Characterization and Controlled Release Formulation of Agrochemical Herbicides Based on Zinc-Layered Hydroxide-3-(4-Methoxyphenyl) Propionate Nanocomposite

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ABSTRACT

Nanocomposite of zinc layered hydroxide-3-(4-methoxyphenyl) propionate (ZLH-MPP) were prepared by intercalation of 3-(4-methoxyphenyl) propionic acid (MPP) into the interlamellae of zinc layered hydroxide (ZLH) by using direct reaction of an aqueous suspension of zinc oxide with MPP solution via one step method. Power x-ray diffraction patterns showed the result of successful intercalation of ZLH-MPP nanocomposite at 27.3 Å at a low angle of reflection. The result was also supported by FTIR spectra and elemental analysis of the nanocomposite. On the basis of EDX and TGA-DTG results, the chemical formula of ZLH-MPP nanocomposite was Zn(OH)1.47(CH3OC6H4CH2CH2COO-)0.53·0.87H2O. The controlled release of MPP from interlayer of ZLH-MPP nanocomposite showed that phosphate medium yielded the highest percentage release compared to sulphate and chloride medium. The release of MPP was found to be in controlled manner governed by pseudo-second order for phosphate medium and first order for sulphate and chloride medium.

Keywords: Nanocomposite ∙ Zinc layered hydroxide ∙ 3-(4-methoxyphenyl) propionic acid ∙ Controlled release

INTRODUCTION

Herbicides are chemical substances that are utilized to specifically kill plants. The mode of action for herbicides is the biochemical or physical mechanism, which includes absorption into plant and translocation to the site action and also disrupting or altering one or more of their metabolic processes resulting in plant death [1]. Lately, particular attention has been focused on the controlled release system on herbicides using layered material hydroxide which is acting as a host for the herbicide. Other systems that are being used in current applications such as layered double hydroxide (LDH) [2], modified clay montmorillonite [3] and kaolinite [4]. Zinc layered hydroxide (ZLH) is a type of layered metal hydroxide (LMH), having the general formula $\text{M}^{2+}_x\text{A}^{m-}_x\text{H}_n\text{O}$ where $\text{M}^{2+}$ is the metal cation, $\text{Zn}^{2+}$ and $\text{A}^{m-}$ is the counter ion. ZLH structure is similar to that of brucite; however, the inorganic layers are composed of only one type of metal cation such as Mg$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$. In this structure, the OH anions on the brucite hydroxide layer are substituted by water molecules and counter anions [5]. There are various synthesis methods that can be used to synthesise the ZLH nanocomposite such as ion-exchange method [6, 7], coprecipitation method [6], structural memory effects [8], and hydrothermal precipitation methods [9]. Above all, direct reaction method is frequently chosen in the preparation of ZLH nanocomposite because it is an easy preparation method, as considerably a fewer steps and chemicals are involved [10, 11]. In this research, we highlighted on the intercalation of MPP into ZLH to form a new nanocomposite, ZLH-MPP by using direct reaction method. The slow release of herbicides would be proven by using the kinetic analysis supported by data from various concentrations with various types of solution.

EXPERIMENTAL SECTION

Synthesis ZLH-MPP nanocomposite

All solutions were prepared using deionised water. ZnO (ACS reagent, Acros Organics) and 3-(4-methoxyphenyl) propionic acid (MPP) (Acros Organics) were used without further purification. The ZLH nanocomposite was prepared by the direct reaction method of ZnO with the guest anions in an aqueous environment as previously done elsewhere [10, 12]. In this experiment, 0.05 g of ZnO was dispersed into 100 ml deionized water. Solutions of
RESULTS AND DISCUSSION

PXRD Analysis

The XRD patterns of ZLH-MPP nanocomposite are shown in Figure 1 (a). The intercalation of MPP herbicides into ZLH exhibited a diffraction pattern characterization with a sharp diffraction peak centred at 27.3 Å for all concentrations of MPP. The turbostratic disorder which were traced to ZnO, has also been observed in PXRD pattern of 0.025 M ZLH-MPP nanocomposite. The presence of ZnO peak indicated by an incomplete reaction which resulted in remaining ZnO phase [14]. None of the crystalline impurities of MPP were detected in the intercalated nanocomposite material. Nanocomposite at 0.05 M concentration of MPP showed high intensity of intercalation at low angle of 20 degree with a very small peak of ZnO that was chosen for further characterization.

