Adsorption of dyes on carbon xerogels and templated carbons: influence of surface chemistry

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Abstract The removal of textile dyes by adsorption onto carbon materials with extended mesoporosity is addressed in the present work. Two types of high surface area carbon adsorbents were prepared, namely a carbon xerogel and a templated carbon. Both materials were subsequently subjected to appropriate treatments in order to modify their surface chemistries, while keeping their textural properties relatively unchanged. The carbon adsorbents were extensively characterized by different techniques in order to correlate their adsorption performances with the corresponding surface properties. The behavior of the different materials was evaluated by determining equilibrium adsorption isotherms of two anionic dyes (Reactive Red 241 and Acid Blue 113) at different pH values. The results are compared with data previously obtained with commercial activated carbons subjected to the same treatments, and discussed in terms of the carbon surface chemistry and the interaction between the dye molecules and the adsorbent surface (dispersive and electrostatic interactions).

1 Introduction

The textile industry is characterized by a large consumption of water, and by producing enormous amounts of contaminated effluents. The removal of colour from these effluents is imperative, in order to be able to reuse water in the process. Since there is no single method capable of removing colour at acceptable costs, the best option is a combination of different techniques. Usually, a biological treatment combined with other physical or chemical processes is capable of removing most of the organic matter in textile effluents; however, a final treatment is generally required in order to remove colour (Marmagne and Coste 1996), so that water can be recycled and reused in the plant. Adsorption methods are efficient for this purpose, and activated carbons have been used in this context (Choy et al. 1999; Walker and Weatherley 2001; Al-Degs et al. 2009).

The use of activated carbons as adsorbents for colour removal is well documented in the literature (Pereira et al. 2003; Faria et al. 2004; Órfão et al. 2006; Gómez et al. 2007; Demirbas 2009; Rodríguez et al. 2009; Mak et al. 2009; Ip et al. 2010). Most of the earlier reports relate the adsorption capacities mainly to the textural properties of the adsorbents (surface area, pore size distribution, micropore volume), overlooking the influence of the surface chemistry of the materials, which can play a decisive role in the process (Leon y Leon and Radovic 1994; Radovic and Rodríguez-Reinoso 1997; Rodríguez-Reinoso 1998; Radovic et al. 2001). Indeed, it may be expected that the various classes of dyes may show different affinities for carbon adsorbents with different surface properties. For instance, Graham et al. (2001) focused their work on the textural properties, although they report some effects of surface chemistry. A more systematic approach to studying the effects of the surface chemical properties of the activated carbons on the adsorption of different classes of dyes or model organic compounds is only found in recent publications (Pereira et al. 2003; Faria et al. 2004; Órfão et al. 2006; Villacañas et al. 2006).

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On the other hand, mesoporous carbons may be advantageous for the adsorption of bulky molecules, such as textile dyes. Indeed, it has been reported that mesoporous carbons can adsorb much larger amounts of dyes than activated carbons, which are essentially microporous materials (Han et al. 2000; Xun et al. 2007; Yang et al. 2008; Zhuang et al. 2009; Asouhidou et al. 2009; Derylo-Marczewska et al. 2010).

There are two major types of mesoporous carbons, namely carbon xerogels (Pekala 1989) and templated carbons (Jun et al. 2000; Ryoo et al. 2001). It is possible to tailor the texture of these materials by selecting the adequate synthesis conditions (Fuertes 2003, 2004; Fuertes and Nevskaia 2003; Job et al. 2004, 2005; Mahata et al. 2007, 2008).

In the present work, a carbon xerogel was prepared from resorcinol and formaldehyde, as previously described (Mahata et al. 2007), and an ordered mesoporous carbon of the type CMK-3 was prepared using a SBA-15 silica template (Zhao et al. 1998) impregnated with polyfurfuryl alcohol by a method described by Fuertes (2004). With the objective of studying the effect of the surface chemistry, both materials were subjected to oxidation with nitric acid in order to introduce oxygenated functional groups, such as carboxylic acids and anhydrides, lactones, phenols and carbonyls; in general, this treatment produces an acidic surface. The materials were subsequently thermally treated at high temperature in order to remove most of the oxygen-containing surface groups (Figueiredo et al. 1999). This methodology has the advantage of minimizing changes in the original textural properties of the materials, in order to isolate the effect of the different surface chemical properties. The different samples were then evaluated in the adsorption of two anionic dyes (Reactive Red 241 and Acid Blue 113) at different pH values.

2 Experimental

2.1 Preparation of templated carbons

The ordered mesoporous carbons were prepared with an SBA-15 silica template (Zhao et al. 1998), according to the following recipe: an aqueous solution of HCl (37%, Riedel de Haën) and surfactant Pluronic P123 (Aldrich) were added to the silicon source, TEOS (tetraethylorthosilicate 99%, Fluka) in the following molar proportions: TEOS/P123/HCl/H_2O = 1/0.017/5.7/193. The mixture was stirred until the TEOS was completely dissolved, and then kept in a closed vessel for 20 hours at 35 °C under stirring. The temperature was subsequently raised to 125 °C, and the mixture was left under stirring for 24 hours. The resultant solid was filtered, washed and dried at 40 °C, and then calcined in air at 600 °C for 4 hours.

The mesoporous silica was impregnated first with a solution of paratoluenesulfonic acid (Aldrich) for 1 h. The solid was filtered and washed with ethanol, and dried at 80 °C. Then, a volume of furfuryl alcohol (99%, Aldrich) equal to the pore volume was added. The sample was kept at 80 °C during 6 hours, and then carbonized under nitrogen (150 Ncm³/min) at 800 °C for 1 hour. The silica template was removed with a solution of HF (40%, Fluka) (Fuertes 2004). The materials prepared in this way were denoted as JC.

2.2 Preparation of carbon xerogels

The carbon xerogels were prepared as follows (Mahata et al. 2007): 40 mL of distilled water were added to 25 g of resorcinol (98%, Aldrich) under stirring. When the resorcinol was dissolved, a few drops of NaOH 2 M were added in order to bring the pH to 6.0. Then, 34 mL of formaldehyde (37%, Aldrich) were added under stirring, and the pH was adjusted to 6.0 by adding a few drops of HCl 0.1 M. The gelation was accomplished in a water bath at 85 °C for 3 days. The gel was crushed and dried in an oven during 4 days (1st day at 60 °C, 2nd day at 80 °C, 3rd day at 100 °C and 4th day at 120 °C). The dried gel was carbonized under nitrogen (100 Ncm³ min⁻¹) at 800 °C in a tubular furnace. The heating protocol comprised the following sequential steps, all at the same heating rate of 2 °C min⁻¹: (1) up to 150 °C and hold for 2 h; (2) up to 400 °C and hold for 1 h; (3) up to 600 °C and hold for 1 h; (4) up to 800 °C and hold for 6 h. The sample was then cooled to room temperature. These materials were designated as CX.

