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BIOSORPTION AND REMOVAL OF CHROMIUM FROM WATER BY USING MORINGA SEED CAKE (*Moringa oleifera* Lam.)

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This study evaluated the adsorption capacity of chromium from contaminated aqueous solutions by using *Moringa oleifera* Lam. seeds. Parameters such as solution pH, adsorbent mass, contact time between solution and adsorbent, isotherms, thermodynamic, kinetics, and desorption were evaluated. The maximum adsorption capacity (Q_m) calculated to be 3.191 mg g^{-1} for the biosorbent. Activated carbon was used for comparison purposes in addition to the biosorbent. The best fit was obtained by the Langmuir model for both adsorbents. The average desorption value indicated that both the biosorbent and activated carbon have a strong interaction with the metal. The results showed that the biosorbent has advantages owing to its low cost and efficiency in Cr^{3+} removal from contaminated waters.

Keywords: natural adsorbent; waters; desorption.

INTRODUCTION

Moringa, the only genus belonging to the Moringaceae family, consists of fourteen species; *Moringa oleifera* Lam. is the most widely known and used worldwide.[1] In Brazil, the plant was introduced for ornamental purposes and later came to be cultivated for its medicinal and industrial importance and high nutritional value. Moreover, oil extracted from moringa seeds is used in biodiesel production.[2]

Aside from these attractive features, the plant has an additional role: a byproduct known as moringa cake, obtained after oil is extracted from the seeds, is used wastewater treatment.[3]

The use of alternative materials in retaining or removing pollutants from aqueous systems has been studied to lower the expenses of materials and to reduce the treatment of some wastes and contaminated solutions.[4]

Activities such as electroplating and industries that process materials such as leather, cement, steel, and fertilizer are responsible for releasing toxic heavy metals that can cause severe damages to human health and the environment.[5] One such pollutant, chromium, and its compounds persist in the environment in oxidization states of Cr^{3+} and the more toxic Cr^{6+}.[6,7]

Although the trivalent form is less toxic, Cr^{3+} can be extremely dangerous in higher concentrations. Moreover, this element is non-biodegradable in living tissues and is a known carcinogen.[8,9]

Many physical and chemical methods have been developed to remove heavy metals from solution such as ion exchange, chemical precipitation, and membrane separation; however, many of these process are expensive, have low selectivity and result in incomplete removal of pollutants.[10]

Adsorption has emerged as a very efficient process considered effective in removing heavy metals from contaminated aqueous solutions.[11]

For this technique, the most commonly used material is activated carbon, which is highly efficient in various situations.[12] However, its high cost often makes this material unfeasible for practical usage.[5]

For this reason, various low-cost adsorbents have gained increasing attention. In particular, agroindustrial wastes are inexpensive and are easily purchased. These materials often do not require chemical or physical modification for highly efficient pollutant removal even at low concentrations.[13]

The aim of this study was evaluate adsorption behavior in the removal of Cr^{3+} from a contaminated aqueous solution by using a cake of moringa seeds under varied conditions of solution pH, adsorbent mass, contact time, and temperature of the system and the desorption process.

MATERIAL AND METHODS

Material

The moringa seeds were collected in the city of Uberlandia, MG, Brazil, and the fortified solutions were prepared from salts of chromium chloride ($CrCl_3$, Vetec, 97%) and distilled and deionized water. The primary fortified solution (stock) had a concentration of 1000 mg L^{-1}.

All experiments and Cr^{3+} content determinations were conducted at the Laboratory of Environmental and Instrumental Chemistry, located at Center of Agricultural Sciences, State University of Western Parana, Marechal Candido Rondon, PR, Brazil. Analyses by infrared spectroscopy (IR) and scanning electron microscopy (SEM) were performed by the Department of Chemistry, State University of Londrina, Londrina, PR, Brazil.

Cr^{3+} content determination was performed by atomic absorption spectrometry, flame mode (FAAS),[14] by using GBC 932 AA equipment (Victoria, Australia) with chromium hollow cathode and deuterium lamps for background correction operated under the conditions recommended by the manufacturer.

Preparation and characterization of adsorbent material

After removing the pericarp from seeds, and thus the permanence of the material, by heating them in an oven (S36 BioPar BD) at 60 ± 2 °C for 36 h, the seeds were crushed, and the oil was extracted with n-hexane (C_6H_{14}, Nuclear) by using the Soxhlet system.[15] The

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seed cake was obtained, and the material was dried at 70 ± 2 °C for 24 h to complete solvent evaporation. The biosorbent was sieved (14 mesh - Bertel) to standardize the particles; no chemical treatment was applied to the moringa seed cake.

