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Effect of sodium stearate and sodium palmitate concentration on the modification of CaAl-layered double hydroxides for the removal of carbaryl and imidacloprid from aqueous solutions

Efecto de la concentración de estearato de sodio y palmitato de sodio en la modificación de CaAl-hidróxidos dobles laminares para la eliminación de carbaril e imidacloprid de soluciones acuosas

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Abstract
Sodium stearate (SS) and sodium palmitate (PS), natural surfactants suitable for human consumption, were used to modify Ca-Al layered double hydroxides (CaAl-LDH) to evaluate their applications in synthesizing an adsorbent material for the removal of carbaryl and imidacloprid from contaminated water. CaAl-LDH materials were produced by the co-precipitation method. Modification of CaAl-LDH was performed with different degree of SS and PS saturation to determine the effect of surfactant concentration in pesticide removal efficiency from aqueous solution. Materials were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS). CaAl-LDH modified with PS at a concentration of 0.01 mol L^{-1} had the highest removal efficiency for both pesticides with improved sorption capabilities three times greater than the inorganic LDH. This novel material exhibits an increase in the basal spacing for the (002) diffraction plane from 8.62 Å in the inorganic LDH to 8.75 Å, along with a well-crystallized phase, a good double layered structure, and hydrophobic properties. Further adsorption studies are required to achieve a better understanding of this material as an adsorbent of carbaryl and imidacloprid from contaminated waters.
Keywords: CaAl-LDH, sodium palmitate, sodium stearate, carbaryl, imidacloprid.

Resumen
El estearato de sodio (SS) y el palmitato de sodio (PS), surfactantes naturales aptos para el consumo humano, se utilizaron en la modificación de CaAl-hidróxidos dobles laminares (CaAl-HDL) para evaluar sus aplicaciones en la síntesis de un material adsorbente para la remoción de carbaril e imidacloprid del agua. Los materiales de CaAl-HDL fueron sintetizados mediante el método de co-precipitación. La modificación de CaAl-HDL se realizó con diferentes grados de saturación de SS y PS para determinar el efecto de la concentración de surfactante en la eficiencia de eliminación de los pesticidas en solución acuosa. Los materiales fueron caracterizados por difracción de rayos X (XRD), microscopía electrónica de barrido de emisión de campo (FESEM) y espectroscopía por dispersión de energía (EDS). CaAl-HDL modificado con PS a una concentración de 0.01 mol L^{-1} tuvo la mayor eficiencia de eliminación para ambos pesticidas con capacidades de sorción tres veces mayores que el HDL inorgánico. Este nuevo material presenta un aumento en el espacio basal para el plano de difracción (002) de 8.62 Å en el LDH inorgánico a 8.75 Å, así como buena cristalinidad, buena estructura laminar y propiedades hidrofóbicas. Se requieren estudios de adsorción adicionales para comprender mejor las aplicaciones de este material como adsorbente de carbaril e imidacloprid de aguas contaminadas.
Palabras clave: CaAl-HDL, palmitato de sodio, estearato de sodio, carbaril, imidacloprid.

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1 Introduction

Pesticides are commonly employed in agriculture to enhance crop productivity and defend against pests; however, their runoff can lead to the contamination of water sources. Exposure to pesticide residues in water can disrupt aquatic ecosystems, harming wildlife, while also resulting in acute and chronic health effects in humans (Lew *et al.,* 2009; Rani *et al.,* 2021). Therefore, research on the development of effective and sustainable methods for the removal of these pollutants from water is of vital importance for safeguarding public health and preserving the environment (Rajmohan, Chandrasekaran & Varjani, 2020; Cadena-Álava, *et al.,* 2024).

Carbaryl and imidacloprid are two insecticides of significant environmental concern due to their widespread use and high toxicity to bees and other essential pollinators. Both compounds have been detected in various water bodies worldwide, with carbaryl concentrations reaching up to 47.73 mg L^{-1} (Pérez *et al.,* 2012) and imidacloprid levels up to 320 μg L^{-1} (Van Dijk *et al.,* 2013). Carbaryl, a synthetic carbamate, acts as an acetylcholinesterase inhibitor and is a suspected endocrine disruptor, while imidacloprid is a systemic neonicotinoid. These pesticides pose substantial risks to ecosystems and human health, underscoring the need for effective removal strategies to mitigate their environmental impact. (USEPA, 2023; De Smedt *et al.,* 2015; Bejarano-Gonzalez, 2017). The chemical structures of both pesticides are presented in Figure 1.

In recent years, researchers worldwide have shown growing interest in layered double hydroxides (LDHs) due to their potential environmental applications. LDHs are a large group of natural and synthetic anionic clays that are represented by the general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$ (Nuramirah *et al.,* 2021; Theiss, Ayoko & Frost, 2016).

These compounds have a particular structure of lamellar hydroxides, usually with two types of metallic cations in the main layers and anions in the interlamellar domain. They consist of octahedral brucite-like layers which are positively charged by the partial substitution of M^{3+} for M^{2+}.

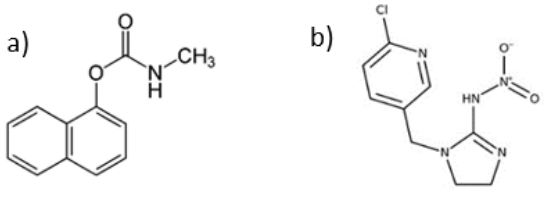

Fig. 1 Chemical structure of a) carbaryl and b) imidacloprid.

The positive charge is compensated by anions intercalated in the interlayer space to achieve charge neutrality (Bukhtiyarova, 2018; Mahboobeh *et al.*, 2010; Wang *et al.,* 2005).

One of the most significant aspects of LDHs is that some anions are preferably intercalated to the interlayer space over others and can therefore be used for targeted anion removal (Tóth *et al.*, 2014). In addition, these materials have numerous properties that make them suitable sorbent materials such as low toxicity, high surface area, anion exchange capabilities, simple and low-cost preparation, and adjustable structures through possible variations in metals, interlayer anions and synthesis techniques (Johnston *et al.*, 2021).

Adsorption in LDHs can occur mainly through two different routes: external surface sorption and interlayer anion exchange. These materials have a strong enthalpy of bond formation within layers, which makes them thermodynamically stable. Conversely, the interlayer domain is less stable, thus it can suffer repeatedly intercalation/deintercalation processes (Bernardo, Moreira & Ribeiro, 2017; Mittal, 2021).

