Reusing Materials: Pb and Cr biosorption

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ABSTRACT

The heavy metals such as chromium and lead are highly toxic and have high persistence in the environment. This has direct implications on the ecosystem and the health of populations not directly exposed to contaminated water. There is a need to reevaluate the residues originated in industrial processes for the production of new raw material, reducing the volume of waste. In this regard, the biosorption is an alternative method for treating effluents more economical compared to conventional methods. The main objectives of this research were: the evaluation of six waste materials biosorbent capacity for the extraction of Cr (VI) and Pb (II) ions from aqueous solutions and, the determination of the adsorption and kinetic parameters for the more efficient system. The materials evaluated were: peanuts shell (Arachis hypagaea), sugarcane bagasse (Saccharum officinarum), avocado peel (Persea americana), pecan nutshell (Carya illinoinensis), wheat bran (Triticum aestivum) and banana peel (Mussa paradisiaca). The highest percentage of lead removal was obtained with wheat bran (89%). For chromium, the percentage was generally much lower compared with lead for all tested biosorbents, being the most efficient the banana peel with a 10% of removal. The models better describes the adsorption processes were: Langmuir and Freundlich. The pseudo-second orden kinetic model allowed obtaining the parameters for both systems. The equilibrium time, in both systems, was reached after 60 minutes.

KEYWORDS

bioadsorption, lead, chromium, reusing waste materials and waters

INTRODUCTION

Reusing industrial wastewater is often precluded due to high levels of toxic substances that may be present depending on the type of industry. The heavy metals such as chromium and lead are highly toxic and have high persistence in the environment; their threats are multiplied as they can bioaccumulate in organisms of lower trophic levels, and reach its biomagnifications [1-3]. This has direct implications on the ecosystem and the health of populations not directly exposed to contaminated water. Lead is widely used in the manufacture of batteries and accumulators, in the manufacture of pigments and paints, in the petrochemical industry as a stabilizer for plastics and as a detonator for explosives, among other applications. Chromium is mainly used in the metallurgical industry, as it provides corrosion resistance and a shiny finish; also it is used in leather tanning and in production of paints and pigments. As ore, chromite is used in molds for the production of refractory material.
The development of new technologies with low environmental impact to eliminate or recover heavy metals is of critical value. There is also a need to **re-evaluate** the residues originated in

industrial processes for the production of new raw material, reducing the volume of waste. In this regard, the biosorption is an alternative method for treating effluents with lower costs compared to conventional techniques.
The main objectives of this research were the evaluation of six waste materials biosorbent capacity for the extraction of Cr(VI) and Pb(II) ions from aqueous solutions and, the determination of the adsorption and kinetic parameters of the most efficient system. The residues evaluated were: peanuts shells (*Arachis hypagaea*), sugarcane bagasses (*Saccharum officinarum*), avocado peels (*Persea americana*), pecan shells (*Carya illinoinensis*), wheat brans (*Triticum aestivum*) and banana peels (*Mussa paradisiaca*).

MATERIALS AND METHODS

The samples of the biosorbent materials were washed with distilled water and dried at 110°C to constant weight. Subsequently the dried biomass was ground and sieved to a particle size between 1.0 and 1.5 mm.
To study the adsorption capacity of these biomasses, triplicate experiments were performed in batch type reactors, with orbital shaking at 150 rpm, in a controlled environment at 25 ± 2 °C and pH = 5.5 ± 0.1. The liquid was then filtrated using a cellulose filter. The presence of Pb (II) and Cr (VI) ions was quantified before and during the experiment at different times by Atomic Absorption Spectrophotometry (210-VGP Buck Scientifc®). Standard Merck® solutions with 1000 mg / L of each metal were used to perform the corresponding calibration curves. Working solutions of 10, 20 and 30 mg / L for Cr (VI) and 20, 40, 60 and 80 mg / L for Pb (II), were prepared from K_2CrO_4 and Pb $(NO_3)_2$ respectively, in distilled water. The working proportion was 0.1 g of adsorbents and 50 mL of metal solutions.Subsequently, with the best of each pollutant absorbent, the absorption and kinetics curves were constructed.The Langmuir [4] and Freundlich [5] models are the most employed to describe the adsorption equilibrium. The linearized Langmuir isotherm equation is:

