

# Adsorption of 1,3,6-Naphthalenetrisulfonic Acid on Activated Carbon in the Presence of Cd(II), Cr(III), and Hg(II). Importance of Electrostatic Interactions

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This work studies the influence of the metals Cd(II), Cr(III), and Hg(II) on the adsorption of 1,3,6-naphthalenetrisulfonic acid (NTS) on ozonized activated carbon. The adsorption capacity ( $K$ ) and adsorption intensity ( $1/n$ ) of NTS on activated carbon is increased in the presence of Cd(II) and Cr(III), whereas the adsorption process is not affected by the presence of Hg(II). This behavior is more marked in ozone-treated activated carbon samples. The presence of the cationic species  $\text{Cd}(\text{OH})^+$  and  $\text{Cr}(\text{OH})^{2+}$  in the medium enhances attractive electrostatic interactions between the carbon surface and NTS. Hg(II), because it is  $\text{Hg}(\text{OH})_2$  as a neutral species, does not affect the adsorption of NTS on activated carbon. Study of the influence of the solution pH on NTS adsorption in the presence of the metals Cd(II), Cr(III), or Hg(II) revealed that greater NTS adsorption is produced when the charge signs of the metal species and NTS in the solution are opposite. Analysis of the amount of metal adsorbed according to the pH, in the presence of NTS, showed that the presence of NTS in the medium increases the adsorption of Cd(II) and Cr(III) but has no effect on the adsorption of Hg(II) on activated carbon. The results obtained indicate that the adsorption of NTS on activated carbon in the presence of Cd(II) and Cr(III) occurs by a cooperative mechanism, in which electrostatic interactions play a key role.

## 1. Introduction

Textile industry effluents are characterized by a high content of sulfonated polyphenols (dyestuffs) and contain a wide variety of chemical compounds, including naphthalenesulfonic acids.<sup>1–6</sup> They also present elevated concentrations of the highly toxic heavy metals Cr(III), Cd(II), and Hg(II).<sup>7</sup>

Activated carbon has been widely used to remove organic compounds and heavy metals from industrial effluents.<sup>8–12</sup> Indeed, recently it has been proposed by the Environmental Protection Agency as a highly effective method to purify waters contaminated with these contaminants. However, the influence of the experimental conditions on the adsorption of these compounds is not fully elucidated.<sup>13,14</sup> Knowledge of the mechanisms underlying naphthalenesulfonic acid adsorption and of the influence

of operational variables is essential to optimize the use of activated carbon on an industrial scale.

Recently, we analyzed<sup>15–17</sup> the processes of adsorption of naphthalenesulfonic acids and the metals Cd(II), Cr(III), and Hg(II) on activated carbon and the interactions involved, in separate studies. Thus, the adsorption of naphthalenesulfonic acids<sup>15</sup> on activated carbon is determined both by  $\pi$ – $\pi$  dispersion interactions between the electrons of the activated carbon surface and the aromatic rings of the adsorbate and by electrostatic interactions between the naphthalenesulfonate anions and the surface charge of the activated carbon. Furthermore, electrostatic interactions<sup>16,17</sup> predominate in the adsorption of Cd(II) and Cr(III) on activated carbon, whereas the adsorption of Hg(II) occurs by an adsorption–reduction mechanism.

To evaluate the efficacy of activated carbon in removing naphthalenesulfonic acids under experimental conditions similar to those of real effluents, the present work was designed to investigate the adsorption capacity of carbon and the predominant interactions in the removal of naphthalenesulfonic acids in the presence of the heavy metals Cd(II), Hg(II), or Cr(III). For this purpose, a study was conducted of the adsorption isotherms and influence of the pH in the adsorption process of 1,3,6-naphthalenetrisulfonic acid (NTS), selected as a model compound, in the presence of these metals on activated carbon with different degrees of oxidation. The carbons were obtained

