

# Role of Carboxylic Sites in the Adsorption of Nickel (II) and Zinc (II) onto Plain and Oxidized Activated Carbon Fibers

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**Abstract** The adsorption mechanism of Ni(II) and Zn(II) onto activated carbon fiber (ACF) cloth and felt plain and oxidized was investigated in this work. The adsorption equilibrium data were obtained in a batch adsorber. The concentration of acidic and basic sites on the ACFS was determined by an acid–base titration method. The experimental adsorption equilibrium data were interpreted with the Redlich–Peterson isotherm, which fitted the data reasonably well. The ACF was oxidized with HNO<sub>3</sub> solution and the concentration of acidic sites increased during oxidation, whereas that of the basic sites diminished. The adsorption capacity of the oxidized ACF was higher than that of the plain ACF because the oxidation of ACF formed more acidic sites on the surface where the metal cations can be adsorbed. The adsorption capacity of the plain and oxidized ACFs was linearly dependent upon the

concentration of carboxylic sites. The adsorption of Ni(II) and Zn(II) on the ACFs was due to both electrostatic interactions and cation- $\pi$  interactions. The contribution of ion exchange to the overall adsorption of Zn(II) and Ni(II) on ACFs was less than 3.3 % and can be considered negligible.

**Keywords** Adsorption · Activated carbon fibers · Carboxylic sites · Zn(II) · Ni(II)

## 1 Introduction

Environmental pollution due to heavy metals is mainly caused by wastes and wastewaters from mining, metallurgical, metal finishing, and chemical industries (Katsou et al. 2012). The main source of metal pollution in surface water is the industrial wastewater discharges. Several heavy-metal ions are toxic and carcinogenic, and represent a hazard to human health and environment (Paul Chen 2013).

Nickel and zinc are toxic metals commonly found in wastewaters because they have many useful applications. Nickel is present in the effluents of several metal-related industries such as silver refining, electroplating, zinc-based casting, and battery manufacturing. At concentrations above the maximum allowed limit (MAL), Ni(II) can cause cancer in the kidney, prostate and stomach, and dermatitis (Kadirvelu et al. 2000). Zinc is very frequently found in effluents from plating, galvanizing, and roller coating processes (Förstner and Wittmann

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1979). Besides, Zn(II) is a trace element that is essential to human health; however, at levels above the MAL, Zn(II) can lead to various health problems such as stomach cramps, skin irritation, vomiting, nausea, and anemia (Samman 2002). Thus, the removal of Zn(II) and Ni(II) from industrial wastewaters to prevent pollution of water sources is of great concern.

Adsorption on granular activated carbon (GAC) is a conventional method for the removal of heavy metals from wastewater (Chaudhuri and Azizan 2012). However, its application has been limited because the rate of adsorption on GAC is slow (Leyva-Ramos et al. 2007). The activated carbon fiber (ACF) is a novel adsorbent that can be used for removing organic as well as heavy metal pollutants from municipal and industrial wastewaters (Brasquet and Le Cloirec 1997; Osmond 2000). The ACF has some advantages over GAC and powdered activated carbon (PAC), which are the traditional forms of activated carbon. The overall rate of adsorption in ACF is much faster than in GAC but as fast as in PAC (Leyva-Ramos et al. 2012). However, ACF does not have the handling problems existing with PAC.

The adsorption of Cd(II) and Pb(II) on ACFs has been investigated extensively (Babic et al. 2002; Leyva-Ramos et al. 2004, 2005b, 2011; Rangel-Mendez and Streat 2002), and it has been demonstrated that the capacity of the ACFs for adsorbing these heavy metals can be enhanced by increasing the pH and temperature.

Adsorption of Ni(II) and Zn(II) onto GAC, PAC, and other adsorbents has been investigated extensively (Paul Chen and Lin 2001; Gupta and Sharma 2003; Leyva-Ramos et al. 2005a; Madhava-Rao et al. 2008). Nevertheless, few works have been aimed at studying the adsorption of Ni(II) and Zn(II) from water solution on ACFs (Alvarez-Merino et al. 2005; Kadirvelu et al. 2000; Faur-Brasquet et al. 2002; Shim et al. 2001; Soo-Jin et al. 2004).

The principal purpose of this work was to investigate the role of the acidic sites on the adsorption of Ni(II) and Zn(II) from aqueous solutions onto several types of ACFs. In addition, the dependence of the adsorption capacity of the ACF upon the surface properties, degree of oxidation, and type of ACF was also examined comprehensively.

## 2 Materials and Methods

### 2.1 Activated Carbon Fibers

Commercial ACFs in the forms of cloth and felt were used in this work. The ACF cloth is commercially known as AW1104 and is fabricated from polyacrylonitrile by KoTHmex, and the ACF felt is traded as ACN211-15 and is produced from Novoloid (phenolic resin) by American Kynol. The ACFs were washed oftentimes with distilled water and then dried in an electric oven set up at 383 K for 24 h.

### 2.2 Textural and Physicochemical Properties of ACFs

The surface area, pore volume, and mean pore diameter were determined by the N<sub>2</sub>-BET method using a surface area and porosimetry analyzer, Micromeritics, model ASAP 2010. The point of zero charge (PZC) and surface charge distribution were determined by the acid–base titration method proposed by Babic et al. (2002). The procedure is described as follows. A mass of 0.1 g of ground ACF and 20 mL of 0.1 M NaCl solution were added to a 50-mL polypropylene bottle. It is important to mention that the ground ACF sample was only used in the determination of the surface charge. A volume, ranging from 0.1 to 5 mL, of 0.1 M NaOH or HCl solution was added to the NaCl solution to adjust the solution pH over the pH range of 1.8–12.0. Next, N<sub>2</sub> was bubbled above the solution for 5 min to avoid the CO<sub>2</sub> present in the air to be absorbed in the solution and form CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-1</sup>. Each bottle was capped and set on the top of a magnetic stirrer, and the solution was stirred for 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. Further details on this method can be found elsewhere (Leyva-Ramos et al. 2011).

