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Preparation of Zinc Layered Hydroxide 2,4-dichlorophenoxyacetate (2,4-D) Nanocomposite

Penyediaan Nano Komposit Zink Hidrosida Berlapis 2,4-dichlorophenoxyacetate (2,4-D)

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Abstract

Recently, layered materials have gained great attention because they can be designed at the nanometer levels. Due to its advantages such as low cost material, easy to synthesize and excellent anion exchange properties, these material exhibit unlimited potential in catalysis, separation technology, medical science, nanocomposite material engineering, agriculture and etc. In this study, Zinc Layered Hydroxide (ZLH) has been intercalated with 2,4-Dichlorophenoxyacetic acid (2,4-D) anion by using ion exchange method. These nanocomposites were synthesized at a different mass of ZLH which are 1 g, 2 g and 3 g also with different concentration of guest anions (2,4-D) which are 0.01 M, 0.02 M, 0.04 M, 0.08 M, 0.16 M and 0.32 M. Powder X-ray Diffraction (PXRD) patterns showed an expansion of interlayer spacing with the value ranging from 26.8 Å to 39.6 Å, 29.4 Å to 37.3 Å, 28.7 Å to 31.6 Å for 1 g, 2 g and 3 g of ZLH at various concentration of 2,4-D respectively. This expansion of basal spacing implies that 2,4-D anion which is bigger size than the prior ZLH was successfully intercalated into the ZLHs. FTIR analysis further confirmed that 2,4-D were successfully intercalated between the interlayers of ZLH with evidence of functional groups of ZLH and 2,4-D in the ZLH-2,4-D nanocomposite (ZN) spectra.

Keywords Zinc Layered Hydroxide, 2,4-Dichlorophenoxyacetic acid (2,4-D), ion exchange, intercalation, nanocomposite

Abstrak

Pada masa kini, bahan berlapis telah mendapat perhatian kerana ia boleh direka bentuk pada skala nano. Kerana kelebihannya seperti murah, mudah disintesis dan sifat pertukaran anion yang baik, maka bahan-bahan ini menunjukkan potensi yang tinggi untuk digunakan bidang katalis, teknologi penapis, sains perubatan, bahan kejuruteraan nano komposit, pertanian dan berbagai kegunaan lagi. Dalam kajian ini, Zink Hidrosida Berlapis (ZLH) telah di sisipkan dengan anion asid 2,4-Dichlorophenoxyacetic (2,4-D) secara kaedah pertukaran ion. Komposit nano ini telah disistesis dengan berlainan jisim ZLH iaitu 1 g, 2 g dan 3 g serta masing-masing dengan berbagai kepekatan anion tumpangan (2,4-D) iaitu 0.01 M, 0.02 M, 0.04 M, 0.08 M, 0.16 M dan 0.32 M. Corak Pembelauan Sinar-X (PXRD) menunjukkan jarak antara lapisan mengembang dari 26.8 Å kepada 39.6 Å, 29.4 Å kepada

37.3 Å dan 28.7 Å kepada 31.6 Å masing-masing bagi 1 g, 2 g dan 3 g ZLH dengan berbagai kepekatan 2,4-D. Pengembangan jarak di antara lapisan ini menunjukkan bahawa anion 2,4-D adalah bersaiz lebih besar daripada saiz ZLH yang berjaya disisip ke dalam lapisan-lapisan ZLH. Analisis FTIR mengesahkan bahawa 2,4-D telah berjaya disisipkan di antara lapisan ZLH dengan bukti terdapatnya kumpulan berfungsi ZLH dan 2,4-D dalam spektrum FTIR komposit nano (ZN)

Kata kunci Lapisan Zink Hidroksida, asid 2,4-Dichlorophenoxyacetic (2,4-D), pertukaran ion, sisipan, komposit nano

INTRODUCTION

Layered single hydroxide salt (LSH) such as zinc layered hydroxide (ZLH) is a layered inorganic compound which has gained attention in wide range of applications, particularly due to its unique anion exchange properties (Abdul Latip *et al*., 2013). Recent studies reported that ZLH has high capacity to accommodate guest molecules and stronger host-guest interaction which leads to high stability; which makes it possible to be used as new host material and delivery system with controlled release rate of active agents (Kasai *et al*., 2006; Yang *et al*., 2007). ZLH structure is high potential host material in forming nanocomposites because it can expand or contract depending on nature of interlayer anions (Mohsin *et al*., 2013). Due to that, the ZLH particularly have been studied extensively and intercalated with various organic anions (Liang *et al*., 2004) mainly via ion exchange process, ranging from anionic dyes (Marangoni R *et al*., 2009), porphyrin sensitizers (Demel J *et al*., 2010) and an anti-corrosive compound (Rocca E *et al*., 2006).

