Biosorption of chromium and nickel from aqueous solution using pine cones, eucalyptus bark, and moringa pods: a comparative study

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Abstract

Low-cost local plants (eucalyptus bark, moringa pods, pine cones) have been successfully used to remove heavy metals from simulated wastewater. Two types of heavy metals were chosen to study the removal capacity, nickel (Ni) and chrome (Cr), with a concentration of 400, 600, 900 ppm. The results show that moringa pods have the best removal capacity for heavy metals with percentages of 90–99% for both metals, Ni and Cr, for the eucalyptus bark the removal capacity percentages reach 50–98%, while for the pine cones revealed a lower removing capacity with percentages of 40–99%, indicating that this is the lowest removal capacity. The data has been best fitted to the Langmuir adsorption model for all plants, while the Freundlich adsorption model could not fit the obtained results at the experimental conditions. The kinetic study has revealed that the first-order kinetic model successfully describes the kinetics of Ni adsorption, while the second-order describes the kinetics of Cr adsorption. The removal of heavy metals (Ni, Cr) was obtained when moringa was used; its highest removal efficiency was reached within 20 minutes. On the other hand, other plants (eucalyptus bark, pine cone) removal efficiency was attained in more than two hours. The removal is remarkable even at a high concentration of heavy metals, especially with the moringa plant.

Key words: eucalyptus bark, adsorption models, heavy metal removal, moringa pods, pine cones, sorbents

Highlights

- A comparison between different local adsorbents which are available at low cost to remove heavy metals from water.
- Introduces three types of adsorbent and compared with moringa as extended results for our previous published study.
- The adsorption kinetics and modeling for heavy metals removal.

NOMENCLATURES

a_L Langmuir constant
C_e final concentration of heavy metal in the solution sample at equilibrium (ppm)
C_i initial concentration of heavy metal in the solution sample before treatment (ppm)
K rate constant of adsorption

K_f Freundlich constant, which is related to the bonding energy (L/mg)
K_L Langmuir equilibrium constant, which is related to the adsorption/desorption energy, the affinity of the
       binding sites
$1/n$ heterogeneity factor and n (g/L)
q_e mass of metal adsorbed at equilibrium (mg of ion/g of metal)
t mixing time in minutes

INTRODUCTION

Sources of heavy metals in natural water include dissolution from natural deposits and discharges of domestic, industrial, or agricultural wastewater. There are two types of metals, non-toxic and toxic metals; non-toxic metals are not harmful to humans and microorganisms, where preferable in small traces in water, such as sodium, iron, manganese, aluminum, copper, and zinc. Toxic metals are harmful to human beings and living organisms in small quantities. These metals can be found in dissolved water like barium, cadmium, chromium, lead, mercury, and silver (Sincero & Sincero 2002). Heavy metal pollution (contamination) can arise from many sources but most commonly from the purification of metals, for example the smelting of copper and the preparation of nuclear fuels. Electroplating is the primary source of chromium and cadmium contamination (Shanker & Venkateswarlu 2011).

The removal of single heavy metals like cobalt (Co) and zinc (Zn) from aqueous solutions using various low-cost adsorbents (Fe_2O_3, Fe_3O_4, FeS, steel wool, coal, and pellets of Mg, Cu, Zn, Al, Fe) was investigated and results show that the pH of the solution was significant and effective on metal adsorption and removal using Fe_2O_3 and Fe_3O_4 (Droste & Gehr 2018)).

Removal of nickel ions from aqueous solutions using pine tree (*Pinus nigra*) materials modified with HCl, was investigated by Argun *et al.* (2005), and the maximum removal efficiency levels obtained were 97% for the modified pine bark and 80% for the modified pine cone. Vikerant Sarin & Pant. (2006) examined the removal of chromium from industrial waste using eucalyptus bark. It was reported that more than 99% of chromium (VI) removal was achieved with a dose of 200 ppm concentration at pH equal to 2. Chromium removal from aqueous solution using peanut shells was also investigated by Tarsina Rabia *et al.* (2012) and found that the maximum chromium removal was 87.5%. Several studies have also investigated the removal of chromium ions using different types of biosorbent, such as Neem leaf powder (Sharma & Krishna (2004), pineapple leaves, (Ponou *et al.* 2011), natural clay, Veli & Alyüz (2007), and eucalyptus roots (Aparna & Gupta 2016).