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**Table 1. Textural and Chemical Characteristics of the Activated Carbon Samples**

sample	$S_{N_2}$ (m <sup>2</sup> /g)	$S_{ext}$ (m <sup>2</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)	$V_2^a$ (cm <sup>3</sup> /g)	$V_3^b$ (cm <sup>3</sup> /g)	pH <sub>PZC</sub>	acidic sites <sup>c</sup> (μequiv/g)	basic sites <sup>d</sup> (μequiv/g)	oxygen (wt %)
F	1000	54	0.474	0.11	0.26	8.82	234	570	1.82
F10	1023	87	0.472	0.12	0.27	5.96	702	437	4.30
F120	632	64	0.297	0.14	0.32	2.59	3370	none	24.9

<sup>a</sup> Volume of pores with diameters from 50 to 6.6 nm. <sup>b</sup> Volume of pores with diameters above 50 nm. <sup>c</sup> Determined by NaOH (0.1 N) neutralization. <sup>d</sup> Determined by HCl (0.02 N) neutralization.

by the ozone treatment of a commercial activated carbon (Filtrisorb 400). The adsorption study was completed with a dynamic study using carbon columns, to construct NTS breakthrough curves in the presence of the previously mentioned metals and to determine column characteristics. The information yielded by this study will be of great value in the design of more efficacious adsorbents for the removal of these contaminants.

## 2. Experimental Section

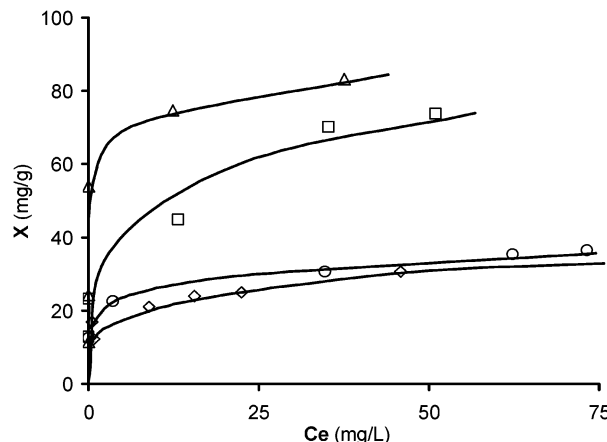
Filtrisorb 400 (Calgon Carbon Corp., U.S.A.) was used, an activated carbon derived from bituminous coal (denominated F) with a particle size of 500–800 μm. To obtain samples of activated carbon with increasing concentrations of oxygenated surface groups, samples were treated with ozone for 10 min (sample F10) or 120 min (sample F120). The carbon samples were texturally and chemically characterized (Table 1). A more detailed description of the equipment and methodology used was previously published.<sup>18</sup>

NTS adsorption isotherms were obtained in the presence of Cd(II), Cr(III), or Hg(II) on activated carbon samples at 298 K. For this purpose, 100 mL of NTS and metal solutions, of different concentrations, was put in contact with 0.1 g of activated carbon in different Erlenmeyer tubes. In all solutions prepared for isotherm measurement, the molar ratio of the NTS/metal concentrations was maintained constant at 2.5. The Erlenmeyer tubes were agitated until equilibrium was attained (72 h). The time to equilibrium 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. The solution pH was monitored, and it did not vary during these experiments.

The influence of the solution pH on the adsorption capacity of the activated carbon was analyzed by placing 100 mL of a solution of  $5.7 \times 10^{-4}$  mol/L metal and  $1.44 \times 10^{-3}$  mol/L NTS of different pH values (2, 4, 6, 8, or 10) with 0.1 g of activated carbon in Erlenmeyer tubes. The tubes were agitated until equilibrium was attained (72 h). The different pH values of the solutions were obtained by adding appropriate amounts of HCl and NaOH. The equilibrium concentrations of the naphthalene-sulfonic acid were determined as described previously. The equilibrium metal concentration was determined by atomic absorption using Variant Spectra A-200 equipment. The solution pH was monitored, and it did not vary during these experiments.

