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ORIGINAL PAPER

Insights into Glyphosate Adsorption in Aqueous Solutions Using Zn-Al Layered Double Oxide

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Abstract Contamination of surface and groundwater with glyphosate, used widely on crops to control weeds, can cause severe environmental damage. Processes for glyphosate removal from water bodies have been developed, but few are effective and all are expensive. This objective of the present study was to investigate the use of a layered double oxide as a potentially effective and inexpensive material to remove glyphosate from water. Equilibrium, kinetics, and adsorption mechanisms were evaluated, in addition to the effects of competing anions and temperature on glyphosate adsorption. Up to 95% of glyphosate was removed from a synthetic solution in 50 min by Zn_2Al-LDO (layered double oxide in Zn/Al ratio of 2:1) at pH 10. The adsorption isotherms were type L and the Langmuir model best fitted the experimental data, with a q_{max} value of 191.96 μg mg^{-1} at 25°C. The XRD pattern did not support the hypothesis of intercalation of glyphosate anions, whereas Fourier-transform infrared and solid-state ^{13}C and ^{31}P magic angle spinning nuclear magnetic resonance confirmed the adsorption of glyphosate anions on the Zn_2Al-LDO surface, through carboxylate and phosphonate moiety interactions with end-on and side-on modes. The degree of removal of glyphosate increased with increasing temperature and decreased with increasing concentration of competing anions, with carbonate anions having the most prominent effect on the inhibition of glyphosate adsorption. The adsorption kinetics fitted a pseudo-first order law. Moreover, the intraparticle diffusion model suggested that the adsorption process depends on the formation and thickness of the film at the solution/solid interface.

Keywords Adsorption mechanism · Anionic competition · Equilibrium · Kinetic

Introduction

Glyphosate, sold under the 'Roundup' brand, is the world's most widely used systemic, post-emergent, non-selective, and broad-spectrum herbicide (Valle et al., 2019). The effectiveness of glyophosate is ascribed to the high efficiency of inhibiting 5-enolpyruvylshikimate-3-phosphate, a very important enzyme for the development of plants (Wang et al., 2012). Glyphosate is well known to have the ability to form complexes with transition metals in aqueous solutions and also shows strong affinity for

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the surfaces of aluminum, iron, and copper oxides, among others (Sheals et al., 2002). In addition to interacting with the inorganic matrix of the soil, the compound can be adsorbed by various portions of organic matter that are also present in the soil (Barrett & McBride, 2006). These properties are important for the fate and rate of transport of glyphosate in the environment. Various physical processes, such as leaching and percolation, can carry glyphosate from the soil to aquatic environments due to its water solubility, causing the contamination of aquifers (Barrett & McBride, 2006). In addition, biodegradation processes can lead to the formation of aminomethylphosphonic acid, an important metabolite that has a longer half-life than glyphosate and contributes significantly to environmental contamination (Borggaard & Gimsing, 2008). Glyphosate contamination of food and water can also be associated with diseases. This compound can cause chronic kidney disease, diabetes, cancer, autism, depression, obesity, intestinal diseases, allergies, and celiac disease, among others (Duke, 2018). For these reasons, controlling glyphosate's negative effects is of great importance (Pompeo Queiroz et al., 2011).

Since conventional methods of water treatment do not effectively remove anionic pollutants, alternatives have been developed (Maroneze et al., 2014). The literature reports the use of various materials for glyphosate adsorption, such as biochar, activated carbon, industrial residues, and cationic clays (Herath et al., 2015; Hu et al., 2011; Khenifi et al., 2010). Layered double oxides (LDOs) and layered double hydroxides (LDHs) are also promising materials (Rives et al., 2014). However, only a few studies involving glyphosate and LDHs have been published, as described below.

LDHs are versatile solids and can be formed easily over a large range of pH levels and synthesized readily on a laboratory scale. These compounds are anionic clays that have a lamellar brucite-like structure, in which some sites of divalent cations are replaced by trivalent cations (Wu et al., 2011; Radha et al., 2014). Due to this substitution, a positive charge density is generated in the lamellae that must be compensated by anions. Water molecules are also present in order to ensure structural cohesion. LDHs have the general formula $[M^{2+}_{1+x}M^{3+}_{X}(OH)_2]^{x+}(A^{n-})_{\frac{x}{n}}.mH_2O$, where M^{2+} (Fe, Co, Cu, Ni or Zn) and M^{3+} (Al, Cr, Ga, Mn or Fe) are di- and trivalent cations, respectively; x is the molar ratio of $M^{2+}/(M^{2+}+M^{3+})$ in the range 0.2–0.33, and A^{n-} is an anion (Liu et al., 2016; Pachayappan & Kamath, 2019; Pan et al., 2019). Different organic or inorganic anions can be inserted into the structure of LDHs. If calcined at moderate temperatures, LDHs are converted into layered double oxides (LDOs). These solids have excellent adsorption capacity in comparison with non-calcined precursors because they have greater specific surface area (Abdellaoui et al., 2017; Extremera et al., 2012; Julianti et al., 2017; Kooli et al., 1997; Zubair et al., 2017). Hydrotalcites can be regenerated after thermal treatment. The reconstruction process can be achieved by immersing calcined hydrotalcite in a solution containing the anions to be intercalated through the so-called 'memory effect.' The regeneration property makes hydrotalcites promising for the adsorption process (Abdellaoui et al., 2017). The results of studies involving the adsorption of glyphosate by calcined Ca-Al and Mg-Al-LDH, in addition to Ni-Al-LDH and Mg-Al-LDH containing intercalated nitrate and chloride, have been reported (Khenifi et al., 2010; Li et al., 2005; Peng et al., 2021).

Because of the deleterious effects of glyphosate on humans and the environment, together with the possible adsorptive properties of layered double oxides (LDO), the present study was undertaken to analyze the application of the LDO Zn/Al 2:1 (hereafter referred to as Zn_2Al-LDO) for glyphosate adsorption. Equilibrium and adsorption kinetics were investigated in order to determine the maximum amount of glyphosate which can be adsorbed, the adsorption mechanism, in addition to evaluating the competition of different anions. A further objective was to obtain fundamental information about the resulting glyphosate adsorbed on the structure of Zn_2Al-LDO (hereafter referred to as Zn_2Al-LDO-gly), by employing powder X-ray diffraction (XRD), ^{13}C and ^{31}P solid-state nuclear magnetic resonance (SSNMR), and infrared spectroscopy methods.

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Materials and Methods

Materials

Reagents

All reagents ($ZnCl_2$, $AlCl_3.6H_2O$, $NaNO_3$, Na_2CO_3, NaH_2PO_4, NaCl, Na_2SO_4, Na_2MoO_4, NaOH. and ninhydrin, with 99% purity, and 37% HCl) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA) and used as received. Glyphosate was extracted and purified from the commercial herbicide, Roundup, from Bayer (Belford Roxo, Rio de Janeiro, Brazil) according to Hottes et al. (2021).

