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Pb^{2+} ADSORPTION FROM AQUEOUS SOLUTIONS ON ACTIVATED CARBONS OBTAINED FROM LIGNOCELLULOSIC RESIDUES

L. Giraldo[1] and J. C. Moreno-Piraján[2*]

[1]Universidad Nacional de Colombia, Departamento de Química,
Facultad de Ciencias, Grupo de Calorimetría, Bogotá, Colombia.
[2]Universidad de los Andes, Department of Chemistry, Sciences Faculty, Group of
Research on Porous Solids and Calorimetry, Phone/Fax: +(57) (1) 3394-94949
Carrera 1 No. 18 A 10 Bogotá, Colombia.
E-mail address: jumoreno@uniandes.edu.co

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Abstract - Activated carbons obtained from cane sugar bagasse (ACB), African palm pit (ACP) and sawdust (ACS) were prepared through an impregnated with HNO_3 and thermal treatment in an atmosphere in N_2/steam water at 1173 K. Adsorption isotherms of N_2 at 77 K and of CO_2 at 273 K were determined for the activated carbons for which surface area and pore volume values were from 868 to 1100 m^2g^{-1} and from 0.27 to 0.55cm^3 g^{-1}, respectively. These results were correlated, with the ones obtained for adsorption the adsorption isotherms of Pb^{2+} in aqueous solutions. Impregnation of the lignocellulosic materials with nitric acid produced acid-type activated carbons with total acid site contents between 4.13 and 6.93 mmol g^{-1} and pH at the point of zero charge values between 2.7 and 4.1, which were within range of the adsorption, at different pH values, since they determined, the surface charge of the activated carbons. Adsorption isotherms of Pb^{2+} at different pH values (2-8) at 298 K were determined. The ion adsorption capacity on ACB, ACP and ACS were 13.7, 15.2 and 17.5 mg.g^{-1}, respectively. Experimental data were fitted to the Langmuir and Freundlich models and all cases the former fit better. The highest values for the quantity adsorbed on the monolayer, qm, were at pH 4, whereas the surface, charge of activated carbons was negative and the lead species mainly present was Pb^{2+}. For higher pHs, the quantity of Pb^{2+} adsorbed decreased, and this had an important effect on adsorption, the surface characteristics of the solids and the hydroxilated lead species that were formed in the system.
Keywords: Adsorption; Activated carbon; Lead(II); Carboxylic sites; Lignocellulosic residues.

INTRODUCTION

Because of its hazardousness, water pollution by heavy metals is considered a serious menace to the environment and especially to human health. Natural waters can be contaminated by metal ions as a result of residual discharges from industries or mining activities (Reddad 2002). The most common toxic metals found in wastewater are copper, cadmium, chromium, nickel, zinc and lead.

The contamination of water by heavy metals has increased over the last few decades due to industrial processes and the development of new technologies. The importance of study of different ways in which heavy metals can be removed from water lies in their toxicity, persistence and accumulation in living organisms.

One of most common toxic metals found in waters waste is leas, which is toxic even at a trace level (Johns 1998). In Figure 1 a diagram of lead species in aqueous solution as a function of pH, is shown. According to Fig. 1, at a pH of about 6, the predominant species is Pb^{2+} and $Pb(OH)_{2(s)}$ and $PbOH^+$ (soluble species) start to form.

Between 7 and 12, the most common species is solid hydroxide and soluble forms $Pb(OH)^{3-}$ and $Pb(OH)_4^{2-}$ (Radovic 2000) begin to appear.

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*To whom correspondence should be addressed