Adsorbent characterization is important for understanding the behavior of the metal removal mechanism from the solid surface[16] and for qualitative assessment of the main functional groups responsible for the metal binding. IR studies were performed by using a spectrometer Infrared Spectrophotometer Shimadzu FTIR-8300 Fourier Transform in the region of 400-4000 cm^{-1} with resolution of 4 cm^{-1}. The spectra were obtained by transmittance with KBr pellets.

Through SEM, the surface morphology of the material was assessed under an FEI Quanta 200 microscope operating at 30 kV. The samples were deposited on a double-sided carbon tape attached to a sample platform and were subsequently coated with gold, using a sputter coater Baltec Scutter SCD 050, to a thickness of approximately 30 nm.

In addition to the aforementioned tests, point of zero change (pH_{PZC}) analysis was performed by adding 50 mg of biosorbent in 50 mL of aqueous potassium chloride (KCl, Vetec, 99%) to 0.05-0.5 mol L^{-1} with initial pH values of 2.0–9.0 were adjusted to 0,1 mol L^{-1} with hydrochloric acid solutions (HCl, Vetec, 37%) and sodium hydroxide (NaOH, Vetec, 99%). After 24 h in contact at 200 rpm, the final pH values of the system were obtained to produce a graph of the initial pH variation depending on the final pH for each KCl concentration; the point at which pH variation was not observed corresponded to pH_{PZC}.[17]

Studies of adsorption depending on the pH and adsorbent mass

The optimal conditions for adsorption were verified by increasing the amounts of adsorbent material from 200 to 1200 mg under various pH conditions of 5.0, 6.0, and 7.0, according to the normal pH range of natural waters; these values were adjusted to 0.1 mol L^{-1} with solutions HCl (Vetec, 37%) or NaOH (Vetec, 99%). In this step, temperature, stirring speed, and contact time of the system were kept constant at 25 °C, 200 rpm, and 90 min, respectively.

The adsorbent material and 50 mL of aqueous solution fortified with metal at 10 mg L^{-1} were placed in 125 mL Erlenmeyer flasks. After 90 min, 10 mL aliquots were removed from this solution and were centrifuged at 3000 rpm (629.77 g) in a centrifuge (Biosystems HT-81C) for 5 min, and determination of Cr^{3+} concentration in the solution was performed through FAAS.[14]

The amount of metal adsorbed on the balance was determined by using Equation 1:

$$Q_{eq} = (C_0 - C_{eq})/mV, \quad (1)$$

where Q_{eq} is the amount of ions adsorbed in the equilibrium (mg g^{-1}), C_0 is the metal initial concentration in the solution (mg L^{-1}), C_{eq} is the remaining concentration of the metal in the solution (mg L^{-1}), V is the volume of solution (L), and m is the mass of adsorbent used (g).

The percentage of metal removed was calculated according to Equation 2:

$$\%R = 100 - (C_{eq}/C_0 \, . \, 100), \quad (2)$$

where % R is the percentage of metal removal from solution by the moringa seeds cake, C_{eq} is the remaining concentration of the metal in the solution (mg L^{-1}), and C_0 is the initial concentration of metal in the solution (mg L^{-1}).

Studies of adsorption depending on contact time with adsorbent

For kinetic studies, the conditions were the same as those used for pH and mass. 400 mg of biosorbent was placed in 125 mL Erlenmeyer flasks containing a 50 mL of solution with metal at 10 mg L^{-1}, and pH was adjusted to 5.0. Stirring speed and temperature were kept constant at 200 rpm and 25 °C, respectively. Aliquots of 10 mL were taken from each flask in 20-min intervals for 3 h. After centrifugation (HT-81C Biosystems) at 3000 rpm (629.77 g) for 5 min, the Cr^{3+} concentration in the solution was determined by FAAS.[14]

Pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion kinetic models were used to analyze the data and to evaluate the predominant mechanism in the process.

Adsorption isotherms

Adsorption isotherms were obtained on the basis on optimal conditions observed in the previous experiments. Aliquots of 50 mL of solution containing 10–90 mg L^{-1} of the metal under pH 5.0 were placed in 125 mL Erlenmeyer flasks with 400 mg of adsorbent and stirred for one period of 120 min at 200 rpm. Subsequently, aliquots were removed and centrifuged (81C-HT Biosystems) at 3000 rpm (629.77 g) for 5 min to determine the metal concentration in solution by FAAS.[14] Mathematical models of Langmuir, Freundlich, and Dubinin–Radushkevich were used to interpret the experimental data.

