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Development of Herbicide Delivery System Based on Magnesium Aluminium – 4-Chlorophenoxyacetic Acid (Mac) Nanocomposite

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Abstract: Layered double hydroxide (LDH)-based nanocomposite, created by interacting LDH with another nanoparticles usually applied in the area of environmental, catalytic, industrial and biomedical field. In this study, a new herbicide delivery system was developed through the intercalation of Magnesium Aluminium-layered double hydroxide (MAN host) with 4-chlorophenoxyacetic acid (4-CPA). This intercalation was done by using co-precipitation method at pH 10 with different concentration of 4-CPA which were 0.5 M and 0.7 M. The successful intercalation was obtained at 0.7 M Magnesium Aluminium-4-chlorophenoxyacetic acid (MAC) and had been confirmed through several analysis. Firstly, the XRD pattern shows expansion of basal spacing shifted from 8.9 Å to 9.3 Å. This result supported by the FTIR-ATR spectrum that shows the disappearance nitrate peak (NO_3^-) and appearance of carboxylate ion (COO^-) peak at 1596 cm^{-1}. Furthermore, this intercalation was validated with the result of surface morphology by FESEM. The controlled release study of 4-CPA from 0.7 M MAC shown sodium carbonate solution released the percentage of 4-CPA higher than tap water. This study has signifies MAC as a safer agent of agrochemicals by reducing the dosage of herbicide in the agriculture field and protect the herbicide through encapsulation system.

Key words: *Intercalation, Controlled release study, 4-chlorophenoxyacetic acid (4CPA), Magnesium layered hydroxide, Agrochemical, Nanocomposite*

INTRODUCTION

Nowadays, agriculture sector is among the important sector that contributes to the earning of many countries on the earth. For many years, this sector has been the backbone of Malaysia economy by yielding the crops and producing agricultural product. Thus, the use of herbicides in farming is extremely difficult to avoid in order to increase the crops productivity.

Layered nanomaterials such as LDH are widely study among researcher due to their unique properties and it has been used in diverse applications such as adsorbents, drug delivery [1], controlled release formulation [2-3] and sensors [4]. LDH has capability as a host to construct organic-inorganic nanomaterials due to high stability and less toxicity properties [5]. Intercalation technique usually use to create nanomaterials without modifying the structure of interlayer by insertion of interest anion toward interlayer space [6]. There are many methods to intercalate anion into LDH interlayer gallery such as co-precipitation, hydrothermal and ion-exchange method.

4-CPA is one of the attractive herbicide that has been widely used in the agricultural field [7]. The chemical structure of 4-CPA has shown in the Fig 1. It used for plants growth regulator and herbicide which increases fruit production [8]. However, according to Reference [9], the use of this herbicide in agricultural field on a large scale can cause water pollution as the herbicide can be swept away or run off to the river. Intercalation of 4-CPA with Magnesium Aluminium-layered double hydroxide (MAN host) can minimized this problem as it increase the efficiency of the

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herbicide thus the dosages of herbicide needed in agricultural will reduced. Moreover, the production of Magnesium Aluminium-4-chlorophenoxyacetic acid (MAC) nanocomposite will protect the herbicide from the physical changes and less efficacy when it exposed to sunlight and heat. So, encapsulation system make the 4-CPA more stable with their properties.

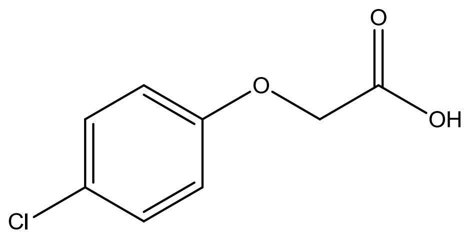


Figure 1: Chemical structure of 4-Chlorophenoxyacetic acid

Owing to this excellent properties, LDH has been explored tremendously for the development of new hybrid materials with great performance. Therefore, this study is conducted to intercalate 4-chlorophenoxyacetic acid (4-CPA) with the Magnesium Aluminium-layered double hydroxide (MAN host) to increase the efficiency of the herbicide.

EXPERIMENTAL

Chemical and Reagents

All chemicals were purchased from R&M Chemical (98 %) except for 4-Chlorophenoxyacetic acid (4CPA, 99 %) that was purchased from Sigma Aldrich and being used without further purification. All the solutions were prepared by using deionized water.

