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## RESEARCH ARTICLE

### CRAMBE PIE MODIFIED FOR REMOVAL OF CADMIUM, LEAD AND CHROMIUM FROM AQUEOUS SOLUTION

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#### ABSTRACT

This study examined the performance of the adsorbents created from the pie of *Crambe abyssinica* Hochst and its adsorption capacity for removal of metal ions Cd(II), Pb(II) and Cr(III) from contaminated water. Firstly, crambe pie was obtained, dried, milled and sifted for standardization of its particle size. The crambe biomass was chemically modified with H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and NaOH by solutions of 0.1 mol L<sup>-1</sup>. After this step were performed the adsorption tests aimed to determine the best conditions of pH, adsorbent mass, and contact time between adsorbent/adsorbate to the removal of the metals Cd, Pb and Cr. From these preliminary results were obtained the adsorption isotherms and thermodynamic parameters, such as  $\Delta H$ ,  $\Delta G$  and  $\Delta S$ . It is observed that the modifying solutions were effective in the modification of adsorbents, resulting in adsorbent materials of high capacity. It is noted an equilibrium time for Cd, Pb and Cr about 40 minutes. By the obtained results can be concluded that the modified crambe pie are excellent adsorbent materials, renewable, with high availability and low cost, being an attractive alternative for industrial use in advanced treatment systems, for removal of metals as Cd, Pb and Cr.

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#### INTRODUCTION

Intensive agriculture has been expanding day by day, reaching new ecosystems and consequently compromising the natural dynamics of the environment. The use of fertilizers and pesticides grows due to the amazing amount of crops in the world. The increase in crops favors the production of grains and food in general, but some consequences are linked to this breakthrough, as the persistence of some compounds in the soil after harvest, such as pesticides and toxic heavy metals from fertilizers (Gonçalves Jr. et al., 2011).

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The crambe (*Crambe abyssinica* Hochst) is an oilseed belonging to the family of Brassicaceae, one striking feature of this culture is the inedible oil content found in the seeds that can reach 36% to 38%, this characteristic associated with facilities of cultivation suggest the culture as a good source to complement the matrix of vegetable oils to produce biofuels such as biodiesel (Pitol et al., 2010). The culture of crambe expresses a productive potential of 1,000 to 1,500 kilograms per hectare, being tolerant to drought and frost after established and has high precocity, those are the main advantages of culture (Pitol, 2008). Nowadays the emphasis on renewable energy promotes the biofuels market, thus increasing the demand for raw materials that can produce biofuels such as crambe.

The by-products arising from the oil extraction of crambe seeds commonly called pie are highly available on market. The fact that it cannot be used as feed even for non-ruminants is due to the presence of substances called glucosinolates that cause damage to the digestive system. However, recently the use of this by-product has been studied as an adsorbent material for removing metal ions from contaminated effluent. Agriculture is one of the most responsible for contamination of water bodies with metal ions. The main releasing metals are fertilizers (Cd, Cr, Pb, Zn), pesticides (Cu, Pb, Mn, Zn), and the waste of large-scale production of bovine, swine and poultry (Cu, As, and Zn) (Gonçalves Jr *et al.*, 2014).

The metals released into the soil are leached into rivers, by laminar erosion or by the flow of surface water from rain, when present in the aquatic environment have free or ionic form, what facilitates their accumulation in fish tissues. The main way of introducing metals such as Cd(II), Pb(II) and Cr(III) in the environment is via contamination of water bodies by human activities such as dumping of municipal wastewater, metallurgy and mining activities, leaching pesticides, among others (Dellamatrice and Monteiro, 2014). It should also be noted that the conventional agricultural system, where the absence of crop rotation is a striking feature, could allow seepage or runoff of metals and consequently contaminate groundwater and rivers, resulting in highly harmful damage to human health, plant and animal. The ongoing need to control the pollutants emitted levels has led to a better study of the processes that make it possible to decrease the concentration of contaminants to tolerable levels assigned by law, such as treatments for adsorption (Vasconcelos *et al.*, 2007), which refers to the accumulation of a substance in a given interface. The purpose of adsorbents for industrial use is to separate or purify a particular chemical species. Various adsorbent materials are used in adsorption techniques to remove organic and inorganic residues (Aklil *et al.*, 2004), being the activated coal the most widely used.

Alternative materials such as by-products and residues from agro-industrial processes has been assessed due to its high availability, accessibility and its high competitiveness, compared to ion exchange resins and activated coal (Valdman *et al.*, 2001), mainly because the coal production costs are very high when considering the treatment of large amounts of effluent (Hsu, 2009). Different types of biomass, such as agricultural by-products, wood, algae, fungi, bacteria among others, also have the capacity to retain metallic ions through adsorption, taking advantage of the commercial resins or activated carbons, being feasible in technical and economic perspective (DiCaprio *et al.*, 2014). Such biomasses when chemically treated with solutions of chemical reactants such as acids or bases, may eventually increase the number of active sites, thereby increasing the contaminant adsorption capacity by means of a low-cost treatment (Miola *et al.*, 2014; Schwantes *et al.*, 2014). Thus, the search for new adsorbent materials is focused on biomass waste, to be economically viable, biodegradable and coming from renewable resources, deserving special mention in this scenario the waste of biodiesel production. The aim of this research was to evaluate the potential use of crambe pie, a solid by-product of biodiesel

agribusiness, as adsorbent chemically modified in the removal of Cd(II), Pb(II) and Cr(III) in aqueous medium.

## MATERIAL AND METHODS

### Adsorbent material and research site

The biosorbent materials used in this study were produced by drying and grinding crambe seed, with extraction of oil by means of chemical extractor (n-hexane), as occurs in the agricultural industry.

The fortified monoelementary solutions with metallic ions Cd(II), Pb(II) and Cr(III) were prepared from salts of cadmium nitrate [ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , P.A.  $\geq 99,0\%$  Sigma-Aldrich], lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ , P.A.  $\geq 99\%$  Sigma-Aldrich], and chromium nitrate [ $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , P.A.  $\geq 99\%$  Sigma-Aldrich]. From monoelementary solutions of  $1000 \text{ mg L}^{-1}$  were prepared other concentrations for each study. The pH was adjusted by adding NaOH  $0,1 \text{ mol L}^{-1}$  e HCl  $0,1 \text{ mol L}^{-1}$ . The adsorption experiments and analysis were performed at the Laboratory of Environmental and Instrumental Chemistry, at the State University of Western Paraná (Unioeste), campus of Marechal Cândido Rondon.

### Preparation and characterization of studied adsorbents

The crambe seeds were submitted to 48 hours at  $60^\circ\text{C}$  in a forced air circulation oven, then they were ground, and the oil was extracted through Soxhlet system (IUPAC, 1988), thereby obtaining pie crambe, which was dried at  $80^\circ\text{C}$  for a period of 24 hours for evaporation of the solvent hexane ( $\text{C}_6\text{H}_{14}$ , nuclear) used in the process. After this step, the milled and dried pie, without oil, was sieved (material retained between 14 and 65 mesh), in order to standardize the particle size, resulted in the adsorbent *in natura* (C. *in natura*). Chemical modifications were performed to C. *in natura*, in order to enhance favorable conditions for adsorption of metals, such as surface contact area, porosity, number of adsorption sites, energy of sorption sites, among others. For that were tested three different chemical reagents, performing washes in C. *in natura* with solutions  $0,1 \text{ mol L}^{-1}$  of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$  and NaOH (Dos Santos *et al.*, 2011; Wan Ngah and Hanafiah 2008; Argun and Dursun 2006).