Thermodynamics of adsorption

The influence of temperature was evaluated in a Dubnoff bath (Nova Técnica, NT232) for five conditions including 25, 35, 45, 55 and 65 °C with a system of 50 mL of fortified solution at pH 5 with 50 mg L^{-1} metal concentration and 400 mg of adsorbent. The system was maintained under stirring at 200 rpm for 120 min. After centrifugation of the aliquots, the Cr^{3+} concentration in the solution was determined by FAAS.[14]

Desorption

The adsorbent material used in the isotherms was separated from the aqueous solution by filtration, washed with distilled and deionized water, and dried in oven at 60 ± 2 °C for 24 h. The mass of biosorbent obtained was placed in contact with 50 mL of HCl (Vetec, 37%) at 0.1 mol L^{-1} and stirred at 200 rpm at 25 °C for 120 min. After this step, the metal concentration in the solution was determined by FAAS, and the desorption percentage was calculated by Equation 3:

$$D = (C_{eq(des.)}/C_{eq(ads.)}) \, 100, \quad (3)$$

where $C_{eq(des)}$ (mg L^{-1}) and $C_{eq(ads)}$ (mg L^{-1}) are the Cr^{3+} concentration desorbed by moringa cake and that adsorbed at equilibrium, respectively.

Comparison with activated carbon

For comparison purposes, synthetic powdered activated carbon, which is a commercial adsorbent widely used for removing pollutants from wastewater,[12] was employed under the same conditions as those used in the isotherms construction of desorption studies for the biosorbent.

RESULTS AND DISCUSSION

Adsorbent characterization

Infrared spectroscopy studies were performed to qualitatively assess the main functional groups responsible for binding with chromium.

This method of analysis provides information about the functional groups that may be present in the structure of the adsorbents.[18] As shown in Figure 1 the adsorbent material showed the following bands: 3328, 2929, 1656, 1535 , 1421, 1234, and 1058 cm^{-1}.

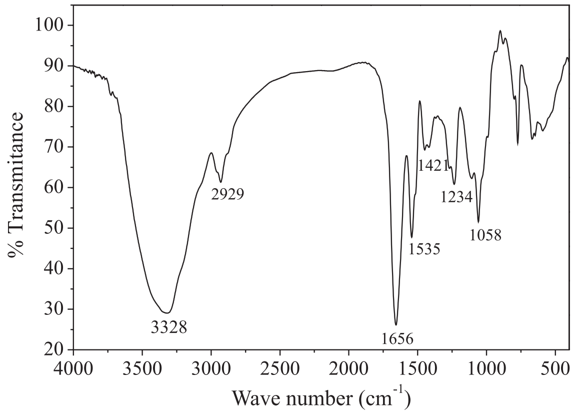

Figure 1. *Infrared spectra of M. oleifera Lam. byproduct*

A strong and broad band at 328 cm^{-1} was observed that may be attributed to the vibration stretching of the O–H bond of hydroxyl groups present in carbohydrates, fatty acids, proteins, units of lignin, cellulose, and absorbed water.[19-21] A contribution in this region for the vibration stretching of the N–H bond of amide groups may be related to the protein content in the moringa seeds.[22] The band at 2929 cm^{-1} characterizes the stretching vibration of the C–H bond of alkane groups.[18] The bands at 1656–1421 cm^{-1} may be attributed to the vibration stretching of C–O bond of amides and carboxylic groups; that at 1234 cm^{-1} can be associated with C–O stretching into phenols.[21] The band at 1058 cm^{-1}, also ascribed to the stretching C–O, suggests the presence of lignin, which includes compounds such as carboxyl groups that provide adsorption sites for the metal ions.[23]

Thus, the adsorption of metals by agricultural waste or industrial byproducts can be attributed to the presence of functional groups of lignin, proteins, carbohydrates, and phenolic compounds that contain carboxyl groups, hydroxyls, phosphates and aminos. Pagnanelli[24] has demonstrated that these groups have the ability to unite heavy metals to form complexes with ions in solution.

SEM analysis revealed that the biosorbent has a fibrous surface with spongy areas and an irregular and heterogeneous structure (Figure 2).

Such a structure facilitates the adsorption process, allowing for the conclusion that the material has a morphological profile suitable for retention of metal species.[22]

Figure 3 shows a graph developed for studying pH$_{PZC}$ for seed cakes of *M. oleifera* Lam.