Characterization

The glyphosate was quantified according to the optimized Ruhemann colorimetric method (Hottes et al., 2021) and the absorbance was measured at 570 nm in glass cuvettes in a Shimadzu 1800 UV-Vis spectrophotometer (Barueri, São Paulo, Brazil),. The Fourier-transform infrared/attenuated total reflectance (FTIR/ATR) spectra were obtained using a Bruker Vertex 70 spectrometer (Atibaia, São Paulo, Brazil) from 400 to 4000 cm^{-1} using 64 scans at room atmosphere and temperature. The Mg/Al ratio was obtained by metal quantification using an Agilent SpectrAA 55B atomic absorption system (Barueri, São Paulo, Brazil). X-ray diffraction patterns were obtained using a Rigaku Ultima IV diffractometer with CuKα, 1.54 Å (Texas, USA), recorded between 5 and 90°2θ with 0.2°2θ steps. Solid-state $^{13}C\{^1H\}$ cross-polarization and $^{31}P\{^1H\}$ cross-polarization NMR spectra were collected at 400 MHz with a Bruker Avance II spectrometer, 9.4 T (Atibaia, São Paulo, Barzil), at operating frequencies of 168 and 100 MHz for ^{31}P and ^{13}C, respectively. Textural analysis (Brunauer Emmett Teller – BET – surface area and pore-size distribution) was performed using a ReoTerm BELSORP HP analyzer (Rio de Janeiro, Brazil). Thermogravimetric analysis (TGA–DTG) was carried out in locally produced synthetic air using a TA Instruments PCT-1A thermal analysis system (Delaware, New Castle, USA). In this analysis, 21-mg samples were heated at a 5°C min^{-1} rate from room temperature to 1000°C.

Methods

Zn_2Al-LDO Preparation

The layered double hydroxides with 2:1 Zn/Al ratio (Zn_2Al-LDH) were prepared by coprecipitation according to Aisawa et al. (2004). Briefly, 0.376 mol of $ZnCl_2$ and 0.188 mol of $AlCl_3.6H_2O$ were added to 250 mL of Milli-Q water, and the resulting solution was added slowly (1 mL min^{-1}) at room temperature and under vigorous stirring to 500 mL of a solution containing 0.9 mol of NaOH and 0.360 mol of Na_2CO_3. The pH of the solution was adjusted to 10 by slow addition of a 1 M NaOH solution, resulting in the formation of white precipitates. The precipitates were then aged for 18 h (65°C), filtered, and washed with water and oven dried for 24 h at 65°C. The Zn_2Al-LDO was obtained by calcining the Zn_2Al-LDH at 450°C for a duration of 4.5 h.

Adsorption Experiments

Adsorption of glyphosate on Zn_2Al-LDO was investigated in batch experiments in triplicate. Standard glyphosate solutions with initial concentrations of 10, 20, 40, 60, 80, 100, 120, 150, 200, 250, and 300 μg mL^{-1} were prepared by diluting the 500 μg mL^{-1} glyphosate stock solution with an appropriate amount of Milli-Q water. Then 25 mg of Zn_2Al-LDO was added to 50 mL of the respective glyphosate solutions in a series of 100 mL Erlenmeyer flasks The mixtures were stirred at 150 rpm. To determine the effect of temperature on adsorption, experiments were performed at 25, 35, and 45°C. After stirring, the solid was separated from the mixture by filtration. Residual glyphosate was determined in the filtrates by the optimized Ruhemann colorimetric method (Hottes et al., 2021). The adsorption capacity and adsorption percent of glyphosate on Zn_2Al-LDO were calculated using Eqs. 1 and 2, respectively:

$$q_e = \frac{(C_o - C_e).V}{m} \quad (1)$$

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

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where, C_o and C_e represent the initial and equilibrium concentrations of glyphosate, respectively (μg mL^{-1}); V denotes the volume of glyphosate solution used (mL); and m represents the mass of the LDO adsorbent (μg) (Rosset et al., 2020). All adsorption experiments were performed at least three times to achieve data accuracy and reproducibility. Adsorption isotherm models were applied to describe the fraction of adsorbate that was partitioned between liquid and solid phases at equilibrium. In this study, Langmuir, Freundlich, and Temkin models were adopted to evaluate the adsorption behavior of glyphosate by Zn_2Al-LDO. Non-linear and linearized equations were used to make appropriate adjustments. For the sake of clarity, non-linear equations (Tan & Hameed, 2017) are given as Langmuir (Eq. 3), Freundlich (Eq. 4), and Temkin (Eq. 5).

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^{1/n} \tag{4}$$

$$q_e = \frac{RT}{b} \ln(a_T C_e) \tag{5}$$

where, Q_{max} (μg mg^{-1}) is the maximum adsorption capacity associated with a monolayer formed over a solid surface, K_L is the equilibrium or Langmuir constant, C_e (μg.mL^{-1}) is the equilibrium concentration, q_e (μg mg^{-1}) is the amount of solute adsorbed at equilibrium, K_F is the Freundlich constant, $1/n$ is a constant related to site heterogeneity, a_T is the Temkin constant, b is a constant related to the heat of adsorption, T is temperature, and R is the universal gas constant (Freundlich, 1907; Langmuir, 1918; Tan & Hameed, 2017). For comparison purposes, the experimental adsorption data were also fitted using linearized equations related to the Langmuir, Freundlich, and Temkin models. These equations are presented in the supplementary material. In addition, the equilibrium data were submitted to χ^2 (chi-square) analysis according to Eq. 6 (Zhang et al., 2019).

$$\chi 2 = \sum \left(qe_{exp} - qe_{cal}\right)^2 / qe_{exp} \tag{6}$$

The kinetics of glyphosate adsorption by the Zn_2Al-LDO was studied using the adsorption capacity obtained from isotherm experiments. The glyphosate adsorption rate after various contact times was measured over the time range 5–200 min, with an initial glyphosate concentration of 300 μg mL^{-1}. The procedure was conducted as detailed in the adsorption isotherms, except that the temperature was controlled at 25 ± 1°C. To understand the glyphosate adsorption mechanism, experimental data were fitted to different kinetics models, corresponding to the pseudo-first order model (Eq. 7), pseudo-second order model (Eq. 8), and the Weber-Morris intraparticle diffusion model (Eq. 9):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{7}$$

$$q_t = \left(q_e^2 k_2 t\right) / \left(1 + q_e k_2 t\right) \tag{8}$$

$$q_t = K_{iff} t^{1/2} + C \tag{9}$$

where, k_1 is the pseudo-first order constant, k_2 is the pseudo-second order constant, K_{iff} is the intraparticle diffusion rate constant, C is a constant, Q_e is the maximum amount of glyphosate adsorbed (μg Mg^{-1}), and Q_t is the amount adsorbed (μg mg^{-1}) at time t (min) (Tan & Hameed, 2017).

