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Assessment of Chemically Modified Lignocellulose Waste for the Adsorption of Cr (VI)

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Abstract

Chromium (Cr(VI)) presents carcinogenic and mutagenic effects in living beings. Biosorption is an alternative to conventional technologies for the treatment of waste water. The aim of this study was to assess the use of corncob and orange peels modified with citric acid and calcium chloride, respectively, for the removal of Cr(VI) using a batch system taking into account pH and particle size. Biomaterial were characterized using an elemental and chemical analysis, and FTIR, in which was evidenced the presence of hydroxyl, carbonyl and carboxyl groups, belonging to the cellulose and lignin that are attributed for the presence of active centers which intervene in the adsorption process. Adsorption experiments through batch system were performed using a solution of potassium dichromate at 100 ppm, 150 rpm, varying pH (2, 3, 4 and 6) and particle size (0.355, 0.5 and 1 mm). From de results was found that maximum removal percentage was obtained at pH 2 and particle size of 0.355 using corncob and orange peels. Final concentration of Cr(VI) was determined by using the standard method ASTM D1687-02 with 1,5-diphenylcarbazide at 540 nm. Adsorption kinetics and isotherms were assessed with the best conditions found, in which the experimental data was adjusted to the Pseudo-second order and Freundlich models, respectively. R^2 value greater than

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0.95 suggests that the process is controlled by a chemical reaction leading the formation of multilayers. The performance of the biomass in terms of q_0 was found to be: corncob>orange peels>corncob modified>orange peels modified.

Keywords: biosorption; chromium (VI); freundlich; pseudo-second order.

Evaluación de residuos lignocelulósicos modificados químicamente en la adsorción de Cr (VI)

Resumen

El Cr(VI) tiene efectos cancerígenos y mutagénicos en seres vivos. La bioadsorción se presenta como alternativa a las tecnologías convencionales para tratamiento de aguas residuales. El objetivo del presente estudio fue evaluar el uso de la tusa de maíz modificada con ácido cítrico y la cáscara de naranja con cloruro de calcio, para la remoción de Cr (VI) en sistema por lotes evaluando el efecto del pH y el tamaño de partícula. Los biomateriales se caracterizaron por análisis químico, elemental y FTIR, evidenciando la presencia de grupos hidroxilo, carbonilo y carboxilo, pertenecientes a la celulosa y la lignina a estos se les atribuye propiedades de centros activos intervinientes en el proceso de adsorción. Los experimentos de adsorción por lotes se realizaron utilizando una solución de Dicromato de potasio a 100 ppm, 150 rpm pH 2, 3, 4 y 6 y tamaños de partícula 0.355, 0.5 y 1 mm, encontrándose que los porcentajes máximos de remoción se obtuvieron a pH 2 y tamaño de partícula 0.355 usando tusa de maíz y cáscara de naranja; la concentración final del metal se determinó por el standard método ASTM D 1687-02 con 1.5-difenilcarbazida a 540 nm. Se evaluó la cinética e isothermas a las mejores condiciones encontradas, obteniéndose que los datos experimentales fueron ajustados al modelo de Pseudo-segundo orden y Freundlich, respectivamente, con $R^2 > 0.95$; esto sugiere que el proceso es controlado por reacción química y sucede en multicapas. Se obtuvo el siguiente desempeño de las biomasas en términos q_0 : tusa de maíz>naranja>tusa de maíz-mod>naranja-mod.

Palabras clave: biosorción; cromo (VI); freundlich; pseudo-segundo orden.

Avaliação de resíduos lignocelulósicos modificados quimicamente na adsorção de Cr (VI)

