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Comparative assessment of Al_2O_3-modified biomasses from agricultural residues for nickel and cadmium removal

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Abstract

The biodiversity of aqueous environments has been affected due to the disposal of wastewater highly contaminated with heavy metal ions, causing much damage to ecosystems. These pollutants are very toxic and bioaccumulate in living organisms. This work attempts to evaluate the adsorption of nickel ad cadmium ions using three biomasses from agricultural residues (corn cob – CC, orange peel – OP, and oil palm bagasse – PB) modified with alumina nanoparticles. The biomasses were characterized via compositional analysis and a point of zero charges to quantify the presence of lignin, cellulose, hemicellulose, and the feasible pH, taking advantage of the biomass charge. After modification with Al_2O_3 nanoparticles. The resulting adsorbents were characterized via FT-IR analysis to identify the functional groups that most contributed to the adsorption performance. Furthermore, the influence of Al_2O_3 nanoparticles was analysed on the adsorption capacities of the evaluated biomasses using batch systems at a temperature of 25°C and pH 6. All biomasses displayed a high content of cellulose, estimating a weight percentage of about 19.9%, 14.3%, and 13.1% for PB, OP, and CC samples, respectively. The FT-IR spectrum confirmed hydroxyl and carboxyl functional groups, which contribute to enhancing the adsorption capacities of the modified biomasses. Functional adsorption capacity was observed for all biomasses after modification with Al_2O_3 nanoparticles, achieving at pH 6.0 a cadmium removal from 92% (CC-Al_2O_3 and PB-Al_2O_3) up to 95.8±0.3% (OP-Al_2O_3). In nickel ions, it was estimated a broader adsorption capacity at pH 6.0 of about 86±0.4% after using the CC-Al_2O_3 sample, 88±0.1% for the PB-Al_2O_3 adsorbent, and 98±0.2% for the OP-Al_2O_3 sample, confirming the suitability of these Al_2O_3-modified biomasses for the removal of heavy metal ions.

Key words: *adsorption, agricultural residues, alumina nanoparticles, cellulose, heavy metal ions*

INTRODUCTION

There is an increasing concern about the contamination of water sources by heavy metal ions coming from different anthropogenic activities [KAVAND *et al.* 2020]. These progressively dangerous pollutants are absorbed by marine animals that are part of the food chain generating a high risk to consumer health [FONSECA-CORREA *et al.* 2019]. Additionally, they affect the environmental conditions of aquatic life in the receiving environments, such as lakes and rivers [ES-SAHBANY *et al.* 2019]. Heavy metals like nickel (Ni) and cadmium (Cd) are characterize by high toxicity, the hardness of degradability, and facile accumulation via the food chain [DENG *et al.* 2020]. Despite this, nickel occurs naturally, higher concentrations above 5–10 $\mu g \cdot dm^{-3}$ in drinking water can produce serious health problems [MADDODI *et al.* 2020]. Illnesses include nervous disorders, neurological problems, bone degeneration, and deficiency of the gastrointestinal system, kidneys, and liver [OLIVERO-VERBEL *et al.* 2007].

Health problems in humans derived from metal exposure and the deterioration in surface water quality have been the motivation to search for alternatives to remove or reduce the content of these pollutants before discharging them into the environment [ES-SAHBANY *et al*. 2019]. The treatment of residual waters in Colombia must comply with environmental regulations; however, only 10% of total wastewater receive proper treatment, despite there being capacity for up to 20% [Twenergy 2014]. There is no strict control in managing wastewater, and wastewaters contaminated with heavy metals end up in surface water above the maximum permissible limit. Various separation technologies are used to reduce the concentration of heavy metal ions in industrial effluents, for example, coagulation, reduction, differential precipitation, ion exchange, electrochemical treatment, separation by a membrane, solvent extraction, and flotation, among others. These methods require a high operating cost, which makes it unattractive for the industry [ISLAM *et al*. 2019].

Among the wastewater treatment technologies, the adsorption technique offers a more attractive alternative in terms of efficiency, economy, and advantages, since no toxic waste is generated [XU *et al*. 2016]. The adsorbents coming from residual biomasses allow the completion of the cycle of exploitation of derived-crops, and the cost associated with their acquisition is low [BHATNAGAR *et al*. 2015]. Besides, its composition as lignocellulosic material has a high affinity for interaction with heavy metals ions. Its presence can be determined by qualitative analysis as infrared spectroscopy, or quantitative as the potentiometric titration of Böehm [TOMAR *et al*. 2014].

