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Adsorbents developed from residual biomass of canola grains for the removal of lead from water

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ABSTRACT

This research aimed to develop modified adsorbents from grains residual biomass of four canola genotypes (canola meal) with H_2O_2, H_2SO_4 and NaOH (0.1 mol L^{-1}) for removal of Pb^{2+} from water. The adsorbents were characterized by the point of zero charge (pH_{PZC}), Fourier-transform infrared spectroscopy, thermal stability and porosimetry (Brunauer–Emmett–Teller and Barrett–Joyner–Halenda). Doses of adsorbent and the pH of the contaminated solution were evaluated. In addition, kinetics, equilibrium and thermodynamics studies were performed. The modified biosorbents presented an irregular appearance regarding its surface morphology, the presence of aldehyde, ketone and carbonyl functional groups (allowing the connection with metallic ions in solution) and pH_{PZC} different from that observed for the precursor material. The adsorption of Pb^{2+} was influenced by the used adsorbent doses. The ideal contact time was found between 80 and 140 min. The adsorption kinetics indicated the predominance of chemical adsorption. The best adjustments occurred for the Langmuir model and genotype 3, which showed the higher value of Q_m, the best adsorption rates (80%) which were found by modification by H_2SO_4. From these results, it is possible to affirm that there are differences in adsorption among different genotypes of canola, and these waste materials are a promising alternative for the treatment of water contaminated with Pb^{2+}.

Keywords: Advanced water treatment; Biosorption; Bioremediation; Canola meal; Modified adsorbents; Toxic metals

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1. Introduction

Currently, the quality of environmental compartments has been highly discussed around the world, mainly because of the importance of these resources in the world and because of its relevance in the maintaining of life and health of all living beings [1,2].

In this sense, water resources have received greater attention, mainly due to the low availability of drinking water in nature, since all freshwater available on the planet accounts for only 0.3%, and it is stored in rivers and lakes; being these the main sources for human consumption [3].

Water has great importance for the maintenance of ecosystems and living beings, however, its quality has been gradually compromised by the different human activities. Among them, industrial and agricultural activities, characterized by the high production of residues with contaminants and toxic substances stand out [4].

Agricultural activities, for example, are responsible for the release of pesticides and fertilizers into water bodies. These products are characterized by high concentrations of toxic compounds [5]. Similarly, industrial activities, depending on the production processes employed, are also responsible for the launch of these compounds [3].

Among the harmful compounds released by these activities, there are toxic metals, which cause great impacts on water resources, mainly due to their capacity of accumulation and distribution between the environmental compartments, besides the possibility of its bioaccumulation in the tissues of living beings, representing great environmental risk. Among all toxic metals, some are responsible for greater damage to the environment and humans, such as lead since this compound has high toxicity [6].

Given the importance of toxic metals, it is necessary to develop low-cost and feasible new technologies for the decontamination of environmental compartments. Although commercial activated carbon has excellent metal removal efficiency, it has a complex production system, which makes it expensive for the treatment of large quantities of water [7].

In order to reduce the cost of the adsorbent, researchers are seeking to evaluate and develop renewable and alternative adsorbent materials to reduce operational costs [8]. This also occurs because the high agricultural and agroindustrial production generates a high amount of waste that results in several environmental problems [9], and these materials are a good source of raw-material for eco-friendly adsorbents.

Canola cultivation tends to expand in Brazil and worldwide and its residues may have in the future a much higher economic value than today. There are some results in the literature that demonstrate that the use of canola grain residues can become sustainable biosorbents for water decontamination [10,11]. However, those articles are not very recent, besides not considering the fact that there are numerous genotypes of canola cultivated worldwide.

Considering the aforementioned, this research aimed: (i) to study the decontamination of Pb^{2+} in water using biosorbents produced with canola grain residues; (ii) to evaluate the differences in Pb^{2+} removal of water contaminated with biosorbents from residues from different genotypes of canola (canola meal); (iii) to evaluate if different chemical activations in biosorbents from canola meal can result in differences in the removal of Pb^{2+} from the aqueous medium.

2. Material and methods

2.1. Development of canola-based adsorbents

The biomass (grains) of canola *in natura* from four distinct genotypes (G1 = Hyola 76; G2 = Hyola 61; G3 = Hyola 411; G4 = Hyola 433) was dried for 48 h at 60°C. The resulted material was smashed and sieved (14 and 65 mesh) aiming at the standardization of the particles between 0.212 and 1.40 mm. After realizing this process, the oil of the grains was extracted using the methodology of the Soxhlet type system [12], and then, the resulting material was dried at 60°C for 24 h for total evaporation of the solvent (*n*-hexane) used to extract the oil.

In order to improve some characteristics of the precursor material (surface area, number of adsorption sites and porosity, for example), chemical modifications were applied in the biosorbent (canola *in natura*). For the modification, the canola biomass of each genotype was placed in immersion with 0.1 mol L^{-1} solution of H_2O_2, H_2SO_4 or NaOH [13], considering a ratio of 1:10 (m v^{-1}) in 125 mL Erlenmeyer with constant stirring of 150 rpm at 60°C for 6 h. After this process, the modified adsorbents were washed with distilled water. The materials originate were: for genotype 1 (Hyola 76): G1 *in natura*, G1 H_2O_2, G1 H_2SO_4 and G1 NaOH; for genotype 2 (Hyola 61): G2 *in natura*, G2 H_2O_2, G2 H_2SO_4 and G2 NaOH; for genotype 3 (Hyola 411): G3 *in natura*, G3 H_2O_2, G3 H_2SO_4 and G3 NaOH; and for genotype 4 (Hyola 433): G4 *in natura*, G4 H_2O_2, G4 H_2SO_4 and G4 NaOH.

Aiming the removal of Pb^{2+} in the solutions, a fortified mono-elementary solution with metallic ions Pb^{2+} (prepared from the salt of lead nitrate [$Pb(NO_3)_2$] P.A. ≥ 99% Sigma-Aldrich, St. Louis, USA) was prepared. For the desired concentrations of the Pb^{2+}, a 1,000 mg L^{-1} solution was used as initial solution. The desired pH rates were adjusted by adding NaOH 0.1 mol L^{-1} or HCl 0.1 mol L^{-1}.

The adsorbent characteristics were also evaluated, for this, the adsorbents pH_{PZC} was obtained. The pH_{PZC} refers to the pH in which the resultant of the adsorbent surface charge is null [14].

Another characteristic that was determined was the vibrational spectroscopy in the infrared region. This parameter evidences the molecular structure of the material from the analysis of vibrational modes related to functional groups in the adsorbent. For the analysis, specters by transmittance were obtained by using KBr pellets, which were analyzed using a Shimadzu 8300 (Kyoto, Japan) Fourier-transform infrared spectroscope, considering the region between 400 and 4,000 cm^{-1} with a resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM) analysis was conducted by using a microscope JEOL JSM 6360-LV (Tokyo, Japan) equipped with energy dispersive microscopy. For the analysis of this parameter, the samples were dispersed in double-sided tape coated with a thin layer of gold (30 nm) using the Bal-Tec SDC sputter coater (Scotia, New York, United States).

The surface analysis, size and pore volume were performed using Quantachrome Nova 1200e equipment

(Boynton Beach, Florida, USA), where 500 mg of material was heated to 200°C under vacuum for approximately 4 h. After this process, it was performed the adsorption and desorption of N_2. The surface size and pore volume were calculated using the standard Brunauer–Emmett–Teller (BET) [15] and pore size was obtained using the method of Barrett–Joyner–Halenda (BJH) [16], as shown in Table 1.

Aiming to evaluate the thermal stability of the materials, thermogravimetric analyzes (TGA) were performed. A TGA 4000 Perkin Elmer thermogravimetric analyzer was used (Waltham, Massachusetts, USA), where the materials were heated to a temperature ranging from 30°C to 900°C, under a heating rate of 10°C min^{-1} under nitrogen atmosphere.

2.2. Adsorption studies on canola-based materials

For the evaluation of the adsorption process, adsorption studies were also conducted. Thus, the study on the influence of the adsorbent dose and the influence of the pH of the Pb^{2+} solution was performed by using a central composite design. For this end, adsorbent masses ranging from 200 to 1,200 mg were evaluated (i.e., proportion of 4 to 28 g L^{-1}).

For these preliminary tests, 50 mL of Pb^{2+} solution (10 mg L^{-1}) in different pH values were set in contact in Erlenmeyers with the adsorbent doses. The Erlenmeyer containing the adsorbent was then placed in a thermostatic Dubnoff system and stirred for 60 min at 200 rpm. After that, in order to determine the Pb^{2+} concentration by flame atomic absorption spectrometry (FAAS) [17], the samples were filtered and aliquots were taken.

Aiming to evaluate the adsorption kinetics, 200 mg of modified canola-based adsorbents were placed in a 125 mL Erlenmeyer bottles and set in contact with 50 mL of 10 mg L^{-1} solutions (adsorbent dose of 4 g L^{-1}), at pH 5.00 at 25°C. Those Erlenmeyers were stirred for periods between 10 to 180 min. After this step, in order to determine the concentration of the residual Pb^{2+} by FAAS and to evaluate kinetics parameters, samples were taken. The results were evaluated by the linear mathematical models of pseudo-first-order [18], pseudo-second-order [19], Elovich [20] and Weber–Morris [21], as described in Table 1.

In order to evaluate the removal of metals in higher concentrations (up to 200 mg L^{-1}) equilibrium studies were conducted. In this way, 200 mg of the mass of the adsorbent was placed in 125 mL Erlenmeyer with 50 mL of Pb^{2+} solution (adsorbent dose of 4 g L^{-1}) in increasing concentrations (from 5 to 200 mg L^{-1}), considering pH equal to 5.00, 25°C and 60 min of stirring. After the stirring, samples were taken and Pb^{2+} concentration was obtained by FAAS. The results were evaluated by the mathematical models of Langmuir [22], Freundlich [23], Dubinin–Radushkevich [24] and Sips [25], as presented in Table 1.

The influence of temperature in the adsorption process was evaluated in five temperature conditions, being them: 15°C, 25°C, 35°C, 45°C, and 55°C. For that purpose, 50 mL of Pb^{2+} solution at 50 mg L^{-1} were added in 125 mL Erlenmeyer containing 4 g L^{-1} of the canola-based adsorbents. The Erlenmeyer was then stirred for 60 min. After this step, samples were taken for the determination of Pb^{2+} by FAAS. The thermodynamics parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were estimated according to Sari et al. [26] and Gonçalves et al. [27].

The last test conducted was performed in order to verify the possibility of the reuse of the materials. For that, the canola-based adsorbents used in isotherms tests were dried for 24 h at 60°C (post-adsorption). The recovered mass was set in contact with 50 mL of HCl 0.1 mol L^{-1} with stirring at 200 rpm for 90 min at 25°C. The final concentration of the desorbed Pb^{2+} was determined by FAAS.

3. Results and discussion

Chemical modifications in the canola-based adsorbents caused changes in pH_{PZC} (Fig. 1). From the chemical point of view, when water or effluent has a higher pH than pH_{PZC}, negative charges predominate on the adsorbent surface [28] favoring cations adsorption, such as Pb^{2+}. As observed, the average pH_{PZC} for canola biosorbent (*in natura*) is 5.98 ± 0.05, for the modification with H_2O_2 is 6.34 ± 0.13, for the modification with H_2SO_4 is 1.49 ± 0.02, and for NaOH is 8.65 ± 0.57.

