Adsorption (2012) 18:173–179
DOI 10.1007/s10450-012-9391-5

Competitive adsorption of the herbicide fluroxypyr and tannic acid from distilled and tap water on activated carbons and their thermal desorption

**C. Moreno-Castilla · M.V. López-Ramón ·
L.M. Pastrana-Martínez · M.A. Álvarez-Merino ·
M.A. Fontecha-Cámara**

Received: 14 December 2011 / Accepted: 8 June 2012 / Published online: 21 June 2012
© Springer Science+Business Media, LLC 2012

Abstract A study was conducted on batch and column competitive adsorption of fluroxypyr (FLX) and tannic acid (TA) from distilled (DW) and tap water (TW) on activated carbon cloth (ACC) and granular activated carbon (GAC). Thermal desorption of the adsorbates from the spent ACC was also studied. FLX adsorption was higher from TW than from DW at low FLX equilibrium concentrations, and the inverse was observed at high FLX concentrations. The presence of TA diminished the amount of FLX adsorbed from both solvents due to partial blocking of the microporosity, but the same trends as before were observed at low and high FLX concentrations. Carbon consumption, obtained from the breakthrough curves, was lower as a function of superficial contact time with ACC than with GAC. The presence of TA increased carbon consumption, which was related to the microporosity of the adsorbents. Thermal desorption profiles of the spent ACC showed two peaks and one peak after adsorption from DW and TW, respectively. Desorption peaks shifted to higher temperatures with an increase in the heating rate, allowing the apparent activation energies and pre-exponential factors of the desorption processes to be determined.

Keywords Batch adsorption · Column adsorption · Fluroxypyr · Tannic acid · Activated carbons · Thermal desorption

1 Introduction

Activated carbons are used in water treatments to remove organic contaminants. Natural organic matter (NOM) is present in all surface waters due to the decay and transformation of vegetation and microbial remains. This NOM is largely in the form of dissolved organic carbon (DOC), whose composition is a complex mixture of humic substances of variable size and molecular weight. DOC competes with the target contaminant by two major mechanisms: direct competition for adsorption sites within the microporosity of the activated carbons; and pore blocking (Li et al. 2003, 2008). Small DOC molecules directly compete with the contaminant molecules if they are of comparable size. Larger DOC molecules can be adsorbed on mesopores or the external surface of activated carbons, blocking entry of contaminant molecules to the micropores. The degree of competition between DOC and contaminants depends on: the surface chemistry and physics of the activated carbons, characteristics of the DOC, and initial relative concentrations of contaminant and DOC (Li et al. 2003).

Water hardness and alkalinity also influence the adsorption of contaminants and DOC on activated carbons. Thus, increased salt concentration affects: (i) adsorbate-adsorbent and adsorbate-adsorbate electrostatic interactions due to screening effects (Stuart et al. 1991; Pastrana-Martínez et al. 2010), (ii) adsorbate solubility (Pastrana-Martínez et al.

Electronic supplementary material The online version of this article (doi:10.1007/s10450-012-9391-5) contains supplementary material, which is available to authorized users.

C. Moreno-Castilla (✉)
Departamento de Química Inorgánica, Facultad de Ciencias,
Universidad de Granada, 18071 Granada, Spain
e-mail: cmoreno@ugr.es

M.V. López-Ramón · L.M. Pastrana-Martínez ·
M.A. Álvarez-Merino · M.A. Fontecha-Cámara
Departamento de Química Inorgánica y Orgánica, Facultad
de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén,
Spain

M.V. López-Ramón
e-mail: mvlro@ujaen.es

2010; Lyklema 1993; Xie et al. 1997), and (iii) the degree of association of humic substances, especially when Ca^{2+} ions are present (Ando et al. 2010). In addition, inorganic compounds in water can accumulate on the activated carbon filters by adsorption on their surface, by the formation of complexes with DOC, or by precipitation due to the creation of insoluble compounds such as $CaCO_3$ (Pastrana-Martínez et al. 2010; McCafferty et al. 2000; Lee et al. 2003).

Herbicides can be found as contaminants in many surface waters and shallow groundwaters due to their extensive use in agriculture. The herbicide FLX, whose chemical formula is 4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid, belongs to the pyridine family. It is widely used in cereals, olive trees, and fallow croplands to control broadleaf weeds. Our group recently studied the effects of the pH, temperature, hardness, and alkalinity of the water on FLX adsorption on activated carbons in the form of grains, fibers, and cloth (Pastrana-Martínez et al. 2010; Pastrana-Martínez et al. 2009).

