

Research Article

Chemical Modifications of Cassava Peel as Adsorbent Material for Metals Ions from Wastewater

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Residues from the processing of cassava roots (*Manihot esculenta* Crantz), or cassava peels, are evaluated as chemically modified adsorbents with H_2O_2 , H_2SO_4 , and NaOH, in the removal of metal ions Cd(II), Pb(II), and Cr(III) from contaminated water. Modified adsorbents were chemically characterized for their chemical composition and pH_{PZC} (point of zero charge), while adsorption tests determined the best conditions of pH, adsorbent mass, and contact time between adsorbent and adsorbate in the process of removal of the metal ions. Isotherms obtained from the preliminary results were linearized by Langmuir's and Freundlich's models. The thermodynamic parameters, such as ΔH , ΔG , and ΔS , were also evaluated. The modifying solutions proposed were effective in the modification of adsorbents and resulted in high capacity sorption materials. Equilibrium time between adsorbent and adsorbate for the solutions contaminated with metals is about 40 minutes. The Langmuir model adjusted to most results, indicating monolayers adsorption of Cd(II), Pb(II), and Cr(III). The values obtained for Langmuir Q_m show a higher adsorption capacity caused by chemical modifications, with values such as 19.54 mg Cd(II) per g of M. NaOH, 42.46 mg of Pb(II) per g of M. NaOH, and 43.97 mg of Cr(III) per g of M H_2O_2 . Results showed that modified cassava peels are excellent adsorbent, renewable, high availability, and low-cost materials and a feasible alternative in the removal of metals in industries.

1. Introduction

Since agroindustries produce several basic products, they have transformed themselves into a symbol of developed societies [1]. However, their various segments are responsible not only for the production of various products but also for several solid wastes. The cassava industry is no exception. Solid wastes are generated in the processing of cassava roots, most of which go to the manufacture of animal feed and biofertilizers. Cassava peel makes up approximately 3 to 5% of the total mass of roots and about 1 million tons of cassava peels is annually produced in Brazil and 11 million tons worldwide [2]. Since cassava is a crop planted worldwide, with great production and an enormous increasing potential,

it is estimated that the above rates will grow considerably in the future.

Another issue also refers to industrial and agricultural activities which cause, directly or indirectly, the contamination of the environment by heavy metals, with great concern and attention for environmental researchers and agencies involved in the control of water pollution [3], especially when the bioaccumulation of metals in aquatic fauna and flora affects human populations and causes irreversible physiological effects with metabolic dysfunctions.

Several techniques reduce contamination but all present disadvantages, especially high installation costs and maintenance. Among the conventional methods, the following are the most employed: chemical precipitation, oxidation or

reduction, filtration, coagulation, electrochemical treatment, membrane separation processes, and solid phase extraction. Some methods are restricted for technical or economic infeasibility, especially when metals are dissolved in large volumes of water at relatively low concentrations [4].

The adsorption process is an alternative to remove polluting waters. In fact, the technology is being used extensively for the removal of organic pollutants from aqueous solutions. Although activated carbon is one of the most widely used adsorbents, its high cost is a great disadvantage [5] since its production involves physical and chemical activation, as well as high temperature and pressure under controlled conditions [6].

Thus, the use of activated carbon on a large scale, for instance, in the decontamination of large volumes of contaminated water or industrial effluents [7], may not be feasible.

Another research comprises the use of milled vegetable biomass to remove metal ions and pesticides. Some advantages in using plant biomass for wastewater treatment include operational easiness, low-cost processing, reasonable adsorption capacity, selective removal of metal ions, facility of disposal of materials, and easy regeneration [8]. Nevertheless, biomass has not always a very high adsorption capacity [7], which is one of the main restrictions for its use in water remediation. However, some bibliographies already report the use of simple chemical modifications and low-cost biosorbents to increase the adsorptive capacity without increasing the cost of final product [9, 10] and, thereby, its widespread use may not be impeded.

Consequently, vegetable biomass is chemically treated with chemical reagents in low-cost solutions such as acids or bases, causing an increase in the pollutant-removing capacity [11, 12].

Several studies report that chemical modifications used as biosorbents may introduce functional groups within the structure of the adsorbents or increase their porosity, with an increase in their adsorption capacity [10, 13].

Current research evaluates the efficiency of chemically modified cassava peels as adsorbent materials for the removal of toxic metal ions Cd(II), Pb(II), and Cr(III) from water.

2. Material and Methods

2.1. Obtaining Raw Material and Preparation of Modified Adsorbents. Cassava peels were obtained directly from a cassava processing agroindustry in Toledo, PR, Brazil. They were dried at 60°C for 48 h, crushed, and sieved (material retained between 14 and 65 mesh) to standardize particle size. Chemical modifications were made to the raw material (cassava peels) such as surface contact area, porosity, number of adsorption sites, and the energy sorption sites, to increase the adsorption of the metals.

Three chemical modifications were evaluated with different chemical reagents by washing with 0.1 mol L⁻¹ solutions of H₂O₂ (Vetec P.A. 36%), H₂SO₄ (Vetec P.A. 98%), and NaOH (Vetec P.A. 99%) [8, 10, 14].

Solutions were prepared in 0.1 mol L⁻¹ of H₂O₂, H₂SO₄, and NaOH, to which 70 mL of solution was added in 125 mL

Erlenmeyer flasks containing 7.0 g of material *in natura* (M. *in natura*).

The Erlenmeyer flasks were placed in a Dubnoff metabolic incubator, at 60°C for 6 hours. The modified adsorbents were subsequently washed with distilled water to remove residual reactants still present in the material.

Three chemical modifications applied to cassava peel were evaluated, totaling 3 new modified adsorbents and an adsorbent in its *in natura* form, namely, M. *in natura*, M. H₂O₂, M. H₂SO₄, and M. NaOH.

Fortified mono-elementary solutions with metallic ions Cd(II), Pb(II), and Cr(III) were prepared from salts of cadmium nitrate [Cd(NO₃)₂·4H₂O P.A. ≥ 99.0% Sigma-Aldrich], lead nitrate [Pb(NO₃)₂ P.A. ≥ 99% Sigma-Aldrich], and chromium nitrate [Cr(NO₃)₃·9H₂O P.A. ≥ 99% Sigma-Aldrich]. Solutions were prepared from the mono-elementary solution of 1000 mg L⁻¹, at the desired concentrations for each study, and buffered in pH rates by adding NaOH 0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹. The water used in all adsorption experiments was ultrapure (Puritech Permution®).

2.2. Characterization of Chemically Modified Adsorbents. The chemical characterization of adsorbents was performed by nitroperchloric digestion of adsorbent materials [15] and concentrations of metals, potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), lead (Pb), and chromium (Cr) were determined by flame atomic absorption spectrometry (FAAS) [16], GBC 932 AA (Victoria, Australia) with deuterium lamp for background correction.

The adsorbent's point of zero charge (pH_{PZC}) or rather the pH at the surface of the adsorbent charges equal to zero was also determined [17].

2.3. Preliminary Studies Involving pH of the Medium and Mass of Adsorbent. A multivariable study was conducted to evaluate the effect of modified adsorbent mass and pH of mono-elementary solutions of Cd(II), Pb(II), and Cr(III). In fact, a univariate test of mass and pH would not be able to determine the possible interactions between the parameters mentioned above. Consequently, the compound center rotational design (CCRD) was employed to determine the influence of each variable and the possible interaction between them, generating an empirical and quadratic mathematical model which is valid within the experimentally tested range [18]. Adsorbents' masses were evaluated between 250 and 1250 mg, while pH ranged between 3.00 and 7.00.

Table 1 shows CCRD planning matrix, displaying the encoded rates and variables of the adsorbent mass and pH configuration for each mass versus pH tested.

The solutions were placed in 125 mL Erlenmeyer flasks containing the mass of the modified adsorbents (Table 1) and subsequently placed in Dubnoff thermostatic system with constant agitation at 200 rpm for 1.5 h.

After performing the sorption process, the samples were filtered and aliquots were removed to determine the concentrations of metals by FAAS [16]. Adsorbed amount

TABLE 1: CCRD planning matrix (coded and real rates).

