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Adsorption of Cadmium(II) from an Aqueous Solution onto Activated Carbon Cloth

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Abstract: The effects of surface properties and solution pH and temperature on the adsorption of cadmium(II) onto activated carbon fiber cloth (ACC) made from poly-acrylonitrile (PAN) were investigated in this work. The ACC was oxidized with HNO_3 solution and the concentration of acidic sites increased during oxidation whereas that of basic ones diminished. The adsorption capacity of the oxidized ACC was higher than that of ACC without oxidation because the ACC contained greater concentration of acidic sites. It was found that the maximum adsorption took place at pH 8 and the adsorption capacity increased near 22 times, augmenting the pH from 2 to 8. The adsorption capacity diminished on the average twofold, increasing the temperature from 15 to 35°C. Cd(II) adsorbed on ACC at pH 6 can be almost completely desorbed by reducing the solution pH to 2. The adsorption capacity is considerably dependent upon the characteristics of the ACC surface and temperature and pH of the solution.

Keywords: Activated carbon cloth, adsorption, cadmium

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INTRODUCTION

In the last years several studies have been carried out about the adsorption of Cd(II) from water solutions onto activated carbon. It has been shown that Cd(II) can be adsorbed on activated carbon but the Cd(II) uptake depends significantly upon the solution pH and surface properties of activated carbon. Various commercial granular and powdered activated carbons, and some manufactured at laboratory scale, have been tested thoroughly (1–5).

Activated carbon is manufactured mainly in the granular (GAC) and powdered (PAC) forms, the first one being the most commonly used. Recently activated carbon in the form of fiber has been developed. This novel form is known as activated carbon fiber (ACF) and is manufactured in the cloth and felt forms. The porous structure of ACF is composed mainly of micropores, while the GAC and PAC contain a complex porous network of macro, meso, and micropores. In the ACF the access to the micropores is directly from the fiber external surface; however, in the GAC and PAC, the macropores are opened to the particle external surface and then branch into the mesopores, which lead in turn to the micropores. Most of the adsorption in all activated carbon forms takes place in the micropores, thus adsorption area in ACF can be accessed more easily than in the other forms (6).

ACF has some advantages over the traditional forms (7). Generally, the intraparticle diffusion in GAC is very slow and therefore it controls the overall rate of adsorption. This causes the adsorption and regeneration stages to be very slow (8). In the PAC processes, the overall rate of adsorption is very fast, but it presents the disadvantage that it is quite difficult to deal with the PAC and it is necessary to filter out the solution to separate it, causing losses and inefficient use of PAC (9). The overall rate of adsorption in ACF is as fast as in the PAC but it does not have the handling problems existing in PAC.

Adsorption of Cd(II) onto GAC and PAC has been investigated very extensively (1, 2, 4, 5, 10, 11) but very limited onto ACC. Rangel-Mendez and Streat (8) investigated the adsorption of Cd(II) on an ACC manufactured from PAN that was oxidized electrochemically and using ozone. These authors noticed that both oxidation processes are effective to enhance the adsorption capacity for Cd(II), increasing the capacity up to 13 times that of the ACC without oxidation (8). Neither the effect of temperature and the reversibility of the Cd(II) adsorption on ACC have been studied nor has the adsorption mechanism been elucidated.

The adsorption of zinc, cadmium, silver, gold, palladium, lead, and mercury from aqueous solution on ACC (12) has been studied recently, and it was found that the adsorption capacity is dependent on the solution pH and temperature, concentration of the metal ion, degree of oxidation, and oxidizing agent (8, 12–14).

The aim of this work is to study the adsorption of Cd(II) from aqueous solution onto ACC, and to evaluate the effect of the solution pH and temperature and degree of oxidation of ACC on its adsorption capacity. The interactions between the ACC surface and the Cd(II) ions in solution are also investigated to elucidate the adsorption mechanism of Cd(II) on ACC and to better understand the desorption of Cd(II) adsorbed on ACC.

EXPERIMENTAL SECTION

Activated Carbon Cloth

The ACC used in this work is manufactured from PAN by KoTHmex (AW1102). The ACC was washed repeatedly with distilled water to remove dust and then dried in an oven set at 383 K during 24 h.

Characterization of ACC

The ACC was characterized physically by the N₂-BET method using a surface area and porosimetry analyzer, Micromeritics, model ASAP 2010. The external surface of the carbon fibers was examined by means of a Scanning Electron Microscope, Leica-Cambridge, model S420-i.

Determination of the Point of Zero Charge

The point of zero charge (PZC) for the ACC was determined by the following procedure: 0.1 g of ACC ground in an agate mortar and 20 mL of a 0.01 M KCl–0.004 M KOH solution were added to a glass beaker. The solution was mixed continuously during 48 h. Then, the solution containing the ACC was titrated with a 0.1 M HCl solution using a burette and bubbling N₂ to avoid that the CO₂ present in the air can be absorbed in the solution and formed CO₃²⁻ and HCO₃⁻¹. On the other hand, the 0.01 M KCl–0.004 M KOH solution was also titrated under the same conditions but without ACC (15).

