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# Performance of Iron-Functionalized Activated Carbon Catalysts (Fe/AC-*f*) on CWPO Wastewater Treatment

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Abstract: Two commercial activated carbon were functionalized with nitric acid, sulfuric acid, and ethylenediamine to induce the modification of their surface functional groups and facilitate the stability of corresponding AC-supported iron catalysts (Fe/AC-f). Synthetized Fe/AC-f catalysts were characterized to determine bulk and surface composition (elemental analysis, emission spectroscopy, XPS), textural (N<sub>2</sub> isotherms), and structural characteristics (XRD). All the Fe/AC-f catalysts were evaluated in the degradation of phenol in ultrapure water matrix by catalytic wet peroxide oxidation (CWPO). Complete pollutant removal at short reaction times (30-60 min) and high TOC reduction  $(X_{TOC} = 80 \% \text{ at} \le 120 \text{ min})$  were always achieved at the conditions tested (500 mg·L<sup>-1</sup> catalyst loading, 100 mg·L<sup>-1</sup> phenol concentration, stoichiometric H<sub>2</sub>O<sub>2</sub> dose, pH 3, 50 °C and 200 rpm), improving the results found with bare activated carbon supports. The lability of the interactions of iron with functionalized carbon support jeopardizes the stability of some catalysts. This fact could be associated to modifications of the induced surface chemistry after functionalization as a consequence of the iron immobilization procedure. The reusability was demonstrated by four consecutive CWPO cycles where the activity decreased from 1st to 3rd, to become recovered in the 4th run. Fe/AC-f catalysts were applied to treat two real water matrices: the effluent of a wastewater treatment plant with a membrane biological reactor (WWTP-MBR) and a landfill leachate, opening the opportunity to extend the use of these Fe/AC-f catalysts for complex wastewater matrices remediation. The degradation of phenol spiked WWTP-MBR effluent by CWPO using Fe/AC-f catalysts revealed pH of the reaction medium as a critical parameter to obtain complete elimination of the pollutant, only reached at pH 3. On the contrary, significant TOC removal, naturally found in complex landfill leachate, was obtained at natural pH 9 and half stoichiometric H<sub>2</sub>O<sub>2</sub> dose. This highlights the importance of the water matrix in the optimization of the CWPO operating conditions.

**Keywords:** functionalized activated carbon; supported iron catalysts; CWPO; hydrogen peroxide; WWTP effluent water matrix; landfill leachate

# 1. Introduction

The stringent national and EU regulations [1–6] force to implement tertiary treatments with the aim to fulfill the adequate harmlessness of discharges [3,7–10]. Advanced oxidation processes (AOPs) have acquired increasing interest as an alternative to refine outlet effluents from wastewater treatment plants (WWTPs) [6,11,12]. Among them, catalytic wet peroxide oxidation (CWPO) has promising characteristics to become efficiently applied to real cases [6,13–20]. AOPs are based on the generation of highly reactive hydroxyl radicals (HO<sup>•</sup>), which have an unselective capability to provoke oxidation of many organic pollutants [1,15,21–27]. Specifically, in the case of CWPO, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is the oxidizing agent used for HO<sup>•</sup> formation (E<sup>0</sup> HO<sup>•</sup>/H<sub>2</sub>O<sub>2</sub> = 2.73 V) [13]. CWPO, considered



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the heterogeneous version of the well-known Fenton process, emerged to palliate the inconveniences of homogeneous treatments, such as the generation of secondary contamination due to iron sludge, or the high reagents consumption [13,19]. Contrarily, heterogeneous CWPO treatment is a more efficient procedure when the catalyst can be recycled and recovered, contributing to reduce the consumption of reactants and therefore, the global cost. However, the immobilization of iron, or alternative metals [14,28], on the support, frequently presents detrimental effects in the activity of the oxidation process [29,30]. The selection of high specific surface area supports has been commonly assumed to distribute a high loading of active metal with high dispersion and particle size uniformity [28,31,32]. Additional advantages are desired for the support to provide multifunctional catalysts with added values as adsorption capacity, low metal loading, regeneration of metal species, wide range of operating pH or in situ generation of hydroxyl radical source [13,16,33]. In this sense, the use of magnetic supports [34,35], or the presence of immobilized magnetic particles could play the double role of CWPO catalytic site and easy recoverability [1,14,36,37], where the coupling of an electro-magnetic field [2] or microwave [4,16,27] has shown to improve the CWPO performance. The objective of many published research focuses on the development and performance of efficient catalysts in the decomposition of  $H_2O_2$  into HO<sup>•</sup>, synchronized with the demand for oxidation of organic compounds in the reaction medium, in order to constrain the costs involved in the process [4,5,21,38,39].

Despite the huge effort dedicated to investigate new, active, stable, and recoverable multifunctional catalysts for the CWPO process, carbonaceous materials (among other high surface area supports) maintain the relevance as polyvalent support which could be customized, inducing changes in their surface [5,8,35,40–44]. The role of chemical nature of carbon surface is important for the adsorption of contaminants and oxidants, the immobilization of metal, the stability and the redox regeneration of active sites, the efficiency in the formation of hydroxyl radicals, and durability of catalysts, among others [8,21,26,27,41]. The surface of carbons has a high reactivity, and development of functionalization is relatively easy, although it could be reversible. Another interesting feature of carbonaceous materials, and more specifically, activated carbons (AC), is the elevated specific surface area, usually >1000 m<sup>2</sup> · g<sup>-1</sup>, and their complex pore network, mainly due to micropore size. Functionalization is frequently accompanied by mesopore generation which could favor the accessibility to inner pores, increase the density of attainable active sites and speed the reaction kinetics by increasing the contact surface.

