INFLUENCE OF AGING TIME ON THE 2,4-D/LDH HYBRID NANOCOMPOSITE SYNTHESIS

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

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

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

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

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

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

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

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

ABSTRACT: Different aging times (1, 2, 4, and 18 h) were used to intercalate the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) into the layered double hydroxide (ZnAl-LDH) using the coprecipitation method to form the 2,4-D/LDH hybrid nanocomposite. The XRD and FTIR results demonstrated that the herbicide was introduced into the layered structure of the LDH, forming an organic-inorganic crystalline nanohybrid in very short aging times, such as one h. The herbicide molecules introduced into the LDH-ZnAl produced an increase in basal spacing, a decrease in crystallinity, and changes in the morphology and particle size of the nanohybrid. The release kinetics obeyed the pseudo-second-order model, and the herbicide release mechanism was done via ion exchange. The analysis of the nanohybrids after herbicide release confirmed the insertion of carbonate anions via ion exchange into the lamellar structure of the LDH by decreasing the basal spacing.
KEYWORDS: Aging time, hybrid nanocomposites, 2,4-D/LDH, direct synthesis, controlled release formulations.

INTRODUCTION

Agrochemicals have become essential to agriculture, protecting crops against pests, diseases, and weeds, thus contributing to increased production and global food security (Carvalho, 2017). However, the indiscriminate and unprepared use of these products raises environmental and health concerns, particularly about the contamination of water resources and human exposure to chemical residues (Celis *et al.*, 2002; Rigotto, Vasconcelos e Rocha, 2014). 2,4-dichlorophenoxyacetic acid (2,4-D) is an herbicide widely used in agriculture to control broadleaf weeds effectively (Khan *et al.*, 2021). It is commonly applied through liquid spraying, facilitating its movement through the soil and eventually leaching into surface and groundwater, resulting in significant environmental risks (Góngora-Echeverría *et al.*, 2019; Phuong *et al.*, 2017; Qurratu e Reehan, 2016).

Given the environmental impact caused by agrochemicals, it is urgent to study alternatives that allow other forms of application. One such alternative is controlled Release Formulations (CRFs). These solid structures encapsulate an active component in a matrix to be released slowly with high delivery efficiency and reduced toxicity (Santilli *et al.*, 2009). CRFs can be used as host-host structures to release the herbicide 2,4-D. Among the materials used as host structures are Layered Double Hydroxides (LDHs), which are structures capable of hosting molecules in the interlayer region, offering a stable and protected environment for the herbicide, then allowing its gradual release during the crop cycle (Kang e Park, 2022).

There are several studies on nanohybrids based on LDHs for the release of herbicides such as 4-chlorophenoxy acetate (Bashi *et al.*, 2016), 3,4-dichlorophenoxyacetate (3,4D) and 2-methyldichlorophenoxyacetate (MCPA) (Sarijo, Ghazali e Hussein, 2015); 2,4,5-Tricholorophenoxy butyric acid (TBA) (Sarijo *et al.*, 2015); cloprop (Hashim *et al.*, 2014); dichlorprop (Hussein *et al.*, 2011); 4-(2,4-dichlorophenoxy)butyrate (DPBA) and 2-(3-chlorophenoxy)propionate (CPPA) (Hussein *et al.*, 2012), 2,4,5-trichlorophenoxybutyric acid (TBA) and 3,4-dichlorophenoxy-acetic acid (3,4D) (Ghazali, Fatimah e Bohari, 2021), 4-(2,4-dichlorophenoxy)butyric acid (DPBA) (Hashim *et al.*, 2007), terbuthylazine (Bruna *et al.*, 2008). Some studies were reported about the nanohybrid based on 2,4-D herbicide (Bashi *et al.*, 2013, 2016; Bashi, Haddawi e Al-Yasari, 2010; Cardoso *et al.*, 2006; Hermosín *et al.*, 2006; Hussein *et al.*, 2009, 2005; Lakraimi *et al.*, 2000; Nadiminti *et al.*, 2019; Phuong *et al.*, 2017).

Most of the studies reported on the nanohybrid based on the herbicide 2,4-D, and LDH studied the release properties of the herbicide in different saline aqueous mediums. Other studies compared nanohybrids formed by different herbicides and 2,4-D. There are no studies in the literature on the synthesis conditions of the hybrid nanocomposites, specifically the influence of the synthesis variables on the physicochemical characteristics of these nanomaterials and their release properties. In addition, the studies carried out on the 2,4-D/LDH nanohybrid reported results of the nanocomposites synthesized by the direct coprecipitation method from the mixture of aqueous solutions of Zn and Al salts, a precipitating agent, usually NaOH, and a solution of the herbicide. All studies reported that the solid formed after mixing the reagents were aged 18 hours. It is worth noting that applying CRFs in small plantations for in situ studies would require larger quantities of CRFs than those produced in laboratory research. Thus, the production of large amounts of the hybrid nanocomposite would be favored if the aging time were to make the nanohybrids much shorter.

With the potential of the 2,4-D/LDH hybrid nanocomposite for controlled herbicide release and the need to understand how shorter aging times can influence the formation of the organic-inorganic nanohybrid, this study investigates the influence of aging time. The focus is on using shorter aging times and comparing the results with the standard 18-hour aging time used in current research. The study also examines the impact of aging time on the physicochemical properties of the nanohybrid and its 2,4-D release properties.