Oxidation of ACC

The ACC was oxidized with HNO₃ by adding 20 g of ACC and 500 mL of a HNO₃ solution in a flask. The oxidation was carried out at three levels that correspond to the HNO₃ concentrations of 10, 20, and 50% v/v. The acid solution containing the ACC was heated to 323 K for 2 h. The oxidized ACC was rinsed several times with deionized water until the pH of the rinsing water remained constant. The ACC was dried in an oven set at 373 K during 24 h and stored in a closed container. Throughout the text the

ACCs oxidized with 10, 20, and 50% v/v HNO₃ solutions are denoted as ACCOx-10, ACCOx-20, and ACCOx-50, respectively.

Determination of Active Sites

Acidic and basic sites on both plain and oxidized ACC were determined by the acid-base titration method proposed by Boehm (16). The acid sites were neutralized with a 0.1 N NaOH solution and the basic sites with a 0.1 N HCl solution. Also the different types of acidic sites were titrated using Na₂CO₃ and NaHCO₃. In this way, the acidic sites neutralized with the NaOH solution correspond to the sum of the carboxylic, phenolic, and lactonic sites; the Na₂CO₃ solution neutralizes both carboxylic and lactonic sites and the NaHCO₃ solution titrates only the carboxylic ones (17).

Determination of Cd(II) Concentration

The concentration of Cd(II) in aqueous solution was determined by atomic absorption spectroscopy using a double beam atomic absorption spectrophotometer, Varian, model SpectrAA-20. The Cd(II) concentration of a sample was estimated using a calibration curve (concentration vs. absorbance) which was prepared for each of the different pH values tested since the curves varied with pH.

Adsorption Equilibrium Data

A solution containing Cd(II) and ACC was introduced into a 500 mL Erlenmeyer flask that served as the experimental batch adsorber. The adsorber was partially submerged into a constant temperature water bath set atop a magnetic stirrer and the adsorber solution was stirred continuously with a Teflon-coated stirring bar.

Experimental adsorption isotherm data were obtained as follows. A predetermined mass of ACC was contacted with a fixed volume of a Cd(II) solution of known initial concentration. The solution remained in contact with the ACC until equilibrium was reached. Preliminary experiments showed that 5 days were enough to reach equilibrium. Samples were taken at various times (3, 4, and 5 days) to follow the progress of adsorption, and Cd(II) concentration for each sample was determined as described previously. The equilibrium was attained when two consecutive samples showed no change in Cd(II) concentration. Solution pH was measured periodically with a pH meter and kept constant by adding 0.01, 0.05, and 0.1 N HNO₃ or NaOH solutions as required. The total volume added of the HNO₃ or NaOH solutions was recorded to be considered in the mass balance.

The mass of Cd(II) adsorbed at equilibrium was calculated by performing a mass balance.

Desorption Equilibrium Data

The reversibility of adsorption was investigated by carrying out desorption experiments which consisted of performing an adsorption experiment as already described. Once equilibrium was reached, the ACC saturated with Cd(II) was removed from the solution, washed with deionized water to eliminate Cd(II) solution caught between the ACC external walls, and then was placed inside a batch adsorber containing 480 mL of a desorbing solution without Cd(II). The washing step was achieved by submerging the ACC into deionized water for 10 sec. The saturated ACC and the desorbing solution were left in contact for 5 days until they reached a new equilibrium. It was assumed that a new equilibrium was reached when the Cd(II) concentration of two consecutive samples remained constant. The initial pH of the desorbing solution was 6 or 2 and the pH was kept constant during desorption, by adding 0.1 M HNO₃ or NaOH solution. The mass of Cd(II) that remained adsorbed on the ACC was estimated by a mass balance.

RESULTS AND DISCUSSION

Textural Properties of ACCs

The textural properties of the ACCs are shown in Table 1. The specific surface areas were slightly greater than 1100 m²/g and the pore volumes were about 0.500 cm³/g. ACCs manufactured from cellulose, pitch, and PAN presented values of specific surface area and pore volume very similar to those reported in this work (6, 18).

As shown in Table 1 the average pore diameter of the ACC is slightly less than 2 nm. This indicates that the porous structure of the ACC is mainly comprised of micropores agreeing with the results reported by other authors (7, 18, 19).

Table 1. Textural properties of ACC without oxidizing and oxidized

ACC	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
ACC	1143	0.45	1.93
ACCOx-10	1184	0.45	1.94
ACCOx-20	1129	0.44	1.96
ACCOx-50	1171	0.45	1.96

Surface Properties of ACCs

The concentrations of active sites for the ACCs are shown in Fig. 1 and the concentration of acidic sites for all ACCs are greater than that of basic ones. Therefore, the surface of all the ACCs is acidic.

The concentrations of the acidic and basic sites for the ACC without oxidizing are 1.055 and 0.296 meq/g, respectively. The concentration of acidic sites is below the range of values reported for a PAN-based ACC (8, 20) and that of basic sites is very close to the value found by Park and Jung (20).