2.3 Modification of the surface chemistry

The oxidation treatment was carried out in a 250 mL Soxhlet loaded with 18 g of sample. The Soxhlet was connected to the condenser and to a bulb containing 400 mL of HNO_3 5 M. The acid was heated to 140 °C and the system kept under reflux for 6 h. Finally, the sample was washed with distilled water until neutral pH.

The thermal treatment consisted in heating 14 g of nitric acid oxidized carbon to 900 °C (heating rate: 10 °C/min) under nitrogen (flow rate: 50 Ncm³/min) in a tubular reactor, and keeping for 1 hour at that temperature.

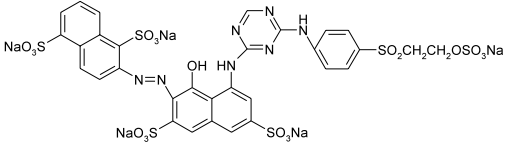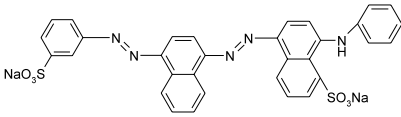Table 1 includes all the samples prepared and their corresponding designations.

2.4 Characterization

The textural characterization of the samples was based on the nitrogen adsorption isotherms determined at −196 °C with a Quantachrom Instruments Nova 4200. The specific volume of micropores (V_{micro}) and the specific surface area

Table 1 Carbon materials used in this study

Sample	Starting material	Further Treatment
CX-O	–	None
CX-HNO$_3$	CX-O	Oxidation with HNO$_3$ 5 M
CX-t	CX-HNO$_3$	Thermal treatment under N$_2$ flow at 900 °C
JC-O	–	None
JC-HNO$_3$	JC-O	Oxidation with HNO$_3$ 5 M
JC-t	JC-HNO$_3$	Thermal treatment under N$_2$ flow at 900 °C

Table 2 Selected dyes and their characteristics

Class	Commercial name / Molecular structure	Generic name	Dimensions[a] (Å × Å)	Chemical class	λ_{max} [nm]
Reactive	Rifafix Red 3BN	C.I. Reactive Red 241	23.6 × 9.8	Monoazo	542
Acid	Erionyl Navy R	C.I. Acid Blue 113	22.1 × 9.2	Diazo	565

[a]Approximate values, considering the largest distances of the two farthest atoms in two perpendicular directions of the molecule after 3D optimization, using the ChemSketch software from ACD

of mesopores (S_{meso}) were calculated by the t-method, using the appropriate standard isotherm; in addition, the specific surface area was calculated by the B.E.T. method (S_{BET}), and the average mesopore diameter by the BJH method.

The materials were observed by Transmission Electron Microscopy on a *LEO 906E* microscope operating at 120 kV.

Temperature programmed desorption (TPD) analyses were carried out with an Altamira Instruments AMI-200 apparatus. The amounts of CO and CO$_2$ evolved from the decomposition of the surface oxygenated groups were analyzed with a mass spectrometer Dymaxion 200 amu, Ametek. The following masses were monitored: 2 (H$_2$), 18 (H$_2$O), 28 (CO) and 44 (CO$_2$). In the case of nitric acid treated samples, the mass signal 30 was also followed in order to check for the eventual decomposition of nitrogen groups as NO$_x$.

The basicity of the carbon materials was determined by adding 0.2 g of each sample to 25 mL of HCl 0.025 M in closed vessels, which were then stirred during 48 h at room temperature. Then, the suspension was decanted and the remaining HCl was titrated with a solution of NaOH 0.025 M. The total acidity of the samples was determined by a similar procedure, where the samples were contacted with NaOH

0.025 M, and a 0.025 M solution of HCl was used for titration (Faria et al. 2004).

To determine the point of zero charge of the samples (pH$_{pzc}$), 50 cm^3 of NaCl 0.01 M were placed in closed vessels, and the pH adjusted to values between 2 and 12, by adding 0.1 M solutions of NaOH or HCl. Then, 0.15 g of the sample was added to each vessel. The suspensions were kept under stirring at room temperature for 48 h, and then the final pH was recorded. The pH$_{pzc}$ of each sample was determined by the intersection of the curve pH$_{final}$ *vs* pH$_{initial}$ with the line pH$_{final}$ = pH$_{initial}$. Blank experiments were carried out, and the pH$_{initial}$ used in each case was that corresponding to the pH$_{final}$ of the blank test (Faria et al. 2004).

2.5 Adsorption tests

Table 2 shows the selected dyes and some of their properties. The dyes used are in their anionic form in the entire pH range studied.

In order to determine the time needed to reach equilibrium, the adsorption kinetics were determined for each material with an initial concentration of the reactive dye of 400 mg/L, at pH = 12. Each kinetic curve was obtained by contacting several portions of 50 mg of sample ($d_p <$

50 μm) with 50 mL of the dye solution in closed vessels under shaking at 25 °C. The vessels were successively removed at predetermined times, the liquid was separated by centrifugation, and the remaining concentration of the dye was determined with an UV/Vis absorption spectrophotometer Jasco V-560. It was found that a contact time of 7 days was needed to make sure that equilibrium was reached.

The adsorption equilibrium isotherms of each dye on the different materials were obtained as follows: 50 mL of dye solution, with a concentration between 50 and 600 mg/L, were contacted with 50 mg of finely ground adsorbent ($d_p <$ 50 μm) in closed vessels of 100 mL. The vessels were wrapped up in aluminium foil, to avoid degradation of the dye by the action of light, and placed in a shaker at room temperature until equilibrium was reached (7 days). Analysis was carried out as described above.

3 Results and discussion

3.1 Characterization of the carbon materials

Table 3 includes the textural and chemical properties of the original and modified carbon materials.

Concerning the textural properties, it may be observed that both treatments lead to changes in the mesopore surface areas, while the micropore volumes and the mesopore sizes remain unchanged. A representative TEM micrograph of the original templated carbon is shown in Fig. 1, where a clearly ordered mesoporosity is observed.

