Journal of Sustainable Development of Energy, Water and Environment Systems

http://www.sdewes.org/jsdewes

Year 2018, Volume 6, Issue 2, pp 341-350

Agroindustrial Waste for Lead and Chromium Biosorption

Susana P. Boeykens*[1], Andrea Saralegui[2], Néstor Caracciolo[3], María N. Piol [4]
[1]Facultad de Ingeniería, Laboratorio de Química de Sistemas Heterogéneos (LaQuíSiHe), Universidad de Buenos Aires, Paseo Colon 850, Buenos Aires, Argentina
e-mail: sboeyke@gmail.com
[2]Facultad de Ingeniería, Laboratorio de Química de Sistemas Heterogéneos (LaQuíSiHe), Universidad de Buenos Aires, Paseo Colon 850, Buenos Aires, Argentina
e-mail: saraleguiandrea@gmail.com
[3]Facultad de Ingeniería, Laboratorio de Química de Sistemas Heterogéneos (LaQuíSiHe), Universidad de Buenos Aires, Paseo Colon 850, Buenos Aires, Argentina
e-mail: nestorcaracciolo@hotmail.com
[4]CONICET, Universidad de Buenos Aires, Paseo Colon 850, Buenos Aires, Argentina
Facultad de Ingeniería, Laboratorio de Química de Sistemas Heterogéneos (LaQuíSiHe), Universidad de Buenos Aires, Paseo Colon 850, Buenos Aires, Argentina
e-mail: natypiol@yahoo.com

Cite as: Boeykens, S. P., Saralegui, A., Caracciolo, N., Piol, M. N., Agroindustrial Waste for Lead and Chromium Biosorption, J. sustain. dev. energy water environ. syst., 6(2), pp 341-350, 2018,
DOI: https://doi.org/10.13044/j.sdewes.d5.0184

ABSTRACT

There is a need to re-evaluate the residues generated in industrial processes for the production of new raw material, reducing the volume of waste. In this regard, the biosorption is a low-cost alternative method for treating effluents compared to conventional methods. The main objectives of this research were: the evaluation of the biosorbent capacity of six waste materials for the extraction of chromium(VI) and lead(II) ions from aqueous solutions and, the determination of the adsorption and kinetic parameters for the more efficient system. The materials evaluated were: peanut 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, the banana peel being the most efficient with a 10% removal. The models that better describe the adsorption processes were: Langmuir and Freundlich. The pseudo-second order kinetic model allowed obtaining the parameters for both systems. The equilibrium time, in both systems, was reached after 60 minutes. The study of Fourier Transformed Infrared spectra and the results of desorption experiments allowed to hypothesize on the mechanisms involved in the adsorption of these metals.

KEYWORDS

Bioadsorption, Lead, Chromium, Reusing waste material.

---

[*] Corresponding author

INTRODUCTION

Reusing industrial wastewater is often precluded due to high levels of toxic substances that may be present depending on the type of industry. Heavy metals such as chromium and lead are highly toxic and have high persistence in the environment [1], their threats are multiplied as they can bio-accumulate in organisms of lower trophic levels, and reach its bio-magnifications [2]. This has direct implications on the ecosystem and the health of populations not directly exposed to contaminated water [3].

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 [4]. Lead is considered a possible carcinogen in humans [5].

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 [6]. There is sufficient evidence to state that Chromium(VI) [Cr(VI)] is carcinogenic to human [7]. For these reasons Argentine legislation considers them as hazardous substances and regulates the content of metals both in the discharge of effluents as in drinking and irrigation water [8].

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, biosorption is an alternative for treating effluents with lower costs compared to conventional techniques [9]. The development of low environmental impact remediation methods that allow the removal or recovery of heavy metals is of crucial value [10]. In addition, there is a great need to value the waste originated in industrial and agricultural processes, as goods for the manufacture of new raw material, thus reducing the volume of waste [11]. The principal parameters needed in finding of the best adsorbent for treating heavy metals in wastewater are the availability and the cost effectiveness [12].

Numerous works using agroindustrial waste have been published [13]. The capacity of these materials to concentrate contaminating metals of the water in their structures is remarkable [14]. Studies of the mechanisms for adsorption are being made continuously in order to understand and predict their adsorption capacity, efficiency and regenerability. Marigold flowers [15], bay leaves [16], different lignocellulosic materials [17], seaweeds [18], neem bark [19], rice flour and starch [20] were used as biosorbents. The common feature of these residues is the presence of natural biopolymers in their structures such as alginate, cellulose, hemicellulose or lignin which are characterized by the presence of different functional chemical groups, mainly carboxyl, hydroxyl or amine. These surface chemical groups play a key role in the adsorption of contaminants [21].

