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Green Nanoparticle-Aided Biosorption of Nickel Ions Using Four Dry Residual Biomasses: A Comparative Study

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Abstract: The green synthesis of titanium dioxide nanoparticles was performed using the sol-gel method for their use in the modification of several agricultural biomasses (orange, lemon, cassava and yam peels) to evaluate the enhancement of adsorption capacity. To this end, different particle sizes (0.355, 0.5 and 1.0 mm) and initial solution pHs (2, 4 and 6) were assessed to identify the optimum conditions for further experimentation with the selected lignocellulosic materials. The defined conditions reporting the highest removal yields were used to perform adsorption experiments for chemically modified biosorbents. The biomaterials were characterized via elemental and bromatological analysis in order to quantify their composition. After the incorporation of TiO₂ nanoparticles, the resulting biosorbents were characterized via FT-IR and SEM techniques. The results revealed that the pH solution significantly affects the nickel ion uptake, reaching the best performance at pH = 6 for all biomasses. Unmodified biomasses shown adsorption capacities between 18–20 mg/g. For chemically modified with TiO₂ orange peels and yam peels biomass, the increase in adsorption capacities was 21.3 and 18.01 mg/g, respectively. For cassava and lemon peels chemically modified, it was found the increasing in adsorption capacities with values of 21.3 and 18.01 mg/g, respectively, which suggested that the incorporation of nanoparticles enhances adsorption capacities.

Keywords: adsorption; heavy metals; biomass; nanoparticles



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1. Introduction

The presence of nickel ions in the environment, as well as other heavy metals such as mercury, cadmium and lead, threatens the biodiversity of flora and fauna since they may generate a series of neurological, physiological and mutagenic disorders [1]. In human beings, exposure to nickel can cause weight loss, anemia, hyperglycemia and heart damage; besides, skin contact or inhalation causes local irritation and asthma pneumoconiosis [2]. Nickel is mainly used in the production of stainless steel and nickel alloys [3]. The contribution of water to total daily intake is unrepresentative. However, the high pollution of water sources may increase the contribution of water to nickel intake. According to the World Health Organization, the maximum allowable limit of nickel in drinking water is 0.07 mg/L [4]. In Colombia, the Ministry of Environment and Sustainable Development regulates the emissions of heavy metal ions into the environment through industrial effluents; for example, the allowed limit concentration of nickel in effluents discharged to superficial water sources is 0.5 mg/L of nickel [5].

Different alternatives have been proposed to face this environmental problem of water pollution due to the presence of nickel ions. In addition to the mechanical treatments of wastewater (sedimentation) or biological materials (active sludge), some physicochemical treatments are used for the removal of these heavy metals. The most common processes

involve precipitation, oxidation-reduction, ion exchange and adsorption [6]. Although effective, such treatment technologies are costly in terms of energy consumption and produce additional discharge streams [7]. Biosorption is the most widely used method for the removal and recovery of heavy metals from liquid effluents owing to the following advantages compared to traditional methods [8]: high capacity to accumulate metal ions efficiently and quickly, high selectivity in relation to specific metals, ability to handle various heavy metals and waste mixtures, and wide operating range under physicochemical conditions such as temperature and pH.

In recent years, the application of several agricultural biomasses and magnetic nanoparticles to adsorb heavy metals is gaining much attention [9]. Biosorption using lignocellulosic residues and agricultural by-products has been identified as a promising alternative to existing technologies for toxic heavy metal ions uptake from aqueous solution. The efficiency of each biosorbent is given by different operating conditions, e.g., temperature, initial metal concentration, biosorbent particle size and its dosage [10]. The chemical modification of lignocellulosic materials may increase the adsorption capacity and enhance thermodynamic and kinetic performance [11,12].

On the other hand, nanotechnology has numerous effective applications in different fields, and its application for wastewater treatment is a fast-developing, fascinating area of interest, the above because at nanoscale, materials show unique characteristics that improve the adsorption capacity of the nanoparticles due of their small size and large surface area [13]. Moreover, nanoparticles show catalytic potential and high reactivity, which make them great adsorbing materials. To obtain better results for the removal of metallic species from wastewater, nanoparticles are becoming new alternatives for the treatment of wastewater [14]. Among them, TiO_2 are one of the most extensively used engineered nanoparticles (ENPs) [15,16], commonly implemented in the adsorption and removal of various metal contaminants, among them Pb [12], Cu [17], Ni [18] and Hg [19]. Hence, nanometric-size metal oxide nanoparticles supported on lignocellulosic material attracts the interest of researchers by their high adsorption rates and high selectivity to heavy metals [20]. Zhao et al. [21] synthesized a nano-biomaterial derived from pine biomass and chemically modified with titanium nanoparticles in order to remove hexavalent and trivalent chromium. They reported an improvement of the adsorption capacity of 1.23 mg/g to 12.8 mg/g for Cr(III) and Cr(VI), respectively. Chen et al. [15] used natural rice straw for the removal of Cu (II) in polluted water systems. This biomass was characterized and pretreated with hydrated TiO_2 . The results showed an increase of adsorption as pH rises from 2.0 to 7.5 with 2 g/L. Ouma et al. [22] used magnetite-pine nanocomposites as an efficient bioadsorbent to remove Cr(VI) ions. The adsorption of heavy metal was both pH- and concentration-dependent, with the highest adsorption percentage occurring at pH 2 and 75 mg/L.