FTIR Analysis

Figure 1 (b) shows the FTIR spectra of MPP, ZLH-MPP, and ZnO. FTIR analysis for MPP herbicide showed the spectra of methoxy group bonding with an aromatic ring displaying an asymmetrical C-O-C stretching band at 1275 cm$^{-1}$-1200 cm$^{-1}$ which centered at 1274 cm$^{-1}$ and symmetrical stretching near 1075-1020 cm$^{-1}$ which centred at 1038 cm$^{-1}$. The bands perceived at around 1410 cm$^{-1}$ and 1300 cm$^{-1}$ were assigned to the stretching vibrations of the aromatic ring C=C bond [10]. The strong and sharp band of C=O for COOH that bonded with the aliphatic alkyl group were centred at 1708 cm$^{-1}$ and 1640 cm$^{-1}$. All the characteristic bands of pure MPP were present in the ZLH-MPP nanocomposite spectra. However, the disappearance of the absorption bands around 1760 cm$^{-1}$ and 1744 cm$^{-1}$ (carboxylic group, COOH) in the ZLH-MPP nanocomposite spectra, was due to the removal of hydrogen ions from the MPP molecule which confirmed that the species which were intercalated into the ZLH layers were in the anionic form of MPP or in other term was known as 3-(4-methoxyphenyl) propionate [12, 13]. FTIR spectra for ZLH-MPP also showed a broad and strong band in the range of 3200-3600 cm$^{-1}$ centred at 3442 cm$^{-1}$ which was due to the O-H stretching vibration mode of hydroxyl groups and water molecules [15]. Peaks at 1412 cm$^{-1}$ and 1563 cm$^{-1}$ were attribute to symmetric and asymmetric stretching vibration of the COO$^-$ group respectively whereas, a strong band at 1034 cm$^{-1}$ and 1238 cm$^{-1}$ were due to symmetric and asymmetric stretching modes of C-O-C [10]. The band at 1334 cm$^{-1}$ was due to a C=C in the benzene ring. The superimpose of ZLH-MPP spectra with ZnO spectra and MPP spectra confirmed the intercalation of the MPP anions and the formation of ZLH-MPP nanocomposite.
the ZLH-MPP nanocomposite was 27.3 Å. Therefore, the width occupied by MPP herbicides in the interlayer space of ZLH was 17.3 Å.

The probable orientation of MPP anions intercalated between the ZLH interlayer for the formation of ZLH-MPP nanocomposite

Thermal Analysis
The TGA-DTG curve for representative herbicide, nanocomposite and ZnO are shown in Figure 3. The weight losses of MPP started at 60.9 °C and completed around 265 °C with 98.8% weight loss in only one stage as shown in Figure 3 (a). Meanwhile, Figure 3 (b) shows the three stages of weight losses of ZLH-MPP nanocomposite. The first stage started between 60.9 °C and 140.4 °C with 7.6% weight loss which was due to the loss of the surface physisorbed water molecule [12, 13] and the intercalated water structure [12, 15] at corresponding peak, 136 °C. The second stage ended at 397 °C with a weight loss of 34.5%. This was due to dehydroxylation of the ZLH lamellae and the decomposition and elimination of MPP at 379 °C [13, 20]. The third stage involved the collapse of ZLH lamellae which ended at 626 °C with a weight loss of 7.8% [8]. The differential thermogravimetric curve showed a peak at 519 °C that indicated the decomposition of the benzene ring of carbon, where collapsing of layered hydroxide salt layers was completed leaving an oxide metal as the combustions were done [8, 12]. There was no thermal decomposition on ZnO which proved that ZnO was a thermally stable compound as shown in Figure 4 (c). An increase in the decomposition temperature of MPP from 265 °C (MPP in free state) to 258 °C (MPP intercalated into the nanocomposite) indicated better thermal stability of ZLH-MPP nanocomposite than MPP itself. This was probably due to electrostatic attraction between the negatively charged functional group of MPP and the positively charges ZLH [13].