As seen in Fig. 1 the concentration of the acidic sites was increased almost twice whereas that of basic sites was diminished to near half when ACC was oxidized with HNO_3 . The total concentration of the active sites was enhanced around 62%. Several investigators (3, 21–24) have found that the chemical oxidation of GAC and ACC with HNO_3 always increased the concentration of acidic sites while it diminished the concentration of basic ones. This behavior can be attributed to the introduction of oxygenated groups making the ACC surface more acidic.

During the oxidation the concentration of phenolic and carboxylic sites almost doubled and tripled, respectively, and the concentration of the lactonic sites increased less than the other sites (Fig. 1). In the oxidized as well as unoxidized ACC the concentrations of acidic sites reduced in the following order: Phenolic > Carboxylic > Lactonic. Similar results have been reported by Rangel Mendez and Streat (8).

Surface charge on the ACC will be generated when the ACC is contacted with an aqueous solution. The charge is caused by the interactions between the ions present in the solution and the functional groups on the surface.

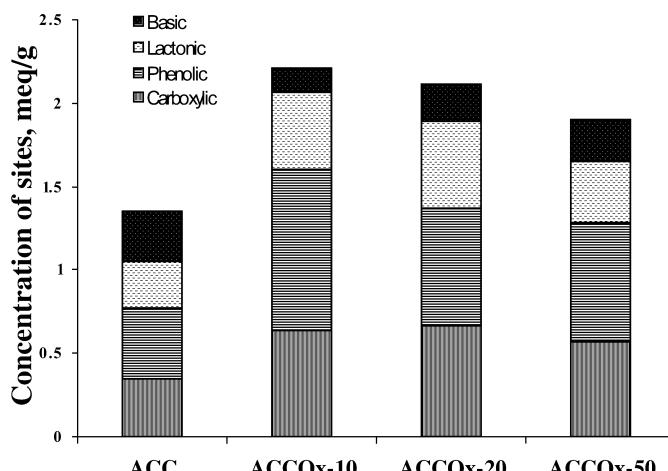


Figure 1. Illustration of the active sites concentrations of ACCs.

The surface charge of ACC is dependent upon the type of ions present, the characteristics of the surface, and the solution pH. The surface is positively charged when the solution pH is below the point of zero charge (PZC), negatively charged at pH above the PZC and neutral when the pH is equal to the PZC.

The PZC of ACC and ACCOx-10 were determined to be 3.8 and 2.9, respectively, indicating that both ACCs are acidic. This result was expected since in both ACCs the concentration of acidic sites was greater than that of basic sites. The PZC of ACC decreased during oxidation with HNO_3 due to the introduction of oxygenated groups on the ACC surface that are of acidic nature.

Morphology of ACCs

An electron micrograph of the ACC is shown in Fig. 2. The morphology of the yarns and woven fabric can be distinguished clearly, and each fiber is an activated carbon. This ACC was prepared by activating a woven fabric of PAN fibers.

The morphology of the individual fibers of the ACC are displayed in Fig. 3. Each ACC fiber is ribbed and its diameter is about 5 μm ; the diameters of ACCs prepared from PAN are in the range 5–10 μm (25). The surface morphology of

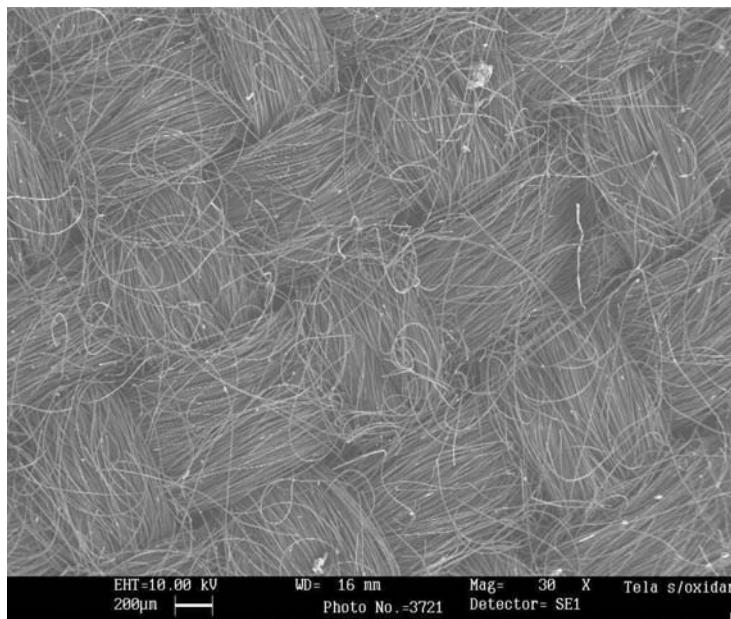


Figure 2. Photomicrograph of the ACC without oxidizing. Magnification factor = 30.

