Removal of Pb²⁺ and Cd²⁺ from Contaminated Water using Activated Carbon from Canola Seed Wastes

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Abstract – The objective of this work was to produce activated carbon chemically from canola seeds wastes and to apply the activated carbon produced in the sorption of Pb²⁺ and Cd²⁺ from contaminated water. The activation of the canola seeds wastes was performed with NaOH (1 mol L⁻¹) for 6 h under constant stirring. Then the activated material was pyrolyzed for 1 h at 750 °C. The activated carbon was subjected to nitroperchloric digestion for the determination of P, K, Ca, Mg, Mn, Zn, Cu and Pb by flame atomic absorption spectrometry (FAAS). It was also realized the thermogravimetric evaluation (TG), infrared spectra (FT-IR), pH$_{PCZ}$ and scanning electron microscopy (SEM). The metals were evaluated for ideal amounts of adsorbent dose and pH and kinetic, thermodynamic and equilibrium parameters. The mass and pH results demonstrated that four grams of adsorbent is needed to decontaminate one liter of contaminated solution. Linearization were obtained by the mathematical models of Langmuir, Freundlich and D-R, with high capacity of removal of both metals. Thus, using canola waste to produce activated carbon it is possible to add value to the canola seed wastes, also, it contributes directly with the economic, social and environmental sustainability of this productive system.

Keywords: Adsorption, adsorbents, agricultural wastes, mathematical modeling, heavy metals.

1. Introduction

Even with the importance of water, anthropic activities release contaminants into the environment that result in pollution of aquatic systems. Among these contaminants, toxic metals have more severity because they do not have metabolic functions known in living organisms. Toxic metals such as Pb²⁺ and Cd²⁺ can accumulate and bioaccumulate in living tissues resulting in anomalies, disorders and cancers [1].

An efficient way to decontaminate contaminated water has been the use of alternative adsorbents, such as activated carbons from agroindustry and agricultural wastes. In this sense, many crops generate large amounts of waste that can be used [2].

Among the residues used to produce activated carbon are, for example, residues of cassava processing industry [3, 4], *Pinus* barks [5, 6], açaí seeds [7, 8], banana barks [9] and others.

Generally, studies that develop alternative activated carbons aim to remove contaminants from the aquatic environment, among the studies of removal; the most studied contaminants are the toxic metals [10]. However, some agricultural wastes were not evaluated for their transformation into activated carbon and consequent removal capacity. This is the case of the canola crop. Although canola has already been evaluated as a biosorbent for the removal of industrial dyes [11, 12] and heavy metals [13], there are no studies focused on the production and decontamination of water using activated carbon from canola.

The increase in canola production in recent years happens to supply the demand for biofuel. This increase results in a greater amount of agricultural waste generated. These residues are generally used to supplement animal nutrition. The use of this material as a precursor for the production of activated carbon could add more value to this residue, besides being able to result in a material with excellent characteristics of adsorption [13].

In this way, in order to add value to canola seed residues and to collaborate directly with the economic, social and environmental sustainability of this productive system, this original study aimed to produce activated carbons from canola crop wastes and to use the carbon produced to decontaminate polluted waters with Pb^{2+} and Cd^{2+}.

2. Material and Methods

2.1. Adsorbents obtainment and preparation

The seeds of canola (*Brassica napus* L.) were given by the State University of Maringá (Maringá - PR, Brazil), after transportation to the Laboratory of Environmental and Instrumental Chemistry of the State University of the West of Paraná – UNIOESTE (Marechal Cândido Rondon - PR, Brazil) the grains were crushed and dried in a greenhouse for 36 h. The oil extraction was carried out using a Soxhlet type system with n-hexane (C_6H_{14}) [14]. After, the materials were dried at 60 °C for 48 h and sieved in 14 and 65 mesh to standardize the particles (0.212 to 1.40 mm). For the chemical modification, the natural material (canola cake) was immersed in NaOH solution (1.0 mol L^{-1}), in the proportion of 1:10 (m/v) with constant agitation at 150 rpm for 6 h at 60 ºC. Then the modified adsorbents were washed in ultrapure water and dried at 60 °C until constant weight [6]. The material was then subjected to pyrolysis for one hour in a constant heating furnace (25 °C min^{-1}) until the temperature stabilized (750 °C).