The objective of the present study was to examine the competitive adsorption of FLX and TA. TA was chosen as model DOC compound because this important humic substance is present in many surface waters. Batch and column adsorption was conducted in DW and TW with a hardness of 315 mg/L as $CaCO_3$, considered to be hard water (Weiner 2000). Adsorption was studied using commercial activated carbons in the form of grains and cloth. Thermal desorption of FLX and FLX plus TA was studied after saturation of the adsorption capacity with DW and TW. Thermal desorption reveals the strength of the adsorption and the possibility of regenerating the activated carbons.

2 Experimental

Two commercial activated carbons were used: GAC from Chemviron Carbon type 208C with particle size of 0.5 mm, and ACC with thickness of 0.45 mm from Kynol Europe. These samples were characterized to determine their BET surface area, micro- and mesoporosity, oxygen content, and pH at the point of zero charge (pH_{PZC}); these results were reported and commented in detail elsewhere (Pastrana-Martínez et al. 2010) and are therefore not discussed in the present paper. Surface characteristics of the two activated carbons are displayed in Table 1.

Table 1 Surface characteristics of the activated carbons

Carbon	S_{BET} (m^2/g)	W_0[a] (cm^3/g)	L_0[b] (nm)	V[c] (cm^3/g)	Ash (%)	O (%)	pH_{PZC}
GAC	1191	0.494	1.41	0.002	2.4	4.1	7.6
ACC	2128	0.913	1.69	0.020	0.2	1.7	8.0

[a] Micropore volume from DR equation applied to N_2 adsorption isotherms at 77 K

[b] Mean micropore width from DR equation applied to N_2 adsorption isotherms at 77 K

[c] Mesopore volume from N_2 adsorption isotherms at 77 K

FLX and TA (molecular weight 1701 g/mol) were supplied by Sigma-Aldrich as high-purity (99 %) and analytic grade reagents, respectively; their molecular structures are depicted in Supplementary Material. Both adsorbates were characterized by potentiometric titrations, as described elsewhere (Pastrana-Martínez et al. 2009; Moreno-Castilla et al. 2004), in order to determine their speciation diagrams as function of pH; the results are given in Supplementary Material. FLX molecular dimensions were obtained from data collected by X-ray diffraction (Pastrana-Martínez et al. 2009).

Adsorption studies were conducted using DW and TW as solvents. TW, from the city of Jaén (Spain), had a hardness and alkalinity measured as $CaCO_3$ of 315 and 202 mg/L, respectively, and Ca^{2+} and Mg^{2+} concentrations were 79 and 28 mg/L, respectively (Pastrana-Martínez et al. 2010)

Batch adsorption experiments were carried out at 298 K using 0.05 g of carbon and 500 mL of herbicide solutions at different concentrations. The effect of TA on FLX adsorption was studied at a fixed TA concentration of 4 mg/L, the typical NOM concentration in many water reservoirs. Thermostated suspensions were mechanically shaken at 300 rpm until equilibrium was attained, which took from one to four days according to the adsorbent used.

Column adsorption was carried out in glass columns (inner diameter of 9 mm) into which GAC or ACC circles were packed after presoaking in DW or TW at 298 K for 3 days. FLX and TA concentrations were 30 and 4 mg/L, respectively, and solutions in the absence or presence of TA were pumped down through columns with different adsorbent bed depths (between 1 and 4 cm) using a peristaltic pump at a flow rate of 2 mL/min. Outlet concentrations were periodically measured and breakthrough curves were obtained, plotting the relative FLX concentration against the volume of solution passed through the bed.

FLX equilibrium concentrations in the presence of TA were determined by HPLC using an LC-10A model Shimadzu machine with UV/VIS detector at 212 nm and a Hypersil Gold C-18 column of 150 mm × 4.6 mm as stationary phase. The mobile phase was a mixture of 30 % HPLC grade acetonitrile and 70 % deionized water containing 0.01 % formic acid with a flow of 1.4 mL/min. FLX equilibrium concentration in the absence of TA was spectrophotometrically determined at 212 nm using a CECIL CE7200 double-beam spectrophotometer.