Numerous studies have demonstrated that LDHs can be modified by incorporating anions with specific functional groups into their structure, thereby enhancing their selectivity for the removal of various water pollutants, including emerging contaminants. Emerging contaminants, such as the pesticides carbaryl and imidacloprid, are part of a group of anthropogenic organic compounds that pose significant environmental and health risks (Guerrero-Martínez, *et al.*, 2024). As these pesticides are neutrally charged and poorly water-soluble (Hashim *et al.*, 2016; Johnston *et al.*, 2021), modifying hydrophilic LDHs with organic anions, such as anionic surfactants, can increase their hydrophobicity, thus significantly improving their adsorption capacity for organic, non-ionic, or low-polarity pollutants (Moyo, Nhlapo, & Focke, 2008; Zhang *et al.*, 2019). Table 1 summarizes some studies on the removal capacities of several organic pollutants using different LDH-based adsorbents, with surfactants incorporated as interlayer anions.

Most research on the removal of organic pollutants using surfactant-modified LDH materials has focused on Mg-Al as cations and synthetic surfactants as interlayer anions. In the present study, we investigate the use of Ca-Al cations, which have been less extensively studied, along with food-grade surfactants sodium palmitate and sodium stearate as interlayer anions. Both surfactants are derived from natural sources and are suitable for human consumption, minimizing the toxicity risks associated with these compounds in potential water treatment applications.

Table 1. Removal capacities of organic pollutants by inorganic LDHs and surfactant-modified LDH-based adsorbents.

Pollutant	Cations	Interlayer anion	Removal capacity		Reference
			Inorganic LDH	Modified LDH	
Carbetamide	Mg-Al	DDS	0 mmol g^{-1}	0.9 mmol g^{-1}	Bruna *et al*., (2006)
Metamitron	Mg-Al	DDS	0.05 mmol g^{-1}	0.48 mmol g^{-1}	Bruna *et al*., 2006
Naphtalene	Mg-Fe	DDS	0.5 mg g^{-1}	2 mg g^{-1}	Ruan *et al*., 2013
Nitrobenzene	Mg-Fe	DDS	2.5 mg g^{-1}	7 mg g^{-1}	Ruan *et al*., 2013
Acetophenone	Mg-Fe	DDS	1.5 mg g^{-1}	3 mg g^{-1}	Ruan *et al*., 2013
Aniline	Mg-Fe	DDS	1.3 mg g^{-1}	2.1 mg g^{-1}	Ruan *et al*., 2013
2,4,5-Trichlorophenol	Mg-Al	SDBS	25 mg g^{-1}	150 mg g^{-1}	Zaghouan-Boudiaf *et al*., 2011
1,2,4-Trichlorobenzene	Mg-Al	SOBS	0 mg g^{-1}	2.2 mg g^{-1}	You *et al*., 2002
1,1,1- Trichloroethane	Mg-Al	SOBS	0 mg g^{-1}	4 mg g^{-1}	You *et al*., 2002
1,2,4-Trichlorobenzene	Mg-Al	SOS	0 mg g^{-1}	2 mg g^{-1}	You *et al*., 2002
1,1,1-Trichloroethane	Mg-Al	SOS	0 mg g^{-1}	2.5 mg g^{-1}	You *et al*., 2002
Methylene blue	Co-Al	Rhamnolipid	ND	54.01 mg g^{-1}	Kheradmand *et al*., 2022
Reactive orange 16	Co-Al	Rhamnolipid	ND	53.04 mg g^{-1}	Kheradmand *et al*., 2022

ND (No data)

Table 2 Designation of the synthesized LDH materials.

Sample name	Intercalated surfactant	Surfactant concentration
CaAl-LDH	-	-
LDH-SS1	Sodium stearate	0.0001 mol L^{-1}
LDH-SS2	Sodium stearate	0.001 mol L^{-1}
LDH-SS3	Sodium stearate	0.005 mol L^{-1}
LDH-SS4	Sodium stearate	0.01 mol L^{-1}
LDH-SS5	Sodium stearate	0.02 mol L^{-1}
LDH-PS1	Sodium palmitate	0.0001 mol L^{-1}
LDH-PS2	Sodium palmitate	0.001 mol L^{-1}
LDH-PS3	Sodium palmitate	0.005 mol L^{-1}
LDH-PS4	Sodium palmitate	0.01 mol L^{-1}
LDH-PS5	Sodium palmitate	0.02 mol L^{-1}

Moreover, sodium palmitate and sodium stearate are safe ingredients with advantageous properties used as surfactants in the manufacture of a wide range of products such as food, cosmetics and pharmaceuticals. Their safety profiles have been extensively evaluated, ensuring compliance with international standards and regulations; both compounds are recognized as safe for consumption by regulatory agencies such as the U.S. Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA) (Burnett, 2019; Saraswat, 2023).

Additionally, sodium palmitate and sodium stearate exhibit compatibility with a wide range of compounds and processing conditions as they function effectively across various pH, temperature, and other parameters, making them versatile for diverse applications (NCBI, 2024c, 2024d). These characteristics make SS and PS interesting surfactants for LDH modification to potentially facilitate their use in treating polluted water while minimizing the risk of toxicity associated with the adsorbent material.

In the present work, modified CaAl-LDH materials were synthesized by the co-precipitation method with anionic surfactants sodium stearate (SS) and sodium palmitate (PS) at different concentrations as interlayer anions. The LDHs were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS). The inorganic CaAl-LDH and the modified LDHs were compared for the removal of non-ionic pesticides carbaryl and imidacloprid from aqueous solutions.

2 Materials and methods

2.1 Synthesis of the LDH materials

CaAl-LDH was synthesized by the coprecipitation method according to Saha *et al.* (2018), by dissolving 32 mmol of $Ca(NO_3)_2{\cdot}4H_2O$ and 16 mmol of $Al(NO_3)_3{\cdot}9H_2O$ in 250 mL of deionized water with constant stirring under N_2 atmosphere. The pH of

the solution was adjusted to 8.5 by dropwise addition of 0.5 mol L^{-1} NaOH solution to obtain a white gelatinous suspension. The gel was allowed to age for 24 hours at room temperature, then it was centrifuged at 3500 rpm for 5 minutes and washed five times with deionized water to separate the precipitate. Finally, the obtained product was dried at 80°C for 12 h.