In these circumstances, the main goal of this work has been the study of Fe/AC-*f* catalysts to assess their application in two real water matrices: effluent of a wastewater treatment plant with a membrane biological reactor (WWTP-MBR) and a landfill leachate. The following targets were sequentially faced: (i) The modification of activated carbons surface to induce acidic/basic properties; (ii) preparation of iron supported on functionalized activated carbons catalysts (Fe/AC-*f*); (iii) evaluation of the influence of the functionalized surface of Fe/AC-*f* catalysts on the stability and CWPO activity in phenol degradation, and, finally; (iv) application of CWPO with Fe/AC-*f* catalysts to degrade phenol spiked in a WWTP effluent matrix and mineralization of organic matter naturally present in a complex landfill leachate. All the steps lead to the ultimate aim to extent the use of these Fe/AC-*f* catalysts to the removal of pollutants from complex effluents by CWPO.

## 2. Result and Discussion

# 2.1. Physicochemical Characterization Studies

XRD pattern of the two series of prepared Fe/AC-*f* catalysts are analogous (Figure S1). They exhibit three principal wide peaks, characteristic of poor crystalline solids, at 20 values of 26°, 43°, and 79°, which correspond to graphite phase (ICDD PDF File 001-0646) and were assigned to (002), (100)-(101), and (110) planes. Additionally, a less intense narrow peak circa 27° was observed in both Fe/AC-*f* catalyst series. It was identified as SiO<sub>2</sub>-Quartz (ICDD PDF File 046-1045). The Fe/CN and Fe/CN-*f* catalysts showed the

presence of secondary narrow peaks at 20 22°, 31°, 36°, 47°, 58°, and 68°, approximately, identified as SiO<sub>2</sub>-Cristobalite (ICDD PFD File 003-0272).

All the functionalized Fe/AC-*f* catalysts exhibited type Ib isotherms with H4 hysteresis loop (Figure S2) [45], previously ascribed to essentially microporous solids with presence of mesoporosity with slit shape [46]. The functionalization process and further catalysts preparation procedure had different detrimental effects on the textural properties, as can be observed in Table 1. Whereas only a 6–16% decrease was observed in the pore volume (<50  $\mu$ m), the micropore volume was more sensitive to the functionalization treatment, ranged almost 40% of loss, probably due to the blockage of narrow porosity by iron deposits and partial loss of the carbon network, by combustion, during heat treatment in the final stage of the catalyst preparation procedure [4,47]. With respect to the BET surface area, 8–28% maximum reduction was found for Fe/CM-*f* and Fe/CN-*f* catalysts, respectively.

Elemental and chemical analyses (Table 2) proved the efficiency of acidic functionalization, quantified by the amount of oxygen present in the catalysts which became between two-fold and five-fold higher than those in the raw AC. The increase in oxygenated groups on Fe/AC-*f* catalysts had a reduction effect on the carbon content. Likewise, the results evidenced the rise of nitrogen and sulfur content in the case of ethylenediamine (Fe/CM-B and Fe/CN-B) or sulfuric acid functionalization (Fe/CM-A and Fe/CN-A), respectively. Nevertheless, the amount of oxygen became significantly increased when compared to bare carbon support. Even in the case of Fe/CM and Fe/CN catalysts an important rise in oxygen content was observed, which has been previously associated to the acidic nature of iron nitrate salt used for the impregnation stage and further heat treatment in air atmosphere. Both circumstances seem to be inherent to the growth of oxygen percentage in the basic functionalized Fe/CN-B and Fe/CM-B catalysts; and all the Fe/AC-f catalysts in general [48]. Contrarily, the nitrogen content of nitric acid treated Fe/AC-f catalysts (Fe/CM-O and Fe/CN-O) showed similar values to those non-modified. The procedure of preparation of Fe/AC-f catalysts was efficient and the iron was quantitatively incorporated despite the functionalization performed on the AC supports.

Sample	$S_{BET}$ (m <sup>2</sup> ·g <sup>-1</sup> )	$A_{External}$ (m <sup>2</sup> ·g <sup>-1</sup> )	${f A_{Micropore}}\ (m^2 {\cdot} g^{-1})$	$V_{Micropore}$ (cm <sup>3</sup> ·g <sup>-1</sup> )	$V_{Total}$ (cm <sup>3</sup> ·g <sup>-1</sup> )
СМ	967	105	862	0.36	0.52
Fe/CM	934	104	830	0.35	0.50
Fe/CM-O	940	169	771	0.30	0.49
Fe/CM-A	827	103	724	0.33	0.43
Fe/CM-B	888	125	763	0.30	0.44
CN	1297	110	1187	0.47	0.57
Fe/CN	1228	193	1035	0.39	0.53
Fe/CN-O	932	176	756	0.29	0.48
Fe/CN-A	1164	141	1023	0.41	0.54
Fe/CN-B	1202	140	1062	0.42	0.55

Table 1. Textural characteristics of Fe/AC-f catalysts and corresponding raw AC.

**Table 2.** Elemental analysis of Fe/AC-*f* and raw AC (%, *w*/*w*, d.b.).

Catalyst	С	Н	Ν	S	0 *	Ashes	Fe
СМ	$89.5 \pm 1.8$	$0.7\pm0.1$	$0.5\pm0.1$	$0.7\pm0.1$	$3.9\pm0.4$	$4.7\pm0.5$	-
Fe/CM	$75.4 \pm 1.5$	$1.3 \pm 0.2$	$0.8\pm0.1$	$0.8\pm0.1$	$12.4 \pm 1.3$	$9.3 \pm 0.9$	$4.3 \pm 0.4$
Fe/CM-O	$72.0 \pm 1.4$	$1.4 \pm 0.2$	$0.7\pm0.1$	$0.7 \pm 0.1$	$18.6 \pm 1.9$	$6.6 \pm 0.7$	$3.9 \pm 0.3$
Fe/CM-A	$79.8 \pm 1.6$	$1.1 \pm 0.2$	$0.7\pm0.1$	$1.0 \pm 0.2$	$11.1 \pm 1.1$	$6.3 \pm 0.6$	$3.6 \pm 0.3$
Fe/CM-B	$72.4\pm1.4$	$1.6\pm0.2$	$2.4\pm0.3$	$0.7\pm0.1$	$14.6\pm1.5$	$7.3\pm0.7$	$4.4\pm0.4$
CN	$86.7 \pm 1.8$	$1.0 \pm 0.1$	$0.6\pm0.1$	$0.7\pm0.1$	$2.7\pm0.4$	$8.3\pm0.3$	-
Fe/CN	$81.2 \pm 1.6$	$1.0 \pm 0.1$	$0.6 \pm 0.1$	$0.6 \pm 0.1$	$5.7\pm0.6$	$10.9 \pm 1.1$	$3.8 \pm 0.3$
Fe/CN-O	$71.8 \pm 1.4$	$1.5 \pm 0.2$	$0.8\pm0.1$	$0.4 \pm 0.1$	$17.9 \pm 1.8$	$7.6 \pm 0.8$	$4.3 \pm 0.4$
Fe/CN-A	$74.4 \pm 1.5$	$1.1 \pm 0.1$	$0.6\pm0.1$	$1.5\pm0.2$	$15.1 \pm 1.6$	$7.3 \pm 0.7$	$4.1\pm0.4$
Fe/CN-B	$75.2 \pm 1.5$	$1.3\pm0.1$	$2.4\pm0.3$	$0.3\pm0.1$	$12.9\pm1.3$	$7.9\pm0.8$	$4.5\pm0.4$

