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Carbonized and activated textile acrylic fibers and melamine foams are tested as catalysts for the wet air oxidation of aniline. The use of carbon materials prepared from foams and fibers enriched with nitrogen improves the rate of aniline removal. Among all the prepared materials, a fiber carbonized at 850°C and activated during 12 h is the most effective material for both aniline and total organic carbon removal. The catalytic activity of this fiber is maintained in consecutive runs. In addition, a strong correlation was observed between the total organic carbon removal and the pyridinic-N group content on the catalyst surface.

Keywords acrylic fibers; aniline; melamine foam; nitrogenated groups; wet air oxidation

INTRODUCTION

The introduction of nitrogenated groups onto the surface of carbon materials has been investigated in order to improve their catalytic and adsorption properties (1–4). Nitrogen functional groups can be introduced onto carbon surfaces by different treatments, such as nitric acid oxidation, reaction of surface carboxyl groups with diamine compounds, and treatment at high temperatures with ammonia, ammonia-air, or ammonia-steam mixtures (5). A different approach consists of the carbonization of polymers containing nitrogen in their structure, such as acrylic fibers and melamine foams (6,7). In this approach chemical treatments for the introduction of nitrogenated groups are not required, decreasing the cost and time consumed for the synthesis of carbon materials enriched with nitrogen. The main common objective of these treatments is to induce surface basicity on porous carbons, thereby enhancing the adsorption properties, but the presence of nitrogen atoms in the carbon matrix has also shown enhancement of the catalytic activity of these materials in different applications, including oxidation reactions (1–4).

Catalytic wet air oxidation (CWAO) is a well-established treatment for waste streams, which are too dilute to incinerate and too concentrated for biological treatment (8). Depending on the reaction conditions and catalyst composition, either a total mineralization of pollutants into CO_2, N_2, and H_2O, or an increase of the effluent biodegradability by producing easily biodegradable by-products, such as low molecular weight carboxylic acids, can be achieved. Several heterogeneous catalysts have been investigated in the last four decades, based either on metal oxides (e.g., Cu, Zn, Co, Fe, Mn, and Bi) or noble metals (e.g., Pt, Pd, Ru, Rh) and usually supported on TiO_2, CeO_2, Al_2O_3, ZrO_2, or carbon materials (e.g., activated carbons, multi-walled carbon nanotubes, carbon xerogels, carbon nanofibers) (8–24). Many of these catalysts exhibit good activity for CWAO, but deactivation problems have been reported, including leaching, poisoning, and fouling or even poor chemical resistance of the support. As a result, researchers are looking for more stable and active catalysts.

Carbons are unequivocally one of the preferred materials for CWAO (12). Due to advances in the knowledge on synthesis and characterization of these materials, recent efforts are focussed in the development of carbons that can be used directly in the process as catalysts on their own (12,20,21). Previous studies show that mesoporous carbon xerogels with a significant amount of oxygen functional groups on their surface exhibit high activity in CWAO (20). Alternatively, activated carbon fibers have interesting advantages such as very high apparent surface areas (up to 2000 m^2/g) and small diameters (10–20 μm), resulting in high adsorption capacities with mass transfer resistances lower than those typically observed for activated carbons, where the particle size is commonly higher than 1 mm. In the present work several fibers and foams were carbonized at different temperatures and exposed to different activation times. These carbon materials, with

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varying nitrogen contents, were tested in the treatment of aniline by CWAO. Aniline was chosen as a model compound since it is widely used in the chemical industry, mainly in the synthesis of rubber additives and polymers such as isocyanate intermediates and polyurethanes, and in the production of dyes, pigments, resins, unsaturated polyesters and sweetening agents. To the best of our knowledge this is the first report using carbonized and activated carbon fibers and foams enriched with nitrogen for the CWAO process.

EXPERIMENTAL

Catalysts Preparation

The fibers were prepared from textile polyacrylonitrile fibers, FISIVON, supplied by FISIPE, Portugal, which were subsequently knitted in the facilities of the Technological Centre for the Textile and Clothing Industries of Portugal (CITEVE). The foams were prepared from a melamine resin, Basotect G, supplied by BASF, Germany. First, stabilization of the fibers was carried out by heating 5 g of the original fibers up to 300°C in a tubular reactor. A heating rate of $1°C\,min^{-1}$ under a constant N_2 flow of $85\,Ncm^3\,min^{-1}$ was used, and the final temperature was maintained for 2 h. The fibers were then carbonized by raising the temperature at a rate of $5°C\,min^{-1}$ up to the desired temperature (800, 850, or 900°C), and maintaining the carbonization temperature for 1 h. Further activation was obtained by raising the temperature again at $15°C\,min^{-1}$ to 800, 850, or 900°C, but then switching the N_2 flow to a CO_2 flow for a specific time (6). In the case of melamine foams, the original material was cut from a parallelepipedic block and subjected to carbonization by raising the temperature at a rate of $5°C\,min^{-1}$ to 700, 800, or 900°C, and maintaining this temperature during 1 h (7).