The main objectives of this research were:

- The evaluation of six waste materials for the extraction of Cr(VI) and Lead(II) [Pb(II)] ions from aqueous solutions;
- The determination of the adsorption and kinetic parameters of the most efficient systems, in order to lay the foundations for the design of treatment reactors with these adsorbents.

The agroindustrial wastes evaluated were: peanut shells (*Arachis hypagaea*), sugarcane bagasse (*Saccharum officinarum*), avocado peel (*Persea americana*), pecan shell (*Carya illinoinensis*), wheat bran (*Triticum aestivum*) and banana peel (*Mussa paradisiaca*).

The highest percentage of lead removal was obtained with wheat bran (89%). The percentage of chromium removal was generally much lower with all tested biosorbents, the most efficient being banana peels with a 10% removal. The models that better describe the adsorption processes were: Langmuir and Freundlich. The pseudo-second order model allowed obtaining the kinetic parameters for both systems. The equilibrium time, in both systems, was reached after 60 minutes. The study of Fourier Transformed Infrared (FTIR) spectra and results of desorption experiments allowed to hypothesize on the mechanisms involved in the adsorption of these metals.

MATERIALS AND METHODS

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 1,000 mgL^{-1} of each metal were used to perform the corresponding calibration curves. Working solutions of 10, 20 and 30 mgL^{-1} for Cr(VI) and 20, 40, 60 and 80 mgL^{-1} for Pb(II), were prepared from Potassium chromate (K_2CrO_4) and Lead nitrate [$Pb(NO_3)_2$] 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.

Equilibrium and kinetics modeling

The Langmuir [22] and Freundlich [23] models are the most employed to describe the adsorption equilibrium. The linearized Langmuir isotherm equation is:

$$\frac{C_\mathrm{e}}{q} = \frac{1}{b\,Q_\mathrm{max}} + \frac{C_\mathrm{e}}{Q_\mathrm{max}} \tag{1}$$

where C_e (mgL^{-1}) is the supernatant concentration after the equilibrium of the system, b (Lmg^{-1}) is the Langmuir affinity constant and Q_max (mg g^{-1}) is the maximum adsorption capacity of the material assuming a monolayer of adsorbate uptaken by the adsorbent.

The linearized Freundlich isotherm equation is:

$$\ln q_\mathrm{e} = \ln K_\mathrm{f} + \frac{1}{n}\ln C_\mathrm{e} \tag{2}$$

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 [24] is expressed as:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_1(q_\mathrm{e} - q_\mathrm{t}) \tag{3}$$

where q_e and q_t (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 $q_\mathrm{t} = 0$ at $t = 0$ and $q_\mathrm{t} = q_\mathrm{t}$ at $t = t$, the equation becomes:

$$q_{\mathrm{t}} = q_{\mathrm{e}}(1 - e^{-k_1 \mathrm{t}}) \tag{4}$$

The pseudo-second order equation [25] is expressed as:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_2(q_{\mathrm{e}} - q_{\mathrm{t}})^2 \tag{5}$$

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

$$q_{\mathrm{t}} = \frac{t}{\frac{1}{k_2 {q_{\mathrm{e}}}^2} + \frac{t}{q_{\mathrm{e}}}} \tag{6}$$

where k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant of the pseudo-second order equation and $k_2 q_{\mathrm{e}}^2$ (mg g^{-1} min^{-1}) is the initial adsorption rate.

Fourier transform – Infrared spectrometry studies

In order to investigate structural modifications in chemical functional groups due to the adsorption process, both adsorbents were analysed before and after the experiments using a Fourier Transform Infrared Spectrometer (FT-IR Nicolet 8700). The characteristic absorption bands of the different functional groups were adjudicated by studying the spectrum obtained and comparing them with those described in the bibliography [26].

Desorption studies

In this case, desorption experiments were performed in order to contribute to elucidation of the processes involved in adsorption and to establish the possibilities of the adsorbent reuse.

For the recovering of the exhausted adsorbent, desorption should be carried out with a saturated solution of a salt, or a strong base or acid which is more efficient for the displacement of the adsorbed ion. The most effective desorbent agent will reveal a predominant mechanism whose equilibrium it was able to displace.