### 2.3 Determination of Active Sites

The acidic and basic sites of ACFs were determined by the volumetric method proposed by Boehm (1966). 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 titrated using 0.1-M Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> solutions. In this way, the acidic sites titrated with the NaOH

solution were the carboxylic, phenolic, and lactonic sites; the  $\text{Na}_2\text{CO}_3$  solution neutralized both carboxylic and lactonic sites, and the  $\text{NaHCO}_3$  solution only titrated the carboxylic ones (Boehm 1966). The procedure for determining the acidic and basic sites consisted of adding 50 mL of 0.1 M neutralizing solution and 1 g of ACF to a polypropylene bottle. The bottle was placed in a constant temperature water bath set up at 298 K for 5 days. The bottle was manually shaken twice a day. Afterwards, a sample was taken and titrated with 0.1 N HCl or NaOH solution, as needed.

#### 2.4 Oxidation of ACF

The cloth AW1104 and felt ACN-211-15 were oxidized with  $\text{HNO}_3$  solution by adding 20 g of ACF and 500 mL of  $\text{HNO}_3$  solution into a flask. The concentration of the  $\text{HNO}_3$  solution was either 7.5 % or 15 % v/v. The solution containing the ACF was heated up to 333 K for 2 h and subsequently, the solution was allowed to cool down to room temperature. The oxidized ACFs were washed oftentimes with deionized water until the pH of the washing solution remained constant. The oxidized ACFs were dried in an electric oven set up at 373 K for 24 h and stored in a closed container. The oxidized ACFs were denominated as ACN211-15OX15, AW1104OX7.5, and AW1104OX15 where the last two digits refer to the concentration of  $\text{HNO}_3$  used during the oxidation.

#### 2.5 Determination of Ni(II) and Zn(II) Concentration

The concentrations of Ni(II) and Zn(II) in aqueous solutions were quantified using a double-beam atomic absorption spectrophotometer, Varian, model SpectraAA-20. The heavy metal concentration of the sample was estimated with a calibration curve (concentration of metal vs. absorbance) prepared with standard solutions of Ni(II) or Zn(II).

#### 2.6 Adsorption Equilibrium Data

The aqueous solutions of Ni(II) and Zn(II) were prepared by dissolving a given mass of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with a solution having a pH=6. This last solution was made by mixing proper volumes of 0.01 M  $\text{HNO}_3$  and NaOH solutions.

The experimental adsorption equilibrium data were obtained by a batch adsorption method. A mass of 0.3 g of the ACF and 40 mL of a metal solution of known initial concentration were added to a 50-mL conical vial (adsorber), which was placed in a vial rack inside a thermostatic bath set up at  $T=25$  °C. The initial concentration of metal varied from 60 to 350 mg/L. Four times a day, the adsorber solution was stirred by placing the rack with the vials in an orbital shaker for 15 min. The solution pH was determined periodically with a pH meter and kept constant by adding few drops of 0.01 N  $\text{HNO}_3$  or NaOH solution, as required. The initial volume of the adsorber solution was assumed to be constant because the total volume of 0.01 M NaOH and  $\text{HNO}_3$  solutions added to the adsorber was less than 0.5 % of the initial volume. The metal solution and the ACF were allowed to attain equilibrium. The equilibrium was reached in 5 days when the metal concentration of two consecutive samples of the adsorber solution did not vary. The mass of metal adsorbed at equilibrium was calculated by performing a mass balance of the heavy metal, which is represented by the following equation:

$$q = \frac{V_0(C_0 - C_F)}{m}, \quad (1)$$

where  $C_0$  is the initial concentration of the metal (milligrams per gram);  $C_F$  is the concentration of metal at equilibrium (milligrams per gram);  $m$  is the mass of ACF (grams);  $q$  is the mass of metal adsorbed on the ACF (milligrams per gram); and  $V_0$  is the initial volume of the metal solution (liters).

All the adsorption experiments were carried out at pH=6 and  $T=25$  °C because the effects of temperature and pH on the adsorption capacity of ACFs towards heavy metals are not being studied in this work.

#### 2.7 Desorption Equilibrium Data

The reversibility of Ni(II) and Zn(II) adsorption on the ACFs was examined by carrying out adsorption-desorption experiments. First, adsorption experiments were completed as already described. Once equilibrium was reached, the desorption experiment was performed by removing the ACF saturated with Ni(II) or Zn(II) from the adsorber solution and placing it inside a batch adsorber containing 40 mL of a desorbing solution without Zn(II) or Ni(II). The ACF loaded with the metal

and the desorbing solution attained equilibrium again in 7 days. The initial pH of the desorbing solution was 4 or 6, and the pH was kept constant during desorption as indicated previously. At the desorption equilibrium, the mass of Ni(II) or Zn(II) that remained adsorbed on the ACF was computed by the following mass balance:

$$q_d = q_0 - \frac{V_0}{m} C_F, \quad (2)$$

where  $q_0$  is the mass of metal adsorbed on the ACF at the beginning of the desorption stage (milligrams per gram) and  $q_d$  is the mass of metal that remained adsorbed on the ACF at the end of the desorption stage (milligrams per gram).

