

## Evidence of lead ions on palygorskite surface after adsorptive process: kinetic and isotherms studies

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### ABSTRACT

Our previous work reported that palygorskite has potential for application as metal cations adsorbent due to its chemical and mineralogical properties. In this work, kinetic study and adsorption isotherms were performed in order to evaluate Pb (II) ions adsorption rate, maximum capacity and type of adsorption by using palygorskite as adsorbent. Adsorption tests were performed in batch, using pH of 5, 2 g of palygorskite, 40 mL of synthetic effluent solution and stirring for 1 hour. Kinetic experiments were performed using 34 mg L<sup>-1</sup> of a lead synthetic effluent at same mass and pH conditions. Furthermore, after adsorption studies, the sample was characterized by X-ray fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray spectroscopy (EDS) analysis, in order to verify and understand the interaction of lead ions in palygorskite. The results demonstrated that palygorskite presented an equilibrium time of 10 min with 99.14% of removal, following pseudo-second order kinetic. The maximum adsorption capacity was 21.65 mg g<sup>-1</sup> and Gibbs' adsorption-free energy was -21.39 KJ mol<sup>-1</sup>, with Langmuir model being the most suitable for adjustment of the data. Thus, its presence was confirmed by characterization techniques, indicating that the metal is distributed homogeneously on palygorskite surface, proving its efficiency as lead ions adsorbent.

**Keywords:** Brazilian palygorskite, kinetic, isotherm, characterization.

### 1. INTRODUCTION

Pollution by heavy metals originating from anthropogenic activities, such as those in industries, commerce and agriculture, poses a threat to ecosystems and human health, and has gradually drawn wide concern across the globe because of their increased discharge, acute toxicity, persistence, bioaccumulation and biomagnification through food chains [1-3].

Industrialization and population growth are identified as key factors responsible for the increase in pollution by heavy metals, expanding the need to treat effluents containing such polluting species [4, 5]. These toxic ions are frequently present in wastewater due to industrial activities such as dyeing textile, hydrometallurgical, tanning, smelting of ores, metal plating, battery industries, fertilizers and herbicides production, motor, electrochemical, house paint, gasoline additives and plumbing pipes. [6] Variety of clays and clay minerals play an important role in the environment and used as an effective adsorbent material for the removal of toxic metal ions from water solution [5, 7].

Lead is a naturally occurring element, found in abundance in the earth crust, almost always as lead sulphide (galena) [8]. Due to its vast industrial application in production of batteries, solder, metal alloys, cable shields, pigments, rust inhibitors, ammunition, glassware and plastic stabilizers, it is one of the most commonly found heavy metals in water bodies [9, 10].

In Brazil, the region of Alto Vale do Ribeira, in the extreme southeast of São Paulo State and northeast of Paraná State, as well as the region of Boquira, in the State of Bahia, are the main Brazilian cases of contamination by this metal. Boquira region covers the most worrying case of lead contamination in Brazil, where lead-zinc mining worked for approximately 30 years, until it was suddenly abandoned. The waste generated, containing toxic metals such as lead, zinc, silver, barium, copper, chromium and nickel, was improperly deposited close to the city [11], damaging not only the commercial activities, but also the living conditions of the population. For this reason, the remediation of soil and water, aiming to minimize environmental risks and human exposure to these contaminated wastes are targets of study until nowadays [12, 13]. In addition, there is a concern to raise awareness and encourage companies in the mining sector, in order to invest in safety measures, as well as comply with the legislative requirements that compete in the companies operating in this sector [14].

Due to this, a few technologies for the removal of heavy metals from aqueous solutions have been studied nowadays. These technologies include chemical precipitation, ion exchange, membrane filtration, carbon adsorption and coprecipitation/adsorption [15-17]. However, these techniques have inherent limitations in practice (such as complicated treatment process, high cost and energy requirement) or pose danger of secondary pollution [18, 19].

Adsorption is an effective method of removing a wide range of contaminants from effluents, especially when adsorbate and adsorbent combination is the best possible [20]. However, the main disadvantage of adsorption methods is the high price of the adsorbents, which increases the cost of wastewater treatment. The most generally used solid adsorbent is activated carbon [21]. However, activated charcoal is expensive and for effluents containing metallic ions it requires chelating agents to enhance its performance, thus increasing treatment cost [22, 23]. Therefore, the need of alternative low cost adsorbents has prompted the search for new and cheaper sorption processes for aqueous effluent treatment, since these materials could significantly reduce the wastewater-treatment cost [24-27].

Thus, the use of clay minerals as adsorbent materials for various contaminants present in aquatic environment emerges as an economically viable alternative [20, 28]. Palygorskite, for example, has been investigated in recent decades as an adsorbent for the removal of organic pollutants and metallic ions from solutions [29-35]. Palygorskite has been used for this purpose due to an excellent adsorptive property, which are inherent in its porous structure associated with its high surface area, generally between 125 and 210 m<sup>2</sup> g<sup>-1</sup> [36], giving it an advantage in the adsorption of heavy metals. Besides that, the increasing interest in the use of this material as adsorbent is related to its high worldwide availability, low cost and possibility of reuse.

The chemical composition of palygorskite unit cell is (Mg,Al)<sub>5</sub>Si<sub>8</sub>O<sub>20</sub>(OH)<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>.4H<sub>2</sub>O. Mineralogically, palygorskite belongs to the group of 2:1 phyllosilicates and has a three-dimensional structure consisting of a double layer composed of silicon oxide tetrahedra bound by octahedral magnesium ions [37, 38]. These tapered layers are joined at the ends by Si-O-Si bonds, resulting in a porous structure with channels [39, 40] which have exchangeable cations and water [41].

In palygorskite structure, the most common substitutions are Si<sup>4+</sup> in the tetrahedra layer, by trivalent cations (Al<sup>3+</sup> or Fe<sup>3+</sup>) and Al<sup>3+</sup> cations in the octahedra layer, by divalent cations (Mg<sup>2+</sup> or Fe<sup>2+</sup>), leading to a deficiency of positive charges and to a negative potential on the clayey surface [42, 43].

Palygorskite is a typical fibrous clay, whose fibers have active sites for adsorption, with the silanol group (SiO-H) being the predominant site in palygorskite. These sites can interact through hydrogen bonds to adsorb cationic species or accumulated molecules at the interfaces [23].

In Brazil, the main palygorskite deposits are in the municipality of Guadalupe, in Piauí's state [44, 45] and in the region of Alcântara, in the state of Maranhão [46, 47]. Among Brazilian palygorskite occurrences, the reserves in the Guadalupe region have the greatest potential for economic use. However, samples from this region are not used for more noble commercial purposes, being a national raw material, free from more technological economic interests. Thus, in this work, the efficiency of the processed Guadalupe's palygorskite sample as an adsorbent for the removal of Pb<sup>2+</sup> from aqueous solutions was investigated by batch tests.

A kinetic study was conducted in order to determine the necessary time to reach the equilibrium of the system, aiming to assess relevant information about its adsorption rate. Besides that, the relationship between the effluent concentration and the amount of adsorbed ions were described by Langmuir and Freundlich isotherms models.

After adsorption tests, X-ray fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray spectroscopy (EDS) of the system were conducted in order to verify the presence of lead ions in palygorskite.

