

Adsorbent-adsorbate interactions in the adsorption of organic and inorganic species on ozonized activated carbons: a short review

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Abstract This objective of this work was to summarize the main results obtained in previous papers related to the adsorbent-adsorbate interactions involved in the adsorption of naphthalenesulphonic acids and heavy metals (Cd(II) or Hg(II)) by modified activated carbons. The adsorption of organic compounds (1-naphthalenesulphonic acid, 1,5-naphthalenedisulphonic acid and 1,3,6-naphthalenetrisulphonic acid) and inorganic species (Cd(II) and Hg(II)) was studied on a series of ozonized activated carbon in aqueous phase. Commercial activated carbon (Filtrasorb 400) was treated with different ozone doses to study the effect of ozone treatment on its surface properties and investigate the behavior of the treated carbon samples in the above adsorption processes. After ozonation, carbonyl- and carboxyl-type groups were generated on the carbon surface. The action of ozone also affected the textural characteristics of the carbon; thus, the surface area diminished due both to the ozone attack and to the increase in oxygenated groups, which prevented the diffusion of nitrogen by obstructing micropore entrances. The capacity of activated carbon to adsorb naphthalenesulphonic acids sharply decreased with a greater number of sulphonic groups in the aromatic rings of these acids. As the concentration of oxygenated electron-withdrawing groups on the carbon surface increased, a significant reduction in adsorption capacity was observed. In all cases, the adsorption uptake decreased with higher solution pH. The adsorption of metallic ions, Cd(II) and Hg(II), by this series of ozonized activated carbons was also studied. In the case of Cd(II), the adsorption capacity and affinity of the adsorbents increased with a higher concentration of

acid oxygenated groups on the activated carbon surface. In the case of Hg(II), the adsorption diminished with an increase in the degree of oxidation of the activated carbon. The adsorption of 1,3,6-naphthalenetrisulphonic acid on the ozonized carbons was also studied in the presence of Cd(II) and Hg(II). The presence of Cd(II) in the medium enhanced the sulphonic acid uptake, mainly for the most ozonized activated carbon sample, whereas the presence of Hg(II) had no significant effect on the adsorption.

Keywords Adsorption · Metal species · Organic micropollutants · Activated carbon surface · Interactions

1 Introduction

A constant flow of new organic products is generating novel contaminants with unknown short-, medium- or long-term effects on the environment and human health that are not governed by regulations on the maximum allowable concentrations in the environment. They include chemical compounds in cosmetics (creams, perfums, make-up), domestic products (degreasants, glass cleaners, detergents) and pharmaceuticals, which are causing the greatest concern due to their very wide variety and elevated consumption (Halling-Sørensen et al. 1998; Calamari 2002; Richardson and Bowron 1985; Adler et al. 2008). They generally have a low biodegradability (Adler et al. 2008) and high toxicity (Adler et al. 2008), and some are reported to have mutagenic and carcinogenic characteristics (Calamari 2002; Adler et al. 2008). Conventional treatment systems, mainly based on the use of microorganisms have proven inadequate to effectively remove this type of organic compound, largely due to its complex molecular structure.

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Adsorption on activated carbon, one of the oldest water treatment (Mars and Rodríguez-Reinoso 2006; Radovic et al. 2001; Zogorski and Faust 1978) has been recognized by the U.S. Environmental Protection Agency as one of the best methods available to remove organic and inorganic compounds from water intended for human consumption. The value of activated carbons in this field resides in the chemical and textural properties of their surface such as a high surface area, well-developed internal microporosity structure, as well as the presence of a wide spectrum of surface functional groups (Radovic et al. 2001). However, this technology is not very widely used to treat wastewater and industrial effluents, mainly because of their high organic matter content. Importantly, some experimental parameters of activated carbon adsorption remain unknown, and the mechanisms involved in each system have yet to be elucidated (Radovic et al. 2001). This knowledge is essential for optimizing the use of activated carbon in water treatments.

Activated carbons are also widely used to treat water contaminated with heavy metals (Radovic et al. 2001; Budinova et al. 1994) because of their great capacity to adsorb these species. The surface chemistry of activated carbons has a major influence on their capacity to adsorb inorganic compounds, especially metallic cations; moreover, it can be appropriately modified by physical or chemical treatments to increase their adsorption capacity. Research efforts to elucidate the role of activated carbon surface chemistry in the mechanism of metallic ion adsorption have also been stimulated by considerable industrial and environmental interest in the use of activated carbon as support for the preparation of metal catalysts. Indeed, the characteristics of these catalysts greatly depend upon the above mechanism. Despite numerous studies on this issue (Radovic et al. 2001), doubts still remain about the influence of the chemical nature of the activated carbon surface on the adsorption of metals in aqueous solution. The adsorption mechanism and the type of adsorbent-adsorbate interactions that govern these processes are not completely understood.