The elemental analysis result is shown in Table 1. The elemental analysis showed that there were no C and N elements found in ZnO. Result of the elemental analysis of ZLH-MPP nanocomposite showed that 27.70% of carbon with a weight percentage of 41.56%. The appearance of C and Zn elements in nanocomposite indicated the success of the intercalation of MPP into the interlayer of ZLH material. Based on the EDX analysis and TGA-DTG analysis, the formula of ZLH-MPP was proposed as Zn(OH)$_{1.47}$(CH$_3$OC$_6$H$_4$CH$_2$CH$_2$COO$^-$)$_{0.53}$.0.87H$_2$O).

Controlled Release Study
The release profile of MPP from ZLH-MPP interlayer into three different concentrations of sodium dihydrogen phosphate, sodium sulphate and sodium chloride are shown in Figure 4. Based on the components of rain water, phosphate solution was chosen as the solution for release of MPP herbicide [21] as well as sulphate and chloride solution. In most cases, the controlled release of herbicides increased with the increasing of concentrations due to the higher rate of ion exchange of herbicides that intercalated in ZLH with PO$_4^{3-}$, SO$_4^{2-}$, and Cl$^-$ ions in the solution. The ion exchange process occurred due to the high affinity of the smaller size and higher charge density of phosphate, sulphate and chloride ions compared to MPP. Previous studies reported that the affinity of smaller size and higher charge density of phosphate anion as compared to DPBA, DPPA, and CPPA resulted in the higher rate of ion exchange process [22]. As shown in the Figure 4 (a to c) the release rate of herbicides increased with the increasing of solution concentration. At higher concentration of the anions in the aqueous media, more ion exchange process could be accomplished, and therefore a faster rate could be observed [5, 23]. The release rate of MPP into phosphate solution was found to be faster at the beginning and slower after 600 minutes. This was due to the high density of phosphate anion leading to a high formation of electrostatic interaction between phosphate anion with the positively charged layer of layered hydroxide material in the ion exchange process [21]. However the release rates were

| Table 1 Analysed Chemical composition of ZnO and ZLH-MPP nanocomposite. |
|------------------|------------------|------------------|------------------|
| Sample           | C (%)            | N (%)            | Anion (w/w)      | Formula                  |
| ZnO              | -                | -                | 85.8             | ZnO                      |
| ZLH-MPP          | 27.70            | 0                | 19.42            | 41.56 Zn(OH)$_{1.47}$(CH$_3$OC$_6$H$_4$CH$_2$CH$_2$COO$^-$)$_{0.53}$.0.87H$_2$O |

$^a$ = estimated from CHNO-S analysis

$^b$ = estimated from EDX and TGA-DTG analysis

Figure 3 TGA-DTG thermograms of (a) MPP, (b) ZLH-MPP nanocomposite, and (c) ZnO

Figure 2 The probable orientation of MPP anions intercalated between the ZLH interlayer for the formation of ZLH-MPP nanocomposite

Figure 4 The probable orientation of MPP anions intercalated between the ZLH interlayer for the formation of ZLH-MPP nanocomposite
lower in sulphate and chloride solutions as shown in Figure 4 (b) and (c). In sulphate and chloride solutions, the release rate achieved equilibrium only after 1260 minutes and 2880 minutes respectively. It could be observed that phosphate (0.3 M) dominated the accumulated release percentages at 93.2% compared to percentage release in sulphate and chloride solutions as previously reported [24]. This was due to the affinity of the compared to percentage release in sulphate and chloride solutions dominated the accumulated release percentages at 93.2% respectively. It could be observed that phosphate (0.3 M) achieved equilibrium only after 1260 minutes and 2880 minutes and (c). In sulphate and chloride solutions, the release rate lower in sulphate and chloride solution as shown in Figure 4 (b) and lastly chloride ions [6, 25].

Figure 4 Release profile of MPP herbicide from ZLH-MPP nanocomposite (a) in aqueous phosphate, (b) sulphate, and (c) chloride solutions.