## 2. MATERIALS AND METHODS

### 2.1 Preparation and characterization of palygorskite (adsorbent)

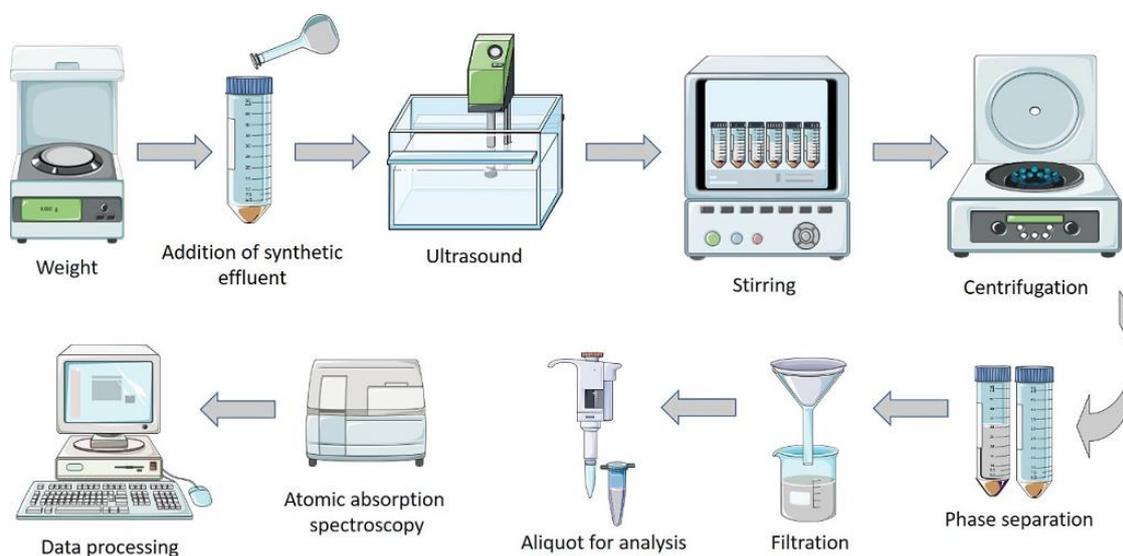
The preparation and characterization of palygorskite was performed as previously described [4]. In this work, it was added the textural properties study, which is an important characteristic of the adsorbent material.

The textural properties were determined by nitrogen ( $N_2$ ) physisorption at  $-196^\circ\text{C}$ . Analyses were performed with a Micrometrics using approximately 400 mg of sample. Pretreatment of the samples consisted of drying at  $100^\circ\text{C}$  under vacuum at  $1 \times 10^{-6}$  mmHg for 24 hours for the elimination of physically adsorbed water. Then the actual analysis was carried out, in which the adsorption and desorption isotherms were obtained by varying the partial pressure of  $N_2$ . With the isotherms, the surface area was calculated by the B.E.T method and the pore size distribution was obtained from the desorption isotherm of  $N_2$  by the B.J.H. (Barret-Joyner-Halenda) method.

### 2.2 Adsorption experiments

Kinetic experiments were previously performed using  $34 \text{ mg L}^{-1}$  of a lead synthetic effluent prepared with lead II nitrate salt ( $\text{Pb}(\text{NO}_3)_2$ ) from Sigma-Aldrich and 2 g of palygorskite at pH 5. For different tested times (from 10 to 50400 min), the samples were agitated on an IKA model KS 4000i orbital shaker table with incubation, rotating at 250 rpm at room temperature (approximately  $21^\circ\text{C}$ ), then centrifuged for 10 minutes in Cientec CT-6000 digital microprocessed bench centrifuge. The supernatant was filtered with qualitative filter paper and submitted to flame atomic absorption spectrometry (FAAS) for  $\text{Pb}^{2+}$  ions quantification. The analyses were performed with a Varian 50B model with acetylene flame and nitric acid solutions ( $\text{HNO}_3$ ) were used to construct the analytical curve.

To batch adsorption tests, palygorskite mass was weighed and transferred to a Falcon tube with 40 mL of synthetic effluent. The pH was adjusted with  $0.1 \text{ mol L}^{-1}$  NaOH and HCl solutions using the Metrohm model 827 pH meter. The samples were then subjected to ultrasonic scattering to disperse the particles in homogeneous condition and then agitated on the same shaker and at equal conditions described for kinetics experiments. A schematic representation of adsorption process steps can be seen in Fig. 1.



**Figure 1:** Representative scheme of adsorption experiments steps.

The lead adsorption isotherm was studied in order to understand the relationship between the effluent's concentration and the amount of  $\text{Pb}^{2+}$  ions adsorbed. The experiments were carried out using the lead solution concentration from 34.1 to  $3360 \text{ mg L}^{-1}$ . The contact time was defined according to the kinetic study, where 2 g of the sample was used at pH 5. All readings were performed in triplicate and accompanied by an analytical blank.

The metal ion adsorption capacity of the adsorbent in batch test was calculated by the Equation (1)

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

Where:

$q_e$  is the equilibrium capacity of lead on the adsorbent ( $\text{mg g}^{-1}$ );

$C_o$  the initial concentration of lead solution ( $\text{mg L}^{-1}$ );

$C_e$  the equilibrium concentration of lead solution ( $\text{mg L}^{-1}$ );

$m$  the mass of adsorbent used (g);

$V$  the volume of lead solution (L).

### 2.3 Characterization after adsorption

In order to characterize the metal ions, present on palygorskite after adsorption process, X-ray fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray spectroscopy (EDS) analyses were conducted.

X-ray fluorescence (XRF) was performed on an X-ray fluorescence spectrometer, (WDS-1), model AXIOS MAX (Panalytical) at X-Ray Fluorescence Laboratory in CETEM. The analysis was conducted with 0.200 g which was subjected to muffle furnace with a temperature of 1,000°C for 16 hours. After cooling in desiccator, the samples were weighed to check the loss of ignition (LOI). For chemical analysis, approximately 5.0 g were placed in an oven at 100°C for 24 hours and cooled in a desiccator. Then 3.0 g of the sample was added to 0.3 g of boric acid and pressed in an automatic press VANEON (20 mm mold) for 3 series of 10 seconds with a pressure of 20 tons.

Fourier Transform Infrared Spectroscopy (FTIR) was performed in the Laboratory of Instruments and Research of the Chemistry Institute at UFRJ using Nicolet 6700 FT-IR spectrophotometer, with records from 4,000 to 400  $\text{cm}^{-1}$  and 4  $\text{cm}^{-1}$  of resolution in KBr tablets.

Scanning electron microscopy (SEM) analysis was performed on Tabletop microscope equipment, brand HITACHI TM303 Plus. 1.0 g of the sample was pressed with carbon in FLUXANA press (Vaneox® Technology) and analyzed in backscattered electron modules and energy dispersive spectrometry (EDS) for chemical elements qualitative determination. The mapping of lead element distribution was carried out in 200 seconds with 5000x of approximation.

