Research article

Adsorption kinetic and thermodynamic studies of the 2, 4 – dichlorophenoxyacetate (2,4-D) by the [Co–Al–Cl] layered double hydroxide

Josiane S. Calisto, Ingrid S. Pacheco, Leonardo L. Freitas, Laiane K. Santana, Wêlique S. Fagundes, Fábio A. Amaral, Sheila C. Canobre *

LAETE - Laboratório de Armazenamento de Energia e Tratamento de Efluentes, Institute of Chemistry, UFU. Uberlândia Federal University, João Naves de Ávila Avenue, 2121, 38400-902, Uberlândia- Minas Gerais, Brazil

A R T I C L E   I N F O

Keywords:
Inorganic chemistry
Environmental science
Layered double hydroxides
Adsorption
Herbicide
dichlorophenoxyacetate

A B S T R A C T

[Co–Al–Cl] layered double hydroxide (LDH) obtained by co-precipitation at constant pH 8 presented a single phase in a hexagonal unit cell parameters similar to the hydrotalcite (JCPDS 14-191) belonging to the rhombohedral crystal system and space group R3C. The adsorption kinetics of 2,4-D onto [Co–Al–Cl] LDH was better described by the Pseudo Second-Order (best adjust R² = 0.9998 for 60 mg L⁻¹ 2,4-D adsorption). Intra-particle diffusion model was not the sole rate-controlling factor, indicating the adsorption of 2,4-D by the [Co–Al–Cl] LDH is a complex process for the experimental conditions performed, involving both boundary layer and intra-particle diffusion. The adsorption isotherm adjusted better to the Freundlich model (R² = 0.9845) and the ΔH° value of - 51.18 kJ mol⁻¹ indicated the predominance of the physical adsorption. The FT-IR spectrum of LDH after adsorption presented 2,4-D bands together with those of LDH and XRD showed an increase in the interlamellar distance (d003) due to the intercalation of 2,4-D in the interlayer structure of the [Co–Al–Cl] LDH, corroborating inter and intra-particle adsorption data. Thus, [Co–Al–Cl] LDH, commonly used as electrodes in supercapacitors, can be effectively used as an adsorbent for the removal of 2,4-D from contaminated waters.

1. Introduction

The current concern with the widespread contamination of soils and groundwater from the application of pesticides in modern agriculture is driving the development of research into recovery and treatment alternative processes. In this context, adsorption is considered one of the most cheap and practical of puriﬁcation and separate processes due versatility and accessibility in residual water treatment, allowing the hazardous compounds removal in wastewater. In addition, is one of the main and accessibility in residual water treatment, allowing the hazardous compounds removal in wastewater. In this context, adsorption is considered one of the most cheap and practical of purification and separate processes due versatility and accessibility in residual water treatment, allowing the hazardous compounds removal in wastewater. In this context, adsorption is considered one of the most cheap and practical of purification and separate processes due versatility and accessibility in residual water treatment. Furthermore, inorganic clays have received special attention in the pesticides adsorption study (Khoei et al., 2019; Ye et al., 2019), pharmaceuticals (Ghemit et al., 2017), metals (Shujun et al., 2018; Khoei et al., 2019) and others substances considered caused environmental damage. In this sense, the search for low cost alternative materials for the removal of environmental pollutants has been growing in recent years. The Layered double hydroxide (LDH) has a basic structure formed by cationic layers, composed of divalent and trivalent cations hexacoordinated to hydroxyl ions in an octahedral arrangement (Crepaldi et al., 2000).

Synthetic compounds of the hydrotalcite type are similar to the structure of the mineral hydrotalcite, which in turn has layers with structures of the brucite Mg(OH)2 type. The general formula \[\text{M}^{2+}_x\text{M}^{3+}_y(\text{O} \text{H})_z\text{Al}^{3+}_m\text{M}^{2+}_n\text{H}_2\text{O}\] describes the chemical composition of hydrotalcite-type compounds, where: \(\text{M}^{2+}\) (divalent metal cation), \(\text{M}^{3+}\) (anion charge), \(\text{M}^{-}\) (charge of the anion) and \(X = \text{M}^{3+}/{(\text{M}^{3+} + \text{M}^{2+})}\) where \(X\) is the Molar ratio. Thus, from different metal ions (divalent and another trivalent) and interlayer species, LDH can be prepared by different methods such as: by coprecipitation at pH constant or variable, hydrolysis of the urea, sol-gel, or by regeneration of the calcined precursor (Crepaldi and Valim, 1998; Crepaldi et al., 2000). Thus, this material presents a variety of applications, such as catalytic process (Bialas et al., 2016) electrochemical application as electrodes in batteries and supercapacitors (Lai et al., 2015) and adsorbents of pesticides (Pavlovic et al., 2016).
et al., 2013). Among the herbicides, 2,4 – dichlorophenoxyacetate (2,4 - D) was the first successful selective herbicide, which quickly became the most widely used in the world. 2,4-D appears predominantly in its anionic form in the pH range that exists in the natural environment and it is highly mobile and poorly biodegradable (Carter, 2000). The half-life of 2,4-D in water ranges from one to several weeks under aerobic conditions, and it can exceed 120 days under anaerobic conditions (WHO, 2003). 2,4-D poses a high threat to surface and ground water supplies due to its high mobility and toxicity. Besides, it is among the priority contaminants of major environmental concern (Hamilton et al., 2003; WHO, 2003). The half-life of 2,4-D in water ranges from one to several weeks under aerobic conditions, and it can exceed 120 days under anaerobic conditions (WHO, 2003). 2,4-D in water ranges from one to several weeks under aerobic conditions, and it can exceed 120 days under anaerobic conditions (WHO, 2003). 2,4-D in water ranges from one to several weeks under aerobic conditions, and it can exceed 120 days under anaerobic conditions (WHO, 2003). 2,4-D in water ranges from one to several weeks under aerobic conditions, and it can exceed 120 days under anaerobic conditions (WHO, 2003). 2,4-D in water ranges from one to several weeks under aerobic conditions, and it can exceed 120 days under anaerobic conditions (WHO, 2003).