Thus, solutions of  $0,1 \text{ mol L}^{-1}$  of NaOH,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  were prepared, being added 70 mL of solution in each erlenmeyers of 125 mL containing 7,0 g of material C. *in natura*. The erlenmeyers were accommodated in the thermostatic shaker at  $60^\circ\text{C}$  for 6 hours. Subsequently the modified adsorbents were now abundantly washed with distilled water, to promote the removal of residual reactants still present in the material. Thus, we evaluated three chemical modifications applied to crambe pie, totaling 3 new modified adsorbents C. *in natura* (unmodified, i.e. the biosorbent) C.  $\text{H}_2\text{O}_2$ , C.  $\text{H}_2\text{SO}_4$  and C. NaOH. The characterization of adsorbent materials was carried out by the determination and quantification of surface charges ( $\text{pH}_{\text{PZC}}$ ) and by determination of levels of the constituent elements of its structure. For the quantification of surface charges present in adsorbent materials was determined the point of zero charge ( $\text{pH}_{\text{PZC}}$ ).

The  $pH_{PZC}$  represents the pH that the charge balance on the adsorbent surface is zero (Mimura *et al.* 2010). To perform the characterization of  $pH_{PZC}$  for each one of the adsorbents, were added 50 mg of weight to 50 L of aqueous solutions of potassium chloride (KCl, Vetec, 99%) at  $0.5 \text{ mol L}^{-1}$  with pH values ranging from 2.0 to 9.0, which was adjusted with hydrochloric acid solution (HCl, Vetec, 37%) or sodium hydroxide (NaOH Vetec, 99%), both at a concentration of  $0.1 \text{ mol L}^{-1}$ . After a period of 24 hours stirring at 200 rpm, the final values obtained for pH were measured, resulting in a graph of pH variation *versus* final pH. The point that reach the value zero for x-axis correspond to  $pH_{PZC}$  (Mimura *et al.*, 2010).

The quantification of the elements in the structure of the adsorbent material was made by nitroperchloric digestion (AOAC, 2005), with subsequent determination of the concentration of potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), cadmium (Cd), chromium (Cr) and lead (Pb) by means of flame atomic absorption spectrometry (AAS) (Welz and Sperling, 1999).

### Studies involving adsorbent mass and pH of the medium

Experiments were performed in order to get the optimal mass of adsorbent to be used, as well as more favorable pH for the adsorptive processes. The different masses used in the process varied between 250 mg and 1.250 g for each of the studied adsorbents. To evaluate the effect of modified adsorbent mass and the pH of Cd(II), Pb(II) and Cr(III) solutions, a study was conducted in conjunction (multivariable study), for mass and pH. Univariate tests would not be able to determine the possible interactions between the above parameters.

For this purpose was used a Central Composite Rotational Design (CCRD) for determining the influence of each variable and the possible interaction between them, generating an empirical mathematical model, quadratic, valid within the range tested experimentally (Barros *et al.*, 2010). The masses of adsorbents were evaluated in the range of 250 to 1,250 mg while the pH was evaluated in the range 3.00 to 7.00. Table 1 shows the matrix of CCR planning, displaying the encoded and the actual values of the variables mass of adsorbent and pH for each configuration mass (mg) *versus* pH tested.

**Table 1. Matrix of planning CCRD**

Test	$X_1$	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

These solutions were placed in 125 mL flasks containing the mass of the modified adsorbents (Table 1), and subsequently packed in Dubnoff thermostatic system with constant shaking

at 200 rpm. After conduction of the sorption process in Dubnoff system, the samples were filtered, and aliquots were removed for the determination of concentrations of metals by AAS/Flame (Welz and Sperling, 1999). From the values obtained for the equilibrium concentration was calculated adsorbed amount at equilibrium (Equation 1).

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

In which:  $Q_{eq}$  and  $q$  is the amount of ions adsorbed per g adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $m$  is the mass of the used adsorbent (g),  $C_0$  represents the initial concentration of ion ( $\text{mg L}^{-1}$ )  $C_{eq}$  is the concentration of ion in solution at equilibrium ( $\text{mg L}^{-1}$ ) and  $V$  is the volume used (L). The results obtained in the above tests were tabulated and evaluated according to multivariate analysis using Statistica 5.0 program.

### Effect of contact time between adsorbent and adsorbate (adsorption kinetics)

With the amount of mass set at 200 mg well as pH of 5.00, the respective masses were placed in 125 mL erlenmeyer flasks and added to 50 ml of mono-elementary solutions at a concentration of  $10 \text{ mg L}^{-1}$ . Keeping the physicochemical conditions listed above, tests were performed to evaluate the effect of contact time between adsorbent and adsorbate for subsequent evaluation of metal removal efficiency. The tested times were 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 min. The results were subjected to evaluation by linear models of pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion. The linear equation pseudo-first order is based on the adsorption capacity of the equation and the concentration of the solution, the first order Lagergren model (Equation 2) is called pseudo-first order.

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

In which:  $Q_{eq}$  ( $\text{mg g}^{-1}$ ) and  $Q_t$  ( $\text{mg g}^{-1}$ ) the quantity of adsorbate retained per gram of adsorbent at equilibrium and at time  $t$ , respectively, and  $K_1$  ( $\text{min}^{-1}$ ) is the pseudo-first order kinetic constant. The model mentioned above considers that the occupancy rate of the active sites are proportional to the number of active sites on the adsorbent material (Aksu, 2001). The applicability of pseudo-first order model is checked when you get a log graph line ( $Q_{eq} - Q_t$ ) in function of  $t$  (Ho and McKay, 1999). The pseudo-second order kinetic model (Equation 3) assumes that the process is of chemical nature, involving the participation of valence forces or electron exchange between adsorbent and adsorbate (Ho and McKay, 1999).

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

In which:  $K_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the constant of pseudo-second order rate. Unlike the pseudo-first order model, the model predicts the kinetic behavior over the entire adsorption time range (Aksu, 2001). The kinetic model Elovich (Equation 4) was first proposed by Roginsky and Zeldovich in 1934 and, as Ho and McKay (2004), this model is used with a high frequency to describe the chemisorption of gases in solids.

$$Q_{eq} = a + b \ln t \quad (4)$$

In which:  $a$  and  $b$  are constants, being  $a$  corresponding to rate of initial chemisorption ( $\text{mg g}^{-1} \text{h}^{-1}$ ) and  $b$  indicates the number of suitable sites for the adsorption, which is related to the surface coverage extension and the activation energy of chemisorption ( $\text{g mg}^{-1}$ ) (Witek-Krowiak *et al.*, 2011). The intraparticle diffusion equation (Equation 5), derived from the Fick's law assumes that the spread of the liquid film that surrounds the adsorbent is negligible and only the intraparticle diffusion controls steps in the adsorption process (Yang e Al-Duri, 2005).

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

In which:  $K_{id}$  is the constant of intraparticle diffusion ( $\text{g mg}^{-1} \text{min}^{-1/2}$ ) and  $C_i$  suggests the thickness of the boundary layer effect ( $\text{mg g}^{-1}$ ) (Han *et al.*, 2010).

### Isotherms of adsorption (equilibrium studies)

Studies were also conducted for the construction of isotherms, for this we used the best conditions above, studying now the effect of increasing initial concentrations for metals (5, 20, 40, 60, 80, 100, 120, 140, 160 e 200  $\text{mg L}^{-1}$ ).

