

CHARACTERIZATION AND USE OF AGROINDUSTRIAL BY-PRODUCTS IN THE REMOVAL OF METAL IONS IN AQUEOUS SOLUTION

Tejada-Tovar Candelaria^a, Villabona-Ortiz Angel^a, Ruiz-Paternina Erika^a, Herrera-Barros Adriana^b, Ortega-Toro Rodrigo^{c*}

^aDepartment of Engineering, Chemical Engineering Program, Process Design and Biomass Utilization Research Group (IDAB), University of Cartagena, 130015, Cartagena, Colombia

^bDepartment of Engineering, Chemical Engineering Program, Nanomaterials and Computer Aided Process Engineering Research Group (NIPAC), University of Cartagena, 130015, Cartagena, Colombia

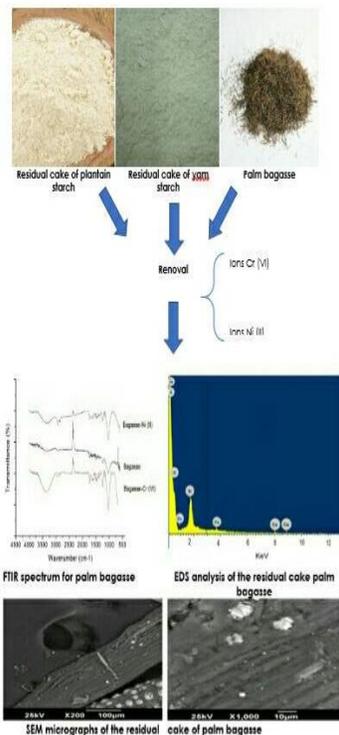
^cDepartment of Engineering, Food Engineering Program, Food Packaging and Shelf Life Research Group (FP&SL), University of Cartagena, 130015, Cartagena, Colombia

Article history

Received
27 February 2019
Received in revised form
16 August 2019
Accepted
22 August 2019
Published online
24 October 2019

*Corresponding author
rortegap1@unicartagena.edu.co

Graphical abstract



Abstract

Contamination of surface waters with heavy metals causes concern due to their toxicity, resistance to degradation and adverse effects on human health and aquatic biota. On the other hand, the search for uses and applications of agroindustrial waste has become a priority in the environmental agenda, due to the large volumes generated. Thus, adsorption is presented as an alternative to using these wastes in the treatment of water contaminated with metal ions. The objective of this work was the study of the use and characterisation of adsorbents of an agroindustrial source (palm bagasse) and by-products of the process of obtaining starch (yam and plantain), for its use in the removal of Cr (VI) and Ni (II) ions in a batch system. The adsorption tests were carried out at an initial concentration of 100 ppm ions at 200 rpm using 1 g of material in 100 mL of solution. The adsorbents were characterised by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, micro-elemental analysis, physicochemical analysis and surface area measurement by Brunauer-Emmett-Teller analysis. From the results, it is established that the palm bagasse has a pore volume twice higher than the other biomaterials. It was determined by the adsorption results, for Cr (VI), were superior in all materials to those obtained for Ni (II). The three agroindustrial residues studied presented high percentages of adsorption efficiency, above 70%, with palm bagasse standing out with an adsorption efficiency of 92%. Therefore, the use of these three biomasses is recommended to treat water contaminated with Cr (VI).

Keywords: Agroindustrial by-products, surface area, chromium (IV), nickel (II), bio-adsorbent

© 2019 Penerbit UTM Press. All rights reserved

1.0 INTRODUCTION

Water is a natural resource of great importance for living beings. The humans perform daily activities that require the constant use of this resource. The cities, industry and agriculture are the most consumers [1]. However, within the industrial sector, some companies discharge untreated wastewater into open water sources, reducing its quality, due to their pollutants, among which the heavy metals come out, the Ni and Cr cations, characterized by having a molecular weight greater than 23, damaging plant and animal life and compromising human life itself because of their toxicity to biota, due to the fact that they are not degraded [2, 3, 4].

A number of technologies for the removal of inorganic and organic contaminants from aqueous solutions have been developed over the years, including adsorption [5], process by which matter is extracted from one phase and concentrated on the surface of another. The substance that is concentrated on the surface is called "adsorbate" and the phase on which the "adsorbent" process takes place; in this process there must be affinity of the adsorbent for the adsorbates, in order for the latter to be transported to the solid, where they will be retained [6].

Thus, the adsorption technique has been highly used for the removal of contaminants such as heavy metals. Although the presence of these does not cause immediate danger in the population, it can lead to a sustained, irreversible or broader damage to the environment [7]. Various residual biomass have been used in the removal of Chromium and Nickel, such as: cane bagasse [8], seaweed *Sargassum* sp., *Padina* sp., *Ulva* sp., and *Gracillaria* sp. [9], *Caryota urens* [10], peanut shells [11], bean shells [12, 13], bilingual seeds [14], *Fumaria indica* [15], rice husk [16], coconut flour copra [17], lotus seeds [18], among others, due to its availability and low cost. The physical and chemical characteristics of the adsorbents used in this process are considered essential.

