formulation with CR capability. Similarly, layered double hydroxide was also used as a soluble inorganic vector for CR purposes [7]. This is due to the advantages of CR formulation compared to its counterpart.

The interactions between the matrix and the active substances are important and this in turn may control the CR properties of the formulation such as diffusion, reaction rates or other physicochemical parameters. In addition, manipulation of the appropriate barriers, the target and the fate of the active agent once beyond these barriers are equally important and contribute to the success of the CR system designed.

Due to the bulky size of the guest and its orientation in the inorganic lamellae together with the presence of water molecule and other species, an expansion of the interlayer distance to a nanometer-sized dimension is usually observed and the formation of the so-called nanohybrid or nanocomposite materials [8] occurred. Depending on its usage, preference of the anions and cations that form the intercalated LDHs are the most important and thus can be chosen according to the resulting properties of the product desired [9]. The insertion of guest anions into the inorganic interlamellae, can be accomplished by spontaneous self-assembly [10] or co-precipitation technique. In this method, the host and the guest species are included in the mother liquor, followed by
aging process to form a well-ordered nanolayered structure. On the other hand, insertion of the guests can also be done by first preparing the host followed by modification or further treatment of the host and finally insertion of the guest molecule into the interlayer [11].

In the present study, we report and discuss the formation of a layered organic–inorganic nanohybrid material by intercalation of 24D into the Zn–Al–LDH (ZAL) for CR formulation (CRF) purposes. Following the intercalation of the 24D moiety into the Zn–Al–LDH inorganic lamella (ZAD), we subsequently study the controlled release property of the resulting intercalated 24D from the CR formulation into the aqueous solution containing various concentrations of chloride and carbonate anions. In addition, release of 24D in distilled water was also studied. The possible mechanism involved was also proposed and will be discussed. To our knowledge, no controlled release study of 24D, in particular from Zn–Al–LDH matrix has been carried out. Due to an herbicide property of 24D, a slow release of 24D from its nanocomposite material, ZAD can be exploited for CRF of an herbicide.

2. Materials and methods

2.1. Synthesis of the LDH and its nanocomposite

All solutions were prepared using decarbonated distilled water. Sample of Zn–Al–24D nanocomposite, in which 24D as the guest anion (ZAD) was directly synthesized by spontaneous self-assembly method of mixed aqueous solutions of Zn(NO₃)₂ and Al(NO₃)₃ with a molar initial ratio of Zn/Al, into the interlayer [11].

The percentage of 24D in ZADs was determined by UV–vis technique. All measurements were carried out at λmax = 283.1 nm using a Perkin–Elmer UV–vis Spectrophotometer Lambda 20. Powder X-ray diffraction (PXRD) patterns were recorded on a Shimadzu XRD-6000 powder diffractometer using Cu–Kα (λ = 1.54 Å) at 40 kV and 20 mA. Fourier transform infrared (FTIR) spectra were recorded using a Perkin–Elmer Model 1725 X spectrophotometer in the range of 400–4000 cm⁻¹. Scanning electron microscope, JEOL JSM-6400 was used to study the surface morphology of the samples at various magnifications.

2.2. Characterizations

The degree of intercalation of 24D for ZAD was estimated to be 49% (w/w) with carbon content of about 20% (w/w). This is in agreement with the FTIR spectra shown in Fig. 1(b), which indicates that FTIR spectrum of ZAD is a combination of bands of FTIR spectra of 24D and ZAL.

3. Results and discussion

3.1. Syntheses and characterization of the CRF

Powder X-ray diffraction patterns (PXRD) for ZAL and the CRF, ZAD are shown in Fig. 1(a). As shown in the figure, ZAL has the interlayer spacing of 9.7 Å. Intercalation is confirmed by the enhancement of the interlayer spacing to 25.1 Å when 0.32 M 24D was used for the synthesis which produced sharp, symmetrical and intense peaks, especially for the 003 reflection at about θ = 3.5°. The resulting ZAD obtained was subsequently used for controlled release study.

