



## Study of the Effect of Temperature in the Remotion of NI (II) on African Palm Bagasse (*Elaeis guineensis*)

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**Abstract :** Heavy metals are pollutants released into the environment, and are highly available as a result of the increase in different activities where they are used, so their presence in aqueous media causes worldwide concern, as they pose a serious threat to ecosystems by being non-biodegradable, toxic and carcinogenic to living beings. The present work evaluated the effect of temperature and pH on the capacity of African palm bagasse (*Elaeis guineensis*) to remove nickel present in aqueous solutions, studying the kinetics, equilibrium and thermodynamic parameters that determine the process. For this purpose, it was tested in batch system by varying the temperature and pH of the solution, keeping constant the agitation rate (200 rpm), adsorbent dose (5 g \*100ml<sup>-1</sup>), initial metal concentration (100 ppm) and the size of the adsorbent (0.1 mm). It was found that the best adsorption conditions were 54.9 °C and pH 5.93, obtaining a maximum adsorption capacity of 17.01 mg g<sup>-1</sup> corresponding to a removal of 85.14 %. The kinetic model that best fits the experimental data was Elovich and the isotherm that best describes the process is Freundlich, with R<sup>2</sup> of 0.9967 and 0.999, respectively. The determined thermodynamic parameters ( $\Delta H^0$ ,  $\Delta G^0$ ,  $\Delta S^0$ ) suggest that the process is favorable, spontaneous, endothermic and reversible under certain operating conditions. The results show that palm bagasse is a good precursor of Nickel adsorbent.

**Keywords :** Freundlich isotherm, Elovich model, thermodynamic parameters, adsorption thermodynamics.

### 1. Introduction

Heavy metals are pollutants released into the environment, and are highly available as a result of the increase in different activities where they are used. This is of global concern, as they pose a serious threat to ecosystems by being non-biodegradable, toxic and carcinogenic to humans<sup>1,2,3</sup>. The gold, tannery and nickel mining industry discharges to natural sources large quantities of highly contaminated liquid waste, its main components being chromium, nickel and mercury affecting the nervous system, digestive tract, skin, lungs, kidneys and eyes<sup>4,5,6</sup>.

Adsorption is a process by which a substance is concentrated on the surface of another solid or liquid phase. It is therefore considered a superficial phenomenon. The substance that concentrates on the surface is called adsorbate and the phase that retains it is called adsorbent. On the other hand, biosorption is an efficient and versatile alternative because it uses lignocellulosic organic waste, which reduces costs, so it is a clean and environmentally friendly technology<sup>7,8</sup>.

Studies conducted by Al-Othman *et al.*<sup>9</sup> and Giri *et al.*<sup>10</sup> in which they study the removal of Cr (VI), using as adsorbent root of *Eichhornia crassipes* and chemically activated walnut shell with KOH respectively, in which temperature and pH variations were made, calculating the thermodynamic parameters for the characterization of the process.

They established that adsorption is spontaneous and endothermic due to the negative values of  $\Delta G$  and by the positive values of  $\Delta H$  and that it is a reversible process due to the positive values found for  $\Delta S$ , besides the increase of temperature and an acidic medium favor the process. Also, the removal of ions from Hg (II), Ismaiel *et al.*<sup>11</sup> used activated palm shell charcoal, making variations in temperature and other parameters, including pH, to evaluate the effects of these on the adsorption process, thus finding that for high temperatures and a basic medium, favor the process, in addition that the thermodynamic parameters evaluated indicate spontaneity and an endothermic nature.

With respect to studies on the implementation of biomasses in the removal of ions Ni (II) Yasmin *et al.*<sup>12</sup>, Tejada-Tovar *et al.*<sup>13</sup> and Singh and Parmar<sup>14</sup>, they used neem leaves, modified matrices, nut shell, among others and made variations in parameters such as temperature and pH. In this sense, this research aimed to evaluate the effect of five different combinations of pH and temperature on the capacity of African palm bagasse (*Elaeis guineensis*) to remove nickel present in aqueous solutions, studying the kinetics, equilibrium and thermodynamic parameters that determine the batch system process.

## 2. Experimental

Stirring of the solution in contact with biomass (rpm), adsorbent dosage ( $\text{g mL}^{-1}$ ), contact time (min) and particle size (mm) were used as the intervening variables; as dependent variables were the percentage of adsorption (%), the maximum metal removal capacity in equilibrium ( $\text{mg g}^{-1}$ ), Gibbs's free energy ( $\text{J mol}^{-1}$ ), enthalpy ( $\text{J mol}^{-1}$ ) and adsorption entropy ( $\text{J m}^{-1}$ ). A  $2^2$  rotatable central composed experimental design with 2 levels of temperature and pH variation was followed, with particle size of 0.1 mm, agitation of 200 rpm and adsorbent dosage of  $0.005 \text{ g mL}^{-1}$  ( $5\% \text{ w v}^{-1}$ ); Table 1 reports the experiments to be performed, determining the number of tests using the software STATGRAPHICS Centurion XVI 16.1.03<sup>14,15</sup>.

