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Adsorption of lead(II) from aqueous solution onto several types of activated carbon fibers

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Abstract In this work, the adsorption of Pb(II) from aqueous solution was investigated on various types of activated carbon fibers (ACFs) manufactured from polyacrylonitrile and phenolic resin. The textural and physicochemical properties of the ACFs were determined by the N_2-BET method and acid-base titration. The experimental adsorption equilibrium data of Pb(II) on the ACFs were obtained in a batch adsorber, and the Langmuir isotherm model better fitted the experimental data. The effects of the type of ACF and precursor of ACF, solution pH and temperature upon the adsorption of Pb(II) on the ACFs were examined in detail. The adsorption capacity was highly dependent upon the precursor of ACF. The Pb(II) adsorption capacity of the ACFs augmented when the solution pH and temperature were increased from 2 to 4 and from 288 to 308 K, respectively. The effect of the pH was attributed to the interactions between the surface of the ACF and Pb^{2+} ions present in the water solution. The Pb(II) adsorption capacity of the ACFs was enhanced by oxidation with HNO_3 solution and the enhancement factor was between 1.1 and 1.4. The reversibility of the adsorption of Pb(II) was investigated by first adsorbing Pb(II) on an ACF and then desorbing the Pb(II). It was noticed that Pb(II) was substantially desorbed from ACF while reducing the solution pH to 2. It was concluded that the Pb(II) was mainly adsorbed on the ACFs by chemisorption, electrostatic interactions and ion exchange.

Keywords Activated carbon fiber · Adsorption · Desorption · Mechanism · Pb(II)

1 Introduction

Lead, cadmium and chromium(VI) are very toxic heavy metals and its presence in water solutions poses a serious hazard to human life. Lead and its complexes have been introduced into superficial water by disposing wastewater from various industrial activities such as acid battery manufacturing, metal plating and finishing, mining, ammunition and ceramic glass (Galvao and Corey 1989). Aqueous solutions polluted with Pb(II) can be treated by chemical precipitation, ion exchange, liquid membrane extraction, electrode deposition, activated carbon adsorption and biological processes (Brooks 1991).

Recently, adsorption has attracted much attention for removing lead and other heavy metals from water solutions because adsorption is a very effective separation process to eliminate pollutants present at trace levels. Various types of adsorbents have been tested to remove Pb(II) from aqueous solution, among the most important are activated carbons from different precursors, zeolites and clays (Babel and Kurniawan 2003; Berber-Mendoza et al. 2006; Bhattacharyya and Sen Gupta 2008; Leyva-Ramos 2007).

Adsorption on activated carbon (AC) is a very popular separation process for wastewater treatment as well as the purification of drinking water. AC is normally produced in the forms of granules, powder and fibers. The activated carbon fiber (ACF) is a novel adsorbent that has been developed for removing pollutants from water solution. The ACF can be manufactured in the forms of cloth, felt and paper, and from different precursors such as cellulose, phenolic resins, pitch and polyacrylonitrile (Leyva-Ramos 2007;

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Suzuki 1994). The ACFs have advantages over the granular and powdered forms of AC. The main advantages are fast adsorption rate and easiness of handling (Le Cloirec et al. 1997; Osmond 2000).

The adsorption of Cd(II), Cu(II), Hg(II), Ni(II) and Zn(II) from water solution on ACFs has been investigated in several works (Alvarez-Merino et al. 2005; Babic et al. 2002; Faur-Brasquet et al. 2002a, 2002b; Harry et al. 2006; Kadirvelu et al. 2000; Ko et al. 2004; Leyva-Ramos et al. 2005; Park and Kim 2005; Rangel-Mendez and Streat 2002; Shim et al. 2001). It has been found that the capacities of the ACFs for adsorbing heavy metals were enhanced by increasing the pH and was highly dependent on the surface properties of the ACFs, particularly, the acidic sites. Furthermore, the adsorption capacity of the ACF was increased by oxidizing the ACF using various methods.

Few works have been aimed at the adsorption of Pb(II) from water solution on ACFs (Faur-Brasquet et al. 2002a; Harry et al. 2006; Kadirvelu et al. 2000). The capacities of the ACFs for adsorbing Pb(II) were greater than those for other heavy metals such as Ni(II) and Cu(II). In all these studies, the ACFs were in the form of cloth and the effect of the precursor of ACF was not analyzed in detail.

The main objectives of the present work were to study the capacity of ACF for adsorbing Pb(II) from water solution and to investigate the effects of type of ACF, precursor of ACF, oxidation with HNO_3, temperature and solution pH on the adsorption capacity.

2 Materials and methods

2.1 Activated carbon fibers

Four commercially marketed ACFs were used in this work, one in the form of cloth and the others in the forms of felt. The ACF cloth was manufactured from polyacrylonitrile (PAN) by KoTHmex and is commercially known as AW1104. The ACFs in the form of felt were produced from a phenolic resin by the American Kynol and are commercially designated as ACN211-15, ACN211-10 and ACN210-15. The ACFs were washed several times with deionized water to remove dust and dried in an oven at 383 K during 24 h.

2.2 The textural and surface properties of ACFs

The textural properties of ACFs were determined by the N_2-BET method using a surface area and porosimetry analyzer, Micromeritics, model ASAP 2010. The morphology of the ACFs was examined by means of a Scanning Electron Microscope, Leica-Cambridge, model S420-i.

The point of zero charge (PZC) and surface charge distribution were determined by a titration method (Babic et al. 1999). The procedure was as follows: a portion of 100 mg of ACF and 20 mL of 0.1 M NaCl solution were added to a 50 mL polypropylene bottle. A volume, ranging from 0.1 to 5 mL, of 0.1 M NaOH or HCl titrating solution was added to the NaCl solution to adjust the solution pH over the pH range of 1.8–12.0. Next, N_2 was bubbled above the solution during 5 minutes to avoid that the CO_2 present in the air can be absorbed in the solution and formed CO_3^{2-} and HCO_3^{1-}. Each bottle was capped and set on the top of a magnetic stirrer, and the solution was stirred during 5 days with a Teflon-coated stirring bar. The final solution pH was measured after 5 days. Blank experiments without ACF were also carried out in the same manner.

In the same figure the potentiometric curves, final pH of the solution vs. volume of titrating solution, were plotted for the solution with ACF and without ACF. The surface charge was calculated using the following equation (Babic et al. 1999):

$$C_S = \frac{C_T F \Delta V}{m} \tag{1}$$

where C_S is the surface charge at a given pH, C/g; C_T is the concentration of titrating solution, mol/L; F is the Faraday constant, 96,500 C/mol; m is the mass of adsorbent, g; and ΔV is the difference between the volume of the titrating solution with ACF and the volume of titrating solution without ACF at the same pH value. The PZC is the solution pH at which the surface charge is neutral.