Anionic Competition

To study the effect of anion concentration on glyphosate adsorption, 25 mg of Zn_2Al-LDO was left in contact with 50 mL of different solutions containing glyphosate at 200 μg mL^{-1} and different anions in various concentrations (10–400 μg mL^{-1}). The solutions were left in contact for 200 min and then were centrifuged and filtered using a Millipore 0.45 mm filter. Experiments were performed at pH 10 (±0.3) and room temperature (≈25°C) in triplicate.

Thermodynamic Parameters

The thermodynamic study was performed by reproducing the adsorption isotherm experiments with glyphosate solutions also at 35ºC and 45°C. The change in free energy of glyphosate adsorption ($\Delta G°$), change in entropy of adsorption ($\Delta S°$), and change in enthalpy of adsorption ($\Delta H°$) were calculated using Eqs. 10, 11, and 12, respectively (Tan & Hameed, 2017).

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$$\Delta G^{\circ} = -RT\ln K \quad (10)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (11)$$

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (12)$$

Results and Discussion

Characterization of Solids Before and After Glyphosate Adsorption

The Zn^{2+} and Al^{3+} contents obtained from the atomic absorption analysis were 29% and 15%, respectively, indicating an experimental Zn/Al ratio of 1.96. This value suggests that the experimental data were in agreement with the nominal mass data used in the experiment. Based on the percentages of cations, the following formula for the solid is proposed: $[Zn_{0.67}Al_{0.33}(OH_2)]^{0.33}(CO_3)_{0.165}$. Three mass-loss peaks were revealed by the thermograms obtained in an oxidizing atmosphere at 80°C, 170°C, and 230°C (Fig. 1) Such peaks between 25°C and 200°C are well known to indicate the loss of water molecules present in the extrinsic and intrinsic domains of the LDH structure. The peak recorded at 230°C suggests the beginning of the breakdown process of the lamellar structure and also the loss of carbonate present in the interlayer region. A wide and low-intensity peak was also observed in the region of 500°C, attributed to the decarbonation process of LDH (Montanari et al., 2010).

The powder XRD patterns for Zn_2Al-LDH, Zn_2Al-LDO, and Zn_2Al-LDO-gly (Fig. 2) were obtained to compare the structures of Zn_2Al-LDH and Zn_2Al-LDO and to map possible changes due to glyphosate adsorption (comparing Zn_2Al-LDO and Zn_2Al-LDO-gly). The positions of the main diffraction peaks of Zn_2Al-LDH ($d_{003} = 0.75$ nm) observed in the XRD pattern (Fig. 2) were in agreement with those predicted in the literature for LDH of the Zn-Al system containing carbonate anions in the interstices (Aisawa et al., 2004). The profile of the diffraction peaks also indicated the high crystallinity of the solid, as well as its structural organization. The crystallite size obtained using the Scherrer equation and the reflection peak (003) was 0.34 nm. A similar value (0.33 nm) was observed by Aisawa et al. (2004) while studying the intercalation of amino acids by LDH of the Zn-Al system. Calcination at 450°C led to the collapse of the precursor structure, so observing the

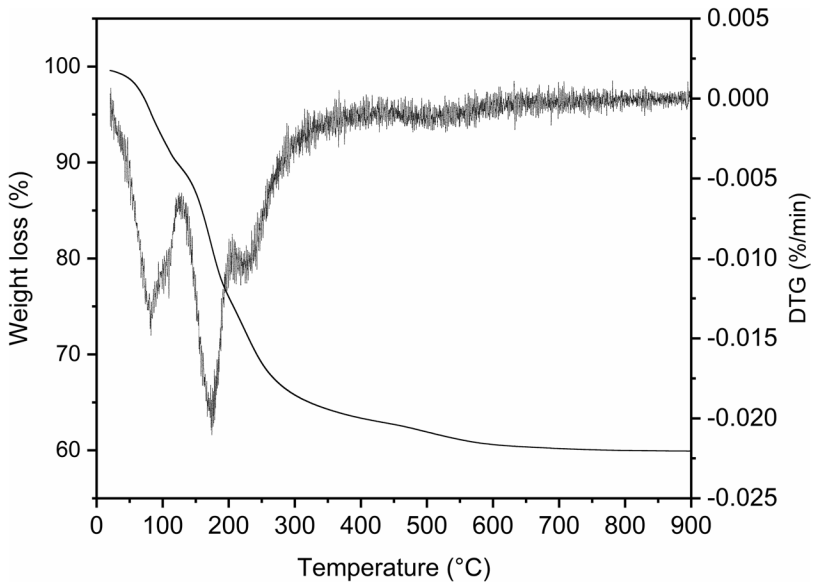


Fig. 1 TGA-DTG curves for Zn_2Al-LDH

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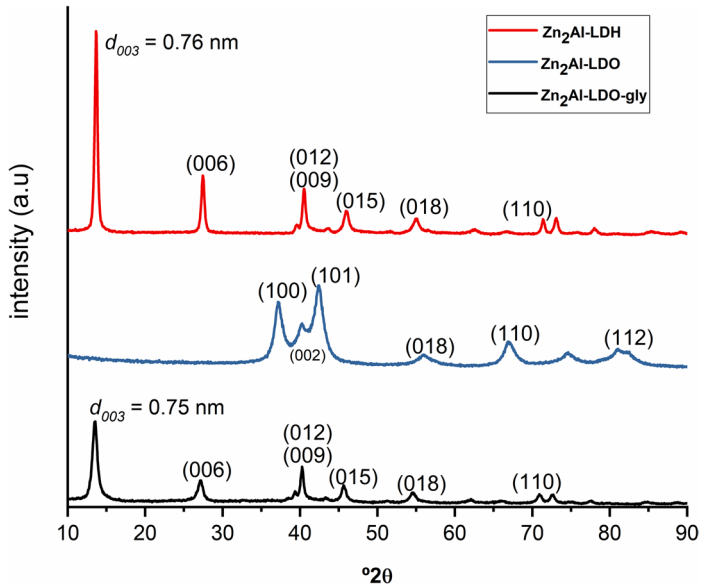


Fig. 2 XRD pattern of calcined, non-calcined, and reconstructed solids in glyphosate solution

presence of reflection peaks (003) and (006) in the XRD patterns, characteristic of LDH, was no longer possible because of the presence of extended peaks typical of ZnO. The diffraction peaks observed in the solid after calcination are in agreement with those present in the literature for LDH of the Zn-Al-CO_3 system calcined at temperatures between 450 and 500°C (Hu et al., 2018; Montanari et al., 2010). After rehydration in aqueous solution, the typical ZnO diffraction peaks disappeared (Fig. 2), accompanied by the formation of peaks with patterns identical to that of the precursor, indicating the solid reversibility and structure regeneration (OH/LDH). However, the basal spacing of ~0.75 obtained after regeneration suggested that glyphosate intercalation was not the main process in the reconstruction. A broadening of the diffraction peaks was observed, suggesting that during the reconstruction step, multiple anions may have been intercalated, such as OH^- to CO_3^{2-} (Aisawa et al., 2004; Montanari et al., 2010; Rosset et al., 2020). Thus, glyphosate may have been superficially adsorbed to the solid and also on the sides of the layer.