Catalyst Characterization

The textural characterization of the materials was based on the N_2 adsorption isotherms determined at −196°C in a Quantachrom NOVA 4200e analyzer. Surface morphological observations were carried out by scanning electron microscopy (SEM) with a JEOL JSM 35C/Noran Voyager microscope. The surface chemistry was characterized by the pH at the point of zero charge (pH_{pzc}), according to a procedure described elsewhere (25), X-ray photoelectron spectroscopy (XPS), elemental analysis, and temperature programmed desorption (TPD). XPS analysis was performed in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized Mg Kα radiation (1253.6 eV). The values of binding energies were calibrated with respect to C1s peak at 285.0 eV. Elemental analysis of carbon, hydrogen, sulphur, nitrogen, and oxygen was carried out using Carlo Erba EA 1108. TPD spectra were recorded with an automated apparatus (Altamira Instruments, AMI-200) equipped with a quadrupole mass spectrometer (Ametek, Dymaxion 200 amu). The sample was placed in a U-shaped quartz tube inside an electrical furnace and heated under a constant flow of helium at $5°C\,min^{-1}$ up to 1100°C. Selected mass signals, $m/z = 28$ and 44, were monitored during the thermal analysis. The amounts of CO and CO_2 were calibrated at the end of each analysis with CO and CO_2 gases. Since one of the fragments in the mass spectrum of CO_2 occurs at $m/z = 28$, the mass signal monitored for quantification of CO ($m/z = 28$) was corrected in order to eliminate the influence of CO_2 on CO evolution.

Reactor and Procedure

The CWAO experiments were performed in a 160 mL 316-stainless steel high pressure batch reactor (Parr Instruments, USA Mod.4564). In a typical oxidation run, 70 mL of ultrapure water and 0.2 g of catalyst were placed into the reactor. The reactor was flushed with pure nitrogen in order to remove dissolved oxygen, pressurized with 0.5 MPa of nitrogen, and pre-heated up to the desired temperature (200°C). As soon as this temperature was reached, 5 mL of an aniline solution with a pre-calculated concentration was injected into the reactor together with pure air ($t = 0$ min), in order to obtain an initial aniline concentration of $2\,g\,L^{-1}$ under an oxygen partial pressure of 0.7 MPa (5.0 MPa of total pressure). The stirring rate was maintained at 500 rpm to avoid mass transfer limitations. A non-catalytic blank experiment was performed in the absence of a catalyst. Adsorption experiments were performed with aniline and the carbon materials, replacing pure air by nitrogen. In another run, the vapor-liquid equilibrium at these conditions was quantified by using aniline without carbon materials in a nitrogen atmosphere.

TABLE 1
Textural properties of fibers and foams

Sample	S_{BET} ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	S_{meso} ($m^2\,g^{-1}$)
FI-800°C-0 h	<0.5	–	–
FI-800°C-10 h	430	0.20	36
FI-800°C-20 h	637	0.30	49
FI-850°C-0 h	<0.5	–	–
FI-850°C-7 h	528	0.21	43
FI-850°C-12 h	845	0.38	58
FI-900°C-0 h	<0.5	–	–
FI-900°C-3 h	76	0.01	49
FI-900°C-5 h	116	0.03	44
FO-700°C-0 h	<0.5	–	–
FO-800°C-0 h	<0.5	–	–
FO-900°C-0 h	<0.5	–	–

The performance of the catalysts was evaluated in terms of the aniline conversion (X_{ANL}) and total organic carbon (TOC) conversion (X_{TOC}).

Analytical Techniques

The concentration of aniline in liquid samples withdrawn from the reactor was followed with a Hitachi Elite LaChrom HPLC system equipped with a Diode Array Detector (L-2450). A method with a flow rate of $1\,mL\,min^{-1}$ was used in a Hydrosphere C18 column ($250\,mm \times 4.6\,mm$; $5\,\mu m$ particles). First, the column was equilibrated with an A:B mixture (98:2) of 20 mM NaH_2PO_4 acidified with H_3PO_4 at pH = 2.80 (A) and methanol (B), followed by a linear gradient run to A:B (30:70) in 7.5 min and finally with isocratic elution during 5 min. Quantification was based on the chromatograms taken by measuring the concentration of aniline at the maximum absorbance value and using the EZChrom Elite chromatography data handling software (Version 3.1.7). Absorbance was found to be linear over the whole range considered