The modified LDH materials were synthesized by the coprecipitation method under N_2 atmosphere. 16 mmol of $Al(NO_3)_3{\cdot}9H_2O$ and 32 mmol of $Ca(NO_3)_3{\cdot}4H_2O$ were dissolved in 250 mL of an aqueous solution containing the surfactants SS or PS, both provided by Sigma-Aldrich, at 5 different concentrations. The following steps were the same as in CaAl-LDH synthesis procedure. Table 2 shows the prepared materials with the sample designations.

2.2 Characterization techniques

The LDH materials were analyzed using X-ray diffraction (XRD) with an Empyrean DY-2516 diffractometer equipped with CuKα irradiation source (λ= 1.5418 Å). All samples were scanned in the 2θ range 4°-60°, with a step size of 0.01°. XRD data was analyzed using Panalytical High Score Plus software. The basal spacing was calculated from the peak arising at the (002) plane of each sample according to equation 1 (Bragg´s equation); where, d is the interlayer distance (Å), λ is the wavelength of the CuKα radiation (1.5418 Å), θ is the diffraction angle and n is the diffraction order.

$$n\lambda = 2d\sin\theta \tag{1}$$

The crystallite size and lattice strain of the LDH materials were determined from the (002) reflection of each sample using the Scherrer equation:

$$\text{Crystallite size} = \frac{K\lambda}{\beta\cos\theta} \tag{2}$$

$$\text{Lattice strain} = \frac{\beta}{4\tan\theta} \tag{3}$$

Where K is the Scherrer constant, β is the full width at half maximum (fwhm), and θ is the diffraction angle.

The particle morphology of the LDH materials was analyzed using a Hitachi SU-8230 field emission scanning electron microscope (FESEM). Additionally, the elemental composition of the samples was determined through energy dispersive spectroscopy (EDS) attached to the FESEM. Prior to analysis, the samples were coated with platinum (Pt) under argon gas using a Q150T sputter coater.

2.3 Pesticide removal from aqueous solution

Pure analytical carbaryl (naphthalen-1-yl *N*-methylcarbamate) and imidacloprid ((*NE*)-*N*-[1-[(6-chloropyridin-3-yl)methyl]imidazolidin-2-ylidene]nitramide) were supplied by Sigma-Aldrich.

Elimination of carbaryl and imidacloprid from aqueous solutions, both at an initial concentration of 50 mg L^{-1} were studied separately. Pesticide removal by the modified materials was compared to that of the unmodified inorganic form of the LDH. Pesticide solutions without adsorbents were used as controls to ensure that pesticide concentrations remained constant over time.

Pesticide concentrations were quantified using a Cary 60 UV-Vis Spectrophotometer by measuring absorbance at λ=280 nm for carbaryl and λ=270 nm for imidacloprid. Calibration curves were first performed showing good linearity (R^2=0.988 for carbaryl and R^2=0.984 for imidacloprid) from 5 mg L^{-1} to 80 mg L^{-1}.

Eleven flasks, each containing 50 mL of carbaryl aqueous solution at a concentration of 50 mg L^{-1} were prepared by adding 0.25 g of each LDH material separately. Reactors were kept under constant magnetic stirring. Aliquots of the mixtures were sampled at different times for 72 h and centrifuged at 3500 rpm for 10 minutes to remove the adsorbent material and the retained pesticide. The supernatant was then analyzed by UV-vis absorbance to measure the pesticide concentration remaining free in solution. The same procedure was repeated to study imidacloprid elimination by the LDH materials. All experimental runs were performed in triplicate for accuracy and reproducibility.

Pesticide removal was calculated by the following equation:

$$qt = \frac{(C_0 - C_t)\cdot V}{m} \tag{4}$$

Where qt is the amount of adsorbed pesticide at time t (mg g^{-1}), V is the volume of the solution (L), C_0 and C_t are the initial and at time t pesticide concentration respectively (mg L^{-1}) and m is the mass of the adsorbent (g).

3 Results and discussion

3.1 Characterization of the LDH materials

3.1.1 XRD patterns

The powder X-ray diffraction (XRD) pattern of CaAl-LDH, LDH-PS4 and LDH-SS5 are shown in Fig.2. The characterization figures focus on the modified LDH samples, LDH-PS4 and LDH-SS5, as they demonstrate better overall performance in pesticide removal, as discussed later in this work.

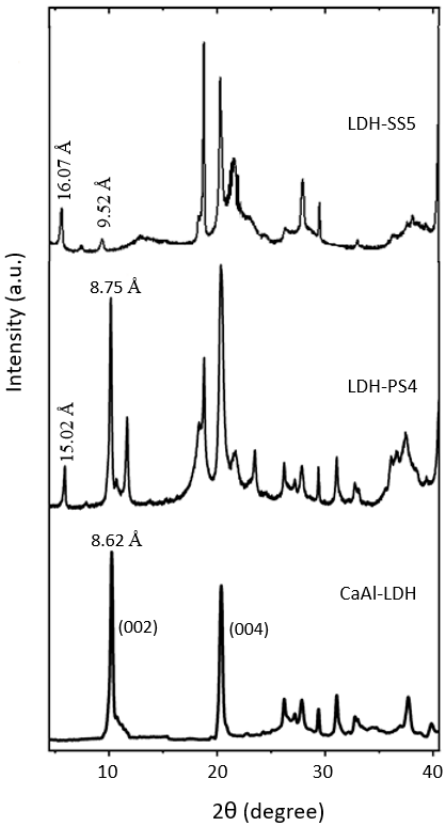

Fig. 2 XRD pattern of CaAl-LDH, LDH-PS4 and LDH-SS5.

Table 3. The basal spacing at the (002) diffraction peaks in the XRD patterns of the LDH materials.

Sample	Basal spacing (Å)
CaAl-LDH	8.62
LDH-PS4	8.75
LDH-PS5	9.05
LDH-SS4	9.52
LDH-SS5	9.62

The basal spacing (d_{002}) of 8.62 Å in the inorganic material corresponds to the (002) diffraction peak of CaAl-LDH (JCPDS 04-012-4448) in the database of the International Center for Diffraction Data (ICDD) with a chemical formula of $Ca_2Al(NO_3)(OH)_6(H_2O)_2$. This confirms the main phase of CaAl-LDH with NO_3^- interlayer anion and a well-formed crystalline layered structure.

