

Activated carbon cloth as adsorbent and oxidation catalyst for the removal of amitrole from aqueous solution

C. Moreno-Castilla · M.A. Fontecha-Cámara ·
M.A. Álvarez-Merino · M.V. López-Ramón ·
F. Carrasco-Marín

Received: 20 July 2010 / Accepted: 28 September 2010 / Published online: 16 October 2010
© Springer Science+Business Media, LLC 2010

Abstract Removal of amitrole from water was studied by adsorption on an activated carbon cloth and by oxidation with hydrogen peroxide using the same activated carbon cloth as catalyst. Study variables included the solution pH, ionic strength, and temperature in the adsorption process and the solution pH and the surface chemistry of the activated carbon cloth in the oxidation process. Results showed that amitrole adsorption on activated carbon cloth was not adequate to remove amitrole from water due to the high solubility and low aromaticity of the herbicide, which reduced its adsorption on the carbon. A higher amitrole removal rate was obtained with the activated carbon/H₂O₂ system. The best results were obtained on basic activated carbon surfaces at pH 7–10, when hydroxyl radical formation is favored, achieving the removal of 35–45% of the AMT, compared with 20–25% under the best adsorption conditions. Importantly, oxygen fixed on the carbon surface during AMT oxidation must be removed by heat treatment in order to regenerate the surface basicity of the carbon before its reutilization in another oxidation cycle.

Keywords Amitrole adsorption · Amitrole oxidation · Activated carbon cloth

1 Introduction

Amitrole (AMT) is a heterocyclic herbicide derived from triazole (3-amino-1,2,4-triazole) that is widely used for weed control in agriculture and along roadsides and railways. It is a non-selective herbicide sometimes used in place of other prohibited herbicides (Oesterreich et al. 1999; Catastini et al. 2004; Da Pozzo et al. 2005). AMT can be found at relatively high levels in surface water and can contribute to ground-water contamination *via* leaching, due to its high solubility.

Contaminated waters can be adequately treated with activated carbon filters to reduce herbicides to permitted levels. Adsorption on activated carbons is one of the most effective methods to remove this type of hazardous compound from polluted waters (Radovic et al. 2001). Activated carbons are generally used in granular or powder form, although activated carbon fibers and cloths recently emerged as better adsorbents than granular activated carbons, generally showing much faster adsorption kinetics and adsorption capacity.

However, adsorption on activated carbons can be inadequate to remove some organic pollutants from water, and advanced oxidation processes (AOP) may be a more effective technology. AOPs are characterized by the production of OH• radicals, which are powerful (2.8 V) unselective oxidants (Zapata et al. 2009) that can oxidize and mineralize organic pollutants in water, yielding CO₂ and other inorganic compounds. Hydroxyl radicals can be generated from H₂O₂ by using activated carbon as decomposition catalyst (Bansal et al. 1988; Kimura and Miyamoto 1994; Khalil et al. 2001; Oliveira et al. 2004; Georgi and Kopinke 2005; Santos et al. 2009).

The aim of this study was to investigate AMT removal from water by adsorption on activated carbon cloth and by oxidation with hydrogen peroxide, using the same activated

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

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

carbon cloth as catalyst. Study variables included the solution pH, ionic strength and temperature in the adsorption process and the solution pH and surface chemistry of the activated carbon cloth in the oxidation process.

2 Experimental

Two activated carbon cloths were used: as-received sample (ACC) supplied by Kynol Europe; and ACC heat-treated at 1173 K in N₂ flow for 4 h, designated ACCN. Samples were cut into 6 mm diameter circles and were characterized by N₂ adsorption at 77 K using an Autosorb 1 analyzer from Quantachrome, after outgassing samples overnight at 383 K under high vacuum (around 10^{−6} mbar). The BET and DR equations were applied to these isotherms to determine the BET surface area, S_{BET} , micropore volume, W_0 , and mean micropore width, L_0 .