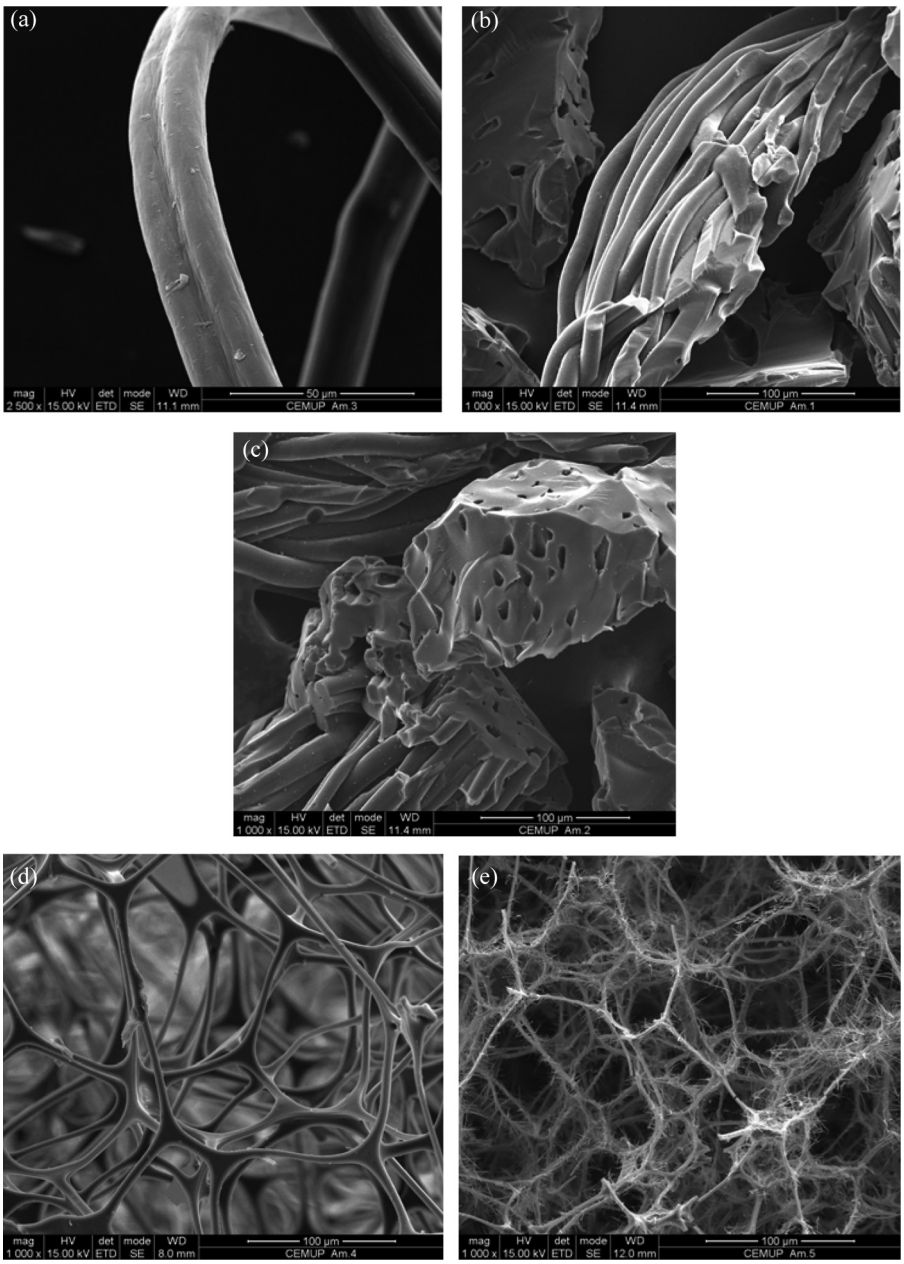

FIG. 1. SEM images of original fiber (a), fiber carbonized at 800°C (b), fiber carbonized at 800°C and activated during 10 h (c), original foam (d), and foam carbonized at 800°C (e).

(maximum relative standard deviation of 2%). The degree of mineralization was determined by total organic carbon (TOC) analysis in a Shimadzu TOC-5000A analyzer. The uncertainty in this parameter, quoted as the relative deviation of three separate measurements, was never larger than 2%.

RESULTS AND DISCUSSION

Characterization of Carbon Fibers and Foams

The textural properties of the materials were determined from the analysis of the corresponding N_2 adsorption-desorption isotherms, and are gathered in Table 1. The reference given to each sample indicates the type of carbon material (fiber-FI or foam-FO) as well as the respective carbonization temperature (700–900°C) and activation time (0–20 h). The carbonized foams and fibers have negligible surface areas regardless of the temperature used. However, activation has a strong impact on the textural properties of the fibers. For these fibers, the BET surface area and the micropore volume increase with the activation time, the fiber carbonized at 850°C and activated for 12 h (FI-850°C-12 h) presenting the highest surface area.

Figure 1 shows SEM micrographs of the original fiber (Fig. 1a) and foam (Fig. 1d), both materials carbonized at 800°C, (Fig. 1b and Fig. 1e, respectively), as well as a representative micrograph of a fiber carbonized at 800°C and activated during 10 h (Fig. 1c). The original and treated fibers have quite similar surface morphologies, since the pores are too small to be clearly visualized by this technique. The original melamine foam (Fig. 1d) consists of struts with triangular cross-sections, and the carbonization treatment seems to promote the weakening of the foam structure (Fig. 1e).