**Tabla 1. Experiments**

No. Experiments	T(°C)	pH
1	55	4
2	40	2
3	70	2
4	40	6
5	70	6
6	33.8	4
7	76.2	4
8	55	1.17
9	55	6.83
10	55	4

Two pH and temperature reference values were used: one high (+1) and one low (-1), which were parameterized using Equation 1 as presented in Table 2.

$$\frac{X_{actual} - \left(\frac{X_{max} + X_{min}}{2}\right)}{\left(\frac{X_{max} - X_{min}}{2}\right)} \quad (1)$$

**Table 2. Experimental ranges and levels of independent variables.**

Independent variables	Range and level				
	$-\alpha$ (-1.41)	-1	0	+1	$+\alpha$ (+1.41)
pH	1.17	2	4	6	6.83
Temperature (°C)	33.8	40	55	70	76.2

### 2.1 Preparation of biomass

The African palm bagasse was obtained as a residue from the pressing process at a palm oil extraction plant located in María la Baja in the Department of Bolívar, Colombia. Initially, distilled water was washed with 5L to remove impurities such as reducing sugars, tannins and minerals that may be involved in the adsorption process, then dried in an Isotherm® brand oven model OFA-32-8 at 60°C for 24 h. The material was then ground and sieved in a 0.1 mm mesh<sup>16</sup>.

### 2.2 Preparation of the synthetic solution

The Ni (II) solution was prepared by dissolving 0.448 g of nickel sulfate hexahydrate (NiSO<sub>4</sub>\* 6H<sub>2</sub>O) in 100 mL deionized H<sub>2</sub>O, to measure up to 1000 mL and obtain a concentration of 100 ppm<sup>16</sup>.

### 2.3 Adsorption tests

To determine the removal rate, adsorption tests were performed in a batch system; initially the pH of the metal solution was stabilized at the interest level (1.17,2,4,6,6 and 6.83) using HCl or NaOH 2 M. 100 mL of solution and 0.5 g of biomass were contacted in each test with 200 rpm agitation and simultaneous heating at 33.8,40,55,70 and 76.2°C<sup>17</sup>.The solution was then filtered and 10 mL was taken from each filtered sample; the analysis of the residual metal concentration was performed on an iCE 3500 Double Beam atomic absorption spectrophotometer and the removal rate was determined using Equation 2 where C<sub>f</sub> and C<sub>i</sub> are the final and initial concentrations, respectively in ppm:

$$\text{Remotion (\%)} = \frac{C_i - C_f}{C_i} * 100 \quad (2)$$

### 2.4 Kinetics and adsorption isotherms

The adsorption kinetics were performed under the most favorable pH and temperature conditions, placing 100 mL of solution with 0.5 g of biomass in contact with 100 mL of solution in a Lab Shaking Incubator model IN-666 at 200 rpm for 170 min<sup>14</sup>. Samples were taken at 10,20,30,50, 80,120 and 170 min. The experimental data were fitted to the kinetic models of pseudo-primer order, pseudo-second order and Elovich for non-linear regression in SS minimization using the Microsoft Office Excel Solver optimization plug-in<sup>18</sup>.The adsorption isotherms were determined to describe the equilibrium of the separated solute between the solid and liquid phase, as well as to determine the phenomenon that controls the adsorption; for this reason the initial metal concentration was varied during 120 min, adjusting the experimental data to the models of Freundlich, Langmuir and Redlich– Peterson<sup>19</sup>.

### 2.5 Thermodynamic parameters

The graphical method based on the Van't Hoff equation was used to determine spontaneity, type of adsorption and predict the magnitude of changes on the surface of the adsorbent, respectively<sup>20</sup>.Therefore, the change in Gibbs's standard free energy ( $\Delta G$ ) was estimated to be enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ), by means of tests of removal percentages of samples at 33.8,40,55,70 and 76.2 °C. The final concentration of the metal was then determined after adsorption and the amount of metal removed was estimated; with this information, a Ln (Kc) versus T<sup>-1</sup> graph was made, which determined the thermodynamic parameters<sup>21</sup>.The analysis of these parameters allowed the feasibility of the adsorption process to be estimated, as well as the effect of temperature on them.