2.3 Oxidation of ACFs

The ACFs were oxidized with a HNO_3 solution by adding 20 g of ACF and 500 mL of a HNO_3 solution in a flask. The concentration of HNO_3 solution was 15% v/v. The acid solution containing the ACFs was heated between 323 and 333 K for 2 h and then allowed cooling to the room temperature. The acid solution was drained, and the oxidized ACF was rinsed several times with deionized water until the pH of the rinsing water remained constant. The ACF was dried in an oven at 383 K during 24 h and stored in a closed container. The ACFs oxidized with 15% v/v HNO_3 solutions were denoted as AC211-15Ox and AW1104Ox.

2.4 Determination of active sites

Acidic and basic sites of ACFs were determined by the acid-base titration method developed by Boehm (1994). The acid sites were neutralized with a 0.1 M NaOH solution and the basic sites with a 0.1 M HCl solution. Furthermore, the different types of acidic sites were neutralized using 0.1 M Na_2CO_3 and $NaHCO_3$ solutions. In this way, the acidic sites neutralized with the NaOH solution corresponded to the sum of the carboxylic, phenolic, and lactonic sites; the Na_2CO_3

solution neutralized both carboxylic and lactonic sites and the $NaHCO_3$ solution neutralized only the carboxylic ones (Boehm 1994). The acidic and basic sites were determined by adding 50 mL of 0.1 N neutralizing solution and 1 g of ACF to a polypropylene bottle. The bottle was partially immersed in a constant temperature water bath set up at 298 K and left there for 5 days. The bottle was manually stirred twice a day. Afterwards, a sample was taken and titrated with 0.1 N HCl or NaOH solution, as required.

2.5 Determination of Pb(II) concentration

The concentration of Pb(II) in an aqueous solution was determined by atomic absorption spectroscopy. The absorbance of a sample was measured using a double-beam atomic absorption spectrophotometer, Varian, model SpectrAA-20. The Pb(II) concentration of a sample was estimated using a calibration curve (concentration vs. absorbance) prepared with standard solutions of Pb(II). The calibration curves had to be prepared at the pH values of 2, 3.2 and 4 since the curves were dependent on pH.

2.6 Adsorption equilibrium data

In this study, all Pb(II) solutions were prepared by dissolving $Pb(NO_3)_2$ in a solution with its pH adjusted to a certain value by mixing predetermined volumes of 0.01 M HCl and NaOH solutions. In a batch adsorber, a portion of 0.3 g of the ACF was contacted with 40 mL of a Pb(II) solution of known initial concentration, which varied from 60 to 450 mg/L. A conical vial of 50 mL served as the experimental batch adsorber and was partially submerged into a constant temperature water bath. The solution with the ACF was manually mixed during 5 minutes 5 times daily. The Pb(II) solution remained in contact with the ACF until equilibrium was attained. Preliminary experiments showed that 7 days were enough to reach equilibrium. The equilibrium was attained when two consecutive samples showed no change in Pb(II) concentration. The solution pH was measured periodically with a pH meter and kept constant by adding 0.01 and 0.1 N HNO_3 or NaOH solutions, as required. The total volume of added HCl or NaOH solutions was recorded to be considered in the mass balance. This total volume was between 0.2 and 1.0 mL, which represented less than 2.5% of the initial total volume. The concentration of Pb(II) in a sample was determined as described earlier. A mass balance of Pb(II) was performed to calculate the mass of Pb(II) adsorbed at equilibrium. This mass balance can be represented by the following equation:

$$q = \frac{V_0 C_0 - C(V_0 + V_a)}{m} \tag{2}$$

where C is the concentration of Pb(II) at equilibrium, mg/L; C_0 is the initial concentration of Pb(II) in the solution, mg/L; m is the mass of adsorbent, g; q is the mass of Pb(II) adsorbed per mass of adsorbent, mg/g; V_0 is the initial volume of the Pb(II) solution added to the adsorber, L; and V_a is the total volume of 0.01 and 0.1 N NaOH and HNO_3 solutions added to the adsorber to keep constant the solution pH in the adsorber, L.

2.7 Desorption equilibrium data

The reversibility of Pb(II) adsorption on the ACFs was studied by carrying out desorption experiments, which consisted of performing an adsorption experiment as already described. Once equilibrium was reached, the ACF loaded with Pb(II) was removed from the Pb(II) solution, and was placed inside a batch adsorber containing 40 mL of a desorbing solution without Pb(II). The saturated ACF and the desorbing solution were left in contact for 7 days until they attained equilibrium; it was assumed that new equilibrium was reached when the Pb(II) concentration of two consecutive samples did not vary. The initial pH of the desorbing solution was 2, and the pH was kept constant during desorption as indicated earlier. The mass of Pb(II) that remained adsorbed on the ACF was computed by a mass balance.

$$q_d = q_0 - \frac{C(V_i + V_a)}{m} \tag{3}$$

where q_0 is the mass of Pb(II) adsorbed at the beginning of the desorption experiment, mg/g; q_d is the mass of Pb(II) that remained adsorbed at the end of the desorption experiment, mg/g; and V_i is the initial volume of the solution without Pb(II) added to the adsorber, L.

2.8 Determination of the amount of the ions exchanged during adsorption

The equivalents of H^+ exchanged during the adsorption of Pb(II) were determined by the following procedure. A solution without Pb(II) and at $pH = 4$ was prepared by mixing proper volumes of 0.01 M HCl and NaOH solutions. A portion of 40 mL of this solution without Pb(II) and 0.3 g of the ACF were placed inside the batch adsorber. The solution pH was measured periodically with a pH-meter and kept constant by adding 0.01, 0.05 and 0.1 N NaOH solutions, as required. Once the solution pH did not change over time, the solution pH was registered as the initial pH, and a 10 mL portion of a solution with a known initial concentration of Pb(II) and at the same pH of the adsorber solution was added to the adsorber. Afterwards, the solution pH was measured periodically but was not adjusted. The equilibrium was attained when the solution pH did not change over time. The final pH of the solution was registered and the final concentration of Pb(II) in the solution at equilibrium was determined as described previously. In preliminary runs, it was found that the concentration of Na^+ ions present in the solution did not change during the adsorption of Pb(II), and it was considered that Na^+ was not exchanged on the surface of the ACF.