The TPD spectra of the different carbon materials are presented in Fig. 2, and the amounts of CO and CO_2 released are included in Table 3. Analysis of the spectra shows that the nitric acid treatment introduces mainly carboxylic acid groups on the surface (which release CO_2 at temperatures below 400 °C), but also carboxylic anhydrides (CO and CO_2 released near to 500 °C), lactones (CO_2 released near

to 650 °C), phenols (CO released at about 700 °C) and carbonyl/quinones (CO released at about 850 °C). The thermal treatment removes almost completely all groups releasing CO_2, leaving only a small amount of CO-releasing groups on the surface, which have a basic character (Figueiredo et al. 1999; Figueiredo et al. 2007).

The total acidity and basicity of the materials, as well as their points of zero charge (pH_{pzc}), are also included in Table 3. Compared to the original, sample CX-HNO₃ shows a remarkable increase in acidity (and a decrease in basicity), which results from the introduction of large amounts of carboxylic acid groups by the nitric acid treatment. Correspondingly, there is also a significant decrease in the pH_{pzc}. On the other hand, sample CX-t shows a basic character. The original templated carbon sample (JC-O) is acidic, since the *template* (SBA-15) was removed with HF. Of the templated materials, sample JC-t is the less acidic ($pH_{pzc} = 6.5$).
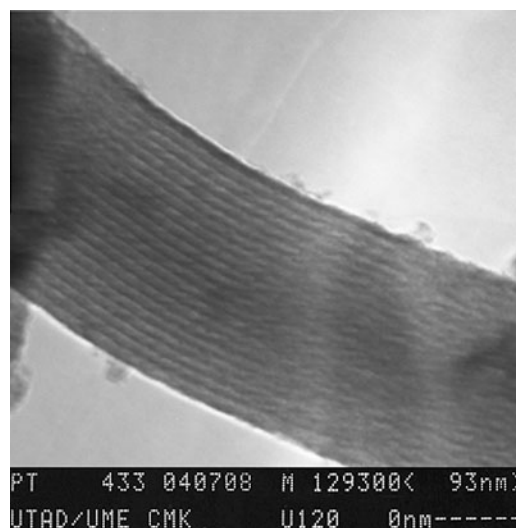

Fig. 1 TEM micrograph of JC-O

Table 3 Chemical and textural properties of the materials used

| Sample	CO [μmol g⁻¹][a]	CO_2 [μmol g⁻¹][a]	Acidity [μeq g⁻¹]	Basicity [μeq g⁻¹]	pH_{pzc}	S_{BET} [m² g⁻¹]	S_{meso} [m² g⁻¹][b]	V_{micro} [cm³ g⁻¹][b]	d_{meso} [nm][c]
CX-O	330	149	584	408	7.8	809	329	0.20	37
CX-HNO₃	3189	1340	1584	136	3.1	1007	440	0.24	37
CX-t	289	166	396	476	8.7	790	252	0.22	36
JC-O	951	501	459	1563	3.5	1120	819	0.13	3.5
JC-HNO₃	5361	928	709	816	3.0	1022	747	0.12	3.2
JC-t	46	50	334	1699	6.5	740	446	0.13	3.7

[a]Calculated by TPD spectra integration

[b]Micropore volume (V_{micro}) and mesopore surface area (S_{meso}) calculated by the *t*-method

[c]Average mesopore diameter (d_{meso}) obtained from the desorption isotherm using the Barrett, Joyner and Halenda (BJH) method

Fig. 2 TPD spectra of:
(**a**) carbon xerogels and
(**b**) templated carbons obtained
via SBA-15
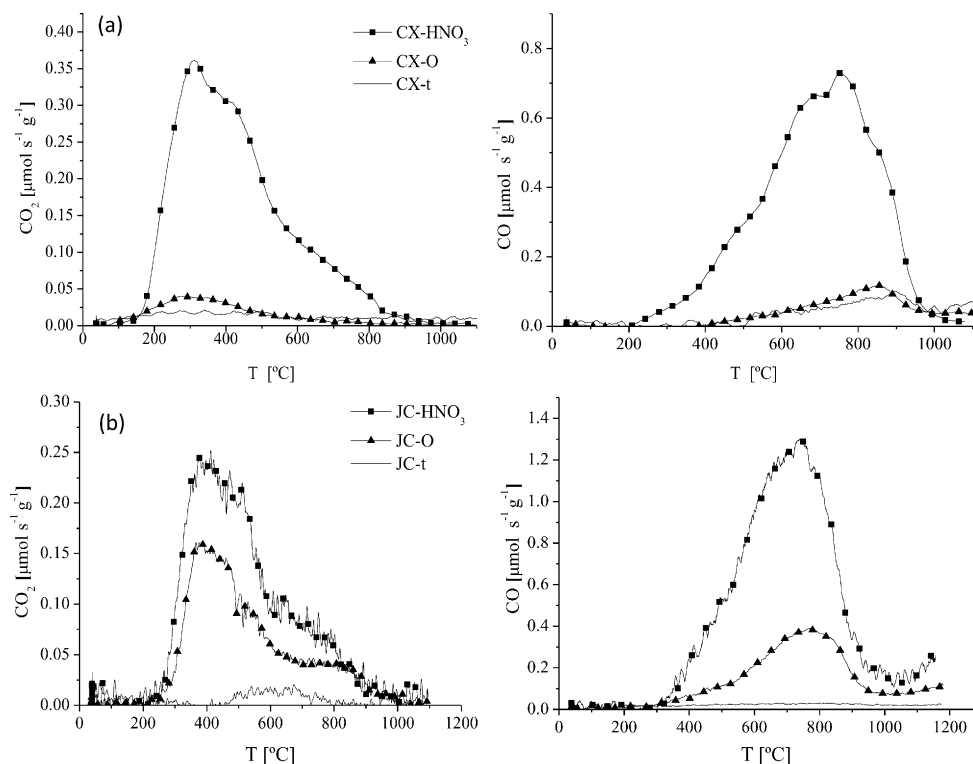
3.2 Adsorption of the reactive dye

The adsorption equilibrium isotherms of the reactive dye at 25 °C were determined at different pH values (2, 7 and 12) on the carbon materials, as shown in Fig. 3. The Langmuir model was used to analyze the isotherms, since it gave a better fit than the Freundlich model. The Langmuir model is described by:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \qquad (1)$$

where C_e and q_e are the equilibrium concentrations of the adsorptive in the liquid phase and in the solid, respectively, q_m is the adsorption capacity, and K_L a constant.

The experimental data were fitted to the model by non-linear regression, in order to minimize the errors in the parameters, which are collated in Table 4. The corresponding model curves are included in Fig. 3.