In Colombia, state policies support the expansion of agribusiness, and the development of more processing plants using plantain, yam starch, among others, appear to be an attractive alternative. The purpose of this investigation was to look for potential use to the residual by-product of the starch extraction process. On the other hand, plants installed and that are producing African palm oil are generating large volumes of waste, for which studies are being conducted that seek the use of the residual fibre of this plant. Thus, the aim of this work was the use of by-products from the process of obtaining yam and plantain starch, as well as palm bagasse as Cr (VI) and Ni (II) adsorbents in a batch system. The adsorbents are characterised by FTIR, SEM, EDS, BET and physicochemical analysis.

2.0 METHODOLOGY

2.1 Preparation of Biomaterials

The Yam and plantain were collected in the rural area of the department of Bolivar (Colombia), geographic coordinates 10°24'N 75°30'O. The materials were washed, peeled and grated. A 0.25% NaOH solution was added to the grated material obtained from each material and placed at 5°C for 18 hours, then they were liquefied and filtered by separating the starch from the residual cake of said process. The pH was adjusted to 7 with 2M HCl, to be removed by a new filtration. These materials were dried in an oven at 313.15 K for 14400 s and exposed to solar radiation for 8 hours to complete their drying [19]. The bagasse was obtained as a product of rejection of the process of extraction of palm oil in an extracting plant of the Department of Bolivar (Colombia), it was subjected to three washes to remove the largest amount of oil retained in the fibre and then dried. The classification of the particle sizes for all biomasses was made through sieves of 0.001 and 0.0005 m. This work was done during the year 2018.

2.1 Characterization Techniques and Adsorption Tests

The materials were characterized by three types of analysis: Fourier Transform Infrared Spectroscopy (FTIR) was carried out to identify the functional groups in the bio-adsorbents. Scanning Electron Microscopy (SEM) was performed on a JEOL JSM-6490 LV Microscope to identify the elemental composition of these samples. The TAPPI T 222 om-83, TAPPI T 203 os-74 chemical composition analyses were also carried out to determine lignin, cellulose and hemicellulose respectively. Also, the Brunauer-Emmett-Teller (BET) analysis was done to know the physical characteristics of the adsorbents. For the adsorption tests, standard solutions of Cr (VI) and Ni (II) were prepared at 1000 ppm each. For Cr (VI), potassium dichromate ($K_2Cr_2O_7$) was used as the base reagent, for Ni (II) nickel sulfate ($NiSO_4$) was used as the base reagent. The adsorption tests were carried out using 0.0001 m³ of each solution at 313.15 K, 200 rpm for 24 hours. The pH was adjusted at 2 and 6 for Cr (VI) and Ni (II) solutions, respectively. The concentration data were determined with UV-VIS spectrophotometry for Cr (VI) ions and with atomic absorption spectrophotometry for Ni (II) ions. The removal efficiency (%) was determined using the Equation 1, according to Wu *et al.* [20].

$$\text{Removal efficiency (\%)} = \left[\frac{C_0 - C_T}{C_0} \times 100 \right] \quad (1)$$

Where C_0 is the initial concentration of the ion in the adsorbent (Kg/m³); and C_T is the final concentration of the ion in solution (Kg/m³).

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Bio-adsorbents

Figure 1 shows the FTIR for the residual cake of plantain starch (RCPS) before and after the adsorption processes of Cr (VI) and Ni (II). The peak observed between the wavelengths of 3000 and 3500 cm^{-1} corresponds to functional groups OH, as well as between 3200 and 3500 cm^{-1} . Amines and carbonyl signals may appear due to stretching vibrations of the OH bond [21]. The peak at 2900 cm^{-1} is attributed to possible vibrations of CH methyl, methylene and methoxy groups [22], while the signals at 2500 correspond to alkyne groups and carboxylic acids. The peak at 1650 cm^{-1} is attributed to the stretching of C = O and CO [23], as well as may indicate hydrogen vibrations that represent the stretching of C = C. On the other hand, the presence of primary, secondary and tertiary alcohols is evidenced between 1000 and 1200 cm^{-1} . These signals are a product of the stretching vibrations of the C-OH bond and the flexions between the planes (1225-950 cm^{-1}), these are only complementary signs, since the stretches CC, CN and CO fall in the same region and appear several signals depending on the number of hydrogens. The interactions among adsorbate and carbonyl groups or surface alkenes of the bio- adsorbents could promote these events [24].

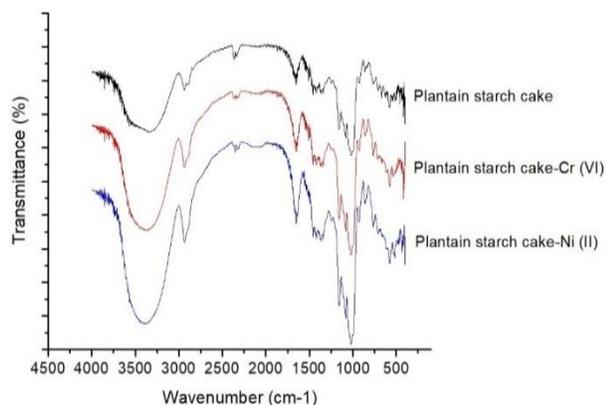


Figure 1 FTIR spectrum for the residual cake of plantain starch before and after the adsorption of Cr (VI) and Ni (II)

Finally, the bands at 600 cm^{-1} show torsional vibrations of the C-OH bond. After the adsorption of Cr (VI) and Ni (II) ions within the surface structure of the biomass, the increase in the width of the spectral bands and the slight decrease in intensity for each of the adsorption processes executed are evidenced. For both metals, this decrease is corroborated in the change in intensity at 2341 cm^{-1} , due to the interaction of hydrogen bonds with over-tone patterns. That indicates the presence of carboxylic acids (-COOH), by the stretching of OH, as is noted in the intensity change of the adsorption peak at 2928 cm^{-1} attributed

to the C-H vibrations present in the biomass that would facilitate the adsorption process and the formation of metal complexes.