The equivalents of H^+ exchanged per mass of adsorbent were estimated by performing a mass balance:

$$\text{equivalents of } H^+ \text{ exchanged} = V_0(10^{-\mathrm{pH}_{\mathrm{final}}} - 10^{-\mathrm{pH}_{\mathrm{initial}}})/m \qquad (4)$$

where V_0 is the initial volume of the adsorber solution after the solution of known initial concentration of Pb(II) was added to the adsorber, L.

3 Results and discussion

3.1 Textural properties of the ACFs

The textural properties of the pristine and oxidized ACFs are given in Table 1. The surface areas and pore volumes of the ACFs varied from 1004 to 1542 m^2/g, and from 0.46 to 0.7 cm^3/g, respectively. The ranges of these values are within the ranges of values reported in the literature for ACFs manufactured from different precursors such as cellulose, phenolic resin, pitch and polyacrylonitrile (Li et al. 1998; Rangel-Mendez and Streat 2002; Park et al. 2003).

In all the ACFs, the average pore diameter was smaller than 2 nm indicating that the porous structures of ACFs were mainly constituted of micropores. Similar results have been reported by other investigators. Hsieh and Teng (2000) characterized a PAN-based ACF and reported average pore diameters ranging between 1.9 and 2.0 nm. The average pore diameter of a phenolic-based ACF was determined to be 1.91 nm (Ko et al. 2004). Furthermore, Diaz-Flores et al. (2006) characterized ACFs in the forms of cloth and felt and found that the average pore diameters varied between 1.93 and 1.96 nm.

Table 1 Textural properties of unoxidized and oxidized ACFs

ACF	Precursor	Form	S_{BET} (m^2/g)	V_P (cm^3/g)	d_P (nm)
AW1104	PAN	Cloth	1004	0.49	1.94
AW1104Ox	PAN	Cloth	1127	0.55	1.94
ACN211-15	Novoloid	Felt	1204	0.58	1.91
ACN211-15Ox	Novoloid	Felt	1335	0.64	1.94
ACN211-10	Novoloid	Felt	1014	0.46	1.89
ACN210-15	Novoloid	Felt	1542	0.70	1.88

d_P = Average pore diameter = $4V_P/S_{\mathrm{BET}}$; S_{BET} = Surface area determined by N_2-BET method; V_p = Total pore volume at $P/P_0 = 0.9954$

3.2 Morphology of ACFs

The SEM images of the felt ACN211-15 and cloth AW1104 are shown in Figs. 1(a) and 1(b), respectively. The marked difference in textile structure between the two forms of ACFs is mainly due to the precursor materials. The cloth AW1104 was prepared by activating a woven fabric of PAN fibers and the morphology of the yarns and woven fabric can be clearly noted. The felt ACN211-15 was prepared from a non-woven cloth of a phenolic resin.

The oxidation of the ACFs with a 15% HNO_3 solution did not influence the morphology of the filaments of both forms of ACFs. Similar results have been reported by other authors for the oxidation of ACFs with HNO_3 solutions (Rangel-Mendez and Streat 2002; Leyva-Ramos et al. 2005). In preliminary runs, it was noticed that the oxidized ACFs turned out to be slightly more fragile when the concentration of HNO_3 was 20% v/v or above. This is why the concentration of HNO_3 in the oxidation was chosen to be 15% v/v.

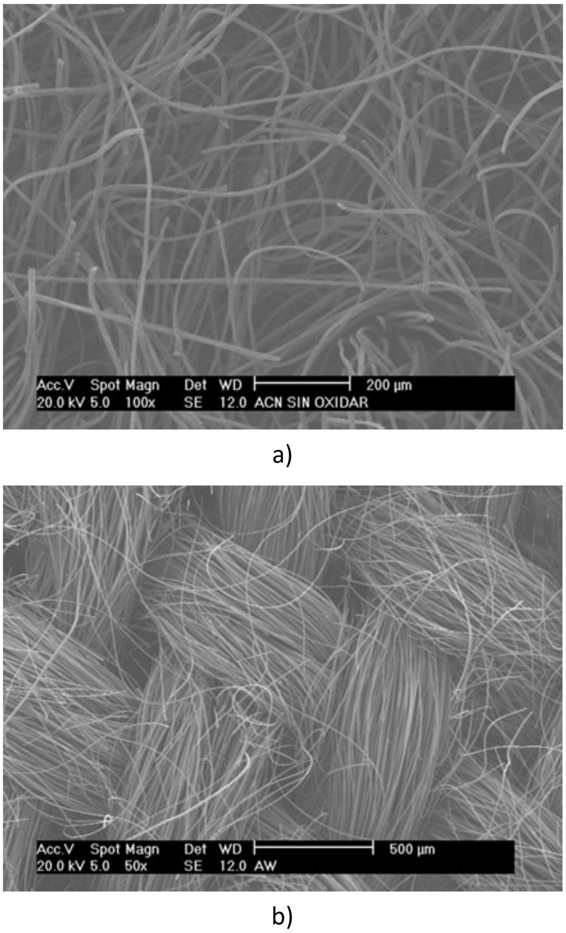

Fig. 1 SEM images of the pristine felt ACN211-15 (**a**) and pristine cloth AW1104 (**b**). Magnification factors 100 and 50, respectively

Table 2 Concentration of active sites in the ACFs

ACF	Concentration of active sites (meq/g)					PZC
	Acidic sites				Basic sites	
	Carboxylic	Lactonic	Phenolic	Total		
AW1104	0.400	0.340	0.385	1.125	0.320	6.10
AW1104Ox	0.516	0.391	0.848	1.755	0.411	3.0
ACN211-15	0.340	0.140	0.470	0.950	0.460	5.20
ACN211-15Ox	0.419	0.391	0.933	1.743	0.495	3.72
ACN211-10	0.220	0.120	0.100	0.440	0.360	7.97
ACN210-15	0.180	0.080	0.115	0.375	0.460	9.40

3.3 Physicochemical properties of ACFs

The concentrations of the active sites for the pristine and oxidized ACFs are displayed in Table 2. Except for the felt ACN-210-15, the surface character of all the ACFs was acidic since the concentration of the total acidic sites was always greater than that of basic sites. The concentrations of the acid sites for the felt ACN210-15 and cloth AW1104 diminished in the following order: Carboxylic > Phenolic > Lactonic, for the felt ACN-211-15: Phenolic > Carboxylic > Lactonic, and for the felt ACN211-10: Carboxylic > Lactonic > Phenolic. This reveals that the surface characteristics of the ACFs are highly dependent on the precursor.