The presence of strong, sharp bands at about 1616 and 1359 cm⁻¹ in the FTIR spectrum of ZAD (Fig. 1(b)), which are absent in both FTIR spectra of ZAL and 24D is due to the formation of carboxylate anions. This is the result of ionization of 24D moiety in the aqueous solution. The two absorption bands actually belong to symmetric and asymmetric carboxylate stretching band, respectively [12].

The morphologies of ZAL and ZAD obtained by SEM are shown in Fig. 1(c) and (d), respectively. They show typical morphology of LDH and its nanocomposite, which are non-uniform irregular agglomerates of compact and non-porous plate-like structure similar to the morphology of Zn/Al–sodium dodecyl sulfate nanocomposite [13].

3.2. Controlled release of 24D into aqueous solutions

A series of aqueous solutions of chloride and carbonate sodium salts with various concentrations; 0.05, 0.005 and 0.0005 M were used to observe the effect on the release rate of 24D from the organic–inorganic nanohybrid, ZAD. In addition, distilled water was also used for comparison.

Fig. 2(a) and (b) show the release profile of 24D from the interlamellae of ZAD into the aqueous solution at various initial concentrations for chloride and carbonate, respectively. In addition, the release profile of 24D into distilled water at various amounts of ZAD is also given in Fig. 2(c).

The accumulated 24D released into the aqueous solution increased with contact time when ZAD was put in contact with the aqueous solutions containing NaCl at various concentrations (Fig. 2(a)). The release rate was found to be faster in the first 10 h from the initial time of the experiment, thereafter
a slower release was observed. Equilibrium was achieved at around 100 h. The amount of accumulated 24D released is generally increased with the concentration of the chloride ion in the aqueous solution.

However, for Na$_2$CO$_3$ aqueous solution, the equilibrium was reached at a faster rate. The release rate was found to be rapid for the first 5 h, followed by a slower one thereafter and the equilibrium was achieved at around 40 h. Similar to the chloride system, the amount of accumulated 24D released is generally increased with the concentration of the carbonate concentration in the aqueous solution.

To study the release of 24D in distilled water, a slightly different strategy was adopted. Different amounts of ZAD, 0.1, 0.2 and 0.4 g were introduced into 500 ml distilled water, so that the effect of the release rate of 24D at different amounts of ZAD when it was put in contact with the release medium can be observed. Similar to carbonate, the release of 24D was found to be rapid for the first 5 h, and a more sustained release thereafter. Equilibrium was achieved at around 120 h. The amount of 24D released was found to be proportional to the amount of ZAD introduced in the distilled water. Similarly, the introduction of more ZAD into the distilled water resulting in more percentage release of 24D into the release medium as a result of ion exchange process between the 24D in the interlayer with the carbonate anion generated due to the carbon dioxide dissolved from the atmosphere into the distilled water. In addition, the affinity of carbon dioxide is also higher than 24D towards the inorganic interlamellae.

The rapid release pattern of higher concentration of the anions, chloride or carbonate is obvious if only ion exchange phenomenon governs the release of 24D into the media, aqueous solutions. At higher concentrations of the anions in the aqueous media, more ion exchange process can be accomplished, and therefore a faster rate can be observed.

The amount of 24D released from ZAD into the aqueous solutions containing Na$_2$CO$_3$ was found to be the highest, as shown in Fig. 2(b). It was observed that at the end of rapid release rate, the amount of 24D released from aqueous solutions at various initial Na$_2$CO$_3$ concentrations were 80% (0.0005 M); 85% (0.005 M) and 90% (0.05 M). The lowest percentage of 24D released was achieved in NaCl aqueous solutions. At equilibrium, it was estimated that only about 60% of 24D could be released from ZAD into the aqueous solutions if the initial concentration of NaCl was set to 0.0005 M, compared to around 80% for 0.05 and 0.005 M. In distilled water, about 70, 80 and 90% of 24D, could be released in 170 h when 0.1, 0.2 and 0.4 g of ZAD, respectively were put in contact with the release medium.

