Removal of nitroimidazole antibiotics from aqueous solution by adsorption/bioadsorption on activated carbon

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A B S T R A C T

The objective of the present study was to analyse the behaviour of activated carbon with different chemical and textural properties in nitroimidazole adsorption, also assessing the combined use of microorganisms and activated carbon in the removal of these compounds from waters and the influence of the chemical nature of the solution (pH and ionic strength) on the adsorption process. Results indicate that the adsorption of nitroimidazoles is largely determined by activated carbon chemical properties. Application of the Langmuir equation to the adsorption isotherms showed an elevated adsorption capacity ($X_m = 1.04$–2.04 mmol/g) for all contaminants studied. Solution pH and electrolyte concentration did not have a major effect on the adsorption of these compounds on activated carbon, confirming that the principal interactions involved in the adsorption of these compounds are non-electrostatic. Nitroimidazoles are not degraded by microorganisms used in the biological stage of a wastewater treatment plant. However, the presence of microorganisms during nitroimidazole adsorption increased their adsorption on the activated carbon, although it weakened interactions between the adsorbate and carbon surface. In dynamic regime, the adsorptive capacity of activated carbon was markedly higher in surface water and groundwater than in urban wastewaters.

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1. Introduction

A constant flow of new 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 [1–5]. They include chemical compounds in cosmetics (creams, perfumes and make-up), domestic products (degreasants, glass cleaners and detergents) and pharmaceuticals, which are causing the greatest concern due to their very wide variety and elevated consumption [4,5]. For example, over 3000 different pharmaceutical substances are used in the UK [6], and the annual production for human consumption in the European Union is estimated to exceed 100 tons per member country [7]. Antibiotics are the most heavily used medical drugs in the European Union, with an estimated annual consumption of around 10,000 tons [7]. It should also be noted that these consumption figures are considerably increased by the use of many of these products in veterinary medicine.

High concentrations of antibiotics are now detected in drinking waters, reducing their quality. They generally have a low biodegrad-

ability [8,9] and high toxicity [10], and some are reported to have mutagenic and carcinogenic characteristics [11]. 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 [9,12].

Nitroimidazole antibiotics were recently detected in waters at concentrations of 0.1–90.2 μg/L [13]. They are widely used to treat infections caused by anaerobic and protozoan bacteria (e.g., *Trichomonas vaginalis* and *Giardia lamblia*) in humans and animals and are added to chow for fish and fowl [14,15], leading to their accumulation in animals, fish-farm waters and, especially, meat industry effluents [10]. Little is yet known about the capacity of current water treatment systems to remove nitroimidazoles [16], but it is not expected to be very high given the complex chemical structure of these compounds. It will be necessary to develop new methods to effectively remove these contaminants from waters in a technologically feasible and economically viable manner.

With this background, the objective of this study was to determine the behaviour of activated carbon with different chemical and textural properties in the removal of nitroimidazoles from surface, groundwater and urban wastewaters, in both static and dynamic regimes. The study also aimed to assess the influence of the chemical nature of the solution (pH and ionic strength) on the nitroimidazole adsorption and the effects on this pro-
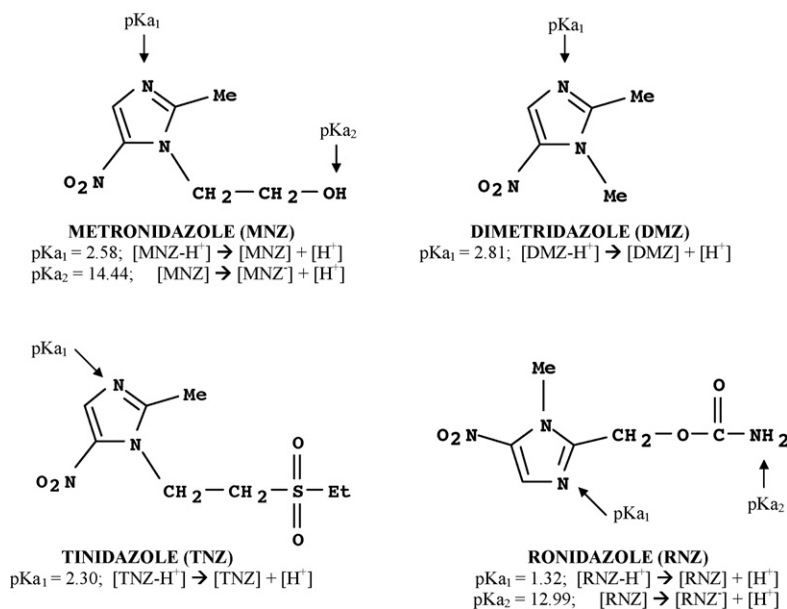
Fig. 1. Chemical structure and acidity constants of nitroimidazoles.

cess of combining microorganisms with the activated carbon (bioadsorption).

2. Experimental

2.1. Pharmaceutical products

Nitroimidazoles used in this study were: (i) metronidazole (MNZ), (ii) dimetridazole (DMZ), (iii) tinidazole (TNZ) and (iv) ronidazole (RNZ), all supplied by Sigma–Aldrich. Fig. 1 and Table 1 show the chemical formulas and properties of these compounds.

2.2. Activated carbon

Three activated carbons were used: two commercial carbons, Sorbo (S) and Merck (M), and a third carbon (sample C) prepared in our laboratory by chemical activation of petroleum coke with KOH

[17]. After sieving and washing the carbon with ultrapure water, they were dried in drying chamber at 110 °C and then stored in a dessicator. Particle size range was 0.45–1 mm.

Activated carbon samples were chemically and texturally characterized (surface area, volume of water-accessible pores, elemental analysis, ash content, surface oxygenated groups and point of zero charge). Detailed descriptions of the techniques and methods used for this characterization were previously reported [18,19]. Tables 2 and 3 depict carbon characterization results.

The hydrophobicity of activated carbon was determined by measuring immersion enthalpies in benzene $\Delta H_i(C_6H_6)$ and water $\Delta H_i(H_2O)$ using a SETARAM C80 calorimeter. For this purpose, 0.1 g of activated carbon was degasified in a glass capsule at a pressure of 10^{-5} mbar and a temperature of 383 K for 12 h. Subsequently, each sample was left to stabilize for 3 h at 303 K in the calorimeter before the experiment. Table 4 shows the results obtained in the calorimetry experiments.