NTS adsorption in the presence of Cd(II), Cr(III), or Hg(II) was also studied in the dynamic regime using activated carbon columns. For this purpose, a solution at pH 6 with concentrations of  $1.1 \times 10^{-4}$  mol/L and  $4.6 \times 10^{-5}$  mol/L of NTS and metal, respectively, was passed through columns 8 cm in height and 1 cm in diameter at a flow of 1.5 mL/min. Samples were then taken from the solution at the outlet of the column until the column reached saturation. The breakthrough curves and carbon column characteristics were determined from these experiments.

The UV–vis spectra of all the prepared solutions were studied, and no differences were found with the original NTS spectrum. These results indicate that no coordination compounds were formed between NTS and the metals Cd(II), Cr(III), or Hg(II) under the experimental conditions studied.



**Figure 1.** NTS adsorption isotherms on carbon F: (◇) without metal; (□) in the presence of Cd(II); (△) in the presence of Cr(III); and (○) in the presence of Hg(II).

**Table 2. Results Obtained by Applying the Freundlich Equation to the Adsorption Isotherms**

sample	NTS		NTS + Cd(II)		NTS + Cr(III)		NTS + Hg(II)	
	K	1/n	K	1/n	K	1/n	K	1/n
F	17.4	0.13	22.62	0.26	58.30	0.56	17.63	0.16
F10	22.6	0.11	28.89	0.30	68.92	0.78	21.94	0.14
F120	0.78	0.09	2.92	0.59	7.41	0.94	0.94	0.08