Although these biomaterials used in the remediation of polluted waters have a particularly good performance during the adsorption process, proposing improvement of this quality generates expectation. According to recent studies, components such as nanomaterials or chemical agents are capable of forming bonds with some heavy metals [HERRERA-BARROS *et al*. 2019; LI *et al*. 2020]. Nanomaterials composed of alumina (Al_2O_3) and titanium dioxide (TiO_2) can absorb nickel and cadmium ions, as confirmed in the literature [FEITOZA *et al*. 2014].

In this work, we modified palm bagasse, corn cob, and orange peel biomasses with alumina nanoparticles which are conventionally obtained by the Sol-Gel method. The primary purpose of this modification is to enhance the specific surface area and pore structure of the biomass allowing for a more efficient adsorption of heavy metal ions.

MATERIALS AND METHODS

ADSORBENT PREPARATION

Biomass preparation. The corn cobs, orange peels, and oil palm bagasse all come from local farms in the Department of Bolivar (Colombia). These biomasses were cut into small pieces, washed thoroughly, and dried in an oven at 70°C for 24 h [LIANG *et al*. 2010]. Then, they were crushed and sieved to a particle size of 0.35 mm, which is within the range stated in the literature [LASHEEN *et al*. 2012]. These, size-reduced particles were washed with ethyl alcohol to remove impurities [HERRERA-BARROS *et al*. 2018a]. The pretreated biomasses were characterized via compositional analysis, and the point of zero charge was estimated.

Preparation of alumina nanoparticles. The synthesis of Al_2O_3 nanoparticles was carried out using the Sol-Gel method, which required the preparation of 0.5 M solution of aluminium nitrate [$Al(NO_3)_3$] and 0.5 M solution of citric acid [$C_6H_8O_7$]. Both solutions were mixed under continuous stirring at 60°C until the overall colour became yellow. Then, the stirring temperature was increased by 10°C until a gel formed. This gel was sent to a muffle at 200°C for two hours and 750°C during the next two hours to improve its crystal structure [LI *et al*. 2006; HERRERA-BARROS *et al*. 2018b].

Incorporation of alumina nanoparticles into the biomass. Modifying biomasses with alumina nanoparticles (Al_2O_3) is performed as follows: a suspension of 0.5 g of the biomasses was dispersed in 20 cm^3 of the organic solvent Dimethylsulfoxide (DMSO) using a shaker for 24 h at 120 rpm. Afterward, 3 cm^3 of Tetra-ethyl-ortho-silicate (TEOS) chemical reagent was added and kept under mechanical stirring at 120 rpm in a shaker for 48 h at room temperature. During this procedure, the (TEOS) molecules are expected to hydrolyse and condense on the surface of the biomasses, forming Polysiloxane (Si-O) bond bridges [HERRERA, RINALDI 2008], which also serves to fix the nanoparticles into the biomaterials matrix. Then, 0.2 g of the synthesized alumina nanoparticles (Al_2O_3) were added under continuous stirring at 120 rpm for 12 h. Once the functionalization process was completed, ethanol washing was conducted followed by vacuum filtration and drying at room temperature. Figure 1 shows the schematic process for the modification of the biomasses with the alumina nanoparticles (Al_2O_3).

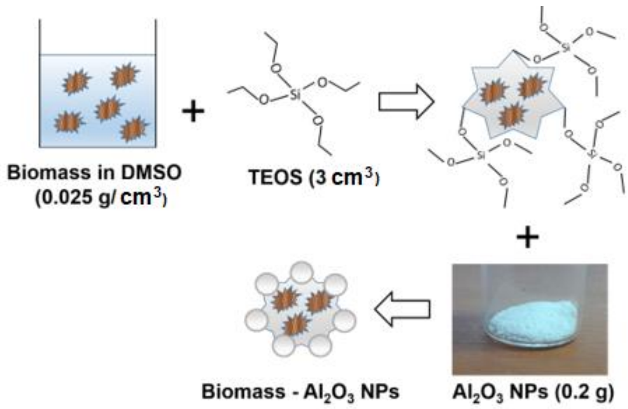


Fig. 1. Schematic representation of biomass modification with alumina nanoparticles; source: own elaboration

CHARACTERIZATION TECHNIQUES

Composition analysis. The composition of lignocellulosic biomass in terms of inorganic and organic components were determined by analytical methods following the methodology proposed by TEJADA-TOVAR *et al.* [2020]. Table 1 lists the compounds considered in each characterization method.