Desorption efficiencies of the following solutions were evaluated: Sodium hydroxide (NaOH) 0.1 M (pH = 12), Sodium chloride (NaCl) 0.1 M (pH = 5), Nitric acid (HNO_3) 0.1 M (pH = 2) and distilled water (pH = 6.5).

For the experiments, a measured mass of five samples of each adsorbent loaded with phosphate were stirred with 50 mL of desorbent solution for 24 h.

Desorption percentage was calculated by eq. (7):

$$\mathrm{Desorption} = 100 \left(\frac{C_{\mathrm{d}} V_{\mathrm{d}}}{q_{\mathrm{a}} m}\right) [\%] \tag{7}$$

where C_{d} (mgL^{-1}) is the ion concentration in the desorbed solution, V_{d} (L) is the volume of the desorption solution, q_{a} (mg g^{-1}) is the adsorption capacity, and m (g) is the adsorbent mass. In all cases the initial solution of phosphate was 30 mgL^{-1}.

RESULTS AND DISCUSION

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

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

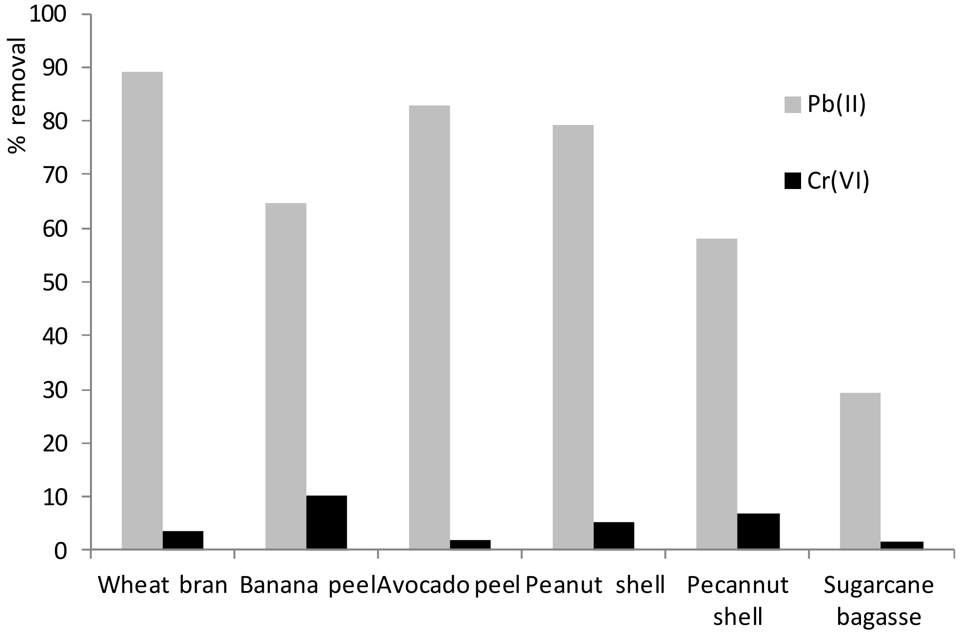

Figure 1. Removal percentage of Pb(II) and Cr(VI) obtained with all tested adsorbents

For chromium, the highest removal percentage was obtained with banana peels, so they were selected as the best adsorbents for chromium, with adsorption capacity of 1.41 mg g^{-1}.

Table 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]
Wheat bran	89	24.7	49.3	3.5	0.5	1.0
Banana peel	65	18.9	35.8	10	1.4	2.8
Avocado peel	83	23.0	45.9	2.1	0.3	0.6
Peanut shell	79	22.6	47.1	5.3	0.8	1.5
Pecan shell	58	17.6	35.2	6.8	1.0	1.9
Sugarcane bagasse	29	8.1	16.2	1.5	0.2	0.4

Results from kinetic studies showed that the equilibrium time was 60 minutes in all cases. The saturation of the adsorbent was observed only with Pb(II) onto wheat bran at 60 mgL^{-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. This could indicate that chemisorption is occurring. 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 data for the adsorption of both 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 (b) were higher for the adsorption of Pb(II) than Cr(VI). This was because values of Q_{max} and b 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 2. Kinetics parameters obtained from the selected systems