### 3. Results and discussions

#### 3.1 Influence of pH and temperature

Preliminary adsorption tests were carried out to determine at which temperature and pH the highest adsorption capacity of Ni (II) is present on bagasse of African palm. The set of data obtained shown in Table 3 were processed using the software Statgraphics Centurion XVI 16.1.03, from which it was found that the combination of temperature and pH at which the palm bagasse removes the largest amount of Nickel under the conditions of adsorption experiments was 55°C and a pH of 5.94.

**Table 3. Preliminary test results**

Experiment	Temperature (°C)	pH	C <sub>f</sub> (mg/L)	Remotion (%)
1	33.8	4	34.91	65.09
2	40	2	45.21	54.79
3	40	6	30.26	69.74
4	55	1.17	40.45	59.54
5	55	4	30.81	69.19
6	55	4	30.46	69.53
7	55	6.83	26.82	73.18
8	70	2	46.23	53.77
9	70	6	33.61	66.39
10	76.2	4	28.74	71.26

In different studies it has been observed that both pH and temperature influence the adsorption process, since both temperature can cause changes in the structure of the adsorbent material, and that the most favourable adsorption conditions depend to a large extent on the type of biomass used, as shown in Table 4. According to these values, Ni (II) tends to have better removal rates at pH between 5 and 7, which is confirmed by the results obtained in the present study, being this factor the most influential in the adsorption process.

**Table 4. Conditions for the removal process of Ni (II), from African palm bagasse**

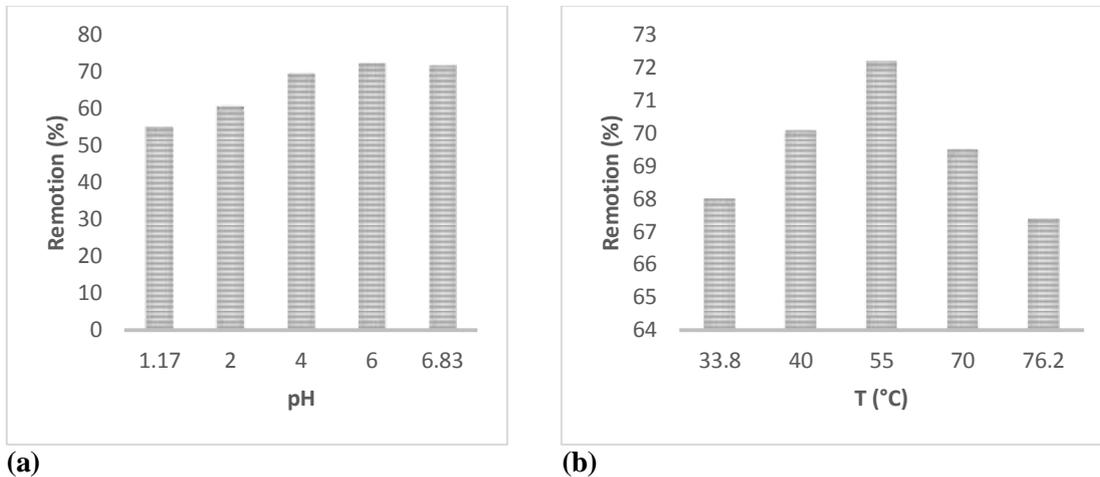
Variable	Low	High	Favourable
Temperature (°C)	33.79	76.21	54.93
pH	1.17	6.83	5.94

Figure 1 shows the relationship between the percentage of removal of Ni (II) with palm bagasse and the pH of the metal solution, which is the most important factor influencing removal rates.

**Table 5. Comparison of the most favorable T and pH conditions for Ni (II) adsorption with different biomasses in preliminary tests.**

Bioadsorbent material	Remotion (%)	pH	T (°C)	Reference
Orange peel	96 %	6	50	(Ajmal et al. <sup>17</sup> )
Bagazo de caña	80.6 %	5	25	(Aloma et al. <sup>18</sup> )
Peat	92.5 %	5	25	(Bartczak, <sup>19</sup> )
Cane bagasse	90.09%	8.5	25	(Bhagyalakshmiand Sarna <sup>20</sup> )
Rice straw	46 %	5	25	(El-Sayed et al. <sup>21</sup> )
Yam shell	77 %	6	25	(Tejada-Tovar et al. <sup>16</sup> )
Tea Waste	94%	5	30	(Singh and Parmar <sup>14</sup> )
Bread yeast	92.1 %	6.75	27	(Padmavaty <sup>22</sup> )
Palm bagasse	72 %	5.9	55	This research

It can be seen that the greater percentages of removal are obtained at pH close to 6, it can be deduced that an increase in pH favours the removal process, but this increase is only favorable up to certain levels, since after 6 the pH has a negative influence on the amount of metal removed. In general, acidification of the aqueous phase leads to an increase of the proton that occupies the active sites in the adsorbent structure. At low pH, the number of H<sup>+</sup> ions exceeds several times the amount of metal ions and Ni (II) ions can hardly compete with H<sup>+</sup> ions for binding sites in the Palm Bagasse. As pH increases, the concentration of H<sup>+</sup> ions decreases and more active sites are available for metal ions<sup>15</sup>.