2.1. Materials

[Co–Al–Cl] LDH were synthesized by coprecipitation method at constant pH 8, using 1.0 mol L\(^{-1}\) CoCl\(_2\).6H\(_2\)O (BIOTEC P.A.) and 0.5 mol L\(^{-1}\) AlCl\(_3\).6H\(_2\)O (BIOTEC P.A.). A basic solution of 1.0 mol L\(^{-1}\) NaOH (VETEC P.A.) was slowly added to control the pH.

The dosage of the 2,4-D (ALDRICH 98%) used were 40, 60 and 80 mg L\(^{-1}\) and masses of [Co–Al–Cl] LDH were 100 and 200 mg in adsorption tests.

2.2. Synthesis of [Co–Al–Cl] LDH by coprecipitation at constant pH

The pHZCP was determined for LDH, in order to check the pH range in which [Co–Al–Cl] LDH behave like cationic or anionic. The procedure for determining the pHZCP consisted of adding 1 g L\(^{-1}\) [Co–Al–Cl] LDH in 0.1 mol L\(^{-1}\) NaCl aqueous solution (increasing ionic strength) in different conditions of starting pH, from 2 to 12 (Regalbuto and Robles, 2004). The solutions were filtered and the final pH of the solution has been determined after 24 h of equilibration at 25 °C (Feigenbrugel et al., 2006). The pHZCP correspond to the range in which the final pH is kept constant regardless of the initial pH. The acid solutions were prepared from HCl 0.1 mol L\(^{-1}\) dilutions and from the NaOH aqueous solution 0.1 mol L\(^{-1}\) dilutions.

2.3. Characterization of materials

2.3.1. Structural characterization of [Co–Al–Cl] LDH by XRD

The structural characterization was performed by X-ray diffraction (XRD) in a Shimadzu diffractometer (Model 6000, radiation Cu K\(_\alpha\), \(\lambda = 1.5406 \text{ Å}\)) with a voltage of 40 kV, current of 30 mA, at 20 min\(^{-1}\) from 5 to 70°. The unit cell parameters, a, c and d were calculated d was calculated using the Fullprof program. The d003-value corresponds to the sum of the thickness and height of the interlayer region.

2.3.2. Surface area characterization of [Co–Al–Cl] LDH by B.E.T

Specific surface area measurements were performed on a Micrometrics equipment, model ASAP 2020, by adsorption of N\(_2\). The samples were pre-treated under vacuum at 90 °C for 4 h.

2.3.3. Microstructural characterization by fourier transform infrared (FT-IR)

FT-IR spectroscopy measurements were performed using an infrared spectrophotometer (FT-IR Frontier Single Range – MIR da Perkin Elmer) in the region between 4000 and 500 cm\(^{-1}\). The measurements were made in solid state, using the Attenuated Total Reflectance (ATR) accessory with diamond crystal.

2.4. Batch adsorption experiments of the 2,4-D by [Co–Al–Cl] LDH

2.4.1. Factorial experiment (2\(^3\))

The optimization of parameters affecting the adsorption was performed using a two-level full factorial experimental design with a central point involving three factors: initial concentration of the 2,4-D (20 mg L\(^{-1}\) (-1) and 100 mg L\(^{-1}\) (+1)), [Co–Al–Cl] LDH adsorbent mass (100 mg (-1) and 200 mg (+1)) and pH 3 (-1) and 5 (+1) at 25 °C, 200 rpm and 60 min of equilibration time. The supernatants were recovered to measure the residual concentration of the herbicide which was determined by UV-Vis spectrophotometry. The absorbance was measured at 230 nm (Feigenbrugel et al., 2006) in a Shimadzu UV-1650D (UV-Visible Spectrophotometer). The experimental data were processed using the Statistica® software, the performance factors and the interactions between them were evaluated on the results obtained by the Pareto graph. To obtain adsorption capacity values (\(q\)), a mass balance is carried out, in which the amount of adsorbate in the adsorbent must be equal to the amount of adsorbate removed from the solution, or, in mathematical terms (Eq. 1) (Kinniburgh, 1986).

\[
q_t = \frac{V (Co – Ce)}{m}
\]

where \(Co\) (mg L\(^{-1}\)) is the initial concentration of 2,4-D, \(Ce\) (mg L\(^{-1}\)) is the 2,4-D concentration at time \(t\) (min), \(m\) (g) is the mass of adsorbent LDH, \(V\) (L) is the volume of adsorbate solution and \(q_t\) (mg g\(^{-1}\)) is the adsorbed amount at time \(t\) (min).