The nitrogen contents obtained from elemental analysis and XPS measurements are summarized in Table 2. The original materials have a large amount of nitrogen. The nitrogen content is larger for the original foam in comparison to the original fiber. The bulk nitrogen (obtained from elemental analysis) decreases with the increase of carbonization temperature or activation time. However, even after the carbonization at 900°C, fibers and foams still contain a significant amount of nitrogen.

XPS analysis was performed for both fibers and foams in order to obtain additional information about the nature of the N bonding. The XPS N 1S spectra (Fig. 2) were decomposed into four peaks based on previous literature data (4,26–27).

The results obtained from the deconvolution of the N1s spectra are shown in Table 3. The first peak identified at around 398 eV, hereafter referred to as N6, is attributed to pyridinic-N, with the nitrogen atom in a six-membered ring and contributing with one p-electron to the aromatic π-system. The second peak situated between 400.0–400.9 eV

TABLE 2
Nitrogen content obtained by elemental analysis, N (wt.%)[a], and surface nitrogen concentration obtained by XPS, N (wt.%)[b]

Sample	N (wt.%)[a]	N (wt.%)[b]
FI-original	24.0	–
FI-800°C-0 h	18.0	11.3
FI-800°C-10 h	11.9	8.5
FI-800°C-20 h	9.7	8.9
FI-850°C-0 h	15.5	12.6
FI-850°C-7 h	11.2	5.2
FI-850°C-12 h	8.1	7.1
FI-900°C-0 h	4.6	7.2
FI-900°C-3 h	4.2	4.9
FI-900°C-5 h	4.0	4.2
FO-original	45.2	–
FO-700°C-0 h	27.1	7.3
FO-800°C-0 h	16.5	6.8
FO-900°C-0 h	10.7	2.7

[a]Elemental analysis.
[b]XPS.

is ascribed to pyrrolic-N or pyridone-N and referred as N5. The next peak identified at 401.4–401.7 eV is attributed to quaternary nitrogen (N-Q), which may involve a large number of different structures, such as a pyridinic group with a nitrogen atom protonated through the formation of an H-bridge. The last peak observed at higher binding energy, between 402–403 eV (N-X), represents certain forms of oxidized nitrogen. Therefore, the fibers have associated two dominant peaks (N5 and N6 groups) plus two smaller contributions (N-Q and N-X groups). Increasing the fiber carbonization temperature leads to a decrease of the pyridinic-N concentration. Regarding the foams, only N6 and N5 peaks were assigned.

Since surface oxygen groups on carbon materials decompose upon heating releasing CO and CO_2, it is possible to identify and estimate the amount of oxygenated groups on the surface of a carbon material from the respective TPD spectra. CO_2 is released from the decomposition of carboxylic acids at low temperatures or from the decomposition of lactones at high temperatures. Phenols and carbonyl/quinone basic groups decompose into CO. Anhydrides release both CO and CO_2 (28,29). The total amounts of CO and CO_2 released from the prepared carbon materials, as well as the respective pH_{pzc} values, are gathered in Table 4. For all the materials, the amount of CO-releasing groups is larger than the amount of groups which decompose into CO_2. Therefore, the carbon samples have associated a basic character which is in agreement with the respective pH_{pzc} values, between 7 and 9 for the fibers, and around 10 for the foams.