**Figure 1. Influence on the percentage of Ni (II) adsorption of the solution's (a) pH; (b) temperature**

In Figure 1b, the influence of temperature on adsorption tests is shown, determining that a temperature of 55 °C generates the highest removal rates of Ni (II) with palm bagasse. Temperatures higher or lower than this will damage the adsorption process, thus generating lower removal %. Although temperature is less likely to affect the % of Ni (II) removal with palm bagasse as shown in Table 9, it is also a factor that must be regulated to improve the amount of nickel removed. These data are consistent with those obtained by Ajmal *et al.*<sup>17</sup>, where they reported a temperature of 50°C for the removal of nickel with orange peel, similar to those obtained, where they determined that for the removal of Ni (II) with barley straw ash an adequate temperature range is between 50°C and 80°C. An increase in temperature causes an activation of the sites available for adsorption and high temperature reduces resistance to mass transfer so that the ions diffuse to bonding sites. After 55°C, the equilibrium adsorption capacity decreases. The reduction could be the cause of ruptured lignin and hemicellulose at high temperature, causing a change in the chemical state of the bonds available for bonding. Most potential adsorption sites are located in cellulose, hemicelluloses. Its sorption characteristic is due to the presence of active functional groups such as hydroxyl and carboxylic groups<sup>23</sup>.

### 3.2 Statistical analysis

Table 6 shows the results obtained from the analysis of variance (ANOVA), which was carried out to determine the statistical significance of each effect by comparing its mean square against an experimental error estimate; In this way, the values of the significant parameters in the adsorption process of Ni (II) with bagasse of African palm are obtained, establishing a 95% confidence level, therefore those effects or parameters with an error P-value < 0.05.

**Table 6. Statistical analysis of variance (ANOVA) for the removal percentage.**

Variable	Sum of squares	GI	Squaremedium	F	P-value
A:Temperature	2.35	1	2.35	0.09	0.78
B:pH	247.55	1	247.55	10.52	0.03
AA	20.49	1	20.49	0.79	0.43
AB	1.36	1	1.35	0.05	0.83
BB	41.79	1	41.79	1.60	0.27
Error total	104.42	4	26.11		
Total	428.25	9			

According to the results reported in the Pareto Diagram in Figure 2, it is shown that the variable with the most positive influence on the Ni (II) adsorption process is pH, which means that as the pH value increases, the removal percentage increases until it reaches a maximum value, which is consistent with the results previously found. In the Pareto diagram it can also be observed that temperature as well as temperature-pH interaction influence the adsorption of Ni (II) in a less significant way than pH and do not exceed the line corresponding to statistically significant effects, which coincides with that reported by Asfaram *et al.*<sup>24</sup> and Dastkhooon *et al.*<sup>25</sup>.

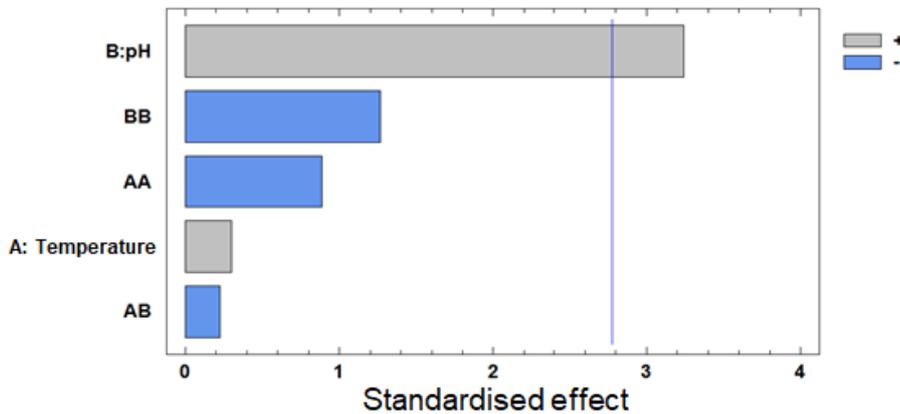


Figure 2. Pareto diagram for the percentage of removal of Ni (II) on palm bagasse.