The results indicated a value of approximately 4.4 for moringa seed cake, (Figure 3); thus, in the case of heavy metals, cation adsorption is favored for pH levels with higher values than the pH$_{PZC}$.[25]

pH dependency and adsorbent mass

The pH levels of the solution influenced the adsorption properties, interfering at the biosorbent surface, and the behavior of the ionic forms of the Cr^{3+} solution. As previously determined, the adsorption of cations is favored for pH values higher than pH$_{PZC}$.

Figure 2. *Image by scanning electron microscopy (SEM) of the adsorbent material under 3,000 magnification*

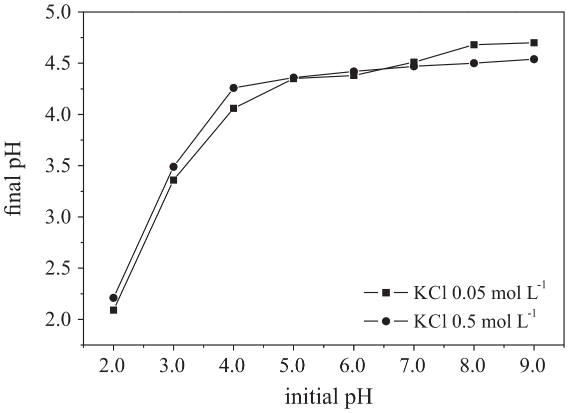

Figure 3. *Plot of zero charge point (pH$_{PZC}$) of* M. oleifera *Lam seeds cake*

Figure 4 shows that the highest rate of metal removal was achieved at pH 5.0. A smaller degree of removal at pH levels of 6.0 and 7.0 can be explained by the fact that the mobility of some elements may be reduced, which can lead to precipitation of insoluble forms[26] at pH values close to neutral. When low pH values are present, H$^+$ and Cr^{3+} ions compete for the active sites of adsorption.[27]

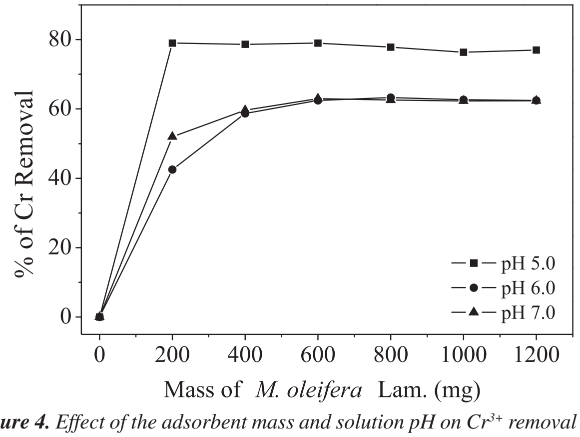

Figure 4. *Effect of the adsorbent mass and solution pH on Cr^{3+} removal (C$_0$: 10 mg L^{-1}, 90 min, 200 rpm, 25 °C)*

The high efficiency of Cr^{3+} removal at pH 5.0 indicates that in the treatment of effluents with various pH ranges, a higher efficiency may not be achieved. However, even under such circumstances, lower adsorption rates of this metal will occur.

In addition, these results may be confirmed by the property of the adsorbent pH_{PZC}, as previously mentioned.

Negligible changes in ion removal were observed when more than 400 mg of adsorbent was used; therefore, this amount was considered optimal for the conditions studied.

Witek–Krowiak[10] reported that the number of active sites available for biosorption depends on the mass of adsorbent used. In this case, for values above 400 mg, a decrease in the adsorbed amount can occur because of reductions in total surface area and therefore in the number of vacant sites available for the process due to agglomerate formation.

Influence of contact time

Figure 5 illustrates the amount of Cr^{3+} removed during the contact time with the adsorbent.

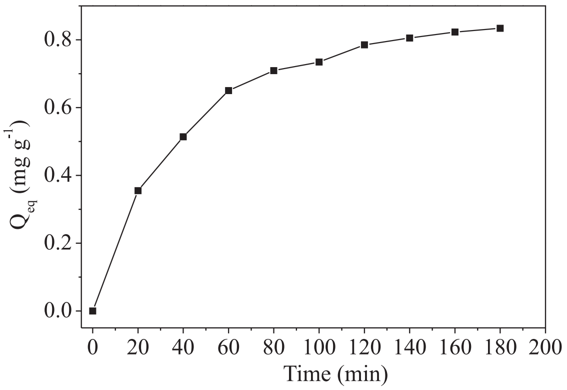

Figure 5. *Amount of Cr^{3+} removed during contact time (C_0: 10 mg L^{-1}; 400 mg, pH 5.0, 200 rpm, 25 °C)*

The rate of removal increased gradually to reach equilibrium at 120 min of contact between the adsorbent and the aqueous solution. The contact time required for the system to reach equilibrium depended on the nature of the biosorbent and amount of available adsorption sites.