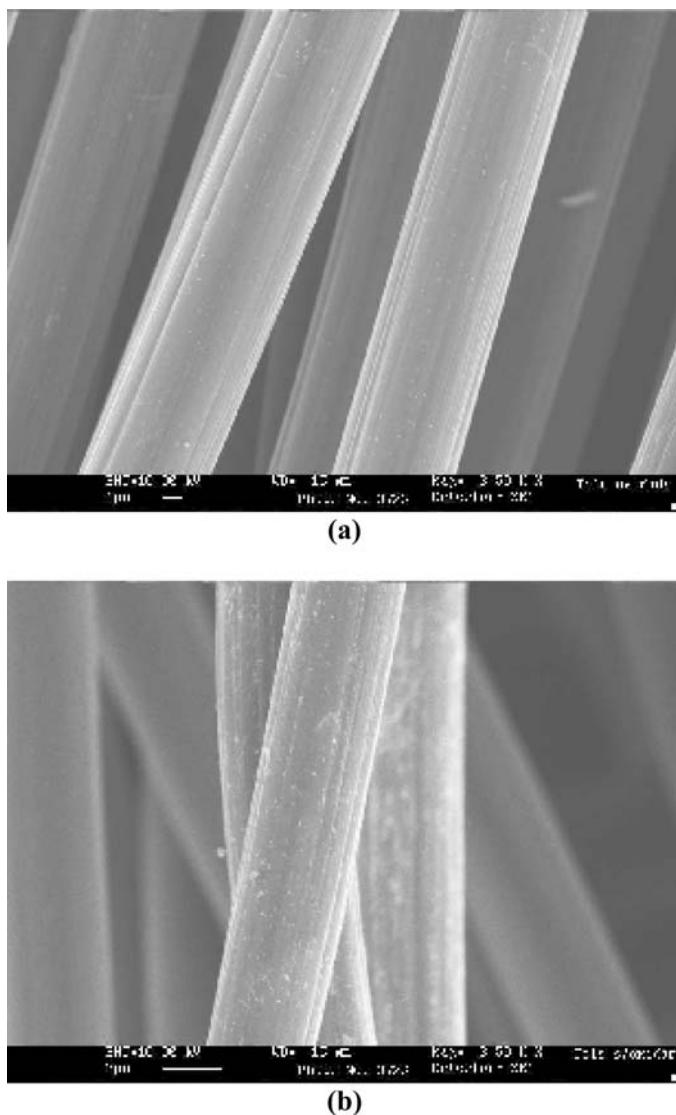


Figure 3. Photomicrographs of ACC without oxidizing (a) and ACCOx-50 (b). Magnification factor = 3500.

the ACC fiber was not affected by oxidation with HNO_3 solution since no surface morphology differences were observed between the ACC without oxidizing (Fig. 3a) and oxidized with 50% HNO_3 (Fig. 3b); however, it was noticed that ACCOx-50 was slightly more fragile than ACC. Physical damage to ACC was reported during oxidation with ozone (8).

Adsorption Isotherm

The experimental equilibrium data for the adsorption of Cd(II) on the ACC were fitted to the adsorption isotherm models of Langmuir, Freundlich, and Prausnitz-Radke. These models are represented by the following equations:

$$q = \frac{q_m K C}{1 + K C} \quad (1)$$

$$q = K C^{1/n} \quad (2)$$

$$q = \frac{a C}{1 + b C^\beta} \quad (3)$$

The values of the isotherm constants were evaluated using a least-squares method based on an optimization algorithm. The average absolute percentage deviation was also calculated as follows:

$$\%D = \left(\frac{1}{N} \sum_{i=1}^N \left| \frac{q_{\text{exp}} - q_{\text{pred}}}{q_{\text{exp}}} \right| \right) \times 100\% \quad (4)$$

The percentage deviation varied from 5.10 to 27.9% for the Langmuir isotherm, 7.51 to 38.9% for the Freundlich isotherm, and 5.26 to 28.6% for the Prausnitz-Radke isotherm. The isotherm best fitting the experimental data was assumed to be that having the lowest average absolute percent deviation. Of the 10 isotherm cases shown in Table 2, 5 were best fit to the Freundlich, 4 to the Prausnitz-Radke, and 1 to the Langmuir isotherm.

Table 2. Constants of the Freundlich isotherm and absolute average percentage deviation

ACC	T (°C)	pH	Freundlich		
			k ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$)	n	%D
ACC	25	W/N ^a	0.85	2.46	10.7
ACCOx-10	25	W/N ^a	3.99	3.59	7.50
ACCOx-20	25	W/N ^a	2.62	2.71	13.6
ACCOx-50	25	W/N ^a	2.97	3.27	7.75
ACCOx-10	25	2	0.02	0.97	24.5
ACCOx-10	25	4	3.22	3.45	11.2
ACCOx-10	25	6	12.6	4.14	19.1
ACCOx-10	25	8	16.3	3.14	38.9
ACCOx-10	15	8	21.7	2.93	16.7
ACCOx-10	35	8	15.7	3.84	9.25

^aW/N = The solution pH was not adjusted.

Moreover, the experimental data were not adjusted satisfactorily to the Langmuir isotherm since the experimental data did not exhibit the asymptotic behavior at higher concentrations that is typical of the Langmuir isotherm.

The Freundlich isotherm was chosen over the other isotherms because this isotherm implies that the adsorption occurs on an energetically heterogeneous surface, and it is very well documented in the literature (26) that the surface of activated carbon is very heterogeneous. The values of the Freundlich isotherm constants as well as the average absolute percentage deviation are all given in Table 2.

