ORIGINAL ARTICLE

Removal of Cd(II), Pb(II) and Cr(III) from water using modified residues of *Anacardium occidentale* L.

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Abstract
The pollution of water has been one of the greatest problems faced by the modern society, due to industrialization and urban growth. Rivers, lakes and seas have been continually suffering from the rising concentration of various pollutants, especially toxic elements. This study aimed to evaluate the use of cashew nut shell (*Anacardium occidentale*) (CNS), after chemical modification with H_2O_2, H_2SO_4 and NaOH, as an new and renewable adsorbent material, for the removal of metals Cd^{2+}, Pb^{2+} and Cr^{3+} in aqueous medium. The adsorbents were characterized by its chemical constitution, structure, infrared spectroscopy, morphology, by means of scanning electron microscopy, determination of the point of zero charge, thermogravimetrical analysis and porosimetry assessments. Tests were conducted to determine the optimal conditions (pH vs. adsorbent mass) for adsorption, by means of multivariate analysis using a central composite design. The adsorption kinetics was evaluated by models of pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion, while adsorption isotherms were linearized by Langmuir, Freundlich and Dubinin–Radushkevich. The effect of initial concentration, temperature and desorption was also performed. The adsorbents exhibited irregular, spongy and heterogeneous structure. FTIR analysis confirms the presence of hydroxyl, aliphatic, phenolic and carboxylic acid groups, which are favorable adsorption characteristics. The pH_{PZC} of adsorbent is 4.35, 2.50 e 6.92, respectively, for CNS H_2O_2, H_2SO_4 and NaOH. The optimum adsorption conditions were as follows: pH 5.0; relation of adsorbent mass/volume of water: 4 g L^{-1}; 40 min of contact time for reaching the equilibration. Results suggest the predominance of chemisorption of Cd^{2+} and Cr^{3+}. Most of biosorbents exhibited good fit by Langmuir and Freundlich, suggesting the occurrence of adsorption on mono- and multilayers. The adsorbents of cashew nut shell exhibited high removal efficiency of Cd, Pb and Cr from waters.

Keywords Biosorbent · Biosorption · Metal adsorption · Remediation · Water pollution

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Introduction

Daily, toxic metals are released into the environment, whether in the form of mining waste, fertilizers and pesticides, or through domestic and industrial waste, as well as activities of tanning leather, wood preservation, paints, textiles and metallurgy, among others. These metals, in most part, are accumulative and characterized by latent toxicity, causing numerous damages into the biological cycles and trophic chain (Perugini et al. 2011; Nacke et al. 2013).

Cadmium (Cd), lead (Pb) and chromium (Cr), for example, are harmful to human health. Cd accumulates easily in the circulatory system, kidney (renal cortex mainly), lung and heart, it is toxic to bones and gonads, while Pb has carcinogenic properties damaging the digestive and respiratory and immune systems; in children it mainly affects the

intelligence and the nervous system (Zhong et al. 2016). Cr can exist in various states of oxidation (Apte et al. 2005), in conditions of pH > 6.0, predominantly at the form of Cr(OH)$_3$. Cr(III) is involved in maintaining levels of glucose, cholesterol and triglycerides, performing, therefore, essential role as a nutrient to living organisms (Apte et al. 2005; Frois et al. 2011). However, under certain conditions it can be oxidized to Cr(VI), causing serious environmental consequences, due to its high solubility and mobility, as well as being harmful to the skin, liver, kidney and respiratory organs, causing diseases such as dermatitis, renal tubular necrosis, perforation of the nasal septum and lung cancer (Apte et al. 2005; Frois et al. 2011; Zhong et al. 2016).

Treatment techniques and processes have been used for the removal of pollutants from water, such as: precipitation, ion exchange, electrochemical treatment, flocculation, filtration and ozonization, which are used for wastewater decontamination with toxic metals. Generally, these techniques are limited by its eventually high costs or its technical viability, especially when used to remove dissolved metals in large volumes of water, generating large amounts of solid wastes, which are maintained and stored, causing another serious problem (Kanitz Junior et al. 2009). One of the most popular methods is adsorption, especially when using activated carbon, although its high cost restricts its usage. In this way, the use of natural adsorbents can represent an excellent alternative, providing in many cases the same efficiency that activated carbon with lower costs (Zhao et al. 2011).

The use of biosorbent is a promising technology for the removal of toxic metals and other pollutants from aqueous solutions, as observed by the solid wastes from cassava industry (Schwantes et al. 2013), pie of *Crambe abyssinca* Hochst (Gonçalves Jr. et al. Gonçalves et al. 2013; Rubio et al. 2013a, b), pie of *Moringa oleifera* Lam. (Gonçalves Jr. et al. 2013b; Meneghel et al. 2013), biomass of Jatropha (*Jatropha curcas*) (Nacke et al. 2016), wheat straw (Coelho et al. 2016), mussel shell, pinus ashes, oak ash, pinus bark and hemp residues (Quintans-Fondo et al. 2016a, b, c). Although the economic benefits of nontransformation of biomass, studies are being carried out in order to increase the potential of biosorbents removal capacity, with the goal of giving new functional groups on the adsorbent surface through superficial chemical modifications on adsorbents mostly from vegetable origin (Wan Ngah and Hanafiah 2008; Schwantes et al. 2015, 2016).

The cashew areas (*Anacardium occidentale* L.) are expanding mainly by its great agronomic potential in Brazil and for its potential use of co-products (Moreira et al. 2013). The cashew tree is a tree native from Tropical America, producer of edible nuts and succulent stems (pseudofruits) widely consumed by the population of many countries (Leitão et al. 2013; Muianga et al. 2016).

The world production of cashew nuts is estimated of 4,280,000 tons, in which 20% of the fruit consists of shell, with world annual bark production estimated of 856,000 tons, being in Brazil 54,000 tons (Coelho et al. 2014).

After obtaining the shell of cashew nut (CNS) and its oil, the solid wastes are disposed inappropriately in the soil, causing environmental problems. As a result, Coelho et al. (2014) evaluated the removal of Cd^{2+}, Pb^{2+} and Cr^{3+} from aqueous solutions by natural cashew nut as a biosorbent, i.e., with no chemical modification, obtaining good results for the removal of these metals from aqueous solutions. Despite the use of biosorbents, many studies highlight that after simple chemical modifications most part of natural adsorbents may have its adsorption capacity increased with little or insignificant increase in costs. In addition, there is still very little information about the efficiency of CNS biosorbent after chemical modifications and its efficiency on the removal of pollutants. In this way, this work aimed to evaluate the increased efficiency of CNS chemically modified for the removal of Cd^{2+}, Pb^{2+} and Cr^{3+}.

Materials and methods

Sampling and preparation of adsorbents

The adsorbents produced from the shells of cashew nut (*Anacardium occidentale* L.) were obtained at Curionópolis (PA), which were transported to the Laboratory of Environmental and Instrumental Chemistry of State University of Western Paraná—UNIOESTE, c*ampus* of Marechal Cândido Rondon.

The shells of cashews (CNS) were separated from the almonds, crushed in a blender and dried at 60 °C for 36 h. Subsequently, the oil from the shell was extracted through the Soxhlet-type system with n-hexane (C_6H_{14}, nuclear). The materials were again dried at 60 °C for 48 h and sieved in mesh 14 and 65, for the standardization of particles size between 0.212 and 1.40 mm, resulting in the *in natura* material. Chemical modifications were carried out by immersing the *in natura* material in 1.0 mol L^{-1} of H_2O_2, H_2SO_4 and NaOH, at a rate of 1:10 (m/v) with constant stirring 150 rpm for 6 h at 60 °C. Then, the modified adsorbents were washed with ultrapure water to remove the excess of modifying solution and finally were dried at 60 °C, until constant weight.

Characterization of adsorbent materials

The concentration of metal elements (K, Ca, Mg, Cu, Fe, Mn, Zn, Cd, Pb and Cr) was determined through nitropercloric digestion (AOAC 2005), followed by determination

by FAAS, with certified standard curves of all metals (GBC 932 AA).

The analysis of scanning electron microscopy (SEM), infrared spectroscopy (FTIR), thermogravimetry (TG/DTG), specific surface area, pore diameter and volume, was carried out in the Department of Chemistry of the Londrina State University (UEL) at Londrina, Paraná.

The surface morphology of the materials was obtained by scanning electron microscopy (SEM), with a microscope JEOL KAL 6360-LV, equipped with energy-dispersive microscopy.

In order to determine the main functional groups in adsorbents, infrared spectroscopy analysis was performed, with a spectrometer FTIR-Fourier Transform 8300 (Infrared Spectrophotometer, Shimadzu), in the region between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}, in which the spectra were obtained by using transmittance KBr pellets.

For the determination of the point of zero charge (pH$_{PZC}$) of the adsorbent, 500 mg of mass was added at 50-mL erlenmeyer, containing KCl solution of 0.5 mol L^{-1}. The solutions had pH adjusted ranging from 2.0 to 9.0, resulting in eight samples per adsorbent. After 24-h stirring (200 rpm), the final pH values were obtained (pH$_f$) in function of the initial pH (pH$_i$), being the pH$_{PZC}$ corresponding to the point of null pH variation (Mimura et al. 2010).

The thermal stability of adsorbents was determined by thermogravimetric analyzer (TGA 4000 PerkinElmer), where samples were heated from 30 to 900 °C with heating rate of 10 °C min^{-1}, under N$_2$ atmosphere. In order to verify the pore structure of adsorbents were determined the specific surface area (SSA), volume and pore size of the adsorbent materials using the equipment Quantachrome NOVA 1200e. To this end, 500 mg of materials was heated to 200 °C under vacuum for about 4 h, followed by adsorption and desorption of nitrogen. The surface size and pore volume were calculated using the standard Brunauer, Emmett and Teller (BET), and a pore size was obtained using the method of Barrett–Joyner–Halenda (BJH), according to Eqs. 1 and 2:

$$\frac{1}{v\left[\frac{p_0}{p} - 1\right]} = \frac{c-1}{v_m c}\left(\frac{p}{p_o}\right) + \frac{1}{v_m c} \tag{1}$$

where p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity, and v_m is the monolayer adsorbed gas quantity. c is the BET constant, adapted from Barrett, Joyner and Halenda (1951).

$$\ln \frac{p}{p^0} = \frac{2\gamma v_1}{RT}\frac{1}{r_m} \tag{2}$$

where γ 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, and p/p^o is the relative pressure, adapted from Brunauer et al. (1938).

Multivariable analysis for the influence of mass and pH

The ideal conditions of adsorption were defined with the use of a central composite design (CCD). Tests of adsorbent mass and pH were performed with 5 increasing values (250.0, 396.4, 750.0, 1103.6 and 1250.0 mg) and 5 pH conditions (3.0, 3.6, 5.0, 6.4 and 7.0), adjusted with HCl or NaOH solutions (0.1 mol L^{-1}) (Table 1). These values are combined with fixed volumes of 50 mL containing 10 mg L^{-1} monoelementary water solutions of Cd^{2+}, Pb^{2+} or Cr^{3+}, prepared from cadmium nitrate salts [Cd(NO$_3$)$_2$4H$_2$O], lead nitrate [Pb(NO$_3$)$_2$] and chromium(III) nitrate [Cr(NO$_3$)$_3$ 9H$_2$O]. Then, they were stirred in thermostatic shaker (200 rpm at 25 °C) for 90 min.