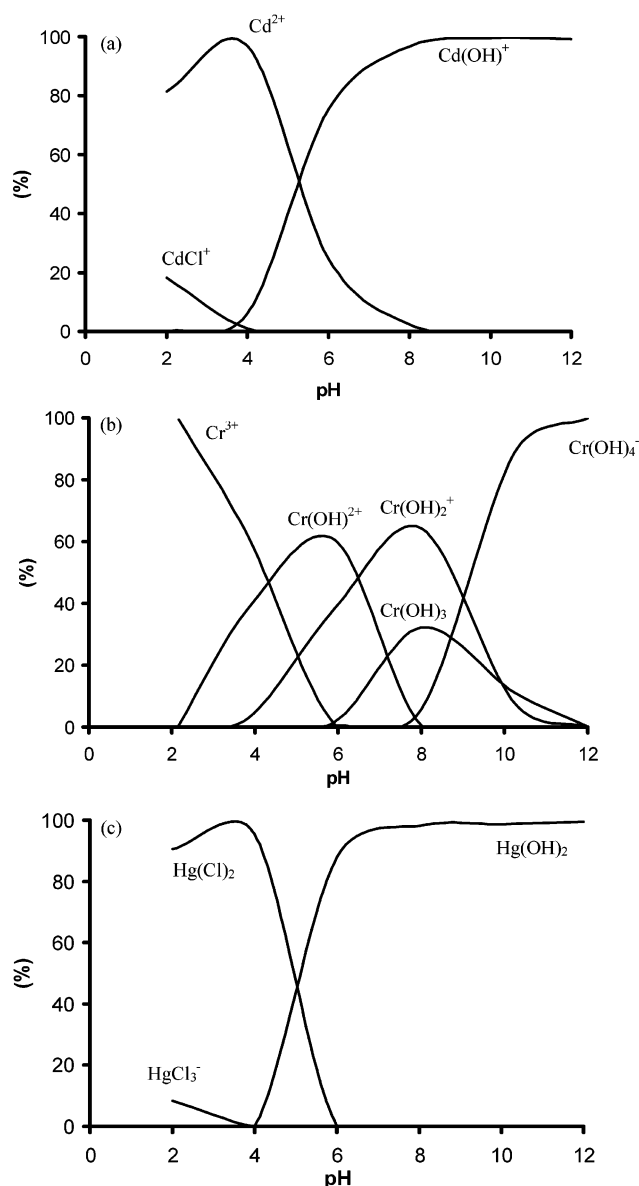
## 3. Results and Discussion

**3.1. Adsorption in the Static Regime.** **3.1.1. NTS Adsorption Isotherms on Activated Carbon in the Presence of Cd(II), Cr(III), or Hg(II).** Figure 1 depicts, as an illustration, the NTS adsorption isotherms on the original activated carbon, F, in the presence and absence of the metals Cd(II), Cr(III), or Hg(II). Similar results have been observed for the rest of the activated carbon samples studied (F10, F120). The Freundlich equation was applied to calculate the adsorption capacity ( $K$ ) and adsorption intensity ( $1/n$ ) of NTS for the different activated carbon samples. These results are displayed in Table 2.

To explain the results obtained, it must be stressed that the surface charge density at the working pH (pH = 6) was different in each activated carbon sample studied. Thus, carbon F presented a positive charge density (pH<sub>PZC</sub> = 8.82), carbon F10 a zero charge density (pH<sub>PZC</sub> = 5.96), and carbon F120 a negative charge density (pH<sub>PZC</sub> = 2.59).

The results presented in Table 2 show that, in absence of metal, the adsorption capacity of the activated carbon was slightly increased when it had been treated with low ozone doses (carbon F10). This was probably due to an increase in the surface area accessible to the adsorbate molecules, produced by gasification of the micropores<sup>18</sup> (Table 1). However, with longer exposure to ozone and, therefore, an increased number of electron-attracting groups in the activated carbon, the NTS adsorption diminished. This is due to a reduction in the electronic density of the basal plane of the activated carbon, producing a weakening of the adsorbate–adsorbent  $\pi$ – $\pi$  dispersion interactions and a strengthening of the repul-

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**Figure 2.** Calculated distribution of metal species present at different solution pH values: (a) Cd(II); (b) Cr(III); and (c) Hg(II).

sive electrostatic interactions between oxygenated surface groups at the working pH and naphthalenesulfonate anions.<sup>15</sup>

In addition, the presence of Cd(II) or Cr(III) in the medium enhanced the adsorption of NTS on activated carbon, increasing the  $K$  and  $1/n$  values (Table 2). This behavior was more marked in the ozone-treated samples. Thus, the presence of Cd(II) and Cr(III) in the medium increased the adsorption capacity of sample F120 by 274 and 850%, respectively. In contrast, the presence of Hg(II) in the medium had no significant effect on the adsorption of NTS on the activated carbon.

To explain the results presented in Table 2, a study was conducted of the species distribution, according to the solution pH, for Cd(II), Cr(III), and Hg(II) (Figure 2). The stability constants given by Stumm and Morgan<sup>19</sup> were used for this calculation. It was observed that, at the working pH (pH = 6), the majority of the species of Cd(II) and Cr(III) presented a positive charge [ $\text{Cd(OH)}^+$  and  $\text{Cr(OH)}_2^+$ ], respectively), whereas the majority of the species of Hg(II) was neutral [ $\text{Hg(OH)}_2$ ]. Analysis of NTS ionization constants ( $\text{p}K_2 \approx 4$ ,  $\text{p}K_3 \approx 10$ ) showed that NTS presented two ionized protons at the working pH (pH = 6) and was, therefore, found in naphthalenesulfonate anion form.

The adsorption of positively charged metal species, in the cases of Cd(II) and Cr(III), enhances attractive electrostatic interactions between naphthalenesulfonate anions and the activated carbon surface, explaining the results in Table 2. Moreover, the fact that the Cd(II) and Cr(III) species are cationic but the NTS species are anionic at the working pH means that a cooperative adsorption is established, favoring the purification efficacy of the activated carbon. This aspect will be discussed in greater depth in the next section. On the other hand, in the case of Hg(II), the adsorption of  $\text{Hg(OH)}_2$ , a species without a charge, has no effect on the adsorption of NTS on the activated carbon.

