Synthesis, characterization and alteration of phenoxyherbicides-based nanocomposites resulted from mixing two herbicides with Zinc Oxide-layered hydroxide

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Abstract

The present study is a part of an investigation of the effect of ZnO supported for two mixed agent (4-chlorophenoxy acetate (4CPA) as plant growth regulator and 2,4-dichlorophenoxyacetates (2,4D) as herbicide) synthesis via the ionic exchange with zinc Oxide layered hydroxide(LH). The product of this process led to the formation of nanocomposites assigned as (Zinc-NCPA). This byproduct represented a mixture of two newly phases was confirmed by X-Ray Diffraction (XRD) which were visualized at 25.6 and 19.14 Å, respectively. These findings were approved by images produced by Scanning Electron Microscopy (SEM). The maximum accumulated release of 4CPA and 2,4D was found to depend on the concentrations of the incoming ions. The accumulated rate of 4CPA was found to be less than 24D. The release behavior of the phenoxy acetate into the aqueous solution was controlled mainly by pseudo-second-order which was followed by pseudo-first order rate expression. This study concluded that Zinc Oxide layered hydroxide (ZLH) have the capability to act as a carrier for mixed active agents of two compounds with two different roles.

Keywords: Controlled release, chlorophenoxy acetates, Zinc Oxide layered hydroxide, organic-inorganic hybrid nanocomposites

1.0. Introduction

Zinc Oxide Layered hydroxide (ZLH) is a 2D material which is similar to the layered double hydroxide (LDH) which has two metals. Replacement of hydroxyl groups by other ions make them exchangeable but only one metal is involved [1-4]. Structure of zinc-hydroxide salts is considered simple hydroxides. This criteria is related to the small distance between the layers which allows molecules with small dimensions to have access to the interlayer space [5, 6]. Alteration of the hypothetical structure of zinc hydroxide may be enhanced by the ion exchange property. This is one of the important properties of ZLHs, which has been used for the formation of their nanocomposite derived products [7].

The organic guest anion intercalated into the ZLHs can be released by in vitro of the ion exchange property which depends on the synthesis methods, [8]. This is useful in designing a controlled release formulation with a specific target property and effect of polymer on Zinc layered [9]. Other studies have shown that preparation of various controlled release formulations using LDH with a specific target property was applicable in plant growth regulators [10-12], biological materials [13], pharmaceutical products [14-16] DNA and ATP storage with layered double hydroxide due to higher stability of the biological materials in the interspaces of LDH. Agrochemicals have been applied in “non-organic” farming practices of modern agriculture with a typical example is ZLH that has been used in friendly environment. Chlorophenoxyacetic acids are agrochemicals in a family of herbicides, which include 2,4-dichlorophenoxyacetic acid (24D) and 4-chlorophenoxy acetic acid (4CPA). The chemical structure of 4CPA and 24D is very similar, but with slightly different functional group/s, in which two chlorine atoms attached to the position 2 and 4 of the benzene ring, while in 4CPA one chlorine atom is attached at position 4 of the benzene ring. This study was undertaken as a continuation to our previous studies (1-4). The main objectives were to determine the physicochemical properties and the controlled release mechanism of well-ordered nanocomposites phases of phenoxyherbicides family interacting with ZHLs.

2.0 Materials and Methods

A mixture of 2,4-dichlorophenoxy acetic acid, (24D) and 4-chlorophenoxy acetic acid (4CPA) purchased from (Merck,Germany). They were prepared for final concentrations 0.05 M for CPA and 0.1M for 24D. Basically these compounds were dissolved in 50 ml of 90% ethanol and 0.5 gm of Zinc oxide (ZnO) obtained from (ACrose, USA ) was added to this mixture. This process was carried out using N\textsubscript{2} gas with magnetic stirring for
two hours followed by incubation into a water bath at 70°C for 18 hours. After cooling at room temperature, the mixture was centrifuged and washed four times with deionized water, dried in oven at 70°C, grinding and used for further analysis.

3.0 Characterizations
X-Ray patterns were obtained using Shimadzu XRD-6000 powder diffractometer (λ=1.540562 Å) at 40 kW and 30 mA, scan rate = 0.5 degrees/min. Fourier transform infrared (FTIR) spectra were recorded by using spectrophotometer thermo Nicolet Ft-IR Nexus self supporting sample in the range of 4000-400 cm⁻¹, the TG/DTG were carried out using a Setaram TG-DSC-11. The surface morphology and bulk structure of the samples were visually observed by scanning electron microscope (SEM) model JOEL (JSM-6400).and transmission electron microscope (TEM) (Hitachi H-7100). The specific surface area of the solids was determined by a Micromeritics surface area and pore size analyzer (ASAP2000) using nitrogen gas adsorption-desorption technique at 77 K together with the BET equation.