Resumo

O Cr (VI) tem efeitos cancerígenos e mutagênicos em seres vivos. A bioadsorção apresenta-se como alternativa às tecnologias convencionais para tratamento de águas residuais. O objetivo do presente estudo foi avaliar o uso do sabugo de milho modificado com ácido cítrico e a casca de laranja com cloreto de cálcio, para a remoção de Cr (VI) em sistema por lotes avaliando o efeito do pH e o tamanho de partícula. Os biomateriais caracterizaram-se por análise química, elementar e FTIR, evidenciando a presença de grupos hidroxilo, carbonilo e carboxilo, pertencentes à celulose e à lignina; a estes se lhes atribui propriedades de centros ativos intervenientes no processo de adsorção. Os experimentos de adsorção por lotes realizaram-se utilizando uma solução de Dicromato de potássio a 100 ppm, 150 rpm pH 2, 3, 4 e 6 e tamanhos de partícula 0.355, 0.5 e 1 mm, encontrando-se que as porcentagens máximas de remoção obtiveram-se a pH 2 e tamanho de partícula 0.355 usando sabugo de milho e casca de laranja; a concentração final do metal determinou-se pelo standard método ASTM D 1687-02 com 1.5-difenilcarbazida a 540 nm. Avaliou-se a cinética e isotermas às melhores condições encontradas, obtendo-se que os dados experimentais foram ajustados ao modelo de Pseudo-segunda ordem e Freundlich, respectivamente, com $R^2 > 0.95$; isto sugere que o processo é controlado por reação química e sucede em multicamadas. Obteve-se o seguinte desempenho das biomassas em termos q_0 : sabugo de milho > laranja > sabugo de milho-mod > laranja-mod.

Palavras chave: bioadsorção; cromo (VI); Freundlich; pseudo-segunda ordem.

I. INTRODUCTION

Surface and underground water pollution by toxic heavy metals is the product of dumping industrial effluents [1]. Chromium is a heavy metal dumped at high concentrations to the environment, which is caused by industrial activities such as the fabrication of fertilizers, textiles, photography, pigments, tannery, electroplating, electronic manufacture, among others [2, 3]. After coming in contact with water, this metal is found in two oxidation states: Cr(III) and Cr(VI). Usually, Cr(VI) is found as chromate ions (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$), which enter easily in contact with biologic barriers, presenting carcinogenic and mutagenic behaviors, besides, Cr(VI) is 500 more times toxic and moves better than Cr(III) [5, 6]. Although Cr(III) is not toxic, when is encountered in aqueous solutions may become toxic by oxi-reduction to Cr(VI) [7].

Several methods have been reported for the removal of this metal due to the high resistance to degradation and biomagnification, such as: precipitation, oxidation, reduction, ionic exchange filtration, electrochemistry treatment, membrane technology, neutralization, electrocoagulation, inverse osmosis, catalytic oxidation, bioremediation, electrokinetic and evaporation [8-10]. However, implementation of these technologies implies high consumption of energy, operational costs, chemical additives, sludge accumulation and low efficiency at low concentrations. In this context, biosorption is an alternative against the elimination of heavy metals from industrial effluents with the aim to achieve high removal percentages, since the adsorbents from agroindustrial wastes present excellent properties for maintenance, low cost, easy processing, good reusability and wide availability [2, 9]. Among the materials widely studied with excellent results for the removal of Cr(VI) in aqueous solutions, are found: peels of lime [7], rice and lychees [4, 5], orange [11], apple [12], nut [13, 14], lemon [15] plantain [10, 16], among others [3, 17, 18]. Hence, this study compares the Cr(VI) adsorption capacity using orange peels and corncob as bioadsorbents, performing a batch system. Biomass was chemically modified with citric acid (corncob) and calcium chloride (orange peel) with the aim to determine the effects of the functional groups to the adsorption capacity of Cr(VI) ions.

II. MATERIALS AND METHODS

A. Preparation and characterization of the bioadsorbents

Orange peels and corncob were washed with distilled water and dried at 70 °C for 24 h, and then the particle size was reduced by using a rolling mill and classified with sieving through 1, 0.5 and 0.555 mm meshes. Biomaterials were characterized through elemental analysis using AOAC 949.14 method to determine the percentage of carbon, nitrogen and hydrogen. The content of lignin was determined by photocalorimetry, and content of pectin and hemicellulose by acid digestion, cellulose and ashes by basic digestion using thermogravimetry. Fourier transformed infrared spectroscopy (FTIR) was performed to determine the functional groups that intervene in the adsorption process by using a NICOLET 6700 with an absorbance range between 4000 and 500 cm^{-1} .