In previous publications,<sup>16,17</sup> it was observed that the adsorption of Cd(II) and Cr(III) on activated carbon was enhanced in ozonized samples, fundamentally when the ozonation time was increased. This is due to the formation of oxygen surface groups, mainly carboxylic groups (Table 1), which, when ionized, potentiate attractive electrostatic interactions between the activated carbon surface and the cationic species of Cd(II) and Cr(III) present. The increased adsorption of the cationic species of Cd(II) and Cr(III) on the surface of ozonized activated carbon samples would intensify attractive electrostatic interactions between the naphthalenesulfonate anions and the activated carbon surface, accounting for the results presented in Table 2. Moreover, in the case of carbon F120, which had a negative charge density ( $\text{pH}_{\text{PZC}} = 2.59$ ) at pH = 6, the presence of cationic species in the medium exerts a screening effect between the carbon surface and the naphthalenesulfonate anions, drastically reducing NTS–carbon electrostatic repulsion. Thus, a greater increase in adsorption was observed in carbon F120 in the presence of Cd(II) and Cr(III).

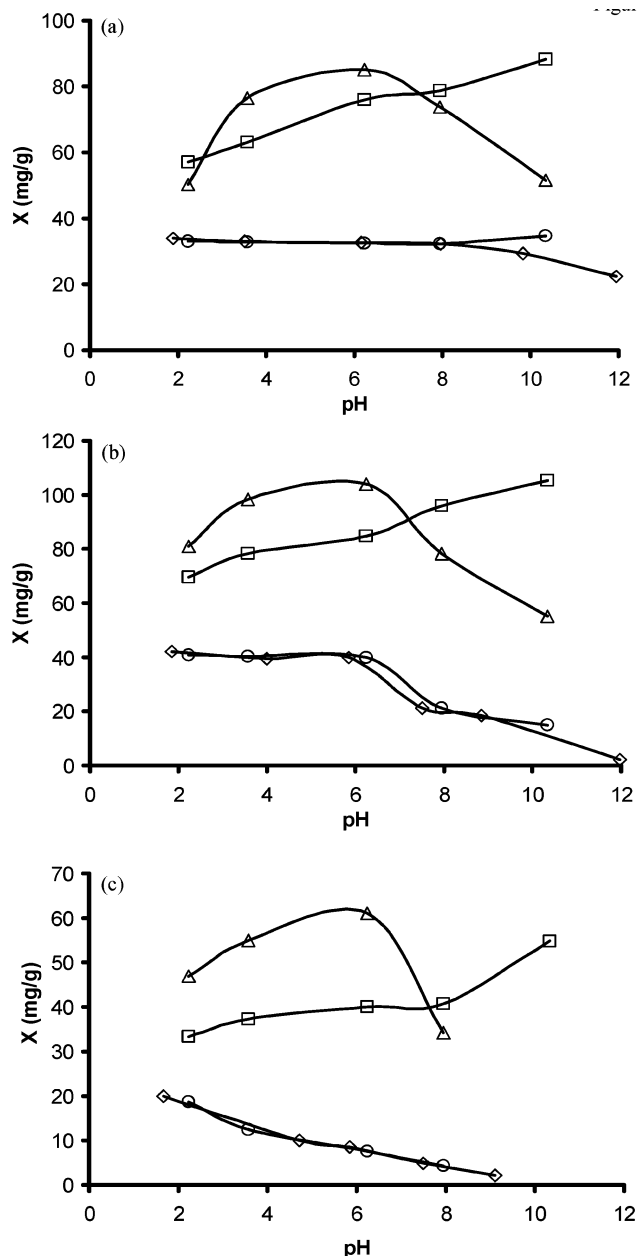
It can also be deduced from the results in Table 2 that NTS adsorption is especially favored in the presence of Cr(III). This is due to a greater adsorption of Cr(III) on the activated carbon surface<sup>16,17</sup> and the resulting intensification of attractive electrostatic interactions between the activated carbon surface and the naphthalenesulfonate anions.

It can be observed that the presence of Cd(II) and Cr(III) in the medium increased the NTS adsorption on the activated carbon, regardless of the carbon sample studied or the pH considered. However, the presence of Hg(II) did not appear to affect this adsorption process.