Table 1. Analytic techniques applied for biomass characterization

Organic/inorganic	Method	Elements	Method
Carbon	AOAC 949.14	calcium sodium potassium iron copper	atomic absorption spectroscopy (AAS)
Hydrogen	AOAC 949.14		
Nitrogen	AOAC 984.13 Kjeldahl		
Pectin	acid digestion – thermogravimetric analysis		
Lignin	photocolorimetric		
Cellulose	acid digestion – thermogravimetric analysis		
Hemicellulose	acid digestion – thermogravimetric analysis		
Ashes	thermogravimetric analysis		

Source: own elaboration.

Point of zero charge (pHz). The procedure to determine the point of zero charge for the biomasses is described as follows: 50 cm^3 of distilled water was pH-adjusted to different values of 3, 4, 5 and 6 using 1 M solutions of NaOH and HCl. Then, 0.5 g of biomass was added to and continually stirred at 30°C for 48 h. The final pH was measured using a pH-meter for all the cases of pH variation. These values of initial and final pH were used to build a plot, from which the point of zero charge could be estimated.

Characterization of biomasses modified with alumina nanoparticles. Fourier-transform infrared spectroscopy (FTIR) was used to identify functional groups on the prepared materials. A Thermo Scientific Nicolet 6700 FTIR spectrometer recorded The FTIR spectra of biomass after modification with Al_2O_3 nanoparticles in a resolution region ranged from 600 to 4000 cm^{-1}. Moreover, a JEOL JSM-6490LV scanning electron microscope (SEM) coupled to an Energy-dispersive X-ray spectroscopy (EDS) was used to determine the morphology of the biosorbent and Al_2O_3 nanoparticles.

ADSORPTION EXPERIMENTS

A 300 cm^3 stock solution of nickel or cadmium was prepared with a concentration of 100 ppm using nickel sulphate ($NiSO_4$) or cadmium sulphate ($CdSO_4$). This solution was adjusted to pH 6 using 1 M NaOH and HCl solutions. This value has shown to provide high removal yields for the selected heavy metal ions [PÉREZ-MARÍN *et al*. 2009]. Then, 0.5 g of biomass was added and kept under continuous agitation for 2 hours at room temperature. After the contact time was over, the adsorbent was filtered. We collected a small sample of this solution to measure the remaining concentration of metals using an ICE 3000 Atomic Absorption Spectrometer with wavelengths of 229 nm and 305 nm for cadmium and nickel detections [LASHEEN *et al*. 2012]. The removal yield was quantified using the Equation (1)

$$R = \frac{(C_0 - C_e)}{C_0} 100\% \tag{1}$$

where: C_0 (mg·cm^{-3}) and C_e (mg·cm^{-3}) are the initial and remaining concentrations of heavy metal ions in aqueous solution, respectively [MORENO-SADER *et al*. 2019].

RESULTS AND DISCUSSION

CHARACTERIZATION TECHNIQUES

Table 2 shows organic and inorganic components in the evaluated biomasses. The palm bagasse showed the highest cellulose and lignin content with 19.90±0.35% and 17.11±0.27%, representing around 37% of the biomass weight. In the corn cobs and orange peels, the lowest amount of cellulose and lignin was measured, achieving only 20% of the total composition of these biomasses among these biopolymers. Additionally, the orange peel displayed a pectin content of 18.15±0.04%, which is twice as much as the amount detected in the corn cob and four times high than that in the palm bagasse samples. We compared the results with those found in the literature for the same biomaterials. RIVAS-CANTU *et al*. [2013] showing that orange peel has high cellulose, pectin, and hemicellulose content with all values reading above 35, 20, and 5%, respectively. For this type of oil palm waste, the reported composition found in literature ranged between 27 and 35% of cellulose, 15 and 19% of hemicellulose, 48 and 55% of lignin, and 1 and 4% of ashes [DUNGANI *et al*. 2018]. Regarding the corn cobs, the chemical composition typically ranged in 42.8% of hemicellulose, 35.1% of cellulose, and 4.8% of lignin [YANNI *et al*. 2010].