Sen *et al.* (2015) have reported in a review of different bark biosorption that pine cones, as well as several types of adsorption where bark is used, offers a green alternative to remove heavy metals from industrial waters. A brief survey of the chemical composition and structure of different bark species has been presented. A recent study by Mahamadi (2019) reported trends in sorption capacities were analyzed using ratios of maximum adsorption of multi-metal systems consisting of Pb, Cu, Cd, Zn, Ni, and Cr in binary, binary sorption capacities obtained using pine cone shell bio sorbent Pb(II) using activated carbon from *Eucalyptus camaldulensis* Dehn bark. Ayesha *et al.* (2020) reported many varieties of low-cost adsorbents such as agricultural and industrial solid wastes, natural materials, and bio sorbents developed and tested as effective and economic adsorbents for the removal of low concentrations of copper, nickel(II) ions, and lead from water and wastewater.

In this study, three different types of local plants were selected to examine the removal of nickel (Ni) and chromium (Cr) cations. Pine tree cones, eucalyptus (known as *Keinya* tree among local Jordanians), and moringa were selected. Pine trees are evergreen conifers that belong to the genus *Pinus* in the family Pinaceae. They have a long lifespan that ranges from 100 years to 1000 years. The bark of pine trees was used to make blankets, capes, and costumes. Pine trees were also an

excellent source of fuel. In modern times, pine trees are used for making pencils and other tools (Kat *et al.* 2016). While the *Eucalyptus camalulensis* tree is an important timber, firewood, shelterbelt, and honey tree. It is one of the most widely distributed trees in most arid and semiarid areas. Eucalyptus is a diverse genus of flowering trees and shrubs (including a distinct group with a multiple-stem mallei growth habit) in the myrtle family, Myrtaceae. Members of the genus dominate the tree flora of Australia. There are more than 700 species of eucalyptus, mostly native to Australia, and a very small number are found in adjacent areas of New Guinea and Indonesia. (Sellers 2018). This kind of tree exists on almost every roadside in Jordan. Moringa peregrine occurs naturally in arid or semi-arid countries bordering Somalia and Yemen. In tropical Africa, it is reported in Sudan, Ethiopia, Eritrea, Djibouti, and Somalia.

Moringa in Jordan grows in the southern part in the vicinity of the Dead Sea in 'Ghore Al-Safi', where suitable weather conditions are available. Studies have been conducted since the early 1970s to test the effectiveness of moringa for treating wastewater (Aravind *et al.* (2013), Vieira *et al.* (2009), Kalavathy & Miranda (2010), Matouq *et al.* (2015), Reddy *et al.* (2010). The choice of using these plants in this work is due to their local availability and cheapness.

This study aims to investigate the removal efficiency of heavy metals from aqueous solutions and eventually from wastewater by using local and cheap plants like moringa pods, pine cones, and eucalyptus bark. The investigation process will be achieved through the following specific objectives: (a) testing several local plants for suitability for removing heavy metals from aqueous solution, and (b) comparing the removal capacities of the different plants used and recommending the best one for further investigation.

MATERIALS AND METHODS

Preparation of bio-sorbents

Eucalyptus and pine cones

Pine cones and eucalyptus were collected from the faculty campus, which is located in the eastern part of Amman city. These were then crushed by an electrical grinder to obtain almost fine particles. The particles were soaked in distilled water for approximately 24 hours and during this period a magnetic stirrer was used to assure that the particles were cleaned from any dust. The water was then removed several times until the color become clear brownish, which was naturally produced from both cones and bark. When the color became clear the particles were then washed with dilute nitric acid (0.1 M) for further cleaning of any oil components that might exist and then were cleaned several times with distilled water again. The cleaned particles were dried overnight using an electrical oven at 80 °C. The dried particles were sieved into different mesh sizes (1 mesh, 2 mesh, 2.8 mesh), and then were ready to use as a sorbent.

Moringa pods

Moringa pods were collected from the southern part of Jordan (Matouq *et al.* 2015). Crushed pods were soaked in distilled water for 10 hours and well mixed using a magnetic stirrer to assure that the plants were cleaned, and their brownish colors disappeared by changing the distilled water several times. Diluted nitric acid (0.1 M) was prepared for washing the pods. The pods were washed with distilled water again. The plants then were dried in an electrical oven at 105 ± 2 °C overnight. The dried particles were sieved to different mesh sizes (1 mesh, 2 mesh, 2.8 mesh) and then were ready to use as sorbent.