Effect of Oxidation on Adsorption Capacity of ACC

The adsorption isotherms of Cd(II) on the ACC without oxidizing and oxidized to different degrees are exhibited in Fig. 4. It can be observed that the adsorption capacity of the ACC was increased more than twice when it was oxidized with HNO_3 solution, and that the adsorption capacity was dependent upon the degree of oxidation (higher concentration of HNO_3).

The adsorption capacity of the ACC oxidized to different degrees can be compared by calculating the mass of Cd(II) adsorbed on ACC at the same equilibrium concentration. At a Cd(II) equilibrium concentration of 50 mg/L, the mass of Cd(II) adsorbed is 4.16 mg/g for the ACC without oxidizing and is 11.9, 10.7, and 9.83 mg/g for the ACCOx-10, ACCOx-20, and ACCOx-50, respectively. This represents an increase in the adsorption

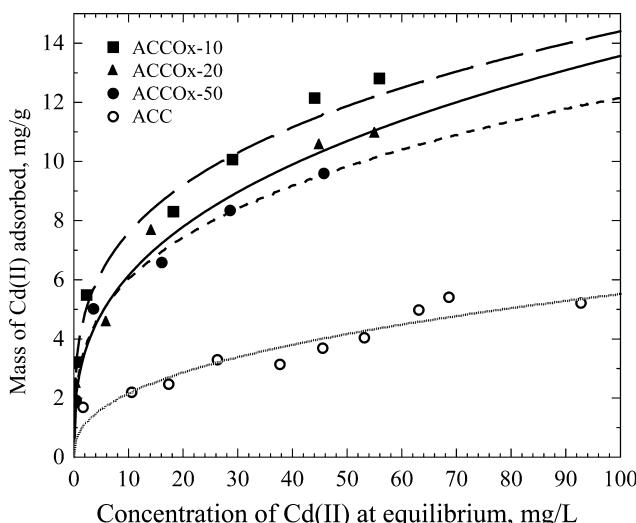


Figure 4. Effect of ACC oxidation on the adsorption isotherm of Cd(II) on ACC. $T = 25^\circ\text{C}$ and solution pH was not adjusted. The lines represent the Freundlich isotherm.

capacity of 2.9, 2.6, and 2.3 times for the ACCOx-10, ACCOx-20, and ACCOx-50, respectively, in comparison to the ACC without oxidizing.

The increase in the adsorption capacity due to oxidation can be explained by recalling that the oxidation increased the concentration of acidic sites on the ACC and that the Cd(II) was mainly adsorbed on these sites. The adsorption capacity of ACCOx-10 was higher than those of ACCOx-20 and ACCOx-50 since ACCOx-10 had more acid sites than the other ACCs. This last effect can be probably related to the consumption and destruction of ACC porous structure during oxidation; however, the textural properties of ACCs (Table 1) did not change significantly and consistently to support this statement.

Effect of pH on the Adsorption Isotherm

It was observed that the solution pH always diminished during the Cd(II) adsorption and it was kept constant by adding 0.01, 0.05, and 0.1 N NaOH or HNO_3 solutions. At the beginning of the adsorption experiments, particularly at initial pH values of 6 or 8, the solution pH fell down considerably to pH values near 3 in the first 2 h. This can be attributed to transfer of H^+ from the ACC surface to the solution.

The effect of pH was investigated by determining the adsorption isotherm of Cd(II) on the ACCOx-10 at the pH values of 2, 4, 6, and 8, the results were plotted in Fig. 5. No adsorption experiments were carried out at pH greater

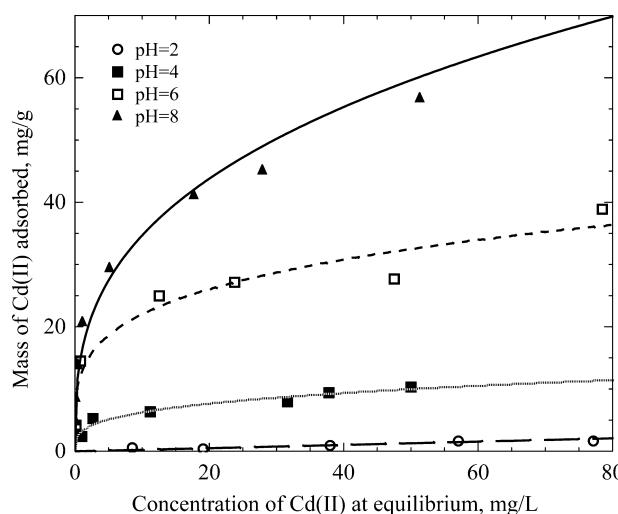


Figure 5. Effect of pH on the adsorption isotherm of Cd(II) on ACCOx-10. $T = 25^\circ\text{C}$. The lines represent the Freundlich isotherm.

than 8 since at these conditions Cd(II) precipitated as Cd(OH)₂. In this figure can be noticed that the adsorption isotherm was affected significantly by the solution pH and that the adsorption capacity was diminished considerably while reducing the pH. The results also revealed that the maximum adsorption capacity occurred at pH 8 and that the capacity increased nearly 22 times increasing the pH from 2 to 8. Similar results have been reported by Reed and Matsumoto (4) and Bhattacharya and Venkobachar (10) for the adsorption of Cd(II) onto GAC and PAC.

