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A *Crambe abyssinica* seed by-product as biosorbent for lead(II) removal from water

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ABSTRACT

This study assessed the performance of a C*rambe abyssinica* Hochst seed by-product as biosorbent for removing lead [Pb(II)] ions from water. The material was characterized by scanning electron microscopy and infrared spectroscopy techniques as well as by point of zero charge (pH_{PCZ}) measurement. The following parameters were determined after adsorption experiments: solution pH, biosorbent mass, contact time, and temperature. The optimal conditions were found to be mass –400 mg, solution pH 7.0, and equilibration time –20 min; they were used for performing isotherm tests. The isotherms were best fitted to the Freundlich and Dubinin–Radushkevich mathematical models. Based on the results of kinetic and thermodynamic studies (pseudo-second-order kinetics, negative change in Gibbs free energy, positive change in enthalpy and low ion desorption rate), it was established that the Pb(II) ions interacted forcefully with the biosorbent, thus confirming that a spontaneous endothermic chemisorption process took place. To check the effectiveness of the novel adsorbent for the Pb(II) removal and retention, comparative studies were carried out with activated carbon. On the basis of the obtained results, it has been possible to conclude that the *C. abyssinica* seed by-product can feasibly be used as an alternative material for the remediation of lead-contaminated water, since it is sustainable and does not require pretreatment.

Keywords: Adsorption; Water; Lead; *Crambe abyssinica* Hochst; Sustainability

1. Introduction

Contamination of water resources with heavy metals is one of the most concern environmental issues, because these elements are not biodegradable and can accumulate in living tissues, thereby inducing a range of diseases and disorders [1,2].

Among the heavy metal ions, lead [ionic form—Pb(II)] is considered highly dangerous due to the fact that it scatters immediately throughout the system when entering the body and brings harmful

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effects to tissues, in which it would accumulate, causing red blood cell and kidney damages, hearing impairment, malaise, anorexia, vomiting, and even mental retardation [3,4]. Pb(II) pollution is produced by industrial activities such as batteries, solders, ammunition, lubricating oil and metal alloys [5].

To minimize heavy metal contamination hazards, water resources have received legal protection. Thus, Resolution No. 357/2005 issued by the Brazilian Environmental Council (CONAMA) has set the maximum allowable limit for Pb(II) at $0.033\,\mathrm{mg\,L^{-1}}$ [6], whereas the limit established by Ordinance 518/2004 of the Brazilian Ministry of Health is $0.01\,\mathrm{mg\,L^{-1}}$ for drinking water [7].

Several methods are commonly used to remove the heavy metals from water: coagulation, chemical precipitation, solvent extraction, reverse osmosis, oxidation and reduction, electrochemical deposition, membrane separation and ion exchange on polymeric resins [8–11]. However, these techniques can be more expensive when compared to adsorption [12].

The latter is based on adhesion of species to surfaces of various materials, even at their very low concentrations ($<100\,\mathrm{mg\,L^{-1}}$) [13]. Activated charcoal appears to be the most common adsorbent for water purification, but lately, materials prepared from agro-industrial wastes have been studied and introduced due to their efficiency and cheapness compared with other commercial adsorbents. The following biosorbents have been used for the Pb(II) removal: almond (*Prumus dulcis*) and hazelnut shell (*Corylus avellana*) [3], pine bark (*Pinus brutia Ten.*) [4], banana peel [12], natural sponge (*Luffa cylindrica*) [14] rice bran [15], sugarcane bagasse [16], peach palm waste [17], and many others.

In order for a biosorbent to be considered feasible, it must come from a renewable source, below-cost and easy to manipulate and have the least possible environmental impact [1].

Given these characteristics, the benefits provided by the culture of *Crambe* (*Crambe abyssinica* Hochst) are immense, considering its easy cultivation, early growth, resistance to pests and diseases; besides, this plant is excellent for producing biodiesel, since its seeds contain high levels (36–38%) of good-quality oil [18,19]. The extraction of oil from *Crambe* seeds gives a large amount of by-product that cannot be used in animal feed, because it has unpalatable features and belongs to the glucosinolates, meaning that it is transformed into toxic substances when entering the digestive system of nonruminant animals [18–22].

Thus, the *Crambe* seed by-product can be alternatively used as biosorbent, since recent studies have demonstrated its effective application for the removal of dyes from aqueous solutions [23]. Therefore, the objective of this research was to evaluate the use of this by-product for the biosorption of the toxic heavy metal ion—Pb(II)—present in water-based solutions.