The behavior observed in relation to the pH can be explained by the charge of the metal species present (Figure 2) and by the surface charge density of each carbon sample at each pH value. The fact that the adsorbate is found as a naphthalenesulfonate anion across the pH range studied must also be taken into account.

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**Figure 3.** Influence of the pH on NTS adsorption on activated carbon samples: (a) F, (b) F10, and (c) F120; ( $\diamond$ ) without metal; ( $\square$ ) in the presence of Cd(II); ( $\triangle$ ) in the presence of Cr(III); and ( $\circ$ ) in the presence of Hg(II).

**Table 3. Influence of the Solution pH on Cd(II) Adsorption**

pH	without NTS			with NTS		
	F (mg/g)	F10 (mg/g)	F120 (mg/g)	F (mg/g)	F10 (mg/g)	F120 (mg/g)
2.23	1.38	1.24	2.95	3.25	5.23	10.26
6.23	2.18	6.73	11.55	5.56	10.25	16.23
7.94	2.18	6.28	10.79	5.69	11.26	18.36

The majority of the species of Cd(II) presented a positive charge across the entire pH range studied (Figure 2). Therefore, the increase in NTS adsorption with higher pH found in all activated carbon samples is due to the progressive ionization of the oxygenated surface functional groups. This implies an increase in the density of the surface negative charge, producing a greater adsorption of Cd(II) cationic species present at each pH (Table 3) and, therefore, intensifying attractive electrostatic interactions between the carbon surface and the naphtha-

**Table 4. Influence of the Solution pH on Cr(III) Adsorption**

pH	without NTS			with NTS		
	F (mg/g)	F10 (mg/g)	F120 (mg/g)	F (mg/g)	F10 (mg/g)	F120 (mg/g)
2.23	0.05	0.05	7.78	5.52	6.20	12.52
6.23	3.14	6.02	13.10	8.56	12.52	20.36
7.94	3.10	4.58	8.22	8.45	10.26	14.59

**Table 5. Influence of the Solution pH on Hg(II) Adsorption**

pH	without NTS			with NTS		
	F (mg/g)	F10 (mg/g)	F120 (mg/g)	F (mg/g)	F10 (mg/g)	F120 (mg/g)
2.23	20.52	6.70	5.90	20.70	17.30	6.90
6.23	25.54	22.80	11.79	26.11	23.20	11.40
7.94	25.29	23.00	10.83	26.10	23.50	11.40

lenesulfonate anions. This behavior was enhanced in the ozone-treated activated carbon samples (F10 and F120) because of the presence of a higher concentration of oxygenated surface groups. Furthermore, the fact that the majority of the Cd(II) species is cationic and the NTS species anionic across the entire pH range studied means that a cooperative adsorption is established.

Interestingly, NTS adsorption in the presence of Cr(III), Figure 3, was reduced at pH values above 6. This is partly because of the repulsive electrostatic interactions established between the carbon surface and the species present at these pH values [ $\text{Cr}(\text{OH})_4^-$  and naphthalene-sulfonates] and partly because both adsorbates present a negative charge, ending the cooperative adsorption.

The presence of Hg(II) did not affect the NTS adsorption on the activated carbon (Figure 3) because the species present were neutral across the pH range studied (Figure 2).

To confirm the cooperative effect in these adsorption processes, the amount of metal adsorbed was also studied as a function of the pH (Tables 3–5). The results show that the presence of NTS increased the adsorption of Cd(II) and Cr(III) on the activated carbon but had no effect on the adsorption of Hg(II). This effect was more pronounced at low pH values. The adsorption of the naphthalenesulfonate anion increases the attractive electrostatic interactions between the activated carbon surface and the cationic metal species, explaining the increase observed in the adsorption of Cd(II) and Cr(III). Interestingly, in the presence of Cr(III), the maximum adsorption of both NTS (Figure 3) and the metal (Table 4) occurred in the pH range (pH 2–6) at which the charges of the two adsorbates were opposed. These results confirm the cooperative character of the mechanism involved in the adsorption of NTS in the presence of Cd(II) and Cr(III).