As observed in Fig. 1, the chemical modifications of canola biomass caused changes, modifying the pH_{PZC} of canola-based adsorbents, the differences found in the pH_{PZC} among the *in natura* and modified materials are related to the characteristics of the material used in the activation. Góes Casqueira and Lima [29], for example, who worked with a stalk of banana *in natura* and physically treated as biosorbent, did not observe changes in the pH_{PZC} value of the treated material relative to the precursor, however, these authors did not use chemical modification in the adsorbents. On the other hand, using chemically activated carbon from olive stones, [30] found differences in the pH_{PZC} values, evidencing that the use of some chemical compounds during the activation can change the values of pH_{PZC} [30].

Hydrogen peroxide, a powerful oxidizing agent, has the potential to cause changes in the surface of the material, similar to what was observed by Schwantes et al. [13] by studying adsorbents modified from pine bark in the removal of diverse toxic metals.

The acid treatment is able to improve the thermal stability of materials. H_2SO_4 exhibits a higher degree of oxidation and removal of lignocellulosic, even at relatively low temperatures (45°C) and low concentrations [31,32].

Alkaline treatment with NaOH tends to remove surface impurities as well as to induce a rough surface of the fibers, improving fiber-matrix adhesion and, consequently, the mechanical properties of the material [33].

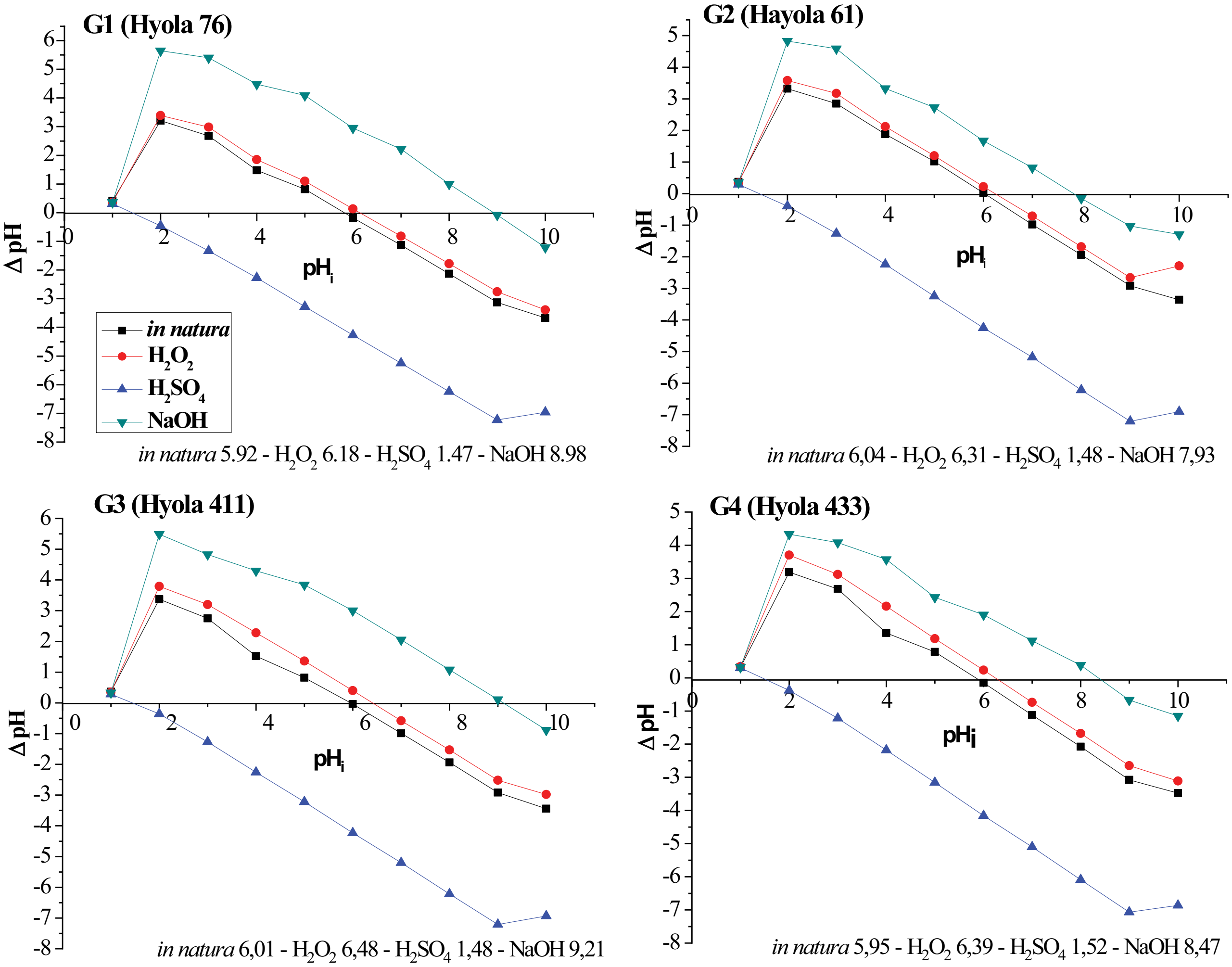
The oxidizing, acidic or alkaline agent reacts with the numerous functional groups in canola biomass, generating reactions of hydrolysis, oxidation, dehydration, protonation/deprotonation, among others.

The modified adsorbents retain the surface characteristics of its precursor (Fig. 2), however, with some remarkable modifications.

The microstructures and morphologies of the canola-based adsorbents G. *in natura* (G1 – *in natura*, G2 – *in natura*, G3 – *in natura*, G4 – *in natura*) and the modified adsorbents (G1 – H_2O_2, G2 – H_2O_2, G3 – H_2O_2, G4 – H_2O_2; G1 – H_2SO_4, G2 – H_2SO_4, G3 – H_2SO_4, G4 – H_2SO_4; G1 – NaOH, G2 – NaOH, G3 – NaOH, G4 – NaOH) were observed under amplification of 2,400 times (Fig. 2).

Table 1
Mathematical linear models used in the current research

Brunauer–Emmett–Teller and Barrett–Joyner–Halenda models		
BET [15]	$\frac{1}{v\left[\frac{p_0}{p}-1\right]}=\frac{c-1}{v_m c}\left(\frac{p}{p_o}\right)+\frac{1}{v_m c}$	p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption; v is the adsorbed gas quantity; v_m is the monolayer adsorbed gas quantity. c is the BET constant; g is the surface tension of liquid nitrogen; v_1 is the molar volume of the liquid; R is the universal gas constant; T is the temperature (77 K); r_m is the radius of the meniscus; p/p^0 is the relative pressure
BJH [16]	$\ln\frac{p}{p^0}=\frac{2\gamma v_1}{RT}\frac{1}{r_m}$	
Kinetics linear models		
Pseudo-first-order [18]	$\log\left(Q_{\text{eq}}-Q_t\right)=\log Q_{\text{eq}}-\left(\frac{K_1}{2.303}\right)t$	Q_{eq} and Q_t (mg g^{-1}): quantities of adsorbate retained per gram of adsorbent in equilibrium and in time (t); K_1 (min^{-1}): the rate constant of pseudo-first-order
Pseudo-second-order [19]	$\frac{t}{Q_t}=\frac{1}{K_2Q_{\text{eq}}^2}+\frac{1}{Q_{\text{eq}}}t$	K_2 (g mg^{-1} min^{-1}): the rate constant of pseudo-second-order
Elovich [20]	$Q_{\text{eq}}=A+B\,\text{In}\,t$	A: the speed of initial chemisorption (mg g^{-1} h^{-1}); B: number of suitable sites, related to the extent of surface coverage and the activation energy of chemisorption (g mg^{-1})
Intraparticle diffusion [21]	$Q_{\text{eq}}=K_{\text{id}}t^{1/2}+C_i$	K_{id}: intraparticle diffusion constant (g mg^{-1} min$^{-1/2}$); C_i: suggests the thickness of boundary layer effect (mg g^{-1}); t: time
Equilibrium linear models		
Langmuir [22]	$\frac{1}{Q_e}=\frac{1}{C_m}+\frac{1}{K_LC_mC_e}$ $\frac{C_{\text{eq}}}{q_{\text{eq}}}=\frac{1}{q_mb}+\frac{C_{\text{eq}}}{q_m}$	C_e or C_{eq}: concentration at equilibrium; Q_e or Q_{eq}: amount adsorbed at equilibrium per unit of mass of the adsorbent; K_L or q_mb and C_m: reflect properly the nature of the adsorbent material and can be used to compare the performance of adsorption; C_m or Q_m: maximum capacity of adsorption; K_L or q_mb: adsorbent–adsorbate interaction forces
Freundlich [23]	$\log q_{\text{eq}}=\log K_f+\left(\frac{1}{n}\right)\log C_{\text{eq}}$	C_{eq}: concentration on balance; Q_{eq}: amount adsorbed at equilibrium per unit of mass of adsorbent; K_F and n: parameters of Freundlich
Dubinin–Radushkevich [24]	$\ln Q_{\text{eq}}=\ln Q_d-Bd\varepsilon^2$ $\varepsilon=RT\ln\left(1+\frac{1}{C_{\text{eq}}}\right)$	Q_{eq}: amount adsorbed ion per unit mass of the adsorbent (mol g^{-1}); Q_d: adsorption capacity (mol L^{-1}); B_d: coefficient related to the energy of sorption (mol^2 J^{-2}); ε: the potential of Polanyi; R: universal gas constant (kJ mol^{-1} K^{-1}); T: temperature (K); C_{eq}: liquid phase equilibrium concentration (mol L^{-1})
Sips [25]	$q_{\text{eq}}=\frac{q_{\max}\left(K_sC_{\text{eq}}\right)^n}{1+\left(K_sC_{\text{eq}}\right)^n}$	Q_{eq} and C_{eq} have the same meanings as in the previous isotherms; $q_{\max}$ corresponds to the maximum sorption capacity (mg g^{-1}); K_s is the equilibrium constant of Sips (L mg^{-1}) and represents the degree of heterogeneity of the system, and can vary from 0 to 1. If $n = 1$ means that the system is homogeneous, matching the Langmuir model, $n < 1$ represents increased heterogeneity
Thermodynamics linear models		
Gibbs free energy [26]	$\Delta G^\circ=-RT\ln K_d$	K_d: the ratio of the quantity adsorbed per unit of adsorbent (Q_{eq}) and solution concentration in equilibrium (C_{eq}); R: universal gas constant (8.314 J mol^{-1} K^{-1}); T: temperature used in the experiment (Kelvin). The values of ΔH° and ΔS° were obtained from the graph of lnK_d in the function of $1/T$
Enthalpy and entropy [26]	$\ln K_d=\frac{\Delta S^\circ}{R}-\frac{\Delta H^\circ}{RT}$	



in natura 5.92 - H_2O_2 6.18 - H_2SO_4 1.47 - NaOH 8.98

in natura 6,04 - H_2O_2 6,31 - H_2SO_4 1,48 - NaOH 7,93

in natura 6,01 - H_2O_2 6,48 - H_2SO_4 1,48 - NaOH 9,21

in natura 5,95 - H_2O_2 6,39 - H_2SO_4 1,52 - NaOH 8,47

Fig. 1. pH_{PZC} for the canola-based adsorbents. ΔpH: final pH – initial pH.

The surface of canola-based *in natura*, according to Figs. 2 (G1, G2, G3 and G4) exhibits irregular and heterogeneous structures, with spongy and fibrous appearance. These characteristics can be indicative of the existence of favorable conditions for adsorption [13].

For adsorbents modified with H_2O_2 (Figs. 2 G1 – H_2O_2, G2 – H_2O_2, G3 – H_2O_2, G4 – H_2O_2), it can be observed irregular surfaces with cracks and porous cavities, all these characteristics are presented in function of the oxidizing power of H_2O_2.

