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Preparation of Zinc Layered Hydroxides-cinnamaldehyde Nanocomposites and Its Physico-Chemical Study

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Abstract

Cinnamaldehyde (CINN) is an organic guest anion, the main constituent of cinnamon oil was intercalated into zinc-layered hydroxides (ZLHs) by ion exchange method. CINN has been reported can killed mosquito larvae. The powder X-Ray diffraction (PXRD) indicates a successful intercalation of CINN into the interlayer galleries of ZLHs matrix when 1.0 g of ZnO with 0.08M of CINN was used forming zinc layered hydroxides-cinnamaldehyde (ZCINN) exhibiting basal spacing expansion, 21.2Å. Fourier transform infrared (FTIR) results supported and confirmed the intercalation of CINN as both ZnO and CINN functional groups appeared in ZCINN spectrum. The thermal stability property of the ZCINN was enhanced as compared to the anion, CINN. Field emission scanning electron microscopy (FESEM) image of ZnO showed a nonuniform granular-like structure transforming into flaky structure with various sizes after intercalation of CINN took place. These results indicate that it is possible to design and develop the nanocomposites containing larvicide for further investigations.

Keywords layered hydroxides, intercalation, cinnamaldehyde, nanocomposites

INTRODUCTION

Nanotechnology is the engineering of molecularly precise structure with nanoscale of 1-100 nanometre (nm) in size. Development of these nanomaterials is a result of progressive fundamental research done by scientists and researchers have shown improvements in the products. Applications and products from nanotechnology have been playing an important role in aiding benefits to society both in expected and unexpected ways mainly in medical care, home care industries and etc. Nowadays, scientists and researchers undertake a lot of work in synthesis, characterizations and applications of nanomaterials in order to find the best possible materials in enhancing its properties from the current one.

Zinc layered hydroxides (ZLHs) is a type of layered hydroxide salts (LHS) that consisted of zinc as metal cation in which only zinc and hydroxyl that represent the inorganic layers such as ZnO. The general formula of ZLH is $M^{2+}(OH)^{2-x}(An^{-})^{x/n}.mH_2O$ where M^{2+} is the metal cation and An^{-} is the counter anion [1]. The structure of ZLHs is similar to that of brucite, boasting a strong structure containing a positively charged layer that can expand or contract depending on the nature of the interlayer anions [2]. In recent years, there have been extensive researches and studies done on the preparations and uses of ZLHs for controlled release formulation (CRF) of agrochemical herbicides [3], adsorbent [4], drug carriers [5, 6, 2], flame retardants [7], catalyst [8], chemical sensor [9] and etc. The selection of anion which is inserted into the ZLHs system determines the applications. Basically, the choice of the guest anion species is based on the resulting properties of the desired product. ZLHs nanocomposites can be synthesised by ion-exchange method [10] with the fact that it is an easy preparation method and only requires minimal procedure [2].

Mosquito is classified from family of small and midge-like flies called Culicidae. Mosquito species population can be found in many parts of the world which has been giving summer nuisance and play predominant role in the transmission of viral diseases such as dengue fever and malaria which are among the greatest health problems in the world [11]. CINN which is the main constituent of cinnamon oils shows a great pungent smell and has the ability of excellent inhibitory effect in killing mosquito larvae [11]. From previous research, cinnamon oil could be used as an effective mosquito repellent, anti-inflammatory agent, anti-oxidant agent, anti-ulcer agent, anti-microbial agent and hypolipidemic properties [12, 13, 14]. Due to the interesting properties of CINN as discussed above, this has brought the idea to intercalate CINN into the interlayer of ZLHs which could be further tested as controlled release formulations (CRF) on mosquito larvicides application.

It is clear that there are many applications that could be brought to reality from the intercalation of key anionic species into ZLHs, particularly if the guest anion can then be released in a controlled manner. In this paper, we report on the intercalation of the cinnamaldehyde into ZLHs layer forming ZLH-cinnamaldehyde (ZCINN) nanocomposites. To date, no intercalation of cinnamaldehyde into ZLHs has been reported. The controlled release of CINN in the form of nanocomposites is hoped to be effective and environmental friendly CRF of larvicide.