The FTIR/ATR spectrum of non-adsorbed glyphosate (Fig. S1, Supplementary Material) revealed absorption bands at 3384, 1633/1581, and 1373 cm^{-1}. Bands in he region of 779–557 cm^{-1} in the Zn_2Al-LDH FTIR spectrum (Fig. 3) correspond to the vibrational modes of the O–H bonds of the LDH structure and interstitial and adsorbed water, O-H-O bending, C-O stretching of carbonate, and structural M-O-M and O-M-O stretching, respectively (Hu et al., 2018; Jiang et al., 2009).

After calcination, complete disappearance of the band at 3384 cm^{-1} and drastic reduction of the 1350 cm^{-1} band, referring to the carbonate, were observed, indicating that these anions may still have been present in small amounts in Zn_2Al-LDO (Fig. 3) even after calcination of the precursor. Concerning Zn_2Al-LDO-gly (Fig. 3), the interaction of glyphosate with the layer was confirmed by the presence of absorption bands at 1573 cm^{-1}, corresponding to vibrational modes of the COO^- bond, and at 1065 cm^{-1} and 967 cm^{-1}, corresponding to the vibrational modes of the P–O bond of the phosphonate group. According to the literature, when glyphosate is not adsorbed, C=O stretching can be observed in the form of two absorption maxima at 1730 and 1713 cm^{-1} (Li et al., 2005; Meng et al., 2005). Concerning Zn_2Al-LDO-gly, the interaction of glyphosate with the layer was confirmed by the presence of absorption bands at 1573 cm^{-1}, corresponding to vibrational modes of the COO^-group, and at 1065 cm^{-1} and 967 cm^{-1}, corresponding to

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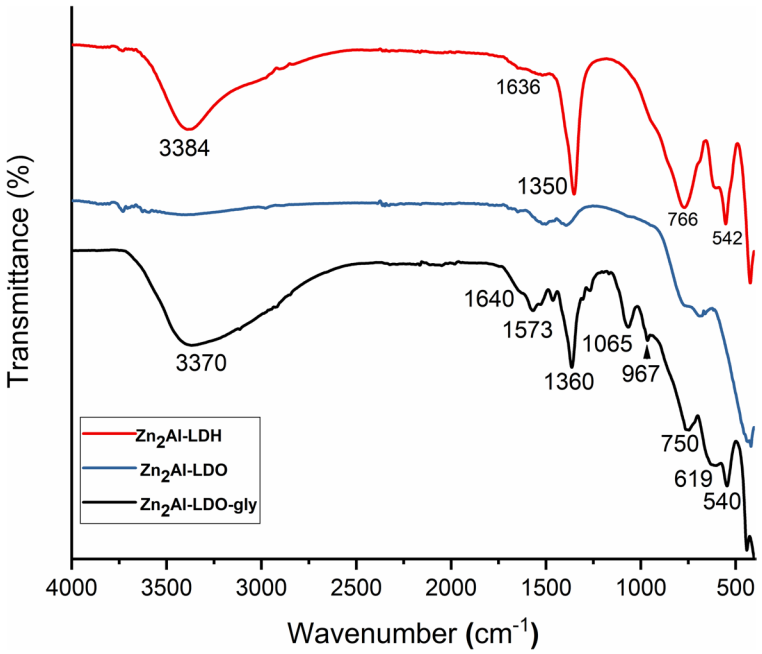


Fig. 3 FTIR/ATR spectra of calcined, non-calcined, and reconstructed solids in glyphosate solution

the vibrational modes of the phosphonate groupFurthermore, vibrational modes referring to P–O bonds of free glyphosate split into five bands with peaks at 1269, 1170, 1065, 1075, and 912 cm^{-1}. But after interaction with the solid surface, these bands were reduced to two or three modes, as also noted in the present study. Li et al. (2005) and Meng et al. (2005) suggested that the band at 1360 cm^{-1} contains contributions from the vibrational modes of the C–O bonds of carbonate adsorbed from the environment during the experiments and also from the complementary vibrational modes of the C=O bond of the carboxylate portion of glyphosate, previously recorded at 1424 cm^{-1} in its non-adsorbed form.

The porosity and surface area of the Zn_2Al-LDH and Zn_2Al-LDO samples were evaluated using the nitrogen desorption-adsorption method (Fig. 4a, b and Table 1). For both samples, type IV adsorption isotherms with type H3 hysteresis were observed, suggesting a mesoporous structure. The solids mostly had a pore size distribution between 2 and 10 nm. After calcination, a significant increase in the surface area of the adsorbent was observed, from 77.01 m^2 G^{-1} in Zn_2Al-LDH to 102 m^2 g^{-1} in Zn_2Al-LDO. The surface areas, obtained for both solids synthesized in the present study, were greater than those reported previously in the literature: 16.6 m^2 G^{-1} for Zn-Al-LDH and 55.9 m^2 G^{-1} for Zn-Al-LD (Hu et al., 2018), indicating that the method in the present work led to the formation of materials with greater adsorptive potential. According to the literature, the substantial increase in the area of the calcined solid compared to the non-calcined solid may be related to the loss of water and interstitial carbonate molecules, as well as changes in porosity. The heat treatment induced the formation of a larger number of pores in the region from 2 to 10 nm in the calcined solid (Fig. 4b).

For a better understanding of the glyphosate/Zn_2Al-LDO interaction mechanism, ^{13}C and ^{31}P SSMR experiments were performed. Experimental and simulated spectra, obtained for free glyphosate and adsorbed/interleaved glyphosate (Figs. S2 and S3), revealed only one peak in free glyphosate, with a chemical shift $\delta_{P\text{-}31} = 18$ ppm. After adsorption on the solid Zn_2Al-LDO, signals with isotropic chemical shifts equal to $\delta_{P\text{-}31} = 23$ to 14 ppm were present. According to Li et al. (2013), the signal at $\delta_{P\text{-}31} = 12$ ppm suggests a chemical environment in which phosphorus is complexed with aluminum sites (Al-O-P) in the solid layers. The