2. Materials and methods

2.1. Material and solutions

Crambe seeds were obtained in the city of Jatai (Region of Cerrado, State of Goiás, Brazil).

Aqueous solutions (based on distilled and deionized water) were synthetically contaminated with Pb(II) using neutral lead acetate salts PA ($(CH_3.COO)$ 2Pb, Vetec, 99%).

2.2. Preparation and characterization of the biosorbent

The *Crambe* seeds were dried in an oven at 60°C for 36 h. Then, they were crushed, and the oil extracted using a Soxhlet apparatus [24] resulted in the production of a by-product. The latter was dried at 70°C for 24 h to evaporate the n-hexane solvent (C_6H_{14}).

Afterwards, this biosorbent material was passed through a 14-mesh sieve to get a standard particle size.

The morphological characterization of the by-product was performed by scanning electron microscopy (SEM); a Bal-Tec SCD 050 sputter coater and FEI Quanta 200 scanning microscope (voltage 30 kV) were employed.

Infrared (IR) spectra were taken with KBr pellets on a Shimadzu FTIR-8300 Fourier transform infrared spectrophotometer (resolution $4\,\mathrm{cm^{-1}}$).

To determine partial charges on the surface of the adsorbent (point of zero charge—pH_{PZC}), the following procedure was carried out: 50 mg of the material was mixed with 50 mL of $0.05–0.5\,\mathrm{mol\,L^{-1}}$ aqueous KCl solutions (Vetec, 99%) at initial pH 2.0–10.0. The mixtures were stirred in a Marconi AM 035 Dubnoff-type thermostat at 200 rpm and 25°C for 24 h. At the end of this period, the final pH values were obtained, resulting in a graph with initial pH depending on the final pH, being the that the pH range where there was no chance to the final pH corresponds to the pH_{PZC} [25].

2.3. Study of the Pb(II) adsorption

2.3.1. Effects of solution pH and adsorbent mass

Ten milligram per litre Pb(II) solutions was adjusted to pH 5.0, 6.0, and 7.0 with $0.1\,\mathrm{mol\,L^{-1}}$ NaOH (Vetec, 99%) or HCl (Vetec, 37%) and then poured (50 mL) into 125-mL Erlenmeyer flasks containing 200–1,200 mg of the biosorbent. The samples remained under constant stirring at 200 rpm and 25˚C for 90 min. Afterwards, 10-mL aliquots were withdrawn, centrifuged in a Biosystems HT-81C device at 3,000 rpm (629.77 g) for 5 min, and then, Pb(II) concentrations were determined by flame atomic absorption spectroscopy (FAAS) using a GBC 932 AA instrument (Victoria, Australia) and calibration curves built with certified standards [26].

The equilibrium adsorption capacity was estimated according to Eq. (1):

$$Q_{eq} = \frac{(C_0 - C_{eq})}{m} V \qquad (1)$$

where Q_{eq} is the Pb(II) amount adsorbed per unit mass of the biosorbent (mg g^{-1}), m is the mass of the biosorbent (*g*), C_0 and C_{eq} are the initial and equilibrium Pb(II) concentrations, respectively, in the solution (mg L^{-1}), and V is the volume of the solution (L).

2.3.2. Effect of contact time

One hundred and twenty five milli litre Erlenmeyer flasks containing 50 mL of 10 mg L^{-1} Pb(II) solutions (pH 7.0) and 400 mg of the adsorbent were stirred at 200 rpm (Thermostat Dubnoff-Marconi MA 035) and 25˚C for 20–180 min. Then, 10 mL aliquots were collected and centrifuged (629.77 g) for 5 min, and subsequently, Pb(II) levels were measured by FAAS [26].

2.3.3. Adsorption isotherms

The optimal pre-established conditions found in the previous studies were used to construct adsorption isotherms. About 50 mL of 10–90 mg L^{-1} Pb(II) solutions was transferred to Erlenmeyer flasks and stirred at 200 rpm and 25˚C, and 10 mL aliquots of the solutions were collected and centrifuged (629.77 g), and after that, Pb(II) concentrations were measured by FAAS [26].

2.3.4. Study of the Pb(II) desorption

To perform the desorption study, the biosorbent material used in the adsorption tests was filtered, rinsed with distilled and deionized water, and dried in a laboratory oven at 60˚C for 24 h. Then, it was weighed and placed into flasks containing 50 mL of 0.1 mol L^{-1} HCl (Vetec, 37%). The mixtures were constantly stirred at 200 rpm, and 25˚C for 20 min, and 10 mL aliquots of the liquid phase were collected and centrifuged for 5 min, and then, Pb(II) levels were measured by FAAS [26].