\* By difference: %O = 100 - (%C + %H + %N + %S + %Ashes).

XPS spectra (Figure 1) were very similar for all the Fe/AC-f catalysts, Fe/CN-Bwas chosen as example to qualitatively show the multiple signals observed for major components, C1s, O1s, and Fe2p. The C1s region presented the typical shape for AC, with the six signals at 284.4 eV, 285.2 eV, 286.0 eV, 287.1 eV, 288.5 eV, and 290.5 eV usually assigned to aromatic C, aliphatic C (defects), C-OH or C-O-C, C=O, COOH, or COOC and  $\pi \rightarrow \pi^*$ , respectively [20,49]. Regarding the O1s spectral region, five contributions could be found (Table 3). The peak at 530.0 eV was identified as Fe-O, and the relative percentage corresponds to the surface iron content encountered (Table 2). 531.5 eV and 532.9 eV signals were assigned to C=O and C-O, with analogous contributions for all the catalysts. The highest difference appeared for oxygen signal at 534.0 eV, due to COOH. In this case Fe/CM-B and Fe/CN-B catalyst, functionalized with ethylenediamine, exhibited a significantly lower contribution, whose formation could be induced during impregnation with  $Fe(NO_3)_3 \cdot 9H_2O$  and further heat treatment [48]. Finally, the contribution of adsorbed H<sub>2</sub>O was at 536.0 eV, also lower in the basic functionalized catalysts (Fe/CM-B and Fe/CN-B). Concerning iron spectral region,  $Fe^{3+}$  was confirmed in all the Fe/AC-*f* catalysts according to Fe2p peaks position (Table 4), at 711.2  $\pm$  0.2 eV and 724.6  $\pm$  0.1 eV and the satellite pike at 718.2  $\pm$  0.2 eV [20,31,50,51].



Figure 1. XPS spectra of C1s, O1s, and Fe2p region for Fe/CN-B catalyst. All the Fe/AC-f catalysts present analogous signals.

Despite the bulk quantitative composition determined by elemental and chemical analyses, the different elements could be non-uniformly distributed, accumulating at the surface or in the inner walls of narrow pore network, which are mostly inaccessible to reactants. For this purpose, oxygen to carbon and iron to carbon ratios in the bulk and surface (from XPS analysis) were calculated (Table 5). The highest surface iron content was found in the basic functionalized catalysts, Fe/CM-B and mostly in Fe/CN-B, both in bulk and even more evidently in the surface. Regarding the distribution of the oxygen, nitric acid functionalized catalysts, Fe/CM-O and Fe/CN-O, exhibited the highest O/C bulk ratio, but the major relative concentration of oxygen in the surface was found in the Fe/CM-O and, a priori more unexpectedly, in the Fe/CN-B catalyst.

Table 3. Contribution (%) of different peaks to the O1s XPS spectrum.

Binding E (eV)	ID	Fe/CM	Fe/CM-O	Fe/CM-A	Fe/CM-B	Fe/CN	Fe/CN-O	Fe/CN-A	Fe/CN-B
530.0	O-Fe	19.5	16.2	20.6	33.3	28.5	19.6	17.9	41.2
531.5	C=O	29.6	26.8	30.9	31.3	31.3	30.5	35.5	28.0
532.9	C-O	27.5	28.9	25.7	21.6	23.5	27.9	26.4	21.2
534.0	COOH	16.4	19.5	16.7	10.4	12.6	16.3	13.8	7.6
536.0	H <sub>2</sub> O ads	7.0	8.6	6.1	3.4	4.1	5.7	6.4	2.0

Catalyst	Fe 2p <sub>3/2</sub> (eV)	Fe 2p <sub>1/2</sub> (eV)	Sat-Fe <sup>3+</sup> (eV)
Fe/CM	711.3	724.5	718.3
Fe/CM-O	711.4	724.5	718.3
Fe/CM-A	711.4	724.6	718.2
Fe/CM-B	711.1	724.6	718.1
Fe/CN	711.1	724.5	718.2
Fe/CN-O	711.3	724.7	718.4
Fe/CN-A	711.4	724.6	718.3
Fe/CN-B	711.1	724.5	718.4

Table 4. Binding energy of Fe2p peaks in the XPS spectrum.

**Table 5.** Surface and bulk O/C and Fe/C atomic ratios on Fe/AC-*f*, and raw AC supports.

Catalyst	(O/C) <sub>bulk</sub>	(O/C) <sub>XPS</sub>	(Fe/C) <sub>bulk</sub>	(Fe/C) <sub>XPS</sub>
СМ	0.044	0.029	0	0
Fe/CM	0.164	0.081	0.057	0.005
Fe/CM-O	0.258	0.159	0.054	0.007
Fe/CM-A	0.139	0.108	0.045	0.005
Fe/CM-B	0.202	0.139	0.061	0.017
CN	0.031	0.046	0	0
Fe/CN	0.070	0.105	0.047	0.010
Fe/CN-O	0.249	0.107	0.060	0.008
Fe/CN-A	0.203	0.121	0.055	0.009
Fe/CN-B	0.172	0.183	0.060	0.043

These results infer with the preferential allocation of iron species on terminal oxygenated groups of oxidized carbon supports, which agree with other previously reported studies [48]. The borders are more accessible sites and should contribute to enhancing the interaction with  $H_2O_2$  and, therefore, HO<sup>•</sup> formation, driving to theoretically higher CWPO activity [36].