From the obtained values for final concentration, graphics were built using the sorbed amount of metal calculated by Eq. 3.

$$Q_{ads} = \frac{(C_0 - C_f)}{m}V \tag{3}$$

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

Table 1 Real and coded values for the planning of the central composite rotatable design (CCRD)

Test	Variable			
	X_1	Mass (mg)	X_2	pH
1	− 1.00	396.39	− 1.00	3.60
2	1.00	1103.61	− 1.00	3.60
3	− 1.00	396.39	1.00	6.40
4	1.00	1103.61	1.00	6.40
5	0.00	750.00	0.00	5.00
6	− 1.41	250.00	0.00	5.00
7	0.00	750.00	1.41	7.00
8	1.41	1250.00	0.00	5.00
9	0.00	750.00	− 1.41	3.00
10	0.00	750.00	0.00	5.00
11	0.00	750.00	0.00	5.00
12	0.00	750.0	0.00	5.00

Experimental conditions: volume: 50 mL, concentration of Cd^{2+}, Pb^{2+} and $^{3+}$ Cr (10 mg L^{-1}), stirring time: 90 min, rotation: 200 rpm; temperature: 25 °C. X_1: encoding for the variable mass; X_2: encoding for the variable pH

Kinetic mechanism of adsorption

With the obtained results from previous tests, we determined the optimal time of sorption of metals. Thus, 200 mg adsorbents were stirred for 12 different time intervals (5, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160 and 180 min) containing 50 mL monoelementary water solutions at 10 mg L^{-1} and pH 5.0. Solutions were filtered through qualitative filter paper, and the equilibrium concentration was found by FAAS determination. To evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order (Eq. 4), pseudo-second-order (Eq. 5), Elovich (Eq. 6) and intraparticle diffusion models (Eq. 7) were used (Ibrahim 2010; Han et al. 2010; Witek-Krowiak et al. 2011).

$$\log \left(Q_{eq} - Q_t \right) = \log Q_{eq} - \left(\frac{K_1}{2303} \right) t \tag{4}$$

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

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{eq}2} + \frac{1}{Q_{eq}} t \tag{5}$$

in which K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second order. Unlike the pseudo-first-order model, this model predicts the kinetic behavior over the entire range of adsorption time (Ho and Mckay 1999).

$$Q_{eq} = A + B\text{Int} \tag{6}$$

in which A and B are constants, and A corresponds to the speed of initial chemisorption (mg g^{-1} h^{-1}) and B is the number of suitable sites for adsorption, which is related to the extent of surface coverage and the activation energy of the chemisorption (g mg^{-1}) (Witek-Krowiak et al. 2011).

$$Q_{eq} = K_{id} t^{1/2} + C_i \tag{7}$$

in which K_{id} is diffusion intraparticle constant (g mg^{-1} min$^{-1/2}$) and $C_{(i)}$ suggests the thickness of the boundary layer effect (mg g^{-1}) (Han et al. 2010).

Efficiency of adsorption and desorption

The experimental conditions were based on results of mass, pH and time obtained in the previous tests. Thus, 200 mg adsorbents containing plus 50 mL of rising concentrations of monoelementary water solutions of Cd^{2+}, Pb^{2+} and Cr^{3+} (5, 20, 40, 60, 80, 100, 120, 140, 160 and 200 mg L^{-1}), at pH 5.0, were stirred at 25 °C and 200 rpm

for 40 min. The solutions were then filtered through qualitative filter paper, and the equilibrium concentration was determined by FAAS. The Q_{ads} was calculated according to Eq. 1, and the percentage of removal of metals was calculated according to Eq. 8:

$$\%R = 100 - \left(\frac{C_f}{C_0} \times 100 \right) \tag{8}$$

in which %R is the percentage of ion removal by adsorbent, C_f is the final concentration of ion (mg L^{-1}), and C_0 is the initial ion concentration in solution (mg L^{-1}).

In order to check the reusability of adsorbents, the already used adsorbents were separated from the aqueous solution by filtration, through a quantitative filter paper and oven-dried at 60 °C for 24 h. The obtained mass was placed with 50 mL HCl solution (0.1 mol L^{-1}) and then stirred for more 40 min (200 rpm at 25 °C). After that, the samples were filtered and the final solution was used for determining the final concentrations of desorbed metal. The desorption percentage was calculated using Eq. 9:

$$D = \left(\frac{c_{eq(des)}}{c_{eq(ads)}} \right) \times 100 \tag{9}$$

in which $C_{eq(des)}$ (mg L^{-1}) and $C_{eq(ads)}$ (mg L^{-1}) are desorbed concentration and adsorbed concentration, respectively.

Adsorption equilibrium

By the influence of initial concentration, adsorption isotherms were constructed by linear mathematical models of Langmuir (Langmuir 1916), Freundlich (Freundlich 1906) and Dubinin and Radushkevich (1947), respectively, according to Eqs. 10, 11, 12, 13 and 14, being the standard error (SE) determined by the method of least squares.

$$\frac{1}{Q_e} = \frac{1}{C_m} + \frac{1}{K_L C_m C_e} \tag{10}$$

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m} \tag{11}$$

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

$$\log q_{eq} = \log K_f + \left(\frac{1}{n} \right) \log C_{eq} \tag{12}$$

in which C_{eq} or C_e is concentration on balance and q_{eq} or Q_e is the amount adsorbed at equilibrium per unit of adsorbent mass; K_F and n are the two parameters of Freundlich.

$$\ln Q_{eq} = \ln Qd - Bd\,\varepsilon^2 \tag{13}$$

in which Q_{eq} is the amount adsorbed ion per unit of adsorbent mass (mol g^{-1}), Q_d is the adsorption capacity (mol L^{-1}), B_d is an coefficient related to the sorption energy (mol^2 J^{-2}), and "ε" is the potential of Polanyi (Eq. 14).

$$\varepsilon = RT \ln\left(1 + 1/C_{eq}\right) \tag{14}$$

in which R is the universal gas constant (kJ mol^{-1} K^{-1}), T is the temperature (K), and C_{eq} is in liquid-phase equilibrium concentration (mol L^{-1}) (Dubinin and Radushkevich 1947; Njoku et al. 2011).

Influence of temperature

Tests aiming to study the influence of temperature on adsorption were performed. For this purpose, 200 mg adsorbent material plus 50 mL solution containing 50 mg L^{-1} Cd^{2+}, Pb^{2+} and Cr^{3+}, at pH 5.0, was shaken at 200 rpm at different temperatures (15, 25, 35, 45 and 55 °C).

With the results, we calculated the parameters of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), in order to evaluate the thermodynamic parameters and investigate the nature of the process (Sari et al. 2007).

$$\Delta G = -RT \ln K_d \tag{15}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{16}$$

in which K_d corresponds to the ratio of the quantity adsorbed per unit of adsorbent (Q_{eq}) and solution concentration in equilibrium (C_{eq}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K). The values of ΔH and ΔS were obtained from the graph of $\ln K_d$ in function of $1/T$.

Results and discussion

Characterization of adsorbent materials

The characterization of the total chemical elements of adsorbents is exhibited in Table 2.

The decrease in amount of K, Ca, Mg, Cu, Zn, Fe and Mn by the solutions H_2O_2, H_2SO_4 and NaOH is observed, i.e., the solutions caused modification on chemical composition of the adsorbent materials. This can be explained by the characteristics of each modifying agents, such as oxidation (H_2O_2), solubilization of organic groups (NaOH) and dehydration (H_2SO_4) (Schwantes et al. 2016). The levels of Cd, Pb and Cr were not detected in CNS *in natura*. There was an increase for the concentration of Cd, Mn and Cr after modification, which might have occurred through contamination of materials due to the modifying agent itself, which in its composition contains low levels of these elements.

The microstructures of CNS *in natura* were observed at 160×, 1200× and 12,000× of amplification and modified adsorbents in resolutions of 50×, 400× and 1600× (Fig. 1). The CNS *in natura* surface, according to Fig. 1a–c, presented lamellar aspect, irregular and heterogeneous structure, which according to Rubio et al. (2013a) and Coelho et al. (2014) favor the adsorption of metal ions.

For the CNS H_2O_2 (Fig. 1d–f) can be observed irregularities on the adsorbent surface, which after modification exhibits sponge-shaped aspect, with cavities in the form of pores due to the oxidizing power of H_2O_2. The CNS H_2SO_4 also configured irregularities, heterogeneous surface with cracks and pore-shaped cavities, probably due to the dehydrating action of sulfuric acid H_2SO_4 (1.0 mol L^{-1}) (Fig. 1g–i). The CNS NaOH presented irregular surface, with heterogeneous surface and cavities (Fig. 1j–l), possible in function to the high solubility of NaOH, which is also a strong base. According to the characteristics observed by micrographs, it can be stated that the adsorbents may have conditions to adsorb metals, in function the modifications on their surfaces.

Table 2 Characterization of the total chemicals of cashew nut shell (CNS) *in natura*, modified with H_2O_2, H_2SO_4 and NaOH

Adsorbent	K	Ca	Mg	Cu	Zn	Mn	Fe	Cd	Pb	Cr
	g kg^{-1}			mg kg^{-1}						
CNS *in natura**	7.65	9.23	1.67	6.73	13.40	52.60	19.30	< LQ	< LQ	< LQ
CNS NaOH	1.30	1.97	1.06	5.20	13.90	21.00	7.70	0.80	33.40	8.10
CNS H_2SO_4	0.81	1.38	0.43	5.40	12.30	1.80	7.00	0.60	11.60	3.70
CNS H_2O_2	2.57	1.91	1.15	9.80	18.00	38.50	4.60	0.50	13.50	7.30

LQ (quantitation limit): K = 0.01; Ca = 0.005; Mg = 0.005 (g kg^{-1}); Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; Cr = 0.01 (mg kg^{-1})
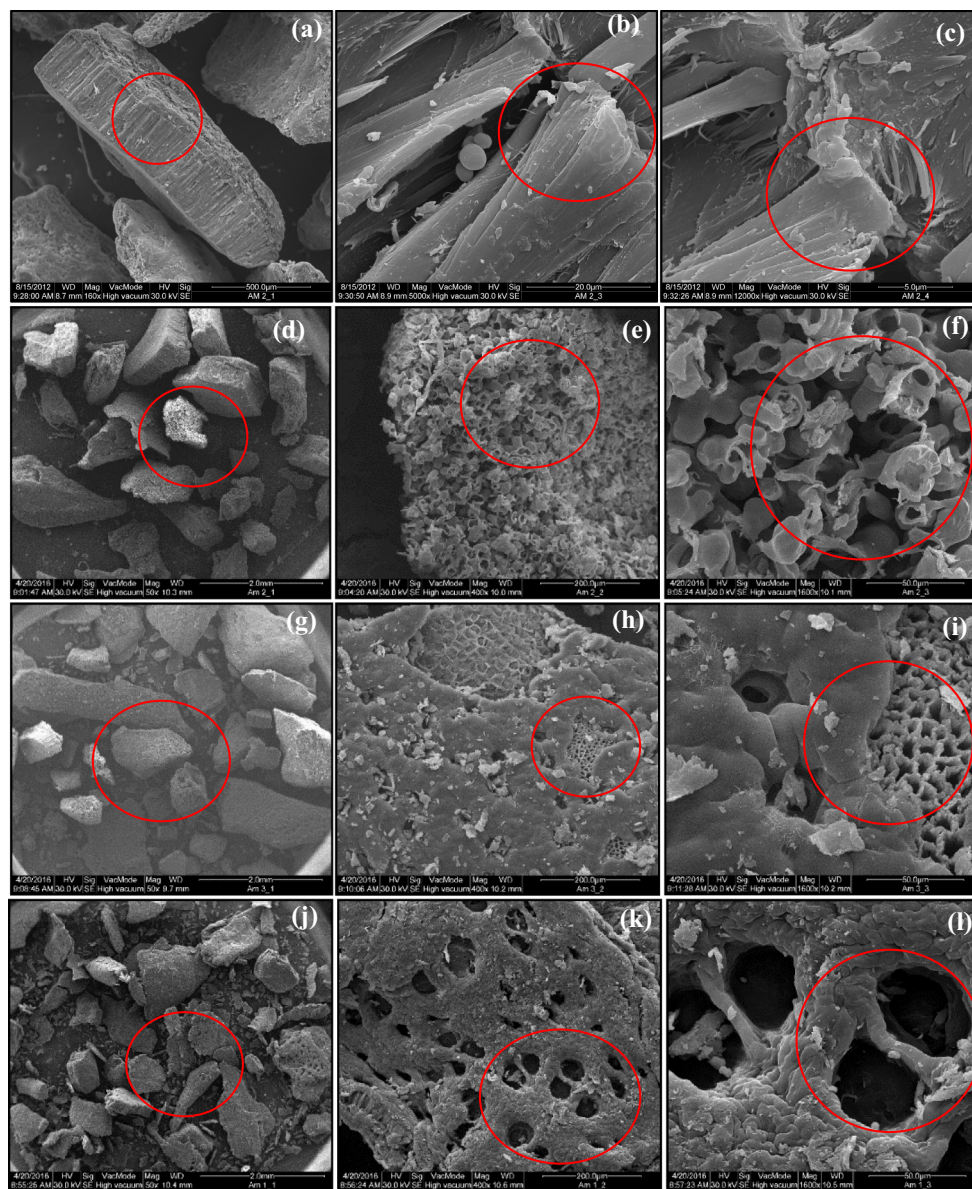
Source: Coelho et al. (2014)

Fig. 1 Scanning electron microscopy to shell of cashew nut (CNS) *in natura* with magnifications of 160 (**a**), 5000 (**b**) and **c** 12,000 times (*source*: COELHO et al. 2014) and chemically modified with H$_2$O$_2$ with magnification of 50 (**d**), 400 (**e**), 1600 (**f**). H$_2$SO$_4$ with magnification of 50 (**g**), 400 (**h**), 1600 (**i**), and NaOH with 50 magnification (**j**), 400 (**k**), 1600 (**l**) times (*source*: the author)

The FTIR spectra in the range of 400–4000 cm^{-1} for the bark of *A. occidentale* L. *in natura* and modified with H$_2$O$_2$, H$_2$SO$_4$ and NaOH (Fig. 2; Table 3) exhibit the possible presence of anionic functional groups (hydroxyl, carboxylic acid and amines) on the adsorbent surface as well as the modification of the surface of CNS by modifying agents.