It should be noted that the optimal conditions laid down in previous studies were used such as adsorbent mass of 200 mg, pH of the monoelementar solution (Cd, Pb and Cr) of 5.00, and contact time between adsorbent and adsorbate 40 minutes. As in previous cases, the agitation speed was kept constant at 200 rpm in Dubnoff thermostatic system with constant temperature at 25°C. Results were analyzed by linear models of Langmuir and Freundlich. The mathematical model of Langmuir is expressed in its linear form by Equation 6 (Njoku *et al.*, 2011).

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

In which:  $C_{eq}$  is the ion concentration in equilibrium in the solution ( $\text{mg L}^{-1}$ ),  $Q_{eq}$  is the adsorbed amount at equilibrium per unit mass of adsorbent ( $\text{mg g}^{-1}$ ),  $Q_m$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ) and  $b$  or  $K_L$  is the constant related to the strength of adsorbent-adsorbate interactions ( $\text{L mg}^{-1}$ ). The favorability of the isotherm, in other words, the favorable behavior or not can be interpreted by the equilibrium constant parameter ( $R_L$ ) (Hall *et al.*, 1966), which is calculated by Equation 7:

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

In which:  $C_0$  is the maximum value of initial concentration ( $\text{mg L}^{-1}$ ) and  $b$  is the Langmuir constant.

Thus, if the value of  $R_L$  is located between 0 and 1, the adsorption process is favorable. The mathematical model of Freundlich (Equation 8) describes a multilayer adsorption with an exponential distribution of active sites and, therefore, a balance in heterogeneous surfaces (Wan Ngah and Hanafiah, 2008).

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

In which:  $K_f$  is the adsorption capacity ( $\text{mg g}^{-1}$ ) and  $n$  indicates the strength of adsorption and is related to the heterogeneity of the adsorbent surface.

### Effect of temperature on adsorptive process (thermodynamics of adsorption)

In order to assess the effect of temperature on the adsorption process, were conducted at different temperature conditions of the solution (15, 30, 45, 60°C). For this purpose, in 125 ml erlenmeyer flasks were added 200 mg of the adsorbent material, plus 50 mL of contaminant solution at a concentration of 50  $\text{mg L}^{-1}$ , maintaining the other physical and chemical parameters of the steps listed above, such as: pH 5.00 and contact time between adsorbent and adsorbate 40 min. The results were evaluated by linear models for the determination of the thermodynamic parameters:  $\Delta G$ ,  $\Delta H$  e  $\Delta S$ , these parameters being obtained by the equations listed below. The variation of enthalpy ( $\Delta H$ ) indicates the adsorption process is endothermic or exothermic and variation of entropy ( $\Delta S$ ) is related to the irreversibility of the adsorption process (Aksu and İşoğlu, 2005). These parameters can be calculated according to Equations 9 and 10 (Sari *et al.*, 2007; Gonçalves *et al.*, 2008).

$$\Delta G = \Delta H - T \Delta S \quad (9)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

In which:  $K_d$  represents the relationship between the amount adsorbed per unit of adsorbent ( $Q_{eq}$ ) and the concentration in equilibrium in the solution ( $C_{eq}$ ),  $R$  refers to the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature of the system (Kelvin). The values for  $\Delta H$  and  $\Delta S$  were obtained from the graph of  $\ln K_d$  in function of  $1/T$ .

## RESULTS

### Characterization of chemically modified adsorbents

Table 2 shows the values for the elements contents for adsorbents C. *in natura*, C.  $\text{H}_2\text{O}_2$ , C.  $\text{H}_2\text{SO}_4$  and C. NaOH. It is observed in Table 2 that the solutions 0,1  $\text{mol L}^{-1}$  of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$  and NaOH were effective for the extraction of some constituents of the biomass, can be regarded as chemical treatments to the plant material, as Table 1 shows decrease on the concentration of elements K, Ca, Mg, Cu, Zn, Mn, Fe, Cd and Pb.

Figure 1 shows the values obtained for  $\text{pH}_{\text{PZC}}$ , or point of zero charge of the adsorbents: C. *in natura*, C.  $\text{H}_2\text{O}_2$ , C.  $\text{H}_2\text{SO}_4$  and C. NaOH. It is observed in Figure 1 the following values of  $\text{pH}_{\text{PZC}}$  for each studied adsorbent: C. *in natura* 5.67, C.  $\text{H}_2\text{O}_2$  6.00, C.  $\text{H}_2\text{SO}_4$  3.16 and C. NaOH 8.03. This indicates that solutions of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$  and NaOH 0,1  $\text{mol L}^{-1}$  were sufficient to result in chemical modifications to the biomass structure of *crambe pie in natura*, as Figure 1 illustrates the resulting

adsorbents differ in its electric arrangement, that is, as the distribution of surface electrical charges dependent of pH.

**Studies involving adsorbent mass and pH of the medium**

Table 3 presents the results obtained for the levels proposed by delineation Central Composite Rotational Design (CCRD) for the variables “adsorbent mass “versus” pH solution “versus” quantity adsorbed at equilibrium”. Table3.

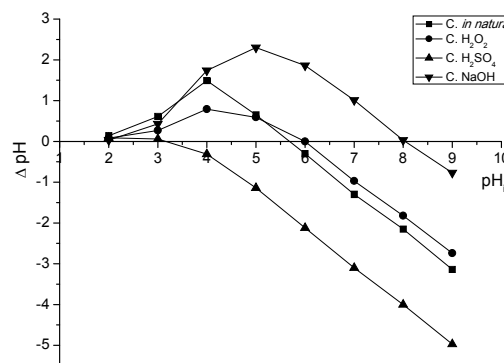
model. It should be noted that the adsorbent C. NaOH to remove Cr(III) showed statistical significance at 1% probability for the source: “adsorbent mass” only on the linear model.

These results show that the adsorbents C. *in natura*, C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH are closely dependent of the quantity of adsorbent available, without depending on the pH (in the studied range).

**Table 2. Average levels of the chemical elements in adsorbents *in natura* and modified with NaOH, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> 0,1mol L<sup>-1</sup>**

Adsorbent	gkg <sup>-1</sup>				mgkg <sup>-1</sup>						
	K	Ca	Mg	Cu	Zn	Mn	Fe	Cd	Pb	Cr	
C. <i>in natura</i>	6.00	15.00	3.40	8.00	56.00	51.60	921.00	0.10	15.30	<LQ	
C. H <sub>2</sub> O <sub>2</sub>	2.37	9.84	2.04	7.70	55.90	43.10	813.60	0.10	10.00	<LQ	
C. H <sub>2</sub> SO <sub>4</sub>	1.54	2.36	0.68	6.00	28.00	6.90	187.20	<LQ	5.40	<LQ	
C. NaOH	5.84	14.15	3.34	5.80	46.10	51.40	894.90	0.10	15.30	<LQ	

LQ (limit of quantification): 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<sup>-1</sup>).