3.1 Results and Discussion
3.1.1 X-Ray Diffractions
The results showed that two distinguished phases were produced with well ordered layered structure of organic-inorganic nanohybrid of phenoxyherbicides. The latter was hybridized with the zinc oxide layered. The analyses results of PXRD patterns are shown in Fig. [1]. Diffraction results of the two phases for the planes (003), (006), (009) and (0012) of the first phase appeared at 25.6, 12.9, 6.5 and 3.22 Å respectively. This phase contributed to the existence of 24D anion. Our results are in agreement with previous study conducted on 24D. The second phase of (003), (006), (009) and (0012) appeared at 19.14, 9.7, 4.7 and 3.2 Å respectively. This phase can be attributed to the existence of 4CPA in the interlamellae. Results from previous study are in support to our finding in here [1]. It is commonly known that the presence of two phases is thermodynamically more stable than single phase of each anions separately. The analysis patterns of zinc-layered hydroxide (ZLH) showed the absence of diffractions within the ranges of 3 to 30 (2θ/ degree) as in Fig.(2). This indicates the intercalation of mixed anions 24D and 4CPA which formed ZCDN nanocomposites. It is well known that layers expansion can be attributed to spatial orientation of these guest anions located into the interlamellae space of the ZLH according to their sizes. These newly hybrids are bigger than the original hosts represented by nitrate and/or H₂O molecules. They are replaced by the counter anions 24D and 4CPA which led to synthesis of ZCDN.

![Fig.[1]. The diffraction patterns of zinc-layered hydroxide (ZLH) intercalated with mixed ions (24D and 4CPA) showing the 003, 006, 009 for two phases.](image-url)
3.1.2 SEM and TEM techniques.

The previous two phases were distinguished on the SEM images. On these images, EDX was arranged at three different positions, reflecting the identical main components of the resulted two different phases table ( ) and Fig [2a]. SEM image, in Fig [2b] showed a bulb-like structures of the intercalated anions distributed on the layered surface of ZnO. Fig[2b,c] shows the TEM image of ZCDN hybrid nanostructures. Numerous organic nano crystals of (24D and 4CPA) are homogenously deposited on the ZnO crystal surfaces.
Fig. 2 a, SEM image of ZLH intercalated with 24D and 4CPA present a (bulb structure).

[3] TEM image of ZCDN is showing b- nanorods like structure and c- nanocrystals have an average size between 23-33nm.

3.1.2 Infrared Study

The FTIR spectrum of ZCDN, ZHL as in Fig.[4] shows the characteristic absorption bands of zinc-layer hydroxide particularly abroad band at 3430 cm$^{-1}$. This can be attributed to the interlayer water molecules as reported in [16,17,18]. The peak at 1378 cm$^{-1}$ assigned to three vibration modes of (NO$_3^-$) with $D_3h$ symmetry. A weak peak at 828 cm$^{-1}$ was shown in this figure reflecting the two modes of the same anion. The presence of the band at 1640 cm$^{-1}$ is due to H–O–H stretching vibration. The weak peak at 1018 cm$^{-1}$ reflected the mode nitrate group. Two bands at 470 and 410 cm$^{-1}$ could be attributed to the Zn–OH and Zn–O lattice vibrations, respectively [19].

The ZCDN spectrum pattern is dominated by a broad absorption band at 3474 cm$^{-1}$. This can be resulted from the vibrations of interlayer water molecules. A shoulder near 3347 cm$^{-1}$ was observed which can be resulted because of the hydrogen bonding stretching vibrations. The peak 1608 cm$^{-1}$ can be assigned to the stretching of νH–O–H. The two peaks 642 cm$^{-1}$ and 470 cm$^{-1}$ represent the M–OH vibrations which caused stretching and bending respectively.

Existing of the phenoxyacetates intercalated with zinc-layer was confirmed by the infra red spectra [Fig. 4]. The presence of the two mixed herbicides anions in the sample was evident by the C–H vibrations band at 2941 and 1493 cm$^{-1}$. Band representing the C=C vibrations of the aromatic ring was showed at 1435 cm$^{-1}$. Other bands at 1100, 1058 and 1010 cm$^{-1}$ were formed due to the symmetric vibration of C–O–C. Strong bands corresponding to the carboxylate νC=O group produced at 1608 cm$^{-1}$ and νC–O at 1659 cm$^{-1}$ for 4CPA. Similar bands were observed at 1744 and 1234 cm$^{-1}$ for 24D which is in consistance with other reported study [21].

The absence of the absorption band at 1384 cm$^{-1}$ on the spectrum of ZCDN was related to the replacement of nitrate ion by the phenoxyacetate ions in the resulted ZCDN. This showed that all phenoxyacetates have higher
affinity than nitrate towards the inorganic interlamellae. This finding was supported by the CHNS result due to the absence of nitrogen in the nanocomposites.