2.2. Characterization of the adsorbents

The chemical elements (K, Ca, Mg, Cu, Fe, Mn, Zn, Zn, Cd, Pb and Cr) were determined by means of a nitroperchloric digestion followed by determination by atomic absorption spectrometry (FAAS), with certified standard curves for all metals (GBC 932 AA). Scanning electron microscopy (SEM), infrared (IR) spectroscopy and thermogravimetric (TG) were also performed.

The surface morphology of the materials was evaluated by scanning electron microscopy (SEM), in a JEO JSM 6360-LV microscope equipped with dispersive energy microscopy. It was determined the main functional groups present in the adsorbents also by means of infrared spectroscopy (IR) in a FTIR-8300 Fourier Transform spectrometer (Shimadzu Infrared Spectrophotometer). It was conduced in the region between 400 and 4000 cm^{-1} with resolution of 4 cm^{-1}, in which the spectra were obtained by transmittance using KBr pellets.

For the determination of the zero load point (pH_{PCZ}), 0.5 g of each material produced was weighed and 50 mL of 0.5 mol L^{-1} aqueous solution of potassium chloride (KCl) was added with pH values between 2.0 and 13.0 (pH adjusted with HCl and NaOH - 0.1 mol L^{-1}), totalling 12 samples per adsorbent. After 4 h of stirring (200 rpm), the final pH values were obtained. The pH variation (ΔpH) occurred during the process (final pH - initial pH) was then determined. When plotting the data, pH_{PCZ} corresponded to the value at which the dependent variable (ΔpH) exceeded the value of the independent variable (initial pH) - adapted methodology [15].

The thermal stability of the mass of the adsorbents with increasing temperature was determined by thermal analysis in a thermogravimetric analyzer (TGA 4000 Perkin Elmer), where the samples were heated from 30 to 900 °C with a heating rate of 10 °C min^{-1}, under N_2 atmosphere, with a flow rate of 20 mL min^{-1}.

2.3. Multivariate evaluation of the adsorbent dose and pH in the sorption of metals

To verify the ideal adsorption dose and pH conditions for adsorption, the Rotational Compound Central Design (RCCD) was used. It was decided to use five adsorbent doses and pH with 4 replicates at the center value (750 mg L^{-1} with pH 5.0) as described by [6]. It was used fixed volumes of monoelement solution (50 mL) containing pH adjusted with 0.1 molar solutions of HCl or NaOH, contaminated with 10 mg L^{-1} of Cd^{2+} and Pb^{2+} from monoelement solutions (1000 mg L^{-1}) were used. For the preparation of the monoelement solutions were used cadmium nitrate salts [$Cd(NO_3)_2 4H_2O$] and lead nitrate [$Pb(NO_3)_2$].

The erlenmeyers containing the contaminated solutions and adsorbents were shaken for 90 min in Dubnoff (200 rpm at constant temperature of 25 °C). The final concentrations of Cd or Pb were determined by atomic absorption spectrometry (FAAS). From the final concentration of Pb^{2+} and Cd^{2+}, response surface plots were constructed using the adsorbed amount of metals calculated by Equation 1.

$$Q_{ads} = \frac{(C_0 - C_f)}{m} V \tag{1}$$

In which: Q_{ads} is the amount of adsorbed metals per gram of the adsorbent (mg g^{-1}), m is the mass of the adsorbents (g), C_0 is related to the initial concentration of the ions in the solution (mg L^{-1}), C_f is the concentration of the ions in solution (mg L^{-1}) and V is the volume of the used solution (L).

2.4. Adsorption kinetics

Based on the best results of the adsorbent dose and pH obtained, the ideal time of the metal sorption process was determined. For this, 50 mL of solutions (10 mg L^{-1}) at pH 5.0 containing 200 mg of the adsorbents were shaken at 12 time intervals (5, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160 and 180 minutes).