For canola adsorbents modified with H_2SO_4 (Figs. 2 G1 – H_2SO_4, G2 – H_2SO_4, G3 – H_2SO_4, G4 – H_2SO_4), it can be observed a heterogeneity on the adsorbent surface, with pore-shaped cavities created by the oxidizing power of H_2SO_4. Due to the dehydrating action of sulfuric acid H_2SO_4 (1.0 mol L^{-1}), it configured an irregular and heterogeneous surface.

As NaOH is a strong base of high solubility, it possibly caused irregular, heterogeneous surface and cavities (Fig. 2 G1 – NaOH, G2 – NaOH, G3 – NaOH, G4 – NaOH). In fact, these characteristics assist in the adsorption of metals by increasing the surface area of the adsorbent. There are some studies in literature, such those conducted by Wan Ngah and Hanafiah [34], Schwantes et al. [35], and de Campos et al. [33], which all evidence the improvement in the metals adsorption rates by using chemical pre-treatments in vegetal origin adsorbents, such as NaOH, H_2SO_4, tartaric acid, reactive orange 13, and among others.

Fig. 3 exhibits the possible functional groups in canola-based adsorbents. The strong and wide bands found in the region of 3,400 to 3,300 cm^{-1} can be attributed to the vibrational stretching of alcohols and phenols (O–H) bonds [36]. Similar results in the region of 3,400 to 3,300 cm^{-1} were observed by [37], when studying biosorbents from *Pinus elliottii* in the removal of chromium (Cr^{3+}).

The vibrational elongations found in the region of 3,000–2,800 cm^{-1} may be related to a vibrational C–H bond, which is found in alkanes or alkyl groups [38].

According to [39], the bands comprised in 1,740 to 1,760 cm^{-1} indicate the presence of aldehyde and ketone carbonyl groups, which are abundant in lignin and cellulose. These results corroborate with those obtained by Schwantes et al. [13], who developed pine barks adsorbents.

The bands located at 1,680–1,620 cm^{-1} and 1,550–1,370 cm^{-1} can be attributed to the presence of vibrational stretches of C=C type bonds found in alkenes [40,41].

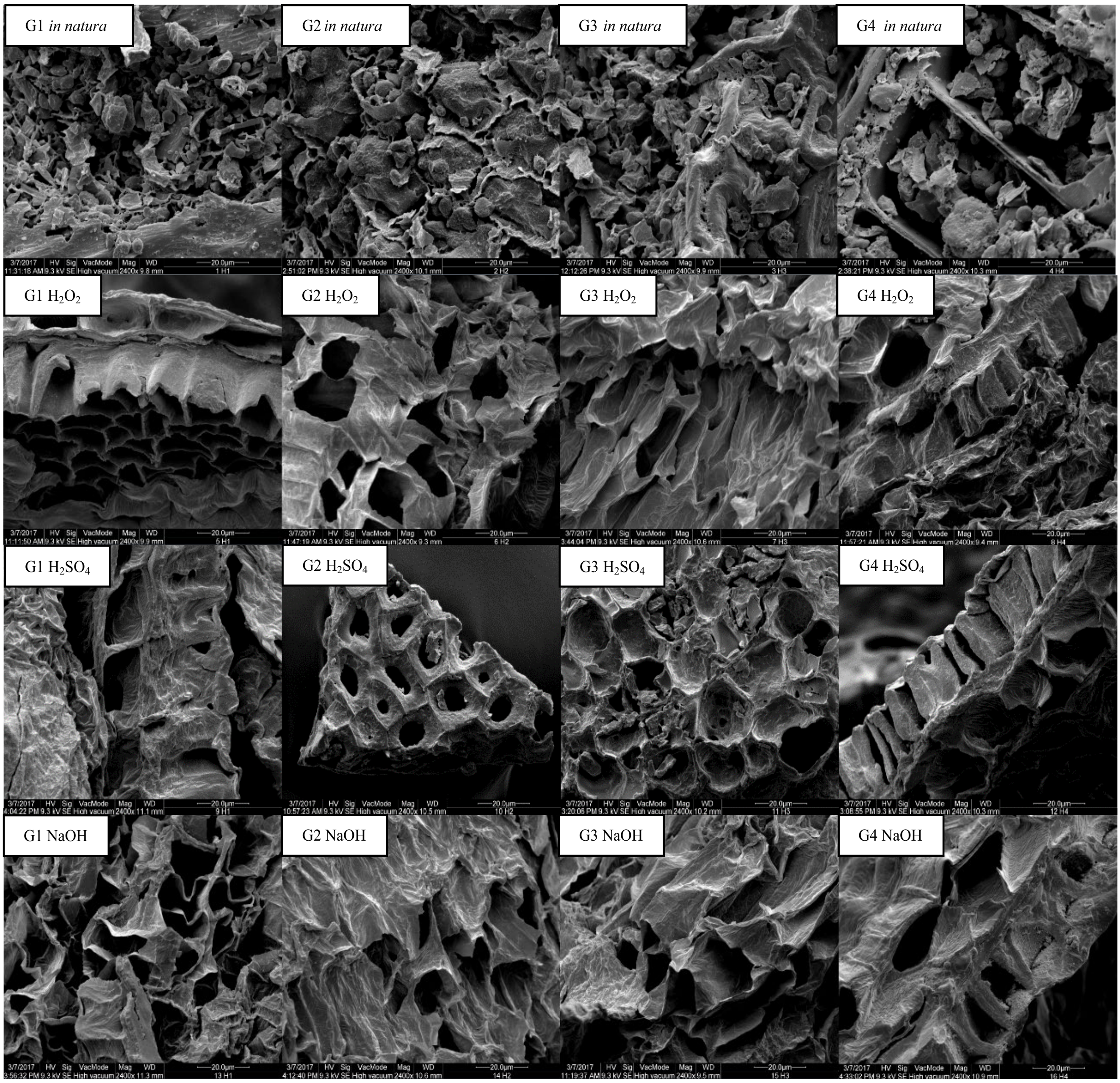


Fig. 2. SEM of canola-based adsorbents in magnification of 2,400 times.

The bands found from 1,070 to 1,150 cm^{-1} can be attributed to the occurrence of C–O bonds, which are abundant in lignin and phenols [38–42,43]. Nacke et al. [44] obtained similar results studying *Jatropha curcas* based adsorbents.

From the infrared spectra, we can also observe that the modification with H_2SO_4 conferred more intense bands to genotype 4, when compared to the other genotypes in the same modification. Similarly, the bands observed for G1, G2 and G4 modified with NaOH were weak compared to genotype 3, which for the same modification showed much more intense bands.

In the first instance, by comparing the infrared spectra of *in natura* with modified materials, several clusters in the *in natura* material are also exposed in the modified adsorbents, demonstrating that the modified materials still have characteristics of the precursor biomass.

However, some bands are only seen in the modified materials, as the bands in 1,740 to 1,760 cm^{-1} for the modifications with H_2O_2, H_2SO_4 and NaOH, in all the genotypes. These bands may be related to the C=O bonds of aldehydes, ketones, carbonyls, amides and esters, respectively [45,46].

It is important to mention that the adsorption of metal ions is related to the presence of functional groups, such as alcohols, carboxylic, carbohydrates and protein groups. Various functional groups found in the natural material

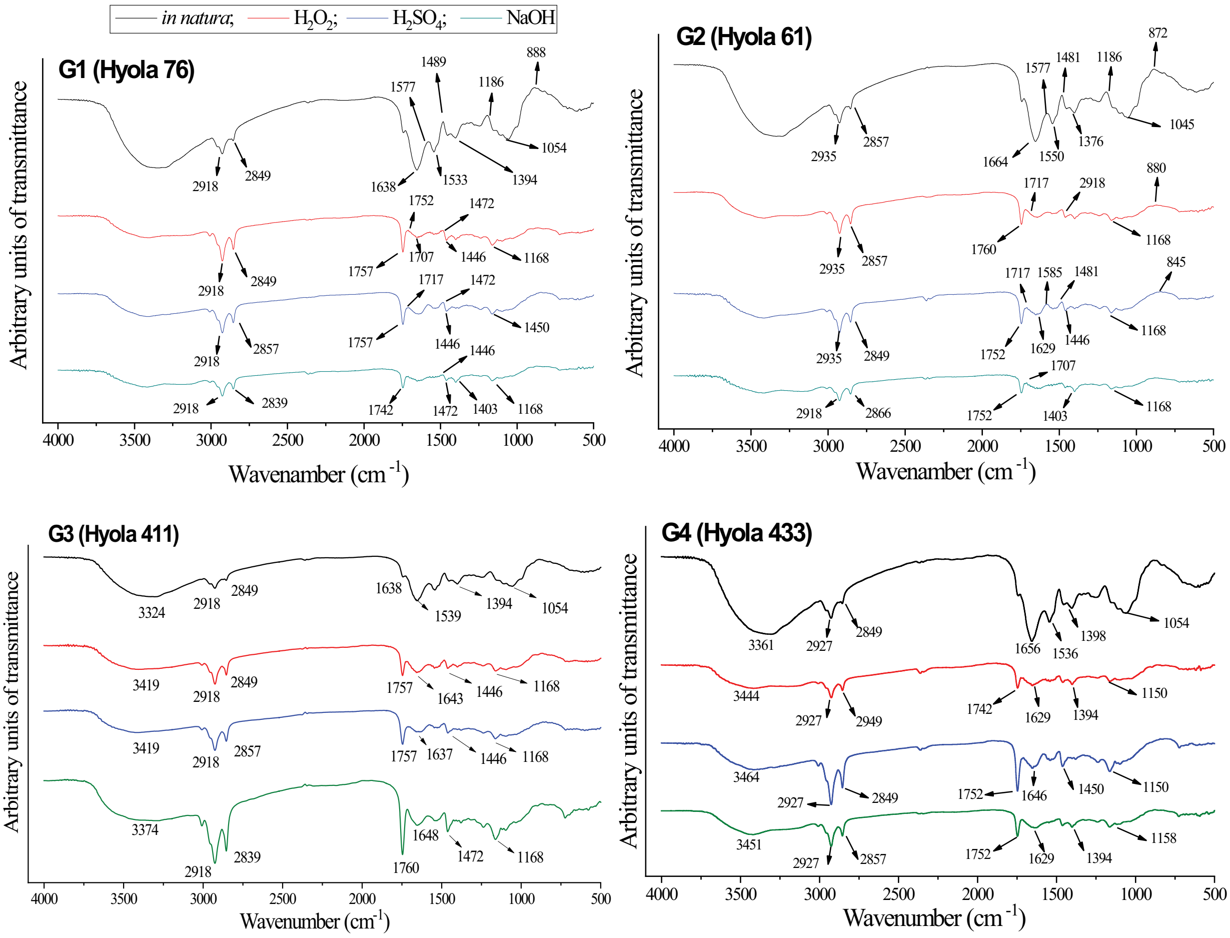


Fig. 3. Infrared spectrum analysis from 4,000 to 400 cm^{-1} for the canola-based adsorbents.

(*in natura*) remained after the treatment with the modifying solutions (H_2O_2, H_2SO_4, NaOH) indicating the presence of cellulose and lignin, which are complex natural polymers and provide many active sites for the adsorption process.

The thermal stability of the adsorbents was performed to verify the dynamics weight loss of after treatment with H_2O_2, H_2SO_4 and NaOH (Table 2 and Fig. 4).

It is observed that the genotypes, in their *in natura* form, exhibit different thermal stability, both in the number of events as in observed temperature ranges. This is possibly due to the genetic characteristics of the genotypes, which may have in their biomass greater or lesser amounts of compounds such as proteins, cellulose, carbohydrates, etc.

For the adsorbents *in natura* and modified with H_2O_2, H_2SO_4 and NaOH the first loss of mass is related to the release of moisture absorbed by the adsorbents.

Modifications with NaOH provided higher thermal stability and uniformization of the canola biomass, as a certain homogeneity is observed in the number of events (3) and the observed temperature ranges.

