INFLUENCE OF 2,4-D CONCENTRATION IN THE 2,4-D/LDH HYBRID NANOCOMPOSITE SYNTHESIS USED AS CONTROLLED RELEASE FORMULATION

Julia Ismerio Cardoso
Universidade do Estado do Rio de Janeiro, Instituto Politécnico (UERJ-IPRJ)

João Luiz Martins Mattoso Câmara
Universidade do Estado do Rio de Janeiro, Instituto Politécnico (UERJ-IPRJ)

Bruno Muniz e Souza
Universidade do Estado do Rio de Janeiro, Instituto Politécnico (UERJ-IPRJ)

Sabrina Guimarães Sanches
Universidade do Estado do Rio de Janeiro, Instituto Politécnico (UERJ-IPRJ)

Marcio Felipe de Oliveira
Universidade do Estado do Rio de Janeiro, Instituto de Química (UERJ - IQ)

Aderval Severino Luna
Universidade do Estado do Rio de Janeiro, Instituto de Química (UERJ - IQ)

José Licarion Pinto Segundo Neto
Universidade do Estado do Rio de Janeiro, Instituto de Química (UERJ - IQ)

Raquel Pires Gonçalves
Centro Brasileiro de Pesquisas Físicas (CBPF)

Jhonny Oswaldo Huertas Flores
Universidade do Estado do Rio de Janeiro, Instituto Politécnico (UERJ-IPRJ)

ABSTRACT: The synthesis of the 2,4-D/LDH hybrid nanocomposite, a novel approach, was carried out using the direct coprecipitation method at three different concentrations of 2,4-D (0.10, 0.20, and 0.40 mol/L). The X-ray diffraction and infrared spectra analyses confirmed the successful incorporation 2,4-D into the ZnAl-LDH matrix at the chosen concentrations. The insertion of 2,4-D into the interlayer increased the basal spacing from 7.8 Å to values above 23 Å. The higher the herbicide concentration, the more 2,4-D was introduced, resulting in increased crystallinity and a higher herbicide release capacity at equilibrium. The release of 2,4-D was primarily governed by the ion exchange mechanism between carbonate ions in solution and interlayer 2,4-D, and the pseudo-second-order kinetic model best described the release profile.

KEYWORDS: 2,4-D, hybrid composites, coprecipitation method, influence of 2,4-D concentration, layered double hydroxides.

INTRODUCTION

Agrochemicals, or phytosanitary products, are substances used in agriculture to protect plants against pests, diseases, and weeds, aiming to increase crop productivity. These products include pesticides, herbicides, fungicides, and chemical fertilizers. Although they play an essential role in large-scale food production, agrochemicals also raise environmental and health concerns due to their potential negative impacts (Elfvendahl *et al.*, 2004; Relyea, 2005; Zhang *et al.*, 2018). For this reason, it is essential to adopt sustainable agricultural practices and adequate regulations to minimize the risks associated with agrochemicals, ensuring food safety and environmental protection. 2,4-dichlorophenoxyacetic acid (2,4-D) is Brazil's second most widely used herbicide, behind only glyphosate (Brovini *et al.*, 2021). It is also widely used worldwide in agriculture to control broadleaf weeds (Lozano *et al.*, 2018). However, its use has been limited due to its persistence in the environment. Due to its high water solubility, the herbicide is not easily absorbed by the soil, undergoes leaching, and causes pollution of surface and groundwater (Cox *et al.*, 2000). In addition, the half-life of 2,4-D in water can exceed 120 days under anaerobic conditions (World Health Organization, 2003). In other words, 2,4-D poses a threat of water contamination and is among the priority contaminants of most significant environmental concern (Hamilton *et al.*, 2003; World Health Organization, 2003).

Studies using Controlled Release Formulations (CRFs) have been carried out to minimize contamination from herbicides applied in liquid form, in which the herbicide is incorporated into the matrix of a crystalline structure forming a solid or nanocomposite before application, facilitating its handling and limiting its use in large quantities in planting areas (Barik, Sahu e Swain, 2008; Celis *et al.*, 2002; Li *et al.*, 2009; Maqueda *et al.*, 2008; Mukhopadhyay, 2014; Phuong *et al.*, 2017). Layered double hydroxides (LDH), which can be hydrotalcite-type materials, have a structure similar to brucite and can be found in nature or produced synthetically. One of their distinctive features is the ability to be synthesized with various cation compositions in the lamellar layer and anions in the interlayer. This versatility has led LDHs to be used in a wide range of applications, such as drug carriers, herbicide carriers, biosensors, and nanocomposites (Benício *et al.*, 2017; Berber e Hafez, 2018; Kuthati, Kankala e Lee, 2015). Several studies have used LDH as a host structure for herbicides such as 2,4,5-trichlorophenoxybutyric acid (TBA) and 3,4-dichlorophenoxy-acetic acid (3,4D) (Ghazali, Hussein e Sarijo, 2013), 4-chlorophenoxy acetate (CPA) (Bashi *et al.*, 2016), 2,4,5-Tricholorophenoxy butyric acid (T BA) (Sarijo *et al.*, 2015), 4-(2,4-dichlorophenoxy) butyrate (DPBA) and 2-(3-chlorophenoxy) propionate (CPPA) (Hussein *et al.*, 2012), 2-(2,4-dichlorophenoxy) propionic acid (Hussein *et al.*, 2011), 3,4-dichlorophenoxyacetate (3,4D) and 2-methyldichlorophenoxyacetate (MCPA) (Sarijo, Ghazali e Hussein, 2015), 4-(2,4-dichlorophenoxy)butyrate (DPBA) (Hussein, M. Z. Bin *et al.*, 2009), terbuthylazine (Bruna *et al.*, 2008) and 4-(2,4-dichlorophenoxy)butyric acid (DPBA) (Hashim *et al.*, 2007).