The band at 3400 cm^{-1} can be attributed to the vibrational stretch of O–H bond, suggesting the presence of hydroxyl groups (OH$^-$) from cellulose, lignin, amine groups (NH$_2$$^-$) and amides (Munagapati et al. 2010; Rubio et al. 2013a; Coelho et al. 2014). The vibrational stretching at 2925 and 1380 cm^{-1} may be from C-H bonds of alkanes and aliphatic

acid groups as described by Coelho et al. (2014) for the shell of cashews *in natura*, and this stretch also found in other biomass adsorbents like the pie of *Crambe abyssinica* H. (Rubio et al. 2013a, b).

The carboxylic groups and amides can also be found in bark of cashews at 1640 cm^{-1} assigned to the stretching vibrational bonds C=O (Monier et al. 2010; Han et al. 2010).

The band at 1076 cm^{-1} suggests the presence of C-O from aromatic groups (Garg et al. 2007), confirming the presence of lignin structure in the shell of the cashew nut. Smaller wavelength at 800 cm^{-1} can also be attributed to N containing bio-binders (Barka et al. 2010).
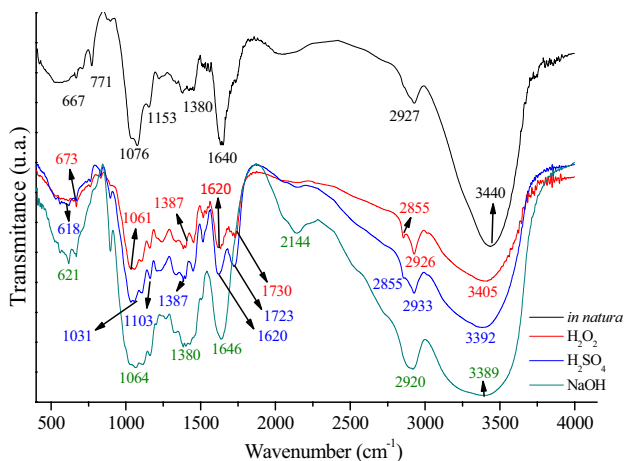
Fig. 2 Infrared spectrum of CNS *in natura* (*source*: COELHO et al. 2014) and chemically modified with H_2O_2, H_2SO_4 and NaOH

Table 3 Surface area, volume of pore and pore radius for the shell of the cashew nut shell (CNS) chemically modified with H_2O_2, H_2SO_4 and NaOH

Parameters	CNS H_2O_2	CNS H_2SO_4	CNS NaOH
Surface area ($m^2\,g^{-1}$)	0.5093	0.0915	0.2612
Pore volume ($cm^3\,g^{-1}$)	4.609e−4	1.370e−3	1.850e−3
Pore radius (nm)	1.731	1.722	2.836

Vibrational elongation of bond C-N can also be found by the presence of a band at 700 and 667 cm^{-1} (Salem and Awwad 2011).

The CNS that received modificant solutions with H_2O_2, H_2SO_4 and NaOH presented, respectively, vibrational stretches at the region of 3405, 3392 and 3389 cm^{-1}, assigned to O–H bonds of primary amides, amines and carboxylic acids and hydroxylic found in lignins, cellulose and water (Smidt and Meissl 2007; Movasaghi et al. 2008; Pavia et al. 2010). The spectra at 2926 cm^{-1} for CNS H_2O_2, 2933 cm^{-1} for H_2SO_4 and 2920 cm^{-1} for NaOH assigned to C-H bonds in alkanes, aliphatic acid groups and aldehydes or CH_2 assigned to lipids.

The 2855 cm^{-1} group found only for CNS H_2O_2 and CNS H_2SO_4 and also refers to the presence of lipids or bonds CH_2. These groups, according to Pavia et al. (2010), are directly related to the carboxylic acid groups encountered by vibrational stretches at 1723 and 1730 cm^{-1}, respectively, for CNS H_2O_2 and CNS H_2SO_4. According to the same author, when acids or peroxides are diluted in solvents the modification of C=O may occur, releasing carboxylic acids in the material. This may have occured due to the adsorbent being modified with H_2SO_4 and H_2O_2. Other vegetable residues have presented the same functional groups as pie of *Crambe abyssnica* H. and *Jatropha*

curcas L. (Rubio et al. 2013a, b; Coelho et al. 2014; Nacke et al. 2016).

For modification with NaOH, it is observed a vibrational stretch in the region of 2144 cm^{-1}, related to the presence of hydrocarbons, alkynes nonterminal groups, with bonds C≡C (Pavia et al. 2010), which may have been produced through saponification reaction due to the presence of derivatives of the LCNS (net of the shell of the cashew nut) (Mazzeto et al. 2009).

The spectra at 1387, 1380 for CNS H_2O_2, H_2SO_4 and NaOH can be related to N–H bonds of amines, CH_3, C–O or CH (Smidt and Meissl 2007; Pavia et al. 2010).

Only for the adsorbents CNS *in natura* and CNS H_2SO_4 are observed a stretch at the region of 1153 and 1103 cm^{-1} and demonstrate the presence of polysaccharides of bonds C–O–P (Pavia et al. 2010). This group is absent in modified adsorbents with H_2O_2 and NaOH, suggesting that the reaction with H_2SO_4 is weaker in comparison with the other modifying agents.

The region stretches from 1061 cm^{-1} for CNS H_2O_2 to 1064 cm^{-1} for CNS NaOH, suggesting the presence of sulfoxides bonds S=O, C–O from polysaccharides (Movasaghi et al. 2008; Smidt and Meissl 2007). The groups at 671, 618, 621 cm^{-1} for CNS H_2O_2, H_2SO_4 and NaOH can be related to S–O bonds of inorganic sulfate (Movasaghi et al. 2008; Smidt and Meissl 2007).

The value of pH$_{PZC}$ for the cashew nut (CNS) *in natura* is 3.69 (Fig. 3). It is observed, after the modifications (Fig. 3), the occurrence of alterations on the point of zero charge for CNS H_2O_2, H_2SO_4 and NaOH, being, respectively, 4.35, 2.50 and 6.92. This change already was expected, since the variation of pH$_{PZC}$ occurs according to power of alkalinization or acidification of each modifying solution, protonation, deprotonation or hydroxylation of chemical groups of the CNS (Schwantes et al. 2016).
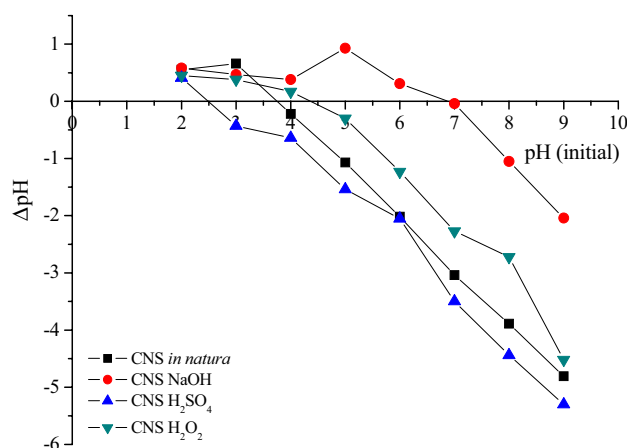

Fig. 3 Point of zero charge (pH$_{PZC}$) of CNS *in natura* (Coelho et al. 2014) and modified with H_2O_2, H_2SO_4 and NaOH

This way when the pH > pH$_{PZC}$, the surface of the adsorbent is electronegative, favoring the adsorption of Cd^{2+}, Pb^{2+} and Cr^{3+}. If the pH < pH$_{PZC}$, the surface of the adsorbent is electropositive; in this state, H$^+$ ions compete with the metal cations, repelling them from possible interactions with the adsorbents surface.

Thermogravimetric analysis (TG) was performed to verify the thermal stability of the adsorbents from CNS after treatment with H$_2$O$_2$, H$_2$SO$_4$ and NaOH (Fig. 4).

For the adsorbents CNS modified with H$_2$O$_2$ (Fig. 4a), H$_2$SO$_4$ (Fig. 4b) and NaOH (Fig. 4c), the first mass loss, related to the release of moisture in the adsorbents, is bounded by the surface tension and started at higher temperatures for CNS H$_2$O$_2$ (81.53–100 °C) when compared with others, 71.43–150 °C for CNS H$_2$SO$_4$ and 73.33–100 °C for CNS NaOH.

The DTG curve for decomposition of hemicellulose, which demonstrates the thermal stability of materials, exhibits the beginning of mass loss at 230, 200 and 230 °C for CNS H$_2$O$_2$, CNS H$_2$SO$_4$ and CNS NaOH, respectively. Already for cellulose, the step where more mass is lost occurred to 370.64 °C for CNS H$_2$O$_2$ and CNS H$_2$SO$_4$ and 362.90 °C for CNS NaOH. The decomposition of lignin and other compounds occurred above 400 °C for CNS H$_2$O$_2$, above 350 °C for CNS H$_2$SO$_4$ and above 400 °C for CNS NaOH (Melzer et al. 2013; Moreira et al. 2017). It is observed in Fig. 4 the loss of about 80% of masses of CNS H$_2$O$_2$, CNS H$_2$SO$_4$ and CNS NaOH. These results demonstrate that the modified adsorbent materials are similar when it comes to its thermal stability.

The adsorption and desorption isotherms of BET for CNS adsorbents have the purpose of determining the specific surface area, as well as volume and pore diameter (Fig. 5).

Figure 5 shows a behavior of the BET type II adsorption isotherm with the negative concavity, characteristic of nonporous or low porous systems, representing the monolayer formation, in this step high energy demand (Khafaloui et al. 2003).