Effects of the presence in the medium of Cd(II), Cr(III), or Hg(II) on the interactions involved in NTS adsorption on activated carbon were investigated. A study was made of the contribution of global dispersive and electrostatic interactions (adsorbent–adsorbate, adsorbate–adsorbate) to NTS adsorption on activated carbon at all the pH values studied.

It was considered that, in the absence of metal, dispersion forces are responsible for adsorption at solution  $\text{pH} = \text{pH}_{\text{PZC}}$  of the carbon samples and electrostatic interactions are negligible.<sup>14,15</sup> Therefore, the amount of acid adsorbed or desorbed as a result of global electrostatic interactions at the different pH values could be calculated from the difference between the amount adsorbed at each pH value and the amount adsorbed at  $\text{pH} = \text{pH}_{\text{PZC}}$  (in absence of metal). The results obtained are exhibited in

**Table 6. Relative Contribution of Electrostatic Interactions to the Overall Adsorption Capacity of NTS on Activated Carbon F as a Function of the pH**

pH	without metal (mg/g)	Cd(II) (mg/g)	Cr(III) (mg/g)	Hg(II) (mg/g)
2.23	0.85	24.80	17.87	0.68
3.57	0.45	30.73	44.17	0.50
6.23	0.12	43.67	52.77	0.19
7.94	0.04	46.37	41.47	0.02
10.33	-1.98	55.87	19.27	2.39

**Table 7. Relative Contribution of Electrostatic Interactions to the Overall Adsorption Capacity of NTS on Activated Carbon F10 as a Function of the pH**

pH	without metal (mg/g)	Cd(II) (mg/g)	Cr(III) (mg/g)	Hg(II) (mg/g)
2.23	0.85	29.65	41.05	0.97
3.57	0.68	38.35	58.45	0.49
6.23	-0.59	44.85	64.15	0.14
7.94	-18.85	56.15	38.35	-18.70
10.33	-30.29	65.45	15.27	-24.81

**Table 8. Relative Contribution of Electrostatic Interactions to the Overall Adsorption Capacity of NTS on Activated Carbon F120 as a Function of the pH**

pH	without metal (mg/g)	Cd(II) (mg/g)	Cr(III) (mg/g)	Hg(II) (mg/g)
2.23	0.00	14.72	28.34	0.07
3.57	-5.88	18.67	36.40	-6.18
6.23	-11.15	21.41	42.57	-11.04
7.94	-14.52	22.14	15.62	-14.27

**Table 9. Characteristics of Activated Carbon Columns (Carbon F)**

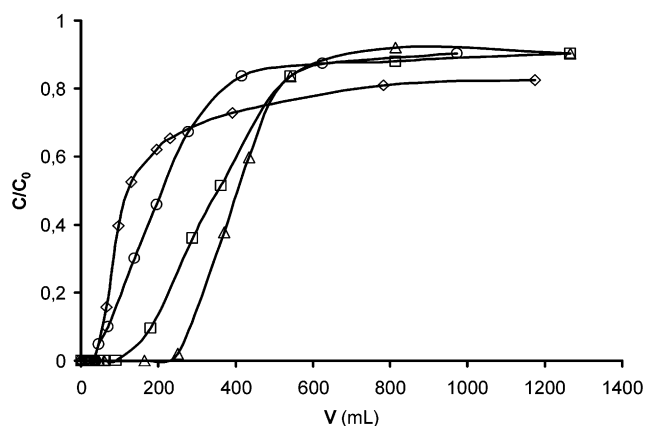
adsorbate	$V_R^a$ (mL)	$X_R^b$ (mg/g)	$X_{0.8}^c$ (mg/g)	$H_{MTZ}^d$ (cm)	$\phi^e$	$G_U^f$ (%)
NTS	36.98	2.62	10.34	21.90	0.30	25.33
NTS + Cd(II)	100.67	8.53	25.66	12.16	0.48	33.24
NTS + Cr(III)	201.00	20.1	37.37	6.67	0.59	53.78
NTS + Hg(II)	39.09	3.9	12.58	15.87	0.35	31.00