The speciation diagram for Cd(II) has been reported in a previous work (3). Accordingly, the predominant ionic species is Cd⁺² for pH below 7 and at pH values just below 9, Cd(II) precipitates as Cd(OH)₂. At pH 8 the species distribution is approximately 90% Cd⁺² and 10% Cd(OH)⁺. Moreover, the solubility diagram of Cd(II) (27) indicated that Cd(II) was not precipitated as Cd(OH)₂ since the pH and Cd(II) concentrations in all the experiments were not in the precipitation region. Hence, Cd(II) was principally adsorbed on ACCOx-10 as Cd⁺².

The effect of pH on the adsorption isotherm was due to interactions between Cd⁺² in solution and the surface charge of ACCOx-10. When the solution pH is above the PZC, Cd⁺² ions were attracted to the negatively charged ACCOx-10 surface, thus favoring Cd⁺² accumulation onto the surface. The surface charge of ACCOx-10 became more negatively charged while increasing the pH above its PZC = 2.9. Then, more Cd⁺² ions were attracted to the surface causing an increase in the adsorption capacity of ACCOx-10. At pH below the PZC, adsorption of Cd(II) was nearly zero since the ACCOx-10 surface was positively charged, causing a mutual repulsion between Cd⁺² ions and the ACC surface. If adsorption occurs at all, it is not due to an electrostatic attraction, but to a chemical interaction with sufficient energy to overcome the surface-ion repulsion.

Effect of Temperature on Adsorption Isotherm

The adsorption isotherm represents the equilibrium relationship between the Cd(II) adsorbed and the Cd(II) in solution, and for this reason it is dependent upon the temperature. The effect of temperature upon the adsorption isotherm of Cd(II) on the ACCOx-10 was investigated by determining the adsorption isotherms at 15, 25, and 35°C, and keeping the solution pH constant at 8. These isotherms are shown in Fig. 6, and it can be observed that the adsorption capacity diminishes when the temperature is increased. Comparing the adsorption isotherms the adsorption capacity is halved on the average while increasing the temperature from 15 to 35°C. This behavior can be attributed to fact that the vibrational energy of the Cd(II) adsorbed increase while elevating the temperature and then more Cd(II) adsorbed possess enough energy to overcome the attractive forces and desorb back to the solution (28).

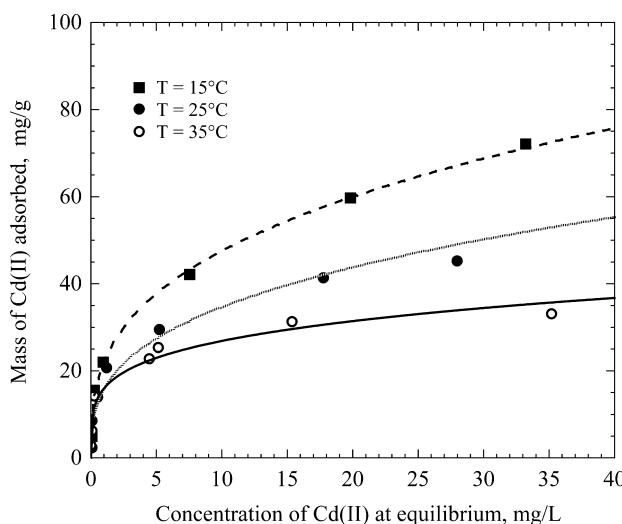


Figure 6. Effect of temperature on the adsorption isotherm of Cd(II) on ACCOx-10. pH = 8. The lines represent the Freundlich isotherm.

Desorption of Cd(II) Adsorbed on ACCOx-10

The Cd(II) was adsorbed on the ACCOx-10 from an aqueous solution at pH 6 and then was desorbed by placing the ACCOx-10 loaded with Cd(II) in an aqueous solution without Cd(II) at either pH 6 or 2. Under these conditions the Cd(II) was now transferred from the ACC to the solution until a new equilibrium was reached.

The results of the adsorption-desorption steps are shown in Fig. 7. The lines in Fig. 7 represent the Freundlich isotherms at pH 6 and 2 evaluated with the isotherm constants reported in Table 2. As expected the adsorption experimental data at pH 6 was on the Freundlich isotherm obtained previously but the desorption equilibrium data was above the Freundlich isotherm except for concentrations lower than 2 mg/L. This means that the new equilibrium reached in the desorption step is not the same as that of the adsorption step.

In the case of desorption with solution at pH 2, the experimental desorption data are very below compared to the experimental adsorption data at pH 6 but are very close to the Freundlich isotherm at pH 2 (see Fig. 7). In other words the equilibrium in the adsorption step is different from that in the desorption step. At pH 2 the concentration of H^+ was much higher than the Cd(II) concentration in solution hence H^+ displaces the Cd⁺² adsorbed on the ACCOx-10 to reach a new equilibrium which corresponds to the Freundlich isotherm at pH 2.