Table 1
Properties of nitroimidazoles.

Nitroimidazole	Molecular weight (g/mol)	Transversal section (A^2)	Volume (A^3)	Solubility in water (mol/L)	pk_{ow}[a]	pk_{a1}	pk_{a2}
MNZ	171.15	101	186	0.041	0.02	2.58	14.44
DMZ	141.13	88	157	0.062	−0.31	2.81	–
TNZ	247.27	138	258	0.008	0.35	2.30	–
RNZ	200.15	113	206	0.015	0.38	1.32	12.99

[a] Octanol–water partition coefficients.

Table 2
Textural characterization of activated carbon.

Activated carbon	S_{N_2}[a] (m^2/g)	S_{ext}[b] (m^2/g)	V_2[c] (cm^3/g)	V_3[d] (cm^3/g)	V_{H_2O}[e] (cm^3/g)	W_o (N_2)[f] (cm^3/g)	W_o (CO_2)[f] (cm^3/g)	L_o (N_2)[g] (nm)	L_o (CO_2)[g] (nm)
S	1225	46.9	0.044	0.481	0.983	0.391	0.279	1.02	0.65
M	1301	41.9	0.101	0.284	0.729	0.423	0.295	1.69	0.70
C	848	28.0	0.061	0.154	0.512	0.361	0.158	0.66	0.49

[a] Surface area determined from adsorption isotherms of N_2 at 77 K.
[b] External surface area.
[c] Volume of pores with diameter of 6.6–50 nm determined by mercury porosimetry.
[d] Volume of pores with diameter >50 nm determined by mercury porosimetry.
[e] Volume of pores accessible to water determined by pycnometric densities.
[f] Volumes of micropores determined by N_2 and CO_2 adsorption, respectively.
[g] Mean widths of micropores determined with Dubinin's equation [45].

Table 3
Chemical characteristics of activated carbon.

Activated carbon	Carboxyl groups[a] (μequiv./g)	Lactone groups[b] (μequiv./g)	Phenol groups[c] (μequiv./g)	Carbonyl groups[d] (μequiv./g)	Total acid groups[e] (μequiv./g)	Total basic groups[f] (μequiv./g)	pH_{pzc} [g]	Oxygen[h] (% wt)	Ashes (%)
S	0.0	56.0	244.0	146.7	446.7	1080.0	9.0	9.8	6.07
M	40.0	120.0	156.0	84.0	400.0	440.0	7.7	7.4	5.30
C	0.0	53.3	433.3	220.0	706.7	986.7	8.8	12.3	0.42

[a] Concentration of carboxyl groups determined by titration with $NaHCO_3$ (0.02N).
[b] Concentration of lactone groups determined by titration with Na_2CO_3 (0.02N)–$NaHCO_3$ (0.02N).
[c] Concentration of phenol groups determined by titration with NaOH (0.02N)–Na_2CO_3 (0.02N).
[d] Concentration of carbonyl groups determined by titration with NaOH (0.1N)–NaOH (0.02N).
[e] Concentration of acid groups determined by titration with NaOH (0.1N).
[f] Concentration of basic groups determined by titration with HCl (0.1N).
[g] pH of point of zero charge.
[h] Percentage in oxygen determined by means of elemental analysis.

Table 4
Results obtained from immersion calorimetry of activated carbon in water and benzene.

Activated carbon	$-\Delta H_i(C_6H_6)$[a]		$-\Delta H_i(H_2O)$[b]		$1 - \frac{\Delta H_i(H_2O)}{\Delta H_i(C_6H_6)}$ [c]
	(J/g)	(mJ/m²)	(J/g)	(mJ/m²)	
S	136.7	111.6	48.4	39.5	0.65
M	114.3	87.8	37.2	28.6	0.67
C	128.5	151.5	62.0	73.1	0.52

[a] Benzene adsorption enthalpy.
[b] Water adsorption enthalpy.
[c] Relative hydrophobicity coefficient.

2.3. Nitroimidazole adsorption on activated carbon

The adsorption isotherms of the four nitroimidazoles were obtained for the three activated carbons (S, M and C). For this purpose, 100 mL of nitroimidazole aqueous solutions at increasing concentrations (50–600 mg/L) were placed in contact with 0.1 g of activated carbon, determining the nitroimidazole concentration after equilibrium was reached (8 days). Adsorption isotherms were obtained at a pH value between 6 and 7.

The influence of pH on the nitroimidazole adsorption process was studied by adding 0.1 g of activated carbon to Erlenmeyer flasks containing 100 mL of nitroimidazole solution with a concentration of 600 mg/L at different pH values (2–11). The working pH was obtained by adding the appropriate volume of HCl (0.1N) and NaOH (0.1N) to the corresponding nitroimidazole solution. The effect of the presence of electrolytes on the adsorption process was analyzed by placing 100 mL of the corresponding nitroimidazole solution (600 mg/L) and increasing concentrations of NaCl (0.0001–0.1 M) in contact with 0.1 g of activated carbon.

The presence of microorganisms has a major influence on the effectiveness of activated carbon in water treatment because they can be adsorbed on the carbon and form bacteria colonies on its surface (biological activated carbon) [20]. In order to determine the efficacy of the combined action of activated carbon and microorganisms (bacteria) in nitroimidazole removal, the corresponding adsorption isotherms in the presence of bacteria (bioadsorption) were obtained. To this end, a mixture of microorganisms obtained from secondary effluents from a wastewater treatment plant was used. We drew 5 mL of this water and added it to an autoclaved

Erlenmeyer flask containing 25 mL of a TSB solution (Tryptone Soy Broth) buffered at pH 7, which was shaken at a temperature of 303 K until turbidity was observed in the solution. This procedure was used to get a suspension with a high concentration of bacteria [21]. Then, following the procedure described above to obtain adsorption isotherms, 1 mL of bacteria suspension was added to each flask after being centrifuged and washed several times with distilled and sterile water.

Nitroimidazole adsorption was also studied in dynamic regime by using activated carbon columns. For this purpose, a solution of nitroimidazole (100 mg/L) was passed through 7-cm high and 1-cm diameter columns at a flow of 1.5 mL/min. As in the isotherm determination, solutions were prepared in the absence of any pH-controlling compound. At different time intervals, solution samples were taken at the column outlet until saturation was reached. Carbon column breakthrough curves and their characteristics were obtained from these experiments [22].