Based on the release of 24D at equilibrium when 0.1 g ZAD was put into 500 ml of various solutions, the order of the
Fig. 2. Release profile of 24D from ZAD interlamellae into the aqueous solutions containing various anions at various concentrations; NaCl (a), Na$_2$CO$_3$ (b) and distilled water (c). The profile of release at the beginning of the process is also shown in the inset.

The accumulated amount of the 24D released at the end of 100 h from the start of ZAD was put in contact with aqueous solution containing various anions and concentrations of the aqueous solution can be summarized as

Na$_2$CO$_3$ > distilled water > NaCl

In aqueous Na$_2$CO$_3$ solutions, the high concentration of CO$_3^{2-}$ ions in the solutions resulted in CO$_3^{2-}$ ions to be ion-exchanged with 24D. As a result, CO$_3^{2-}$ ions will be incorporated into the interlayer of ZAD and at the same time, the 24D would then be released into the solution, i.e. the formation of LDH. At the beginning of the experiment, the ion exchange process is rapid. When a small species, CO$_2$ was exchanged with a bigger anion, 24D a decrease in the basal spacing occurred and this phase transformation will first cover the external part of the nanohybrid crystals. As the reaction proceeded, a smaller and a larger basal spacing co-existed in the same crystal and therefore a formation of phase boundary between internal zone containing the nanohybrid and the external zone containing LDH occurred. As a result of the formation of this new phase (LDH), a sort of ‘barrier’ builds up between the CR formulation, ZAD and the aqueous solution, and consequently this will further decrease the rate of the 24D that could be released from the formulation into the aqueous solution, hence the amount of 24D released declined progressively [1].

The amount of the 24D released at equilibrium is higher for Na$_2$CO$_3$ solutions than that for NaCl, 80–90 and 60–80%, respectively. In general, several factors such as the affinity of the anion towards the Zn–Al–LDH inorganic interlamellae, the extent of the dissolution of the inorganic LDH with the collapse of the nanolayered structure and the actual composition of the controlled release formulation are important and these will contribute to the amount of 24D released into the aqueous solution. As we know that the affinity of carbonate is higher than chloride towards the Zn–Al–LDH inorganic interlamellae, with the other factors being constant, then the former factor is the most important that govern the released amount of 24D.

In distilled water, the amount of the 24D released at equilibrium at the same loading of ZAD, i.e. 0.1 g in 500 ml solution is around 60%. The amount increased with the increase of the loading, 80 and 90% for 0.2 and 0.4 g, respectively. As the solution was left under atmospheric condition during the experiment, it is obvious that the anion responsible for the ion exchange process is carbonate, due to the carbon dioxide dissolved in the distilled water during the experiment.

3.3. First order kinetics

The 24D release profiles suggested that the first order kinetic equation given in Eq. (1) could be used to describe the release behavior,

$$\ln (1 - M_i/M_f) = (1)$$

in which $M_i$ and $M_f$ are the initial and final concentrations of 24D, respectively.

Attempt has been made to fit the data obtained from the 24D released into the aqueous solution into the first order kinetic and the result obtained is shown in Fig. 3(a)–(c). The extent of time and the regression value are also given. As shown in the figure, the release of 24D nicely followed the first order kinetic for the first 12 h or so for all of the solutions used, with a value of 23, 16 and 22% of 24D released from ZAD into the aqueous solutions for NaCl, Na$_2$CO$_3$ and distilled water, respectively.

3.4. Powder X-ray diffraction

In order to obtain some insight on the ion exchange phenomenon, we subsequently recovered the resulting samples from the aqueous solutions after the 24D release experiment. Solutions with 0.005 M NaCl and Na$_2$CO$_3$ and 0.2 g ZAD in distilled water were selected and the contact times chosen were at 5 min, 60 min and 24 h. The recovered samples were dried, thoroughly washed and characterized by PXRD. The PXRD patterns for the recovered samples from solutions are shown in
Fig. 4, and the basal spacing and phases observed are summarized in Table 1. The PXRD of the CRF, ZAD is also given at the bottom of the figure (indicated by 0 min) for comparison.