Synthesis of MAN host

About 6 g of $Mg(NO_3)_2.6H_2O$ and 5 g of $Al(NO_3)_2.9H_2O$ were mixed together with additional of deionized water. Then, the mixture was stirred vigorously under nitrogen gas (N_2). This is an important step to avoid the contamination with atmospheric CO_2 and water that could formed carbonate ion in the interlayer of the MAN host. Next, sodium hydroxide (NaOH) was added slowly into the mixture solution until the pH 10. The mixture was aged for 18 hours at 70 ºC in oil bath shaker before being centrifuged. This mixture had been centrifuged for 5 mins and washed with deionized water three times to remove impurities. The precipitate was collected and dried in oven for 72 hours at 70 ºC.

Synthesis of MAC via co-precipitation

The MAN host was mixed 0.7 M 4-CPA anion in the Erlenmeyer flask. Then, the pH of solution was adjusted to 10.0 ± 0.5 by adding a dropwise of 2 M of NaOH. Next, the mixture was aging for 18 hours in oil bath shaker at 70 ºC, centrifuged at 180 rpm for 5 minutes, washed for three times with deionized water and dried in oven for 72 hours. This synthesized procedure was repeated by using different concentration of 4-CPA which was 0.5 M.

Controlled Release Procedure

The release of 4-CPA from MAC nanocomposite were prepared with different aqueous medias which were sodium carbonate (Na_2CO_3) and tap water. 3 mg of MAC nanocomposite was placed in quartz cuvette on top of aqueous media. The percentage release of 4-CPA from MAC nanocomposite was measured by using UV-Vis instrument.

RESULT AND DISCUSSION

PXRD analysis

This analysis was done to determine the crystallinity properties of the MAN host and MAC. It also can be used to determine the successful intercalation of 4-CPA with MAN host labelled as 0.5 M MAC and 0.7 M MAC. Fig 2 shows the XRD pattern obtained for the prepared MAN host and MAC at different concentration of 4-CPA. From the pattern of MAN host, a very intense and sharp peak was appeared with the basal spacing of 8.9 Å. This basal spacing was contained water molecules and nitrate as counter anions between its interlayer gallery that had been reported previously by [10-12]. The water molecules were attached to the nitrate and metal hydroxide through extensive hydrogen bonds that would continuously breaking and forming into the new bond. There are several factors that affect the amount of water molecules in the interlayers such as the characteristics of the counter anions, the water vapour pressure and surrounding temperature [10].

For the nanocomposite synthesized at 0.5 M of 4-CPA, the result has indicated that the nitrate ion was remain in the interlayer of MAN host since the basal spacing was being unchanged at 8.9 Å. Therefore, we can concluded that 4-CPA wasn't fully intercalated into MAN host as there is the presence of nitrate ions. In contrast, the basal spacing of 0.7 M MAC was slightly shifted downward to 9.3 Å with the wider basal spacing after the intercalation process took place. The increases in the basal spacing of nanocomposite showed the expansion of the interlayers of the MAN host due to the inclusion of a new guest anion, 4-CPA [13-14]. Thus, this intercalation was assumed to be success since there was an absence of nitrate peak ion in the XRD pattern of 0.7 M MAC.