B. Modification of biomaterials

Corn cob was modified chemically by mixing 13.5 g of biomass with 33.75 mL of a 0.6 M citric acid solution at 60 °C for 2 h [14]. Orange peels crosslinking was achieved by putting in contact 20 g of biomass with 500 mL of 0.2 calcium chloride solution at 200 rpm for 24 h [19]. After the treatment with citric acid and calcium chloride, the products were washed several times with distilled water to remove the excess of reactants, and then were filtered and dried at 60 °C for 24 h [1].

C. Adsorption experiments using a batch system

A 100 ppm solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was used for the adsorption experiments, in which 0.5 g of bioadsorbent was added to 100 mL of the solution at different pH (2, 3, 4 and 6) and the particle size defined previously. The solution was placed into an incubator shaker IN-666 at 150 rpm and room temperature for 2h. Then, 0.5 N solutions of HCl and NaOH were used to adjust pH. Moreover, Cr(VI) concentration was measured following the standard method ASTM D 1687-02, in which 1.5-Diphenylcarbazide was used to be read at 540 nm

in an UV-Vis spectrophotometer Shimadzu UV 17000. Quantity of adsorbed Cr(VI) in the biomass was determined through the Equation (1).

$$q(\text{mg/g}) = \frac{(C_o - C_f)V}{m} \quad (1)$$

Where C_o and C_f (mg/L) are the initial and final concentration of Cr(VI), respectively, V (L) is the solution volume and m (g) is the bioadsorbent mass used in the experiments.

D. Adsorption kinetics and isotherms

Adsorption kinetic was studied to determine the equilibrium time in which the biologic material reaches the highest adsorption of Cr(VI). Experiments were performed putting in contact 0.5 g of biomass with 100 mL of Cr(VI) solution at 100 ppm, using the best conditions for pH and particle size as determined previously. Aliquots of 5 mL were taken each certain time between 10 and 330 minutes [10].

Adsorption isotherms were performed to describe the equilibrium of the solute between the solid and liquid phases. Experiments consisted in using different initial concentrations of Cr(VI) (25, 50, 75 and 100 ppm), taking 0.5 g of biomass with the best condition established previously. The contact time between the biomass and the solution depended on the equilibrium time achieved in the adsorption kinetics [11].

III. RESULTS

A. Characterization of biomaterials

Elemental composition of the biomass is shown in Table 1. Carbon content was determined to be 44.4% for the orange peels and 40.0% for the corncob. Results provided the presence of hydrogen, nitrogen and other biopolymers which are usual in this type of biomass, showing similar information as is reported in the literature by other authors [13, 20].

Table 1. Elemental composition of Orange peels and corncob.

Parameters	Orange peels	Corncob	Analytical method
Carbon	44.40 %	40.00 %	AOAC 949.14
Hydrogen	6.21 %	3.28 %	AOAC 949.14
Nitrogen	0.81 %	0.45 %	AOAC 984.13
Pectin	18.10 %	4.88 %	Acid digestion – thermogravimetric
Lignin	7.14 %	17.11 %	Photocolorimetry
Cellulose	14.28 %	19.90 %	Digestion - thermogravimetry
Hemicellulose	7.02 %	7.00 %	Acid digestion – thermogravimetric
Ashes	2.04 %	4.23 %	Digestion - thermogravimetry
Minerals and others	6.39 %	3.15 %	EAA graphite furnace

Biomass was analyzed through FTIR with the aim to determine the chemical structure of the bioadsorbent materials, and those functional groups with affinity towards heavy metal ions such as Cr(VI). In Figure 1, the infrared spectra show the results for the unmodified and modified corncob after the adsorption process.