Fig. [3] Spectrum of FTIR is showing the characteristic absorption bands of zinc-layer hydroxide (ZnO) and ZCDN nanocomposite.

3.1.3. Thermal properties

Fig. [5] shows DTA-DTG thermograms of ZLH and its nanocomposites ZCDN synthesized in this work. The thermograms of the guest molecule, phenoxyherbicides are also indicated in the comparison with the pure zinc oxide. Results of the analyses are given in table [1]. Nanocomposites ZCDN shows higher thermal stability than the zinc oxide. This is seems to be due to the newly electrostatic forces formed between the anion and the zinc-layers as a result of the intercalation of the anions into the interlamellae [23]. The hydrogen bonding formed between H₂O and Cl attached to the benzene ring may also contributes to the thermal stability of the synthesized nanomaterial.
Fig. 5 TGA/DTG thermograms for ZLH (top) and ZCDN is showing the different losses in relation to temperatures.

In the ZCDN there are four major weight losses at maximum temperatures of 98, 144, 293 and 901 °C with weight loss of 5.3, 3, 46.2 and 2% respectively. The first two weight losses processes were due to the loss of water physisorbed on the external surface of the zinc-layered and on the anion while the third weight loss was due to the decomposition of 4CPA and 24D intercalated into the interlamellae. The state of weight loss at 901 °C was apparently due to the removal of remaining traces of organic materials.
3.1.4. Surface properties

The results from isotherm of adsorption-desorptions of N\textsubscript{2} gas at 77 °K and the JBH method for pores distribution are shown in Fig 6a. Effects of surface property of the resulting nanocomposites upon successful intercalation of 4CPA and 24D with the ZnO resulted a well-ordered ZCDN nanolayered structure as they are shown in Fig. 5a. The BET surface area of ZCDN synthesized in this work is 2.27 m\textsuperscript{2}g\textsuperscript{-1}.

The adsorption-desorption isotherms for the ZCDN nanocomposites are of type IV as in Fig. 6a. This is in agreement with other reported study[24]. Occurrence of this isotherm is associated with a slow uptake of gas followed by a sharp increase closer to the saturated relative pressure > 0.9. The isotherms have similar characteristics indicating the mesoporous nature of the resulting ZCDN nanocomposites.

The BJH desorption pore size distribution for ZCDN nanocomposites is shown in Fig. 6b. The summaries of pore volume and pore diameter are given in Table 1. Two-peaked pores sizes distribution was centered at around 10 and 20 nm, respectively.

![Fig.6a isotherm of gas adsorption on the surfaces of the resulted nanocomposite ZCDN](image)

![Fig.6b show the microspores distributions(top) and adsorptions desorption’s isotherm(down)](image)
3.1.5. Controlled release of phenoxyherbicides into aqueous solutions

3.1.5.1 Kinetic Study

The simultaneous release of 4CPA and 24D in sodium phosphate media of (0.005 M) are shown in Table 1. The kinetics of the release process studied by UV-Vis at a fixed lambda max for each anion using Pierre Lambert law to calculate the accumulated concentration. Our results showed similar behavior to previous studies reported on release of the organic moieties which were evaluated using various models such as zero order [18], first order [19], Bashkar et al [20] and Pseudo second order equation [21].

The released amount (qt) with time (t) was plotted at constant temperature. Usually, the release process can be described better with pseudo-second-order kinetic model as shown in Fig. 7.

The correlation coefficient ($r^2$) values obtained from straight lines are listed in Table 1. The $r^2$ values of the released data fitting with pseudo-second order model at 0.99-1 while those with pseudo-first-order are within a range of 0.90-0.94. The application of parabolic diffusion using Bashker equation produced non-linear results which are not consistent with our finding. The accumulated release of 24D and 4CPA were 98 and 75 respectively. This may suggests that the release of both active agents (4CPA and 24D) from the host (Zinc-LH) followed a pseudo second order reaction model.

![Graphs showing release kinetics](image)

**Fig. 7** shows the adapting of different models of kinetic study to determine the controlled release.
Table 1. Summary of micro analysis, thermal properties and kinetic studies.

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Thermal analysis

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Kinetic study

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3.1 Conclusions

Phenoxyherbicides-intercalated with ZnO led to the formation of organic-inorganic hybrid ZCDN nanocomposite materials. The controlled release formulations of the anions as two guests resulted from the interlamellae of the host was found to be sacrificial ion-dependent. The release of 4CPA and 24D is best described by pseudo-second-order rate expression. In addition, the release profile of the two an ions could be different from each other. The findings in this study suggest that Zinc Oxide layered hydroxide (ZLH) can be used as a carrier for mixed active agents of phenoxyherbicides. Also the chemical structure of the intercalated moiety can be used to tune the desired release profile of the beneficial agent.

Acknowledgement

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Reference


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