



**HAL**  
open science

## Regeneration of Activated Carbon by (Photo)-Fenton Oxidation

Cynthia Tiemi Muranaka, Carine Julcour-Lebigue, Anne-Marie Wilhelm,  
Henri Delmas, Claudio A. O. Nascimento

► **To cite this version:**

Cynthia Tiemi Muranaka, Carine Julcour-Lebigue, Anne-Marie Wilhelm, Henri Delmas, Claudio A. O. Nascimento. Regeneration of Activated Carbon by (Photo)-Fenton Oxidation. Industrial and Engineering Chemistry Product Research and Development, 2010, 49 (3), pp.989-995. 10.1021/IE900675D . hal-03474305

**HAL Id: hal-03474305**

**<https://hal.science/hal-03474305>**

Submitted on 10 Dec 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>  
Eprints ID: 5849

**To link to this article:** DOI:10.1021/IE900675D

URL: <http://dx.doi.org/10.1021/IE900675D>

**To cite this version:** Muranaka, Cinthia T. and Julcour-Lebigue, Carine and Wilhelm, Anne-Marie and Delmas, Henri and Nascimento, Claudio A. O (2010) Regeneration of Activated Carbon by (Photo)-Fenton Oxidation. *Industrial & Engineering Chemistry Research*, vol. 49 (n°3). pp. 989-995. ISSN 0196-4321

Any correspondence concerning this service should be sent to the repository administrator: [staff-oatao@listes.diff.inp-toulouse.fr](mailto:staff-oatao@listes.diff.inp-toulouse.fr)

# Regeneration of Activated Carbon by (Photo)-Fenton Oxidation

Cíntia T. Muranaka,<sup>\*,†,‡</sup> Carine Julcour,<sup>\*,‡</sup> Anne-Marie Wilhelm,<sup>‡</sup> Henri Delmas,<sup>‡</sup> and Claudio A. O. Nascimento<sup>†</sup>

*Departamento de Engenharia Química, Escola Politécnica—Universidade de São Paulo USP, Cidade Universitária, São Paulo 05508-900, Brazil, and Laboratoire de Génie Chimique UMR CNRS 5503, Université de Toulouse, 4, allée Emile Monso, BP 84234, Toulouse cedex 4 - 31432, France*

This work aims to study the adsorption of phenol on activated carbons (ACs) and the consecutive in situ regeneration of carbon by Fenton oxidation. Two different operations have been carried out: (1) a batch procedure in order to investigate the influence of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations; (2) continuous fixed bed adsorption, followed by a batch circulation of the Fenton's reagent through the saturated AC bed, to examine the efficiency of the real process. Two different activated carbons have been also studied: a both micro- and mesoporous AC (L27) and an only microporous one (S23). In the batch reactor the best conditions found for pollutant mineralization in the homogeneous Fenton system are not the best for AC regeneration: a continuous reduction of adsorption capacity of L27 is observed after 3 oxidations, due to the decrease of both AC weight and surface area. Higher concentration of  $\text{Fe}^{2+}$  and lower concentration of  $\text{H}_2\text{O}_2$  (2 times the stoichiometry) lead to a 50% recovery of the initial adsorption capacity during at least four consecutive cycles for L27, while about 20% or less for S23. In the consecutive continuous adsorption/batch Fenton oxidation process, the regeneration efficiency reaches 30–40% for L27 after two cycles whatever the feed concentration and less than 10% for S23. A photo-Fenton test performed on L27 shows almost complete mineralization (contrary to "dark" Fenton) and further improves recovery of AC adsorption capacity although not complete (56% after two cycles).

## 1. Introduction

The study of advanced technologies for wastewater treatment has been intensified owing to the raising of public concern about health and related environmental effects.

Phenol and phenolic compounds are among the most prevalent chemical pollutants found in industrial wastewaters, due to their extensive use in petrochemical units, oil refineries, and the polymer and pharmaceutical industries.

Inhibitory effects of phenol on microbial activity have been reported for concentrations larger than 500 ppm.<sup>1,2</sup> Therefore high loaded effluents requires additional solutions to conventional biological treatment. Among possible techniques, adsorption on activated carbon (AC) is extensively applied, as it is most effective for removing relatively low-molecular-weight organic compounds such as surfactants, pesticides, dyes, and aromatic molecules.<sup>3</sup>

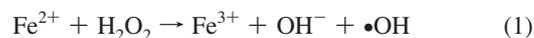
However, after adsorption of toxic compounds, activated carbon becomes itself a hazardous waste that must be treated or disposed properly. Incineration of spent activated carbons is often used, but it has some major drawbacks: its operating costs, the destruction of the adsorbent, as well as the emission of possibly toxic compounds, such as chlorodioxines and chlorodibenzofuranes when the activated carbon is saturated with organochloro compounds.<sup>4</sup>

The economical viability of processes using adsorption is thus directly related to their efficiency in regenerating and recycling the activated carbon. The most widely used technology is thermal regeneration. However, it presents the disadvantage of high energy consumption in keeping the temperature above 800 °C and carbon loss by burnoff. Another method used to

regenerate activated carbons is based on solvent extraction. Studies have shown that activated carbons generally do not recover their full adsorption capacity by this method due to residual solvent.<sup>5</sup> Moreover, it only again displaces pollution.

Advanced oxidation processes (AOPs) have been considered a promising alternative technology for the remediation of toxic organic compounds. AOPs are characterized by the production of free radicals, mainly the hydroxyl radical ( $\bullet\text{OH}$ ) that offers a high oxidation potential (2.8 V) and is able to oxidize a wide range of organic compounds. AOPs can be classified according to the different systems used to generate free radicals, such as the following:  $\text{O}_3/\text{UV}$  radiation,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$  radiation,  $\text{H}_2\text{O}_2/\text{UV}$  radiation,  $\text{TiO}_2/\text{UV}$  radiation,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$  radiation.<sup>6–8</sup> Those last two processes have been largely studied, known as the so-called Fenton and photo-Fenton systems, respectively.