METHODOLOGY

Synthesis of the samples

Samples were synthesized by mixing two solutions, one of $ZnCl_2$ and $AlCl_3$ with a Zn/Al molar ratio of 4 and a concentration of 1.50 mol L^{-1} and the other of NaOH with a concentration of 2.0 mol L^{-1}. The solutions were added simultaneously by droplet into a beaker containing 0.02 mol of 2,4-D diluted in 200 mL of deionized water under constant stirring and at 70 ºC. The dripping was conducted to maintain the mixture's pH around 7 ± 0.5. After the consumption of the reagents, the solid formed was aged for different times of 1, 2, 4, and 18 h, maintaining the temperature at 70 ºC. Then, the solid was separated from the mother liquor and washed with approximately 600 mL of deionized water heated to 50 ºC to eliminate soluble impurities. The solid was dried in an oven for 24 hours at 80 °C. The samples were coded as 2,4-D/LDH-x, where x assumes 1, 2, 4, and 18 (aging times used in the synthesis). For comparative purposes, a sample of LDH without herbicide was synthesized under the conditions mentioned above but with an aging time of 18 h.

Characterizations

The samples were characterized by X-ray Diffraction (XRD) in a Panalytical Empyrean X-Ray Diffractometer with CuKα radiation (45 kV and 40 mA), scanning rate of 0.0131º per step and an angular range of 2º to 70º. The resulting samples' mole ratio Zn to Al fraction was determined by an inductively coupled plasma spectrometry (ICP-AES) using a Perkin Elmer Spectrophotometer model Optima 5300 DV under standard conditions. Fourier transform infrared spectra (FTIR-ATR) were obtained in the wavenumber region between 4000-400 cm^{-1}, from the average of 60 acquisitions and with a resolution of 4 cm^{-1} using Perkin Elmer Frontier equipment. The morphological analysis obtained by scanning electron microscopy images was performed in a high-resolution scanning electron microscope, SEM-FEG model JSM-7100F from JEOL.

Release study of 2,4-D into aqueous solutions

The release of 2,4-D from hybrid nanocomposite was carried out according to Hussein et al. (2009) work. Initially, 150 mg of the nanocomposite was added to 500 mL of a sodium carbonate solution (0.05 mol L^{-1}) under constant stirring at room temperature. The accumulated 2,4-D released into the solution was measured at a specific time using a UV–vis Cary 60 UV/VIS spectrophotometer. The wavelength used for the analyses was 283 nm. In addition, the hybrid nanocomposite recovered from the aqueous solutions at various contact times was also subjected to XRD and SEM analysis.

DISCUSSION AND RESULTS

Characterization of the materials

Intense and narrow peaks of the ZnAl-hydrotalcite phase were found in the sample synthesized without herbicide and aged for 18 h. Samples of the nanohybrids synthesized at different aging times showed well-defined (003), (006), and (009) peaks, but less intense ones of the ZnAl-hydrotalcite phase shifted to smaller angles, Figure 1. This result represents a well-ordered nanolayer structure. As shown in Table 1, the basal spacing for LDH-18 was 7.8 Å and increased to values around 23 Å for the hybrid nanocomposites. The expansion was attributed to the spatial orientation of the 2,4-D anion in the interlayer space of LDH in the ‘c’ direction and the larger molecule size. It is worth mentioning that the only difference found in the XRD patterns was the intensity of the (003) plane peak. It is clear from these results that it was possible to synthesize the nanohybrids in times 18 times shorter than the time conventionally used in several studies (Bashi *et al.*, 2016; Cardoso *et al.*, 2006; Hussein *et al.*, 2009, 2005; Lakraimi *et al.*, 2000; Phuong *et al.*, 2017). The values of the interlayer distance found in the nanohybrids exceed the size of the 2,4-D molecule, which is 8.9 Å in the vertical position (Pavlovic *et al.*, 2005). This information indicates that the interlayer is possibly formed by more than one layer of stacked 2,4-D molecules.

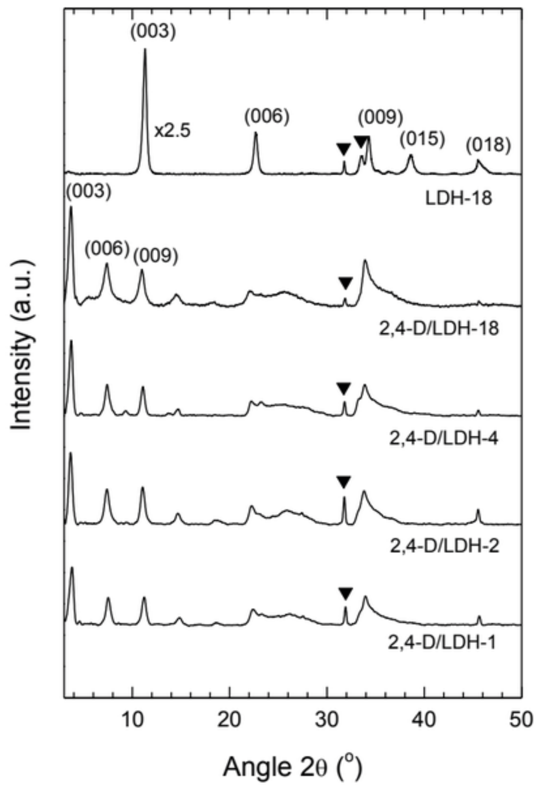

Figure 1. XRD patterns of samples synthesized at different aging times (▼ ZnO phase)