According to Table 3, the specific surface area of adsorbents followed the order CNS H$_2$O$_2$ > CNS NaOH > CNS H$_2$SO$_4$, being their values, respectively, 0.5093, 0.2612 and 0.0915 m^2 g^{-1}, which represent low values when compared to commercial activated carbon, with 894 m^2 g^{-1} (Merck®), and nonsilicated clay minerals, such as goethite, 41.73 m^2 g^{-1}, and hematite, 38.36 m^2 g^{-1} (Cessa et al. 2009). The pore volume (cm^3 g^{-1}) found was 5.268 e^{-4}, 5.074 e^{-4} and 3.330 e^{-4} for the adsorbents CNS NaOH > CNS H$_2$SO$_4$ > CNS H$_2$O$_2$, with pore diameter greater for CNS NaOH (2.836 nm) > CNS H$_2$O$_2$ (1.731 nm) > CNS H$_2$SO$_4$ (1.722 nm). These results demonstrate that adsorption may
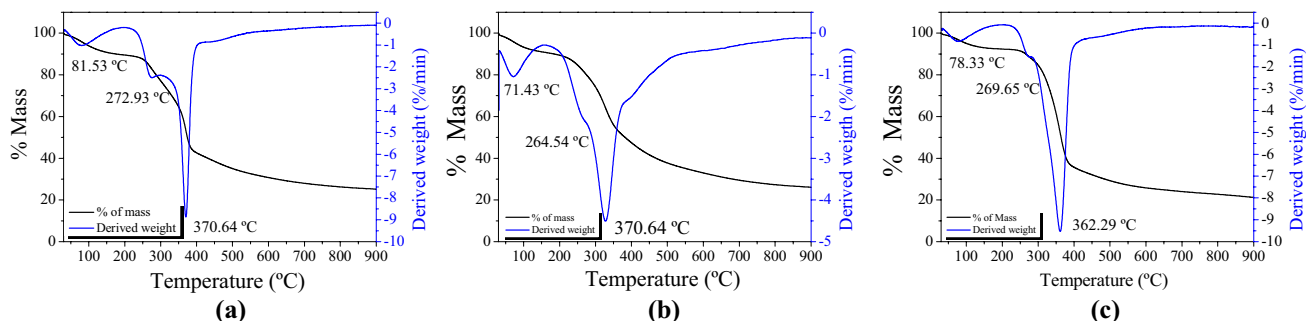
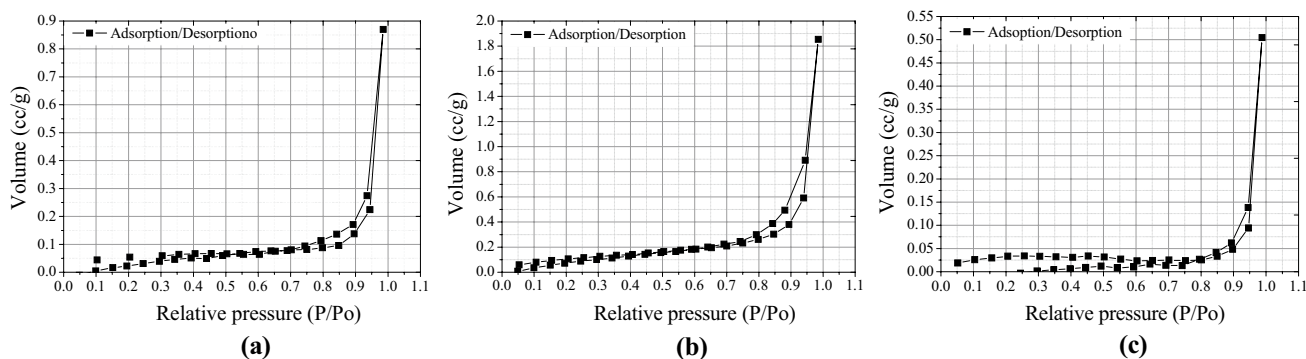**Fig. 4** Loss of mass (TG) and derived weight (DTG) of CNS chemically modified with H$_2$O$_2$ (**a**), H$_2$SO$_4$ (**b**) and NaOH (**c**)

Fig. 5 Adsorption and desorption isotherms of BET to CNS chemically modified with NaOH (**a**), H$_2$SO$_4$ (**b**) and H$_2$O$_2$ (**c**)

occur predominantly superficially, with low possibility of intraparticle diffusion.

The results in Table 3 suggest that the adsorbents have been effectively changed, showing that the modification process, in certain temperatures, can change the CNS biomass differently and may be favorable or not to the adsorption of metal ions.

Multivariate analysis of the influence of adsorbent mass and solution pH

According to Tables 4 and 5, there was a significant difference at 5% of significance for the variable mass, for all the

adsorbents at all cases. For Cr^{3+} adsorption on CNS NaOH, significant differences for the variable mass, pH and interaction between both variables were found, and the same can be observed by Pareto graphs (Fig. 6).

The Pareto graph (Fig. 6) also exhibits the results for variables mass and pH on adsorption of CNS adsorbents, highlighting the significance for both variables, except for Pb^{2+} by CNS NaOH (Fig. 6 h). Table 6 expresses the mathematical equations from the graphs exhibited in Fig. 7.

Higher values of Q_{eq} occurred with lower quantities of adsorbent material, i.e., 200 mg, or 4 g L^{-1}, CNS *in natura* and chemically modified with H_2O_2, H_2SO_4 and NaOH. The increase in adsorbent mass can even in some cases decrease

Table 4 CCRD planning matrix with triplicate in central point in their coded values and real values for absorption of Cd^{2+}, Pb^{2+} and Cr^{3+} by adsorbents *in natura* and modified with H_2O_2, H_2SO_4 and NaOH

Variable			Q_{ads} (mg g^{-1}) Cd^{2+}				Q_{ads} (mg g^{-1}) Pb^{2+}				Q_{ads} (mg g^{-1}) Cr^{3+}			
Test	Mass (mg)	pH	CNS *in natura*	CNS H_2O_2	CNS H_2SO_4	CNS NaOH	CNS *in natura*	CNS H_2O_2	CNS H_2SO_4	CNS NaOH	CNS *in natura*	CNS H_2O_2	CNS H_2SO_4	CNS NaOH
1	396.39	3.60	1.155	1.167	0.911	1.240	1.234	1.261	1.263	0.293	1.071	1.003	0.935	1.127
2	1103.61	3.60	0.426	0.428	0.281	0.439	0.440	0.452	0.453	0.103	0.426	0.363	0.306	0.212
3	396.39	6.40	1.185	1.189	0.987	1.235	1.226	1.260	1.258	0.305	0.591	0.734	0.763	0.396
4	1103.61	6.40	0.428	0.430	0.288	0.436	0.439	0.453	0.411	0.134	0.181	0.242	0.342	0.022
5	750.00	5.00	0.630	0.632	0.473	0.647	0.648	0.666	0.648	0.180	0.618	0.620	0.557	0.142
6	250.00	5.00	1.843	1.863	1.587	1.950	1.939	1.994	1.931	0.586	1.768	1.718	1.812	1.141
7	750.00	7.00	0.631	0.635	0.436	0.645	0.654	0.664	0.652	0.399	0.438	0.496	0.558	0.279
8	1250.00	5.00	0.377	0.381	0.219	0.387	0.387	0.400	0.392	0.125	0.367	0.372	0.335	0.000
9	750.00	3.00	0.601	0.592	0.345	0.653	0.645	0.666	0.651	0.261	0.448	0.405	0.287	0.613
10	750.00	5.00	0.627	0.631	0.427	0.647	0.644	0.664	0.651	0.224	0.619	0.611	0.559	0.172
11	750.00.	5.00	0.626	0.635	0.428	0.648	0.644	0.664	0.660	0.192	0.618	0.625	0.582	0.176
12	750.00	5.00	0.628	0.627	0.422	0.647	0.647	0.664	0.656	0.229	0.618	0.624	0.584	0.142

Q_{ads}: amount sorbed of metal ions (mg g^{-1}). Experimental conditions: volume of 50 mL, concentration of Cd^{2+}, Pb^{2+} and $^{3+}$Cr (10 mg L^{-1}), stirring time of 90 min, rotation of 200 rpm; temperature of 25 °C

Table 5 Analysis of variance (ANOVA) for cashew nut shell (CNS) *in natura*, CB H_2O_2, CNS H_2SO_4 and CNS NaOH and pH on the removal of Cd^{2+}, Pb^{2+} and Cr^{3+}

FV	DF	Cd(II)				Pb(II)				Cr(III)			
		CNS *in natura*	CNS H_2O_2	CNS H_2SO_4	CNS NaOH	CNS *in natura*	CNS H_2O_2	CNS H_2SO_4	CNS NaOH	CNS *in natura*	CNS H_2O_2	CNS H_2SO_4	CNS NaOH
Mass (L)	1	1.581*	1.869*	1.3295*	1.8123*	1.7795*	1.8696*	1.8343*	0.1280*	1.1502*	1.149*	1.229*	1.051*
Mass (Q)	1	0.323*	0.391*	0.3241*	0.3764*	0.3700*	0.3914*	0.3641*	0.0107	0.2017	0.189*	0.284*	0.227*
pH (L)	1	0.0007	0.0000	0.0057	0.0000	0.0000	0.0000	0.0002	0.0071	0.0680	0.0084	0.0077	0.241*
pH (Q)	1	0.0032	0.0022	0.0062	0.0019	0.0017	0.0022	0.0017	0.0050	0.1169	0.1013	0.0845	0.102*
Mass × pH	1	0.0002	0.0000	0.0012	0.0000	0.0000	0.0000	0.0003	0.0008	0.0136	0.0053	0.0106	0.078*
Error	6	0.0086	0.0104	0.0083	0.0095	0.0096	0.0104	0.0069	0.0085	0.0401	0.0267	0.0369	0.0081
Total	11												

FV factors of variation, *DF* degrees of freedom, *L* linear, *Q* quadratic

*Significant at 5% probability for Fisher's test, obtained through degrees of freedom and treatment of error (Barros et al. 2010)
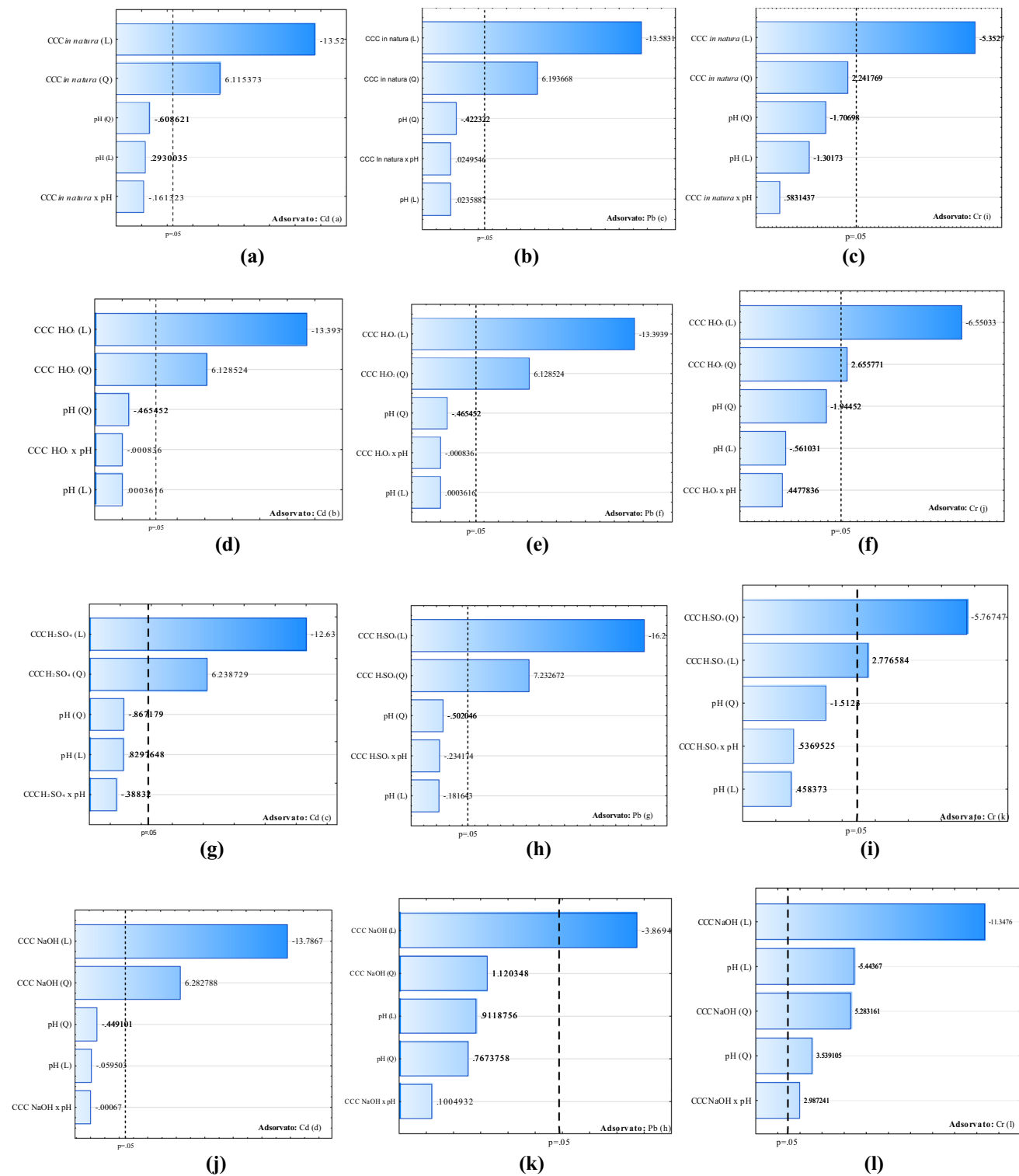
[ns]No significant at 5% probability by Fisher's test

Fig. 6 Pareto graph from CCRD analysis for the adsorbent masses and solution pH on sorption of Cd^{2+} (**a–d**), Pb^{2+} (**e–h**) and Cr^{3+} (**i–l**) on cashew nut shell (CNS) *in natura*, modified with H_2O_2, H_2SO_4 and NaOH

Q_{ads} by forming clusters, reducing the total contact surface area and, therefore, the number of places available assets to the process (Rubio et al. 2013a; Kiran et al. 2013).