MATERIALS AND METHODS

All the chemicals used in the study were obtained from different chemical suppliers (Sigma-Aldrich and Acros Organics) were used as received. ZCINN was prepared by ion-exchange method. About 1.0 g of ZnO was dispersed into 100 mL of deionised water. CINN solutions with various concentrations (0.01-0.08 M) were added into the ZnO mixture. Stirring of solution was carried out for 2 hours. Then, it was subsequently agitated for 18 hours in an oil bath shaker at 70°C. The resulting slurry was centrifuged, thoroughly washed and dried in an oven at 70°C for overnight. The prepared ZCINN was grinded to fine powder and stored in sample bottle for further characterisations.

Powder X-Ray diffraction (PXRD) patterns of the samples were obtained using filtered Cu-Kα radiation in a Shimadzu diffractometer D-600. Fourier transform infrared (FTIR) spectra were recorded in 400-4000 cm^{-1} wavenumber range by a Perkin-Elmer 1750 spectrophotometer. KBr disc method with a 1.0 % sample in 200 mg of spectroscopic-grade KBr pellets was made by pressing at 10 tons. Thermogravimetric and differential thermogravimetric analyses (TGA-DTG) were carried out in the alumina crucibles using a Metter-Toledo instrument model TGA851e (Greifensee, Switzerland) at a heating rate of 10^o per minute in the range of 25-1200ºC with the sample amount around 5-10 mg in nitrogen atmosphere. The surface morphology of the samples was observed by field emission scanning electron microscope (FESEM), FEI Nova Nanosem 230 with an acceleration voltage of 25 kV. Prior to analysis, the samples were mounted on aluminium stub over double-coated carbon film and were gold coated.

RESULTS AND DISCUSSIONS

X-ray Diffraction Analysis

Figure 1 shows the PXRD pattern of ZLH and ZCINN nanocomposites prepared via ion exchange method with fixed mass of 1.0 g and various concentration of CINN (0.01 M to 0.08 M). Based on all of the PXRD patterns, it can be observed that there is an intercalation occurred when 0.08 M of CINN was used. Previous studies of ZLH intercalated with nitrate ions show sharp diffraction peak with basal spacing of 9.6-9.9˚A recorded around $2\theta = 9.3$ [15, 16]. The basal spacing of ZCINN is shifted to lower 2θ, indicating successful intercalation of CINN into the interlayer of ZLH. The peak at low 2θ angle reflection is due to the dissociation-deposition mechanism [2]. Expansion of the basal spacing was recorded at the lowest 2θ of 21.2 Å. ZLH phase appears in the PXRD diffraction which is due to incomplete reaction [3]. Based on PXRD results, ZCINN prepared using 1.0 g with 0.08 M and CINN was chosen for further characterisations.

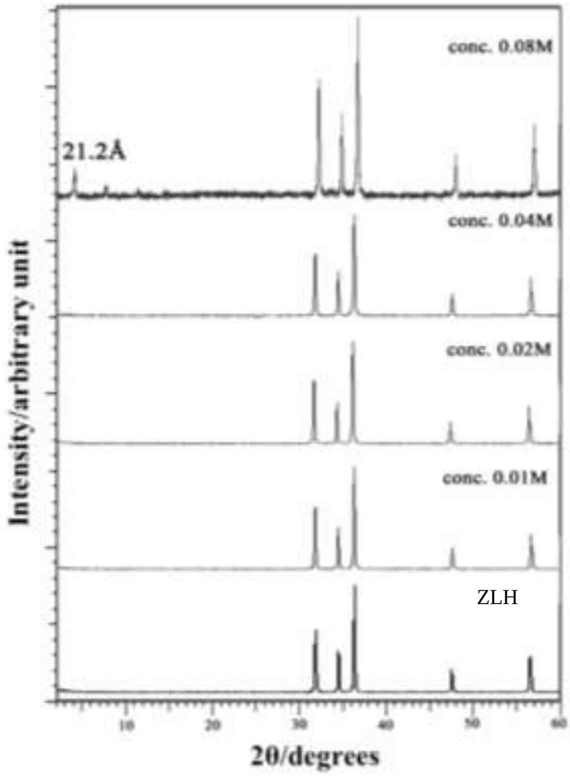

Figure 1 PXRD pattern of ZLH-cinnamaldehyde nanocomposites synthesised at different concentration of CINN (0.01-0.08 M) with fixed mass of ZLH (1.0 g)