From the residual cake of yam starch (RCYS) (Figure 2) before and after the adsorption of the metals studied a wide band at 3400 cm^{-1} is observed due to the vibrations of the OH bond [21].

Signals produced by the C-H bond at 2950 cm^{-1} and 1350 cm^{-1} are observed too. The vibrations at 1650 cm^{-1} , 1400 cm^{-1} and 900 cm^{-1} are assigned to carboxylic acids. The strong signal at 1150 cm^{-1} refers to the carboxylate ion COO^- , the peaks at 1080 and 1030 cm^{-1} show the presence of C-O and C-O-C respectively caused by the ester group. The medium bands at 900 and 750 cm^{-1} correspond to the N-H group produced by the torsion present in the amines [25]. After the adsorption of Cr (VI), a lower intensity from 3500 to 3250 cm^{-1} is observed due to the vibrations of the OH group and to 1030 cm^{-1} with the functional group C-O-C. For Ni (II) adsorption only a lower intensity at 3400 cm^{-1} produced by the vibrations of the OH bond is evidenced, which would indicate the possible formation of complexes with Ni (II).

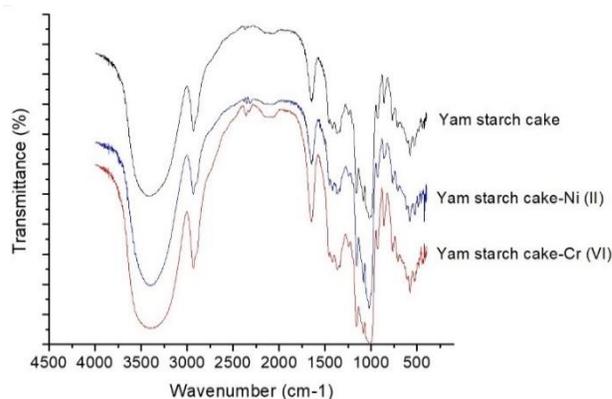


Figure 2 FTIR spectrum for the residual cake of yam starch before and after the adsorption of Cr (VI) and Ni (II)

Figure 3 shows the FTIR of palm bagasse before and after the adsorption of the metals under study. For the unmodified palm bagasse, a pronounced peak is observed at 3330 cm^{-1} which refers to the hydroxyl group. The interval between 3000-2800 cm^{-1} is assigned to the alkanes group, at 2300 cm^{-1} to the carboxylic acids, 1850-1540 cm^{-1} to the carbonyl groups, and finally the peaks of 1233 and 1025 cm^{-1} corresponding to the alcohol group [25, 26]. After the adsorption, it is concluded that the hydroxyl groups, alkanes and carboxylic acids are those that participate in the retention of Cr (VI) and Ni (II) on the palm bagasse.

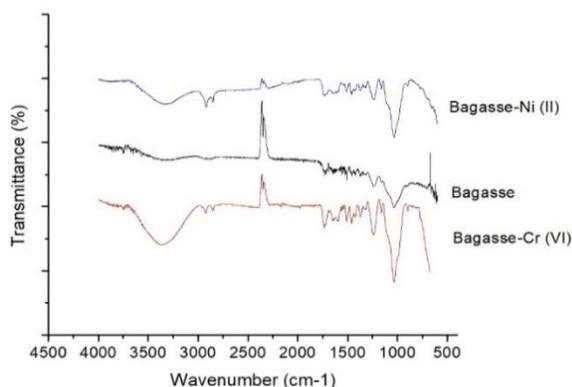


Figure 3 FTIR spectrum for palm bagasse before and after the adsorption of Cr (VI) and Ni (II) ions

Table 1 shows the results of the BET analysis of the bio-adsorbents. The current pore classification of the IUPAC indicates three groups according to the pore size. Micropores, diameters less than 2×10^{-9} m; mesoporous, diameters between 2 nm and 50 nm, and macropores, diameters higher than 50 nm. Considering the noted above, the palm bagasse and the RCPS are mesoporous, while RCYS is macroporous [26]. It is observed that the palm bagasse has a volume of pore two times greater than the other biomaterials, and a surface area about ten times higher than that of RCYS but lower than the surface area of RCPS. These results indicate a higher adsorbent capacity of the bagasse, as they could offer a higher volume and a larger contact area between the metal ions and the biomaterial [27].