## 2.2. Catalytic Activity

Prior to CWPO runs, for comparison purpose, the evolution of phenol concentration was followed during adsorption and CWPO runs with bare AC and functionalized AC-*f* (Table 6). Adsorption in original AC reached the highest values, 54% and 51%, for CM and CN supports, respectively, that became hardly reduced with the acidic functionalization, and only basically treated CM-B and CN-B supports suffered a drastic loss of adsorption, with values under 20% (14% and 18%, respectively). CWPO activity on AC and AC-*f* supports showed an evolution of phenol concentration only at short times, later, a plateau, characteristic of adsorption behavior, was observed (Figure 2a,b). The phenol concentration reached on bare AC showed 2–15% additional loss due to some CWPO activity, which has been frequently related to the chemical composition and surface functional groups present in AC [24,44,49,52], but AC-*f* supports, barely could remove an extra 0–7% phenol amount, due to degradation, during CWPO reaction.

Analogously, the adsorption of phenol was evaluated to discriminate the different contributions to phenol removal on Fe/AC-*f* prepared catalysts (Figure 2c,d). Between 24 and 40% of initial phenol concentration was eliminated from the aqueous effluents due to adsorption on the Fe/AC-*f* catalysts, following the sequence: Fe/CM~Fe/CM-A~Fe/CM-B > Fe/CN-A~Fe/CN-B > Fe/CN-O > Fe/CM-O (Table 6), where it could be concluded that the functionalization procedure reduced the adsorption mostly related to loss in BET surface area. Despite that, functionalization of supports on Fe/CN-*f* catalysts seems to reduce the phenol adsorption capability. Meanwhile, Fe/AC-O catalysts, prepared as from nitric acid modified AC supports, seem to adsorb the lowest amount of phenol, in



the studied operating conditions, which could be associated to accessibility and/or polarity of surface groups [44,48].

**Figure 2.** Evolution of phenol CWPO reaction on AC and AC-*f* supports: (**a**) CM-*f* and (**b**) CN-*f*. And evolution of phenol adsorption on Fe/AC-*f* catalysts: (**c**) Fe/CM-*f* catalysts and (**d**) Fe/CN-*f* catalysts. Reaction conditions: 50 mL reaction volume, 100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> catalyst, 500 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, pH 3, 200 rpm, 50 °C.

All the synthetized Fe/AC-*f* catalysts showed a high activity in the degradation of phenol by CWPO (Figure 3). Conversion of phenol achieved 100% with most of the catalysts, specifically, all Fe/CM-*f* and acidic functionalized Fe/CN-A and Fe/CN-O, which exceeds that obtained by bare Fe/CN catalyst. Only Fe/CN-B achieved poor results (X<sub>Phenol</sub> = 65%). The use of H<sub>2</sub>O<sub>2</sub> was efficient for most of the catalysts, all the Fe/CM-*f* catalysts exhibited curves over theoretical stoichiometric line (Figure 3a). The use of H<sub>2</sub>O<sub>2</sub> resulted improved for Fe/CN-A, which reached circa 100% X<sub>Phenol</sub> with 50% X<sub>H2O2</sub>. The Fe/CN-O catalyst followed theoretical behavior, and only Fe/CN-B poorly use H<sub>2</sub>O<sub>2</sub>, even worse than Fe/CN (Figure 3b). These performances were emphasized over 50% X<sub>H2O2</sub>. Therefore, at 50% X<sub>H2O2</sub>, the X<sub>Phenol</sub> reached by the catalysts followed the sequence: Fe/CN-A (97%) >> Fe/CM-O (70%) > Fe/CM (62%)~Fe/CM-A (60%) > Fe/CM-B (53%) > Fe/CN-O (48%)~Fe/CN (48%) > Fe/CN-B (39%), demonstrating the ability of synthetized Fe/AC-*f* catalysts to generate sufficient HO<sup>•</sup> radicals to oxidize phenol in the mild studied conditions.



**Figure 3.** Degradation of phenol with the consumption of  $H_2O_2$ : (a) Fe/CM-*f* catalysts and (b) Fe/CN-*f* catalysts. Reaction conditions: 50 mL reaction volume, 100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> catalyst, 500 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, pH 3, 200 rpm, 50 °C.

The removal of TOC, when high surface area catalysts are involved, could not be directly related to mineralization degree, even when adsorbed pollutants could undergo further degradation [39]. Then, the contribution of adsorption and CWPO to TOC removal has been itemized in Table 6, where  $H_2O_2$  consumption,  $H_2O_2$  direct decomposition, and iron release, were also quantified. The Fe/AC-*f* catalysts speeded up the TOC removal due to CWPO contribution, compared to AC-*f* or raw AC. Acidic functionalization with nitric acid showed the highest enhancement of CWPO results for both AC supports, but only Fe/CN-O showed stability with low iron release. Fe/CN-A, despite exhibiting higher CWPO than Fe/CN, presented the important drawback of iron loss.

**Table 6.** TOC removal due to adsorption, CWPO and total contribution,  $H_2O_2$  consumption,  $H_2O_2$  direct decomposition, and iron release, for raw AC, AC-*f* supports and Fe/AC-*f* catalysts. Operating conditions: 50 mL reaction volume, 100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 500 mg·L<sup>-1</sup> catalyst, pH 3, 50 °C, 200 rpm, 240 min reaction time, when corresponding.