The adsorption and desorption BET and BJH isotherms by *in natura* adsorbents and adsorbents modified with H_2O_2, H_2SO_4 and NaOH, are used for the estimate of the specific surface area (SSA) of the adsorbents, as well as pore volume and diameter (Table 3).

The results of SSA evidenced that the modification with H_2SO_4 has improved the SSA in the genotypes G2, G3 and G4 when compared to the *in natura* material. The adsorbent G4 H_2SO_4 exhibited the highest values for surface area (0.879 m^2 g^{-1}), followed by G2 H_2SO_4 (0.786 m^2 g^{-1}) while the smaller SSA was observed for G3 H_2O_2 (0.003 m^2 g^{-1}). Similar results were found in the literature, such as the study with biosorbents of Pinus barks modified with H_2SO_4 (0.33 m^2 g^{-1}) and NaOH (0.48 m^2 g^{-1}) and cassava barks modified with H_2SO_4 (0.4637 m^2 g^{-1}) [13].

The observed values for SSA are lower from those obtained for sugarcane bagasse modified with acetic anhydride (10.72 m^2 g^{-1}) [47]. The observed volume of pores, although small, are higher than those obtained by Schwantes et al. [13] in modified cassava residues (0.00307 cm^3 g^{-1}).

According to International Union of Pure and Applied Chemists (IUPAC) [48], the pores of some material can be classified into three groups, being them, microporous (diameter smaller than 2 nm), mesoporous (diameter bigger than 2 nm and smaller than 50 nm), and macroporous (diameter bigger than 50 nm). In this sense, it can be evidenced that the adsorbents *in natura* and modified are classified, in most part, as microporous and mesoporous.

According to Boniolo [8], the presence of microporosity is a desirable feature in relation to the adsorptive process.

Table 2
Thermal stability of canola-based adsorbents

Number of events				Temperature (°C)				Weight loss (%)				Weight loss rate (% min^{-1})			
G1	G2	G3	G4	G1	G2	G3	G4	G1	G2	G3	G4	G1	G2	G3	G4
In natura materials															
1	1	1	1	7.3	81.6	86.7	85.6	6.9	6.2	6.6	8.2	0.86	0.70	0.73	0.12
2	2	2	2	319	318.3	318.4	309.0	40.0	32.6	60.9	62.3	3.10	2.72	2.83	0.37
3	3	3	3	401.9	413.8	851.2	852.0	24.0	29.4	13.7	11.1	1.97	2.97	0.74	0.10
4	4			797.8	879.3			8.2	11.5			0.93	0.62		
5				880.7				4.0				0.82			
Materials modified with H_2O_2															
1	1	1	1	82.5	73.0	82.6	85.5	8.9	8.9	7.0	7.2	0.89	1.00	0.67	0.70
2	2	2	2	343.6	180.0	407.0	333.3	59.2	1.6	65.6	63.6	2.65	0.39	3.58	2.55
3	3	3	3	858.7	327.9	877.4	415.8	9.3	56.2	4.1		0.61	2.71	0.53	3.82
	4		4		388.0		880.8				3.83		3.08		3.83
	5				877.0				10.5				10.50		
Materials modified with H_2SO_4															
1	1	1	1	79.3	80.8	89.3	87.1	6.7	7.5	6.4	6.4	0.74	0.78	0.64	0.66
2	2	2	2	257.1	312.1	333.9	334.8	10.2	57.1	63.3	61.8	2.28	2.86	3.10	2.84
3	3	3	3	305.8	439.8	859.7	870.4	30.8		5.8	1.9	3.20	1.32	0.42	0.37
4	4			408.1	856.9			15.5	3.4			1.71	0.46		
5				886.6				3.8				0.50			
Materials modified with NaOH															
1	1	1	1	88.4	90.0	82.3	101.4	9.2	9.0	9.8	6.7	0.85	0.83	0.94	0.59
2	2	2	2	356.8	371.9	362.8	386.6	59.6	61.4	60.4	65.2	2.95	2.96	2.84	3.34
3	3	3	3	827.3	853.1	817.2	845.2	13.6	13.9	15.8	9.6	0.77	0.89	1.00	0.78

G1 = genotype 1 (Hyola 76); G2 = genotype 2 (Hyola 61); G3 = genotype 3 (Hyola 411); G4 = genotype 4 (Hyola 433).

Considering the importance of the microporosity, the modified genotypes G2 and G4 exhibited characteristics of microporosity in relation to the *in natura* material. It can be observed that for G1 all the chemical modification improved the pore diameter in terms of microporosity. For the genotype G3, the materials *in natura*, modified with H_2O_2 and NaOH showed mainly mesoporosity, while the genotype modified with H_2SO_4 exhibited microporosity.

Considering that this investigation aims Pb^{2+} removal, the presence of microporous and mesoporous in the material favor the adsorption process, since the estimate ionic radius of Pb^{2+} is 0.118 nm [49], allowing the intraparticle diffusion as a possibility. The results demonstrate that adsorbents were effectively altered, thus demonstrating that the modification process may alter the canola-based biomass differently, and therefore may be favorable or not to adsorption of metal ions.

In tests that aim to verify the adsorption efficiency, the adsorbent dose and the pH are important parameters that influence the removal capacity [50]. The lower doses of canola-based adsorbents showed the highest Pb^{2+} removal rates (Fig. 5). In most cases, the use of 4 g L^{-1} of canola-based adsorbents removes around 1.5–2.0 mg g^{-1} of Pb^{2+}. For the modifications with H_2O_2 the evaluated pH range has an influence on the adsorbent rate, the same was observed in other studies [13,27].

Table 3
Specific surface area (SSA), the average diameter of pores and pore volume of canola-based adsorbents by BET and BJH method

Adsorbents	SSA (m^2 g^{-1})	Pore average diameter (nm)	Pore volume (cm^3 g^{-1})
G1 *in natura*	0.290	1.546	0.00147
G2 *in natura*	0.258	2.492	0.00106
G3 *in natura*	0.194	8.487	0.00755
G4 *in natura*	0.288	1.912	0.00124
G1 H_2O_2	0.103	14.850	0.00048
G2 H_2O_2	0.074	1.549	0.00070
G3 H_2O_2	0.003	3.306	0.00150
G4 H_2O_2	0.066	14.020	0.00065
G1 H_2SO_4	0.145	3.299	0.00182
G2 H_2SO_4	0.786	1.542	0.00137
G3 H_2SO_4	0.433	1.550	0.00061
G4 H_2SO_4	0.879	1.727	0.00122
G1 NaOH	0.111	2.832	0.00066
G2 NaOH	0.062	1.685	0.00029
G3 NaOH	0.062	2.416	0.00026
G4 NaOH	0.225	1.186	0.00079

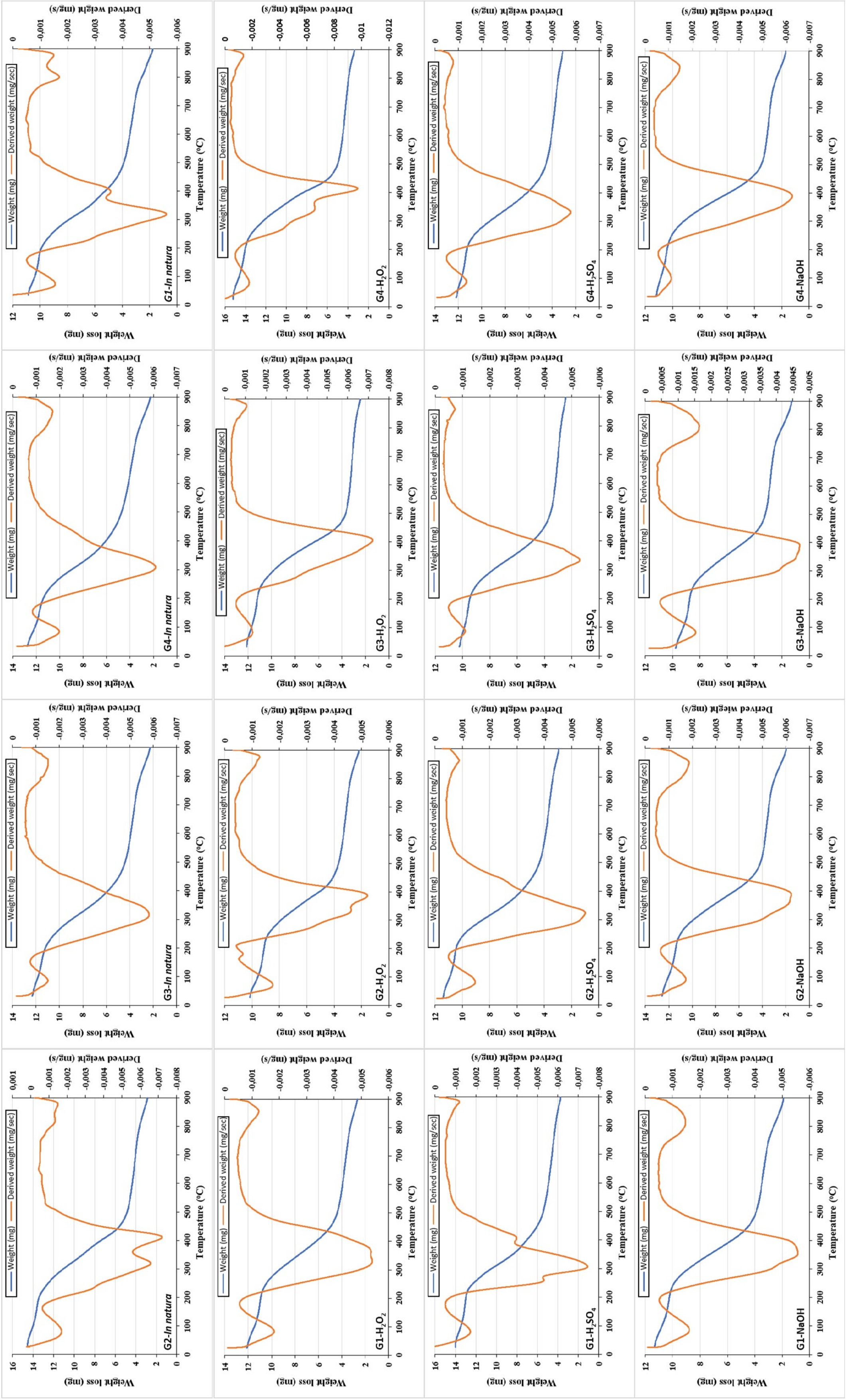


Fig. 4. Thermal stability of canola-based adsorbents.