Layered double hydroxides (LDHs) have been emerging as suitable hosts for the herbicide 2,4-D because they have layered structures containing compensation anions in the interlayer space ideal for receiving 2,4-D molecules and forming a hybrid organic-inorganic nanocomposite structure (Bashi *et al.*, 2013; Kang e Park, 2022; Phuong *et al.*, 2017). 2,4-D/ LDH nanocomposites can be synthesized directly via coprecipitation. No studies report the influence of coprecipitation synthesis conditions that favor the formation of the 2,4-D-based nanocomposite. Hashim et al. (2014) (Hashim *et al.*, 2014) present an analysis of the impact of cloprop concentration using coprecipitation and direct reaction methods. Bashi et al. (2016) (Bashi *et al.*, 2016) conducted a study on the influence of 2,4-D concentration on the synthesis of nanohybrid via direct reaction of ZnO with 2,4-dichlorophenoxyacetic acid (2,4-D) solutions. Lakraimi et al. (2000) (Lakraimi *et al.*, 2000) also studied the influence of 2,4-D concentration on nanocomposite formation using the ion exchange method.

This study is part of a broader investigation to understand the influence of variables during synthesizing the 2,4-D/LDH hybrid nanocomposite using the direct coprecipitation method. Specifically, this work studied the impact of the concentration of 2,4-D during the synthesis of the nanohybrid on its physicochemical characteristics and release properties. Samples with different herbicide concentrations (0.10, 0.20, and 0.40 mol/L) were synthesized, keeping the pH, temperature, and aging time constant. The synthesis was carried out using Zn and Al chloride salts with a molar ratio of 4/1. The samples were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) techniques. The release properties were studied using a sodium carbonate solution.

METHODOLOGY

Synthesis of the samples

Hybrid nanocomposite samples were synthesized using the direct coprecipitation method using different concentrations of the herbicide 2,4-D. Solution I containing Cl_2Zn (1.2 mol/L) and Cl_3Al (0.2 mol/L) and Solution II containing NaOH (2.0 mol/L) were slowly and simultaneously added to 200 mL of Solution III containing the herbicide 2,4-D at 70 °C, maintaining the pH at 7 ± 0.5 and under intense stirring. Three concentrations of the 2,4-D herbicide solution (0.10, 0.20, and 0.40 mol/L) were used. After consumption of the reagents, the suspension formed was aged for four h at 70 °C. The solid formed was separated from the mother liquor by filtration and washed with approximately 600 mL of distilled water heated to 50 °C to eliminate soluble impurities. The samples were oven-dried for 24 h at 80 °C. The samples were labeled as 2,4-D/LDH-x, where 2,4-D is the herbicide, LDH is the layered double hydroxide, the host structure, and 'x' corresponds to the herbicide concentration during synthesis. 'x' assumes values of 0.10, 0.20, and 0.40, which correspond to the herbicide concentrations used in the synthesis. For comparative purposes, the LDH without herbicide was synthesized under the same conditions as the nanocomposite samples.

Characterization

The samples were characterized by X-ray diffraction (XRD) on a Panalytical Empyrean X-Ray Diffractometer with CuKα radiation (λ = 1.5406 Å) at 45 kV and 40 mA. Fourier transform infrared (FTIR-ATR) spectra were obtained in the 4000–400 cm^{-1} wavenumber region using an average of 60 scans with a resolution of 4 cm^{-1} on a Perkin Elmer Frontier instrument. The morphology of the samples was studied using a high-resolution scanning electron microscope (SEM-FEG) model JSM-7100F from JEOL. Transmission electron microscopy (TEM) imaging was performed to analyze the samples of nanocomposites. The samples were prepared by diluting the nanocomposites powder in water and sonicating it for 5 min. A drop of the supernatant was then deposited on a glow-discharged copper grid and air dried. Samples were investigated using TEM in a JEOL 2100F operated at an accelerating voltage of 200 kV and equipped with an energy-dispersive X-ray spectrometer, EDS. The samples elemental composition was determined using a Perkin Elmer Spectrophotometer model Optima 2000DV under standard conditions and a CHNS analyzer CHNS-932 (LECO).

Release studies in aqueous solution

The release of 2,4-D from the interlayer region of the nanocomposite was carried out according to the work of Hussein et al. (2009b) (Hussein, M. Z. *et al.*, 2009). 150 mg of the synthesized solid was added to 500 mL of an aqueous sodium carbonate solution (0.05 mol/L) under constant stirring at room temperature. The accumulated 2,4-D released in the solution was measured using a UV/VIS spectrophotometer model Cary 60 at lmax = 283 nm.

DISCUSSION AND RESULTS

The LDH sample synthesized without herbicide showed reflections characteristic of layered double hydroxides, Figure 1(a). The (003) peak indicates the basal reflection of an inorganic counter-anion in the interlayer, in this case, Cl⁻ ions, whose basal spacing was 7.8 Å (Table 1). The reflections found in the LDH were narrow, symmetrical, and intense, demonstrating the formation of a well-crystallized structure. The XRD patterns of the hybrid nanocomposites showed reflections characteristic of LDH shifted to smaller 2θ angles. These reflections were less intense, indicating a decrease in crystallinity. It was also found that with the increase in the concentration of 2,4-D, the intensity of the XRD reflections of the hybrid nanocomposites increased. As shown in Table 1, the hybrid nanocomposites presented an expansion of the basal d003 spacing from 7.8 Å in LDH to 23.6, 23.7 and 23.9 Å in 2,4-D/LDH-0.1, 2,4-D/LDH-0.2 and 2,4-D/LDH-0.4, respectively. This result demonstrates that the 2,4-D molecules were intercalated between the brucite layers of LDH, as identified in literature (Hussein, M. Z. *et al.*, 2009; Hussein *et al.*, 2005). From the results found in the values of the lattice parameter 'c', shown in Table 1, it is confirmed that the expansion shows a specific spatial orientation characteristic of the larger 2,4-D anions in the LDH interlayer (Bashi *et al.*, 2013; Phuong *et al.*, 2017). The observed increase in the basal spacing value with increasing 2,4-D concentration was due to the rise in interlayer

thickness, Table 1, which can be attributed to a specific arrangement of herbicide molecules in the LDH interlayer region. Weak reflections assigned to ZnO were observed in the 2q (in the range 30-35°) samples.