HPLC/MS study of the stability of FLX solution in the presence of TA showed that the herbicide was stable for at least the time required to complete the adsorption isotherms.

TA solutions in TW acquired a yellow color due to the formation of tannates at the basic pH (around 8) of TW, which shifted the maximum absorption peak from 275 to 320 nm (Markovic et al. 2003).

ACC was selected to study the thermal desorption of FLX in the presence and absence of TA after adsorption from DW and TW solutions. For this purpose, 0.05 g of ACC was soaked in 500 mL solution containing 30 mg/L of FLX or 30 mg/L of FLX and 4 mg/L of TA. After equilibrium was reached, the amount adsorbed was determined by HPLC. After adsorption, the sample was oven-dried at 383 K for 24 h and the cooled sample was then carefully weighed, calculating the percentage weight loss at 383 K, W_{383}.

DTG profiles of the oven-dried spent ACC were obtained using a Mettler-Toledo TGA-STDA 851 thermobalance. Samples were heated to 1073 K in dry nitrogen (80 cm^3/min) at heating rates of 10–40 K/min following a method described elsewhere (Pastrana-Martínez et al. 2009; Ferro-García et al. 1995). After heating at 1273 K, the percentage of weight loss, W_{1273}, and the residue left on the carbon surface, R_{1273}, were obtained from these experiments. All weight loss calculations were made with respect to the amount of adsorbed fluroxypyr obtained from HPLC.

3 Results and discussion

3.1 Competitive adsorption

FLX molecular dimensions are 1.15–0.89–0.36 nm (length-width-height); therefore, micropores of the activated carbons are accessible to FLX molecules. TA molecules are approximately circular, with an estimated diameter of 3 nm (Ariga et al. 2007); therefore, they cannot access the micropores and can block their entrances.

Figure 1 depicts adsorption isotherms of FLX on ACC at 298 K from DW and TW in the absence and presence of TA, as an example. FLX and FLX plus TA solutions were unbuffered. The initial pH was between 4 and 5 and once the equilibrium was attained, the final pH was between 4.4 and 6 with the use of DW as solvent. The initial and final solution pHs were equal and varied between 8 and 8.4 with the use of TW as solvent. Therefore, by taking account of the speciation diagrams of FLX and TA and the pH_{PZC} of carbons, it is possible to determine the surface charge of the adsorbates and adsorbents. When DW was used as solvent, FLX and TA were negatively charged and practically uncharged, respectively, whereas both activated carbons were positively charged. In contrast, when TW was used as solvent, both adsorbates and GAC were negatively charged and ACC was practically uncharged.

With the utilization of TW as solvent, the FLX adsorption was always higher at low solution concentrations, whereas this trend was reversed at higher solution concentrations. Adsorption isotherms were fitted to Freundlich and Langmuir equations (1) and (2), respectively.

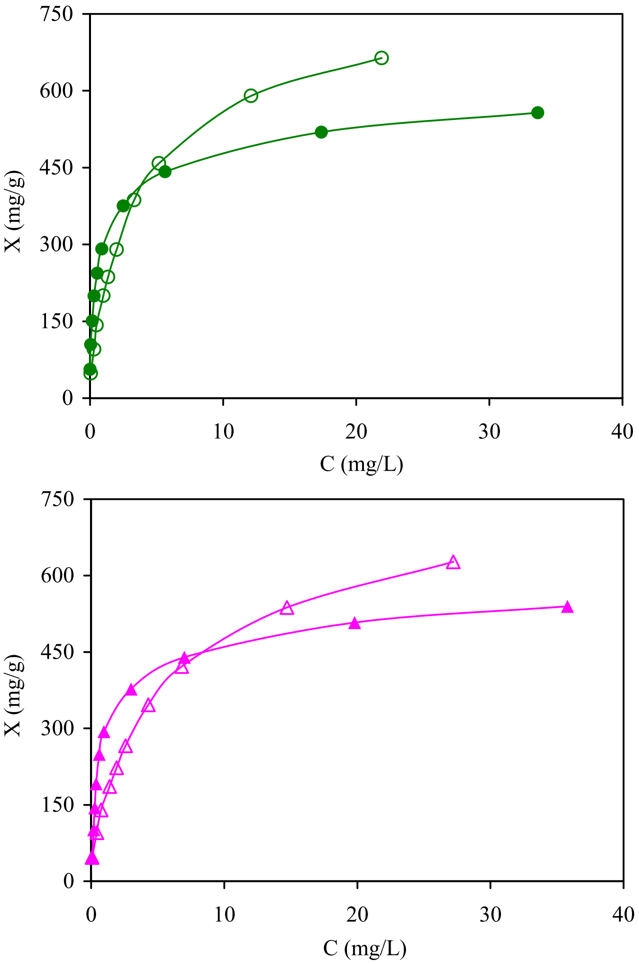

Fig. 1 Adsorption isotherms of FLX on ACC in the absence (○) and presence (△) of TA (4 mg/L) from DW (*open symbols*) and TW (*closed symbols*) at 298 K