The Pb(II) desorption rate (*D*, %) was calculated according to Eq. (2):

$$D = \left(\frac{C_{eq(des)}}{C_{eq(ads)}}\right) \times 100 \qquad (2)$$

where $C_{eq(des.)}$ and $C_{eq(ads.)}$ are the desorbed and adsorbed Pb(II) amounts, respectively (mg).

2.3.5. Thermodynamic parameters

The effect of temperature on the Pb(II) adsorption on the *Crambe* seed by-product was estimated at 25, 35, 45, 55, and 65˚C under the optimal conditions found: adsorbent mass—400 mg, solution (50 mg L^{-1}) pH of 7.0, and stirring time—20 min (200 rpm, 25˚C).

2.3.6. Comparative study with activated charcoal

The comparative study was performed with powdered activated charcoal PA (Synth), since it is the most common commercial adsorbent [9,27,28], under the same optimal conditions as those employed for the Pb(II) adsorption and desorption studies with the *Crambe* biosorbent.

3. Results and discussion

3.1. Characterization of the biosorbent

The scanning electron micrographs of the *Crambe* seed by-product (Fig. 1) demonstrate its irregular and heterogeneous surface that can enable the retention of metal ions present in aqueous solutions.

Molecular IR spectroscopy is an analysis technique that allows to indicate the incidence of various functional groups on the biosorbent surface based on the number of absorption peaks [29].

In Fig. 2, it is possible to observe peaks at 3,328, 2,925, 1,647, 1,537, 1,429, 1,251, and 1,053 cm^{-1} obtained after the spectral analysis of the *Crambe* seed by-product.

The strong band at 3,328 cm^{-1} may be attributed to the OH stretching vibrations of carbohydrates, proteins, fatty acids, celluloses, lignins, and absorbed water [30–32]. The thin band at 2,925 cm^{-1} assumes the CH stretching vibrations of alkanes, whereas the peaks at 1,647, 1,537, and 1,429 cm^{-1} are due to the CO stretching vibrations of amide and carboxyl groups [32]. Besides, the band at 1,537 cm^{-1} may also be assigned to the NH stretching of proteins. The band at 1,251 cm^{-1} is attributed to the CO stretching vibrations of phenols [32], and the band at 1,053 cm^{-1}

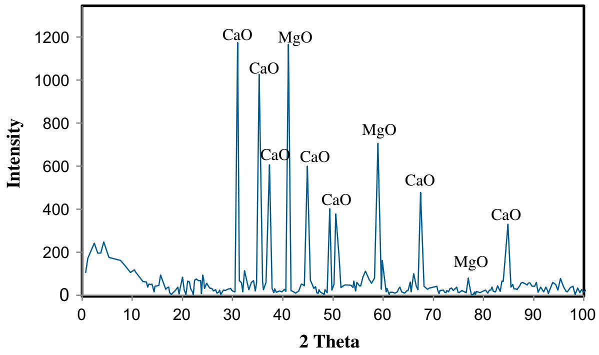

Fig. 1. Scanning electron micrographs of the *C. abyssinica* seed by-product.

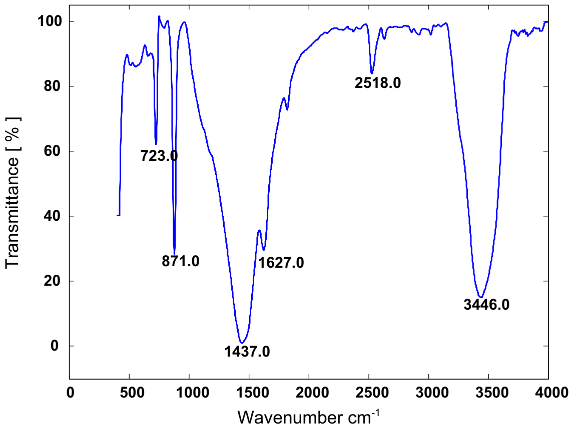

Fig. 2. IR spectra of the *C. abyssinica* seed by-product.

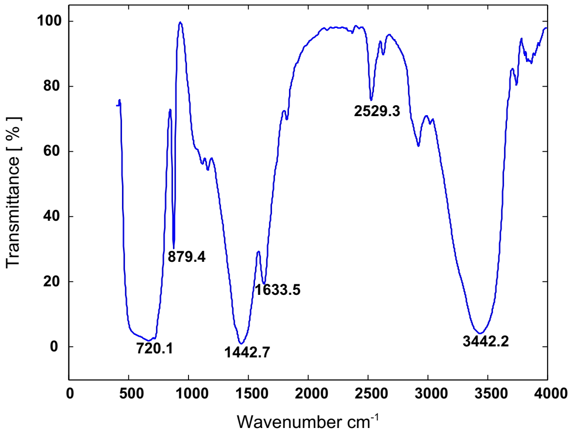

Fig. 3. Experimental determination of pH_{PZC}.

may be ascribed to the CO stretching vibrations of lignins [32,33], which appears to be a significant factor, since lignins have been used for the metal adsorption [34,35].