2.4.2. Determination of equilibration time and adsorption kinetics

50 mL of 2,4-D solution at different concentrations (40, 60 and 80 mg L\(^{-1}\)) at pH 5 received a mass of 150 mg of [Co–Al–Cl] LDH in erlenmeyers. At room temperature 298 K under 200 rpm shaking until the collection time previously set at 10, 20, 30, 40, 60, 90, 120, 150, 180 and 240 min. Then, each collected sample aliquot was measured in a UV-Vis at the maximum wavelength of 230 nm. To investigate the adsorption kinetics of 2,4-D onto LDH, used linear models, denoted Pseudo-First-Order, Pseudo- Second-Order, Intraparticle and Film Diffusion models.

2.4.3. Determination of adsorption isotherms

50 mL of 2,4-D solution at different concentrations (40, 60 and 80 mg L\(^{-1}\)) at pH 5 were maintained in contact with 150 mg of [Co–Al–Cl] LDH under agitation of 200 rpm for 60 min. The experiment was carried out at
4 temperatures (298, 308, 318 and 328 K). Adsorption isotherms were adjusted using the Langmuir and Freundlich models in linearized forms.

2.4.4. Effect of temperature on adsorption thermodynamic parameters

The thermodynamic parameters were estimated from the data of isotherms of de Freitek, since they were exposed to four different temperatures (298, 308, 318 and 328 K). Thermodynamic parameters can evaluate the orientation and feasibility of the adsorptive reaction. The three thermodynamic parameters considered were in Gibbs free energy ($\Delta G^\circ$), standard enthalpy ($\Delta H^\circ$) and standard entropy ($\Delta S^\circ$).

3. Results and discussion

3.1. Structural characterisation of [Co–Al–Cl] LDH

Fig. 1 (a) show the X-ray diffractogram for [Co–Al–Cl] LDH synthesized at pH constant 8. It was observed diffraction peaks at $2\theta = 22.72^\circ$, 44.43° and 60.12°, corresponding to the reflections 006, 018 and 110, respectively, can being indexed to the layered structure, consistent with the JCPDS No. 14-191, concerning the hydrotalcite. Inorganic layers of LDH resulted in a hexagonal unit cell belonging to the rhombohedral crystal system and space group $R$-3m. Besides, it was realized the Rietveld refinement for this [Co–Al–Cl] LDH. The experimental points (in red), the calculated curve (in black) and the difference between them (in green) are represented in the XRD pattern. The vertical bars indicate the positions of the Bragg reflections for each crystalline phase, noting the presence of the single-phase hydrotalcite type.

Then, to evaluate the quality of the refined structural model, it was calculated $R_{\text{Bragg}}$ and $\chi^2$, which showed values of 1.61 and 1.73, respectively (Table 1).

3.2. Specific surface area characterisation of [Co–Al–Cl] LDH by B.E.T

The pore classification of [Co–Al–Cl] LDH was mesopores considering that the average diameter of the pores and average width of the pores is between 2 nm < diameter < 50 nm (Gregg and Sing, 1982). The specific surface area and pore volume values for [Co–Al–Cl] LDH were 43.48 m$^2$ g$^{-1}$ and 0.048 cm$^3$g$^{-1}$, respectively. These values are coherent with those obtained by Mostafa and Mohamed (2016) and Bernardo et al. (2016).

3.3. Determination of the pH of zero charge point (pH$_{ZCP}$)

In order to prescribe the pH range wherein the adsorbent [Co–Al–Cl] LDH possessed a cationic character which would favor the adsorption with herbicide that has a negative charge density 2,4-D. The pH of zero charge point of [Co–Al–Cl] LDH was determined between the pHs 2 and 12. In Fig. 2 is shown the final pH after 24 h of adsorption as a function of pH prior to adsorption.

The pH$_{ZCP}$ was calculated from the arithmetic average of the final pH. The [Co–Al–Cl] LDH synthesized at pH constant 8 showed a pH$_{ZCP}$ value of 5.99. This specific pH range occurs with electroneutral charges on the surface of the adsorbent. At pH values below pH$_{ZCP}$, the surface active sites are protonated, presenting a surface with positive charge density. Thus, the herbicide adsorption process was conducted at pHs below 5.99, to enhance the electrostatic attraction between [Co–Al–Cl] LDH and 2,4-D (anionic herbicide).

3.4. Adsorption test of the 2,4-D by [Co–Al–Cl] LDH

3.4.1. Factorial experiment (2$^3$)

The treatment of the data obtained using analysis of variance (ANOVA) and statistical probability ($p = 0.05$) resulted in the Pareto graph shown in Fig. 3. The results show that adsorbent mass and 2,4-D concentration were effects more significant in the adsorption process. The adsorbent mass was the most significant factor, revealing a positive effect. Based on this observation, it can be inferred that when the ratio between sorbent and sorbate is high there are more active sites available, favoring the adsorption efficiency.

It is well known that the concentration of the 2,4-D solution is the main factor affecting the adsorption properties. This variable showed a negative effect, indicating that an increase in the concentration value results in an decrease in the rate de 2,4-D adsorption due to saturation of the active sites of the adsorbent by the adsorbate molecules (Table 2).

Table 2 show the experimental matrix of the factorial design ($2^3$) and capacity adsorption of the herbicide 2,4-D by [Co–Al–Cl] LDH.