Temperature-programmed desorption (TPD) was used to determine the oxygen content (O_{TPD}) of carbon samples from the amount of CO and CO₂ evolved after their heat treatment in He flow at 1273 K, by means of a model Prisma mass spectrometer from Pfeiffer. Samples were also characterized by potentiometric titration to determine the variation of surface charge with solution pH and hence their pH at the point of zero charge (pH_{PZC}). Surface acidity and basicity were determined by titration with NaOH and HCl, respectively. All of these methods are described in detail elsewhere (Moreno-Castilla et al. 2004).

Analytical reagent grade AMT was supplied by Sigma-Aldrich. Its molecular size was determined from the CIF file deposited in the Cambridge Structural Database. The molecular area and dipolar moment were established by using the SCF AM1 semi-empirical method of the Gaussian03 program (Frisch 2004). The herbicide was also characterized by potentiometric titrations to determine its speciation diagram as a function of the pH, showing the distribution of the different forms (neutral, anionic or cationic) of AMT in aqueous medium at different pH values.

Adsorption isotherms of AMT were obtained by using 0.1 g of carbon and 100 mL of AMT solutions at concentrations ranging from 2 to 90 mg/L. Effects of ionic strength and solution pH on adsorption were investigated by utilizing different KCl concentrations and adding either HCl or KOH

to adjust the pH, except in the case of pH 7, when a phosphate buffer composed of monobasic potassium phosphate and dibasic sodium phosphate was added. Suspensions were mechanically shaken at the chosen temperature, between 288 and 308 K, until equilibrium was reached. Concentrations were spectrophotometrically determined at 202 nm by using an UV-V Perkin-Elmer double beam spectrophotometer, model Lambda 19. Lambert-Beer's law was determined for each KCl concentration and pH used.

AMT oxidation experiments were carried out using 0.1 L of a 1.07 mM AMT solution in thermostated flasks at 298 K shaken at 300 rpm. Oxidation was carried out at pH values of 3, 7, and 10, which were adjusted by adding HCl or NaOH and using 0.05 g of carbon and 6 mmol of H₂O₂ (30% w/w, from Merck). Blank experiments were also carried out to determine the percentage of AMT adsorbed by the activated carbon with respect to the total amount of AMT removed from the solution. AMT concentrations were measured by high-performance liquid chromatography (HPLC) using an LC-10A model Shimadzu system, with UV/VIS detector at 202 nm and a Hypersil 50-DS C-18 column of 200 mm × 5.6 mm as stationary phase. The mobile phase was 70% HPLC grade acetonitrile: 30% ultrapure water at a flow of 1.1 mL/min. All samples were diluted ten-fold before their analysis.

AMT mineralization was followed by measurement of the total organic carbon (TOC), using a TOC-5000A model Shimadzu analyzer. TOC results are the average of at least three analyses. Concentrations of nitrate and ammonium ions in solution were determined with specific Merck Spectroquant kits. Methods were based on the formation of 4-nitro-2,5-dimethylphenol for nitrate ions and of an indophenol blue derivative for ammonium ions, determining these compounds with a double-beam spectrophotometer at 330 and 690 nm, respectively. When necessary, mass-HPLC and ¹³C-nuclear magnetic resonance (¹³C-NMR) were used to determine the presence of AMT degradation products.

3 Results and discussion

3.1 Characteristics of the activated carbons and herbicide

Surface characteristics of the activated carbons used are compiled in Table 1. Heat treatment of ACC at 1173 K in

Table 1 Surface characteristics of activated carbons

Sample	S_{BET} (m ² /g)	W_0 (cm ³ /g)	L_0 (nm)	Acidity (meq/g)	Basicity (meq/g)	pH _{PZC}	CO (mmol/g)	CO ₂ (mmol/g)	O_{TPD} (%)
ACC	2128	0.92	1.6	0.20	0.50	8.0	1.10	0.06	1.9
ACCN	1876	0.77	1.8	0.10	0.69	9.0	0.19	0.05	0.5

inert atmosphere to obtain ACCN produced a decrease in total oxygen content, O_{TPD} , reducing the surface acidity and increasing the surface basicity and pH_{PZC} . Therefore, as expected, the heat treatment of ACC gives rise to a more basic carbon surface. There was also a decrease in S_{BET} and W_0 and an increase in L_0 as a result of the slight gasification produced by the removal of surface oxygen complexes (SOCs).