Tests	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	750.00	0.00	5.00

at equilibrium was calculated from rates obtained for the equilibrium concentration:

$$Q_{eq} = \left[\frac{(C_0 - C_{eq})}{m} \right] V \quad (1)$$

in which Q_{eq} is the amount of ions adsorbed per 1g of adsorbent at equilibrium (mg g^{-1}); m is the mass of the adsorbent used (g); C_0 is the initial concentration of the ion (mg L^{-1}); C_{eq} is the concentration of ion in solution at equilibrium (mg L^{-1}); V is the volume of solution used (L).

The results of the tests were tabulated and evaluated according to multivariate analysis with Statistica 5.0.

2.4. Studies Involving the Adsorption Kinetics. The adsorption kinetics of metals Cd(II), Pb(II), and Cr(III) by modified adsorbents was evaluated by studies in which the modified biomass was placed in contact with contaminated mono-elementary solutions of the evaluated metals.

A constant mass of 200 mg of the modified adsorbents (determined in Section 2.3, Figure 2) was placed in 125 mL Erlenmeyer flasks, to which was added 50 mL of the mono-elementary solutions at a concentration of 10 mg L^{-1} , pH 5.0 (determined in Section 2.3, Figure 2), and temperature at 25°C .

In the above-mentioned physico-chemical conditions, the absorbed amount of metal was assessed by the following contact times between the modified adsorbent and adsorbate: 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, and 180 minutes. Results were evaluated by the mathematical models of linear pseudo-first order, pseudo-second order, and Elovich and intraparticle diffusion.

The linear pseudo-first order equation, Lagergren's model, is based on the solid adsorption capacity of the equation and the concentration of the solution:

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - \left(\frac{K_1}{2.303} \right) t \quad (2)$$

in which Q_{eq} (mg g^{-1}) and Q_t (mg g^{-1}) are the quantity of adsorbate retained per gram of adsorbent at equilibrium

at time t , respectively; K_1 (min^{-1}) is the rate constant for pseudo-first order.

The model's occupancy velocity of the active sites is proportional to the number of active sites on the adsorbent material [19]. The applicability of pseudo-first-order model is checked when there is a log graph line ($Q_{eq} - Q_t$) versus t [20].

The kinetic model of pseudo-second order (see (3)) is a chemical process, involving the participation of valence forces or electron exchange between the adsorbent and adsorbate [20]:

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

in which K_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the constant of velocity of pseudo-second order. Unlike the pseudo-first-order model, the model predicts the kinetic behavior over the entire adsorption time range [19].

Elovich's kinetic model (see (4)) was first proposed by Roginsky and Zeldovich in 1934 and, according to [21], it has often been employed to describe the chemisorption of gases in solids:

$$Q_t = a + b \ln t \quad (4)$$

in which a and b are constant, wherein a represents the initial chemisorption velocity ($\text{mg g}^{-1} \text{ min}^{-1}$) and b indicates the number of suitable sites for the adsorption, which is related to the surface coverage extension and activation energy of chemisorption (g mg^{-1}) [22].

The intraparticle diffusion equation (see (5)), derived from Fick's Law, reveals that the distribution of the liquid film surrounding the adsorbent is negligible and the intraparticle diffusion is the only rate that controls the stages of the adsorption process [23]:

$$Q_{eq} = K_{id} t^{0.5} + C_i \quad (5)$$

in which K_{id} is the intraparticle diffusion constant ($\text{mg g}^{-1} \text{ min}^{-1/2}$) and C_i suggests the thickness of the boundary layer effect (mg g^{-1}) [24].

2.5. Studies of Adsorption Isotherms. Equilibrium studies were developed to assess removal of metals at higher concentrations. Thus, 200 mg of the modified adsorbent masses (determined in Section 2.3, Figure 2) was weighed and placed in 125 mL Erlenmeyer flasks; 50 mL of mono-elementary solutions was added with increasing concentrations, at constant conditions, such as pH 5.00 (determined in Section 2.3, Figure 2), constant temperature system 25°C , and contact time between adsorbent adsorbate of 40 min (determined in Section 2.4, Figure 3).

The adsorption of metals in the above-mentioned physico-chemical conditions was reported at the following pollutant concentrations: 5, 20, 40, 60, 80, 100, 120, 140, 160, and 200 mg L^{-1} . Results were evaluated by Langmuir's and Freundlich's linear models.

Langmuir's mathematical model is expressed in its linear form by (6) [25]. Consider

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{(Q_m K_L)} + \frac{C_{eq}}{Q_m} \quad (6)$$

in which C_{eq} is the ion concentration in equilibrium in the solution (mg L^{-1}); (Q_{eq}) is the adsorbed amount at equilibrium per unit of mass (mg g^{-1}); Q_m is the maximum adsorption capacity (mg g^{-1}); K_L is a constant related to the strength of adsorbent-adsorbate interactions (L mg^{-1}).

The favorability of the isotherm, or rather the favorable or unfavorable behavior of adsorption isotherm, may be interpreted by a constant called equilibrium parameter (R_L) [26] calculated by

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (7)$$

in which C_0 is the initial concentration of higher value (mg L^{-1}); K_L is the Langmuir constant (L mg^{-1}). Thus, if the rate of R_L lies between 0 and 1, the adsorption process is favorable.

Freundlich's mathematical model (see (8)) describes a multilayer adsorption with an exponential distribution of active sites and, therefore, an equilibrium on heterogeneous surfaces [8].

$$\log Q_{eq} = \log K_f + \frac{1}{n \log C_{eq}} \quad (8)$$

in which K_f represents the adsorption capacity (mg g^{-1}); n indicates the strength of adsorption, related to the heterogeneity of the adsorbent surface.

2.6. Effect of Temperature on the Adsorption Process. The effect of temperature on the metal sorption process by modified adsorbents was also studied by determining some of the thermodynamic parameters. A constant 200 mg mass of modified adsorbents was weighed in 125 mL Erlenmeyer flasks and 50 mL of mono-elementary solutions was added at a concentration of 50 mg L^{-1} , at pH 5.00 and contact time between adsorbent and adsorbate at 40 min.

In the above-mentioned experimental conditions, the system temperature was evaluated at 15, 25, 35, 45, and 55°C . Results were evaluated by linear models to determine the thermodynamic parameters: ΔG , ΔH , and ΔS .

The variation of enthalpy (ΔH) indicates that the adsorption process is endothermic or exothermic and variation of entropy (ΔS) is connected to the system after the order of the adsorption process [27]. These parameters may be calculated according to (9) [28, 29]. Consider

$$\Delta G = \Delta H - T\Delta S$$

$$\ln K_d = \left(\frac{\Delta S}{R} \right) - \left(\frac{\Delta H}{RT} \right) \quad (9)$$

in which K_d is the division between the amount adsorbed per unit of adsorbent (Q_{eq}) and concentration in equilibrium

(C_{eq}); R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the temperature in the experiment (Kelvin). ΔH and ΔS rates were obtained from the graph of $\ln K_d$ versus $1/T$.

2.7. Acid Elution for Adsorbents Reuse. The adsorbent masses from the isotherm study (Section 2.5) were recovered and deposited in Erlenmeyer flasks with 50 mL of HCl 0.1 mol L^{-1} at 200 rpm and 25°C , in order to determine the possibility of reuse of those modified adsorbents. The Erlenmeyer flasks were stirred for 1.5 h in acid solution, the solution was filtered, and the remaining desorbed concentration of the metal was calculated.

3. Results

3.1. Characterization of Chemically Modified Adsorbents. Further, pH corresponding to the point of zero charge (pH_{PZC}) of the adsorbents M. *in natura*, M. H_2O_2 , M. H_2SO_4 , and M. NaOH was determined, as illustrated in Figure 1.

According to Figure 1, the zero charge point for the adsorbents 6.02 M. *in natura*, 3.98 M. H_2O_2 , and 2.05 M. H_2SO_4 7.07 for M. NaOH may be observed.

The composition of the adsorbents studied by nitroperchloric digestion [15] and the metals by FAAS were determined [16], as Table 2 shows.

According to Table 2, the chemical modifications on the adsorbent (modifications with acid, base, and peroxide) were sufficient to cause changes in the chemical composition of the adsorbent, showing its effectiveness as a modifier solution.