It may be observed that there are significant differences in the adsorption capacities of the materials, and that there is also a strong influence of the pH.

The samples which have been thermally treated are those that present better adsorption performances, while those which have large amounts of surface oxygen-containing groups have lower adsorption capacities. This shows that dispersive forces are involved in the adsorption mechanism, resulting from the interaction of the delocalized π electrons in the carbon basal planes, and the free electrons of the aromatic rings and multiple bonds of the dye molecules. Some

oxygenated groups of the nitric acid treated samples are electron-attractors, which may hinder the interactions with the dye molecules; therefore, the acid samples exhibit lower adsorption capacities (Órfão et al. 2006). It is also possible that the oxygenated groups may obstruct the access to the smaller pores (Pereira et al. 2003).

Independently of the sample considered, the adsorption capacity increases in the sequence pH 12 < pH 7 < pH 2. This indicates that electrostatic interactions also play a role in the adsorption mechanism (Órfão et al. 2006; Faria et al. 2004). When the solution pH is higher than the pH$_{pzc}$, the surface of the adsorbent is negatively charged, favoring the adsorption of cationic species, while for a solution pH lower than the pH$_{pzc}$ the surface is positively charged, favoring the adsorption of anionic species (Radovic and Rodríguez-Reinoso 1997), which is the case of the reactive dye used in the present work. Samples CX-O (pH$_{pzc}$ = 7.8) and CX-t (pH$_{pzc}$ = 8.7) are positively charged at pH = 2 and pH = 7, while at pH = 12 they are charged negatively. Therefore, the results shown in Fig. 3 and Table 4 are not surprising, since the adsorption capacities obtained at pH = 2 and pH = 7 are higher than those at pH = 12, since in this case there is an electrostatic repulsion between the anionic dye and the carbon surface. The surface of the carbon xerogel oxidized with nitric acid (pH$_{pzc}$ = 3.1) is positively charged only at pH = 2; therefore, this sample presents its best performance under these conditions.

In the case of the templated carbons, their surfaces are positively charged at pH= 2, while they are negatively
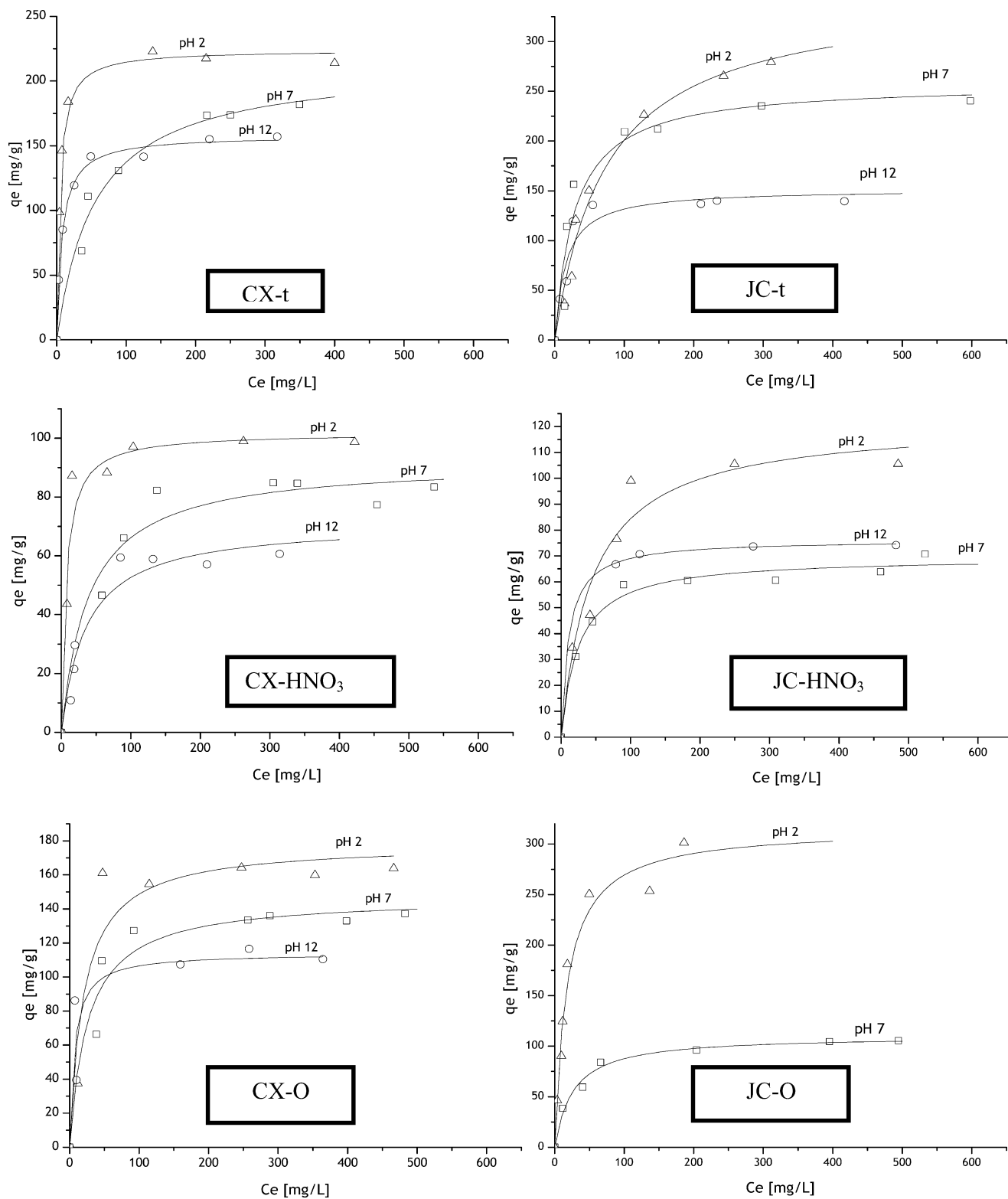
Fig. 3 Equilibrium adsorption isotherms of reactive dye at 25 °C and pH 2, 7 and 12 on the mesoporous carbon materials

charged at pH = 7 and pH = 12. Therefore, the results of Fig. 3 and Table 4 are also as expected for these samples: the adsorption capacities at pH = 2 exceed those measured

at pH = 7 and pH = 12, because in the later case there are electrostatic repulsive forces between the anionic dye and the surface of the materials.

3.3 Adsorption of the acid dye

The adsorption equilibrium isotherms of the acid dye at 25 °C were determined at pH= 7 on the carbon materials, as shown in Fig. 4, and the corresponding parameters of the Langmuir model are included in Table 5.