3.4.2. Determination of equilibrium time and adsorption kinetics

The contact time indicates the kinetic behavior of the adsorption for a given adsorbent at a given initial adsorbate concentration. Fig. 4 shows the effect of the contact time for 2,4-D adsorption on [Co–Al–Cl] LDH at
pH = 5 as a function of different dosages of the adsorbent. The removal of 2,4-D increases rapidly during the initial 2,4-D adsorption stages due to sites available for sorption on the surface. However, with increasing surface coverage, the number of remaining binding sites decrease downing to the repulsive forces between the adsorbed and free molecules, leading to the equilibrium state being achieved (Yu et al., 2017). The equilibrium state was achieved after 60 min, which was used for Kinetic and Thermodynamic studies.

Two kinetic models were considered (Fig. 5(a) and (b)) Pseudo-First-Order and Pseudo-Second-Order) to investigate the mechanism of 2,4-D adsorption (Eq. 2 and Eq. 3, respectively). These models are the most commonly used to describe the adsorption of organic and inorganic pollutants onto solid adsorbents. Linear kinetic models were compared using the $R^2$ value as reference.

\[
\ln \left( \frac{q_e}{C_0} - \frac{q_t}{C_0} \right) = -k_1t
\]

(2)

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t
\]

(3)

where $q_e$ and $q_t$ are the amounts of 2,4-D adsorbed at equilibrium, in mg g\(^{-1}\), and at time $t$, in min, respectively, $k_1$ and $k_2$ are the pseudo first order rate constant (min\(^{-1}\)) and second order rate constant (g mg\(^{-1}\) min\(^{-1}\)) respectively.

According to the linear fitted plots presented in Fig. 5 (a) and (b) and kinetic parameters, the adsorption kinetics of 2,4-D onto [Co–Al–Cl] LDH is better described by the Pseudo Second-Order kinetic model (R\(^2\) 0.9998 for 2,4-D 60 mg L\(^{-1}\) adsorption) than the Pseudo First-Order (R\(^2\) 0.4026 for 2,4-D 60 mg L\(^{-1}\) adsorption). The correlation coefficient for the pseudo-second-order model (R\(^2\) > 0.99, Table 3), suggesting that the sorption process was mainly dominated by multiplex mechanisms involved in herbicide removal (Yu et al., 2018).

A plot that expresses the amount of adsorbate adsorbed, $q_t$ (mg g\(^{-1}\))
as a function of the square root of the time, gives the rate constant by calculating the plot slope. This model can be described by Eq. (4) (Weber and Morris, 1963):

\[ q_t = k_{id} \sqrt{t} + C \] (4)

where \( k_{id} \) (mg g\(^{-1}\) \cdot min\(^{-0.5}\)) and C are diffusion coefficient and intraparticle diffusion constant, respectively. C is directly proportional to the thickness of the boundary layer.

According to Weber and Morris (1963) if intraparticle diffusion is the determinant of velocity, the removal of the adsorbate varies with the square root of time and passes through the origin. Fig. 6 (a) shows the plot of amount adsorbed of 2,4-D, \( q_t \) (mg g\(^{-1}\)), versus \( t^{1/2} \). Film diffusion model (Fig. 6 (b)) was also used to investigate if transport of 2,4-D from the liquid phase up to the solid phase boundary also plays a role in the adsorption process Eq. (5) (Boyd et al., 1947):

\[
-\ln \left(1 - \frac{q_t}{q_e}\right) = K_{fd} t
\] (5)

Where \( K_{fd} \) is the liquid film diffusion constant.

The plots (Fig. 6 (a)) are nonlinear for the whole range of studied concentrations, indicating that intraparticle diffusion is not the only rate-limiting step, but other process may also be involved in the adsorption. The adsorption process is not a one-step process as evidenced by the curvature in these plots and two different sharp stages are clearly observed. The first stage, including the adsorption period from 0 to 40 min \( (t^{1/2} < 6.3) \), describes the instantaneous adsorption stage where 2,4-D adsorption rate is high due to low competition between the 2,4-D molecules. Intraparticle diffusion was not the predominant mechanism in the adsorption in the range up to 40 min \( (t^{1/2} = 6.3) \), since the first stage the linear coefficient was different of zero and the intraparticle diffusion constant \( C \) varied from 0.85 to 2.3 mg g\(^{-1}\)). The second stage, ranging from 40 to 240 min \( (6.3 < t^{1/2} < 15.5) \), is attributed to the low adsorption stage caused by the low concentration gradients, producing the equilibrium condition. When diffusion equilibrium is reached in the second stage, the intra-particle diffusion slows down due to saturation of most of the adsorption sites and this is evidenced by the plateaus.

| 2,4 D (mg L\(^{-1}\)) | Pseudo First Order | Pseudo Second Order |
|------------------------|---------------------|---------------------|
|                        | \( K_1 \) (min\(^{-1}\) \cdot 10^4) | \( K_2 \) (g mg\(^{-1}\) \cdot min\(^{-1}\) \cdot 10^2) |
| 40                     | 1.2524              | 0.3361              |
| 60                     | 2.2584              | 0.4026              |
| 80                     | 3.8411              | 0.8502              |

Table 3

Kinetic parameters predicted by pseudo-first order, pseudo-second order and for adsorption of 2,4 D by [Co–Al–Cl] LDH.
film diffusion mechanism on the adsorption rate. Likewise, by comparing the data presented in Table 4, the $R^2$ values for the intraparticle diffusion values were similar to those of the film diffusion model. These results suggest that both processes occur simultaneously during the 2,4-D adsorption process. Then, intraparticle diffusion model was not the sole rate-controlling factor, indicating the adsorption of 2,4-D by the [Co–Al–Cl] LDH is a complex process, involving both boundary layer and intra-particle diffusion.