Samples of natural waters (groundwater and surface) were drawn from the drinking water treatment plant, and wastewaters were collected from the wastewater treatment plant in Motril (Granada). Samples were supplied by the company "Aguas y Servicios de la Costa Tropical de Granada". After being characterized, waters were filtered and stored in cold until use. Table 5 shows the characterization parameters determined for these waters.

Nitroimidazoles were spectrophotometrically analyzed at a wavelength of 320 nm using a Genesys 5 spectrophotometer. The elemental analysis of activated carbon was conducted in a Fisons Instruments 1108 CHNS elemental analyser.

Table 5
Chemical characteristics of waters used.

Water	pH	TOC (mg/L)	$[HCO_3^-]$ (mequiv./L)	$[Ca^{2+}]$ (mmol/L)	$[Mg^{2+}]$ (mmol/L)	Total hardness $CaCO_3$ (mg/L)	Conductivity[a] (μS/cm)
Ultrapure	6.80	0.0	0.0	0.0	0.0	0.0	0.055
Surface	8.30	14.9	6.4	1.55	1.11	266	688
Groundwater	7.45	29.7	8.8	2.53	2.18	471	1623
Waste	7.77	88.9	7.2	2.12	1.53	365	1578

[a] Conductivity at 298 K.

3. Results and discussion

3.1. Characteristics of activated carbon

Table 2 depicts the textural characteristics of activated carbon used in this study: they have a large surface area (>848 m^2/g) and a highly developed porosity, with a very large volume of pores accessible to water, ranging from 0.512 cm^3/g (carbon C) to 0.983 cm^3/g (carbon S). The pore size distribution of carbon is an important parameter for the adsorption of a compound in aqueous solution, since pores that are inaccessible to water will not be effective for adsorption.

Micropore volumes deduced from N$_2$ adsorption were very high, ranging from 0.361 cm^3/g (carbon C) to 0.423 cm^3/g (carbon M), but were considerably lower than those from CO$_2$ adsorption (Table 2), indicating a very heterogeneous micropore distribution in the activated carbon. Because CO$_2$ is only adsorbed in smaller size micropores (ultramicropores), whereas N$_2$ is adsorbed on the surface of all micropores [23,24], N$_2$ adsorption data yield the total micropore volume, W_o (N$_2$). Thus, the mean micropore size (L_o) was higher when determined by N$_2$ versus CO$_2$ adsorption (Table 2).

Table 3 lists the chemical characteristics of carbon, showing that the study carbons are predominantly basic, with pH of point of zero charge values ranging from 7.7 (carbon M) to 9.0 (carbon S). The carbon from petroleum coke (carbon C) had an ash content of only 0.42%.

Table 4 shows the results obtained in water and benzene immersion calorimetry experiments with the different activated carbons. Adsorption enthalpies determined by immersion calorimetry of an activated carbon in water depend on the interactions with polar sites (acid or basic), the micropore filling and the external surface wetting. Hence, the first process is specific and corresponds to relatively high energies, whereas the other two are due to lower energy non-specific interactions [25,26]. Due to this specific interaction, a relationship can be established between the water immersion enthalpy and surface oxygen content of different carbons [27,28]. Thus, when water adsorption heat is expressed per gram of carbon, there is a linear relationship (0.9979 correlation coefficient) with the oxygen percentage of activated carbon (Table 3). Furthermore, the adsorption enthalpy of the non-polar benzene molecule, ΔH_i(C$_6$H$_6$), does not depend so directly on the chemical nature of carbon surface but rather on the distribution of its porosity [25,26]. Thus, data obtained from calorimetry with benzene show an inverse relationship with mean L_o (N$_2$) and L_o (CO$_2$) micropore size (Table 2).

If the polar character of the water molecule is related to the non-polar character of benzene, the relative hydrophobicity of carbon can be determined by means of the hydrophobicity coefficient given by Eq. (1)

$$1 - \frac{\Delta H_i(H_2O)}{\Delta H_i(C_6H_6)} \tag{1}$$

Table 4 shows the relative hydrophobicity coefficients for activated carbon. Carbon hydrophobicity is a very important characteristic for its use as adsorbent in an aqueous solution because it enhances the adsorption process. These carbons showed intermediate hydrophobicity, with values of 0.52–0.67, and the hydrophobicity coefficient increased with a decrease in oxygen content of the carbon (Table 3).

3.2. Nitroimidazole adsorption processes

The mechanisms involved in the process of nitroimidazole adsorption and the adsorption capacity of carbon were determined by obtaining the corresponding adsorption isotherms. Fig. 2 depicts, as an example, the normalized adsorption isotherms of the four
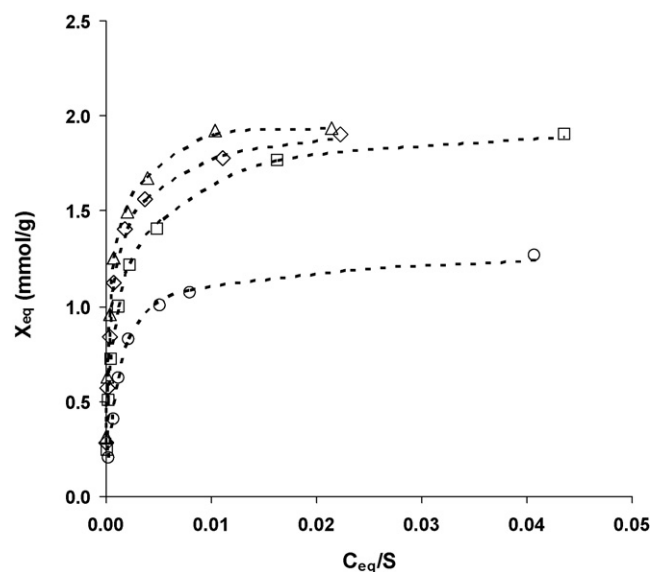

Fig. 2. Adsorption isotherms of nitroimidazoles on carbon S. pH 7, T 298 K. [S] = 1 g/L. (◇) MNZ; (△) DMZ; (○) TNZ; (□) RNZ.

nitroimidazoles for activated carbon S. It shows the millimoles of nitroimidazole adsorbed per gram of carbon (X_{eq}) versus the equilibrium concentrations normalized for the solubility of each nitroimidazole in water at 298 K (C_{eq}/S). Isotherms show the L form of the classification by Giles et al. [29,30], suggesting that the aromatic rings of nitroimidazole molecules are adsorbed in parallel to the carbon surface and that there is no major competition between nitroimidazoles and water molecules for the active adsorption centres on the carbon.