The thermally treated samples exhibit the best performances for the adsorption of the acid dye, and those treated with nitric acid show the worst performances. Once more, this behavior highlights the importance of the surface chem-

ical properties in the adsorption process, since the best samples in each group are those with a lower surface area (cf. Table 3).

3.4 Comparative analysis of the results and correlations with surface properties

We could not find any correlation between the adsorption capacities (for both dyes) and the textural properties of the carbon adsorbents (mesopore surface areas and micropore volumes). The molecular dimensions of the dyes are not too different (see Table 2) and both can easily enter into the mesopores of both carbon samples; therefore, the surface area will be the dominant textural parameter. Significant correlations were found with the basicity of the materials, for all values of pH studied, as shown in Fig. 5.

Moreover, we can compare the results obtained in the present work, using mesoporous carbon materials, with those previously reported with activated carbons (which are essentially microporous adsorbents). We have taken for comparison the data of Órfão et al. (2006) for the adsorption of the reactive dye on an activated carbon Norit ROX 0.8 (labelled here as AC1), and the data reported by Faria

Table 4 Parameters of Langmuir model for adsorption of the reactive dye on mesoporous carbon materials

Sample	pH	$10^{-2} q_m$ [mg g^{-1}]	K_L [L mg^{-1}]
CX-O	12	1.14 ± 0.12	0.14 ± 0.08
	7	1.47 ± 0.09	0.04 ± 0.01
	2	1.79 ± 0.15	0.05 ± 0.02
CX-HNO$_3$	12	0.71 ± 0.06	0.03 ± 0.01
	7	0.92 ± 0.05	0.03 ± 0.01
	2	1.02 ± 0.06	0.15 ± 0.05
CX-t	12	1.58 ± 0.02	0.13 ± 0.01
	7	2.14 ± 0.14	0.02 ± 0.01
	2	2.24 ± 0.04	0.23 ± 0.02
JC-O	12	–	–
	7	1.10 ± 0.04	0.04 ± 0.01
	2	3.16 ± 0.19	0.06 ± 0.01
JC-HNO$_3$	12	0.76 ± 0.01	0.10 ± 0.01
	7	0.70 ± 0.02	0.04 ± 0.01
	2	1.22 ± 0.11	0.02 ± 0.01
JC-t	12	1.52 ± 0.11	0.07 ± 0.02
	7	2.58 ± 0.20	0.04 ± 0.01
	2	3.49 ± 0.25	0.01 ± 0.01

Table 5 Parameters of Langmuir model for adsorption of the acid dye on mesoporous carbon materials

Sample	pH	$10^{-2} q_m$ [mg g^{-1}]	K_L [L mg^{-1}]
CX-O	7	1.56 ± 0.09	0.10 ± 0.03
CX-HNO$_3$	7	1.34 ± 0.08	0.14 ± 0.05
CX-t	7	2.68 ± 0.12	0.09 ± 0.03
JC-O	7	6.44 ± 0.28	0.04 ± 0.01
JC-HNO$_3$	7	4.86 ± 0.45	0.26 ± 0.09
JC-t	7	6.57 ± 0.42	0.06 ± 0.01
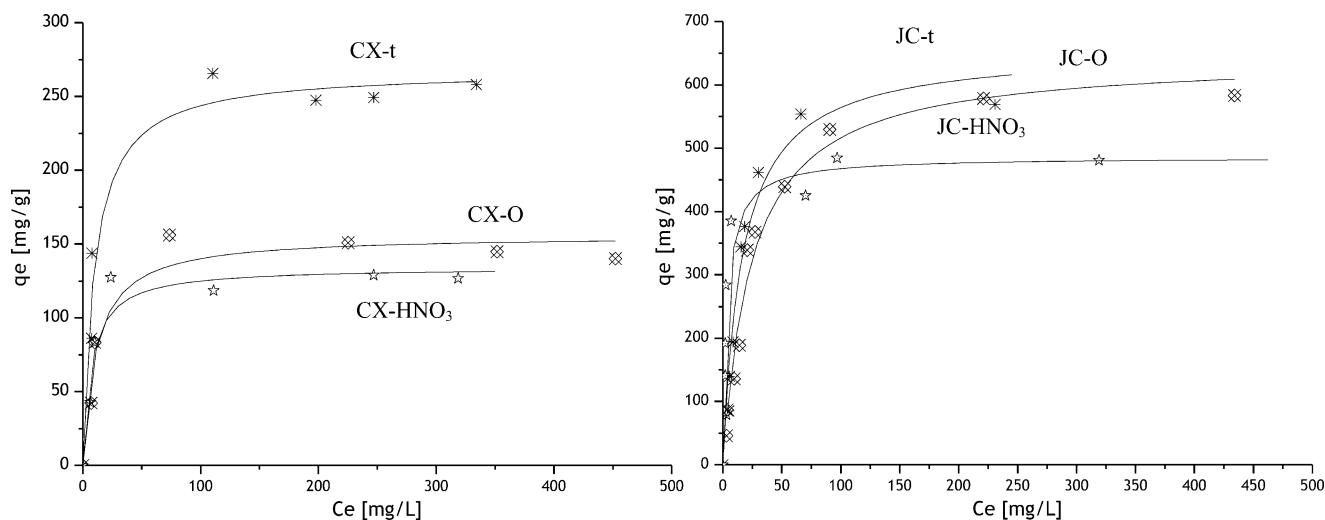
Fig. 4 Equilibrium adsorption isotherms of acid dye at 25 °C and pH 7 on the mesoporous carbon materials