**Figure 1. Point of zero charge (pH<sub>PZC</sub>) of adsorbent *in natura* and modified adsorbents**

**Table 3. Matrix CCRD with quadruplicate at the midpoint and average values of the adsorption of Cd(II), Pb(II) and Cr(III) to adsorbents *in natura* and chemically modified with H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and NaOH solutions**

Tests	Variables		Q <sub>eq</sub> (mg g <sup>-1</sup> ) Cd(II)				Q <sub>eq</sub> (mg g <sup>-1</sup> ) Pb(II)				Q <sub>eq</sub> (mg g <sup>-1</sup> ) Cr(III)			
	Mass (mg)	pH	C. <i>in natura</i>	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. <i>in natura</i>	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. <i>in natura</i>	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH
1	396.39	3.6	0.912	1.184	1.042	0.950	1.152	1.142	1.136	0.956	0.651	1.129	0.747	0.818
2	1103.61	3.6	0.323	0.426	0.357	0.341	0.411	0.404	0.409	0.330	0.227	0.396	0.288	0.199
3	396.39	6.4	0.919	1.210	1.032	0.988	1.141	1.127	1.151	0.909	1.166	0.760	0.940	0.355
4	1103.61	6.4	0.321	0.424	0.350	0.356	0.410	0.405	0.422	0.325	0.424	0.281	0.315	0.071
5	750.00	5.0	0.473	0.634	0.529	0.527	0.612	0.595	0.623	0.476	0.450	0.563	0.559	0.286
6	250.00	5.0	1.479	1.926	1.645	1.586	1.802	1.744	1.880	1.447	1.263	1.718	1.745	1.118
7	750.00	7.0	0.465	0.635	0.532	0.516	0.610	0.603	0.624	0.490	0.633	0.493	0.502	0.428
8	1250.00	5.0	0.278	0.378	0.310	0.307	0.363	0.359	0.375	0.283	0.274	0.335	0.333	0.181
9	750.00	3.0	0.472	0.632	0.541	0.438	0.605	0.609	0.629	0.479	0.415	0.604	0.204	0.481
10	750.00	5.0	0.478	0.633	0.529	0.529	0.608	0.604	0.632	0.476	0.444	0.573	0.563	0.290
11	750.00	5.0	0.482	0.633	0.537	0.519	0.607	0.594	0.632	0.472	0.449	0.576	0.563	0.325
12	750.00	5.0	0.472	0.631	0.532	0.523	0.608	0.602	0.628	0.479	0.444	0.575	0.573	0.326

The results shown in Table 3 were subjected to analysis of variance (ANOVA) (Table 4) in order to find significant difference for the evaluated parameters with respect to the adsorbent *in natura* C. *in natura*, C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH in removing Cd(II), Pb(II) and Cr(III) from contaminated solutions. Significant differences were found at a 1% level (Table 4) for all the studied adsorbents in relation to the variation source: “adsorbent mass”, by linear and quadratic

In Figure 2 are illustrated the response surface for adsorption of Cd(II), Pb(II) and Cr(III) by means of adsorbents C. *in natura*, C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH. It is observed in Figure 2 and Table 4 that the pH ranges studied did not influence the adsorption of Cd(II), Pb(II) or Cr(III), however, it is noted that the higher removal efficiencies of the metals Cd(II), Pb(II) and Cr(III) (measured by the adsorbed amount Q<sub>eq</sub> or Q<sub>ads</sub>) were

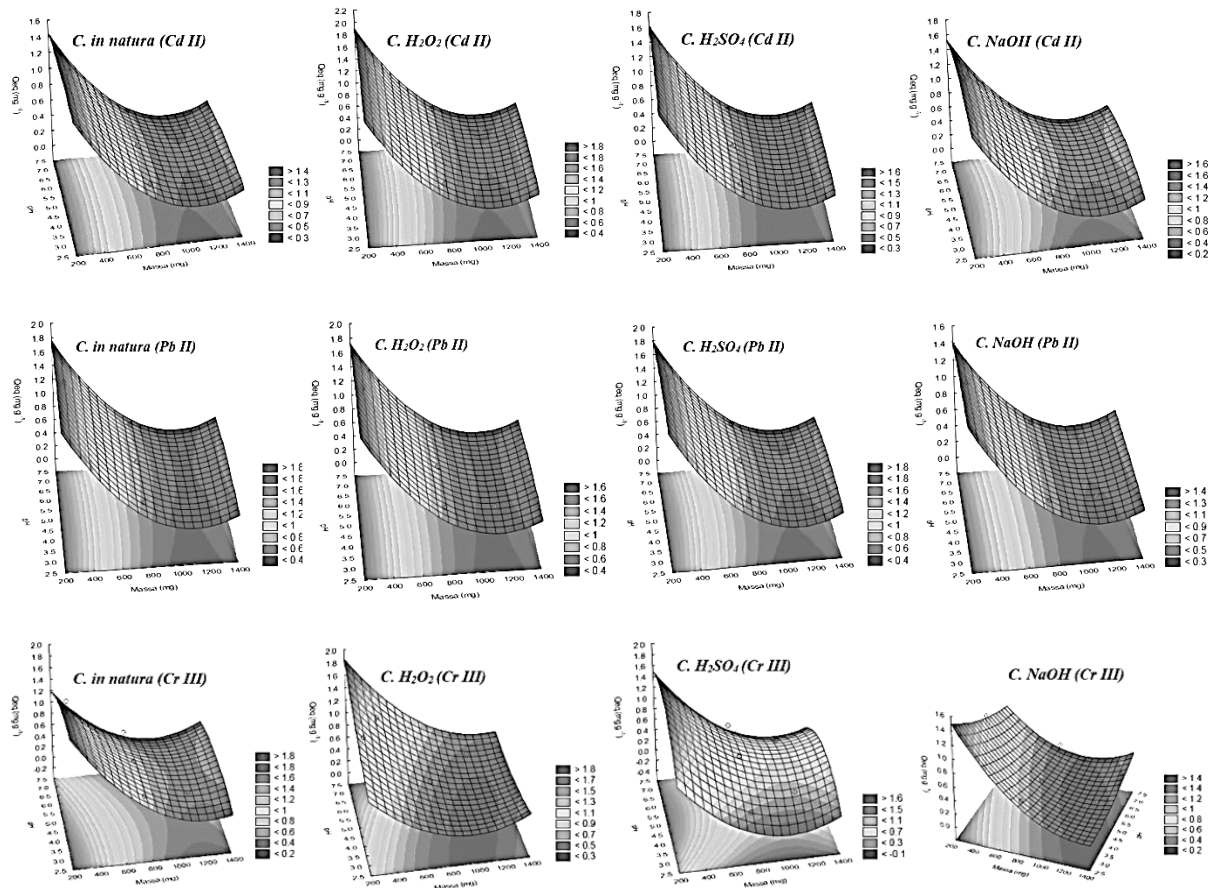
obtained for adsorbent masses closest to 200 mg, in other words, to the smaller masses evaluated.

The graphs shown in Figure 2 are mathematically expressed by the multiple linear regression equations ( $x, y, z$ ) for the removal of Cd(II), Pb(II) and Cr(III) for the modified adsorbent and *in natura* and in Table 5.

Regarding the results of the adsorption kinetics (Figure 3), these were linearized by mathematical models of pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion for the adsorbents C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH, used in removal of Cd(II), Pb(II) and Cr(III) on contaminated water. The obtained kinetic parameters will be discussed below

**Table 4. Mean squares for the influence of adsorbent masses of crambe pie and pH of the solution for the removal of Cd(II), Pb(II) and Cr(III) for adsorbents *in natura* and modified with H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and NaOH**

SV	DOF	Cd(II)				Pb(II)				Cr(III)			
		C. <i>in natura</i>	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. <i>in natura</i>	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. <i>in natura</i>	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH
Mass (L)	1	1.039**	1.741**	1.323**	1.162**	1.537**	1.461**	1.605**	1.020**	0.822**	1.253**	1.187**	0.620**
Mass (Q)	1	0.224**	0.366**	0.275**	0.250**	0.310**	0.286**	0.324**	0.215**	0.151**	0.233**	0.272**	0.097
pH (L)	1	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.129	0.051	0.051	0.055
pH (Q)	1	0.002	0.002	0.001	0.008	0.001	0.000	0.004	0.000	0.006	0.015	0.119	0.004
Mass pH	1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.025	0.016	0.006	0.028
Residue	6	0.006	0.010	0.006	0.007	0.008	0.006	0.012	0.004	0.004	0.020	0.023	0.021
Total	11												



**Figure 2. Response surfaces for the effect of adsorbent mass based on crambe *in natura* and modified *versus* pH of the contaminant solution *versus* adsorbed amount of metal (Cd, Pb and Cr) in equilibrium**

**Adsorption kinetics studies**

The results obtained for removal of the metals Cd(II), Pb(II) and Cr(III) by C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH adsorbents, and the effect of contact time between the modified adsorbents and contaminants monoelementar solutions shown in Figure 3.