### 3.3 Kinetic modeling

The kinetic study was carried out to investigate the adsorption mechanism of Ni (II) on residual biomass of African palm, using the kinetic models of pseudo-primer order or equation of Lagergren, pseudo-second order and Elovich considering the following stages: mass transfer from the solution sinus ion to the adsorbent surface, adsorption of the ion in the adsorbent and internal diffusion of the contaminant in the adsorbent<sup>26</sup>. In order to find the model that best fits the experimental data, an adsorption capacity ( $q_t$ ) vs. time (min) curve was made; the adjustment of the models was made by non-linear regression in SS minimization<sup>27</sup>.

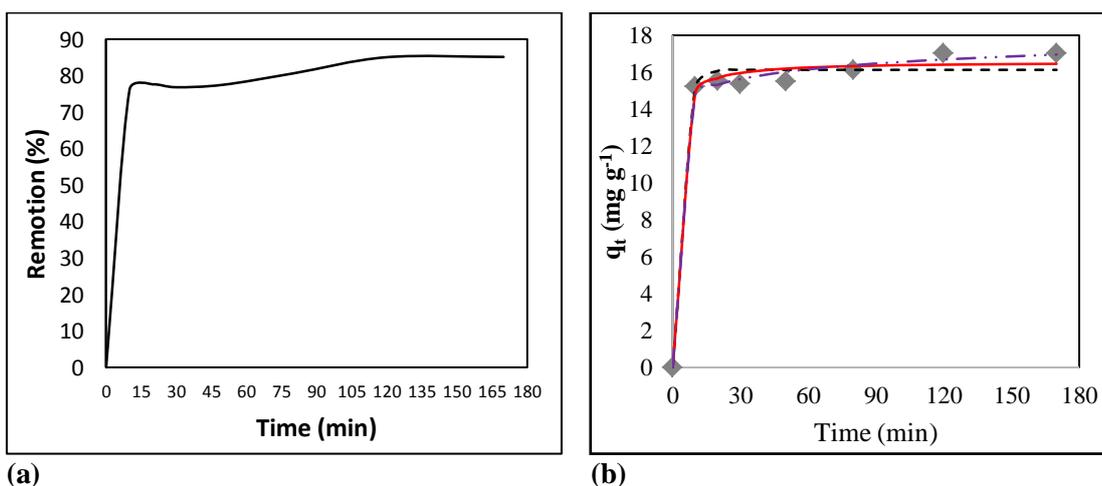


Figure 3. (a) Ni (II) adsorption process balancing time; (b) fit to kinetic models. (♦) experimental, (-----) Pseudo-first order, (—) Pseudo-second order, (---) Elovich.

The Pseudo-first model assumes that the limiting stage in an adsorption process is the mass transfer of the metal ion from the solution sinus to the adsorbent surface<sup>28</sup>. It is expressed according to Equation 3 where  $k_1$

( $\text{min}^{-1}$ ) is the kinetic velocity constant of Lagergren,  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities in equilibrium and at time  $t$ , respectively.

$$\log(q_e - q_t) = \log(q_e) - \left( \frac{k_1}{2.303} \right) \cdot t \quad (3)$$

This kinetic model establishes that the determining stage of the adsorption processes is the reaction itself and not the mass transference. In addition, the metal ion can be adsorbed by two active biomass sites. It is defined according to Equation 4 where  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities in equilibrium and at a given time  $t$ , respectively, and  $k_2$  ( $\text{g}^{-1}\text{min}^{-1}$ ) is the second order adsorption velocity constant.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The Elovich model, which is generally applied in chem-adsorption processes, assumes that the active sites of the adsorbent are heterogeneous and therefore exhibit different activation energies, based on a second-order reaction mechanism for a heterogeneous reaction process<sup>29</sup>. It is defined according to Equation 5 where  $q_t$  ( $\text{mg g}^{-1}$ ) is the adsorption capacity for a time  $t$  ( $\text{mg. g}^{-1} \cdot \text{min}^{-1}$ ) is the initial adsorption speed and  $\beta$  ( $\text{g mg}^{-1}$ ) is the desorption constant related to the surface range<sup>30</sup>.

$$q_t = \alpha \cdot \ln(\alpha \cdot \beta) + \alpha \cdot \ln(t) \quad (5)$$

**Table 7. Adjustable parameters of kinetic models of Ni (II) adsorption on palm bagasse**

Model	Parameter	Value
Pseudo-first order	$q_e$ ( $\text{mg g}^{-1}$ )	16.12
	$k_1$ ( $\text{min}^{-1}$ )	0.65
	SS	2,87
	$R^2$	0.98
Pseudo-Second Order	$q_e$ ( $\text{mg g}^{-1}$ )	16,55
	$k_2$ ( $\text{min}^{-1}$ )	0.053
	SS	1.73
	$R^2$	0.992
Elovich	$\beta$ ( $\text{g. mg}^{-1}$ )	1.31
	$\alpha$ ( $\text{mg g}^{-1}\text{min}^{-1}$ )	18186622
	SS	0.76
	$R^2$	0.997