The Fenton process consists in the generation of hydroxyl radicals by the reaction between ferrous ions and hydrogen peroxide (Fenton's reagent), according to eq 1:<sup>9</sup>



The degradation efficiency of this oxidation process is accelerated by UV light irradiation. UV radiation results not only in the formation of additional hydroxyl radicals but also in an improved regeneration of the ferrous catalyst by reduction of  $\text{Fe}^{3+}$  and destruction of ferric complexes. In this way, the overall reaction is accelerated and mineralization yield increased.<sup>10,11</sup>

Recently Fenton oxidation has been successfully applied for the recovery of carbons exhausted with chlorinated organic compounds<sup>12</sup> and methyl tert-butyl ether.<sup>13</sup>

$\text{H}_2\text{O}_2/\text{UV}$  radiation has also been reported for the regeneration of activated carbon saturated with acetone and isopropyl alcohol.<sup>14</sup>

The present work aims to destroy adsorbed phenol in order to in situ regenerate activated carbon by Fenton and photo-

\* To whom correspondence should be addressed. E-mail: cinthia.muranaka@poli.usp.br (C.T.M.); carine.julcour@ensiacet.fr (C.J.).

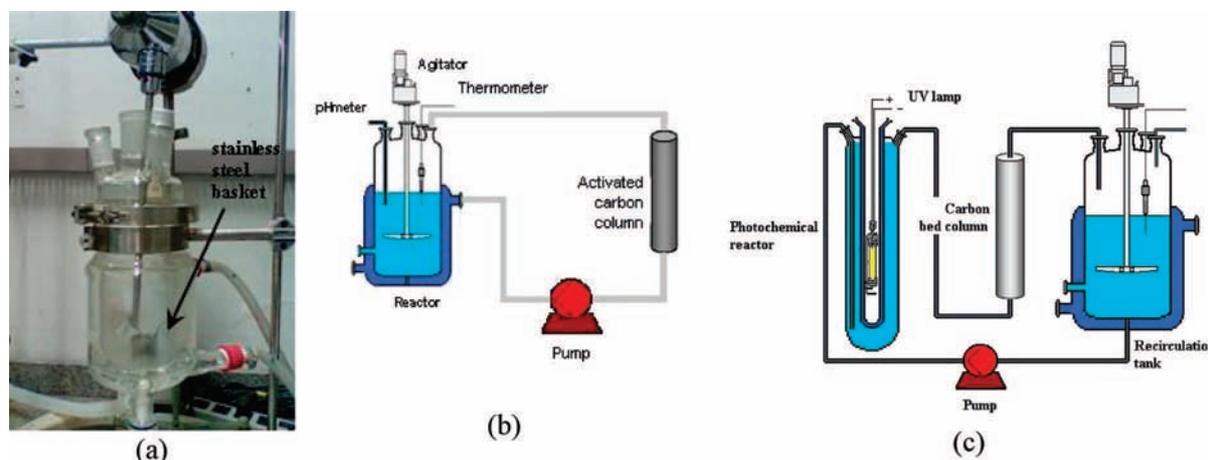
<sup>†</sup> Universidade de São Paulo.

<sup>‡</sup> Université de Toulouse.

**Table 1. Physical and Surface Chemical Properties of the Activated Carbons**

properties	specific surface area (m <sup>2</sup> /g)	microporous volume <sup>a</sup> (cm <sup>3</sup> /g)	mesoporous volume <sup>b</sup> (cm <sup>3</sup> /g)	C <sub>a</sub> <sup>c</sup> (mmol/g)	C <sub>b</sub> <sup>c</sup> (mmol/g)	pH <sub>PZC</sub> <sup>d</sup>
L27	1860	0.77	0.48	1.9	0.6	6.2
S23	1230	0.49	0.04	0.3	1.0	9.7

<sup>a</sup> Calculated from the Horvath–Kawazoe model.<sup>15</sup> <sup>b</sup> Calculated from the Barret–Joyner–Halenda method.<sup>16</sup> <sup>c</sup> C<sub>a</sub> and C<sub>b</sub> are the total concentrations of acidic and basic groups per gram of activated carbon, determined from Boehm titration.<sup>17</sup> <sup>d</sup> pH<sub>PZC</sub> is the pH at the point of zero charge (PZC).

**Figure 1.** Fenton ((a) batch reactor, (b) loop reactor) and photo-Fenton (c) setups used for the regeneration of activated carbon.

Fenton oxidations in very mild conditions. Compared to usual continuous oxidation treatment, very high conversion is no longer required in this sequential adsorption/oxidation process as water quality is provided by the adsorption step. Moreover, the preconcentration of target pollutants on the AC may minimize radical scavenging and there is no need to remove iron from the purified water (consumption of Fe<sup>2+</sup> is minimized).

The two-step process has been conducted using either a batch system (preliminary experiments to study the influence of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations) or a continuous fixed bed adsorption, followed by a batch circulation of the Fenton's reagent through the spent AC bed.

## 2. Materials

Ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>; 30%) were used as Fenton's reagents. Phenol was chosen as a model pollutant and the pH of the synthetic wastewater was adjusted by concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). During Fenton experiments, samples of the reactant mixture were withdrawn at different reaction times, and a quenching solution containing potassium iodide (KI, 0.1 mol/L), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>, 0.1 mol/L), and sodium hydroxide (NaOH, 0.1 mol/L) was added to stop the reaction. KI and Na<sub>2</sub>SO<sub>3</sub> decompose H<sub>2</sub>O<sub>2</sub>, and NaOH precipitates Fe<sup>2+</sup> ions. All reagents were analytical grade.

Two types of activated carbons were used, in the form of 1–1.6 mm diameter particles: a both micro- and mesoporous AC (PICA L27 from wood) and an essentially microporous AC (PICA S23 from coconut shell). Their physicochemical properties are given in Table 1.

## 3. Apparatus

The experimental setup used for Fenton experiments consisted in a 650 mL stirred Pyrex reactor, equipped with a jacket to control the temperature of the solution.