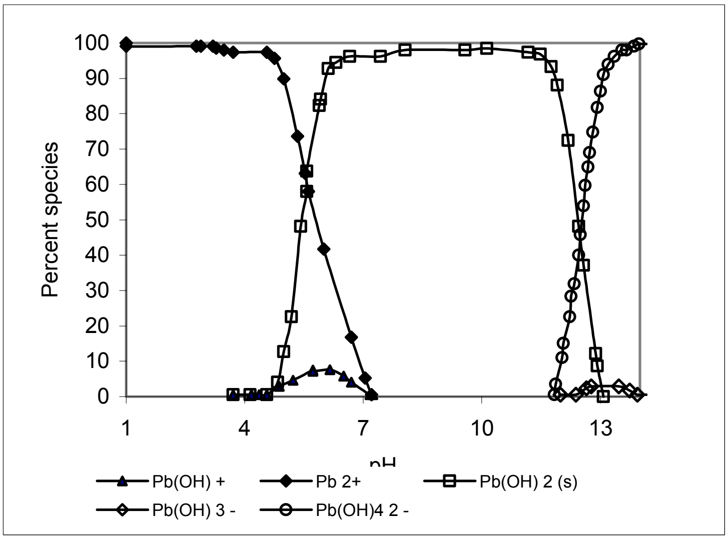

Figure 1: Lead species as a function of pH

Although there are several methods used for the removal of heavy metals from waters, one of the most effective is adsorption on activated carbon, which is a versatile adsorbent due to its large specific surface, pore size distribution and the presence of different functional groups on its surface. The activated carbons that are used for liquid phase adsorption must have a given volume of macropores to facilitate the diffusion of liquids into smaller pores. Activated carbon is the most versatile adsorbent because of its large area, polymodal porous structure (essentially microporous), high adsorption capacity and variable surface chemical composition. As a consequence, there are numerous applications in many fields, for example in gas or liquid phases. (Rodríguez-Reinoso 1997).

Therefore, it is necessary to investigate and develop new adsorbent materials that inexpensive and highly capable of retaining heavy metals by adsorption. Thus, the production of activated carbon from agricultural or agroindustrial waste materials has been the purpose of several studies, among which we can mention activated carbons prepared from nut shells (Kim 2001), rice husks (Yalcin and Sevinc 2000), peach stones (Bello 1999), cane sugar bagasse (Girgis 1994), fruit rind (Namasivayam and Kadirvelu 1997) and peanut husks (Periasamy and Namasivayam 1994).

As agricultural by products are produced in large quantities, their cost is low and is their disposal pose a serious problem. They become an advantageous starting material for obtaining several types of carbonaceous materials; for example, where is produced, several hundreds of tons of cane sugar bagasse wastes may be produced per day and these constitute cellulosic material whose carbon content can be enriched by heat treatment that enables the formation of a number of pores of different sizes, depending on the activation method (Wing and Sessa 1997). Agricultural lignocellulosic wastes have been widely studied and shown to be good precursors for the production of activated carbon for the removal of metal ions from aqueous solutions (Cordero 2001).

It is also known that the activated carbons that are most effective for the adsorption of positively charged species are the oxidized carbons with functional groups of oxygen on their surfaces that play a role as ion exchangers. The chemical composition of the activated carbon has an impact on its properties; carbons located on the ends of an aromatic layer are likely to form C-O bonds, so a appreciable amount of oxygen and other atoms can be added onto the activated carbon surface and thus, the development of acid groups can take place with oxygen (air) or other oxidizing compounds.

In this study, three lignocellulosic materials were chosen as precursors, which were chemically activated by the use of nitric acid as activating agent. The activated carbons thus obtained have a high adsorption capacity for the Pb^{2+} ions. The adsorption capacity for this ion is associated with the type and number of oxygenated groups developed on the surfaces of the different carbons obtained. Results on the effect of nitric acid on the texture and surface chemistry of each carbon obtained are presented; in addition, how the adsorption capacity of the Pb^{2+} ion in the activated carbons prepared is affected by varying the pH of the solution.

EXPERIMENTAL

Pre-Treatment of Raw Material

The precursors, cane sugar bagasse, African palm pit and sawdust, were sieved to give particles of an average diameter of 0.551 mm (U.S. meshes -30 +50). These materials were washed several times with distilled water and then dried for 24 hours in an oven at 90ºC.' Finally, they were packaged in dry and closed plastic containers.

Activated Carbons Obtained by Chemical Activation

For chemical activation, cane sugar bagasse, African palm pit and sawdust were impregnated with a 50% v/v HNO_3 solution for 5 hours. During activation, a 200 $mL.min^{-1}$ flow of N_2/steam was maintained for a period of 2 hours at a temperature of 1173 K with a heating ramp of 4 $Kmin^{-1}$ for all precursors. The activated carbons obtained were later washed with water until a neutral pH was reached.