Identification of the functional groups in the biomass is important, since biosorption is the result of electrostatic interaction and formation of complexes between the metal ions and the functional groups found in the biosorbent [29,36]. From the spectral analysis of the *Crambe* seed by-product, it can be suggested that this material has the following functional groups that enable the metal adsorption: hydroxyl, amide, carbonyl, and carboxyl [36].

To understand the adsorption mechanism, the point of zero charge (pH_{PZC}) of the adsorbent should be determined. Adsorption of cations is favored at $pH > pH_{PZC}$, whereas adsorption of anions is favored at $pH < pH_{PZC}$ [37]. Fig. 3 shows the experimental determination of the pH_{PZC} using two KCl concentrations. It can be seen that the pH_{PZC} of the *Crambe* seed by-product was found to be close to 5.5, thus corroborating the value obtained by Oliveira et al. [23] for this biosorbent.

3.2. Study of the Pb(II) adsorption

3.2.1. Effects of solution pH and adsorbent mass

The solution pH is the most important parameter that controls the adsorption process, because it influences the charge distribution at the active site surface and the speciation of metal ions [4,38]. Considering the pH_{PZC} value found in the present research, it should be expected that at $pH < 5.5$, the surface bearing ionizable groups become protonated, thus generating a net positive charge, which can cause repulsion between the surface and the cations in the solution, and consequently, discouraging the adsorption [25,38].

Therefore, for further experiments, the pH of the solutions was adjusted to values higher than that found for the pH_{PZC} (Fig. 3), and pH 7.0 was the optimal one, at which higher Pb(II) removal rate was obtained (Fig. 4).

Despite knowing that metal precipitation can take place at $pH > 6.0$ [9], the solution pH value of 7.0 was selected due to the results obtained from the pH test (Fig. 4). Moreover, the experimental concentrations were below those used in several previous adsorption tests, and no precipitation features, such as the presence of crystals and turbidity in the solution were observed [38].

The studies performed by Pehlivan et al. [3], Gundogdu et al. [4] and Tarley and Arruda [14], in which biosorbents of vegetable origin were employed, showed high Pb(II) adsorption capacity at pH 7.0.

Regarding the variation in the biosorbent mass, it is known that the greater the mass, the larger the surface, and more active sites become available for the metal adsorption. Nevertheless, as shown in Fig. 4, for masses > 400 mg, the percent removal (adsorption) was constant. From this point on, partial aggregation of the adsorbent took place, leading to a decrease in the surface area and in the metal amount adsorbed per unit mass of the biosorbent (Q_{eq}, mg g^{-1}) due to repulsive forces between the solute particles in the solid and those remaining in the solution [15,39,40].

Since the adsorption sites became saturated, it is possible to assume that for economic removal of any metal amount, small batches of the adsorbent should be used rather than only a single batch [15].

Hence, as demonstrated by the results, the biosorbent mass of 400 mg was used in further studies.

3.2.2. *Effect of contact time*

The kinetics of the Pb(II) adsorption was very rapid, since > 94% of the Pb(II) ions was removed by the *Crambe* seed by-product from the 10 mg L^{-1} water-based solution after 20 min of contact (Fig. 5). These data corroborate the findings of Tarley and Arruda [14] observed for the Pb(II) adsorption on a natural sponge (*L. cylindrica*).

The kinetics of the Pb(II) adsorption on the *Crambe* seed by-product was investigated by implementing four mathematical models: pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion.

The pseudo-first-order equation assumes that the adsorption rate is proportional to the number of sites that remain unoccupied by solute (metal) particles [8,9]. The linear form of this model is presented by Eq. (3).

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - \frac{K_1 \times t}{2.303} \tag{3}$$

where Q_{eq} is the Pb(II) amount adsorbed at equilibrium (mg g^{-1}); Q_t is the Pb(II) amount adsorbed at time t (mg g^{-1}); K_1 is the pseudo-first-order rate constant (min^{-1}).