For preliminary batch experiments, AC was kept inside the reactor in a small basket (Figure 1a), whereas continuous

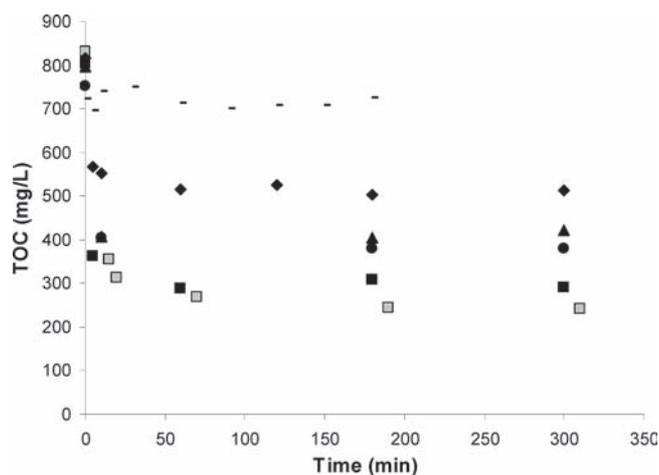
adsorption was carried out in a stainless steel column (18.5 cm high and 1.5 cm internal diameter) packed with AC. A peristaltic pump achieved the continuous feed of the phenol solution through the AC column during the adsorption step. The same pump was used to feed the column with the Fenton solution from the stirred reactor and back to it during the regeneration step (cf. Figure 1b).

For photo-Fenton experiments, an annular photochemical reactor was employed (cf. Figure 1c). A 80 W low pressure mercury UV lamp (Philips HPLN) was used as light source. It was placed in jacketed quartz well, immersed in a borosilicate vessel. The photochemical reactor was connected to the activated carbon column and to a stirred Pyrex tank. The total liquid volume of 2 L was circulated through the reactor and the column by a peristaltic pump.

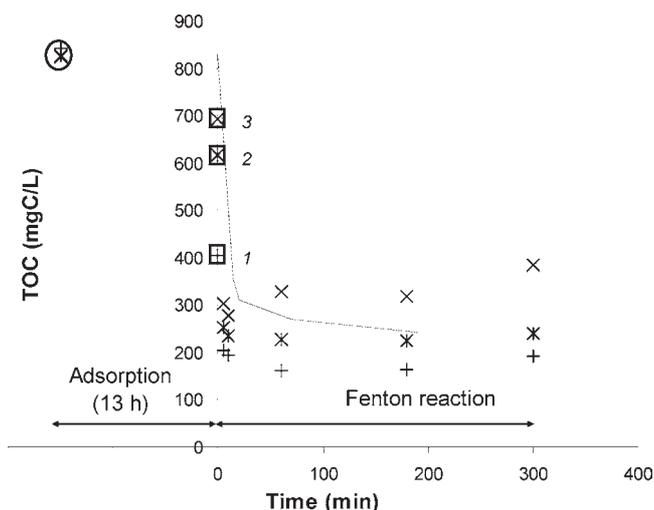
## 4. Experimental Procedures

**4.1. Batch Adsorption System.** The procedure consisted of two steps: (1) batch adsorption of phenol on activated carbon (contained in a basket); (2) Fenton oxidation. The weight of AC (S23 or L27) was chosen in order to adsorb half of the pollutant amount initially in the solution.

During the first step, 500 mL of 1 g/L phenol solution was contacted at 30 °C with the activated carbon under stirring until adsorption equilibrium was reached (after 13 h). Then, the pH of the solution was adjusted to 3.0 and the Fenton reaction was initiated by simultaneous addition of FeSO<sub>4</sub>·7H<sub>2</sub>O and hydrogen peroxide. After the reaction step, the solution was withdrawn and another batch adsorption was carried out with a new phenol solution using the same activated carbon. This procedure was repeated three consecutive times with the same operating conditions. Liquid samples were taken just after adsorption and regularly during oxidation (up to 5 h). Different concentrations of Fe<sup>2+</sup> (10–20 mmol/L) and H<sub>2</sub>O<sub>2</sub> (300–1000 mmol/L), corresponding to 2 to 6.5 times the stoichiometric amount for complete mineralization [The stoichiometric amount of H<sub>2</sub>O<sub>2</sub> required for the total oxidation of phenol was calculated based



**Figure 2.** TOC evolution during Fenton oxidation without AC:  $\text{H}_2\text{O}_2 = 0.50$  mol, no iron (-);  $\text{H}_2\text{O}_2 = 0.50$  mol,  $[\text{Fe}^{2+}] = 10$  mmol/L ( $\square$ );  $\text{H}_2\text{O}_2 = 0.15$  mol,  $[\text{Fe}^{2+}] = 1$  mmol/L ( $\blacklozenge$ );  $\text{H}_2\text{O}_2 = 0.15$  mol,  $[\text{Fe}^{2+}] = 10$  mmol/L ( $\blacksquare$ );  $\text{H}_2\text{O}_2 = 0.15$  mol,  $[\text{Fe}^{2+}] = 20$  mmol/L ( $\bullet$ );  $\text{H}_2\text{O}_2 = 0.15$  mol,  $[\text{Fe}^{2+}] = 25$  mmol/L ( $\blacktriangle$ ).



**Figure 3.** TOC evolution during batch adsorption–Fenton oxidation cycles with L27: exp 1 ( $\text{H}_2\text{O}_2 = 0.50$  mol,  $[\text{Fe}^{2+}] = 10$  mmol/L); (line) Fenton reaction without AC, (dots) successive regeneration cycles [first (+), second (\*), and third (x) cycles]. Empty circles and squares correspond to the beginning and end of adsorption, respectively.

**Table 2.** Regeneration Efficiency of L27 and S23 after Fenton Treatment (Batch Adsorption)

exp	AC	$m_{\text{AC}}$ (g)	$[\text{Fe}^{2+}]$ (mmol/L)	$\text{H}_2\text{O}_2$ (mol)	regeneration efficiency (%)			
					2nd cycle	3rd cycle	4th cycle	5th cycle
1	L27	1.70	10	0.50	52.3	43.0	22.8	
2	L27	1.70	20 <sup>a</sup>	0.15	40.3	52.7	43.6	37.0
3	L27	1.70	20	0.15	51.9	46.6	50.7	44.9
4	S23	0.87	20	0.15	30.6	24.8	22.1	16.6

<sup>a</sup> Added in two equal parts at  $t = 0$  and 60 min.

on following equation:  $\text{C}_6\text{H}_5\text{OH} + 14\text{H}_2\text{O}_2 \rightarrow 6\text{CO}_2 + 17\text{H}_2\text{O}$ ) were tested for AC regeneration.