## 3. RESULTS AND DISCUSSION

### 3.1 Determination of Textural Properties

Table 1 presents the textural properties (surface area, pore volume and average pore size). According to the results, palygorskite sample has a surface area of 71.29  $\text{m}^2 \text{g}^{-1}$ . In the kinetic and isothermal study of lead adsorption, the surface area obtained using a Chinese palygorskite of 200 mesh (75  $\mu\text{m}$ ) was 48.66  $\text{m}^2 \text{g}^{-1}$  [31]. Thus, it is possible to conclude that previous ore dressing corroborates with the increase of the surface area. The pore volume is 0.24  $\text{cm}^3 \text{g}^{-1}$ , which is in accordance with the values obtained for this clay mineral in literature [48, 49]. The average pore size is 12.23 nm, which characterizes this clay mineral as a mesoporous material, which covers pores with an internal width between 2 and 50 nm [50].

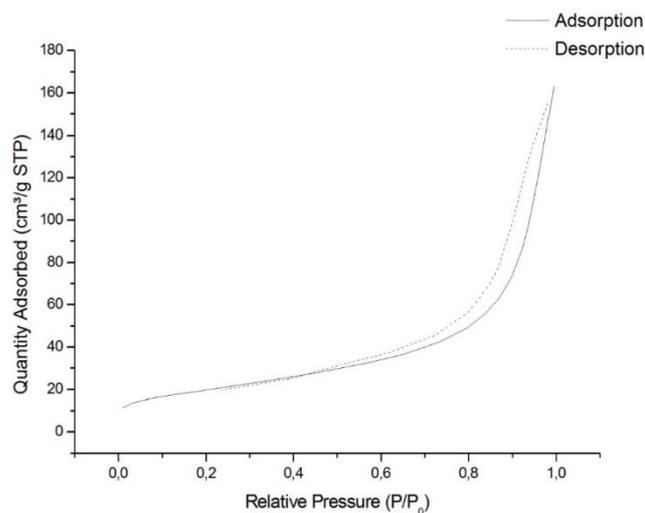
**Table 1:** Textural properties of Guadalupe's palygorskite.

Textural properties	
Surface área	71.29 $\text{m}^2 \text{g}^{-1}$
Pore volume (B.J.H. method)*	0.24 $\text{cm}^3 \text{g}^{-1}$
Average pore size (B.J.H. method)*	12.23 nm

\*Average desorption pore size

According to the International Union of Pure and Applied Chemistry (IUPAC) [50], isotherms can be

classified into six different characteristic types according to the nature of the solid. The hysteresis presence, observed in two types of isotherm, occurs because the saturation pressures are not the same for condensation and evaporation inside the pores, that is, the adsorption and desorption isotherms do not coincide. The isotherm profile obtained (Fig. 2) is classified as type IV, characteristic of mesoporous materials.

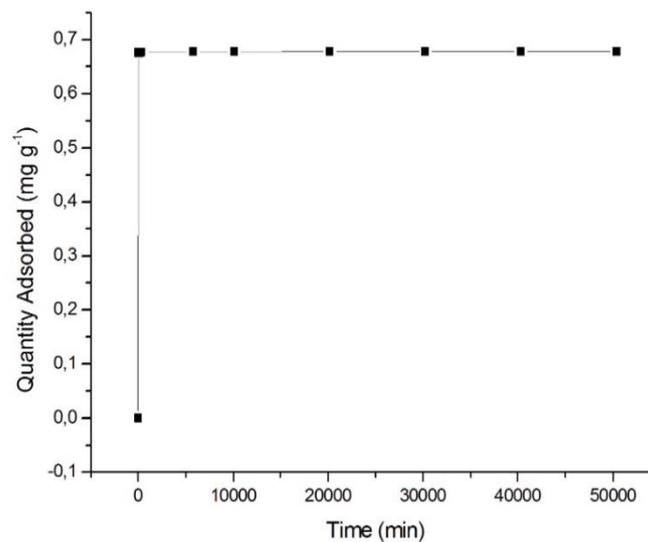


**Figure 2:** Isotherm profile obtained by B.E.T method.

It can be observed in the adsorption isotherm, that the initial process occurs in monolayer at low pressures, followed by adsorption in multilayers. At this point, the amount of gas adsorbed increases rapidly with little pressure variation. Considering that the predominant class of pores in a solid material is the one where the largest amount of  $N_2$  was released to fill the pores volume with a certain diameter, and that for palygorskite sample, the average pore size largest distribution was between the range of 2 to 50 nm, this sample is classified as being a mesoporous material, corroborating with the obtained isotherm. Hysteresis provides important information about pores shape. The type of hysteresis in the studied sample according to IUPAC was classified as hysteresis type H3 and indicates the presence of pores in cracks, which format is associated with non-rigid particles aggregates in the form of plates originating this type of pore.

### 3.2. Kinetics studies

Fig. 3 shows the amount of lead ions adsorbed by palygorskite sample according to contact time. Equilibrium was reached in 10 min, with  $1.2492 \text{ mg g}^{-1}$  of  $Pb^{2+}$  adsorbed, representing a removal of 99.14%. The same values were found for 60 min of contact and in order to guarantee the equilibrium conditions of the system, the tests were performed with a longer equilibrium time than that observed, since 60 min could be considered a viable time for the development of the process on an industrial scale. Besides that, it is a way of ensuring a complete adsorption of lead ions to the active sites present in palygorskite structure.



**Figure 3:** Equilibrium time of palygorskite sample.

According to CHEN and WANG [31], in their lead ions adsorption kinetic study by a 200 mesh (75  $\mu\text{m}$ ) palygorskite determined that the equilibrium time was reached in 8 hours of contact time and remained constant. FAN *et al.* [32], on the other hand, using the same clay mineral granulometry, verified that the equilibrium was reached at 3 hours of contact. Although both palygorskite samples are from the same location (Gansu, China), the shorter equilibrium time obtained by FAN *et al.* [32], may be associated with the heat treatment carried out, since with the increase in temperature the loss of water molecules occurs, providing more adsorption sites.

POTGIETER *et al.* [30], investigated the removal of Pb (II) from an aqueous solution of palygorskite and found that the equilibration time for this ion was only 30 min for Pb (II) concentrations of 20 to 100  $\text{mg L}^{-1}$ . According to the authors the balance was quickly reached, indicating that the adsorptive sites were more exposed. The rapid adsorption (10 min) obtained in this study may be associated with the previous ore dressing carried out on palygorskite sample [4], promoting a purification and reduction of particle size (20  $\mu\text{m}$ ) that allowed the active sites to become more available for the studied ion.

Aiming to investigate palygorskite adsorption process characteristics on lead removal and the controlling step of the potential rate (chemical reaction, diffusion control and mass transfer), the kinetic data were analyzed by using pseudo-first order and pseudo-second order linear models, as presented in Equations 2 e 3, respectively [51].

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{k_1}{2,303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where:

$q_e$  is the amount adsorbed per gram of adsorbent at equilibrium ( $\text{mg g}^{-1}$ );

$q_t$  is the amount adsorbed per gram of adsorbent at time  $t$  ( $\text{mg g}^{-1}$ ).