The shape and dimensions of AMT are depicted in Fig. 1. Its molecular area is $0.39 \text{ nm}^2/\text{molecule}$ (Fontecha-Cámara et al. 2007), and this molecule is completely accessible to the microporosity ($\theta < 2 \text{ nm}$) of the carbons used. The AMT speciation diagram (Fontecha-Cámara et al. 2007) indicates that it exists as neutral species (AMT) at pHs of 6–8, as protonated species ($AMTH^+$) at $pH < 6$, and as deprotonated species (AMT^-) at pHs 8–13.

3.2 Amitrole adsorption

AMT adsorption isotherms at 298 K on ACC are depicted in Fig. 2. Results of application of the Langmuir equation to these isotherms at different pHs are displayed in Table 2, which additionally includes the correlation coefficient, R^2 , of the Langmuir plots. This table also shows that AMT solubility markedly decreases with a rise in the pH; this reduction was pronounced between pH 5 and 7 and remained practically constant between pH 7 and 11. According to

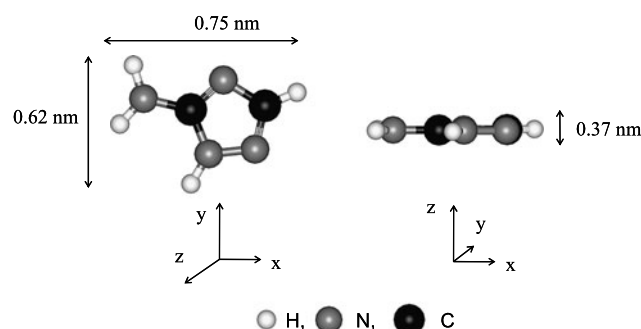


Fig. 1 Molecular dimensions of amitrole

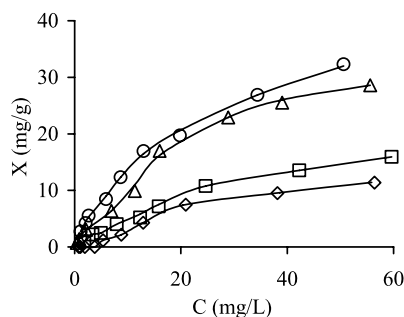


Fig. 2 Adsorption isotherms of amitrole on ACC at different pHs: (\diamond) pH 3, (\square) pH 5, (\triangle) pH 7, (\circ) pH 9

the AMT speciation diagram (Fontecha-Cámara et al. 2007) AMT molecules are predominantly protonated (about 95% as $AMTH^+$) at pH 3. The rise in pH increases the percentage of uncharged AMT molecules, finding 100 and 90% as AMT at pHs 7 and 9, respectively. Hence, the rise in pH increases the AMT hydrophobicity due to a decrease in the heat of hydration of the AMT molecules (López-Ramón et al. 2010).

X_m increased when the pH rose from 3 to 7, especially from 5 to 7, remaining virtually unchanged from pH 7 to 9. Variations in X_m can be explained by hydrophobic and electrostatic interactions. Thus, the decrease in solubility increases hydrophobic interactions between the AMT molecules and the hydrophobic parts of the adsorbent. In addition, AMT molecules are 95% and 30% protonated as $AMTH^+$ at pH 3 and 5, respectively, whereas the carbon surface is also positively charged, since the pH_{PZC} of ACC is 8. In this situation, repulsive adsorbent-adsorbate and adsorbate-adsorbate electrostatic interactions predominate, reducing AMT adsorption on the carbon surface. Conversely, the neutral form of the AMT molecule predominates at pH 7 and 9, with a disappearance of the electrostatic repulsions that negatively affect the adsorption.