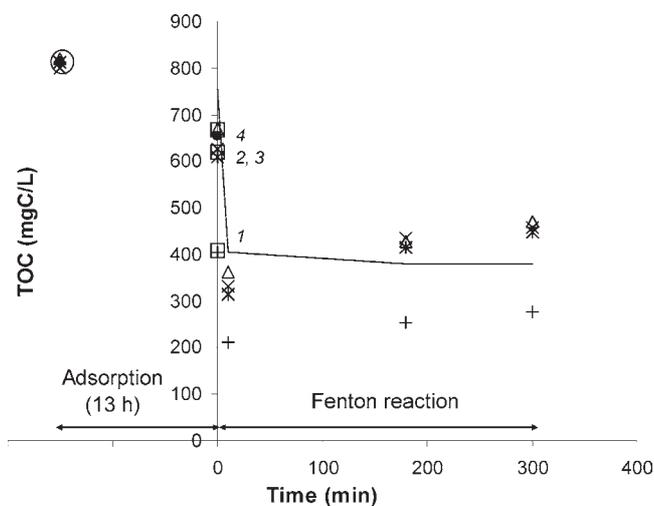
**4.2. Continuous Adsorption System.** In this operation, a 0.1 or 1 g/L phenol solution was continuously fed to the column with a flow rate of 2 L/h until saturation of the AC bed. Then, the stirred reactor was loaded with 500 mL of the same phenol solution which was recycled through the bed at 2–6 L/h. The reactor temperature was set to 30 °C, and the pH was adjusted to 3. The Fenton reaction was initiated by simultaneous addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and hydrogen peroxide. The oxidative regeneration step was carried out for 5–24 h. Then, the AC bed was drained to operate a new adsorption–oxidation cycle. Samples were regularly withdrawn at the column outlet during the two steps.

**4.3. Analytical Methods.** During the oxidation step, samples of the reacting solution were withdrawn and treated with the quenching solution (NaOH 0.1 mol/L, KI 0.1 mol/L and  $\text{Na}_2\text{SO}_3$  0.1 mol/L) in order to stop the oxidation process. After precipitation of iron and filtering, samples were analyzed for remaining total organic carbon (Shimadzu TOC 5050A analyzer).

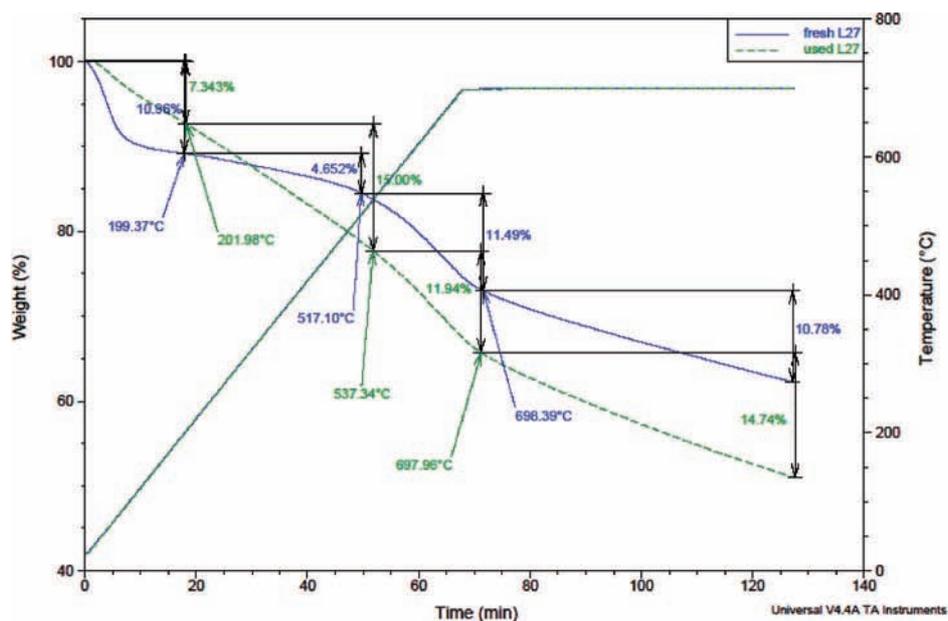
The samples were also analyzed by HPLC. The separation was achieved by a C18 reverse phase column (ProntoSIL C18 AQ) using a mobile phase of variable composition (acidified deionized water/acetonitrile). The dual wavelength UV detector (UV2000 Thermo Finnigan) was set at 210 and 254 nm. In this case, the quenching solution was made of NaOH 0.1 mol/L only (so that to precipitate  $\text{Fe}^{2+}$  and remove it from the samples), because KI and  $\text{Na}_2\text{SO}_3$  peaks detected by HPLC may interfere with the peaks of phenol and oxidation intermediates. As shown by the results of experiment without  $\text{Fe}^{2+}$  (Figure 2), removal of  $\text{Fe}^{2+}$  from the solution is enough to avoid any further decrease

of TOC within a few hours. Moreover, the samples were injected in the chromatograph immediately after the addition of NaOH.

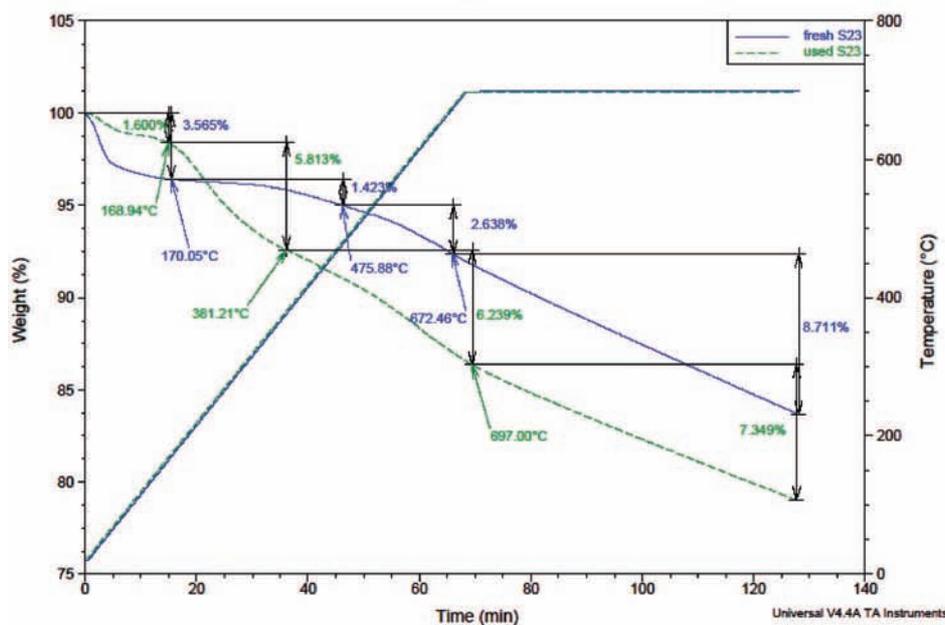
After the last adsorption–oxidation cycle, the spent activated carbons were characterized for BET surface area by measuring nitrogen adsorption isotherms at 77 K with an ASAP 2010 analyzer (Micromeritics). Thermogravimetry analysis (TGA) of the ACs was also performed under nitrogen flow from room temperature to 700 °C at a heating rate of 10 °C/min (Q600 SDT, TA Instrument). To further identify the compounds