		Pseudo-first order				Pseudo-second order			
	q_{exp}	C_i [mgL^{-1}]	k_1 [min^{-1}]	R^2	q_e [mg g^{-1}]	C_i [mgL^{-1}]	k_2 [g min mg^{-1}]	R^2	q_e [mg g^{-1}]
Wheat bran/ Pb(II)	12	20	0.07	0.9595	1.4	20	0.09	1	11
	18	40	0.06	0.9511	6.7	40	0.02	0.9998	19
	24	60	0.08	0.9998	15	60	0.01	0.9999	25
	24	80	0.07	0.8972	3.8	80	0.03	0.9999	23
Banana peel/ Cr(VI)	0.3	10	0.07	0.9649	2.7	10	0.31	0.9975	0.3
	0.5	20	0.08	0.8493	2.0	20	0.17	0.9967	0.6
	0.8	30	0.08	0.7954	1.5	30	0.09	0.9946	0.8

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 bran/Pb(II)	23.8	2	0.9969	5.1	13.5	0.9408
Banana peel/Cr(VI)	3.0	0.07	0.8808	1.2	0.2	0.9892

Although the complex molecular structure of these biosorbents, the study of the FT-IR spectra obtained from the biomasses before and after the adsorption process permits to identify which of them are active during chemisorption by analyzing the position, width and intensity of their characteristic bands [27].

Figure 2 presents the FT-IR spectra obtained from the wheat bran before and after the adsorption of lead and Figure 3 presents the corresponding from banana peels before and after adsorption of chromium. In both cases, the following bands are noted: a broad band at frequencies between 3,500-3,300 cm^{-1}, assigned to intermolecular stretching O-H overlapped with N-H, two narrow bands at 2,900-2,800 cm^{-1}, assigned to asymmetric stretching C-H, a band at 1,700 cm^{-1}, assigned to asymmetric stretching of C = O, a band between 1,500 and 1,300 cm^{-1}, assigned to different symmetrical and asymmetrical scissor type overlapped vibrations of the groups CH_3 and an intense band at 1,000 cm^{-1}, assigned to bending C-N. The decrease of the intensities and a slight variation in the adsorption frequency of all these bands would indicate that the carbonyl, amino and alcohol groups were preventing their vibrations modes due to the binding with the heavy metal ions. Similar results were observed by other authors [28].

Several authors agree that one of the mechanisms involved in the adsorption of metal ions would be the exchange of protons or light metal with heavy metal ions taken from water [29]. This mechanism would be consistent with the results found in this study for adsorption of lead by wheat bran. For Cr(VI) instead, it is proposed that it is removed from the aqueous system through the banana peel by an indirect reduction mechanism. It is one of the widely accepted mechanisms for the removal of Cr(VI) using bioadsorbents under acidic conditions [30]. The indirect reduction mechanism consists of three steps:

- The Cr(VI) anionic binding to the positively charged groups present on the surface of the banana peel;
- The reduction of Cr(VI) to Cr(III) by adjacent electron donor groups;
- The release of Cr(III) reduced to the aqueous phase due to the electron repulsion with the positively charged groups, or the binding of Cr(III) with another adjacent group.

The results of this study showed that chromium was retained on the surface of the material, so the amino and the carboxyl groups could participate in the mechanism described.

Results obtained by desorption of lead from wheat bran experiments showed that acid solution have the ability to release lead from its adsorptive bonds (Figure 4). It is also observed that solutions with high sodium concentration can release lead from the surface of the adsorbent. These results agree with the hypothesis of the ion exchange adsorption model in the case of lead.

Desorption of chromium from the banana peels could not be detected with the tested solutions. This confirms the hypothesis of the irreversible reduction of chromium on the surface of the adsorbent.