Kinetic Study
Kinetic study of the MPP release from the interlayer of ZLH-MPP nanocomposite was further performed and quantitative analysis of the data obtained from the release study were fitted to zeroth order (x = t + c), first order (\(-\log (1 - (M_i/M_f)) = t + c\)) [26], pseudo second order (\(t/M_f = 1/(M_i/M_f)^2 + t/M_f\)) [27], parabolic diffusion model \((M_i/M_f = kt^{0.5} + c)\) [28], and Fickian diffusion model \((M_i/M_f = kt^n)\) [29] as previously reported [10, 20, 30, 31] for which the equations are given below. The x is the percentage release of the herbicides anion at time \(t\), \(M_i\) and \(M_f\) are the initial and final concentration of MPP anions respectively and c is a constant. Meanwhile \(M_i/M_f\) represents the fraction of release herbicide at time \(t\), and \(n\) is an empirical parameter describing the release mechanism [31].

The rate constants, \(k\), and \(t_{1/2}\) are calculated from the corresponding equation where \(t_{1/2}\) is the time required for 50% of MPP herbicide to be release from ZLH-MPP nanocomposite. The diffusional exponents, \(n\) and \(k\) for Fickian diffusion model are evaluated from the slope of the plot \(\log (M_i/M_f)\) versus \(\log t\).

The obtained fitting curve between 0 to 1000 min are presented in Figure 5. The best fit graph can be obtained through the resulting correlation coefficients, \(r^2\) values where the closest value to 1 was considered as best fit as listed in Table 2. The correlation coefficient, \(r^2\) for the release of MPP into phosphate solution was shown to have a value near to 1 which indicated the release profile of MPP herbicide into phosphate solution followed the pseudo second order. This was due to the release of herbicide from the inorganic ZLH interlayer involved in the dissolution of nanocomposite as well as ion exchange between the intercalated anions in the interlayer ZLH and the phosphate anions in the aqueous solution which were controlled by pseudo second order [22]. The \(t_{1/2}\) of release profile of MPP into aqueous phosphate solution was lower than sulphate and chloride solutions, and \(t_{1/2}\) decreased as the concentration of solution increased. This showed that the herbicides were more easily released into a medium if the available anions in the media had higher affinity towards the ZLH inorganic interlayers [30]. The decrease of \(t_{1/2}\) was obvious because, as the concentration of the phosphate increased, when more phosphate anions were available to be ion exchanged with MPP herbicides anions, resulting in a lower value of \(t_{1/2}\) [21].

Based on \(r^2\), obtained, first order was the best fit for the released profile of MPP herbicide in both sulphate and chloride solutions, that indicated the released herbicide to the sulphate and chloride solutions was in a way proportional to the amount of MPP herbicides that remained in the interlayer ZLH. In such way, the amount of MPP herbicides released by unit of time diminished as described in [26]. Generally, both pseudo second order and first order show that the exchangeable anion either incoming and outgoing from the solution could be exploited for controlling release herbicides which is available for agricultural purposes.

![Image](36x533 to 314x630)

Figure 5 Fitting of the data for MPP release from ZLH-MPP nanocomposite to the (a) pseudo second order (aqueous phosphate solution), (b) first order kinetic (aqueous sulphate solution), and (c) first order kinetic (aqueous chloride solution).

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CONCLUSION

A nanocomposite of ZLH-MPP was obtained by a simple and profitable separation method using ZnO as starting material in which an aqueous suspension was directly reacted with an MPP solution via one step method. The resultant nanocomposite had a basal spacing of 27.3 Å indicating that MPP encapsulated perfectly into the ZLH interlayer. The FTIR study showed the presence of functional groups for both guest anions and inorganic host which also confirmed the intercalation of MPP into the interlayer of ZLH and the MPP anions were estimated to be 41.56% (w/w). An enhanced thermal stability of ZLH-MPP nanocomposite was highlighted in the thermogravimetry analysis as it had a higher decomposition temperature (379 ºC) compared to MPP anions (258 ºC). The release of MPP anions from interlayer ZLH was higher in phosphate solution compared to sulphate and chloride solutions. 93.2% of MPP anions were released from 0.3 M of ZLH-MPP nanocomposite into the aqueous phosphate solution and the percentage yield was reduced with the decreasing of nanocomposite concentration. The released behavior of MPP herbicides from its nanocomposite into phosphate solution 10. followed the pseudo second order and whereas, in both sulphate and chloride solution it was governed by first order kinetic. Based on this study, the method used was very practical as well as 11. producing a good result without costing a lot of money. Besides that, ZLH is strongly suggested to be used as a carrier for MPP herbicides with controlled release capability which is environmentally friendly towards a new safer agrochemical field. 12.

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