With the above background, the present work aimed to outline results obtained during the development of a wider project where activated carbons were used as adsorbents of organic and inorganic compounds in order to dilucidate the type of interactions (electrostatic attraction or repulsion, specific interactions such as complex formation, or non-specific van der Waals interactions) that govern the mechanism of each adsorption system and, thus, to know both how to “activate” the carbon surface, and the optimum aqueous solution conditions to achieve maximum removal efficiencies. For that, the adsorption of three naphthalenesulphonic acids and metallic species of Cd(II) and Hg(II) on ozonized activated carbons was studied. The adsorption capacity of these ozonized carbon samples and the predominant interactions in the removal of naphthalenesulphonic

acids in the presence of the heavy metals Cd(II) or Hg(II) were also studied. Some of these results have been already published elsewhere (Valdés et al. 2002; Sánchez-Polo and Rivera-Utrilla 2002a, 2002b; Rivera-Utrilla and Sánchez-Polo 2003a, 2003b; Rivera-Utrilla et al. 2003).

2 Experimental

2.1 Materials

Bituminous coal-based activated carbon Filtrasorb 400 (Calgon Carbon Corp., USA), particle size range 0.2–0.5 mm, was used in this study (denominated carbon F). Ozone was produced from pure oxygen using a Ozokav generator rated at 5 g O₃/h.

2.2 Activated carbon treatments

Activated carbon F was treated with ozone for different periods of time, ranging from 10 to 120 min (i.e., F, F10, F60 and F120), in a fixed bed reactor loaded with 2 g of activated carbon at a constant flow of approximately 76 mg/min at 25 °C and 1 atm. Experimental details were given elsewhere (Sánchez-Polo and Rivera-Utrilla 2002a).

2.3 Carbon samples characterization

Activated carbon samples were texturally and chemically characterized using N₂ adsorption at 77 K, mercury porosimetry, determination of the pH of the point of zero charge (pH_{PZC}), temperature program desorption (TPD), and X-ray photoelectron emission spectroscopy (XPS). These techniques have been described in detail elsewhere (Sánchez-Polo and Rivera-Utrilla 2002a). Estimation of acid and basic group contents was conducted by the method proposed by Boehm (1966) based on selective neutralization analysis. The pH at the point of zero charge (pH_{PZC}) was estimated by mass titration (Noh and Schwartz 1990).

2.4 Naphthalene sulphonic acid adsorption experiments

The adsorption equilibrium data of 1-naphthalenesulphonic acid (NS), 1,5-naphthalenedisulphonic acid (NDS) and 1,3,6-naphthalenetrisulphonic acid (NTS) on activated carbon samples were determined at 298 K in aqueous solutions. Typically, a 0.1 L aqueous solution containing 25–200 mg/L of naphthalenesulphonic acid was mixed with 0.1 g activated carbon in stirred Erlenmeyer flasks and maintained at 298 K for 72 h. This was the time needed to reach equilibrium, as determined by confirming that no additional adsorption occurred following this extended period. These experiments were carried out in the absence of any pH setting; the starting solutions had a pH of 5.5–6. Ultrapure water was used

to make the solutions. Further adsorption experiments were conducted at initial pH values of 2, 4, 6, 8, 10 and 12. HCl and NaOH were used to adjust the initial solution pH to the set value. The initial concentration of sulphonic acid in these experiments was 100 mg/L. The naphthalenesulphonic acid concentration was determined using a Spectronic Genesys 5 spectrophotometer. The wavelengths used were 223 nm, 286 nm and 223 nm for NS, NDS, and NTS, respectively.

2.5 Heavy metals adsorption experiments

The adsorption equilibrium data, in aqueous solution, of Cd(II) and Hg(II) on the activated carbon samples were obtained at 298 K using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Merck), respectively, as precursor salts. In Erlenmeyer flasks, 0.05 L of metal solution (5–80 mg/L) was put in contact with 0.1 g of activated carbon. The flasks were agitated until equilibrium was reached (72 h) (Sánchez-Polo and Rivera-Utrilla 2002b). The time required to achieve equilibrium was determined from previous experiments, by measuring the adsorbate concentration versus adsorption time. It was observed that the adsorbate concentration was constant after 72 h. The metal equilibrium concentration was determined by atomic absorption, using a Varian Spectra A-200 equipment. All adsorption experiments were performed in ultrapure water at pH 6; this pH was reached by adding the appropriate amounts of NaOH and HCl.

2.6 NTS adsorption in the presence of Cd(II) or Hg(II)

The NTS adsorption equilibrium data were obtained in the presence of Cd(II) or Hg(II) on activated carbon samples at 298 K. For this purpose, 0.1 L of NTS and metal solution, of different concentrations, were put in contact with 0.1 g of activated carbon in different Erlenmeyer flasks. In all solutions prepared for isotherms measurement, the NTS/metal concentration molar ratio was maintained constant at 2.5. The flasks were agitated until equilibrium was attained (72 h). The equilibrium time was obtained from the adsorption kinetics. The equilibrium concentration of NTS was determined by UV-visible spectrophotometry, using Spectronic

Genesys 5 equipment. All adsorption experiments were performed in ultrapure water at pH 6, adjusted by the addition of appropriate amounts of NaOH and HCl.