It is a well-known fact that the concentration of acidic sites increases oxidizing the ACFs with HNO_3 (Leyva-Ramos et al. 2005; Park et al. 2003; Shim et al. 2001). This behavior can be attributed to the introduction of oxygenated groups making the ACF surface more acidic. The oxidation of the cloth AW1104 and felt ACN211-15 augmented the concentrations of the acidic sites.

The surface charge of all the forms of activated carbon is dependent on the type of ions present in solution, characteristics of the surface and the solution pH. The PZC is the solution pH at which the surface of the ACF is neutral. The surface is positively charged when the solution pH is below the PZC and is negatively charged when the pH is above the PZC. The behavior of the surface charge regarding the solution pH is illustrated in Fig. 2 for the felt ACN211-15 and cloth AW1104. The surface charge distributions of the other ACFs were not included because they presented the same behavior as that shown in Fig. 2.

The PZC of the pristine ACFs augmented in the following order: ACN211-15 < AW1104 < ACN211-10 < ACN210-15. The surfaces of the felt ACN211-15 and cloth AW1104 were both acidic since their PZCs were below 7 whereas the surfaces of the felts ACN211-10 and ACN210-15 were basic. It is obvious that the surface character depended on the concentrations of the acidic and basic sites. The surface character of the felt ACN211-10 presented an unreasonable behavior. Its PZC indicated that its surface was basic; however, the concentration of the acidic sites was greater than those of the basic sites revealing that its surface was supposed to be acidic.

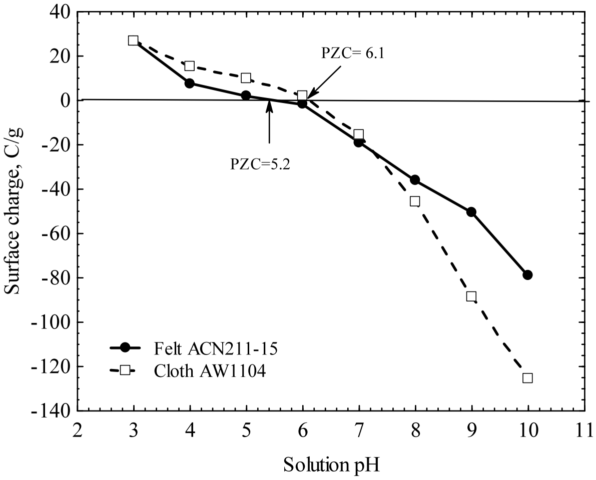

Fig. 2 Surface charge distribution of the felt ACN211-15 and cloth AW1104

The PZC of the felt ACN211-15 and cloth AW1104 diminished while oxidizing the ACFs with a HNO_3 solution. Similar results were reported for the oxidation of pitch-based ACF with HNO_3 (Shim et al. 2001). This was attributed to the generation of oxygen complexes during the oxidation which were mainly acidic functional groups.

3.4 Adsorption isotherms of Pb(II) on ACFs

The adsorption isotherm models of Langmuir and Freundlich were used to fit experimental equilibrium data for the adsorption of Pb(II) on the different types of ACFs. These isotherm models can be formulated as follows:

$$q = \frac{q_m KC}{1 + KC} \tag{5}$$

$$q = kC^{1/n} \tag{6}$$

where C is the concentration of Pb(II) at equilibrium, mg/L; k is the Freundlich constant related to the adsorption capacity, $\mathrm{mg}^{1-1/n}\,\mathrm{L}^{1/n}\,\mathrm{g}^{-1}$; K is the Langmuir constant related to the energy of adsorption, L/mg; n is the Freundlich constant related to the heterogeneity of the adsorbent surface; q is the mass of Pb(II) adsorbed per mass of adsorbent, mg/g; and q_m is the Langmuir constant related to the maximum adsorption capacity, mg/g.

The parameters for these isotherms were assessed by a non-linear estimation method with Statistica software. This method was based upon minimizing the following least-squares function:

$$\text{Minimum} = \sum_{i=1}^{N} (q_{\text{exp}} - q_{\text{pred}})^2 \tag{7}$$

The isotherm constants are shown in Table 3. Besides, the average absolute percentage deviation, %D, was computed by the following equation and its values are also given in Table 3:

$$\%D = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_{\text{exp}} - q_{\text{pred}}}{q_{\text{exp}}} \right| \times 100\% \tag{8}$$

where N is the number of experimental data points; q_{exp} is the experimental mass of Pb(II) adsorbed, mg/g; and q_{pred} is the mass of Pb(II) adsorbed predicted with the isotherm model, mg/g.

The values of $\%D$ for the Langmuir and Freundlich isotherms ranged from 5.8 to 26% and from 8.6 to 45%, respectively. The Langmuir isotherm better fitted the experimental data since the Langmuir isotherm presented lower %D than the Freundlich isotherm in 9 out of the 11 isotherm cases shown in Table 3. Furthermore, in some cases, the adsorption equilibrium data exhibited an undoubtedly asymptotic behavior that can be only represented by the Langmuir isotherm. From the above, the Langmuir isotherm was chosen to interpret the adsorption equilibrium data of Pb(II) on ACFs.

3.5 Effect of type of ACF on adsorption capacity

The adsorption equilibrium of Pb(II) on various types of ACFs as well as the Langmuir isotherms are plotted in Fig. 3. The decreasing order of the Pb(II) adsorption capacity of these ACFs was as follows: ACN211-15 > AW1104 > ACN211-10 > ACN210-15. The total acidic and carboxylic sites decreased in the following order: AW1104 > ACN211-15 > ACN211-10 > ACN210-15. Hence, the ACFs that presented greater adsorption capacities were the ACFs with higher concentrations of total acidic and carboxylic sites. This result can be explained recalling that the Pb^{2+} cations were adsorbed on the acidic sites. At pH = 4, the adsorption capacity of ACN211-15 was greater than that of the AW1104 because of the electrostatic interactions between the Pb^{2+} in solution and the surface charge of the ACN211-15. The PZC of the ACN211-15 (PZC = 5.20) was lower