Langmuir (Eq. (2)) and Freundlich (Eq. (3)) models were applied to the experimental adsorption isotherm data. They are the most widely used models for describing this type of process and are represented mathematically as:

$$\frac{C_{eq}}{X_{eq}} = \frac{C_{eq}}{X_m} + \frac{1}{BX_m} \tag{2}$$

$$X_{eq} = K_f C_{eq}^{1/n} \tag{3}$$

The correlation coefficients obtained were >0.99 for all systems with the Langmuir equation (Table 6) but ranged from 0.842 for the TNZ-carbon S system to 0.987 for DMZ-carbon M when the Freundlich equation was applied (Table 7). Although both models served to explain our results, the Langmuir model fitted better the experimental data.

The adsorption capacity was very elevated for all carbons and nitroimidazoles (Table 6), with X_m values ranging from 1.04 mmol/g for TNZ-carbon C to 2.04 mmol/g for DMZ-carbon C. In general, relative affinity values, BX_m, were also higher than those usually reported in aromatic compound adsorption [31], indicating the high chemical affinity of nitroimidazoles for carbon. Interestingly, the constant B value in Langmuir's equation (related to adsorption energy) increased in the order DMZ < MNZ < RNZ < TNZ, which may be related to the solubility of these nitroimidazoles in water, with an increase in their adsorption energy as solubility decreases (Table 1). The corresponding values of the Freundlich exponential coefficient, $1/n$, were low, ranging from 0.214 to 0.295 (Table 7), which also indicates strong adsorbent–adsorbate interactions [32].

The adsorption capacity of carbon for the different nitroimidazoles was expressed per unit of carbon surface area, X'_m, to enable comparisons among them (Table 6). Except in the case of TNZ, the adsorption capacity of carbon increased in the order M < S < C, which may be related to the oxygen content of carbon, which increased

Table 6
Parameters obtained by applying Langmuir's equation to the adsorption isotherms of nitroimidazoles on activated carbon S, M and C.

Nitroimidazole	X_m (mmol/g)			X'_m ($\times 10^3$ mmol/m^2)			B (L/mmol)			BX_m (L/g)		
	S	M	C	S	M	C	S	M	C	S	M	C
MNZ	1.92	1.25	1.68	1.56	0.96	1.98	52.11	9.44	23.50	100.00	11.82	39.37
DMZ	1.99	1.32	2.04	1.62	1.01	2.40	43.84	9.38	23.29	87.24	12.39	47.62
TNZ	1.37	1.56	1.04	1.12	1.20	1.23	75.79	94.24	56.45	104.17	147.06	58.82
RNZ	1.97	1.82	1.89	1.61	1.40	2.23	52.85	25.49	24.57	104.11	46.51	46.51

X_m = adsorption capacity; B = Langmuir's constant; BX_m = adsorbent–adsorbate relative affinity.

Table 7
Parameters obtained by applying Freundlich's equation to the adsorption isotherms of nitroimidazoles on activated carbon S, M and C.

Nitroimidazole	S			M			C		
	$1/n$	K_f (L/g)	r^2	$1/n$	K_f (L/g)	r^2	$1/n$	K_f (L/g)	r^2
MNZ	0.247	403.27	0.925	0.268	171.67	0.968	0.282	248.42	0.932
DMZ	0.235	408.97	0.901	0.261	191.20	0.987	0.260	345.46	0.893
TNZ	0.295	268.47	0.842	0.214	439.44	0.915	0.280	200.26	0.885
RNZ	0.223	479.40	0.935	0.262	317.03	0.967	0.240	361.80	0.928

$1/n$ = exponential Freundlich's coefficient; K_f = Freundlich's affinity parameter; r^2 = correlation coefficient.

in the same direction (Table 3). Thus, in the case of carbon C and S, this oxygen is mainly forming phenolic groups (Table 3), which are electronic activators of the aromatic rings of carbon graphene planes; this favours the adsorption of aromatic compounds like nitroimidazoles, which can be adsorbed by dispersion interactions of π electrons of their aromatic rings with π electrons of the carbon graphene planes [33]. Furthermore, the presence of oxygen in the carbon favours the establishment of hydrogen bridge bonds between nitroimidazoles and the carbon surface. These bonds may be responsible for the strong adsorbent–adsorbate interactions detected in these systems and commented above.

Comparison of the adsorption capacity of carbon for each nitroimidazole (X'_m) shows that, with the exception of carbon M, X'_m decreased in the order DMZ > RNZ > MNZ > TNZ. These results show some relationship with the size of the nitroimidazole molecules (Table 1) and hence with their accessibility to the carbon porosity. Thus, TNZ has the largest molecule size and was the least adsorbed, whereas DMZ has the smallest molecule size and therefore highest accessibility to the carbon surface and showed the highest adsorption. Besides the accessibility of nitroimidazoles to the carbon surface, the electronic density of their aromatic ring also increases their adsorption, since it enhances the above-mentioned π–π adsorbate–adsorbent dispersion interactions. Based on the chemical composition of these nitroimidazoles and the electronic activating/deactivating power of the groups they contain, the electronic density of aromatic rings decreases in the order DMZ > RNZ ≈ MNZ > TNZ, the same order found for the increase in adsorption capacity of these nitroimidazoles. These results demonstrate that the adsorption process is mainly determined by the adsorbent–adsorbate dispersion interactions described above.

3.3. Influence of medium pH on nitroimidazole adsorption

Fig. 3 shows, as an example, the influence of solution pH on nitroimidazole adsorption of activated carbon M. The solution pH did not significantly affect the process of adsorption of nitroimidazoles on carbon M between pH 4 and 11, but all four nitroimidazoles showed a slight decrease at pH 2. According to their pk_{a1} values (Fig. 1), this is because of the protonation of nitroimidazoles at pH values close to 2. As a result, repulsive electrostatic interactions are established between the carbon surface, positively charged at pH 2 ($pH_{solution} < pH_{PZC}$) and the nitroimidazoles, positively charged at pH values close to 2. Similar results were observed for the other carbon samples.

