

# Characterization and Modification of a Clay Mineral Used in Adsorption Tests

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## Abstract

Clay minerals are widespread in natural systems and have been widely used for the removal of pollutants. In this study, natural expanded vermiculite was used in adsorption tests to remove ammonium nitrogen from landfill leachate. The modification of vermiculite was carried out using NaOH and HCl, and for both modifications the best concentration was 0.1 mol/L. The results produced by XRD (X-ray diffraction) showed that Al replaced K after modification of the vermiculite using HCl and that Mg and Na replaced K after modification using NaOH. It was observed that the adsorption capacity increased as the percentage in mass of K diminished. The Langmuir is the isotherm that presents the best fit of the data, and the values of  $R_L$  (the Langmuir coefficient) suggest that the adsorption is linear. The thermodynamic parameters indicate that the process is spontaneous and endothermic, that there is a high affinity between the adsorbate and the adsorbent, and that physical adsorption is prevalent.

## Keywords

Adsorption Isotherms, Adsorption Thermodynamics, Clay Minerals, Expanded Vermiculite, Landfill Leachate, Vermiculite

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## 1. Introduction

Adsorbents are solid particles that present porous structure and volume of pores up to 50% of the total volume of particles, which justify their use in adsorption processes. Various materials can be used as adsorbents, such as activated carbon, silica gel (sodium silicate and sulfuric acid), activated alumina, zeolite (aluminum silicate), vermiculite (aluminum-iron-magnesium silicate, and phyllosilicate), bentonite (aluminum phyllosilicate), and

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organic and synthetic polymers [1].

Vermiculite is found in various parts of the world, but currently the major mines are located in South Africa, China, Brazil, Zimbabwe and the United States. Vermiculite clays are weathered micas (**Figure 1** and **Figure 2**) with structural formula  $\{(Mg, Fe)_3 [(Si, Fe, Al)_4 O_{10}] [OH]_2 4H_2O\}$  in which the potassium ions among molecular sheets are replaced by magnesium and iron ions [2]-[4]. Aluminum, hydrogen, magnesium and oxygen are essential elements, whereas calcium, sodium and potassium are common impurities [5]. **Table 1** and **Table 2** present some physical and chemical characteristics of vermiculite.

Expanded vermiculite is obtained by exfoliation or thermal expansion that consists of heating the natural mineral to a temperature ranging from 540°C to 810°C. The exfoliation process converts the dense flakes of ore into lightweight and porous granules [5]. In its expanded form, vermiculite is chemically active and biologically inert [8] [9].

The adsorption capacity of metals by vermiculite has been studied. The cationic exchange capacity (CEC) is one of the factors that characterizes the adsorption capacity of ions. Amongst the mechanisms that can be related to the adsorption of metal ions onto vermiculite is the cationic exchange that occurs on the planar sites. This exchange is the result of the interaction between the metal ions and the outer-sphere complexes [10] [11]. However, as a result of competitiveness, which is a function of the affinity amongst the ions and the vermiculite, the adsorption of some ions may result in the reduction of the adsorption capacity of others. According to the results found by the authors who studied the CEC of vermiculite, values varied from 40 meq/100 g to 250 meq/100 g [12]-[15]. Barshad [14] studied the competition between K and  $NH_4^+$ , and found out that the adsorption onto vermiculite was proportional to the CEC.