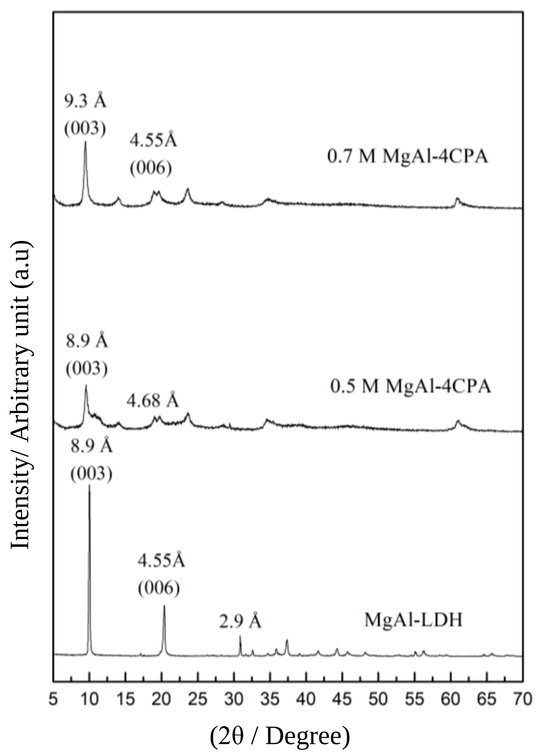


Figure 2: XRD pattern of LDH host, 0.5 M MgAl-4CPA and 0.7 M MgAl-4CPA

FTIR-ATR spectroscopy

The successful formation of nanocomposite can be validated by using FTIR spectra with the presence of functional groups observed. Through the FTIR spectra analysis, the presence of 4-CPA was confirmed intercalate into the interlayer gallery of nanocomposite at the concentration of 0.7 M MAC. Fig 3 summarizes the FTIR spectra for MAN host, 0.5 M MAC, 0.7 M MAC and pure 4-CPA. For 4-CPA spectrum, CH_3 stretching with sp^3 character was observed at 2924 cm^{-1} [15]. The strong peaks at 1732 cm^{-1} and 1233 cm^{-1} represent the carboxylic group which were C=O and OH respectively. In addition, the symmetric and asymmetric stretching mode of C-O-C vibration can be seen at the peak of 1088 cm^{-1}. Other than that, the peaks at 1489.30 cm^{-1} and 1233.50 cm^{-1} were corresponding to the C=C vibration of the aromatic ring. All of these peaks have defined the structure of 4-CPA accordingly.

From the results obtained, the spectrum for MAN host showed a strong and broad peak at 3488 cm^{-1} due to the hydroxyl group (O-H) stretching vibration. It also corresponding to the presence of water molecules within the layers. Not only that, a low intense peak at wavenumber of 1640 cm^{-1} also ascribed to the distortion mode of water. Next, the strong peaks at 1353 cm^{-1} and 826 cm^{-1} attributed to the nitrate peak that present as an initial anion in the interlayer gallery [16].

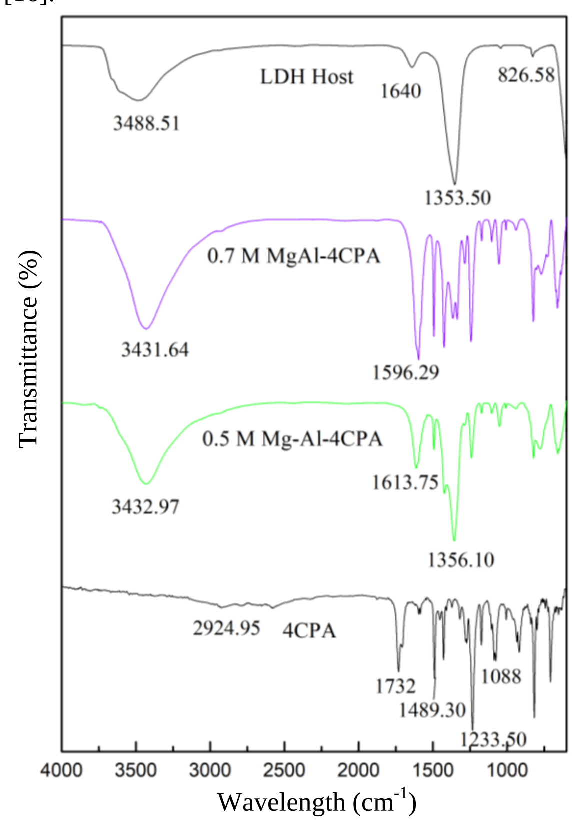
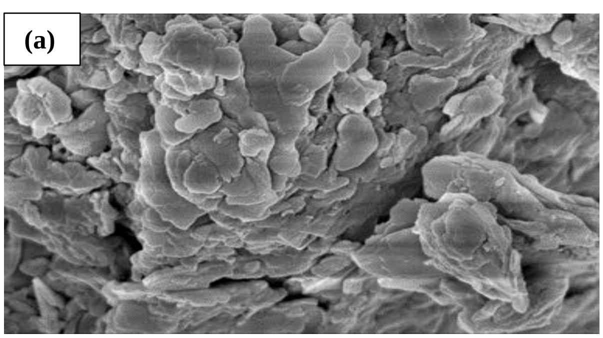


Figure 3: FTIR-ATR spectra for LDH host, pure 4CPA, 0.5 M MgAl-4CPA and 0.7 M MgAl- 4CPA

The intercalation of 4-CPA into MAN host was lead to different spectra of MAC by comparing to the spectra of pure 4-CPA and MAN host as they exhibited both spectra and characteristics [17]. For 0.5 M MAC, the nitrate peak was still remained in the FTIR spectrum at 1356 cm^{-1} that brings the fact 4-CPA was not completely intercalated into the layers of MAN host. However, in the 0.7 M MAC spectrum, the absence of nitrate peak was observed. This spectrum indicating that 4-CPA was successfully occupied in the MAN host layers. In addition, the peaks of carboxylic group at 1732 cm^{-1} and 1233 cm^{-1} were diminished and a strong new peak, carboxylate ion (COO^-) was appeared at 1596 cm^{-1}. This peak is belongs to the anionic form of 4-CPA which is very necessary to confirm the intercalation process was completely took place [2].