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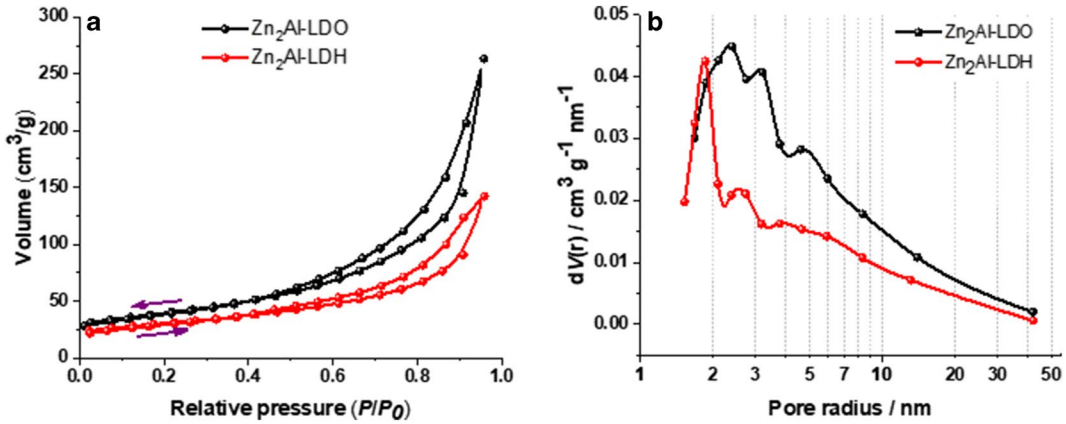


Fig. 4 **a** Nitrogen adsorption isotherms and **b** pore-size distribution (BJH)

Table 1 Specific surface area (S_{BET}), pore radius (r_p), and pore volume (V_p) of the Zn_2Al-LDH and Zn_2Al-LDO samples. Data fitting based on the BET and BJH methods (desorption branch) (Sing, 1982)

Sample	S_{BET} ($m^2\ g^{-1}$)	r_p (nm)	V_p ($cm^3\ g^{-1}$)
Zn_2Al-LDO	102.30	2.41	0.40
Zn_2Al-LDH	77.10	1.86	0.21

broadened signal which shifted to greater frequency at $\delta_{P\text{-}31} = 24$ ppm suggests a chemical environment where the phosphonate moiety is associated with the solid surface by electrostatic interactions. As pointed out by Li et al., (2004, 2013), when investigating the adsorption of phosphate by various minerals, the broadening of NMR signals is related to stronger dipolar interactions between molecules as well as interactions with the solid surface, decreasing their mobility, in addition to being influenced by the formation of hydrogen bonds with neighboring molecules or with surrounding water molecules.

In the ^{31}C-CPMAS spectrum, signal were observed at $\delta_{C\text{-}13} = 169$ ppm (carboxylate) and a doublet at 48 and 46 ppm. After adsorption, the signal at $\delta_{C\text{-}13} = 169$ ppm split into three signals at $\delta_{C\text{-}13} = 180$, 171, and 172 ppm. These displacements may be explained by the participation of carboxylate groups in a network of hydrogen bonds and/or non-bonded bridge interactions on the solid surface, as well as possible electrostatic interactions and complexation by the carboxyl with lamellar zinc atoms (C-O-Zn) (Li et al., 2013).

Adsorption of Glyphosate as a Function of pH

The surface charge and the adsorbate–adsorbent interactions are influenced directly by the pH of the aqueous solution (Zubair et al., 2017). Glyphosate solutions are naturally acidic and, thus, can promote the leaching of Al^{3+} and Mg^{2+} cations due to the attack on the octahedral sheets, promoting deterioration of the solids and reducing their efficiency as adsorbents (Rosset et al., 2019, 2020). Glyphosate has different anionic forms depending on the pH of the medium, which is also important for its interaction with the solid matrix. According to Peixoto et al. (2015), in aqueous solutions with pH values ≈10, the anionic forms gly^{2-} and gly^{3-} are observed, with trivalent anions being in greater proportion. These theoretical data were later confirmed experimentally by Liu et al. (2016). Furthermore, Li et al. (2005) observed good efficiency of glyphosate adsorption by both LDH and LDO, occurring at pH values ≥ 9 and < 11 and decreasing dramatically at pH > 11, thus suggesting that the glyphosate–solid interaction is highly unstable. Recent studies have indicated that good glyphosate adsorption can be achieved by LDH-type materials at pH values close to 10. Cardoso and Valim (2006) reported that the adsorption of acidic pesticides on LDO-type solids was satisfactorily efficient at pH close to 9. Because a higher anionic charge density may contribute to greater adsorption potential due to greater chemical interaction and the distribution of glyphosate ionic species as a function of the pH, experiments in the present study were conducted at

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pH ≈ 10. A relevant aspect is that aqueous suspensions containing LDO and low concentrations of glyphosate will reach pH values close to the working pH, requiring the addition of minimal amounts of a basic solution to adjust the pH to 10. Buffer solutions were avoided because they might introduce unwanted anions into the reaction medium, leading to possible competition for the adsorption sites.

Equilibrium Study

Experimental adsorption curves of glyphosate by solid Zn2Al-LDO at different temperatures were fitted to non-linear (Fig. 5) and linear equations (Fig. S4, and Fig. 6) according to the Langmuir, Freundlich, and Temkin models. Regression parameters from non-linear and linear fits are shown in Table 2.

The analysis of the adsorption isotherms (Fig. 5a) suggests H-type isotherms, according to the Giles classification, and strong interaction between the adsorbent and adsorbate, which can occur mainly by electrostatic interactions in view of the nature of the species (Giles & Smith, 1974). However, other forms of interactions must also be considered, such as hydrogen bonds and complexation, as already mentioned. According to the literature, an H-type isotherm is considered a special case of