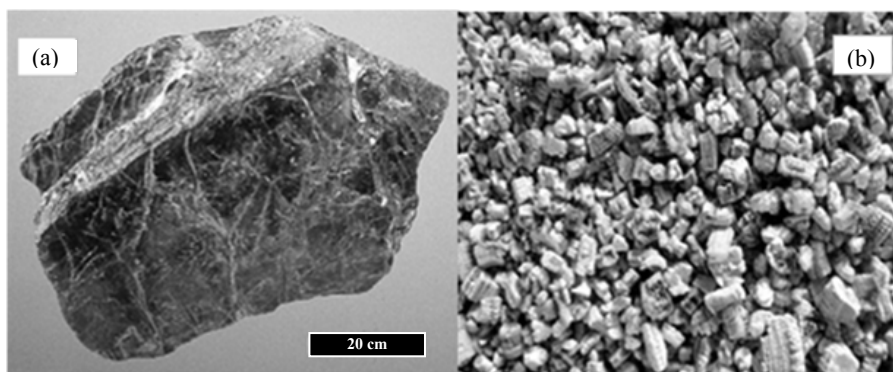
Other authors studied the vermiculite as an agent of adsorption of ions, in particular metal ions, for instance, results produced by Foscolos [12]. This author determined the equilibrium constants of  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Al^{3+}$ , using five different concentrations of HCl, NaCl,  $MgCl_2$  and  $CaCl_2$ , and pointed out that there was a hierarchic organization among the studied ions:  $Mg^+ < Ca^{2+} < H^+ < Al^{3+} < Na^+$ . Thus, the author concluded that  $Na^+$  was the ion that presented the greatest capacity of reposition on the surface of vermiculite, and that  $K^+$  also could present a high capacity of reposition. On the other hand, Abollino *et al.* [13] observed that the capacity of metal retention by vermiculite presented the following order:  $Pb^{2+} < Cu^{2+} < Cd^{2+} < Zn^{2+} < Ni^{2+} < Mn^{2+}$ . According to these authors, this hierarchy is a function of the chemical properties of the ions and not of the characteristics of the vermiculite. These authors also concluded that the vermiculite could be effectively utilized as an adsorbent for the treatment of high ionic strength wastewaters and high pH. It was also mentioned that the vermiculite could be used to treat low salinity solutions in any pH value.

The use of expanded vermiculite as a supporting agent to wastewater treatment has been presented in the literature. The use of expanded vermiculite as adsorbent has been particularly related to the removal of dyes, hydrocarbons and other hydrophobic substances [16]-[22].

Adsorbents can be modified by various means, and the objective is to increase their adsorption capacity. This increase can be obtained by intensifying the linkage strength between the adsorbent and the adsorbate, substituting a cation with higher affinity to the adsorbate, increasing the porosity of the adsorbent, increasing the specific surface area and activating the adsorbent. Acidic, basic, pillaring and hydrothermal treatments are ways to modify adsorbents [23]-[29].

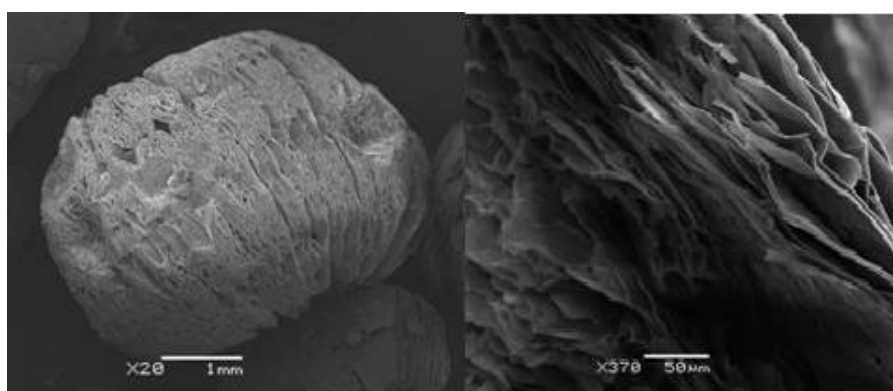
Adsorption is a transfer process of a substance (adsorbate) that is in solution in a liquid phase to the surface of a solid phase (adsorbent). The adsorption process can occur by means of physical forces, in which the van der Waals forces are involved. It can also occur by means of chemisorption, which involves chemical interaction between the adsorbate molecules and the surface of the adsorbent [1].

In the adsorption process, the isotherm represents the equilibrium relationship between the concentration in the liquid phase and the concentration on the adsorbent at a given temperature. The isotherm provides information to evaluate the affinity and the adsorption capacity of an adsorbent by an adsorbate [30]. In order to produce the best evaluation, the models most frequently used are those of Langmuir and Freundlich. The Langmuir isotherm model considers that the adsorption is restricted to a monolayer, and it is assumed that the surface of the pores of the adsorbent is homogeneous. One important feature of this model is the consideration that the forces of interaction amongst the adsorbed molecules are negligible and that the adsorption is reversible [1] [31]. The separation factor is the main characteristic of the Langmuir isotherm ( $R_L$ —the Langmuir coefficient). This coefficient is dimensionless and inversely proportional to the highest initial concentration of the adsorbate [31]. The results produced by the calculation of the Langmuir coefficient allow evaluating the adsorption process in terms



Source: (a) Vermiculite Mineral Data [6]; (b) the author.