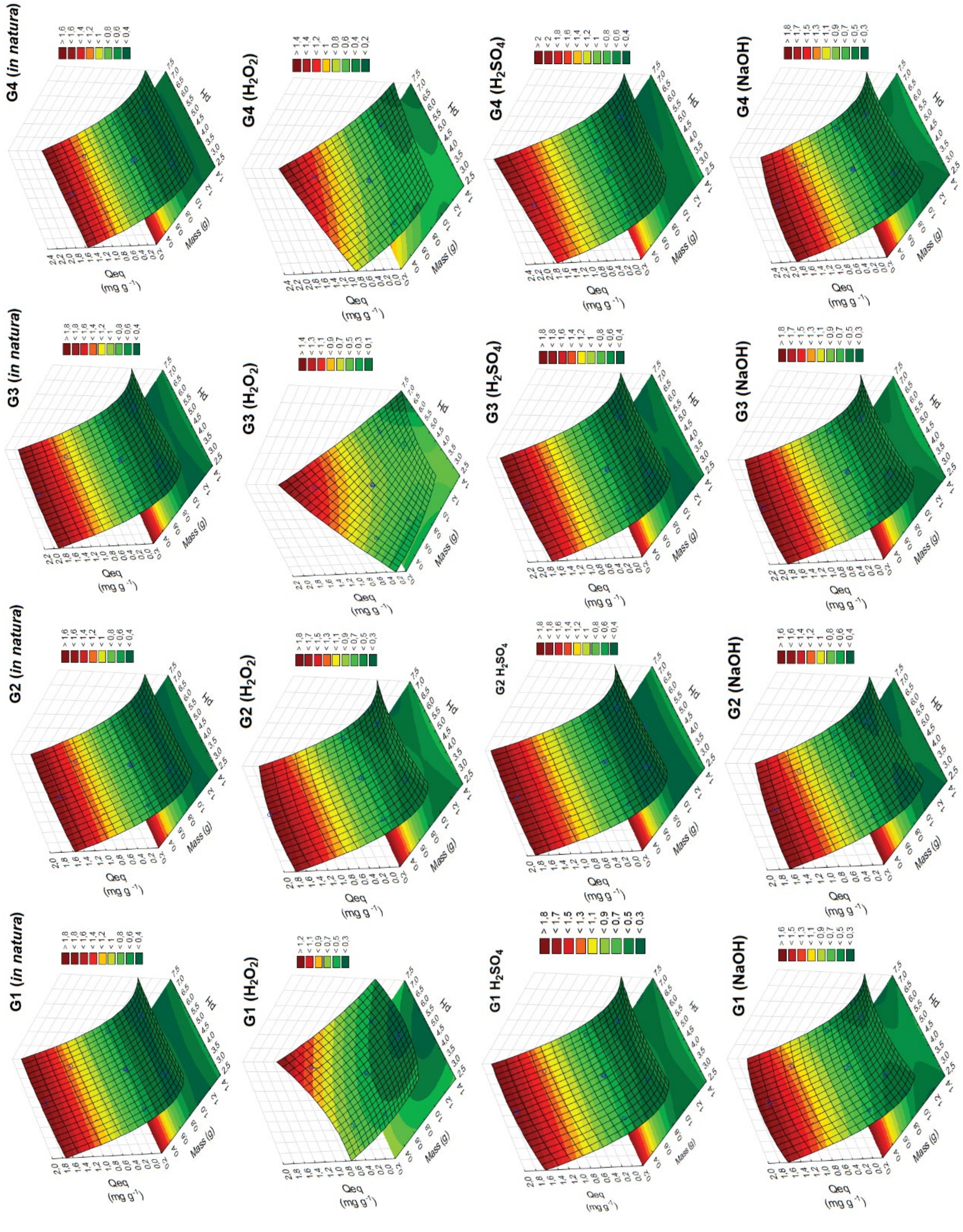


Fig. 5. Response surfaces for removal of Pb^{2+} (10 mg L^{-1}) by canola-based adsorbents (doses from 4.0 to 25 g L^{-1}).

However, for all other studied cases, the evaluated pH range 3.0–7.0 does not have an influence on the Pb^{2+} removal, that is, the canola adsorbents, when modified with H_2SO_4 or NaOH have great flexibility, removing high amounts of Pb^{2+} in the pH spectrum of 3.0–7.0. Therefore, pH 5.0 was chosen as the ideal pH to perform the equilibrium, thermodynamics and kinetics, because, as described and studied by [44] evaluating adsorbents from jatropha fruit wastes (*Jatropha curcas* L.), [37] pine bark (*Pinus elliottii*) adsorbents, [35,13] cassava barks wastes (*Manihot esculenta*), above this pH ranges, heavy metals in solution such Pb^{2+} tend precipitate more easily.

Values of R^2 closer to 1 were observed for the pseudo-second-order model, which presupposes chemical adsorption between Pb^{2+} ions and canola-based adsorbents, with R^2 values of all genotypes higher than 0.99 for this model. In this case, in addition to good mathematical adjustments, we also observe convergent values for Q_{eq} (cal.) and Q_{eq} (exp.), in most cases. The results obtained by the pseudo-second-order model suggest the occurrence of Pb^{2+} chemisorption by adsorbents based on canola grains residue [19].

Thus, according to Table 4, despite the satisfactory values obtained for R^2 in the Elovich model in some cases, it is evidenced that the pseudo-second-order model provided the best adjustments for the kinetics study of Pb^{2+} ions on canola-based adsorbents. This situation indicates that the control of the velocity mechanism is based on chemical adsorption [19], promoted by the sharing or exchange of electrons between adsorbent and adsorbate [51].

Adsorption isotherms can be classified into classes and subgroups as proposed by Giles et al. [52] and are exhibited in Fig. 6.

The *in natura* materials of genotypes 2, 3 and 4 exhibited Langmuir type "L-type" isotherms [52], showing an initial tendency to bend down due to decreased availability of the active sites. They show the difficulty of filling vacant sites and the poor interaction between the solvent molecules and the sites of the adsorbent. This is the most common type and its characteristic is adsorption in monolayers, being represented mainly by Langmuir and Freundlich models.

For genotype 1, only the *in natura* material presented an "S-type" isotherm [52], which has a curvature facing upwards, presenting a point of inflection because there is a competition of the molecules of the solvent or other molecules by the site of the adsorbent solid making them weaker than the adsorbate–adsorbent and solvent-adsorbent interactions.

All genotypes modified with H_2O_2 showed Langmuir type "L-type" isotherms [52], except for genotype 3 where there was not isotherm formation, all other genotypes modified with H_2SO_4 showed "S-type" isotherms [52].

For the genotype 2 modified with NaOH, isotherm formation was not achieved, the other genotypes modified with NaOH exhibited the "type L", that is, isotherms of Langmuir [52], these isotherms show an initial tendency to bend down due to decreased availability of active sites. This isotherm model also evidence the difficulty of filling vacant sites and the poor interaction between solvent molecules and adsorbent sites, this is the most common type and its characteristic is adsorption in monolayers.

By the obtained results (Table 5), good adjustments (R^2) were found for Langmuir and Freundlich, however with predominance in Pb^{2+} monolayers, according to the best fit by Langmuir model [25].

Langmuir's R_L values indicate that there is favorability in the adsorptive system [22], thus, in the studied cases of canola adsorbents, the sorption systems are favorable for the toxic metal uptake, with values ranging from 0.003 [G1 (Hyola 76) NaOH] to 0.196 [G1 (Hyola 76) H_2SO_4].

According to Dada et al. [53], values of Freundlich's n parameter higher than 1 indicate highly energetic active sites in the adsorbent surface. In our study, all adsorbents exhibited $R_L > 1$, with values observed from 0.0001 [G2 (Hyola 61) H_2SO_4; and G4 (Hyola 433) *in natura*] to 8.136 (G4 (Hyola 433) H_2O_2).

These results corroborate with those obtained by Nacke et al. [44], where jatropha adsorbents exhibited good R^2 values for the Langmuir and Dubinin–Radushkevich, suggesting the formation of monolayers and chemisorption of Cd^{2+}. It is worth mentioning the results for G1 NaOH, with the highest values of $Q_m = 48.78$ mg g^{-1}. It is observed that the highest values of Q_m always occurred for canola *in natura* and activated with NaOH, independent of the genotype.

In the case of genotype analysis, G3 presented the highest values of Q_m, except for the activation with H_2SO_4 (activation with H_2SO_4 resulted in lower values of Q_m for all genotypes). The preparation of the activated carbons from sunflower oil cake by sulfuric acid activation with different impregnation ratios was carried out by Karagöz et al. [54]. In that study $10 < Q_m > 17$, similar values to those obtained in current research.

Dubinin–Radushkevich also exhibited good adjustments, suggesting the occurrence of chemisorption on canola-based adsorbents, with values $E > 8$ kJ mol^{-1}, except for G1 NaOH, G2 *in natura* and G4 *in natura*, with $E < 8$ kJ mol^{-1} [34].

For G1 NaOH the value of $E = 0.144$ kJ mol^{-1}, this is well below the obtained for other activations and genotypes, suggesting purely physical adsorption, the physical adsorption is also evidenced by the value of n obtained in the linearization of the Freundlich model. When $1/n > 1$ the adsorption tends to be physical or cooperative [55].

The nature of the adsorption process can be evaluated by thermodynamics parameters [56]. As can be seen in Table 6, the $\Delta G°$ value for ion Pb^{2+} on genotypes G1, G2 and G4 *in natura*, G1, G2, G3 and G4 H_2O_2, G2 H_2SO_4, and G1 and G4 for NaOH were positive for all studied temperatures, suggesting that the process, in these cases, are spontaneous and favorable. The opposite was observed for Pb^{2+} on genotype 3 *in natura*, G1, G3 and G4 H_2SO_4, and G2 and G3 for NaOH.

When the enthalpy values ($\Delta H°$) are positive the system is endothermic, as observed for genotypes G1, G2 and G3 for the *in natura* material, G1, G2, G3 and G4 for H_2O_2, G2 for H_2SO_4, and G1 and G4 for NaOH. In turn, the negative values of $\Delta H°$ for the remaining material show that the process was exothermic. The results in Table 6 also demonstrate values of $\Delta H°$ greater than 40 kJ mol^{-1}. These results suggest possible chemisorption [57].

The entropy values ($\Delta S°$), for G3 *in natura*, G1, G3 and for H_2SO_4 and G2 and G3 for NaOH, suggest a slight increase in system disorder. In these cases, according to Rao and Khan [58], there is an increasing disorder of the solid-solution interface, indicating increased randomness

Table 4
Kinetics parameters for Pb^{2+} removal by canola-based adsorbents

Kinetics parameters	G1 *in natura*	G2 *in natura*	G3 *in natura*	G4 *in natura*	G1 H_2O_2	G2 H_2O_2	G3 H_2O_2	G4 H_2O_2	G1 H_2SO_4	G2 H_2SO_4	G3 H_2SO_4	G4 H_2SO_4	G1 NaOH	G2 NaOH	G3 NaOH	G4 NaOH
Pseudo-first-order [18] $\log\left(Q_{eq}-Q_t\right)=\log Q_{eq}-\left(\frac{k_1}{2.303}\right)t$																
K_1 (min^{-1})	–0.008	–0.005	–0.016	–0.016	–0.009	–0.014	–0.011	–0.019	–0.024	–0.031	–0.025	–0.024	–0.033	–0.019	–0.024	–0.017
Q_{eq} (cal.) (mg g^{-1})	0.866	0.293	0.273	0.669	0.309	0.725	0.944	0.988	1.637	1.112	1.304	1.086	0.908	0.627	0.96	0.283
R^2	0.694	0.767	0.966	0.945	0.951	0.968	0.937	0.934	0.989	0.957	0.977	0.964	0.970	0.915	0.960	0.819
Pseudo-second-order [19] $\frac{q}{Q_t}=\frac{1}{k_2Q_{eq}^2}+\frac{1}{Q_{eq}}t$																
K_2 (g mg^{-1} min^{-1})	2.264	1.555	0.935	1.463	1.228	1.205	1.619	1.323	0.024	0.067	0.054	0.051	0.914	0.947	0.942	0.937
Q_{eq} (cal.) (mg g^{-1})	0.134	1.48	2.461	1.573	1.874	1.911	1.422	1.739	2.375	2.335	1.723	2.317	2.518	2.429	2.443	2.456
R^2	0.993	0.994	0.998	0.993	0.997	0.992	0.997	0.99	0.997	0.999	0.991	0.999	0.999	0.998	0.998	0.999
Elovich [20] $Q_{eq}=A+B\ \text{In}\ t$																
A (mg g^{-1} h^{-1})	0.307	0.084	0.120	0.347	0.200	0.325	0.528	0.452	1.093	0.763	0.795	0.746	0.593	0.378	0.607	0.210
B (g mg^{-1})	2.109	15.969	13.179	5.088	23.478	12.72	3.034	3.642	0.647	4.636	4.246	4.116	16.928	32.299	12.354	98.31
R^2	0.937	0.308	0.729	0.862	0.958	0.865	0.955	0.919	0.962	0.957	0.987	0.981	0.971	0.813	0.980	0.935
Intraparticle diffusion – Weber–Morris model [21] $Q_{eq}=k_{id}t^{1/2}+C_i$																
K_{id} (g mg^{-1} min$^{-1/2}$)	0.004	0.063	0.023	0.061	0.001	0.018	0.072	0.076	1.015	1.215	1.004	1.393	0.003	0.065	0.091	0.034
C_i (mg g^{-1})	0.602	1.631	1.140	0.777	1.620	1.200	0.816	0.708	0.008	0.054	0.118	0.068	2.049	1.486	1.377	2.062
R^2	0.934	0.873	0.931	0.956	0.966	0.602	0.986	0.979	0.654	0.896	0.809	0.865	0.644	0.839	0.811	0.744
Q_{eq} (exp.) $_{(\text{mg g}^{-1})}$	0.899	1.343	1.318	1.296	1.707	1.641	1.354	1.308	2.207	2.133	2.095	2.330	2.207	2.133	2.095	2.33

K_1: pseudo-first-order velocity constant; Q_{eq}: amounts of adsorbate retained per gram of adsorbent at equilibrium; K_2: pseudo-second-order velocity constant; A: constant indicating the initial chemisorption rate; B: number of sites suitable for adsorption. Related to the extent of surface coverage and the activation energy of chemisorption; K_{id}: intraparticle diffusion constant; C: suggests the thickness of the boundary layer effect; R^2: coefficient of determination.