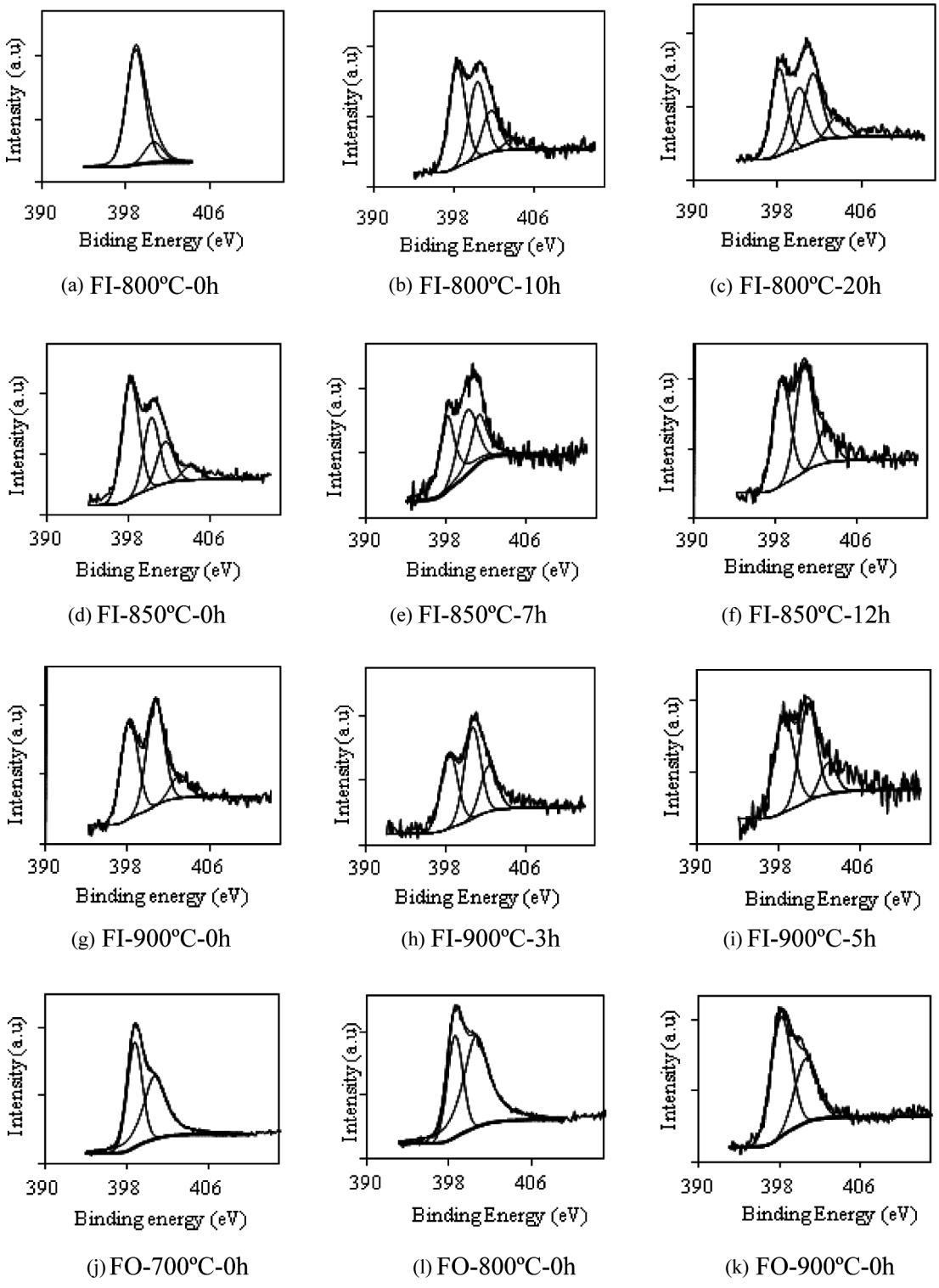

FIG. 2. N1s XPS spectra for all carbons studied.

CWAO of Aniline with Carbon Fibers and Foams

The prepared carbon materials were tested in the CWAO of aniline aqueous solutions. Figures 3a and 3b show the aniline (X_{ANL}) and TOC (X_{TOC}) removals after 5 h of reaction, respectively. At the conditions used, the non-catalytic oxidation of aniline cannot be neglected.

TABLE 3
Binding energies and relative surface concentrations of nitrogen species obtained by fitting the N1s core level XPS spectra

	N6 groups		N5 groups		N-Q groups		N-X groups	
Sample	B.E. (eV)	%	B.E.(eV)	%	B.E. (eV)	%	B.E. (eV)	%
FI-800°C-0 h	398.9	9.6	400.6	1.7	–	–	–	–
FI-800°C-10 h	398.4	3.7	400.4	2.7	401.7	1.6	404.0	0.4
FI-800°C-20 h	398.1	2.9	400.0	2.5	401.4	2.6	403.7	0.9
FI-850°C-0 h	398.4	6.2	400.3	3.4	401.7	2.3	404.2	0.8
FI-850°C-7 h	398.3	2.2	400.7	2.4	–	–	403.1	0.52
FI-850°C-12 h	398.5	3.0	400.8	3.1	–	–	402.9	0.1
FI-900°C-0 h	398.1	3.3	400.6	3.3	–	–	402.7	0.6
FI-900°C-3 h	398.4	1.8	400.7	2.1	–	–	402.4	1.1
FI-900°C-5 h	398.6	2.0	400.9	1.7	–	–	402.0	0.6
FO-700°C-0 h	398.8	3.3	400.7	4.0	–	–	–	–
FO-800°C-0 h	398.5	2.2	400.5	4.6	–	–	–	–
FO-900°C-0 h	398.1	1.7	400.5	0.1	–	–	–	–

However, it is evident that the efficiencies of aniline and TOC removal are increased, in general, when the carbon materials are used. In addition, for the fibers, both the aniline and TOC removal increase with the activation time for a given temperature of carbonization, and decrease with the temperature of carbonization for the same activation time (0 h). In the case of the foams, the removal of aniline was quite similar regardless of the temperature of carbonization used, while small increases on TOC removal were observed for carbonizations at higher temperatures. The highest efficiencies were obtained with the fiber carbonized at 850°C and activated during 12 h (FI-850°C-12 h). Several small peaks were observed in the HPLC chromatogram of the reaction samples indicating a complex reaction network, some traces corresponding to phenol and hydroquinone.