Elemental Analysis of the Activated Carbons Obtained

Carbon, hydrogen and nitrogen contents of the activated carbons were determined with a CHNS Vario type, EI, elemental analyzer. The oxygen content of the samples was calculated by subtracting. Before carrying out the BAC analysis, the sample was dried for 2 houes at 363 K.

Textural Characterization of the Activated Carbons Obtained

The textural characteristics were established by determination of the N_2 adsorption isotherms at 77 K and CO_2 at 273 K in a conventional volumetric apparatus (Autosorb 3B, Quantachrome).

Determination of Active Sites

For determination of the acid and basic sites in activated carbons, the titration method proposed by Boehm (Boehm, 1994) is used. The total acid sites were neutralized by means of a 0.1 N NaOH solution, and the basic sites were neutralized with a 0.1 N HCl solution. The carboxylic and lactonic sites were titrated with a 0.1 N Na_2CO_3 solution the carboxylic sites were titrated with a 0.1 N $NaHCO_3$ solution and the phenolic sites were estimated by the difference (Bandoz 1993).

For each determination, 50 milliliters of the solution were added to 1.000 g of activated carbon in a glass container. The container was partially immersed in a water bath at a temperature of 298 K for five days and was manually agitated four times a day. A 10 mL sample was titrated with 0.1 N HCl or NaOH solutions. Titration was by means of a CG 840B Shott potentiometer.

Determination of the Point of Zero Charge

For determination of the point of zero charge, PZC, for activated carbons, a 0.500 g sample of these carbons was weighed and then transferred to a 25 mL Erlenmeyer flask to which 10 milliliters of CO_2-free distilled water were added. The Erlenmeyer flask was capped and then was continuously agitated in an automatic Mistral apparatus (Multi-Mixer, Lab-Line Instruments, Inc. Designers and Manufacturers) for 48 hours at a temperature of 298 K. The pH of the solution corresponded to the point of zero charge, PZC, is measured. This method was satisfactorily used by Leon y Leon and Radovic (Leon 1994) and Moreno-Castilla et al. (Moreno-Castilla 1995).

Adsorption Equilibrium Data

Pb^{2+} solutions were prepared from $Pb(NO)_3$ within a concentration range from 5 to 120

mgL^{-1} and the pH was adjusted to 2, 4, 5, 6 and 8, depending on the case, with 0.01M HNO_3 and 0.01M NaOH solutions.

The equilibrium concentrations for the adsorption of Pb^{2+} were obtained in a batch-type adsorber having a 1000 mL capacity into which 480 mL of a solution of known Pb^{2+}concentration and pH were transferred. The activated carbon mass, varying from 0.100 to 1.000 g, was transferred into a *Pyrex* glass container and then put into the solution by means of an appropriate coupling in the adsorber. The solution was shaken and kept at 298 K. temperature.

Solution concentrations were determined periodically until the Pb^{2+} concentration between two consecutive samples did not vary significantly, which indicated that equilibrium had been reached.

The Pb^{2+} concentration in the aqueous solution was determined by atomic absorption spectroscopy by means of Perkin-Elmer Analyst 300 equipment; and it was assessed by means of a calibration curve (Giraldo and Moreno 2004). Calibration curves were prepared for each of the pH valued tested in this work.

RESULTS

The activated carbons obtained are referred to as follows, ACB, activated carbon obtained from cane sugar bagasse, CCP, activated carbon obtained from African palm pit, and ACS, activated carbon derived from sawdust. The results of the elemental analysis of the activated carbons are shown in Table 1. It may be seen the materials from the lignocellulosic precursors, which are considered agroindustrial wastes, have a high content of carbon and from them carbonaceous solids with good adsorbent characteristics are derived. The modification using nitric acid increased the lead ion adsorption capacity. This agrees with the increase in acidic functional surface groups with oxidation of the carbon and to the increase in total charge on the carbon surface, as mentioned in the literature (Soto-Garrido 2003). The surface chemical structure of the ACs obtained is characterized by the formation of acid-type oxygenated groups, which affect their behavior when used as adsorbents or as catalyst supports.

For the adsorption of inorganic compounds by this kind of porous solids, such as metal ions in aqueous solution, the most important variable was the nature of the surface complexes, even more than the surface area and the porosity of the adsorbent.