The surface area of ACC covered by AMT, calculated from the X_m values and molecular size of AMT, was 7% at pH 7–9. This is a very low value in comparison to other herbicides (Fontecha-Cámara et al. 2007; Pastrana-Martínez et al. 2009). Hence, despite the small molecular dimensions of AMT, which make it accessible to the microporosity of the adsorbent, it is not extensively adsorbed, mainly due to its high water solubility. In addition, the aromaticity of the AMT cycle is much lower than that of other pollutants with a benzene cycle, markedly reducing the dispersion interactions between electrons of the pentagonal AMT cycle and π electrons of the carbon graphene layers.

The BX_m value is a measurement of AMT-carbon interactions and increased with higher pH, with a much steeper increase between pH 5 and 7. This is related to a marked decrease in amitrole solubility, most notably from pH 5 to 7, which enhances hydrophobic AMT-carbon interactions.

Table 2 Results of application of the Langmuir equation to adsorption isotherms of AMT on ACC at 298 K and at different pHs

pH	X_m (mg/g)	R^2	BX_m (L/g)	Solubility (g/L)	θ (%)	AMT _{removed} ^a (%)
3	20	0.940	0.45	1600	3	9
5	30	0.970	0.58	1000	4	12
7	51	0.988	1.27	280	7	21
9	53	0.980	1.74	279	7	24

^aPercentage of AMT removed from a solution with an initial concentration of 90 mg/L

Table 3 Results of application of the Langmuir equation to adsorption isotherms of AMT on ACC at 298 K, pH 7 and different KCl concentrations

[KCl] (mol/L)	X_m (mg/g)	R^2	BX_m (L/g)	θ (%)	AMT _{adsorbed} ^a (%)
0.00	51	0.927	1.27	7	21
0.01	60	0.930	1.38	8	25
0.05	68	0.921	1.43	9	26

^aPercentage of AMT removed from a solution with an initial concentration of 90 mg/L

Table 4 Results of application of the Langmuir equation to adsorption isotherms of amitrole (AMT) at different temperatures on ACC at pH = 7 and at 0.01 M KCl concentration

T (K)	X_m (mg/g)	R^2	BX_m (L/g)	Solubility (g/L)	ΔH (kJ/mol)	ΔS (J/mol K)
288	64	0.950	1.52	210		
298	60	0.930	1.38	280	-7.5 ± 0.4	14.3 ± 1.2
308	48	0.950	1.24	357		

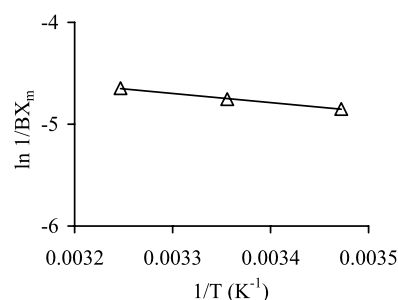
A study was also performed on the effect of ionic strength on AMT adsorption on ACC at pH 7 and 298 K. Table 3 displays the results of applying the Langmuir equation (and R^2) to the adsorption isotherms obtained, showing an increase in X_m with greater ionic strength of the solution. Hence, since amitrole is neutral at pH 7, an increase in KCl concentration could reduce the solubility of AMT, which would enhance AMT-adsorbent hydrophobic interactions. BX_m values also increased with higher KCl concentrations, and the surface area of ACC covered by amitrole at a concentration of 0.05 M KCl was 9%, again a very low value.

The last column of Tables 2 and 3 show the percentages of AMT removed by adsorption from a solution with an initial AMT concentration of 90 mg/L. The highest percentages, which depended on the pH and ionic strength, were only 20–25%, which is a very low percentage removal.

AMT adsorption on ACC at pH 7 and between 288 and 308 K was exothermic, as evidenced by the decrease in X_m (Table 4) at higher adsorption temperatures within this range. This is due to the increased solubility (Table 4) and vibrational energy of adsorbed molecules with higher temperature. Hence, more adsorbed molecules have sufficient energy to overcome the attractive interactions and desorb back into solution (Cooney 1998).