After stirring, the samples were filtered with qualitative filter paper and the equilibrium concentration was determined by EAA/flame. In order to verify the kinetic mechanism that controls the adsorption process, the models of pseudo-first order and pseudo-second order, Elovich and intraparticle diffusion were used, according to Equations 2, 3, 4 and 5 respectively [16, 17, 18].

$$\log\left(Q_{eq} - Q_t\right) = \log Q_{eq} - \left(\frac{K_1}{2,303}\right) t \tag{2}$$

In which: Q_{eq} (mg g^{-1}) and Q_t (mg g^{-1}) are the amounts of the adsorbate retained per gram of adsorbent at equilibrium and at time t, respectively, and K_1 (min^{-1}) is the rate constant of the pseudo first order.

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t \tag{3}$$

In which: K_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo second order. In contrast of the pseudo first order model, this model predicts the kinetic dynamics over the entire adsorption time [16].

$$Q_{eq} = A + B \text{ Int} \tag{4}$$

In which: A and B are constants, being A corresponding to the initial chemisorption rate (mg g^{-1} h^{-1}) and B indicates the number of sites suitable for adsorption, which is related to the extent of surface coverage and the activation energy of the chemisorption (g mg^{-1}) [17].

$$Q_{eq} = K_{id} t^{1/2} + C_i \tag{5}$$

In which: K_{id} is the constant of the intraparticle diffusion (g mg^{-1} min$^{-1/2}$) and C_i suggest the thickness of the boundary layer effect (mg g^{-1}) [18].

2.5. Adsorption thermodynamics

In order to verify the influence of the temperature in the adsorption process, 200 mg of adsorbent materials were stirred in 50 mL of contaminated solution (50 mg L^{-1} of Pb^{2+}), pH 5.0, rotated at 200 rpm at different temperatures (15, 25, 35, 45 and 55 °C).

From the results, the free energy of Gibbs (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated according to Equations 13 and 14 [19]:

$$\Delta G = -RT \ln K_d \tag{6}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

In which: K_d corresponds to the ratio between the adsorbed amount per unity of the adsorbent (Q_{eq}) and the equilibrium concentration in the solution (C_{eq}), R is the universal constant of the gas (8,314 J mol^{-1} K^{-1}) and T is the temperature used in the experiment. The values of ΔH and ΔS were obtained from the graph of ln K_d in function of 1/T.

2.6. Adsorption equilibrium

From the obtained results by the test of influence of the initial concentration, the adsorption isotherms were determined by linear mathematical models of Langmuir, Freundlich and Dubnin-Radushkevich, respectively, according to Equations 8, 9, 10, 11 and 12.

$$\frac{1}{Q_e} = \frac{1}{C_m} + \frac{1}{K_L C_m C_e} \tag{8}$$

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{1}{q_m} \tag{9}$$

In which: C_e and C_{eq} represent the concentration at equilibrium and Q_e or q_{eq} is the quantity adsorbed at equilibrium per unit mass of the adsorbent. The two parameters of the Langmuir isotherm K_L or b and C_m reflect the nature of the adsorbent material and can be used to compare adsorption performance. The Langmuir C_m parameter is related to the maximum adsorption capacity and K_L or b with the adsorbent-adsorbate interaction forces.

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

In which: C_{eq} or C_e is the concentration in the equilibrium and q_{eq} or o Q_e is the quantity adsorbed in the equilibrium per unity mass of the adsorbent. K_F and n are two parameters of Freundlich model.

$$\ln Q_{eq} = \ln Q_d + B_d \varepsilon^2 \tag{11}$$

In which: Q_{eq} is the amounto of ion adsorbed per unity mass of the adsorbent (mol g^{-1}), Q_d is the adsorption capacity (mol L^{-1}), B_d is a coefficient related to the sorption energy (mol^2 J^{-2}) and 'ε' is the Polanyi potential (Equação 12).

$$\varepsilon = RT \ln (1+1)/C_{eq} \tag{12}$$

In which: R is the universal constant of gas (kJ mol^{-1} K^{-1}), T is the temperature (K) and C_{eq} is the concentration of equilibrium in liquid phase (mol L^{-1}).

3. Results and discussion

The characterization of the total chemical compounds present in the precursor material (canola cake) and activated carbon from canola waste are described in Table 1.

Table 1: Chemical characterization of precursor material (PM) and activated carbon from waste of canola seeds (C.C. NaOH).