et al. (2004) for the adsorption of the acid dye on the activated carbon Norit GAC 1240 plus (labelled as AC2). Both
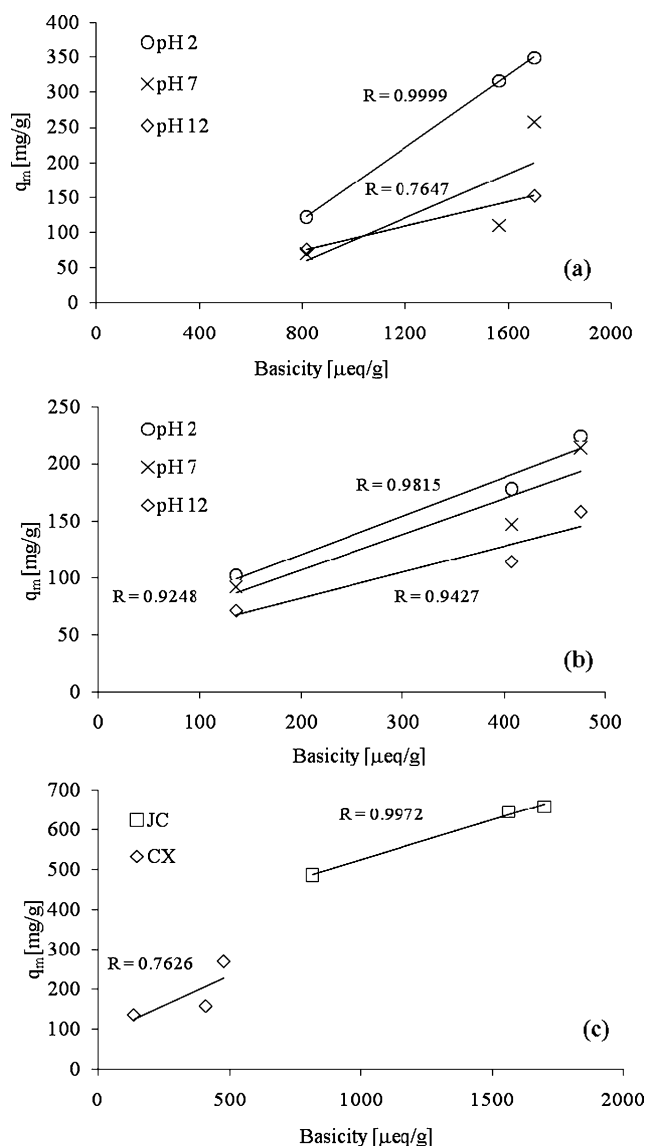
Fig. 5 Correlation between the maximum adsorption capacity of reactive dye (at pH 2, 7 and 12) and the basicity of templated carbons (**a**) and carbon xerogels (**b**), and the maximum adsorption capacity of acid dye (at pH 7) and the basicity of mesoporous carbons (**c**)

samples were subjected to similar treatments (nitric acid and thermal treatment) as we have done in the present work. The properties of these activated carbon samples are collated in Table 6.

The performances of the different materials are compared in Fig. 6 for the reactive dye at different values of pH (2, 7, 12) and in Fig. 7 for the acid dye at pH $= 7$. The dyes uptake values were normalized by the BET surface area.

Among the acid treated materials, sample AC1-HNO$_3$ is the best for the adsorption of the reactive dye, independently of the pH (Fig. 6a). The dispersive interactions are dominant here, and the activated carbon possibly has a higher electron density than the mesoporous materials, which could be due to a dissimilar structure of the carbon matrices as a consequence of the synthesis route followed. At pH $= 2$, both mesoporous carbons have their surfaces positively charged, and so there are electrostatic attractive forces which enhance the adsorption of the reactive dye (anionic). The adsorption capacity of JC-HNO$_3$ slightly exceeds that of CX-HNO$_3$, possibly as a result of its higher fraction of mesoporous surface area. However, this effect is suppressed at higher pH.

The results obtained with the original (untreated) samples are compared in Fig. 6b. At pH $= 7$ sample JC-O adsorbs less than the other materials, because it is the only one that has a negative surface charge (pH$_{pzc}$ = 3.5), and so there are repulsive forces between the dye and this adsorbent. At pH $= 7$ the adsorption of the reactive dye is favored in all samples, due to the electrostatic interactions. The best performance is shown by JC-O, since it has a higher fraction of mesoporous surface area.

The results obtained with the thermally treated samples are compared in Fig. 6c. At pH $= 2$ all samples are positively charged, which favors the adsorption of the reactive dye. The higher fraction of mesoporous surface area of the templated sample explains its higher adsorption capacity. At pH $= 7$, sample JC-t exhibits an almost neutral surface, while CX-t and AC1-t are positively charged. Nevertheless, sample JC-t still shows the best performance, although the differences are marginal. At pH=12, samples JC-t and CX-t have the same performance, suggesting that the effect of the textural properties becomes progressively less important as the pH increases.

Table 6 Chemical and textural characteristics of the activated carbon samples

Sample	Acidity [μeq g^{-1}]	Basicity [μeq g^{-1}]	pH$_{pzc}$	S_{BET} [m^2 g^{-1}]	S_{meso} [m^2 g^{-1}]	V_{micro} [cm^3 g^{-1}]
AC1-O	370	457	8.4	1032	138	0.38
AC1-HNO$_3$	1720	−65	2.0	893	102	0.35
AC1-t	86	640	10.0	987	129	0.38
AC2-O	149	302	9.7	972	125	0.37
AC2-HNO$_3$	716	34	2.7	909	91	0.35
AC2-t	89	437	10.8	972	103	0.38