As shown in Table 2, the concentration of K, Ca, Mg, Cu, Zn, and Pb in the composition of the modified adsorbents was effectively reduced and demonstrated that the modifying solutions (H_2O_2 , H_2SO_4 , and NaOH) were extracting solutions, predigesting the biomass, and extracting certain chemical elements of its structure.

It is also notable that the modifier solution H_2SO_4 , a strong acid recognized as a potent dehydrator, resulted in a higher extraction of metallic elements from cassava peels; this is noted because lower concentrations of the elements K, Ca, Mg, Cu, Zn, Fe, and Pb were found in its composition.

3.2. Preliminary Studies Involving pH of the Medium and Mass of Adsorbent. Results obtained at the proposed levels are provided (Table 3) for the compound center rotational design (CCRD) for the variables: mass of adsorbent versus pH of the solution versus quantity adsorbed at equilibrium.

Results shown in Table 3 were subjected to analysis of variance (ANOVA) and are presented in Table 4. There were significant differences ($\alpha = 1\%$) for all parameters evaluated with regard to the adsorbents *in natura* M. H_2O_2 , M. H_2SO_4 , and M. NaOH in the removal of Cd(II), Pb(II), and Cr(III) from contaminated solutions.

Table 4 reveals a significant difference of 1% in all adsorbents studied for the source of mass variation, both as a linear and as a quadratic model. These results showed that the adsorbents M. *in natura*, M. H_2O_2 , M. H_2SO_4 , and M. NaOH depended closely on the amount of available adsorbent, but not on the pH, at least in this experiment, at the studied range.

TABLE 2: Mean concentration of elements of the adsorbents.

Adsorbent	K	Ca g kg ⁻¹	Mg	Cu	Zn	Mn	Fe mg kg ⁻¹	Cd	Pb	Cr
<i>M. in natura</i>	24.10	35.03	6.83	14.33	32.00	123.33	335.66	>0.005	13.00	>0.01
M. H ₂ O ₂	7.84	5.68	1.27	10.60	32.20	121.50	333.70	>0.005	10.40	>0.01
M. H ₂ SO ₄	5.78	3.41	0.43	4.30	20.40	115.70	330.90	>0.005	5.10	>0.01
M. NaOH	11.22	6.52	1.49	4.80	32.60	122.00	331.60	>0.005	11.50	>0.01

QL (quantification limit): K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; Cr = 0.01 (mg kg⁻¹).

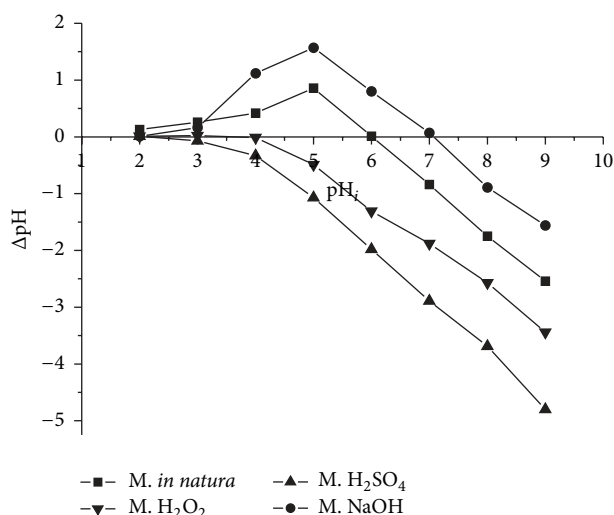


FIGURE 1: pH_{PZC} for the adsorbents *M. in natura*, M. H₂O₂, M. H₂SO₄, and M. NaOH.

This result is excellent, because the modified adsorbents studied in this research may be used in a wide pH range, still maintaining high efficiency removal of these metals.

Figure 2 illustrates the response surfaces for the adsorption of Cd(II), Pb(II), and Cr(III) by adsorbents *M. in natura*, M. H₂O₂, M. H₂SO₄, and M. NaOH.

As may be seen in Figure 2 and Table 4, within the experimental conditions of this study, the pH ranges did not influence the adsorption of Cd(II), Pb(II), or Cr(III). However, higher adsorption rates of the metals Cd(II), Pb(II), and Cr(III), measured by the adsorbed amount (Q_{eq} or Q_{ads}), occurred closer to the adsorbent mass 200 mg.

The number of active sites available depends on the amount of the adsorbent; then studies to verify the ideal mass adsorption are fundamental, because according to Rubio et al. [30] in certain cases there may be a decrease of the amount adsorbed due to formation of agglomerates which would reduce the total surface area and the number of active sites available for the process.

Response surfaces in Figure 2 are adjusted mathematically by the multiple linear regression equations (x, y, z) for the removal of Cd(II), Pb(II), and Cr(III) by the modified adsorbents and *in natura* (Table 5).

3.3. Studies Involving Adsorption Kinetics. Figure 3 shows the results obtained for removal of metals Cd(II), Pb(II),

and Cr(III) by adsorbents M. H₂O₂, M. H₂SO₄, and M. NaOH and the effect of contact time between the adsorbent-modified solutions and Cd(II), Pb(II), and Cr(III).

Results in Figure 3, or rather the influence of contact time between adsorbate and adsorbent, were linearized by mathematical models of pseudo-first order, pseudo-second order, and Elovich and intraparticle diffusion for the adsorbents M. H₂O₂, M. H₂SO₄, and M. NaOH used for the removal of Cd(II), Pb(II), and Cr(III) from contaminated water.

Tables 6 and 7 present the results of the kinetic parameters inherent to linearization by the models of pseudo-first order, pseudo-second order, and Elovich and intraparticle diffusion.

In a preliminary analysis of the data of all the kinetic models evaluated (Tables 6 and 7), the pseudo-second-order model proved to be the best mathematical adjustment for adsorption of Cd(II), Pb(II), and Cr(III) by modified adsorbents M. H₂O₂, M. H₂SO₄, and M. NaOH.

The intraparticle diffusion model presupposes the occurrence of diffusion of the adsorbate particle (Cd, Pb, and Cr in this study) into the adsorbent particle (M. H₂O₂, M. H₂SO₄, and M. NaOH in this study). Data reveal the possibility of the occurrence of diffusion intraparticle at various stages in this way; straight line fragmentation was performed in two segments, so that adjustment diffusion model occurs in at least one of the intervals at the evaluated time, as shown in Table 7 for the M. H₂SO₄ adsorbent in removing Cd(II).

Similarly, in Table 6, straight fragmentation was also performed for the better model adjustments of Elovich for the adsorbent M. H₂SO₄ in removing Cd(II). However, despite the straight fragmentation, a good adjustment (R^2) was not found for the observed data, so that the models of pseudo-first order, Elovich, and intraparticle diffusion failed to demonstrate a satisfactory adsorption of Cd(II), Pb(II), and Cr(III) by M. H₂O₂ materials, M. H₂SO₄ and M. NaOH.

Only one exception was observed; the adsorbent M. H₂SO₄ in the removal of Cr(III) showed good adjustment (R^2) of the model Elovich. These results will be described and discussed in the following sections.

3.4. Studies of Adsorption Isotherms. Results for sorption equilibrium tests constructed Cd(II), Pb(II), and Cr(III) adsorption isotherms, which were linearized by Langmuir's and Freundlich's mathematical models, as shown in Table 8.