$$X = K_F C^{1/n} \tag{1}$$

$$\frac{C}{X} = \frac{1}{BX_m} + \frac{C}{X_m} \tag{2}$$

where X (mg/g) is the amount adsorbed at a given equilibrium concentration, C (mg/L); K_F is the so-called unit capacity factor, equivalent to the amount adsorbed at an equilibrium concentration of 1 mg/L; and n (dimensionless) is an empirical parameter. In the Langmuir equation, C and X have the same meaning, X_m (mg/g) is the adsorption capacity, and B (L/mg) is the Langmuir constant. Unlike the Langmuir isotherm, the Freundlich isotherm does not indicate an adsorption limit at which the surface coverage is sufficient to fill a monolayer and is therefore expected to fail at high adsorbate concentrations (Crittenden and Thomas 1998). Consequently, K_F values give the adsorption capac-

Table 2 Results from Freundlich and Langmuir equations applied to the adsorption isotherms of FLX on ACC and GAC at 298 K from distilled (DW) and tap (TW) water in presence and absence of tannic acid (TA)

Carbon	Solvent	Freundlich equation*			Langmuir equation			
		K_F	n	R^2	X_m (mg/g)	B (L/mg)	R^2	θ (%)
ACC	DW	210 ± 3	2.1 ± 0.3	0.920	746 ± 19	0.40 ± 0.05	0.994	60
	TW	290 ± 1	3.0 ± 0.1	0.992	565 ± 9	0.93 ± 0.11	0.998	46
	DW + TA	156 ± 1	1.8 ± 0.1	0.999	701 ± 16	0.26 ± 0.02	0.997	57
	TW + TA	250 ± 3	2.2 ± 0.3	0.970	549 ± 8	0.82 ± 0.12	0.999	45
GAC	DW	78 ± 1	2.3 ± 0.1	0.980	451 ± 20	0.12 ± 0.02	0.982	65
	TW	156 ± 1	5.6 ± 0.1	0.999	286 ± 4	1.22 ± 0.15	0.999	41
	DW + TA	34 ± 1	1.4 ± 0.1	0.998	419 ± 8	0.08 ± 0.01	0.998	61
	TW + TA	81 ± 1	2.7 ± 0.2	0.970	262 ± 1	0.40 ± 0.03	0.999	38

* Freundlich parameters are based on units of X (mg/g) and C (mg/L)

ity of carbons at low equilibrium concentrations, whereas X_m gives their maximum adsorption capacity.

Results of the two equations are reported in Table 2, together with the surface area of carbon covered by FLX molecules, θ, obtained by taking into account the FLX molecular area, 0.73 nm^2/molecule (Pastrana-Martínez et al. 2009), and the X_m value. In all cases: (i) the K_F values obtained, both in the absence and presence of TA, were higher with the use of TW *versus* DW as solvent, and this effect was more marked with the GAC sample, observing the inverse effect on X_m values; (ii) the presence of TA (in both solvents) reduced K_F values due to partial blocking of the microporosity by TA molecules. The K_F decrease was more pronounced in the GAC sample, which has a lower microporosity *versus* ACC. X_m also decreased but to a lower extent *versus* K_F, because competition between TA and FLX is more apparent at lower than higher FLX concentrations (iii) The B value, which is related to the curvature of the adsorption isotherm "knee", was higher (i.e., the knee point was closer) with the use of TW *versus* DW, indicating higher adsorbate-adsorbent interactions in TW.

TW shows higher K_F values in comparison to DW. This is because the presence of different inorganic salts in the TW, responsible for its hardness and alkalinity, screens electrostatic repulsions between charged FLX and TA molecules and between these molecules and the GAC carbon surface, increasing adsorbate-adsorbent interactions (as shown by B values) and hence the amount of FLX adsorbed.

