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# Evaluation of *Theobroma cacao* Waste Performance in Nickel Removal (II) in Continuous System*

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**Abstract :** The objective of this research was to evaluate the performance of cocoa shell residual biomass as an adsorbent of Ni (II) dissolved in aqueous solution, in a continuous fixed bed system determining the effect of bed height on the removal of this contaminant. The experimental work was based on: biomass preparation, design and assembly of the adsorption unit and mathematical modeling, considering as variables incidents in the process; the initial concentration of metal, pH, flow rate and particle size. In FTIR to shell analysis, the presence of functional groups favourable for metal adsorption was observed in the spectrum. The residual concentration of the solution was measured by atomic adsorption spectroscopy where the maximum adsorption capacity was 99.02% for the 10g (7.5 cm) bed. In addition, Thomas's model was the one that best adjusted the experimental data. The cocoa shell has the potential to be used as a solution bio-adsorbent of Ni (II) and the increased height of the bedding in the continuous system favours removal of the contaminant.
**Keywords :** Bio-adsorbent, cocoa shell, continuous system, molecular adsorption, mathematical modeling.

## 1. Introduction

The discharge of industrial effluents increases the concentration of heavy metals in the water, which generates sanitary alarm because the concentrations of metals in wastewater have exceeded the maximum permitted rates. This poses a threat to the environment and public health from water-soluble salts of heavy metals such as Nickel (Ni), which are toxic and accumulable by the organisms ingesting them [1]. The development of industrial activities such as mining, cement, dyestuffs, tannery, electroplating, steel production, photographic material, anti-corrosive paints, nuclear power production, textile manufacturing, and aluminum anodizing present a high concentration of heavy metals such as chromium, nickel, cadmium, lead and mercury in their effluents, which are discharged without adequate treatment [2, 3, 4].

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Nickel exists mainly as Ni (II) in aqueous solution, causing poisoning of various life forms due to its high neurotoxicity; it is also associated with health effects such as dermatitis, nausea, bronchitis and cancer [4, 5]. The discharge to the public sewerage system is controlled by environmental authorities in Colombia according to Decree 1594 of 1984, which establishes limits for the discharge of 0.02 mg $L^{-1}$ of Ni into aqueous solutions[4, 6].According to the World Health Organization (WHO), the maximum concentration of heavy metal ions in water should be in the range of 0.01-1 ppm, however, concentrations of heavy metal ions up to 450 ppm in effluents are currently reported [7, 8].

In this context, technologies have been developed for the removal of metals in solution such as: precipitation, oxidation-reduction, ion exchange, filtration, electrochemical treatment, membrane technologies and evaporative recovery. These methods can remove up to 99% of these metals; however, the high cost of installation and maintenance makes their application unfeasible[3, 9].In this order of ideas, bioadsorption is an alternative treatment due to the advantages it presents in comparison with conventional techniques: low cost, high efficiency, minimization of chemical products and biological sludge, no additional nutrients are required, regeneration of biosorbents and possibility of metal recovery [3, 10].

The efficiency of agricultural and agro-industrial adsorbents has been studied and evaluated as an alternative for the adsorption of heavy metals in aqueous solution. Tejada et al., [5], studied the use of yam shell and palm bagasse as Ni (II) bioadsorbents in aqueous solution at a concentration of 100 ppm in batch system, finding that the adsorption process is highly pH dependent, with an optimal value of 6. Obtaining the maximum adsorption capacity of 68.14; 47.93 mg $g^{-1}$ for the yam shell and palm bagasse respectively. Quiñones et al., [11], made adsorption tests of Ni (II) obtaining that the bark of Acacia, with a removal capacity of 294.1 mg $g^{-1}$ has been the bioadsorbent with greater efficiency. Ardila and Carreño [12],studied the use of cocoa cob shell as a nickel bioadsorbent obtaining a removal rate of 88% and concluded that the adsorbent material at this time was not yet saturated.

Cocoa (*Theobroma cacao L.)* is an agricultural product of neotropical origin with a high participation in the international market, from which the seed is economically harvested, which represents 10% of the mass of fresh fruit, wasting shells and pulp, generating the propagation of a fungus of the genus Phytophoraspp, the main cause of economic losses in cocoa activity[13].The present research aimed to evaluate the application of cocoa shells, based on their use as a nickel bioadsorbent in aqueous solution in a fixed bed system.