3 Results and discussion

3.1 Effect of ozone treatment on the surface properties of activated carbon

The adsorptive activity of activated carbon is closely related to its chemical and textural properties; this section summarizes the modifications in these properties produced by ozone. The effect of ozonation on textural and chemical surface properties of carbon F is shown in Tables 1 and 2. A slight increase in surface area can be observed at 10 min (F10) of ozone exposure, followed by a gradual reduction as the time of exposure lengthens. The external surface area in untreated carbon is relatively low, and slightly increased at 10 min of ozone exposure (F10) and then decreased with the treatment time. These results indicate that in a first stage (sample F10), the O_3 slightly develops the porosity of the carbon opening its porosity and increasing its surface area. As the time of exposure to ozone lengthens, from 10 to 120 min, the pore walls are destroyed by the gasification of the carbon, with a resulting reduction in the surface area. Moreover, the increasing formation of surface oxygen groups (discussed below) at the entrance to the

Table 1 Textural characteristics of the carbon samples

Sample	S_{N_2} (m^2/g)	V_{mic} (cm^3/g)	V_{me} (cm^3/g)	S_{ext} (m^2/g)
F	1000	0.474	0.019	53.7
F10	1023	0.472	0.031	87.1
F60	815	0.380	0.025	71.6
F120	632	0.297	0.023	64.4

S_{N_2} : Surface area determined from N_2 adsorption. V_{mic} : Micropore volume determined from N_2 adsorption. V_{me} : Mesopore volume determined from N_2 adsorption. S_{ext} : External surface area determined from N_2 adsorption

Table 2 Chemical characteristics of the carbon samples

Sample	pH_{PZC}	Carboxyl ($\mu\text{eq/g}$)	Lactone ($\mu\text{eq/g}$)	Phenol ($\mu\text{eq/g}$)	Carbonyl ($\mu\text{eq/g}$)	Acid sites ($\mu\text{eq/g}$)	Basic sites ($\mu\text{eq/g}$)	CO/CO_2	Oxygen %
F	8.82	None	38	57	139	234	570	4.64	1.82
F10	5.96	228	76	228	170	702	437	2.62	4.30
F60	3.89	998	342	57	672	2069	171	1.68	14.54
F120	2.59	1330	494	1028	518	3370	None	1.03	24.90

Table 3 XPS results. Surface composition of untreated and 60 minutes ozonized activated carbon

Element	Peak	Functional groups	Binding energy (eV)	Activated carbon (% atomic)	
				F	F60
C1s	(1)	Graphitic, Aromatic (C–C)	284.6	52.28	41.57
C1s	(2)	C in Hydroxyl, Ethers (C–OH, C–O–C)	286.0	16.07	14.55
C1s	(3)	C in Carbonyl (C=O)	287.3	5.03	2.29
C1s	(4)	C in COOR (R=H or alkyl)	288.6	3.58	10.27
C1s	(5)	π – π^* transitions in aromatic	291.0	3.95	3.03
O1s	(1)	Carbonyl, Quinone (C=O)	530.7	5.30	1.59
O1s	(2)	Hydroxyl, Ethers (C–OH, C–O–C)	532.1	6.96	12.15
O1s	(3)	Anhydride, Lactone, Carboxylic acids	533.3	1.95	9.86
O1s	(4)	Chemisorbed H ₂ O or O ₂	535.3	0.00	0.67

pores with the ozonation time may obstruct N₂ access to the micropores, resulting in a decrease of surface area. Thus, ozonation also produced a change in the chemical nature of the carbon from basicity (carbon F: pH_{PZC} = 8.82) to acidity (carbon F120: pH_{PZC} = 2.59) due to the fixation of these surface oxygen groups.

The results showed in Table 2 indicate that acid groups are massively formed due to ozonation, whereas basic groups are significantly reduced. Acid groups appear to be associated with oxygenated functional groups such as carboxyl, phenol, carbonyl, lactone and carboxylic anhydride (Moreno-Castilla et al. 1998). On the other hand, the basic behavior of activated carbon has been related with oxygen containing species, such as chromene and γ -pyrone-like structures, and with π electron system of the basal planes of the carbon (Radovic et al. 2001; Biniak et al. 1997).

XPS analysis yields a clearer picture of the chemical composition of the carbon surface. Table 3 compares XPS analysis results for the untreated carbon and the sample ozonated for 60 min. The XPS spectra present two distinctive peaks due to carbon (C1s) and oxygen (O1s), respectively. In turn, the C1s peak was deconvoluted into five peaks and the (O1s) peak into four peaks, all of which are identified in Table 3. The results show that ozone treatment for 60 min leads to an increase in lactone, anhydride and/or carboxylic groups on the carbon surface, and to a reduction of the number of carbon atoms of graphitic nature in the surface. The total atomic oxygen content increased from 1.82% in untreated carbon to 24.90% in ozonized sample F120, which could be mainly accounted for by the increase in surface carboxylic groups. Moreover, the O1s:C1s ratio increased from 0.18 to 0.34 due to ozonation, thereby showing the increase in the extent of surface oxidation. More data related to activated carbon ozonation can be found elsewhere (Valdés et al. 2002).