**Figure 4.** TOC evolution during batch adsorption–Fenton oxidation cycles with L27: exp 3 ( $\text{H}_2\text{O}_2 = 0.15$  mol,  $[\text{Fe}^{2+}] = 20$  mmol/L); (line) Fenton reaction without AC, (dots) successive regeneration cycles [first (+), second (\*), third (x), and fourth ( $\Delta$ ) cycles]. Empty circles and squares correspond to the beginning and end of adsorption, respectively.



(a)



(b)

**Figure 5.** Thermograms of fresh/spent L27 (a) and fresh/spent S23 (b) (conditions of exps 2 and 4).

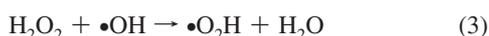
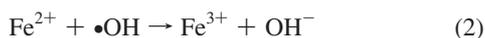
adsorbed on the activated carbon after the adsorption–oxidation cycles, pyrolysis–GC/MS of used carbons was carried out on a PY-2020iD coupled with a GCMS-QP2010 Plus (Frontier Lab) (590 °C pyrolysis temperature, 320 °C GC injector temperature, and 230 °C MS ion source temperature). Finally, scanning electron microscopy energy dispersive X-ray (SEM/EDX) analysis of the particles (on the surface and in the core) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of acidic leachates after contacting a few days with the ground particles were used to determine the iron content in the activated carbon after Fenton oxidation.

## 5. Results and Discussion

**5.1. Fenton Reaction without AC.** The homogeneous Fenton reaction was first investigated for the treatment of a 1 g/L

phenol solution (500 mL), varying the concentration of  $\text{Fe}^{2+}$  (from 0 to 25 mmol/L) and the amount of  $\text{H}_2\text{O}_2$  (from 0.15 to 0.50 mol). As shown in Figure 2, the highest mineralization was obtained for 10 mmol/L of  $\text{Fe}^{2+}$  and 0.50 mol of  $\text{H}_2\text{O}_2$ , leading to a steady TOC conversion of 71% after about 1 h of reaction. In all experiments with  $\text{Fe}^{2+}$ , phenol was depleted within 10 to 30 min.

A positive effect could be expected on TOC removal by raising the concentrations of Fenton's reagents. However, it has been observed that an excess of  $\text{Fe}^{2+}$  or  $\text{H}_2\text{O}_2$  can be detrimental for the process performance, because those species can subsequently react with the most active radical intermediates like  $\bullet\text{OH}$ , resulting in a competition with the organic compounds to be degraded,<sup>18,19</sup> as indicated in eqs 2 and 3.



Such an effect is noticeable here for  $\text{Fe}^{2+}$ , leading to a better TOC removal with 10 mmol/L than with higher concentrations.

**5.2. Batch Adsorption System.** The best Fenton conditions without AC were applied for the regeneration of L27 after it had reached adsorption equilibrium with the phenol solution (exp 1). As shown in Figure 3, the TOC reduction obtained in liquid phase by this sequential adsorption–oxidation process was higher than that observed without AC, at least during the first cycle. However in this case, the TOC vs time plot exhibited a minimum, due to desorption of both phenol and oxidation intermediates from AC.

For simplicity the regeneration efficiency was defined as the ratio of phenol amount re-adsorbed on AC after Fenton treatment to the initial amount adsorbed, even if a more proper definition should consider values at same equilibrium aqueous phase concentration. The calculations were also based on the initial weight of AC. Corresponding results are given in Table 2.

Using the Fenton conditions which led to the highest mineralization of the phenol solution, a continuous decrease of adsorption capacity of L27 from 100% to 23% was observed after three oxidations (exp 1). It could be explained not only by some remaining physisorbed pollutants, but also by a decrease of both surface area (from 1860 to 590  $\text{m}^2/\text{g}$ ) and AC weight (from 1.7 to 1.45 g after three cycles).

The modification of the chemical surface properties of the ACs by the Fenton's reagent could also be a reason for the lower adsorption observed after regeneration. A blank test (without pollutant) showed that this phenomenon contributed for 25% of the total capacity loss of L27 carbon in the conditions of exp 1.

A lower concentration of  $\text{H}_2\text{O}_2$  was used to reduce AC weight loss. Iron was added in two equal parts (at  $t = 0$  and 60 min) leading to a final concentration of 20 mmol/L (exp 2). Actually, a slight improvement was found when adding it in once at  $t = 0$  (exp 3). The results of exp 3 showed that the efficiency of phenol adsorption remained then practically constant at 50% for at least four adsorption–oxidation cycles (Table 2). The TOC evolution in the liquid phase exhibited also the same behavior from the second to the fourth adsorption–oxidation cycles (with an overall reduction of about 60% after 10 min), as shown in Figure 4.

No AC weight loss was observed and the surface area only decreased to 1020  $\text{m}^2/\text{g}$  in this case. A blank test in the same Fenton conditions resulted in a loss of adsorption capacity of only 2.5%.

These results confirm that the best conditions of Fenton's reagent without AC do not correspond to those leading to the highest regeneration yield of the activated carbon. A probable explanation is the attack of activated carbon surface by an excess of  $\text{H}_2\text{O}_2$  resulting in a loss of AC weight.