$t$  is the contact time;

$k_1$  is the constant rate of pseudo-first order adsorption ( $\text{min}^{-1}$ );

$k_2$  is the constant rate of pseudo-second order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ );

The values of  $k_1$  and  $q_e$  were calculated from slope and intercept of the plot of  $\text{log}(q_e - q_t)$  vs.  $t$ , while the values of  $k_2$  and  $q_e$  were evaluated from the intercept and slope of a plot  $t/q_t$  vs.  $t$ . Both kinetic constants  $k_1$  and  $k_2$  are interpreted as a time scale factor, which aim to indicate the speed with which the system reaches

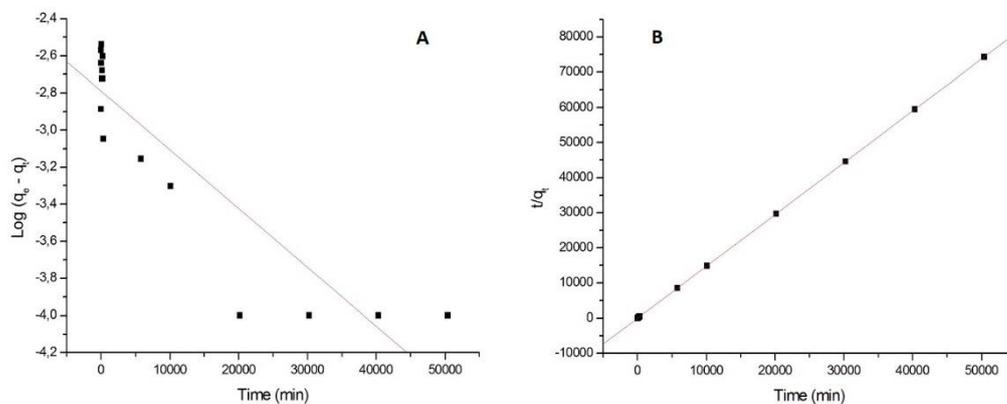
equilibrium. The applicability of the model with the best fit of the data is conditioned to a linear relationship close to 1.

Table 2 shows the kinetic parameters obtained for both kinetic models and the linearized graphs of pseudo-first order and pseudo-second order models are presented in Figure 4, respectively.

**Table 2:** Kinetic parameters of pseudo-first order and pseudo-second order models.

	Pseudo-first order			Pseudo-second order		
* $q_{\text{exp}}$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$q_c$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$q_c$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$
0.6781	$6.9\times 10^{-5}$	615.74	0.8178	1.31	0.6780	1.0000

\* $q_{\text{exp}}$  lead ions adsorbed by palygorskite experimentally



**Figure 4:** Linearized pseudo-first order model (A) and linearized pseudo-second order model (B).

According to analysis of the results, it is observed that the rate correlation coefficients of pseudo-second order kinetic model ( $R^2 = 1.0000$ ) is higher than that obtained for pseudo-first order model ( $R^2 = 0.8178$ ). In addition, pseudo-second order parameters  $q_{\text{ex}}$  and  $q_c$  demonstrated a good agreement with each other, indicating that this model is the one that best describes the adsorption kinetics of lead ions by palygorskite.

As stated by WANG and GUO [52], a system that better fits a pseudo-second order model indicates that the adsorbent is abundant with active sites. This fact corroborates with the short equilibrium time obtained in this work that was due to an efficient ore dressing step that increased the adsorptive sites availability. This result indicated that the sorption process was complex and involved more than one mechanism [53].

### 3.3. Adsorption studies

In order to study the relationship between the amount of ions adsorbed by work sample and lead solution concentration (adsorption isotherm), the contact time of 60 min was fixed, and solution concentration was varied until reaching balance. Among mathematical models of isotherms used in liquid systems that involve the treatment of wastewater and industrial effluents, the main models to describe the adsorption equilibrium are the Langmuir and Freundlich isotherms [54].

Langmuir isotherm is a theoretical equilibrium isotherm which relates the amount of solute adsorbed on a surface to the concentration of the solute in the solution. This model is based on the hypothesis that the interaction forces between the adsorbed molecules are negligible and that each site can be occupied by only one molecule. All molecules are adsorbed on a fixed number of sites. For high concentrations of solute, the

equation predicts a limited capacity by the formation of the monolayer.

Freundlich isotherm is an empirical adsorption isotherm for non-ideal adsorption on heterogeneous surfaces, as well as for multilayer adsorption.

The adsorption capacity of a saturated monolayer (Langmuir) can be represented by Equation 4 [31]. The Equation 5 represents the linearized form for the Freundlich model [31].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

Where:

$C_e$  is the concentration of the solution in equilibrium ( $\text{mg L}^{-1}$ );

$q_e$  is the amount of solute adsorbed at equilibrium ( $\text{mg g}^{-1}$  of adsorbent);

$q_m$  represents the maximum amount of solute adsorbed to form a complete monolayer ( $\text{mg g}^{-1}$ );

$b$  is the adsorption constant of Langmuir, which is related to free energy of adsorption;

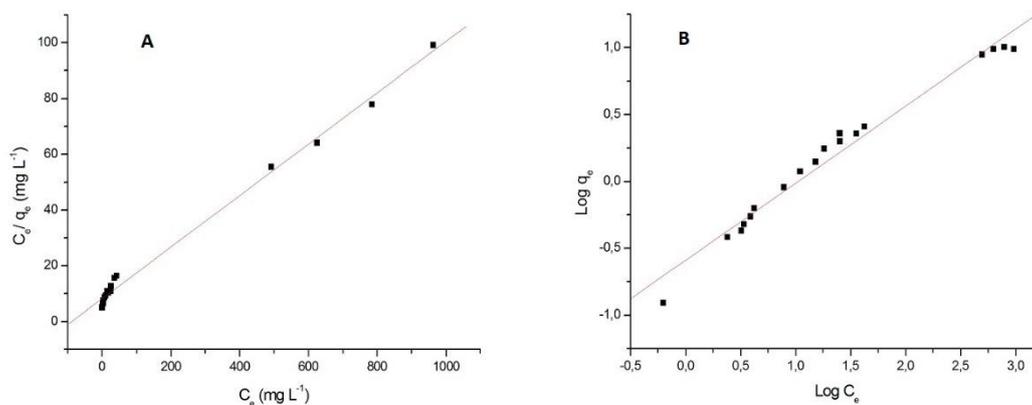
$K_f$  and  $n$  are Freundlich's constants;

$K_f$  indicates the adsorption capacity of the adsorbent and  $n$  indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity.

Adsorption isotherms were obtained from the experimental data using Equations 4 and 5. The isotherms constants and the correlation coefficients were calculated from the linearization of the Langmuir and Freundlich equations by plotting  $C_e/q_e$  vs.  $C_e$  and  $\log q_e$  vs.  $\log C_e$ . These results are shown in Table 3 and Figure 5.

**Table 3:** Langmuir and Freundlich constants and correlation coefficients associated with Pb (II) adsorption isotherms by palygorskite.

Langmuir's model			Freundlich's model		
$Q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$	$n$	$R^2$
21.65	0.018	0.9943	1389.00	2.52	0.9838



**Figure 5:** Linearized adsorption isotherm for lead ions using Langmuir model (A) and Freundlich model (B).

For the adsorption of lead ions, the most suitable model was the Langmuir isotherm model, considering the higher value of  $R^2$  (0.9943) in relation to the Freundlich isotherm (0.9838). This can occur due to the homogeneous distribution of active sites on the palygorskite surface. The maximum adsorption value ( $q_m$ ) of 21.65 mg g<sup>-1</sup> and the value of  $b$  equal to 0.0185 indicate that the studied sample can be used to adsorb lead ions in effluents.