$$\boldsymbol{C_e/q = 1/bQ_{max} + C_e/Q_{max}} \qquad (1)$$

where, Ce is the supernatant concentration after the equilibrium of the system (mg L^{-1}), b the Langmuir affinity constant (L mg^{-1}), and Q_{max} the maximum adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbate uptaken by the adsorbent.
The linearized Freundlich isotherm equation is:

$$\boldsymbol{lnq_e = lnK_f + \frac{1}{n} lnC_e} \qquad (2)$$

where, K_F is the Freundlich constant and n is the Freundlich exponent related to the adsorption intensity.
To fit the experimental kinetics data two models were used: the pseudo-first order equation [6] is expressed as:

$$\boldsymbol{dq_t/dt = k_1(q_e - q_t)} \qquad (3)$$

Where, qe and qt (mg g^{-1}) are the amount of cadmium sorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first order equation.
After integration and applying the boundary conditions, for $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes:

$$\boldsymbol{q_t = q_e\left(1 - e^{-k_1 t}\right)} \qquad (4)$$

The pseudo-second order equation [7] is expressed as:

$$ {dq_t}/{dt} = k_2(q_e - q_t)^2 \qquad (5) $$

Integration of this equation, for the same boundary conditions, gives:

$$ q_t = t/\left[\left(1/{k_2 {q_e}^2}\right) + \left(t/q_e\right)\right] \qquad (6) $$

where, k_2 is the equilibrium rate constant of the pseudo-second order equation (g mg^{-1} min^{-1}) and k_2qe^2 is the initial adsorption rate (mg g^{-1} min^{-1}).

RESULTS AND DISCUSION

The comparative removal percentages obtained with the tested adsorbents from the solutions with Pb and Cr are shown in Figure 1. The adsorption capacities, the experimental removal percentages and the equilibrium concentrations obtained are shown in Table 1.

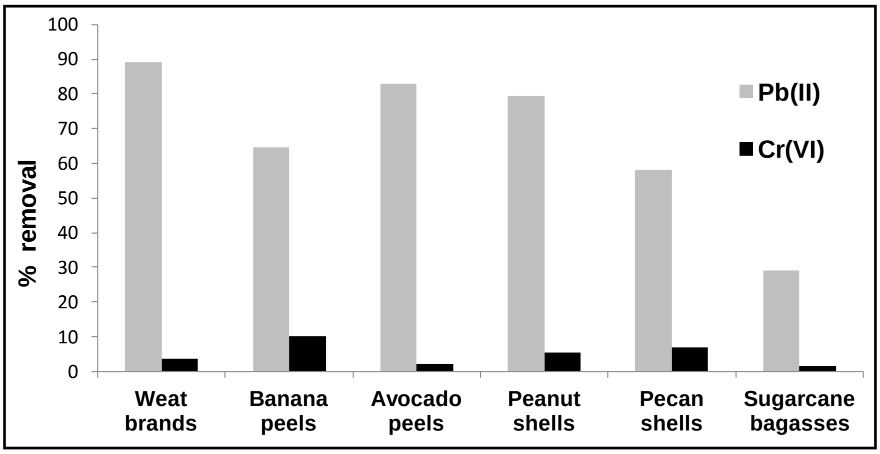

Figure 1. Removal percentage of Pb (II) and Cr (VI) with all tested adsorbents.

Tabla 1. Experimental removal percentages, adsorption capacities (q_e) and equilibrium concentrations (C_{eq}) obtained in all the studied systems.

Adsorbent	Pb (II)			Cr (VI)		
	Removal %	q_e (mg/g)	C_{eq} (mg/L)	Removal %	q_e (mg/g)	C_{eq} (mg/L)
Weat brands	89	24.7	49.3	3.5	0.5	1.0
Banana peels	65	18.9	35.8	10	1.4	2.8
Avocado peels	83	23.0	45.9	2.1	0.3	0.6
Peanut shells	79	22.6	47.1	5.3	0.8	1.5
Pecan shells	58	17.6	35.2	6.8	1.0	1.9
Sugarcane	29	8.1	16.2	1.5	0.2	0.4

Lead had reached a greater adsorption percentage than chromium with all the tested adsorbents. Wheat brans were selected as the most efficient adsorbent to remove lead, with an adsorption capacity of 24.7 mg g^{-1}. However, avocado and peanut peels, with 83% and 79% removal respectively, have good removal percentages so they can be studied in future work. For chromium, the highest removal percentage was obtained with banana peels, so they were selected as the best adsorbents for chromium, with an adsorption capacity of 1.41 mg. g^{-1}.