TiO_2 nanoparticles are widely used as a substrate for the adsorption and removal of various metal contaminants; however, in the literature there are few biomass-based adsorbents modified with TiO_2 nanoparticles. In this work, an integral alternative is proposed to remove nickel ions from aqueous solution by implementing biochemical and nanotechnological principles to develop nano-biomaterials based on residual biomass typical of the Colombian Caribbean region, such as the orange peels, lemon, cassava and yam modified with titanium dioxide nanoparticles. It is reported that these biomasses could reach higher levels of metal ion uptake with the incorporation of functional groups in their molecular structure through nanomaterials such as nanoparticles [17].

2. Materials and Methods

2.1. Biomass Preparation

The biomasses biomasses (orange peels (OP); lemon peels (LP); yam peels (YP); cassava peels (CP)) were collected from food markets located in North-Colombia and washed with water to remove impurities that may interfere with the adsorption process. These lignocellulosic materials were subjected to drying at 70 °C; grounded; and mesh-sieved

to reduce particle size to 0.355, 0.5 and 1 mm [23]. For the classification of biomaterial sizes, mesh numbers 45, 35 and 18 were used, which select size ranges of 0.3–0.355 mm, 0.425–0.5 mm and 1.0–1.18 mm, respectively.

2.2. Modification with TiO₂ Nanoparticles

The titanium dioxide (TiO₂) nanoparticles were synthesized via green chemistry following the sol-gel methodology proposed by Herrera-Barros et al. [24]. The reduction of titanium isopropoxide was performed using lemon leaf extract, which was obtained by mixing 100 g leaves with 500 mL of water. Then, 85 mL of precursor at 5 mM was mixed with 15 mL of lemon leaf extract under continuous stirring at 175 rpm. After forming the nanoparticles, centrifugation was conducted at 5000 rpm to separate the desired products from the remaining solution. The nanoparticles were washed thoroughly with water and ethanol and dried in an oven at 550 °C for 3 h. For biomass modification, 3 mL of tetraethyl-ortho-silicate (TEOS) was added after mixing biomass with dissolvent at 8000 rpm and 2 h. The resulting mixture was kept under continuous stirring at 100 rpm and 3 h. The biomasses were subjected to centrifugation and mixed with 0.3 g of TiO₂ nanoparticles. The chemically modified materials were centrifuged, washed with ethanol and finally dried. Modification mechanism followed Equation (1).



2.3. Characterization Techniques

The agricultural residues were characterized by elemental and compositional analysis to quantify the composition of carbon, hydrogen, lignin, pectin, cellulose and hemicellulose by using the analytical methods shown in Table 1; all the experiments were made in triplicate. The chemically modified biomasses (CM-OP, CM-LP, CM-YP, CM-CP) were characterized via Fourier-Transform Infrared Spectroscopy (FT-IR) to identify the functional groups most contributing to the adsorption of heavy metal ions [18]. The Scanning Electron Microscopy (SEM) was also conducted to study the morphology of the resulting biosorbents.

Table 1. Analytical methods for chemical characterization of biomasses.

Parameter	Method	Description
Carbon (%)	AOAC 972.43	A Thermo Scientific FLASH 2000 Analyzer, Organic Elemental Analyzer was used; 5 g of the sample was burnt in excess of oxygen, and the carbon and hydrogen present in it were oxidized to carbon dioxide and water. For this, the sample was dropped into a combustion tube containing chromium (III) oxide and silvered cobaltous/cobaltic oxide catalysts. An aliquot of purified oxygen was added to the quartz tube, generating a flash combustion reaction and increasing the reaction temperature from 1020 °C to 1800–2000 °C.
Hydrogen (%)	AOAC 972.43	
Nitrogen (%)	AOAC 984.13 KJELDAHL	Two grams of the sample with particle size <1 mm was placed into a digestion flask along with 40 mL of sulphuric acid at 98%, adding 7 g of potassium sulfate and copper. The mixture was heated at 370 °C during 180 min until white fumes could be seen, continuing the heating for about 60–90 min. The digestion is finished when the sample will be totally transparent with a slightly blue color due to the Cu from the catalyst. The tube flask was cooled at room temperature, and 250 mL of water was added cautiously. During the distillation, 50 mL of sodium hydroxide 50% w/w solution was added to the sample to neutralize the pH and to convert NH ₄₊ into NH ₃ ; NH ₃ was captured in a 50 mL of boric acid solution 4% that contains 6–7 drops of Tashiro's indicator, and the solution turns from red violet to green (pH 4.4–5.8) due to the color change of the indicator from acid to basic medium. Then, the solution was titrated with HCl 0.25 mol/L until the solution had a slightly violet color.
Ashes (%)	Thermogravimetry	Five grams of dry material (M ₁) was placed at 700 °C and left for 1 h to determine the ash content (M ₄). The percentage of ash was determined using the following equation: $\%Ashes = \left(\frac{M_4}{M_1} \right) \times 100 \quad (2)$

Table 1. Cont.