Table 1 Analysis of surface area and porosity of the bio-adsorbents

Bio-adsorbents	Surface area (m ² /g)	Volume of pores (m ³ /Kg)	Size de pores (m)
Residual cake of yam starch	2.461	55x10 ⁻⁷	8.371x10 ⁻⁸
Residual cake of plantain starch	3.859	4x10 ⁻⁷	4.86x10 ⁻⁹
Palm bagasse	2.732	112x10 ⁻⁷	1.641x10 ⁻⁸

The removal of heavy metals from an aqueous solution in lignocellulosic materials is related to the presence of several functional groups on their surface (hydroxyl, carbonyl, phosphate, amino, thiol). Although their presence does not guarantee an efficient removal of metals, since this process is affected by several factors such as the number of active sites, its accessibility, chemical status and affinity for the metal, it much depends on the type of compounds and elements present. Among them, cellulose is relevant because of its chemical stability and mechanical strength [28].

In Table 2, the percentage of these components is shown, it is highlighted that cellulose is the component

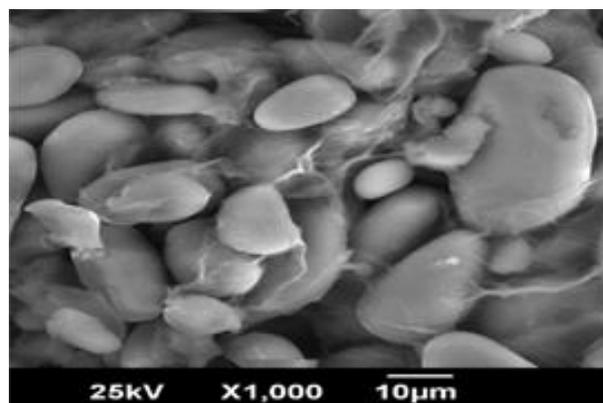
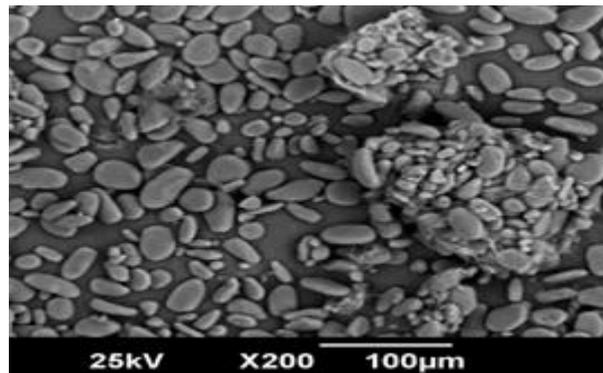
with the most significant presence. The existence of different functional groups in the structure of cellulose could promote the efficiency in the adsorption process [29].

Table 2 Chemical analysis of bio-adsorbents

Component	Residual cake of yam starch	Residual cake of plantain starch	Palm bagasse
Lignin (%)	19.53	26.22	17.11
Cellulose (%)	39.24	41.80	17.90
Hemicellulose (%)	27.41	15.81	7.00

Figure 4A shows the SEM micrographs of the RCPS, observing a uniform and cylindrical appearance. The RCYS (Figure 4B) exhibits a cylindrical and agglomerated structure. In the case of bagasse (Figure 4C) shows an irregular and porous surface typical of lignocellulosic materials, this morphology is desirable to improve the adsorption process due to the availability of active porous surface sites [30]. In this same figure, the presence of white lumps can be observed, which can be attributed to the presence of Silicon and Calcium that has palm bagasse, according to what is shown in the EDS analysis of Figure 5C. It is noteworthy that in the residues of plantain and yam starches, these two elements are not present on its surface, and there is no presence of white lumps, as seen in Figure 4.

A.