Van't Hoff equation (1) was used to obtain the enthalpy, ΔH , and entropy, ΔS , of the adsorption process.

$$\ln K = -\Delta H/RT + \Delta S/R \quad (1)$$

**Fig. 3** Application of Van't Hoff equation to AMT adsorption on ACC between 288 and 308 K and at pH 7

The value of K is defined as

$$K = \gamma_a X / \gamma_s C \quad (2)$$

where γ_a and γ_s are the activity coefficients of the adsorbate on the adsorbent and in solution, respectively, and X is the amount adsorbed at equilibrium concentration C . When C approaches zero, the activity coefficients approach unity, and K can therefore be obtained by extrapolating C to zero (Aksu and Kabasakal 2004; Chingombe et al. 2006). Thus, K is the inverse of the intercept (BX_m) value of the plot of C/X against X , which is the linearized form of the Langmuir equation. The plot of $\ln 1/BX_m$ against $1/T$ is depicted in Fig. 3, and the adsorption enthalpy and entropy data are compiled in Table 4.

In conclusion, AMT adsorption on activated carbon is very low, and this technology is not sufficiently effective to remove this herbicide from aqueous solutions. Consequently, a study was then performed on the removal of AMT by oxidation with hydroxyl radicals generated by activated carbon/ H_2O_2 systems.

3.3 AMT removal by activated carbon/ H_2O_2 systems

The activated carbons ACC and ACCN were used to study AMT removal by the activated carbon/ H_2O_2 system. ACCN was used immediately after its preparation to avoid reoxidation from prolonged contact with the atmosphere. In these systems, removal of the herbicide can occur by both adsorption and oxidation.

Several blank runs were performed before the study was undertaken. The first was to determine the stability of the AMT solution at the pHs studied. ^{13}C -NMR spectra and mass-HPLC results showed that AMT was the only product in solution at pH 3 and 7, while ~20% of 5-hydroxy amitrole, 5-HAMT, was also detected at pH 10.

Figure 4 depicts the ^{13}C -NMR spectra of AMT solutions at the pH values studied. AMT signals appear at pH 3 and 7. In the case of the last pH the signals are shifted to a higher field due to AMT is as neutral molecule. AMT signals are again shifted to a higher field (150.2 and 162.2 ppm)

at pH 10, due to its partial dissociation, and signals of 5-HAMT (155.5 and 169.3 ppm) can also be seen.

Studies were also undertaken on the ability of H_2O_2 to oxidize AMT in the absence of activated carbon, finding that AMT degradation was below 2% at pHs 3, 7, and 10 and remained constant throughout all experiments (10 h).

Figure 5 depicts AMT removal with the ACCN/ H_2O_2 system at pH 7, as an example, and AMT removal by adsorption on ACCN. Table 5 displays the results obtained from these curves after 10 h. In all cases, $\text{TOC}_{\text{removed}}$ is similar to the sum of $\text{AMT}_{\text{degraded}}$ and $\text{AMT}_{\text{adsorbed}}$, indicating that all $\text{AMT}_{\text{degraded}}$ was completely mineralized. AMT oxidation is higher in the presence of activated carbons than in their absence because they act as catalysts of H_2O_2 decomposition, producing hydroxyl radicals (Kimura and Miyamoto 1994; Khalil et al. 2001; Oliveira et al. 2004; Georgi and Kopinke 2005; Santos et al. 2009).