Meanwhile, the 002 peaks of LDH-PS4 and LDH-SS5, modified with PS concentration of 0.01 mol L^{-1}, and SS concentration of 0.02 mol L^{-1} respectively, have an increase in the basal spacing from 8.62 Å in CaAl-LDH to 8.75 Å in LDH-PS4 and 9.52 Å in LDH-SS5. This indicates an increase in the interlayer spacing of the modified LDHs achieved by a successful surfactant intercalation.

Table 4 Crystallite size and lattice strain of LDH materials determined by the Scherrer formula.

Product	Crystallite size (nm)	Lattice strain (%)
CaAl-LDH	31.21	0.00563
LDH-PS4	30.16	0.01301
LDH-SS5	39.69	0.01230

Additionally, sample LDH-PS4 exhibits strong reflections for the 001 and 002 diffraction planes, indexed for layered clays, indicating a well-crystallized phase and a good double-layer structure similar to the inorganic LDH (Saha *et al.,* 2018). Moreover, a new diffraction peak is observed for both modified LDHs, with d-spacing of 15.02 Å in LDH-PS4 and 16.07 Å in LDH-SS5. This suggests an important change in the layered material structure due to the intercalation of organic molecules, which produce various forms of supramolecular arrangements in the LDH interlayer (Zhang *et al.,* 2012). Layered lattices can adapt to the geometry of the inserted compound by adjustment of the interlayer separation (Szekeres *et al.,* 2005).

Overall, at higher surfactant concentrations of 0.01 mol L^{-1} and 0.02 mol L^{-1} used in the LDH modification, the 002 peak exhibit an increase in basal spacing, and a well-formed double-layered structure. However, at lower concentrations, the intensity of the 002 reflection greatly decreased, suggesting notable structural changes and reduced crystallinity. Table 3 presents the basal spacing at the 002 reflection for LDH materials modified with higher surfactant concentrations.

Calculated by the Scherrer formula (Eq. 2 and 3), Table 4 shows the crystallite size and lattice strain of CaAl-LDH, LDH-PS4 and LDH-SS5. The inorganic LDH and the LDH modified with PS exhibit similar crystallite sizes. In contrast, the LDH modified with SS shows a slightly increased crystallite size. Additionally, microstrain increases following surfactant modification.

3.1.2 Morphology

Figure 3 exhibits the FESEM images of CaAl-LDH (a), LDH-SS5 (b) and LDH-PS4 (c, d). Figure 3a shows the typical "sand rose" arrangement of LDH materials (Adachi-Pagano, Forano & Besse, 2000). After surfactant modification, samples LDH-PS4 and LDH-SS5 are comprised of flake-like crystals, as shown in Figures 3b, 3c and 3d. The crystalline particles have a few nm thicknesses and a lateral distance of the order of μm which is the characteristic feature of layered materials (Nhlapo *et al.*, 2007; Shamitha, Mahendran & Anandhan, 2019). Aditonally, LDH-SS5 exhibits a slightly larger particle size than LDH-PS4.

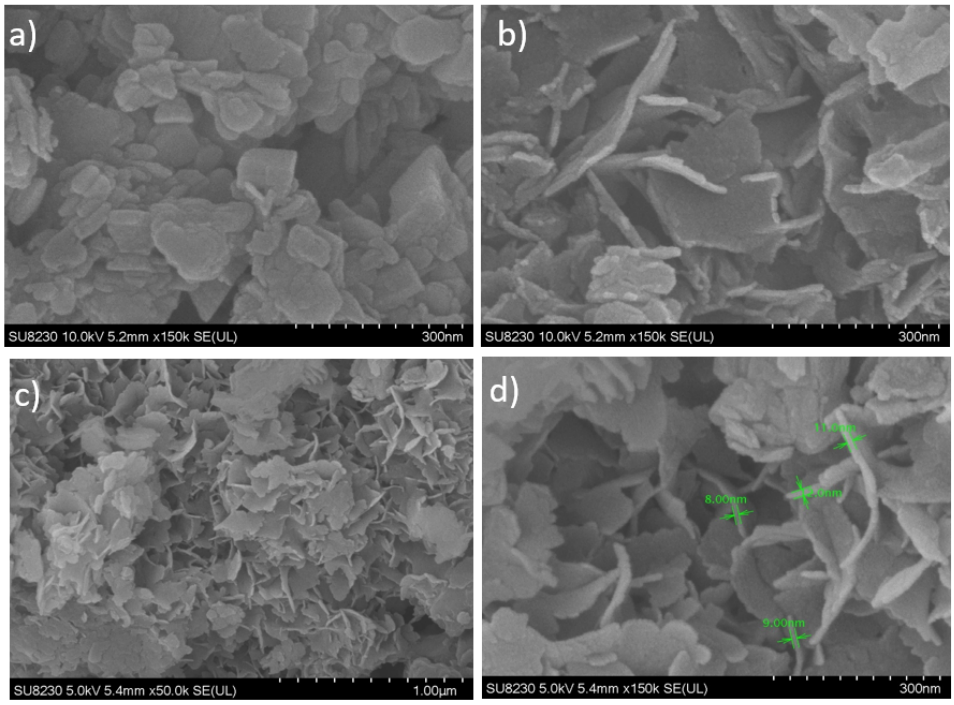

Fig. 3 FESEM images show: a) the "sand rose" morphology of CaAl-LDH; b) the flake-like morphology of LDH-SS4; and c), d) the flake-like morphology of LDH-PS4 crystallites at different magnifications.

3.1.3 Elemental composition

The EDS analysis of LDH-PS4 is shown in Figure 4, comprising the component elements of Ca, Al, O, and C. Figures 4a and 4b respectively show a homogeneous distribution of Al and Ca in the sample, confirming the presence of the modified LDH. In addition, C and O signals occurring in the EDS spectra are due to the insertion of the organic surfactant PS ($C_{16}H_{31}NaO_2$) into the LDH structure. The composition of LDH-SS5, consisting of Ca, Al, O and C was also confirmed by EDS analysis.