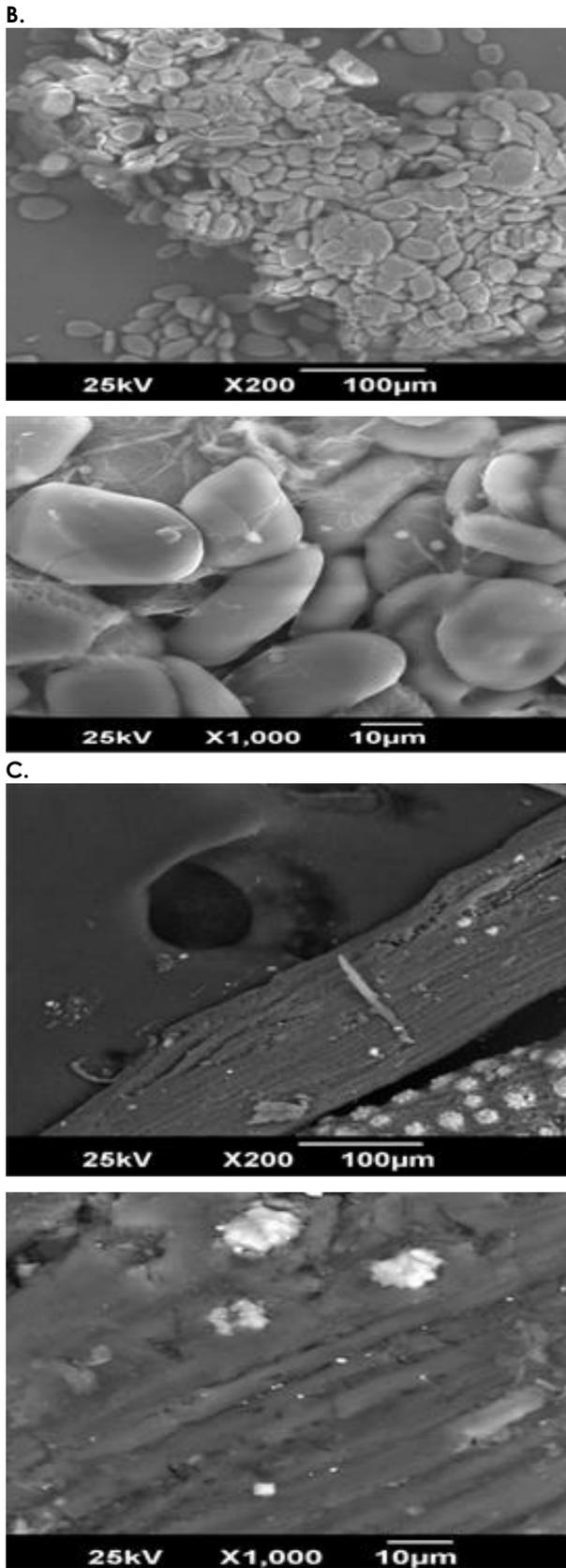


Figure 4 SEM micrographs of the residual cake of plantain starch (A), residual cake of yam starch (B), and palm bagasse (C)

The EDS analysis shown in Figure 5 revealed that the elemental composition of the bio-adsorbents is mainly carbon and oxygen, with traces of impurities in the case of the RCYS, and elements such as Cu, K, Ca, Na, K in the other biomaterials that can be attributed to the organic nature of them. The main elements in percentage of weight for the RCYS were C (65.90), O (34.02), Al (0.05) and Ni (0.03), for the RCPS they were C (58.32), O (41.07), K (0.24), Na (0.20), Cl (0.10) and Cu (0.07), and for the palm bagasse C (58.31), O (41.23), Si (0.34), Cu (0.07) and Ca (0.04).

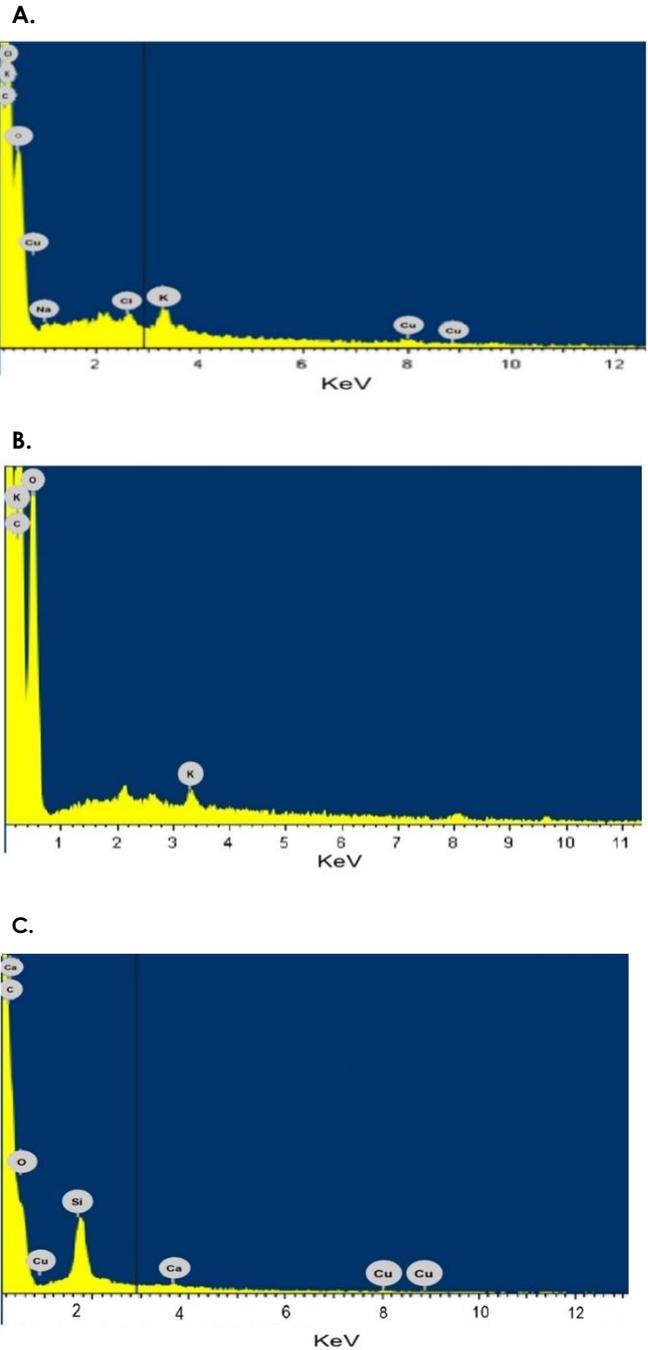


Figure 5 EDS analysis of the residual cake of plantain starch (A), residual cake of yam starch (B) and palm bagasse (C)

3.2 Adsorption Tests

Table 3 shows the adsorption data for Ni (II) and Cr (VI) ions. The positively charged ions (cations) present in the solution can be adsorbed to the surface of these materials by electrostatic forces, forming exchange complexes and chelates. Some metals once they form chelates or complexes can migrate more easily along the profile [31].