The values of $k_{id}$ and $K_{fd}$ were determined from the slopes of the linear plots (second stage) and presented in Table 4.

### 3.5. Determination of adsorption isotherms

In order to establish the type of adsorption prevailing between the herbicide and [Co–Al–Cl] LDH, two types of isotherms were tested (Freundlich and Langmuir models).

To better understand the characteristics of the adsorption process, the equilibrium adsorption data were analyzed by well-known Langmuir (Eq. 6) and Freundlich (Eq. 7) linear models (Langmuir, 1918; Freundlich, 1906).

$$
\frac{C_e}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} C_e
$$

(6)

$$
\ln(q_e) = \ln(k_f) + \frac{1}{n} \ln(C_e)
$$

(7)

where $C_e$ (mg/L) is the equilibrium concentration of 2,4-D remained in the solution, $q_e$ (mg/g) is the amount 2,4-D adsorbed on per weight unit of solid after equilibrium, $q_{max}$ (mg/g) is the maximum adsorption capacity, $K_L$ is adsorbate/adsorbent interaction constant (L mg$^{-1}$); $K_F$ is a measure of adsorvent capacity and the slope $1/n$ is the adsorption intensity.

Fig. 7 (a) and (b) shows that adsorption isotherm adjusted to the Freundlich ($R^2 = 0.9845$) rather than Langmuir ($R^2 = 0.9023$), particularly at low concentrations and at 308 K (where was the best adjust), indicating the occurrence of physical and chemical and adsorptions, respectively. Thus, this adjustment preferably to the Freundlich model demonstrates the formation of multilayer interaction action between adsorbent and adsorbate.

Table 5 show parameters of both model adjusts in different temperatures. The $q_{max}$ and $K_L$ parameters obtained from Langmuir isotherm represent the maximum adsorption capacity and adsorbate/adsorbent interaction constant, respectively. Table 5 shows that the $q_{max}$ value decreases with increasing temperature and the $K_L$ increases, since the adsorption process of 2,4-D by [Co–Al–Cl] LDH is exothermic. The $K_F$ and $1/n$ represent the Freundlich constants, referring to the maximum adsorption capacity and adsorption intensity, respectively. The parameter $1/n$ calculated from the Freundlich model is in the interval from 0 to 1, suggesting that the 2,4-D adsorption onto LDH is favorable and also that there are minimum interactions between the adsorbed molecules (Fytianos et al., 2000; Tsai et al., 2005). The $K_F$ value decreases with increasing temperature, because this constant is related to the maximum adsorption capacity, which decreases with increasing temperature.

Table 6 shows that the adsorption capacity of the [Co–Al–Cl] LDH is consistent with that obtained for other materials tested as adsorbent for the removal of 2,4-D.

### 3.6. Effect of temperature on adsorption thermodynamic parameters

The effect of temperature of the 2,4-D adsorption on the [Co–Al–Cl] LDH was investigated under isothermal conditions in the temperature range 298–328 K. The 2,4-D adsorption capacity onto [Co–Al–Cl] LDH decreases with increasing temperature, suggesting that the adsorption reaction is exothermic. The change in standard free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) of adsorption were calculated using Eqs. (8) and (9). The Freundlich constant $K_F$ can be obtained as a dimensionless value using Eq. (10) (Tran et al., 2016).

### Table 4

| 2,4-D (mg L$^{-1}$) | Intraparticle Diffusion model | Film Diffusion model |
|---------------------|-------------------------------|----------------------|
|                     | $K_{id}$ (mg g$^{-1}$ min$^{-0.5}$) | $R^2$ | $K_{fd}$ (min$^{-1}$) | $R^2$ |
| 40                  | 1.161                         | 0.8910               | 5.150                | 0.9133 |
| 60                  | 1.331                         | 0.8674               | 5.210                | 0.8587 |
| 80                  | 6.211                         | 0.8855               | 2.730                | 0.8775 |

### Table 5

| Model          | Parameters | 298 K | 308 K | 318 K | 328 K |
|----------------|------------|-------|-------|-------|-------|
| Langmuir       | $q_{max}$ (mg g$^{-1}$) | 30.120 | 27.174 | 25.974 | 23.364 |
|                | $K_L$ (10$^2$.L mg$^{-1}$) | 0.9428 | 1.1240 | 1.2233 | 1.3895 |
|                | $R^2$      | 0.8785 | 0.9023 | 0.8494 | 0.6973 |
| Freundlich     | $K_F$ (10$^1$.mg g$^{-1}$) (L mg$^{-1}$.min$^{-n}$) | 8.536 | 8.146 | 5.969 | 5.532 |
|                | $1/n$      | 0.603 | 0.627 | 0.719 | 0.704 |
|                | $R^2$      | 0.9722 | 0.9845 | 0.9689 | 0.9637 |

---

Fig. 7. (a) Langmuir adjust and (b) Freundlich adjust models for 2,4-D adsorption by the [Co–Al–Cl] LDH at 308 K.
\[
\Delta G = -RT \ln K_c, 
\]

\[
\ln K_c = \frac{-\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}, 
\]

\[
K_c = K_F \rho \left( \frac{10^p}{\rho} \right)^{(1-t/14)} 
\]

where \( \rho \) is the density of pure water (assumption on 1.0 g mL\(^{-1} \)), \( R \) is the gas constant (8.314 J K\(^{-1} \) mol\(^{-1} \)), \( T \) the temperature in K and \( K_c \) is the equilibrium constant (L mg\(^{-1} \)).