### 3 Results and Discussion

#### 3.1 Textural Properties of ACFs

The textural properties of the plain and oxidized ACFs are given in Table 1. The  $N_2$ -BET surface areas ranged from 1,156 to 1,370  $m^2/g$ , and these values are within the range reported for other ACFs (Diaz-Flores et al. 2006; Leyva-Ramos et al. 2004; Rangel-Mendez and Streat 2002). Besides, the average pore diameters of all the ACFs were smaller to 2 nm, revealing that the ACFs were mainly composed of micropores. It was noted that the surface area increased as the pore volume was augmented. This behavior is expected in a porous adsorbent since the surface area is mainly related to its porosity. During the oxidation, the pore volume and the surface area of the ACF increased, meanwhile the pore diameter remained constant. This result can be explained assuming that the average length of the pores was enlarged because the bottom of the pore was partly consumed during the oxidation.

#### 3.2 Physicochemical Properties of ACFs

The concentrations of active sites for the ACFs are presented in Table 2. The concentrations of the acidic sites in all the ACFs were greater than those of basic sites; hence, the surface of the ACF was acidic. Moreover, the oxidation of the ACFs with a  $HNO_3$  solution enhanced the concentrations

of acidic sites and reduced the concentration of basic sites. It is well documented that the concentration of acidic sites increases during oxidation of the ACFs with  $HNO_3$ , caused by the introduction of oxygenated groups on the ACF surface (Leyva-Ramos et al. 2005b; Park et al. 2004).

The concentrations of the different types of acidic sites are illustrated in Fig. 1. As seen in this figure, the concentration of phenolic and carboxylic sites of AW1104 increased during the oxidation with  $HNO_3$ , whereas the concentration of lactonic sites did not change. For ACN-211-15, the concentrations of the carboxylic and lactonic sites almost doubled and tripled, respectively, and the concentration of the phenolic increased less than the other sites.

The PZC of all the ACFs are shown in Table 2. The PZC is the solution pH at which the surface charge of the ACF is neutral. The surface charge in the ACFs is due to the interaction between the ions in the solution and the functional groups present on the surface of the ACF. 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 at  $pH=PZC$ . The PZCs of the plain and oxidized AW1104 cloth and ACN 211-15 felt were below  $pH=7$ , indicating that both ACFs are acidic.

The PZC of the ACFs augmented in the following order: AW1104 < ACN211-15. The surfaces of the cloth AW1104 and felt ACN211-15 were both acidic since their PZCs were below 7. It is obvious that the surface character depended on the concentrations of both acidic and basic sites.

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

#### 3.3 Adsorption isotherm

The experimental adsorption equilibrium data of Zn(II) and Ni(II) on the plain and oxidized ACFs were interpreted using the Freundlich, Langmuir, and Redlich–Peterson adsorption isotherms. These

**Table 1** Textural properties of plain and oxidized ACFs

| ACF           | Precursor | Form  | Surface area (m <sup>2</sup> /g) | Pore volume (cm <sup>3</sup> /g) | Mean pore diameter (nm) |
|---------------|-----------|-------|----------------------------------|----------------------------------|-------------------------|
| AW1104        | PAN       | Cloth | 1,172                            | 0.568                            | 1.93                    |
| AW1104OX7.5   | PAN       | Cloth | 1,306                            | 0.646                            | 1.96                    |
| AW1104OX15    | PAN       | Cloth | 1,156                            | 0.574                            | 1.97                    |
| ACN211-15     | Novoloid  | Felt  | 1,236                            | 0.576                            | 1.91                    |
| ACN211-15OX15 | Novoloid  | Felt  | 1,370                            | 0.639                            | 1.91                    |

PAN polyacrylonitrile

isotherm models can be mathematically represented as follows:

$$q = kC^{1/n}, \tag{3}$$

$$q = \frac{q_m KC}{1 + KC}, \tag{4}$$

$$q = \frac{K_R C}{1 + a_R C^\beta}, \tag{5}$$

where  $a_R$  is a constant of the Redlich–Peterson isotherm (L<sup>β</sup>/mg<sup>β</sup>);  $β$  is a constant of the Redlich–Peterson isotherm;  $C$  is the metal concentration in aqueous solution at equilibrium (milligrams per liter);  $k$  is a constant of the Freundlich isotherm (L<sup>1/n</sup>/mg<sup>1-1/n</sup>g<sup>-1</sup>);  $K$  is a constant of the Langmuir isotherm (liters per milligram);  $K_R$  is a constant of the Redlich–Peterson isotherm (liters per milligram);  $n$  is a Freundlich isotherm related to the adsorption intensity;  $q$  is the mass of metal adsorbed on ACF (milligrams per gram); and  $q_m$  is a Langmuir constant representing the maximum

mass of metal adsorbed on ACF (milligrams per gram).

The adsorption isotherm constants were evaluated by a least-squares nonlinear method, and the values of the isotherm constants as well as the average absolute percentage deviation are presented in Table 2. The average absolute percentage deviation, %D, was computed with the following equation:

$$\%D = \frac{1}{N} \sum_{i=1}^N \left| \frac{q_{\text{exp}} - q_{\text{pred}}}{q_{\text{exp}}} \right| \times 100\%, \tag{6}$$

where  $N$  is the number of experimental data points,  $q_{\text{pred}}$  is the mass of metal adsorbed predicted with the adsorption isotherm, and  $q_{\text{exp}}$  is the experimental mass of metal adsorbed.