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

Sample	Zn/Al ratio	$d_{(003)}$ (Å)	Lattice parameter (Å)			Interlayer distance (Å)
			a	B	c	
2,4-D/LDH-1	2.05	23.2	3.05	3.05	69.53	18.4
2,4-D/LDH-2	2.01	23.9	3.06	3.06	71.85	19.2
2,4-D/LDH-4	2.10	23.6	3.04	3.04	70.78	18.8
2,4-D/LDH-18	2.04	23.9	3.06	3.06	70.32	19.1
LDH-18	2.06	7.8	3.08	3.08	23.47	3.01

The FTIR spectra of the samples are illustrated in Figure 2. The intense band centered at 3440 cm^{-1} that appears in the hybrid nanocomposites and pristine LDH is due to the stretching vibration of the OH^- groups of the hydroxide or interlayer water molecules. The bending vibration at 1627 cm^{-1} found in the pristine LDH corresponds to the deformation mode of interlayer water (δH2O). The band at 1400 cm^{-1} corresponds to the deformation mode of interlayer water. The bands found between 606 cm^{-1} and 420 cm^{-1} are related to the stretching vibrations of the metal-oxygen bond. (Zn-O e Al-O) (Shabanian, Hajibeygi e Raeisi, 2020). The spectra of the 2,4-D/LDH hybrid nanocomposite showed a high absorption band at 1614 cm^{-1}, which can be attributed to the antisymmetric stretching vibration of the COO^- group. The bands at 1484 and 1427 cm^{-1} corresponding to the vibrations of the C=C bond of the aromatic ring of 2,4-D were also found. The herbicide's antisymmetric and symmetric C-O-C stretching bands appear at 1285 and 1065 cm^{-1}, respectively. The band at 866 cm^{-1} was attributed to the C-Cl vibration (Cardoso *et al.*, 2006). This result confirms that 2,4-D herbicide molecules stably intercalate between the brucite layers of LDH (Phuong *et al.*, 2017).

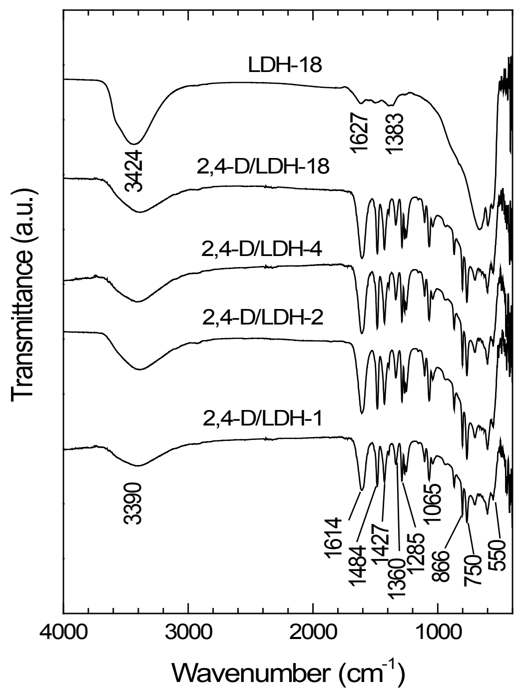

Figure 2. FTIR spectra of the samples synthesized at different aging times

Figure 3 shows the micrographs of the nanocomposites and LDH-18. Clusters of particles with irregular morphology resembling petals or folded sheets with thicknesses less than 100 nm can be observed in the images of the hybrid nanocomposites. It was impossible to distinguish the influence of aging time on the morphology of the nanocomposites. Sheet-shaped particles larger than those found in the nanohybrids can be observed in the LDH-18 sample. The insertion of 2,4-D into the LDH structure modifies its morphology, producing aggregates of smaller particles.

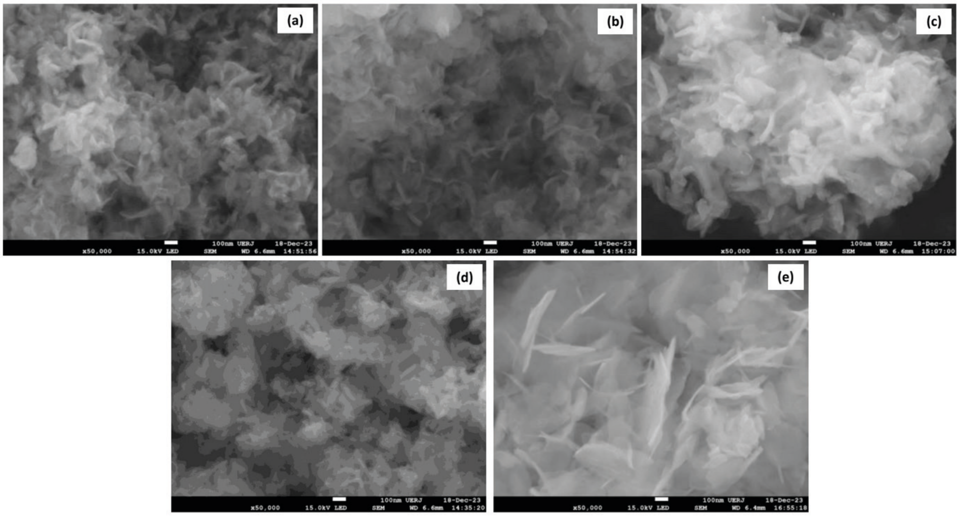

Figure 3. SEM micrographs of samples: (a) 2,4-D/LDH-1, (b) 2,4-D/LDH-2, (c) 2,4-D/LDH-4, (d) 2,4-D/LDH-18 and (e) LDH-18.