The slope and intercept of the Van’t Hoff plot is equal to \(-\Delta H/R\) and \(\Delta S/R\), respectively. Thermodynamic parameters obtained are summarized in Fig. 8.

The heat of adsorption \( \Delta H \) for the sorption of 2,4-D onto [Co-Al-Cl] LDH can be calculated from the temperature dependence of the equilibrium adsorption constant, \( K \). A plot of \( \ln K_c \) vs. \( 1/T \) (Fig. 8), should be linear with slope \(-\Delta H/R\) and intercept \(\Delta S/R\). \( \Delta H \) was found to be -51.2 kJ mol\(^{-1} \) while \( \Delta S \) was -126.6 J K\(^{-1} \) mol\(^{-1} \).

The \( \Delta G \) values (obtained from Eq. (9) using equilibrium constant \( K_c \) derived from the Freundlich constant \( K_F \)) at different temperatures are negative and decrease with an increase in the temperature, revealing an adsorption process more effective under raised temperatures. The \( \Delta H \) value of -51.2 kJ mol\(^{-1} \), lower than the value of -40 kJ mol\(^{-1} \), indicated the exothermic process and predominance of physical adsorption. Besides, the low value of \( \Delta H \) implies that there was loose bonding between the adsorbate molecules and the adsorbent surface (Singh, 2000). Then, activation energy for physisorption is also very low and hence it is practically a reversible process. The \( \Delta S \) value of -126.6 J K\(^{-1} \) mol\(^{-1} \) suggesting a decrease in the degree of freedom of the adsorbed species (Dogan et al., 2006).

### 3.7. Characterization of the [Co-Al-Cl] LDH before and after 2,4-D adsorption

The FT-IR spectra of [Co-Al-Cl] LDH, before and after 2,4-D adsorption, are shown in Fig. 9.

The broad strong absorption band at region from 3671 to 3087 cm\(^{-1} \) is attributed to the stretching vibrations of surface and interlayer water molecules and hydroxyl groups (Wei et al., 2006). This is related to the formation of hydrogen bonds of interlayer water with guest anions as well as with hydroxide groups of layers. The weaker band at 1623 cm\(^{-1} \) is due to the bending mode of water molecules and the bands centered at 540 and 420 cm\(^{-1} \) are attributed to M-O-H and O-M-O lattice vibrations, respectively (Li et al., 2004; Nejati and Rezvani, 2012). In the FT-IR spectrum of 2,4-D (shown in Fig. 9 (a)) absorption band at 1477 cm\(^{-1} \).

### Table 6

Comparison of 2,4-D adsorption of this work and previous studies.

| Adsorbent                          | Adsorption capacity, \( q_m \) (mg g\(^{-1} \)) | Reference                      |
|-----------------------------------|-----------------------------------------------|--------------------------------|
| Commercial AC (F-300)             | 181.82                                        | (Salman and Hameed, 2010)      |
| Chitin                            | 6.07                                          | (El Harmoudi et al., 2014)     |
| Chitosan                          | 11.16                                         | (El Harmoudi et al., 2014)     |
| CB-C carbon black                 | 68.60                                         | (Kuśmierzek et al., 2016)      |
| CB-V carbon black                 | 72.20                                         | (Kuśmierzek et al., 2016)      |
| Nano-sized Rice Husk (n-RH)       | 76.92                                         | (Ivy and Chidambaran, 2016)    |
| Biochar from Switchgrass         | 133.00                                        | (Essandoh et al., 2017)        |
| Carbon Nanotubes (CNTs)           | 83.33                                         | (Hue et al., 2018)             |
| LDH [Co-Al-Cl]                    | 27.174                                        | (This study)                   |

Fig. 8. Variation of \( K_c \) and \( \Delta G \) as a function of temperature for 2,4-D adsorption by the [Co-Al-Cl] LDH.

Fig. 9. FT-IR spectra of: (a) 2,4-D; (b) [Co-Al-Cl] LDH before 2,4-D adsorption and (c) [Co-Al-Cl] LDH after 2,4-D adsorption.

Fig. 10. X-ray patterns of: (a) [Co-Al-Cl] HDL before 2,4-D adsorption and (b) [Co-Al-Cl] HDL after 2,4-D adsorption.
corresponds to the C–C vibration of the aromatic ring. The two other bands centered at 1310 cm⁻¹ and 1091 cm⁻¹ cause by the antisymmetric and symmetric vibrations of C–O–C, respectively. On the other hand, absorption bands centered at 1725 cm⁻¹ and 1230 cm⁻¹ are attributed to the stretching vibrations of the C=O and O–H deformation coupled with C–O groups, respectively. (Pavlovic et al., 2005). The FT-IR spectrum of LDH after adsorption of 2,4-D (shown in Fig. 9(c)) indicated the 2,4-D related bands present in conjunction with those of LDH. In 2,4-D adsorbed on LDH, the two bands at 1725 and 1230 cm⁻¹, have disappeared and new band of the 2,4-D has appeared at 1085 cm⁻¹ which indicates symmetric vibrations of 2,4-D.