The values of %D for the Langmuir, Freundlich, and Redlich–Peterson isotherms varied within 3.36 to 29.6 %, 4.46 to 17.4 % and 2.41 to 13.1 %, respectively. It was considered that the Redlich–Peterson isotherm best fitted the experimental data due to that the average absolute percentage deviation for this isotherm was the lowest in more isotherm cases than those of the Langmuir and Freundlich isotherms (see

**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          | 0.408                                 | 0.232    | 0.611    | 1.251       | 0.201 | 5.16  |
| AW1104 OX7.5    | 0.555                                 | 0.290    | 0.818    | 1.663       | 0.273 | 3.34  |
| AW1104 OX15     | 0.596                                 | 0.332    | 0.900    | 1.828       | 0.280 | 3.42  |
| ACN-211-15      | 0.340                                 | 0.140    | 0.470    | 0.950       | 0.460 | 6.13  |
| ACN-211-15 OX15 | 0.600                                 | 0.400    | 0.600    | 1.600       | 0.300 | 3.84  |

**Fig. 1** Illustration of the concentrations of acidic sites in the ACFs

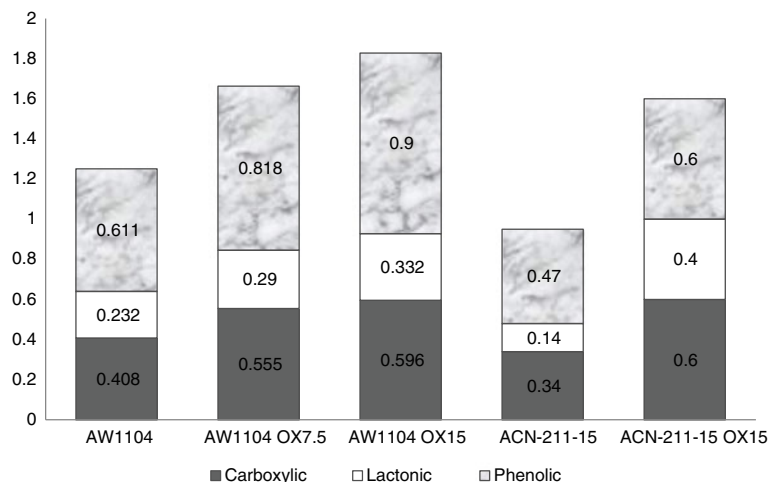


Table 3). Furthermore, the Langmuir and Freundlich isotherms are special cases of the Redlich–Peterson isotherm. From the above-mentioned, the Redlich–Peterson isotherm was chosen to represent the adsorption equilibrium data of Ni(II) and Zn(II) on ACFs.

### 3.4 Effect of ACF Type on the Adsorption Isotherm

At pH=6 and  $T=25$  °C, the adsorption isotherms of Zn(II) and Ni(II) on the plain ACFs are shown in Fig. 2a and b. The capacities for adsorbing Zn(II) and Ni(II) decreased in the following order: AW1104 > ACN-211-15. The surface areas diminished in the following order: ACN-211-15 > AW1104. Hence, the adsorption capacity was not exclusively dependent on the

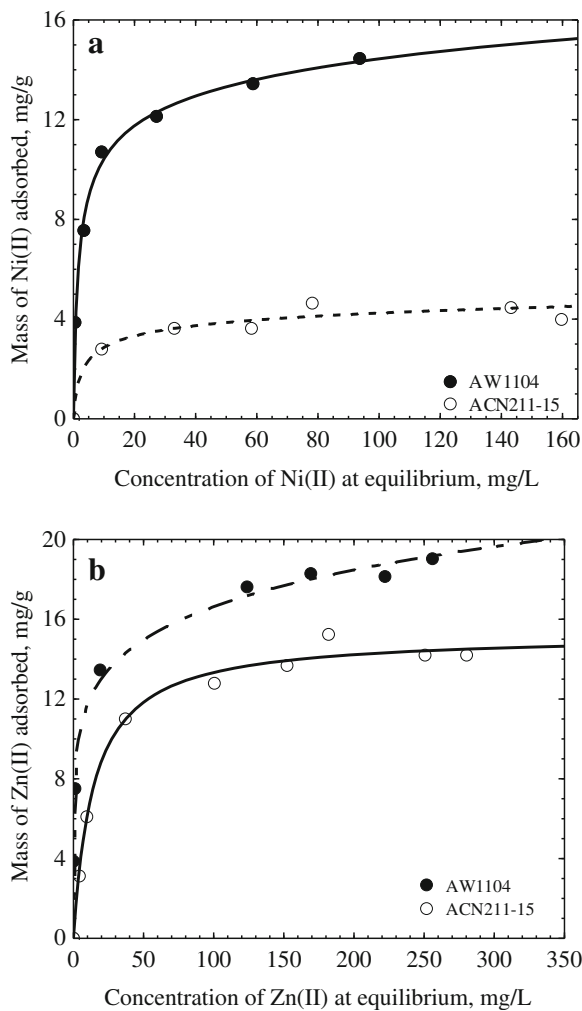
surface area. Moreover, the total acidic and carboxylic sites decreased in the following order: AW1104 > ACN211-15. Hence, the adsorption capacities of the ACFs followed the same order as the total acidic and carboxylic sites. Thus, the adsorption of heavy metal cations on ACFs is highly dependent on the surface properties such as concentration of acidic sites.

At pH=6, the  $Zn^{2+}$  and  $Ni^{2+}$  cations were mainly adsorbed on the carboxylic as well as on the phenolic sites of ACFs. The capacity of AW1104 cloth for adsorbing Zn(II) and Ni(II) at pH=6 was 1.2 and three times greater than that of ACN-211-15 felt. This result can be explained arguing that the  $Ni^{2+}$  and  $Zn^{2+}$  cations were attracted more strongly to the AW1104 surface because the PZC of the AW1104 was lower than that of the ACN-211-15.