**Figure 1.** Vermiculite (a) natural raw; (b) natural expanded.



Source: The author.

**Figure 2.** Scanning electron micrograph of the expanded vermiculite.

**Table 1.** Properties of exfoliated vermiculite.

Property	Typical data	Property	Typical data
color	light to dark brown	combustibility	non combustible
bulk density <sup>a</sup>	64 - 160 kg/m <sup>3</sup>	Mohs hardness	1 - 2 (2.1 - 2.8) [3]
specific gravity	2.5 g/cm <sup>3</sup> [3]	cation exchange capacity <sup>b</sup>	50 - 100 meq/100 g
moisture loss at 110°C	4% - 10%	waterholding capacity <sup>a</sup>	220% - 325% (by weight) 20% - 50% (by volume)
pH in water	6 - 9	thermal conductivity at 25°C	60 cal/m <sup>2</sup> ·h °C [3] [4]

**Note:** <sup>a</sup>Bulk density and water holding capacity vary with grain size; <sup>b</sup>Exchangeable ions are Mg<sup>2+</sup> and Ca<sup>2+</sup> (sodium acetate saturation/ammonium acetate substitution method). **Source:** Adapted from The Vermiculite Association (2014) [7].

**Table 2.** Typical chemical analysis.

Component	Percent by weight	Component	Percent by weight
SiO <sub>2</sub>	38 - 46	Fe <sub>2</sub> O <sub>3</sub>	6 - 13
Al <sub>2</sub> O <sub>3</sub>	10 - 16	TiO <sub>2</sub>	1 - 3
MgO	16 - 35	H <sub>2</sub> O	8 - 16
CaO	1 - 5	Other	0.2 - 1.2
K <sub>2</sub> O	1 - 6		

Source: The Vermiculite Association (2014) [7].

of the favorability of occurrence, linearity and reversibility. If  $R_L$  values vary from zero to the unit ( $0 < R_L < 1$ ), the adsorption process is favorable; if it is higher than the unity ( $R_L > 1$ ), it is unfavorable; if it equals the unit ( $R_L = 1$ ), it is linear; if it equals zero ( $R_L = 0$ ), it is irreversible. The Freundlich isotherm model establishes that there is no limit for the adsorption capacity of the adsorbent, and that it is because the amount adsorbed tends to infinite when the concentration of the solution increases. This model is often the most frequently used for the description of the adsorption characteristics of wastewater treatment [1]. The characteristics of the Freundlich isotherm are expressed in terms of intensity of the adsorption process (“ $n$ ”). The results using this variable allow evaluating if chemical ( $n < 1$ ) or physical ( $n > 1$ ) adsorption is prevalent [31] [32].

According to Castilla [33], when there are more than one adsorbent to choose, the adsorption isotherms represent a tool to identify the one that is most adequate for one particular condition.

Another fundamental condition to the evaluation of the adsorption process is the determination of the thermodynamic parameters, Gibbs free energy variation ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy variation ( $\Delta S^0$ ). The results produced by the calculation of these parameters are of great importance to understand whether an adsorbent presents characteristics to carry out the adsorption process. On one hand, if negative values of  $\Delta G^0$  are obtained, there is an indication that the adsorption process is spontaneous. On the other hand, if positive values of  $\Delta H^0$  are obtained, there is an indication that the process is endothermic. These results are associated with the understanding that the adsorption capacity increases with an increase in the temperature. However, one of the most significant results is referred to the association between values of entropy and Gibbs free energy. If positive values of  $\Delta S^0$  are associated with negative values of  $\Delta G^0$ , there is an indication that there is a high affinity between the adsorbent and the adsorbate [34]-[36].

Notwithstanding, information on the adsorption kinetics is relevant because as a result of kinetic experiments the time to reach the equilibrium will be determined. This information is of fundamental importance for the determination of the adsorption isotherms [37].