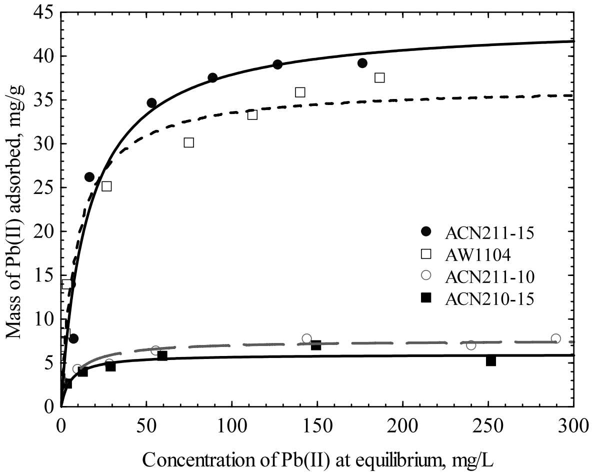

Fig. 3 Effect of type of ACF on the adsorption of Pb(II) at $T = 298$ K and pH = 4

Table 3 The Freundlich and Langmuir isotherm parameters for the adsorption of Pb(II)

ACF	T (K)	pH	Langmuir			Freundlich		
			q_m (mg/g)	K (L/mg)	$\%D$	k ($L^{1/n}\,mg^{1-1/n}\,g^{-1}$)	n	$\%D$
AW1104	298	4	36.6	0.109	9.2	8.11	3.34	9.7
AW1104	298	2	9.68	0.005	11	0.18	1.67	11
AW1104Ox	298	4	52.7	0.318	5.8	21.9	5.47	11
AW1104Ox	298	2	21.1	0.002	9.0	0.065	1.20	10
ACN211-15	298	4	43.9	0.063	16	8.24	3.11	24
ACN211-15Ox	298	4	48.0	0.101	18	10.9	3.30	36
ACN211-10	298	4	7.59	0.120	9.7	2.8	5.68	8.6
ACN210-15	298	4	5.98	0.174	8.8	2.90	7.89	11
ACN211-15	288	4	45.5	0.029	11	3.73	2.15	16
ACN211-15	308	4	42.1	0.128	26	9.27	3.18	45
ACN211-15	298	2	11.6	0.002	13	0.07	1.40	12

than that of AW1104 (PZC = 6.10) so that at pH = 4, the repulsion between the Pb^{2+} cations and the positively charged surface was lower in the felt ACN211-11 than in the cloth AW1104.

3.6 Effect of oxidation on adsorption capacity

In several works, it has been shown that the adsorption capacity of the ACFs can be considerably enhanced by oxidizing the ACFs with a HNO_3 solution (Harry et al. 2006; Leyva-Ramos et al. 2005; Park et al. 2003; Shim et al. 2001). The oxidation created oxygen complexes on the surface of the ACFs, which were mainly acidic sites. The effect of oxidation on the adsorption capacity of the cloth AW1104 and felt ACN211-15 was investigated by oxidizing them with a 15% HNO_3 solution.

At pH = 4 and $T = 298$ K, the adsorption equilibrium and Langmuir isotherms of Pb(II) on the pristine and oxidized ACFs are shown in Fig. 4. The adsorption capacities decreased in the following order: AW1104Ox > ACN211-15Ox > ACN211-15 > AW1104. Comparing the values of q_m (Table 3), the Pb(II) adsorption capacity of the cloth AW1104 and felt ACN211-15 increased 1.4 and 1.1 times, respectively, due to oxidation. The concentration of total acidic and carboxylic sites decreased in the following order: AW1104Ox > ACN211-15Ox > AW1104 > ACN211-15. Again, the Pb(II) adsorption capacity of the pristine and oxidized ACFs could be related to the concentrations of total acidic and carboxylic sites.

At $T = 298$ K, the maximum capacity of the AW1104Ox for adsorbing Pb(II) can be compared to those of other traditional and novel carbonaceous adsorbents reported in the literature. The maximum adsorption capacities of granular activated carbon (GAC) from coconut shell and sulfurized GAC (Goel et al. 2005), carbon nanotubes oxidized with HNO_3 (Li et al. 2005), multiwalled carbon nanotubes (MWCNTs) and MWCNTs oxidized with HNO_3 (Wang et al. 2007), activated alumina (AA) (Naiya et al. 2009), and clinoptilolite (Berber-Mendoza et al. 2006) are 21.9 (pH = 5), 29.4 (pH = 5), 35 (pH = 5), 4 (pH = 5), 49.1 (pH = 5), 83.3 (pH = 5), and 120 mg/g (pH = 4). Thus the AW1104Ox presented lower adsorption capacity than AA and clinoptilolite and higher adsorption capacity than GACs, CNTs and MWCNTs.

3.7 Effect of pH on adsorption capacity

The solution pH plays a very important role in the adsorption of heavy metals on the ACFs because the interactions between the metal ions in solution and the oxygenated complexes on the surface of ACFs are considerably influenced by the solution pH. The metal species present in the water solution and the surface charge of the ACFs are relying on the solution pH.

The effect of the solution pH on the Pb(II) adsorption capacity of the cloth AW1104 and felt ACN211-15 is shown in Fig. 5. These two pristine ACFs were chosen because both presented the highest Pb(II) adsorption capacities. The effect of pH was only examined at pH values of 2 and 4 because Pb(II) precipitated forming a white solid, which was visually observed in the solution at pH = 5. Similar results have been noticed in the adsorption of Pb(II) on clinoptilolite (Berber-Mendoza et al. 2006). Accordingly to the speciation diagram of Pb(II) in aqueous solution (Berber-Mendoza et al. 2006), the Pb(II) was solely present as the Pb^{2+} cations at pH not higher than 4. This meant that the Pb(II) was adsorbed on the ACFs as Pb^{2+} cations in all the adsorption experiments.

The adsorption capacities of the cloth AW1104 and felt ACN211-15 were dramatically enhanced by increasing the

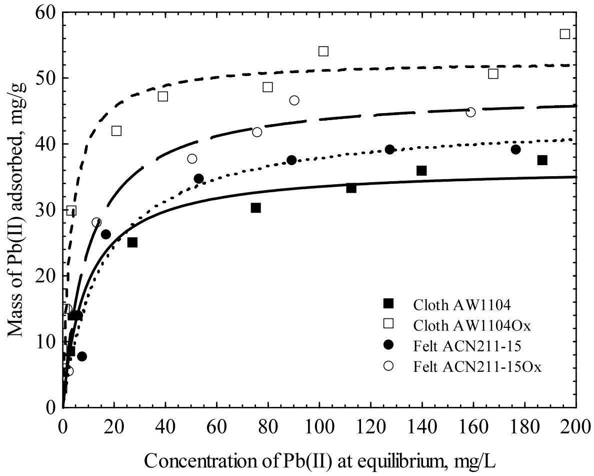

Fig. 4 Effect of oxidation on the adsorption capacity of the cloth AW1104 and felt ACN211-15 at pH = 4 and $T = 298$ K