**Table 3** Constants for the Freundlich, Langmuir, and Redlich–Peterson isotherms

| Ion       | ACF            | Langmuir     |              |      | Freundlich                           |      |      | Redlich–Peterson   |                              |         |      |  |
|-----------|----------------|--------------|--------------|------|--------------------------------------|------|------|--------------------|------------------------------|---------|------|--|
|           |                | $q_m$ (mg/g) | $K_L$ (L/mg) | %D   | $K_F$ ( $L^{1/n}/mg^{1-1/n}g^{-1}$ ) | $n$  | %D   | $K_R$ (L/g)        | $a_R$ ( $L^\beta/mg^\beta$ ) | $\beta$ | %D   |  |
| $Ni^{2+}$ | AW1104         | 14.0         | 0.391        | 7.28 | 5.81                                 | 4.77 | 10.5 | 9.71               | 1.04                         | 0.902   | 2.41 |  |
|           | AW1104OX7.5    | 16.3         | 0.574        | 29.5 | 6.90                                 | 5.09 | 11.8 | $1.55 \times 10^3$ | $2.23 \times 10^2$           | 0.805   | 13.1 |  |
|           | AW1104OX15     | 21.0         | 2.64         | 15.2 | 11.5                                 | 5.76 | 16.4 | $1.39 \times 10^2$ | 9.55                         | 0.892   | 6.36 |  |
|           | ACN-211-15     | 4.60         | 0.147        | 7.92 | 2.09                                 | 6.57 | 6.08 | 2.10               | 0.82                         | 0.887   | 5.66 |  |
|           | ACN-211-15OX15 | 18.9         | 0.106        | 29.6 | 5.89                                 | 4.36 | 10.8 | $6.86 \times 10^2$ | $1.14 \times 10^2$           | 0.775   | 10.8 |  |
| $Zn^{2+}$ | AW1104         | 22.7         | 1.78         | 13.0 | 10.5                                 | 5.99 | 17.4 | 80.2               | 5.50                         | 0.902   | 11.3 |  |
|           | AW1104OX7.5    | 23.7         | 0.105        | 23.9 | 6.57                                 | 4.20 | 5.57 | 77.1               | 10.8                         | 0.779   | 3.98 |  |
|           | AW1104OX15     | 22.7         | 1.78         | 13.0 | 10.4                                 | 5.99 | 17.4 | 80.2               | 5.50                         | 0.902   | 11.3 |  |
|           | ACN-211-15     | 15.2         | 0.069        | 3.36 | 3.63                                 | 3.86 | 15.2 | 1.06               | 0.07                         | 1.000   | 3.66 |  |
|           | ACN-211-15OX15 | 26.3         | 0.039        | 21.1 | 6.53                                 | 4.19 | 4.46 | $8.83 \times 10^2$ | $1.34 \times 10^2$           | 0.763   | 4.33 |  |





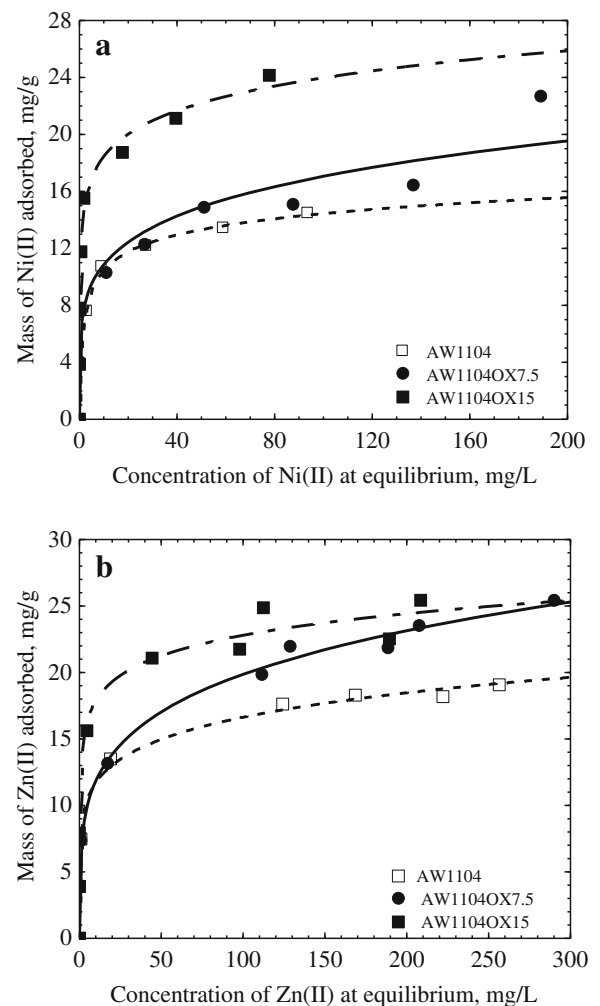
**Fig. 2** Adsorption isotherms of Ni(II) (a) and Zn(II) (b) on the plain ACFs at pH=6 and  $T=25$  °C. The lines represent the adsorption isotherms of Redlich–Peterson

### 3.5 Effect of Degree of Oxidation on the Adsorption Capacity

In several works, it has been shown that the adsorption capacity of the ACFs can be considerably enhanced by oxidizing the ACFs using a  $\text{HNO}_3$  solution (Harry et al. 2006; Leyva-Ramos et al. 2005b, 2011; Park and Kim 2005; Shim et al. 2001). The oxidation formed 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 7.5 % and 15 %  $\text{HNO}_3$  solution.

The adsorption isotherms of Zn(II) and Ni(II) on the plain AW1104 and AW1104 oxidized at different

degrees are exhibited in Fig. 3a and b, respectively. The degree of oxidation was referred to the concentration of  $\text{HNO}_3$  used in the oxidizing solution. In Fig. 3a, it can be seen that the Ni(II) adsorption capacity of AW1104 was increased from 1.4 to 1.5 times when the ACF was oxidized with 7.5 % and 15 %  $\text{HNO}_3$  solution, respectively. Also, the adsorption capacity of AW1104 towards Zn(II) was augmented from 1.1 to 1.3 at concentration at equilibrium of 100 mg/L when the ACF was modified with 7.5 % and 15 %  $\text{HNO}_3$  solutions (see Fig. 3b). The ACFs AW1104OX7.5 and AW1104OX15 exhibited the same capacity for adsorbing when the concentration at equilibrium was near 300 mg/L.