Researches have proven this LSH is currently gaining attention due to its simple method of synthesis, as a precursor for a wide band gap of ZnO and its anion exchange properties (Thomas N *et al*., 2011). LSH also has demonstrated the ability to extend the release period of drug molecules and bioactive molecules (Hussein, M., *et al*., 2010) that prompting more investigations towards potential applications of LSH in drug delivery systems. LSH are thought to be ideal candidates for agricultural applications (Choy *et al.,* 2007). Others active agents such as drugs, vitamins and dyes need to be released in controlled manner to reduce their toxicity or other side effects to increase its durability and stability (Hwang *et al*., 2001).

Recently, the study on the intercalation of phenoxy herbicides into the interlayer of LDH (Layered Double Hydroxide) using various synthesis methods been reported. 2,4-D is highly selective herbicide which is toxic to broad leaved plants but less harmful to grasses. This chemical has complex mechanism of action against weeds, resembling those of auxins (growth hormones). Once adsorbed 2,4-D is translocate within the plant and accumulates at the growing points of roots and shoots where it inhibits growth (Kenneth, 1983). In this paper, we reported the preparation of Zinc Layered Hydroxide 2,4-Dichlorophenoxyacetate (2,4-D) nanocomposite.

MATERIALS AND METHODS

Synthesis of materials

The chemicals used in the synthesis were of analytical grade, obtained from various chemical suppliers and were used without any further purification. The chemicals are

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2,4-dichlorophenoxyacetic acid > 98% from Merck and Zinc Oxide > 99% from Acros Organics. All of the solutions were prepared using deionised water. The synthesis of ZN 1 was prepared by ion exchange method. 1 g Zinc Oxide, ZnO (which then referred as ZLH material) in 100 ml of water was mixed with 2,4-D solution at chosen concentrations (ranging from 0.01 M to 0.32 M). The solution mixture was stirred for 2 hours with magnetic stirring and was conducted under atmospheric conditions. Once stirring was completed, the precipitate was aged at 70 °C for 18 hours in an oil bath shaker, cooled, thoroughly washed and dried overnight in an electric oven at 70 °C. Finally, the dried sample was ground into fine powder by using mortar and pestle, then kept in bottle sample for further used and characterizations. Similar procedure was repeated for ZN 2 and ZN 3 with 2 g and 3 g of ZnO respectively.

Characterisation of material

Powder X-ray diffraction (PXRD) patterns of the samples were recorded between 2^o and 60^o on a Shimadzu 6000 model analytical powder diffractometer using Cu Kα radiation at 30 kV and 30 mA at the rate of 4^o min^{-1}. FTIR spectra of the materials were recorded over the range 400 - 4000 cm^{-1} on a Perkin-Elmer 1752X Spectrophotometer using KBr disc method.

RESULTS AND DISCUSSION

Powder X-ray Diffraction Analysis

Figure 1 show PXRD patterns of ZN 1 synthesised at different concentration of 2,4-D with 1 g of ZLH. The basal spacing showed increasing in the expansion from 26.75 Å to 31.75 Å, 33.08 Å, 35.57 Å, 37.10 Å, and 39.58 Å with the increasing concentration. Figure 2 also shows the same trends. ZN 2 gives the harmonic increasing in the expansion of basal spacing ranging from 29.43 Å to 37.25 Å. PXRD patterns of these two prepared samples display a high intensity diffraction peak indicating a pure phase material without any ZnO phase. This shows that a well-ordered nano-layered structure with good crystallinity was obtained at this optimum condition. The increase of the basal spacing is associated with the spatial orientation and revealed that the size of 2,4-D is bigger than nitrate in the interlayer region (Kuh and Huh, 1998). Meanwhile, in Figure 3, the poor trends detected with 3 g of ZLH. It shows the disorder expansion of basal spacing of 30.87 Å, 28.66 Å, 29.53 Å, 30.23 Å, 31.75 Å, and 27.76 Å due to poor crystallinity obtained.

According to all values of basal spacing, it is proven that 2,4-D was intercalated into ZLH interlayers. In Figure 4, comparison study on various masses of ZLH used in nanocomposite at 0.01 M of 2,4-D. It shows the increases of the basal spacing expansion is proportional with the increases mass of ZLH. The obtained basal spacing value is higher than those reported for the intercalation of other type of herbicides into the LDH interlayers (Cardoso *et al*., 2006; Sarijo *et al*., 2010). ZLH reportedly has larger interspacing than LDH to accommodate a greater number of incoming guest anions of varying sizes, due to its higher charge density (Kasai *et al*., 2006; Hwang *et al*., 2001; KoreYang *et al.,* 2007). Thus it is possible to simultaneously intercalate 2,4-D anions into the ZLH interlayers.