Fig. 6 Maximum adsorption capacity of the reactive dye on different carbon materials as a function of pH: (**a**) samples oxidized with nitric acid, (**b**) original samples and (**c**) thermally treated samples
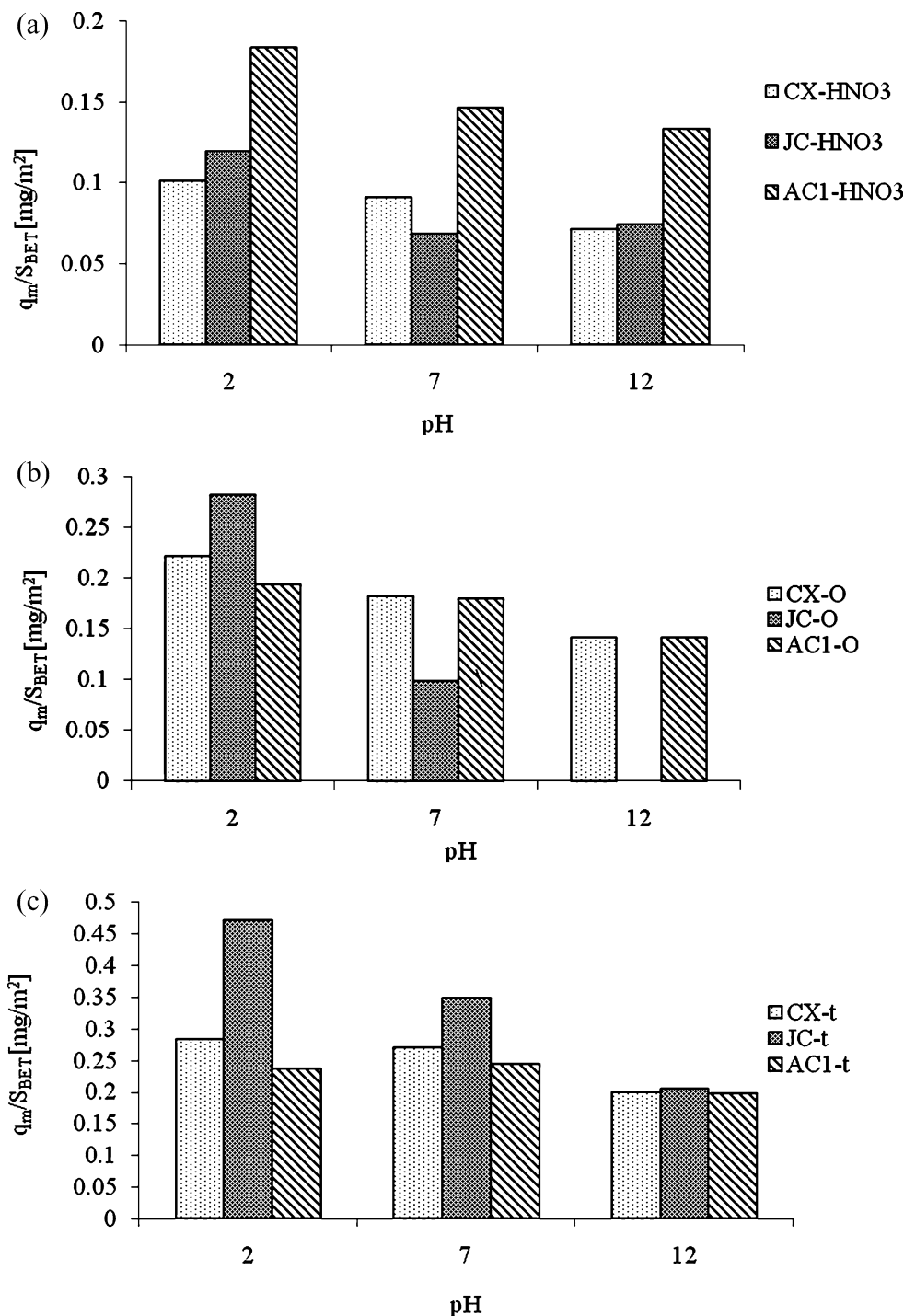

The lower mesoporosity of the activated carbon does not seem to be a limiting factor for the adsorption of these dyes. In fact, they present approximately a cylindrical shape with an average diameter lower than 1 nm (see Table 2), which allows their access to most of the microporous structure of the activated carbon; indeed, values of 1.0 and 1.1 nm were obtained for the average width of the small micropores, re-

spectively for sample AC1-O (Órfão et al. 2006) and AC2-O (Faria et al. 2004).

Analysis of Fig. 7 shows that the templated carbons are the best for adsorption of the acid dye at pH = 7, possibly as a result of their higher fraction of mesoporous surface areas. The activated carbon performs better than the carbon xerogels in this case.

Fig. 7 Maximum adsorption capacity of the acid dye at pH 7 on different carbon materials
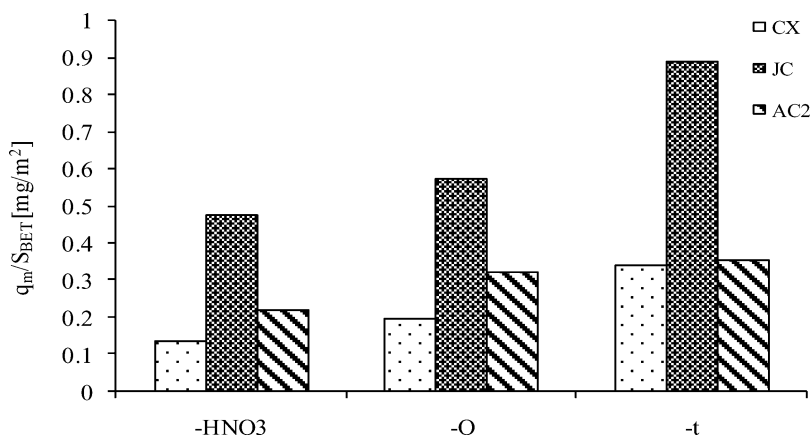
4 Conclusions

The following conclusions can be drawn from the present work:

- The surface chemistry of the adsorbents plays a major role in the adsorption process. The thermally treated carbons (thus with few oxygenated surface groups) are the most efficient, since the dispersive interactions between the delocalized π electrons of the carbon materials and the free electrons of the dye molecules (aromatic rings and N=N bonds) are most important. The samples oxidized with nitric acid are the worst adsorbents, because they present large amounts of surface oxygenated groups, which are capable of attracting the π electrons, an effect which decreases the dispersive interactions with the adsorptive molecules.

- The pH is a most important parameter, because it determines the surface charge of the carbon materials, and therefore, the intensity of the electrostatic interactions (attractive or repulsive) between the dye molecules and the adsorbents. The solution pH must be lower than the pH_{pzc} of the carbon materials, in order to maximize the adsorption of the anionic dyes.

- Strong correlations were established between the adsorption capacity and the basicity of the materials, both for the acid and for the reactive dye.

- Carbon xerogels do not seem to be an option to remove colour from the effluents, since their performances are worst or similar to activated carbons. On the other hand, templated carbons perform better than activated carbons in some cases, as a result of their higher mesopore surface areas. That is the case for adsorption of the acid dye, at least at pH = 7, and of the reactive dye at pH = 2.

References

Al-Degs, Y.S., Khraisheh, M.A.M., Allen, S.J., Ahmad, M.N.: Adsorption characteristics of reactive dyes in columns of activated carbon. J. Hazard. Mater. **165**, 944–949 (2009)

Asouhidou, D.D., Triantafyllidis, K.S., Lazaridis, N.K., Matis, K.A., Kim, S.S., Pinnavaia, T.J.: Sorption of reactive dyes from aqueous solutions by ordered hexagonal and disordered mesoporous carbons. Microporous Mesoporous Mater. **117**, 257–267 (2009)

Choy, K.K.H., McKay, G., Porter, J.F.: Sorption of acid dyes from effluents using activated carbon. Resour. Conserv. Recycl. **27**, 57–71 (1999)

Demirbas, A.: Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. J. Hazard. Mater. **167**, 1–9 (2009)

Derylo-Marczewska, A., Marczewski, A.W., Winter, S., Sternik, D.: Studies of adsorption equilibria and kinetics in the systems: Aqueous solution of dyes–mesoporous carbons. Appl. Surf. Sci. **256**, 5164–5170 (2010)

Faria, P.C.C., Órfão, J.J.M., Pereira, M.F.R.: Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Res. **38**, 2043–2052 (2004)