To evaluate the kinetic mechanism controlling the biosorption process, the models of pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion were applied.[21]

According to Liu and Liu,[28] the pseudo-first order model, also known as the Lagergren Equation, is represented in its linear form by Equation 4:

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - (K_1/2.303)t, \quad (4)$$

where, Q_{eq} and Q_t is the amount adsorbed in the equilibrium and a particular time (mg g^{-1}), respectively, and K_1 is the constant for pseudo-first order (min^{-1}). Q_{eq} and K_1 values were calculated from the graph of log ($Q_{eq} - Q_t$) by time.

The pseudo-second order model[29] is expressed in the linear form by Equation 5:

$$t/Q_t = 1/K_2Q_{eq}^2 + 1/Q_{eq}, \quad (5)$$

where K_2 is the constant of pseudo-second order (g mg^{-1} min^{-1}). The values of K_2 and Q_{eq} were calculated from the graph of t/Q_t by time.

The Elovich equation represented by Equation 6 is appropriate for systems with heterogeneous adsorption surfaces:

$$Q_{eq} = A + B \ln t, \quad (6)$$

where A and B are constants; A represents the initial velocity of chemisorption and B is related to the extent of surface coverage and chemisorption activation energy.[10] In addition, the intraparticle diffusion mathematical model was employed:

$$Q_{eq} = K_{id}\, t^{1/2} + Ci, \quad (7)$$

where k_{id} (g mol^{-1} $min^{-1/2}$) is the constant of intraparticle diffusion speed and C_i is related to thickness or resistance of the boundary layer in the adsorption process.[30]The obtained graphics and the values of pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion models are illustrated in Figure 6 and in Table 1.

The graphs for the intraparticle diffusion model (6d) initially indicate that the adsorption process is controlled by more than one step; the first portion of the line suggests diffusion by macropores, and the second suggests diffusion by mesopores and micropores of adsorbent.[31] However, the R^2 values for this mathematical model, shown in Table 1 to be 0.954 and 0.914, indicate that this kinetic model does not effectively explain the observed adsorption process.

Table 1 shows the parameters set by the models studied.

For the pseudo-first order model, the values of Q_{eq} (exp.) and Q_{eq} (calc.) did not approach each other even though the coefficient of determination (R^2) is considered satisfactory; thus, the best fit was obtained for the pseudo-second order model. The agreement between the high R^2 value and the proximity between Q_{eq} (exp.) and Q_{eq} (calc.) suggests that the adsorption process has the characteristic of chemisorption as a limiting step.[29]

Adsorption isotherms

The distribution of ions between the solution and biosorbent describes the balance mechanism and can be expressed by one or more isotherm models to provide information about the nature of the adsorption process and the maximum capacity of the sorption material.[26] The adsorption isotherms of the moringa seeds cake and of activated carbon are illustrated in Figure 7.

The equilibrium isotherms show favorable behavior, indicating that the adsorption capacity increased with increasing solution concentration. Adsorption data were adjusted according to mathematical models of Langmuir, Freundlich, and Dubinin–Radushkevich.

The mathematical model of Langmuir considers that the adsorbent has a defined number of active sites, each of which retains only one molecule of adsorbate. In this model, the adsorption energy does not dependent on the amount of material adsorbed, and adsorbed species do not react with each other; adsorption is restricted to the monolayer.[32] The linear expression of the model is given by Equation 8:

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m, \quad (8)$$

where C_{eq} is the equilibrium metal concentration in the solution (mg L^{-1}), Q_{eq} the amount adsorbed at equilibrium per unit mass of adsorbent (mg g^{-1}), Q_m is the maximum adsorption capacity (mg g^{-1}), and b is the biosorption constant related to adsorbent–adsorbate interaction forces (mg L^{-1}).

The essential feature of the isotherm can be expressed by the constant (dimensionless) known as the equilibrium parameter (R_L), expressed by Equation 9:

$$R_L = 1/(1 + bC_0), \quad (9)$$

where C_0 the highest initial concentration (mg L^{-1}) and b the Langmuir constant. If $0<R_L<1$, adsorption is considered favorable.[33]