Table 2. Compositional analysis of biomasses

Organic/inorganic	Composition		
	orange peels (OP)	corn cob (CC)	palm bagasse (PB)
% wt.			
Carbon	44.43±0.12	39.89±0.41	38.27±0.45
Hydrogen	6.21±0.02	3.28±0.09	4.71±0.05
Nitrogen	0.81±0.02	0.46±0.04	2.03±0.11
Pectin	18.15±0.04	7.98±0.33	4.88±0.17
Lignin	7.14±0.03	6.51±0.18	17.11±0.27
Cellulose	14.28±0.07	13.08±0.25	19.90±0.35
Hemicellulose	7.02±0.05	6.47±0.07	7.00±0.12
Ashes	2.08±0.02	1.20±0.08	4.23±0.14
mg·g^{-1}			
Calcium	5.26±0.09	0.06±0.002	1.21±0.04
Sodium	2.22±0.14	0.24±0.02	0.35±0.03
Potassium	0.44±0.008	0.03±0.005	2.73±0.08
Iron	0.23±0.009	0.0002±0.00003	0.0002±0.00002
Copper	0.01±0.003	0.002±0.0001	0.04±0.005

Source: own study.

Point of zero charge (pHz). The point of zero charge provides information about the solution's pH that will promote the predominance of the negative charges in the adsorbent surface. Solution pH value lower than the pHz requires that the biomass surface be positively charged, affecting the adsorption of cations due to electrostatic repulsion by equal charges [MARTIN LARA 2008]. Intersecting the curve for initial pH versus final pH with the line $y = x$ (Fig. 2) leads to the estimation of pHz value. The pHz of palm bagasse was 4.5, while for corn cobs and orange peel, it was 4.8 and 4.1, respectively. These values revealed that the biomasses have an acidic surface, i.e., the concentration of acidic sites is higher than the basic sites. In this sense, the selected pH value for adsorption experiments will be adequate to reach high removal yields

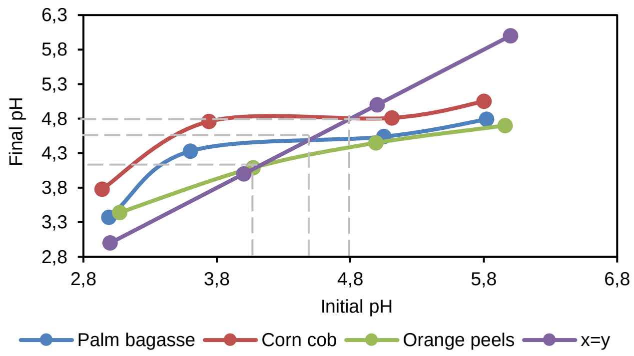


Fig. 2. Point of zero charge of biomasses; source: own study

because of the biomasses' acid charge. As the corn cobs achieved the highest value of point of zero charge, it may require a higher solution pH to have the same adsorption performance than the orange peels and the palm bagasse. A comparison of these results with those found in previous works (Tab. 3) validates the measurement accuracy. The accuracy of pHz for palm bagasse and orange peels ranged around 7–8 % compared to the estimations of [ROMERO-CANO *et al*. 2016; SATHORN *et al*. 2008].

Table 3. Comparison of point of zero charge for palm bagasse, corn cob and orange peels biomasses

Biomass	Previous works	This work	Reference
Palm bagasse	4.20	4.5	PANUMATI *et al*. [2008]
Corn cob	4.08	4.8	SEPÚLVEDA *et al*. [2015]
Orange peels	4.50	4.1	ROMERO-CANO *et al*. [2016]

Source: own study.

Characterization of biomasses modified with alumina nanoparticles. Figure 3 depicts the Fourier-transform infrared spectroscopy (FTIR) spectra of biomasses chemically modified with alumina nanoparticles. Similar trends appear for all the spectrum with sharp absorptive peaks around 650–670 cm^{-1}, 1000–1100 cm^{-1}, 1500–1550 cm^{-1}, and 3700–3800 cm^{-1}. Such peaks correspond to the bonds between alumina nanoparticles and functional groups characteristic of the lignocellulosic materials like carboxyl and hydroxyl. The following functional groups are present by stretching vibrations in the adsorbents associated with the incorporation of nanoparticles into the biopolymer matrix: O-Al-O (650–700 cm^{-1}), Al-O-M; M=Al or Si (950–1200 cm^{-1}), Al-C=O (1500–1700 cm^{-1}), Al-COOH (2600–3800) [CARMONA TÉLLEZ 2008].