## 2. Experimental

The following equipment was used to carry out the investigation: blade mill, screening machine, Shaker, pH meter, analytical balance, refrigerator, Oven model IFA-54-8 Escode Brand (400 - 600°C), atomic absorption spectrometer Agilent 5975C.

### 2.1 Bioadsorbent preparation and characterization

The cocoa shell was washed with distilled water to remove impurities until the washing water did not show any colouring. The material was then dried in the kiln at 90 °C for 24 h, then ground and sieved to obtain the selected particle size of 0.5 mm[14].The biomaterial was characterized by atomic adsorption spectroscopy (AAS) to determine the presence of Calcium, Sodium, Potassium, Iron, Copper and Magnesium. Elemental analysis to determine the percentage of Carbon, Hydrogen, Nitrogen percentage, Sulphur content, Ash percentage, Pectin percentage, lignin percentage, cellulose percentage and hemicellulose percentage. FTIR analyses were also performed using a Fourier transform infrared spectrometer to each of the biomasses, before and after the metal removal process to identify the functional groups responsible for adsorption.

### 2.2 Preparation of synthetic wastewater

0.6 g of Nickel Sulphate II ($NiSO_4$) dissolved in 6 L of deionized water was used to prepare the synthetic wastewater, obtaining the desired concentration of 100 ppm. Sodium hydroxide and hydrochloric acid were used for pH adjustment to 6 [5].

### 2.3 Adsorption tests in continuous system

The adsorption tests were carried out in a pilot unit that consists of four columns, with a diameter of 3.5 cm and height of 18.5 cm, equipped with a feeding tank which contains the prepared synthetic water, a submersible pump that feeds the water to the distribution tank where it is kept at a constant level by overflow; then by gravity the water is distributed to the columns and manual flow control. The experimental set-up was carried out by varying the height of the bed (4 cm and 7.5 cm), through which the synthetic water solution passed with a flow rate of 6 mL $min^{-1}$. The first sample was taken to be analyzed in the atomic absorption equipment at 10 min to operate the system, the second at 20 min and the next every half hour until the saturation time of the biomass was completed [15].All tests were performed in duplicate for the reliability of the results, the average value was calculated between the data obtained and with this the percentage of metal removal.

The performance of the column was represented by adjusting the rupture curve, which determines the behaviour of the impregnated metal in the cocoa bed, expressed in terms of initial concentration and time, $C_t/C_o$, as a function of the time or volume of the effluent at a given height, thus generating the respective curve[16, 17].The experimental data from the rupture curve were adjusted to Yoon-Nelson, Thomas and Bohart-Adams models [18].

## 3. Results and discussions

### 3.1 Biomass characterization

Table 1 shows the results of the elemental analysis of cocoa shell, in which the chemical composition of carbon, nitrogen, ash, pectin, lignin, cellulose and hemicellulose was determined by gravimetric methods.

**Table 1.**Elemental analysis of the cocoa shell

| **Parameters** | **Value** | **Analitical method** |
|---|---|---|
| Carbon (%) | 50.35 | AOAC 949.14 |
| Hydrogen (%) | 5.08 | AOAC 949.14 |
| Nitrogen (%) | 1.28 | AOAC 984.13 |
| Sulfur (ppm) | 0.59 | Digestion-Nephelometrics |
| Ash (%) | 7.75 | Thermogravimetry |
| Pectin (%) | 9.54 | Acid Digestion-Thermogravimetry |
| Lignin (%) | 12.66 | Photodorimetry |
| Cellulose(%) | 19.82 | Acid Digestion-Thermogravimetry |
| Hemicellulose (%) | 9.45 | Acid Digestion-Thermogravimetry |

A physicochemical analysis of biomass was performed by the EAA method (atomic adsorption spectroscopy) to determine the chemical components that prevailed in the analyzed sample (See Table 2).