Parameter	Method	Description
Pectin (%)	Digestion-thermogravimetry	Ten grams of sample was degraded with a mixture of nitric acid and acetic acid and boiled at 80 °C for 30 min in an apparatus that contained a condenser. The solution was then filtered through a funnel. Then the filter paper containing an insoluble residue was dried in the oven and measured for determining the cellulose content. The extraction process of pectin was carried out under reflux using acidified water at 97 °C for 30 min. The hot acid extract was then filtered using a cheese cloth to remove the pulp. The filtrate was then cooled to 4 °C and precipitated using double the volume of ethanol. The solvent precipitate mixture was then mixed until the pectin floated and removed by using cheese cloth followed by drying.
Cellulose (%)	Digestion-thermogravimetry	Separation of hemicelluloses was performed using a two-stage separation process based on a prehydrolysis step with a weak acid dilution (H ₂ SO ₄ ⁺ water) where the hemicellulose was dissolved in water, followed by an organosolv process with ethanol.
Hemicellulose (%)	Digestion-thermogravimetry	
Lignin (%)	Photocalorimetry	Five grams of biomass oven-dry mass was placed into a flask, where a potassium hydroxide 0.2% water solution of 2,3,5-triphenyltetrazolium chloride was added. The flask was heated in a water bath (during this time the sample obtains red color) and cooled afterwards. Then, the sample was filtered and washed with ethanol unless formed dye transferred to the solution

Adapted from: [25–27].

2.4. Adsorption Study

Stock solutions of nickel sulfate (NiSO₄) were prepared at 100 ppm according to the methodology suggested by Moreno-Sader et al. [28]. Initial solution pH was adjusted to 1, 4 and 6 using solutions of NaOH and HCl. Then, 0.5 g of biomass was kept in contact with nickel solution for 2 h, room temperature and 150 rpm. The samples were centrifuged, and the remaining concentration of heavy metal ions was measured using an atomic absorption technique. The removal yield of nickel ions was calculated by Equation (3) and the adsorption capacity by Equation (4):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (4)$$

where C_0 (mg/L) is the initial concentration of heavy metal ions, C_e (mg/L) the remaining concentration, m the adsorbent amount (g) and V is the sample volume (L) [24].

3. Results and Discussion

3.1. Biomass Characterization

Table 2 shows the elemental analysis of agricultural biomasses studied in this work. The highest carbon content was observed for orange peels, followed by yam peels and lemon peels. The hydrogen and nitrogen compositions were low for all lignocellulosic materials. Similar results are available in open literature for the same biomasses. Pathaket al. [29] reported an elemental composition of lemon peels with C (wt.%) 39.61, H (%) 5.96 and N (%) 1.27. For the orange peel biomass, Wan et al. [30] quantified the composition in 42.2, H (wt.%) 5.3 and N (wt.%) 2.98. For yam peels, Asuquo et al. [31] reported the following composition as C (wt.%) 41.5, H (wt.%) 6.26 and N (wt.%) 0.82.

Table 2. Elemental analysis of raw biomasses.

Biomass	Carbon (%)	Hydrogen (%)	Nitrogen (%)
OP	44.43 ± 0.39	6.21 ± 0.18	0.81 ± 0.03
LP	38.48 ± 0.28	4.98 ± 0.09	1.21 ± 0.06
YP	48.14 ± 0.47	5.44 ± 0.12	0.18 ± 0.05
CP	39.96 ± 0.36	3.98 ± 0.08	0.26 ± 0.03
OP	44.43 ± 0.93	6.21 ± 1.05	0.81 ± 0.02

As shown in Table 3, the lignin content varied significantly among the biomasses showing highest composition for yam peels (27%). The cellulose biopolymer reached values within 13–18.5%, while hemicellulose varied in the range 6.0–7.0%. These results were compared with those found in the literature for the same biomasses. For example, Ibeto et al. [32] reported that the composition of yam peels reaches values of lignin, cellulose and hemicellulose of 6.70%, 39.90% and 29.76%, respectively. Damma et al. [33] quantified the presence of biopolymers in lemon peels and obtained the following results: cellulose (23.1%), pectin (13%), hemicellulose (8.09) and lignin (7.6%). Cellulose, hemicelluloses and lignin have a wide variety of active functional groups as aromatics, phenolic hydroxyl and alcoholic hydroxyl, carbonyl, methoxy, carboxyl, amino, conjugated double bond among others, which can act as adsorption sites for heavy metals [34]. Hence, active functional groups, can be used as union points for chemical modifications, allowing the incorporation of more sites that improve the affinity of the biosorbents and adsorption capacity [35].

Table 3. Compositional analysis of evaluated agricultural biomasses.

Biomass	Pectin	Cellulose	Ashes	Lignin	Hemicellulose
OP	18.15 ± 0.06	18.49 ± 0.05	2.08 ± 0.03	7.22 ± 0.15	7.02 ± 0.23
LP	5.41 ± 0.01	14.28 ± 0.07	3.68 ± 0.06	7.14 ± 0.11	6.07 ± 0.18
YP	10.98 ± 0.01	13.08 ± 0.04	4.85 ± 0.08	27.73 ± 0.07	6.47 ± 0.28
CP	2.84 ± 0.04	18.47 ± 0.06	1.58 ± 0.04	2.2 ± 0.15	6.01 ± 0.19

The FT-IR spectra of orange peels chemically modified with TiO₂ nanoparticles (Figure 1a) exhibited characteristic peaks of lignocellulosic materials. The peaks around 602.0 and 1300 cm⁻¹ were attributed to stretching vibrations of C≡C and C-CH₃, respectively. The carbonyl and hydroxyl functional groups were identified around 1700 and 3300 cm⁻¹, respectively. The incorporation of carbon dioxide nanoparticles was confirmed by the presence of Ti-O-C around 1040–1500 cm⁻¹, as well as Ti-COOH around 3600 cm⁻¹.