Coelho et al. (2014) studied the removal of Cd^{2+}, Pb^{2+} and Cr^{3+} by the shell of the cashew nut *in natura* and found that 600 mg was enough to occur removal of metal ions from

Table 6 Equation for adsorbed quantity (Q_{ads}) of Cd^{2+}, Pb^{2+} and Cr^{3+} by CNS adsorbents

CNS	Q_{ads}	Adj. R^2
Cd^{2+}		
in natura:	$2.21458 + 0.12968x - 0.011165x^2 - 0.00388y + 0.0000017y^2 - 0.00001495xy$	0.974
H_2O_2	$2.57000 + 0.093847x - 0.009377x^2 - 0.004335y + 0.0000019y^2 - 0.000000085xy$	0.974
H_2SO_4	$1.69901 + 0.20156x - 0.01561x^2 - 0.003677y + 0.0000017y^2 - 0.0000353xy$	0.974
NaOH	$2.54068 + 0.08514x - 0.008654x^2 - 0.00425y + 0.0000019y^2 - 0.000000065xy$	0.974
Pb^{2+}		
in natura:	$2.53173 + 0.080597x - 0.00818x^2 - 0.004232y + 0.0000019y^2 + 0.0000024xy$	0.974
H_2O_2	$2.57000 + 0.09384x - 0.009377x^2 - 0.004335y + 0.0000019y^2 - 0.000000085xy$	0.973
H_2SO_4	$2.48390 + 0.09349x - 0.008266x^2 - 0.004119y + 0.0000019y^2 - 0.000019xy$	0.981
NaOH	$0.9391 - 0.1259x + 0.01400x^2 - 0.000895y + 0.00000032y^2 + 0.0000092xy$	0.743
Cr^{3+}		
in natura:	$1.2984 + 0.5224x - 0.0674x^2 - 0.003786y + 0.000001419y^2 + 0.0001165xy$	0.871
H_2O_2	$1.01747 + 0.5504x - 0.06282x^2 - 0.00350y + 0.0000013y^2 + 0.00007309xy$	0.904
H_2SO_4	$1.19506 + 0.51846x - 0.05737x^2 - 0.004155y + 0.00000168y^2 + 0.000102917xy$	0.884
NaOH	$4.9784 - 0.9557x + 0.0631x^2 - 0.00463y + 0.0000015y^2 + 0.0002691xy$	0.971

CNS Cashew nut shell, Q_{ads} sorbed amount (mg g^{-1}), adj. R^2 adjusted coefficient of determination
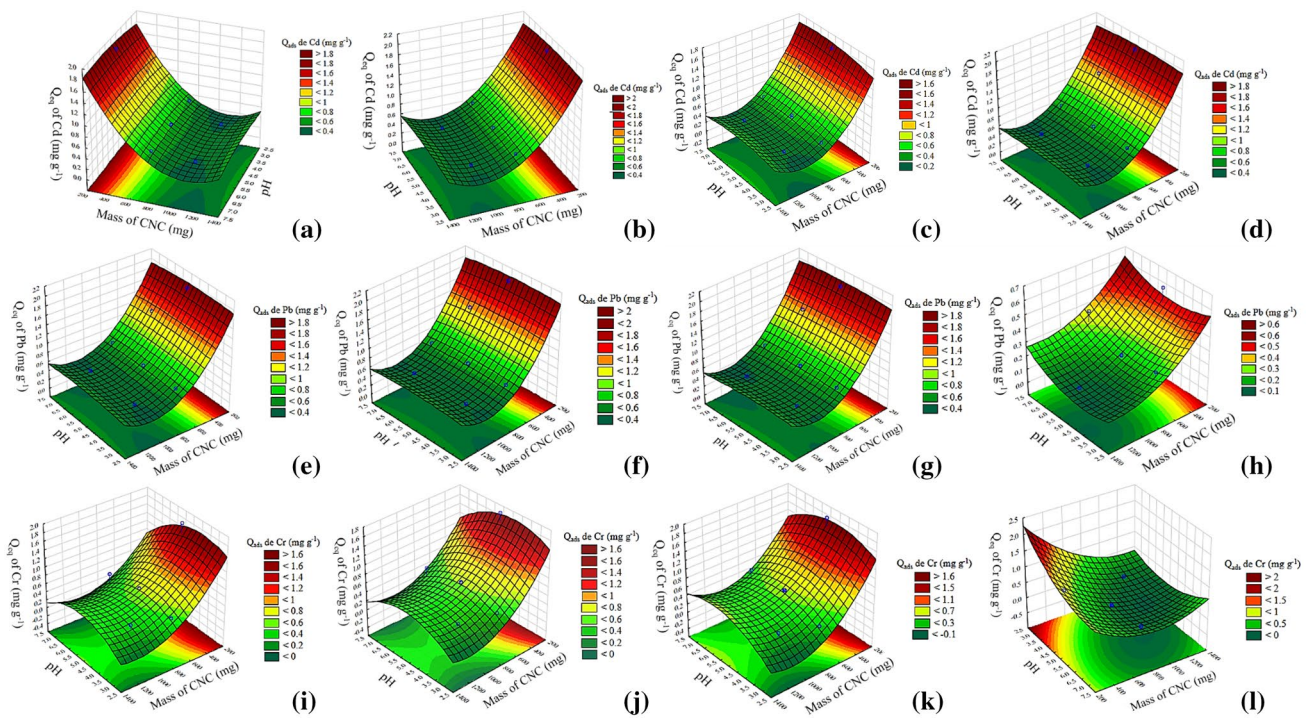

Fig. 7 Graph of response surface for multivariate analysis for adsorbent masses and pH of the solution by the amount adsorbed (Q_{ads}) of Cd^{2+} (**a–d**), Pb^{2+} (**e–h**) and Cr^{3+} (**i–l**) on the shell of cashews (CNS) *in natura*, modified with H_2O_2 (**b**), H_2SO_4 (**c**) and NaOH (**d**)

water. Nacke et al. (2016) and Gonçalves Jr. et al. (2016) checked different amounts of *Jatropha curcas* L. *in natura* and lump of Acai *in natura*, respectively, on adsorption of Cu^{2+} and Zn^{2+} and found that 8 g L^{-1} was enough to achieve high removal efficiency. Schwantes et al. (2015) and Schwantes et al. (2016) performed, respectively, the chemical modification, with solutions of H_2O_2, H_2SO_4 and NaOH,

in crambe pie and cassava peel, and found that 5 g L^{-1} was the ideal proportion adsorbent/adsorbate solution, for removing Cd^{2+}, Pb^{2+} and Cr^{3+} from aqueous solution at pH 5.0.

Regarding metals adsorption, it is recommended to be carried with pH values lower than 5.0, in function of the possibility of precipitation (Yang and Al-Duri 2005; Ercan and Aydin 2013). Coelho et al. (2014) studying the shell of

cashews for the removal of Cd^{2+}, Pb^{2+} and Cr^{3+} also used pH 5.0. As in the present work there was no significant difference for the variable pH, and the experiment was carried out at pH 5.0.

Influence of contact time and evaluation of the kinetic mechanism of adsorption

The influence of the contact time of ions Cd^{2+}, Pb^{2+} and Cr^{3+} on the adsorbents CNS H_2O_2, CNS H_2SO_4 and CNS NaOH features fast adsorption, decreasing with the increase in time (Fig. 8).

For CNS H_2O_2, the occurrence of equilibrium in adsorption process at 40 min of stirring, with insignificant variations at higher periods of time, is observed in Fig. 8a. For CNS H_2SO_4 (Fig. 8b), the equilibrium also occurs at 40 min, with little variations among 160–180 min. For CNS NaOH (Fig. 8c), the equilibrium is again observed at 40 min, with insignificant variations after this period. There is a tendency of depletion of the adsorption sites, suggesting that periods higher than 40 min may be impractical for large-scale systems.

The parameters of pseudo-first and second order, Elovich and intraparticle diffusion for Cd^{2+}, Pb^{2+} and Cr^{3+} on the CNS modified with H_2O_2, H_2SO_4 and NaOH are exhibited in Table 7 and Fig. 9.

The pseudo-first-order, Elovich and intraparticle diffusion models not exhibited good fit to experimental data. Only the model of pseudo-second-order model exhibited good fitting, with values of $Q_{eq(exp.)}$ and $Q_{eq(calc.)}$ next to each other, suggesting the occurrence of chemisorption (Feng et al. 2011). Only for Pb, the pseudo-second order did not exhibited values of $Q_{eq\ (exp.)}$ and $Q_{eq\ (calc.)}$ next to each other, and we cannot infer the same. Several experiments report good fits for pseudo-second-order models like Gonçalves Jr. et al. (2016) and Nacke et al. (2016), when studying the kinetics of adsorption of the lump of Acai *in natura* and *Jatropha curcas* for Cu^{2+}, Zn^{2+}. Also Schwantes et al. (2015) and

Schwantes et al. (2016) for Cd^{2+}, Pb^{2+} and Cr^{3+} in crambe pie and cassava peel chemically modified found similar results.

Efficiency of adsorption and desorption

The adsorbents *in natura* and H_2O_2 exhibited a tendency to decrease the adsorption efficiency (%) of Pb with the increase in initial concentration of lead. For the adsorption of Cd by CNS H_2SO_4 initially occurred adsorption increase, leading to a decrease soon followed, which may be related to the fact that the higher energy sites become saturated with the increase in the metal concentration and, only then, occur adsorption in lower energy sites, resulting in a decrease in adsorption efficiency (Bhattacharya et al. 2006). The aforementioned result occurred for all evaluated cases, except for the adsorption of Pb by CNS NaOH, where there has been an increase in the removal efficiency, a fact that can be explained by the change of pH by the adsorbent material that alkalined the middle which may have precipitated the Pb.

In the case of Cd^{2+} adsorption by CNS *in natura*, CNS H_2O_2, CNS H_2SO_4 and CNS NaOH, the efficiency of adsorption was, respectively, 69, 87, 85, 99%; in the case of Pb^{2+} CNS *in natura*, CNS H_2O_2, CNS H_2SO_4 and CNS NaOH , respectively, 54, 51, 88 and 34%, in the case of Cr^{3+} by CNS *in natura*, CNS H_2O_2, CNS H_2SO_4 and CNS NaOH, respectively, 80, 68, 69 and 86%. In this way, Fig. 10 demonstrates that there has been an increase in the rate of adsorption for Cd^{2+} when the CNS was with H_2O_2 and NaOH.