From Table 2, it is clear that the pseudo second-order kinetics model fits better than the pseudo first-order model for both the adsorption processes studied. The pseudo second-order constant k_2 decreases with the increase in metal concentration for both cases. From this table it can also be found that the calculated q_e values with the pseudo second-order model were on par with the experimental q_{exp} values for both the observed processes unlike the pseudo first-order equation. The equilibrium time was 60 minutes in all cases. Saturation of the adsorbent was observed with Pb (II) onto wheat brans at 60 mg L^{-1}.

Table 2. Kinetics parameters obtained for the selected systems.

		Pseudo-first order				Pseudo-second order			
	q_{exp}	C_i (mg L^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	C_i (mg L^{-1})	k_2 (g min mg^{-1})	R^2	q_e (mg g^{-1})
Wheat brans/ Pb (II)	12	20	0.066	0.9595	1.42	20	0.089	1	10.6
	18	40	0.061	0.9511	6.72	40	0.018	0.9998	18.5
	24	60	0.077	0.9998	14.6	60	0.014	0.9999	24.7
	24	80	0.070	0.8972	3.78	80	0.029	0.9999	23.4
Banana Peels/ Cr (VI)	0.3	10	0.074	0.9649	2.65	10	0.309	0.9975	0.33
	0.5	20	0.078	0.8493	2.04	20	0.170	0.9967	0.56
	0.78	30	0.075	0.7954	1.45	30	0.090	0.9946	0.83

The equilibrium data for the adsorption of both the metals were fitted with the Langmuir and Freundlich isotherm models. It can be inferred from Table 3 that the maximum adsorption capacity (Q_{max}) and the Langmuir constant (K_L) were higher for the adsorption of Pb (II) than Cr (VI). This was because values of Q_{max} and K_L are directly proportional to the adsorption percentage. The Freundlich exponent (n) and Freundlich constant (K_F) were also higher for the adsorption of Pb (II) than Cr(VI). Here the value of n was between *1* and *10* which proves that the processes are favourable.

Table 3. Langmuir and Freundlich models parameters obtained for the selected systems.

	Langmuir			Freundlich		
	Q_{max} (mg g^{-1})	b	R^2	n	K_f	R^2
Wheat brans/ Pb (II)	23,81	2	0,9969	5,08	13,49	0,9408
Banana Peels/ Cr (VI)	3,01	0,07	0,8808	1,19	0,21	0,9892

CONCLUSION

The highest removal percentage of lead was obtained with wheat brans. For chromium, the removal percentage was much lower compared with lead for all the tested biosorbents, being the banana peels the most efficient. The adsorption processes were described by the Langmuir and by the Freundlich models showing favourable adsorption behaviour. The experimental kinetics data from both systems were well fitted using the pseudo-second order model, with correlation coefficients above 0.99. The equilibrium concentration values calculated by this model were very close to those obtained in laboratory experiments. The equilibrium time was 60 minutes in all cases. Saturation of the adsorbent was observed with Pb (II) onto wheat brans at 60 mg L^{-1}.
Despite the advantages, there are unresolved issues within the experimental applications of biomaterials as adsorbents. The adsorption capacity for Cr (VI) by biomaterials is low. In such a way there is a need to find new biomaterials capable of adsorbing Cr (VI) more efficiently.

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NOMENCLATURE

C_e	concentration of the solution at equilibrium state	[mg/L]
t	time	[min]
q_e	amount of adsorbed species per unit mass of adsorbent at the equilibrium state	[mg/g]
q_t	amount of adsorbed species per unit mass of adsorbent at the time t	[mg/g]
q_m	Langmuir parameter related to the maximum capacity of the adsorbent	[mg/g]
b	Langmuir parameter related to the energy of adsorption	[L/mg]
K_f	Freundlich parameter related to the adsorption capacity	
n	Freundlich parameter related to the intensity of adsorption	
k_1	velocity constant in the pseudo-first order model	[min^{-1}]
k_2	velocity constant in the pseudo-second order model	[min^{-1}]

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