The results of the kinetic parameters inherent to the linearization models pseudo-firstorder, pseudo-secondorder, Elovich and intraparticle diffusion are shown in Table 6 and 7.

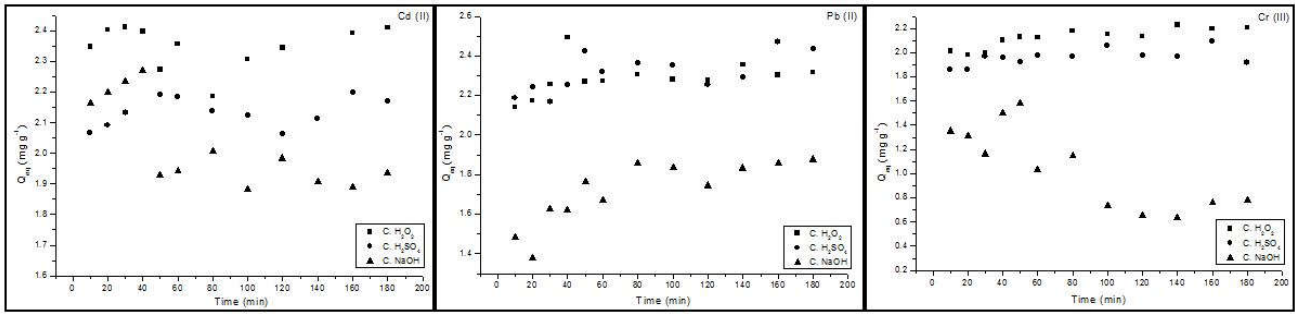


Figure 3. Effect of contaminant monoelemental solution of Cd(II), Pb(II) and Cr(III) and the contact time between adsorbent/adsorbate

Table 5. Multiple linear regressions obtained from the response surfaces for adsorption of Cd(II), Pb(II) and Cr(III) by adsorbents based on crambe pie chemically modified and *in natura*

Cd	<i>C. in natura</i>	$z = 1.8464 - 0.003244x + 0.00000149x^2 + 0.09186y - 0.00885y^2 - 0.0000048xy$	0.970
	C. H <sub>2</sub> O <sub>2</sub>	$z = 2.3808 - 0.0041179x + 0.0000019x^2 + 0.11378y - 0.01006y^2 - 0.000014xy$	0.970
	C. H <sub>2</sub> SO <sub>4</sub>	$z = 2.1801 - 0.0036430x + 0.0000016x^2 + 0.06244y - 0.00658y^2 + 0.0000009xy$	0.974
	C. NaOH	$z = 1.6459 - 0.0033970x + 0.0000015x^2 + 0.20813y - 0.01852y^2 - 0.0000111xy$	0.969
Pb	<i>C. in natura</i>	$z = 2.3342 - 0.0039092x + 0.0000017x^2 + 0.08276y - 0.00871y^2 + 0.0000052xy$	0.974
	C. H <sub>2</sub> O <sub>2</sub>	$z = 2.3573 - 0.0037890x + 0.0000016x^2 + 0.04820y - 0.00562x^2 + 0.0000080xy$	0.978
	C. H <sub>2</sub> SO <sub>4</sub>	$z = 2.2570 - 0.0039609x + 0.0000018x^2 + 0.13110y - 0.01281y^2 - 0.0000013xy$	0.962
	C. NaOH	$z = 2.0687 - 0.0033193x + 0.0000014x^2 + 0.01544y - 0.00346y^2 + 0.000021xy$	0.977
Cr	<i>C. in natura</i>	$z = 2.4237 - 0.0040426x + 0.0000015x^2 + 0.09028y - 0.0241y^2 + 0.0001264xy$	0.927
	C. H <sub>2</sub> O <sub>2</sub>	$z = 1.1635 - 0.0019572x + 0.0000012x^2 + 0.05292y + 0.0155y^2 - 0.0001585xy$	0.975
	C. H <sub>2</sub> SO <sub>4</sub>	$z = 0.0081 - 0.0031501x + 0.0000016x^2 + 0.80203y - 0.0683y^2 - 0.0000830xy$	0.925
	C. NaOH	$z = 2.6947 - 0.0031064x + 0.0000009x^2 - 0.312235y + 0.0683y^2 + 0.000167xy$	0.860

x = adsorbent mass (mg); y = pH of contaminant solution; z = amount of metal adsorbed at equilibrium (mg g<sup>-1</sup>).

Table 6. Kinetic parameters relating to the linear models of pseudo-firstorder, pseudo-secondorder and Elovich, to remove the metals Cd(II), Pb(II) and Cr(III) by adsorbents C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH

Parameters/Adsorbent	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH (Line A)	C. NaOH (Line B)	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH
Pseudo-first order										
$K_1$ (min <sup>-1</sup> )	0.0176	-0.0050896	0.000808	x	-0.0030169	-0.0119525	-0.0177561	-0.0129658	0.00137001	0.01091622
$Q_{eq}$ (cal.) (mg g <sup>-1</sup> )	0.0215	0.1329382	0.304319	x	0.28920779	0.31867647	0.44806394	0.24617276	0.11634561	0.233367299
$R^2$	0.4633	0.3102	0.0782	x	0.6744	0.9518	0.8234	0.9671	0.2979	0.9147
Pseudo-second order										
$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.4712	-0.2214365	1.324414	x	1.32875299	0.20670057	0.12622977	0.23544531	1.29165940	-0.17247076
$Q_{eq}$ (cal.) (mg g <sup>-1</sup> )	2.1623	1.89207598	2.300013	x	2.31679911	2.41493395	1.89204018	2.22103766	1.99290525	0.695270078
$R^2$	0.9985	0.9984	0.9856	x	0.99932	0.99638	0.99763	0.9995	0.9967	0.9226
Elovich										
a (mg g <sup>-1</sup> h <sup>-1</sup> )	2.4212	2.0022	2.08031	2.0053	2.0834	1.77349	1.0971	1.74437	1.76779	1.79752
b (g mg <sup>-1</sup> )	-0.0081	0.0427	0.05138	-0.01831	0.04502	0.13148	0.1522	0.09367	0.04432	-0.22517
$R^2$	0.1098	0.9359	0.9994	0.2434	0.8914	0.9618	0.8375	0.9089	0.9089	0.795
$Q_{eq}$ (exp.) (mg g <sup>-1</sup> )	2.319	2.120	2.028	2.028	2.286	2.313	1.712	2.120	1.959	1.054

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

Table 7. Results of the adsorption kinetics of Cd(II), Pb(II) and Cr(III) linearized by intraparticle diffusion model