The adsorption data of lead ions by palygorskite also fit in the Freundlich model, but not as well as in the Langmuir model. The adsorption profile of palygorskite is well described by the Langmuir equation [30-32, 34, 55].

The coefficient correlation value was very close to the unit ( $R^2 = 0.9943$ ) indicating that the obtained adsorption curve really obeys the Langmuir model. Therefore, the apparent equilibrium constant can be estimated to be 5630.40 L mol<sup>-1</sup> and Gibbs' adsorption-free energy, calculated according to Equation 6, using  $T = 298\text{K}$ , was -21.39 KJ mol<sup>-1</sup>. This calculated  $\Delta G$  value indicated that in this case a chemical and spontaneous adsorption process occurs through interactions between the adsorbed cation and the basic centers of the adsorbent [42, 56], at 25°C.

$$-\Delta G = RT \ln K \quad (6)$$

Where  $R$  is the gas constant (8.31451 J K<sup>-1</sup> mol<sup>-1</sup>) and  $T$  the temperature in Kelvin.

### 3.4. Characterization after adsorption

Table 4 presents the chemical composition of palygorskite sample after adsorption. In our previous work [4], the sample before adsorption presented 50.50, 15.50, 4.50, 7.10 and 18.6% w/w of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub> and Loss on Ignition (LOI), respectively. It can be observed that before adsorption, the content of these oxides increased due to a decrease in (LOI). The presence of lead oxides (PbO), not present before, confirms its adsorption onto palygorskite.

**Table 4:** XRF of palygorskite sample after lead adsorption.

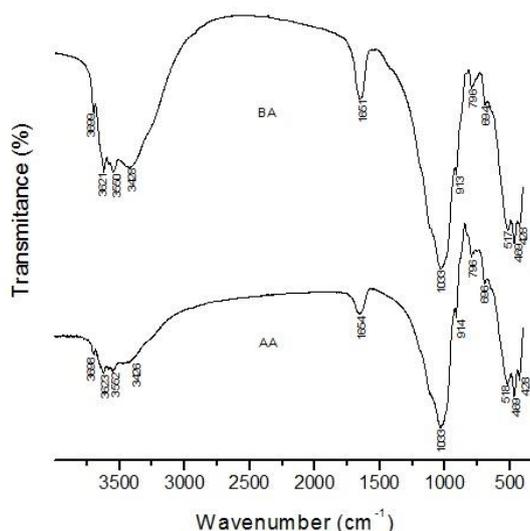
Oxide	(% w/w)
SiO <sub>2</sub>	55.70
Al <sub>2</sub> O <sub>3</sub>	17.40
MgO	4.70
Fe <sub>2</sub> O <sub>3</sub>	7.60
PbO	2.70
K <sub>2</sub> O	2.20
TiO <sub>2</sub>	0.74
MnO	0.32
CaO	0.12
Na <sub>2</sub> O	0.10
LOI*	7.90
Total	99.48

\*LOI – Loss on ignition

According to Figure 6, it is possible to observe the results obtained for spectroscopy in the Infrared Region with Fourier transform (FTIR) for the systems before adsorption (BA) and after adsorption (AA). According to the BA spectrum, there is a 3699 cm<sup>-1</sup> band that can be attributed to the vibrational stretching of Mg-OH palygorskite group, followed by the same vibrational species of Al-O-H group at 3621 cm<sup>-1</sup> characteristics of palygorskite. The bands at 3550 and 3428 cm<sup>-1</sup> can be attributed to coordination and zeolitic waters [57], while the band at 1651 cm<sup>-1</sup> was attributed to water molecules angular deformation [58]. Characteristic bands of Si-O-Si vibrations can be seen in 1033, 913 cm<sup>-1</sup> and the bands in 517 and 469 cm<sup>-1</sup>

refers to the vibration of the Si-O-Al and Si-OH respectively [42], The bands at 694 and 428  $\text{cm}^{-1}$  correspond to the Si-O-Mg vibrations [59].

By spectra analysis, displacements of the bands are observed in the AA spectrum, which may indicate the presence of lead ions on the clay mineral surface. These displacements are probably due to ion exchange between  $\text{Pb}^{2+}$  and  $\text{H}^+$  presented in  $-\text{OH}$  groups of palygorskite, since the bands containing deformations and stretches related to this functional group were precisely those that obtained the greatest displacements, in addition, to a possible electrostatic interaction between  $\text{Pb}^{2+}$  with the silanol (Si-OH) and aluminol (Al-OH) groups present on the palygorskite surface. Besides that, such changes in wavelength and intensity of transmittance are addressed in literature as being indicative of the presence of contaminants in the adsorbent [60-63].



**Figure 6:** FTIR of palygorskite sample after lead adsorption.

Mapping and EDS obtained by SEM for palygorskite sample after lead adsorption is shown in Fig. 7 and 8, respectively. The blue image represents the mapping of Mg, characteristic palygorskite element, and the red image represents the lead present on the sample surface. Thus, it was observed that the metal is distributed homogeneously on palygorskite surface. Besides that, EDS result confirmed the presence of lead, corroborating with the results of adsorption, XRF and FTIR presented, evidencing that lead had been adsorbed by the clay mineral.

It is worth mentioning that modification of clay minerals, such as thermal activation [64], acid treatment [65] and pillarization [66], can be achieved by using any of the available modification methods, but there are challenges associated with each method that needs to be considered before making a decision. Although clay mineral for heavy metal remediation is being used because it is cost-effective and environmentally friendly, however, modification may result in additional costs and release of new chemical agents into the environment [67, 68]. Thus, a previous physical treatment, such as an ore dressing to reduce granulometry and consequently existing impurities, already consists of an efficient process to increase the removal capacity of these contaminants, especially lead ions, as presented in this work.