Material	Phenol Removal: Adsorption <sup>(1)</sup>	Phenol Removal: Total <sup>(2)</sup> (ads + CWPO)	Phenol Mineralization <sup>(3)</sup> (CWPO)	H <sub>2</sub> O <sub>2</sub> Consumption <sup>(4)</sup>	H <sub>2</sub> O <sub>2</sub> Direct Decomposition <sup>(5)</sup>	Fe <sub>rel</sub> <sup>(6)</sup>
	X <sup>Adsorption</sup> (%)	$X_{ ext{TOC}}^{Adsorption+CWPO}$ (%)	$X_{\text{TOC}}^{CWPO} = X_{\text{TOC}}^{Ads+CWPO} - X_{\text{TOC}}^{Ads}(\%)$	X <sub>H2O2</sub> (%)	(X <sub>H2O2</sub> ) <sub>direct</sub> (%)	(%)
AC						
CM CN	$\begin{array}{c} 54\pm2\\51\pm2\end{array}$	$\begin{array}{c} 64\pm3\\ 53\pm2 \end{array}$	5–15 2-6	$\begin{array}{c} 55\pm3\\ 28\pm2 \end{array}$	$\begin{array}{c} 80\pm3\\ 100\pm3 \end{array}$	-
AC-f						
CM-A CM-O CM-B CN-A CN-O CN-B	$\begin{array}{c} 47\pm 2\\ 41\pm 2\\ 14\pm 1\\ 47\pm 2\\ 51\pm 2\\ 18\pm 1\end{array}$	$\begin{array}{c} 47 \pm 2 \\ 41 \pm 2 \\ 19 \pm 1 \\ 47 \pm 2 \\ 50 \pm 2 \\ 18 \pm 1 \end{array}$	0-4 0-4 3-7 0 0-4 0-4	$5 \pm 1 \\ 3 \pm 1 \\ 5 \pm 1 \\ 23 \pm 2 \\ 34 \pm 2 \\ 9 \pm 1$	$76 \pm 3 \\ 45 \pm 3 \\ 8 \pm 3 \\ 100 \pm 3 \\ 99 \pm 3 \\ 80 \pm 3$	
Fe/CM Fe/CM-A Fe/CM-O Fe/CM-B Fe/CN-B Fe/CN-A Fe/CN-A Fe/CN-O Fe/CN-B	$\begin{array}{c} 39 \pm 2 \\ 40 \pm 2 \\ 24 \pm 2 \\ 40 \pm 2 \\ 39 \pm 2 \\ 33 \pm 2 \\ 26 \pm 1 \\ 32 \pm 1 \end{array}$	$\begin{array}{c} 80 \pm 2 \\ 78 \pm 2 \\ 77 \pm 2 \\ 80 \pm 2 \\ 76 \pm 2 \\ 82 \pm 2 \\ 83 \pm 2 \\ 64 \pm 2 \end{array}$	$\begin{array}{c} 41 \pm 4 \\ 38 \pm 4 \\ 53 \pm 4 \\ 40 \pm 4 \\ 37 \pm 4 \\ 49 \pm 4 \\ 57 \pm 3 \\ 32 \pm 3 \end{array}$	$\begin{array}{c} 96 \pm 2 \\ 87 \pm 2 \\ 90 \pm 2 \\ 88 \pm 2 \\ 100 \pm 2 \\ 89 \pm 2 \\ 97 \pm 2 \\ 100 \pm 2 \end{array}$	- - - - - - - - - - -	$11 \pm 1 \\ 4 \pm 1 \\ 26 \pm 2 \\ 6 \pm 1 \\ 8 \pm 1 \\ 24 \pm 2 \\ 4 \pm 1 \\ 0.8 \pm 0.2$

<sup>(1)</sup> Calculated as:  $((C_{TOC_{t=0} \min} - C_{TOC_{t=240} \min})/C_{TOC_{t=0} \min}) \cdot 100$ . <sup>(2)</sup> Maximum TOC removal by adsorption and further CWPO reaction. <sup>(3)</sup> Phenol mineralization estimated from:  $((C_{TOC_{t=240} \min}^{Adsorption} - C_{TOC_{final}}^{CWPO})/C_{TOC_{t=0} \min}) \cdot 100$ . <sup>(4)</sup> Accumulated H<sub>2</sub>O<sub>2</sub> consumption at the maximum total TOC removal, in column 3. <sup>(5)</sup> Capability for H<sub>2</sub>O<sub>2</sub> decomposition in the absence of phenol. <sup>(6)</sup> Iron released to the aqueous medium at the end of 240 min reaction time. Regarding the evolution of TOC along reaction time, Figure 4 shows a very fast reduction of organic matter in the aqueous effluents, with >70% of TOC removal in less than 30 min in the case of Fe/CN-A catalyst, and 60 min for all the Fe/CM-*f* catalysts (Fe/CM-A, Fe/CM-O and Fe/CM-B). Fe/CN-A and Fe/CM-A even showed a residual  $H_2O_2 > 30-20\%$ , respectively at this high TOC conversion values. Fe/CN-B obtained the poorest TOC removal, 60% approximately, with total depletion of  $H_2O_2$  within 60 min of reaction. Analogously, it could be observed that all the Fe/CN-*f* catalysts consumed the stoichiometric amount of  $H_2O_2$  in 120 min of reaction without total TOC removal. Contrarily, Fe/CM-*f* catalysts reached a maximum 80% of TOC removal, even when significant amount of  $H_2O_2$  remained in the reaction medium, which pointed out some limitation to keep propagation stage of the reaction, probably due to some blockage in the active sites of the catalysts, unable to continue the formation of HO<sup>•</sup> radicals [7,18,53,54].



**Figure 4.** Evolution of TOC and consumed  $H_2O_2$  along reaction time: (a) Fe/CM-*f* catalysts and (b) Fe/CN-*f* catalysts. Reaction conditions: 50 mL reaction volume, 100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> catalyst, 500 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, pH 3, 200 rpm, 50 °C.