**Table 2.Chemical components in the cocoa shell**

| **Parámetros** | **Valor** | **Método Analítico** |
|---|---|---|
| Calcium, (mg $g^{-1}$) | 11.20 | EAA |
| Sodium, (mg $g^{-1}$)$^{+}$ | 0.50 | EAA |
| Potasium, (mg $g^{-1}$) | 47.00 | EAA |
| Iron, (mg $g^{-1}$) | 0.0014 | EAA |
| Copper, (mg $g^{-1}$)$^{+}$ | 0.008 | EAA |
| Magnesium, (mg $g^{-1}$)$^{+}$ | 2.20 | EAA |
| Cromo, (mg $g^{-1}$)$^{+}$ | 0.0006 | EAA- Graphite furnace |

### 3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The spectra of the FTIR analysis of cocoa shell shown in Fig. 1 were recorded between 4000 $cm^{-1}$ and 400 $cm^{-1}$.

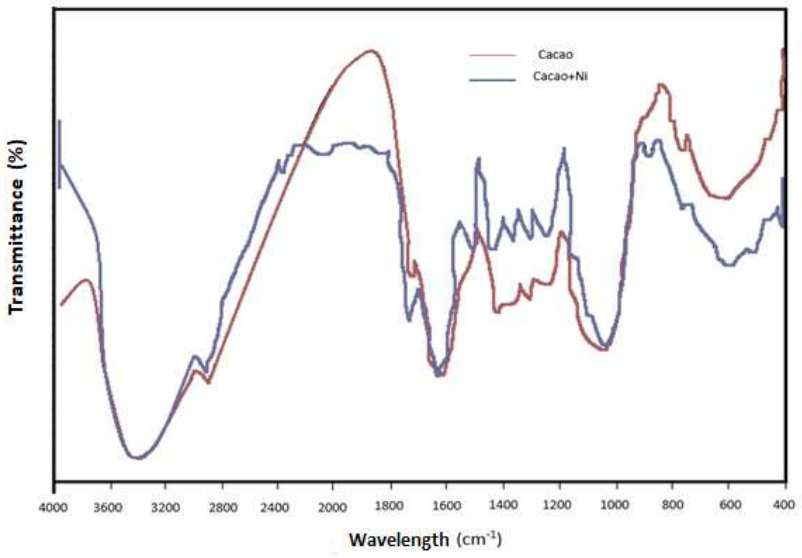



**Figure 1.FTIR of cocoa biomass before and after being used as a Nickel adsorbent (II)**

### 3.3 Effect of bed height on adsorption

The effect of cocoa bed height was evaluated by determining the removal percentage and rupture time of each column for Ni (II) adsorption, as shown in Table 5.

**Table 5.Nickel Removal Results**

| Time (min) | Bed height 5 g (mg $L^{-1}$) | | Bed height 10 g (mg $L^{-1}$) | |
|---|---|---|---|---|
| | Average | Adsorption (%) | Average | Adsorption (%) |
| 10 | 6.873 | 93.127 | 1.133 | 98.867 |
| 30 | 6.057 | 93.943 | 0.984 | 99.016 |
| 60 | 5.504 | 94.496 | 1.310 | 98.690 |
| 90 | 6.921 | 93.079 | 2.107 | 97.893 |
| 120 | 7.977 | 92.023 | 2.766 | 97.234 |
| 150 | 8.609 | 91.391 | 2.914 | 97.086 |
| 180 | 9.649 | 90.351 | 3.904 | 96.096 |
| 210 | 10.676 | 89.324 | 4.275 | 95.725 |
| 240 | 12.430 | 87.570 | 4.494 | 95.506 |
| 270 | 13.294 | 86.706 | 7.440 | 92.560 |

The saturation time was determined from the rupture curves (see Fig. 2).