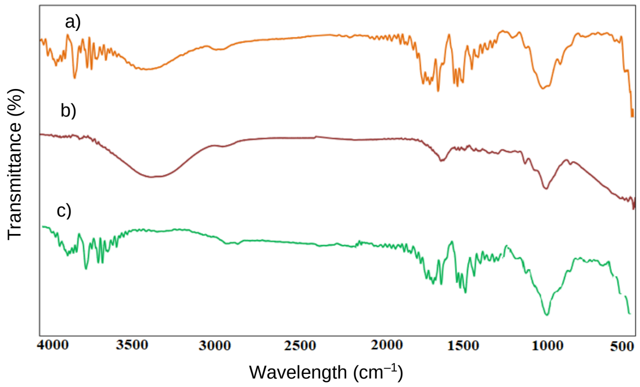


Fig. 3. Fourier-transform infrared spectroscopy spectra: a) Al_2O_3-modified orange peels, b) Al_2O_3-modified corn cob, c) Al_2O_3-modified palm bagasse; source: own study

Figure 4 shows the appearance of biomasses modified with alumina nanoparticles, observing an amorphous morphology characteristic of the lignocellulosic materials. The EDS (Fig. 4d) confirmed the incorporation of Al_2O_3 nanoparticles, from which the highest weight percentage of aluminium (Al) was estimated at 7.5% and 7.0% for the OP-Al_2O_3 and CC-Al_2O_3 samples. In comparison, the PB-Al_2O_3 adsorbent displayed the lowest aluminium content of 2.3%.

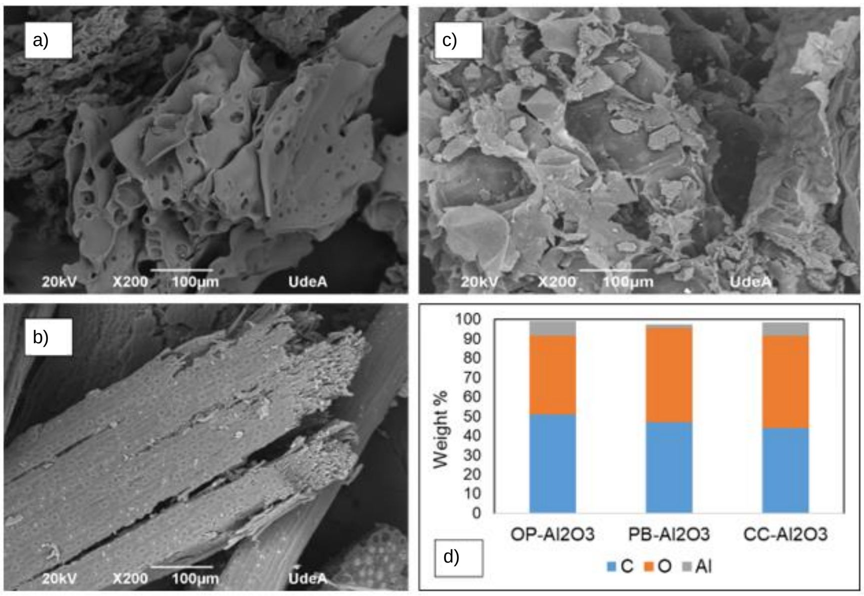
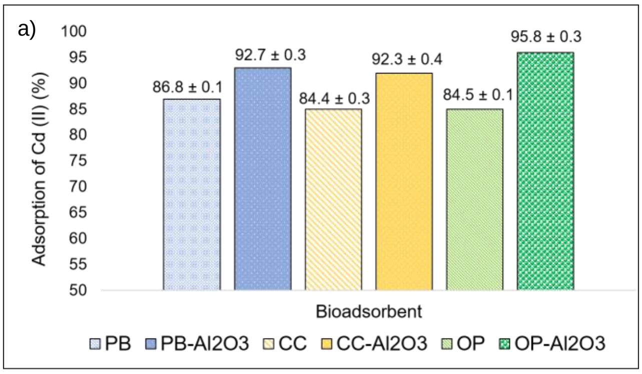


Fig. 4. Scanning electron microscope images and Energy-dispersive X-ray spectroscopy (EDS) weight percentage for biomasses chemically modified with Al_2O_3 nanoparticles: a) orange peels (OP-Al_2O_3), b) palm bagasse (PB-Al_2O_3), c) corn cobs (CC-Al_2O_3), d) weight percentage according to EDS measurements; source: own study