Fourier Transform Infrared Spectroscopy

Figure 2 shows the FTIR spectra of ZLH host material, CINN guest anion and ZCINN nanocomposite. FTIR of pure ZLH host material showed a strong peak at 361 cm^{-1} due to vibration of zinc and oxygen sublattices [17]. In FTIR spectrum of the guest anion, the CINN, the peak observed at 3336 cm^{-1} can be attributed to the C-H stretching, 1685 cm^{-1} to C=O stretching vibrations of carbonyl groups; aldehyde [6] and 1556 cm^{-1} to C=C stretching. Meanwhile, the R-H and R=C stretching band could be observed at 1122 cm^{-1}. Trans C-H-out-of-plane bend for CINN was detected at 971 cm^{-1}. C-H monosubstitution band for phenyl group could be detected at 748 cm^{-1} and 689 cm^{-1} [2]. This is due to C-H vibration of benzene ring in the CINN molecule [3]. On the other hand, the ZCINN exhibits most of the vibrations assigned for CINN molecule, although some of vibrations shifted due to the interaction of CINN with the host material interlayer. In particular, vibrations due to trans-C-H-out-plane bend are observed at 969 cm^{-1} and C-H monosubstitution band is observed at 743 cm^{-1} and 683 cm^{-1}. Band at 1449 cm^{-1} that appeared in the ZCINN was due to the stretching vibrations of the aromatic ring C=C [3]. A strong band detected at 1668 cm^{-1} is due to the highly overlapped C=C stretching of CINN molecule with the C=O stretching in the intercalated ZCINN compound. The only band in ZLH host material appeared in the ZCINN compound at 361 cm^{-1}.

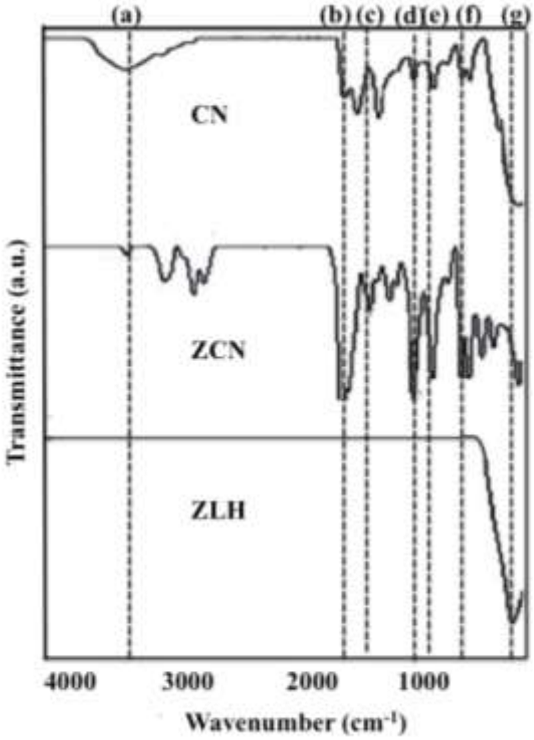

Figure 2 FTIR **spectra** of CINN, ZCINN intercalation compound and ZLH.
(a) = 3336-3343 cm^{-1}, (b) = 1668-1685 cm^{-1}, (c) = 1449-1556 cm^{-1}, (d) = 1117-1122 cm^{-1},
(e) = 969-971 cm^{-1}, (f) = 748-683 cm^{-1} and (g) = 361 cm^{-1}

The spectrum of ZCINN displays both characteristic bands of ZLH and CINN that some are overlapped and shifted from their initial positions as the result of multiple chemical interactions such as the electrostatic interactions between CINN anions and ZLH lattice [18] and as well as the hydrogen bonding effect between the water molecules and CINN anions. Thus, these results indicate that CINN anions are successfully intercalated between the positively charged ZLH layers as indicated by the characteristics of PXRD pattern.