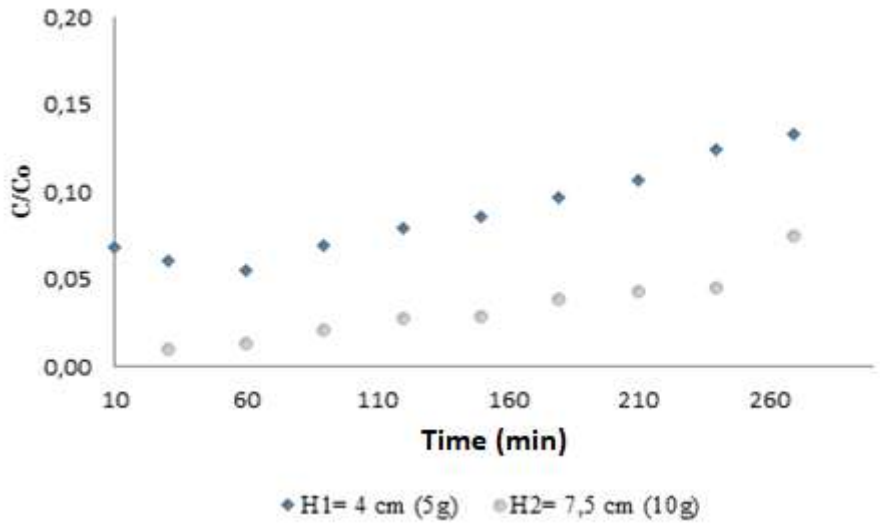



**Figure 2.Rupture curves of Ni adsorption**

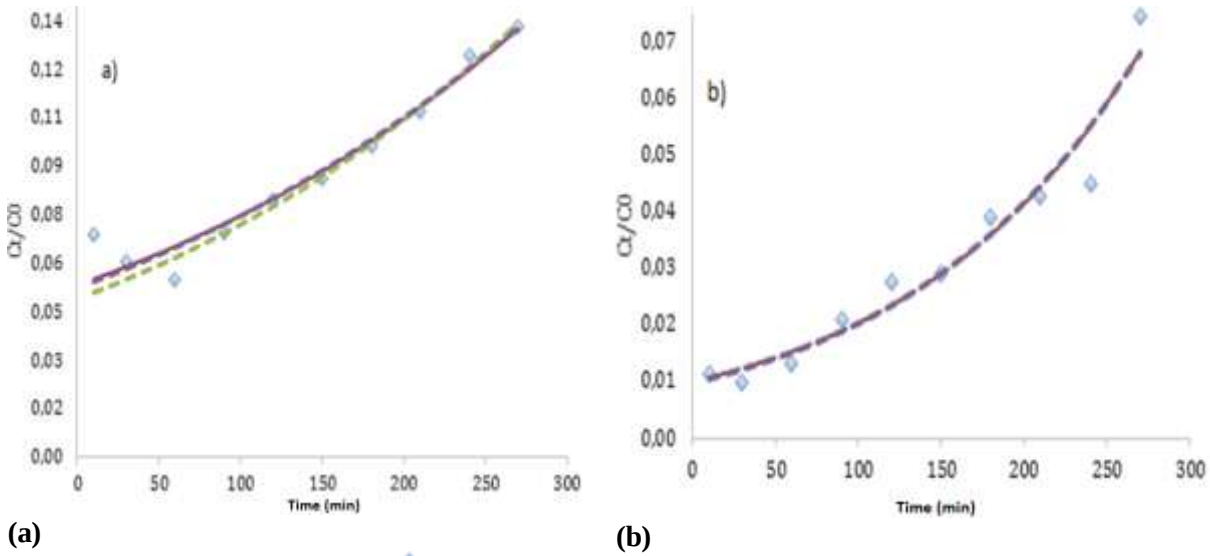
Table 6 shows the parameters of the Ni (II) adsorption rupture curve on cocoa shell, noting that the higher the bed height, the longer the rupture time; this means that more solute per gram of adsorbent is adsorbed.

**Table 6. Rupture curve parameters**

| Z (cm) | x (g) | $T_{rup}$ (min) | $Q_{rup}$ (mg $g^{-1}$) | Maximum removal rate (%) |
|---|---|---|---|---|
| 4 | 5 | 30 | 7.2 | 94.49 |
| 7.5 | 10 | 240 | 14.4 | 99.02 |

### 3.4 Modelling of bed rupture curves

Fig. 3 (a) showed the behaviour of the rupture curve of the 4 cm column treated with nickel and predicted by the models under study for a time of 270 min. In Fig. 3 (b) the behaviour of the 7.5 cm column rupture curve was observed for the same operating time and adsorbate, it can be observed that the models show a low discrepancy with the experimental data of the metal studied. The models were applied by making an adjustment to the rupture curve from its initial part, up to the region of relative concentration $Ct/C_0 = 0.05$ (5%).