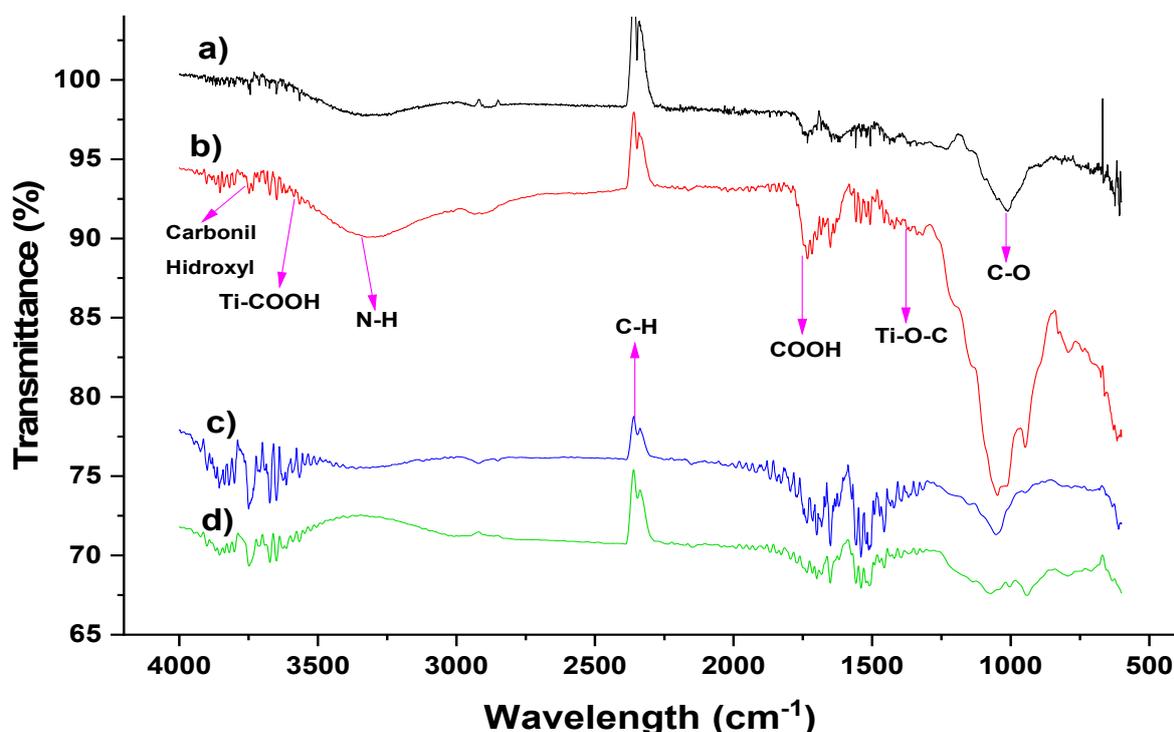


Figure 1. FT-IR spectra of: (a) CM-OP, (b) CM-LP, (c) CM-YP and (d) CM-CP.

The spectra of lemon peels chemically modified (Figure 1b) showed a carbonyl functional group around peaks at $1600\text{--}1700\text{ cm}^{-1}$. The presence of amine and ester was confirmed by the absorption bands at 3200 and 1730 cm^{-1} , respectively. The stretching vibrations of Ti-O-C were observed at 1047 and 1500 cm^{-1} . The spectra of CM-YP (Figure 1c) show absorption bands around $1600\text{--}1700\text{ cm}^{-1}$ attributed to -NH_2 and -COOH functional groups that are characteristic of this biomass. The presence of nanoparticles was confirmed by stretching vibrations of Ti-OH and Ti-O-Ti around $1400\text{--}1600\text{ cm}^{-1}$. The functional groups of Ti-O and Ti-O-C were observed around 800 and 1050 cm^{-1} , respectively [13]. The cassava peels biomass chemically modified with nanoparticles exhibited peaks around $2900\text{--}3300\text{ cm}^{-1}$, corresponding to the amine functional group. The carbonyl, hydroxyl and amide groups were also observed in the spectra at 1100 , 1090 and 1500 cm^{-1} , respectively. The metal carboxylated complexes (R-COO-Ti) formed by interactions between TiO_2 nanoparticles and biomass were identified around 1300 cm^{-1} [36].

Figure 2 shows the scanning electron microscopy (SEM) images of the four raw adsorbents under study. OP, YP and CP have a irregular and porous surface, which allows a large interface for heterogeneous biosorption, while LP has smoother surface, which presents a certain porosity in its structure that is typical of lignocellulosic materials [37]. Similar structural and morphological features were observed in other biosorbents, which played a key role in retaining metal ions [37,38]. At large, the presence of the observed cages and surface cracks can have a positive impact on the removal efficiency by providing pathways towards the reactive adsorption sites and helping the mass transfer phenomena within the body of the material [39].