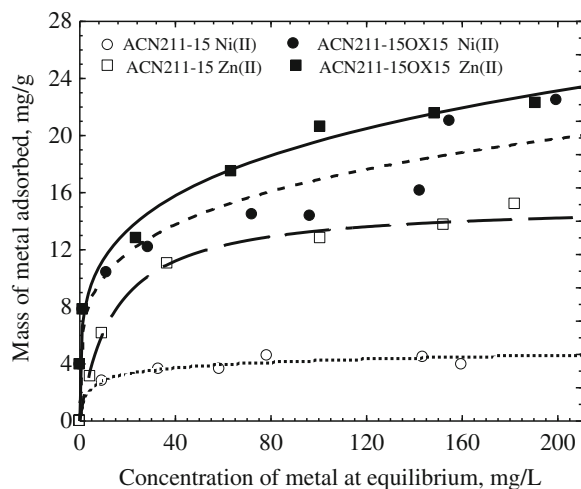
**Fig. 3** Effect of the oxidation degree on the adsorption of Ni(II) (a) and Zn(II) (b) on AW1104 at pH=6 and  $T=25$  °C. The lines represent the adsorption isotherms of Redlich–Peterson

The capacities of ACN-211-15 and ACN-211-15OX15 for adsorbing Ni(II) and Zn(II) are presented in Fig. 4, and the adsorption capacity was augmented 4.1 and 1.7 times when the ACF was oxidized with 15 % HNO<sub>3</sub>, respectively. In addition, the oxidized ACF was more selective towards Zn(II) than Ni(II). Therefore, the adsorption capacity of ACF was dependent upon the degree of oxidation. This result was attributed to the enhancement of the concentrations of acidic sites caused by the oxidation.

The Ni(II) and Zn(II) adsorption capacities of plain and oxidized AW1104 decreased in the following order: AW1104OX15 > AW1104OX7.5 > AW1104. As it can be noted in Fig. 1, the concentration of carboxylic sites decreased in the same order. This order indicated that the Ni<sup>2+</sup> and Zn<sup>2+</sup> were mainly adsorbed on the carboxylic sites. This result was expected because the carboxylic sites were deprotonated at pH below 6, whereas the phenolic sites were normally deprotonated at pH above 6 (Mironov and Taushkanou 1974).

### 3.6 Reversibility of Adsorption of Ni(II) and Zn(II) on ACF

A solute adsorbed on a material is normally desorbed by placing the adsorbent saturated with a metal in a solution without the metal. In this way, the metal adsorbed on the surface would be desorbed and diffused back to the solution. The desorption studies can be useful to elucidate



**Fig. 4** Effect of oxidation degree on the adsorption of Zn(II) and Ni(II) on ACN-211-15 at pH=6 and  $T=25$  °C. The lines represent the adsorption isotherms of Redlich–Peterson

the adsorption mechanism and find a procedure for regenerating the saturated adsorbent.

The Ni(II) and Zn(II) were adsorbed on the cloth AW1104OX7.5 from an aqueous solution at pH=6, and then the Ni(II) and Zn(II) were desorbed by placing the AW1104OX7.5 loaded with Zn(II) or Ni(II) in an aqueous solution without Ni(II) or Zn(II) at pH=6 and pH=4. At this condition, the adsorbed Ni<sup>2+</sup> or Zn<sup>2+</sup> ions were now transferred from the cloth AW1104OX7.5 to the solution until equilibrium was attained again.

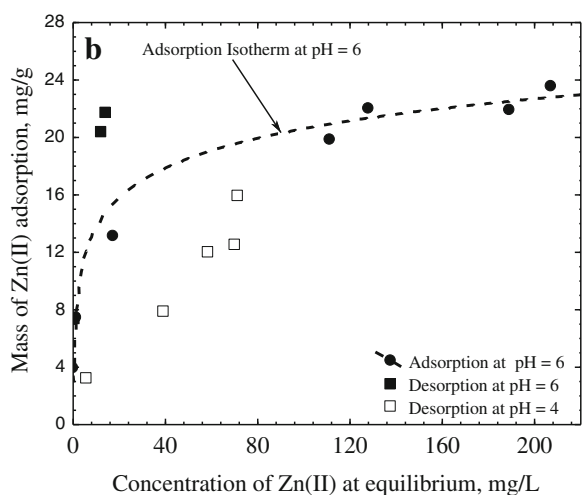
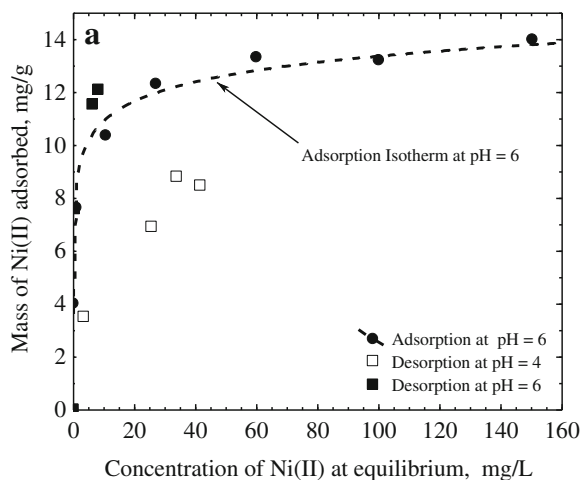
The results of the adsorption and desorption steps for Ni(II) and Zn(II) are shown in Fig. 5a and b, respectively. The line drawn in both figures represents the Redlich–Peterson isotherm at pH=6 (Table 3). For both metals, the experimental desorption equilibrium data at pH=6 were above the Redlich–Peterson isotherm except for concentrations below 2 mg/L. This means that the desorption equilibrium is not the same as that of the adsorption step. On the other hand, the desorption with a solution at pH=4 was slightly below the experimental adsorption equilibrium data and adsorption isotherm at pH=6. This indicated that an amount of the Ni(II) or Zn(II) adsorbed at pH=6 was desorbed by contacting the saturated ACF with a solution at pH=4. At pH=4, the concentration of H<sup>+</sup> was higher than the Ni(II) or Zn(II) concentration in the solution, hence the H<sup>+</sup> ions displaced the Ni<sup>2+</sup> or Zn<sup>2+</sup> ions adsorbed on the ACF to reach equilibrium again. Thus, the ions H<sup>+</sup> compete with the Ni<sup>2+</sup> or Zn<sup>2+</sup> ions for the acidic sites available for adsorption.