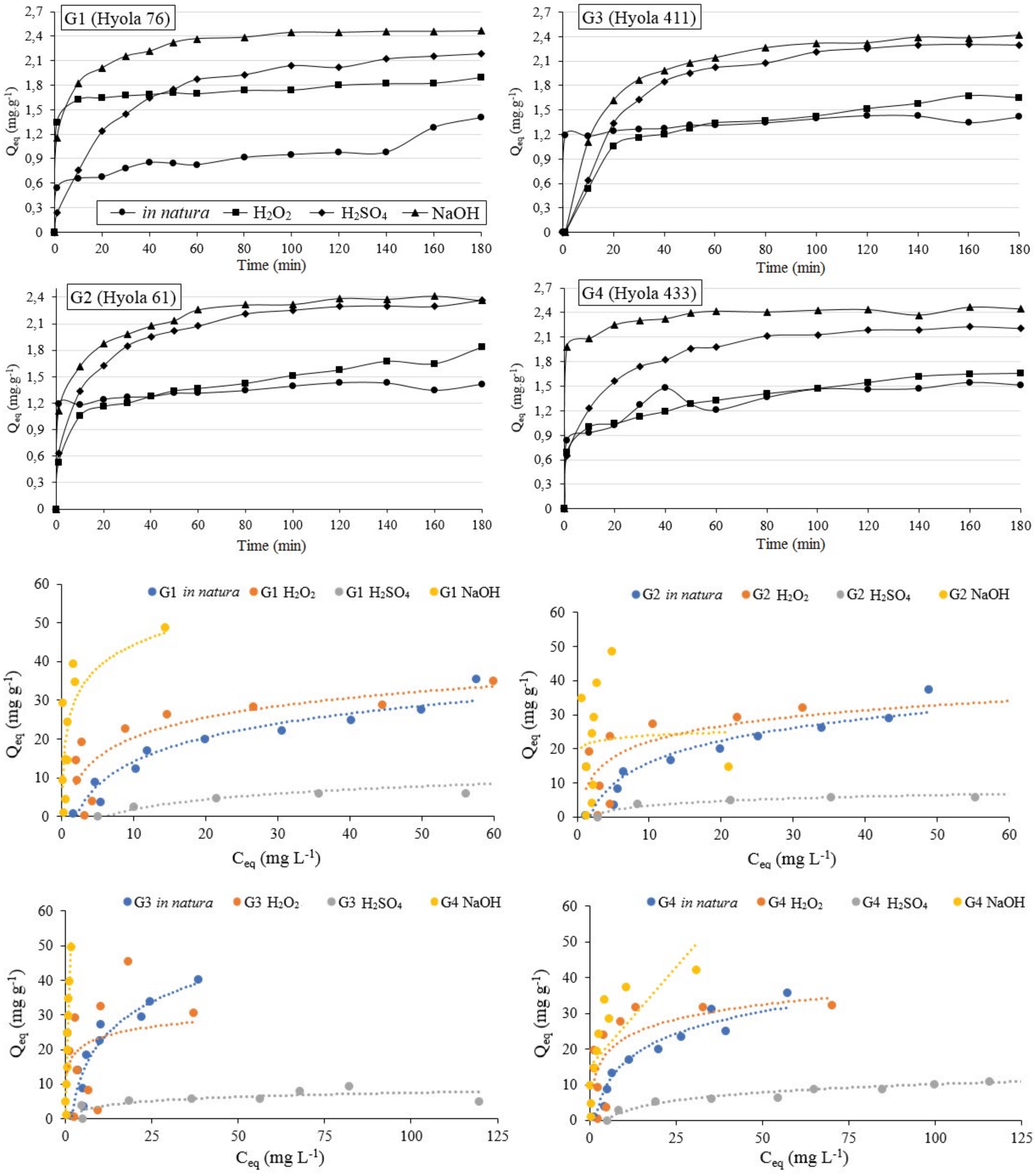


Fig. 6. (a) (Q_{eq} vs. time): kinetics (200 mg L^{-1}) and (b) (Q_{eq} vs. C_{eq}): equilibrium studies (from 5 to 200 mg L^{-1}) of canola-based adsorbents in Pb^{2+} removal.

Table 5
Adsorption parameters for linear models of Langmuir [22], Freundlich [23], Dubinin–Radushkevich [24] and Sips [25] in the removal of Pb^{2+} by canola-based adsorbents

Canola – G1 (Hyola 76)		*In natura*	H_2O_2	H_2SO_4	NaOH
Langmuir	Q_m (mg g^{-1})	34.843	30.864	14.513	48.780
$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$	b or K_L (L mg^{-1})	0.066	0.074	0.020	1.357
	R_L	0.070	0.062	0.196	0.003
	R^2	0.982	0.996	0.978	0.988
Freundlich	K_F (mg g^{-1})	4.238	15.584	0.272	23.222
$\log q_{eq} = \log k_f + \left(\frac{1}{n_F}\right)\log C_{eq}$	n	2.059	5.230	1.268	0.0003
	R^2	0.984	0.983	0.986	0.900
Dubinin–Radushkevich $\ln Q_{eq} = \ln Q_d - Bd\varepsilon^2$	Q_d (mol g^{-1})	0.0008	0.0003	0.0003	0.0009
$\varepsilon = RT \ln\left(1+\frac{1}{C_{eq}}\right)$	E (kJ mol^{-1})	10.783	17.149	9.534	0.144
	R^2	0.960	0.970	0.983	0.935
Sips	n	1.097	1.556	1.034	0.335
$\ln\left(\frac{Q_{eq}}{Q_{max}-Q_{eq}}\right) = \frac{1}{n_s}\ln C_{eq} + \frac{1}{n_s}\ln k_L$	K_s or L (L mg^{-1})	0.067	0.312	0.019	0.947
	R^2	0.984	0.979	0.984	0.961
Canola – G2 (Hyola 61)		*In natura*	H_2O_2	H_2SO_4	NaOH
Langmuir	Q_m (mg g^{-1})	44.843	15.898	12.674	30.120
$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$	b or K_L (L mg^{-1})	0.043	0.121	0.029	0.479
	R_L	0.103	0.039	0.144	0.010
	R^2	0.994	0.999	0.982	0.985
Freundlich	K_F (mg g^{-1})	0.875	18.749	0.959	13.436
$\log q_{eq} = \log k_f + \left(\frac{1}{n_F}\right)\log C_{eq}$	n	1.023	6.729	0.0001	1.115
	R^2	0.989	0.978	0.986	0.928
Dubinin–Radushkevich $\ln Q_{eq} = \ln Q_d - Bd\varepsilon^2$	Q_d (mol g^{-1})	0.004	0.0002	0.0002	0.023
$\varepsilon = RT \ln\left(1+\frac{1}{C_{eq}}\right)$	E (kJ mol^{-1})	7.955	19.611	10.206	8.638
	R^2	0.986	0.989	0.994	0.935
Sips	n	0.771	1.007	1.245	0.149
$\ln\left(\frac{Q_{eq}}{Q_{max}-Q_{eq}}\right) = \frac{1}{n_s}\ln C_{eq} + \frac{1}{n_s}\ln k_L$	K_s or L (L mg^{-1})	0.060	0.672	0.021	0.468
	R^2	0.996	0.984	0.997	0.991
Canola – G3 (Hyola 411)		*In natura*	H_2O_2	H_2SO_4	NaOH
Langmuir	Q_m (mg g^{-1})	50.000	31.056	5.061	133.333
$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$	b or K_L (L mg^{-1})	0.099	0.160	0.327	0.381
	R_L	0.048	0.030	0.015	0.013
	R^2	0.988	0.999	0.993	0.977
Freundlich	K_F (mg g^{-1})	8.317	23.399	2.345	36.914
$\log q_{eq} = \log k_f + \left(\frac{1}{n_F}\right)\log C_{eq}$	n	2.321	5.263	3.412	1.621
	R^2	0.992	0.768	0.933	0.998
Dubinin–Radushkevich $\ln Q_{eq} = \ln Q_d - Bd\varepsilon^2$	Q_d (mol g^{-1})	0.0009	0.0004	0.0001	0.005
	E (kJ mol^{-1})	11.624	18.898	13.608	11.470
$\varepsilon = RT \ln\left(1+\frac{1}{C_{eq}}\right)$	R^2	0.992	0.746	0.914	0.997

Sips	n	8.210	0.493	2.810	0.641
$\ln\left(\frac{Q_{eq}}{Q_{max}-Q_{eq}}\right)=\frac{1}{n_s}\ln C_{eq}+\frac{1}{n_s}\ln k_L$	K_s or L (L mg^{-1})	1.18 e^{-9}	0.065	3.4 e^{-4}	1.935
	R^2	0.998	0.979	0.975	0.978
Canola – G4 (Hyola 433)		*In natura*	H_2O_2	H_2SO_4	NaOH
Langmuir	Q_m (mg g^{-1})	48.543	33.557	13.947	46.511
$\frac{C_{eq}}{q_{eq}}=\frac{1}{q_m b}+\frac{C_{eq}}{q_m}$	b or K_L (L mg^{-1})	0.049	0.071	0.027	0.342
	R_L	0.092	0.065	0.151	0.014
	R^2	0.989	0.995	0.984	0.993
Freundlich	K_F (mg g^{-1})	3.296	20.197	0.300	19.098
$\log q_{eq}=\log k_f+\left(\frac{1}{n_F}\right)\log C_{eq}$	n	0.0001	8.136	1.304	4.016
	R^2	0.989	0.960	0.992	0.991
Dubinin–Radushkevich	Q_d (mol g^{-1})	0.0044	0.0002	0.0002	0.0004
$\ln Q_{eq}=\ln Q_d-B d\varepsilon^2$	E (kJ mol^{-1})	7.905	22.360	10.206	16.666
$\varepsilon=RT\ln\left(1+\frac{1}{C_{eq}}\right)$	R^2	0.991	0.979	0.983	0.991
Sips	n	1.026	0.809	1.033	0.745
$\ln\left(\frac{Q_{eq}}{Q_{max}-Q_{eq}}\right)=\frac{1}{n_s}\ln C_{eq}+\frac{1}{n_s}\ln k_L$	K_s or L (L mg^{-1})	0.068	0.627	0.032	0.448
	R^2	0.978	0.989	0.983	0.999

Q_m (mg g^{-1}): maximum adsorption capacity; K_L or b (L mg^{-1}): constant related to the adsorbent/adsorbate interaction forces; R_L: Langmuir constant; K_F (L mg g^{-1}): related to adsorption capacity; n (Freundlich or Sips – dimensionless): related to the heterogeneity of the solid; Q_d: maximum adsorption capacity; E: mean sorption energy. K_s or L (L mg^{-1}): constant of Sips; R^2: coefficient of determination.