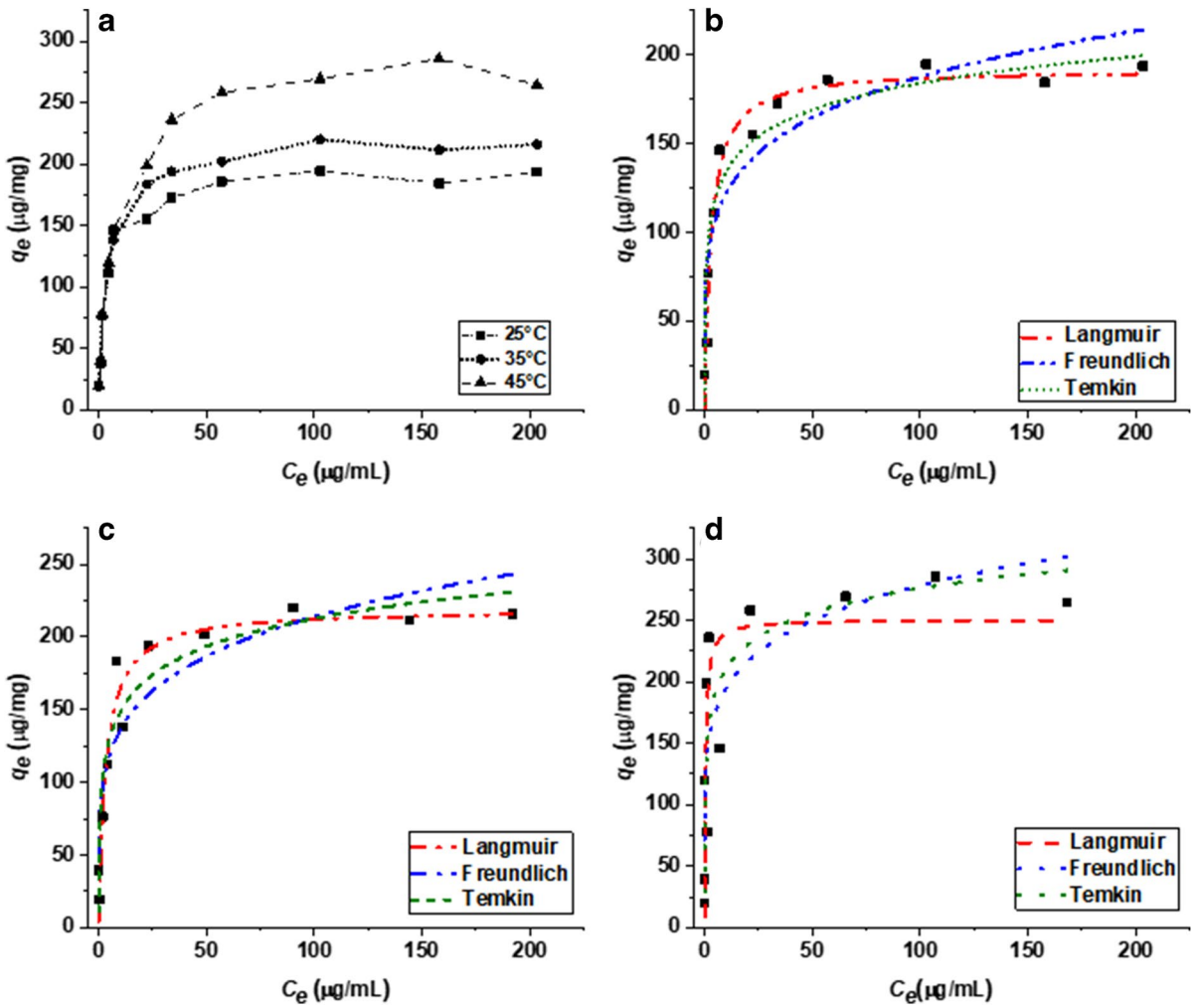


Fig. 5 **a** Experimental adsorption isotherms at 25, 35, and 45°C. Fitting of the Langmuir, Freundlich, and Temkin non-linear models **b** 25°C, **c** 35°C, and **d** 45°C

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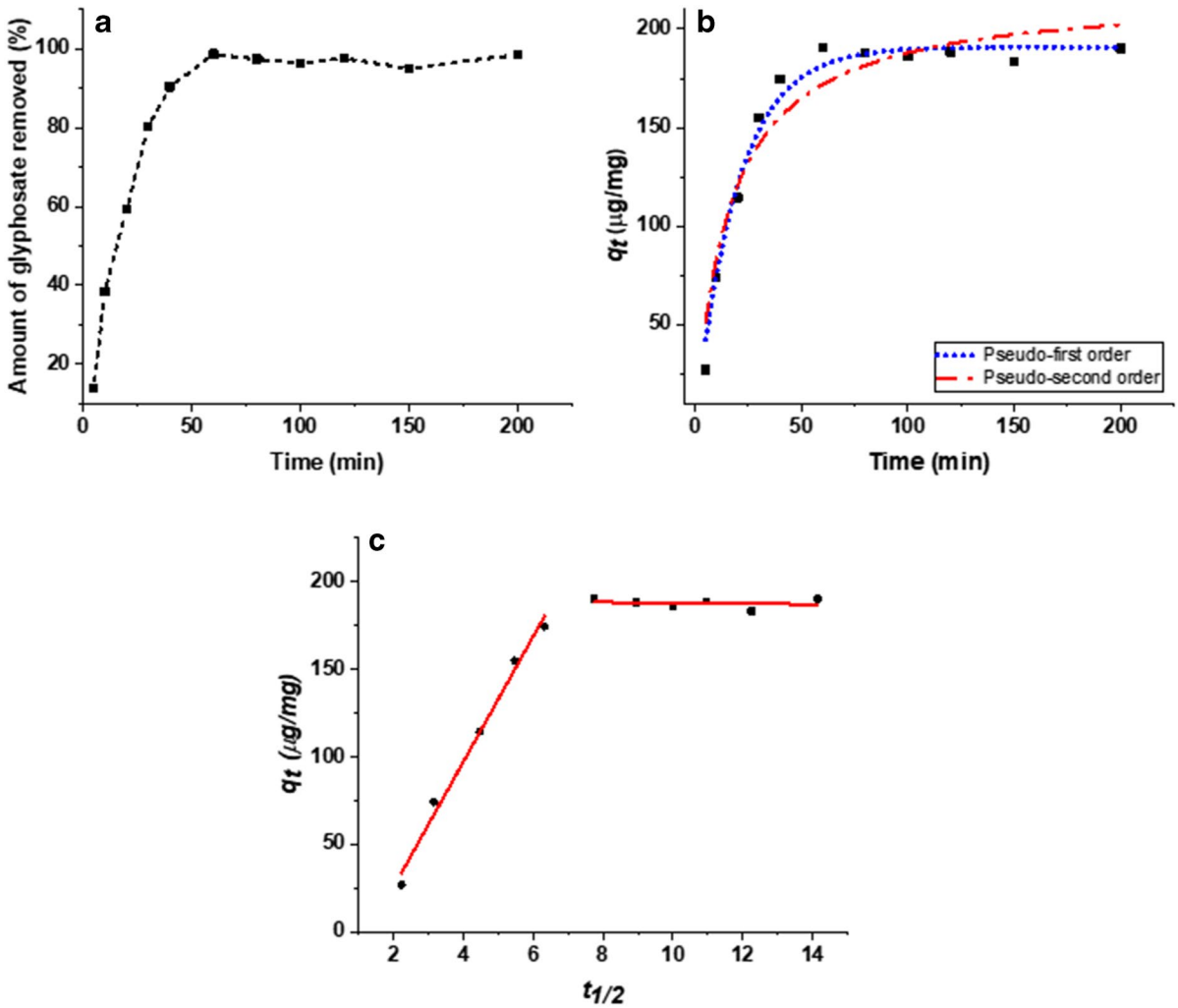


Fig. 6 Experimental kinetics curves of glyphosate adsorption on Zn_2Al LDO: **a** pseudo-first order kinetics model; **b** pseudo-second order kinetics model; and **c** Weber-Morris intraparticle diffusion model

an L-type isotherm, where the initial section of the curve is vertical (Abdellaoui et al., 2017; Aisawa et al., 2004; Giles & Smith, 1974; Rosset et al., 2019, 2020). The correlation coefficients clearly indicated that the Langmuir model best fits the adsorption isotherms (Fig. 5b, d). Through this analysis, obtaining information about the nature of the adsorptive process was possible. The analysis of data (Table 2) indicates that the K_L values obtained by the linear and non-linear equations increased when the adsorption temperature changed from 25 to 45°C, reflecting an increasing adsorption capacity of the solid. This process is endothermic and can be explained by ion exchange with the medium. The greater adsorption efficiency was attributed to better dispersion of the adsorbent in the medium and exposure of adsorption sites.