The model proposed by Freundlich considers that the adsorption

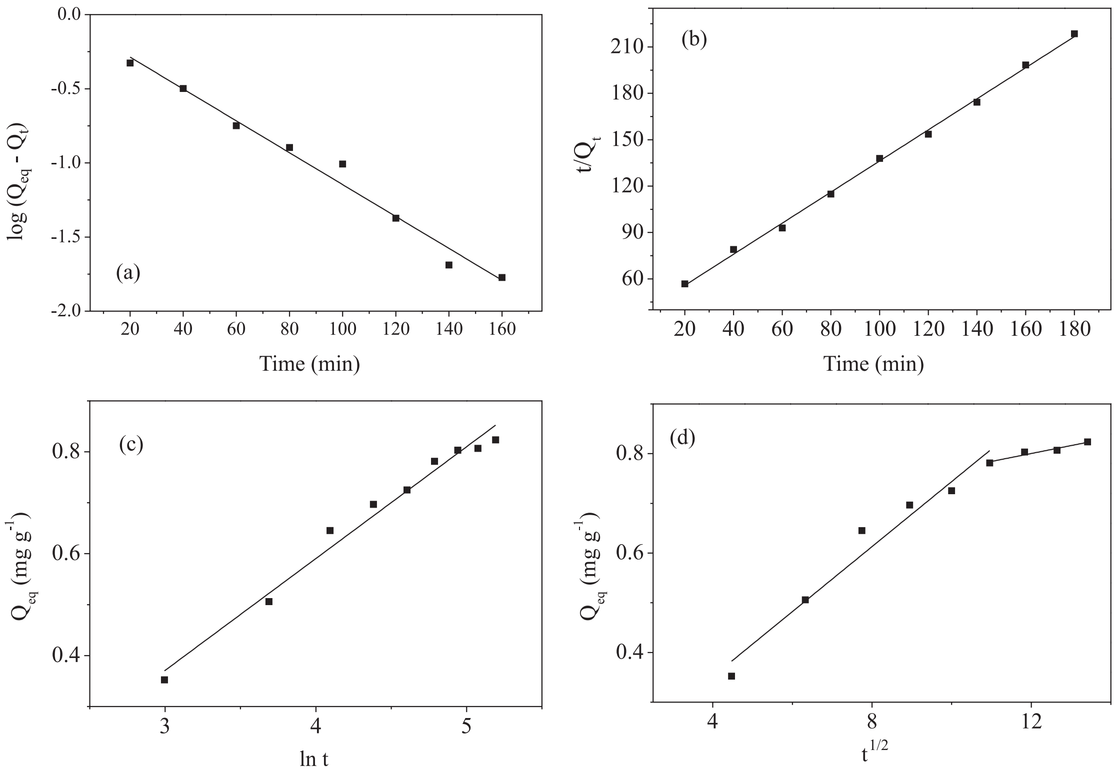

***Figure 6.** Models of (a) pseudo-first order, (b) pseudo-second order, (c) Elovich, and (d) intraparticle diffusion for Cr^{3+} adsorption by moringa seeds cake*

Table 1. Kinetic parameters obtained by studying Cr^{3+} adsorption on the seeds cake of *M. oleifera* Lam

Pseudo-first order		Q_{eq} (exp.) (mg g^{-1})	*Pseudo-second order*		
K_1 (min^{-1})	–0.025	0.824	K_2 (g mg^{-1} min^{-1})		0.039
Q_{eq} (cal.) (mg g^{-1})	0.995		Q_{eq} (cal.) (mg g^{-1})		0.848
R^2	0.979		R^2		0.998
Elovich		*Intraparticle diffusion*			
A	–0.288	K_{t1} (mg g^{-1}min$^{-1/2}$)	0.065	K_{t2}(mg g^{-1}min$^{-1/2}$)	0.016
B	0.219	C_{i1} (mg g^{-1})	0.090	C_{i2} (mg g^{-1})	0.609
R^2	0.978	R^2	0.954	R^2	0.914

of a given substance occurs in multiple layers and is therefore useful for describing adsorption in highly heterogeneous surfaces.[34] The linear expression of the model is expressed by Equation 10:

$$\log Q_{eq} = \log K_f + (1/n)\log C_{eq}, \quad (10)$$

where K_f is the Freundlich constant (mg L^{-1}) and n (dimensionless) indicates adsorption intensity, which is related to the heterogeneity of the adsorbent surface.[35]

The mathematical model of Dubinin–Radushkevich is based on the heterogeneity of the adsorbent surface. This model is widely used for differentiation of a process of physical or chemical nature[5] and is represented by Equation 11:

$$\ln Q_{eq} = \ln Q_d - B_d e^2, \quad (11)$$

where Q_{eq} is the amount of adsorbed metal per unit mass of adsorbent (g mol^{-1}), Q_d is the adsorption capacity (mol L^{-1}), and B_d is a coefficient related to the sorption energy (mol^2 J^{-2}). $\varepsilon$is the Polanyi potential (ε = RT ln (1 + 1/Ceq), in which R is the universal gas constant (kJ mol^{-1} K^{-1}), T is temperature (Kelvin), and C_{eq} is the equilibrium concentration in liquid phase (L mol^{-1}).