The N_2 adsorption isotherms of the activated carbons, ACB, ACP and ACS at 77 K, are shown in Figure 2. Table 2 includes the values of micropore volume, V_o, of N_2 at 77 K and of CO_2 at 273 K and the total volume, V_T, for activated carbons. Volumes were deduced by means of analysis of the physical adsorption isotherms of N_2 at 77 K and of CO_2 at 273 K, using the Dubinin-Raduskevich (DR) equation. The three materials have surface area values suitable for adsorption in solution, and it can be seen that the activated carbon with the largest surface area was that 1100 m^2g^{-1}, that obtained from sawdust. The values of Vo (CO_2) and Vo (N_2) are similar for all the activated carbons; the fact that similar values of micropore volume were obtained by nitrogen and carbon dioxide adsorption for the two aforementioned carbons indicates that the microporosity of these carbons is narrow and uniform (Gun´ko and Mekhalovsty 2004). For ACS, micropores volume and with both adsorbates (N_2 and CO_2) were higher with larger differences between them, indicating that microporosity was grater too. Thus, it is worth mentioning that, as far as the subject matter of this research paper is concerned, surface chemistry as well as the origin the raw materials chemistry played a predominant role in the adsorption of the lead ion.

The shape of the isotherms changed, a indicating that the pores were modified whenever the precursor material was changed. It can be seen that sawdust (ACS) had a larger pore volume and surface area than the other two activated carbons. These surface characteristics of the carbons had a direct effect on the adsorption capacity of the Pb^{2+} ion.

Table 1: Elemental composition of the activated carbons

Activated Carbon	**Starting Material**	**C**	**N**	**H**	**O**	**Ashes**
		($g\ kg^{-1}$)				
ACB	Cane Sugar bagasse	490	14	32	445	19
ACP	Palm pit	502	13	41	426	18
ACS	Sawdust	468	16	38	457	21

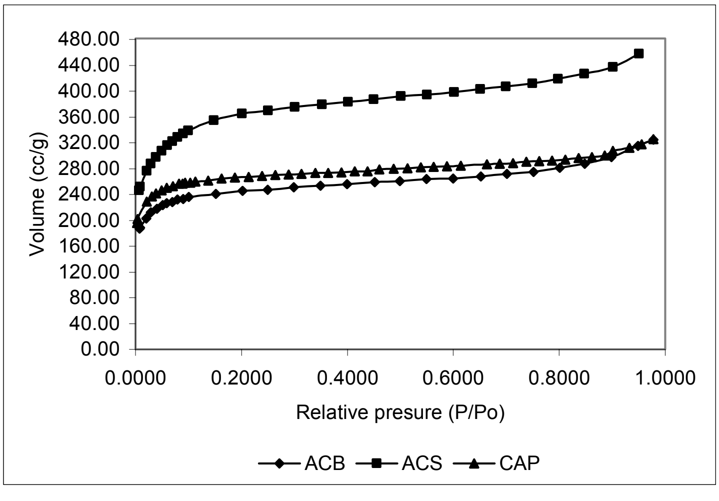

Figure 2: Isotherms of chemically activated carbons

Table 2: Textural characteristics of the activated carbons obtained.

Sample	Starting material	% Burn-off	S_{BET} (m^2g^{-1})	N_2 77 K	V_T (cm^3g^{-1})	CO_2 273 K
				V_o(cm^3g^{-1})		V_o(cm^3g^{-1})
ACB	Cane Sugar bagasse	46	868	0.39	0.39	0.37
ACP	Palm pit	46	967	0.27	0.27	0.24
ACS	Sawdust	46	1100	0.55	0.55	0.49

Results for the total content of acid and basic sites and the distribution of the oxygenated groups are shown in Table 3. There was a greater development of acid sites in the carbon obtained from sawdust, ACS, making it more capable of adsorbing metal cations from aqueous solution on those sites. Impregnating the precursor materials with HNO_3 caused the content of acid groups to be higher than the content of basic groups. A similar behavior occurs when activated carbons undergo oxidation processes after being obtained (Leyva-Ramos 2002; Leyva-Ramos and Rangel-Mendez). The difference between the content of acid and basic groups is explained by the production of the oxygenated groups that were formed with nitric acid introduced by means of the activation process.

