



HAL
open science

Improvement of (transition metal-modified) activated carbon regeneration by H₂O₂-promoted catalytic wet air oxidation

Imane Benhamed, Laurie Barthe, Rachid Kessas, Henri Delmas, Carine Julcour-Lebigue

► To cite this version:

Imane Benhamed, Laurie Barthe, Rachid Kessas, Henri Delmas, Carine Julcour-Lebigue. Improvement of (transition metal-modified) activated carbon regeneration by H₂O₂-promoted catalytic wet air oxidation. *Environmental Technology*, 2018, 39 (21), pp.2761-2770. 10.1080/09593330.2017.1365942 . hal-01879931

HAL Id: hal-01879931

<https://hal.science/hal-01879931>

Submitted on 24 Sep 2018

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.







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's version published in: <http://oatao.univ-toulouse.fr/20422>

Official URL: <http://doi.org/10.1080/09593330.2017.1365942>

To cite this version:

Benhamed, Imane  and Barthe, Laurie  and Kessas, Rachid and Delmas, Henri  and Julcour-Lebigue, Carine  *Improvement of (transition metal-modified) activated carbon regeneration by H₂O₂-promoted catalytic wet air oxidation.* (2018) *Environmental Technology*, 39 (21). 2761-2770. ISSN 0959-3330

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

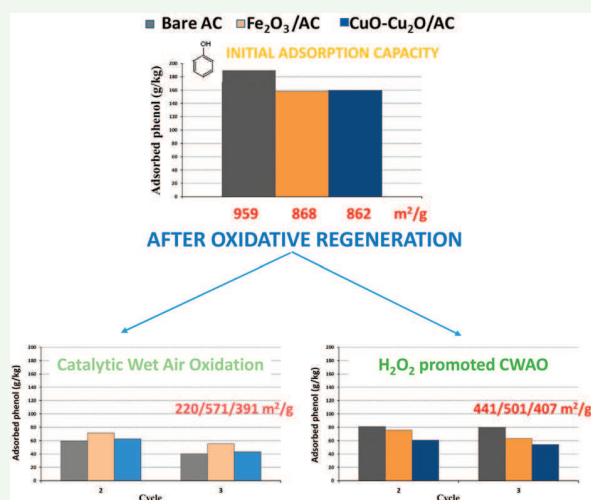
Improvement of (transition metal-modified) activated carbon regeneration by H₂O₂-promoted catalytic wet air oxidation

Imane Benhamed^{a,b}, Laurie Barthe^a, Rachid Kessas^b, Henri Delmas^a and Carine Julcour^a

^aLaboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France; ^bLaboratoire de Génie Chimique et de Catalyse Hétérogène, Université des Sciences et de la Technologie d'Oran, Oran, Algeria

ABSTRACT

Oxidative regeneration of activated carbon (AC) exhausted with phenolic compounds is still a challenging issue due to the frequent porosity loss. Addition of low H₂O₂ amount is investigated as a way to promote catalytic wet air oxidation (CWAO) of adsorbed pollutants and thereby to recover adsorbent properties. Commercial AC and transition metal (iron or copper)-modified counterparts are tested in repeated adsorption/batch peroxide-promoted CWAO of phenol. Cycles are operated in both fixed bed and slurry reactors to vary the initial pollutant distribution in between the two phases. Influence of metal location is also studied by adding iron salt to the pollutant solution prior to perform peroxide-promoted oxidation on bare carbon. Regeneration results are analyzed through a detailed analysis of both the solid and the liquid phases during the oxidative treatment. It is proved that a convenient H₂O₂ dosage can increase the lifetime of adsorbent in adsorption-oxidation cycles, but coupling with (un)supported metal oxide does not provide significant gain.



1. Introduction

Phenol is widely used in petroleum refining, plastic, synthetic fiber, pharmaceutical and agri-food industries. Highly toxic, it is known for its persistence and ability for bioaccumulation. Phenolic compounds are therefore among the main pollutants found in wastewaters and phenol is a model molecule in many works related to water pollution remediation [1–3].

Adsorption onto activated carbon (AC) is a well-established method for the treatment of aromatic-containing

wastewaters due to its low cost, simple implementation and high efficiency, even at low concentrations.

However, as the pollutants are not destroyed, the solid becomes itself a waste to be discharged or incinerated. Therefore regeneration of the adsorbent is an important issue in order to improve competitiveness and sustainability of adsorption processes.