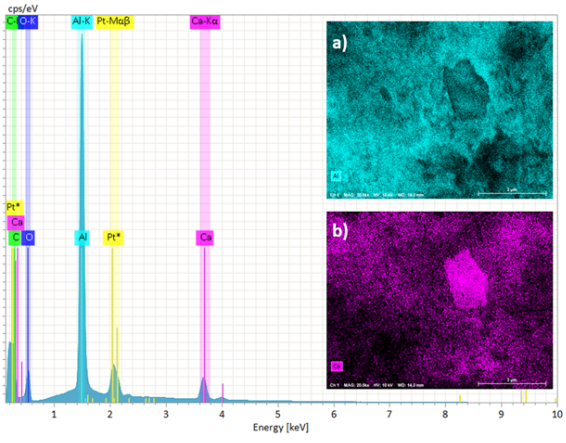

Fig. 4 Energy dispersive spectroscopy analysis (EDS) of sample LDH-PS4 showing the component elements of Al, Ca, O and C. Images a) and b) show the elemental distribution of Al and Ca, respectively.

3.2 Pesticide removal from aqueous solution

As shown in Figure 5, each one of the synthesized LDH based materials was able to remove a determined amount of carbaryl from water compared to the control. Sample LDH-PS4 had the highest removal efficiency of 67.08% in 24 h (Fig. 8), with carbaryl concentration decreasing from 50 mg L^{-1} to 16.4 mg L^{-1} in 72h. On the other hand, sample LDH-SS4 had the lowest removal efficiency of 21.76% in 24 h with carbaryl concentration in solution decreasing from 50 mg L^{-1} to 31.86 mg L^{-1} in 72h. Sample CaAl-LDH had a removal efficiency of carbaryl of 22.32% in 24h, meaning that after modification of this material with PS at a concentration of 0.01 mol L^{-1}, carbaryl removal efficiency was improved by 300%.

Figure 6 illustrates that each of the synthesized LDH-based materials removed a certain amount of imidacloprid from water compared to the control, although to a lesser degree than carbaryl. Sample LDH-PS4 had the highest removal efficiency of 23.9% in 24 h and, imidacloprid concentration was decreased from 50 mg L^{-1} to 24.45 mg L^{-1} in 72h (Fig. 8). Meanwhile, sample LDH-PS2 had the lowest removal efficiency of only 4.42% in 24 h and imidacloprid concentration decreased from 50 mg L^{-1} to 47.52 mg L^{-1} in 72h. Sample CaAl-LDH had a removal efficiency of imidacloprid of 7.84% in 24h, meaning that after modification of this material with PS at a concentration of 0.01 mol L^{-1}, imidacloprid removal efficiency was improved by 304%.

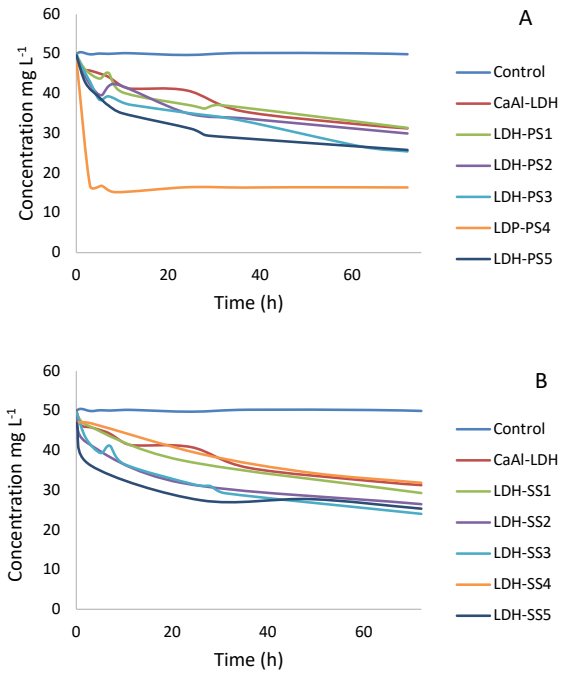

Fig. 5 Carbaryl removal over time by A) LDH materials modified with PS and B) LDH materials modified with SS.

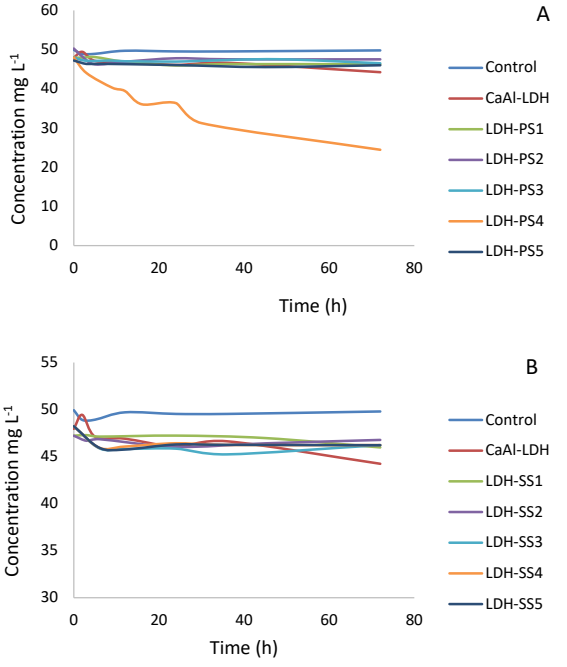

Fig. 6 Imidacloprid removal over time by A) LDH materials modified with PS and B) LDH materials modified with SS.

The effect of contact time on the amount of carbaryl and imidacloprid adsorbed by every LDH material was evaluated at an initial pesticide concentration of 50 mg L^{-1} as shown in Figure 7. The pseudo-first-order and pseudo-second-order kinetic models were evaluated. The agreement between the experimental data and the model-predicted values was determined by means of the correlation coefficients R^2. The experimental uptake values ($q_{e,exp}$) and the kinetic parameters for the adsorption of carbaryl and imidacloprid onto each LDH material are presented in Tables 5 and 6, respectively.

The highest pesticide uptake was achieved by LDH-PS4, with $q_{e,exp}$ = 6.72 mg of carbaryl per gram of adsorbent (Fig. 7A). The adsorption of carbaryl by LDH-PS4 occurred quickly; the maximum adsorption of the pollutant was achieved within 2h after the beginning of the experiments.

The solid-liquid adsorption process comprises three steps: external transfer, intraparticle transfer, and surface adsorption via physical or chemical mechanisms. Pseudo-first-order kinetics, primarily involving the first two steps, assumes a high initial adsorbate concentration relative to available adsorption sites and describes mass transfer or physisorption. In contrast, pseudo-second-order kinetics involves all three steps, incorporating chemisorption and assuming the initial adsorbate concentration is comparable to the available adsorption sites (Benjelloun *et al.*, 2021; Azizian, 2004).