Table 6
Thermodynamics parameters for canola-based adsorbents

Modification	Temperature (°C)	Average Q_{eq} (mg g^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1})
G1 *in natura*	15	7.97	22.59 ± 0.67	10.35	–0.04
	25	7.69	23.02 ± 0.67		
	35	6.87	23.44 ± 0.67		
	45	6.57	23.87 ± 0.67		
	55	6.54	24.29 ± 0.67		
G2 *in natura*	15	5.99	10.72 ± 0.38	3.62	–0.02
	25	5.40	10.96 ± 0.38		
	35	10.01	11.21 ± 0.38		
	45	5.6	11.46 ± 0.38		
	55	5.43	11.70 ± 0.38		
G3 *in natura*	15	5.16	–20.16 ± 0.44	–12.09	0.02
	25	6.13	–20.44 ± 0.44		
	35	7.05	–20.72 ± 0.44		
	45	6.8	–21.00 ± 0.44		
	55	7.05	–21.28 ± 0.44		
G4 *in natura*	15	6.13	85.38 ± 2.42	41.16	–0.15
	25	5.48	86.91 ± 2.42		
	35	5.63	88.45 ± 2.42		
	45	1.99	89.98 ± 2.42		
	55	1.57	91.52 ± 2.42		
G1 H_2O_2	15	10.58	70.27 ± 1.90	35.64	–0.12
	25	9.74	71.47 ± 1.90		
	35	8.05	72.67 ± 1.90		
	45	7.88	73.87 ± 1.90		
	55	8.92	75.07 ± 1.90		

(Continued)

Table 6 Continued

Modification	Temperature (°C)	Average Q_{eq} (mg g^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})
G2 H_2O_2	15	7.68	18.22 ± 0.56	7.97	–0.03
	25	6.90	18.58 ± 0.56		
	35	5.34	18.93 ± 0.56		
	45	7.10	19.29 ± 0.56		
	55	6.44	19.65 ± 0.56		
G3 H_2O_2	15	3.24	78.41 ± 2.06	40.93	–0.13
	25	3.06	79.72 ± 2.06		
	35	10.53	81.02 ± 2.06		
	45	9.73	82.32 ± 2.06		
	55	8.37	83.62 ± 2.06		
G4 H_2O_2	15	7.30	162.91 ± 4.34	83.75	–0.27
	25	10.66	165.66 ± 4.34		
	35	9.10	168.41 ± 4.34		
	45	6.15	171.16 ± 4.34		
	55	6.60	173.91 ± 4.34		
G1 H_2SO_4	15	4.50	–6.06 ± 0.04	–5.35	0.002
	25	4.88	–6.08 ± 0.04		
	35	5.76	–6.11 ± 0.04		
	45	4.79	–6.13 ± 0.04		
	55	5.34	–6.16 ± 0.04		
G2 H_2SO_4	15	8.50	67.18 ± 1.88	32.81	–0.11
	25	7.19	68.37 ± 1.88		
	35	4.65	69.57 ± 1.88		
	45	5.48	70.76 ± 1.88		
	55	5.57	71.95 ± 1.88		
G3 H_2SO_4	15	7.30	–52.55 ± 1.29	–28.93	0.08
	25	5.27	–53.37 ± 1.29		
	35	5.83	–54.19 ± 1.29		
	45	6.36	–55.01 ± 1.29		
	55	8.75	–55.83 ± 1.29		
G4 H_2SO_4	15	3.91	–36.89 ± 0.86	–21.09	0.05
	25	3.66	–37.44 ± 0.86		
	35	4.54	–37.99 ± 0.86		
	45	5.13	–38.54 ± 0.86		
	55	7.19	–39.09 ± 0.86		
G1 NaOH	15	11.87	42.83 ± 1.06	23.34	–0.06
	25	10.06	43.50 ± 1.06		
	35	11.11	44.18 ± 1.06		
	45	11.53	44.86 ± 1.06		
	55	10.60	45.53 ± 1.06		
G2 NaOH	15	8.02	–108.29 ± 2.92	–55.04	0.18
	25	10.01	–110.14 ± 2.92		
	35	10.98	–111.99 ± 2.92		
	45	9.90	–113.84 ± 2.92		
	55	10.07	–115.69 ± 2.92		
G3 NaOH	15	9.92	–47.44 ± 1.30	–23.63	0.08
	25	10.84	–48.27 ± 1.30		
	35	6.79	–49.09 ± 1.30		
	45	7.97	–49.92 ± 1.30		
	55	11.35	–50.75 ± 1.30		
G4 NaOH	15	11.83	84.11 ± 2.13	45.17	–0.13
	25	11.97	85.46 ± 2.13		
	35	11.84	86.81 ± 2.13		
	45	11.01	88.16 ± 2.13		
	55	10.75	89.51 ± 2.13		

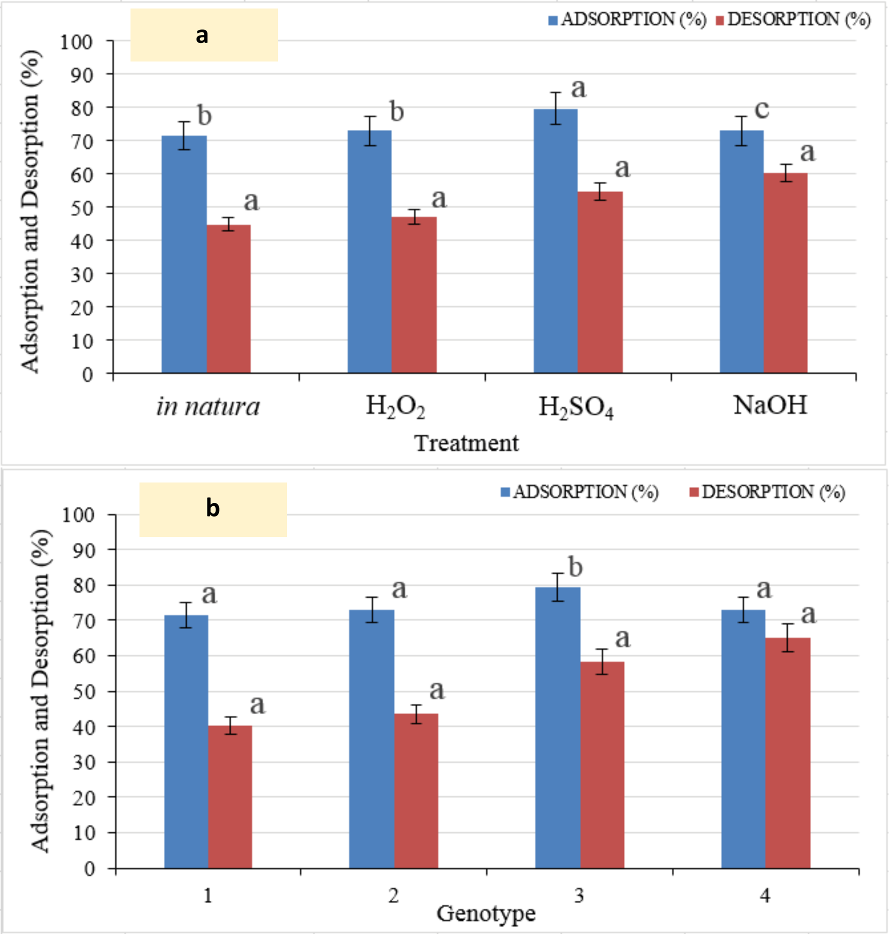


Fig. 7. Average % of adsorption and desorption rates for canola-based adsorbents. (a) The effect of the modifying solution in the adsorption and desorption rate of Pb^{2+}. (b) The effect of the evaluated genotypes (1 to 4) in the adsorption and desorption rates of Pb^{2+}. Different letters in the bars show a statistical difference among treatments at 5% by the Tukey's test.

at the solid/solution interface, which may occur due to the substitution of water molecules of the solution previously adsorbed by metal ions. In other cases, the values of $\Delta S°$ smaller than 0, indicate no disorder in the system.

From the initial concentration of the influence tests, it was possible to evaluate the efficiency of Pb^{2+} adsorption (%) and desorption (%) for the canola-based adsorbents.

The following desorption rates were obtained by acid elution of Pb^{2+}, for genotype 1: C. *in natura* (40%); C. H_2O_2 (41%); C. H_2SO_4 (71%) and C. NaOH (81%); For genotype 2: C. *in natura* (48%); C. H_2O_2 (32%); C. H_2SO_4 (43%) and C. NaOH (38%); For genotype 3: C. *in natura* (52%); C. H_2O_2 (75%); C. H_2SO_4 (56%) and C. NaOH (77%); For genotype 4: C. *in natura* (39%); C. H_2O_2 (41%); C. H_2SO_4 (49%) and C. NaOH (45%). The averages and the standard deviations from 240 analytical determinations that estimate the adsorption and desorption rates are exhibited in Figs. 7a and b, showing the average values for each modifying solution and its effect in adsorption and desorption rates, as well as the effect of the different genotypes.

Although some acceptable values for desorption (G1 C. H_2SO_4 and C. NaOH, G3 C. H_2O_2 and C. NaOH) were observed, the majority of the materials had low elution rates. These results suggest that the adsorption process is in most of the cases a chemical nature, since, according to Albadarin et al. [59], low elution rates indicate that the metal ion is strongly bound to the active sites of the adsorbent by means of chemical bonds.

4. Conclusion

In general, it can be concluded that the adsorbents from *Brassica napus* L. *in natura* (canola meal) and chemically modified with H_2O_2, H_2SO_4 and NaOH showed differences in structure, morphology, porosity, point of zero charge and thermal stability. The evaluated pH range only influences the adsorption of Pb^{2+} when it is used H_2O_2 as a modifying agent. For other adsorbents, the pH studied range (3.0–7.0) did not influence the Pb^{2+} adsorption. However, there was a significant difference in the used adsorbent dose, with the use of 4 g L^{-1} as the ideal ratio for the efficient removal of Pb^{2+} from aqueous medium.

In addition, it was observed that the canola-based adsorbents have surface functional groups as aldehyde, ketone and carbonyl, which allow the connection with metallic ions in solution.

The ideal contact time range was found between 80 and 140 min. The obtained results in adsorption kinetics indicate that the biosorbents presented better adjustment by the pseudo-second-order model suggesting the occurrence of chemisorption. The best adjustments (R^2) were observed for the Langmuir, and genotype 3 (Hyola 411) exhibited a better average of Q_m 54.86 mg g^{-1} (average of Q_m from *in natura*, H_2O_2, H_2SO_4 and NaOH) as well as the highest percentage of adsorption (80%).

The application of the Dubinin–Radushkevich model demonstrates that the removal of Pb^{2+} by the canola-based adsorbents occurs by chemisorption, with a predominance of monolayers. The adsorbents modified with NaOH demonstrated a higher percentage of desorption. However, the percentage of desorption between the different genotypes and treatments did not differ statistically. The high desorption rates suggest the possibility of reuse of the canola-meal adsorbents for several cycles of adsorption.