Adsorbent	K	P	Ca	Mg	Cu	Zn	Mn	Fe	Cd	Pb	Cr
	------------------- g kg^{-1} ------------------------				-- µg g^{-1} ---						
MP	15.50	1.83	6.60	5.60	16.00	91.00	85.00	243.00	< LQ	21.00	< LQ
C.C. NaOH	1.20	3.48	22.65	12.45	23.00	352.00	507.00	1489.00	< LQ	36.00	< LQ

PM: Precursor material, LQ (limits of quantification): In g kg^{-1}: K = 0.01, Ca = 0.005 e Mg = 0.005. In µg kg^{-1}: Cu = 0.005, Fe = 0.01, Mn = 0.01, Zn = 0.005, Cd = 0.005, Pb = 0.01 and Cr = 0.01.

In general, it can be observed that the K content decreased in the activated carbon. Similar dynamic was observed by [6], for these authors, the contact between the precursor material and the chemical activator results in the extraction of this element, decreasing its concentration. The contents of P, Cu, Zn, Fe, Ca, Mg, Mn and Pb were elevated in the activated carbon in relation to the natural material. Contents of Cd and Cr were not detected. The concentration of these elements in the precursor material may be related to the boiling point, which is extremely high for most metals [20].

In the Figure 1 it is possible to observe the microstructure of the canola activated carbon with NaOH (C.C. NaOH), with amplifications of 100, 3000 and 10000 times. It can be observed with irregular aspect, with superficial pores and openings of different sizes and proportions.
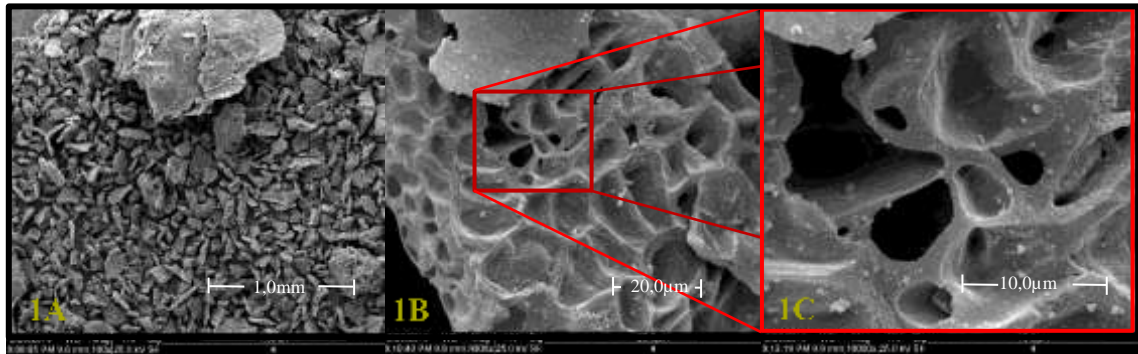

Fig. 1: Scanning electron microscopy for NaOH activated carbon (C.C. NaOH) with amplifications of: 100X (1A), 3000X (1B) and 10000X times (1C).

IR spectra (Figure 2A) in the 1385 regions may be related to N-H bonds of amines, CH_3, C-O or CH. The bands around 1385 are related to the degradation of CH_2 and CH_3. The band at 896 is related to NH_2 groups. Bands 1760 and 1771 are related to the C=O group, bound to the presence of esters, and bands 720 and 728 are related to CH groupings [21].
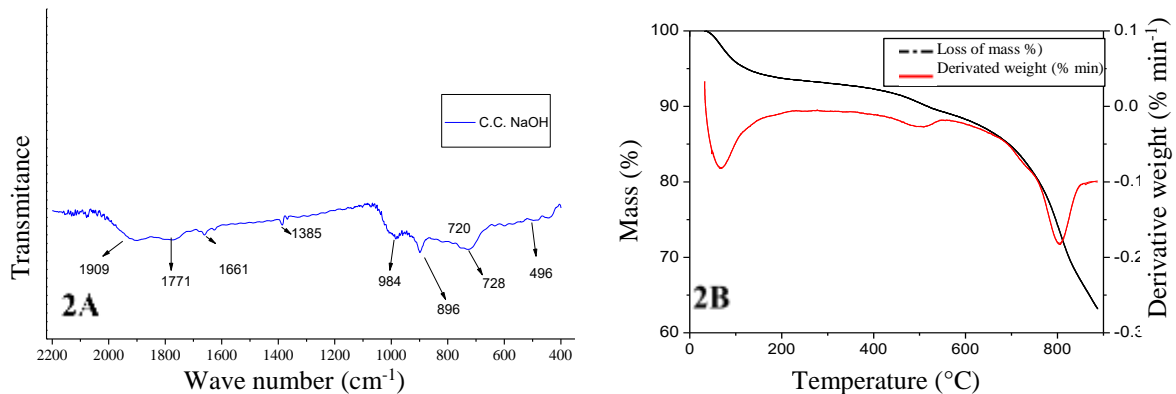