Several techniques are available for AC regeneration, with varied performances (depending on the adsorbate) and drawbacks.

One of the most usual methods uses an inert gas stream at temperatures above 700°C for thermal decomposition of the adsorbates. However, this process is generally operated *ex situ* involving additional transport costs and significant carbon losses. Wet air oxidation also requests high energy consumption and expensive equipment due to the severe applied conditions (temperature > 200°C, total pressure > 20 bar). Moreover, its regeneration efficacy is reduced when the pollutants are chemisorbed as often observed with aromatic molecules [4]. A promising way comes from the fact that AC itself can act as a catalyst [5–7] or can be impregnated with cheap metal oxides [8], allowing to temper the reaction conditions.

Using ozone also permits a treatment under near-ambient conditions, but this strong oxidant might be aggressive for AC surface properties, as suggested by several studies [9–11]. Likewise advanced oxidation processes have been proposed for removing adsorbates, as they generate free radicals (such as HO[•]) known for their high oxidation potential. In particular, the application of hydrogen peroxide in combination with a catalyst and/or UV irradiation is encouraging. For instance, from 86% to 93% regeneration efficiency was achieved over 3 cycles by H₂O₂/UV following acetone or isopropanol adsorption [12]. Similarly, Fenton-type oxidative treatment (at pH close to 3) allowed over 80% re-adsorption yield in the case of methyl tert-butyl ether [13], ethylene glycol [14], phenol [15] and organochloro compounds [16]. On the other hand, homogeneous photo-Fenton oxidation only permitted to recover 56% of AC adsorption capacity after 2 recycles in the case of phenol, due to the reduction of specific surface area [17].

A sequential process was previously developed by our research team which treats phenol-polluted water by adsorption onto AC, followed by adsorbent regeneration in mild conditions using catalytic wet air oxidation (CWAO) [7,18,19]. Our last work [20] aimed to improve the long-term efficacy of this process by impregnating AC with transition metals (iron and copper). The addition of metal oxide showed a beneficial effect on AC regeneration by CWAO, but not as high as expected with respect to the better recovery of specific area for the treated solids and/or the reduction of carbon oxygen demand (COD) measured in solution during the regenerative oxidation. Indeed, the presence of metal also increased the adverse effects of CWAO on the carbon properties, with a phenol uptake reduced by one half after oxidative treatment without any pollutant (vs. 20% for bare AC). Therefore the balance in between the two effects (reduction of oligomer deposition on the one hand, but increase in surface acidity and pore size on the other hand) was only slightly positive. In accordance with previous works on the application of transition metal-based catalysts

[21,22], copper was found particularly efficient to promote CWAO, mainly as a consequence of significant metal leaching initiating parallel homogeneous reaction. Conversely, iron oxide catalyst was found stable and proved to hinder oxidative coupling on the carbon surface.

As CWAO onto AC was reported to involve radical mechanisms [23,24], hydrogen peroxide could act as a promoter to improve the oxidation rate of the pollutants, reducing reaction time and allowing milder conditions.

Several authors showed the beneficial effect of sub-stoichiometric H₂O₂ addition on phenol conversion and mineralization in the presence of AC [25,26]. Rubalcaba et al. [25] more than doubled the mineralization yield when applying peroxide-promoted instead of classical CWAO. Quintanilla et al. [26] also proved a synergy effect between the two oxidants: reaction between adsorbed O₂ and H₂O₂ led to the formation of HO₂[•] radical, both in solution and in adsorbed phase, which contributed to phenol oxidation.

Moreover, in combination with hydrogen peroxide, iron or copper oxide deposit would promote the formation of hydroxyl radicals in Fenton-like systems [27–31]. These additional effects could further help the removal of oligomers, while the oxidation of AC surface might not be worsened if a low amount of co-oxidant is used.

In this context, the aim of the present work is to investigate the effect of H₂O₂ addition on the regeneration of transition metal-modified ACs by CWAO. Modified ACs are tested in batch peroxide-promoted CWAO (PP-CWAO) of phenol, as well as in repeated adsorption–oxidation cycles in a fixed bed reactor. The pollutant degradation and adsorbent regeneration performances are compared to that observed with conventional CWAO.