Kinetics Study

The contact time of glyphosate with Zn_2Al-LDO was 200 min, for a glyphosate concentration of 300 µg mL^{-1}, with adsorbent dosage of 0.5 mg mL^{-1}, and pH equal to 10 (±0.3). The amount of glyphosate adsorbed on LDO as a function of time (Fig. 6a) suggests that the removal of glyphosate from the aqueous

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Table 2 Adsorption parameters obtained from various linearized equations for glyphosate adsorbed on Zn_2Al-LDO: Langmuir (K_L, Langmuir constant; Q_{max}, maximum adsorption capacity); Freundlich (K_f, Freundlich constant); and Temkin (A and B, Temkin parameters)

Isotherms	Parameters	25°C		35°C		45°C	
		Linear	Non-linear	Linear	Non-linear	Linear	Non-linear
Langmuir	K_L	0.37	0.34	0.33	0.30	0.92	2.17
	Q_{max}	193.79	191.96	218.81	219.21	217.73	250.55
	R^2	0.99	0.97	0.99	0.95	0.99	0.73
	χ^2	26.27	24.35	43.48	42.49	266.53	235.36
Freundlich	K_f	61.13	79.51	62.61	86.46	104.68	136.10
	n	3.86	5.37	3.49	5.08	4.06	6.44
	$1/n$	0.26	0.17	0.29	0.19	0.25	0.15
	R^2	0.91	0.88	0.80	0.85	0.72	0.72
	χ^2	59.70	76.74	111.94	171.36	230.73	347.24
Temkin	A	48.52	48.56	20.60	20.60	164.51	164.51
	B	21.67	21.67	27.88	27.88	28.42	28.42
	R^2	0.90	0.90	0.89	0.89	0.78	0.78
	χ^2	94.48	94.48	152.19	152.19	112.63	112.63

solution increased dramatically in the first 50 min, when it reached its maximum, and then remained constant and in an equilibrium state until at least 200 min. The different steps of the adsorption curve as a function of time were affected by the concentration of the adsorbate in the medium. The high initial concentration of glyphosate favored a process of rapid mass transfer from the liquid phase to the surface or pores of the solid, which explains the steep slope of the curve in the initial period. As the adsorbate concentration decreases, the mass transfer rate tended to decrease until the equilibrium state was achieved and a dynamic adsorption-desorption process was established.

Peng et al. (2021) investigated glyphosate adsorption on Ca_Al-LDO and reported a fast rate of adsorption in the first 80 min. They obtained an adsorption rate of 40 µg of glyphosate per mg of adsorbent during 50 min. In the present study, for the same time interval, a greater adsorption rate of 190 µg mg^{-1} was attained over a period of 50 min. The greater adsorption rate of the analyte to the solid phase observed in the present study when compared to that of Peng et al. (2021) can be explained by the large difference in the surface area of the materials used, which were 14.37 m^2 g^{-1} of the solid Ca_AL-LDO versus 102.30 m^2 g^{-1} of the solid Zn_2Al-LDO in the current study.

Khenifi et al. (2010) studied the adsorption of glyphosate on $NiAlNO_3$-LDH and observed a rapid mass transfer of the adsorbate to the surface, with ~180 µg of solution being removed from the glyphosate solution/mg of adsorbent in an average time of 30 min. In the present study, in the same period the diffusion process led to the adsorption of only 160 µg of glyphosate per mg of solid adsorbent. However, the higher diffusion rate observed by Khenifi et al. (2010) can be explained by the use of a greater adsorbent load in their experiments (1 mg mL^{-1}) compared to the mass used in the present study (0.5 mg mL^{-1}). Unlike the current observations and those previously reported, Li et al. (2005) verified that the step with the greatest percentage of glyphosate adsorption by the solid they studied ($MgAlNO_3$-LDH) took place over an average time of 150 min, reaching a state of equilibrium after that period.

To obtain information about the mechanism of glyphosate adsorption on Zn_2Al-LDO, the experimental adsorption as a function of time was fitted to the non-linear pseudo-first order and pseudo-second order models and to the Weber-Morris intraparticle diffusion model (Fig. 6b, c and Table 3).

The best fit was obtained with the pseudo-second order model (Fig. 6b and Table 3). This result indicates that the decisive step in the adsorption rate of glyphosate on Zn_2Al-LDO passed through a

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chemisorption process, i.e. distinct chemical interactions occurred that led to structural variations in the solid formed by the adsorbate–adsorbent adduct. This conclusion was corroborated by the explicit changes in the FTIR-ATR and SSNMR spectra of ^{13}C and ^{31}P, indicating that glyphosate was bound chemically to the solid. Moreover, the Weber-Morris intraparticle diffusion model was used (Fig. 6c) and the multilinearity observed in the graph referring to the diffusion adjustment indicated that the adsorptive process occurred at least in one of the steps being controlled by the formation of the intrafilm.

Also noted was a reduction in the value of the diffusion constant from step 1 to step 2. This effect indicates that the diffusion of glyphosate decreased from the liquid phase to the surface of the adsorbent due to the reduction of its concentration in solution and suggests that the system was moving toward a state of equilibrium. A non-zero value of C indicates that the line does not pass through the origin. This behavior may be due to the difference in the mass-transfer rate variation at the beginning and end of the adsorptive process. These data indicate further that an external diffusion process rather than pore diffusion is the rate-limiting step.

Thermodynamic Study

The thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy were estimated from equilibrium data obtained from isotherm experiments at 25, 35, and 45°C, as reported in Table 4. The equilibrium experiments performed at these temperatures showed an increase in the amount of glyphosate adsorbed with increasing temperature, indicating the endothermic nature of the adsorption. The negative ΔG value indicates that the nature of the adsorption was spontaneous and that the affinity of the glyphosate/LDO increased with increasing temperature. The increase in glyphosate adsorption was accompanied by an increase in medium disorder, indicating that the process depends on surface anion exchange. The positive enthalpy value also confirmed that the adsorption process was strictly dependent on entropy (Extremera et al., 2012; Marangoni et al., 2009).