FESEM

Surface morphology of MAN host and 0.7 M MAC nanocomposite are shown in Fig 4. The micrographs in Figure 4 were obtained using field emission scanning electron microscope at 25,000x. The nature of MAN host roughly consist of some smooth region and non-porous plate-like particles in a big size of shape. The morphology of 0.7 M MAC nanocomposite was changed contrarily to an agglomerate and porous with granule structure compared to the compact morphology of MAN host. Observation on some flakes on the nanocomposite structure identifies a new phase discovery from arrangement of crystalline phase of MAN host with the presence of 4-CPA.



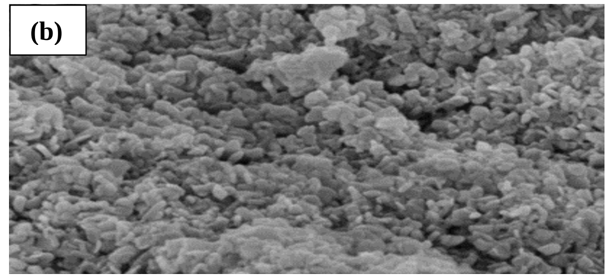


Figure 4: FESEM images of (a) LDH host and (b) 0.7 M MgAl-4CPA

Controlled release study by UV-Vis spectrometer

The release profile of 4-CPA from 0.7 M MAC nanocomposite in sodium carbonate solution (Na_2CO_3) and tap water are displayed in Figure 5. This release was ascribed due to the ion exchange of anions, electrostatic attraction and charge-density between anion of aqueous media solution and nanocomposite [18]. This is important to ensure the efficiency of herbicide by minimizing the usage of it from leaching into water and air [19]. In Na_2CO_3 solution, the burst effect was occurred at first 50 mins before a slow release ensue until it achieved equilibrium. The burst effect release rapidly to create the therapeutic dose that can kept for a long lasting [20]. The burst effect might be happened due to the surface characteristics of MAN host material, the herbicide interactions and porous structure of the material.

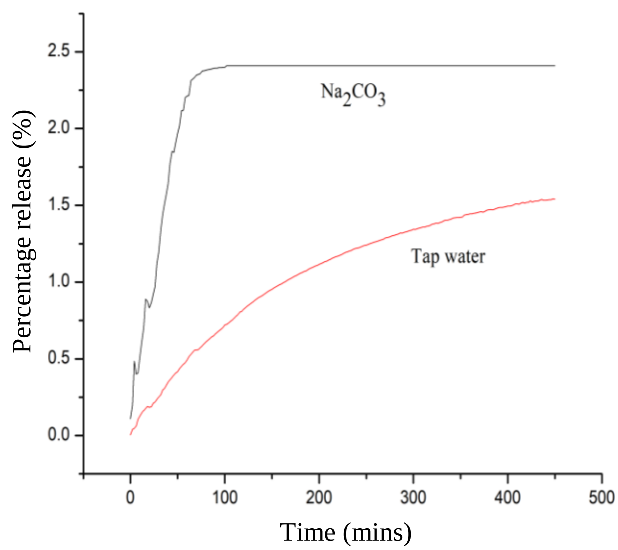


Figure 5: The release study of 4CPA in aqueous media solution

In comparison, percentage of 4-CPA release into the Na_2CO_3 solution higher than in tap water which was 19.72 % and achieved equilibrium at 102 minutes. As for tap water, it does not achieved equilibrium and needed longer time. However, percentage of controlled release during that period was 18.72 %. The release study depending to the availability of an anion in the aqueous solutions as carbonate ion is more easily intercalated compared to the chloride anion contained in tap water. It is due to the affinity of carbonate and chloride ions against the interlayer gallery [3]. The affinity of anions gave a great contribution to the process of anion exchange in order to examine the quantity of 4-CPA released into the aquoeus solution.

CONCLUSION

The novel MAC nanocomposite was developed via co-precipitation method at pH 10 (± 0.5) as an effective nanocarrier for the herbicide delivery system. Through this method, the most successful intercalation was obtained at the concentration of 0.7 M 4-CPA. PXRD analysis, FTIR-ATR spectroscopy and FESEM images indicated the 4-CPA was successfully intercalated into the MAN host. Moreover, further investigation was done with the controlled release study showing the percentage of release 4-CPA in Na_2CO_3 solution and tap water to be 19.72 % and 18.72 % respectively. This study show that MAN is a good nanocarrier for 4-CPA in controlling the rate of dosage release especially in agricultural field in order to save the environment.

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