The sorption energy (E (kJ mol^{-1})) is calculated by Equation 12:

$$E = 1/\sqrt{-2B_d} \quad (12)$$

The parameters obtained by linearization according the mathematical models studied are shown in Table 2.

The coefficients of determination (R^2) indicate that the adsorbents show similarity among the models studied. That of Langmuir most effectively described the adsorption data for both materials such that the process occurred in the monolayer with sorption energy equivalent to all active sites.[36] Moreover, the value of R_L indicates that the adsorption was favorable in the concentration range studied for the materials prepared.[37]

The maximum adsorption capacity (Q_m) calculated and estimated was 3.191 mg Cr^{3+} per g of moringa seed cake, and the b value (or K_L) was 0.089 mg L^{-1}. The activated carbon showed a maximum adsorption capacity of 12.048 mg g^{-1}, which, given its high cost, is an unfeasible material for certain locations or treatments in larger quantities.

The parameter n (Table 2) resulted in a value of 2.121 for moringa seed cake and 2.218 for activated carbon, suggesting that the metal

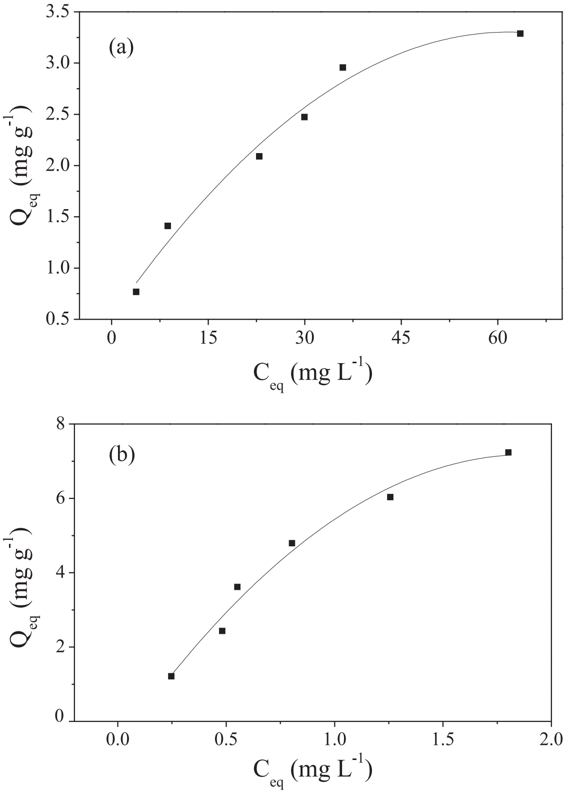

Figure 7. *Adsorption isotherms of Cr^{3+} for (a) moringa seeds cake and (b) activated carbon (C_0: 10 to 90 mg L^{-1}; 400 mg, pH 5.0, 120 min; 200 rpm, 25 °C)*

Table 2. Parameters of the mathematical models of Langmuir, Freundlich, and Dubinin-Radushkevich for Cr^{3+} adsorption on *M. oleifera* Lam. seeds cake and activated carbon

Parameters	Adsorbent	
	M. oleifera Lam.	Activated carbon
Langmuir		
Q_m (mg g^{-1})	3.191	12.048
b ou K_L (L mg^{-1})	0.089	0.814
R_L	0.120	0.013
R^2	0.993	1.000
Freundlich		
K_f (L mg^{-1})	0.457	5.162
n	2.121	2.218
R^2	0.953	0.955
Dubinin-Radushkevich		
Q_d (mol g^{-1})	2.0 e^{-4}	3.0 e^{-4}
E (kJ mol^{-1})	10.000	13.948
R^2	0.968	0.961

adsorption process on the adsorbent occurred favorably once when the n value was between 1 and 10. This result indicates adsorption of ions on the relatively strong biosorbent surface and suggests the presence of high energetic sites occupied first by metals.[10]

The average sorption energy (E) obtained through the mathematical model of Dubinin–Radushkevich differentiates a process of chemical or physical nature.[13] Values of E between 1 and 8 kJ mol^{-1} indicates physical adsorption; those higher than 8 kJ mol^{-1} indicate that the process has a chemical nature.[38] The values obtained in this experiment were 10.000 kJ mol^{-1} for the biosorbent and 13.948 kJ mol^{-1} for the activated carbon; therefore, the type of Cr^{3+} adsorption on the adsorbent materials was likely chemisorption.