Fig. 2: A) Infrared spectra and B) Thermogravimetric (TG) and Thermogravimetric Derivative (DTG) analysis for the NaOH activated carbon from the canola seed waste (C.C. NaOH).

In TG (Figure 2B), two major events are observed, the first one related to water loss (close to 100 °C) [22], an event occurring near 500 °C. Likewise, the observed event at 800 °C is linked to the reactions at 800 are both related to dehydroxylation [23].

It was obtained $pH_{PCZ} = 10.83$. This pH_{PCZ} value is directly related to the basic nature of the activated agent. The alkalinization of activated carbons with strong bases such as NaOH is common due to release of hydroxylates from the chemical reagent [6].

It is necessary to emphasize that, when pH of the solution > pH_{PCZ}, the surface of the adsorbent is electronegative, favouring the adsorption of metallic cations like Cd^{2+} and Pb^{2+}. In the case of pH < pH_{PCZ}, the surface of the adsorbent is electropositive, in which H^+ ions effectively compete with the metal cations, repelling them from the surface reducing the adsorption efficiency [23].

It can be observed, in Figure 3, the adsorption dynamic of Pb^{2+} ions (Figure 3A) and Cd^{2+} (Figure 3B) as a function of the adsorbent doses and pH of the solution. The figure shows that higher Pb and Cd removals occurred, in both cases, for smaller ones doses of adsorbent used in the present study (5 g L^{-1}). However, when using even lower doses, it can be raised to the adsorption efficiency (approaching even more of the red area). This dynamic was also observed by [6]. In that study, the author states that 4 g L^{-1} is the ideal dose to decontaminate one liter of contaminated solution. It is noteworthy that this author used the same design used in the present study.
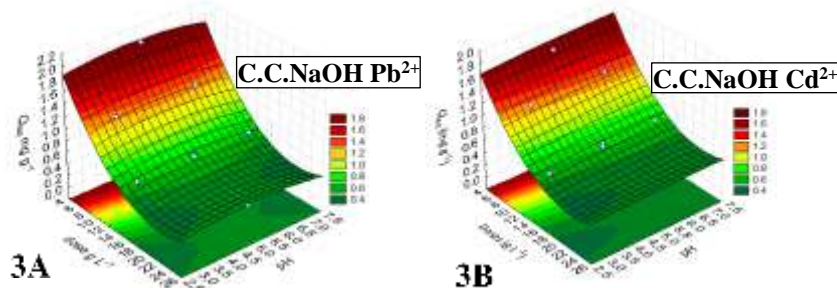
Fig. 3: Response surfaces of the activated carbon doses versus the pH of the solution by the adsorbed amount (Q_{eq}) of Pb^{2+} (3A) and Cd^{2+} (3B).

Regarding the kinetic parameters (Table 2), it was possible to verify that the equilibrium occurred at 40 min. According to [22], there is a tendency to deplete the active sites of the adsorbents in the removal of $Cd2+$ and Pb^{2+}. It suggest that times greater than the equilibrium (40 min) are not justified, as this would result in greater time and unnecessary expenses. In addition, the kinetic models of pseudo first order and Elovich did not fit the experimental data. Better adjustments were observed for pseudo second order, for both metals, and adjustment of intraparticle diffusion for Pb^{2+} removal.

Table 2: Kinetic parameters of pseudo first order, pseudo second order, Elovich and intra-particle diffusion models and quantity of the adsorbed material in the equilibrium ($Q_{eq(exp.)}$) obtained in the adsorption studies of Cd^{2+} and Pb^{2+} by activated carbon from canola wastes.