It can be pointed out that in the desorption step, the Cd⁺² adsorbed on the ACCOx-10 was transferred from the ACC to the solution and the H^+ ions in the

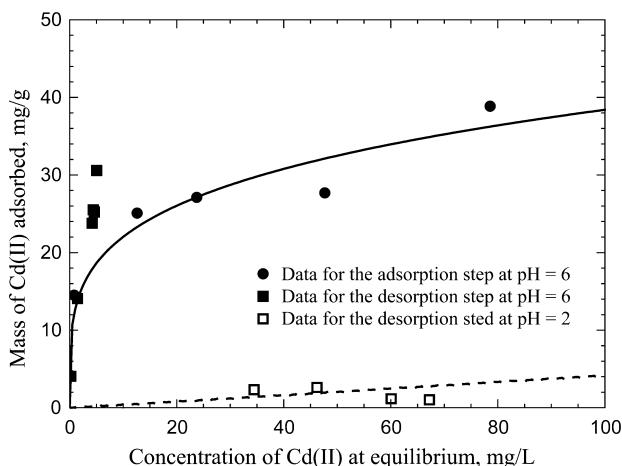


Figure 7. Reversibility of the adsorption isotherm of Cd(II) on ACCOx-10 at $T = 25^\circ\text{C}$. The lines represent the Freundlich isotherm predicted using the constants reported in Table 2.

desorbing solution in the other direction. The amount of Cd(II) desorbed at pH 6 was very small compared to that at pH 2 because the concentration of H^+ at pH 2 was 10^4 times bigger than that at pH 6. Thus, at pH 2 the H^+ ions compete strongly with the Cd^{+2} ions for the acidic sites available for adsorption.

Adsorption Mechanism of Cd(II) on ACC

To elucidate the adsorption mechanism of Cd(II) on the ACCOx-10, it is necessary to understand the interactions among the Cd^{+2} ions in aqueous solution with the surface complexes of the ACC.

Mass balances of ions in the adsorption experiments were performed once equilibrium was attained. It was found that one Cd^{+2} ion was adsorbed for every two H^+ ions released from the ACCOx-10 surface. This indicated that an ion exchange mechanism was taking place and explained why the solution pH decreased during Cd(II) adsorption. The ion exchange mechanism in the carboxylic sites ($\text{S}-\text{COOH}$) can be represented by the following reaction: $2(\text{S}-\text{COOH}) + \text{Cd}^{+2} \leftrightarrow (\text{S}-\text{COO})_2\text{Cd} + 2\text{H}^+$, where S stands for surface of ACC.

The adsorption capacity was reduced while increasing the concentration of H^+ (decreasing pH). This behavior can be explained by considering that the exchange of Cd^{+2} on the ACC was not favored when diminishing the pH since there were more H^+ ions competing with the Cd^{+2} ions for the available acidic sites on the surface. This also explains why the Cd(II) adsorption on ACC was almost null at very acidic pH values.

CONCLUSIONS

The Cd(II) adsorption capacity of ACC increased 2.9, 2.6, and 2.3 times when it was oxidized with 10, 20, and 50% v/v HNO₃ solutions, respectively. This effect was due to the increase of acidic sites caused by oxidation.

The solution pH plays a very important role on the adsorption of Cd(II) on ACC. The adsorption capacity of ACCOx-10 increased about 22 times augmenting pH from 2 to 8, and the maximum adsorption was observed at pH 8. The effect of pH on the adsorption capacity was attributed to the electrostatic interactions between the Cd⁺² ions in solution and the surface charge of ACCOx-10.

The adsorption capacity of ACC was reduced by increasing the temperature from 15 to 35°C. Less Cd⁺² ions were adsorbed on ACC at higher temperatures since the vibrational energy of the Cd⁺² adsorbed was increased, raising the temperature, then more-adsorbed Cd⁺² ions had enough energy to overcome the attracting forces from the ACC surface.

Mass balances of ions carried out in the equilibrium adsorption experiments revealed that two H⁺ ions were released from the surface for every Cd⁺² ion adsorbed on the surface. Thus, Cd(II) was adsorbed on ACC by an ion exchange mechanism. Moreover, the Cd⁺² ions adsorbed on ACCOx-10 at pH 6 were desorbed almost completely by reducing pH to 2. At pH 2 the H⁺ ions in solution competed for the acidic sites and displaced the Cd⁺² ions adsorbed on the ACC surface.