The pH at the point of zero charge, pH_{PZC}, for the activated carbons obtained is shown in Table 3. The pH_{PZC} value is the point at which surface functional groups do not contribute to the pH of the solution. The activated carbons produced are effective adsorbents for removing the Pb^{2+} ion at $pH \geq pH_{PZC}$. The pH_{PZC} values determined for activated carbons indicate their acid nature, which was expected due to the treatment applied to the carbons, which caused the introduction of oxygenated groups as shown in Table 3.

As regards the distribution of acid sites, the number of carboxylic groups was larger in carbons ACB and ACS, which also had the smaller acid pH_{PZC} values, since these groups correspond to higher strength acids. African palm pit (ACP) has a higher content had a higher content of phenolic groups and its pH_{PZ} was the highest, 4.1.

Once the activated carbons had been prepared and characterized, the adsorption isotherms of ion Pb^{2+} were obtained at different pH values, ranging between 2 and 8, at 298 K. Isotherms are shown in Figures 3 through 5, in which it can be seen that for the three activated carbons, the pH for the highest adsorption was 4.

Table 3: Chemical characterization of the activated carbons. Determination of acid and basic sites and point of zero charge (PZC).

Sample	Starting material	TOTAL Acid Sites (mmol g^{-1})	Phenolic Groups (mmol g^{-1})	Carboxylic Groups (mmol g^{-1})	Lactonic Groups (mmol g^{-1})	TOTAL Basic Sites (mmol g^{-1})	PZC
ACB	Cane Sugar bagasse	4.13	1.47	0.78	1.88	0.83	4.1
ACP	Palm pit	5.00	0.24	3.44	1.32	0.76	3.5
ACS	Sawdust	6.93	1.32	4.45	1.16	1.22	2.7