Unlike the pseudo-first-order model, the pseudo-second-order kinetic model (Eq. (4)) represents the chemical nature of adsorption.

$$\frac{t}{Q_t} = \frac{1}{K_2 \times Q_{eq}^2} + \frac{1t}{Q_{eq}} \tag{4}$$

where K_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

The Elovich model (Eq. (5)) allows to describe chemisorption [8,41], and it is often validated for systems, in which the adsorbent surface is heterogeneous [27].

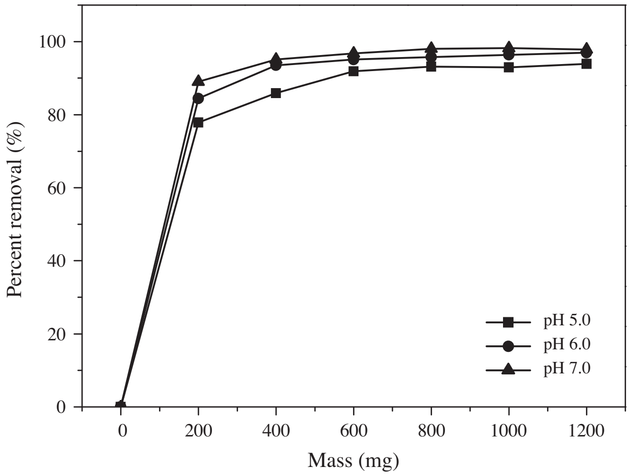

Fig. 4. Pb(II) percent removal for the *C. abyssinica* seed biosorbent as a function of the variation in its mass and the solution pH (C_0: 10 mg L^{-1}, 50 mL, 90 min, 200 rpm, 25˚C).

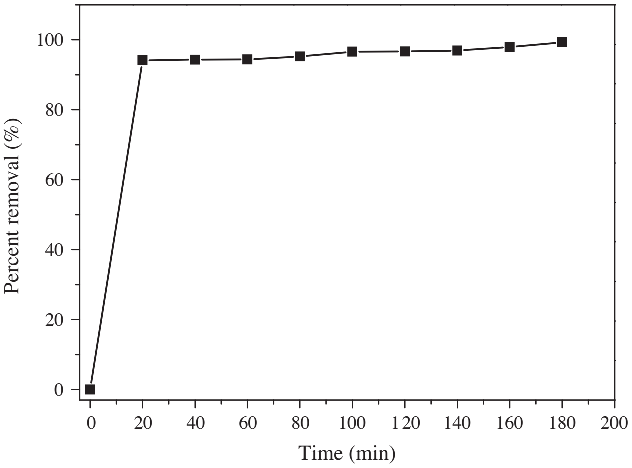

Fig. 5. Pb(II) percent removal for the *C. abyssinica* seed by-product as a function of the contact time (C_0: 10 mg L^{-1}, 50 mL; 400 mg, 200 rpm, 25˚C).

$$Q_{\mathrm{eq}} = A + B \ln t \tag{5}$$

where A and B are constants: A represents the initial rate of chemisorption, and B is related to the extent of surface coverage and the activation energy for chemisorption.

The intraparticle diffusion model (Eq. (6)) is derived from the Fick's law; it presumes that diffusion through liquid film surrounding the adsorbent is meaningless, and the adsorption process is controlled by intraparticle diffusion [42].

$$Q_{\mathrm{eq}} = K_{\mathrm{id}} t^{1/2} + C_{\mathrm{i}} \tag{6}$$

where K_{id} is the intraparticle diffusion constant ($\mathrm{g\,mg^{-1}\,min^{-1/2}}$); C_{i} is the boundary layer thickness constant ($\mathrm{mg\,g^{-1}}$).

Table 1 shows that the pseudo-first-order and Elovich models ($R^2 = 0.875$ and 0.772, respectively) were not suitable for describing the kinetics of the Pb(II) adsorption on the *Crambe* seed by-product.

Herein, the intraparticle diffusion was not the controlling factor in the biosorption kinetics due to the fact that the straight line shown on the graph (Fig. 6(d)) does not go through the origin [43,44], and the $C_{\mathrm{i},}$ value is different from zero (Table 1). Besides the determination coefficient found for this model ($R^2 = 0.946$) is inadequate when compared to the pseudo-second-order model ($R^2 = 0.999$) that showed the proximity of the values predicted for the Pb(II) adsorption at equilibrium [Q_{eq}(pred.)] and determined experimentally [Q_{eq}(exp.)] (Table 1).

Therefore, the pseudo-second-order model provided the best fit to the kinetic data obtained for the Pb(II) adsorption on the *Crambe* seed by-product, assuming that the adsorption rate was governed by chemisorption through sharing or exchange of electrons between the adsorbent and the adsorbate (Pb(II) ions) [13,45].