For the adsorption of carbaryl by LDH-PS4, both models provided a good fit to the experimental data (Table 5). Additionally, the calculated value q_e closely matched the experimental value $q_{e,exp}$. Moreover, k_1 and k_2 values are higher for this sample due to the fast adsorption rate of carbaryl, which allows it to reach equilibrium quickly.

Regarding the adsorption of imidacloprid, the highest pesticide uptake was also achieved by LDH-PS4, with $q_{e,exp}$ = 2.73 mg of imidacloprid per gram of adsorbent (Fig. 7C). The R^2 values, indicate that the pseudo-second order model provides a better fit. Similarly, the calculated value q_e, is in good agreement with the experimental $q_{e,exp}$ value (Table 6). For instance, Jain et al. (2017) reported that the adsorption kinetics of imidacloprid on organobentonites had a better fit to the pseudo-second-order model as well.

For the LDHs modified with SS, the sample with the best overall removal capacity is LDH-SS5, achieving a $q_{e,exp}$ value of 4.51 mg g^{-1} for carbaryl and 0.75 mg g^{-1} for imidacloprid. Although LDH-SS5 did not exhibit the highest uptake capacity for imidacloprid, it performed better in terms of the quicker time to reach equilibrium, which is crucial since fast sorption rates are preferable for the practical application of organo-LDHs in polluted water treatment at water treatment sites (Zhang *et al.*, 2019).

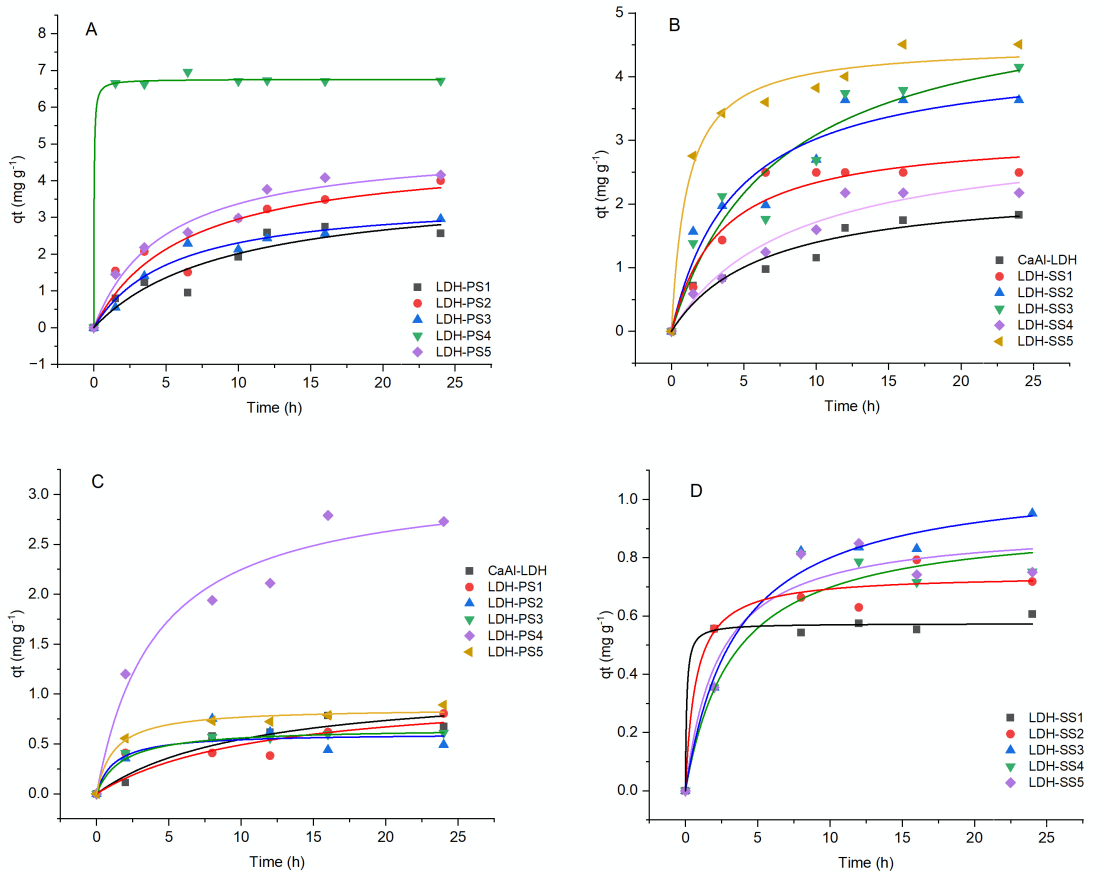

Fig. 7 Adsorption kinetics of A) carbaryl by sodium palmitate modified CaAl-LDHs; B) carbaryl by sodium stearate modified CaAl-LDHs; C) imidacloprid by sodium palmitate modified CaAl-LDHs and D) imidacloprid by sodium stearate modified CaAl-LDHs.

Table 5 Kinetic parameters for carbaryl adsorption.

		Pseudo-first-order			Pseudo-second-order		
Product	$q_{e,exp}$	q_e	k_1	R^2	q_e	k_2	R^2
CaAl-LDH	1.83	2.09	0.096	0.946	2.28	0.068	0.924
LDH-SS1	2.50	2.76	0.169	0.929	3.11	0.095	0.945
LDH-SS2	3.63	3.99	0.125	0.925	4.36	0.051	0.917
LDH-SS3	3.74	4.81	0.090	0.919	5.35	0.025	0.908
LDH-SS4	2.18	2.66	0.092	0.936	3.14	0.038	0.959
LDH-SS5	4.51	4.29	0.287	0.976	4.50	0.202	0.981
LDH-PS1	2.59	2.92	0.119	0.887	3.88	0.027	0.884
LDH-PS2	3.23	3.95	0.140	0.861	4.79	0.033	0.883
LDH-PS3	2.44	2.80	0.188	0.969	3.55	0.051	0.971
LDH-PS4	6.72	6.74	2.88	0.998	6.77	6.127	0.998
LDH-PS5	3.77	4.11	0.183	0.956	5.01	0.041	0.976

q_e (mg g^{-1}); k_1 (min^{-1}); k_2 (g mg^{-1} min^{-1})

According to the results, the sorption efficiency of carbaryl and imidacloprid by the surfactant modified LDH materials does not increase linearly with respect to the concentrations of PS and SS utilized in the synthesis process, as depicted in Figure 8. Moreover, LDH-PS4 demonstrated the highest removal efficiency for both pesticides, achieving 67.08% for carbaryl and 23.9% for imidacloprid. On the other side, LDH-SS5 exhibited a significant removal efficiency for carbaryl at 45.08%, and a lower efficiency of 7.4% for imidacloprid.