TABLE 4
Amounts of CO and CO_2 obtained from the TPD spectra and pH_{pzc} values of carbon materials

Sample	pH_{pzc}	CO ($\mu mol\,g^{-1}$)	CO_2 ($\mu mol\,g^{-1}$)	CO/CO_2
FI-800°C-0 h	7.5	3852	150	25.6
FI-800°C-10 h	7.2	607	110	5.5
FI-800°C-20 h	7.2	1495	141	10.6
FI-850°C-0 h	8.5	2945	144	20.4
FI-850°C-7 h	7.5	1253	152	8.3
FI-850°C-12 h	7.8	1415	95	14.9
FI-900°C-0 h	8.2	2261	142	15.9
FI-900°C-3 h	7.8	935	185	5.1
FI-900°C-5 h	7.9	952	263	3.6
FO-700°C-0 h	10.0	667	60	11.1
FO-800°C-0 h	10.0	480	146	3.3
FO-900°C-0 h	9.6	333	204	1.6

Figure 4 shows the evolution of the dimensionless aniline concentration as a function of reaction time in experiments performed:

(i) in the absence of any carbon material and using 5.0 MPa of pure N_2 (N_2),

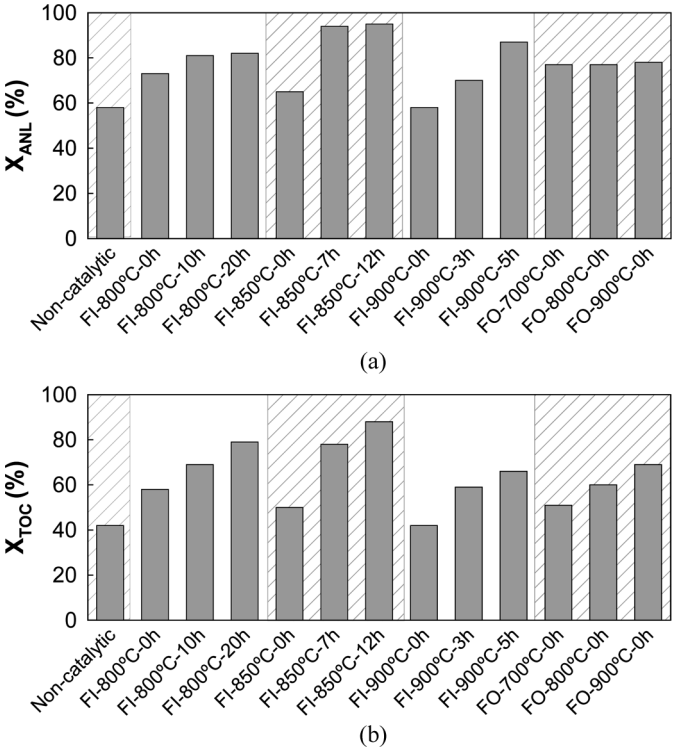

FIG. 3. Aniline removal X_{ANL} (a) and TOC removal X_{TOC} (b) after 5 h of reaction for non-catalytic and catalytic experiments.

(ii) in the presence of the fiber with the highest surface area and using the same N_2 atmosphere (N_2-FI-850°C-12 h), and
(iii) in the presence of the fibers carbonized at the same temperature with different activation times and using 5.0 MPa of pure air instead of N_2 (Air-FI-850°C-0 h, Air-FI-850°C-7 h and Air-FI-850°C-12 h).

Without a carbon material under inert atmosphere (N_2), part of the aniline (ca. 20%) seems to be transferred to the gas phase at the conditions employed, suggesting that a vapor-liquid equilibrium occurs. Aniline is thermally stable at the temperature used (200°C) since the aniline concentration reached after vapor-liquid equilibrium (ca. 80% of the initial load) is maintained until the end of the experiment. For comparative purposes, the results of aniline adsorption on the FI-850°C-12 h were obtained in the same N_2 atmosphere. The results suggest that this fiber adsorbs ca. 32% of aniline at these conditions. When oxygen is used, an additional decrease of the aniline concentration (ca. 34%) is observed due to oxidation. Therefore, there are three different contributions for the decay of the aniline concentration: vapor-liquid equilibrium, adsorption on the fiber, and oxidation reaction. Among all the carbon materials tested, the fiber carbonized at 850°C and activated for 12 h (FI-850°C-12 h) was the most efficient, which seems to be due, to some extent, to its higher surface area ($S_{BET} = 845\,m^2/g$). The total aniline and TOC removals were 95 and 88% after 5 h, while the values observed under non-catalytic conditions were 58% for aniline and 42% for TOC removal. The same run was repeated three times and the experimental errors determined for the aniline and TOC removals were never higher than 6 and 3%, respectively.