This research was focused on the evaluation of a Brazilian clay mineral, natural expanded vermiculite. To reach the goal, the chemical characteristics of the vermiculite were determined, and the adsorption characteristics of the adsorbent were also determined in order to assess its capability to remove ammonium nitrogen from landfill leachate.

## 2. Materials and Methods

The important remarks related to the methods used to characterize both the vermiculite and the adsorption process are presented hereafter.

### 2.1. Chemical Characterization of Expanded Vermiculite

The characteristics of expanded vermiculite were determined by Energy-dispersive X-ray spectroscopy and also by X-ray diffraction, as presented below.

#### 1) Energy-dispersive X-ray spectroscopy (EDS)

EDS tests were carried out in a Jeol JSM-636OLV electronic microscope. Samples of expanded natural vermiculite, before and after washing, were oven-dried at 40°C for 24 hours and stored in a vacuum desiccator. Subsequently, 5 grains of expanded vermiculite were placed on aluminum support and metalized with golden powder in a Balzer Union FL 9496 (SCD 030) Critical Point Dryer, under the pressure of 0,1 mbar.

The software Noran System Six was used to determine the atomic percentage of each analyzed sample.

#### 2) X-ray diffraction (XRD)

In order to carry out the XRD analysis a sample of expanded vermiculite was pulverized in a container coated with tungsten carbide. Subsequently, a 7 g-sample from the pulverized material mixed with 1.4 g of organic wax was used to produce tablets. For the determination of the chemical composition of the expanded vermiculite these tablets were placed in a Philips-Panalytical PW 2400 equipment, operating with a Rhodium X-ray source of 3 kW.

### 2.2. Modification of Expanded Vermiculite

According to the methodology proposed by Okada *et al.* (2005) [25], basic and acidic media were used for the modification of expanded vermiculite.

The modification of the expanded natural vermiculite was carried out using three different concentrations of sodium hydroxide (NaOH) and hydrochloric acid (HCl) (0.1 mol/L, 1 mol/L and 2 mol/L). The experiments were carried out at room temperature and at 60°C, the samples were continuously stirred, and the contact time was 2 hours. After each treatment, the expanded vermiculite was washed five times with distilled and deionized water, and oven-dried at 40°C in a porcelain dish.

### 2.3. Adsorption Experiments

Adsorption tests were carried out with samples of landfill leachate collected from the treatment system of Curitiba's Sanitary Landfill, Paraná, Brazil (25°37'29.98"S; 49°20'01.66"W).

The adsorption capacity of ammonium nitrogen from landfill leachate onto expanded vermiculite at three temperatures (288 K, 296 K, 303 K) was determined using natural expanded and modified adsorbent as well.

Tests for the determination of adsorption isotherms and thermodynamic characteristics were carried out only for the natural expanded vermiculite. After each step of the assay, the concentrations of ammonium nitrogen were determined.

All tests were carried out in triplicate. Blank samples composed of vermiculite and deionized water were processed under the same experimental conditions.

#### Batch tests

The adsorption batch tests consisted of transferring 50 mL of leachate and 0.83 g of natural expanded and modified vermiculite to Erlenmeyer flasks, covered with three layers of Parafilm® and placed in an orbital shaker (Tecnal TE-421). The rotational speed in which the equipment operated was 150 rpm. These conditions were adopted for the determination of the type of vermiculite to be used in the tests. For the determination of ammonium nitrogen concentrations samples were collected every 2 hours, for 24 hours, and filtered through qualitative filter paper (0.205 mm, 80 g/m). These concentrations were determined according to the method 4500-NH<sub>3</sub>F. Phenate Method [38]. Subsequently, the mass of solute adsorbed per mass of adsorbent at equilibrium ( $q_{eq}$ ), in mg/g, was calculated using Equation (1).

$$q_{eq} = \frac{(C_0 - C_{eq})V}{M} \quad (1)$$

where,  $C_{eq}$  is the final adsorbate concentration in solution at equilibrium (mg/L).