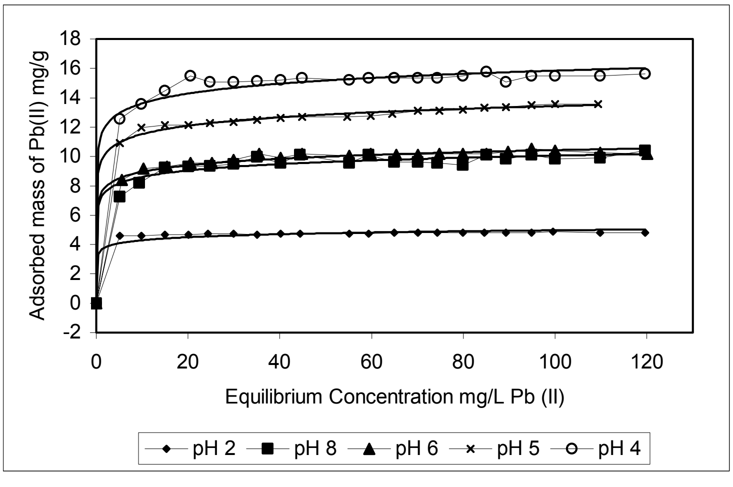

Figure 3: Pb(II) adsorption isotherm for ACP

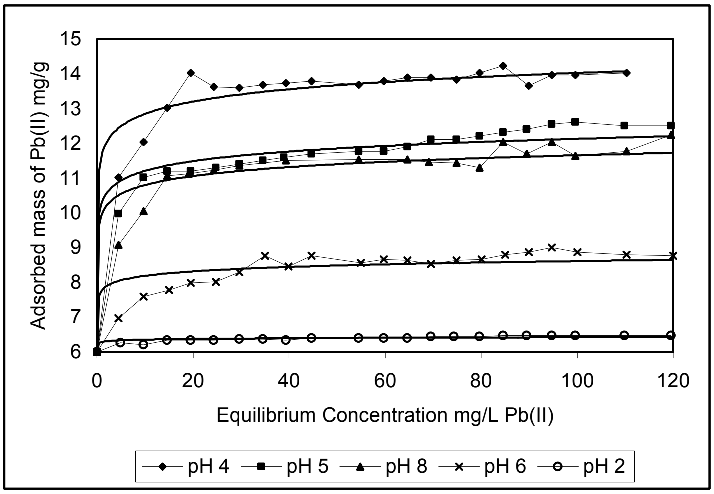

Figure 4: Pb(II) adsorption isotherm for ACB

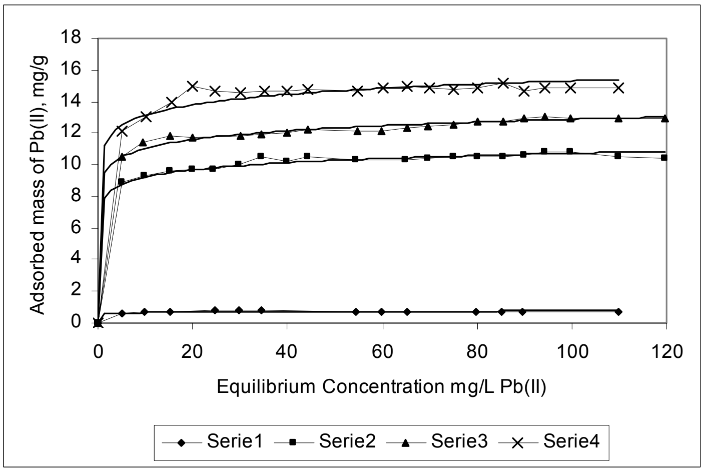

Figure 5: Pb(II) adsorption isotherm for ACS.

The greatest adsorption observed was for activated carbon ACS, in which the surface characteristics had an effect on said adsorption capacity, while carbons ACP and ACB, which have surface areas and micropore volumes of the same magnitude, had similar adsorption capacities. The Pb^{2+} adsorption on ACS was approximately 17.5 mgg^{-1}, and may be associated with the content of surface acid groups, since it had highest total acidity value, 6.93 $meqg^{-1}$, and in turn, the highest content of carboxylic groups, 4.45 $meqg^{-1}$.

Experimental data adjusts to the models of Freundlich and Langmuir isotherms. Isotherms are mathematically represented as

$$q = \frac{q_m KC}{1 + KC}$$

$$q = kC^{1/n}$$

where q at $meqg^{-1}$ is the mass of adsorbed Pb^{2+}, C at mgL^{-1}, is the Pb^{2+} equilibrium concentration, q_m at $meqg^{-1}$ and K at Lmg^{-1} are the Langmuir constants for the highest adsorption capacity and energy, respectively.

Table 4 shows the constants for the Freundlich model are k at $L^{1/n}mg^{1-1/n}g^{-1}$ and 1/n, for the adsorption capacity and intensity, respectively.

Constants obtained for these models at different pH values, were determined by aligning the isotherm variables and fitting them by the MS method. For each line, a correlation coefficient congruent with the proposed model was obtained. The percentage of absolute deviation, %D, was also calculated for each isotherm as follows:

$$\%D = \left(\frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_{exp} - q_{calc}}{q_{exp}} \right| \right) .100\%$$

where N is the number of experimental plots, q_{calc} is the adsorbed Pb^{2+} mass that was calculated with the isotherm model and q_{exp} is the adsorbed Pb^{2+} experimental mass (Berber-Mendoza 2006).

From correlation coefficients, R^2, it may deduced that experimental data the fit of the Langmuir model the is better, since the values range between 0.9972 and 0.9999. For the Freundlich model, the R^2 values are smaller, 0.7045 to 0.9488, indicating greater experimental data scattering around the average line for all carbons. For most carbons, smaller percentages of deviation were found when the experimental data were analyzed using the Langmuir model. For Pb^{2+} adsorption, the percentage of deviation shown to be smaller when pH was near 4 in all cases.

The applying Langmuir model, it may be seen that values obtained for the quantity of adsorbed Pb^{2+} on the monolayer, q_m, for activated carbon samples at different pHs, are they similar for ACB and ACP since to increase a pH value of 4 and then decrease higher pH values. For ACS, whose adsorption value is the highest, the quantity adsorbed increases up to pH 4 and for higher pH values, decreases. K values obtained for activated carbons are high for pH 2 and decrease to values around 2.00 Lmg^{-1}.