Thermodynamic parameters

The state of a solid–liquid system can be set by thermodynamic parameters.[39] The Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated from Equations 13 and 14:

$$\Delta G = -RT \ln K_d, \tag{13}$$

$$\ln K_d = \Delta S/R - \Delta H/RT, \tag{14}$$

where K_d is the ratio between Q_{eq} and C_{eq}, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature used in the experiment (Kelvin). By means of the linear plot of ln K_d depending on the 1/T (where T is the temperature in Kelvin), the values of ΔH and ΔS can be estimated. The obtained line equation shows a slope coefficient corresponding to ΔH/R and a linear coefficient corresponding to ΔS /R.[40]

The increase in temperature caused an increase of the amount adsorbed at equilibrium, thus indicating an endothermic process.[37]

The values of thermodynamic parameters obtained for the adsorption process at various temperatures are shown in Table 3.

Table 3. Thermodynamic parameters for Cr^{3+} adsorption on the seeds cake of *M. oleifera* Lam

Temperature (°C)	Q_{eq} (mg g^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1})
25	2.915	5.273	13.674	28.194
35	3.337	4.991		
45	3.698	4.710		
55	3.828	4.428		
65	3.863	4.146		

Although positive ΔG values are indicated, it can be noted that increases in temperature cause slight decreases of these values; hence, a tendency toward negative values can be observed. Farooq[26] demonstrated that a decrease in ΔG values with increasing temperature results in an increase in process spontaneity.

Positive ΔH values confirm the endothermic nature of the process[37] and indicate increased randomness in the solid–solution interface, which may occur because of the substitution of water molecules previously adsorbed by Cr^{3+} ions.[13]

Although an enthalpy value of less than 40 kJ mol^{-1} characterizes a process of physical adsorption,[41] the other observed parameters such as the value of E and the best fit obtained by the pseudo-second model confirm a chemical nature.

Desorption

Reversibility of the adsorption process, known as desorption, corresponds to the removal of metal binding sites on the surface of the adsorbent whereby H^+ ions are expected to replace cations adsorbed by the ion exchange mechanism.[17] This process gains importance when the employed adsorbent material has high costs relative to the lower costs generated by the process. Depending on the characteristics presented by the material, its reuse it can be ensured in other cycles of adsorptive process.[42]

The data obtained from the adsorption isotherms indicate an average Cr^{3+} removal percentage of 40.48%, of which approximately 16.43% was desorbed. For activated carbon, the average percentage of adsorption was 96.47%, of which approximately 4.33% was desorbed, indicating the occurrence of a strong interaction between the metal and adsorbent. Therefore, ion removal was difficult, which corroborates the results of pseudo-second order model and the values of the

E) obtained by the mathematical model of Dubinin–Radushkevich. Namasivayam[43] determined that low rates of desorption suggest a chemisorption process as the primary mode of pollutant removal by the adsorbent. Therefore, the percentage desorbed cannot be considered satisfactory for a possible reuse of this biosorbent for new adsorption processes.

Other solutions such as sulfuric acid, acetic acid, and nitric acid can be utilized in the desorption process. Under acidic conditions, Cr^{3+} ions are displaced by protons in the active binding sites.[42] In addition to using other extraction solutions or even HCl in other concentrations, the incineration process is an alternative to the final disposal of biosorbent containing this contaminant.

Owing to the low cost and biodegradable nature of the biosorbent, in addition to its abundance after an appropriate treatment such as incineration, the resulting volume of the adsorbent may be introduced in the composition of concrete, bricks, and ceramics. Such usage reduces costs and yields source material with superior mechanical properties.[44] However, such processes may emit toxic gases into the environment.

Therefore, a new cost-effective and efficient system for contaminated water body treatment is necessary to appropriately dispose of waste containing toxic heavy metals from the adsorption processes.

CONCLUSIONS

It can be concluded that moringa seed cake satisfactory removes Cr^{3+} from contaminated solutions.

The obtained results of the pseudo-second order model and the E value indicate that the adsorption process are chemical in nature.

The best fit was observed by the mathematical model of Langmuir for both adsorbents used, demonstrating monolayer adsorption with maximum adsorption capacities (Q_m) of 3.191 mg g^{-1} and 12.048 mg g^{-1} for the biosorbent and activated carbon, respectively. Owing to its low cost, high availability, and biodegradable nature, this byproduct can be considered a viable alternative for the treatment of contaminated aqueous solutions.

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