Sample	Zn/Al ratio	Basal distance d(003) (Å)	Lattice parameter (Å) c	Interlamellar distance (Å)
2,4-D/LDH-0.1	4.05	23.6	70.85	18.6
2,4-D/LDH-0.2	4.01	23.7	70.79	18.8
2,4-D/LDH-0.4	4.10	23.9	71.25	19.1
LDH	4.06	7.8	23.44	3.01

Table 1. Zn/Al molar ratio, basal spacing, and lattice parameters.

Figure 1(b) presents the infrared spectra of LDH and 2,4-D/LDH-x hybrid nanocomposites. The FTIR spectra of LDH reveal a broad band at 3440 cm^{-1}, attributed to the stretching vibrations of the O-H bond in water molecules or hydroxyl groups (OH$^-$) (Paiva *et al.*, 2008). The band at 1740 cm^{-1} can be attributed to the vibrations of the hydroxyl groups of water molecules in the interlayer. The band at 1627 cm^{-1} found in LDHs without herbicide corresponds to the deformation mode of interlayer water (δH2O) (Shabanian, Hajibeygi e Raeisi, 2020). The characteristic band near 1380 cm^{-1} corresponds to the interlayer water deformation mode, while the intense bands observed between 800 cm^{-1} and 400 cm^{-1} are related to the stretching vibrations of the metal-oxygen bond (Zn-O and Al-O) present in the LDH structure (Meng *et al.*, 2005; Shabanian, Hajibeygi e Raeisi, 2020). The distortion of Cl$^-$ in the interlayer of Zn-Al-Cl is reflected in the IR spectra at 1215 cm^{-1} and 650 cm^{-1}, respectively (Mahjoubi *et al.*, 2017). These FTIR spectra provide a comprehensive understanding of the LDH and 2,4-D/LDH-x hybrid nanocomposites, enhancing our knowledge in this field.

The FTIR results play a pivotal role in confirming the insertion of 2,4-D into the LDH interlayer and the subsequent formation of the 2,4-D/LDH hybrid nanocomposite. These results complement the XRD findings and provide strong evidence for forming hybrid nanocomposites. The FTIR spectra of the hybrid nanocomposites show a combination of the FTIR spectra of the LDH, host structure, and 2,4-D guest molecule. In the nanohybrid samples, a band was found at 3400 cm^{-1} corresponding to the internal OH hydrogen bond. The band observed at 1614 cm^{-1} corresponds to the carboxylate ion. This band overlapped with the deformation mode of the water molecules in the interlayer domain found at 1627 cm^{-1} (Hussein, M. Z. *et al.*, 2009). The bands found at 1484 cm^{-1} and 1427 cm^{-1} were attributed to the C=C bond vibrations of the 2,4-D aromatic ring, while the bands at 1285 cm^{-1} and 1065 cm^{-1} are the antisymmetric and symmetric vibrations of C–O–C, respectively. A band at 866 cm^{-1} corresponds to the C–Cl vibration, while the C–H deformation vibration of the out-of-plane benzene group appeared at 750 cm^{-1} and 804 cm^{-1} (Cardoso *et al.*, 2006; Lakraimi *et al.*, 2000). The bands between 650 cm^{-1} and 400 cm^{-1} can be attributed to the Al–OH and Zn–Al–OH bond vibrations, respectively. These results provide a solid foundation for our research findings and conclusions.
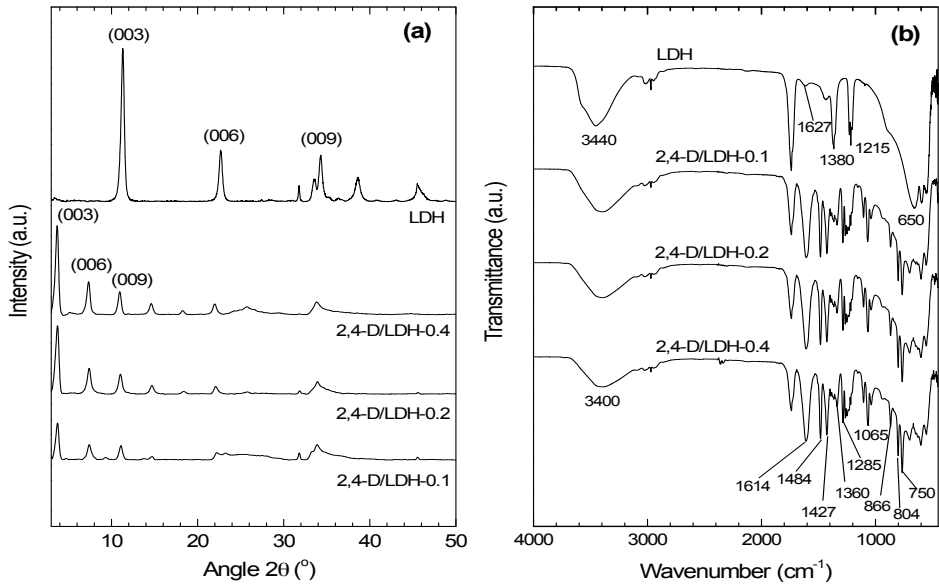
Figure 1. (a) XRD patterns and (b) FTIR spectra of the samples synthesized at different 2,4-D concentrations.