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Órfão, J.J.M.: Modification of the surface chemistry of activated carbons. Carbon **37**, 1379–1389 (1999)

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Órfão, J.J.M.: Characterization of active sites on carbon catalysts. Ind. Eng. Chem. Res. **46**, 4110–4115 (2007)

Fuertes, A.B.: Template synthesis of mesoporous carbons with a controlled particle size. J. Mater. Chem. **13**, 3085–3088 (2003)

Fuertes, A.B.: Synthesis of ordered nanoporous carbons of tunable mesopore size by templating SBA-15 silica materials. Microporous Mesoporous Mater. **67**, 273–281 (2004)

Fuertes, A.B., Nevskaia, D.M.: Control of mesoporous structure of carbons synthesised using a mesostructured silica as template. Microporous Mesoporous Mater. **62**, 177–190 (2003)

Gómez, V., Larrechi, M.S., Callao, M.P.: Kinetic and adsorption study of acid dye removal using activated carbon. Chemosphere **69**, 1151–1158 (2007)

Graham, N., Chen, X.G., Jayaseelan, S.: The potential application of activated carbon from sewage sludge to organic dyes removal. Water Sci. Technol. **43**, 245–252 (2001)

Han, S., Sohn, K., Hyeon, T.: Fabrication of new nanoporous carbons through silica,templates and their application to the adsorption of bulky dyes. Chem. Mater. **12**, 3337–3341 (2000)

Ip, A.W.M., Barford, J.P., McKay, G.: A comparative study on the kinetics and mechanisms of removal of Reactive Black 5 by adsorption onto activated carbons and bone char. Chem. Eng. J. **157**, 434–442 (2010)

Job, N., Pirard, R., Marien, J., Pirard, J.P.: Porous carbon xerogels with texture tailored by pH control during sol–gel process. Carbon **42**, 619–628 (2004)

Job, N., Théry, A., Pirard, R., Marien, J., Kocon, L., Rouzaud, J.N., Béguin, F., Pirard, J.P.: Carbon aerogels, cryogels and xerogels: Influence of the drying method on the textural properties of porous carbon materials. Carbon **43**, 2481–2494 (2005)

Jun, S., Joo, S.H., Ryoo, R., Kruk, M., Jaroniec, M., Liu, Z., Ohsuna, T., Terasaki, O.: Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure. J. Am. Chem. Soc. **122**, 10712–10713 (2000)

Leon y Leon, C.A., Radovic, L.R.: Interfacial chemistry and electrochemistry of carbon surfaces. In: Thrower, P.A. (ed.) Chemistry and Physics of Carbon, vol. 24, pp. 213–310. Dekker, New York (1994)

Mahata, N., Silva, A.R., Pereira, M.F.R., Freire, C., Castro, B., Figueiredo, J.L.: Anchoring of a [Mn(salen)Cl] complex onto mesoporous carbon xerogels. J. Colloid Interface Sci. **311**, 152–158 (2007)

Mahata, N., Pereira, M.F.R., Suárez-García, F., Martínez-Alonso, A., Tascón, J.M.D., Figueiredo, J.L.: Tuning of texture and surface chemistry of carbon xerogels. J. Colloid Interface Sci. **324**, 150–155 (2008)

Mak, S.M., Tey, B.T., Cheah, K.Y., Siew, W.L., Tan, K.K.: Porosity characteristics and pore developments of various particle sizes palm kernel shells activated carbon (PKSAC) and its potential applications. Adsorption **15**, 507–519 (2009)

Marmagne, O., Coste, C.: Color removal from textile plant effluents. Am. Dyest. Report. **85**, 15–21 (1996)

Órfão, J.J.M., Silva, A.I.M., Pereira, J.C.V., Barata, S.A., Fonseca, I.M., Faria, P.C.C., Pereira, M.F.R.: Adsorption of a reactive dye on chemically modified activated carbons—Influence of pH. J. Colloid Interface Sci. **296**, 480–489 (2006)

Pekala, R.W.: Organic aerogels from the polycondensation of resorcinol with formaldehyde. J. Mater. Sci. **24**, 3221–3227 (1989)

Pereira, M.F.R., Soares, S.F., Órfão, J.J.M., Figueiredo, J.L.: Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon **41**, 811–821 (2003)

Radovic, L.R., Rodríguez-Reinoso, F.: Carbon materials in catalysis. In: Thrower, P.A. (ed.) Chemistry and Physics of Carbon, vol. 25, pp. 243–358. Dekker, New York (1997)

Radovic, L.R., Moreno-Castilla, C., Rivera-Utrilla, J.: Carbon materials as adsorbents in aqueous solutions. In: Radovic, L.R. (ed.) Chemistry and Physics of Carbon, vol. 27, pp. 227–405. Dekker, New York (2001)

Rodríguez, A., García, J., Ovejero, G., Mestanza, M.: Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: equilibrium and kinetics. J. Hazard. Mater. **172**, 1311–1320 (2009)

Rodríguez-Reinoso, F.: The role of carbon materials in heterogeneous catalysis. Carbon **36**, 159–175 (1998)

Ryoo, R., Joo, S.H., Kruk, M., Jaroniec, M.: Ordered mesoporous carbons. Adv. Mater. **13**, 677–681 (2001)

Villacañas, F., Pereira, M.F.R., Órfão, J.J.M., Figueiredo, J.L.: Adsorption of simple aromatic compounds on activated carbons. J. Colloid Interface Sci. **293**, 128–136 (2006)

Walker, G.M., Weatherley, L.R.: COD removal from textile industry effluent: pilot plant studies. Chem. Eng. J. **84**, 125–131 (2001)

Xun, Y., Ping, Z.S., Wei, X., You, C.H., Dong, D.X., Mei, L.X., Feng, Y.Z.: Aqueous dye adsorption on ordered mesoporous carbons. J. Colloid Interface Sci. **310**, 83–89 (2007)

Yang, W., Wu, D., Fu, R.: Effect of surface chemistry on the adsorption of basic dyes on carbon aerogels. Colloids Surf. A **312**, 118–124 (2008)

Zhao, D.Y., Huo, Q.S., Feng, J.L., Chmelka, B.F., Stucky, G.D.: Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. J. Am. Chem. Soc. **120**, 6024–6036 (1998)

Zhuang, X., Wan, Y., Feng, C., Shen, Y., Zhao, D.: Highly efficient adsorption of bulky dye molecules in wastewater on ordered mesoporous carbons. Chem. Mater. **21**, 706–716 (2009)