Kinetic and thermodynamic modeling of nickel adsorption onto adsorbent derived from banana peels

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Abstract- The use of agricultural wastes has gain attention for the development of novel materials with remarkable adsorption properties. In this work, adsorption of nickel ions was performed using banana peels biomass in order to evaluate the effect of temperature, initial concentration, adsorbent dosage and particle size on adsorption capacity. Kinetic modeling and thermodynamic study was also carried out to calculate parameters of kinetic models as well as change of Gibbs free energy and enthalpy. Batch system was used for adsorption tests at fixed solution volume (100 mL), pH (6), stirring (200 rpm). The remaining concentration of heavy metal was measured by atomic absorption at 305.1 nm. Results revealed good adsorption performance of banana peels biomass using initial concentration of 200 ppm, temperature of 76°C, adsorbent dosage of 0.1 g and particle size of 1 mm. Kinetic studies showed that pseudo-second order and Elovich models best fitted experimental results reaching a maximum capacity of 167 mg/g. The thermodynamic of adsorption process revealed to be endothermic and non-spontaneous. This research provided insights about the use of banana peels to uptake nickel from aqueous solution and hence, mitigate the environmental impacts of water pollution.

Keywords – adsorption, heavy metals, thermodynamic, biomass

I. INTRODUCTION

The presence of heavy metal ions in aqueous sources has become a global environmental issue due to the high toxicity of such pollutants and their tendency to bioaccumulate in different ecosystems and living organisms. It also features a public health concern due to the ability of heavy metals to be transferred into human body through food chain [1]. According to the World Health Organization (WHO), heavy metals of greater concern are cadmium, zinc, nickel, cobalt, chromium, copper and mercury [2]. Nickel ions in groundwater can be attributed to mining, smelting, metal plating, or metal recycling facilities[3]. Extensive application of such metal in several industries may generate residues that converge in water sources exceeding the allowed levels (0.02 mg/L) [4, 5]. High concentration of nickel in drinking water is associated to several health diseases such as gastrointestinal insufficiency, chest pain, shortness of breath and damage to the lungs and kidney [6].

Several chemical, physical and biological technologies have been evaluated to face the environmental problems of heavy metal water pollutants (e.g. precipitation, adsorption, ion exchange, reverse osmosis, filtration), however, their uses are limited by disadvantages such as high cost, secondary contamination or complexity [7]. Nowadays, adsorption features an attractive method to uptake contaminants and many contributions are being focused on the development of novel materials with high adsorption efficiency and low cost. Agricultural wastes are widely recognized as source of adsorbents with high removal yields providing a good alternative for the problem of biomass disposal. Adsorbents derived from fruit peels, oil palm residues or other sources, act as active sites for metal ions uptake due to the presence of characteristic functional groups [1, 8, 9]. Developing novel materials from banana peels is also a promising alternative because they are easily and cheaply collected from markets, agricultural industries, hotels, farms and chip factories [10]. In this work, a green adsorbent derived from banana peels was employed to remove nickel ions from aqueous solution in a batch system. The effects of several operating parameters such as initial concentration, adsorbent dosage and particle size were evaluated. In addition, thermodynamic analysis and kinetic modeling were performed to provide insights about adsorption performance of such biomaterial.

The rest of the paper is organized as follows. The methodology of bio-adsorbent synthesis and batch tests are explained in section II. Experimental results are presented in section III. Concluding remarks are given in section IV.

II. MATERIALS AND METHODS

2.1. Biomass preparation and adsorption study-

Banana peels biomass was collected from local food industries in Cartagena de Indias (Colombia). The peels were washed thoroughly, cut into small pieces and dried at 60°C for 8 hours. Then, this biomass was grounded and sieved to different particle sizes (0.5, 1 and 2 mm).