It can be seen from the micrograph of the LDH without herbicide, Figure 2(a), that the morphology found is typical of LDHs, formed by irregular, plate-shaped particles with a thickness of less than 100 nm (Phuong *et al.*, 2017). The images of the hybrid nanocomposites, Figure 2(b-d), clearly show aggregates of more minor, irregular, and disordered particles in the shape of leaves or petals, characteristics of the 2,4-D/LDH nanocomposite, in agreement with the findings in literature (Ghazali, Hussein e Sarijo, 2013; Hussein *et al.*, 2005). The thickness of these particles was less than 100 nm, and an increase in thickness was found with increasing herbicide concentration. This morphology was attributed to 2,4-D in the LDH host structure. The results obtained by microscopy confirm the XRD results. The change in the morphology of the samples when passing from the LDH without herbicide to the nanocomposites and its evolution as the concentration of the 2,4-D herbicide increases reveals a progressive transformation of the LDH into a lamellar structure intercalated with 2,4-D [28]. These results are consistent with the results presents in literature (Bashi *et al.*, 2013; Hussein, M. Z. Bin *et al.*, 2009; Phuong *et al.*, 2017).
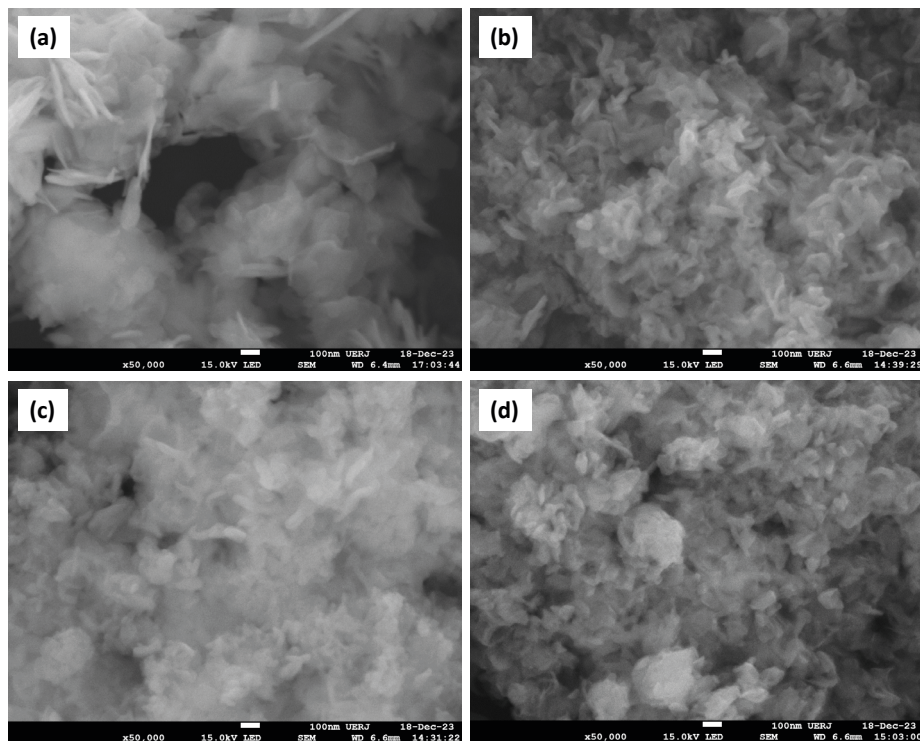
Figure 2. SEM micrographs of (a) LDH, (b) 2,4-D/LDH-0.1, (c) 2,4-D/LDH-0.2, and (d) 2,4-D/LDH-0.4.

The TEM image of the 2,4-D/LDH-0.4 sample shows the insertion of 2,4-D into the LDH's lamellar structure, causing an expansion of the basal spacing, Figure 3. In the micrograph, particles showing stripes can be observed, which would be the layers of the hybrid nanocomposite's lamellar structure. The thickness of the stripes would be around 2 nm (~20 Å), which agrees with the basal spacing values found in the XRD results in Table 1.