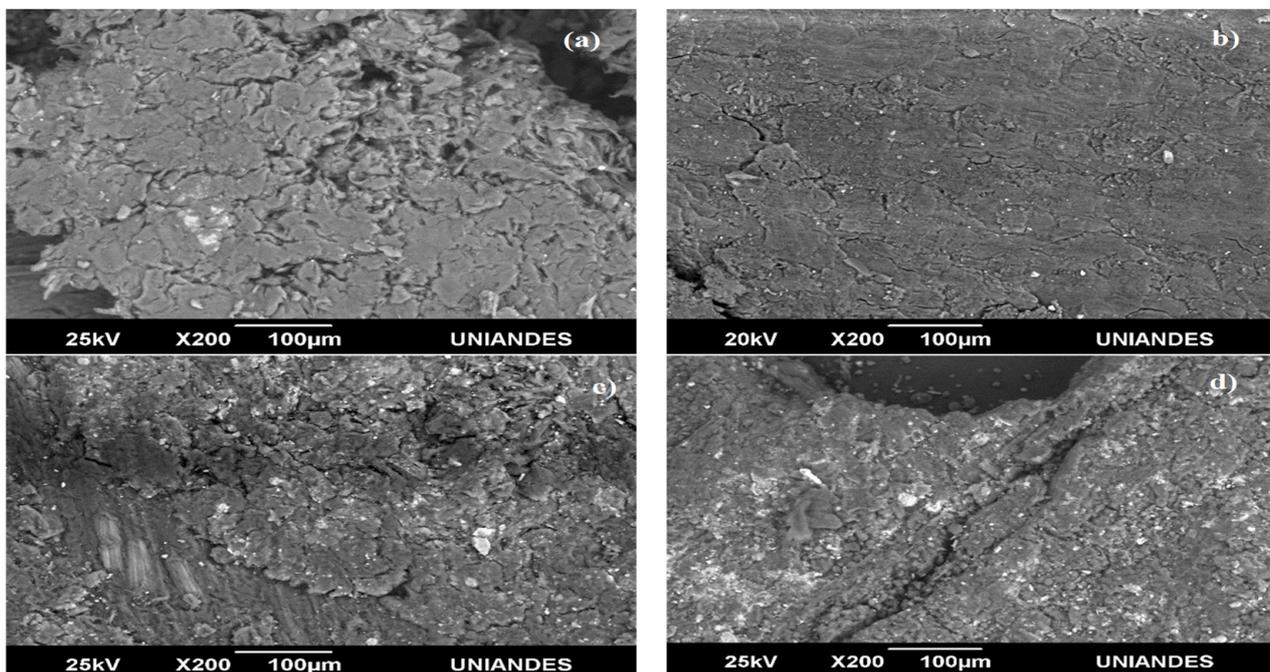


Figure 2. SEM micrograph of: (a) OP, (b) LP, (c) YP, (d) CP.

Figure 3 depicts the micrographs of the chemically modified biomasses obtained by SEM analysis, in which the incorporation of nanoparticles varied the morphology of lignocellulosic materials by the presence of agglomerates onto biomass surface against the raw materials shown in Figure 4 [6]. For all agricultural wastes modified with TiO_2 nanoparticles, it was observed a porous surface that may enhance the adsorption of heavy metal ions owing to the increased surface. It was previously reported that synthesized TiO_2 nanoparticles present a crystallinity of $19 \pm 4\text{ nm}$ with the presence of an anatase phase of 80% and rutile phase of 20% [40]. The diameter of the analyzed samples was calculated by Image J processing software (IJ 1.46) from the SEM images shown in Figure 4.

The measurement was made in triplicate to certify the reproducibility of the obtained data, showing an average particle size of 19.03 ± 1.7 nm. This findings are very similar to the results obtained from XRD, with an average particle size of 19.13 ± 4.1 nm for the synthesized TiO_2 nanoparticles [24].