The X-ray diffractogram of the [Co–Al] LDH before adsorption showed well-defined diffraction peaks, which were indexed to JCPDS 14-191 card Fig. 10(a). In the X-ray diffractogram of [Co–Al] LDH after adsorption (Fig. 10(b)) there is a shift of the value of 2θ to lower values when compared to that obtained for [Co–Al] LDH. This displacement of plane (003) corresponds to an increase in the interlamellar distance d_{003} (Arai and Ogawa, 2009) due to the intercalation of 2,4-D in the interlayer structure of the [Co–Al] LDH. Thus, [Co–Al] LDH can be effectively used as an adsorbent for the removal of 2,4-D from contaminated waters.

### Declarations

**Author contribution statement**

Canobre Sheila: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Josiane Calisto: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Leonardo Freitas: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Ingrid Pacheco: Performed the experiments; Analyzed and interpreted the data.

Laiane Santana: Conceived and designed the experiments; Analyzed and interpreted the data.

Wélitique Fagundes: Analyzed and interpreted the data.

Amaral Fabio: Contributed reagents, materials, analysis tools or data; Wrote the paper.

### Funding statement

This work was supported by FAPEMIG [grant numbers: APQ-02249-14 and APQ-03219-14], CNPq, CAPES and Rede Mineira de Química.

### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

### References

Arai, Y., Ogawa, M., 2009. Preparation of Co–Al layered double hydroxides by the hydrothermal urea method for controlled particle size. Appl. Clay Sci. 42 (3-4), 601–604.

Aumeier, B.M., Dang, A.H.Q., Ohs, B., Yüce, S., Wessling, M., 2019. Aqueous-phase temperature swing adsorption for pesticide removal. Environ. Sci. Technol. 53, 919–927.

Bernardo, M.P., Moreira, F.K.V., Colnago, L.A., Ribeiro, C., 2016. Physico-chemical assessment of (Mg-Al-PO₄)LDHs obtained by structural reconstruction in high concentration of phosphate. Colloids Surf., A 497, 53–62.

Biaín, A., Mazur, M., Natkanski, P., Dudeka, B., Kozak, M., Wacha, A., Kustrowski, P., 2016. Hydrotalcite-derived cobalt–aluminomixed oxide catalysts for toluene combustion. Appl. Surf. Sci. 362, 297–303.

Boyd, W.J., Adamson, A.W., Myers, L.S., 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites. II Kinetics. J. Am. Chem. Soc. 69, 2836–2848.

Carter, A.D., 2000. Herbicide movement in soils: principles, pathways and processes. Weed Res. 40, 113–122.
Feng, C.Y., Chen, P.C, Li, W.S., 2008. Adsorption of 2,4-D on Mg/Al-NiO layered double hydroxides with varying layer charge density. Appl. Clay Sci. 40, 193–200.

Crepaldi, E.L., Pavan, P.C, Valin, J.B., 2000. Comparative study of the coprecipitation methods for the preparation of Layered Double Hydroxides. J. Braz. Chem. Soc. 11, 64–70.

Crepaldi, E.L., Valin, J.B., 1998. Layered double hydroxides: structure, synthesis, properties and applications. Quim. Nova 21, 300–311.

Dogan, M., Alkan, M., Demirbas, O., Ozdemir, Y., Ozmetin, C., 2006. Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions. Chem. Eng. J. 124, 89–101.

El Harmouzi, H., El Gaïnì, L., Daoudi, E., Rchi, M., Boughaleb, Y., El Mhammedi, M., Migalska-Zelas, A., Bakasse, M., 2014. Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties. Opt. Mater. 36, 1471–1477.

Easa, M., Wolgemuth, D., Pittman Jr., C.U., Mohan, D., Milne, T., 2017. Phenoxo herbicide removal from aqueous solutions using fast pyrolysis switchgrass biochar. Chemosphere 174, 49–57.

Evry, A.A.M., Chidambaram, R., 2016. Rice husk as a low cost nanosorbent for 2,4-dichlorophenoxyacetic acid removal from aqueous solutions. Ecol. Eng. 92, 97–105.

Feigenbruch, V., Le Calvé, S., Mirabel, P., 2006. Molar absorptivities of 2, 4 - D, cymoxanil, fenpropidin, isoproturon and pyrimethanil in aqueous solution in the near-UV. Spectrochim. Acta A. 63, 103.

Feng, C.Y., Chen, P.C, Li, W.S., 2008. Adsorption of 2,4-D on Mg/Al-NiO layered double hydroxides with varying layer charge density. Appl. Clay Sci. 40, 193–200.

Crepaldi, E.L., Pavan, P.C, Valin, J.B., 2000. Comparative study of the coprecipitation methods for the preparation of Layered Double Hydroxides. J. Braz. Chem. Soc. 11, 64–70.

Crepaldi, E.L., Valin, J.B., 1998. Layered double hydroxides: structure, synthesis, properties and applications. Quim. Nova 21, 300–311.

Dogan, M., Alkan, M., Demirbas, O., Ozdemir, Y., Ozmetin, C., 2006. Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions. Chem. Eng. J. 124, 89–101.