Fig. 3a shows that the contact time for the biological material to reach the adsorption equilibrium is between 105 and 135 min and a maximum adsorption percentage of 85.14%. The values of the parameters of the previously mentioned models and the corresponding SS and  $R^2$ , are shown in Table 7 and the graphs are shown in Fig. 3b, finding that the Elovich model was the one that best fitted the experimental data of Nickel adsorption with an  $R^2=0.997$  and  $SS=0.76$ ; determining that the chem-adsorption process is controlled by a second-order reaction mechanism for a heterogeneous reaction process. The results of the application of the Elovich kinetic model are very different from those obtained in other investigations since each adsorption system is limited by a different stage, either the transfer of mass of the metal ion from the sinus of the solution to the adsorbent surface, the adsorption of the metal ion in the adsorbent and the internal diffusion of the metal ion in the adsorbent<sup>29</sup>. In a study where the biosorption process of Ni (II) by yam shells and palm bagasse was analyzed, they obtained an SS value of 0.8046 and 0.8590 respectively<sup>8</sup>.

### 3.4 Balance modeling

In order to describe the equilibrium of the separated solute between solid and liquid phases, data obtained in the adsorption process of Ni (II) from African palm bagasse (fibrilla) were evaluated using Langmuir, Freundlich and Redlich-Peterson (R-P) models. Freundlich's model is based on adsorption over a

heterogeneous surface, which implies that active sites where adsorption can be carried out have different behavior from each other, presenting different adsorption energies towards the metal ions and the possibility of multi-layer formation due to the interaction between active sites and non-adsorbicods metal molecules or ions. It is represented in Equation 6 where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of metal adsorbed in the equilibrium,  $C_{e,q}$  ( $\text{mg L}^{-1}$ ) is the residual concentration of metal in the solution in the equilibrium and  $K_f$  ( $\text{mg g}^{-1}$ ) ( $\text{mg L}^{-1}$ ) and  $n$  is a measure of adsorption intensity, which lies in the range 1 to 10, and is a reference point for evaluating adsorbent-adsorbent interaction, determining the magnitude of  $1 \times n^{-1}$  and the favorability of adsorption<sup>31</sup>.

$$q_e = K_f \cdot C_{e,q}^{1/n} \quad (6)$$

The Langmuir model assumes that adsorption occurs on a homogeneous surface, which implies that the active sites of the adsorbent surface are equal to each other, have the same adsorption energy towards the metal ions, do not affect the neighbouring active sites and that a monolayer of the adsorbed metal will be formed, which means that the ions of the adsorbed metal will not interact with the metal ions. It is represented by Equation 7 where  $q_e$  ( $\text{mg. g}^{-1}$ ) is the amount of adsorbate retained in the adsorbent in the equilibrium,  $C_f$  ( $\text{mg L}^{-1}$ ) is the residual concentration of the metal in the equilibrium,  $q_{\text{max}}$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption for saturation sites and  $K_1$  ( $\text{L mg}^{-1}$ ) is the ratio between adsorption/disposition rates<sup>32</sup>.

$$q_e = q_{\text{max}} \frac{K_1 C_f}{1 + K C_f} \quad (7)$$

The Redlich-Peterson (R-P) model suppose an intermediate between the Freundlich and Langmuir models, making it easy to apply the model to systems where the adsorbent has a homogeneous or heterogeneous surface<sup>21, 33</sup>. It is represented by the equation where  $q_e$  ( $\text{mg g}^{-1}$ ) is the adsorption capacity in equilibrium,  $C_e$  ( $\text{mg L}^{-1}$ ) is the residual concentration of adsorbate in equilibrium,  $K_{RP}$  ( $\text{L mg}^{-1}$ ),  $\alpha_{RP}$  ( $\text{L mg}^{-1}$ ) <sup>$\beta_{r-p}$</sup>  and  $\beta_{r-p}$  are the parameters of Redlich-Peterson.  $\beta_{r-p}$  determines the degree of surface heterogeneity, being more homogeneous when approaching 1. The values of  $\beta$  must be between  $0 < \beta_{r-p} \leq 1$ ; in the case that  $\beta_{r-p}=1$ , it tends to the equation of the isotherm of Langmuir and when  $\beta_{r-p}=0$  it tends to the isotherm of Freundlich<sup>34</sup>. The constants and correlation coefficient obtained for the mathematical model of the isotherms of Langmuir, Freundlich and R-P are recorded in Table 8.