Preparation of Ni, Cr cations

Two cation solutions ($NiCl_2.6H_2O$ (light green), $K_2Cr_2O_3$ (yellow)) Cr (VI) were prepared, with different concentrations of 400 ppm, 600 ppm, and 900 ppm for both cations. The different concentrations of ppm for Ni and Cr were obtained by preparing a stock solution of 1,000 ppm of Ni, through dissolving 0.405 grams of $NiCl_2.6H_2O$ in 100 volumetric flasks and diluting it to the mark by water to make a 1,000 ppm stock solution. The same procedure was followed with $Cr+$, to prepare a stock solution of 1,000pm, Cr(VI), dissolving 0.283 g of potassium dichromate ($K_2Cr_2O_7$) and diluting to 100 mL in a volumetric flask. The pH value for $NiCl_2.6H_2O$ after dissolving in water was maintained between 3.5 and 4.5, while for $K_2Cr_2O_3$ the pH value was around 6.5. In all experimental work, the temperature was fixed at room temperature (25 °C).

Methods

A calibration curve representing the relationship between concentration and conductivity for each solution were prepared as indicated in Figure 1. Five grams of each sorbent particle was placed in 100 ml solution with different concentrations (400 ppm, 600 ppm, 900 ppm) and then mixed using an overhead stirrer at 700 rpm mixing speed, the reading of the conductivity meter was measured every three minutes. Mixing was stopped after obtaining a constant reading for at least three successive conductivity readings.
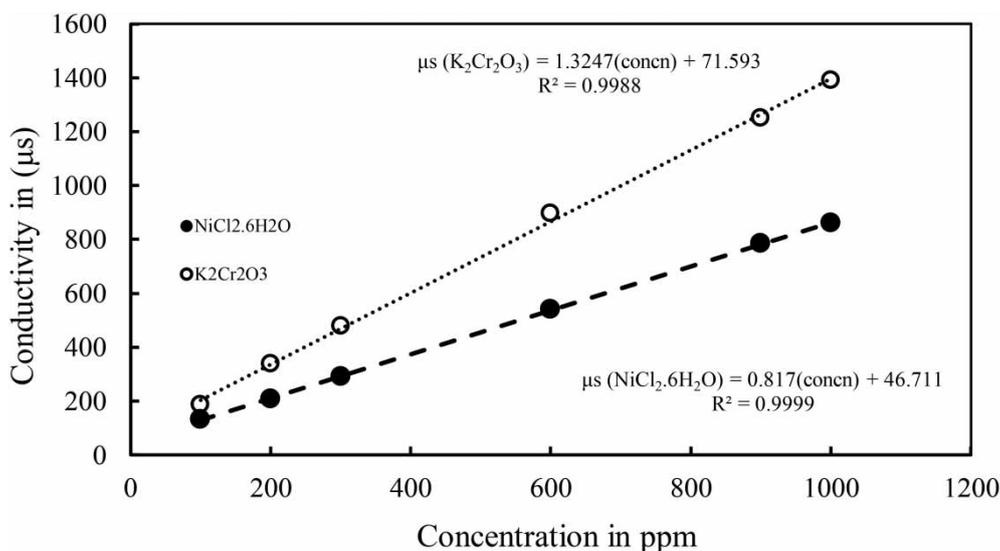
Figure 1 | values of conductivity versus concentration.

Experimental methods

The experimental work was conducted as follows:

1. All bio-sorbent powders were fixed at 5 gm in all the experimental work
2. The batch experimental work took place in a beaker of 200 ml, a solution of 100 of both Cr and Ni was added to 5-gram bio-sorbent at different concentrations.
3. The overhead electrical motor stirrer was placed to keep the solid-liquid mixture in a good homogeneity with mixing at speed of 700 rpm.
4. Concentration readings of the solution were taken every half an hour.
5. The mixing was stopped after 3 hours, depending on the last three readings of conductivity, when it was identical or almost the same reading.