ADSORPTION RESULTS

Results showed the promising adsorption performance of the evaluated adsorbents for nickel and cadmium ions removal. As depicted in Figure 5, all biomasses displayed adsorption capacity for nickel and cadmium ions, determining an average uptake of 76% for nickel and 85% for cadmium at pH 6.0. After modification with the Al_2O_3 nanoparticles, it was observed that an adsorption increase of 7% for cadmium uptake using corn cobs (92.3±0.4%) and palm bagasse (92.7±0.3%), while for the nickel adsorption this increase was around 10–12% (86±0.4% for corn cobs and 88±0.1% for palm bagasse). In orange peels functionalized with the Al_2O_3 nanoparticles, an adsorption increase of 10% was observed for cadmium removal (95.8±0.3%) and 22% for nickel uptake (98±0.2%). For palm bagasse and the corn cobs biomasses before and after modification with nanoparticles, the adsorption yield follows the order Cd(II) >Ni(II). The fact they were adsorbing more efficiently one metal more than others may be attributed to the several characteristics of heavy metal ions such as atomic number, valence, and degree of ionization [KOCAOBA 2008]. This adsorption specificity of biomasses towards cadmium and nickel ions was also reported by MERRIKHPOUR and JALALI [2013] using natural zeolite in the competitive study.



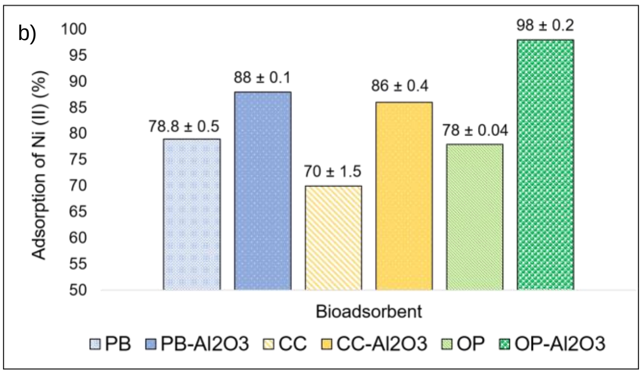


Fig. 5. Adsorption of heavy metal ions at pH 6.0 using palm bagasse (PB), corn cobs (CC) and orange peels (OP) biomasses modified with alumina nanoparticles: a) cadmium uptake, b) nickel removal; source: own study

CONCLUSIONS

This work was focused on comparing the performance of three different adsorbents prepared from oil palm bagasse, corn cob, and orange peel biomasses were modified with alumina nanoparticles. The metal-oxide nanomaterials were incorporated into the biomasses through a polysiloxane matrix. The characterization of these biomasses allowed us to estimate the content of cellulose, lignin, and pectin, and determine the point of zero charges. These points of zero charges ranged between pH 4 to 5, which were lower than the selected initial solution pH of 6. The adsorption experiments conducted in batch mode revealed the potential of these biomasses for nickel and cadmium uptake. The orange peel modified with alumina nanoparticles allowed the highest adsorption capacity (>95%) for both metal cations. Comparing these results with available experimental data for the same biomasses, a possible enhancement in adsorption performance can be identified due to the incorporation of alumina nanoparticles.

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REFERENCES

BHATNAGAR A., SILLANPÄÄ M., WITEK-KROWIAK A. 2015. Agricultural waste peels as versatile biomass for water purification – A review. Chemical Engineering Journal. Vol. 270 p. 244–271.

CARMONA TÉLLEZ S. 2008. Elaboración y caracterización de películas delgadas de óxido de aluminio: Propiedades ópticas, estructurales y eléctricas [Preparation and characterization of aluminum oxide thin films: Optical, structural and electrical properties]. MSc Thesis. México D.F. Instituto Politécnico Internacional pp. 87.

DENG Y., HUANG S., DONG C., MENG Z., WANG X. 2020. Competitive adsorption behaviour and mechanisms of cadmium, nickel and ammonium from aqueous solution by fresh and ageing rice straw biochars. Bioresource Technology. Vol. 303, 122853. DOI 10.1016/j.biortech.2020.122853.

DUNGANI R., ADITIAWATI P., APRILIA S., YUNIARTI K., KARLIATI T., SUWANDHI I., SUMARDI I. 2018. Biomaterial from oil palm waste: Properties, characterization and applications. In: Palm oil. Ed. V. Waisundara. IntechOpen, 76412. DOI 10.5772/intechopen.76412.