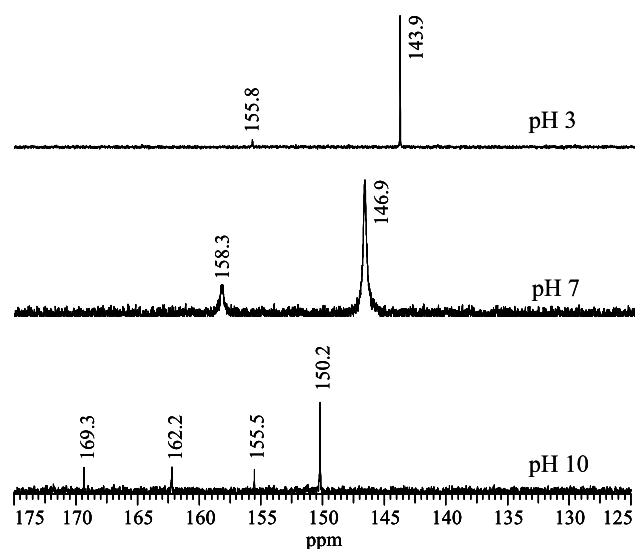


Fig. 4 ^{13}C NMR spectra of AMT solutions (D_2O solvent) at different pHs

$\text{TOC}_{\text{removed}}$ is higher with greater solution pH and surface basicity of the activated carbon cloth because of an increase in both oxidized and adsorbed AMT. Thus, the increase in solution pH enhances H_2O_2 decomposition (Khalil et al. 2001) and reduces AMT solubility, with the former favoring AMT oxidation and the latter AMT adsorption.

In addition, carbon surface basic sites promote H_2O_2 decomposition into hydroxyl and perhydroxyl radicals, thereby enhancing the oxidation of organic compounds in aqueous media (Kimura and Miyamoto 1994; Khalil et al. 2001; Oliveira et al. 2004; Georgi and Kopinke 2005; Santos et al. 2009). These surface basic sites may be delocalized π -electrons from the graphene layers ($\text{C}-\pi$), which transfer electrons according to the mechanism given by reactions (3) and (4) proposed by (Kimura and Miyamoto 1994), similar to the Fenton reaction and Haber-Weisz mechanism.



The only AMT degradation products found in solution after 10 h of treatment were nitrate and virtually negligible concentrations of ammonium ions. The experimental

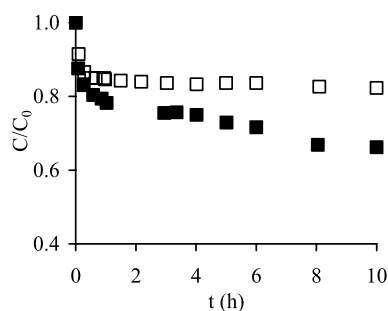


Fig. 5 Adsorption and degradation kinetics of amitrole with ACCN at 25°C . $V = 0.1$ L, $C_{\text{carbon}} = 0.5$ g/L, $C_{\text{H}_2\text{O}_2} = 60$ mM, $C_{\text{AMT}} = 1.07$ mM, pH = 7. (□) without H_2O_2 (by adsorption); (■) with H_2O_2

Table 5 AMT removal at 25°C with activated carbon/ H_2O_2 systems after 10 h reaction and at different pHs. $V = 0.1$ L, $C_{\text{carbon}} = 0.5$ g/L, $C_{\text{H}_2\text{O}_2} = 60$ mM, $C_{\text{AMT}} = 1.07$ mM

Sample	pH	$\text{TOC}_{\text{removed}}$ (%)	$\text{AMT}_{\text{degraded}}$ (%)	$\text{AMT}_{\text{adsorbed}}$ (%)	NO_3^- (exp) (mM)	NO_3^- (theor) (mM)	NH_4^+ (exp) (mM)
ACC	3	11	5	4	0.11	0.10	0.01
	7	17	8	12	0.18	0.17	0.01
	10	30	13(2)*	9(3)	0.29	0.31	0.02
ACCN	3	14	8	10	0.16	0.19	0.01
	7	34	16	18	0.31	0.34	0.01
	10	45	20(3)	15(6)	0.42	0.43	0.02

*Values in parentheses refer to 5-HAMT

Table 6 Results obtained from TPD experiments of fresh and used ACC and ACCN at pHs 7 and 10