Results depicted in Fig. 3 verify that electrostatic interactions do not play a major role in the adsorption of nitroimidazoles on activated carbon surface between pH 4 and 11, since nitroimidazole molecules are neutral under these conditions and surface oxygenated groups of the activated carbon progressively ionize with higher solution pH. Therefore, the increase in negative surface charge does not produce a reduction in the adsorption of the contaminants. These data confirm that non-electrostatic interactions are largely responsible for the adsorption of these compounds on activated carbon, as reported in the above section.

3.4. Influence of ionic strength on nitroimidazole adsorption process

The interactions involved in this process were investigated by studying the influence of ionic strength on nitroimidazole adsorption. Radovic et al. [31] reported that the presence of electrolytes in the solution may modify the strength of adsorbate–adsorbent interactions due to a screening effect.

Fig. 4 shows, as an example, the results of nitroimidazole adsorption on carbon M in the presence of increasing NaCl concentrations. The presence of ionic strength in the solution did not change the
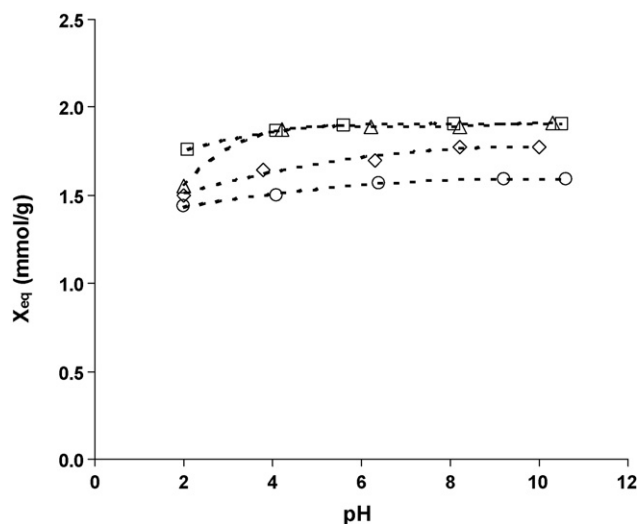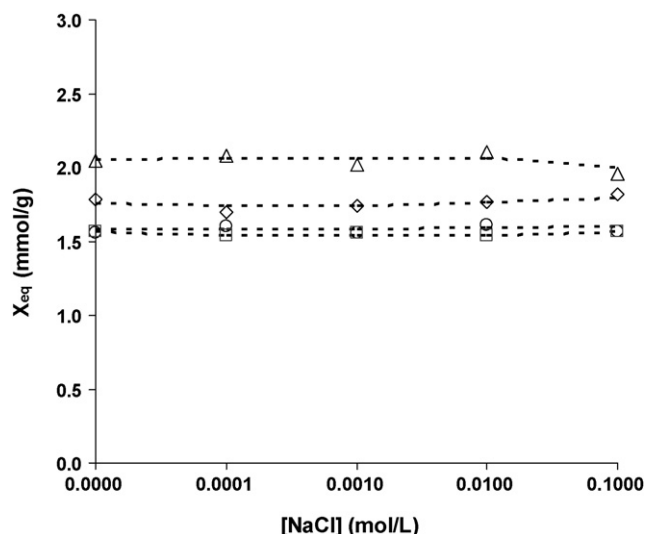

Fig. 3. Influence of pH in nitroimidazole adsorption process on carbon M. T 298 K. [M] = 1 g/L. (◇) MNZ; (△) DMZ; (○) TNZ; (□) RNZ. [Nitroimidazole]$_o$ = 600 mg/L.

Fig. 4. Influence of ionic strength on nitroimidazole adsorption on carbon M. pH 7, T 298 K. [M] = 1 g/L. ($\diamond$) MNZ; ($\triangle$) DMZ; ($\bigcirc$) TNZ; ($\square$) RNZ. [Nitroimidazole]$_o$ = 600 mg/L.

capacity of carbon M to adsorb any of the compounds, and similar results were obtained for the other activated carbon samples. These results confirm that the interactions governing these adsorption processes are not electrostatic.

3.5. Influence of the presence of microorganisms on nitroimidazole adsorption (bioadsorption)

The presence of microorganisms has a major influence on the effectiveness of activated carbon in water treatment because they can be adsorbed on the carbon and form bacteria colonies on its surface (biological activated carbon) [20,34]. Their presence on the carbon surface can have beneficial effects, including: (1) prolongation of carbon bed life due to the transformation of organic biodegradable matter into biomass, carbon dioxide and waste products, avoiding carbon saturation [35] and (2) formation by the adsorbed microorganisms of a biofilm that changes the texture of the carbon and its surface charge, which can improve the adsorption of some contaminants [20]. Bacteria range in size from 0.3 to 30 µm [36,37], therefore their adsorption on the carbon has a direct effect on the largest micropores, although they also exert an indirect effect by blocking the entrance of smaller pores.