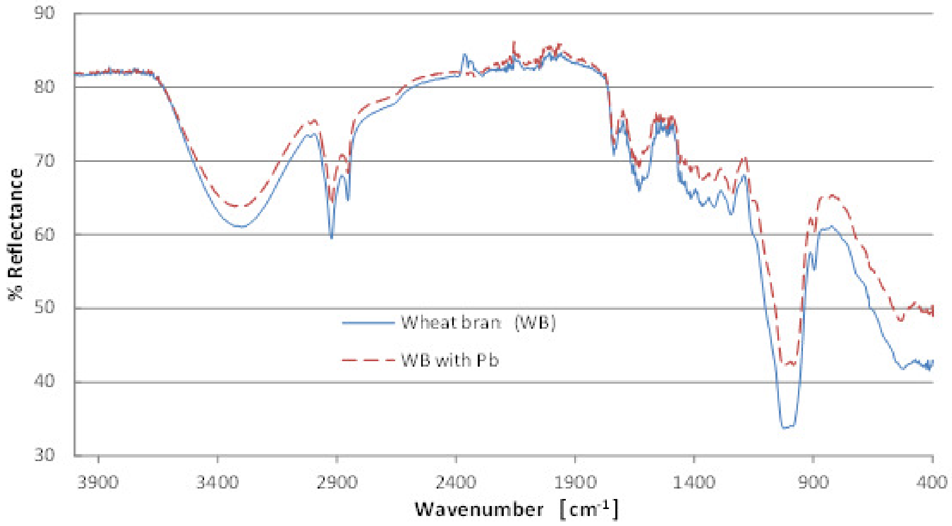

Figure 2. FTIR spectra from wheat bran before and after lead adsorption

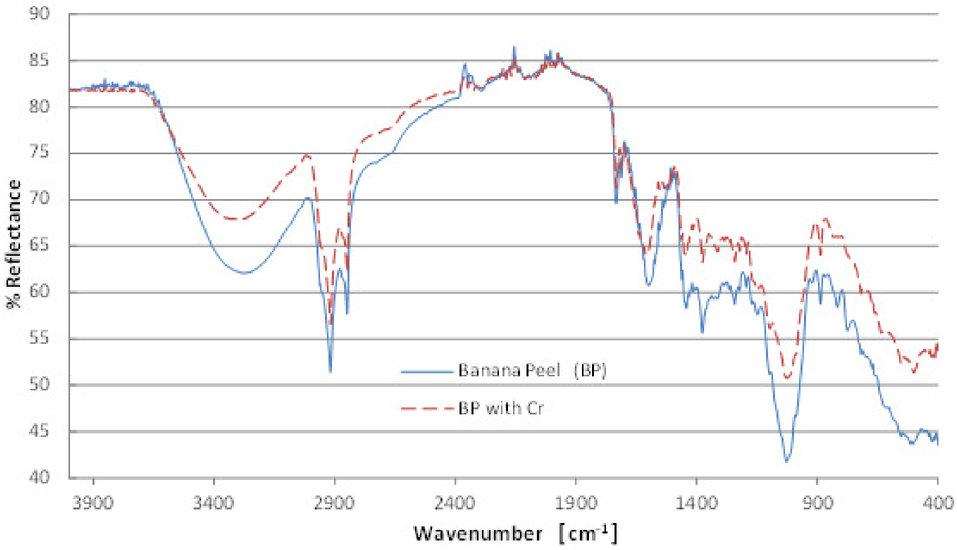

Figure 3. FTIR spectra from banana peel before and after chromium adsorption

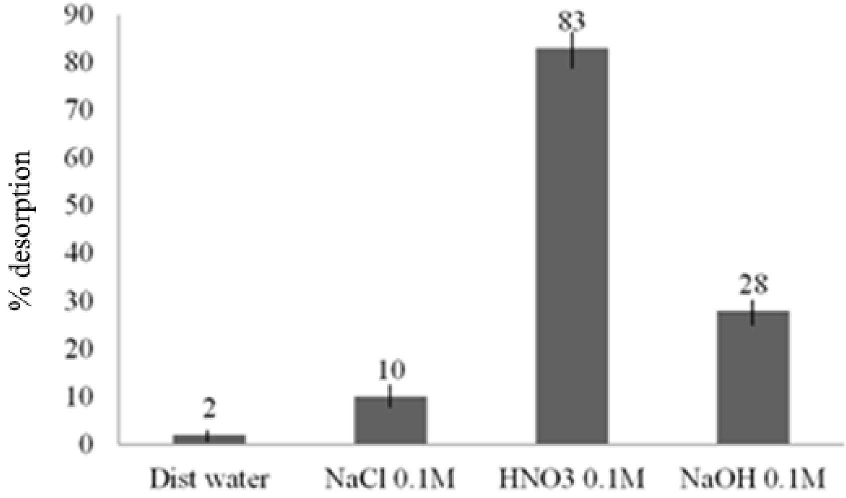

Figure 4. Desorption efficiencies of various reagents for removing lead from wheat bran

CONCLUSIONS

The highest removal percentage of lead was obtained with wheat bran. For chromium, the removal percentage was much lower compared with lead for all the tested biosorbents, the banana peel being 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 bran at 60 mgL^{-1}.