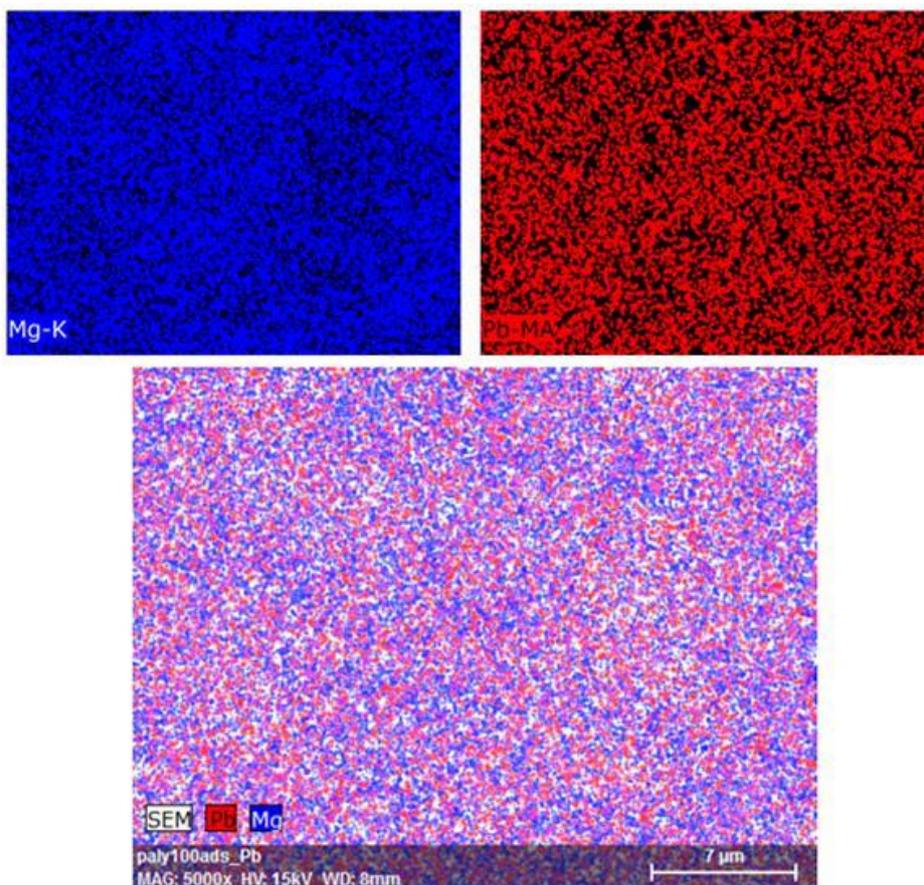


Figure 7: Mapping of magnesium (blue) and lead (red) distribution for palygorskite sample.

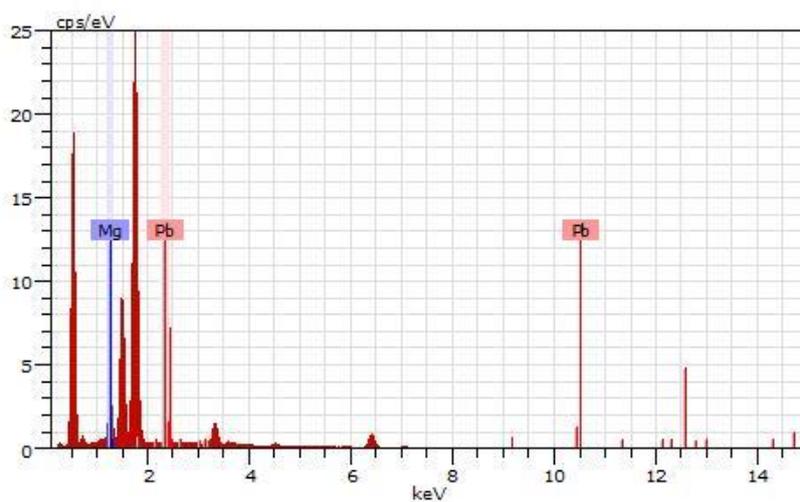


Figure 8: EDS of palygorskite sample after lead adsorption.

#### 4. CONCLUSIONS

The determination of the textural properties indicates that Brazilian palygorskite has a surface area of 71.29 m<sup>2</sup> g<sup>-1</sup>, a pore volume of 0.24 cm<sup>3</sup> g<sup>-1</sup> and an average pore size of 12.23 nm, characteristic of mesoporous

materials.

The kinetic study revealed that Pb (II) adsorption onto palygorskite clay reached rapid equilibrium (10 min) and was well represented by pseudo-second order kinetic model. Batch adsorption assays were efficient (99.14%) for lead ions with 60 min shaking on an orbital shaker table, and pH = 5.

Langmuir isotherm model was most suitable to fit the data obtained in the adsorption process, since the R<sup>2</sup> value was higher than that obtained for the Freundlich model. Thus, the results obtained suggest that the adsorption process occurs in a monolayer on the active sites of each adsorbent. The studied sample presented adsorption capacity of 21.65 mg g<sup>-1</sup> and Gibbs' adsorption-free energy was -21.39 KJ mol<sup>-1</sup>.

Therefore, the data obtained for both kinetic study and adsorption isotherm indicate a chemisorption process, and according to the free energy of adsorption, the reaction occurs spontaneously, evidencing palygorskite adsorptive potential.

XRF, FTIR and mapping coupled with EDS results after adsorption confirmed the presence of the metal on clayey surface, ratifying palygorskite efficiency in lead ions removal.

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## 6. REFERENCES

- [1] XU, P., ZENG, G.M., HUANG, D.L., *et al.* "Adsorption of Pb (II) by iron oxide nanoparticles immobilized phanerochaete chrysosporium: equilibrium, kinetic, thermodynamic and mechanisms analysis", *Chemical Engineering Journal*. v. 203, pp. 423-431, Sep. 2012.
- [2] BARZEGAR, R., MOGHADDAM, A.A., ADAMOWSKI, J., *et al.* "Assessing the potential origins and human health risks of trace elements in groundwater: A case study in the Khoy plain, Iran", *Environmental Geochemistry and Health*. v. 41, pp. 981-1002, Sep. 2018.
- [3] MGBENU, C.N., EGBUERI, J.C., "The hydrogeochemical signatures, quality indices and health risk assessment of water resources in Umunya district, southeast Nigeria", *Applied Water Science*. v. 9, n. 22, Jan. 2019.
- [4] SIMÕES, K.M.A., NOVO, B.L., FELIX, A.A.S., *et al.* "Ore Dressing and Technological Characterization of Palygorskite from Piauí/Brazil for Application as Adsorbent of Heavy Metals", In: ed. Springer International Publishing, *Characterization of Minerals, Metals and Materials*, chapter 7, California, USA, 2017.
- [5] PYRGAKI, K., MESSINI, P., ZOTIADIS, V., "Adsorption of Pb and Cu from Aqueous Solutions by Raw and Heat-Treated Attapulgitic Clay". *Geosciences*. v. 8, n. 5, pp. 157, Apr. 2018.
- [6] JAISHANKAR, M., TSETEN, T., ANBALAGAN, N., *et al.* "Toxicity, mechanism and health effects of some heavy metals", *Interdisciplinary Toxicology*. v. 7, n. 2, pp. 60-72, Nov. 2018.
- [7] UDDIN, M.K., "A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade". *Chemical Engineering Journal*. v. 308, pp. 438-462, Jan. 2017.
- [8] AZEVEDO, F.A., CHASIN, A.A.M., "Chumbo", In: Atheneu, *Metals: gerenciamento da toxicidade*, 1 ed., chapter 12, Rio de Janeiro, Brazil, 2003.
- [9] AXTELL, N.R., CLAUSSEN, K., STERNBERG S.P.K., "Lead and nickel removal using *Microspora* and *Lemna minor*", *Bioresource Technology*. v. 89, n. 1, pp. 41-48, Aug. 2003.
- [10] MASINDI, V., MUEDI, K.L., "Environmental Contamination by Heavy Metals", In: Hosam El-Din M. Saleh and Refaat F. Aglan, *Heavy Metals*, Jun. 2018.
- [11] DALTRO, R.R., DOS ANJOS, J.A.S.A., GOMES, M.C.R., "Avaliação de metais pesados nos recursos hídricos do município de Boquira, no semiárido baiano – Brasil", *Geosciências*. v. 39, n. 1, pp. 139-152, May. 2020.
- [12] FANG, C., ACHAL, V., "The Potential of Microbial Fuel Cells for Remediation of Heavy Metals from Soil and Water-Review of Application", *Microorganisms*. v. 7, n. 12, pp. 697, Dec. 2019.
- [13] MARQUES, J.P., RODRIGUES, V.G.S., RAIMONDI, I.M., *et al.* "Increase in Pb and Cd adsorption by the application of peat in a tropical soil", *Water, Air & Soil Pollution*. v. 231, pp. 136, Mar. 2020.
- [14] MIRANDA, L.S., ANJOS, J.A.S.A., "Occupational impacts and adaptation to standards in accordance with Brazilian legislation: The case of Santo Amaro, Brazil", *Safety Science*. v. 104, pp. 10-15, Apr. 2018.