RELEASE OF 2,4-D FROM THE HYBRID NANOCOMPOSITE

Properties of release

The release profile of 2,4-D from the hybrid nanocomposite interlayer in an aqueous sodium carbonate solution (0.05 mol.L^{-1}) is shown in Figure 4. The cumulative release of 2,4-D increases rapidly in the first 30 min of the experiment and reaches equilibrium around 60 min. The amount released corresponds to 80% of the initial 2,4-D content in the hybrid nanocomposite. This amount released is similar to the value reported in the literature, where equilibrium was reached in about two hours in an aqueous sodium carbonate medium (0.005 mol.L^{-1}) (Hussein *et al.*, 2009, 2002). The curves showed a similar release profile, indicating that the aging time did not influence the release of the herbicide into the medium. Hydrogen bonding mechanisms likely trapped approximately 40% of the herbicide content in the LDH intermediate layer (Phuong *et al.*, 2017). The release of the 2,4-D herbicide from the hybrid nanocomposite in the carbonated medium can be explained by the anion exchange mechanism with and hydroxyl anions present in the médium (Bashi *et al.*, 2013; Hussein *et al.*, 2005). It is known that ZnAl-LDH, as a host material, has a high affinity for . The observed 2,4-D release results from a weaker electrostatic interaction of the anionic 2,4-D species with the ZnAl-LDH layers. On the other hand, carbonate is known to have the strongest affinity for the interlayer in layered double hydroxides (Miyata, 1980).

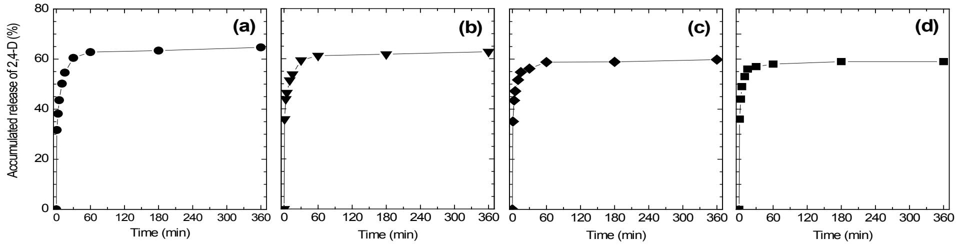

Figure 4. Release profiles of 2,4-D from the interlamellae of hybrid nanocomposite synthesized at different aging times: (a) 2,4-D/LDH-1, (b) 2,4-D/LDH-2, (c) 2,4-D/LDH-4 and (d) 2,4-D/LDH-18.

Release kinetic

The mechanism of the 2,4-D herbicide's release from the hybrid compound is complicated and has not been fully understood. There are two types of mechanisms for the release of the herbicide: the anion exchange process and the dissolution of the LDH layers in the solution. Either of these mechanisms can control the release process (Zhang, Pan e Duan, 2009). Four models are selected to determine the release kinetics of 2,4-D: zero-order kinetics (Costa e Lobo, 2001), first order (Wagner, 1969), pseudo-second order (Lv *et al.*, 2006), and parabolic diffusion (Kodama *et al.*, 2001).

The data of the released 2,4-D were fitted to four kinetic models to understand the release behavior of 2,4-D in aqueous sodium carbonate solution. The parameters obtained from the fitting can be seen in Figure 5. The kinetic models used in the fitting were:

Zero order: $x = t+c$ (1)

First order: $-log(1-M_t/M_f) = t+c$ (2)

Pseudo-second order: $t/Mt = 1/kM_f^2 + t/M_f$ (3)

Parabolic diffusion: $Mt/Mf = kt^{0.5}+C$ (4)

where x represents the percentage release of 2,4-D at the time t, C is a constant, M_t represents the concentration of 2,4-D at the time t, M_f represents the final concentration of 2,4-D and k is a rate constant, and at t = 0, M_t is M_i, the initial concentration of 2,4-D.

The 2,4-D release profile of the nanohybrid is governed by pseudo-second-order kinetics comparing the coefficient of determination and r^2 values obtained from the fit. The pseudo-second-order model describes the release process based on anion exchange in a disaggregation step (Phuong *et al.*, 2017). Furthermore, the release rate would depend on the amount of 2,4-D inserted into the LDH structure. The pseudo-second order kinetics means that the release of the herbicide from the intermediate layer of inorganic LDH involved the dissolution of nanohybrids, as well as the ion exchange between the anions intercalated between the brucite layers of the LDH and the carbonate anions in the aqueous solution (Hussein *et al.*, 2011).