3.2 Adsorption of naphthalenesulphonic acids on ozonized activated carbons. Main interactions involved

The adsorption capacity (X_m) of each carbon sample for the three naphthalenesulphonic acids was determined by applying the Langmuir equation to the adsorption isotherms. Table 4 lists these data and the relative affinities (B_{Xm}) of these compounds to be adsorbed on the carbon samples. For the original carbon, sample F, the adsorption capacity (X_m) and relative affinity (B_{Xm}) decreased as the number of sulphonic groups in the aromatic rings of the acids increased (Table 4). Under these experimental conditions, NS and NDS molecules have their sulphonic groups deprotonated, whereas NTS presents two dissociated sulphonic acid groups (i.e., pK₁ \approx 2, pK₂ \approx 4, pK₃ \approx 10). Thus, at a pH of 6 there would be two negative charges on both NDS and NTS molecules, as compared with only one in the case of NS. This suggests that, since, at the working pH, carbon F shows a positive charge density, there should be a greater adsorption affinity for NDS and NTS than for NS. However, the actual adsorptive behavior, as shown in Table 4 contradicts this logic, because the experimental results show that the adsorption affinities decrease in the following order:

$$\text{NS} > \text{NDS} > \text{NTS}$$

Thus, electrostatic interactions alone cannot explain the adsorption behavior of these aromatic sulphonic acids on untreated carbon at an initial pH around 6.

The adsorption mechanism of organic compounds on activated carbon is controversial (Radovic et al. 2001). According to Leon y Leon et al. (1992), basic carbons are characterized by a high content of electron rich sites on their basal planes, and a low concentration of electron-withdrawing groups. Thus, aromatic ring deactivation due to the increase in the number of electron-withdrawing sulphonic groups seems to be the main cause for the reduction in adsorption affinity of activated carbon F towards the

Table 4 Results obtained by applying the Langmuir equation to naphthalenesulphonic acids adsorption isotherms on untreated and ozone-treated carbons

Sample	NS		NDS		NTS	
	Xm (mg/g)	BXm (L/g)	Xm (mg/g)	BXm (L/g)	Xm (mg/g)	BXm (L/g)
F	84.03	69.44	38.46	8.13	34.97	7.63
F10	89.28	212.76	43.10	9.38	39.53	8.92
F60	75.75	6.23	36.36	1.11	29.16	1.42
F120	56.49	1.00	13.05	0.24	8.04	0.01

sulphonic acids in the above order. Therefore, the present results suggest that the adsorption of naphthalenesulphonic acids on basic activated carbon, such as carbon F, occurs via $\pi-\pi$ dispersion interactions between aromatic ring electrons in the acids and those present in the carbon graphene planes, which is consistent with the mechanism suggested by Coughlin and Ezra (1968).

As ozone exposure of activated carbon increased, a sharp reduction in adsorption capacity was observed for the three sulphonic acids tested. Furthermore, a reduction in the affinity parameter was detected, indicating a weakening in adsorbate-adsorbent interactions. The above observations indicate that the decrease in adsorption capacity of ozonated carbons for NS, NDS and NTS is produced by the increase in the concentration of oxygenated groups on the carbon surfaces. These oxygenated groups may be responsible for two simultaneous effects: (i) a weakening of $\pi-\pi$ dispersive interactions due to a reduction in electron density on the carbon surface; and (ii) an increase in repulsive electrostatic interactions, between the sulphonate groups and the negative charge of the carbon surface of samples F60 ($pH_{PZC} = 3.89$) and F120 ($pH_{PZC} = 2.59$) at the experimental conditions employed.

The effect of solution pH on the adsorption of naphthalenesulphonic acids on untreated and ozonized activated carbons is shown in Fig. 1 for NTS as an example. In all cases, adsorption decreases with an increase in the initial solution pH. This behavior can be explained on the basis of adsorbate-adsorbent electrostatic interactions: these interactions will be attractive at pH values that are lower than the pH_{PZC} of the carbon sample, and will be repulsive at values that are higher. Thus, for each carbon sample, greater adsorption is found at $pH < pH_{PZC}$ than at $pH > pH_{PZC}$. At $pH > pH_{PZC}$, the carbon surface presents a greater overall negative charge because of the ionization of oxygenated functional groups. Thus, in general, for each carbon sample a step in the adsorbed amount is observed at pH values around its pH_{PZC} . This step occurs because at this pH the carbon surface changes its effective charge sign and, therefore, the net sign of the electrostatic interaction between the ionized adsorbate molecules and the activated carbon

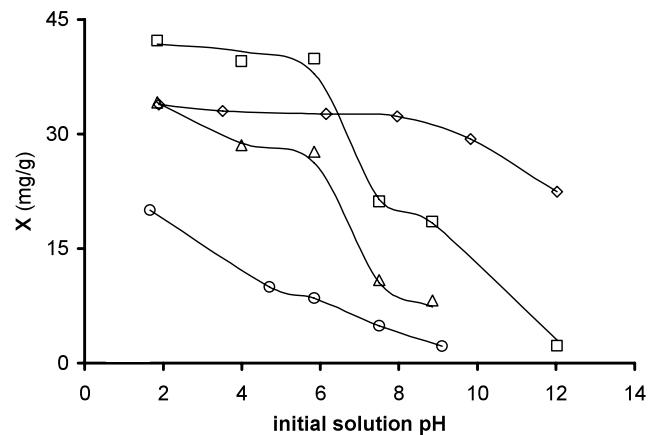


Fig. 1 Influence of pH on 1,3,6-naphthalenetrisulphonic acid adsorption on untreated and ozonized activated carbon. (◊), F; (□), F10; (△), F60; (○), F120 (Sánchez-Polo and Rivera-Utrilla 2002a)

surface also changes. The small plateaus observed in some cases (Fig. 1) may correspond to the range of pH where there are no net charge changes in either adsorbate or adsorbent. More information related to the adsorption of naphthalene sulphonic acid on ozonized activated carbon can be found elsewhere (Sánchez-Polo and Rivera-Utrilla 2002a, 2002b).