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta_{r-p}}} \quad (8)$$

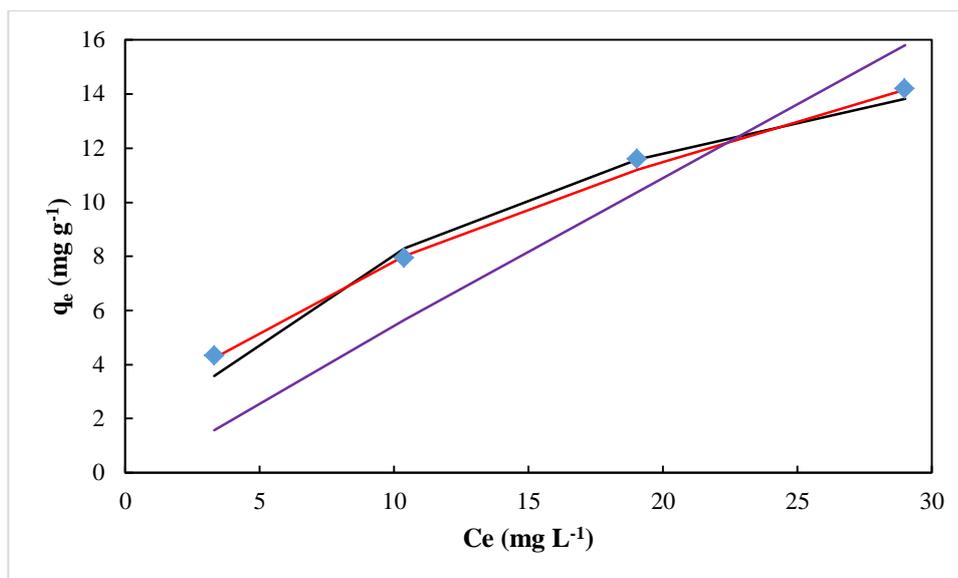


Figure 4. Adjustment of experimental data to the isothermal models. (♦) Experimental, (—) Langmuir, (—) Freundlich, (—) Redlich-Petersen.

For the R-P isotherm, the value of  $\beta_{r-p}$  being closer to zero indicates that the adsorption process tends more towards the Freundlich model, thus proving that it is this model that best fits the data. From a mathematical point of view, the isotherm that best adjusts the experimental data is Freundlich's with  $R^2=0.99$ , which means that the adsorption mechanism is controlled by chemadsorption according to Gupta and Balomajumder<sup>35</sup> and Sepehr, et al.<sup>36</sup>. This result differs from that reported in previous studies by Tejada-Tovar et al.<sup>16</sup>, Uthra and Kadirvelu<sup>37</sup>, and Farhan et al.<sup>38</sup>, who determined that the model that best fits nickel adsorption is Langmuir.

**Table 8. Characteristic parameters of the different models of isotherms.**

Isotherm	Parameter	Value
Langmuir	$q_{max}$	21.96
	$K_l$	0.06
	SS	1.04
	$R^2$	0,98
Freundlich	$K_f$	2.19
	N	1.80
	SS	0.018
	$R^2$	0.99
Redlich-Peterson	$K_{rp}$	0.83
	$\alpha_{rp}$	0.51
	$\beta_{r-p}$	0.30
	SS	16.03
	$R^2$	0.97

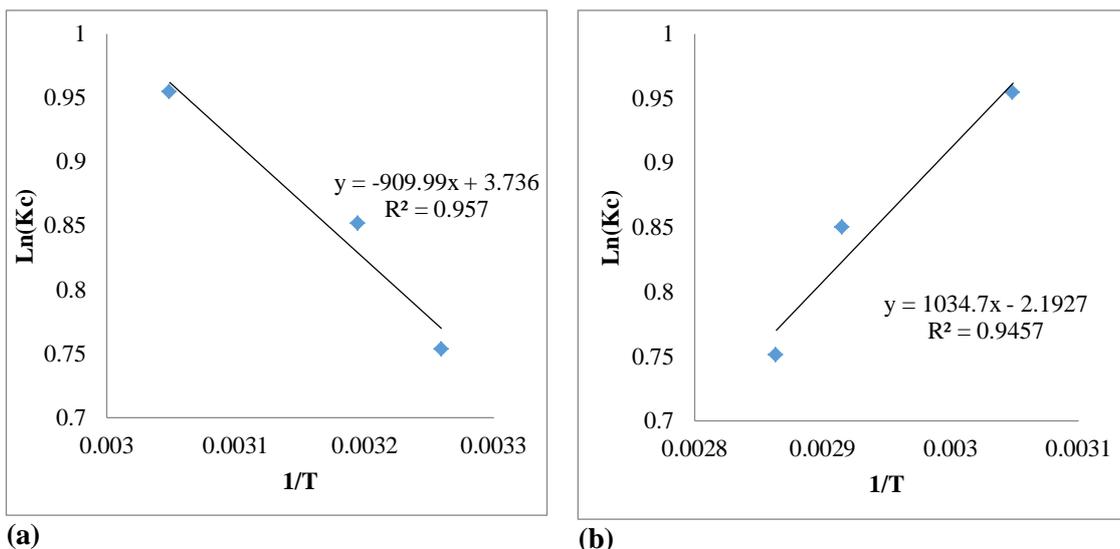
From the physical point of view of the system, Freundlich's model is also the one that best predicts the behavior of the bagasse palm-nickel adsorption system, since the concentration being worked on is sufficiently high to favour the formation of several layers of adsorbed material, which is complemented by the analysis of biomass composition (Table 5), since the presence of different functional groups implies different adsorption energy in the active sites, since they do not behave in the same way to the pH and temperature conditions worked. The Freundlich isotherm indicates that the surface of the adsorbent presents heterogeneous adsorption energies, i. e. there is no uniform adsorption surface due to the presence of different functional groups acting on the adsorption, for this reason the adsorption sites are not equivalent, the adsorbed molecules interact with each other due to the amount of Ni (II) present in the solution, thus affecting the sites.