To perform adsorption batch experiments, synthetic solutions at 100 ppm were prepared by adding 4.48 g $Ni(NO_3)_2$ into 1000 ml water. This standard solution was employed to prepare solutions at 200 ppm. Different adsorbent dosages (0.1, 0.5 and 1 g) and particle sizes (0.5, 1 and 2 mm) were studied at fixed stirring rate (200 rpm), pH (6), temperature (30°C) and contact time (24 h). The remaining concentration of heavy metal ions after adsorption process was measured through an atomic absorption spectrophotometer ICE3000 at 305.1 nm [11]. The adsorption capacity was calculated by Equation 1, where C_0 (mg/L) is the initial concentration of nickel ions, C_t (mg/L) is the final concentration, m is the adsorbent dosage (g) and V is the solution volume (L) [12].

$$q_t = \frac{(C_o - C_t)V}{m} \qquad (1)$$

After selecting the most appropriate operating conditions, the effect of temperature and heavy metal concentration was tested using a central composite experimental design shown in Table 1. The software STATGRAPHICS CENTURION 18.1.02 was used to perform the statistical analysis providing analysis of variance, Pareto diagram, estimated response surface and optimization of such response that allows to maximize the adsorption capacity.

Table-1 Experimental ranges and levels of variation

Independent variables	**Unit**	**Ranges and levels**				
		- α	-1	0	+1	+α
Temperature	°C	29,77	40	55	70	80,23
Concentration	ppm	31,82	100	200	300	368,18

2.2. Kinetic modeling-

The kinetic study describes how quickly the pollutants are removed from aqueous solution using fitting models such as pseudo first order, pseudo second order and Elovich [13]. The fundamental kinetic interactions between metal ions and charged surface are represented by simple equations summarized in Table 2.

Table-2 Mathematical expressions of kinetic models

Kinetic model	**Equation**	**Parameters**
Pseudo-1st-order	$q_t = q_e(1 - e^{-kt})$	q_e, Adsorption capacity at equilibrium (mg/g) k_1, pseudo-1st-order constant (min^{-1})

Pseudo-2nd-order	$q_t = \frac{t}{\left(\frac{1}{(k_2 q_e^2)}\right) + \left(\frac{t}{q_e}\right)}$	k_2 pseudo-2nd-order constant (g/mg.min) q_e, Adsorption capacity at equilibrium (mg/g)
Elovich equation	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	α, Elovich constant (mg/g min) β, Elovich exponent (g/mg)

2.3. Thermodynamic of adsorption process

To calculate thermodynamic parameters, graphical method based on the Van't Hoff equation was employed. So, change in standard Gibbs free energy (ΔG) was quantified by Equations 2 and 3, while enthalpy (ΔH) and standard entropy (ΔS) were determined using Equation 4

$$\Delta G = \Delta H - T\Delta S \quad (2)$$
$$\Delta G = -RT * lnk_c \quad (3)$$
$$lnK_c = \frac{-\Delta H}{R * T} + \frac{\Delta S}{R} \quad (4)$$

Where $Kc = Cac/Cse$; Cac is the adsorbate concentration at equilibrium, Cse is the solution concentration at equilibrium, R is the universal gas constant (8.314 J/mol.K) [13]. The selected temperatures for this study were 30, 55 and 80°C, and initial concentration of heavy metals at 200 ppm.

III. Experiment and Result

3.1. Adsorption study-

The amount of adsorbent is a key parameter during adsorption process affecting the removal yield under defined operating conditions [14]. The effect of adsorbent dosage on Ni (II) ions uptake is shown in Figure 1. The maximum adsorption capacity of Ni (II) onto banana peels (26.1 mg/g) was reached using 0.1 g of adsorbent. Higher dosages than 0.1 g reduce the adsorption capacity due to the saturation of active sites. Particles aggregation onto adsorbent surface reduce the adsorption area, as well as the availability of active sites, reducing the electrostatic interactions between heavy metal ions and biomass [15, 16].