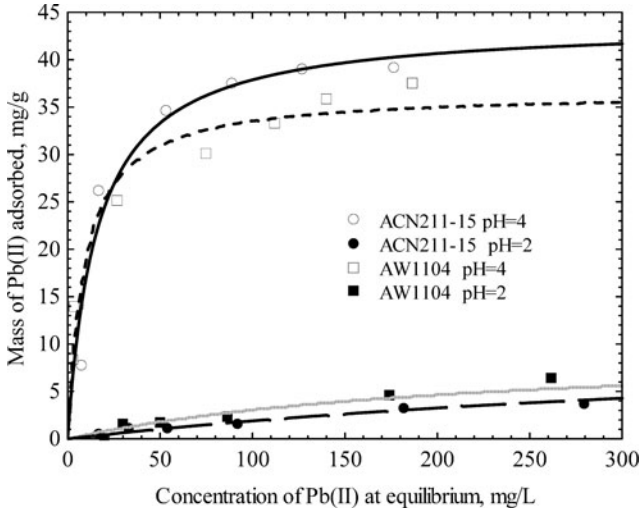

Fig. 5 Effect of the solution pH on the Pb(II) adsorption capacity of the cloth AW1104 and felt ACN211-15 at $T = 298$ K

solution pH from 2 to 4. The maximum adsorption capacities of the cloth AW1104 and felt ACN211-15 for adsorbing Pb(II), q_m, were augmented 3.8 times when the solution pH was increased from 2 to 4.

The electrostatic interactions between the Pb^{2+} cations and the surface charge of the ACFs played a key role on the adsorption capacity of the ACFs. In the pH range 2–4, the surfaces of the cloth AW1104 and felt ACN211-15 were positively charged and the magnitude of the surface charge was reduced while the pH was increased from 2 to 4. Hence, the increment in the adsorption capacity was attributed to that the repulsion between the surface of the ACFs and the Pb^{2+} cations was reduced when the pH was raised from 2 to 4.

3.8 Effect of temperature on the adsorption capacity

The adsorption of a molecule can be due to the interactions between the surface and the molecules in solution and these interactions are influenced by the temperature. The effect of temperature was studied by determining the adsorption equilibrium of Pb(II) on the felt ACN211-15 at the temperatures of 288, 298 and 308 K and pH = 4. The adsorption equilibrium data and the Langmuir isotherm are graphed in Fig. 6, and it can be noticed that the adsorption capacity was enhanced by increasing the temperature for concentrations of Pb(II) at equilibrium less than 50 mg/L. However, the adsorption capacity was not affected by temperature at concentrations of Pb(II) above 160 mg/g. The temperature did not influence the adsorption capacity at high concentrations of Pb(II) because all the acidic sites of the felt ACN211-15 were possibly saturated with Pb(II) and there were no more acidic sites available for adsorption.

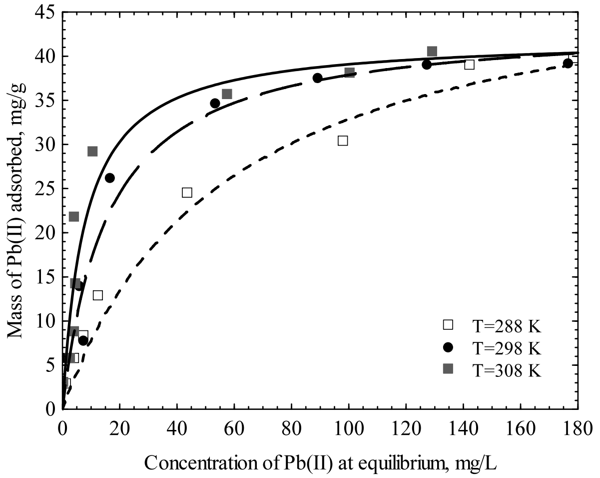

Fig. 6 Effect of temperature on the adsorption of Pb(II) on the felt ACN211-15 at pH = 4

The Langmuir constant K can be related to the temperature (Ruthven 1984) by the van't Hoff equation:

$$K = K_0 e^{-\Delta H_{\mathrm{ads}}/RT} = e^{\Delta S/R} e^{-\Delta H_{\mathrm{ads}}/RT} \tag{9}$$

The heat of adsorption, ΔH_{ads}, and entropy of adsorption, ΔS, were computed from this equation and were 54.8 KJ/mol and 0.16 KJ/mol K, respectively. The adsorption of Pb(II) on the felt ACN211-15 was endothermic. This explained why the capacity of the felt ACN211-15 for adsorbing Pb(II) was raised by increasing the temperature. Besides, the adsorption was spontaneous because the entropy change of adsorption was positive.

The Gibbs free energy of adsorption ΔG was computed from the following equation:

$$\Delta G = \Delta H_{\mathrm{ads}} - T\Delta S \tag{10}$$

At $T = 298$ K, the value of ΔG was estimated to be −40.6 KJ/mol indicating that the adsorption of Pb(II) on the felt ACN211-15 was spontaneous.

3.9 Reversibility of adsorption of Pb(II) on ACF

A solute adsorbed on a material is normally desorbed by placing the saturated adsorbent in a solution without the solute. In this way, the solute adsorbed on the surface would be desorbed and diffused back to the solution. The desorption studies can provide very useful information about the adsorption mechanism and procedure for regenerating the saturated adsorbent.

The Pb(II) was adsorbed on the cloth AW1104Ox from an aqueous solution at pH = 4 and then was desorbed by placing the AW1104Ox loaded with Pb(II) in an aqueous solution without Pb(II) at pH = 2. At this condition, the adsorbed Pb^{2+} ions were now transferred from the cloth AW1104Ox to the solution until equilibrium was attained again. The cloth AW1104Ox was used in the desorption studies because it presented the highest adsorption capacity of all the ACFs studied in this work.