### 3.5 Calculation of thermodynamic parameters

In order to characterize the adsorption process of Ni (II) with palm bagasse from the thermal point of view, the free energy thermodynamic parameters of Gibbs ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and adsorption entropy ( $\Delta S$ ) were calculated graphically using equations 9 and 10.

$$\Delta G = -RT \ln k_c \quad (9)$$

$$\Delta G = \Delta H - T \Delta S \quad (10)$$



**Figure 5. Ln (Kc) vs. 1\*T<sup>-1</sup> graph for Ni (II) adsorption: (a) process favored by temperature increase, (b) process not favored by temperature increase**

It was found that after 55 °C the process was negatively affected, so two graphs were obtained for the determination of thermodynamic parameters as shown in Figure 5; one for the process stage where the temperature has a positive effect (Figure 5a), and another for the process stage where the temperature has a negative effect (Figure 5b). The values calculated for the process steps are shown in Table 9. For the stage of the process where adsorption capacity is favoured with the increase in temperature, a positive value of ΔH is obtained, which indicates that the process is endothermic; negative values of ΔG reveal that the adsorption process of Ni (II) with palm bagasse occurs spontaneously according to Mushtaq *et al.*<sup>39</sup>, Saleh *et al.*<sup>40</sup> and Saman *et al.*<sup>41</sup>. The magnitude of the value of ΔH indicates that the process occurs by physical adsorption. Meanwhile the value obtained for ΔS, sign and magnitude, indicates that the process is reversible (disruption)<sup>42</sup>.

**Table 9. Effect of temperature on thermodynamic parameters for the adsorption of nickel on palm bagasse**

Favourable effect				Negative effect			
T (K)	ΔG (J mol <sup>-1</sup> )	ΔH (J mol <sup>-1</sup> )	ΔS (J mol <sup>-1</sup> K <sup>-1</sup> )	T (K)	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/mol.K)
306.8	-845.69	7565.66	31.06	328	-3009.49	-8602.49	-18.23
313	-1038.27			343	-2896.47		
328	-1504.18			349.2	-2623.02		

For the process stage where the adsorption capacity decreases with temperature increase, values of ΔH and ΔG were negative, which indicated that the process is exothermic and spontaneous, respectively; for its part, the magnitude of ΔH shows that the process occurs through physical adsorption<sup>43</sup>. Meanwhile, the sign and magnitude of S indicate that the process is hardly reversible<sup>42</sup>. The fact that the adsorption process of Ni (II) with palm bagasse presents this behavior under the effect of temperature, suggests that a control system be implemented to prevent system conditions from exceeding this maximum value and avoid a decrease in the amount of nickel removed.

#### 4. Conclusion

African palm bagasse was used as a precursor for a biosorbent in the adsorption of Ni (II) ions present in aqueous solution in a batch system, which showed high efficiency in removal; it reached equilibrium between 105 and 135 min and its best performance at 55°C and pH 5.94 with a removal percentage of 85.14%, with Elovich's kinetic model and Freundlich's isothermal being the ones that best adjusted the experimental adsorption data indicating that the active surface adsorption sites are heterogeneous, exhibit different activation energies and therefore change the adsorption velocity as the process develops. Calculated thermodynamic

parameters  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) indicate that the process occurs spontaneously, energetically stable in nature, endothermic, favorable and reversible. Therefore, palm bagasse under the conditions studied can be used as a Nickel adsorbent material in solution, is an alternative for the treatment of wastewater contaminated with this metal and raises an alternative for the large volumes of waste generated by industry that exploits the wax palm.

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