Table 3 Adsorption results

Metal	Adsorbent	Efficiency (%)
Cr (VI)	Palm bagasse	92.24
	Residual cake of yam starch	79.92
	Residual cake of plantain starch	71.4
Ni (II)	Palm bagasse	26.28
	Residual cake of yam starch	13.35
	Residual cake of plantain starch	44.07

Also, from the laws of surface chemistry can be explained the fact that it is obtained the higher capacity of chromium than the nickel. In general, the adsorption power of different heavy metals depends on their oxidation state and of the hydrated radius of the ion. The larger and smaller the load, the less strongly they are retained in the adsorbent.

The Cr (VI) removal efficiency results shown in Table 3 are consistent, since this ion is presented in an aqueous solution in the form of chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions, and easily exceeds resistance to mass transfer, and they diffuse in the adsorbent material through the porous surface. Thus, the African palm bagasse, which had the highest porous surface according to the SEM and BET analysis, is the one with the highest percentage of removal of this ion. Also, at pH 2 the surface of the adsorbent tends to protonate to a greater extent, which is why the adsorption of Cr (VI) ions is more effective [32].

On the other hand, the Ni (II) ions behave differently from those of Cr (VI), while their adsorption percentage was lower using the three adsorbents, which could be explained due to the selectivity of the active sites by of Nickel ions [32]. It could also be due to the formation of soluble hydroxylated metal complexes under study at pH 6, which compete with the active sites of the biomaterial surface and decrease the net concentration of Ni (II) in the solution, causing a decrease in the motive force to boosts the process of mass transfer from the solution to the adsorbent, and as a consequence, ion retention is reduced [11]. The structure of the material also influences the removal efficiency of the metal, so the residual plantain starch cake exhibits a better behavior due to its mesoporous nature and the surface area close to $4 \text{ m}^2/\text{g}$ [33].

In the literature, the use of agricultural residues, such as seeds, stems and husks, has been established for the removal of metal ions present in solution [34, 35]. The contribution of this study is to use materials that, even after the physicochemical treatments to which they are subjected during agro-industrial processes such as the extraction of palm oil and plantain starch and yam, this biomass still retain their lignocellulosic properties, which makes them a good precursor as a chromium and nickel adsorbent.

4.0 CONCLUSION

Based on the results found, it is established that the bioadsorbents studied have an excellent performance in the removal of Cr (VI), all higher than 70%, highlighting the behaviour of palm bagasse due to its adsorption efficiency, greater than 90%. This fact is not the case for Ni (II), finding that none of the biomass exceeds 45% adsorption efficiency, so this biomass is recommended for use primarily for the removal of Cr (VI). Cellulose is the most relevant component of the lignocellulosic materials due to its chemical stability and chemical structure, although it has limited free hydroxyl groups since most are involved in the formation of hydrogen bonds. This fact could be related to the formation of complexes with the metal ions.

Acknowledgement

The authors thank the Universidad de Cartagena for its support in laboratories, software and research time for professors. Also, Erika Ruiz thanks Colciencias for its sponsorship through the Young Researchers program.

References

- [1] FAO. 2017. Food and Agricultural Organization. El futuro de la alimentación y la agricultura. In: www.fao.org/3/a-i6583e.pdf.
- [2] UNESCO. 2009. United Nations Educational, Scientific, and Cultural Organization. World water assessment program. In: <http://www.unesco.org/new/en/natural-sciences/special-themes/global-climate-change/adaptation-forum/world-water-assessment-programme/>.
- [3] Moammadi S., Karimi M., Afzali D. & Mansouri F. 2010. Removal of Pb (II) from Aqueous Solutions Using Activated Carbon from Sea-buckthorn Stones by Chemical Activation. *Desalination*. 262(1-3): 86-93. DOI: <http://dx.doi.org/10.1016/j.desal.2010.05.048>.
- [4] Jiménez Ramos, I., Rondón, W., Rojas de Astudillo, L., Rojas de Gáscue, B., Prin, J. L., Freire, D., ... & González, O. 2017. Síntesis de carbón activado a partir de epicarpio de *Attalea macrolepis* y su aplicación en la remoción de Pb^{2+} en soluciones acuosas. *Revista internacional de contaminación ambiental*. 33(2): 303-316. DOI: <http://dx.doi.org/10.20937/rica.2017.33.02.11>.
- [5] Mittal, A., Mittal, J., Malviya, A., & Gupta, V. K. 2010. Removal and Recovery of Chrysoidine Y from Aqueous Solutions by Waste Materials. *Journal of Colloid and Interface Science*. 344(2): 497-507.