3.3 Adsorption of heavy metals on ozonized activated carbons

The aim of this section was to determine the adsorption capacity and investigate the predominant interactions in the adsorption processes of metallic species on activated carbon.

3.3.1 Adsorption of cadmium

Figure 2 shows the adsorption isotherms of Cd(II) on the three activated carbon samples (F, F10 and F120). The Langmuir equation was applied to calculate the adsorption capacity (Xm) and the relative affinity of Cd(II) for the different carbon samples (BXm). These data are presented in Table 5.

The adsorption capacity of the oxidized carbon (F120) was much greater than that of the original carbon (F), Table 5, despite the reduction in surface area of the former

produced by the oxidation process (Table 1). Ozonation produced a change in the chemical nature of the carbon from basicity (carbon F: $pH_{PZC} = 8.82$) to acidity (carbon F120: $pH_{PZC} = 2.59$), which enhances the adsorption process because of the greater attractive electrostatic interactions between the surface of the activated carbon and the Cd(II) species present at the pH of the experiments. The shapes of the isotherms (Fig. 2) suggest that for the sample F120, and to a lesser extent for sample F10, there are high energy adsorption sites that lead to strong adsorption at low equilibrium concentrations. The presence, in the ozonized

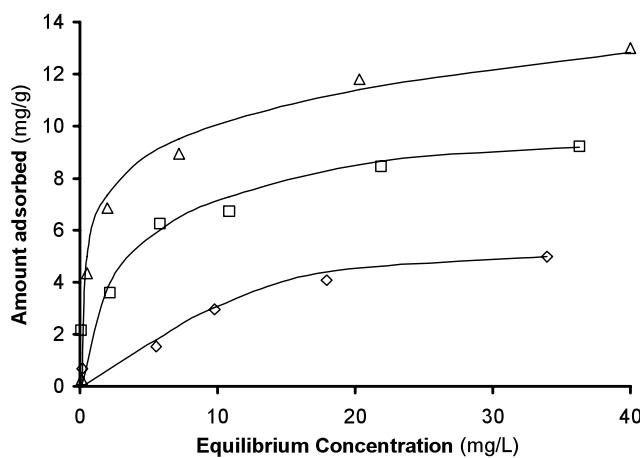


Fig. 2 Adsorption isotherms of Cd(II) on activated carbon. (◊), F; (□), F10; (△), F120 (Sánchez-Polo and Rivera-Utrilla 2002b)

Table 5 Results obtained by applying Langmuir equation to the Cd(II) adsorption isotherms

Sample	Xm (mg/g)	BXm (L/g)
F	6.75	0.61
F10	9.48	4.74
F120	13.38	7.23

carbon samples, of a higher amount of acidic groups, ionized at the working pH ($pH = 6$), mainly carboxylic groups ($pK_a \approx 3–6$) would justify this behavior observed in Fig. 2. In fact, some authors (Aggarwal et al. 1999; Cigdem et al. 2000) have proposed that cationic species are specifically adsorbed on carboxyl and lactone groups present on the carbon surface.

Table 6 displays the calculated distribution of Cd(II) species present in aqueous solution at different pH values. These calculations were made using the stability constants proposed by Stumm and Morgan (1996). Regardless of the pH used, all the species presented a positive sign. At pH 2 and 4, the predominant species was Cd_{aq}^{+2} (81.35% and 96.81%, respectively), whereas at pH values above 4, the predominant species was $Cd(OH)^+$.

Because Cd(II) species are cationic at the working pH, the adsorption interactions must have been of an electrostatic type. Depending on the pH_{PZC} value of the activated carbon sample (Table 2), the surface charge density was positive (carbon F), almost zero (carbon F10) or negative (carbon F120) at a pH of 6. Thus, electrostatic attractions between Cd(II) species and carbon increased in the order F < F10 < F120, which was the order in which the values of Xm and BXm increased (Table 5).

We highlight the adsorption of Cd(II) on carbon F. Carbon F is basic ($pH_{PZC} = 8.82$) and presented a charge positive sign at the working pH, so that Cd(II) adsorption should be impeded by repulsive electrostatic interactions between the activated carbon surface and the Cd^{+2} and $Cd(OH)^+$ species present at this pH. However, carbon F showed an adsorption capacity of 6.75 mg Cd(II)/g activated carbon. These results indicate that other types of interactions, besides electrostatic ones, must be established in the adsorption of Cd(II). It is widely accepted (Radovic et al. 2001) that the adsorption of metallic ions on activated carbons is produced by a mechanism of ionic exchange between ionizable protons of surface oxygen groups and metallic cations. The experimental data in Table 7, which describe the relationship between the Cd(II) ion equivalents adsorbed and