From the results obtained in this research, it is possible to affirm that the modified adsorbents of canola present themselves as a promising alternative for the industry, through their use in systems of treatment of contaminated water, especially for the removal of Pb^{2+}, increasing the sustainability of its productive chain.

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References

[1] M. Kuroda, K. Hara, M. Takekawa, M. Uwasu, M. Ike, Historical trends of academic research on the water environment in Japan: evidence from the academic literature in the past 50 years, Water, 10 (2018) 1456.

[2] A.E. Duncan, N. de Vries, K.B. Nyarko, Assessment of heavy metal pollution in the sediments of the River Pra and its tributaries, Water Air Soil Pollut., 229 (2018) 1–10.

[3] D. Schwantes, A.C. Gonçalves Jr., A. De Varennes, A.L. Braccini, Modified grape stem as a renewable adsorbent for cadmium removal, Water Sci. Technol., 78 (2018) 2308–2320.

[4] E.G. Lisboa, R.L.R. Mendes, L.A.L. Bello, Mapping of risk of contamination of groundwater in urban areas: proposal of a fuzzy-AHP, Rev. Univ. Vale Rio Verde, 14 (2016) 238–252.

[5] P.M. Dellamatrice, R.T.R. Monteiro, Main aspects of the pollution in Brazilian rivers by pesticides, Braz. J. Agric. Environ. Eng., 18 (2014) 1296–1301.

[6] A.C. Gonçalves Jr., D. Schwantes, R.F.B. de Sousa, T.R.B. da Silva, V.F. Guimarães, M.A. Campagnolo, E.S. de Vasconcelos, J. Zimmermann, Phytoremediation capacity, growth and physiological responses of *Crambe abyssinica* Hochst on soil contaminated with Cd and Pb, J. Environ. Manage., 262 (2020) 110342.

[7] E. Conradi Jr., A.C. Gonçalves Jr., D. Schwantes, J. Manfrin, A. Schiller, J. Zimmerman, G.J. Klassen, G.L. Ziemer, Development of renewable adsorbent from cigarettes for lead removal from water, J. Environ. Chem. Eng., 7 (2019) 103200.

[8] M.R. Boniolo, L.M.N. *Yanuli, D.A. Mortari, A.A. Menegário, M.L. Garcia, B*razilian biomass applied to uranium removal from acid mine drainage by biosorption process, Holos Environ., 17 (2015) 149–167.

[9] F.L. Seixas, L.G. Marcelino, N.R.C. Machado, Treatment of vinasse by adsorption on sugarcane bagasse coal, Quim. Nova, 39 (2016) 172–179.

[10] D. Balarak, J. Jafari, G. Hasani, Y. Mahdavi, I. Tyagi, S. Agarwal, 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, Colloid Interface Sci. Commun., 7 (2015) 16–19.

[11] D. Balarak, F.K. Mostafapour, Adsorption behavior of acid red 97 dye on canola stalks, J. Sci. Eng. Res., 3 (2016) 148–154.

[12] IUPAC, Standard Methods for the Analysis of Oils, Fats and Derivatives, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, London Edinburgh Boston Melbourne Paris Berlin Vienna, 1988, pp. 99–102.

[13] D. Schwantes, A.C. Gonçalves Jr., M.A. Campagnolo, C.R.T. Tarley, D.C. Dragunski, J. Manfrin, A. da Paz Schiller, Use of co-products from the processing of cassava for the development of adsorbent materials aiming metal removal, IntechOpen, (2018), doi: 10.5772/intechopen.71048.

[14] A.M.S. Mimura, T.V. de Almeida Vieira, P.B. Martelli, H. de Fátima Gorgulho, Utilization of rice husk to remove Cu^{2+}, Al^{3+}, Ni^{2+} and Zn^{2+} from wastewater, Quim. Nova, 33 (2010) 1279–1284.

[15] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc., 60 (1938) 309–319.

[16] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, J. Am. Chem. Soc., 73 (1951) 373–380.

[17] B. Welz, M. Sperling, Atomic Absorption Spectrometry, John Wiley & Sons, Hoboken, New Jersey, 2008.

[18] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens Handlingar, 24 (1898) 1–39.

[19] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[20] S.Z. Roginski, Adsorption and Catalysis on Inhomogeneous Surfaces, USSR Academy of Science Publications, Moscow-Leningrand, 1948.

[21] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div., 89 (1963) 31–60.

[22] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[23] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 1100–1107.

[24] M.M. Dubinin, L.V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, Zhurnal Fizicheskoi Khimii, 21 (1947) 151–162.

[25] R. Sips, The structure of a catalyst surface, J. Phys. Chem., 16 (1948) 490–495.

[26] 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. Hazard. Mater., 149 (2007) 283–291.

[27] A.C. Gonçalves Jr., C. Selzlein, H. Nacke, Use of water hyacinth (*Eichornia crassipes*) dry biomass for removing heavy metals from contaminated solutions, Acta Sci. Technol., 31 (2009) 103–108.

[28] G.V. Tagliaferro, P.H. Pereira, L.Á. Rodrigues, M.L.C.P. da Silva, Cadmium, lead and silver adsorption in hydrous niobium oxide prepared by homogeneous solution method, Quim. Nova, 34 (2011) 101–105.

[29] R. de Góes Casqueira, A.C. Lima, Avaliação da remoção de Cr(III) empregando o pseudocaule da bananeira (*Musa paradisíaca*) como biossorvente, Engevista, 18 (2016) 174–188.

[30] T. Bohli, A. Ouederni, N. Fiol, L. Villaescusa, Evaluation of an activated carbon from olive stones used as an adsorbent for heavy metal removal from aqueous phases, C.R. Chim., 18 (2014) 1–12.

[31] N. Díez, P. Álvarez, M. Granda, C. Blanco, R. Santamaría, R. Menéndez, CO_2 adsorption capacity and kinetics in nitrogen-enriched activated carbon fibers prepared by different methods, Chem. Eng. J., 281 (2015) 704–712.

[32] E. de M. Teixeira, C. Lotti, A.C. Corrêa, K.B.R. Teodoro, J.M. Marconcini, L.H.C. Mattoso, Thermoplastic corn starch reinforced with cotton cellulose nanofibers, J. Appl. Polym. Sci., 120 (2011) 2428–2433.
[33] A. de Campos, K.B.R. Teodoro, J.M. Marconcini, L.H.C. Mattoso, S.M. Martins-Franchetti, Effect of fiber treatments on properties of thermoplastic starch/polycaprolactone/sisal biocomposites, Polymers, 21 (2011) 217–222.
[34] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresour. Technol., 99 (2008) 3935–3948.
[35] D. Schwantes, A.C. Gonçalves Jr., G.F. Coelho, M.A. Campagnolo, D.C. Dragunski, C.R.T. Tarley, A.J. Miola, E.A.V. Leismann, Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater, J. Chem., 2016 (2016) 1–15, doi: 10.1155/2016/3694174.
[36] K.M.D. da Silva, L.C.S.H. Rezende, C.A. da Silva, R. Bergamasco, D.S. Gonçalves, Caracterização físico-química da fibra de coco verde para a adsorção de metais pesados em efluente de indústria de tintas, Engevista, 15 (2013) 43–50.
[37] A.C. Gonçalves Jr., L. Strey, C.A. Lindino, H. Nacke, D. Schwantes, E.P. Seidel, Applicability of the Pinus bark (*Pinus elliottii*) for the adsorption of toxic heavy metals from aqueous solutions, Acta Sci. Technol., 34 (2012) 79–87.
[38] R.M. Silverstein, F.X. Webster, D.J. Kiemle, Spectrometric Identification of Organic Compounds, John Wiley & Sons, Hoboken, New Jersey, 2005.
[39] W. Tongpoothorn, M. Sriuttha, P. Homchan, S. Chanthai, C. Ruangviriyachai, Preparation of activated carbon derived from *Jatropha curcas* fruit shell by simple thermo-chemical activation and characterization of their physico-chemical properties, Chem. Eng. Res. Des., 89 (2011) 335–340.
[40] R.P. Han, L.J. Zhang, C. Song, M. Zhang, H.M. Zhu, L.J. Zhang, Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode, Carbohydr. Polym., 79 (2010) 1140–1149.
[41] N.C. Feng, X.Y. Guo, S. Liang, Y.S. Zhu, J.P. Liu, Biosorption of heavy metals from aqueous solutions by chemically modified orange peel, J. Hazard. Mater., 185 (2011) 49–54.
[42] X.Y. Guo, S.Z. Zhang, X.-Q. Shan, Adsorption of metal ions on lignin, J. Hazard. Mater., 151 (2008) 134–142.
[43] N. Barka, M. Abdennouri, A. Boussaoud, A.M. El Makhfouk, Biosorption characteristics of Cadmium(II) onto *Scolymus hispanicus* L. as low-cost natural biosorbent, Desalination, 258 (2010) 66–71.
[44] H. Nacke, A.C. Gonçalves Jr., G.F. Coelho, D. Schwantes, M.A. Campagnolo, E.A.V. Leismann, É. Conradi Jr., A.J. Miola, Removal of Cd(II) from water using the waste of jatropha fruit (*Jatropha curcas* L.), Appl. Water Sci., 7 (2017) 3207–3222
[45] E. Smidt, K. Meissl, The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, Waste Manage., 27 (2007) 268–276.
[46] D.L. Pavia, G.M. Lampman, G.S. Kriz, J.R. Vyvyan, Introdução à espectroscopia, 4th ed., Cengage Learning, São Paulo, 2010.
[47] V.V. da S. Guilarduci, H.F. Gorgulho, P.B. Martelli, V.S. Santos, W.G. Corrêa, Avaliação do bagaço de cana natural e modificado como potencial sorvente de óleo vegetal, Rev. Verde de Agroec. e Desenv. Sust., 11 (2016) 129–134.
[48] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquérol, T. Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure Appl. Chem., 57 (1985) 603–619.
[49] Y. Marcus, Thermodynamics of solvation of ions. Part 6.–The standard partial molar volumes of aqueous ions at 298.15 K, J. Chem. Soc., Faraday Trans., 89 (1993) 713–718.
[50] S.V. Yadla, V. Sridevil, M.V.V.C. Lakshmi, A review on adsorption of heavy metals from aqueous solution, J. Chem. Biol. Phys. Sci., 2 (2012) 1585–1593.
[51] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.-H. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies, J. Hazard. Mater., 162 (2009) 616–645.
[52] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, J. Chem. Soc., (1960) 3973–3993.
[53] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, J. Appl. Chem., 3 (2012) 38–45.
[54] S. Karagöz, T. Tay, S. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, Bioresour. Technol., 99 (2008) 6214–6222.
[55] A.F. Taiwo, N.J. Chinyere, Sorption characteristics for multiple adsorption of heavy metal ions using activated carbon from Nigerian bamboo, J. Chem. Eng. Mater. Sci., 4 (2016) 39–48.
[56] P. Senthilkumar, S. Ramalingam, R.V. Abhinaya, S. Dinesh Kirupha, T. Vidhyadevi, S. Sivanesan, Adsorption equilibrium, thermodynamics, kinetics, mechanism and process design of zinc(II) ions onto cashew nut shell, Can. J. Chem. Eng., 90 (2012) 973–982
[57] W.S. Wan Ngah, S. Fatinathan, Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: kinetic, equilibrium and thermodynamic studies, J. Environ. Manage., 91 (2010) 958–969.
[58] R.A.K. Rao, M.A. Khan, Biosorption of bivalent metal ions from aqueous solution by an agricultural waste: kinetics, thermodynamics and environmental effects, Colloids Surf., A, 332 (2009) 121–128.
[59] A.B. Albadarin, C. Mangwandi, A.H. Al-Muhtaseb, G.M. Walker, S.J. Allen, M.N.N. Ahmad, Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent, Chem. Eng. J., 179 (2012) 193–202.