The adsorption and corresponding desorption equilibrium data are graphed in Fig. 7 and are labeled as Ad and Des, respectively. The lines drawn in this Figure represent the Langmuir isotherms at pH = 4 and pH = 2 and are plotted using the Langmuir constants given in Table 3. The adsorption and desorption steps are illustrated for one of the data points (3Ad and 3Des) in Fig. 7 and are designated as the adsorption and desorption lines, respectively. In this case, the experimental desorption equilibrium data at pH = 2 were very below the experimental adsorption equilibrium data and adsorption isotherm at pH = 4 and were slightly above the adsorption isotherm at pH = 2. This indicated that an important amount of the Pb(II) adsorbed at pH = 4 was desorbed by contacting the saturated ACF with

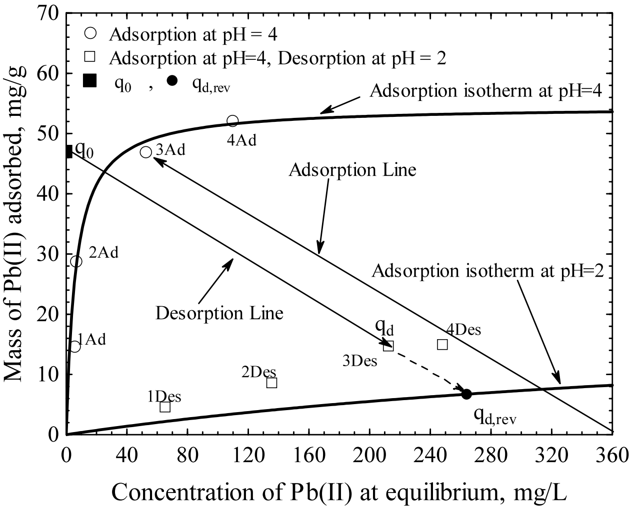

Fig. 7 Adsorption of Pb(II) at pH = 4 and desorption at pH = 2 on the cloth AW1104Ox at $T = 298$ K

a solution at pH = 2. At pH = 2 the concentration of H^+ was much higher than the Pb(II) concentration in solution hence the H^+ ions displaced the Pb^{2+} ions adsorbed on the ACF to reach equilibrium again. Furthermore, the adsorption of Pb(II) was not reversible at pH = 2 because the desorption equilibrium data at pH = 2 is slightly above the adsorption isotherm at pH = 2.

The percentage desorption of Pb(II) can be estimated from the following equation:

$$\%\text{Desorption} = \frac{q_0 - q_d}{q_0 - q_{d,\text{rev}}} \times 100\% \tag{11}$$

where $q_{d,\text{rev}}$ is the mass of Pb(II) that remained adsorbed at the end of the desorption experiment if the adsorption was reversible, mg/g. Accordingly to (11), the desorption percentage would be 100% if the adsorption was reversible. The values of $q_{d,\text{rev}}$ were computed by solving simultaneously the mass balance (3) and the Langmuir isotherm model (AW1104Ox at pH = 2). The values of q_0, q_d and $q_{d,\text{rev}}$ are shown in Fig. 7 for one of the desorption experiments. The values of % desorption were very close to 82%. This revealed that the 82% of Pb(II) was adsorbed by reversible mechanisms such as electrostatic attractions and ion exchange and 18% by non-reversible mechanisms such as chemisorption.

From the above, a large percentage of the Pb(II) adsorbed on the ACF at pH = 4 can be desorbed by reducing the solution pH from 4 to 2.

3.10 Adsorption mechanism of Pb(II) on ACFs

The adsorption mechanism of Pb(II) on the ACFs can be elucidated if the interactions between the Pb^{2+} ions in aqueous solution and the surface complexes of the ACF are well understood.

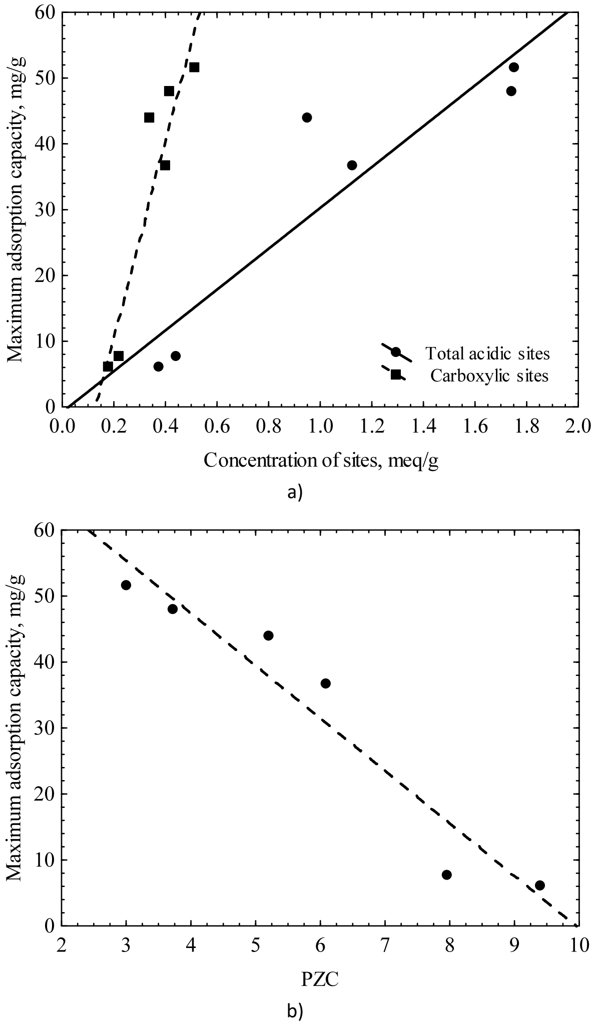

Fig. 8 Dependence of the adsorption capacity on the concentration of acidic sites (**a**) and PZC (**b**) of ACFs

In the previous sections, it has been demonstrated that the Pb(II) adsorption capacity of the ACFs was highly influenced by the concentrations of total acidic and carboxylic sites. The effect of the concentrations of total acidic and carboxylic sites upon the maximum adsorption capacity, q_m, was graphed in Fig. 8a), and the results clearly showed that the adsorption capacity of the ACFs was proportional to the concentration of the total acidic and carboxylic sites. As it is seen in this figure, the concentration of carboxylic sites affected the Pb(II) adsorption capacity more pronouncedly than that of total acidic sites. This last effect was due to that the carboxylic sites of the ACFs played a more important role than the other acidic sites since the carboxylic sites deprotonated in the pH range of 3–6 (Mironov and Taushkanou 1974) and the adsorption was carried out at pH = 4.

The effect of the surface charge on the adsorption capacity was also analyzed by plotting the maximum adsorption capacity vs. the PZC (Fig. 8b). The adsorption capacity was linearly reduced by raising the PZC. This result corroborated that the Pb(II) adsorption capacity of the ACFs was proportional to the electrostatic interactions between the surface charge of the ACF and the Pb^{2+} ions in solution.