The effect of particle size on adsorption performance was assessed by varying such parameter between 0.5 and 2 mm. The highest adsorption capacity was achieved by 1 mm-biomass. Smaller particle sizes provide high adsorption rates due to the transfer of heavy metal ions through a short path inside the adsorbent pores, however, the size of 0.5mm may generate particle agglomeration affecting the adsorption capacity results [17]. Thus, an adsorbent dosage of 0.1 g and particle size of 1 mm were selected as parameter values for further adsorption tests.

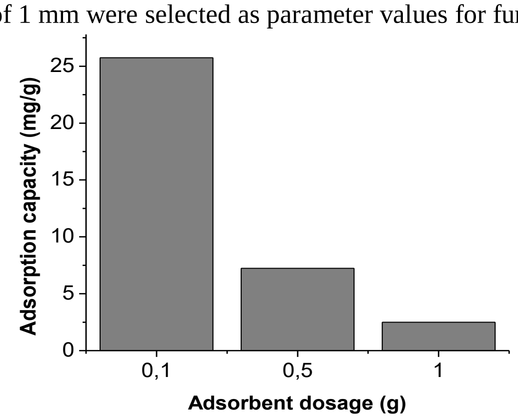

Figure 1. Influence of adsorbent dosage on nickel uptake

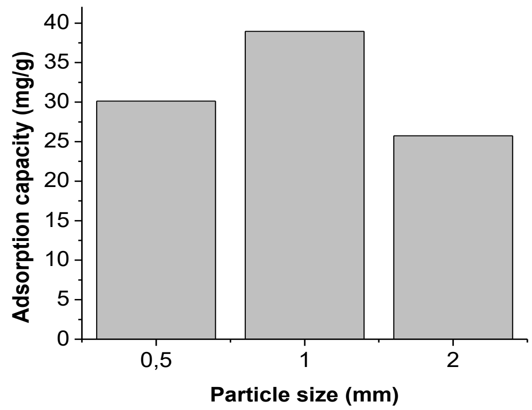

Figure 2. Effect of biomass particle size on adsorption performance

3.2. Statistical analysis for adsorption parameters of temperature and initial concentration-

The statistical study using Statgraphics Centurion software provides information about the importance of both adsorption parameters on nickel removal yields, as well as their interactions. Table 3 lists the results of ANOVA analysis indicating that such parameters are not significant for adsorption experiments purpose because the P-value is greater than 0.05 for temperature and initial concentration.

Table-3 ANOVA results for nickel ions uptake using banana peels biomass

Source	*Sum of squares*	*Gl*	*Average of square*	*F-ratio*	*P-value*
A:Temperature	1087.48	1	1087.48	0.60	0.495
B: Initial concentration	0.1598	1	0.1598	0.00	0.993
AA	3516.96	1	3516.96	1.94	0.258
AB	0.1260	1	0.1260	0.00	0.994
BB	1803.47	1	1803.47	0.99	0.392
Total error	5449.79	3	1816.6		
Total (corr.)	17624.3	8			

Figure 3 shows the Pareto diagram for temperature and initial concentration of nickel ions. The factors that are significant must overcome vertical line that represents 95% of the results reliability. In this sense, it is confirmed that such parameters have no influence on the removal of Ni (II) using the banana peel. Interactions between variables also did not report significant results to be considered as key adsorption factors. As depicted by Figure 4, gradual increase in the initial concentration of metal ions decreased the adsorption capacity of the biomass. This result may be explained by the fact that adsorption occurs at adsorbent active sites, and for constant dosage, the number of sites keeps constant leading to saturation of biomass surface and blocking of active adsorption sites when initial concentration increases. The additional particles of metal ions in the aqueous solution will not be adsorbed due to blocking of adsorption sites [18]. On the other hand, results also revealed gradual decrease in the removal capacity until reaching a temperature of 55 ° C, which is attributed to a decrease in the attractive forces and surface mobility, however, higher temperatures enhance adsorption performance due to a better interaction of heavy metal ions with the binding sites of biomass [14, 19, 20].