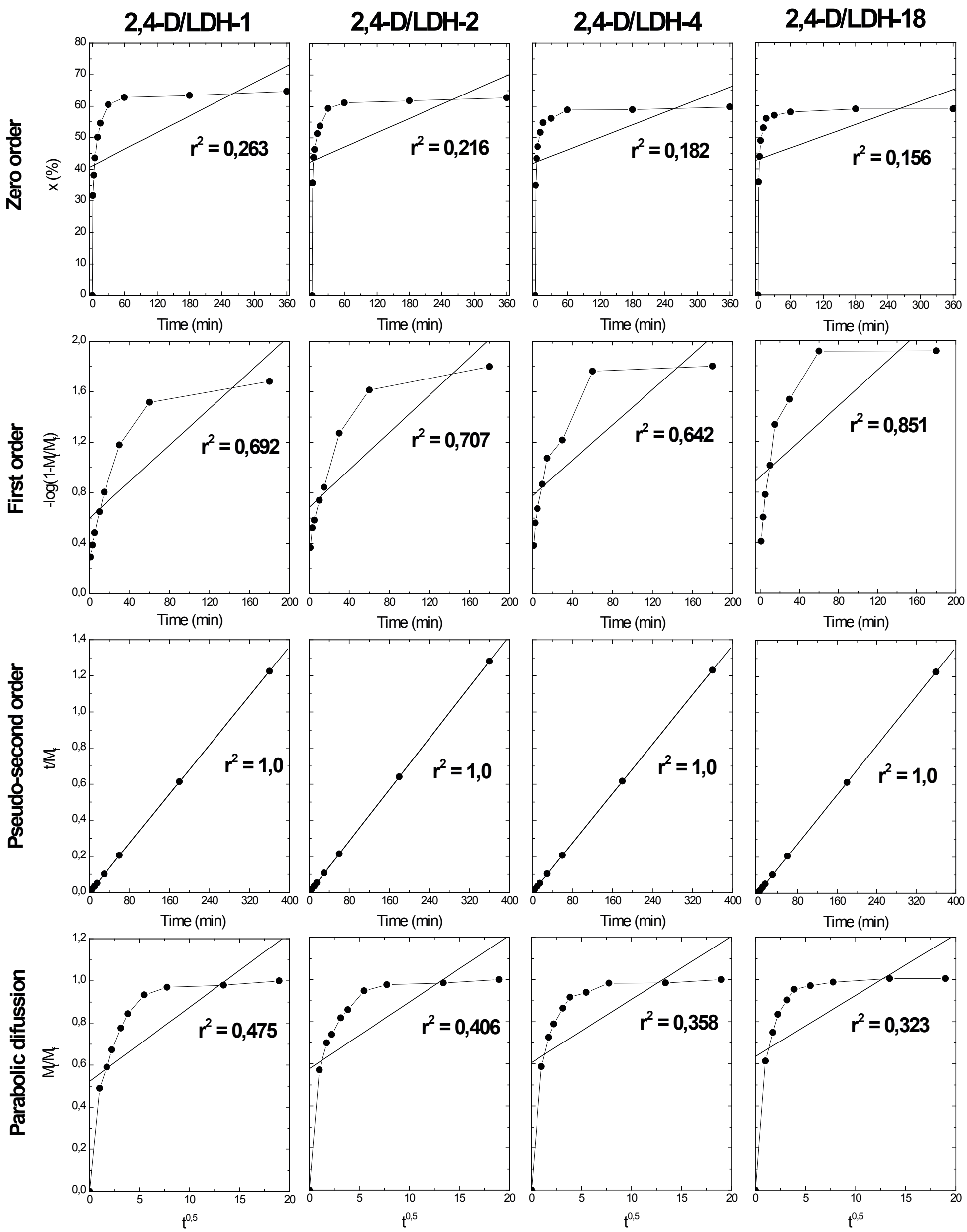

Figure 5. Fitting the release of 2,4-D from hybrid nanocomposite.

Release and interruption tests were performed at 7, 18, and 40 min. The hybrid nanocomposite samples were recovered, dried, and analyzed by XRD, Figure 6. The analyses revealed that the release of 2,4-D modifies the structure of the nanocomposite, favoring the formation of a structure like that of pure LDH, with the peak of the (003) plane shifted to larger angles. The basal spacing values can be observed in the figure. The patterns of the hybrid nanocomposites at zero time correspond to the sample obtained in the synthesis. It is worth noting that due to the rapid release of 2,4-D into the medium, the structure is modified in the first minutes of the test. A notable change was observed at 7 min of contact time; the basal spacing decreased from approximately 23 Å to around 7.4 Å.

Furthermore, two new phases can be observed, the ZnAl-hydrotalcite and ZnO phases and the formation of these phases increases with the herbicide release time. The peaks of the ZnO phase can be observed at 2q from 30° to 40°. These results confirm that after the release of 2,4-D from the nanohybrid structure, there is a collapse of this structure caused by the ionic exchange between the 2,4-D molecules and the ions of the medium, giving rise to the formation of new phases (ZnO and ZnAl-hydrotalcite). The formation of the ZnAl-hydrotalcite phase after 7 min of release time confirms the occurrence of the mechanism. No influence of the aging time was found on the observed results.

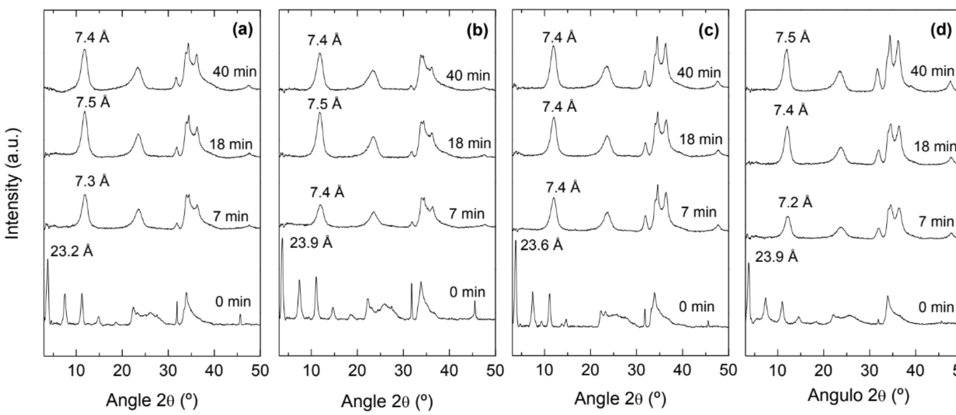

Figure 6. XRD patterns of the samples synthesized at different aging times recovered from Na2CO3 saline solution during the release test at various times. (a) 2,4-D/LDH-1, (b) 2,4-D/LDH-2, (c) 2,4-D/LDH-4 and (d) 2,4-D/LDH-18