Fig. 5 depicts the adsorption/bioadsorption isotherms of DMZ and RNZ on carbon S in the presence and absence of microorganisms. Application of Langmuir's equation to these isotherms (Table 8) showed that the presence of microorganisms during the adsorption of these nitroimidazoles increases the adsorption capacity of carbon S by 22% and decreased the adsorbate–adsorbent relative affinity values (BX_m) by around 60%. These results suggest that the presence of bacteria produces a change in the main interactions responsible for the adsorption and may therefore affect the adsorption mechanism. Nitroimidazole biodegradation kinetics by the bacteria under study were investigated before obtaining
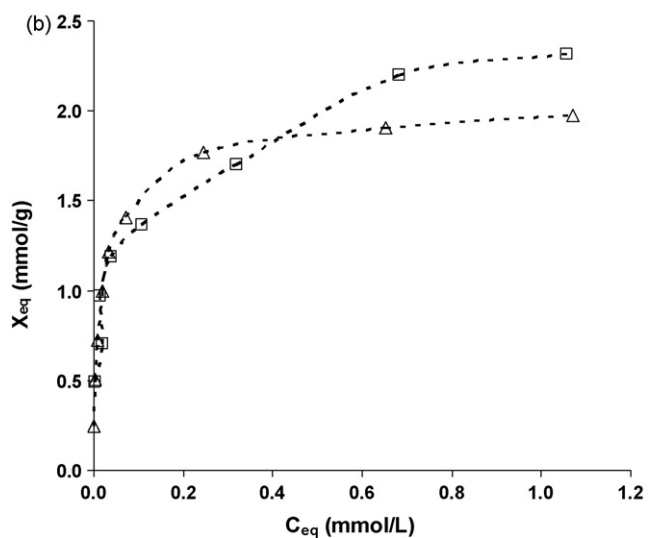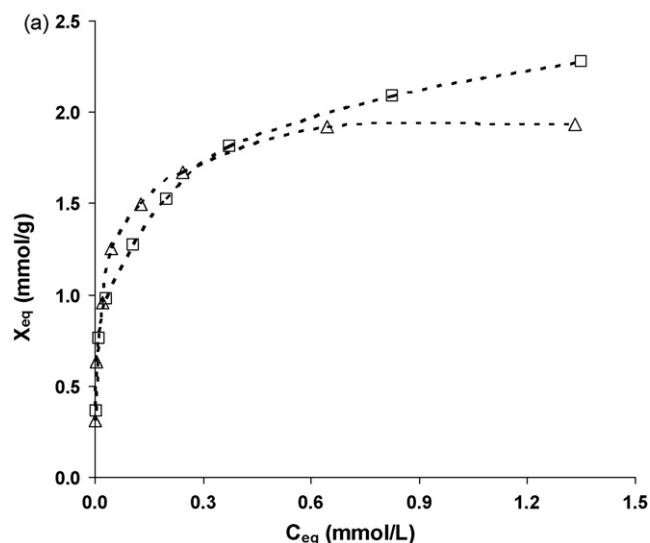

Fig. 5. Adsorption isotherms of DMZ (a) and RNZ (b) in the presence ($\square$) and absence ($\triangle$) of microorganisms on carbon S. pH 7, T 298 K. [S] = 1 g/L.

the bioadsorption isotherms, observing no biodegradation of these compounds under the experimental conditions used.

Previous papers [34,20] reported that the effect of microorganism adsorption on the chemical and textural properties of activated carbon S included: (i) a decrease in the external surface area, due to pore blocking and (ii) a reduction in the pH_{PZC} value, increasing the negative charge density on the activated carbon surface. Moreover, because the external walls of bacteria are formed by phospholipids [38], their adsorption on activated carbon increases the hydrophobicity of the carbon surface. Thus, results shown in Fig. 5 and Table 8 may be explained by this increase in the hydrophobicity of the activated carbon surface, which is known to considerably favour the adsorption process.

Table 8
Results obtained by applying Langmuir's equation to the adsorption isotherms of DMZ and RNZ on carbon S in the presence and absence of microorganisms.

Activated carbon	DMZ				RNZ			
	With bacteria		Without bacteria		With bacteria		Without bacteria	
	X_m (mmol/g)	BX_m (L/g)	X_m (mmol/g)	BX_m (L/g)	X_m (mmol/g)	BX_m (L/g)	X_m (mmol/g)	BX_m (L/g)
S	2.44	31.06	1.99	87.24	2.42	44.25	1.97	104.11

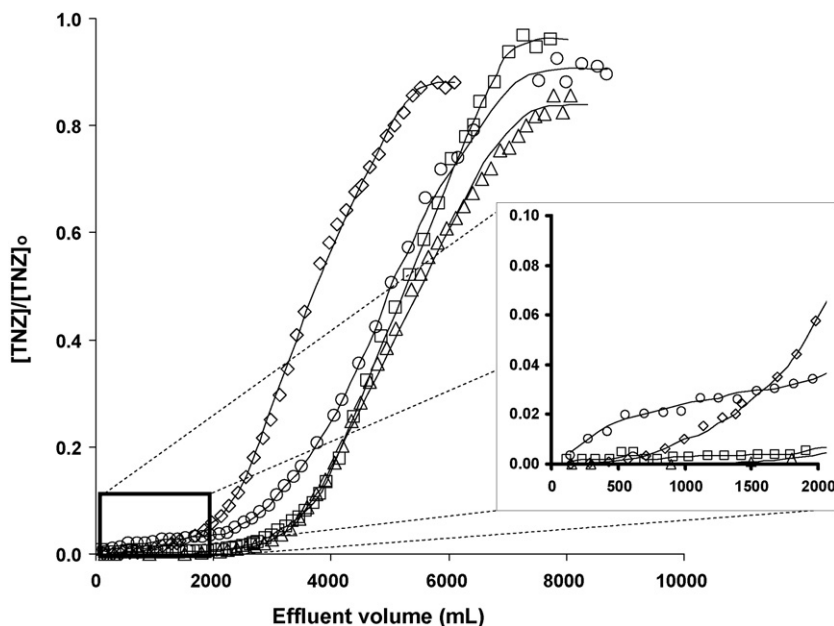**Fig. 6.** Breakthrough curves of TNZ on carbon M as a function of the type of water used. T 298 K. (◇) Ultrapure water; (□) surface; (△) groundwater; (○) wastewater. [Nitroimidazole]$_o$ = 100 mg/L.

Table 9
Characteristics of carbon M columns in the adsorption of TNZ as a function of the type of water used.

Water	$X_{0.02}$[a] (mmol/g)	$V_{0.02}$[b] (mL)	Φ[c]	H_{MTZ}[d] (cm)	Du[e] (%)
Ultrapure	0.35	1377	0.636	6.044	41.14
Surface	0.64	2693	0.660	4.341	56.13
Groundwater	0.73	2870	0.591	4.697	57.50
Waste	0.17	700	0.694	7.670	15.77

[a] Amount of TNZ adsorbed in the point of breakthrough of the column.
[b] Volume treated in the point of breakthrough of the column.
[c] Fractional capacity of the mass transference zone.
[d] Height of the mass transference zone.
[e] Degree of utility.

3.6. Adsorption of TNZ nitroimidazole on activated carbon in dynamic regime: influence of the chemical characteristics of the water

The adsorption of nitroimidazole in dynamic regime was studied in surface, groundwater and wastewaters with different chemical characteristics (Table 5). The wastewater sample had a high concentration of organic matter, while the surface water had high concentrations of calcium and magnesium ions, and the groundwater also showed a high degree of mineralization with high electric conductivity and hardness.