Conversely, FLX adsorption was higher from DW than from TW at high solution concentrations, as demonstrated by the higher X_m values obtained with the use of DW as solvent. This is likely because there is no competition between inorganic salts and FLX molecules for adsorption sites on the sorbent at high FLX solution concentrations in DW (Pastrana-Martínez et al. 2010).

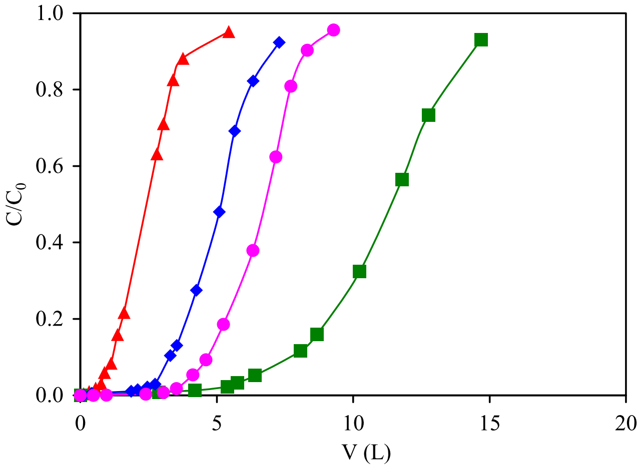

Fig. 2 Breakthrough curves of fluroxypyr on ACC at 298 K in the presence of TA (4 mg/L) from TW. $C_0 = 30$ mg/L, flow 2 mL/min and bed depth 1.0 (▲), 2.0 (◆), 3.0 (●), and 4.0 cm (■)

Table 3 Breakthrough volume values, $V_B(L)$, of carbon beds to remove FLX at 298 K from distilled (DW) and tap (TW) water in presence (4 mg/L) and absence of tannic acid (TA). C$_0$ (FLX) = 30 mg/L. Flow rate = 2 mL/min

Carbon	m (g)	h (cm)	DW		TW	
			FLX	FLX + TA	FLX	FLX + TA
ACC	0.115	1	1.13	0.65	0.79	0.58
	0.256	2	4.14	3.58	3.03	2.37
	0.505	4	n.d.	8.08	6.19	5.11
GAC	0.308	1	0.90	0.56	0.71	0.43
	0.620	2	4.05	3.07	3.42	2.46
	1.255	4	n.d.	6.36	6.94	5.91

n.d.: not determined

Breakthrough curves obtained from column adsorption experiments as a function of bed depth are depicted in Fig. 2, as an example. The breakthrough volume for FLX, V_B, was arbitrarily chosen at a relative concentration of 0.02 from these curves, and it is reported for some of the columns in Table 3. Results show that, at the same bed depth, V_B values were higher for ACC than for GAC, and that V_B values were lower in the presence *versus* absence of TA and in TW

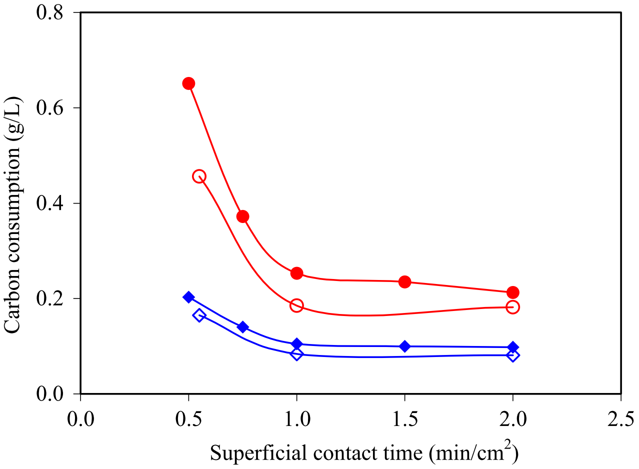

Fig. 3 Carbon consumption as a function of superficial contact time at 298 K for FLX solved in TW in the presence (*closed symbols*) of TA (4 mg/L) and in the absence (*open symbols*). $C_0 = 30$ mg/L, flow 2 mL/min, ACC (◇) and GAC (○)

versus DW, due to the competition of TA and inorganic salts with FLX in TW.