Rates in Table 8 reveal a predominance of good mathematical adjustments to Langmuir's model, which suggests the occurrence of the adsorption of monolayers of Cd(II), Pb(II),

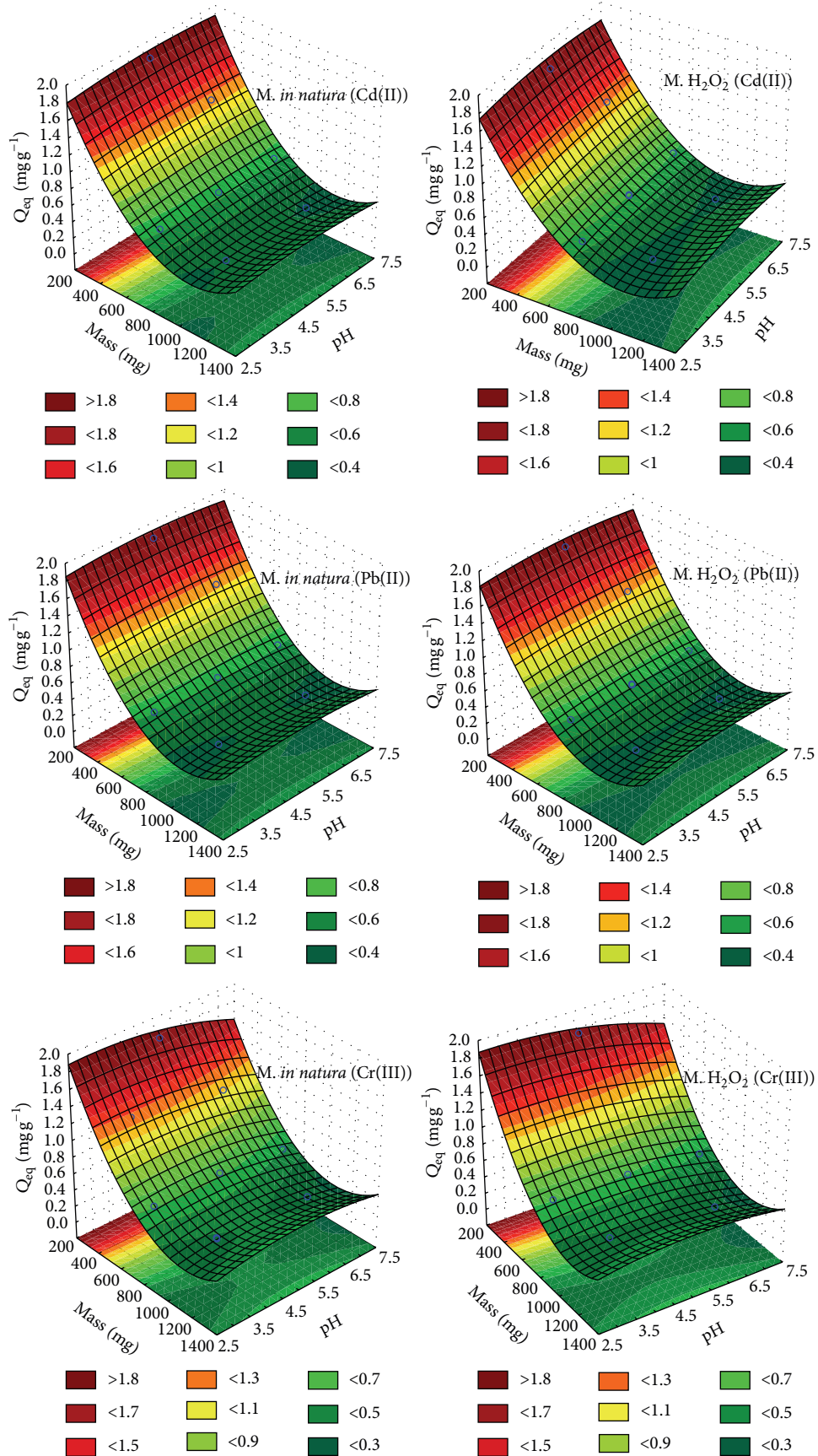


FIGURE 2: Continued.

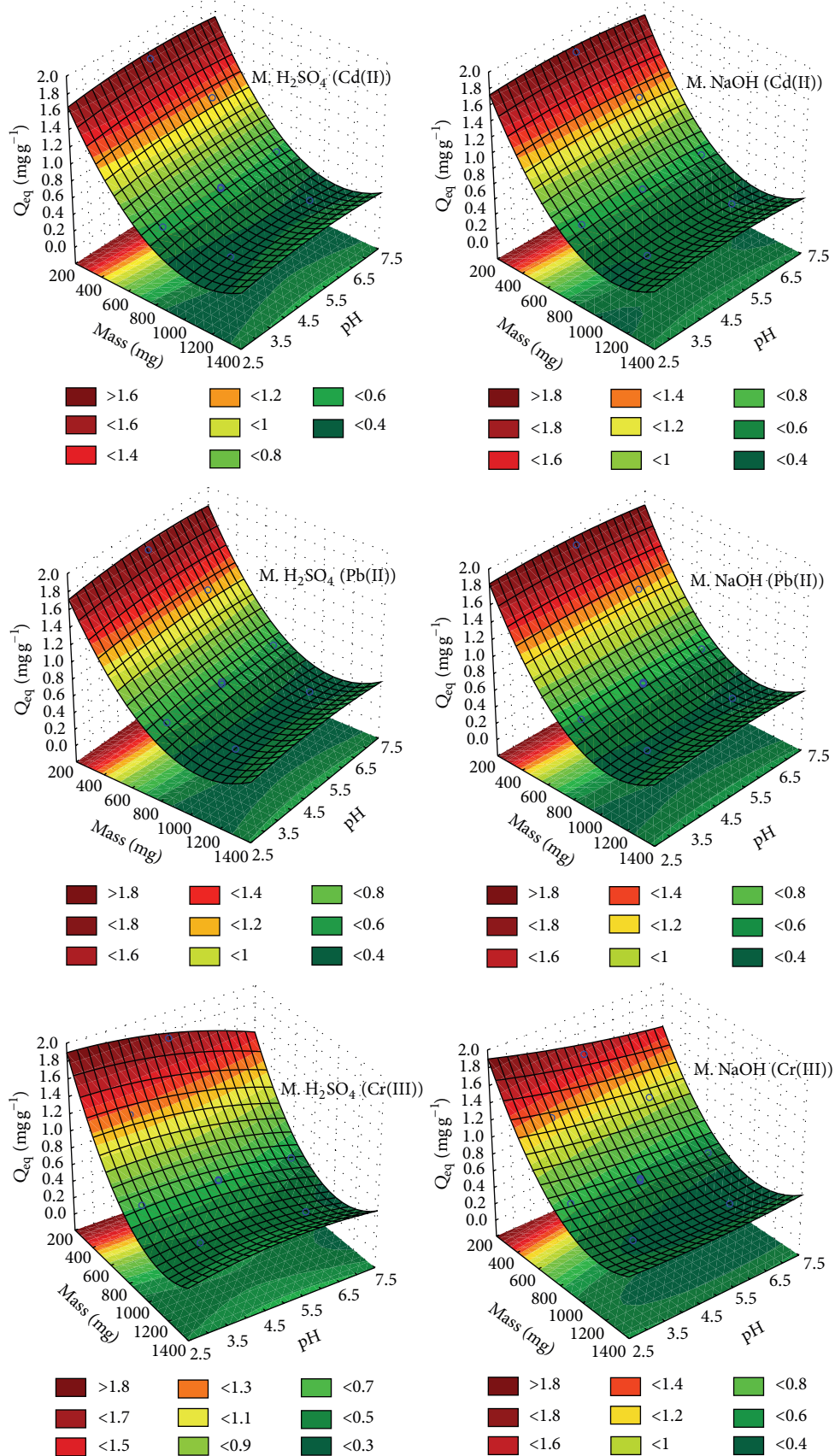


FIGURE 2: Graphs of response surfaces obtained in the adsorption of Cd(II), Pb(II), and Cr(III) by modified materials from cassava peels depending on adsorbent mass and pH of the mono-elementary solutions.