Additional experiments performed under inert atmosphere with fibers and foams presenting negligible surface areas (i.e., without activation −0 h) led to similar results (not shown) as those obtained for the vapor-liquid equilibrium (Fig. 4). As expected, the adsorption contribution is insignificant for these materials. However, when these materials were used in the catalytic experiments with air, differences were found in comparison with the non-catalytic experiment, in particular for the TOC removal (Fig. 3b). With these materials, the TOC removal is mainly due to the oxidation reaction and, therefore, it is possible to conclude that the fibers and foams submitted to carbonization without further activation (0 h) have similar textural properties (Table 1) but different performances in the oxidation of aniline. In this context, the presence of nitrogenated groups seems to influence the catalytic reaction. For instance, the fibers carbonized at 800 and 900°C, with nitrogen contents of 18 and 4%, show aniline conversions of 73 and 58%, respectively (Fig. 3a), and TOC removals of 58 and 42% (Fig. 3b). The advantage of using carbon

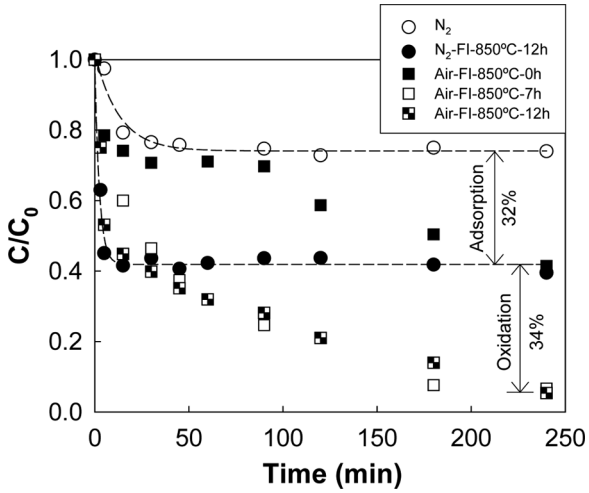

FIG. 4. Evolution of dimensionless aniline concentration during blank and catalytic wet air oxidation experiments for the fiber carbonized at 850°C and activated during 12 h (FI-850°C-12 h).

fibers enriched with nitrogen becomes obvious when the TOC conversions obtained with the fibers are plotted *versus* the N6 content, referred to the pyridinic-N group (Fig. 5). The white dot in this figure corresponds to a fiber that was prepared with a different amount of N6 groups and tested in the CWAO of aniline, just with the aim to corroborate the other results obtained with the three fibers that were thoroughly characterized in this work. Therefore, Fig. 5 shows that the total organic carbon removal is truly dependent on the content of pyridinic-N groups of the fiber through a linear function, since they are Lewis bases inducing basicity at the carbon surface by increasing the electron density (1,30) and, therefore, increasing the respective active sites for the removal of organic compounds.

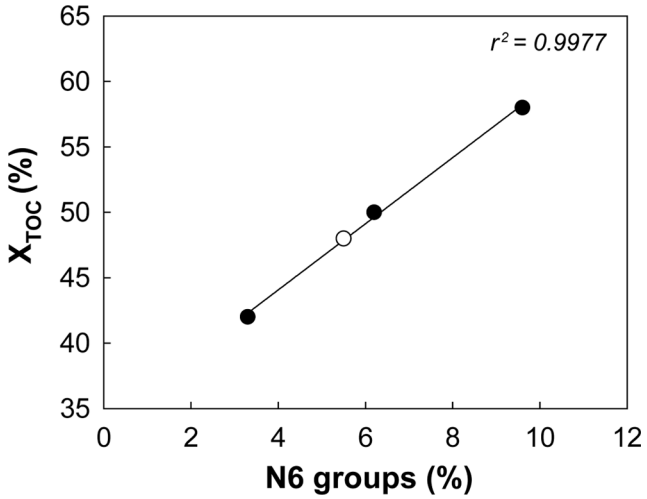

FIG. 5. TOC removal *vs* pyridinic-N content for the fibers submitted only to carbonization (0 h).

Regarding the foams, a different behavior was observed. The aniline removal (Fig. 3a) is not affected by the N6 content on the foam (Table 3) and the TOC removal increases when the N6 content of these materials decreases. In view of these results, it seems that the influence of N6 groups is dependent on the precursor used.

Since the stability of a catalyst is one important aspect in the global evaluation of its catalytic performance, the most efficient catalyst of this work (FI-850°C-12 h) was reused three times in consecutive CWAO reactions (Fig. 6a). Similar results were obtained in the second and third runs, indicating that the catalytic activity was maintained in consecutive experiments and that the actual removal of aniline with this fiber is around 80%. However, a decrease in the removal of aniline was observed from the first to the second run, which seems to be due to the lower adsorption capacity of the used catalyst. In fact, at the end of the experiment, a fraction of organic compounds will remain adsorbed onto the catalyst under the employed operating conditions. These compounds can be either a fraction of aniline and/or a fraction of the intermediates formed during the oxidation reaction. In order to analyze this effect, the measured adsorption contribution (Fig. 4) was suppressed from the aniline concentrations measured in the first CWAO run, namely $(C/C_0)_{1st\ run}$-$(C/C_0)_{ads}$. Figure 6b gathers all the differences observed during the three consecutive runs, and one can observe that they are usually lower than 15%. Regarding TOC removal, the values obtained after 5 h in the second and third runs were 58 and 60%, respectively, while in the first run the TOC removal was 88%, indicating that a fraction of organic compounds are adsorbed on the surface of the fiber.