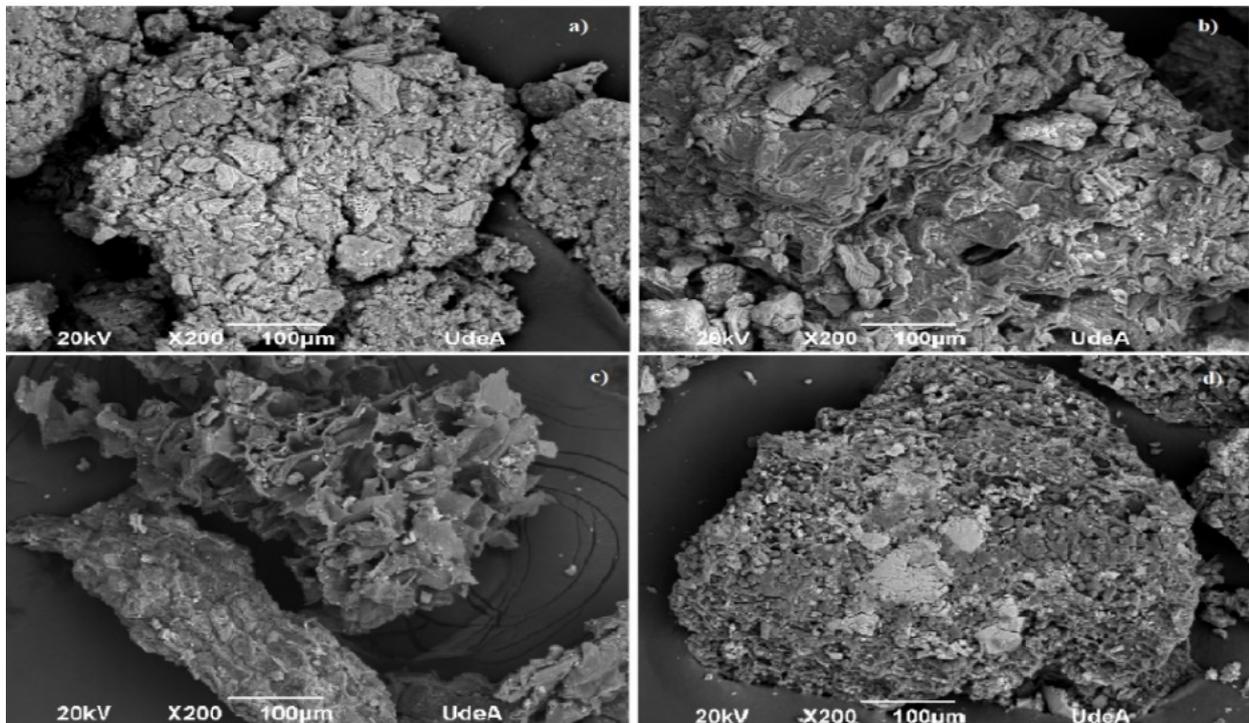


Figure 3. SEM micrograph of: (a) CM-OP, (b) CM-LP, (c) CM-YP and (d) CM-CP.

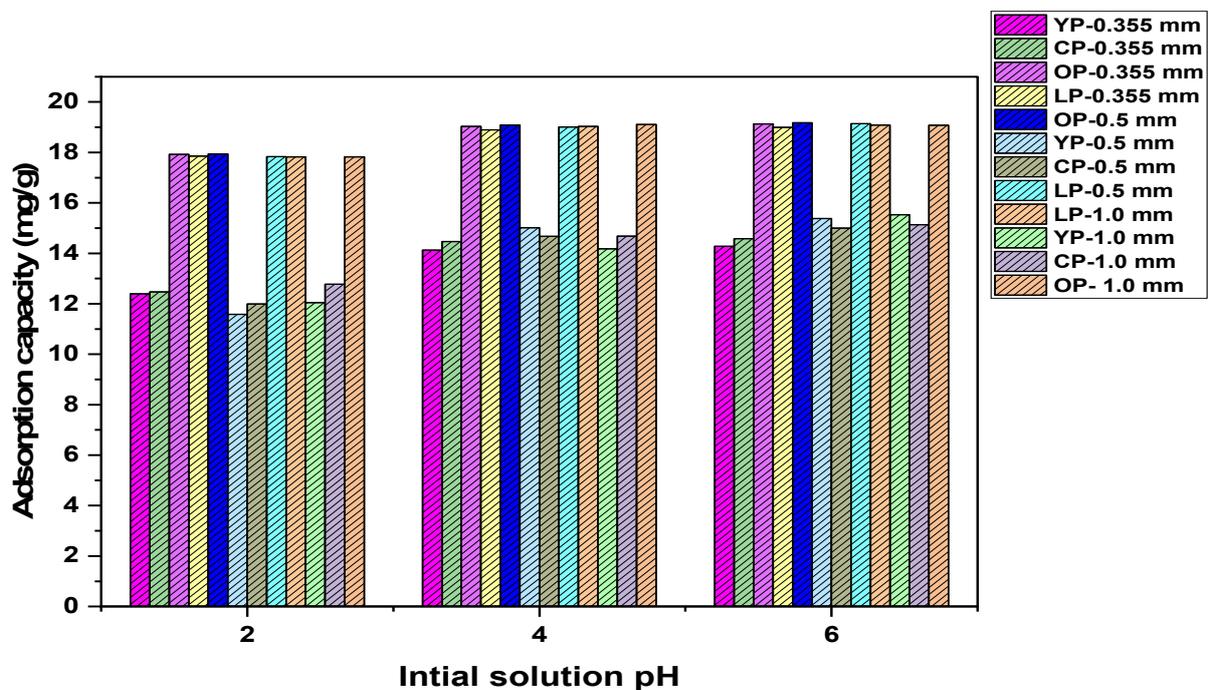


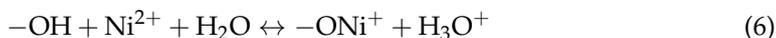
Figure 4. Effect of initial pH on adsorption performance for raw biomass at 0.355, 0.5 and 1 mm of particle size, 100 mg/L of initial concentration, 5 g/L of adsorbent dose and 24 h of contact time.

3.2. Adsorption Study

The adsorption study was conducted to analyze the effect of the solution pH and particle size on the removal of nickel ions from aqueous solution using different agricultural biomasses. The optimum operating conditions were selected to evaluate the performance of chemically modified materials. Figure 4 depicts the influence of the initial solution pH using particles sized 0.355, 0.5 and 1 mm. The adsorption capacities varied in the range 12–20 mg/g. However, for all biomasses, the highest removal yields were reached at pH = 6. Orange peels reported the best performance on nickel ion uptake followed by lemon peels at a pH above 4, while for pH = 2, yam peels and cassava peels reached the optimum results. To remove nickel ions from aqueous solution, 0.355 mm OP biomass at pH = 6 achieved the highest results of 78.23%. This can be explained because the increase in pH gives an increase in the OH concentration on the surface of the biomass, which also increases the adsorption of metallic ions.