The morphology analyses of the samples recovered after 40 minutes of 2,4-D release revealed aggregates of particles with a flower petal-shaped shape, as found in the synthesized samples, but with reduced particle thickness, Figure 7. These results were attributed to the release of the herbicide by the ion exchange mechanism forming the ZnAl-hydrotalcite phase with the interlayer containing carbonate ions, which has a smaller size than the herbicide molecules. Smaller, rounded particles can be observed in Figure 7(c) and (d). These particles would be of the ZnO phase. This result is consistent with that found in Figure 7(c) and (d), where the peaks of the ZnO phase are more intense and well-defined.

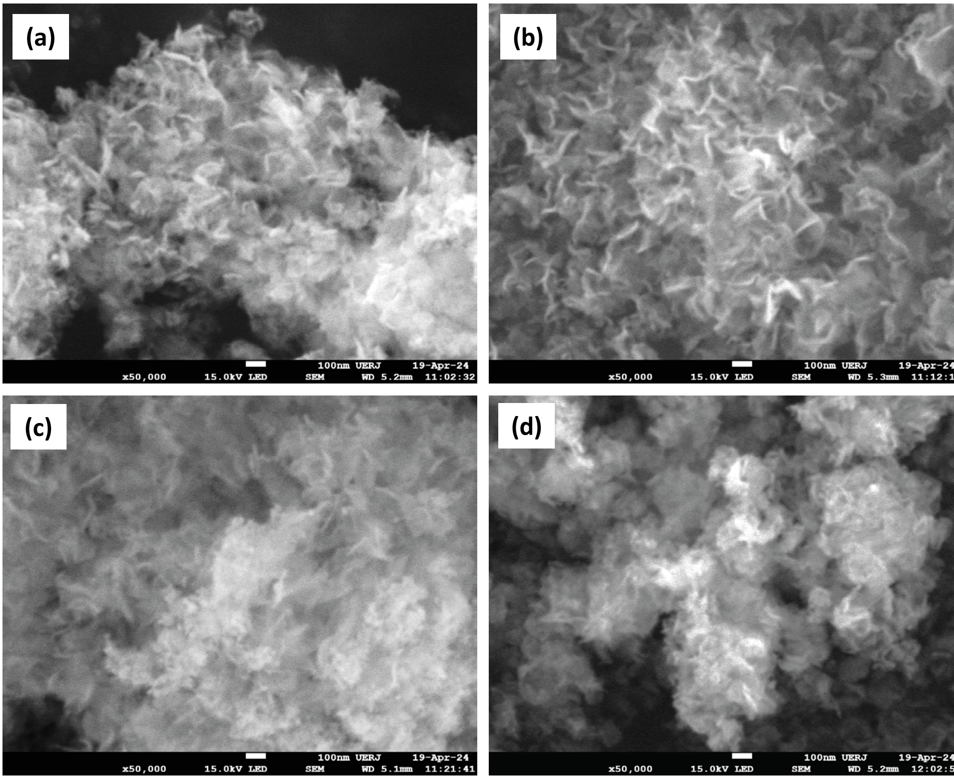

Figure 7. SEM micrographs of samples after 40 min of the release tests: (a) 2,4-D/LDH-1, (b) 2,4-D/LDH-2, (c) 2,4-D/LDH-4 and (d) 2,4-D/LDH-18

CONCLUSION

Samples of 2,4-D/LDH hybrid nanocomposites can be synthesized with aging times much shorter than that reported in the literature of 18 h. The LDH nanostructure with the herbicide inserted into its structure can be synthesized with only one hour of aging. The insertion of 2,4-D strongly modified the LDH structure, increasing the basal spacing from 7.4 Å to values of approximately 23 Å. Likewise, a change in the morphology of the nanohybrids was observed. It was deduced from the interlayer thickness that 2,4-D was inserted into the interlayer, forming an arrangement of two 2,4-D molecules stacked one on top of the other. Approximately 60% of the herbicide was released in aqueous sodium carbonate medium. The r^2 values obtained from the fit confirmed that the herbicide release followed pseudo-second-order kinetics. The ZnAl-hydrotalcite phase formed after 7 min of the release test, and the decrease in particle thickness after 40 min confirmed that the ion exchange mechanism dominated the herbicide release.

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REFERENCES

BASHI, A. M.; HADDAWI, S. M.; AL-YASARI, A. H. Kinetics Study and controlled release of Synthesized Phenoxy herbicides-Based Nanocomposites from; 2, 4-dichloro-and 2, 4, 5-trichlorophenoxy acetates with Zn/Al Layered double hydroxide interlamellae (NJC). Iraqi National Journal of Chemistry, v. 38, p. 279–292, 2010.