Despite the advantages, there are unresolved problems within the experimental applications of biomaterials as adsorbents. For example, in our study the Cr(VI) adsorption capacity obtained with the materials used is low, which implies the need to continue testing different materials to find those that are able to more effectively adsorb Cr(VI). Another question to be solved will be to quantify the magnitude of the interferences that the different pollutants produce on the surface of these new adsorbents, impeding a good efficiency in the adsorption.

ACKNOWLEDGEMENTS

Financial support from Universidad de Buenos Aires (UBACyT 2017-2019 N° 20020160100143BA; 2016-2017 N° 20020150200151BA and PDE 2016-2017 N°13).

NOMENCLATURE

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

REFERENCES

1. Di Giulio, R. T. and Newman, M. C., *Ecotoxicology*, Casarett and Doull's, *Toxicology, The Basic Science of Poisons* (7th ed.), Klaasen, C. D., Mc Graw-Hill, New York, USA, 2008.
2. Liu, J., Goyer, R. A. and Waalkes, M. P., *Toxic Effects of Metals*, Casarett and Doull's, *Toxicology, The Basic Science of Poisons* (7th ed.), Klaasen, C. D., Mc Graw-Hill, New York, USA, 2008.
3. Gadd, G. M., Biosorption: Critical Review of Scientific Rationale, Environmental Importance and Significance for Pollution treatment, *J. Chem. Technol. Biotechnol.*, Vol. 84, No. 1, pp 13-28, 2008, https://doi.org/10.1002/jctb.1999
4. Agency for Toxic Substances and Disease Registry (ATSDR), Division of Toxicology and Human Health Science, Lead, 2007, https://www.atsdr.cdc.gov/, [Accessed: 24-May-2017]
5. International Agency for Research on Cancer (IARC), Monographs on the evaluation of the Carcinogenic Risk of Chemicals in Humans, Vol. 87, Inorganic and Organic Lead Compounds, Lyon, France, 2006.
6. Agency for Toxic Substances and Disease Registry (ATSDR) Division of Toxicology and Human Health Science, Chromium, 2012, https://www.atsdr.cdc.gov/, [Accessed: 24-May-2017]
7. Barnhart, J., Occurrences, uses, and properties of Chromium, *Regulatory Toxicology and Pharmacology*, Vol. 26, No. 1, S3-S7, 1997, https://doi.org/10.1006/rtph.1997.1132
8. Hazardous Waste, Regulation of Law 24051 (in Spanish), Boletín Oficial de la República Argentina, N° 27630 (3/5/93), pp 4-22, 1993.
9. Volesky, B., *Sorption and Biosorption*, BV-Sorbex, Inc., Montreal, Canada, 2004.
10. Naja, G. M., Volesky, B. and Murphy, V., *Biosorption, Metals* (Flickinger, M., ed.), Encyclopedia of Industrial Biotechnology, Wiley Interscience, NY, USA, 2010.
11. Vásquez Chimarro, S., Bioadsorption of Lead and Chromium by the use of Agroindustrial Residues in the treatment of Waste Water (in Spanish), *Mg. Thesis*, Universidad de Buenos Aires, Argentina, 2015.
12. Femina Carolin, C., Senthil Kumar, P., Saravanan, A., Janet Joshiba, G. and Naushad, Mu., Efficient Techniques for the removal of Toxic Heavy Metals from Aquatic Environment: A Review, *Journal of Environmental Chemical Engineering*, Vol. 5, No. 3, pp 2782-2799, 2017, https://doi.org/10.1016/j.jece.2017.05.029
13. Gupta, V. K. and Suhas., Application of Low-cost Adsorbents for Dye removal – A Review, *J. Environ. Manag.*, Vol. 90, No. 8, pp 2313-2342, 2009, https://doi.org/10.1016/j.jenvman.2008.11.017
14. Bhatnagar, A. and Sillanpää, M., Utilization of Agro-industrial and Municipal Waste Materials as Potential Adsorbents for Water treatment – A Review, *Chemical Engineering Journal*, Vol. 157, No. 2-3, pp 277-296, 2010, https://doi.org/10.1016/j.cej.2010.01.007
15. Mondal, M. K., Mishra, G. and Kumar, P., Adsorption of Cadmium (II) and Chromium(VI) from Aqueous Solution by Waste Marigold Flowers, *Journal of Sustainable Development of Energy, Water and Environment Systems*, Vol. 3, No. 4, pp 405-415, 2015, https://doi.org/10.13044/j.sdewes.2015.03.0030
16. Basso, M. C., Cerrella, E. G. and Cukierman, A. L., Lignocellulosic Materials as Potential Biosorbents of Trace Toxic Metals from Wastewater, *Ind. Eng. Chem. Res.*, Vol. 41, No. 15, pp 3580-3585, 2002, https://doi.org/10.1021/ie020023h
17. Laskar, M., Ali, S. K. and Siddiqui, S., A Potential Bio-Sorbent for Heavy Metals in the Remediation of Waste Water, *Journal of Sustainable Development of Energy, Water and Environment Systems*, Vol. 4, No. 4, pp 320-332, 2016, https://doi.org/10.13044/j.sdewes.2016.04.0025