3.2.3. Adsorption isotherms

The data obtained after the adsorption tests performed under the optimal conditions were used to construct isotherms, which show the relationship between the Pb(II) amount adsorbed onto the adsorbent surface (Q_{eq}) and the Pb(II) equilibrium concentration in the liquid phase (C_{eq}).

Besides, to interpret these data, linear Langmuir, Freundlich and Dubinin–Radushkevich models were employed.

The Langmuir model (Eq. (7)) assumes that adsorption takes place onto a monolayer-covered surface composed of a finite number of homogenous sites [8]:

$$\frac{C_{\mathrm{eq}}}{Q_{\mathrm{eq}}} = \frac{1}{q_{\mathrm{m}} \times b} + \frac{C_{\mathrm{eq}}}{q_{\mathrm{m}}} \tag{7}$$

where C_{eq} is the Pb(II) equilibrium concentration ($\mathrm{mg\,L^{-1}}$); Q_{eq} is the Pb(II) equilibrium amount adsorbed per unit mass of the adsorbent ($\mathrm{mg\,g^{-1}}$); q_{m} is the maximum adsorption capacity; and b (or K_{L}) is related to the interaction forces between the adsorbent and the adsorbate.

Unlike the Langmuir model, the Freundlich model (Eq. (8)) describes multilayer adsorption occurring at heterogeneous surfaces [8]:

$$\log Q_{\mathrm{eq}} = \log K_{\mathrm{f}} + \left(\frac{1}{n}\right) \times \log C_{\mathrm{eq}} \tag{8}$$

where K_{F} is the adsorption capacity, and n is related to the intensity of adsorption and the adsorbent/adsorbate interaction.

The Dubinin–Radushkevich (DR) model (Eq. (9)) allows to determine the adsorption energy and distinguish between physical and chemical adsorption [38,46]:

Table 1
Pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic parameters obtained for the Pb(II) biosorption on the *C. abyssinica* by-product

Pseudo-first-order		Q_{eq} (exp.) ($\mathrm{mg\,g^{-1}}$)	Pseudo-second-order	
K_1 ($\mathrm{min^{-1}}$)	−0.007		K_2 ($\mathrm{g\ mg^{-1}\ min^{-1}}$)	0.316
Q_{eq} (pred.) ($\mathrm{mg\,g^{-1}}$)	0.081	1.228	Q_{eq} (pred.) ($\mathrm{mg\,g^{-1}}$)	1.227
R^2	0.875		R^2	0.999
Elovich			Intraparticle diffusion	
A	1.104		K_{id} ($\mathrm{mg\,g^{-1}\ min^{-1/2}}$)	0.048
B	0.018		C_{i} ($\mathrm{mg\,g^{-1}}$)	1.141
R^2	0.772		R^2	0.946