### 2.4. Langmuir and Freundlich Isotherms Determination

Five dilutions of raw leachate were used (130 mg/L; 340 mg/L; 760 mg/L; 1200 mg/L; 1700 mg/L) for the determination of adsorption isotherms of ammonium nitrogen onto expanded vermiculite. For each experiment, a 100 mL-diluted leachate sample was transferred to Erlenmeyer flasks containing 3.33 g of expanded vermiculite, covered with three layers of Parafilm® and placed in an orbital shaker (Tecnal TE-421). The rotational speed in which the equipment operated was 50 rpm for 10 hours, or the equilibrium time determined by adsorption kinetics experiments. The amount adsorbed at equilibrium ( $q_{eq}$ ), in mg/g, was calculated using Equation (1).

The isotherms experimental data were modeled by linear regression using the Langmuir and Freundlich models (Equation (2) and Equation (3)).

$$\ln \frac{q_e - q_t}{q_e} = -k_1 t \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

After the determination of the equilibrium data, the statistical parameter SS (Sum of Squares) Equation (4) was applied to identify the model that presented the best fit of the data.

$$SS = \frac{1}{n} \sqrt{\sum_{i=1}^n (q_{teórico} - q_{experimental})^2} \quad (4)$$

### 2.5. Adsorption Thermodynamics

Data on concentration and adsorption capacity at equilibrium ( $q_{eq}$ ) were used for the calculation of the ther-

thermodynamic parameters of the adsorption process, Gibbs Free Energy ( $\Delta G^0$ ), internal energy variation ( $\Delta H^0$ ) and entropy variation ( $\Delta S^0$ ). The assessment and estimation of the thermodynamic characteristics were based on information presented in **Table 3**.

The thermodynamic parameters  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  are related through the fundamental equation of thermodynamics (Equation (5)).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

The variation of the Gibbs free energy was calculated by Equation (6), whereas the Van't Hoff Equation (7), produced by the combination of Equation (5) and Equation (6), and related to the equilibrium constant  $K_a$ , was used to calculate the internal energy variation and the entropy variation.

$$\Delta G_{\text{ads}} = -RT\ln K_a \quad (6)$$

where,  $T$  is temperature (K),  $R$  is the constant of ideal gases (8.314 J/mol.K) and  $K_a$  is the thermodynamic equilibrium constant.

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

### 3. Results and Discussion

#### 3.1. Characterization of Expanded Vermiculite

**Table 4** presents the results produced by EDS for the chemical characteristics of the expanded vermiculite used to carry out adsorption tests.

As it can be observed from the data presented in **Table 4**, washing with distilled and deionized water is recommended prior to the use of vermiculite when the matrices present nitrogen and/or phosphorus. Otherwise, the

**Table 3.** Adsorption characteristics as a function of thermodynamic parameters.

Adsorption process	Thermodynamic characteristics
spontaneous	$\Delta G^0$ (-)
non spontaneous	$\Delta G^0$ (+)
exothermic	$\Delta H^0$ (-)
endothermic	$\Delta H^0$ (+)
affinity between adsorbent and adsorbate	$\Delta S^0$ (+) and $\Delta G^0$ (-)
no affinity between adsorbent and adsorbate	$\Delta S^0$ (+) and $\Delta G^0$ (+)

**Table 4.** Chemical characteristics of the expanded vermiculite by XRD.

Element	Before washing		After washing	
	Mass (%)	Standard deviation (%)	Mass (%)	Standard deviation (%)
C	27.01	±1.22	32.23	±1.18
N	16.87	±2.04	0	-
O	33.33	±0.69	35.04	±0.63
Mg	4.15	±0.10	2.19	±0.09
Al	1.22	±0.22	2.13	±0.05
Si	7.48	±0.19	11.54	±0.11
P	3.34	±0.01	0	-
Ti	0.78	±0.16	3.7	±0.11
Cr	-	-	1.17	±0.11
Fe	5.82	±0.33	12.00	±0.41
Total	100		100	

results could be biased if the intent is to evaluate nitrogen removal using vermiculite as adsorbent.

### 3.2. Modification of Expanded Vermiculite

After the modification using HCl 2 mol/L, at 2 hours of contact time and 60°C, it could be visually observed that the expanded vermiculite lost color and structural features. Results produced by Lopez-Gonzalez and Barrell-Ruiz [39] corroborate these observations. These authors found a total dissolution of the vermiculite and also reported obtaining a white silicate after modification using HCl 5 mol/L, at a 30-minute contact time. It is worth mentioning that even using a lower concentration it was possible to observe a change in color of the gel formed as a result of the modification using HCl 2 mol/L.