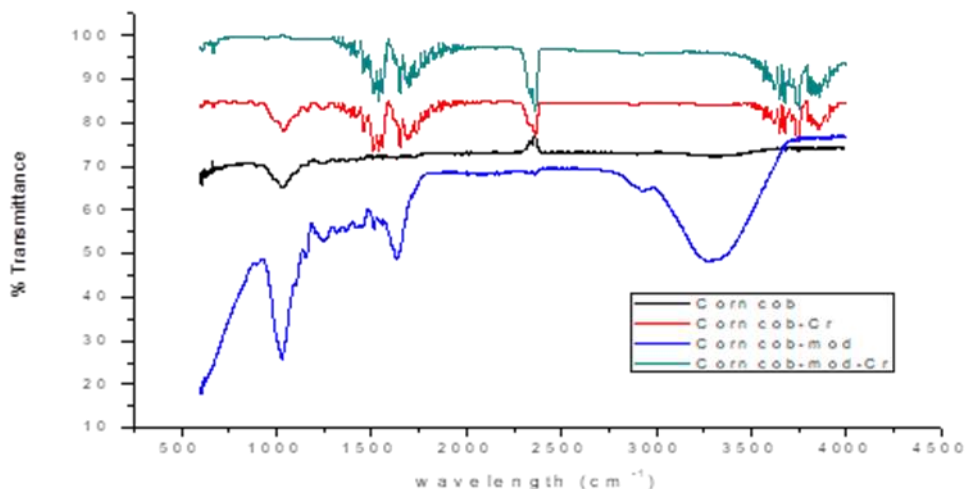


Fig. 1. FTIR analysis for the unmodified and modified corncob and after the adsorption of Cr(VI).

In Figure 2, FTIR spectra shows the results for the unmodified and modified orange peels, before and after the adsorption process.

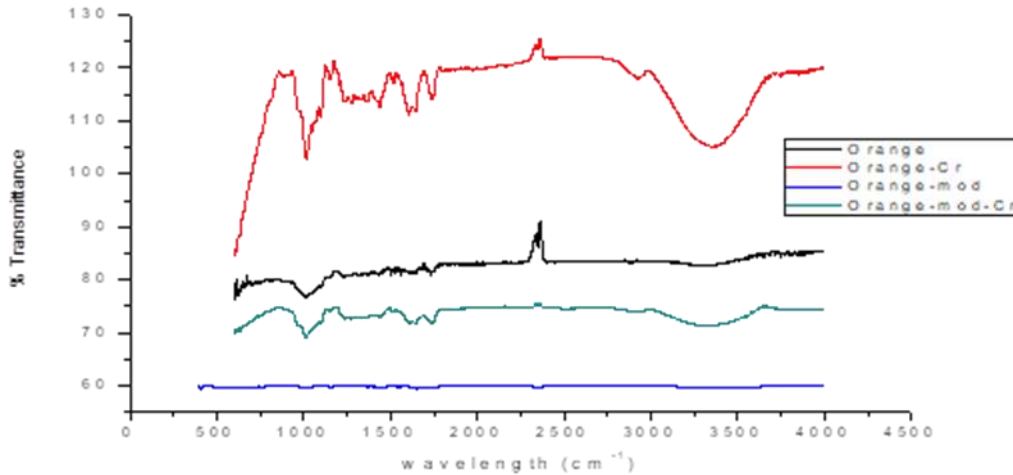


Fig. 2. FTIR analysis of the unmodified and modified orange peels and the adsorption of Cr(VI).

B. Effect of pH and particle size

Adsorption is influenced by the pH of the solution affecting the superficial charge of the adsorbent, the ionization grade and the specie of the sorbate [16]. In Figure 3a is evidenced the effect of pH in the removal percentage of Cr(VI), observing an increasing in the adsorption percentage of the biomaterial as pH decreases in the solution. Removal percentages of 39.8% and 30.6% were achieved for corncob and orange peels at pH 2, respectively.