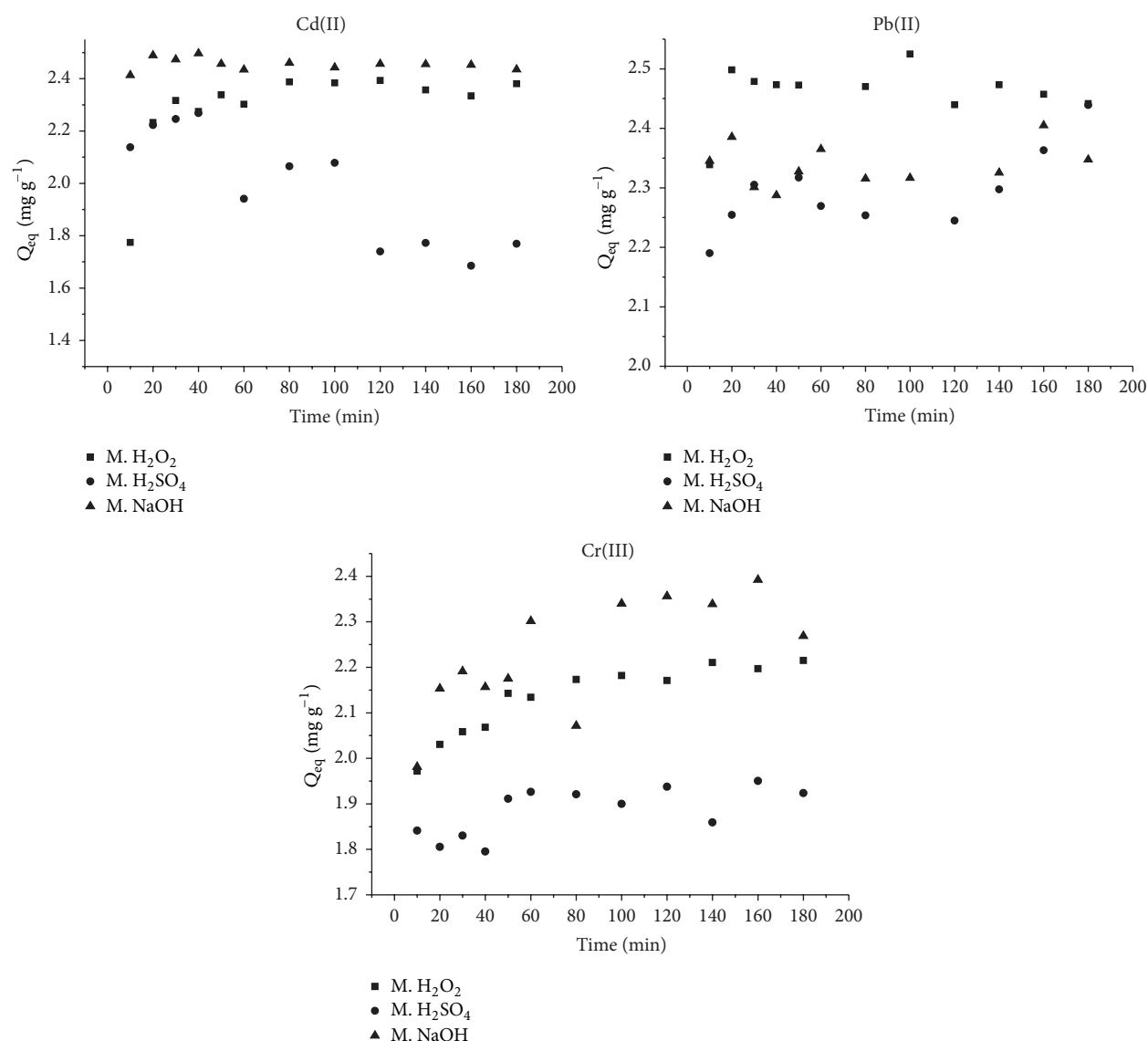


FIGURE 3: Physical-chemical equilibrium time between modified adsorbents and mono-elementary solutions of Cd(II), Pb(II), and Cr(III).

and Cr(III) in current study. This is due to R^2 rates being close to 1.0, indicating good mathematical adjustment, as noted in the following modified adsorbents: M. H_2O_2 , M. H_2SO_4 , and M. NaOH in adsorption of Cd(II); M. H_2O_2 and M. NaOH in adsorption of Pb(II); and M. H_2O_2 and M. H_2SO_4 in adsorption of Cr(III).

However, there was a good adjustment (R^2) to the Freundlich's model in some specific cases, which suggests the occurrence of multilayer adsorption: M. H_2SO_4 adsorption of Cd(II); M. H_2O_2 and M. H_2SO_4 in adsorption of Pb(II).

When data are confronted (Table 8), they suggest the occurrence of adsorption in mono- or multilayer used as the adsorbent M. H_2SO_4 in removing Cd(II), similar to M. H_2O_2 removing Pb(II). Therefore, these cases reveal good mathematical adjustments to Langmuir's and Freundlich's

model. This behavior and other linear parameters of these mathematical models will be discussed below.

3.5. Effect of Temperature on the Adsorption Process. The influence of temperature on the removing process of metals Cd(II), Pb(II), and Cr(III) by modified adsorbents M. H_2O_2 , M. H_2SO_4 , and M. NaOH was evaluated. Results are given in Table 9.

Table 9 demonstrates that the amount of adsorbed metal (Q_{eq}) was different for the adsorbents studied. Higher removal rates occurred by raising the system temperature in the removal of Cd(II) adsorbents M. H_2SO_4 and M. H_2O_2 , and adsorbent for adsorption M. NaOH Cr(III).

Contrastingly, the removal of Cd(II) by the adsorbent M. NaOH and the removal of Pb(II) and Cr(III) by the adsorbent

TABLE 3: Planning matrix CCRD with quadruplicate at the midpoint and average adsorption rates of Cd(II), Pb(II), and Cr(III) to adsorbents *in natura* and chemically modified with H₂O₂, H₂SO₄, and NaOH solutions.

Tests	Variable		Q _{eq} (mg g ⁻¹) Cd(II)				Q _{eq} (mg g ⁻¹) Pb(II)				Q _{eq} (mg g ⁻¹) Cr(III)			
	Mass (mg)	pH	M. <i>in natura</i>	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. <i>in natura</i>	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. <i>in natura</i>	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH
1	396.39	3.60	1.158	1.157	1.065	1.231	1.191	1.179	1.089	1.176	1.220	1.201	1.242	1.217
2	1103.61	3.60	0.434	0.418	0.379	0.448	0.428	0.421	0.397	0.421	0.440	0.437	0.447	0.437
3	396.39	6.40	1.210	1.163	1.120	1.239	1.198	1.175	1.131	1.177	0.950	0.992	1.066	0.986
4	1103.61	6.40	0.435	0.419	0.413	0.449	0.427	0.422	0.404	0.419	0.339	0.342	0.376	0.340
5	750.00	5.00	0.646	0.596	0.602	0.661	0.630	0.621	0.590	0.617	0.595	0.597	0.623	0.561
6	250.00	5.00	1.875	1.783	1.748	1.983	1.890	1.856	1.795	1.855	1.766	1.795	1.809	1.596
7	750.00	7.00	0.638	0.623	0.606	0.659	0.629	0.607	0.590	0.615	0.532	0.535	0.534	0.520
8	1250.00	5.00	0.388	0.369	0.365	0.392	0.378	0.369	0.356	0.366	0.358	0.358	0.368	0.335
9	750.00	3.00	0.647	0.549	0.582	0.658	0.626	0.611	0.578	0.614	0.599	0.611	0.607	0.639
10	750.00	5.00	0.598	0.604	0.605	0.658	0.622	0.614	0.585	0.613	0.580	0.594	0.612	0.542
11	750.00	5.00	0.644	0.613	0.576	0.659	0.627	0.612	0.588	0.607	0.591	0.595	0.619	0.531
12	750.00	5.00	0.648	0.612	0.588	0.656	0.629	0.615	0.567	0.603	0.589	0.597	0.620	0.538

TABLE 4: Mean square and summary of analysis of variance (ANOVA) are displayed to forecast model for the influence of the masses of cassava and pH solution on the removal of Cd(II), Pb(II), and Cr(III) to the adsorbents *in natura* and modified.

FV	GL	Cd(II)					Pb(II)				Cr(III)		
		M. <i>in natura</i>	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. <i>in natura</i>	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. <i>in natura</i>	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH
Mass (L)	1	1.621**	1.516**	1.401**	1.827**	1.685**	1.633**	1.492**	1.635**	1.430**	1.483**	1.549**	1.287**
Mass (Q)	1	0.335**	0.322**	0.287**	0.382**	0.356**	0.348**	0.332**	0.350**	0.302**	0.310**	0.319**	0.267**
pH (L)	1	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.027	0.021	0.015	0.030
pH (Q)	1	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.001	0.006	0.006	0.008	0.000
Mass × pH	1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.003	0.002	0.004
Total	6	0.009	0.006	0.008	0.011	0.009	0.008	0.009	0.008	0.011	0.010	0.007	0.003
Residue	11												

**Significant at 1%.

TABLE 5: Multiple quadratic mathematical equations obtained from the response surfaces for adsorption of Cd(II), Pb(II), and Cr(III) by adsorbents based on cassava peels, chemically modified and *in natura*.