Table 6 Calculated distribution of Cd(II) species present at different solution pH values

	pH					
	2 (%)	4 (%)	6 (%)	8 (%)	10 (%)	12 (%)
Cd^{2+}	81.35	96.81	24.57	0.33	0.01	0.00
$Cd(OH)^+$	0.07	2.97	75.43	99.67	99.99	99.99
$Cd(OH)_2$	0.00	0.00	0.00	0.00	0.00	0.00
$Cd(OH)_3^-$	0.00	0.00	0.00	0.00	0.00	0.01
$CdCl^+$	18.21	0.22	0.00	0.00	0.00	0.00
$CdCl_2$	0.14	0.00	0.00	0.00	0.00	0.00
$CdCl_3^-$	0.23	0.00	0.00	0.00	0.00	0.00

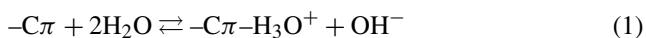
Table 7 Values of the ratio of metal ion adsorbed to H⁺ released per one gram carbon (R) as a function of the amount of Cd(II) adsorbed (X)

F X (mg/g)	R (eq Cd/eq H ⁺)	F10		F120	
		X (mg/g)	R (eq Cd/eq H ⁺)	X (mg/g)	R (eq Cd/eq H ⁺)
0.69	0.94	2.17	0.91	2.33	0.98
1.53	1.08	3.60	0.86	4.35	1.04
2.96	1.03	6.25	0.95	6.85	0.89
4.08	1.04	6.72	0.97	8.93	0.88
4.99	0.86	8.46	0.96	11.81	0.94
6.40	0.90	9.23	0.96	13.00	1.06

the proton equivalents released by the activated carbon, indicate that the above mechanism determines the adsorption process of Cd(II) in the three activated carbon samples studied. These results were obtained by determining the pH of Cd(II) solutions before adding carbon and again when equilibrium was reached after adding carbon. In this way, the number of protons given up by 1 g of carbon was calculated and the relationship (R) between the latter and the known number of metallic ion equivalents adsorbed per gram of carbon was determined. The value of R was obtained for different amounts of Cd(II) adsorbed (X). In all cases, R was close to unity (Table 7), which suggests that adsorption occurred by a mechanism of ionic exchange between carbon surface protons and Cd(II) ions, in the three carbon samples at the range of concentrations studied.

Ionic exchange can be expected in carbons of acidic nature, such as sample F120. This mechanism is harder to explain in the case of basic carbons, such as sample F, which do not have enough oxygenated groups with ionizable protons (Table 2). However, in a previous paper (Rivera-Utrilla and Sánchez-Polo 2003a), we recently demonstrated that delocalized π electrons, responsible for the basicity of these carbons, play a determinant role in the adsorption mechanism.

These delocalized π electrons ($-\text{C}\pi$) are known (Leon y Leon and Radovic 1994; Dougherty 1996; Montes-Morán et al. 1998) to be largely responsible for the basicity of the carbon, because the following equilibrium is established in aqueous solution:



Thus, we have proposed that in basic carbons, like carbon F, $-\text{C}\pi-\text{H}_3\text{O}^+$ interaction protons must exchange with Cd(II) cations for Cd(II) adsorption to take place. This hypothesis was supported by the values of R obtained for carbon F, which were close to unity (Table 7). More information related to the adsorption of Cd(II) on ozonized activated carbon can be found elsewhere Sánchez-Polo and Rivera-Utrilla (2002b).

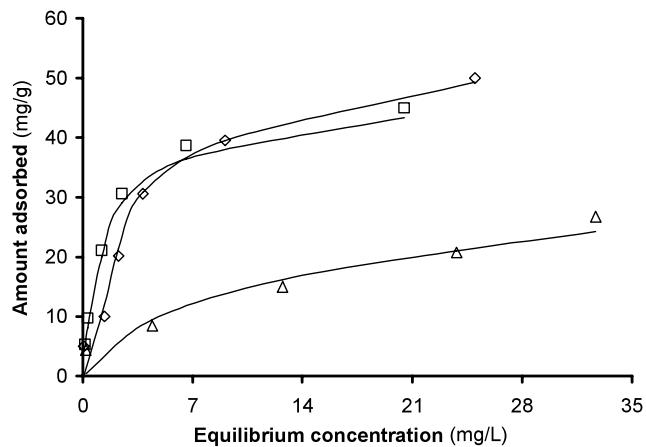


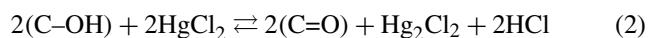
Fig. 3 Adsorption isotherms of Hg(II) on activated carbon. (◇), F; (□), F10; (△), F120 (Sánchez-Polo and Rivera-Utrilla 2002b)

3.3.2 Adsorption of mercury

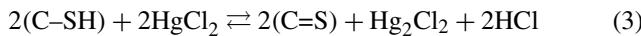
Figure 3 shows the adsorption isotherms of Hg(II) on the three activated carbon samples (F, F10 and F120). The Langmuir equation was applied to calculate Xm and BXm values. These findings are presented in Table 8.

In contrast to the case of Cd(II), the Xm values reduced with increased oxidation of the activated carbon. The predominant Hg(II) species at the pH of the isotherm determinations (pH = 6) was Hg(OH)₂ (Table 9). This species presents no charge, so that the influence of electrostatic interactions does not seem to be determinant in Hg(II) adsorption, unlike in the case of Cd(II).