REFERENCES

1. Huang, C.P. and Ostovic, F.B. (1978) Removal of cadmium (II) by activated carbon adsorption. *J. Environ. Eng. Div.*, 104 (EE5): 863–879.
2. Huang, C.P. and Wirth, P.K. (1982) Activated carbon for treatment of cadmium wastewater. *J. Environ. Eng. Div.*, 108 (EE6): 1280–1299.
3. Levy-Ramos, R., Rangel-Mendez, J.R., Mendoza-Barron, J., Fuentes-Rubio, L., and Guerrero-Coronado, R.M. (1997) Adsorption of cadmium (II) from aqueous solution onto activated carbon. *Water Sci. Technol.*, 35 (7): 205–211.
4. Reed, B.E. and Matsumoto, M.R. (1993) Modeling cadmium adsorption by activated carbon using the Langmuir and Freundlich isotherm expressions. *Sep. Sci. Technol.*, 28 (13&14): 2179–2195.
5. Reed, B.E. and Nonavinakere, S.K. (1992) Metal adsorption by activated carbon: effect of complexing ligands, competing adsorbates, ion strength, and background electrolyte. *Sep. Sci. Tech.*, 27 (14): 1985–2000.
6. Suzuki, M. (1994) Activated carbon fiber: fundamentals and application. *Carbon*, 32 (4): 577–586.
7. Carrott, J.A., Nabais, J.M.V., and Ribeiro Carrott, M.M.L. (2001) Preparation of activated carbon fibres from acrylic textile fibres. *Carbon*, 39: 1543–1555.
8. Rangel-Mendez, J.R. and Streat, M. (2002) Adsorption of cadmium by activated carbon cloth: influence of surface oxidation and solution pH. *Water Res.*, 36 (5): 1244–1252.

9. Cheremisinoff, P.N. and Cheremisinoff, N.P. (1993) *Carbon adsorption for pollution control*; Prentice Hall: New Jersey, 53.
10. Bhattacharya, A.K. and Venkobachar, C. (1984) Removal of cadmium (II) by low cost adsorbents. *J. Environ. Eng.*, 110 (1): 110–122.
11. Reed, B.E. and Arunachalam, S. (1994) Removal of lead and cadmium from aqueous waste streams using granular activated carbon (CAG) columns. *Environ. Prog.*, 13 (1): 60–64.
12. Babic, B.M., Milonjic, S.M., Polovina, M.J., Cupic, S., and Kaludjerovic, B.V. (2002) Adsorption of zinc, cadmium and mercury ions from aqueous solutions on an activated carbon cloth. *Carbon*, 40: 1109–1115.
13. Yue, Z.R., Jiang, W., Wang, L., Toghiani, H., Gardner, S.D., and Pittman, C.U. (1999) Adsorption of precious metal ions onto electrochemically oxidized carbon fibers. *Carbon*, 37: 1607–1618.
14. Xiu, G. and Li, P. (2000) Prediction of breakthrough curves for adsorption of lead(II) on activated carbon fibers in a fixed bed. *Carbon*, 38: 975–981.
15. Babic, B.M., Milonjic, S.M., Polovina, M.J., and Kaludjerovic, B.V. (1999) Point zero charge and intrinsic equilibrium constants of activated carbon cloth. *Carbon*, 37: 477–481.
16. Boehm, H.P. (1966) Chemical identification of surface groups. *Adv. Catal.*, 16: 179–274.
17. Bandosz, T.J., Jagiello, J., and Schwarz, J. (1992) Comparison of methods to assess surface acidic groups on activated carbons. *Anal. Chem.*, 64: 891–895.
18. Li, M., Kruk, M., Jaroniec, M., and Ryu, S-K. (1998) Characterization of structural and surface properties of activated carbon fibers. *J. Colloid Interface Sci.*, 204: 151–156.
19. Le Cloirec, P., Brasquet, C., and Subrenat, E. (1997) Adsorption onto fibrous activated carbon: applications to water treatment. *Energy & Fuels*, 11: 331–336.
20. Park, S-J. and Jung, W-Y. (2001) Removal of chromium by activated carbon fibers plated with copper metal. *Carbon Sci.*, 2 (1): 15–21.
21. Shim, J-W., Park, S-J., and Ryu, S-K. (2001) Effect of modification with HNO_3 and NaOH on metal adsorption by pitch-based activated carbon fibers. *Carbon*, 39: 1635–1642.
22. Rangel-Mendez, J.R. (2001) Adsorption of toxic metals from water using commercial and modified granular and fibrous activated carbons. Ph. D Thesis, Loughborough University, Loughborough, England.
23. Hernandez Orta, M.M.G. (2003) Remocion de pentaclorofenol presente en agua por medio de adsorcion sobre carbon activado. M. Sc Thesis, Universidad Autonoma de San Luis Potosi, Mexico.
24. Leyva-Ramos, R., Bernal-Jacome, L.A., Mendoza-Barron, J., Fuentes-Rubio, L., and Guerrero-Coronado, R.M. (2002) Adsorption of zinc(II) from an aqueous solution onto activated carbon. *J. Hazardous Mat.*, 90 (1): 27–38.
25. Park, S-J. and Kim, K-D. (2001) Influence of activation temperature on adsorption characteristics of activated carbon fiber composites. *Carbon*, 39: 1741–1746.
26. Leon y Leon, C.A. and Radovic, L.R. (1994) Interfacial Chemistry and Electrochemistry of Carbon Surfaces. In *Chemistry and physics of carbon*; Thrower, P.A., ed.; Marcel Dekker, Inc.: New York; Vol. 24, 213–310.
27. Baes, C.F. and Mesmer, R.E. (1976) *The hydrolysis of cations*; Krieger Publishing: Malabar, FL, 295–301.
28. Cooney, D.O. (1998) *Adsorption Design for Wastewater Treatment*; Lewis Publishers: Washington, D.C., 29.