	Pseudo first order			Pseudo second order			Elovich		
	K_1 (min^{-1})	$Q_{eq (cal.)}$ (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	$Q_{eq (cal.)}$ (mg g^{-1})	R^2	A (mg g^{-1} h^{-1})	B (g mg^{-1})	R^2
C.C.NaOH Pb^{2+}	0.0129	2.3747	0.8976	-0.1876	1.3208	0.9223	2.145	1.4779	0.830
C.C.NaOH Cd^{2+}	0.0389	1.5460	0.8945	0.1200	2.6344	0.9984	2.017	0.0614	0.839

	Intraparticle diffusion									
	-------------- K_{id} ----------------- (g mg^{-1} min$^{-1/2}$)			--------------- C_i --------------- (mg g^{-1})			------------ R^2 --------------			$Q_{eq(exp.)}$ (mg g^{-1})
	Reta A	Reta B	Reta C	Reta A	Reta B	Reta C	Reta A	Reta B	Reta C	
C.C.NaOH Pb^{2+}	1.54730	0.88119	2.39544	0.07452	0.17457	0.00830	0.9877	0.9826	0.758	1.206
C.C.NaOH Cd^{2+}	1.0194	0.9574	-	0.35540	0.05763	-	0.8734	0.859	-	2.2013

K_1: constant velocity of first order. Q_{eq}: amounts of adsorbate retained per gram of adsorbent in the equilibrium. K_2: constant velocity of pseudo second order. A: constant that indicates the velocity of initial chemisorption. B: number of active sites adequate for adsorption, related to the extent of surface coverage and the activation energy of the chemisorption. R^2: adjusted coefficient of determination. K_{id}: intraparticle diffusion constant. C_i: suggests the thickness of the boundary layer effect.

In the intraparticle diffusion, the straight line A shows that the initial adsorption with fast sorption velocity where the cadmium ions are rapidly sorbed in the surface layer of the adsorbent. 2) the adsorption velocity decreases following intraparticle diffusion [6] does not occur in the line C, the values of Kid, show that adsorption continues to occur in adsorption and not desorption [23].

It is observed that the Q_{eq} in the adsorption of Pb^{2+} decreased with the temperature increase. Similar results were found in adsorption of Cd^{2+} by [24]. With adsorbents of well-developed surfaces, adsorbent adsorption sites are efficiently exposed to the solute, and this can raise the Q_{eq} over time as shown by the Q_{eq} values for Cd^{2+} adsorption [25].

Table 3: Q_{eq} values and thermodynamic parameters obtained in the adsorption of Cd^{2+} and Pb^{2+} by activated carbon from canola wastes.

	T °C	------------------- Cd²⁺ -------------------					------------------ Pb²⁺ -----------------				
		Q_{eq}	ΔG	ΔH	ΔS	R^2	Q_{eq}	ΔG	ΔH	ΔS	R^2
C.C. NaOH	15	10.100	39.0				11.47	-2.4			
	25	10.800	39.7				11.00	-3.1			
	35	11.300	40.5	21.841	74.422	0.955	9.163	-3.5	32.016	101.622	0.815
	45	11.300	41.0				8.565	-4.0			
	55	11.600	41.8				8.777	-4.7			

Q_{eq}: amount adsorbed per unity of adsorbent (mg g⁻¹). $ΔG$: variation of free energy of Gibbs (KJ mol⁻¹). $ΔH$: enthalpy variation (KJ mol⁻¹). $ΔS$: entropy variation (J mol⁻¹ K⁻¹). T: Temperature (ºC).

Values for ΔH up to 25 kJ mol⁻¹, as observed for adsorption of Cd^{2+} indicate physiosorption. However, to be considered chemisorption it is necessary to reach 40 kJ mol⁻¹, the value of ΔH for adsorption of Pb^{2+} did not reach this value, showing load sharing or transfer of the loads of the biomass surface [24].

Table 4: Parameters of mathematical linear models of Langmuir, Freundlich and D-R related to the adsorption of Cd^{2+} and Pb^{2+} by activated carbon produced from canola seed wastes.