Similar results to ours (Table 8) were reported by Macías-García et al. (1995) in their study of the adsorption of HgCl₂ on H₂O₂-oxidized carbons. They proposed that Hg(II) was adsorbed on the activated carbon via a mechanism of HgCl₂ molecular adsorption with the subsequent reduction of the HgCl₂, thanks to the presence of phenol and hydroquinone groups on the carbon surface:



Sinha and Walker (1972) postulated a similar mechanism to explain the increase in Hg(II) adsorption on sulphuration-treated carbons. In an electronic microscopy study Adams (1991) confirmed the presence of Hg^+ and Cl^- on the surface of activated carbons in contact with HgCl_2 , supporting the reduction mechanism:



This mechanism had already been presented in studies carried out by Lopez-Gonzalez et al. (1982). Prior to the above studies, Rivin (1971) had discussed the possibility that π electrons of the basal plane may be involved in the reduction of Hg on the activated carbon surface. In the present study, X_m values decreased with the reduction in basicity of the activated carbon and thus with a reduction in its surface electronic density (Table 8). These results may indicate that dispersion interactions between the activated carbon surface and the Hg(II) species present in solution [$\text{Hg}(\text{OH})_2$] play a major role in the adsorption process.

The basicity of an activated carbon should be due to the presence of basic oxygen-containing functional groups (e.g. pyrones or chromenes) and/or graphene layers that act as Lewis bases and form electron donor-acceptor (EDA) complexes with H_2O molecules (reaction 1) (Radovic et al. 2001). The latter basic sites are located at π electron-rich regions within the basal planes of carbon crystallites away from the crystallite edges (Radovic et al. 2001). In our view,

Table 8 Results obtained by applying Langmuir equation to the Hg(II) adsorption isotherms

Sample	X _m (mg/g)	BX _m (L/mg)
F	62.11	10.55
F10	48.78	27.80
F120	38.61	2.31

Table 9 Calculated distribution of Hg(II) species present at different solution pH values

	pH					
	2 (%)	4 (%)	6 (%)	8 (%)	10 (%)	12 (%)
Hg^{2+}	0.00	0.00	0.00	0.00	0.00	0.00
$\text{Hg}(\text{OH})^+$	0.00	0.00	0.03	0.00	0.00	0.00
$\text{Hg}(\text{OH})_2$	0.00	0.04	99.97	100	99.99	99.87
$\text{Hg}(\text{OH})_3^-$	0.00	0.00	0.00	0.00	0.01	0.13
HgCl^+	0.00	0.31	0.00	0.00	0.00	0.00
HgCl_2	90.49	99.56	0.00	0.00	0.00	0.00
HgCl_3^-	8.44	0.09	0.00	0.00	0.00	0.00
HgCl_4^{2-}	1.07	0.00	0.00	0.00	0.00	0.00

this delocalized π electron system ($-\text{C}\pi$) can act as a reduction center of different species (reaction 4).



Thus, the decrease in Hg(II) adsorption with more oxygen (electron-withdrawing) functional groups on the carbon surface (Table 8) may be due to: (i) a reduction in the basicity of the carbon, due to the decrease in its surface electronic density, weakening dispersion interactions between the activated carbon surface and $\text{Hg}(\text{OH})_2$; (ii) a decrease in the reductive properties of the activated carbon (because of a diminished π electron density), impeding reduction of the $\text{Hg}(\text{OH})_2$ adsorbed. More information related to the adsorption of Hg(II) on ozonized activated carbon can be found elsewhere (Sánchez-Polo and Rivera-Utrilla 2002b).

3.4 Adsorption of 1,3,6-naphthalenetrisulphonic acid on activated carbon in the presence of Cd(II) and Hg(II). Importance of electrostatic interactions

In the previous sections, we have analyzed the independent processes of adsorption of naphthalensulphonic acids and metal species of Cd(II) or Hg(II) on activated carbon and the adsorbent-adsorbate interactions involved. In order to investigate the predominant interactions in the removal of naphthalensulphonic acids by activated carbon in the presence of the heavy metals, a study was conducted of the adsorption isotherms and influence of the pH in the adsorption process of 1,3,6-naphthalenetrisulphonic acid (NTS), selected as model compound on activated carbons F, F10 and F120 in the presence of Cd(II) or Hg(II).

From the adsorption isotherms and applying Langmuir equation, the adsorption capacity (X_m) and relative affinity (BX_m) of NTS for the different activated carbon samples both in the absence and in the presence of Cd(II) or Hg(II) were determined. These results are displayed in Table 10.

Table 10 Results obtained by applying Langmuir equation to the adsorption isotherms

Sample	NTS		NTS + Cd(II)		NTS + Hg(II)	
	Xm	BXm	Xm	BXm	Xm	BXm
	(mg/g)	(L/mg)	(mg/g)	(L/mg)	(mg/g)	(L/mg)
F	34.97	7.63	74.62	31.34	36.49	14.81
F10	39.53	8.92	79.36	49.50	42.37	20.20
F120	8.04	0.01	36.78	8.65	11.40	0.28

The presence of Cd(II) in the medium enhanced the adsorption of NTS on the activated carbon samples, increasing Xm and BXm values (Table 10). This increase was more marked in the ozone-treated samples. Thus, the presence of Cd(II) increased the adsorption capacity of sample F120 by 457%. However, the presence of Hg(II) in the medium had a lower effect on the adsorption of NTS on the activated carbon samples, showing an increase of 42% in the case of sample F120.