When later Fenton oxidation was applied to S23, the recovery of its adsorption capacity was found significantly lower and always decreasing. It was probably due to S23 microporous character, access to the micropores being partially blocked by condensation products resulting in a surface area divided by a factor of 6 (from 1230 to 210  $\text{m}^2/\text{g}$ ).

Deposit of such low-volatile compounds was also indicated by the comparison between TGA spectra of fresh and spent ACs: the weight loss between 200 and 700  $^\circ\text{C}$  increased from 16% to 27% for L27 (exp 2) and from 4% to 12% for S23 (exp 4). Corresponding thermograms are shown in Figure 5. This point was later investigated by pyrolysis–GC/MS of the carbons (cf. section 5.3).

**5.3. Continuous Adsorption System.** To mimic a real process, a continuous adsorption was achieved prior to the in situ regeneration. However the adsorption step was carried out up to complete AC saturation, so that the adsorption capacity of (fresh/regenerated) ACs could be calculated from numerical integration of the breakthrough curves (cf. Figure 8a). According to the previous results, the amount of  $\text{H}_2\text{O}_2$  added for the regeneration corresponded to about 2 times the stoichiometry for complete mineralization of phenol—adsorbed and in solution (exps 5–7). Results are shown in Table 3.

In accordance with previous batch observations, the Fenton treatment was much more efficient for L27 than for S23. An interesting result is that the recovery yield appeared to be almost independent of the feed concentration used in adsorption (0.1 or 1 g/L), despite the finding that the decrease of  $S_{\text{BET}}$  was higher when increasing the adsorbed pollutant amount.

Pyrolysis–GC/MS analysis at 590  $^\circ\text{C}$  identified the main compounds adsorbed on L27 AC during continuous adsorption–batch Fenton oxidation cycles. Phenol mostly but also oxidation intermediates (hydroquinone, resorcinol, and acetic acid) and phenolic dimer were detected on L27 after the last breakthrough (Figure 6). EGA-MS analysis mode indicated that acetic acid is released from 150 to 350  $^\circ\text{C}$  and should mainly result from acidic surface functions of the carbon. Phenol is also removed at relatively high temperatures (between 150 and 300  $^\circ\text{C}$ ). Phenol seems indeed to interact with AC through a chemisorption mechanism based on the bonding between phenol and oxygen-containing surface groups, which can progress to form phenol-derived polymers by an oxidative coupling mechanism. As reported previously, this mechanism could be one of the responsible for the pore blockage.<sup>20</sup>

The ICP-AES and SEM/EDX analyses showed very low amount of iron in the Fenton regenerated carbons (about 0.5 wt % in conditions of exp 5), due to some deposit on the surface, but not detected in the core of the particle.

**5.4. Photo-Fenton Regeneration.** During the Fenton oxidation, mineralization yield reached its maximum after 10 min to 1 h and never decayed afterward (cf. Figures 2–4). Such reaction inhibition could be explained by the formation of  $\text{Fe}^{3+}$ /carboxylic acids complexes with the degradation products (eq

**Table 3. Regeneration Efficiency of L27 and S23 after Fenton Treatment (Continuous Adsorption)<sup>a</sup>**

exp	AC	$m_{\text{AC}}$ (g)	phenol feed (g/L)	$[\text{Fe}^{2+}]$ (mmol/L)	$\text{H}_2\text{O}_2$ (mol)	regeneration efficiency (%)			$S_{\text{BET}}$ decrease (%)
						2nd cycle	3rd cycle	4th cycle	
5	S23	6.0	0.1	20 <sup>b</sup> –40 <sup>c</sup>	0.25 <sup>b</sup> –0.35 <sup>c</sup>	11.8	7.8		60.0
6	L27	9.8	0.1	20	0.25	37.7	29.5	29.9	39.6
7	L27	9.8	1.0	20	0.74 <sup>d</sup>	47.3	31.2		71.3
8 <sup>e</sup>	L27	8.4	1.0	2	0.62 <sup>f</sup>	49.4	40.5		48.3

<sup>a</sup>  $t_{\text{oxidation}} = 5$  h with  $Q_{\text{recirculation}} = 6$  L/h if not mentioned otherwise. <sup>b</sup> 1st cycle ( $t_{\text{oxidation}} = 24$  h,  $Q_{\text{recirculation}} = 2$  L/h). <sup>c</sup> 2nd cycle ( $Q_{\text{recirculation}} = 2$  L/h). <sup>d</sup> Added in four equal parts. <sup>e</sup> Liquid volume = 2 L. <sup>f</sup> Added in four equal parts and equivalent to 1.1 times the stoichiometry for complete mineralization ( $Q_{\text{recirculation}} = 2$  L/h).

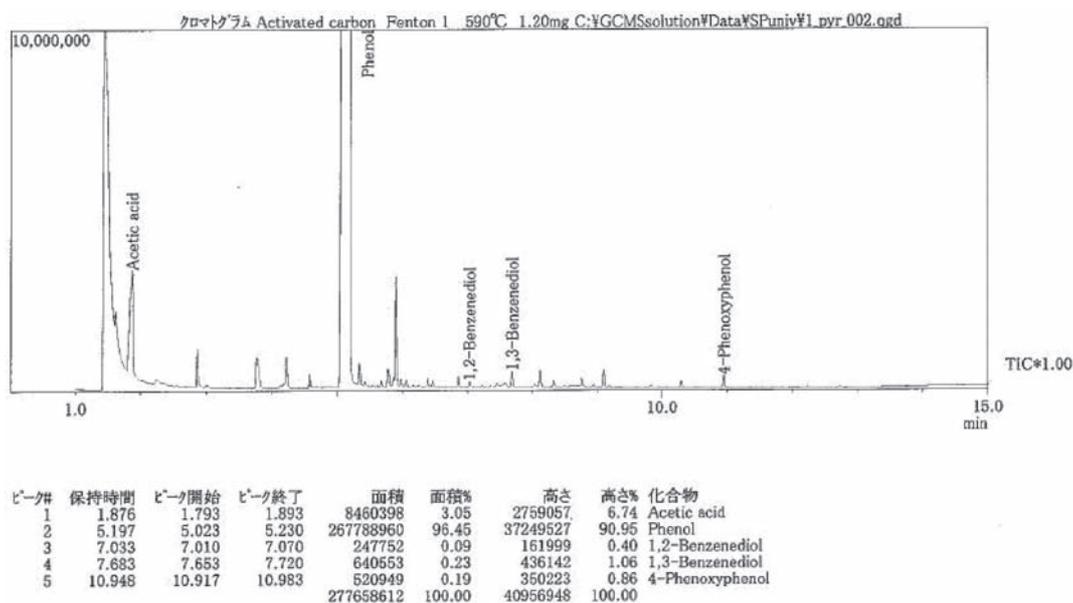


Figure 6. Pyrogram of spent L27 (conditions of exp 8).