- DOI: <https://doi.org/10.1016/j.jcis.2010.01.007>.
- [6] Quiñones, E., Tejada, C., Arcia, C., & Ruiz, V. 2013. Remoción de plomo y níquel en soluciones acuosas usando biomasa lignocelulósicas: una revisión. *Revista UDCA Actualidad & Divulgación Científica*. 16(2): 479-489. DOI: <https://doi.org/10.1016/j.arabjc.2011.02.030>.
- [7] Ghorbel-Abid, I., & Trabelsi-Ayadi, M. 2015. Competitive Adsorption of Heavy Metals on Local Landfill Clay. *Arabian Journal of Chemistry*. 8(1): 25-3.
- [8] Garg, U. K., Kaur, M. P., Garg, V. K., & Sud, D. 2008. Removal of Nickel(II) from Aqueous Solution by Adsorption on Agricultural Waste Biomass Using a Response Surface Methodological Approach. *Bioresource Technology*. 99(5): 1325-1331. Doi: <https://doi.org/10.1016/j.biortech.2007.02.011>.
- [9] Sheng, P. X., Ting, Y.-P., Chen, J. P., & Hong, L. 2004. Sorption of Lead, Copper, Cadmium, Zinc, and Nickel by Marine Algal Biomass: Characterization of Biosorptive Capacity and Investigation of Mechanisms. *Journal of Colloid and Interface Science*. 275(1): 131-141. Doi: <https://doi.org/10.1016/j.jcis.2004.01.036>.
- [10] Rangabhashiyam, S., & Selvaraju, N. 2015. Evaluation of the Biosorption Potential of a Novel Caryota Urens Inflorescence Waste Biomass for the Removal of Hexavalent Chromium from Aqueous Solutions. *Journal of the Taiwan Institute of Chemical Engineers*. 47: 59-70. Doi: <https://doi.org/10.1016/j.jtice.2014.09.034>.
- [11] Burevska, K. A., Memedi, H., Lisichkov, K., Kuvendziev, S., Marinkovski, M., Ruseska, G., & Grozdanov, A. 2018. Biosorption of Nickel Ions from Aqueous Solutions by Natural and Modified Peanut Husks: Equilibrium and Kinetics. *Water and Environment Journal*. 32(2): 276-284. Doi: <https://doi.org/10.1111/wej.12325>.
- [12] Panda, G. C., Das, S. K., Bandopadhyay, T. S., & Guha, A. K. 2007. Adsorption of Nickel on Husk of Lathyrus Sativus: Behavior and Binding Mechanism. *Colloids and Surfaces B: Biointerfaces*. 57(2): 135-142. Doi: <https://doi.org/10.1016/j.colsurfb.2007.01.022>.
- [13] Guyo, U., Sibanda, K., Sebata, E., Chigondo, F., & Moyo, M. 2016. Removal of Nickel (II) from Aqueous Solution by Vigna Unguiculata (Cowpea) Pods Biomass. *Water Science and Technology*. 73(10): 2301-2310. Doi: <https://doi.org/10.2166/wst.2016.012>.
- [14] Omorogie, M. O., Babalola, J. O., Unuabonah, E. I., Song, W., & Gong, J. R. 2016. Efficient Chromium Abstraction from Aqueous Solution Using a Low-cost Biosorbent: Nauclea Diderrichii Seed Biomass Waste. *Journal of Saudi Chemical Society*. 20(1): 49-57. Doi: <https://doi.org/10.1016/j.jscs.2012.09.017>.
- [15] Iqbal, M., & Khera, R. A. 2015. Adsorption of Copper and Lead in Single and Binary Metal System onto Fumaria indica biomass. *Chem. Int.* 1(3): 157b-163b.
- [16] Kieling, A. G., Mendel, T., & Caetano, M. O. 2018. Efficiency of Rice Husk Ash to Adsorb Chromium (VI) using the Allium Cepa Toxicity Test. *Environmental Science and Pollution Research*. 1-9. Doi: <https://doi.org/10.1007/s11356-018-3722-3>.
- [17] Saleem, M., Wongsrisujarit, N., & Boonyarattanakalin, S. 2016. Removal of Nickel (II) ion by Adsorption on Coconut Copra Meal Biosorbent. *Desalination and Water Treatment*. 57(12): 5623-5635. Doi: <https://doi.org/10.1080/19443994.2015.1005155>.
- [18] Shi, X., Gong, B., Liao, S., Wang, J., Liu, Y., Wang, T., & Shi, J. 2019. Removal and Enrichment of Cr (VI) from Aqueous Solutions by Lotus Seed Pods. *Water Environment Research*. Doi: <https://doi.org/10.1002/wer.1187>. DOI: <https://doi.org/10.1016/j.arabjc.2011.02.030>.
- [19] Maniglia, B. C., & Tapia-Blácido, D. R. 2016. Isolation and Characterization of Starch from Babassu Mesocarp. *Food Hydrocolloids*. 55: 47-55. DOI: <https://doi.org/10.1016/j.foodhyd.2015.11.001Get>.
- [20] Wu, Y., Fan, Y., Zhang, M., Ming, Z., Yang, S., Arkin, A., & Fang, P. 2016. Functionalized Agricultural Biomass as a Low-Cost Adsorbent: Utilization of Rice Straw Incorporated with Amine Groups for the Adsorption of Cr (VI) and Ni (II) from Single and Binary Systems. *Biochemical Engineering Journal*. 105: 27-35. DOI: <https://doi.org/10.1016/j.bej.2015.08.017>.
- [21] Wahab, M. A., Jellali, S., & Jedidi, N. 2010. Ammonium Biosorption onto Sawdust: FTIR Analysis, Kinetics and Adsorption Isotherms Modeling. *Bioresource Technology*. 101(14): 5070-5075. DOI: <https://doi.org/10.1016/j.biortech.2010.01.121>.