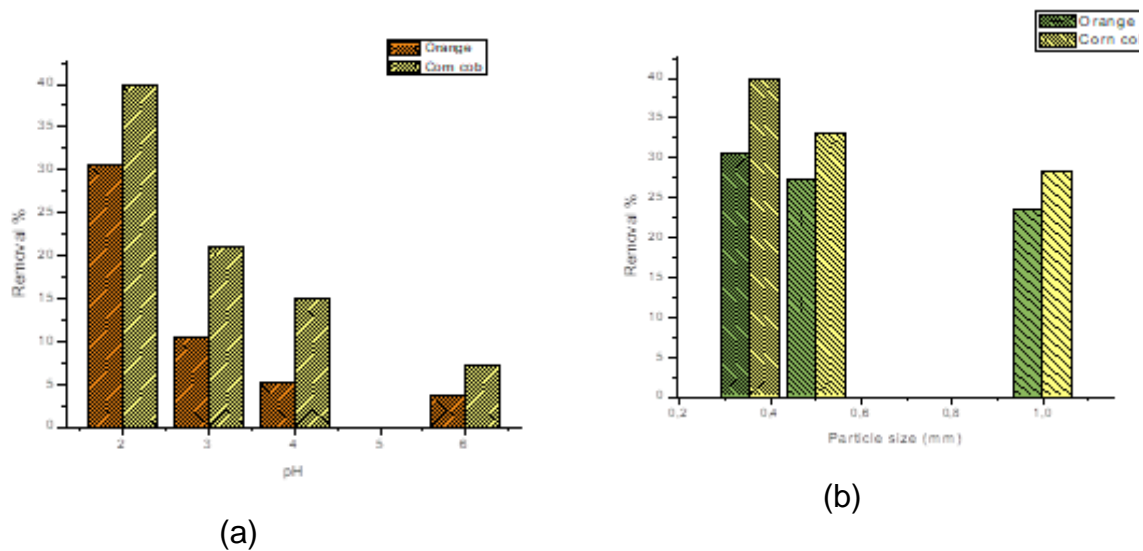


Fig. 3. Effect of (a) pH and (b) particle size in the removal percentage of Cr(VI).

C. Effect of contact time

The study of contact time provides information related to the practical uses of the sorbent, as well as the velocity of the sorption process [25]. The effect of contact time during the removal of Cr(VI) using orange peels and corncob before and after modification, is shown in Figure 4. From the curve is evidenced that the elimination of Cr(VI) increased and the equilibrium was achieved at 270 min.

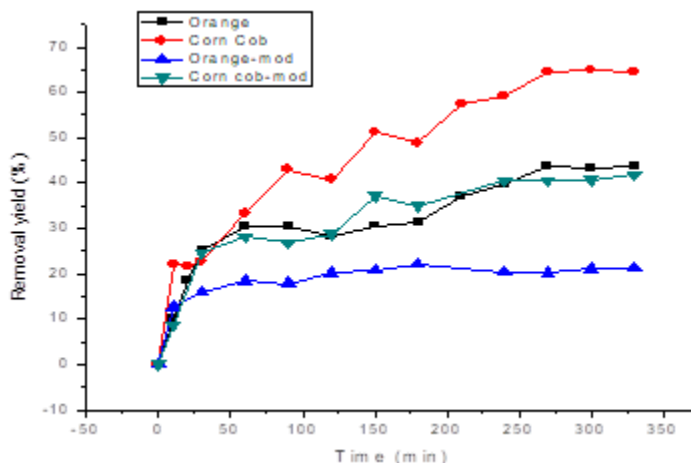


Fig. 4. Kinetics in the removal of Cr(VI).

D. Kinetic adsorption

Experimental data obtained was adjusted to the kinetic models of Pseudo-first order [23], Pseudo-second order [26] and Elovich [13]. In Figure 5a is shown the curves for the unmodified and modified orange peels after the adsorption of Cr(VI), and in Figure 5b is presented the curve for the case of corncob.