Adsorbents	Intraparticle diffusion	Cd(II)		Pb(II)	Cr(III)
		Line A	Line B		
C. H <sub>2</sub> O <sub>2</sub>	$K_{id}$ (g mg <sup>-1</sup> min <sup>-1/2</sup> )	-0.0027	x	0.01308	0.03075
	$C_i$ (mg g <sup>-1</sup> )	2.40158	x	2.15326	1.8887
	$R^2$	0.0715	x	0.7659	0.9784
C. H <sub>2</sub> SO <sub>4</sub>	$K_{id}$ (g mg <sup>-1</sup> min <sup>-1/2</sup> )	0.02591	-0.02149	0.03103	0.02386
	$C_i$ (mg g <sup>-1</sup> )	2.0111	2.33651	2.05595	1.78741
	$R^2$	0.9945	0.6309	0.9337	0.9466
C. NaOH	$K_{id}$ (g mg <sup>-1</sup> min <sup>-1/2</sup> )	0.02559	0.00258	0.0326	-0.07797
	$C_i$ (mg g <sup>-1</sup> )	2.11283	1.92215	1.45927	1.54393
	$R^2$	0.9729	0.0912	0.8015	0.928

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

The intraparticle diffusion model assumes the occurrence of diffusion of the adsorbate particle (in this case Cd, Pb and Cr) into the adsorbent particle (C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH). In the present study, for adsorbents C. H<sub>2</sub>SO<sub>4</sub> e C. NaOH in removing Cd(II) (Table 7), was realized the fragmentation of the line in two segments in order to observe the diffusion model adjustment in at least one of the evaluated ranges.

When these data are compared, as observed for Cr(III) adsorption, the obtained results suggest the occurrence of mono and multilayers when is employed C. H<sub>2</sub>O<sub>2</sub>, because in this case occurs good mathematical adjustments to Langmuir and Freundlich. Such behavior, as well as other linear parameters of these mathematical models will be discussed further ahead.

**Table 8. Parameters referred to the linear models for the Langmuir and Freundlich for adsorption of Cd(II), Pb(II) and Cr(III) by modified adsorbents of crambe**

Parameters		C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH	C. H <sub>2</sub> O <sub>2</sub>	C. H <sub>2</sub> SO <sub>4</sub>	C. NaOH
		Cd(II)			Pb(II)			Cr(III)		
Langmuir	Q <sub>m</sub>	21.949	18.437	31.636	-12.102	23.674	-9.454	8.855	5.706	14.358
	K <sub>L</sub>	0.005	0.080	0.009	-0.129	0.012	-0.325	0.052	-0.014	0.006
	R <sub>L</sub>	0.505	0.059	0.359	-0.040	0.298	-0.016	0.088	-0.540	0.456
	R <sup>2</sup>	0.987	0.991	0.992	0.521	0.996	0.945	0.986	0.973	0.987
Freundlich	K <sub>f</sub>	3.634	1.042	1.352	1.526	6.489	0.220	1.420	0.226	4.460
	n	1.678	1.664	0.892	1.131	3.260	0.666	1.277	0.960	1.903
	R <sub>2</sub>	0.934	0.932	0.929	0.973	0.951	0.978	0.975	0.943	0.916

Q<sub>m</sub> (mg g<sup>-1</sup>): maximum adsorption capacity; K<sub>L</sub> or b (L mg<sup>-1</sup>): constant related to the strength of adsorbent/adsorbate interaction; R<sub>L</sub>: Langmuir constant; R<sup>2</sup>: coefficient of determination; K<sub>f</sub> (L mg<sup>-1</sup>): related to the adsorption capacity; n: related to the heterogeneity of the solid.

**Table 9. Thermodynamic parameters for crambe pie adsorbent in removing Cd(II), Pb(II) and Cr(III)**

Materials	Temp. °C	Cd(II)					Pb(II)					Cr(III)				
		Q <sub>eq</sub>	ΔG	ΔH	ΔS	R <sup>2</sup>	Q <sub>eq</sub>	ΔG	ΔH	ΔS	R <sup>2</sup>	Q <sub>eq</sub>	ΔG	ΔH	ΔS	R <sup>2</sup>
C. H <sub>2</sub> O <sub>2</sub>	15	8.2	1.6				10.2	-0.3				10.3	-0.4			
	25	8.7	0.4				7.7	0.9				9.4	0.2			
	35	11.0	-0.8	36.4	120.9	0.82	7.7	2.1	-35.3	-121.6	0.99	8.9	0.8	-17.7	-60.3	0.82
	45	11.2	-2.0				6.7	3.3				8.9	1.5			
	55	11.8	-3.2				5.4	4.5				9.8	2.1			
C. H <sub>2</sub> SO <sub>4</sub>	15	6.5	3.6				10.8	1.2				9.8	0.2			
	25	6.1	3.4				9.3	0.9				8.6	0.4			
	35	6.9	3.3	7.5	13.7	0.85	9.3	0.6	10.8	33.5	0.82	9.4	0.5	-4.1	-14.8	0.80
	45	6.6	3.1				9.5	0.2				9.2	0.7			
	55	7.3	3.0				10.1	-0.1				9.4	0.8			
C. NaOH	15	10.9	-2.4				8.9	6.1				12.2	-6.5			
	25	11.5	-2.1				3.8	5.7				12.3	-7.5			
	35	10.5	-1.7	-13.2	-37.5	0.65	3.8	5.3	18.8	44.0	0.90	12.1	-8.4	20.2	92.9	0.99
	45	10.7	-1.3				4.9	4.8				12.1	-9.3			
	55	11.4	-0.9				5.7	4.4				12.3	-10.3			

Q<sub>eq</sub> (mg g<sup>-1</sup>); ΔG (KJ mol<sup>-1</sup>); ΔH (KJ mol<sup>-1</sup>); ΔS (J mol<sup>-1</sup> K<sup>-1</sup>)

## Equilibrium studies

The results obtained for equilibrium adsorption of Cd(II), Pb(II) and Cr(III) for the modified adsorbents of crambe pie were used to build the adsorption isotherms. The results of this study were linearized by linear models of Langmuir and Freundlich, as shown in Table 8. When analyzing the obtained mathematical adjustments (Table 8) is observed the predominance of good mathematical adjustments for Langmuir, suggesting the monolayer adsorption of Cd(II), Pb(II) and Cr(III).

This behavior, which suggests the occurrence of metal monolayer adsorption can be clearly observed by values of R<sup>2</sup> on the following modified adsorbents: C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH in adsorption of Cd(II), C. H<sub>2</sub>SO<sub>4</sub> in adsorption of Pb(II), and C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH in adsorption of Cr(III). However, it also noted that in some specific cases occur good mathematical adjustments to the model Freundlich, suggesting occurrence of multilayer adsorption, mentioning C. H<sub>2</sub>O<sub>2</sub> and C. NaOH for Pb(II) adsorption, and C. H<sub>2</sub>O<sub>2</sub> for adsorption of Cr(III).

## Thermodynamic studies

Based on previous studies here above, we evaluated the influence of temperature to the removal process of the metals Cd(II), Pb(II) and Cr(III) through the use of modified adsorbents C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH, and such results are presented in Table 9. By the obtained Q<sub>eq</sub> values, it is observed that each modified adsorbent was influenced by the temperature increase. Important to note that for removal of Cd(II), the adsorbents C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH showed higher removal with increasing system temperature.

By contrast, it is observed that for removal of Pb(II), the adsorbents C. H<sub>2</sub>O<sub>2</sub>, C. H<sub>2</sub>SO<sub>4</sub> and C. NaOH show reduction of amount adsorbed (Q<sub>eq</sub>) with elevation of the system temperature. Other modified adsorbent did not present large difference in the amount of adsorbed metal versus system temperature. It should also be noted that other obtained thermodynamic parameters shown in Table 9 will be discussed in the following topics.