### 3.7 Adsorption Mechanism of Ni(II) and Zn(II) on ACFs

The adsorption mechanism of Ni(II) and Zn(II) on the ACFs can be explained if the interactions between the ions in aqueous solution, and the acidic sites of the ACF are fully understood.

In the previous sections, it has been shown that the capacities of the ACFs for adsorbing Ni(II) and Zn(II) were highly influenced by the concentrations of the total acidic and carboxylic sites. The effects of the concentrations of total acidic and carboxylic sites upon the maximum adsorption capacity (Langmuir isotherm constant),  $q_m$ , were graphed in Fig. 6, and the results showed that the adsorption capacity of the ACFs towards Ni(II) and Zn(II) was linearly dependent on the concentration of the carboxylic sites.



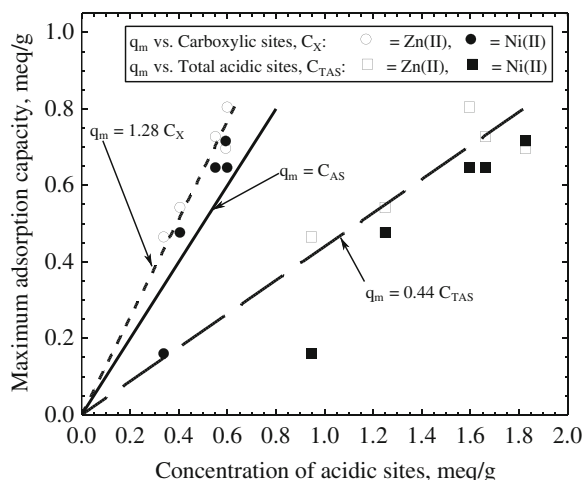


**Fig. 5** Adsorption of the metal at pH=6 and desorption of the metal from cloth AW1104OX7.5 at pH=6 and pH=4,  $T=25\text{ }^{\circ}\text{C}$ . **a** Ni(II) and **b** Zn(II)

Similar results were also reported by Leyva-Ramos et al. (2011) for the adsorption of Pb(II) on ACFs. Except for one data point, the  $q_m$  was well correlated to the concentration of carboxylic sites,  $C_X$ , by the following linear equation:

$$q_m = 1.29C_X \tag{7}$$

It is important to highlight that the maximum adsorption capacities,  $q_m$ , in milliequivalent per gram of the ACFs plain and oxidized for adsorbing Ni(II) are almost the same as those for adsorbing Zn(II). This result was expected since both metal cations can be adsorbed on the same acidic sites of the ACFs.



**Fig. 6** Effect of the concentrations of carboxylic and total acidic sites on the maximum adsorption capacity of the ACFs towards Ni(II) and Zn(II)

As a comparison, the straight line  $q_m=C_X$  was also drawn in Fig. 6. This line represents the case when the metal cations adsorb solely on the carboxylic sites. As seen in Fig. 6, the line  $q_m=1.29C_X$  is above the line  $q_m=C_X$ , so that the adsorption was not only occurring on the carboxylic sites.

Furthermore, it is shown in Fig. 6 that the  $q_m$  is also influenced by the concentration of the total acidic sites. The relationship between the  $q_m$  and the concentration of total acidic sites,  $C_{TAS}$ , can be represented by the following equation:

$$q_m = 0.44C_{TAS} \tag{8}$$

As depicted in Fig. 6, Eq. (8) did not correlate satisfactorily the experimental data, and the experimental data deviated considerably from Eq. (8) and did not exhibit a linear behavior. Hence, the adsorption capacity of ACFs was more pronouncedly affected by the concentration of carboxylic sites than that of the total acidic sites. This last effect revealed 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 Tauskhanou 1974) and the adsorption was carried out at pH=6 for both ions.

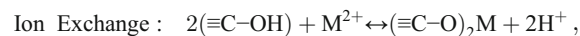
The amount of protons,  $H^+$ , released from the ACF to the solution,  $q_H$ , and the uptake of metal adsorbed on the ACF,  $q_{Me}$ , were determined to evaluate the contribution of ion exchange to the overall adsorption of the metals on the ACFs. In this case, the adsorption

experiments were performed by contacting 0.3 g of AW1104 with 40 mL of a free-metal solution at pH=6. The pH of the solution was measured periodically and kept constant at pH=6 as described previously. Once the solution pH did not vary over time, it was assumed that the free-metal solution and the AW1104 have attained equilibrium. Then, an aliquot of the free-metal solution was taken and was replaced by another aliquot of the metal solution with known concentration and having the same pH of the free-metal solution. The adsorption experiment proceeded as before except that the solution pH was not kept constant. The final pH of solution and the final concentration of the metal were determined as described before. The  $q_H$  and  $q_{Me}$  were calculated from a mass balance of H and metal Me, and then  $q_H$  and  $q_{Me}$  were converted to milliequivalents per gram divided by the equivalent weight of the metal cation and  $H^+$ . The experimental conditions and the values of  $q_H$  and  $q_{Me}$  can be found in Table 4.