Transmission electron microscopy was used to analyze the nanohybrid sample in more detail. Figure 4(a) shows a representative TEM image of an aggregate of particles from the 2,4-D/LDH-0.4 sample. The EDS maps show the distinct chemical composition of the particles in Figure 4(b-e). The particles of the hybrid nanocomposite present a high concentration of Cl and Zn, Figure 4(b and c). The Cl concentration is attributed to the herbicide 2,4-D (2,4-Dichlorophenoxyacetic acid, $C_8H_6Cl_2O_3$) inserted in the interlayer region, and in the case of Zn, the high concentration found would be related to the presence of the metal in the octahedrons that form the brucite layers. The lower Al content observed is consistent with the Zn/Al molar ratio of 4/1 used in the synthesis. The EDS energy is also shown in Figure 4(f).
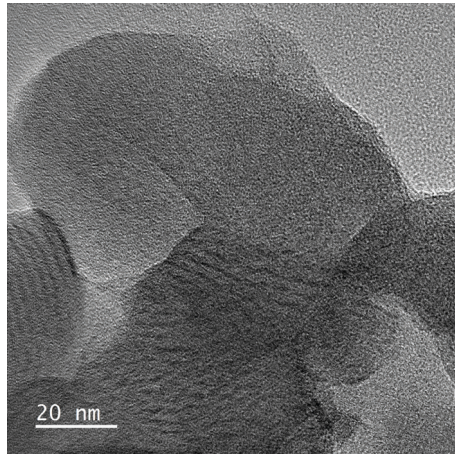
Figure 3. High-resolution transmission electron microscopy image of the 2,4-D/LDH-0.4 sample.
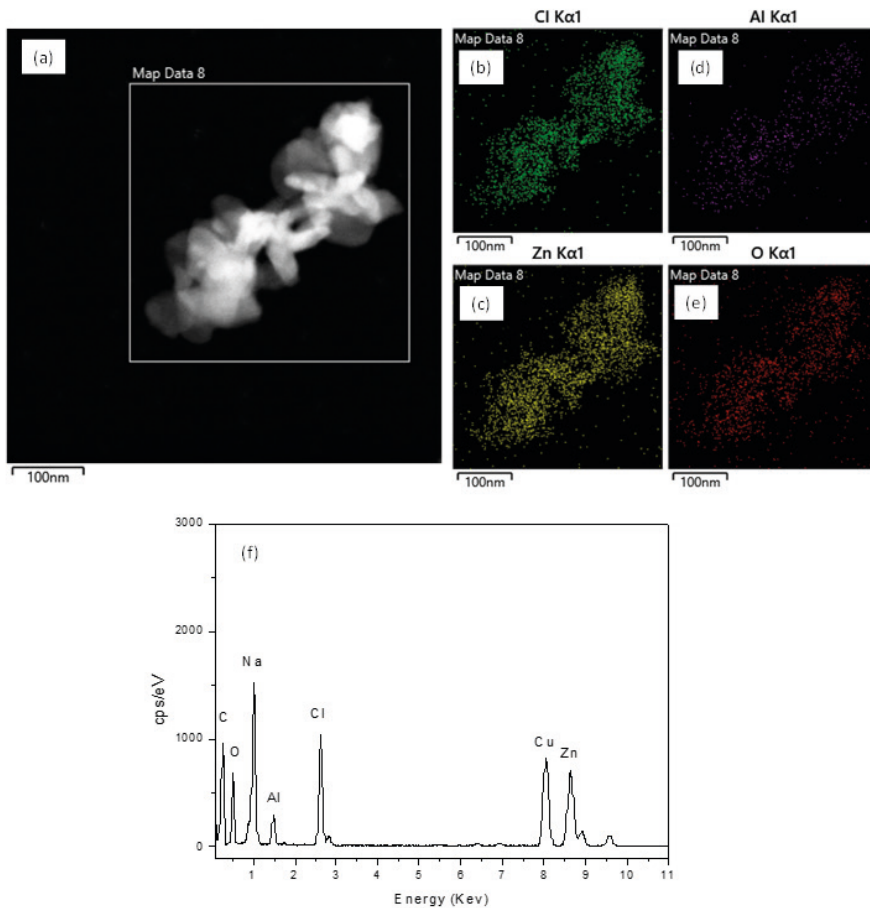
Figure 4. Transmission electron microscopy of a 2,4-D/LDH-0.4 sample. Morphology and chemical analysis using different imaging modes: (a) STEM images using the high-angle annular dark-field detector (HAADF); (b-e) EDS maps showing the distribution of relevant chemical elements (Cl in green, Zn in yellow, Al in purple, and O in red); and (f) EDS energy peaks.
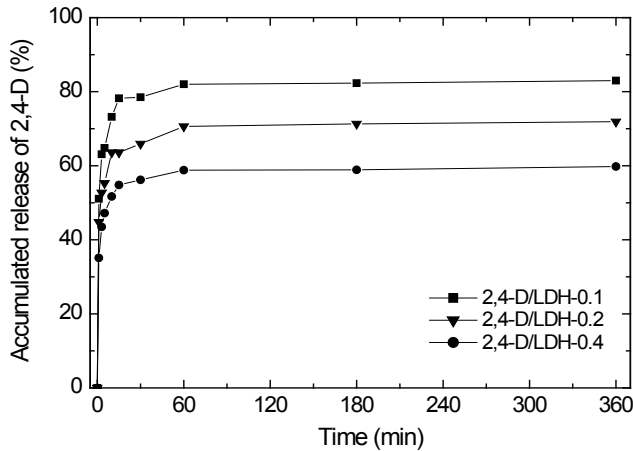
RELEASE OF 2,4-D FROM THE 2,4-/LDH HYBRID NANOCOMPOSITE

Controlled release study

Figure 5 shows the release profile 2,4-D from the 2,4-D/LDH hybrid nanocomposites synthesized with different concentrations of 2,4-D in aqueous sodium carbonate solution with a concentration of 0.05 mol/L. The accumulated 2,4-D released in the aqueous solution increased with time. The release rate was found to be faster in the first 30 min, then the release was slower. Equilibrium was reached around 60 min. Equations are fast when the hybrid nanocomposite is suspended in aqueous Na_2CO_3 solutions (Hussein *et al.*, 2005). The 2,4-D contents inserted into the LDH interlayer determined by CHNS analysis were 53.9, 55.9 and 59.5% for samples 2,4-D/LDH-0.1, 2,4-D/LDH-0.2 and 2,4-D/LDH-0.4, respectively. Hybrid nanocomposites with higher 2,4-D content in the nanohybrid structure showed higher levels of 2,4-D released accumulated at equilibrium. The percentage of 2,4-D released at equilibrium was 59.8, 71.9, and 83% for samples 2,4-D/LDH-0.1, 2,4-D/LDH-0.2, and 2,4-D/LDH-0.4, respectively.

In aqueous solutions of Na_2CO_3, the high concentration of ions cause an ion exchange with 2,4-D within the nanocomposite structure. ions are incorporated into the nanohybrid interlayer, allowing the simultaneous release of 2,4-D; in other words, the formation of a -LDH would occur (Hussein *et al.*, 2005). The exchange of a smaller anion for a larger 2,4-D anion decreases the basal spacing, which would be easily observed in an XRD analysis. The amount of 2,4-D released at equilibrium was more significant in nanohybrids with a higher herbicide content in their structure. This observation may be related to the orientation and arrangement of the anion in the matrix interlayer. An anion well organized in the host structure during intercalation is believed to form a nanohybrid with much more excellent crystallinity. The release of the intercalated guest in the nanohybrid with high crystallinity and larger particle size would be slower than those with lower crystallinity and smaller size. It can be due to the stability of the anionic arrangement, as previously discussed. However, the results of this study show the opposite behavior. The increase in the 2,4-D content in the nanohybrid favored the formation of a structure with higher crystallinity, which produced a higher release at equilibrium conditions. That said, the results obtained show that the release of 2,4-D from nanohybrids with different herbicide contents may be due to two specific factors: (i) the higher herbicide content within the nanohybrid structure facilitates more significant dissolution of the nanohybrid, allowing the structure to collapse more efficiently, contributing to a more significant amount of 2,4-D released at equilibrium and (ii) a more ordered arrangement of 2,4-D molecules in the interlayer region in nanohybrids with higher 2,4-D content facilitates more efficient ion exchange.