ES-SAHBANY H., BERRADI M., NKHILI S., HSISSOU R., ALLAOUI M., LOUTFI M. 2019. Removal of heavy metals (nickel) contained in wastewater-models by the adsorption technique on natural clay. In: Materials Today. Proceedings. Vol. 13 p. 866–875. DOI 10.1016/j.matpr.2019.04.050.

FEITOZA N.C., GONÇALVES T.D., MESQUITA J.J., MENEGUCCI J.S., SANTOS M.-K.M.S., CHAKER J.A., CUNHA R.B., MEDEIROS A.M.M., RUBIM J.C., SOUSA M.H. 2014. Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater. Journal of Hazardous Materials. Vol. 264 p. 153–160. DOI 10.1016/j.jhazmat.2013.11.022.

FONSECA-CORREA R.A., GIRALDO L., MORENO-PIRAJÁN J.C. 2019. Thermodynamic study of adsorption of nickel ions onto carbon aerogels. Heliyon. Vol. 5. No. February e01789. DOI 10.1016/j.heliyon.2019.e01789.

HERRERA A., RINALDI C. 2008. Synthesis and functionalization of magnetite nanoparticles with aminopropylsilane and carboxymethyldextran. Journal of Material Chemistry. Vol. 18 p. 3650–3654.

HERRERA-BARROS A., TEJADA-TOVAR C., VILLABONA-ORTÍZ A., GONZÁLEZ-DELGADO A.D., ALVAREZ-CALDERON J. 2018a. Adsorption of nickel and cadmium by corn cob biomass chemically modified with alumina nanoparticles. Indian Journal of Science and Technology. Vol. 11 p. 1–11. DOI 10.17485/ijst/2018/v11i22/126125.

HERRERA-BARROS A., TEJADA-TOVAR C., VILLABONA-ORTÍZ A., GONZÁLEZ-DELGADO Á.-D., RUIZ-PATERNINA E. 2018b. Application of lemon peels biomass chemically modified with Al_2O_3 nanoparticles for cadmium uptake. Indian Journal of Science and Technology. Vol. 11 p. 1–5.

HERRERA-BARROS A., TEJADA-TOVAR C., VILLABONA-ORTÍZ A., GONZALEZ-DELGADO Á., MEJIA-MEZA R. 2019. Assessment of the effect of Al_2O_3 and TiO_2 nanoparticles on orange peel biomass and its application for Cd (II) and Ni (II) uptake. Transactions of the ASABE. Vol. 62 p. 139–147.

ISLAM A., AWUAL R., ANGOVE M.J. 2019. A review on nickel (II) adsorption in single and binary component systems and future path. Journal of Environmental Chemical Engineering. Vol. 7. No. 5, 103305. DOI 10.1016/j.jece.2019.103305.

KAVAND M., ESLAMI P., RAZEH L. 2020. The adsorption of cadmium and lead ions from the synthesis wastewater with the activated carbon: Optimization of the single and binary systems. Journal of Water Process Engineering. Vol. 34, 101151. DOI 10.1016/j.jwpe.2020.101151.

KOCAOBA S. 2008. Adsorption of nickel (II) and cobalt (II) ions and application of surface complex formation model to ion exchange equilibria. Environmental Engineering Science. Vol. 25. No. 5 p. 697–702. DOI 10.1089/ees.2007.0081.

LASHEEN M., AMMAR N., IBRAHIM H. 2012. Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: Equilibrium and kinetic studies. Solid State Sciences. Vol. 14 p. 202–210. DOI 10.1016/j.solidstatesciences.2011.11.029.

LI J., PAN Y., XIANG C., GE Q., GUO J. 2006. Low temperature synthesis of ultrafine A-Al_2O_3 powder by a simple aqueous sol–gel process. Ceramics International. Vol. 32 p. 587–591.

LI X., WANG C., TIAN J., LIU J., CHEN G. 2020. Comparison of Adsorption Properties for Cadmium Removal from Aqueous Solution by Enteromorpha Prolifera Biochar Modified with Different Chemical Reagents. Environmental Research. Vol. 186, 09502. DOI 10.1016/j.envres.2020.109502.

LIANG S., GUO X., FENG N., TIAN Q. 2010. Effective removal of heavy metals from aqueous solutions by orange peel xanthate. Transactions of Nonferrous Metals Society of China. Vol. 20 p. 187–191. DOI 10.1016/S1003-6326(10)60037-4.