The importance of the ion exchange to the overall adsorption of the metals was estimated by evaluating the ratio  $q_H/q_{Me}$  and the values of this ratio are also shown in Table 4. The  $q_H/q_{Me}$  ranges from 0.008 to 0.033 and 0.006 to 0.022 for Ni(II) and Zn(II), respectively. These ranges imply that the contribution of ion exchange is less than 3.3 % of the overall adsorption. Leyva-Ramos et al. (2011) reported that the ion exchange mechanism contributed from 17 % to 43 % to the overall adsorption of Pb(II) on an ACF at pH=4. This contribution may be relatively high compared to the value estimated in this work, but the contribution in this work was evaluated at pH=6, whereas Leyva-Ramos et al. (2011) determined the contribution at

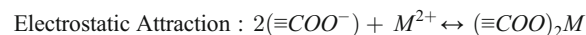
pH=4. The difference in these contributions can be attributed to the differences in the concentration of  $H^+$ .

The ion exchange mechanism of  $Ni^{2+}$  or  $Zn^{2+}$  can be represented by the following reaction:



where  $\equiv\text{C-OH}$  stands for the phenolic or lactonic sites on the surface of ACF and  $M^{2+}$  is the divalent cation  $Zn^{2+}$  or  $Ni^{2+}$ . The carboxylic groups were not considered because all of them were deprotonated at pH=6.

The adsorption mechanism due to the electrostatic interactions consisted of the following steps. First, the acidic site was deprotonated and then the  $Ni^{2+}$  or  $Zn^{2+}$  ions were electrostatically attracted to the ACF surface, and subsequently adsorbed on the acid site on the ACF. This mechanism was suggested by Leyva-Ramos et al. (2011) and can be illustrated as follows:



Another adsorption mechanism of the metal cations on the surface of the ACFs is the  $\pi$ -metal cation interactions that occurred between the aromatic rings of the graphene layer of the ACFs and the metal cation (Rivera-Utrilla and Sanchez-Polo 2003).

## 4 Conclusions

The Redlich–Peterson isotherm fitted the ion adsorption equilibrium data for both ions better than the

**Table 4** Amount of protons exchanged during the adsorption of Ni(II) or Zn(II) on AW1104

| Metal  | Run no. | $C_0$ (mg/L) | pH <sub>i</sub> | pH <sub>f</sub> | $q_{Me}$ (meq/g) | $q_H$ (meq/g)         | $\frac{q_H}{q_{Me}}$ |
|--------|---------|--------------|-----------------|-----------------|------------------|-----------------------|----------------------|
| Ni(II) | 1N      | 30           | 6.00            | 5.07            | 0.14             | $1.04 \times 10^{-3}$ | 0.008                |
|        | 2N      | 60           | 6.02            | 4.63            | 0.20             | $3.19 \times 10^{-3}$ | 0.016                |
|        | 3N      | 90           | 6.06            | 4.52            | 0.25             | $4.27 \times 10^{-3}$ | 0.017                |
|        | 4N      | 160          | 6.01            | 4.08            | 0.39             | $12.8 \times 10^{-3}$ | 0.033                |
| Zn(II) | 1Z      | 60           | 6.07            | 5.1             | 0.17             | $1.00 \times 10^{-3}$ | 0.006                |
|        | 2Z      | 120          | 5.96            | 4.36            | 0.30             | $6.39 \times 10^{-3}$ | 0.022                |
|        | 3Z      | 200          | 5.98            | 4.46            | 0.40             | $5.40 \times 10^{-3}$ | 0.014                |
|        | 4Z      | 300          | 6.05            | 4.2             | 0.66             | $10.9 \times 10^{-3}$ | 0.016                |

Langmuir and Freundlich isotherms. The capacity of ACFs for adsorbing Zn(II) and Ni(II) on the ACFs decreased in the following order: AW1104>ACN-211-15.

The capacity of ACFs for adsorbing Ni(II) and Zn(II) depends mainly on the surface chemistry of the ACFs. The adsorption capacity of ACF is increased when the ACF is oxidized with HNO<sub>3</sub> because the acidic sites were augmented. The concentrations of acidic sites increased with the oxidation level. The concentration of phenolic and carboxylic sites of AW1104 increased during the oxidation with HNO<sub>3</sub>, whereas the concentration of lactonic sites did not change.

The Ni(II) and Zn(II) adsorption capacities of plain and oxidized AW1104 decreased in the following order: AW1104OX15>AW1104OX7.5>AW1104, and the concentration of carboxylic sites decreased in the same order. This result indicated that both ions were mainly adsorbed on the carboxylic sites.

The Ni(II) or Zn(II) adsorbed on ACF at pH=6 were desorbed with a solution at pH=4 because at this pH level the ions H<sup>+</sup> in solution competed for the acidic sites and displaced the Ni<sup>2+</sup> or Zn<sup>2+</sup> ions adsorbed on the ACF surface.

The maximum adsorption capacity of the plain and oxidized ACFs towards Ni(II) and Zn(II) was linearly dependent upon the concentration of carboxylic sites. The adsorption of both metals occurred by ion exchange and electrostatic interactions mainly on the carboxylic sites.

Further studies are needed to understand the adsorption–desorption mechanism of Ni(II) and Zn(II) on ACFs. Besides, the investigation of adsorption kinetics of Ni(II) and Zn(II) may provide additional information regarding the adsorption–desorption mechanism.

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