After these observations tests with lower HCl concentrations (1 mol/L; 0,1 mol/L) were carried out. The modification using 0.1 mol HCl/L, at a 2-hour contact time at room temperature, produced the best modification condition. The treatment using this concentration allowed observing a slight loss of color whereas the vermiculite did not present structural loss.

In spite of having not been observed alterations in the vermiculite treated with 2 mol NaOH/L, to compare results obtained for the modification with HCl and NaOH the treatment was also processed with 0.1 mol NaOH/L, at the same contact time, at room temperature.

**Table 5** presents results produced by XRD for the chemical characterization of modified expanded vermiculite using HCl and NaOH. These results allow pointing out that there was an increase of the mass percentage of Al and reduction of the percentage of K in the expanded vermiculite modified using HCl. Thus, the observation that K was substituted by Al is corroborated by the results presented by Carter *et al.* [40], who observed the substitution of K by Al when the vermiculite was modified by HCl. It was also possible to observe that the modification using NaOH produced the replacement of K by Mg and Na when vermiculite was modified using NaOH. Results by Raman and Jackson [41] corroborate the results produced by this research. The authors also found out that, as a consequence of hydration, K ions were replaced by Mg and Na ions after treating vermiculite with a solution of MgCl<sub>2</sub>.

Regarding the competition between K and NH<sub>4</sub> ions, when vermiculite was modified using HCl and NaOH it was observed a reduction in the percentage of the mass of K. These results are confirmed by those of Barshad [14]. This author pointed out that the adsorption of K and NH<sub>4</sub> were proportional to the cation exchange capacity. Thus, when K is removed there is an increase in the adsorption capacity of NH<sub>4</sub>.

**Table 5.** Chemical characteristics of expanded vermiculite by XRD.

Component	Natural*	Modified (HCl)*	Modified (NaOH)*
SiO <sub>2</sub>	34.19	35.70	34.10
MgO	23.65	23.70	24.20
Al <sub>2</sub> O <sub>3</sub>	11.32	12.00	11.20
Fe <sub>2</sub> O <sub>3</sub>	9.03	9.20	9.70
Na <sub>2</sub> O	0.00	0.00	3.10
TiO <sub>2</sub>	1.65	1.80	1.80
Cr <sub>2</sub> O <sub>3</sub>	0.78	0.90	0.80
NiO	0.27	0.30	0.30
Cl	0.00	0.10	0.00
CaO	0.13	0.10	0.10
MnO	0.05	<0.10	0.10
V <sub>2</sub> O <sub>5</sub>	0.02	<0.10	<0.10
SO <sub>3</sub>	0.01	-	-
K <sub>2</sub> O	0.01	-	-
ZnO	0.01	-	-

Note: \*Concentration in mass per mass percentage.

### 3.3. Adsorption Batch Tests

Figure 3 presents the results produced for the assessment of ammonium nitrogen adsorption onto natural expanded and modified vermiculite.

As presented in Figure 3, after a 6-hour contact time the concentration of ammonium nitrogen decreased as the adsorption time increased. After 24 hours of experiment efficiencies of ammonium nitrogen adsorption onto expanded natural vermiculite, vermiculite modified by HCl and also by NaOH were 84%, 82% and 64%, respectively. Therefore, it can be stressed that natural expanded vermiculite is the most appropriate adsorbent for the adsorption of ammonium nitrogen because it saves time and financial resources of the laboratory.

In all experiments, it was possible to observe that until 6 hours of contact time, approximately, there was a variation in the concentration of ammonium nitrogen. This variation can be related to the possibility of adsorption followed by desorption due to the functional characteristics of the expanded vermiculite.

### 3.4. Langmuir and Freundlich Isotherms

Table 6 and Table 7 present results produced for the determination of adsorption isotherms.