## DISCUSSION

### Characterization of modified adsorbents

Table 2 shows that the concentrations of chemical elements constituents of *Crambe pie in natura* (*C. in natura*) has been changed through the use of modifier solution  $0.1 \text{ mol L}^{-1}$  of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$  e  $\text{NaOH}$ . Also observed that the modifying agents ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ ) caused changes to the electrical potential of the material *in natura*, i.e., the point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of the modified adsorbent was moved, mention: *C. in natura* 5.67, *C. H<sub>2</sub>O<sub>2</sub>* 6.00, *C. H<sub>2</sub>SO<sub>4</sub>* 3.16 and *C. NaOH* 8.03. According to Tagliaferro *et al.* (2011), the adsorption of cations, in this case Cd(II) ions, Pb(II) and Cr(III) should be favored by pH of the medium above the  $\text{pH}_{\text{PZC}}$ , since in these cases the surface of the adsorbent has predominance of negative charges. In this sense, the lower the values of  $\text{pH}_{\text{PZC}}$ , most favored will be the adsorption of cations by the modified adsorbent.

However, it is noteworthy that  $\text{pH}_{\text{PZC}}$  is presented as indicative of the electric potential of adsorbent, influencing the adsorption process. Important to point out that many other factors affect the adsorption process, such as the contact time between adsorbent/adsorbate, the size of the adsorbent pores, the affinity between adsorbate/adsorbent, among many others. Such results are of great interest because they demonstrate that the simple washing of vegetable residual biomass with chemical agents, with added energy to the system ( $60 \text{ }^\circ\text{C}$ ) can cause deep chemical modifications to biomass. It should be noted that these modifications are favorable or unfavorable to the adsorption process by further studies, once that adsorption process tends to be specific for each adsorbent/adsorbate.

### Studies involving adsorbent mass and pH of the medium

The smaller evaluated masses (200 mg) were more effective in removing the metals Cd(II), Pb(II) and Cr(III) by the adsorbent *in natura*, *C. H<sub>2</sub>O<sub>2</sub>*, *C. H<sub>2</sub>SO<sub>4</sub>* e *C. NaOH*, as illustrated in Figure 2. According to Meneghel *et al.* (2013) and Rubio *et al.* (2013a) in some cases may occur a decrease in the amount adsorbed due to formation of agglomerates which can reduce the total surface area and therefore the number of active sites available for the process. As it is observed in Figure 2, the modified adsorbents showed higher values of  $Q_{\text{eq}}$ , when compared to the *C. in natura* in adsorption of Cd(II) and Cr(III). Deserving emphasis adsorbent *C. H<sub>2</sub>O<sub>2</sub>* in removing Cd(II) and Cr(III) ( $1.9$  and  $1.8 \text{ mg g}^{-1}$ ), respectively. Such removal is 26% and 33% higher than the adsorbent *C. in natura*, for Cd(II) and Cr(III), respectively.

These results demonstrate that, in general, at low metal concentrations ( $10 \text{ mg L}^{-1}$ ) chemical modifications applied to biomass generates more efficient adsorbents for the removal of these metals, especially the adsorbent *C. H<sub>2</sub>O<sub>2</sub>*, which had the highest averages. Regarding the adsorption of Pb(II), the adsorbent *C. H<sub>2</sub>SO<sub>4</sub>* presented  $Q_{\text{eq}}$  value only 2% greater than *C. in natura*, and the remaining adsorbents showed similar results or slightly below this.

### Adsorption kinetics studies

According to the obtained results for adsorbents *C. H<sub>2</sub>O<sub>2</sub>*, *C. H<sub>2</sub>SO<sub>4</sub>* and *C. NaOH* to remove Cd(II), Pb(II) and Cr(III), it is observed that after 40 minutes of stirring, the system enters in kinetic balance. There was no significant increase in adsorption rates of these metals for time intervals longer than 40 min. The pseudo-first order model (Table 6) did not show good mathematical adjustment ( $R^2$  values) for removal of Cd(II), Pb(II) and Cr(III) by the modified adsorbents (*C. H<sub>2</sub>O<sub>2</sub>*, *C. H<sub>2</sub>SO<sub>4</sub>* e *C. NaOH*). Thus, such model is unsatisfactory at predicting the observed sorption phenomenon. In contrast, the model of pseudo-second order presented excellent values of  $R^2$ , very close to 1, which is an indication that the model fits on the observed experimental data. The model of pseudo-second order suggests that the adsorption is primarily of chemical nature, with covalent chemical bonds between the adsorbent/adsorbate (Farooq *et al.*, 2011). It should be noted that for proper interpretation of kinetic parameters (Table 6 and 7), besides the values of determination coefficient ( $R^2$ ) must show good adjustment, it is necessary that the  $Q_{\text{eq (cal)}}$  values are close to the experimental values [ $Q_{\text{eq (exp)}}$ ] (Febrianto *et al.*, 2009). In this regard, the model of pseudo-second order present once again best adjustment, because the calculated values [ $Q_{\text{eq (cal)}}$ ] by the model are very close to those obtained experimentally ( $Q_{\text{eq exp}}$ ).

The model Elovich showed good mathematical adjustment only for the adsorption of Cd(II) by *C. NaOH* (Line A). In this particular case, the line is fractionated into two (Line A and Line B), seeking better fit for at least some range of evaluated time. From the results, it is observed that, for the adsorption of Cd(II) using *C. NaOH*, at the initial instants, occurs predominance of chemisorption, as proposed by Elovich model. According to Tseng *et al.* (2003), the model of Elovich is usually used to evaluate the gas chemisorption on solid surfaces without desorption products, because in these cases adsorption rates decrease with time due to the increase of the contact surface. Although the present experiment employs liquid and not gaseous fluids, similar behavior was observed in this particular case, at the beginning of the adsorption process while the adsorption rate decreased with time.

With respect to intraparticle diffusion model, the evaluated time was fragmented in attempt to observe the adsorbate movement phenomenon into the adsorbent particle, as can be seen in Table 7 for adsorption of Cd(II) by adsorbents *C. H<sub>2</sub>SO<sub>4</sub>* and *C. NaOH*. Thus, the data are best represented by two linear stages, while the initial phase is the boundary layer effect, with external mass transfer, where Cd(II) ions are rapidly adsorbed by the adsorbent *C. H<sub>2</sub>SO<sub>4</sub>* and *C. NaOH*. After a certain time, the speed of adsorption decreases, resulting in the second phase, which refers to the diffusion of molecules to the innermost adsorption sites of the adsorbent (Neta *et al.*, 2012). According to the experimental data shown in Table 7, in the early stages there is a fast adsorption of Cd(II) by material *C. H<sub>2</sub>SO<sub>4</sub>* and *C. NaOH*, with good mathematical adjustments ( $R^2$ ), suggesting the occurrence of movement of Cd particles on the surface of *C. H<sub>2</sub>SO<sub>4</sub>* and *C. NaOH* (Line A), occurring shortly after, the movement of the particles to the inner regions of the adsorbent, i.e., the

intraparticle diffusion itself (Line B). In similar research, Rubio *et al.* (2013a), obtained values for  $K_{id}$  of:  $0.013 \text{ g mg}^{-1} \text{ min}^{-1/2}$  for *crambe in natura* for adsorption of Cd(II), lower values than the obtained here ( $0.026 \text{ g}$  and  $0.025 \text{ mg}^{-1} \text{ min}^{-1/2}$  respectively for C.  $\text{H}_2\text{SO}_4$  and C. NaOH for adsorption of Cd), showing that the modified adsorbent had higher rates of intraparticle diffusion than C. *in natura*. Likewise, when the results obtained for adsorption of Cr(III) for *crambe in natura*,  $0.05 \text{ g mg}^{-1} \text{ min}^{-1/2}$  (Rubio *et al.*, 2013b), we observed that the values obtained of  $K_{id}$  for the present experiment are quite close  $0.03 \text{ g mg}^{-1} \text{ min}^{-1/2}$ .