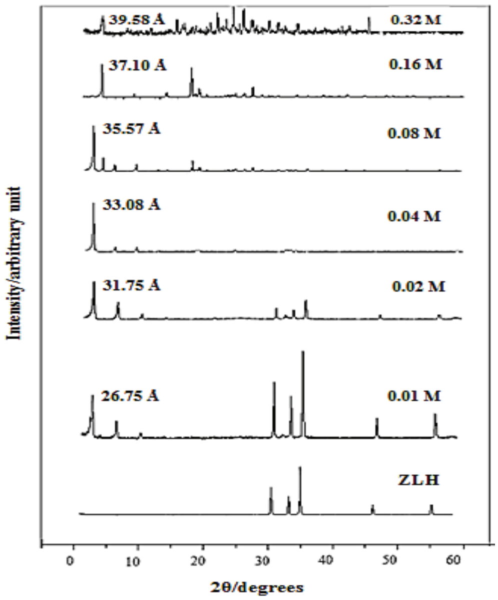

Figure 1 PXRD pattern for ZN 1

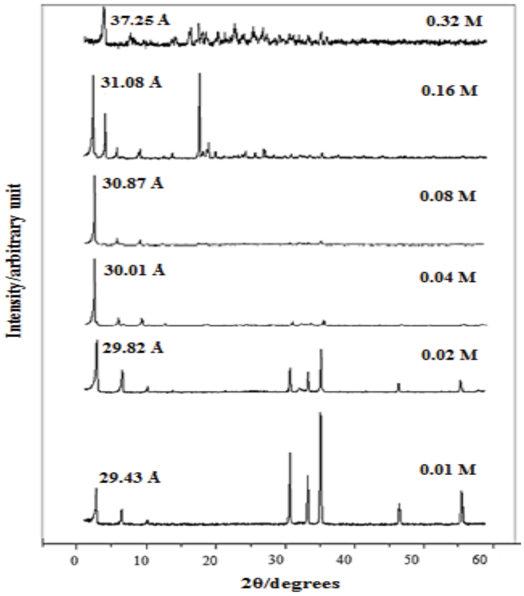

Figure 2 PXRD pattern for ZN 2

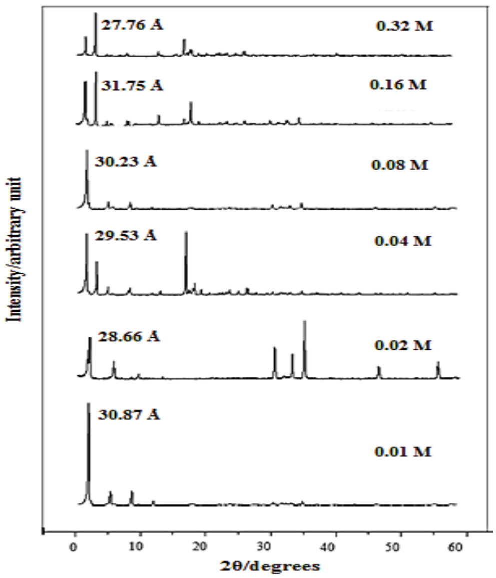

Figure 3 PXRD pattern for ZN 3

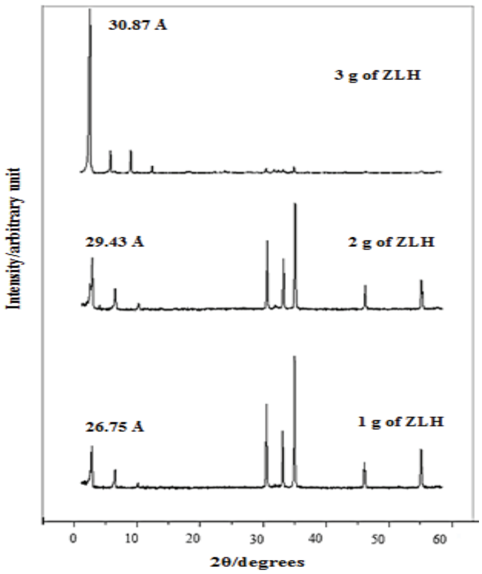

Figure 4 PXRD pattern for ZN 1, 2, 3 at constant 0.01 M of 2,4-D concentration

Fourier Transform Infrared Spectroscopy

Figure 5 shows the FTIR spectra of ZLH, pure 2,4-D and ZLHs. The insertion of 2,4-D into the interlayer ZLH was confirmed by the FTIR spectrum, which is complementary to that of PXRD results. All of the nanocomposites display similar absorption bands as the parent material, ZLH and guest ion, 2,4-D anion that are intercalated into the host interlayer galleries. The presence of 2,4-D anion are shown in the typical broad absorption bands of 2,4-D at 3078 cm^{-1} and 2969 cm^{-1}, corresponding to the O-H stretching vibration of the COOH, while a strong band at 1717 cm^{-1} corresponds to the stretching of C=O. The bands at 1471 cm^{-1} corresponds to the stretching that are attributed to C=C vibrations of the aromatic ring of phenoxy. Absorption band is observed at about 1230 cm^{-1} of FTIR spectra due to C-O-C symmetric stretching modes.