Fig. 6 depicts the breakthrough curves for TNZ adsorption on columns of activated carbon M in the waters described in Table 5. These curves were used [22] to determine the characteristics of the different columns (Table 9). In all types of water, the amount adsorbed at the breakthrough point of the column ($X_{0.02}$) was much lower than the amount adsorbed in static regime (Table 6). This less effective adsorption in dynamic versus static regime can be attributed to problems of TNZ diffusion to the interior of carbon pores. The differences in the values of the column characteristics as a function of the chemical composition of the different waters were analyzed. $V_{0.02}$ and $X_{0.02}$ values and the degree of utility of the column (Du) were much higher in surface water and especially in groundwater than in ultrapure water (Table 9), and the height of the mass transference zone was lower in the former waters, indicating an increase in the effectiveness of the treatment. Two effects may explain these findings: (i) lower

solubility of nitroimidazoles in surface and groundwater as a consequence of their higher alkalinity and salinity, since non-polar organic compounds are known to markedly decrease their solubility in the presence of salts [39,40], explaining the increase in $V_{0.02}$, $X_{0.02}$ and Du and (ii) the presence of Ca^{2+} ions may modify the adsorption of organic molecules on activated carbon, since this ion can react as a co-adsorbate by creating a bridge between the structure of activated carbon and adsorbed molecules [41,42].

Markedly lower $V_{0.02}$, $X_{0.02}$ and Du values and a higher H_{MTZ} value were obtained for TNZ adsorption in wastewaters, because adsorption of dissolved organic matter on carbon surface would reduce the surface area available for the adsorption of TNZ molecules. The effectiveness of treatment would be reduced by the competition between dissolved organic matter and TNZ molecules for active sites on the activated carbon, as previously reported [43,44]. Similar values for the fractional capacity of the mass transference zone (Φ) were observed in all water samples studied (Table 9).

The results presented in Table 9 and Fig. 6 are very interesting from application point of view. Thus, according to the results obtained nitroimidazoles could be efficiently removed from surface and groundwater by adsorption on activated carbon; however, due to the high concentration of organic carbon dissolved in wastewater, activated carbon adsorption would not be the best technological alternative to remove nitroimidazoles from wastewater.

4. Conclusions

The capacity of carbon to adsorb nitroimidazoles is directly related to the density of delocalized π electrons in the graphene layers of the carbon and the electronic density of the nitroimidazole aromatic ring. This indicates that π–π dispersion type interactions between carbon graphene layers and nitroimidazole aromatic rings are responsible for the adsorption process. Hence, adsorption is favoured by electron activating groups in both the carbon surface and the nitroimidazoles.

The pH of the medium and the concentration of the electrolyte present do not have a major effect on the adsorption of these compounds on activated carbon, indicating that adsorbent–adsorbate electrostatic interactions do not play an important role in the adsorption processes studied.

Nitroimidazoles are not degraded by the microorganisms used in the biological treatment stage of a wastewater treatment plant. However, the presence of these microorganisms during the adsorption of these compounds increases their adsorption/bioadsorption on the activated carbon, although interactions between adsorbate and carbon surface are weakened. These results are explained by the increase in hydrophobicity of the carbon surface through adsorption of some of the bacteria present.

Results obtained in dynamic regime show that the adsorption capacity of the activated carbon was markedly higher in surface and groundwater than in ultrapure water and urban wastewaters. These results may be explained by the low nitroimidazole solubility in waters with high alkalinity and the reduction in available surface area that results from the adsorption of dissolved organic matter present in wastewaters.

Acknowledgements

References

[1] B. Halling-Sørensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lützhøft, S.E. Jørgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—a review, Chemosphere 36 (1998) 357–393.

[2] D. Calamari, Assessment of persistent and bioaccumulating chemicals in the aquatic environment, Toxicology 181–182 (2002) 183–186.

[3] M.L. Richardson, J.M. Bowron, The fate of pharmaceutical chemicals in the aquatic environment, J. Pharm. Pharmacol. 37 (1985) 1–12.

[4] N.E. Adler, J. Koschorreck, B. Rechenberg, Environmental impact assessment and control of pharmaceuticals: the role of environmental agencies, Water Sci. Technol. 57 (2008) 91–97.

[5] E.R. Cooper, T.C. Siewicki, K. Phillips, Preliminary risk assessment database and risk ranking of pharmaceuticals in the environment, Sci. Total Environ. 398 (2008) 26–33.

[6] N.J. Ayscough, J. Fawell, G. Franklin, W. Young, Review of human pharmaceuticals in the environment, R&D Technical Report, Environment Agency, Bristol, UK, 2000.

[7] K. Kümmerer, Antibiotics in the environment, in: K. Kümmerer (Ed.), Pharmaceuticals in the Environment. Sources, Fate, Effects and Risks, third revised and enlarger edition, Springer, Berlin, Heidelberg, 2008, pp. 73–93.

[8] A. Al-Ahmad, F.D. Daschner, K. Kümmerer, Biodegradability of cefotiam, ciprofloxacin, meropenem, penicillin G, and sulfamethoxazole and inhibition of waste water bacteria, Arch. Environ. Con. Tox. 37 (1999) 158–163.

[9] K. Kümmerer, A. Al-Ahmad, V. Mersch-Sundermann, Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test, Chemosphere 40 (2000) 701–710.

[10] K. Kümmerer, Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources—a review, Chemosphere 45 (2001) 957–969.

[11] A. Bendesky, D. Menéndez, P. Ostrosky-Wegman, Is metronidazole carcinogenic? Mutat. Res-Rev Mutat. 511 (2002) 133–144.

[12] M. Carballa, F. Omil, J.M. Lema, M. Llompart, C. García-Jares, I. Rodríguez, et al., Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant, Water Res. 38 (2004) 2918–2926.

[13] R. Lindberg, P. Jarnheimer, B. Olsen, M. Johansson, M. Tysklind, Determination of antibiotic substances in hospital sewage water using solid phase extraction and liquid chromatography/mass spectrometry and group analogue internal standards, Chemosphere 57 (2004) 1479–1488.