BASHI, A. M.; HUSSEIN, M. Z.; ZAINAL, Z.; RAHMANI, M.; TICHIT, D. Simultaneous intercalation and release of 2,4-dichloro- and 4-chloro-phenoxy acetates into Zn/Al layered double hydroxide. Arabian Journal of Chemistry, v. 9, p. S1457–S1463, 1 nov. 2016.

BASHI, A. M.; HUSSEIN, M. Z.; ZAINAL, Z.; TICHIT, D. Synthesis and controlled release properties of 2,4-dichlorophenoxy acetate-zinc layered hydroxide nanohybrid. Journal of Solid State Chemistry, v. 203, p. 19–24, 2013.

BRUNA, F.; PAVLOVIC, I.; CELIS, R.; BARRIGA, C.; CORNEJO, J.; ULIBARRI, M. A. Organohydrotalcites as novel supports for the slow release of the herbicide terbuthylazine. Applied Clay Science, v. 42, n. 1–2, p. 194–200, dez. 2008.

CARDOSO, L. P.; CELIS, R.; CORNEJO, J.; VALIM, J. B. Layered double hydroxides as supports for the slow release of acid herbicides. Journal of Agricultural and Food Chemistry, v. 54, n. 16, p. 5968–5975, 9 ago. 2006.

CARVALHO, F. P. Pesticides, environment, and food safety. Food and Energy Security, v. 6, n. 2, p. 48–60, 9 maio 2017.

CELIS, R.; HERMOSÍN, M. C.; CARRIZOSA, M. J.; CORNEJO, J. Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone. Journal of Agricultural and Food Chemistry, v. 50, n. 8, p. 2324–2330, 10 abr. 2002.

COSTA, P.; LOBO, J. M. S. Modeling and comparison of dissolution profiles. European Journal of Pharmaceutical Sciences, v. 13, n. 2, p. 123–133, maio 2001.

GHAZALI, S. A. I. S. M.; FATIMAH, I.; BOHARI, F. L. Synthesis of hybrid organic-inorganic hydrotalcite-like materials intercalated with duplex herbicides: The characterization and simultaneous release properties. Molecules, v. 26, n. 16, 2 ago. 2021.

GÓNGORA-ECHEVERRÍA, V. R.; MARTIN-LAURENT, F.; QUINTAL-FRANCO, C.; LORENZO-FLORES, A.; GIÁCOMAN-VALLEJOS, G.; PONCE-CABALLERO, C. Dissipation and Adsorption of 2,4-D, Atrazine, Diazinon, and Glyphosate in an Agricultural Soil from Yucatan State, Mexico. Water, Air, and Soil Pollution, v. 230, n. 6, 1 jun. 2019.

HASHIM, N.; HUSSEIN, Z.; YAHAYA, A. H.; ZAINAL, Z. Formation of zinc aluminium layered double hydroxides-4(2,4-dichlorophenoxy)butyrate nanocompisites by direct and indirect methods. The Malaysian Journal of Analytical Sciences, v. 11, n. 1, p. 1–7, 2007.

HASHIM, N.; ZOBIR HUSSEIN, M.; MD ISA, I.; KAMARI, A.; MOHAMED, A.; MOHAMAD JAAFAR, A.; TAHA, H. Synthesis and controlled release of cloprop herbicides from cloprop-layered double hydroxide and cloprop-zinc-layered hydroxide nanocomposites. Open Journal of Inorganic Chemistry, v. 04, n. 01, p. 1–9, 2014.

HERMOSÍN, M. C.; CELIS, R.; FACENDA, G.; CARRIZOSA, M. J.; ORTEGA-CALVO, J. J.; CORNEJO, J. Bioavailability of the herbicide 2,4-D formulated with organoclays. Soil Biology and Biochemistry, v. 38, n. 8, p. 2117–2124, ago. 2006.

HUSSEIN, M. Z. BIN; YAHAYA, A. H.; ZAINAL, Z.; KIAN, L. H. Nanocomposite-based controlled release formulation of an herbicide, 2,4-dichlorophenoxyacetate incapsulated in zinc-aluminium-layered double hydroxide. Science and Technology of Advanced Materials, v. 6, n. 8, p. 956–962, nov. 2005.

HUSSEIN, M. Z. BIN; ZAINAL, Z.; YAHAYA, A. H.; FOO, D. W. V. Controlled release of a plant growth regulator, α-naphthaleneacetate from the lamella of Zn–Al-layered double hydroxide nanocomposite. Journal of Controlled Release, v. 82, n. 2–3, p. 417–427, ago. 2002.

HUSSEIN, M. Z.; HASHIM, N.; YAHAYA, A. H.; ZAINAL, Z. Synthesis of Dichlorprop-Zn/Al-hydrotalcite Nanohybrid and its Controlled Release Property. Sains Malaysiana, v. 40, n. 8, p. 887–896, 2011.

HUSSEIN, M. Z.; JAAFAR, A. M.; YAHAYA, A. H.; ZAINAL, Z. The effect of single, binary and ternary anions of chloride, carbonate and phosphate on the release of 2,4-dichlorophenoxyacetate intercalated into the Zn-Al-layered double hydroxide nanohybrid. Nanoscale Research Letters, v. 4, n. 11, p. 1351–1357, out. 2009.

HUSSEIN, M. Z.; RAHMAN, N. S. S. A.; SARIJO, S. H.; ZAINAL, Z. Synthesis of a monophasic nanohybrid for a controlled release formulation of two active agents simultaneously. Applied Clay Science, v. 58, p. 60–66, abr. 2012.