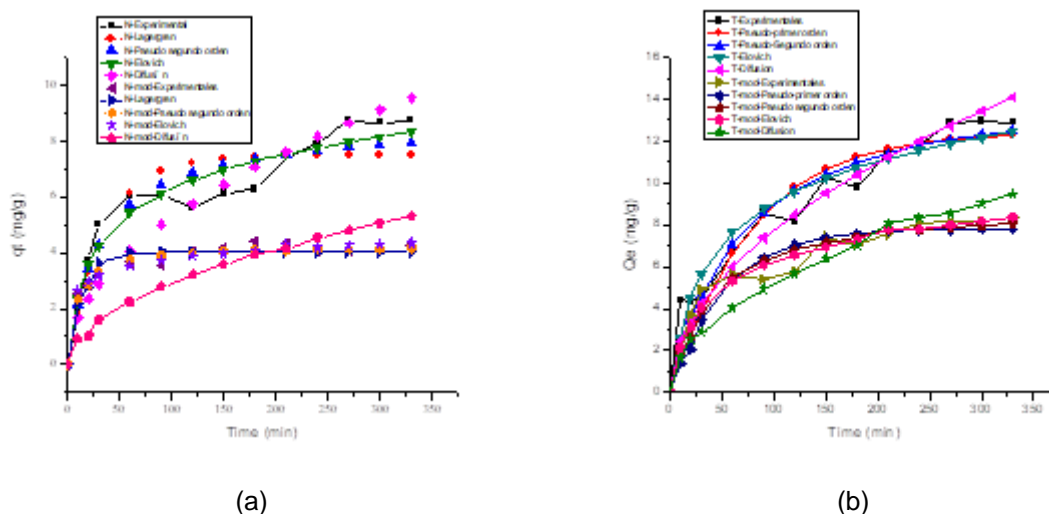


Fig. 5. Experimental data adjusted using (a) unmodified and modified orange peels and (b) unmodified and modified corncob.

The parameters valued for the adjustment of the models, the sum of the error (SS) and the correlation coefficient (R^2) are shown in Table 2.

Table 2. Parameters for the adjustment of the adsorption of Cr(VI) using unmodified and modified orange peels and corncob.

Model	Parameter	Orange	Modified orange	Corncob	Modified corncob
Pseudo-first order	q_{e1}	7.479	4.022	12.483	7.809
	k_1	0.028	0.079	0.0127	0.019
	SS	11.762	0.872	17.478	6.285
	R^2	0.930	0.974	0.969	0.961
Pseudo-second order	k_2	0.004	0.029	0.001	0.003
	q_{e2}	8.664	4.268	15.052	9.000
	SS	7.192	0.331	11.841	3.560
Elovich	R^2	0.957	0.989	0.975	0.977
	β	0.592	2.062	0.353	0.559
	α	0.699	11.581	0.695	0.578
	SS	4.887	0.351	10.545	2.471
	R^2	0.971	0.989	0.974	0.984

E. Adsorption equilibrium

The adjustment of the experimental adsorption equilibrium data of Cr(VI) ions using modified and unmodified orange peel and corncob are shown in Figure 6. The Langmuir and Freundlich isothermal models were evaluated by nonlinear regression in order to establish the driving forces governing the interaction

between adsorbate and adsorbent and the adjustment parameters are shown in Table 3.

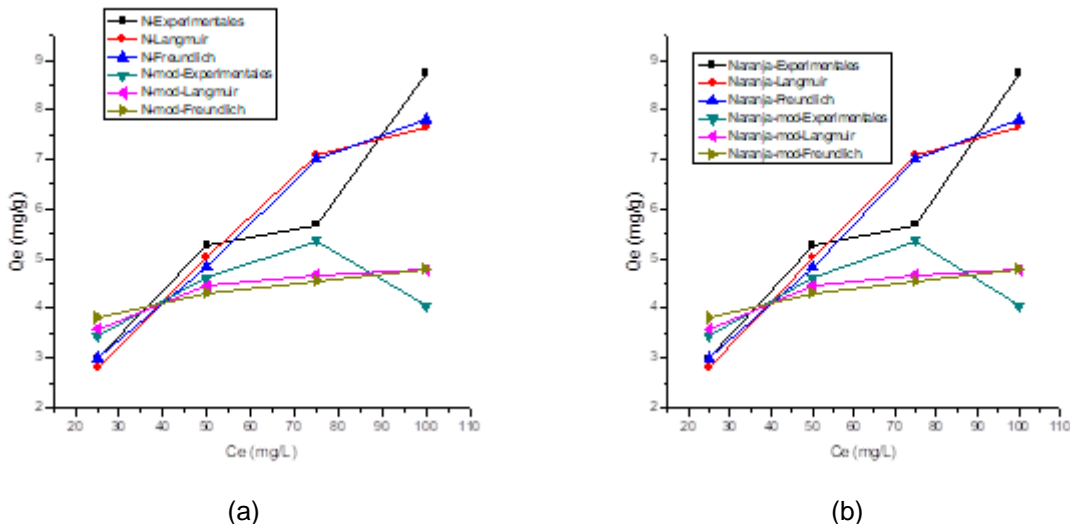


Fig. 6. Adjustment to adsorption isothermal models using: (a) orange before and after modification with CaCl₂ and (b) corncob before and after modification.