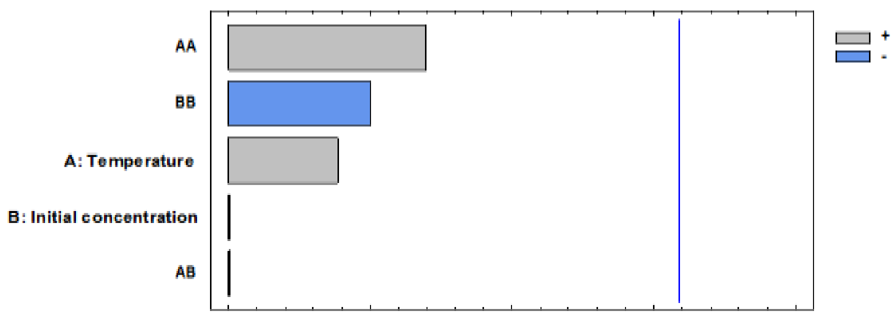

Figure 3. Pareto diagram for nickel adsorption process

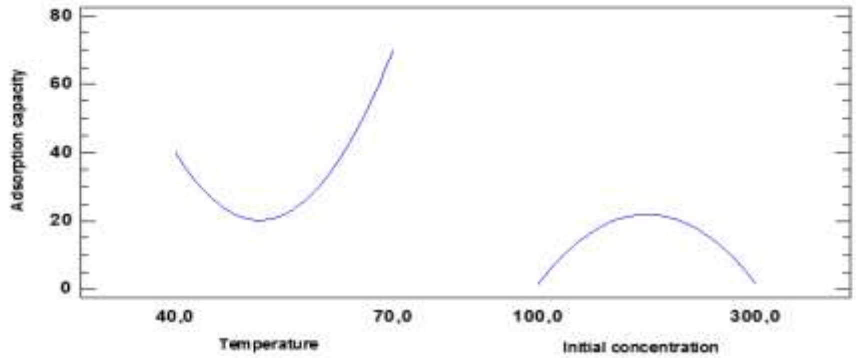

Figure 4. Influence of temperature and initial concentration of heavy metal ions on adsorption capacity

The statistical analysis also provides a fitting model that best describes the experimental results of temperature (°C) and initial concentration (ppm) effects on adsorption capacity, which is given by the following equation:

$$q_t = 332.12 - 15.23\ \mathrm{T} + 0.81\ C_o + 0.15\ T^2 + 0.000118\ \mathrm{T}\ C_o - 0.0020\ C^2$$

This fitting equation was used to build a response surface plot to determine the optimum values for both parameters. As shown in Figure 5, the highest adsorption capacity is reached at 76°C and 200 ppm, hence, such values were selected as optimum for nickel adsorption onto banana peels biomass.

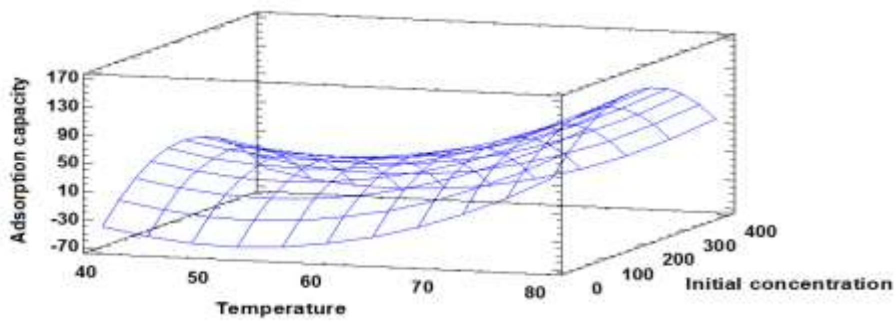

Figure 5. Response surface of Ni (II) ions adsorption under temperature and initial concentration variations

3.3. Adsorption kinetic modelling-

It is important to know the rate at which heavy metal ions are adsorbed onto adsorbent surface to provide valuable data for understanding the mechanism of adsorption reactions [21]. The contact time at which equilibrium is reached was determined from adsorption tests over time as shown in Figure 6. These results exhibited that equilibrium was reached after approximately 120 min, attributed to a rapid initial adsorption that made easier to reach the equilibrium [22].