	-------- Constants of Langmuir -------				------ Constants of Freundlich ------			------------- D-R -------------		
	Q_m (mg g⁻¹)	b ou K_L (L mg⁻¹)	R_L	R^2	K_f (mg g⁻¹)	n	R^2	Q_d	E	R^2
Pb²⁺	44.248	0.310	0.129	0.991	2.460	1.574	0.965	0.0013	11.471	0.992
Cd²⁺	52.356	0.528	0.149	0.992	3.739	4.354	0.992	0.0001	17.678	0.990

Q_m (mg g⁻¹): maximum capacity of adsorption. K_L or b (L mg⁻¹): constant related to the adsorbent/adsorbate interaction forces. R_L: Langmuir constant. R^2: coefficient of determination. K_f (L mg⁻¹): related to the adsorption capacity. n: related to the heterogeneity of the solid. Q_d (mol g⁻¹): maximum adsorption capacity. E: (KJ mol⁻¹): average energy of sorption.

It can be observed by the values of R^2 that for the adsorption of Pb^{2+} and Cd^{2+}, there were good mathematical adjustments by the Langmuir, Freundlich and D-R model, for all the adsorbents. However, the R^2 value for Cd^{2+} adsorption by the model of Freundlich presented lower value of R^2.

4. Conclusion

With the production of NaOH activated carbon from canola seed wastes, it was possible to remove large quantities of Pb^{2+} and Cd^{2+} from polluted waters. The mathematical models of Langmuir, Freundlich and D-R obtained by linearization showed high capacity of removal of both metals and chemical adsorption (values of $n > 1$).

According to the results of adsorbent doses and pH of the solution, it is possible to conclude that four grams of adsorbent are needed to decontaminate one liter of contaminated solution. Thus, using the canola wastes to produce activated carbon. It is possible to add value to the canola seed wastes, directly collaborating with the economic, social and environmental sustainability of this productive system.

Acknowledgements

References

[1] C. H. Lin, Y. T. Hun, C. C. Yen, H. H. Chen, C. J. Tseng, Y. K. Lo, J. Y. H. Chan, "Association between heavy metal levels and acute ischemic stroke," *J. Biom. Scienc.*, vol. 25, no. 1, pp. 1-8, 2018.

[2] G. M. Al-Senani, F. F. Al-Fawzan, "Study on Adsorption of Cu and Ba from Aqueous Solutions Using Nanoparticles of Origanum (OR) and Lavandula (LV)," *Bioinorg. Chem. Applic.*, pp.1–8, 2018.

[3] N. S. Sulaiman, R. Hashim, A. Mohamad, M. Danish, O. Sulaiman, "Optimization of activated carbon preparation from cassava stem using response surface methodology on surface area and yield," *J. Clean. Prod.,* vol. 198, pp. 1422–1430, 2018.

[4] D. Schwantes, A. C. Gonçalves, G. F. Coelho, M. A. campagnolo, D. C. Dragunski, R. T. Tarley, A. Miola Jr, E. A. V. Leismann, "Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater," *J. Chem.*, pp. 1-15, 2016.

[5] S. Valizadeh, H. Younesi, N. Bahramifar, "Preparation and Characterization of Activated Carbon from the Cones of Iranian Pine Trees (Pinus eldarica) by Chemical Activation with H_3PO_4 and Its Application for Removal of Sodium Dodecylbenzene Sulfonate Removal from Aqueous Solution," *Water conservat. Sc. Eng.*, vol. 3, no. 4, pp. 253–265, 2018.

[6] D. Schwantes, A. C. Gonçalves, M. A. Campagnolo, C. R. T. Tarley, D. Dragunski, Conradi, E. "Chemical modifications on pinus bark for adsorption of toxic metals," *J. Environ. Chem. Eng.*, vol. 6, no. 1, pp. 1271–1278, 2018.

[7] J. V. Berni, J. P. V. de Cesaro, F. B. Scheufelle, M. F. Vieira, "Produção e caracterização de carvão ativado proveniente do caroço de açaí," *Cong. Bras. Eng. Quim.*, vol. 20, 2018.

[8] A. C. Goncalves Jr, G. F. Coelho, D. Schwantes, A. L. Rech, M. A. Campagnolo, A. Miola Jr, "Biosorption of Cu (II) and Zn (II) with acai endocarp Euterpe oleracea M. in contaminated aqueous solution," *Acta Scient. Technol.,* vol. 38, no. 3, pp. 361-371.