Table 3. Parameters of Freundlich and Langmuir for Cr(VI) adsorption.

Model	Parameters	Orange	Modified Orange	Corncob	Modified Corncob
Langmuir	Q _{max}	12.292	4.952	14.813	208.925
	B	0.029	0.334	0.127	0.001
	SS	3.239	1.075	1.645	7.057
	R ²	0.899	0.685	0.979	0.830
Freundlich	K _f	0.833	3.117	3.035	0.161
	1/n	0.555	0.098	0.399	0.940
	N	1.801	10.204	2.506	1.064
	SS	2.845	1.447	0.767	6.974
	R ²	0.911	0.534	0.990	0.828

IV. DISCUSSION

The spectra of unmodified biomasses before the adsorption process show peaks at wavelengths of 3300 cm⁻¹, characteristic of hydroxyl group (-OH) stretching which according to the literature are in the range of 3400-3000 cm⁻¹ [21]. In addition, peaks around 1732 cm⁻¹, 1615-1684 cm⁻¹, 1558 cm⁻¹, and 1235 cm⁻¹ were also detected, corresponding to the stretching of the carbonyl groups (C=O), double bonds between carbons (C=C), bonds between carbon atoms and hydrogen (C-H), and bonds between carbons and oxygen (C-O), respectively [20]. These functional

chemical groups are characteristic of the chemical structures of the carboxylic, aromatic, alcohol, methyl and methoxy groups present in the pectin, hemicellulose and lignin components of the studied biomasses [3].

The corncob and orange peel after modification with citric acid and calcium chloride, respectively, show a widening in the peaks between 3000 to 3500 cm^{-1} corresponding to the vibration of the hydroxyl groups; it is also observed that the peak about 1300 cm^{-1} corresponding to the bonds between carbon and oxygen. In the corncob modified with citric acid the creation was presented in 1680 corresponding to the presence of carboxylic acids, confirming that the modification was effective. On the other hand, in the spectrum of the orange peel after the modification with calcium chloride a peak between 540 and 700 cm^{-1} appeared corresponding to the presence of chloroalkanes in the structure of the material, thus confirming the effectiveness of cross-linking with CaCl_2 [19]. The spectra of the biomaterials after the adsorption process show that most of the peaks present a considerable increase in the intensity and width of the bands, due to a slight variation in the frequency of adsorption, which could be attributed to the union of the Cr (VI) ions with the different chemical groups present in the biosorbents [15].

The results obtained can be attributed to the fact that at lower pH, the surface of the biosorbent is highly protonated by the H^+ ions, so there is a greater attraction between these and the chromium ions; in the pH range 2-6, the predominant form is $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , this last one being the predominant species at acid pHs [6]. The diminution of electrostatic attraction causes the decrease of adsorption as the pH of the solution increases, which is caused by the competition between the anionic species of chromium (HCrO_4^- and CrO_4^{2-}) and the OH^- ions in the solution for adsorption in active spots which leads to the generation of repulsive forces between the Cr (VI) ions and the biosorbent, which inhibits adsorption and consequently decreases adsorption of Cr (VI), being the electrostatic interaction a predominant mechanism in the elimination of Cr (VI) using orange peel and corncob [5]. A similar behavior has also been reported previously using rice husks [5], walnut shells [13], and other materials of vegetal origin [3, 22].

The adsorption takes place mainly inside the particles, on the walls of the pores at specific points. The amount of adsorbate (solute) that can be adsorbed is directly proportional to the volume of the pores, and this volume is directly proportional to the external area. In Figure 3b, the particle size is related to the percentage of adsorption of Cr (VI) using orange peel and corncob. The highest removal percentage obtained for both biomasses at pH 2.0 was achieved using the smallest particle size evaluated, that is 0.35 mm (~31% for orange peels and ~40% for corncob). This behavior may indicate the possibility that adsorption of metal ions may also occur inside biomass particles through the porosities of these biomaterials. In addition, a small particle has a larger surface area, increasing the number of pores per unit mass [24]. This means that as the size of the particles decreases, the number of active centers per unit increases and the adsorption capacity increases [15]. In the present study, corncob showed a higher percentage of Cr (VI) ion removal than the orange peel, at the pH conditions and particle size evaluated; this may be due to the higher content of cellulose and lignin in the structure of the material [22].