Figure 5. Release profiles of 2,4-D from the interlamellae of hybrid nanocomposite synthesized at different 2,4-D concentrations.

KINETIC STUDY

Investigating the kinetics of 2,4-D release from hybrid nanocomposites is essential to understanding the mechanisms involved, highlighting the importance of kinetic models in predicting and controlling the release behavior of these materials. The release of the herbicide could be described either by the dissolution of the LDH or by diffusion through the LDH (Hussein, M. Z. *et al.*, 2009). The kinetics of this release can be evaluated through several models: zero-order, first-order, pseudo-second-order, and parabolic diffusion. Following, respectively, Equations (1), (2), (3), and (4).

$$x = t + C \tag{1}$$

$$-\log(1 - M_i / M_f) = t + C \tag{2}$$

$$t / M_t = 1 / kM_f^2 + t / M_f \tag{3}$$

$$M_i / M_f = kt^{0.5} + C \tag{4}$$

where x is the release percentage at time t, and C is a constant. Mt represents the concentration of 2,4-D at time t, M_f represents the final concentration of 2,4-D, and k is a rate constant. At t = 0, M_t is M_i, the initial concentration of 2,4-D. M_i and M_f in equation (4) are the herbicide's initial and final concentrations, respectively.

For comparative purposes of the study of 2,4-D release kinetics, the four different kinetic models were applied to study the behavior of the release process. Based on the results presented in Figure 6, it is observed that the pseudo-second-order model presents a better fit to the experimental data, as can be seen by the values of the correlation coefficients (r^2) equal to 1. The pseudo-second-order model fits better than others for short intervals (Hussein, M. Z. *et al.*, 2009). By linearizing the other models, it can be observed that they

do not fit well with the experimental data. The study of the kinetic behavior of a process in which the pseudo-second-order model is identified as the most appropriate suggests that the release of 2,4-D from the inorganic interlayer of LDH involved the dissolution of the nanohybrids, as well as the ion exchange between the anions intercalated in the LDH interlayer and the carbonate anions in the aqueous solution, which is controlled by the pseudo-second-order (Hussein *et al.*, 2011). These results indicate that LDH can host 2,4-D due to its controlled release properties.
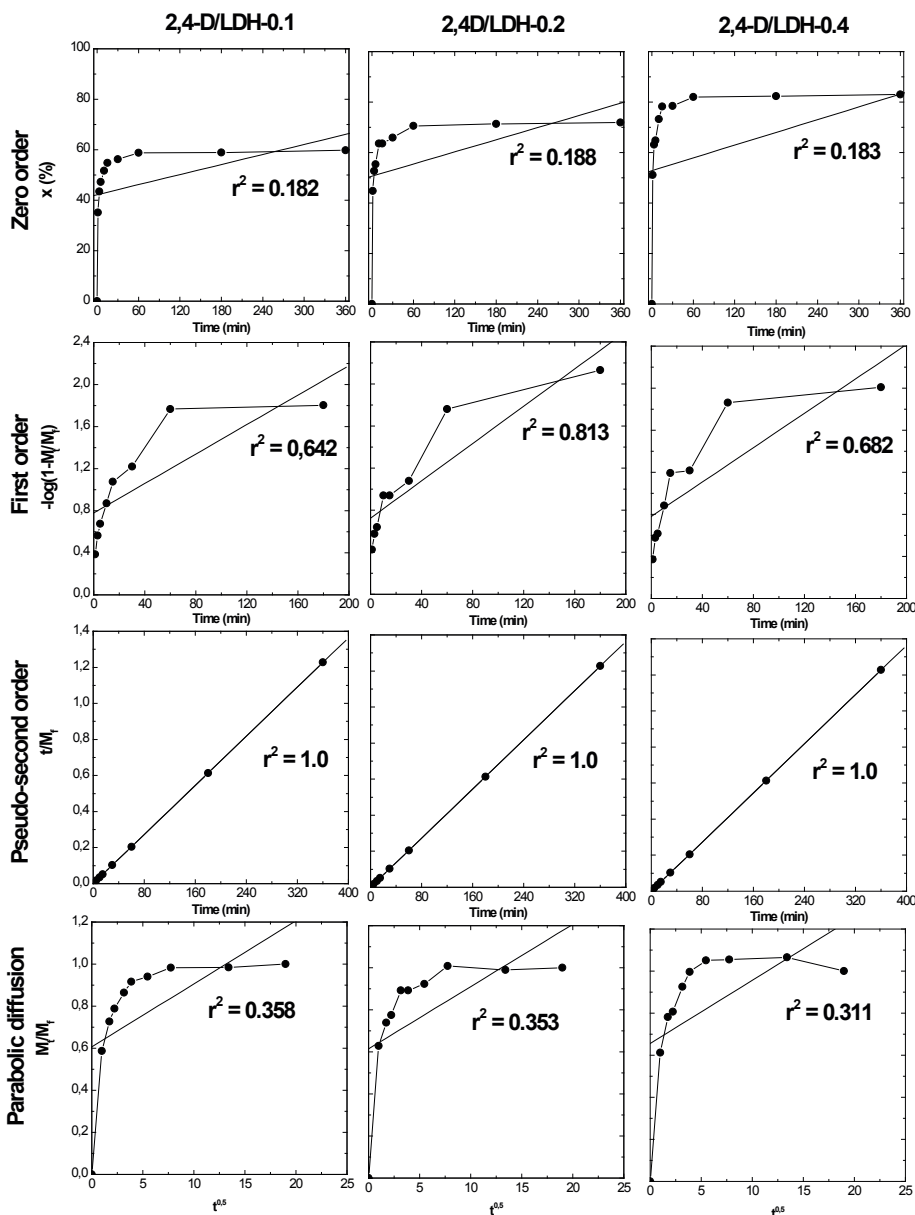

Figure 6. Fitting the release of 2,4-D from hybrid nanocomposite.