El Harmouzi, H., El Gaïnì, L., Daoudi, E., Rchi, M., Boughaleb, Y., El Mhammedi, M., Migalska-Zelas, A., Bakasse, M., 2014. Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties. Opt. Mater. 36, 1471–1477.

Easa, M., Wolgemuth, D., Pittman Jr., C.U., Mohan, D., Milne, T., 2017. Phenoxo herbicide removal from aqueous solutions using fast pyrolysis switchgrass biochar. Chemosphere 174, 49–57.

Evry, A.A.M., Chidambaram, R., 2016. Rice husk as a low cost nanosorbent for 2,4-dichlorophenoxyacetic acid removal from aqueous solutions. Ecol. Eng. 92, 97–105.

Feigenbruch, V., Le Calvé, S., Mirabel, P., 2006. Molar absorptivities of 2, 4 - D, cymoxanil, fenpropidin, isoproturon and pyrimethanil in aqueous solution in the near-UV. Spectrochim. Acta A. 63, 103.

Feng, C.Y., Chen, P.C, Li, W.S., 2008. Adsorption of 2,4-D on Mg/Al-NiO layered double hydroxides with varying layer charge density. Appl. Clay Sci. 40, 193–200.

Crepaldi, E.L., Pavan, P.C, Valin, J.B., 2000. Comparative study of the coprecipitation methods for the preparation of Layered Double Hydroxides. J. Braz. Chem. Soc. 11, 64–70.

Crepaldi, E.L., Valin, J.B., 1998. Layered double hydroxides: structure, synthesis, properties and applications. Quim. Nova 21, 300–311.

Dogan, M., Alkan, M., Demirbas, O., Ozdemir, Y., Ozmetin, C., 2006. Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions. Chem. Eng. J. 124, 89–101.

El Harmouzi, H., El Gaïnì, L., Daoudi, E., Rchi, M., Boughaleb, Y., El Mhammedi, M., Migalska-Zelas, A., Bakasse, M., 2014. Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties. Opt. Mater. 36, 1471–1477.

Easa, M., Wolgemuth, D., Pittman Jr., C.U., Mohan, D., Milne, T., 2017. Phenoxo herbicide removal from aqueous solutions using fast pyrolysis switchgrass biochar. Chemosphere 174, 49–57.

Evry, A.A.M., Chidambaram, R., 2016. Rice husk as a low cost nanosorbent for 2,4-dichlorophenoxyacetic acid removal from aqueous solutions. Ecol. Eng. 92, 97–105.

Feigenbruch, V., Le Calvé, S., Mirabel, P., 2006. Molar absorptivities of 2, 4 - D, cymoxanil, fenpropidin, isoproturon and pyrimethanil in aqueous solution in the near-UV. Spectrochim. Acta A. 63, 103.

Feng, C.Y., Chen, P.C, Li, W.S., 2008. Adsorption of 2,4-D on Mg/Al-NiO layered double hydroxides with varying layer charge density. Appl. Clay Sci. 40, 193–200.

Crepaldi, E.L., Pavan, P.C, Valin, J.B., 2000. Comparative study of the coprecipitation methods for the preparation of Layered Double Hydroxides. J. Braz. Chem. Soc. 11, 64–70.

Crepaldi, E.L., Valin, J.B., 1998. Layered double hydroxides: structure, synthesis, properties and applications. Quim. Nova 21, 300–311.

Dogan, M., Alkan, M., Demirbas, O., Ozdemir, Y., Ozmetin, C., 2006. Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions. Chem. Eng. J. 124, 89–101.

El Harmouzi, H., El Gaïnì, L., Daoudi, E., Rchi, M., Boughaleb, Y., El Mhammedi, M., Migalska-Zelas, A., Bakasse, M., 2014. Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties. Opt. Mater. 36, 1471–1477.

Easa, M., Wolgemuth, D., Pittman Jr., C.U., Mohan, D., Milne, T., 2017. Phenoxo herbicide removal from aqueous solutions using fast pyrolysis switchgrass biochar. Chemosphere 174, 49–57.

Evry, A.A.M., Chidambaram, R., 2016. Rice husk as a low cost nanosorbent for 2,4-dichlorophenoxyacetic acid removal from aqueous solutions. Ecol. Eng. 92, 97–105.

Feigenbruch, V., Le Calvé, S., Mirabel, P., 2006. Molar absorptivities of 2, 4 - D, cymoxanil, fenpropidin, isoproturon and pyrimethanil in aqueous solution in the near-UV. Spectrochim. Acta A. 63, 103.

Feng, C.Y., Chen, P.C, Li, W.S., 2008. Adsorption of 2,4-D on Mg/Al-NiO layered double hydroxides with varying layer charge density. Appl. Clay Sci. 40, 193–200.

Crepaldi, E.L., Pavan, P.C, Valin, J.B., 2000. Comparative study of the coprecipitation methods for the preparation of Layered Double Hydroxides. J. Braz. Chem. Soc. 11, 64–70.

Crepaldi, E.L., Valin, J.B., 1998. Layered double hydroxides: structure, synthesis, properties and applications. Quim. Nova 21, 300–311.

Dogan, M., Alkan, M., Demirbas, O., Ozdemir, Y., Ozmetin, C., 2006. Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions. Chem. Eng. J. 124, 89–101.