Anionic Competition

The effects of anionic competition of the glyphosate in the presence of Cl–, NO_3, HPO_4^{2-}, CO_3^{2-}, and SO_4^{2-} anions using the Zn_2Al-LDO adsorbent have

Table 4 Thermodynamics parameters for glyphosate adsorption by Zn_2Al-LDO: $\Delta G°$, standard free energy of adsorption; $\Delta H°$, standard enthalpy of adsorption; $\Delta S°$, standard entropy of adsorption

$\Delta G°$ (kJ mol^{-1})			$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
25°C	35°C	45°C		
–27.15	–27.96	–31.06	38.82	219.90

Table 3 Kinetics parameters and intraparticle diffusion parameters for adsorption of glyphosate by Zn_2Al-LDO: calculated adsorption capacity ($Q_{e,cal}$, μg mg^{-1}); pseudo-first order rate constant (K_1, min^{-1}); pseudo-second order rate constant (K_2, mg μg^{-1} min^{-1}); diffusion constant (K_{diff}, μg mg^{-1} min$^{-1/2}$); and intraparticle diffusion parameter, C

Models	Parameters	Values
Pseudo-first order	$Q_{e,cal}$ (μg mg^{-1})	190.85
	K_1 (min^{-1})	5.02×10^{-2}
	R^2	0.94
Pseudo-second order	$Q_{e,cal}$ (μg mg^{-1})	218.50
	K_2(mg μg^{-1} min^{-1})	2.819×10^{-4}
	R^2	0.99
Intraparticle diffusion (step one)	K_{diff} (μg mg^{-1} min$^{-1/2}$)	35.80
	C	−46.21
	R^2	0.98
Intraparticle diffusion (step two)	K_{diff} (μg mg^{-1} min$^{-1/2}$)	1.56
	C	202.07
	R^2	0.98

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not been published previously, but are presented here in order to quantify any adsorption inhibition which might be caused by the competing anions. The results (Fig. 7) indicated that the gradual increase in the concentration of all anions induced a reduction in the adsorption of glyphosate anions, as their equilibrium concentration tended to increase in the medium. However, the extent of inhibition of glyphosate adsorption was not equivalent in all cases. According to Abdellaoui et al. (2017), anions that present adequate symmetry and high charge-radius ratio can stabilize the LDH structure during the reconstruction process. Moreover, anions with greater charge density, such as sulfate, hydrogen phosphate, and carbonate, inhibited glyphosate adsorption on LDO more efficiently than nitrate and chloride anions. The trend observed was that, among the anions with higher charge density, the competitive effect varied and greater glyphosate adsorption inhibition was promoted by carbonate, hydrogen phosphate, and sulfate anions.

According to Constantino and Pinnavaia (1995) and Abdellaoui et al. (2017), this variation can be attributed to the greater symmetry observed in the carbonate anions which, when added to the charge, provides greater efficiency in the stabilization of the lamellae in the case of intercalation. Sulfate and hydrogen phosphate, although less symmetrical than carbonate, induce greater inhibition of adsorption due to their high charge and smaller size compared to glyphosate. A study investigating the effect of anionic competition involving the anions mentioned above in relation to amaranth dye indicated that anions with greater charge density and symmetry, such as carbonate, sulfate, and phosphate, were responsible for promoting greater inhibition of adsorbate adsorption (Abdellaoui et al., 2017).

Conclusions

Based on the powder XRD, IR, and atomic absorption data, the synthesis method adopted to obtain the Zn_2Al-LDH precursor led to the formation of material with good phase purity, experimental cation ratio equivalent to the nominal one, and good crystallinity. The BET analysis indicated that the calcination process induced a considerable increase in the surface area of the solid, which went from 77.1 $m^2\ g^{-1}$ to 102.2 $m^2\ g^{-1}$. The analysis of the adsorption isotherms indicated that the Langmuir model provided the best fit to the experimental data, and variation in the adsorption temperature showed that the saturation capacity of the solid increased with increasing temperature, going from 191.96 μg mg^{-1} at 25°C to 250.55 μg mg^{-1} at 45°C, in both cases at pH 10. Comparatively, the linear and non-linear forms of the Langmuir equation yielded similar results at 25 and 35°C, but greater discrepancies were noted at 45°C. The kinetics indicated that the adsorption followed the pseudo-second order model and that > 90% of the glyphosate was adsorbed in the first 50 min, suggesting a fast adsorptive process that reaches the dynamic adsorption/desorption equilibrium

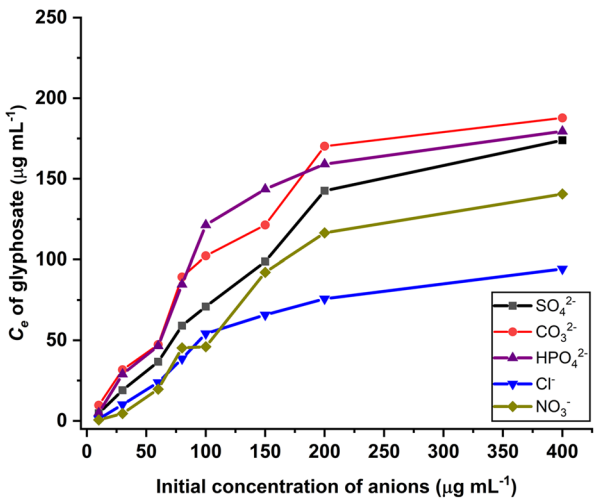


Fig. 7 Influence of the concentration of the various anions on the adsorption of glyphosate

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soon afterward. The negative variation of the Gibbs free energy indicated the spontaneity of the adsorptive process, and according to Eq. 11, the adsorption is entropically favored, given the positive value of $\Delta S°$. Analysis by XRD suggested strongly that the adsorption process was not accompanied by ion exchange between carbonate and glyphosate anions, as no variation was detected in the basal spacing before and after the contact time. On the other hand, FTIR/ATR and ^{13}C and ^{31}P NMR analyses suggested that glyphosate interacts with the LDO surface through its carboxylate and phosphonate groups, and that in addition to the possible charge interactions typical for the system, complexation is also an interaction mechanism.

Finally, the solid LDO was not selective for glyphosate, as its adsorption was reduced when the concentration of competing anions was increased in the medium, with a greater effect on the reduction of glyphosate adsorption being verified in the presence of carbonate and hydrogen phosphate anions.

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Authors' Contributions All authors read and approved the final manuscript. Material preparation, experiments and data analysis were performed by Emanoel Hottes. The first draft of the manuscript was written by Emanoel Hottes and all authors commented on subsequent versions of it. Conceptualization: Emanoel Hottes, Rosane Nora Castro, Glauco Favilla Bauerfeldt, Clarissa Oliveira da Silva and Marcelo Hawrylak Herbst. Methodology: Emanoel Hottes, Glauco Favilla Bauerfeldt, Clarissa Oliveira da Silva, Rosane Nora Castro and Marcelo Hawrylak Herbst. Material characterization: Emanoel Hottes, Rosane Nora Castro and Marcelo Hawrylak Herbst. Equilibrium, kinetics and thermodynamics studies: Emanoel Hottes, Glauco Favilla Bauerfeldt and Clarissa Oliveira. Supervision: Rosane Nora Castro and Marcelo Hawrylak Herbst.

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Declarations

Ethics Approval and Consent to Participate Not applicable (this paper does not contain studies involving human or animal aubjects).

Consent for Publication Not applicable.

Competing Interests The authors declare no competing interests. Availability of data and materials: The authors are responsible for providing additional information not included in the article.

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