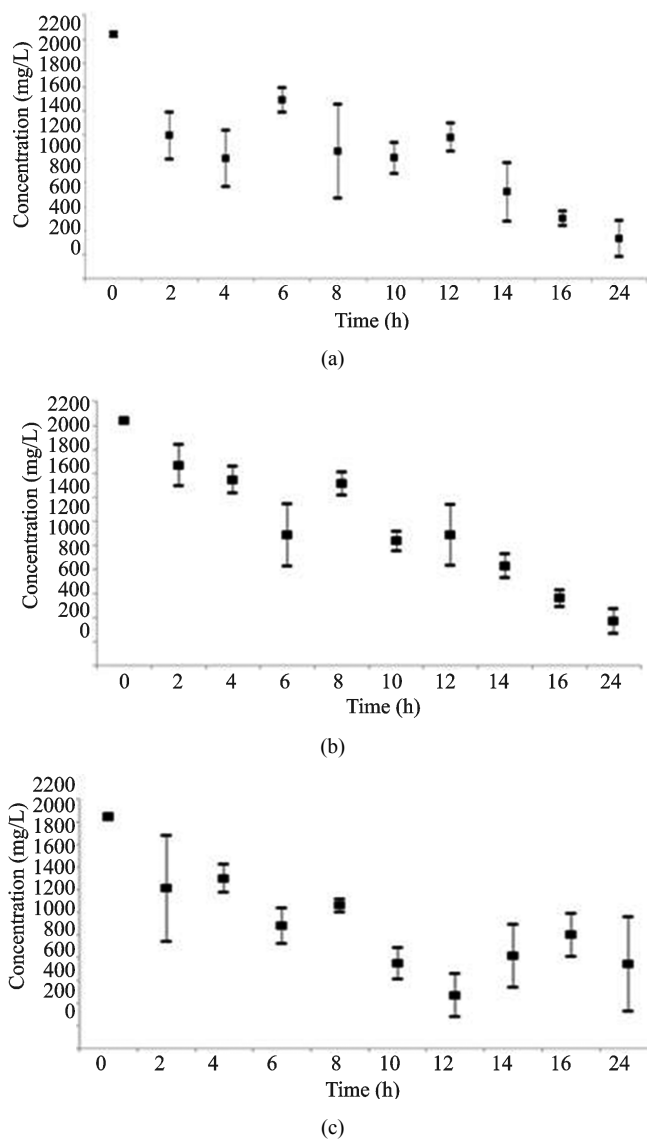


Figure 3. N-NH<sub>3</sub> adsorption onto vermiculite: (a) natural expanded; (b) modified with HCl; (c) modified with NaOH.



As it can be observed from the data presented in **Table 6**, the adsorption capacity increases with an increase in temperature.

In order to produce a more refined correlation and to estimate the parameters of the isotherms the experimental data were adjusted to the models of Langmuir (Equation (2)) and Freundlich (Equation (3)). **Table 7** presents the values estimated for the adsorption isotherms of ammonium nitrogen onto expanded natural vermiculite.

According to the data presented in **Table 7**, it is possible to observe that the values of  $R_L$  equaled the unity. These results suggest that the adsorption process is linear and indicates that the active sites are homogeneous in terms of energy and that there is no interaction amongst the adsorbed species [32]. As the results for the correlation coefficient ( $R^2$ ) for all temperatures were similar, it was necessary to apply the Sum of Squares (SS) statistical method to the equilibrium data (**Table 8**). The SS method provides a strong statistical argument because the lower the SS value, the better the adjustment of the data to the isotherm model.

According to the results it can be affirmed that the experimental data best fitted the Langmuir isotherm, in particular those produced at the temperatures 288 K and 296 K. The Langmuir isotherm is monolayered and hence, only a fixed number of sites are accessible and available on the surface of the adsorbent. Furthermore, all sites present the same energy for adsorption [1].

**Table 6.** Adsorption capacity at 288 K, 296 K and 303 K.

Temperature (K)	288	296	303
Concentration (mgN-NH <sub>3</sub> /L)	$q_{eq}$ (mgN-NH <sub>3</sub> /g <sub>vermiculite</sub> )		
130	0.11 ± 0.01	0.45 ± 0.01	0.63 ± 0.01
340	1.57 ± 0.16	1.75 ± 0.85	1.39 ± 0.66
760	3.52 ± 0.35	6.18 ± 0.69	7.04 ± 0.25
1200	10.04 ± 0.85	12.09 ± 0.16	13.89 ± 0.74
1700	13.24 ± 1.67	15.36 ± 0.18	16.00 ± 0.50