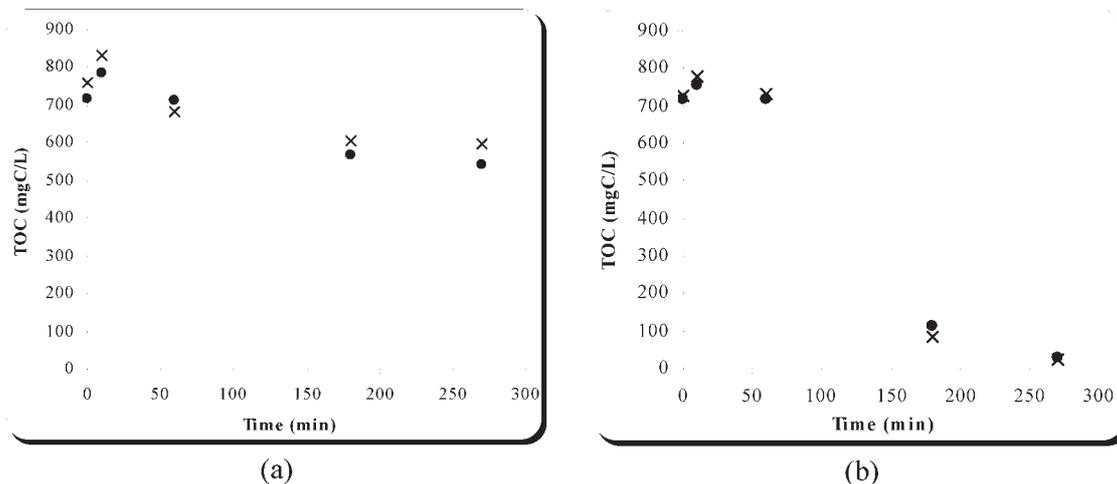


Figure 7. TOC evolution in solution during regeneration of L27 using Fenton (a) and photo-Fenton (b) oxidation (conditions of exp 8): first (•) and second (x) oxidation.

4). These complexes are stable in usual Fenton conditions, hindering the  $\text{Fe}^{2+}$  regeneration:<sup>21,22</sup>



UV radiation is expected to play an important role in the destruction of  $\text{Fe}^{3+}$ /carboxylic acids complexes according to eq 5.



The radical  $\text{R}\cdot$  can react with oxygen and degrade further.

UV light can also enhance mineralization by the photoreduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (eq 6), accelerating  $\text{Fe}^{2+}$  regeneration and generating additional hydroxyl radicals.



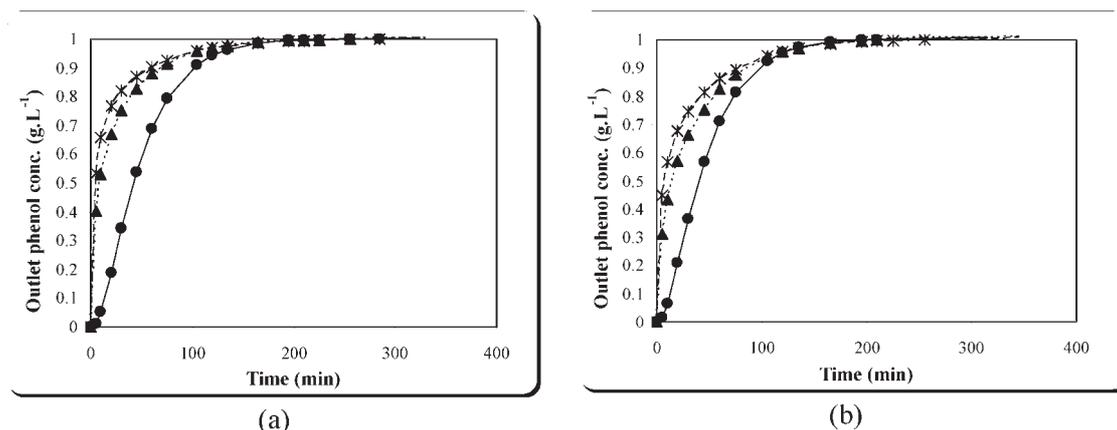
The photogenerated  $\text{Fe}^{2+}$  from eqs 5 and 6 can participate in Fenton's reaction (eq 1), generating additional hydroxyl radicals.

Another UV contribution to enhanced mineralization, but to a less extent, is the photolysis of hydrogen peroxide, as shown in eq 7.



The effect of UV radiation was investigated for the conditions of exp 8. During the oxidation step, 95% mineralization was achieved in solution after 4 h with photo-Fenton, while only 25% with the usual ("dark") Fenton, as shown in Figure 7.

Figure 8a and b compare the corresponding adsorption curves after Fenton and photo-Fenton treatments. Although the adsorption capacity of L27 decreased upon recycling in both cases, it could be maintained to 56% of its original capacity after two cycles with photo-Fenton oxidation (against 40% with dark Fenton). The change in BET surface area appeared to be the same after both treatments, as well as the nature of adsorbed compounds (from pyrolysis-GC/MS analysis).



**Figure 8.** Successive breakthrough curves of phenol with L27 carbon after Fenton (a) and photo-Fenton (b) regeneration (adsorption step: flow rate = 2 L/h, solution feed = 1 g/L; oxidation step: conditions of exp 8): fresh AC (●), AC after first (▲), and second (\*) adsorption-oxidation cycle.

## 6. Conclusions

The experimental results presented in this work proved Fenton and photo-Fenton processes to be applicable to regenerate spent activated carbons saturated with phenol.