In order to explain the results presented in Table 10, it is necessary to consider the charge sign of NTS, Cd(II) and Hg(II) species, as well as the charge density of the surface of each carbon sample. In Tables 6 and 9, it was observed that at the working pH (pH = 6), the majority species of Cd(II) presented positive charge whereas the majority species of Hg(II) was neutral (Hg(OH)_2). Analysis of NTS ionization constants ($\text{pK}_2 \approx 4$, $\text{pK}_3 \approx 10$) showed that NTS presented two ionized protons at the working pH (pH = 6) and was therefore found in naphthalenesulphonate anion form. The surface charge density at this pH was different in each activated carbon sample studied. Thus, carbon F presented a positive charge density ($\text{pH}_{\text{PZC}} = 8.82$), carbon F10 a zero charge density ($\text{pH}_{\text{PZC}} = 5.96$), and carbon F120 a negative charge density ($\text{pH}_{\text{PZC}} = 2.59$). Therefore, the adsorption of positively charged metal species, as in the case of Cd(II), enhances attractive electrostatic interactions between naphthalenesulphonate anions and the activated carbon surface, explaining the results in Table 10. Moreover, the fact that the Cd(II) species are cationic but the NTS species are anionic at the working pH means that a cooperative adsorption is established, favoring the adsorption process. On the other hand, in the case of Hg(II), the adsorption of Hg(OH)_2 , a species without charge, has no effect on the adsorption of NTS on the activated carbon.

In the previous section it was discussed that the adsorption of Cd(II) on activated carbon was enhanced in ozonized samples, fundamentally when the ozonation time was increased. The increased adsorption of cationic species of Cd(II) on the surface of ozonized activated carbon samples would intensify attractive electrostatic interactions between the naphthalenesulphonate anions and the activated carbon surface, accounting for the results presented in Table 10.

Moreover, in the case of carbon F120, which had a negative charge density, the presence of cationic species in the medium exerts a screening effect between the carbon surface and the naphthalenesulphonate anions, drastically reducing NTS–carbon electrostatic repulsion. Thus, a greater increase in adsorption was observed in carbon F120 in the presence of Cd(II). More data related to the adsorption of 1,3,6-naphthalenetrisulphonic acid on activated carbon in the presence of Cd(II) and Hg(II) can be found elsewhere (Rivera-Utrilla et al. 2003).

4 Conclusions

Ozone treatment increases the number of oxygenated electron withdrawing groups (mostly carboxylic) on activated carbon surfaces. As the number of electron withdrawing surface groups increased, the adsorption capacity and the affinity of naphthalenesulphonic acids on activated carbon decreased. Furthermore, as the number of electron-withdrawing groups (sulphonic groups) in the aromatic rings increased, the adsorption capacity and the affinity of carbon for the sulphonic acids was significantly reduced. These results could be explained by a reduction in $\pi-\pi$ interactions between the aromatic rings of the naphthalenesulphonic acids and the activated carbon graphene planes.

The adsorption capacity of carbon for naphthalenesulphonic acids is highly dependent on pH. Thus, the adsorption capacity when $\text{pH} < \text{pH}_{\text{PZC}}$ is higher than when $\text{pH} > \text{pH}_{\text{PZC}}$, because of repulsive electrostatic interactions between the ionized sulphonic groups in the adsorbate and the ionized groups on the carbon surface when the pH is higher than pH_{PZC} .

The present study confirms that the adsorption mechanism of aromatic compounds on carbon involves a complex interplay of electrostatic and dispersive interactions. In the case of naphthalenesulphonic acids, the dispersion (nonelectrostatic) forces govern adsorption.

Electrostatic interactions play a major role in the mechanism of Cd(II) adsorption, especially on acidic carbons. The adsorption capacity of ozonated carbon for Cd(II) ions is enhanced because an increase in: (i) attractive electrostatic

adsorbent-adsorbate interactions and (ii) the number of protons available for ion-exchange with Cd(II). The adsorption of Cd(II) on basic carbons is accounted, in part, for by exchange between metallic ions and $-\text{C}\pi-\text{H}_3\text{O}^+$ interaction protons of the activated carbon surface.

The adsorption of Hg(II), unlike Cd(II), decreases with greater oxidation of the activated carbon. Oxygenated (electron-withdrawing) functional groups reduce the basicity and reductive properties of the activated carbon, therefore impeding the adsorption-reduction mechanism that determines this process. Adsorbent-adsorbate dispersion interactions also play an important role in the Hg(II) adsorption process.

The presence of Cd(II) in the medium increases the contribution of electrostatic interactions to the overall NTS adsorption process. In contrast, the presence of Hg(II) has no significant effect on the NTS adsorption. The presence of metal cationic species in the medium establishes attractive electrostatic interactions that increase the adsorption of NTS on activated carbon. Moreover, because of the greater negative surface charge density of the drastically ozonized carbons, the electrostatic contribution to the overall NTS adsorption process, due to the presence of cationic metal species, is increased in these carbons.

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