**Table 7.** Model parameters of the Langmuir and Freundlich isotherms.

Temperature (K)	Langmuir			Freundlich		
	$R^2$	$K_L$	$R_L$	$R^2$	$K_F$	$n$
288	0.95	$3.7 \times 10^{-8}$	1	0.97	$5.2 \times 10^{-4}$	0.74
296	0.97	$5.1 \times 10^{-8}$	1	0.98	$2.9 \times 10^{-3}$	0.87
303	0.95	$3.6 \times 10^{-7}$	1	0.96	$4.7 \times 10^{-3}$	0.91

Note:  $K_L$  = Langmuir constant;  $R_L$  = equilibrium parameter;  $K_F$  = Freundlich distribution coefficient;  $n$  = intensity of the adsorption process.

**Table 8.** SS values for the models and temperatures evaluated.

Model	Temperature (K)		
	288	296	303
Langmuir	0.39	0.35	0.59
Freundlich	0.56	0.41	0.61

**Table 9.** Thermodynamics of the adsorption process.

Temperature (K)	Thermodynamic parameters		
	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)
288	-6.0		
296	-10.6	100.9	372.8
303	-11.5		

### 3.5. Adsorption Thermodynamics

**Table 9** presents results on the thermodynamics conditions of the ammonium nitrogen adsorbed onto vermiculite.

As it can be observed, negative values were obtained for the Gibbs free energy ( $\Delta G^0$ ) and positive values for both the enthalpy ( $\Delta H^0$ ) and the entropy ( $\Delta S^0$ ) for the three temperatures studied. According to the literature [42]-[48] negative values confirm the viability and spontaneity of the adsorption process. Also according to the literature [49], the range between  $-20$  kJ/mol and  $0$  kJ/mol indicates that the interaction between the adsorbate and the adsorbent occurs via physical adsorption. The experimental data are consistent with the information provided by the results of the Langmuir isotherm to which the data best fitted.

On one hand, positive values for entropy indicate that the adsorption process is irreversible and stable, which reflects the affinity between the adsorbate and the adsorbent. On the other hand, positive values for enthalpy indicate the endothermic nature of the adsorption process, *i.e.*, the adsorption capacity increases when there is an increase in temperature. Thus, the results presented in **Table 6** allow pointing out that the nature of the adsorption of ammonium nitrogen onto expanded vermiculite is an endothermic process.

## 4. Conclusions

The results presented allow concluding that pre-washing of vermiculite is an important step prior to using it as an adsorbent and that it also releases adsorption sites. The observed interference can be due to the presence of impurities from the production process of extraction or can also be related to the conditions of storage. The presence of impurities, in particular the presence of nitrogen, can bias the results of the research, especially in the case of evaluating the removal of ammonium nitrogen from landfill leachate.

Regarding the modification of the expanded mineral, the best results produced were related to the concentration  $0.1$  mol/L of both HCl and NaOH. This concentration at a 2-hour contact time at room temperature allowed observing that there was no loss of either color or structural characteristics of the expanded vermiculite. However, the results of the adsorption test proved that the highest efficiency of ammonium nitrogen removal of 84% was produced using natural expanded vermiculite that was unmodified.

The results produced by XRD made it possible to observe that Al substituted K when the expanded vermiculite was modified using HCl, whereas Mg and Na substituted K when the adsorbent was modified using NaOH.

The use of the SS method allowed concluding that the experimental data best fitted the Langmuir isotherm. The conclusion on the linearity of the adsorption and the interaction amongst the adsorbed species was made possible by the observation of the  $R_L$  values, which equaled the unit.

The values of the thermodynamic parameters,  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ , indicate that the adsorption process of ammonium nitrogen onto natural expanded vermiculite is spontaneous and endothermic and that there is a high affinity between the adsorbent and the adsorbate. The results also allow concluding that the interaction between ammonium nitrogen and natural expanded vermiculite is favorable and occurs via physical adsorption.

Based on these results, it was demonstrated that the expanded vermiculite was an alternative adsorbent material, which was effective in the adsorption process, and that it could be used in the pre-treatment of wastewaters containing ammonium nitrogen.

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