RESULTS AND DISCUSSION

Effect of contact time on the removal of heavy metals

The effect of contact time on the adsorption of cations from solution at different cation concentrations is depicted in Figures 2–7 for two different cation concentrations of Cr and Ni, on adsorption rate. Three different concentrations of Cr and Ni cations in aqueous solution (400, 600, and 900 ppm) were tested. The concentration profiles for all sorbents decrease with increasing contact time, and after a certain period, an equilibrium phase is reached. These figures show that nickel and chrome adsorption is higher during the first five minutes using moringa pod powder particles as an adsorbent, while pine and eucalyptus take longer time (50 minutes); the adsorption then becomes slower. The adsorption rate reached equilibrium after 100 minutes, while for moringa the equilibrium was achieved after 10 minutes only. It is clear from these figures that moringa powder particles give a higher adsorption rate, and after 10 minutes. Both Ni and Cr cations were completely adsorbed, while pine cones took a longer time than moringa but were still better than eucalyptus bark as both took 150 and 210 minutes to adsorb Cr and Ni cations respectively, and come to equilibrium. These results indicate that the adsorption of ions is in the order of:
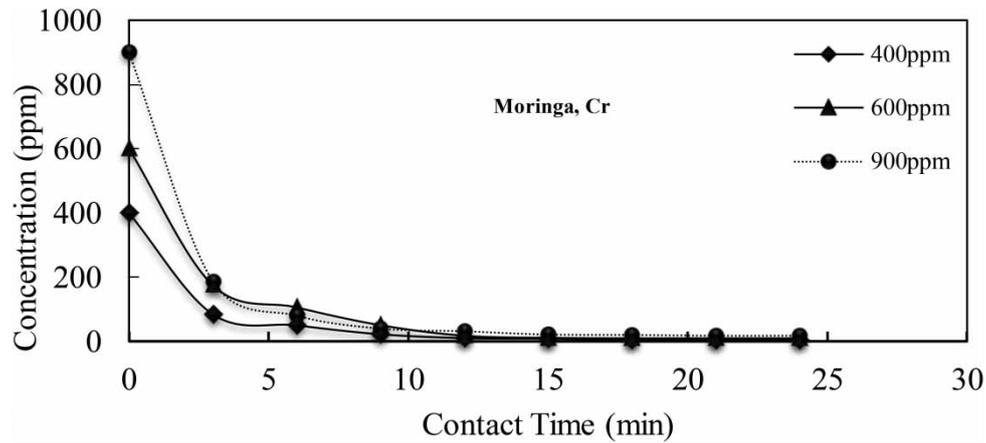
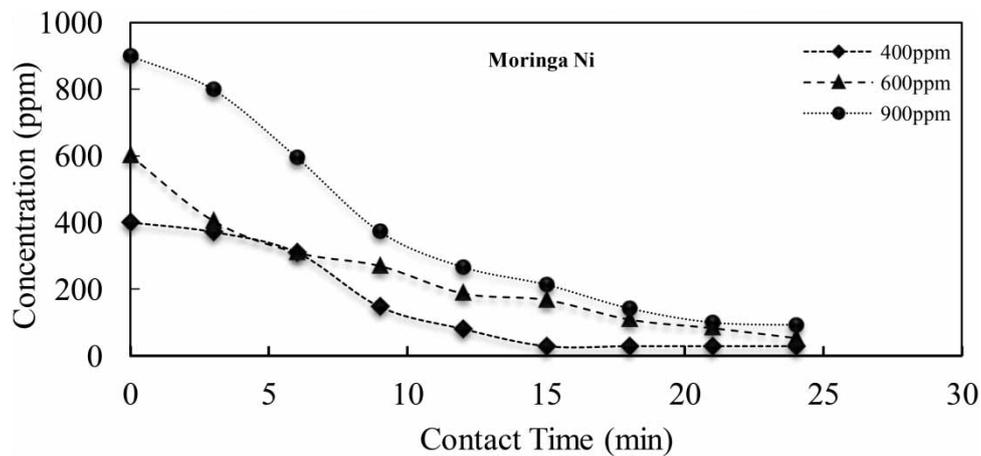$$moringa > eucalyptus > pine\, cone$$
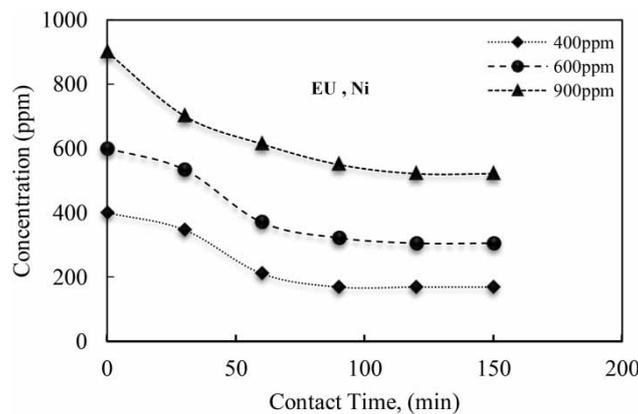
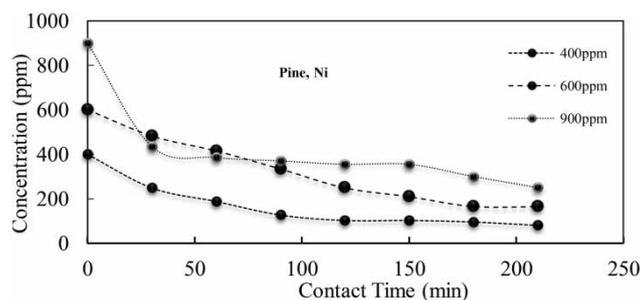Figure 2 | Concentration profiles for Ni with contact time using eucalyptus bark (EU).
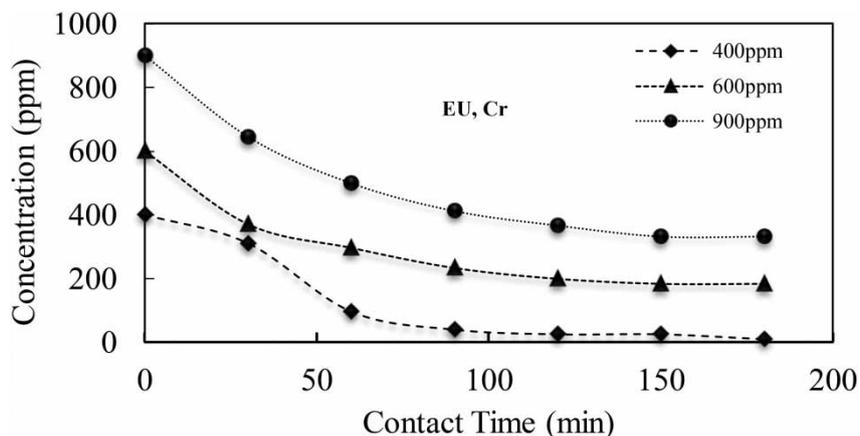
Figure 3 | Concentration profiles for Cr with contact time using eucalyptus bark (EU).