The percentages of desorption for Cd^{2+} CNS *in natura*, CNS H_2O_2, CNS H_2SO_4 and CNS NaOH were 56, 50, 97 and 77%; for Pb^{2+} CNS *in natura*, CNS H_2O_2, CNS H_2SO_4 and CNS NaOH the desorption rates were 76, 55, 85 and 60%. For Cr^{3+} were found lower desorption rates such as 2.9, 9.9, 2 and 0.7%, respectively, for CNS *in natura*, CNS H_2O_2, CNS H_2SO_4 and CNS NaOH (Fig. 10i–l). Meneghel et al. (2013), Rubio et al. (2013b), Coelho et al. (2014) and Schwantes et al. (2015) also found lower desorption rates for
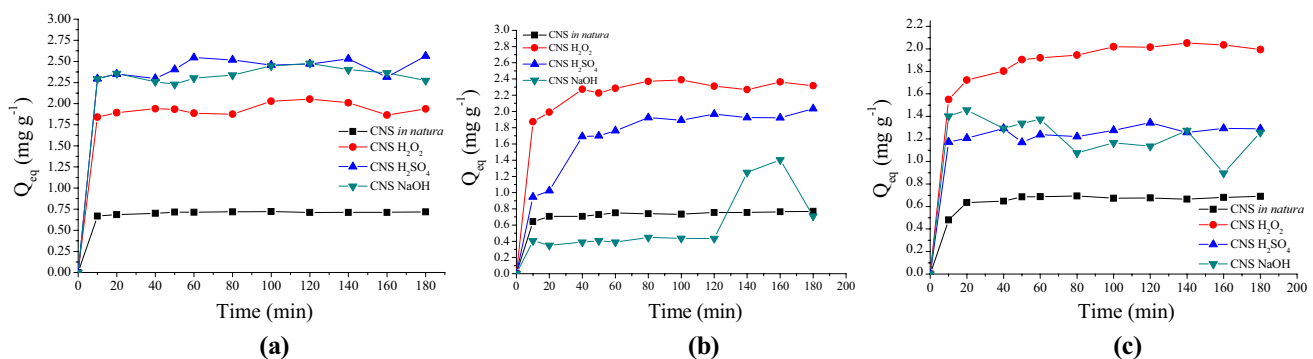

Fig. 8 Effect of contact time of CNS *in natura* (Coelho et al. 2014) and modified with H_2O_2, H_2SO_4 and NaOH in the removal of Cd^{2+} (**a**), Pb^{2+} (**b**) and Cr^{3+} (**c**)

Table 7 Kinetic parameters of pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion and quantity of metal adsorbed at equilibrium ($Q_{eq(exp.)}$) obtained for adsorption of Cd²⁺, Pb²⁺ and Cr³⁺ on CNS *in natura* and chemically modified with H₂O₂, H₂SO₄ and NaOH

		Pseudo-first order			Pseudo-second order			Elovich			$Q_{eq(exp.)}$ (mg g⁻¹)
		K_1 (min⁻¹)	$Q_{eq(cal.)}$ (mg g⁻¹)	Adj. R^2	K_2 (g mg⁻¹ min⁻¹)	$Q_{eq(cal.)}$ (mg g⁻¹)	Adj. R^2	A (mg g⁻¹ h⁻¹)	B (g mg⁻¹)	Adj. R^2	
Cd²⁺	*In natura**	− 0.0109	0.0233	0.406	4.8991	0.7166	0.999	0.6590	0.0121	0.776	0.7174
	H₂O₂	− 0.0143	0.2155	0.754	7.5946	1.9497	0.995	2.0469	0.1017	0.821	1.9367
	H₂SO₄	− 0.0171	0.3149	0.868	0.3181	2.4932	0.994	2.0336	0.0766	0.731	2.42399
	NaOH	− 0.0264	0.6873	0.690	0.9559	2.3640	0.996	1.6599	0.0762	0.913	2.3334
Pb²⁺	*In natura**	− 0.0144	0.0855	0.815	0.6810	0.7690	0.999	0.6198	0.0283	0.867	0.7323
	H₂O₂	− 0.1526	0.3820	0.676	− 5.7751	0.1496	0.967	1.8856	0.0942	0.580	2.2372
	H₂SO₄	− 0.2491	1.3061	0.937	− 35.660	0.1400	0.957	0.0376	0.3978	0.889	1.6746
	NaOH	− 0.0263	1.1176	0.524	− 67.911	0.0336	0.973	0.1510	0.0727	0.329	0.5855
Cr³⁺	*In natura**	− 0.0118	0.0551	0.320	1.5167	0.6856	0.999	0.4962	0.0403	0.580	0.6560
	H₂O₂	− 0.0067	0.1751	0.780	0.1015	2.0823	0.999	1.1827	0.1716	0.929	1.8890
	H₂SO₄	0.0053	0.1725	0.322	0.3165	1.3074	0.997	1.0771	0.0417	0.438	1.2487
	NaOH	− 0.0230	0.5727	0.957	− 0.3729	1.2007	0.986	1.7578	− 0.1234	0.410	1.2695

Intraparticle diffusion

		K_{id} (g mg⁻¹ min⁻¹ᐟ²)			Adj. R^2			C_i (mg g⁻¹)		
		Line A	Line B	Line C	Line A	Line B	Line C	Line A	Line B	Line C
Cd²⁺	*In natura**	0.0112	0.0031	0.0028	0.945	0.998	0.461	0.6474	0.6895	0.6790
	H₂O₂	0.0599	− 0.0273	− 0.0298	0.898	0.802	0.624	1.6423	2.1137	2.3519
	H₂SO₄	0.0020	0.1740	0.0340	− 0.487	0.978	0.910	2.3110	1.1870	2.1130
	NaOH	− 0.0110	0.0679	− 0.0460	0.879	0.929	0.778	2.3246	1.7558	2.9230
Pb²⁺	*In natura**	0.0276	0.0080	0.0093	0.367	0.627	0.831	0.5954	0.6773	0.6457
	H₂O₂	0.0249			0.524			0.0242		
	H₂SO₄	0.0215			0.393			2.0902		
	NaOH	0.8201			0.776			0.1005		
Cr³⁺	*In natura**	0.0427	0.0029	0.0045	0.546	0.566	0.249	0.4395	0.6671	0.6244
	H₂O₂	0.0437			0.830			1.5166		
	H₂SO₄	0.0111			0.437			1.1537		
	NaOH	− 0.0335			0.415			1.5374		

K_1: first order rate constant; Q_{eq}: quantities of adsorbate retained per gram of adsorbent at equilibrium; K_2: second order rate constant; A: constant that indicates the speed of initial chemisorption; B: number of suitable sites for adsorption, related to the extension of coverage of the surface and the activation energy of chemisorption; Adj. R^2: adjusted coefficient of determination; K_{id}: intraparticle diffusion constant; C_i: suggests the thickness of the boundary layer effect
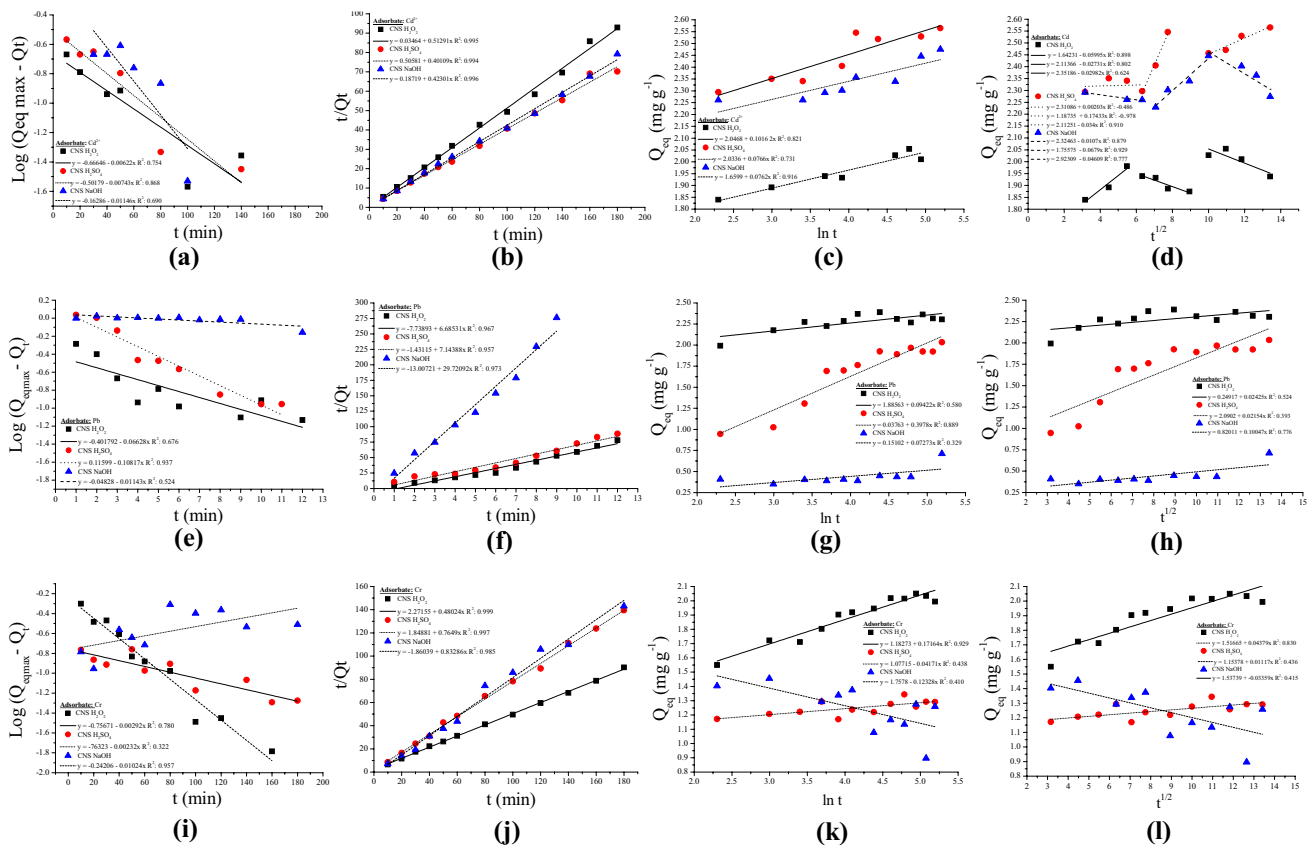
Source: Coelho et al. (2014)

Fig. 9 Kinetic models of pseudo-first order (**a**, **e**, **i**), pseudo-second order (**b**, **f**, **j**), Elovich (**c**, **g**, **k**) and intraparticle diffusion (**d**, **h**, **l**) for sorption of Cd^{2+}, Pb^{2+} and Cr^{3+}, respectively, by CNS modified with H_2O_2, H_2SO_4 and NaOH

Cr^{3+}, respectively, using the adsorbents: *Moringa oleífera* L., *Crambe abyssina* H., cashew nut shell, cassava peels *in natura*; all authors state the Cr is probably chemisorbed by the biomass.

In most tests (Fig. 10), the acidification of pH medium after adsorption was observed, being the adsorbents modified with H_2SO_4 with greater acidification of medium. This process is usually related to the ion exchange (physics), such as the exchange of a cation (H^+) by other ions. For the adsorption of Cd^{2+} and Cr^{3+} by CNS H_2SO_4, there has been a slight alkalinization of the middle, fact that may be related to chemisorption, demonstrating that the adsorption process is complex, due to the influence of various mechanisms. When changes on pH occur, ionic exchange may happen in solution, due to the presence of organic functional groups (Mohan and Pittman, 2007; Bartczak et al. 2015).

According to Fig. 11, the isotherms exhibited for Cd^{2+} adsorption by CNS *in natura*, H_2O_2 and NaOH, Pb^{2+} by all adsorbents and Cr^{3+} by CNS H_2SO_4, are all classified as "L," in function of a decrease in the availability of active sites with the increase in metal concentration (Giles et al. 1960).

The class "*L*" demonstrates a tendency to equilibrium by the saturation of the active sites, as in monolayer system,

that allows to infer the adsorption capacity (Montanher et al. 2005; Foo and Hameed 2010). For the Cd^{2+} adsorption by CNS H_2SO_4, and for Cr^{3+} adsorption by CNS *in natura*, CNS H_2O_2 and CNS NaOH (Fig. 11), we found curves of C type, so-called Constant partition, which have a linear start, featuring a partition between the solute and the surface of the adsorbent, indicating a decreased availability of active sites (Giles et al. 1960).

The mathematical parameters of Langmuir and Freundlich were obtained by linear models in accordance with Fig. 12.

The adsorption results showed good fit for Langmuir for the adsorption of Cd^{2+} by CNS *in natura*, CNS H_2O_2 and CNS NaOH, while for adsorption of Pb^{2+} all adsorbents exhibited good fit for Langmuir.