The regeneration efficiency was found to be a complex interplay between the mineralization yield and the modification of both textural and chemical surface properties of the activated carbons.

Concerning Fenton treatment, a lower recovery of phenol adsorption capacity was obtained for the microporous AC (S23) than for the both meso- and microporous AC (L27), whatever the system considered (spent AC immersed in the Fenton solution or circulation of the reagent through the saturated AC bed). It may be explained by a significant decrease of S23 specific area after the oxidation steps, even if in case of L27 similar performances could be obtained for different aging of the AC.

It was also found that UV irradiation improved the mineralization yield and the subsequent readsorption (by more than 15% compared to dark Fenton treatment).

## Acknowledgment

The authors express their gratitude to the ALFA-Programme, the sixth FP "REMOVALS", INP-ENSIACET, and ANR (Precodd "PHARE") for financial support. They also thank PICA (Veolia group) for supplying S23 and L27 ACs, M. Auriol and C. Rouch (SAP, LGC, Toulouse) for AC characterization, and J. L. Labat for the design and implementation of the Fenton experimental setup.

**Note Added after ASAP Publication:** Changes have been made to Table 3 in the version of this paper that was published on the Web November 4, 2009. The corrected version was reposted December 15, 2009.

## Literature Cited

- (1) Uygur, A.; Kargi, F. Phenol Inhibition of Biological Nutrient Removal in a Four-step Sequencing Batch Reactor. *Process Biochem.* **2004**, *39*, 2123.
- (2) Amat, A. M.; Arques, A.; Beneyto, H.; García, A.; Miranda, M. A.; Seguí, S. Ozonisation Coupled with Biological Degradation for Treatment of Phenolic Pollutants: a Mechanistically Based Study. *Chemosphere* **2003**, *53*, 79.
- (3) Juang, R. S.; Wu, F. C.; Tseng, R. L. Characterization and Use of Activated Carbons Prepared from Bagasses for Liquid-phase Adsorption. *Colloids Surf. A* **2002**, *201*, 191.
- (4) Okawa, K.; Suzuki, K.; Takeshita, T.; Nakano, K. Regeneration of Granular Activated Carbon with Adsorbed Trichloroethylene Using Wet Peroxide Oxidation. *Water Res.* **2007**, *41*, 1045.
- (5) Martin, R. J.; Ng, W. J. The Repeated Exhaustion and Chemical Regeneration of Activated Carbon. *Water Res.* **1987**, *21* (8), 961.

- (6) Zhang, F.; Zhao, J.; Shen, T.; Hidaka, H.; Pelizzetti, E.; Serpone, N. TiO<sub>2</sub>-assisted Photodegradation of Dye Pollutants II. Adsorption and Degradation Kinetics of Eosin in TiO<sub>2</sub> Dispersions under Visible Light Irradiation. *Appl. Catal., B* **1998**, *15*, 147.

- (7) Alnaizy, R.; Akgerman, A. Advanced Oxidation of Phenolic Compounds. *Adv. Environ. Res.* **2000**, *4*, 233.

- (8) Azbar, N.; Yonar, T.; Kestioglu, K. Comparison of Various Advanced Oxidation Processes and Chemical Treatment Methods for COD and Color Removal from a Polyester and Acetate Fiber Dyeing Effluent. *Chemosphere* **2004**, *55*, 35.

- (9) Walling, C. Fenton's Reagent Revisited. *Acc. Chem. Res.* **1975**, *8*, 125.

- (10) Momani, F. A.; Sans, C.; Esplugas, S. A Comparative Study of the Advanced Oxidation of 2,4-dichlorophenol. *J. Hazard. Mater. B* **2004**, *107*, 123.

- (11) Kavitha, V.; Palanivelu, K. The Role of Ferrous Ion in Fenton and photo-Fenton Processes for the Degradation of Phenol. *Chemosphere* **2004**, *55*, 1235.

- (12) Toledo, L. C.; Bernades Silva, A. C.; Augusti, R.; Montero Lago, R. Application of Fenton's Reagent to Regenerate Activated Carbon Saturated with Organochloro Compounds. *Chemosphere* **2003**, *50*, 1049.

- (13) Huling, S. G.; Jones, P. K.; Ela, W. P.; Arnold, R. G. Fenton-driven chemical regeneration of MTBE-spent GAC. *Water Res.* **2005**, *39*, 2145.

- (14) Horng, R. S.; Tseng, I. C. Regeneration of Granular Activated Carbon Saturated with Acetone and Isopropyl Alcohol via a Recirculation Process under H<sub>2</sub>O<sub>2</sub>/UV Oxidation. *J. Hazard. Mater.* **2008**, *154*, 366.

- (15) Horvath, G.; Kawazoe, K. Method for Calculation of Effective Pore Size Distribution in Molecular Sieve Carbon. *J. Chem. Eng. Jpn.* **1983**, *16*, 470.

- (16) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373.

- (17) Boehm, H. P. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon* **1994**, *32* (5), 759.

- (18) Maciel, R.; Sant'Anna, G. L., Jr.; Dezotti, M. Phenol Removal from High Salinity Effluents using Fenton's Reagent and Photo-Fenton Reactions. *Chemosphere* **2004**, *57*, 711.

- (19) Torrades, F.; Pérez, M.; Mansilla, H. D.; Peral, J. Experimental Design of Fenton and photo-Fenton Reactions for the Treatment of Cellulose Bleaching Effluents. *Chemosphere* **2003**, *53*, 1211.

- (20) Santiago, M.; Stüber, F.; Fortuny, A.; Fabregat, A.; Font, J. Modified Activated Carbons for Catalytic Wet Air Oxidation of Phenol. *Carbon* **2005**, *43*, 2134.

- (21) Safarzadeh-Amiri, A. S.; Bolton, J. R.; Cater, S. R. Ferrioxalate-mediated Photodegradation of Organic Pollutants in Contaminated Water. *Water Res.* **1997**, *31* (4), 787.

- (22) Balanosky, E.; Herrera, F.; Lopez, A.; Kiwi, J. Oxidative Degradation of Textile Wastewater. Modeling Reactor Performance. *Water Res.* **2000**, *34* (2), 582.