Figure 4 shows that it gives a fast elimination of Cr (VI) in the initial stages of the process using unmodified biomass, which may be due to the availability of the uncovered surface and the active sites on the adsorbent surface [22]. The results obtained from the different Cr (VI) adsorption tests carried out with the modified biomass, reflected a decrease in the adsorption potential of both biomass according to Figure 3. The highest removal percentage obtained by the corncob without modify was 64.5% after 270 min and modified it was 41.8% after 330 min; on the other hand, the unmodified orange peel obtained 43.7% removal and a modified 21.2%, after 330 min. This could occur due to the surface coating of the biomass instead of chemical modification [9, 25].

The maximum adsorption capacity for the orange peel and the unmodified corncob was determined with equation 1 and was obtained after 270 minutes after the start of the process, when equilibrium was reached. From the adjustment of the data obtained, the sum of errors (SS) and the correlation coefficient (R^2) of Table 2, it was established that the Pseudo-Second order model describes the behavior of

the adsorption process using the orange peel and the unmodified corncob, therefore it is established that the ion can be adsorbed by two active sites of the biomass and that the process occurs by chemisorption due to the formation of chemical bonds between adsorbent and adsorbate on the surface [12]. However, the Elovich model is also a good fit, so it can be said that the adsorption of Cr (VI) also takes place inside the pores of the bioadsorbent material particles and that their active sites are heterogeneous, so they exhibit different activation energies throughout the adsorption process [24]. The adsorption kinetics of Cr (VI) on orange peel modified with Calcium Chloride and corncob modified with citric acid, was adjusted by the Pseudo-Second order and Elovich models, this suggests that the speed limiting step of this adsorption system can be controlled by chemisorption that involves valence forces by sharing or exchanging electrons between sorbent and sorbate [18, 21, 24]. Similar conclusions were documented in the removal of Cr (VI) for ground biosorbents of ground tea and coffee [20], pineapple peels [26], and sweet lime peel [18].

From Figure 6, it is established that the isothermal model that describes in a better way the adsorption of Cr (VI) for the orange peel and the modified and unmodified corncob, considering values recorded for the statistical error (SS) and the coefficient regression (R^2) (Table 3), is that of Freundlich. According to this model the surface of the biomass is heterogeneous, in addition during the adsorption process multilayers are formed on the surface of the biomaterials with an uneven distribution of heat and adsorption affinities on the heterogeneous surface, and that the active sites of Sorption are first occupied by strong bonds, and such force decreases as they are occupied by Cr (VI) ions [20, 26].

The value of the Freundlich constant n is in the range 1-10 which indicates that the chemical bonds formed between Cr (VI) and adsorbent are strong, and that the adsorption process is favorable. The adsorption intensity, given by the Freundlich parameter (n) is high compared to other works using adsorbent materials of plant origin for Cr (VI) [24, 26]. The Freundlich parameter (n) confirmed that the process can be classified as favorable for adsorption [10, 21].

V. CONCLUSIONS

The characterization of the biomaterials shows the presence of hydroxyl, carbonyl and carboxyl groups, belonging to cellulose and lignin, which are attributed to participation in the adsorption process. It was found that the best conditions for the removal of Cr (VI) using corncob and orange peel are pH 2 and particle size 0.355. The adsorption kinetics were adjusted by the Pseudo-Second order model, and the isotherms by the Freundlich model, which suggests that the process is controlled by chemical reaction and occurs in multilayers. The corncob has a Cr(VI) adsorption capacity greater than the orange peel under all the conditions tested in this study.

AUTHOR'S CONTRIBUTION

Tejada-Tovar performed the chemical modification of the corncob and adsorption tests in the batch system. Also made the writing of the manuscript and set standards journal. Villabona-Ortíz carried out the construction of the pilot equipment in columns, and the adsorption tests in continuous system and the adjustment to models of kinetics, isotherms and rupture curves. Herrera-Barros performed the chemical modification of the orange peel and adsorption tests in batch system. Also made the manuscript edition.

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