<sup>a</sup>  $V_R$ : volume of effluent treated to initial breakthrough. <sup>b</sup>  $X_R$ : amount of NTS acid adsorbed to initial breakthrough. <sup>c</sup>  $X_{0.8}$ : amount of NTS adsorbed at the 0.8 breakthrough value. <sup>d</sup>  $H_{MTZ}$ : height of the mass transfer zone. <sup>e</sup>  $\phi$ : fractional capacity of NTS within the mass transfer zone. <sup>f</sup>  $G_U$ : utility degree.

Tables 6–8. According to these results, the presence of Cd(II) and Cr(III) 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 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 ozonized carbons, the electrostatic contribution to the overall NTS adsorption process, due to the presence of cationic metal species, is increased in these carbons.

**3.2. Adsorption in the Dynamic Regime.** To evaluate the effectiveness of the original activated carbon, NTS adsorption in the presence of Cd(II), Cr(III), or Hg(II) was studied in the dynamic regime using activated carbon columns. Carbon F breakthrough curves for NTS were obtained in the presence of each of the three metals studied (Figure 4).

The characteristics of the columns were determined from these curves (Table 9). The breakthrough volume ( $V_R$ ) and the amount adsorbed at a breakthrough volume of 0.8 ( $X_{0.8}$ ) were increased in the presence of Cd(II) and Cr(III). However, the adsorption capacity in the dynamic regime

**Figure 4.** Breakthrough curves of the carbon F column for NTS: (◇) without metal; (□) in the presence of Cd(II); (△) in the presence of Cr(III); and (○) in the presence of Hg(II).

was lower than that obtained in the static regime, as a result of problems of the adsorbate diffusing within the microporosity of the carbon when adsorption is carried out in the dynamic regime. In addition, the presence of Cd(II) and Cr(III) produced a reduction in the height of the mass transfer zone ( $H_{MTZ}$ ), whereas the degree of utility of the columns ( $X_R/X_{0.8}$ ) and the fractional capacity ( $\phi$ ) were increased, especially in the presence of Cr(III).

The results presented in Table 9 indicate that the interactions established between naphthalenesulfonate anions and the activated carbon surface are increased in the presence of Cd(II) and especially in the presence of Cr(III). As stated previously, the presence of these cations strengthens attractive electrostatic interactions between the activated carbon surface and naphthalenesulfonate anions through a cooperative effect.

All these results indicate that the presence of Cd(II) and Cr(III) improves the efficacy of activated carbon in removing NTS from waters.

## 4. Conclusions

NTS adsorption on activated carbon is favored in the presence of Cd(II) and Cr(III), whereas the presence of Hg(II) has no effect on the adsorption process. The presence of Cd(II) and Cr(III) cationic species on the activated carbon surface enhances attractive electrostatic interactions between the carbon surface and NTS, producing an increase in the  $K$  and  $1/n$  values.

In presence of Cd(II) and Cr(III), the NTS adsorption capacity increases with greater oxidation of the activated carbon. The rise in the number of oxygenated surface groups on carbon increases the adsorption of metal cationic species, intensifying attractive electrostatic interactions between the carbon surface and NTS.

The adsorption of NTS in the presence of Cd(II) and Cr(III) is a cooperative process in which electrostatic interactions play a key role. Thus, the presence of metal cationic species favors the adsorption of naphthalenesulfonate anions and vice versa.

Analysis of the influence of the pH on the adsorption of NTS in the presence of the metals shows that the NTS adsorption is favored when the charge signs of the adsorbates (NTS and metal species) are opposite.

Breakthrough values of the carbon columns and the height of the mass transfer zone indicate that the purification efficacy of activated carbon is improved in the presence of Cd(II) and Cr(III).