Figure 7 shows the TPD spectra of the same fiber before (FI-850°C-12 h) and after (Air-FI-850°C-12 h) the CWAO experiment with aniline. The amount of CO_2 released after the reaction is higher than the amount released with the fresh sample, and the CO/CO_2 ratio of the fresh catalyst (14.9) was higher than that of the used catalyst (5.2). The change in the TPD spectra can be attributed to the decomposition of organic compounds adsorbed on the surface or to some modification on the fiber surface during the CWAO process.

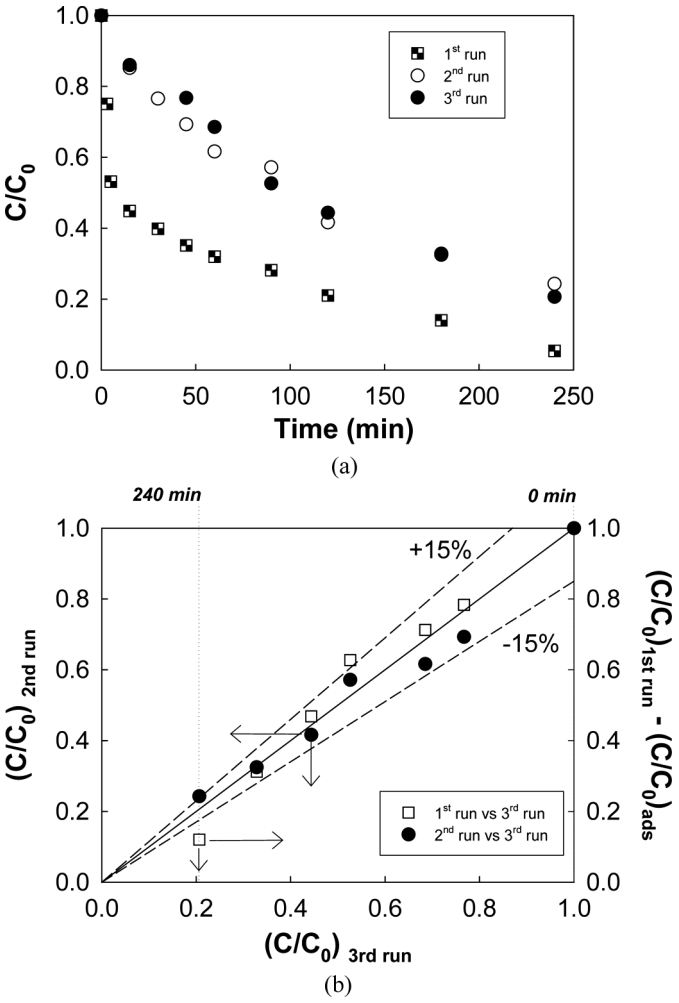

FIG. 6. Evolution of dimensionless aniline concentration during consecutive reutilization runs of the fiber carbonized at 850°C and activated during 12 h (FI-850°C-12 h).

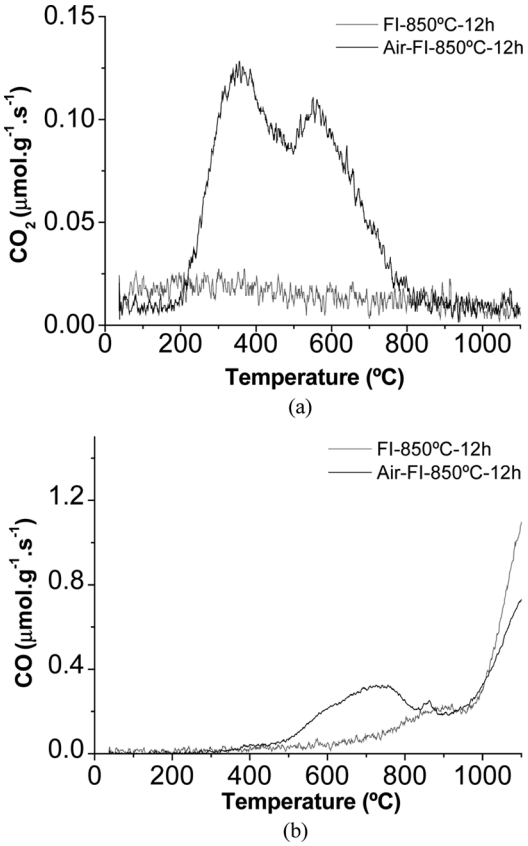

FIG. 7. TPD spectra for the fresh and used catalysts in terms of CO_2 (a) and CO (b) evolutions.

CONCLUSIONS

The use of carbonized and activated carbon foams and fibers enriched with nitrogen in catalytic wet air oxidation improves the removal of aniline and total organic carbon when compared to non-catalytic wet air oxidation. The N-containing carbon fiber treated at 850°C during 12 h shows the best performance in the removal of both aniline and total organic carbon content. This fiber is stable in three consecutive oxidation runs. A linear correlation was found between the total organic carbon removal and the pyridinic-N group content of the fibers carbonized without activation, indicating that the presence of this group increases the fiber efficiency. The same behavior was not observed for the foams tested.

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