Adsorbents		Equations	R ²
Cd	M. <i>in natura</i>	$z = 2.31392 - 0.00389216x + 0.00000183x^2 + 0.0994207y - 0.00765268y^2 - 0.00002575xy$	0.970
	M. H ₂ O ₂	$z = 2.22661 - 0.00391300x + 0.00000179x^2 + 0.1135094y - 0.010198y^2 - 0.0000021231xy$	0.979
	M. H ₂ SO ₄	$z = 2.09311 - 0.00367333x + 0.00000169x^2 + 0.117596y - 0.0099065y^2 - 0.00001022567xy$	0.969
	M. NaOH	$z = 2.49556 - 0.00426238x + 0.00000195x^2 + 0.106341y - 0.01022994y^2 - 0.00000413033xy$	0.969
Pb	M. <i>in natura</i>	$z = 2.42402 - 0.00410920x + 0.00000188x^2 + 0.091384y - 0.00873871y^2 - 0.00000392186xy$	0.973
	M. H ₂ O ₂	$z = 2.40349 - 0.00408627x + 0.00000186x^2 + 0.090141y - 0.0092527y^2 + 0.0000022304xy$	0.975
	M. H ₂ SO ₄	$z = 2.20750 - 0.00386993x + 0.00000182x^2 + 0.108006y - 0.008937y^2 - 0.0000172072xy$	0.969
	M. NaOH	$z = 2.44355 - 0.00408057x + 0.00000187x^2 + 0.0706209y - 0.006958y^2 - 0.0000014771xy$	0.974
Cr	M. <i>in natura</i>	$z = 2.60020 - 0.00422655x + 0.00000173x^2 + 0.04990993y - 0.015409y^2 + 0.00008415263xy$	0.964
	M. H ₂ O ₂	$z = 2.49313 - 0.00414079x + 0.00000176x^2 + 0.08114590y - 0.015967y^2 + 0.00005636427xy$	0.965
	M. H ₂ SO ₄	$z = 2.46274 - 0.00418541x + 0.00000178x^2 + 0.10776064y - 0.0177875y^2 + 0.0000522846xy$	0.977
	M. NaOH	$z = 2.92410 - 0.00392245x + 0.00000163x^2 - 0.149982207y + 0.005562y^2 + 0.00006738493xy$	0.986

x = adsorbent mass (mg); y = pH of the contaminant solution; z = adsorbed quantity (mg g⁻¹).

TABLE 6: Kinetic parameters referred to linear models of pseudo-first order, pseudo-second order, and Elovich obtained by adsorbents M. H₂O₂, M. H₂SO₄, and M. NaOH in the removal of Cd(II), Pb(II), and Cr(III) from water.

Parameters/adsorbents	M. H ₂ O ₂	M. H ₂ SO ₄ (Line A)	M. H ₂ SO ₄ (Line B)	M. NaOH	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH
		Cd(II)				Pb(II)			Cr(III)	
Pseudo-first order										
K_1 (min ⁻¹)	-0.0397	0.0084		0.0008	-0.0059	-0.0046	-0.0053	-0.0161	-0.0218	-0.0184
Q_{eq} (cal.) (mg g ⁻¹)	0.3846	0.1339		0.0425	0.1757	0.2365	0.2338	0.2160	0.1404	0.3513
R^2	0.778	0.707		0.034	0.740	0.578	0.857	0.921	0.908	0.878
Pseudo-second order										
K_2 (g mg ⁻¹ min ⁻¹)	0.4051	-0.0922		-1.4705	-2.3101	0.2235	0.6637	0.2546	0.5264	0.1757
Q_{eq} (cal.) (mg g ⁻¹)	2.3833	1.7042		2.4428	2.4549	2.3867	2.3820	2.2247	1.9309	2.3540
R^2	0.999	0.990		0.999	0.999	0.997	0.998	0.999	0.999	0.996
Elovich										
a (mg g ⁻¹ min ⁻¹)	2.1465	2.0601	4.1905	2.5142	2.5306	2.1624	2.2250	1.8690	1.7040	1.8696
b (g mg ⁻¹)	0.0454	0.0599	-0.4842	-0.0139	-0.0153	0.0211	0.0211	0.0667	0.0474	0.1019
R^2	0.639	0.883	0.712	0.610	0.687	0.768	0.709	0.982	0.850	0.949
Q_{en} (exp.) (mg g ⁻¹)	2.2896	1.9629		2.4556	2.4557	2.3010	2.3526	2.1296	1.8835	2.2273

K_1 : constant of pseudo-first-order velocity; Q_{eq} : adsorbate amounts retained by adsorbent mass in equilibrium; K_2 : constant pseudo-second-order velocity; a : constant indicating chemisorption initial speed; b : number of suitable sites for the adsorption of the surface related to the coverage extension and the activation energy of chemisorption; R^2 : coefficient of determination.

TABLE 7: Kinetic parameters inherent to the intraparticle diffusion model for the removal of the metals Cd(II), Pb(II), and Cr(III) by adsorbents M. H₂O₂, M. H₂SO₄, and NaOH.

Adsorbents	Intraparticle diffusion	Cd(II)		Pb(II)	Cr(III)
		Line A	Line B		
M. H ₂ O ₂	K_{id} (g mg ⁻¹ min ^{-1/2})	0.0116		-0.0041	0.0183
	C_i (mg g ⁻¹)	2.2346		2.5030	1.9834
	R^2	0.5552		0.6676	0.9082
M. H ₂ SO ₄	K_{id} (g mg ⁻¹ min ^{-1/2})	0.0284	-0.0710	0.0086	0.0134
	C_i (mg g ⁻¹)	2.1038	2.6272	2.1815	1.7690
	R^2	0.7800	0.6781	0.7094	0.9280
M. NaOH	K_{id} (g mg ⁻¹ min ^{-1/2})	-0.0035		0.0049	0.0323
	C_i (mg g ⁻¹)	2.4865		2.2744	1.9919
	R^2	0.5127		0.6265	0.8472

K_{id} : intraparticle diffusion constant; C_i : suggesting the thickness of the boundary layer effect; R^2 : coefficient of determination.

TABLE 8: Parameters related to the linear models for Langmuir and Freundlich adsorption of Cd(II), Pb(II), and Cr(III) by M. H₂O₂, M. H₂SO₄, and M. NaOH materials.

Parameters		M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH	M. H ₂ O ₂	M. H ₂ SO ₄	M. NaOH
		Cd(II)			Pb(II)			Cr(III)		
Langmuir	Q_m	13.421	7.058	19.539	21.678	24.004	42.463	43.975	10.074	54.645
	K_L	0.026	0.017	0.006	0.022	0.019	0.002	0.013	0.049	0.010
	R_L	0.163	0.224	0.467	0.188	0.207	0.667	0.273	0.093	0.329
	R^2	0.993	0.980	0.996	0.994	0.938	0.996	0.990	0.964	0.870
Freundlich	K_f	1.967	1.565	3.634	2.510	1.692	3.393	2.025	1.420	5.448
	n	2.287	1.020	1.678	1.764	1.488	0.762	2.700	3.031	3.580
	R^2	0.934	0.977	0.902	0.980	0.977	0.931	0.855	0.862	0.834

Q_m (mg g⁻¹): maximum adsorption capacity; K_L or b (L mg⁻¹): constant related to the strength of adsorbent/adsorbate interaction; R_L : Langmuir constant; R^2 : coefficient of determination; K_f (mg g⁻¹): related to the adsorption capacity; n : related to the solid heterogeneity.

TABLE 9: Thermodynamic parameters for modified adsorbents from cassava peels in the removal of Cd(II), Pb(II), and Cr(III).