Sample	CO (mmol/g)	CO ₂ (mmol/g)	CO/ O CO ₂ (mmol/g)	O _{fixed} (mmol/g)
Fresh ACC	1.10	0.06	18.3 1.22	–
Used ACC at pH 7	1.41	1.15	1.2 3.71	2.49
Used ACC at pH 10	1.34	1.37	1.0 4.08	2.86
Fresh ACCN	0.19	0.05	3.8 0.29	–
Used ACCN at pH 7	2.57	0.59	4.3 3.75	3.46
Used ACCN at pH 10	2.56	0.95	2.7 4.46	4.17

amount of nitrate ions, NO_3^- (exp), was similar to the theoretical amount, NO_3^- (theor), which was obtained by assuming that only two nitrogen atoms per oxidized amitrole molecule are converted to nitrate ions. The agreement between these values indicates that the rest of N is mainly converted to gaseous nitrogen compounds such as N_2 , which can be formed (Da Pozzo et al. 2005) from the two proximate N atoms in the pentagonal AMT cycle (see Fig. 1).

Oxygen is also fixed on the carbon surface during AMT oxidation as shown in Table 6 for oxidation reactions at pH 7 and 10, with higher amounts of fixed O, O_{fixed} , at pH 10 than at pH 7 and with higher amounts on ACCN than on ACC at both pHs. This is because H_2O_2 decomposition is more favored at pH 10 and there are fewer SOC in the basic fresh ACCN versus fresh ACC samples. The percentage of oxygen fixed on the carbon surface was a very small percentage of the total available oxygen from H_2O_2 , ranging from 1 to 2% according to the pH and surface basicity.

The percentage of oxygen consumed in the degradation or mineralization of AMT could also be calculated. Thus, if each degraded AMT molecule ($\text{C}_2\text{H}_4\text{N}_4$) yields two carbon dioxide and two water molecules and two nitrate ions, the percentage of oxygen used in AMT degradation was 2–5% according to the pH and surface basicity. Hence, more oxygen was used in the AMT degradation than in the SOC formation on the carbon.

AMT removal was more effective with the activated carbon/ H_2O_2 system than with adsorption. The best results were obtained on basic activated carbon surfaces at pH 7–10, conditions favorable to hydroxyl radical formation, achieving 35–45% AMT removal (versus 20–25% by adsorption). Importantly, the oxygen fixed on the carbon surface during AMT oxidation must be removed by heat treatment in order to regenerate the surface basicity of the carbon before its reutilization in another oxidation cycle.

4 Conclusions

AMT adsorption was exothermic and increased at higher pH values between 3 and 9, which is explained by changes in

hydrophobic and electrostatic interactions. Despite the small molecular dimensions of AMT, it was not widely adsorbed due to its high solubility in water. Furthermore, the aromaticity of the AMT cycle is much lower than that of other pollutants with a benzenic cycle, implying very low dispersion interactions between electrons of the pentagonal AMT cycle and π electrons of the carbon graphene layers. Consequently, carbon adsorption cannot effectively remove this herbicide from aqueous solutions. AMT removal by oxidation with carbon/ H_2O_2 -generated hydroxyl radicals proved to be more effective. The best results were obtained on basic activated carbon surfaces at pH 7–10, when hydroxyl radical formation is favored, achieving AMT removal of 35–45% compared with 20–25% by adsorption. Oxygen fixed on the carbon surface during AMT oxidation must be removed by heat treatment to regenerate the surface basicity of the carbon before its reutilization in another oxydation cycle.

Acknowledgements Authors are grateful to MEC and FEDER project CTQ2007-67792-C02-02.