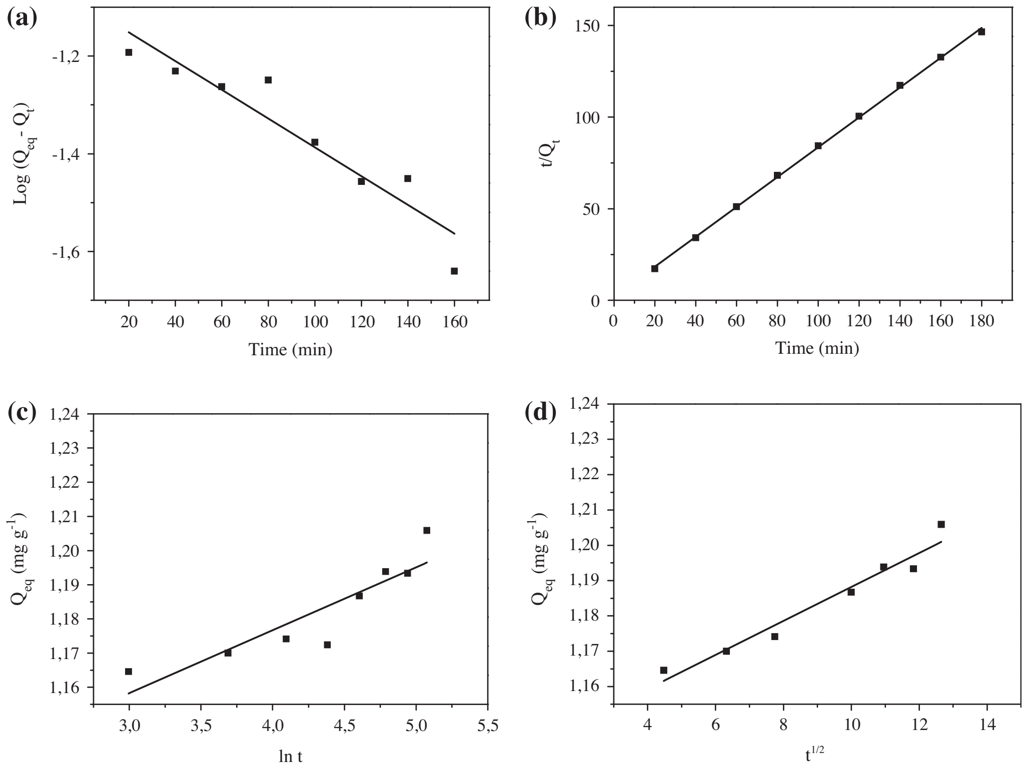

Fig. 6. Kinetic models: (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich, and (d) intraparticle diffusion implemented for the Pb(II) adsorption on the *C. abyssinica* seed by-product.

$$\ln Q_{\mathrm{eq}} = \ln Q_{\mathrm{d}} - B_{\mathrm{d}} \times \varepsilon^2 \tag{9}$$

where Q_{eq} is the Pb(II) amount adsorbed per unit mass of the adsorbent (mol g^{-1}), Q_{d} is the maximum adsorption capacity (mol g^{-1}); B_{d} is the adsorption energy (mol^2 J^{-2}), and ε is the Polanyi potential, which can be evaluated according to Eq. (10):

$$\varepsilon = \mathrm{RT} \ln\left(1 + \frac{1}{C_{\mathrm{eq}}}\right) \tag{10}$$

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

The constant B_{d} is related to the adsorption mean free energy (E), which can be estimated according to Eq. (11):

$$E = \frac{1}{\sqrt{-2B_{\mathrm{d}}}} \tag{11}$$

Table 2 presents the Langmuir, Freundlich and DR isotherm constants. Taking into account the determination coefficients (R^2) of the linear isotherms (Table 2), it can be observed that the Freundlich and DR models gave a better fit to the adsorption data than the Langmuir model.

The nonlinear behavior of dots indicates that the Langmuir model cannot be recommended for determining the maximum monolayer adsorption capacity of the biosorbent. A similar result was obtained by Tarley and Arruda [14] for the Pb(II) adsorption on a vegetable sponge. Unlike that, this model succeeded in describing the Pb(II) adsorption on the activated charcoal ($R^2 = 0.940$), thus indicating the monolayer adsorption and the maximum capacity (q_{m}) of 8.555 mg g^{-1}; besides, the charcoal showed the strong interaction with the Pb(II) ions confirmed by the b (or K_{L}) value of 52.183 L mg^{-1}.

Considering the free energy and the fact that chemisorption occurs at $E > 8$ kJ mol^{-1} [46], the chemical nature of the Pb(II) adsorption on the biosorbent could be elucidated, since $E = 8.427$ kJ mol^{-1}.

As seen in Table 2, the Freundlich and DR models failed to explain the Pb(II) adsorption on the activated charcoal ($R^2 = 0.671$ and 0.680, respectively).

Table 2
Langmuir, Freundlich and Dubinin–Radushkevich parameters obtained for the Pb(II) biosorption on the *C. abyssinica* seed by-product and activated charcoal

	Adsorbents	
	Crambe abyssinica	*Activated charcoal*
Langmuir		
q_m (mg g^{-1})	−16.366	8.555
b ou K_L (L mg^{-1})	−0.092	52.183
R^2	0.712	0.940
Freundlich		
K_F (L g^{-1})	2.093	18.020
n	0.984	2.189
R^2	0.985	0.671
Dubinin–Radushkevich		
Q_d (mol g^{-1})	6.2 e^{-2}	3.4 e^{-4}
E (kJ mol^{-1})	8.427	13.975
R^2	0.985	0.680

3.2.4. Study of the Pb(II) desorption

The desorption tests were performed to clarify the Pb(II) adsorption behavior, estimate the percent recovery of the adsorbed Pb(II) ions and assess the possible reuse of the adsorbent [9].

After these tests, it was established that of 97% of the Pb(II) ions adsorbed (isotherms tests), about 35% was desorbed (desorption tests), thus demonstrating that the Pb(II) adsorption on the *Crambe* biosorbent was irreversible due to the strong chemical interaction between the adsorbent and the Pb(II) ions. This finding was confirmed by the obtained pseudosecond-order kinetic parameters and the DR mean free energy value. Similar results were presented by Pehlivan et al. [3] for the Pb(II) adsorption/desorption by hazelnut and almond shells.