FTIR spectra of ZN 1, ZN 2 and ZN 3 at a constant 0.01 M concentration are observed. The same typical broad absorption bands were observed at 3388 cm^{-1} for ZN 2 and ZN 3, while ZN 1 showed broad absorption bands at 3542 cm^{-1}, 3437 cm^{-1}, and 3263 cm^{-1}. These absorption bands are corresponding to the vibrations of the hydroxyl groups at surface, interlayer water molecules and the water bending mode (Lakraimi *et al.,* 2000; Palmer *et al.,* 2009). Meanwhile, the bands observed at 1595 cm^{-1} for ZN 1, 1599 cm^{-1} for ZN 2, and 1604 cm^{-1} for ZN 3, corresponds to the stretching vibration of aromatic ring C=C. The disappearance of bands in the nanocomposites spectrum at 1717 cm^{-1} and 1230 cm^{-1} indicated C=O stretching vibration of the protonated carboxylic groups of the herbicides respectively (Cardoso *et al*., 2006), shows that anions in host material were completely exchanged with 2,4-D anions for the formation of the ZN.

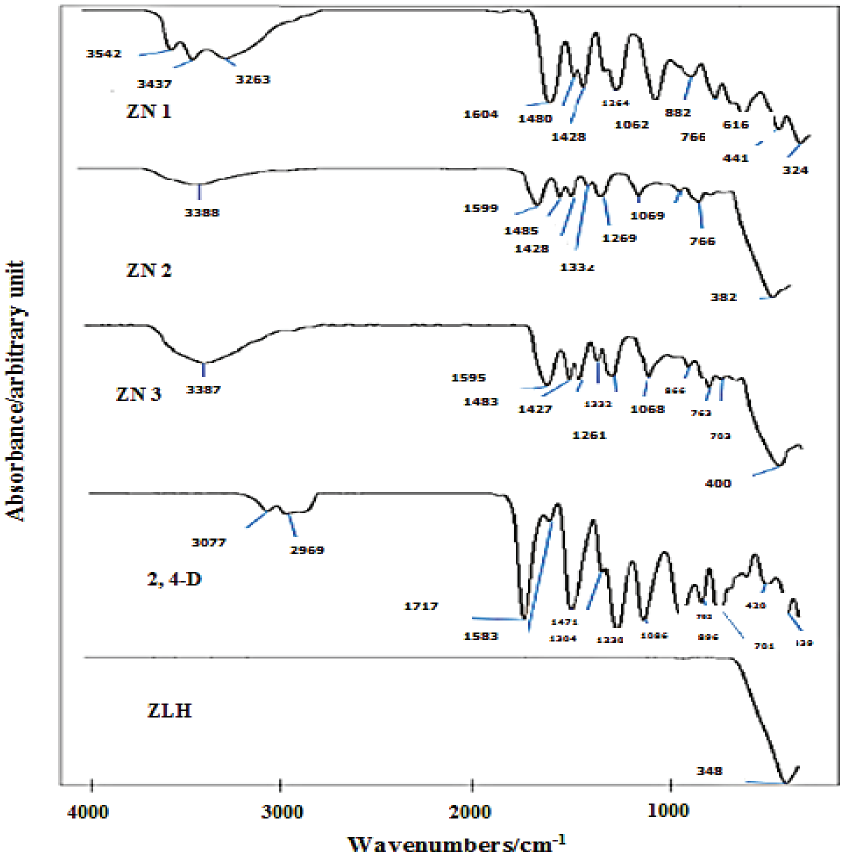

Figure 5 FTIR spectra for ZN 1, ZN 2 and ZN 3 at constant 0.01 M of 2,4-D concentration

CONCLUSION

A series of ZLH-2,4-D (ZN) nanocomposites prepared at different masses of ZLH (1 g to 3 g) and various concentration of 2,4-D (0.01M to 0.32M) have been successfully done via ion-exchange method. This study suggests that the layered hydroxide can be used as a carrier for the 2,4-dichlorophenoxyacetic acid (2,4-D) for further used as herbicide.

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