Carbon consumption was plotted against the superficial contact time for each column (Fig. 3) in order to compare the effectiveness of the two carbons to remove FLX from TW in the absence and presence of TA. Carbon consumption was calculated by dividing the mass of carbon by the breakthrough volume. These curves allow the optimum combination of superficial contact time and carbon saturation rate to be determined. Results obtained show a lower consumption of ACC than of GAC. Carbon consumption was increased by the presence of TA but to a lesser extent in the case of ACC, which can be related to the micropore structure of the two sorbents. ACC has a higher volume of micropores and pores accessible to water in comparison to GAC; therefore, for the same concentration of TA, the blocking effect was lower in ACC than in GAC.

3.2 Thermal desorption

Table 4 gives the percentage weight losses of the spent ACC, W_{383} and W_{1073}, and of the residue (R_{1073}). The W_{383} value derives from the release of FLX and TA molecules dragged by water evaporation and from the removal of weakly adsorbed adsorbates. The presence of TA had virtually no influence on W_{383}, W_{1073} and R_{1073} values. However, the percentage weight loss was lower with TW versus DW, resulting in a higher percentage of the residue. This is mainly due to deposition/adsorption on the carbon surface of the mineral matter contained in the TW, which would not be desorbed at 1073 K. Thus, Mg^{2+} and Ca^{2+} ion uptakes in competition with FLX molecules were 21 and 59 mg/g ACC, respectively (Pastrana-Martínez et al. 2010). Therefore, the value of the residue left by these ions (as MgO and CaO after heating at 1073 K) is around 12 %, which is close to the difference of 9–10 % in R_{1073} found between DW and TW.

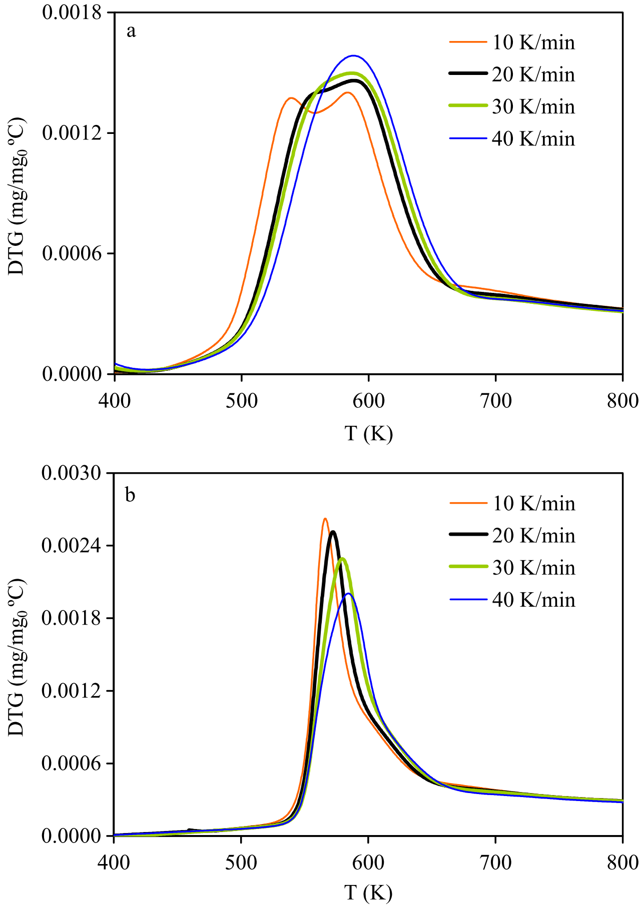

Fig. 4 DTG profiles of the oven-dried spent ACC obtained at different heating rates after adsorption of FLX in the presence of TA from DW (**a**) and from TW (**b**)

DTG profiles of oven-dried spent ACC samples after FLX and AT competitive adsorption from DW and TW are plotted in Figs. 4a and 4b, respectively. Their shapes differ, showing two desorption peaks in the case of DW and only one peak for TW. The DTG profiles with two peaks were deconvoluted to determine their correct position.