The source of TOC, along CWPO reaction, was analyzed (Figure 5). Aromatic by-products were identified in the phenol degradation pathway as hydroquinone, pbenzoquinone, resorcinol, and catechol [54–56]. Those identified aromatic reaction intermediates were formed by the initiation stage of the AOP, where a HO<sup>•</sup> radical was added in preferential relative positions of the phenol aromatic ring [3,7], following the mechanism previously described [39,43]. The concentration of aromatic intermediates was always very low, <10% initial TOC, and the evolution showed the elimination of those aromatics, by further degradation, in the Fe/CM-*f* catalysts, while still remained at 240 minutes in Fe/CN and Fe/CN-B, and Fe/CN-O, although at lower concentration. Contrarily, with respect to the evolution of the degradation route through short-chain organic acids (mainly maleic, malonic, oxalic, acetic, and formic acid), Fe/CM-*f* catalysts showed a higher concentration of these simplest compounds (approximately 16% of initial TOC), while the presence of short-chain organic acids in Fe/CN-*f* catalysts was hardly quantifiable (<5% initial TOC).



**Figure 5.** Evolution of CWPO intermediates along reaction time: Aromatics on (**a**) Fe/CM-*f* catalysts, and (**b**) Fe/CN-*f* catalysts. Short-chain organic acids on (**c**) Fe/CM-*f* catalysts and (**d**) Fe/CN-*f* catalysts. Iron leachate on: (**e**) Fe/CM-*f* catalysts and (**f**) Fe/CN-*f* catalysts. Reaction conditions: 50 mL reaction volume, 100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> catalyst, 500 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, pH 3, 200 rpm, 50 °C.

Concerning the stability of the Fe/AC-*f* catalysts, non-functionalized supports, Fe/CM and Fe/CN, together with Fe/CM-A and Fe/CN-B showed a high stability with iron release under 1%, in the initial 60 min of reaction, when phenol was mostly degraded. After that

initial period, Fe/CN-A, Fe/CM-O, and Fe/CM-B became importantly altered with high concentration of iron released into the reaction medium. Nevertheless, the contribution of homogeneous Fenton should achieve a low rate, mainly two causes support this assessment: (i) the increasing concentration of released iron concurred with the plateau observed in the evolution of phenol and TOC conversion, that is, with the reaction almost stopped as from 120 minutes. (ii) The concentration of dissolved iron in the reaction medium at short times was low to mainly degrade phenol by homogeneous Fenton reaction [4,51].

Fe/CN-O and Fe/CN-B catalysts were reused along four CWPO runs (Figure 6). A decrease in TOC and phenol removal was observed in both catalysts during cycles 1st to 3rd, but a recovery of catalytic activity was clearly observed in the 4th cycle for both catalysts. This behavior could be related to the accumulation of adsorbed organic compounds (phenol and degradation intermediates) on catalysts surface, blocking the catalytic active sites. Further, mineralization of adsorbed TOC could proceed leaving some active sites available to contribute to CWPO activity [39].



**Figure 6.** Evolution of TOC and phenol conversion along for reused cycles for Fe/CN-B and Fe/CN-O catalysts. Reaction conditions: 50 mL initial reaction volume, 100 mg·L<sup>-1</sup> phenol in ultrapure water, 500 mg·L<sup>-1</sup> catalyst, 500 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, pH 3, 200 rpm, 50 °C, 120 min reaction time.

#### 2.3. CWPO in WWTP Effluent and Landfill Leachate Matrices

The application of prepared Fe/AC-*f* catalysts to real effluents was the ultimate pursued objective; therefore, the performance of selected Fe/AC-*f* catalysts was evaluated. Fe/CN-*f* and Fe/CM-O catalysts were chosen after comparison of mineralization degree by CWPO (after adsorption subtraction) and stability of the catalysts (Table 6). Two different water matrices were chosen: the outlet effluent from a WWTP with MBR stage and a landfill leachate water (see Table 7 for main characteristics). Landfill leachate waters are very complex matrices with mixtures of organic and inorganic origin contaminants, with high content of suspended solids, color, and frequent segregation of phases. Meanwhile, WWTP effluent has a much simpler matrix, where basic pH and high TOC should be underlined. First, WWTP water was studied after pH modification, it was adjusted to pH 3 to reproduce previous operating conditions with phenol as the model pollutant. The WWTP water was spiked with 100 mg·L<sup>-1</sup> of phenol to evaluate the role of effluent composition in the CWPO performance. Results on Figure 7 showed the effect of pH

modification and the  $H_2O_2$  dose. As supposed, the basic pH had a detrimental effect on phenol removal that was essentially due to adsorption. The effect of CWPO was hardly observed when stoichiometric or half stoichiometric amount of  $H_2O_2$  were used. On the contrary, at pH 3 the adsorption was reduced but removal of phenol by CWPO was 100% for Fe/CN-A and Fe/CN-O, and very close to this complete elimination for Fe/CN-B and Fe/CM-O. Surprisingly, the removal of phenol in WWTP water matrix at acidic pH was even 30% higher for Fe/CN-B, than that observed in ultrapure water.



**Figure 7.** Effect of water matrix and pH of the reaction medium in the phenol removal by CWPO reaction (240 min). Reaction conditions: 50 mL reaction volume, 500 mg·L<sup>-1</sup> catalyst, 500/250 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 200 rpm, 50 °C, 240 min reaction time. Initial TOC: 80 mg·L<sup>-1</sup> ultrapure water matrix, 90 mg·L<sup>-1</sup> WWTP effluent.

Regarding landfill leachate, it was previously 1:20 diluted with deionized water to obtain a TOC concentration (100 mg·L<sup>-1</sup>) in the range of previous experiments, which also facilitate the analytical measurements [23,57], without any pH modification. Figure 8 shows a significant removal of the TOC, naturally present in the landfill leachate, by CWPO, at original pH 9 [58]. The degradation of organic matter was higher than in the case of WWTP effluent at unmodified pH 8, and even in the ultrapure water at pH 3, where the adsorption step had a higher contribution to TOC elimination than CWPO. Therefore, it could be concluded that the sequence for TOC reduction by CWPO follows the order: Landfill leachate water, pH 9 > WWTP effluent, pH 3 > ultrapure water, pH 8. The obtained results reinforce the robustness of CWPO treatment for removal of contaminants applied to real water matrices but their composition also plays an important role in the process.