Table 4: Langmuir and Freundlich isotherms constants

Sample	**pH**	**Langmuir**			
		q_m (mgg^{-1})	**K (Lmg^{-1})**	**%D**	**R^2**
ACB	8	11.6	1.76	7.8	0.9998
	6	8.60	2.35	5.2	0.9993
	5	11.9	2.79	18.2	0.9987
	4	13.7	2.42	4.2	0.9995
	2	6.40	22.1	12.5	0.9999
ACP	8	9.74	1.33	3.9	0.9972
	6	10.1	2.91	4.3	0.9995
	5	12.9	3.09	11.4	0.9989
	4	15.2	2.77	3.9	0.9996
	2	4.73	16.1	12.5	0.9999
ACS	8	10.1	1.43	12.4	0.9976
	6	12.2	4.16	8.4	0.9997
	5	14.1	2.14	6.9	0.9991
	4	17.5	3.14	4.7	0.9997
	2	2.93	16.2	16.2	0.9997
Sample	**pH**	**Freundlich**			
		K	**N ($mg^{1-1/n}L^{1/n}/g$)**	**%D**	**R^2**
ACB	8	8.16	11.60	5.8	0.7429
	6	6.33	13.23	6.9	0.8913
	5	9.10	14.85	19.6	0.9463
	4	10.36	14.26	3.9	0.7045
	2	6.12	88.63	10.3	0.9004
ACP	8	6.29	9.36	4.8	0.7267
	6	7.82	15.84	5.5	0.8919
	5	10.09	16.21	12.6	0.9398
	4	6.29	17.23	4.8	0.7078
	2	4.46	65.28	14.6	0.9005
ACS	8	5.18	9.71	16.4	0.7296
	6	8.72	10.62	12.3	0.8924
	5	9.63	12.44	8.9	0.9488
	4	10.58	15.32	5.6	0.7198
	2	4.46	55.42	17.2	0.9006

For the Pb^{2+} adsorption, it can be seen that during the pH was decreasing. This may be explained by assuming that H^+ ions were released from the surface of the activated carbon. On the other hand, lead ions were adsorbed on the ACs.

From the pH_{pzc} values obtained for three samples, it may be seen that for pH 2, the charge of the solids was positive, so the process of adsorption of the Pb^{2+} species was not favored, since the activated carbon and the lead both had the same charge, which had a remarkable effect on low values for the quantity adsorbed.

At pH 4, the activated carbons ACP and ACS had a negative charge congruent with their pH_{PZC}. Besides, the predominant species was Pb^{2+}, therefore, indicating that there was an attractive the force between the adsorbent and the adsorbate. Surface characteristics of the activated carbons (i.e. surface area and pore volume) started to have an effect evidenced by the increased Pb^{2+} adsorption at this pH for the ACS activated carbon.

For pH values higher that 5, 6 and 8 (see Fig. 1), the species began to diminish and hydroxilated species, such as $Pb(OH)_2(s)$, precipitated on the surface of the activated carbon, leaving the solution and establishing a new equilibrium that resulted in a similar quantity adsorbed which at these pHs. Lead species found between pH 2 and 8 are Pb^{2+}, $Pb(OH)_{2(S)}$ and $Pb(OH)^+$, which may interact with the solid surface due to its textural and electrostatic characteristics, with these latter affected by the surface chemical groups and the pH of the solution.

CONCLUSIONS

Activated carbons were obtained by chemical treatment, showing a high adsorption capacity for lead ions. The chemical treatment with nitric acid on three lignocellulosic materials produced activated carbons with surface areas between 860 and 1100 m^2g^{-1} and pore volumes between 0.27 and 0.55 $cm^3.g^{-1}$, surface characteristics contribute to ion adsorption. For the ACS, impregnation with nitric acid generated an increased content of total groups, 4.13 to 6.93 $mmolg^{-1}$, on the carbon surface with a higher proportion of carboxylic groups which favored Pb^{2+} adsorption at pH 4.

For the activated carbons obtained, the adsorption capacity varied from 13.7 to 17.5 $mg.g^{-1}$, with ACS being the activated carbon with the greatest adsorption due to its high values for surface area, pore volume and total acidity.

The variation in solution shows that for the range assessed, 2-8, at pH 2, the activated carbons were positively charged, causing an electrostatic repulsion between the surface and the Pb^{2+} ions. When pH $>pH_{PZC}$, solids were negatively charged negatively and this condition were favored the interaction between Pb^{2+} ions and the surface, thus increasing the adsorption of Pb^{2+} ions on the activated carbons with the highest surface areas and volumes. When pH>4, lead hydroxilated species affected the adsorption process, particulary the solid hydroxide that precipitated on the activated carbon surface.

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