Adsorbents	Temp. °C	Cd(II)					Pb(II)					Cr(III)				
		Q_{eq}	ΔG	ΔH	ΔS	R^2	Q_{eq}	ΔG	ΔH	ΔS	R^2	Q_{eq}	ΔG	ΔH	ΔS	R^2
M. H ₂ O ₂	15	6.4	3.0				11.8	-3.6				10.9	-1.4			
	25	6.1	2.6				10.7	-1.7				10.5	-1.2			
	35	7.8	2.1	15.5	43.6	0.93	10.0	0.3	-59.5	-194.2	0.92	10.7	-1.1	-5.7	-15.1	0.93
	45	8.7	1.7				10.5	2.2				10.5	-0.9			
	55	9.0	1.3				10.7	4.1				10.1	-0.8			
M. H ₂ SO ₄	15	5.6	3.8				10.9	-1.0				10.1	-0.2			
	25	6.0	3.7				7.7	1.1				8.6	0.2			
	35	6.3	3.7	5.6	6.5	0.98	7.5	3.1	-59.6	-203.9	0.80	9.2	0.5	-9.9	-34.0	0.98
	45	6.2	3.6				8.6	5.2				9.6	0.8			
	55	6.9	3.5				8.4	7.2				8.8	1.2			
M. NaOH	15	12.5	-5.2				11.8	21.5				11.6	-3.2			
	25	11.6	-4.3				11.7	22.2				11.7	-4.0			
	35	11.5	-3.5	-29.7	-85.2	0.87	11.6	23.0	-0.26	-75.5	0.89	11.7	-4.7	18.1	74.1	0.87
	45	11.9	-2.6				11.5	23.8				11.9	-5.4			
	55	11.2	-1.8				11.7	24.5				12.0	-6.2			

Q_{eq} (mg g⁻¹); ΔG (KJ mol⁻¹); ΔH (KJ mol⁻¹); ΔS (J mol⁻¹ K⁻¹).

M. H₂SO₄ show a reduction of the amount adsorbed (Q_{eq}), with increasing system temperature.

In the case of other modified adsorbents, a great difference was observed in the amount of adsorbed metal versus system temperature. Other thermodynamic parameters shown in Table 9 will be discussed in the following sections.

4. Discussion

4.1. Characterization of Chemically Modified Adsorbents. Figure 1 shows that the modifier solution (H₂O₂, H₂SO₄, and NaOH) and stirring time and temperature (65°C) caused changes in the superficial charge of the modified adsorbents since the pH_{PZC} of the adsorbent was changed to lower or higher rates to pH_{PZC} material *in natura*.

The adsorption of Cd(II), Pb(II), and Cr(III) ions would be favored by pH rates higher than pH_{PZC}, since in these cases, according to [31], the surface of the adsorbent has a predominance of negative charges.

Table 2 demonstrates the occurrence of changes in the chemical constitution of the biomass originated from cassava peels after treatment with solutions containing 0.1 mol L⁻¹ H₂O₂, H₂SO₄, and NaOH for 6 hours at 200 rpm and 60°C. The chemical solutions removed great quantities of chemical elements in biomass *in natura* and caused changes in the chemical structure, resulting in modified adsorbents M. H₂O₂, M. H₂SO₄, and M. NaOH.

It may be noted that a consistent decrease in K, Ca, Mg, and Cu concentrations (Table 2) in the chemical composition of biomass showed that solutions have been applied to produce effective modified chemical adsorbents.

The results (Figure 1 and Table 2) demonstrated that the simple washing of vegetable residual biomass with chemical agents, with energy added to the system (60°C), was sufficiently capable of causing modifications in the biomass.

One may also note that these modifications are favorable or unfavorable to the adsorption process by further studies since the adsorption process tends to be specific for each adsorbent/adsorbate.

4.2. Preliminary Studies Involving pH of the Adsorbent's Medium and Mass. A significant difference was found at 1% to the source of mass variation adsorbent for linear (L) and quadratic (Q) templates (Table 4), with regard to adsorbents M. *in natura*, M. H₂O₂, M. H₂SO₄, and NaOH for adsorption of Cd(II), Pb(II), and Cr(III).

Since no significant differences were found for the source of variation pH, this fact indicated that the conditions on which the surveys were conducted at the pH range studied had no influence on the adsorption process, either to adsorbents *in natura* or to adsorbents modified for the removal of Cd(II), Pb(II), and Cr(III).

This result indicates that each adsorbent when assessed separately for each metal presents significant difference as regards the mass of adsorbent that was used. From the obtained results, it was observed that lower adsorbent masses result in higher adsorption capacity.

When the response surfaces (Figure 2) and the resulting multivariable equations (Table 4) were evaluated, M. NaOH showed the highest removal rate of Cd(II) 1.95 mg g⁻¹, approximately 8% higher than M. *in natura*.

In the case of the removal of Pb(II), the modified adsorbents M. H₂O₂, M. H₂SO₄, and M. NaOH showed equal or slightly higher average than M. *in natura* adsorbent.

As for the removal of Cr(III), M. H₂SO₄ modified adsorbent showed higher removal rate, adsorbing more than 12% of M. *in natura*, reaching 1.60 mg g⁻¹ in the preliminary test.

The studied pH range did not influence the adsorption process, which is an excellent result, because these modified

adsorbents may be used in a wide pH range, such as contaminated waters or effluents containing metals, and still maintaining high efficiency removal of these metals.

4.3. Studies Involving Adsorption Kinetics. According to results (Figure 3), the sorption system is in chemical equilibrium after 40 minutes of stirring, with no great increments for adsorption of Cd(II), Pb(II), or Cr(III) by the adsorbents M. H_2O_2 , M. H_2SO_4 , and M. NaOH.

In the case of the kinetics models performed to results in Figure 3, good mathematical adjustments (R^2) to the pseudo-second-order model were reported, satisfactorily applicable in all studied adsorbents (M. H_2O_2 , M. H_2SO_4 , and M. NaOH) in removing Cd(II), Pb(II), and Cr(III). It must be emphasized that the $Q_{eq (calc.)}$ rates obtained for the pseudo-second-order model are very close to the experimental ones ($Q_{eq exp.}$) and demonstrated the excellent adjustment and precision [32] to estimate the chemically adsorbed amount of Cd(II), Pb(II), and Cr(III) [33].

However, the model of pseudo-first order did not provide satisfactory mathematical adjustments and failed to explain satisfactorily the sorption phenomenon observed. K_1 observed generally has negative values and indicates that the concentration of solute in the solution decreases with increasing time [34].

The pseudo-first- and pseudo-second-order models reveal that the difference between the concentration adsorbed at a given time and concentration adsorbed on equilibrium is the movement force for adsorption, and the overall adsorption rate, proportional to the movement force in the case of pseudo-first-order equation, is the square of movement force to the pseudo-second-order model. These models also indicate that the adsorption process is a "false" order chemical reaction, and adsorption rate may be determined by the reaction equations of the first-order and second-order reaction [23].

The values of K_2 obtaining angular coefficients of the line were -0.0922 , -1.4705 , and $-2.3101 \text{ g mg}^{-1} \text{ min}^{-1}$ for M. H_2SO_4 for adsorption of Cd(II), M. NaOH for adsorption of Cd(II), and M. H_2O_2 for adsorption of Pb(II), respectively. The negative values for K_2 suggest that the metal adsorbed quantity (Q_t) decreases with increasing time [35].

The kinetics of the pseudo-second order describes chemical adsorption processes involving donating or electron exchange between the adsorbate and adsorbent, such as covalent and ionic exchange forces [20]; in this type of adsorption, the molecules are not attracted by the solid surface points, but specifically for the active centers, to form initially a single layer; then there may be the formation of other layers by physisorption.

The Elovich model showed good mathematical adjustment only for the adsorption of Cr(III) by M. H_2SO_4 . Results reveal that, for the adsorption of Cr(III) by M. NaOH in the initial moments of the adsorption, chemisorption is predominant, as proposed by the Elovich's model.

Results in Table 7 demonstrate that the model predicts the intraparticle diffusion, or rather when there is a movement of the metal particle into the adsorbent pores, adequate

mathematical adjustments were not provided, in a limiting step for adsorption of Cd(II), Pb(II), or Cr(III).

In a similar research, Schwantes et al. [36] evaluated Cd(II) adsorption kinetics by M. *in natura* and found better mathematical adjustments to the model of pseudo-second order. According to the authors, this result suggests chemical adsorption of the element by the adsorbent.