Considering these results, it was not possible to satisfactorily reuse the studied biosorbent. It should be stated that this material was not pretreated, and thus, there is a need for further studies of the Pb(II) removal by the biosorbent using different treatment techniques and extraction solutions (e.g. H_2SO_4, HNO_3, and EDTA) [9,47].

Incineration can be another alternative, since the biosorbent is a co-product, low-cost and available for large-scale testing. However, this technique is expensive, and environmental harm may be caused as a result of emissions of toxic pollutants if proper care is not taken [48,49].

As for the Pb(II) desorption from the activated charcoal, about 57% of 99.8% of the adsorbed Pb(II) ions was desorbed, assuming the possible reuse of this adsorbent [29].

3.2.5. Effect of temperature

The effect of the temperature on the Pb(II) adsorption by the biosorbent was evaluated at 25, 35, 45, 55, and 65°C.

The following thermodynamic parameters: enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) were measured and estimated according to Eqs. 12 and 13:

$$\Delta G = -\mathrm{RT} \times \ln K_d \tag{12}$$

$$\ln(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{\mathrm{RT}} \tag{13}$$

where K_d is the Pb(II) distribution coefficient, *T* is the temperature (*K*), and *R* is the universal gas constant (8,314 10^{-3} kJ mol^{-1} K^{-1}).

As seen in Fig. 7, more Pb(II) ions were adsorbed when the temperature rose, thus characterizing the process as endothermic.

The endothermic behavior of the system can be confirmed with the positive ΔH value (40.738 kJ mol^{-1}), since $\Delta H > 20$ kJ mol^{-1} indicates chemisorption (Table 3) [4,50,51].

The ΔG values decreased with the increase in the temperature, demonstrating that the Pb(II) ions were more easily adsorbed at higher temperatures. Since these values were found to be negative, the process was spontaneous and favorable, and larger negative values (by module) stand for its greater energetic

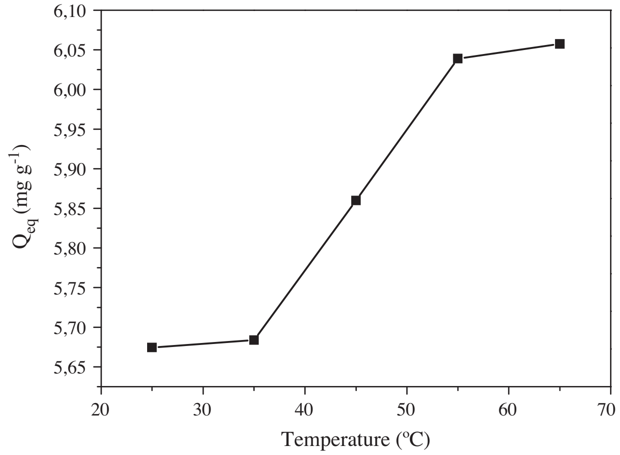

Fig. 7. Pb(II) adsorption capacity of the *C. abyssinica* by-product as a function of the variation in temperature (C_0: 50 mg L^{-1}; 50 mL, 20 min; 400 mg; 200 rpm).

Table 3
Thermodynamic parameters obtained for the Pb(II) biosorption on the *C. abyssinica* seed by-product

Temperature (℃)	ΔS ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	ΔH ($\mathrm{kJ\,mol^{-1}}$)	ΔG ($\mathrm{kJ\,mol^{-1}}$)
25	140.739	40.738	−41.899
35			−43.307
45			−44.714
55			−46.122
65			−47.529

favorability [52].

The other thermodynamic feature—ΔS—was found to be positive, thus revealing randomness at the solid/solution interface during the biosorption [13].

4. Conclusions

The *Crambe* seed by-product can be successfully used for the metal adsorption due to its favorable structure, as seen from the SEM and IR measurements that disclosed its morphology and elucidated the functional groups present.

The Freundlich and DR models provided the best fit into the adsorption data, thus allowing to establish the existence of the strong interaction between the biosorbent and the Pb(II) ions and assume that chemisorption took place, which was confirmed by the pseudo-second-order model parameters as well as by the DR free energy, enthalpy, and desorption rate values.

Based on the obtained results, it is possible to conclude that the *Crambe* seed by-product can be used as an effective biosorbent for removing Pb(II) ions from water-based solutions without any previous treatment, thus presenting itself as an alternative tool for the remediation of Pb(II)-contaminated environmental compartments.

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