MADDODI S.A., ALALWAN H.A., ALMINSHID A.H., ABBAS M.N. 2020. Isotherm and computational fluid dynamics analysis of nickel ion adsorption from aqueous solution using activated carbon. South African Journal of Chemical Engineering. Vol. 32 p. 5–12. DOI 10.1016/j.sajce.2020.01.002.

MARTIN LARA M.A. 2008. Caracterización y aplicación de biomasa residual a la eliminación de metales pesados [Characterization and application of residual biomass to the removal of heavy metals]. Universidad de Granada. ISBN 9788469140956 pp. 424.

MERRIKHPOUR H., JALALI M. 2013. Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. Clean Technologies and Environmental Policy. Vol. 15 p. 303–316. DOI 10.1007/s10098-012-0522-1.

MORENO-SADER K., GARCÍA-PADILLA A., REALPE A., ACEVEDO-MORANTES M., SOARES J. 2019. Removal of heavy metal water pollutants (CO_2^+ and Ni_2^+) using polyacrylamide/sodium montmorillonite (PAM /Na-MMT) nanocomposites. ACS Omega. Vol. 4 p. 10834–10844. DOI 10.1021/acsomega.9b00981.

OLIVERO-VERBEL J., DUARTE D., ECHENIQUE M., GUETTE J., JOHNSON-RESTREPO B., PARSONS P. 2007. Blood lead levels in children aged 5–9 years living in Cartagena, Colombia. Science of the Total Environment. Vol. 372 p. 707–716. DOI 10.1016/j.scitotenv.2006.10.025.

PÉREZ-MARÍN A., AGUILAR M., MESEGUER V., ORTUÑO J., SÁEZ J., LLORÉNS M. 2009. Biosorption of chromium (III) by orange (*Citrus cinensis*) waste: Batch and continuous studies. Chemical Engineering Journal. Vol. 155 p. 199–206.

RIVAS-CANTU R.C., JONES K.D., MILLS P.L. 2013. A citrus waste-based biorefinery as a source of renewable energy: Technical advances and analysis of engineering challenges. Waste Management & Research. Vol. 31 p. 413–420. DOI 10.1177/0734242X13479432.

ROMERO-CANO L., GONZALEZ-GUTIERREZ L.V., BALDENEGRO-PÉREZ L.A., MEDINA-MONTES M. 2016. Preparation of orange peels by instant controlled pressure drop and chemical modification for its use as biosorbent of organic pollutants. Revista Mexicana de Ingeniería Química. Vol. 15. No. 2 p. 481–491.

SATHORN P., CHUDECHA K., VANKHAEW P., CHOOLERT V., CHUENCHOM L., INNAJITARA W., SIRICHOTE O. 2008. Adsorption of phenol from diluted aqueous solutions by activated carbons obtained from bagasse, oil palm shell and pericarp of rubber fruit. Songklanakarin Journal of Science and Technology. Vol. 30. No. 2 p. 185–189.

SEPÚLVEDA L.A., CUEVAS F.A., CONTRERAS E.G. 2015. Valorization of agricultural wastes as dyes adsorbents: Characterization and adsorption isotherms. Environmental Technology. Vol. 36. No. 15 p. 1913–1923. DOI 10.1080/09593330.2015.1016119.

TEJADA-TOVAR C., HERRERA-BARROS A., VILLABONA-ORTÍZ A. 2020. Assessment of chemically modified lignocellulose waste for the adsorption of Cr (VI). Revista Facultad de Ingeniería. Vol. 29. No. 54, e10298. DOI 10.19053/01211129.v29.n54.2020.10298.

TOMAR V., PRASAD S., KUMAR D. 2014. Adsorptive removal of fluoride from aqueous media using *Citrus limonum* (Lemon) leaf. Microchemical Journal. Vol. 112 p. 97–103.

Twenergy 2014. Una iniciativa de endesa por la eficiencia y la sostenibilidad [An endesa initiative for efficiency and sustainability] [online]. [Access 10.10.2017]. Available at: https://twenergy.com/

XU M., LIU J., HU K., XU C., FANG Y. 2016. Nickel(II) removal from water using silica-based hybrid adsorbents: Fabrication and adsorption kinetics. Chinese Journal of Chemical Engineering. Vol. 24 p. 1353–1359.

YANNI S.F., WHALEN J.K., MA B. 2010. Crop residue chemistry, decomposition rates, and CO_2 evolution in Bt and Non-Bt corn agroecosystems in North America: A review. Nutrient Cycling in Agroecosystems. Vol. 87 p. 277–293. DOI 10.1007/s10705-009-9338-8.