DTG profiles shifted to higher temperatures with an increase in the heating rate. The activation desorption energy, E_a, can be calculated from the shift of temperature, T_m, with heating rate, β, according to a first-order desorption process (Cvetanovic and Amenomiya 1967; Thomas and Thomas 1967; Perrard and Joly 1989) given by (3)

$$\frac{\beta E_a}{RT_m^2} = A\exp\left(-\frac{E_a}{RT_m}\right) \qquad (3)$$

In the case of physisorption, E_a corresponds to the heat of adsorption, whereas the pre-exponential factor, A, depends on the desorption mechanism. According to the absolute reaction rate theory, the pre-exponential factor is a

Table 4 Percentage of weight loss after heating the spent ACC at 383 K (W_{383}) and 1073 K (W_{1073}) and residue left on the carbon (R_{1073}). Peak desorption temperature (T_m), activation energy of desorption (E_a) and preexponential factor (A). Heating rate of DTGs: 10 K/min

System	W_{383}	W_{1073}	R_{1073}	T_m (K)	E_a (kJ/mol)	A (s^{-1})
FLX + DW	8	78	22	510	81 ± 8	$(1.4 \pm 0.1) \times 10^6$
				574	231 ± 20	$(1.7 \pm 0.2) \times 10^{19}$
FLX + TA + DW	7	76	24	529	80 ± 9	$(5.4 \pm 0.3) \times 10^5$
				584	223 ± 4	$(1.2 \pm 0.1) \times 10^{19}$
FLX + TW	5	68	32	567	222 ± 2	$(3.7 \pm 0.3) \times 10^{18}$
FLX + TA + TW	5	67	33	568	228 ± 15	$(1.5 \pm 0.1) \times 10^{19}$

frequency factor equal to kT_m/h, where k and h are the Boltzman and Planck constants, respectively. The T_m value ranged between 510 and 584 K; therefore, A must be in the order of 10^{13} s^{-1} for an elementary desorption process without resorption (Cvetanovic and Amenomiya 1967; Thomas and Thomas 1967; Perrard and Joly 1989). E_a and A values obtained are compiled in Table 4.

The presence of TA had practically no influence on T_m, E_a and A values in adsorption from DW. Thus, the first desorption peak had an activation energy of around 80 kJ/mol and a pre-exponential factor of 10^5–10^6 s^{-1}. The boiling points of FLX and TA are 673 and 471 K, respectively (Chemnet 2012). Therefore, the first desorption peak can be assigned to the evolution of weakly adsorbed FLX and TA. The value of the pre-exponential factor was lower than the theoretical 10^{13} s^{-1}, and indicates that FLX and TA were readsorbed during the TGA runs, which is likely given the high microporosity of the adsorbents (Pastrana-Martínez et al. 2009; Ferro-García et al. 1995). The second desorption peak had a higher activation energy, 223–231 kJ/mol, and a higher pre-exponential factor, 10^{19} s^{-1}, than the theoretical value. This peak would correspond to the desorption of strongly adsorbed FLX and TA that took place with an irreversible chemical reaction (Pastrana-Martínez et al. 2009; Ferro-García et al. 1995) caused by their decomposition, leading to a carbonaceous residue on the carbon surface.

Likewise, the presence of TA had practically no influence on the T_m, E_a and A values in adsorption from TW. In this case, these values were close to those found for the second desorption peak in the adsorption from DW, indicating that desorption only took place with the decomposition of the adsorbates. These results were obtained because the solution pH during adsorption from TW was around 8, given that similar findings have been reported (Pastrana-Martínez et al. 2009) for the thermal desorption of FLX previously adsorbed at pH 7–10.

Hence, according to our results, the adsorbates were more strongly bound to the carbon surface when adsorption was carried out from TW than from DW, in agreement with the shape of the isotherms and the higher B values of TW than of DW.

4 Conclusions

K_F values calculated with the Freundlich equation were higher in the absence or presence of TA with the use of TW rather than DW as solvent, because of the screening of electrostatic repulsions by inorganic salts in TW. The presence of TA (in both solvents) reduced K_F values due to partial blocking of the microporosity by TA molecules. Conversely, FLX adsorption was higher from DW than from TW at high solution concentrations.

ACC showed lower carbon consumption as a function of the individual superficial contact time obtained from column adsorption in comparison to GAC. The presence of TA increased the carbon consumption, but this effect was less marked for ACC because of the micropore structure of the sorbents.

The amount of residue left after heating oven-dried spent activated carbon samples to 1073 K was higher with TW than with DW, due to deposition of the mineral matter contained in the TW. The DTG profile of oven-dried spent ACC samples after FLX and AT competitive adsorption showed two peaks when DW was used. The first peak corresponded to the desorption with resorption of weakly adsorbed FLX and TA, and the second peak to the desorption of strongly adsorbed FLX and TA which occured with their decomposition, leaving a carbonaceous residue on the carbon surface. Only one desorption peak was observed when TW was used, attributable to decomposition of the adsorbates. According to these findings, FLX and TA were more strongly bound to the carbon surface in adsorption from TW than in adsorption from DW.