**(a)** **(b)**

**Figure 3. Rupture curves of (◇) experimental and predicted data using the (– – –) Thomas, (——) Adams-Bohart and (– – –) Yoon-Nelson model for Ni (II) bioadsorption with an initial concentration of 100 mg/L and Q = 6 mL/min, in figure a) for a height of 4 cm b) height of 7.5 cm**

Based on the data reported in Table 7 it can be said that the considered models (Thomas, Yoon-Nelson and Adams Bohart) satisfactorily adjust the experimental adsorption data of Ni (II) on cocoa shell in continuous system, showing R2 higher than 0.97; however, Thomas's model shows a slightly better fit for milk height of 4cm0 and Adams-Bohart's for 7.5cm.

**Table 7. Adjustment parameters of experimental data to adsorption models**

| **Model** | **Parameters** | **Bed height** | |
|---|---|---|---|
| | | **H= 4cm** | **H= 7.5cm** |
| Adams-Bohart | $K_{AB}$ (L $mg^{-1}min^{-1}$) | 0.0000 | 0.0001 |
| | $N_0$ (mg $L^{-1}$) | 3814.6616 | 1511.4242 |
| | $R^2$ | 0.9739 | 0.9732 |
| Thomas | $K_{TH}$ (mL $mg^{-1}min^{-1}$) | 0.0408 | 0.0740 |
| | $q_0$ (mg $g^{-1}$) | 87.1584 | 37.4335 |
| | $R^2$ | 0.9741 | 0.9727 |
| Yoon Nelson | $K_{YN}$ (mL $mg^{-1}min^{-1}$) | 0.0037 | 0.0075 |
| | t (mg/g) | 773.2823 | 620.4520 |
| | $R^2$ | 0.9728 | 0.9727 |

In table 7 it was observed that for the 4 cm bed height the Thomas Model was the one that best adjusted the experimental data, with a correlation value of $R^2$ = 0.97413089. For the height of 7.5 cm the three models predict the behavior of the experimental data with a decimal difference of the correlation coefficient value. Adams Bohart's model came closest to fitting the data with an $R^2$ = 0.973174182.

The results show that carbon is the element with the highest percentage in biomass with a composition of 50.35%, cellulose, lignin, pectin and hemicellulose content represent a percentage of 19.82%, 12.66%, 9.54% and 9.45% respectively (Table 1), which are mainly responsible for the adsorption of metal ions because they have a large number of hydroxyl and phenolic groups that favour the adsorption of metals[19].Table 3 reports the vibrational energy status and wavelength of the FTIR spectrum of cocoa shell before and after adsorption of Ni (II) ions, which allowed these characteristics to be associated with the different components.

**Tabla 3. FTIR spectrum bands for biomass before continuous adsorption process**

| **Wavewlenght** | **Type of vibration** | **Functional group** |
|---|---|---|
| 422.43, 439.79, 457.15 | Si–O extension | Silica Functional Group |
| 668.36–518.87 | C–X extension | Organohalogenic |
| 780.24, 817.85 | C=C–H deformation | Unsaturated Aliphatics |
| 896.94 | C–H bending | Aromatic |
| 1155.41–1035.82 | C=S extension | Thioester, thioureas, thioamides |
| 1260.54, 1284.65, 1318.40 | C–O–C extension | Ethers (aromatic, olefinic or aliphatic) |
| 1372.41, 1453.43 | H-C-H bending | Methyl, methylene |
| 1543.12–1506.47 | -NOz asymmetric stretching | Nitro- organic compounds |
| 1873.93–1558.55 | C=O extension | Esters, ketones, amides, carboxylic acids and their salts, acid anhydrides |
| 1998.34–1926.97 | C=C | Aromatic hydrocarbons |
| 2026.31, 2165.19, 2196.05 | C≡C | Aliphatic Hydrocarbons: Alkyl, alene, cyanate, isocyanate, nitrile, isocyanides, diazonium azides, salts, ketones, thiocyanates, isothiocyanates. |
| 2374.47–2216.30 | C≡N | Functional group Nitrogen |

| | | |
|---|---|---|
| 2928.07, 2993.65 | C–H extension | Aliphatic Hydrocarbons: Methyl, methylene, methylene groups |
| 3167.25, 3187.51 | C–H extension | Unsaturated: Aromatic and olefin compounds |
| 3952.31–3265.63 | $OH^-$ | Hydroxyl group |