To study the contribution of ion exchange to the overall adsorption, the amount of H^+ released or exchanged from the surface were determined during the adsorption of Pb(II). First of all, the surface of the ACF was equilibrated in a solution without Pb(II) and pH = 4. The solution pH decreased and was adjusted to pH = 4 by adding 0.1 or 0.01 N NaOH solution. The decrease in the pH indicated that some H^+ ions were released or exchanged from the surface of the ACF. Once the pH did not vary over time and was kept constant at 4, the ions on the surface of the ACF were equilibrated with the ions in the solution. Thereupon, the concentration of Pb(II) in the solution was brought up to a certain initial value and the pH of the solution was not adjusted during the adsorption. It was observed that the solution pH decreased from 4.0 to near 3.3, meanwhile the concentration of Pb(II) also diminished over time. This behavior revealed that H^+ ions were exchanged from the surface to the solution while the Pb^{2+} ions were adsorbed on the surface of the ACF.

The equivalents of H^+ exchanged per mass of adsorbent were estimated using (4). The equivalents of Pb^{2+} adsorbed due to ion exchange from solution to the surface of ACF were considered to be the same as those of the H^+ exchanged in the opposite direction since, as discussed earlier, Na^+ cations were not exchanged during the adsorption. Hence, the equivalents of Pb^{2+} exchanged were calculated with the following equation:

$$\text{Equivalents of } Pb^{2+} \text{ exchanged} = \text{Equivalents of } H^+ \text{ exchanged} \tag{12}$$

The total mass of Pb(II) adsorbed was computed with the initial and final concentrations of Pb(II). The mass of the Pb^{2+} adsorbed by other mechanisms except ion exchange was calculated by subtracting the mass of Pb^{2+} exchanged from the total amount of Pb^{2+} adsorbed. The other mechanisms of adsorption include electrostatic interaction and chemical adsorption.

The total mass of Pb^{2+} adsorbed, mass of Pb^{2+} exchanged and mass of Pb^{2+} adsorbed by other mechanisms except ion exchange are graphed in Fig. 9. The total mass of Pb(II) was much less that the mass adsorbed at pH = 4 because the final pH of the solution was within the range 3.2–3.3. The mass of Pb(II) exchanged was essentially constant at 2 mg/g and represented from 17 to 42% of the total amount of Pb(II) adsorbed. The adsorption by other mechanisms except ion exchange contributed significantly to the adsorption of Pb(II).

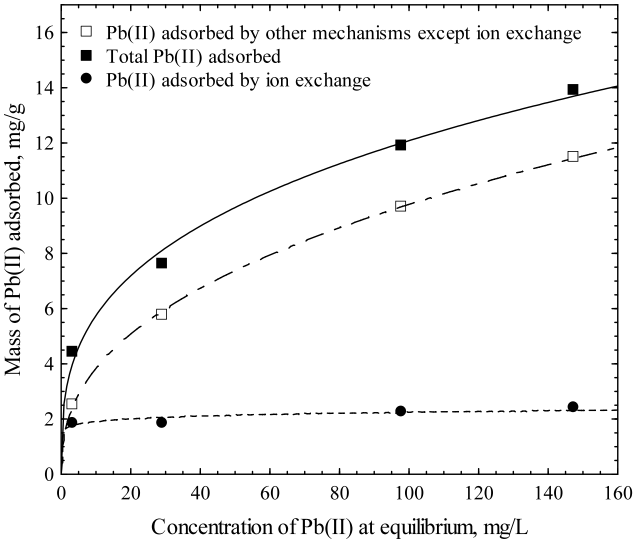

Fig. 9 Contribution of the adsorption mechanisms of Pb(II) on AW1104Ox at $T = 298$ K

The ion exchange mechanism of Pb^{2+} can be represented by the following reaction:

$$2(\equiv COOH) + Pb^{2+} \leftrightarrow (\equiv COO)_2Pb + 2H^+$$

where ≡COOH stands for the carboxylic sites on the surface of ACF. The adsorption mechanism due to electrostatic interactions consisted of two steps. First, the acidic site was deprotonated and second the Pb^{2+} ions were adsorbed on the acid site of the surface by electrostatic interactions. The two steps of this mechanism can be illustrated as follows:

$$\equiv COOH \leftrightarrow \equiv COO^- + H^+$$

$$2(\equiv COO^-) + Pb^{2+} \leftrightarrow (\equiv COO)_2Pb$$

The adsorption capacity was reduced while increasing the concentration of H^+ (decreasing pH). This behavior can be explained by considering that the adsorption of Pb^{2+} on the ACF was not favored when diminishing the pH since more H^+ ions were competing with the Pb^{2+} ions for the acidic sites of the ACF surface. This is the reason the Pb^{2+} was not adsorbed on ACF at very acidic pH values.

4 Conclusions

The concentrations of active sites, PZC and textural properties of the ACFs were dependent on the precursor of the ACF. The oxidation of the ACFs with HNO_3 modified the surface properties due to the origination of oxygenated complexes. The concentration acidic sites of the ACFs increased during the oxidation whereas the PZC decreased.

The Pb(II) adsorption capacity of ACFs was dependent on the surface properties of the ACFs, oxidation, solution pH and temperature. The capacity of ACFs for adsorbing Pb(II) was proportional to the concentration of carboxylic sites. The adsorption capacity of the ACF increased when the ACF was oxidized with a 15% HNO_3 solution. This behavior was explained recalling that the oxidation caused an increase in the concentration of acidic sites.

The adsorption of Pb(II) on the ACF was substantially enhanced by raising the solution pH. This effect was attributed to the electrostatic interaction between the Pb^{2+} ions in solution and the surface charge of ACF. The Pb(II) adsorption capacity of ACF was also extended by increasing the temperature from 288 to 308 K. The adsorption capacity was favored by increasing the temperature because the adsorption was endothermic.

The Pb(II) adsorbed can be significantly desorbed from the ACF and 82% of the Pb(II) was desorbed by diminishing the solution pH from 4 to 2. The desorption studies showed that 82% of the mass of Pb(II) adsorbed on ACF was due to reversible mechanisms, and the rest was by irreversible mechanisms.

The adsorption mechanisms of Pb(II) on the ACFs were ion exchange, chemisorption and electrostatic interactions. The contribution of the ion exchange was assessed by performing a mass balance of the H^+ exchanged from the surface to the solution during the adsorption of Pb(II). The contribution of other mechanisms except ion exchange to the overall adsorption was estimated to be between 58 and 83%.

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