For NaCl (Fig. 4(a) and Table 1), the nanohybrid phase of ZAD showed a reduction in the interlayer spacing from 25.1 to 24.0 Å, after 24 h release time. No obvious change was observed for the first 5 and 60 min, except the intensity of the 003 reflection, in which the 003 reflection peak and other associated peaks generally decreased, indicating lower crystallinity of the resulting material compared to the starting material, ZAD. A similar behavior was also observed for distilled water (Fig. 4(c)) with the basal spacing reduced to 23.4 Å, after 24 h release time.

For Na2CO3, a remarkable change was observed even after 5 min contact time, in which the 003 reflection reduced in intensity and basal spacing decreased to 23.9 Å. In addition, two new phases can be clearly observed, LDH and ZnO phases and the formation of these phases increased with contact time. Although ZAD phase can still be observed up to 60 min, but this phase completely collapsed after 24 h. For the sample recovered from NaCl and distilled water, the decrease of the

![Fig. 3. Fitting of 2D release data into the aqueous solutions containing various anions at various concentrations with first order kinetics; NaCl (a), Na2CO3 (b) and distilled water (c).](image)

![Fig. 4. PXRD patterns for the samples recovered from the aqueous solutions at various release times, 5 min, 60 min and 24 h for NaCl (a), Na2CO3 (b) and distilled water (c), conditions: 0.1 g of ZAD in 500 ml aqueous solutions at room temperature for NaCl and Na2CO3, and 0.2 g of ZAD in 500 ml for distilled water. Peaks labeled ‘o’ indicates the ZnO phase, the PXRD pattern of ZAD (labeled as ‘0 min’) is also given for intensity comparison.](image)
The extent of 24D released from the formulation in which the first order kinetic give a good fit is also indicated in Fig. 3d, basal spacing; NC, nanocomposite.

The release of the 24D anion from the interlayer of ZAD into the aqueous solution containing sodium carbonate could also have occurred. The release of 24D anions from the interlayer of ZAD into the aqueous solution could have also occurred via ion exchange mechanism, in which the 24D ions was exchanged with CO$_3^{2-}$ and OH$^{-}$ ions and finally released into the aqueous solution. As a result, the dissolution of the inorganic LDH followed by the collapse of the layered structure and the ion exchange of the 24D with the CO$_3^{2-}$ in the nanocomposite for the formation of an LDH phase is expected to be observed. PXRD of ZAL (Fig. 1(a)) shows that the basal spacing of LDH with nitrate as the counter anion is 9.7 Å. However, the corresponding peak for the newly formed LDH as a result of the deintercalation of 24D and the formation of new LDH is 7.6 Å. The discrepancy is attributed to the different in the counter anion (carbonate instead of nitrate), which was reintercalated into the resulting LDH material together with its spatial orientation.

### 4. Conclusion

The release of the 24D anion from the interlamellae of an organic–inorganic nanohybrid material, Zn–Al–24D nanocomposite could be controlled by adjusting the type and the concentration of the anion in the release medium, the aqueous solution or the amount of the nanocomposite, the controlled release formulation. The release rate of the anion from the interlamellae of the nanocomposite was found to be dependent on the type of anion and its concentration in the release media. The highest percentage of 24D released was achieved from the highest concentration of carbonate solution. In aqueous solution with carbonate, release of 24D ions from the interlamellae of ZAD was followed by the formation of two new phases, LDH and ZnO. This happened fairly rapidly, even after 5 min contact time. However, in distilled water and NaCl aqueous solutions, release of 24D anions from the nanohybrid did not destroyed the layered structure for at least 24 h. This shows the higher affinity of carbonate than chloride towards the LDH inorganic interlamellae. It was also found that the release of 24D anions from the lamella of ZAD was controlled by the first order kinetic at least at the beginning of the deintercalation process.
up to 12 h or so, regardless of the structure of the resulting CRF.

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