[9] Ç. Sarici-Özdemir, Y. Önal, "Synthesis of new activated carbons produced from polymer waste, Fullerenes," *Nanot. Carb. Nanostruc.*, vol. 26, no. 7, pp. 451-457, 2018.

[10] R. A. Olaoye, O. D. Afolayan, O. I. Mustapha, O. G. H. adeleke, "The Efficacy of Banana Peel Activated Carbon in the Removal of Cyanide and Selected Metals from Cassava Processing Wastewater," *Advances Res.*, vol. 16, no. 1, pp. 1-12, 2018.

[11] D. Balarak, J. Jaafari, G. Hassani, Y. Mahdavi, I. Tyagi, V. K. Gupta, "The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies," *Col. and Interf. Sc. Com.*, vol. 7, pp. 16–19, 2015.

[12] D. Balarak, F. Mostafapour, "Adsorption of Acid Red 97 Dye on Canola," *J. Sc. Eng. Res.*, vol. 3, no. 3, pp. 148-154, 2016.

[13] M. Feizi, M. Jalali, "Removal of heavy metals from aqueous solutions using sunflower, potato, canola and walnut shell residues," *J. Taiwan Inst. Chem. Eng.,* vol. 54, pp. 125–136, 2015.

[14] IUPAC. "International Union of Pure and Applied Chemistry. Rep. Physis. data for gas/solid systems with special reference to the determination of surface area and porosity," *Pure App. Chem.*, vol. 57, pp. 603-619, 1985.

[15] A. M. S. Mimura, T. V. A. Vieira, P. B. Martelli, H. F. gorgulho, "Utilization of rice husk to remove Cu^{2+}, Al^{3+}, Ni^{2+} and Zn^{2+} from wastewater," *Quím. Nova.,* vol. 33, no. 6, pp. 1279-1284, 2010.

[16] Y. S. Ho, G. McKay, "Pseudo-second-order model for sorption," *Process Biochem.*, vol. 34, no. 5, pp. 451-465, 1999.

[17] A. Witek-Krowiak, R. G. Szafran, S. Modelski, "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent," *Desalination*, vol. 265, no. 1-3, pp. 126-134. 2011.

[18] R. Han, L. Zhang, M. Zhang, H. Zhu, L. Zhang, "Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode," *Carbohyd. Polym.*, vol. 79, pp. 1140-1149, 2010.

[19] A. Sari, M. Tuzen, D. Citak, M. Soylak, "Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay," *J. Hazardous Mat.,* vol. 149, no. 2, pp. 283–291, 2007.

[20] L. Calabria, E. T. Balbinot, M. Bonattoc, "Transferência das ligas de soldas estanho (Sn) e chumbo (Pb) na indústria eletrônica: implicações no bem-estar do trabalhador e na performance Ambiental," *Resp. Socioamb.*, vol. 1, no. 1, 2015.

[21] M. F. Queiroz, K. Melo, D. Sabry, G. Sassaki, H. Rocha, "Does the Use of Chitosan Contribute to Oxalate Kidney Stone Formation?" *Marine Drugs*, vol. 13, no. 1, pp. 141–158, 2014.

[22] G. F. Coelho, A. C. Gonçalves, D. Schwantes, C. R. T. Tarley, D. Dragunski, E. Conradi Jr., "Removal of Cd(II), Pb(II) and Cr(III) from water using modified residues of Anacardium occidentale L," *Appl. Water Sc.,* vol. 3, no. 1, pp. 1–21, 2018.

[23] M. F. Brigatti, S. Colonna, D. Malferrari, L. Medici, L. Poppi, "Mercury adsorption by montmorillonite and vermiculite: a combined XRD, TG-MS, and EXAFS study," *Applied Clay Sc.,* vol. 28, no. 1-4, pp. 1–8, 2005.

[24] Y. Chang, J-Y. Lai, D-J. Lee, D-J, "Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters: Research updated," *Biores. Techn.*, vol. 222, pp. 513–516, 2016.

[25] X. Liu, & D-J. Lee, "Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters," *Biores. Techn.*, vol. 160, pp. 24–31, 2014.