Acknowledgements The authors are grateful to MICINN and FEDER, project CTQ2011-29035-C02-01, for financial support.

References

Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T.: Comparison of natural organic matter adsorption capacities of superpowdered activated carbon and powdered activated carbon. Water Res. **44**, 4127–4136 (2010)

Ariga, K., Vinu, A., Miyahara, M., Hill, J.P., Mori, T.: One-pot separation of tea components through selective adsorption on pore-engineered nanocarbon, carbon nanocage. J. Am. Chem. Soc. **129**, 11022–11023 (2007)

Chemnet: http://www.21chemnet.com/. Accessed 19 April 2012 (2012)

Crittenden, B., Thomas, W.J.: Adsorption Technology & Design. Butterworth-Heinemann, Oxford (1998)

Cvetanovic, R.J., Amenomiya, Y.: Advances in Catalysis Vol 17. Academic Press, New York (1967)

Ferro-García, M.A., Joly, J.P., Rivera-Utrilla, J., Moreno-Castilla, C.: Thermal desorption of chlorophenols from activated carbons with different porosity. Langmuir **11**(7), 2648–2651 (1995)

Lee, S.H., Nishijima, W., Lee, C.H., Okada, M.: Calcium accumulation on activated carbon deteriorates synthetic organic chemicals adsorption. Water Res. **37**, 4631–4636 (2003)

Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos, C.: Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. Water Res. **37**, 773–784 (2003)

Li, D., Snoeyink, V.L., Mariñas, B.J., Yue, Z., Economy, J.: Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous atrazine and natural organic matter. Environ. Sci. Technol. **42**, 1227–1231 (2008)

Lyklema, J.: Fundamentals of Interface and Colloid Science. Fundamentals, vol. I. Academic Press, New York (1993)

Markovic, J.M.D., Ignjatovic, L.M., Markovic, D.A., Baranac, J.M.: Antioxidative capabilities of some organic acids and their copigments with malvin, Part II. J. Electroanal. Chem. **553**, 177–182 (2003)

McCafferty, N.D., Callow, M.E., Hoggert, L., Holden, B., Leadbeater, B.S.C.: Application of method to quantify carbonate precipitated on granular activated carbon used in potable water treatment. Water Res. **34**, 2199–2206 (2000)

Moreno-Castilla, C., Álvarez-Merino, M.A., López-Ramón, M.V., Rivera-Utrilla, J.: Cadmium ion adsorption on different carbon adsorbents from aqueous solutions. Effect of surface chemistry, pore texture, ionic strength and dissolved natural organic matter. Langmuir **20**(19), 8142–8148 (2004)

Pastrana-Martínez, L.M., López-Ramón, M.V., Moreno-Castilla, C.: Adsorption and thermal desorption of the herbicide fluroxypyr on activated carbon fibers and cloth at different pH values. J. Colloid Interface Sci. **33**, 2–7 (2009)

Pastrana-Martínez, L.M., López-Ramón, M.V., Fontecha-Cámara, M.A., Moreno-Castilla, C.: Batch and column adsorption of herbicide fluroxypyr on different types of activated carbons from water with varied degress of hardness and alkalinity. Water Res. **44**, 879–885 (2010)

Perrard, A., Joly, J.P.: A classical model for temperature-programmed superficial reactions. Vacuum **39**, 551–556 (1989)

Stuart, M.A., Fleer, G.J., Lyklema, J., Norde, W., Scheutjens, J.M.H.M.: Adsorption of ions, polyelectrolytes and proteins. Adv. Colloid Interface Sci. **34**, 477–535 (1991)

Thomas, J.M., Thomas, W.J.: Introduction to the Principles of Heterogeneous Catalysis. Academic Press, New York (1967)

Weiner, E.R.: Ed. Applications of Environmental Chemistry. A Practical Guide for Environmental Professionals. Lewis, Washington (2000)

Xie, W.H., Shiu, W.Y., Mackay, D.: A review of the effect of salts on the solubility of organic compounds in seawater. Mar. Environ. Res. **44**, 429–444 (1997)