In the analysis of the FTIR spectrum (Figure 1) and Table 3, it is observed that the biomass analysed has a greater presence of: aliphatic, aromatic and unsaturated hydrocarbons with a variable vibrational energy, organic compounds, halogens, methyl, silica and nitrogen and hydroxyl groups. The presence of hydroxyl groups was reported in the region between 3900 $cm^{-1}$ and 3200 $cm^{-1}$, which favors the adsorption of heavy metals, since the groups with negative charge on the surface of the adsorbent are responsible for electrostatic attraction between cations and those groups, the OH- group is also present in activated carbons for commercial use, a product used for the removal of contaminants [20].

When comparing the spectrum of the original biomass with that obtained after the biomass was treated with the nickel solution (Figure 1), it is reported that the functional groups that were maintained after the biomass was used as adsorbent (Table 4). This is because after the biomass was subjected to nickel adsorption, several of the main functional groups in the chain were retained. On the other hand, in the wavelength with values below 600 $cm^{-1}$, a low intensity of the peaks is observed, this is due to the deformation of the carbonyl bonds of the carboxyl functional groups and to the formation of C-O bands[21].

**Table 4. Functional groups present in the biomass treated with Nickel**

| **Wavelenght** | **Type of vibration** | **Functional group** |
|---|---|---|
| 1034.85, 1057.04 | C=S extension | Thioester, thioureas, thioamides |
| 1621.24 | C=O extension | Esters, ketones, amides, carboxylic acids and their salts, acid anhydrides |
| 2928.07 | C–H extension | Aliphatic Hydrocarbons: Methyl, methylene, methylene groups |
| 3998.61-3338.92 | $OH^-$ | Hydroxyl group |

As can be seen in table 5, as the contact time increases, the percentage of removal decreases, this occurs because the fluid with a constant content of adsorbate that feeds the solid bed is initially adsorbed in the lower zone of the adsorbent, therefore the fluid at the exit, does not contain adsorbate in this period. However, by increasing the contact time, adsorbate is bound to the adsorbent in higher and higher areas. This is equivalent to the migration of the mass transfer zone over time. Once the mass transfer zone reaches the highest point of the solid bed, the bed saturation occurs[22].

Fig. 2 shows the bed advance curve of 4 cm and 7.5 cm, which have a rupture time of 60 min and 240 min respectively. It can therefore be considered that the increased height of the packed bed favours the breaking time. The behaviour shown in table 6 allows us to state that the adsorption process is dependent on the height of the packed bed in a proportional way, as the surface area available and the contact time between Ni ions and the cocoa biomass is increased. Therefore the highest bed height is best for adsorption of this metal as reported by Lara *et al.*,[23].

Different models have been used to investigate the mechanism of metal bio-adsorption. The values of $R^2$ higher than 0.97 according to table 6 for the two heights evaluated, indicates a good adjustment of the experimental data to the models of Thomas, Yoon-Nelson and Adams-Bohart which coincides with that reported byLara et al., [23]and Bulgariu and Bulgariu [24] This is validated by observing the graphs in Figure 3 in which the predicted rupture curves and experimental points at different input concentration are shown.

Decreased values of initial adsorption capacity of cocoa shell by increasing bed height for the Thomas model, $q_0$, could indicate that mass transfer was slower, lower concentration and increased adsorption capacity of material due to the increase in adsorption active adsorption sites due to the increased amount of biomaterial, consistent with Yuan et al.,[25].

## 4. Conclusions

Based on the characterization carried out, it was established that the most representative functional group in metallic ion adsorption is the hydroxyl group (OH-) present on the surface of the cocoa shell. Results obtained from adsorption tests showed the effectiveness of cocoa shell as an adsorbent of Ni (II) in aqueous solution, with a maximum removal concentration for bed height of 7.5cm of 99.02%. It was also observed that the bed height has a great influence on the operating time of the column, the best adsorption results and rupture time were obtained in the 7.5 cm high bed compared to the 4 cm bed. Thomas's model was the one that best fitted the experimental data.

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