It should be noted that the kinetics of the pseudo-second order describes well the chemical adsorption processes involving donation or exchange of electrons between the adsorbate and the adsorbent as covalent forces and ion exchange [35].

4.4. Studies of Adsorption Isotherms. Results obtained in studies of adsorption equilibrium Cd(II), Pb(II), and Cr(III) by the base adsorbent-modified cassava peels were used to construct the adsorption isotherms. The results obtained were linearized by Langmuir's and Freundlich's mathematical models (Table 8).

Good adjustments to Langmuir's model were reported (Table 8), suggesting adsorption of monolayers of Cd(II) by M. H_2O_2 , M. H_2SO_4 , and M. NaOH, Pb(II) by M. NaOH and M. H_2O_2 , and Cr(III) by M. H_2O_2 and M. H_2SO_4 . It should be underscored that the adsorbent M. NaOH provided the highest removal capacity of Cd(II) 19.5 mg g^{-1} , when compared to 7.0 mg g^{-1} and 13.4 mg g^{-1} of adsorbents M. H_2O_2 and M. H_2SO_4 .

Higher rates were detected for M. NaOH adsorbent in removing Pb(II), with Q_m at 42.5 mg g^{-1} , 1.45 times the removal reported by Schwantes et al. [36] in a similar experiment, where Q_m with 29.26 mg g^{-1} for M. *in natura* was obtained.

Regarding the removal of Cr(III), the high adsorption capacity of M. H_2O_2 material should be emphasized, or rather 43.9 mg g^{-1} to Q_m , which is 15 times higher than results by Schwantes et al. [2] to evaluate the use of M. *in natura* materials removing the Cr(III) with Q_m of 2.85 mg g^{-1} . The result is remarkable since the adsorbent M. H_2O_2 increased sorption capacity by 15 times with only minor chemical modifications, especially in the case of the trivalent ion Cr(III), which required 3 positive active sites on the adsorbent.

However, Table 8 shows that modified adsorbents exhibited high Q_m rates, but lower K_L rates are observed. The above indicated that the strength of the interaction between adsorbent and adsorbate was not enough for any of the metals studied.

In the adsorption of Cr(III), the modified adsorbents revealed lower rates for K_L , though some studies have shown that activated carbon, an excellent adsorbent for most pollutants, may also have a low interaction to adsorbent/adsorbate (K_L), as Schwantes et al. [2] with K_L rate of 0.010 L mg^{-1} and Rubio et al. [37] with K_L rate of 0.094 L mg^{-1} showed.

It should also be noted that the adsorption procedure laid down by Langmuir's model was favorable due to R_L rates between 0 and 1 [38].

In some cases, adsorption seems to occur in single and multilayer, as shown in Table 8. Good fits to Langmuir's and Freundlich's models have been reported for the adsorption of

Cd(II) by the adsorbent M. H_2SO_4 and adsorption of Pb(II) by M. H_2O_2 .

Nacke et al. [39] report that research on the adsorption of metals by *in natura* *Jatropha* biomass obtained good adjustment (R^2) for both models and suggested the occurrence of mono- or multilayer adsorption, as has been reported for the adsorption of Cr(III) by adsorbent M. H_2O_2 in current study.

Fine adjustments to Freundlich's model were obtained, suggesting multilayer adsorption of Cd(II) by M. H_2SO_4 , Pb(II) by M. H_2O_2 , and M. H_2SO_4 . In the cases above, Freundlich's rate of $n > 1$ is a strong indication of high reactivity of the active sites of the adsorbent [40] and indicates modified adsorbents recommended for the removal of Cd(II) and Pb(II).

When K_f rates were compared, M. H_2SO_4 adsorbent obtained 1.56 mg g^{-1} , or rather 2.6 times higher than that obtained by Rubio et al. [41] with K_f rate of 0.582 mg g^{-1} for the removal of Cd(II) using crambe pie *in natura*.

In the case of the adsorbent M. H_2O_2 for removal of Pb(II) K_f values of 2.51 mg g^{-1} higher than other adsorbents such as *in natura* crambe pie [41] with $K_f = 2.03 \text{ mg g}^{-1}$, biosorbent of *Saccharomyces* [42] with $K_f = 0.03 \text{ mg g}^{-1}$, and even activated carbon synthesized of melon rinds [43] with $K_f = 0.026$ the 0.015 mg g^{-1} were obtained. These results demonstrate that the chemical modifications which resulted in the adsorbent M. H_2O_2 were effective, providing a favorable multilayer adsorption of Pb(II).

4.5. Effect of Temperature on the Adsorption Process. Studies were conducted to evaluate the influence of temperature on modified adsorbents and their relationship in removing Cd(II), Pb(II), and Cr(III). However, it must be underscored that research determined the best temperature for the removal of metals, and that this too would raise operating costs [44], which is impractical. Consequently, the studies aimed at producing information on the thermodynamic nature of the sorption process through ΔG , ΔH , and ΔS parameters.

ΔH rates indicate endothermic ($\Delta H > 0$) or exothermic ($\Delta H < 0$) reaction systems [45]. Results in Table 9 show that the adsorption of Cd(II) by M. H_2O_2 and M. H_2SO_4 and the adsorption of Cr(III) by M. NaOH are endothermic. On the other hand, the adsorption of Cd(II) by M. NaOH, the removal of Pb(II) by M. H_2O_2 , M. H_2SO_4 , and NaOH, and the adsorption of Cr(III) by M. H_2O_2 and M. H_2SO_4 are exothermic processes, according to the negative rates by ΔH .

According to Wan Ngah and Hanafiah [8], when ΔG has negative rates, it indicates the spontaneous nature of the reaction, while positive rates for ΔS indicate an increase in disorder and randomness of solid/solution interface during the sorption process.

Consequently, Table 9 reveals that the adsorption of Cd(II) by M. H_2SO_4 and M. H_2O_2 and the removal of Pb(II) by M. NaOH are not constituted by the spontaneous sorption process, while the adsorption of Cd(II) by M. NaOH and the adsorption of Cr(III) by M. H_2O_2 and M. NaOH constitute spontaneous adsorptive processes due to negative rates by ΔG .

It is worth mentioning that the sorption process may become spontaneous or not depending on the temperature of the medium, such as Pb(II) adsorption by M. H_2O_2 and M. H_2SO_4 , or in the removal of Cr(III) by M. H_2SO_4 . In these cases, ΔG shows negative rates due to lower temperatures and does not tend towards spontaneity of the system with increasing temperature.

According to Wan Ngah and Fatinathan [45], positive rates of ΔS indicate increased randomness disorder and the solid/solution interface during the adsorption process, as occurred in the removal of Cd(II) by M. H_2O_2 , M. H_2SO_4 , and Cr(III) by M. NaOH.

4.6. Acid Elution for Adsorbents Reuse. The elution in an acid solution demonstrates that the modified adsorbents show significant desorption of Cd(II) and Pb(II), allowing its reuse in new adsorption process. Modified adsorbents had the following values for desorption percentage of Cd(II): M. H_2O_2 (60%), M. H_2SO_4 (62%), M. NaOH (74%), and M. *in natura* (63%); and they had the following percentages of desorption of Pb(II): M. H_2O_2 (65%), M. H_2SO_4 (53%), M. NaOH (56%), and M. *in natura* (77%) [36]. The modified and M. *in natura* [2] adsorbents showed no desorption of Cr(III) greater than 3%, even in acid solution 0.1 mol/L HCl, suggesting a strong ligation with this metal with biomass by chemical bounds.

5. Conclusion

The use of modifying agents in cassava peels is an alternative for the production of adsorbents with high metal adsorption capacity (Cd, Pb, and Cr) without burdening the final product.

Results suggest that, in general, the chemisorption of metals (Cd, Pb, and Cr) occurs in monolayer or multilayer or, in some cases, simultaneously.

The modified adsorbents presented better results when compared to the use of M. *in natura* (biosorbent), with increase of 45% in Pb(II) adsorption by M. NaOH and the increase of 1500% of Cr(III) by the use of M. H_2O_2 .

The use of solid waste (cassava peels) as raw material for modified adsorbents production is a relevant alternative for disposal of this waste and even enables added value to waste which is normally disposed of.

Competing Interests

The authors declare that they have no conflict of interests.

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