- [22] Mitra, T., Singha, B., Bar, N., & Das, S. K. 2014. Removal of Pb (II) Ions from Aqueous Solution Using Water Hyacinth Root by Fixed-bed Column and ANN Modeling. *Journal of Hazardous Materials*. 273: 94-103. DOI: <https://doi.org/10.1016/j.jhazmat.2014.03.025Get>.
- [23] Mahamadi, C., & Nharingo, T. 2010. Competitive Adsorption of Pb2+, Cd2+ and Zn2+ ions onto Eichhornia crassipes in Binary and Ternary Systems. *Bioresource Technology*. 101(3): 859-864. DOI: <https://doi.org/10.1016/j.biortech.2009.08.097>.
- [24] Roh, H., Yu, M. R., Yakkala, K., Koduru, J. R., Yang, J. K., & Chang, Y. Y. 2015. Removal Studies of Cd (II) and Explosive Compounds Using Buffalo Weed Biochar-alginate Beads. *Journal of Industrial and Engineering Chemistry*. 26: 226-233. DOI: <https://doi.org/10.1016/j.jiec.2014.11.034>.
- [25] Li, X., Tang, Y., Cao, X., Lu, D., Luo, F., & Shao, W. 2008. Preparation and Evaluation of Orange Peel Cellulose Adsorbents for Effective Removal of Cadmium, Zinc, Cobalt and Nickel. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 317(1-3): 512-521. DOI: <https://doi.org/10.1016/j.colsurfa.2007.11.031>.
- [26] Ahmad, F., Daud, W. M. A. W., Ahmad, M. A., & Radzi, R. 2012. Cocoa (Theobroma cacao) Shell-based Activated Carbon by CO2 Activation in Removing of Cationic Dye from Aqueous Solution: Kinetics and Equilibrium Studies. *Chemical Engineering Research and Design*. 90(10): 1480-1490. DOI: <https://doi.org/10.1016/j.cherd.2012.01.017>.
- [27] Liu, Q. S., Zheng, T., Li, N., Wang, P., & Abulikemu, G. 2010. Modification of Bamboo-based Activated Carbon Using Microwave Radiation and Its Effects on the Adsorption of Methylene Blue. *Applied Surface Science*. 256(10): 3309-3315. DOI: <https://doi.org/10.1016/j.apsusc.2009.12.025>.
- [28] Šošarić, T. D., Petrović, M. S., Pastor, F. T., Lončarević, D. R., Petrović, J. T., Milojković, J. V., & Stojanović, M. D. 2018. Study of Heavy Metals Biosorption on Native and Alkali-Treated Apricot Shells and Its Application in Wastewater Treatment. *Journal of Molecular Liquids*. 259: 340-349. DOI: <https://doi.org/10.1016/j.molliq.2018.03.055>.
- [29] Asuquo, E. D., & Martin, A. D. 2016. Sorption of Cadmium (II) Ion from Aqueous Solution onto Sweet Potato (Ipomoea Batatas L.) Peel Adsorbent: Characterisation, Kinetic and Isotherm Studies. *Journal of Environmental Chemical Engineering*. 4(4): 4207-4228. DOI: <https://doi.org/10.1016/j.jece.2016.09.024>.
- [30] Singh, S. A., & Shukla, S. R. 2016. Adsorptive Removal of Cobalt Ions on Raw and Alkali-treated Lemon Peels. *International Journal of Environmental Science and Technology*. 13(1): 165-178. DOI: <https://doi.org/10.1007/s13762-015-0801-6>.
- [31] Gustafsson, J. P., Pechová, P., & Berggren, D. 2003. Modeling Metal Binding to Soils: The Role of Natural Organic Matter. *Environmental Science & Technology*. 37(12): 2767-2774. DOI: <https://doi.org/10.1021/es026249t>.
- [32] Sha, H., Wu, Y., & Fan, Y. 2017. Utilization of Industrial Waste as a Novel Adsorbent: Mono/Competitive Adsorption of Chromium(VI) and Nickel(II) using Diatomite Waste Modified by EDTA. *Applied Organometallic Chemistry*. 32(1): e3977. Doi: <https://doi.org/10.1002/aoc.3977>.
- [33] Ranasinghe, S. H., Navaratne, A. N., & Priyantha, N. 2018. Enhancement of Adsorption Characteristics of Cr(III) and Ni(II) by Surface Modification of Jackfruit Peel Biosorbent. *Journal of Environmental Chemical Engineering*. 6(5): 5670-5682.

- Doi: <https://doi.org/10.1016/j.jece.2018.08.058>.
- [34] Dai, Y., Sun, Q., Wang, W., Lu, L., Liu, M., Li, J., Yang, S., Sun, Y., Zhang, K., Xu, J., Zheng, W., Hu, Z., Yang, Y., Gao, Y., Chen, Y., Zhang, X., Gao, F., & Zhang, Y. 2018. Utilizations of Agricultural Waste as Adsorbent for the Removal of Contaminants: A Review. *Chemosphere*. 211: 235-253.
- Doi: <https://doi.org/10.1016/j.chemosphere.2018.06.179>.
- [35] De Gisi, S., Lofrano, G., Grassi, M., & Notarnicola, M. 2016. Characteristics and Adsorption Capacities of Low-cost Sorbents for Wastewater Treatment: A Review. *Sustainable Materials and Technologies*: 9: 10-40.
- Doi: <https://doi.org/10.1016/j.susmat.2016.06.002>.