Nevertheless, when comparing the  $C_i$  values, kinetic parameter that refers to estimated thickness of the boundary layer effect for diffusion ( $\text{mg g}^{-1}$ ), it is observed that the use of modified adsorbents present much higher values of  $C_i$  than those cited in bibliography. Rubio *et al.*, (2013a) found  $C_i$  values of approximately 0.70 for Cd, in current research when employed C.  $\text{H}_2\text{SO}_4$  and C. NaOH on adsorption of Cd(II), there were obtained the following values for  $C_i$ : 2.01 and  $2.11 \text{ mg g}^{-1}$ . This result shows that by employing the adsorbents C.  $\text{H}_2\text{SO}_4$  and C. NaOH in medium containing Cd(II), the intraparticle diffusion process occurs within the first moments of the sorption process and in occurs in a rapid manner.

### Equilibrium studies

As seen in Table 8, in general the results suggest the occurrence of monolayer adsorption of Cd(II) and Cr(III) by C.  $\text{H}_2\text{O}_2$ , C.  $\text{H}_2\text{SO}_4$  and C. NaOH, due to the good mathematical adjustments obtained for the Langmuir model. It is noteworthy in this context, the adsorbent C. NaOH, which showed the highest values for  $Q_m$  parameter:  $31.63$  and  $14.35 \text{ mg g}^{-1}$  for adsorption of Cd(II) and Cr(III) (Table 8). When compared to the values obtained by Rubio *et al.*, (2013a), the maximum observed value was  $19.34 \text{ mg Cd(II)}$  per g of C. *in natura*, showing that, in the present study, the adsorbent C. NaOH showed 38% higher adsorption capacity Cd(II). In relation to adsorption of Cr(III), the adsorbent C. *in natura* evaluated by Rubio *et al.*, (2013b), was only  $6.89 \text{ mg g}^{-1}$  for the parameter  $Q_m$ , compared to  $14.35 \text{ mg g}^{-1}$  adsorbed by C. NaOH, i.e., the modified adsorbent showed monolayer adsorption capacity 51% higher than the *in natura* material. In general, Table 8 shows that the modified adsorbents showed higher  $Q_m$  values, however, lower  $K_L$  values are observed, indicating that the strength for the interaction between adsorbent/adsorbate are not strong for any of the metals studied.

In adsorption of Pb(II), it is observed that the adsorbents C.  $\text{H}_2\text{O}_2$  and C. NaOH have best fit ( $R^2$ ) by Freundlich model, suggesting Pb(II) multilayer adsorption. While the adsorbent C.  $\text{H}_2\text{SO}_4$  presented best fit by Langmuir, suggesting monolayers of Pb(II). It is noteworthy that in the case of C.  $\text{H}_2\text{SO}_4$  for adsorption of Pb(II) was obtained  $Q_m$  value of  $23.67 \text{ mg g}^{-1}$ , which was the second largest adsorption capacity of all the adsorbents tested in this experiment.

It should also be noted that the adsorption procedure foreseen by the Langmuir model is favorable when  $R_L$  varied between 0 and 1 (Bhattacharyya and Sarma, 2003), as noted in Table 8 for cases where Langmuir showed satisfactory mathematical adjustment, that is, in large majority of cases.

The adsorbents C.  $\text{H}_2\text{O}_2$  and C. NaOH for removal of Pb(II) showed lower values of  $K_f$  ( $1.13$  and  $0.66 \text{ L mg}^{-1}$ ) compared to the values obtained by Rubio *et al.*, (2015) using the C. *in natura* ( $2.09 \text{ L mg}^{-1}$ ), demonstrating that, in this case, the modified adsorbents show reduced capacity for multilayer adsorption. It is also observed that C. NaOH presents value of  $n$  lesser than "1", which is a strong indication of low reactivity of the active sites of the adsorbent (Gonçalves Jr. *et al.*, 2012), setting this particular case a modified adsorbent not recommended for the removal of Pb(II). The values in Table 8 indicate the occurrence of mono and multilayer adsorption of Cr(III) by C.  $\text{H}_2\text{O}_2$  since the Langmuir model and Freundlich have satisfactory values of  $R^2$ . To evaluate the adsorption of metals by biomass *in natura* of *Jatropha*, Nacke *et al.* (2013) obtained good adjustment ( $R^2$ ) for both models, suggesting the occurrence of adsorption in mono and multilayer, as is observed for the adsorption of Cr(III) by the adsorbent C.  $\text{H}_2\text{O}_2$  in the present study.

### Thermodynamic studies

The study of temperature influence on sorption systems is not intended to determine the optimal temperature for the removal of metals, because it would greatly increase the operating costs (Crini and Badot, 2008). Such studies aim to bring out information concerning the thermodynamic nature of sorption process, through the  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  parameters. According to the values of the thermodynamic parameters, it is observed for the removal of Cd(II) by C.  $\text{H}_2\text{O}_2$  and C.  $\text{H}_2\text{SO}_4$  positive values of  $\Delta H$ , in other words, an endothermic system that absorbs heat from the reaction medium (Wan Ngah and Fatinathan, 2010). Similar results are found for the removal of Pb(II) by C.  $\text{H}_2\text{O}_2$  and C. NaOH and adsorption of Cr(III) by C. NaOH, in all these cases positive values for  $\Delta H$  indicate endothermic sorption systems. In all other cases negative values for  $\Delta H$  occur, indicating that the adsorption of metals by these adsorbents are from exothermic nature, i.e., with the release of heat (Wan Ngah and Fatinathan, 2010).

According to Wan Ngah and Hanafiah (2008), negative values for  $\Delta G$  indicate spontaneous nature of the reaction, while positive values for  $\Delta S$  indicate an increase in disorder and randomness of solid/solution interface during the sorption process.

Thus, in Table 9 it is observed that the adsorption of Cd(II) and Cr(III) by C. NaOH occurs spontaneously, i.e., without free energy absorption, according to the negative values of  $\Delta G$ .

It should also be noted that in some cases the sorptive phenomenon can be spontaneous or not depending on the temperature of the medium, examples are the adsorption of Cd(II) by C.  $\text{H}_2\text{O}_2$ , Pb(II) by C.  $\text{H}_2\text{O}_2$  and C. NaOH, and Cr(III) by C.  $\text{H}_2\text{O}_2$ . In these cases, the  $\Delta G$  assumes negative values from a given temperature, indicating the spontaneity of adsorption for this condition.

Positive values for  $\Delta S$  indicate an increase in disorder and randomness of solid/solution interface during the sorption process (Wan Ngah and Fatinathan 2010), as occurred in the removal of Cd(II) by C.  $\text{H}_2\text{O}_2$  and C.  $\text{H}_2\text{SO}_4$ , Pb(II) by C.  $\text{H}_2\text{SO}_4$  and C. NaOH, Cr(III) by C. NaOH.

## Conclusion

The obtained results at the current research indicate that the modified adsorbents of crambe pie are excellent alternatives for removal of Cd(II), Pb(II) and Cr(III) in contaminated water, with higher capacities for removal of these pollutants when compared to the use of the natural adsorbent. The chemical modifications applied to crambe pie profoundly influenced the new adsorbents, making them, in general, superiors to the use of biomass in natura as biosorbent.

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