When the particle size of biosorbent changed to 0.5 mm, the results varied between 18–20 mg/g, and OP biomass reported a similar performance to LP biomass at pH = 6. For pH = 4, there is a slight increase in adsorption results for OP. Despite the non-significant differences, the optimum removal yield increased by 1.3% when varying the particle size from 0.355 mm to 0.58 mm. When using a particle size of 1 mm, the adsorption performance was similar for both pH = 4 and pH = 6. The highest removal yield was reached by OP biomass at pH = 4, followed by YP biomass at pH = 6. In general, the adsorption results varied from 43.63% to 77.69%, which are lower than those obtained when considering a particle size of 0.5 and 0.355 mm.

The pH of the solution also plays a vital role in the speciation of nickel, determining its presence in different forms based on reactions with surface acidic functional groups while pH varies, as is described in Equations (5) and (6) [41]:



In order to evaluate the individual interaction and the quadratic effects of the variables that influence the Ni(II) removal efficiency, an analysis of variance (ANOVA) was performed. An R² adjusted for degrees of freedom (LG) of 99% was obtained for orange peel, 95% for lemon peel, 93% for yam peel and 83% for cassava peel. F-factor values are shown in Table 2 for percent Ni(II) removals. A confidence level of 95% was established for the *p*-Value, so variables with a *p*-Value less than 0.05 were considered significant [42]. From the variance analysis of Table 4, it can be established that the variable with a significant statistical influence on the Ni(II) removal process using the four biomasses was the pH.

Table 4. Analysis of variance (ANOVA) for nickel removal efficiency on cassava and lemon peels.

Parameter	OP			LP			YP			CP		
	Sum of Squares	Factor-F	Value- <i>p</i>	Sum of Squares	Factor-F	Value- <i>p</i>	Sum of Squares	Factor-F	Value- <i>p</i>	Sum of Squares	Factor-F	Value- <i>p</i>
A: pH	4117.41	3701.25	0.00	2.10	10.86	0.05	357.34	36.20	0.009	110.34	9.43	0.05
B: Particle size	2.12	1.90	0.18	0.070	0.36	0.59	3.86	0.39	0.58	0.07	0.01	0.94
AA	1195.35	1074.54	0.00	2.24	11.58	0.04	40.98	4.15	0.13	10.02	0.86	0.42
AB	0.79	0.71	0.41	0.00	0.01	0.92	8.11	0.82	0.43	0.12	0.01	0.23
BB	5.31	4.77	0.04	1.25	6.48	0.08	4.73	0.48	0.54	19.26	1.65	0.29
Error total	21.14	0.06	0.95	0.58			29.61			35.11		
Total (corr.)	5509.17			6.25			435.83			174.91		

Based on the adsorption performance of the lignocellulosic materials, the optimum conditions were identified and summarized in Table 5.

Table 5. Optimum conditions for the selected biomasses.

Biomass	Optimum Initial Solution pH	Optimum Particle Size (mm)	Removal Yield (%)
OP	6	0.5	79
LP	6	0.5	79
YP	6	1	78
CP	6	1	76

The effect of incorporating the TiO₂ nanoparticle on the biopolymer matrix of the biosorbents was assessed at the defined conditions shown in Table 1. The adsorption results for modified materials are depicted in Figure 5. The biosorbent performance was increased for the cassava peel and lemon peel biomasses chemically modified with TiO₂ nanoparticles to 17.3 and 20 mg/g, respectively. For the chemically modified orange peels and yam peels biomasses, the increase in adsorption capacity was 21.3 and 18.01, respectively. The superior performance of the orange peel, with respect to the other biomasses evaluated, can be explained because of the higher presence of cellulose in its structure, which would increase the amount of active adsorption centers and binding points for the successful modification with TiO₂ [14].

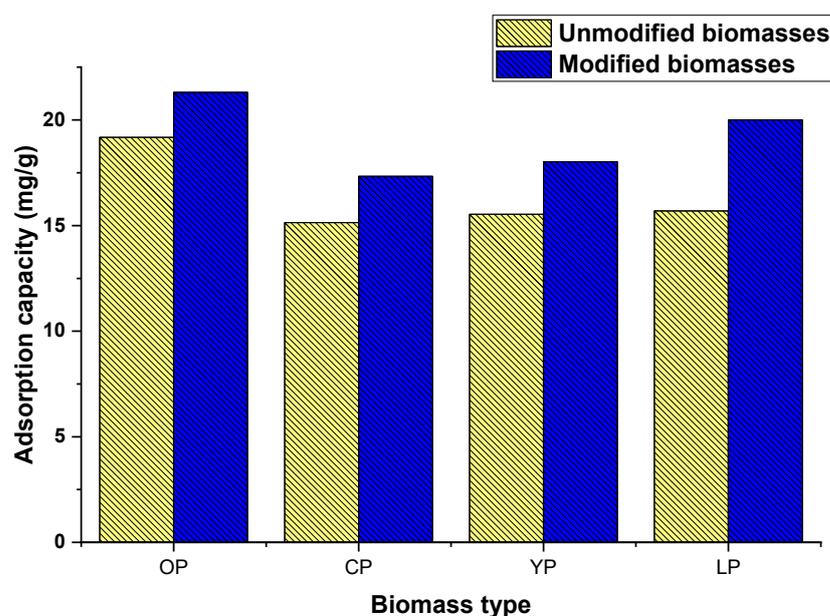
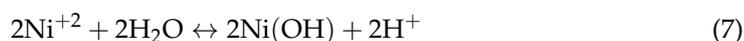