Figure 4 | Concentration profiles for Cr with contact time using moringa pod particles.
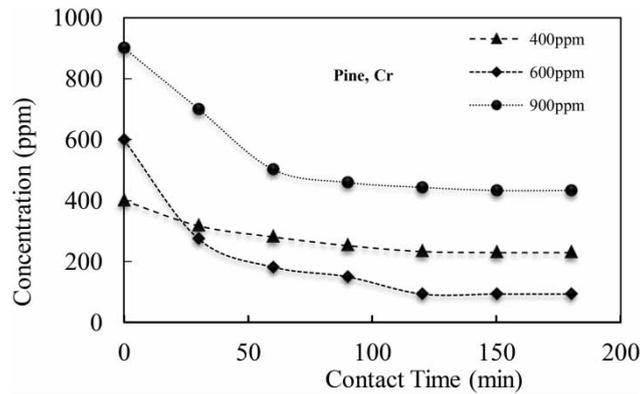

Figure 5 | Concentration profiles for Ni with contact time using moringa pod particles.

Figure 6 | Concentration profiles for Ni with contact time using pine cone particles.

These figures also indicate that as the concentration of the ions increased (900 ppm) the adsorption rate decreased, which indicates the lower concentration (400 ppm) is preferable over higher ones. This could be explained that with higher ion concentration in the solution the number of collisions between ions in the solution and the adsorbed on the sorbent results in the desorption of metal ions from the binding sites which will reduce the absorption rate.

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Figure 7 | Concentration profiles for Ni with contact time using pine cone particles.