For Cr^{3+}, no good fit was found by Langmuir. However, for Freundlich, good fit was found for Cd^{2+} adsorption by CNS *in natura* and CNS H_2O_2, for Pb^{2+} adsorption by CNS NaOH and for Cr^{3+} adsorption by CNS *in natura* and CNS H_2O_2. The parameter R_L of Langmuir indicates a favorable adsorption process by the values between $0 < R_L < 1$, except for Pb^{2+} adsorption by CNS NaOH and Cr^{3+} CNS *in natura*, CNS H_2O_2 and CNS H_2SO_4 (Sun et al. 2013) (Table 8).
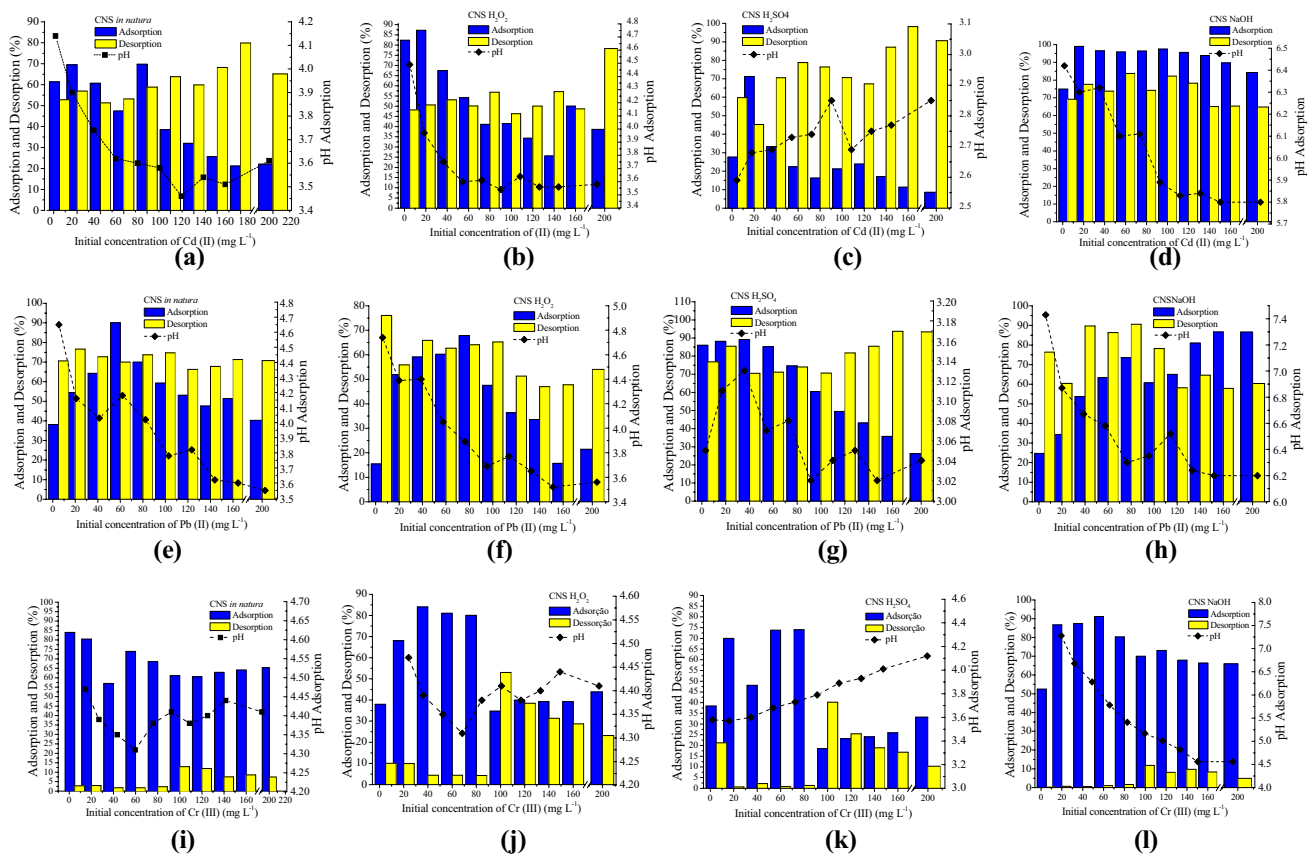
Fig. 10 Adsorption (%), desorption (%) and pH after adsorption of Cd^{2+} (**a–d**), Pb^{2+} (**e–h**) and Cr^{3+} (**i–l**), respectively, by CNS *in natura* and modified with H_2O_2, H_2SO_4 and NaOH

The higher Q_m values for CNS at adsorption of Cd^{2+} followed the order CNS NaOH > CNS *in natura* > CNS H_2O_2, with values of 47.5059, 12.5455 and 10.0301 mg g^{-1}. The adsorption of Pb^{2+} followed the order CNS *in natura* (27.1297 mg g^{-1}) > CNS H_2SO_4 (13.45501 mg g^{-1}); however, these values underestimate those found by isotherms (Fig. 11). The sequence of Q_m for Cr^{3+} was higher for CNS NaOH, with 42.6803 mg g^{-1}. The parameter b or K_L demonstrated low binding energy between Cd^{2+}, Pb^{2+} and Cr^{3+} and the CNS *in natura* and chemically modified with H_2O_2, H_2SO_4 and NaOH (Table 8), with low affinity/selectivity of metal–ligand interaction, suggesting that these ions are released into solution very easily.

The n parameter determines the Freundlich reactivity of active sites, and it is related to the solid heterogeneity. As can be seen in this research, n values below 1 are found only for Pb^{2+} adsorption by CNS NaOH and Cr^{3+} CNS *in natura*, CNS H_2O_2 and CNS H_2SO_4, and all other values were higher than 1 (Table 8). In cases where n values approach 1, it is a strong indication of the presence of highly energetic sites or the occurrence of cooperative adsorption, involving interactions between molecules of the own adsorbate (Khezami and

Capart 2005). But to Skopp (2009), when $n > 1$, that do not reflect a good fit, for lack of physical sense.

Dubinin–Radushkevich model (D–R), according to Abd El-Latif and Elkady (2010), is used to verify that the nature of the adsorption process is chemical or physical (Table 9).

In Table 9, we can observe the average energy of sorption (E). If the value of $E > 8$ kJ mol^{-1}, there is a predominance of chemical adsorption in the system; however, if $E < 8$ kJ mol^{-1} the nature of the process is physical (Wan Ngah and Hanafiah 2008). According to the values of E occurs the predominance of chemisorption for the removal of Cd^2, corroborating the results found by the pseudo-second order (Table 7). For Pb^{2+}, E values suggest chemisorption only for CNS *in natura* and Cr^{3+} for CNS *in natura*, CNS H_2SO_4, CNS NaOH (Table 9) (Wan Ngah and Hanafiah 2008).

The differences found between the evaluated materials are due to the different applied modifications, as already observed in Tables 2 and 3, Figs. 1, 2, 3, 4 and 5, referring to the characterization of the adsorbent materials, since the solutions of H_2O_2, H_2SO_4 and NaOH caused changes in the behavior of the resulting adsorbents (Schwantes et al. 2016).
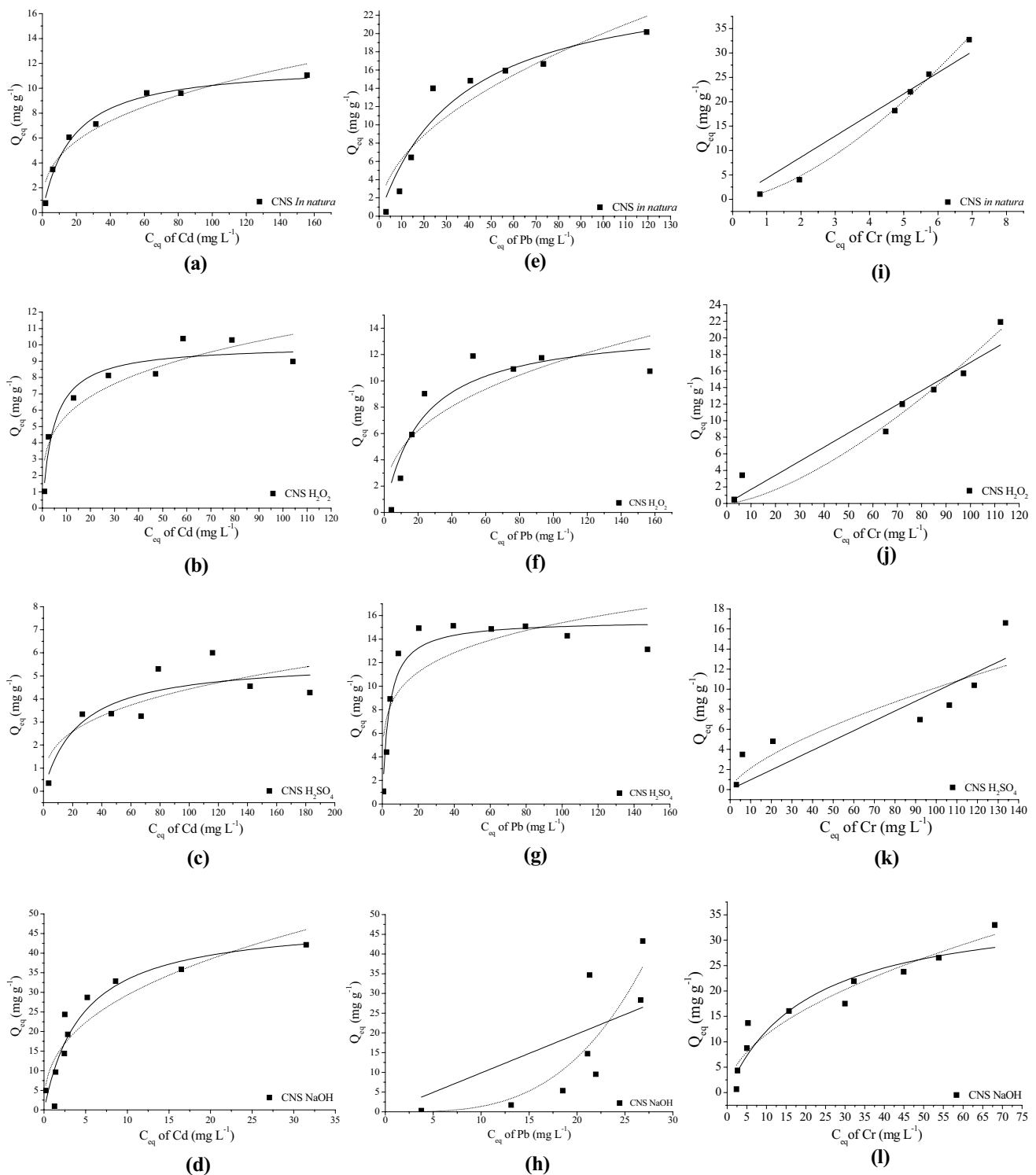
Fig. 11 Langmuir and Freundlich isotherms for sorption of Cd^{2+} (**a–d**), Pb^{2+} (**e–h**) and Cr^{3+} (**i–l**), respectively, by the CNS *in natura* (Coelho et al. 2014) and modified with H_2O_2, H_2SO_4 and NaOH. *Source*: the author

The sodium hydroxide, by dissolving the biomass and modifying the superficial structure of the adsorbent, apparently favored the adsorption of Cd^{2+} and Cr^{3+} in monolayers, according to data presented by the Langmuir model,
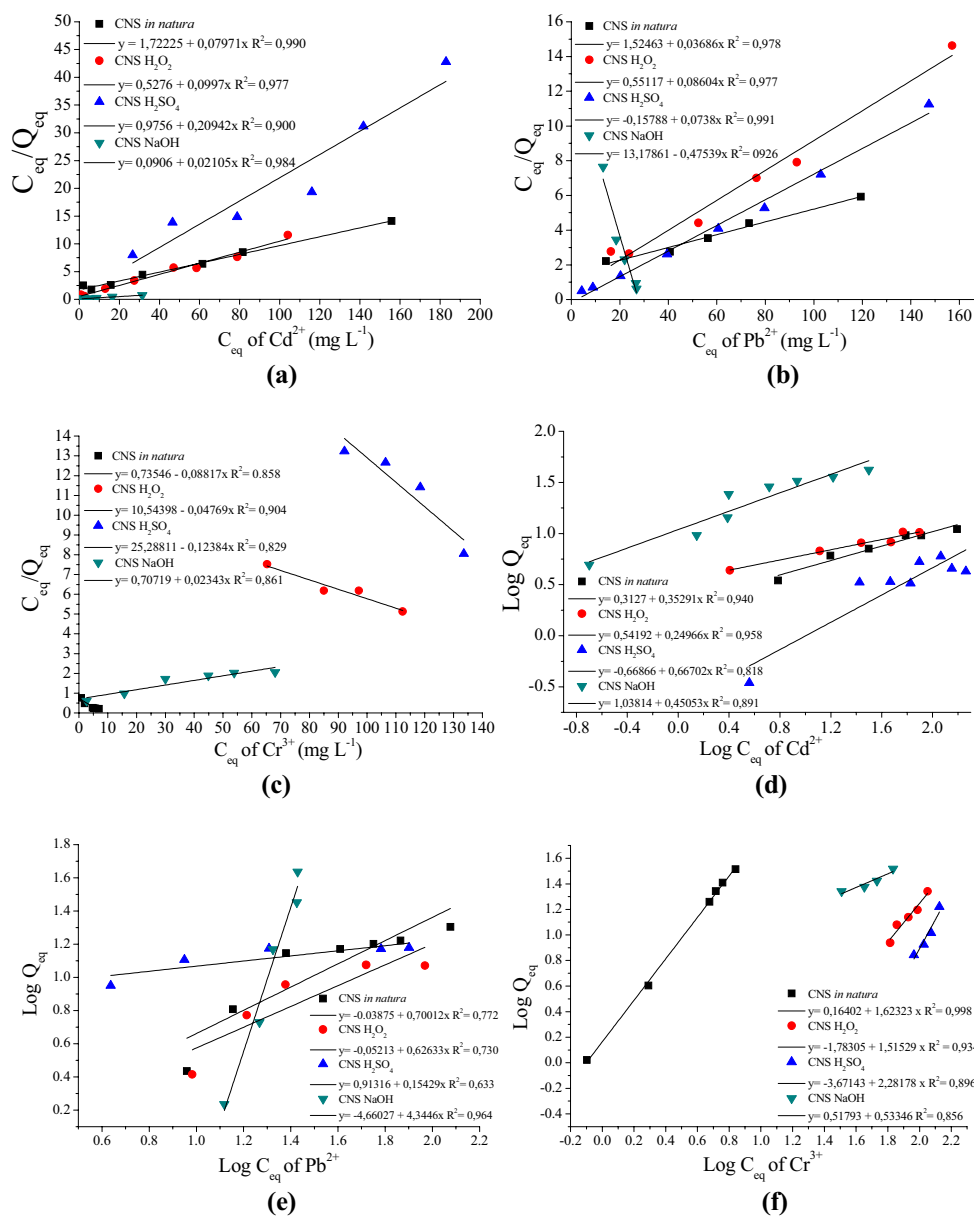
Fig. 12 Linearization of the mathematical models of adsorbent materials: CNS *in natura* (Coelho et al. 2014) and modified with H_2O_2, H_2SO_4 and NaOH by Langmuir for Cd^{2+} (**a**), Pb^{2+} (**b**), Cr^{3+} (**c**) and Freundlich for Cd^{2+} (**d**), Pb^{2+} (**e**) and Cr^{3+} (**f**)