Figure 5. Comparison of the influence of modifications with TiO₂ nanoparticles on adsorption capacities onto OP, CP, YP and LP at pH 6, 100 mg/L of initial concentration, 5 g/L of adsorbent dose and 24 h of contact time.

Apart from the surface properties of the adsorbent and the environment of the aqueous solution, the most relevant studies of the retention mechanisms do not consider the existing ionic form of heavy metals, which includes complex cations, free cations, free oxyanions [43] or the formation of interphase precipitates as insoluble hydroxides or oxides, which is one of the most important aspects affecting the elimination mechanism. It is well known that trace level adsorption (ion exchange) is often completely different compared to macro-level processes. Therefore, a deep exploration of the key control parameters and retention mechanism in more dilute systems could be favorable for developing accurate sorption models that can effectively predict the transport and fate of heavy metal ions and gain a better understanding of the sorption process. The adsorption potential of lignocellulosic adsorbents is postulated mainly due to the chelating behavior of the amino groups present on their surface [44].

Likewise, the presence of titanium dioxide nanoparticles on its surface represents a mechanism related to the site-binding theory, taking into account that heavy metal ions hydrolyze in an aqueous medium and the negative surface charge of TiO₂ nanoparticles promotes the electrolytic ion adsorption of metal cations on metal oxide nanomaterials by electrostatic attraction [16], as described in Equations (7)–(9).



The negative surface charge of the TiO₂ nanoparticles during the proton exchange reaction in an aqueous medium allows the formation of the (TiO[−])₂Ni⁺² species, increasing the adsorption capacity of the treated biomasses.

Table 6 shows the adsorption capacities data reported for removing Ni(II) with adsorbents of a different nature modified with TiO₂ nanoparticles. The results obtained in the present study were in the low range for bioadsorbents modified with TiO₂; nevertheless, the method used to produce the biomasses modified with TiO₂ is simple and unexpensive, compared with the synthesis of the biocomposites.

Table 6. Adsorption capacities of Ni(II) using various adsorbents modified with TiO₂.

Contaminant	Adsorbent	Experimental Conditions	q _{max} (mg/g)	References
Ni(II)	Hybrid biocomposite based on amino-thiocarbamate derivative of alginate/carboxymethyl chitosan/TiO ₂	pH 6, 25 °C, 30 % TiO ₂ /TSC-CMC mass ratio, 750 rpm, 5 h, 6 g/L of adsorbent, 100 mg/L	91	[45]
	TiO ₂ nanofibers	pH 6, 100 mg of adsorbent, 25 °C, 28 min of contact time, 1000 mg/L and 100 mL of solution	80	[46]
	Alginate-chitosan-TiO ₂ composites	pH 6, 25 mL of solution, 180 mg of adsorbent, 3 h of contact time, 100 mg/L	76	[47]
	Orange peels modified with TiO ₂		21.3	
	Lemon peels modified with TiO ₂	pH 6, 100 mg/L, 5 g/L of adsorbent dose, 0.5 mm of particle size and 24 h of contact time	20	This study
	Yam peels modified with TiO ₂		18.01	
	Cassava peels modified with TiO ₂		17.33	
	Polyacrylonitrile-TiO ₂ nanofiber	pH 6, 0.05 g of adsorbent., 50 mL of solution, 25 °C, 100 mg/L	11	[48]
	TiO ₂ NPs modified with humic acid		20	
	TiO ₂ NPs modified with extractant of Walnut shell	25 mL of solution, 25 mg of adsorbent, pH 8, 50 mg/L, 22 h of contact time	18.5	[49]
TiO ₂ NPs modified with 1, 5 diphenyl-Carbazon		10.5		

4. Conclusions

The aim of this work was to analyze the effect of incorporating titanium dioxide nanoparticles into biomasses (orange, lemon, cassava and yam peels) on the removal of nickel ions. From the characterization it was found that the raw biomasses under study

have a high content of carbon and hydrogen, with an irregular and porous surface. After modification with TiO₂ nanoparticles, it was evidenced the presence of titanium at 1047 and 1507 cm⁻¹, proving the success of the modification process. Results revealed that the pH solution significantly affected the nickel ions uptake reaching the best performance at pH = 6 for all biomasses. Unmodified biomasses shown adsorption capacities between 18–20 mg/g. For chemically modified with TiO₂ orange peels and yam peels biomass, the increase in adsorption capacities was 21.3 and 18.01 mg/g, respectively. For cassava and lemon peels chemically modified, it was found the increasing in adsorption capacities with values of 21.3 and 18.01 mg/g, respectively, which suggested that the incorporation of nanoparticles enhances adsorption capacities.

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