18. Kratochvil, D., Pimentel, P. and Volesky, B., Removal of Trivalent and Hexavalent Chromium by Seaweed Biosorbent, *Environ. Sci. Technol*, Vol. 32, No. 18, pp 2693-2698, 1998, https://doi.org/10.1021/es971073u
19. Bhattacharya, A. K., Naiya, T. K., Mandal, S. N. and Das, S. K., Adsorption, Kinetics and Equilibrium Studies on Removal of Cr(VI) from Aqueous Solutions using different Low-cost Adsorbents, *Chemical Engineering Journal*, Vol. 137, No. 3, pp 529-541, 2008, https://doi.org/10.1016/j.cej.2007.05.021
20. Torres, M. D. and Seijo, J., Water Sorption behaviour of by-products from the Rice Industry, *Industrial Crops and Products*, Vol. 86, pp 273-278, 2016, https://doi.org/10.1016/j.indcrop.2016.04.014
21. Ofomaja, A. E. and Ho, Y. S., Effect of pH on Cadmium Biosorption by Coconut Copra Meal, *J. Haz. Mat.*, Vol. 139, No. 2, pp 356-362, 2007, https://doi.org/10.1016/j.jhazmat.2006.06.039
22. Langmuir, I., The adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J. Am. Chem. Soc.*, Vol. 40, No. 9, pp 1361-1403, 1918, https://doi.org/10.1021/ja02242a004
23. Freundlich, H., Adsorption in Solutions (in German), Z. Phys. Chem., Vol. 57, pp 385-470, 1906.
24. Lagergren, S., *About the Theory of So-called adsorption of Soluble Substances* (in German), Supplement of the Royal Swedish Science Academiens Documents (in Swedish), Vol. 24, No. 2, Article No. 4, pp 1-39, 1898.
25. Ho, Y. S. and McKay, G., Pseudo-second Order Model for Sorption Processes, *Process Biochemistry*, Vol. 34, No. 5, pp 451-465, 1999, https://doi.org/10.1016/S0032-9592(98)00112-5
26. Silverstein, R. M., Webster, F. X. and Kiemle, D., *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, USA, 2005.
27. Tejeda Benitez, L., Tejada Tovar, C., Marimón Bolivar, W. and Villabona Ortiz, Á., Study of Chemical and Physical modification of Biomass (*Citrus Sinensis and Musa Paradisiaca*) for the adsorption of Heavy Metals in Solution (in Spanish), *Revista Luna Azul*, Vol. 39, pp 124-142, 2014.
28. Miretzky, P., Saralegui, A. and Fernández Cirelli, A., Simultaneous Heavy Metals removal Mechanism by Dead Macrophytes, *Chemosphere*, Vol. 62, No. 2, pp 247-254, 2006, https://doi.org/10.1016/j.chemosphere.2005.05.010
29. Park, D., Lim, S.-R., Yun, Y.-S. and Park, J., Reliable Evidences that the removal Mechanismo of Hexavalent Chromium by Natural Biomaterials is Adsorption-coupled reduction, *Journal of Hazardous Materials*, Vol. 137, pp 1254-1257, 2007, https://doi.org/10.1016/j.jhazmat.2006.04.007
30. Park, D., Park, J. and Yun, M., Mechanism of the removal of Hexavalent Chromium by Biomaterials or Biomaterial-based activated Carbons, *Journal of Hazardous Materials*, Vol. 137, No. 2, pp 1254-1257, 2006, https://doi.org/10.1016/j.jhazmat.2006.04.007

Paper submitted: 02.06.2017
Paper revised: 27.08.2017
Paper accepted: 29.08.2017