The success of CWPO on landfill leachate water could be explained by the presence of dissolved metals or complexes which could contribute to catalyzing homogeneous Fenton degradation [58,59].



**Figure 8.** Effect of water matrix (ultrapure, WWTP effluent, landfill leachate) on the removal of TOC by CWPO. Reaction conditions: 50 mL reaction volume, 500 mg·L<sup>-1</sup> catalyst, 250 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 200 rpm, 50 °C, 240 min reaction time. Initial TOC: 80 mg·L<sup>-1</sup> ultrapure water, 90 mg·L<sup>-1</sup> WWTP, and 100 mg·L<sup>-1</sup> landfill leachate.

WWTP Effluent	Landfill Leachate
$8.2\pm0.1$	$8.2\pm0.1$
$2.1\pm0.1$	$17.3\pm0.1$
colorless	$27.5\pm0.1$
-	$17300\pm200$
n.d.	$5000\pm500$
n.d.	$150\pm50$
n.d.	$0.03\pm0.01$
$5\pm 1$	$2000\pm10$
n.d.	$21300\pm1000$
n.d.	$1370\pm20$
$1020\pm20$	$18970\pm230$
$440\pm20$	$13250\pm100$
$16\pm 2$	$1600\pm10$
$210\pm50$	$3000 \pm 150$
$370\pm20$	$120\pm30$
n.d.	$5.5\pm0.1$
n.d.	$8.5\pm0.1$
n.d.	$1.9\pm0.1$
$290\pm 60$	$2150\pm220$
$48\pm1$	$1220\pm120$
$52\pm5$	$98\pm 6$
$150\pm14$	$134\pm4$
n.d.	$15\pm 1$
n.d.	$0.6\pm0.1$
n.d.	$0.3\pm0.1$
n.d.	$0.03\pm0.01$
	WWTP Effluent $8.2 \pm 0.1$ $2.1 \pm 0.1$ colorless           -           n.d.           n.d.           n.d.           n.d.           n.d.           n.d.           1020 $\pm 20$ 440 $\pm 20$ 16 $\pm 2$ 210 $\pm 50$ 370 $\pm 20$ n.d.           n.d.

**Table 7.** Characteristics of the wastewater treatment plant effluent (Garray, Soria, Spain) and landfillleachate (Golmayo, Soria, Spain).

# 3. Experimental

# 3.1. Materials

All the materials used in the functionalization of activated carbons, preparation of catalysts, and CWPO reaction were provided by Merck (Darmstadt, Germany). Ultrapure water was produced by a Millipore equipment. Wastewater effluent was collected from Garray WWTP in Soria, Spain, after WWTP-MBR processes of industrial and urban wastewater. Landfill leachate water was gathered from Golmayo landfill, in Soria, Spain. The main characteristics of these effluents have been collated in Table 7.

## 3.2. Functionalization of Activated Carbons

Two commercial activated carbons (Norit RX-3 Extra, provided by Cabot Corporation, Alpharetta, Georgia, USA, and Merck food quality) were the raw materials, named as CN and CM, respectively.

The functionalization was performed as from these AC by modification with sulfuric acid, nitric acid, and ethylenediamine, as follows: (a) 1 g of each AC was treated with 20 mL of sulfuric acid (98 %) at room temperature and stirring for 90 min. Later, the modified AC supports were filtered, washed with water until no sulfate ions were detected (test with barium chloride (BaCl<sub>2</sub>) solution), and dried for 24 h at 110 °C. The modified supports were named as CN-A and CM-A, respectively. (b) Other portion of pristine AC materials was analogously treated with nitric acid (65 %). Later, the products obtained were filtered, washed with deionized water until a constant neutral pH was reached, which indicates all the loosely bonded acid was removed from AC-*f* surface, and, then, dried for 24 h at 110 °C. The modified AC (CN-O and CM-O) were used to prepare the CN-B and CM-B supports. Total of 1 g of nitric acid modified carbons were treated with 15 mL of ethylenediamine at room temperature, and stirred for 90 min. The products were filtered, washed with water until constant neutral pH, which indicates all the loosely bonded ethylenediamine at room temperature, and stirred for 90 min. The products were filtered, washed with water until constant neutral pH, which indicates all the loosely bonded ethylenediamine at room temperature acid modified for 24 h at 110 °C.

# 3.3. Catalysts Preparation

AC-*f*-supported iron catalysts were prepared by incipient wetness impregnation of previously modified or raw activated carbons, at room temperature, using an aqueous solution of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) to obtain Fe/AC-*f* catalysts with the same nominal iron content (4%, w/w). Briefly, 0.3 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O/g of support were dissolved in a volume of deionized water 130% of the support pore volume. The impregnation volume specified in Supporting Information Table S1 (0.67–1.17 mL, depending on the used carbon support) was added dropwise uniformly distributed on the solid surface, previously dried at 60 °C for 12 h. All the samples were left overnight at room temperature, dried for 12 h at 60 °C, and finally heat-treated at 250 °C for 4 h in air atmosphere, using a slow heating rate of 0.7°·min<sup>-1</sup>. Finally, eight catalysts (two bare AC and three functionalized AC-*f*) were prepared: Fe/CN, Fe/CN-A, Fe/CN-O, Fe/CN-B, and Fe/CM, Fe/CM-A, Fe/CM-O, Fe/CM-B (Supporting Information Table S1). The catalysts were ground and fraction under 100 µm was selected by sieving for characterization and catalytic activity tests.

# 3.4. Catalysts Characterization

Elemental analyses were performed by an LECO CHNS-932 Analyzer. Iron present on the catalysts was determined by inductively coupled plasma technique (ICP-OES, Optima 3300DV, Perkin Elmer, Waltham, Massachusetts, USA) after acid digestion in a high pressure microwave oven (Multiwave 3000, Anton Paar, Graz, Austria). XRD patterns were registered between 4–90° 20, 0.04°/step and 50 s accumulation time (XPert Pro, XCelerator detector, PANalytical, Malvern, UK).