- [15] MARTINS, R.J.E., VILAR, V.J.P., BOAVENTURA, R.A.R., “Kinetic modelling of cadmium and lead removal by aquatic mosses”, *Brazilian Journal of Chemical Engineering*. v. 31, n. 1, pp. 229-242, Mar. 2014.
- [16] KHULBE, K.C., MATSUURA, T., “Removal of heavy metals and pollutants by membrane adsorption techniques”, *Applied Water Science*. v. 8, pp. 19, Jan. 2018.
- [17] DUAN, C., MA, T., WANG, J., *et al.* “Removal of heavy metals from aqueous solution using carbon-based adsorbents: A review”, *Journal of Water Process Engineering*. v. 37, Oct. 2020.
- [18] SÖNMEZAY, A., SALIM ÖNCEL, M., BEKTAŞ, N., “Adsorption of lead and cadmium ions from aqueous solutions using manganoxide minerals”, *Transactions of Nonferrous Metals Society of China*. v. 22, n. 12, pp. 3131-3139, Dec. 2012.
- [19] BHAGAT, S.K., PARAMASIVAN, M., AL-MUKHTAR, M., *et al.* “Prediction of lead (Pb) adsorption on attapulgite clay using the feasibility of data intelligence models”, *Environmental Science and Pollution Research*. v. 28, pp. 31670-31688, Feb. 2021.
- [20] TEODORO, L., PARABOCZ, C.R.B., ROCHA, R.D.C., “Caracterização da argila vermiculita expandida: avaliação dos padrões físico-químicos e mineralógicos para aplicação como adsorvente”, *Matéria*, v. 25, n. 4, pp. 1-8, 2020.
- [21] SALEEM, J., SHAHID, U., HIJAB, M., *et al.* “Production and applications of activated carbons as adsorbents from olive stones”, *Biomass Conversion and Biorefinery*. v. 9, pp. 775-802, Aug. 2019.
- [22] DENIZ, F., KEPEKCI, R.A., “Dye biosorption onto pistachio by-product: A green environmental engineering approach”, *Journal of Molecular Liquids*. v. 219, pp. 194-200, Jul. 2016.
- [23] SILVA, T.L., RONIX, A., PEZOTI, O., *et al.* “Mesoporous activated carbon from industrial laundry sewage sludge: Adsorption studies of reactive dye Remazol Brilliant Blue R”, *Chemical Engineering Journal*. v. 303, pp. 467-476, Nov. 2016.
- [24] YAVUZ, O., ALTUNKAYNAK, Y., GUZEL, F., “Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite”, *Water Research*. v. 37, n. 2, pp. 948-952, Feb. 2003.
- [25] ERDEM, E., KARAPINAR, N., DONAT, R., “The removal of heavy metal cations by natural zeolites”, *Journal of Colloid and Interface Science*. v. 280, n. 2, pp. 309-314, Dec. 2004.
- [26] MESHKO, V., MARKOVSKA, L., MARINKOVSKI, M., “Experimental study and modelling of zinc adsorption by granular activated carbon and natural zeolite”, *International Journal of Environment and Pollution*. v. 27, n. 4, pp. 285-299, Jan. 2006.
- [27] LEAL, T.W., LOURENÇO, L.A., SCHEIBE, A.S., *et al.* “Textile wastewater treatment using low-cost adsorbent aiming the water reuse in dyeing process”, *Journal of Environmental Chemical Engineering*. v. 6, n. 2, pp. 2705-2712, Apr. 2018.
- [28] SILVA, V.C., ARAÚJO, M.E.B., RODRIGUES, A.M., *et al.* “Adsorption Behavior of Acid-Treated Brazilian Palygorskite for Cationic and Anionic Dyes Removal from the Water”, *Sustainability* 2021, 13, 3954.
- [29] AGUIAR, M.R.M.P., NOVAES, A.C., GUARINO, A.W.S., “Remoção de metais pesados de efluentes industriais por aluminossilicatos”, *Química Nova*. v. 25, n. 6B, pp. 1145-1154, Dec. 2002.
- [30] POTGIETER, J.H., POTGIETER-VERMAAK, S.S., KALIBANTONGA, P.D., “Heavy metals removal from solution by palygorskite clay”, *Minerals Engineering*. v. 19, n. 5, pp. 463-470, Apr. 2006.
- [31] CHEN, H., WANG, A., “Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay”, *Journal of Colloid and Interface Science*. v. 307, n. 2, pp. 309-316, Mar. 2007.
- [32] FAN, Q., LI, Z., ZHAO, H., *et al.* “Adsorption of Pb (II) on palygorskite from aqueous solution: Effects of pH, ionic strength and temperature”, *Applied Clay Science*. v. 45, n. 3, pp. 111-116, Jul. 2009.
- [33] HE, M., ZHU, Y., YANG, Y., *et al.* “Adsorption of cobalt (II) ions from aqueous solutions by palygorskite”, *Applied Clay Science*. v. 54, n. 3-4, pp. 292-296, Dec. 2011.
- [34] OLIVEIRA, A.B.M., COELHO, L.O., GOMES, S.S., *et al.* “Brazilian Palygorskite as Adsorbent of Metal Ions from Aqueous Solution – Kinetic and Equilibrium Studies”, *Water Air Soil Pollution*. v. 224, n. 1687, Aug. 2013.
- [35] WANG, J., SUN, T., SALEEM, A., *et al.* “Enhanced adsorptive removal of Cr (VI) in aqueous solution by polyethyleneimine modified palygorskite”, *Chinese Journal of Chemical Engineering*. v. 28, pp. 2650-2657, Oct. 2020.
- [36] LUZ, A.B., ALMEIDA, S.L.M., “Atapulgita e Sepiolita”, In: CETEM/MCT, *Rochas e Minerais Industriais, Usos e Especificações*, 2 ed., chapter 10, Rio de Janeiro, Brasil, 2008.
- [37] SANTOS, P. S., In: Edgard Blucher, *Ciência e Tecnologia de Argilas*, 2 ed, São Paulo, Brazil, 1989.
- [38] BERTOLINO, L.C., SILVA, F.A.N.G., BRANDÃO, V.S., *et al.* “Use of Brazilian palygorskite as adsorbent of lead and cadmium ions from aqueous solutions”, In: XVI International Clay Conference, pp. 82, Granada, Jul. 2017.
- [39] HADDEN, W., SCHWINT, I., “Attapulgite: its properties and applications”, *Industrial Engineering*. v. 59, n. 9, pp. 58-69, Sep. 1967.
- [40] GALAN, E., “Properties and applications of palygorskite-sepiolite clays”, *Clay Minerals*. v. 31, n. 4, pp. 443-453, Dec. 1996.
- [41] OLIVEIRA, C., “Caracterização tecnológica de atapulgitas do Piauí”, In: XX Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa, p. 49-56, Florianópolis, Jun. 2004.