The results of the removal capacity of each sorbent at equilibrium at different ion concentrations is given in Table 1. The removal capacity is calculated as indicated in Equation (1)

$$Removal~\% = \frac{(C_i - C_e)}{C_i} \tag{1}$$

where, C_i is the initial concentration of heavy metal in the solution sample before treatment (ppm), C_e is the final concentration of heavy metal in the solution sample at equilibrium (ppm). The removal percentage varied according to the type of ion, concentration, and sorbent type as indicated in Table 1. Removal of Ni cations shows the lowest percentage (42–58%) when eucalyptus bark is used, while pine cone indicated the lowest removal percentage (43–84%) when Cr is used. The moringa shows the highest removal percentage for both Cr and Ni cations within a very short period in comparison with other sorbents and the removal percentage is within 86–99% range. Moringa particles have shown the highest and fastest removal capacity among examined sorbents regardless of cations concentration.

Table 1 | Removal percentage comparison for Cr and Ni ions using different sorbents

Concentration (ppm)		Eucalyptus bark removal (%)	Pine cones removal (%)	Moringa pods removal (%)
Cr	400	98	43	99
	600	70	84	99
	900	63	52	98
Ni	400	55	80	93
	600	50	72	86
	900	44	72	89

Biosorption isotherms

Langmuir model

The equilibrium distribution of metal ions between the sorbents and the solution is important to determine the maximum sorption capacity. Several isothermal models are available to describe equilibrium sorption distribution. In the present work, two models are used here to fit the experimental data: the Langmuir model and the Freundlich model. The Langmuir model was chosen for the estimation of maximum adsorbent capacity corresponding to removal capacity surface saturation, the Langmuir

model for equilibrium ion removal is given according to the following equations:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) Ce \tag{2}$$

K_L: is the Langmuir equilibrium constant, which is related to the adsorption/desorption energy, the affinity of the binding sites. a_L: is the Langmuir constant. The constants K_L and a_L are the characteristics of the Langmuir equation and can be determined from a linearized form of the Langmuir Equation (2), by a plot of the quantity $\left(\frac{Ce}{qe}\right)$ versus Ce, results in a straight line of slope $\left(\frac{a_L}{K_L}\right)$, and intercept $\left(\frac{1}{K_L}\right)$. The results of plotting Equation (2) are given in Table 2, which shows the value of slope and intercept, where K_L and a_L are given for three sorbents with a different type of metal ions. Considering correlation coefficient R^2, for Ni and Cr in Table 3, it is clear the adsorption by moringa, eucalyptus, and pine particles follow Langmuir isotherm.

Table 2 | Langmuir model constant values

	Moringa		Pine cone		Eucalyptus	
	Cr	Ni	Cr	Ni	Cr	Ni
K_L	0.27	0.03	0.11	0.01	0.03	0.31
a_L	0.1	0.008	0.08	0.006	0.02	0.025
R^2	0.94	0.96	0.97	0.98	0.94	0.99

Table 3 | Freundlich model values

Constants	Moringa		Pine cone		Eucalyptus	
	Cr	Ni	Cr	Ni	Cr	Ni
K_f	0.43	0.02	0.79	0.001	0.44	0.05
n	2.07	0.69	11.86	1.3	7	2.29
R^2	0.98	0.90	0.83	0.82	0.59	0.99

Freundlich model

The Freundlich model was tested to estimate the adsorption intensity of the sorbet towards the plants. Freundlich model is an empirical equation based on adsorption on a heterogeneous surface. The Model is commonly represented by Equation (3):

$$q_e = K_f C_e^{1/n} \tag{3}$$

where K_f is the Freundlich constant, which is related to the bonding energy (L/mg), $1/n$ is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Equation (3) is rearranged in linear form to give Equation (4):

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \tag{4}$$

Freundlich equilibrium constants were determined from the plot of $\log(q_e)$ vs. $\log(C_e)$, the basis on the linear of the Freundlich model Equation (4), where the n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, the adsorption is

linear; $n < 1$, the adsorption is a chemical process; and $n > 1$, the adsorption is physical adsorption. The n value in the Freundlich equation was found to be greater than 1 for almost all performed experiments here, indicating biosorption of Cr and Ni onto sorbents is physical adsorption. Since n is less than 1, for the only system of Ni-Moringa, the adsorption is chemical; elsewhere, it is a physical process. Table 3 presents the different values obtained from Equation (4).