Thermal Analysis

Figure 3 shows TGA-DTG profiles for pure CINN (a) and ZCINN (b). A single weight loss of 99.1 % was observed for CINN with maximum temperature at 218.2°C as compared to 350.2°C for ZCINN with weight loss 17.0 %. The decomposition temperature of CINN intercalated into the ZLH interlayer is higher as compared to CINN solely. This suggests that the thermal stability of CINN in the nanocomposites of ZCINN is enhanced due to the interaction between the anion itself and the ZLH host. The intercalation process leads to the formation of electrostatic reaction between the anion and the inorganic layers of ZLH [19].

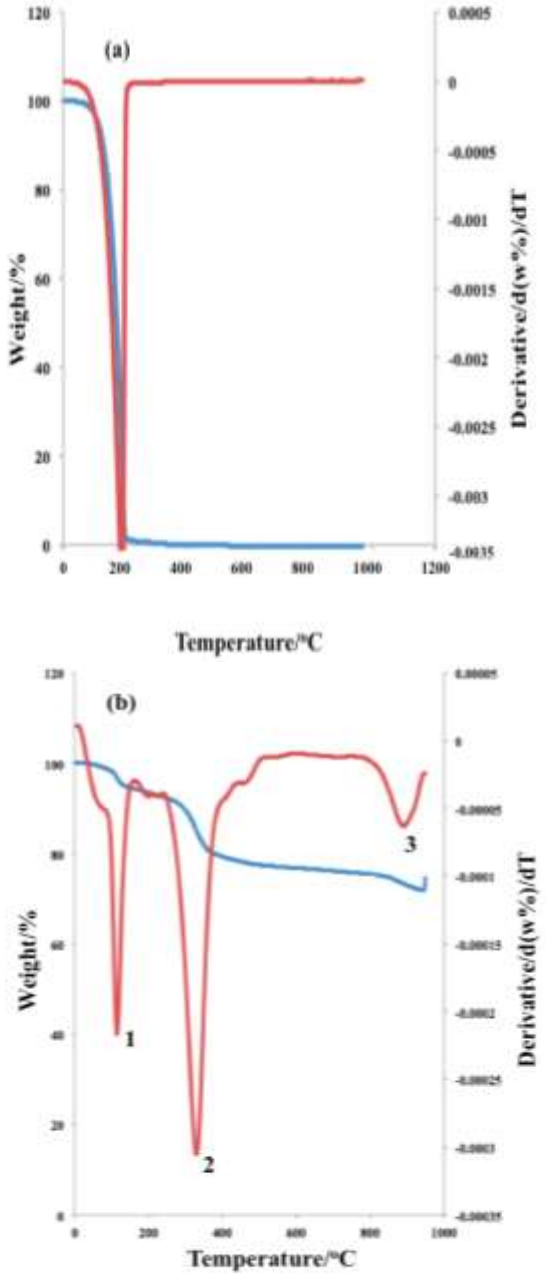

Figure 3 (a) TGA profile for CINN and (b) TGA profile for ZCINN

ZCINN follows the general route of ZLH intercalated with organic anions [1]. For ZCINN, three stages of weight loss were observed. Table 1 reports on the maximum temperature and weight loss of ZCINN. The first step occurs from the temperature up to 200 °C with respective to the weight loss of 5.7 % which is due to the removal of adsorbed and intercalated water [20]. At 207-564°C, the nanocomposites undergoes of 17.0 % weight loss. This is attributed to the dehydroxylation of the hydroxide layers as well as partial decomposition of the intercalated CINN anions. The final step records a 3.9 % weight loss with the major peak occurs around 930°C (temperature range 800-1144°C) which is characterised by combustion of the organic species, leaving only a relatively less volatile, metal oxide.