- [42] GUERRA, D.L., LEMOS, V.P., ANGÉLICA, R.S., *et al.* “Influência de argilas pilarizadas na decomposição catalítica do óleo de andiroba”, *Eclética Química*. V. 32, n. 4, pp. 19-26, Nov. 2007.
- [43] EL-MOFTY, S.E., ASHOUR, F.H., EL-SHALL, H., “Adsorption mechanism of toxic metal ions by clay (attapulgite)”, In: Twelfth International Water Technology Conference, p. 403–414, Alexandria, Mar. 2008.
- [44] BALTAR, C.A.M., BALTAR, L.M., BEZERRA, F.J., *et al.* “Influence of morphology and surface charge on the suitability of palygorskite as drilling fluid”, *Applied Clay Science*. v. 42, n. 3-4, pp. 597-600, Jan. 2009.
- [45] BERTOLINO, L.C., ALMEIDA, S.L.M., LUZ, A.B., *et al.* “Estudo de ativação ácida da atapulgita do Piauí para clarificação de óleos”, In: XXIV Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa, p. 530-36, Salvador, Oct. 2011.
- [46] AMORIM, K.B., ANGELICA, R.S., “Mineralogia e geoquímica da ocorrência de palygorskita de Alcântara, Bacia de São Luis-Grajaú, Maranhão”, *Cerâmica*. v. 57, pp. 483-490, Dec. 2011.
- [47] RODRIGUES, G.M.A., NEVES, R.F., ANGÉLICA, R.S., “Beneficiamento de uma argila tipo palygorskita da bacia de S. Luis-Grajaú, região de Alcântara, MA, e sua utilização como adsorvente de fósforo”, *Cerâmica*, v. 60, pp. 117-126, Mar. 2014.
- [48] ZHANG, J., WANG, Q., CHEN, H., *et al.* “XRF and nitrogen adsorption studies of acid-activated palygorskite”, *Clay Minerals*, v. 45, n. 2, pp. 145-156, Jun. 2010.
- [49] WANG, Y., QIN, Z., GUO, P., *et al.* “Preparation of attapulgite carriers with different pore structures and their effects on thermophysical properties of composite phase change materials”, *AIP Advances*. v. 9, Oct. 2019.
- [50] SING, K.S.W., EVERETT, D.H., HAUL, R.A.W., *et al.* “Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity”, *Pure and Applied Chemistry*. v. 57, n. 4, pp. 603-619, 1985
- [51] NASCIMENTO, R.F., LIMA, A.C.A., VIDAL, C.B., *et al.* *Adsorção: aspectos teóricos e aplicações ambientais*, Fortaleza, Imprensa Universitária, 2014.
- [52] WANG, J., GUO, X., “Adsorption kinetic models: Physical meanings, applications, and solving methods”, *Journal of Hazardous Materials*. v. 390, May. 2020.
- [53] JINTAKOSOL, T., NITAYAPHAT, W., “Adsorption of Silver (I) From Aqueous Solution Using Chitosan/Montmorillonite Composite Beads”, *Materials Research*. v. 19, n. 5, pp.1141-1121, Jul. 2016.
- [54] SILVA, J.C., “Desenvolvimento de processo integrado utilizando processos de separação por membrana e adsorção em carvão ativado para o tratamento de água associada à produção de petróleo”, M.Sc. Dissertation., COPPE/UFRJ, Rio de Janeiro, RJ, Brazil, 2010.
- [55] ÁLVAREZ-AYUSO, E., GARCÍA-SÁNCHEZ, A., “Palygorskite as a feasible amendment to stabilize heavy metal polluted soils”, *Environmental Pollution*. v. 125, n. 3, pp.337-344, Oct. 2003.
- [56] CHEN, H., ZHAO, J., “Adsorption study for removal of Congo red anionic dye using organo-attapulgite”, *Adsorption*. v. 15, pp. 381-389, Feb. 2009.
- [57] SUÁREZ, M., GÁRCIA-ROMERO, E., “FTIR spectroscopic study of palygorskite: Influence of the composition of the octahedral sheet”, *Applied Clay Science*. 31, n. 1-2, pp. 154-163, Jan. 2006.
- [58] SRASRA, N.F., SRASRA, E., “Acid treatment of south Tunisian palygorskite: Removal of Cd (II) from aqueous and phosphoric acid solutions”, *Desalination*. v. 250, n. 1, pp. 26-34, Jan. 2010.
- [59] LAZAREVIÉ, S., JANKOVIÉ-CASTVAN, I., DJOKIÉ, V., *et al.* “Iron-modified sepiolite for Ni<sup>2+</sup> sorption from aqueous solution: An Equilibrium, kinetic, and thermodynamic study”, *Journal of Chemical Engineering Data*. v. 55, n. 12, pp. 5681-5689, Nov. 2010.
- [60] MOYO, M., NYAMHERE, G., SEBATA, E., *et al.* “Kinetic and equilibrium modelling of lead sorption from aqueous solution by activated carbon from goat dung”, *Desalination and Water Treatment*. v. 57, n. 2, pp.765-775, Oct. 2014.
- [61] CHATTERJEE, S., DE, S., “Application of novel, low-cost, laterite-based adsorbent for removal of lead from water: Equilibrium, kinetic and thermodynamic studies”, *Journal of Environmental Science and Health*. Part. A, v. 51, n. 3, pp. 1-11, Dec. 2015.
- [62] TANG, C., SHU, Y., ZHANG, R., *et al.* “Comparison of the removal and adsorption mechanisms of cadmium and lead from aqueous solution by activated carbons prepared from *Typha angustifolia* and *Salix matsudana*”, *RSC Advances*. v. 7, n. 26, pp 16092-16103, Mar. 2017.
- [63] BOMBUWALA DEWAGE, N., FOWLER, R.E., PITTMAN, C.U., *et al.* “Lead (Pb<sup>2+</sup>) sorptive removal using chitosan-modified biochar: batch and fixed-bed studies”, *RSC Advances*. v. 8, n. 46, pp. 25368-25377, Jul. 2018.
- [64] TORRES-LUNA, J.A., CARRIAZO, J.G., “Porous aluminosilicic solids obtained by thermal-acid modification of a commercial kaolinite-type natural clay”, *Solid State Sciences*. v. 88, pp. 29-35, Feb. 2019.
- [65] ESPAÑA, V.A.A., SARKAR, B., BISWAS, B., *et al.* “Environmental applications of thermally modified and acid activated clay minerals: Current status of the art”, *Environmental Technology & Innovation*. v. 13, pp. 383-397, Feb. 2019.

- [66] BARAKAN, S., AGHAZADEH, V., “The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review”, *Environmental Science and Pollution Research*. v. 28, pp. 2572–2599, Oct. 2020.
- [67] ROES, A.L., MARSILI, E., NIEUWLAAR, E., *et al.* “Environmental and Cost Assessment of a Polypropylene Nanocomposite”, *Journal of Polymers and the Environment*. v. 15, pp. 212-226, Aug. 2007.
- [68] LI, J., WANG, X., ZHAO, G., *et al.* “Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions”, *Chemical Society Reviews*. v. 47, pp. 2322-2356, Mar. 2018.

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