KANG, G. H.; PARK, I. K. Reconstruction and intercalating anion exchange of ZnAl-layered double hydroxide. Ceramics International, v. 48, n. 3, p. 3030–3036, 1 fev. 2022.

KHAN, M. M.; KHAN, A.; BHATTI, H. N.; ZAHID, M.; ALISSA, S. A.; EL-BADRY, Y. A.; HUSSEIN, E. E.; IQBAL, M. Composite of polypyrrole with sugarcane bagasse cellulosic biomass and adsorption efficiency for 2,4-dicholrophonxy acetic acid in column mode. Journal of Materials Research and Technology, v. 15, p. 2016–2025, 1 nov. 2021.

KODAMA, T.; HARADA, Y.; UEDA, M.; SHIMIZU, K. I.; SHUTO, K.; KOMARNENI, S. Selective exchange and fixation of strontium ions with ultrafine Na-4-mica. Langmuir, v. 17, n. 16, p. 4881–4886, 7 ago. 2001.

LAKRAIMI, M.; LEGROURI, A.; BARROUG, A.; ANDRÉ, R. DE; BESSE, J. P. Preparation of a new stable hybrid material by chloride-2,4- dichlorophenoxyacetate ion exchange into the zinc-aluminium-chloride layered double hydroxide. Journal of Materials Chemistry, v. 10, n. 4, p. 1007–1011, 2000.

LV, L.; HE, J.; WEI, M.; EVANS, D. G.; DUAN, X. Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetic studies. Water Research, v. 40, n. 4, p. 735–743, 2006.

MIYATA, S. Physico-Chemical Properties of Synthetic Hydrotalcites in Relation to Composition. Clays and Clay Minerals, v. 28, n. 1, p. 50–56, 1 fev. 1980.

NADIMINTI, P. P.; SHARMA, H.; KADA, S. R.; PFEFFER, F. M.; O'DELL, L. A.; CAHILL, D. M. Use of Mg–Al Nanoclay as an Efficient Vehicle for the Delivery of the Herbicide 2,4-Dichlorophenoxyacetic Acid. ACS Sustainable Chemistry & Engineering, v. 7, n. 12, p. 10962–10970, 17 jun. 2019.

PAVLOVIC, I.; BARRIGA, C.; HERMOSÍN, M. C.; CORNEJO, J.; ULIBARRI, M. A. Adsorption of acidic pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite. Applied Clay Science, v. 30, n. 2, p. 125–133, set. 2005.

PHUONG, N. T. K.; HA, H. N. N.; DIEU, N. T. P.; HUY, B. T. Herbicide/Zn-Al-layered double hydroxide hybrid composite: synthesis and slow/controlled release properties. Environmental Science and Pollution Research, v. 24, n. 23, p. 19386–19392, 1 ago. 2017.

QURRATU, A.; REEHAN, A. A Review of 2,4-Dichlorophenoxyacetic Acid (2,4-D) Derivatives: 2,4-D Dimethylamine Salt and 2,4-D Butyl Ester. International Journal of Applied Engineering Research, v. 11, p. 9946–9955, 2016.

RIGOTTO, R. M.; VASCONCELOS, D. P. E.; ROCHA, M. M. Pesticide use in Brazil and problems for public health. Cadernos de Saude Publica, v. 30, n. 7, p. 1360–1362, 1 jul. 2014.

SANTILLI, C. V.; CHIAVACCI, L. A.; LOPES, L.; PULCINELLI, S. H.; OLIVEIRA, A. G. Controlled drug release from ureasil-polyether hybrid materials. Chemistry of Materials, v. 21, n. 3, p. 463–467, 10 fev. 2009.

SARIJO, S. H.; GHAZALI, S. A. I. S. M.; HUSSEIN, M. Z. Synthesis of dual herbicides-intercalated hydrotalcite-like nanohybrid compound with simultaneous controlled release property. Journal of Porous Materials, v. 22, n. 2, p. 473–480, 1 abr. 2015.

SARIJO, S. H.; GHAZALI, S. A. I. S. M.; HUSSEIN, M. Z.; AHMAD, A. H. Intercalation, Physicochemical and Controlled Release Studies of Organic-inorganic -Herbicide (2, 4, 5 Tricholorphenoxy Butyric Acid) Nanohybrid into Hydrotalcite-like Compounds. Materials Today: Proceedings, v. 2, n. 1, p. 345–354, 2015.

SHABANIAN, M.; HAJIBEYGI, M.; RAEISI, A. FTIR characterization of layered double hydroxides and modified layered double hydroxides. Em: THOMAS, S.; DANIEL, S. (Eds.). . Layered Double Hydroxide Polymer Nanocomposites. [s.l.] Woodhead Publishing, 2020. p. 77–101.

WAGNER, J. G. Interpretation of Percent Dissolved-Time Plots Derived from In Vitro Testing of Conventional Tablets and Capsules. Journal of Pharmaceutical Sciences, v. 58, n. 10, p. 1253–1257, out. 1969.

ZHANG, H.; PAN, D.; DUAN, X. Synthesis, characterization, and magnetically controlled release behavior of novel core-shell structural magnetic ibuprofen-intercalated ldh nanohybrids. Journal of Physical Chemistry C, v. 113, n. 28, p. 12140–12148, 16 jul. 2009.