Table 6 Kinetic parameters for imidacloprid adsorption.

Product	$q_{e,exp}$	Pseudo-first-order			Pseudo-second-order		
		q_e	k_1	R^2	q_e	k_2	R^2
CaAL-LDH	0.78	0.80	0.121	0.932	1.12	0.085	0.914
LDH-SS1	0.80	0.57	1.256	0.991	0.57	20.325	0.992
LDH-SS2	0.79	0.70	0.502	0.964	0.74	1.889	0.970
LDH-SS3	0.95	0.94	0.180	0.986	1.19	0.151	0.978
LDH-SS4	0.75	0.79	0.257	0.960	1.08	0.260	0.986
LDH-SS5	0.75	0.81	0.253	0.955	0.90	0.480	0.942
LDH-PS1	0.80	0.94	0.068	0.784	1.06	0.082	0.801
LDH-PS2	0.44	0.57	0.414	0.801	0.61	1.380	0.758
LDH-PS3	0.61	0.59	0.387	0.996	0.66	0.853	0.997
LDH-PS4	2.73	2.67	0.194	0.946	3.16	0.077	0.966
LDH-PS5	0.89	0.78	0.601	0.966	0.86	0.969	0.981

q_e (mg g^{-1}); k_1 (min^{-1}); k_2 (g mg^{-1} min^{-1})

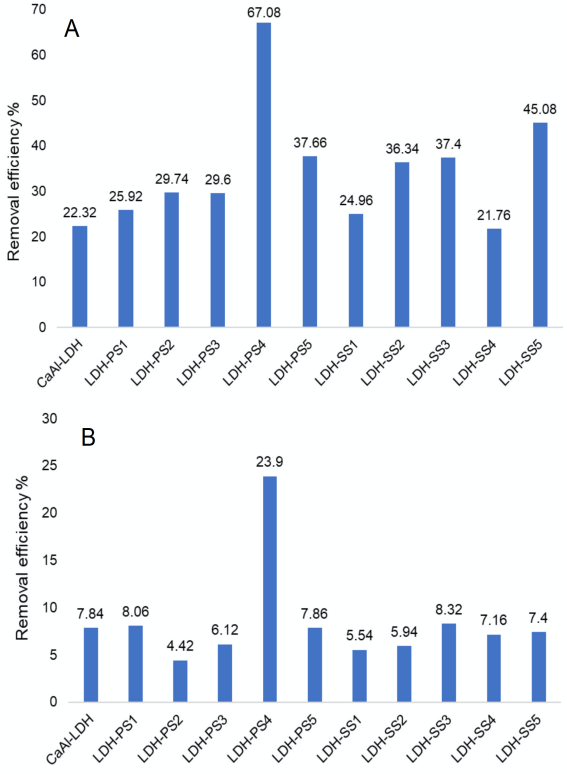

Fig. 8 Pesticide removal efficiency by the LDH materials in 24h. A) Carbaryl; B) Imidacloprid.

Furthermore, LDH-SS4 exhibited the lowest removal efficiency of carbaryl. As shown in Table 3, its basal spacing (d_{002}) had the largest increase, from 8.62 Å to 9.62 Å, compared to 8.75 Å in LDH-PS4. Similarly, LDH-SS5 and LDH-PS5, which also exhibited larger basal spacing at the (002) reflection than LDH-PS4, had lower removal efficiencies for both pesticides than LDH-PS4. This suggests that at higher concentration of surfactant used in the synthesis, an excessive interlayer space was produced, creating an inadequate space for the pollutant molecules to be retained, thus decreasing the sorption capacity of the material. Furthermore, an excessive concentration of surfactant molecules may occupy a disproportionate number of adsorption sites, thereby reducing the material's overall efficiency in removing pollutants.

For instance, Zhang *et al*. (2019) found that with increasingly high surfactant concentration (sodium dodecyl sulfonate), the laminar structure of a modified MgAl-LDH gradually disappeared. In addition, the surface areas of the material decreased due to the hindrance of the exposed surface of the LDH by the incorporated surfactant. Even though, in this study, the authors determined that the sorption efficiency of phenanthrene and pyrene by the modified LDHs increased almost linearly with the increase of SDS concentration used in the LDH modification. However, they concluded that partitioning dominated the sorption process rather than adsorption.

Meanwhile, LDHs modified with PS rather than SS demonstrated overall better performance in the adsorption process. LDH-SS5 exhibited a larger crystallite size and greater basal spacing compared to LDH-PS4. This indicates that the nature of the intercalated surfactant plays a crucial role in the adsorption capacity of the material. In this case, the larger molecular size of SS, due to its greater number of carbon atoms in the alkyl chain, results in a more extended molecular structure, which can negatively affect adsorption efficiency.

Balayeva *et al*. (2019), also obtained a wide basal spacing, increasing from 7.36 Å to 25.21 Å, by intercalating SS at a concentration of 0.3% into CoCr-LDH, due to the solubility of this surfactant in water. On the other hand, Zhang *et al*. (2012) indicated that the interlayer space in CaAl-LDH increased with the intercalation of sodium dodecyl sulfate, and at higher concentrations of the surfactant the crystalline form of the LDH was reduced and a different layered material was formed.

Conversely, LDH-PS4 has a similar crystallite size to that of CaAl-LDH (table 4). Other authors have

reported a decrease in the removal of pollutants with the increase of the particle size of LDHs due to a decreased surface area (Kim, *et al.,* 2022), and to a site availability diminution (Rojas, 2016).

Moreover, at lower surfactant concentrations used in the LDHs modification, reduced pesticide removal efficiencies were observed. In the case of LDH-PS2, the uptake of imidacloprid was even lower than that of the unmodified CaAl-LDH. This can be attributed to the lower crystallinity achieved at reduced surfactant concentrations, indicating that crystallinity plays an important role in determining the sorption capacity of the material.

The sorption capacity of LDH materials depends on factors such as the interlayer space, surface area, hydrophobicity, crystalline lattice, and supramolecular structure, among others. These properties are significantly influenced by the chemical nature and concentration of the interlayer anion (Zaghouane-Boudiafa *et al*, 2011; Chubar *et al*., 2017).