The Langmuir model contains assumptions such as all binding sites that should possess an equal affinity for the adsorbate and adsorption should be limited to the formation of a monolayer. The other assumption is that the number of adsorbed species should not exceed the total number of surface sites and it also assumes that the number of uniform adsorption sites should be finite and that there should be an absence of lateral interactions between adsorbed species compared to other models; for this reason, the Langmuir model could fit the data well compared with the Freundlich model, which takes surface roughness into account (Igwe & Abia 2007).

Kinetic relation

The study of adsorption dynamics describes the solute uptake rate and, evidently, this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of heavy metal adsorption on sorbents was analyzed using a pseudo-first-order reaction. The conformity between experimental data and the model predicated values was expressed by the correlation coefficient R^2. A relatively higher R^2 value indicates that the model successfully describes the kinetics of heavy metal adsorption. Quantifying the change in sorption with the time requires that an appropriate kinetics model is used and traditionally the first order Lagergren's equation is generally expressed to sorption kinetics as follows (Kowanga et al. 2016):

$$\log (q_e - q_t) = \log (q_e) - \frac{Kt}{2.303} \tag{5}$$

where q_e is the mass of metal adsorbed at equilibrium (mg of ion/g of metal), K is the rate constant of adsorption and t is the mixing time in minutes.

Another useful model for the analysis of sorption kinetics is pseudo-second-order; the rate law for this system is expressed as:

$$\frac{t}{q_t} = \left(\frac{1}{Kq_e^2}\right) + \frac{1}{tq_e} \tag{6}$$

where q_e is the mass of metal adsorbed at equilibrium, q_t is the mass of metal adsorbed at the time t, K is the rate constant of adsorption, and t is the mixing time. The removal kinetics were evaluated with the pseudo-first-order and pseudo-second-order. The results show that the sorption of Ni was best described by the Lagergren-first order kinetic model with correlation coefficient R^2 of 97% and the rate constant of adsorption K with a range of ($0 < K < 1$), while sorption of Cr was best described by the pseudo-second-order kinetic model with a coefficient of R^2 of 99% and the constant K has a range of ($0 < K < 1$).

The pseudo-first-order model was attributed to the fast initial uptake of Ni(II) onto the powder biomass before slow adsorption, while for a second-order the biosorption of Cr a slow initial uptake and slow adsorption. These results, as given in Table 4, suggested also that the adsorption process of Cr ion on bio-sorbents is controlled by the pseudo-second-order model and supports that the adsorption is due to chemical adsorption. The kinetics results obtained can be used to know if the intraparticle diffusion is the limiting step in the adsorption of ions on biosorbents, where it is clear in the Ni ion that intraparticle diffusion is not a limiting step so the kinetics are almost pseudo-first-order compared to Cr ion adsorption, which is pseudo-second-order.

Table 4 | Kinetic parameters for biosorption of Cr and Ni ions

		Sorbent					
		Moringa		Pine cone		Eucalyptus	
Order		Cr	Ni	Cr	Ni	Cr	Ni
First	K (min^{-1})	0.71	0.3	0.06	0.04	0.06	0.1
	R^2	0.97	0.95	0.95	0.96	0.96	0.99
Second	K (g mg^{-1} min^{-1})	0.54	0.16	0.03	0.007	0.04	0.03
	R^2	0.99	0.92	0.99	0.87	0.99	0.91

CONCLUSIONS

The results presented in this study showed that moringa pods, pine cones, and eucalyptus can efficiently remove heavy metals Nickel (Ni) and Chrome (Cr) present in aqueous solutions at high concentrations. The removal order was found to be Cr > Ni with removal percentages of 90–99% for moringa, which had the best removal capacity in a very short period, while for the pine cones the removal was 60–99%, and for eucalyptus was 42–94%. The adsorption equilibrium isotherms of Ni and Cr were determined and correlated with common isotherm equations such as Langmuir and Freundlich models, the results indicate that the Langmuir model fits the data better with the range of K_L constant (0 < KL < 1) and a_L (0 < aL < 1) with correlation R^2 of higher than 90% for all sorbents.

The results show that the sorption of Ni was best described by the Lagergren-first-order kinetic model with correlation coefficient R^2 of 97% and the rate constant of adsorption K with a range of (0 < K< 1), while sorption of Cr was best described by the pseudo-second-order kinetic model with coefficient R^2 of 99% and the constant K has a range of (0 < K < 1).

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