The specific surface areas,  $S_{BET}$ , were calculated from nitrogen adsorption at -196 °C (Tristar 3000, Micromeritics, Norcross, Georgia, GA, USA), after application of the BET equa-

tion [60] in the 0.02–0.15 range of relative pressures. Samples were previously outgassed overnight at 250  $^{\circ}$ C under vacuum.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer (Thermo Fisher Inc, Waltham, MA, USA) equipped with a hemispherical electron analyzer and X-ray source of Mg K $\alpha$  (h $\nu$  = 1254.6 eV, 120 W). C 1s peak from carbon samples (284.6 eV) was used as reference for binding energies values. Peaks were adjusted to a combination of Gaussian and Lorentzian functions using the XPSPeak 4.1 software.

## 3.5. Catalytic Activity: CWPO

Catalytic wet peroxide oxidation runs were carried out in a 100 mL batch reactor at 50 °C, atmospheric pressure and 200 rpm stirring rate. 50 mL of reaction mixture were poured into the reactor and pH 3 was adjusted with hydrochloric acid. Initial concentrations of 100 mg·LL<sup>-1</sup> of phenol in ultrapure (MilliQ, Merck, Darmstadt, Germany) water, and 500 mg·L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> were used, that corresponds to the stoichiometric amount for complete oxidation of phenol, or 250 mg·L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> in the case of half-stoichiometric experiments [51]. Powdered and sieved (d<sub>particle</sub> < 100 µm) Fe/AC-*f* catalyst was added into the reactor at a concentration of 500 mg·L<sup>-1</sup> (25 mg).

In the case of real water matrices, WWTP-MBR water matrix was spiked with 100 mg·L<sup>-1</sup> phenol without any modification for natural pH 8 runs, whereas sulfuric acid was used to shift the pH to 3 in corresponding runs. Landfill lixiviate matrix was diluted 1:20 with ultrapure water to obtain equivalent initial TOC and minimize analytical errors, and no additional pollutant was added.

Identification and quantification of phenol and aromatic intermediates (catechol, hydroquinone, p-benzoquinone and resorcinol) were followed by HPLC with photo-diode array detector (Azura Plus, Knauer, Berlin, Germany). Nucleosil C18 5µm (Merck, Darmstadt, Germany) column ( $150 \times 4.6 \text{ mm}^2$ ) was used as the stationary phase. The mobile phase was composed by methanol/acidic water (0.1 % phosphoric acid) at 0.8 mL·min<sup>-1</sup> flow rate. Ion chromatography (883 Basic IC Plus, Metrohm, Herisau, Switzerland) with conductivity detector was used for short-chain organic acids and anions (chemical suppression, Metrosep A supp 7-250/4.0 (Metrohm, Herisau, Switzerland) column as stationary phase, and 3.6 mM sodium carbonate as eluent) and cations (Metrosep C6 250/4.0 column, Metrohm, and nitric acid/dipicolinic acid 1.7 mM as eluent). Total organic carbon (TOC) was measured with a TOC-VSHs Analyzer (Shimadzu, Kyoto, Japan). Hydrogen peroxide concentration was quantified by a colorimetric titration method [61] based on the absorbance intensity of a yellow Ti(IV)- $H_2O_2$  complex, measured at 410 nm (UV/Vis 2100 Shimadzu, Kyoto, Japan). Iron released into the reaction media was evaluated by the spectrophotometric method [62] based on the absorbance measurement at 510 nm of the colored complex formed with o-phenantroline (Shimadzu UV/Vis 2100).

Blank experiments were performed to investigate phenol adsorption (100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> of catalysts and absence of hydrogen peroxide), hydrogen peroxide decomposition (500 mg·L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, 500 mg·L<sup>-1</sup> of catalysts and no contaminant), and CWPO degradation by supports (100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, 500 mg·L<sup>-1</sup> of AC-*f*), in identical conditions as CWPO reactions (50 mL total reaction volume, 100 mL batch reactor volume, 50 °C, 200 rpm, pH 3) and using the same analytical procedures.

Reusability experiments were performed with Fe/CN-B and Fe/CN-O catalysts, checking four consecutive cycles. The initial reaction conditions were the previously defined 50 mL reaction volume, 100 mg·L<sup>-1</sup> phenol, 500 mg·L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, 500 mg·L<sup>-1</sup> catalyst, 50 °C, 200 rpm and 120 min reaction time. The catalyst was recovered after each cycle by filtration, washed with deionized water, and dried at 70 °C for 3 h.

### 4. Conclusions

Fe/AC-*f* catalysts prepared from functionalized activated carbon supports showed a high mineralization ability, removing around 80% TOC when phenol was used as the model pollutant in ultrapure water matrix. Despite acidic and basic functionalization was

introduced in the original activated carbons, the activity and stability of Fe/AC-*f* catalysts could not be straightforwardly related with the new induced characteristics. The stage of impregnation with iron nitrate and further heat treatment during the preparation of catalysts, could probably explain the neutralization of previously functionalized supports, as observed by XPS spectroscopy.

Fe/CN-*f* catalysts showed a remarkable CWPO activity in the elimination of phenol in a WWTP matrix after pH acidification, underlining the importance of pH in the studied AOP degradation process. But, impressively, the application of Fe/AC-*f* catalysts to real matrices revealed the best CWPO performance in the removal of TOC from a complex effluent matrix such as a landfill leachate water at its natural basic pH 9.

These findings open the opportunity to extend the use of Fe/AC-*f* catalysts to the treatment of real complex wastewater effluents by CWPO.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/2073-4 344/11/3/337/s1. Figure S1: XRD of Fe/AC-f catalysts: (a) Fe/CM-f catalysts and (b) Fe/CN-f catalysts. Figure S2: N2 isotherms of Fe/AC-f catalysts: (a) Fe/CM-f catalysts and (b) Fe/CN-f catalysts. Table S1: Catalysts nomenclature and characteristics.

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