CHARACTERIZATION OF HYBRID NANOCOMPOSITES AFTER 2,4-D RELEASE

Following the model proposed by Hussein et al. (2005) (Hussein *et al.*, 2005), to obtain an insight into the ion exchange phenomenon, samples resulting from release tests interrupted at 7, 18, and 40 min from aqueous Na_2CO_3 solutions were recovered, dried, and analyzed by XRD, SEM, and FTIR. Samples of the nanohybrid from the release tests performed in deionized water at the exact times as the tests performed in saline aqueous solution were also recovered. The results of the XRD analyses can be seen in Figure 7(a-c). The results obtained for the samples after the release tests in Na_2CO_3 saline solution show that there was an angular dephasing of the peak corresponding to the atomic plane (003) after 7 min of testing compared to the samples at 0 min. The peaks found after 7 min of release test correspond to the peaks of the hydrotalcite phase with basal spacing smaller than that of the nanohybrids (from ~23.7 Å to ~7.4 Å), suggesting that the carbonate ions replaced the herbicide anions causing a decrease in the basal spacing due to the smaller size of the carbonate anion when compared to the size of the herbicide molecule. However, when comparing the patterns of the samples after the release test in deionized water, Figure 8(a-c), at different test times, it is observed that the recovered samples did not present a shift in the diffraction peaks, indicating that there was no release of the herbicide and the structure remained the same compared to the initial material as found in literature (Hussein *et al.*, 2005). It demonstrates that the basic crystalline structure of the nanocomposites is maintained regardless of the concentration of 2,4-D within the nanohybrid.
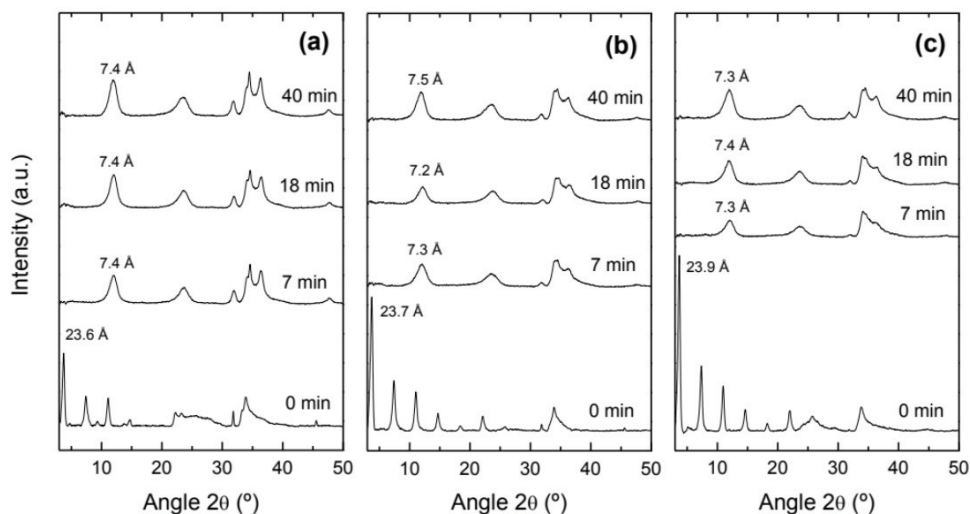

Figure 7. Diffraction patterns of the samples synthesized at different aging times recovered from Na2CO3 saline solution during the release test at various times: (a) 2,4-D/LDH-0.1, (b) 2,4-D/LDH-0.2 and (c) 2,4-D/LDH-0.4.
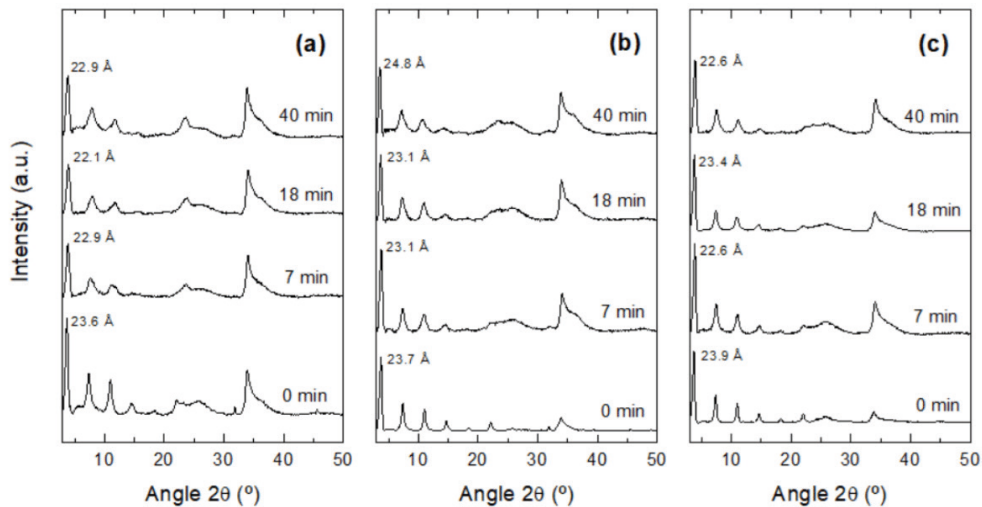
Figure 8. Diffraction patterns of the samples synthesized at different aging times recovered from deionized water at various release times: (a) 2,4-D/LDH-0.1, (b) 2,4-D/LDH-0.2, and (c) 2,4-D/LDH-0.4.