Clay particles have two different interactions with surfactants; the first one commonly referred to as "adsorption' ', which involves the accumulation of the surfactant on the external surfaces of the clay particles; and the second one being ' 'intercalation' ', in which the surfactant molecules are reversibly incorporated inside the interlayer space (Moyo, Nhlapo & Focke, 2008; Ruan *et al*., 2013).

The findings indicate that a PS concentration of 0.01 mol L^{-1} and a SS concentration of 0.02 mol L^{-1} are optimal for the modification of CaAl-LDH, as they facilitate effective intercalation of the surfactant within the interlayer space, and result in enhanced pesticide removal performance. The modification increased the basal spacing and enhanced the hydrophobicity of the material, allowing a better intercalation of non-polar pesticides carbaryl and imidacloprid and improving the sorption of these pollutants.

The above agrees with the two most common mechanisms reported for organic pollutant sorption by LDHs which are external surface adsorption and interlayer anion exchange (Johnston *et al*., 2021). Anion exchange is a result of the replacement of the interlayer anion with the pollutant molecules present in the aqueous medium. On the other hand, surface adsorption involves the adhesion of the targeted pollutants to the surface of the LDH primarily through electrostatic interactions, which promotes the formation of a molecular or atomic film (Hashim *et al*., 2016; Zhang *et al*., 2012). Additionally, hydrophobic interactions take place between the anionic surfactant intercalated in the interlayer space and the pollutants (Zaghouane-Boudiafa *et al.*, 2011).

Moreover, the differences in the removal efficiency of carbaryl and imidacloprid by the modified LDHs is since the adsorption capacity of LDHs also depends on the type and characteristics of the contaminant to be retained (Bruna *et al.*, 2006; Ruan *et al.,* 2013; Zhang *et al*., 2012).

Carbaryl is a non-ionic organic compound with bipolar characteristics due to its structure consisting of a lipophilic naphthyl moiety and a hydrophilic carbonyl group. This pesticide has a biplanar structure and the thickness of the molecule in the solid-state conformation is 6.54 Å (NCBI, 2023a; Sandoz et al., 2000). Being the naphthalene ring the lipophilic part of the molecule, LDH-PS4 and LDH-SS5 have the adequate interlayer space and hydrophobicity to greatly increase carbaryl adsorption compared to the unmodified LDH.

In a similar way, in imidacloprid structure, the imidazolidine nitrogen is partially positively charged and can interact with the anions in LDH-PS4, while the pyridyl part has the function to improve molecular lipophilicity (Kagabu & Matsuno, 1997; NCBI, 2023b). The lower removal efficiency of this pesticide in the LDH materials could be attributed to the size and structure of imidacloprid which contains two heterocyclic rings.

Bruna *et al*. (2006) also reported different removal efficiencies by dodecyl sulfate modified LDH, owing to the differences in the molecular structures of low polarity pesticides carbetamide and metamitron.

Conversely, the rest of the synthesized samples exhibited lower efficiency in removing both pesticides compared to LDH-PS4 and LDH-SS5. This indicates that the surfactant concentrations used in the synthesis process were less adequate. As a result, carbaryl and imidacloprid were less likely to be included within the interlayer space, and the sorption capacity of the materials was less effective.

Furthermore, the adsorption of carbaryl and imidacloprid on LDH materials has not been extensively studied. Therefore, Table 7 compares the adsorption capacities of LDH-PS4 and LDH-SS5 for carbaryl and imidacloprid with other clay and mineral-based adsorbents reported in the literature.

The results of this study reveal that both LDH-PS4 and LDH-SS5 are effective for carbaryl removal from water, with LDH-PS4 also demonstrating suitability for imidacloprid removal.

Future research will focus on detailed adsorption studies on these materials to achieve a better understanding of the sorption mechanisms and to determine their applications as adsorbents for removing carbaryl and imidacloprid from contaminated waters.

Conclusions

CaAl–LDHs containing SS and PS as interlayer anions were synthesized by the co-precipitation method at

Table 7 Adsorption of carbaryl and imidacloprid by LDH-PS4 and LDH-SS5 compared to other clay and mineral adsorbents.

Adsorbent	Pesticide	Adsorption capacity (mg g^{-1})	Reference
LDH-PS4	Carbaryl	6.72	This work
LDH-SS5	Carbaryl	4.51	This work
Montmorillonite	Carbaryl	3.7	Chen *et al*., 2009
Kaolinite	Carbaryl	1.6	Chen *et al*., 2009
Goethite	Carbaryl	2.1	Chen *et al*., 2009
Bentonite	Carbaryl	0.145	Eldurini *et al*., 2010
Natural clay	Carbaryl	3.25	Ouardi *et al*., 2013
Smectite	Carbaryl	3.0	Arroyo *et al*., 2004
LDH-PS4	Imidacloprid	2.73	This work
LDH-SS5	Imidacloprid	0.75	This work
Montmorillonite composite	Imidacloprid	2.0	Narayanan *et al*., 2017
Zeolite Y	Imidacloprid	9.89	De Smedt *et al*., 2015
Bentonite	Imidacloprid	0.18	Jain *et al*., 2017
Organobentonite	Imidacloprid	0.71	Jain *et al*., 2017
Micelle-clay complex	Imidacloprid	11.76	Qurie *et al*., 2021

different surfactant concentrations. The sorption efficiency of carbaryl and imidacloprid by the surfactant modified LDHs does not increase linearly with the concentration of PS and SS used in the synthesis process.

The morphological and interlayer characteristics of CaAl-LDH were modified using natural food-grade surfactants SS and PS, resulting in the development of novel materials; LDH-PS4 with enhanced capabilities for the adsorption of carbaryl and imidacloprid, and LDH-SS5 presenting a significant capacity for carbaryl removal.

CaAl-LDH modified with PS at a concentration of 0.01 mol L^{-1} (LDH-PS4) had the best removal efficiency of carbaryl and imidacloprid from aqueous solutions. This material has an adequate increased interlayer space, a well-crystallized phase, a good double layered structure, and hydrophobic properties, improving its sorption capabilities about three times for both pesticides.

Nevertheless, detailed adsorption studies on these materials are required to achieve a better understanding of the sorption mechanisms and to determine their applications as adsorbents of non-ionic pesticides from contaminated waters.

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