[14] F.P. Tally, B. Goldin, N.E. Sullivan, Nitroimidazoles: in vitro activity and efficacy in anaerobic infections, Scan. J. Infect. Dis. 13 (1981) 46–53.

[15] A.H. Lau, N.P. Lam, S.C. Piscitelli, L. Wilkes, L.H. Danziger, Clinical pharmacokinetics of metronidazole and other nitroimidazole anti-infectives, Clin. Pharmacokinet. 23 (1992) 328–364.

[16] A. Wennmalm, B. Gunnarsson, Public health care management of water pollution with pharmaceuticals: environmental classification and analysis of pharmaceutical residues in sewage water, Drug Inf. J. 39 (2005) 291–297.

[17] M. Sánchez-Polo, J. Rivera-Utrilla, Ozonation of naphthalenetrisulphonic acid in the presence of activated carbons prepared from petroleum coke, Appl. Catal. B: Environ. 67 (2006) 113–120.

[18] M. Sánchez-Polo, J. Rivera-Utrilla, Effect of the ozone-carbon reaction on the catalytic activity of activated carbon during the degradation of 1,3,6-naphthalenetrisulphonic acid with ozone, Carbon 41 (2003) 303–307.

[19] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of naphthalenesulphonic acid in the aqueous phase in the presence of basic activated carbons, Langmuir 20 (2004) 9217–9222.

[20] J. Rivera-Utrilla, I. Bautista-Toledo, M.A. Ferro-García, C. Moreno-Castilla, Bioadsorption of Pb(II), Cd(II), and Cr(VI) on activated carbon from aqueous solutions, Carbon 41 (2003) 323–330.

[21] D.J. Brenner, N.R. Krieg, J.T. Staley, G.M. Garrity, Bergey's Manual of Systematic Bacteriology, Springer, New York, 2005.

[22] J.S. Zogorski, S.D. Faust, Operational parameters for optimum removal of phenolic compounds from polluted waters by columns of activated carbon, in: P.H. Cheremesinoff, E. Ellerbusch (Eds.), Carbon Adsorption Handbook, Ann Arbor Science Publishers Inc., Michigan, 1978, pp. 753–763.

[23] J. Garrido, A. Linares-Solano, J.M. Martín-Martínez, M. Molina-Sabio, F. Rodríguez-Reinoso, R. Torregrosa, Use of N_2 vs. CO_2 in the characterization of activated carbons, Langmuir 3 (1987) 76–81.

[24] F. Rodríguez-Reinoso, A. Linares-Solano, Microporous structure of activated carbons as revealed by adsorption methods, Chem. Phys. Carbon 21 (1989) 1–146.

[25] M.V. López-Ramón, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marín, On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon 37 (1999) 1215–1221.

[26] M.V. López-Ramón, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marín, Specific and non-specific interactions of water molecules with carbon surfaces from immersion calorimetry, Carbon 38 (2000) 825–829.

[27] R.H. Bradley, I. Sutherland, E. Sheng, Relationship between carbon black surface chemistry and energy, J. Chem. Soc., Faraday Trans. 91 (1995) 3201–3207.

[28] S.S. Barton, M.J.B. Evans, J.A.F. MacDonald, Adsorption of water vapor on nonporous carbon, Langmuir 10 (1994) 4250–4252.

[29] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, J. Colloid Interface Sci. 47 (1974) 755–765.

[30] C.H. Giles, A.P. D'Silva, I.A. Easton, A general treatment and classification of the solute adsorption isotherm. Part II. Experimental interpretation, J. Colloid Interface Sci. 47 (1974) 766–778.

[31] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents in aqueous solutions, Chem. Phys. Carbon 27 (2001) 227–403.

[32] H. Freundlich, Colloid and Capillary Chemistry, Ed. Metheun & Co., London, 1926.

[33] R.W. Coughlin, F.S. Ezra, Role of surface acidity in the adsorption of organic pollutants on the surface of carbon, Environ. Sci. Technol. 2 (1968) 291–297.

[34] J. Rivera-Utrilla, I. Bautista-Toledo, M.A. Ferro-García, C. Moreno-Castilla, Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption, J. Chem. Technol. Biot. 76 (2001) 1209–1215.

[35] D.P. Wilcox, E. Chang, K.L. Dickson, K.R. Johansson, Microbial growth associated with granular activated carbon in a pilot water treatment facility, Appl. Environ. Microb. 46 (1983) 406–416.

[36] T.J. Beveridge, R.J. Doyle, Metal Ions and Bacteria, Wiley, New York, 1989.

[37] M.N. Hughes, R.K. Poole, Metal speciation and microbial growth—the hard (and soft) facts, J. Gen. Microbiol. 137 (1991) 725–734.

[38] H. Mikaido, H. Vaara, Outer membrane in *Escherichia coli* and *Salmonella typhimurium*, in: F.C. Neidhardt (Ed.), Cellular and Molecular Biology, American Society for Microbiology, Washington, DC, 1987, pp. 3–22.

[39] C.C. West, J.H. Harwell, Surfactants and subsurface remediation, Environ. Sci. Technol. 26 (1992) 2324–2330.

[40] J.E. Flaming, R.C. Knox, D.A. Sabatini, T.C. Kibbey, Surfactant effects on residual water and oil saturations in porous media, Vadose Zone J. 2 (2003) 168–176.

[41] P. Lafrance, M. Mazet, Adsorption of humic substances in the presence of sodium salts, J. Am. Water Works Assoc. 81 (1989) 155–162.

[42] F.S. Cannon, V.L. Snoeyink, R.G. Lee, G. Dagois, Reaction mechanism of calcium-catalyzed thermal regeneration of spent granular activated carbon, Carbon 32 (1994) 1285–1301.

[43] M.C. Carter, W.J. Weber Jr., K.P. Olmstead, Effects of background dissolved organic matter on TCE adsorption by GAC, J. Am. Water Works Assoc. 84 (1992) 81–91.

[44] J.E. Kilduff, A. Wigton, Sorption of TCE by humic-preloaded activated carbon: incorporating size-exclusion and pore blockage phenomena in a competitive adsorption model, Environ. Sci. Technol. 33 (1999) 250–256.

[45] M.M. Dubinin, Generalization of the theory of volume filling of micropores to nonhomogeneous microporous structures, Carbon 23 (1985) 373–380.