References

- Aksu, Z., Kabasakal, E.: Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon. *Sep. Purif. Technol.* **35**, 223–240 (2004)
- Bansal, R.C., Donnet, J.B., Stoeckli, F.: *Active Carbon*. Dekker, New York (1988) p. 441
- Catastini, C., Rafqah, S., Mailhot, G., Sarakha, M.: Degradation of amitrole by excitation of iron(III) aquacomplexes in aqueous solutions. *J. Photochem. Photobiol. A* **162**, 97–103 (2004)
- Chingombe, P., Saha, B., Wakeman, R.J.: Effect of surface modification of an engineered activated carbon on the sorption of 2,4-dichlorophenoxy acetic acid and benazolin from water. *J. Colloid Interface Sci.* **297**, 434–442 (2006)
- Cooney, D.O.: *Adsorption Design for Wastewater Treatment*. Lewis Publishers/CRC Press, Boca Raton (1998)
- Da Pozzo, A., Merli, C., Sirés, I., Garrido, J.A., Rodríguez, R.M., Brillas, E.: Removal of the herbicide amitrole from water by anodic oxidation and electro-Fenton. *Environ. Chem. Lett.* **3**, 7–11 (2005)
- Fontecha-Cámara, M.A., López-Ramón, M.V., Álvarez-Merino, M.A., Moreno-Castilla, C.: Effect of surface chemistry, solution pH and ionic strength on removal of herbicides diuron and amitrole from water by an activated carbon fiber. *Langmuir* **23**(3), 1242–1247 (2007)
- Frisch, M.J.: *Gaussian 03. Revision C.02*. Gaussian Inc. Wallingford CT (2004)
- Georgi, A., Kopinke, F.D.: Interaction of adsorption and catalytic reactions in water decontamination processes. Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. *Appl. Catal. B Environ.* **58**, 9–18 (2005)
- Khalil, L.B., Girgis, B.S., Tawfik, T.A.M.: Decomposition of H_2O_2 on activated carbon obtained from olive stones. *J. Chem. Technol. Biotechnol.* **76**, 1132–1140 (2001)
- Kimura, M., Miyamoto, I.: Discovery of the activated-carbon radical AC^+ and the novel oxidation-reactions comprising the AC/AC^+ cycle as a catalyst in an aqueous solution. *Bull. Chem. Soc. Jpn.* **67**, 2357–2360 (1994)

- López-Ramón, M.V., Partal-Ureña, F., Moreno-Castilla, C., Fontecha-Cámara, M.A., Álvarez-Merino, M.A., Pastrana-Martínez, L.M.: Relación de la energía de hidratación y estado electrónico de herbicidas con su adsorción sobre carbones activados. In: XXXV Reunión Ibérica de Adsorção, Lisboa, Portugal (2010)
- Moreno-Castilla, C., Álvarez-Merino, M.A., López-Ramón, M.V., Rivera-Utrilla, J.: Cadmium 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)
- Oesterreich, T., Klaus, U., Volk, M., Neidhart, B., Spiteller, M.: Environmental fate of amitrole: influence of dissolved organic matter. *Chemosphere* **38**, 379–392 (1999)
- Oliveira, L.C.A., Silva, C.N., Yoshida, M.I., Lago, R.M.: The effect of H₂ treatment on the activity of activated carbon for the oxidation of organic contaminants in water and the H₂O₂ decomposition. *Carbon* **42**, 2279–2284 (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.* **331**(1), 2–7 (2009)
- Radovic, L.R., Moreno Castilla, C., Rivera Utrilla, J.: Carbon materials as adsorbents in aqueous solutions. In: L.R. Radovic (Ed.) *Chemistry and Physics of Carbon*, vol. 27, Ch. 4, pp. 227–406. Dekker, New York (2001)
- Santos, V.P., Pereira, M.F.R., Faria, P.C.C., Órfao, J.J.M.: Decolourisation of dye solutions by oxidation with H₂O₂ in the presence of modified activated carbons. *J. Hazard. Mater.* **162**, 736–742 (2009)
- Zapata, A., Velegraki, T., Sánchez-Pérez, J.A., Mantzavinos, D., Maldonado, M.I., Malato, S.: Solar photo-Fenton treatment of pesticides in water: effect of iron concentration on degradation and assessment of ecotoxicity and biodegradability. *Appl. Catal., B Environ.* **88**, 448–454 (2009)