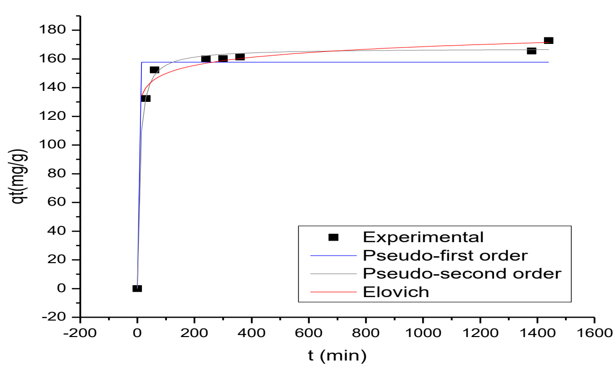

Figure 6. Kinetic experiments for nickel adsorption onto banana peels

The parameters of kinetic modelling are summarized in Table 4, where k_1 (min^{-1}) is the pseudo first order constant [23]; k_2 (g^{-1} min^{-1}) is the pseudo second constant order [24]; α (mg/g min) is the adsorption rate for Elovich model and β (g/mg) is a constant related to the surface coverage and activation energy in the chemisorption [25]. Both Pseudo-second order and Elovich models showed the best fitting results to describe experimental data of nickel adsorption onto banana peels. The value for k_2 revealed a limiting steps in adsorption process attributed to chemical adsorption where there is covalent bond formation through the exchange or exchange of electrons between heavy metal ions and adsorbent binding sites. This phenomenon occurs due to the complexation of Ni (II) ions with functional groups available in the banana peels biomass [26]. The parameter β also revealed the multilayer adsorption process, in which each layer has its own activation energy [27].

Table-4 Fitting results for kinetic modeling

	Pseudo –first order	**Pseudo-second order**	**Elovich**
Model	$q_t = q_e\,(1 - e^{-k_1 t})$	$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	$q_t = \frac{1}{\beta}\ln(\alpha\beta t)$
Parameters	q_e: 157.79 k_1: 1.047E13	q_e: 167.37 k_2: 6.19E5	α: 8.55E6 β: 0.1232
R^2	0.9496	0.9961	0.9923

3.4. Thermodynamic study-

Table 5 shows positive values for the change of Gibbs free energy (ΔG °) indicating a non-spontaneous and energy-unfeasible adsorption process. In addition, the positive change of enthalpy (ΔH °) less than 20 kJ/mol suggested that adsorption process is endothermic. A process of such nature is attributed to chemical adsorption (chemisorption) with strong forces. This result is due to Ni (II) ions must displace more than one molecule of water for adsorption that causes the endotherm of such process [25, 28, 29]. In addition, negative values of entropy ΔS° between 0.10 and 0.27 kJ/mol suggests the non-reversibility of adsorption process [25, 30].

Table-5 Thermodynamic parameters for nickel adsorption onto banana peels biomass

Thermodynamic parameters	**J/mol**	**kJ/mol**
ΔH	269,215	0,269
ΔS	-110,343	-0,110
ΔG1	34,138	
ΔG2	36,478	
ΔG3	38,795	

IV.CONCLUSION

This work was focused on the preparation of a green adsorbent from banana peels for nickel adsorption. The results showed that operating variables such as temperature and initial concentration of heavy metal ions do not present significant effects on the adsorption capacity of biomass. In addition, adsorption equilibrium was reached after 120 minutes and kinetic models that best fitted experimental results were Pseudo-second order and Elovich models. The thermodynamic study indicated an endothermic process, not spontaneous and not reversible. These results suggest that banana peels can be efficiently used to remove nickel ions from aqueous solutions.

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