Table 1 Maximum temperature and weight loss of ZCINN from TGA-DTG profile

Peak/Step	Temperature range (ºC)	Maximum temperature (ºC)	Weight loss (%)
1	55-200	156.5	5.7
2	207-564	350.2	17.0
3	800-1144	930.0	3.9

Field Emission Scanning Electron Microscope (FESEM)

The surface morphologies of ZnO and ZCINN are shown in Figure 4 (a) and (b) respectively. As shown in this figure, all samples showed typical, non-uniform and irregular sizes of layered hydroxides structures. ZnO particles can be observed (Figure 4 (a)) to have granular structure with various shapes, sizes and stacked on top of each other. In comparison to ZnO, Figure 4 (b) of ZCINN micrographs showed more flaky, dense and compact structure. Besides that, ZCINN also exhibits plate-like particles and displays larger size of particles. Similar image observations had been reported between hippuric acid nanohybrid (HAN) and valarate nanohybrid (VAN) with the ZLH host material [21, 22].

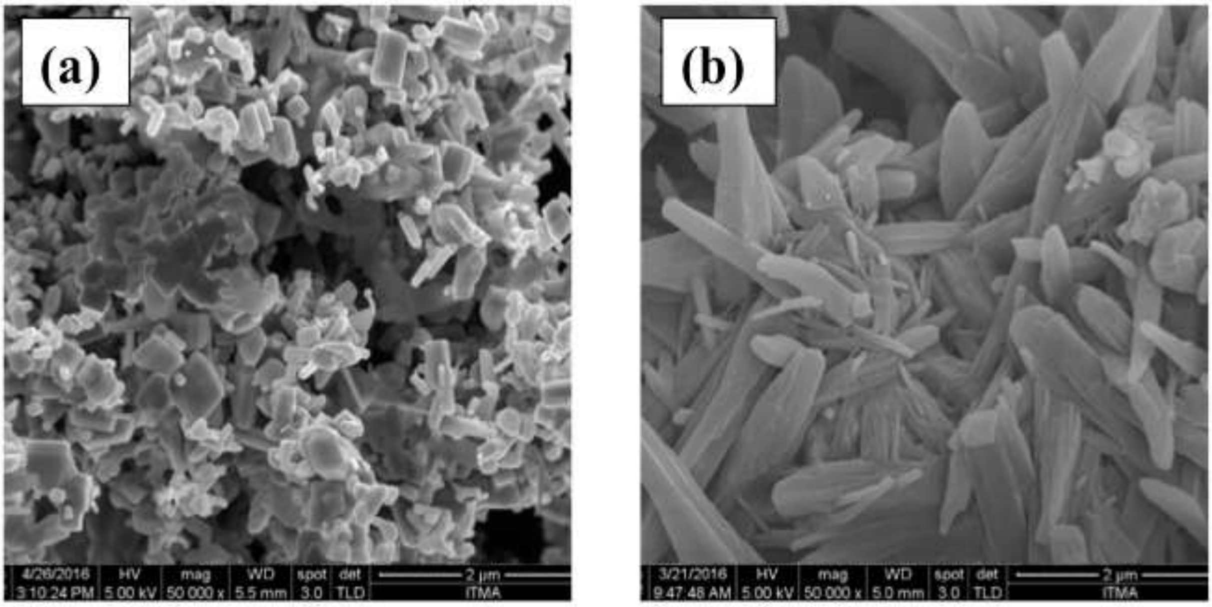

Figure 4 Field emission scanning electron micrographs of (a) ZnO and (b) ZCINN nanocomposites at 50,000x magnification

CONCLUSIONS

New nanocomposites compound, ZCINN has been successfully synthesised via ion exchange method at 1.0 g of ZnO with 0.08 M of CINN. PXRD analysis showed an expansion in basal spacing of 21.2 Å. FTIR results further confirmed the CINN intercalation into the ZLH interlayer due to the existence of all functional groups of CINN and ZnO in ZCINN spectrum. TGA-DTG profiles of ZCINN showed that the thermal stability of CINN in the form of nanocomposites, ZCINN is enhanced. FESEM image of ZCINN showed difference in structure as compared to ZnO image. It is hoped that this work will mark on the new research which will lead to controlled release formulations (CRF) study on mosquito control and larvicides.

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