increasing the estimated adsorption capacity by 370× when compared to the biosorbent values.

Adsorption thermodynamics

In Table 10 can be observed the thermodynamics parameters for adsorption of Cd^{2+}, Pb^{2+} and Cr^{3+} on the shell of cashews (CNS) *in natura* and chemically modified with H_2O_2, H_2SO_4 and NaOH.

As can be observed in Table 10, for Cd^{2+} on CNS H_2O_2, CNS H_2SO_4 and CNS NaOH, for Pb^{2+} adsorption for all studied adsorbents and for Cr^{3+} adsorption by CNS *in*

natura, CNS H_2O_2 and CNS H_2SO_4, the values of ΔG were positive in all studied temperatures, suggesting a nonspontaneous and nonfavorable adsorption process. The opposite was observed for Cr^{3+} adsorption by CNS NaOH. For Cd^{2+} adsorption by CNS *in natura,* it is found a spontaneous process at temperatures between 15 and 25 °C, becoming negative above 25 °C.

The values of enthalpy (ΔH) predict if the system is endothermic, when ΔH is positive, or exothermic, when ΔH is negative (Wan Ngah and Fatinathan 2010). We can observe positive values of ΔH (endothermic system) for all adsorbents, except for Cd^{2+} adsorption by CNS *in natura*. Also,

Table 8 Parameters of Langmuir and Freundlich adsorption parameters on the shell of cashews (CNS) *in natura* and modified with H_2O_2, H_2SO_4 and NaOH

Experimental conditions		Langmuir constants						Freundlich constants				
		Q_m (mg g^{-1})	SE	b ou K_L (L mg^{-1})	SE	R_L	Adj. R^2	K_f (mg g^{-1})	SE	n	SE	Adj. R^2
Cd^{2+}	*in natura**	12.545	0.229	0.137	0.003	0.035	0.990	2.054	0.064	2.834	0.039	0.940
	H_2O_2	10.030	0.309	0.052	0.005	0.086	0.977	3.482	0.033	4.005	0.249	0.958
	H_2SO_4	4.775	3.461	0.204	0.030	0.023	0.900	0.214	0.211	1.499	0.117	0.818
	NaOH	47.505	0.014	0.001	0.001	0.723	0.985	10.917	0.050	2.220	0.058	0.891
Pb^{2+}	*in natura**	27.129	0.1933	0.056	0.002	0.081	0.978	0.914	0.240	1.428	0.151	0.772
	H_2O_2	11.622	0.4900	0.047	0.005	0.095	0.977	0.886	0.272	1.597	0.182	0.730
	H_2SO_4	13.550	0.1959	0.011	0.002	0.751	0.991	8.187	0.076	6.481	0.054	0.633
	NaOH	0.230	0.5499	− 2.024	0.417	− 0.000	0.926	0.012	0.408	0.456	0.337	0.964
Cr^{3+}	*in natura**	11.341	0.0746	− 0.064	0.015	− 0.083	0.858	1.458	0.016	0.616	0.026	0.998
	H_2O_2	20.968	0.8037	− 0.502	0.008	− 0.502	0.904	0.016	0.384	0.660	0.199	0.934
	H_2SO_4	8.074	3.5660	− 3.131	0.031	− 0.001	0.829	0.000	0.900	0.438	0.439	0.864
	NaOH	42.680	0.1743	0.016	0.004	0.231	0.861	3.295	0.207	1.875	0.122	0.856

Q_m: adsorption capacity; b or K_L: constant interaction forces-related adsorbent/adsorbate; R_L: Langmuir constant; Adj. R^2: adjusted coefficient of determination; K_f: related to the adsorption capacity; n: related to the heterogeneity of the solid, SE standard error

Source: Coelho et al. (2014)

Table 9 Parameters of Dubinin–Radushkevich (D–R) related to adsorption of Cd^{2+}, Pb^{2+} and Cr^{3+} on the shell of the cashew nut (CNS) *in natura* and modified with H_2O_2, H_2SO_4 and NaOH

D–R	CNS *in natura** Cd	CNS H_2O_2	CNS H_2SO_4	CNS NaOH	CNS *in natura** Pb	CNS H_2O_2	CNS H_2SO_4	CNS NaOH	CNS *in natura** Cr	CNS H_2O_2	CNS H_2SO_4	CNS NaOH
Qd	2.89e^{-3}	2.0e^{-6}	3.2e^{-6}	10.9e^{-5}	1.41e^{-2}	2.06e^{-4}	6.01e^{-5}	0.0804	6.66e^{-3}	1.84e^{-4}	5.19e^{-5}	7.72e^{-5}
E	10.435	12.539	8.214	12.109	8.513	7.240	10.494	5.654	9.834	7.344	8.305	10.648
Adj. R^2	0.989	0.706	0.933	0.907	0.992	0.692	0.808	0.910	0.985	0.986	0.879	0.875

Q_d: maximum capacity of adsorption (mol g^{-1}); E: average energy of sorption (kJ mol^{-1}); adj. R^2: adjusted coefficient of determination

Source: Coelho et al. (2014)

the results exhibit values of ΔH higher than 40 kJ mol^{-1}, suggesting possible chemisorption of Pb^{2+} by CNS H_2SO_4 (84.77 kJ mol^{-1}) and physisorption for all other processes (Mimura et al. 2010).

Positive values of entropy (ΔS), as observed for Pb^{2+} adsorption by CNS NaOH, and Cr^{3+} adsorption by CNS *in natura* and CNS NaOH (Table 10), suggest a system disorder, probably due to an increase in the disorder of solid–solution interface, indicating randomness on solid–solution interface (Rao and Khan 2009).

Conclusion

The adsorbents from the cashew nut shell (CNS) chemically modified with NaOH, H_2SO_4 and H_2O_2, exhibited differences between the presence of chemical elements,

morphology, porosity, point of zero charge, except for thermal stability.

The infrared spectra demonstrated the existence of anionic functional groups (hydroxyl, carboxylic acid and amines) with differences in structure between the modified adsorbents, such as the presence of polysaccharides of bonds C–O–P for CNS H_2SO_4, carboxylic acids to CNS H_2O_2 and CNS H_2SO_4 and hydrocarbons to CNS NaOH.

The variation of pH caused little influence in adsorption tests; however, the mass of 200 mg (4 g L^{-1}) demonstrated the best adsorption rate, occurring in time of 40-min balance.

The kinetic models of pseudo-first order, Elovich and intraparticle diffusion did not fit to experimental data, and good fiting was only found by the model of pseudo-second order, suggesting chemisorption.

The parameters of Langmuir were satisfactory for Cd^{2+} adsorption by CNS *in natura*, CNS H_2O_2 and CNS NaOH,

Table 10 Q_{eq} obtained values and thermodynamic parameters for adsorption of Cd^{2+}, Pb^{2+}, Cr^{3+} on the shell of the cashew nut (CNS) *in natura* and chemically modified with H_2O_2, H_2SO_4 and NaOH

	T °C	Cd^{2+}					Pb^{2+}					Cr^{3+}				
		Q_{eq}	ΔG	ΔH	ΔS	Adj. R^2	Q_{eq}	ΔG	ΔH	ΔS	Adj. R^2	Q_{eq}	ΔG	ΔH	ΔS	Adj. R^2
CNS *in natura*	15	3.85	− 0.32				3.072	3.44				2.18	5.69			
	25	3.84	− 0.06				3.11	3.53				1.85	5.62			
	35	3.81	0.19	− 7.84	− 26.10	0.99	3.08	3.62	0.79	− 9.18	1.00	1.77	5.55	7.76	7.18	0.97
	45	3.79	0.45				3.18	3.72				2.52	5.47			
	55	3.76	0.71				3.08	3.81				3.06	5.40			
CNS H_2O_2	15	7.15	54.87				11.31	15.80				0.15	62.54			
	25	7.09	55.94				9.94	16.12				0.08	63.81			
	35	7.20	57.02	24.04	− 107.1	0.53	11.86	16.45	6.37	− 32.71	0.84	0.06	65.07	26.03	− 126.7	0.97
	45	6.95	58.09				3.62	16.78				0.04	66.34			
	55	0.00	59.16				11.08	17.10				0.04	67.61			
CNS H_2SO_4	15	2.17	14.34				8.09	166.90				6.23	31.37			
	25	2.13	14.54				3.72	169.76				7.06	31.55			
	35	1.23	14.73	8.75	− 19.39	0.75	10.91	172.60	84.77	− 285.2	0.99	7.01	31.73	26.17	− 18.06	0.99
	45	1.65	14.93				5.41	175.46				6.88	31.91			
	55	7.72	15.12				6.15	178.31				8.67	32.09			
CNS NaOH	15	11.43	2.52				6.61	6.15				11.4	− 2.52			
	25	11.03	2.56				0.05	5.55				11.7	− 3.11			
	35	11.36	2.60	1.457	− 3.69	0.05	10.66	4.96	23.38	59.80	1.00	11.6	− 3.69	14.32	58.46	1.00
	45	11.92	2.63				5.64	4.36				12.0	− 4.28			
	55	10.78	2.67				5.69	3.76				12.0	− 4.86			

Q_{eq}: amount adsorbed per unit of adsorbent (mg g^{-1}); ΔG: Gibbs free energy variation (kJ mol^{-1}); ΔH: variation of enthalpy (kJ mol^{-1}); ΔS: variation of entropy (J mol^{-1} K^{-1}); T: temperature (°C)

just as for Pb^{2+} adsorption by CNS *in natura*, CNS H_2O_2 and CNS H_2SO_4, and for Cr^{3+} adsorption tests we found no good fit. For Freundlich, good fit was found for Cd^{2+} adsorption by CNS *in natura* and CNS H_2O_2, for Pb^{2+} adsorption by CNS NaOH and for Cr^{3+} adsorption by CNS *in natura* and CNS H_2O_2.

The model of Dubinin–Radushkevich suggested the predominance of chemisorption, according to the values of energy sorption (E) for the adsorption of Cd^{2+} on all studied adsorbents. D-R suggests also the chemisorption of Pb^{2+} by CNS *in natura* and for the Cr^{3+} adsorption by CNS *in natura,* CNS H_2SO_4, CNS NaOH.

When compared to CNS *in natura*, the shell of the cashew nut modified with H_2O_2 and H_2SO_4 and NaOH has potential for high efficiency removal of metal from water, being the best adsorption rates of Cd^{2+} obtained after modification with H_2O_2 and NaOH, and for Pb^{2+} adsorption best results were found for CNS H_2SO_4 and for Cr^{3+} with CNS NaOH.

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