The morphology of the hybrid nanocomposites after 40 min of release is formed by aggregates of particles with a flower petal shape, similar to the samples before the release of the herbicide, Figure 9(a-c). Aggregates of larger particles with longer sheets were found in the samples synthesized with higher 2,4-D content. The thickness of the lamellar particles was found to be less than 100 nm. This result demonstrates that during the 2,4-D release process, the structure of the nanocomposite formed by brucite lamellae intercalated by 2,4-D molecules, after the release via anion exchange of the herbicide by the anion, regenerates, forming a lamellar structure characteristic of ZnAl-hydrotalcite containing a smaller anion in the interlayer, but maintaining the particle size without altering its morphology like thin folded sheets.
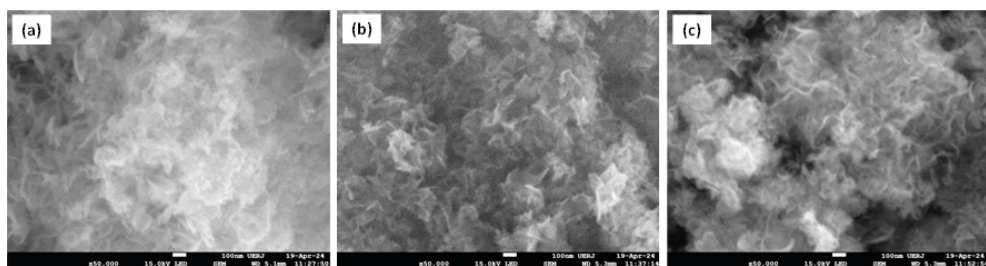
Figure 9. SEM micrographs of nanohybrid samples after 40 min of the release tests: (a) 2,4-D/LDH-0.1, (b) 2,4-D/LDH-0.2, and (c) 2,4-D/LDH-0.4.

The infrared spectra of the hybrid nanocomposites after 40 min of release showed a broad and robust band centered at 3450 cm^{-1} and attributed to the stretching of the OH bond of the hydroxyl groups and H$_2$O molecules, Figure 10. The weak band at 1630 cm^{-1} can be attributed to the H$_2$O bending vibration of the interlayer water. The bands recorded at 550 cm^{-1} and 790 cm^{-1} are attributed to the Zn/Al-OH translation and Al-OH deformation, respectively (Mahjoubi *et al.*, 2017; Meng *et al.*, 2005). The band found at 1365 cm^{-1} is attributed to carbonate's antimetric stretching mode (n_3). The bands observed around 870 cm^{-1} and 600 cm-1 are attributed to the weak nonplanar bending mode (n_2) and angular bending mode (n_4) of carbonate, respectively (Yasaei *et al.*, 2019). These results confirm that 2,4-D was exchanged for anions during the release process.
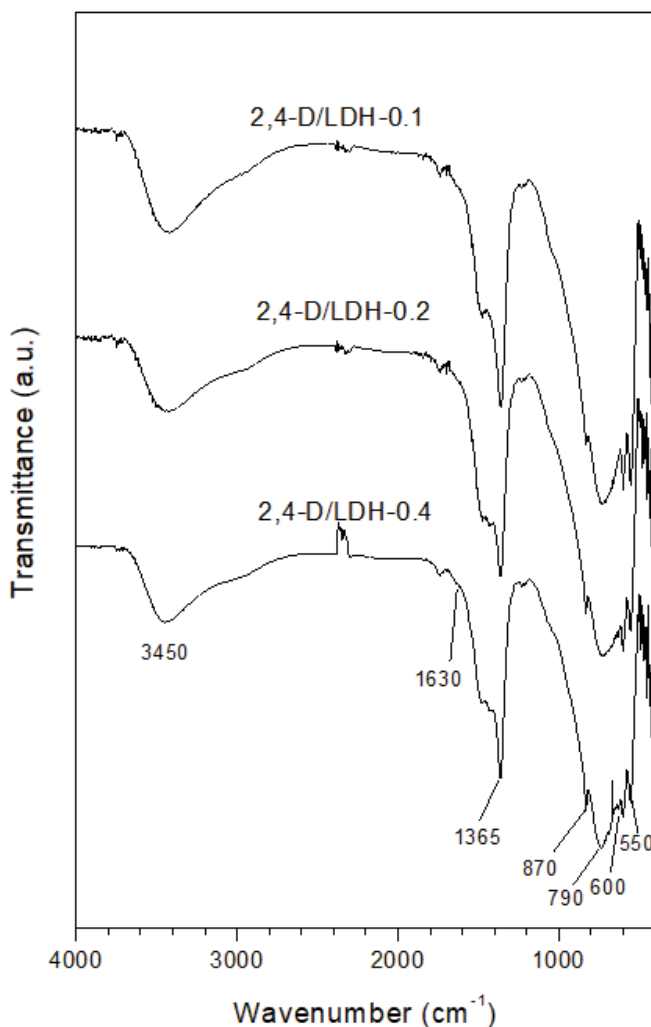
Figure 10. FTIR spectra of samples recovered after 40 min of 2,4-D herbicide release test.

CONCLUSION

It can be concluded from this work that different levels of 2,4-D were introduced into the ZnAl-LDH structure, forming a 2,4-D/LDH hybrid nanocomposite. 2,4-D produces structural and morphological changes in the host material. The increase in the basal spacing of the lamellar structure confirms that 2,4-D was inserted between the brucite lamellae with a spatial orientation defined by the increase in the lattice parameter 'c'. Particles with lamellar shape and irregular morphology were found in all samples of the hybrid nanocomposite. The increase in the concentration of the 2,4-D herbicide allowed the encapsulation of higher levels of the herbicide in the interlayer, favoring a more crystalline structure with greater 2,4-D release capacity. The release kinetics found were pseudo-second-order, and the herbicide release mechanism from the nanohybrid was dominated by the ion exchange between carbonate anions and 2,4-D molecules.

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