2. Materials and methods

2.1. Materials

Three catalysts were used in this study. The first one was a commercial granular AC (Merck 2514) sieved to get the 1.2–1.6 mm fraction. The other catalysts (labeled Fe/AC and Cu/AC) were synthesized by impregnation of Merck AC with iron or copper nitrate, followed by calcination under nitrogen flow at 350°C. Details about their preparation were described in our previous work [20]. Some of their properties are given in Table 1. Transmission electron microscopy (TEM) images of ultramicrotome slices and X-ray diffraction (XRD) analysis (see Figures S1 and S2 in Supplementary Information) also showed the presence of individual oxide nanoparticles of 10–15 nm (Fe₂O₃ or CuO/Cu₂O mixture).

Table 1. Textural properties and metal content of bare AC and prepared catalysts.

Catalyst label	BET surface area (m ² /g) ^a	Micropore volume (cm ³ /g) ^a	Mesopore volume (cm ³ /g) ^a	Measured metal content (wt%) ^b
Bare AC	959	0.38	0.17	Fe: 0.1 Cu: -
Fe/AC	868	0.34	0.13	4.3 ± 0.1
Cu/AC	862	0.34	0.15	4.0 ± 0.2

^aSpecific surface area (Brunauer–Emmett–Teller equation), mesoporous volume (Barrett–Joyner–Halenda method) and microporous volume (Horváth–Kawazoe method) measured by N₂ porosimetry on Micromeritics ASAP 2010 instrument.

^bIron content determined from ICP-AES analysis (Ultima 2, Horiba Jobin-Yvon) after combustion and acid attack at 150°C.

Phenol (99.5%), iron sulfate heptahydrate (FeSO₄·7H₂O, purity ≥ 99%) and hydrogen peroxide solution (30 wt %) were purchased from Sigma Aldrich. All chemicals were used as received without further purification.

2.2. Analytical methods for liquid samples

Phenol concentration was measured by liquid phase chromatography (HPLC) with UV detection (UV2000 detector, Thermo Finnigan). Before analysis, a phosphate buffer (0.5 mL) was added to the reacting solution (1 mL) in order to precipitate dissolved/leached metal.

During oxidation, the extent of mineralization was monitored by total organic carbon (TOC) using a Shimadzu TOC-VCSN analyzer. Prior to TOC analysis, 2 mL of a quenching solution (KI 0.1 mol/L; Na₂SO₃ 0.1 mol/L; KH₂PO₄ 0.05 mol/L; Na₂HPO₄·2H₂O 0.05 mol/L) was added to the reacting solution (5 mL) to stop any homogeneous oxidation by reducing remaining H₂O₂ and precipitating dissolved/leached metal. The sample was filtered and diluted with ultrapure water to 40 mL. The TOC concentration was obtained from the difference between total carbon and inorganic carbon.

2.3. Experimental procedures

Each catalyst was evaluated in a fixed bed reactor under repeated adsorption–oxidation cycles using PP-CWAO. In addition, oxidation performance was measured in a batch autoclave using a lower catalyst amount. These latter tests aimed at reducing the contribution of adsorbed organic compounds and better comparing the oxidation efficiency based on liquid phase analyses.

2.3.1. Fixed bed experiments

About 7 g of catalyst was packed in a small fixed bed reactor (18 cm high and 1 cm internal diameter) for successive adsorption–oxidation cycles. The corresponding setup was described in Julcour-Lebigue et al. [32]. In these assays, phenol solution (0.5 g/L) was circulated

through the AC bed at 0.23 L/h until saturation of the adsorbent. The total adsorbed amount for each cycle was calculated from the corresponding breakthrough curves.

The AC was then regenerated by CWAO, the same phenol solution (0.5 g/L) circulating at 1 L/h between the fixed bed and a pressurized tank (350 mL capacity). Constant oxygen pressure (9.5 bar) was achieved by continuous air flowing at 30 NL/h, while temperature was set to 150°C by thermofluid circulation in the reactor jacket and in the gas–liquid preheater.

During the oxidative regeneration, a total amount of either 44 or 253 mmol of hydrogen peroxide was added to the recycled phenol solution. It corresponded to 20% and 115% respectively, of the stoichiometric amount required for complete mineralization of phenol (both in solution and adsorbed on AC), according to the following equation:



In the case of Fe/AC and Cu/AC, hydrogen peroxide was introduced in three equal parts (at 30, 180 and 330 min) by means of an HPLC pump to prevent radical scavenging in a Fenton-like process [27,33]. For bare AC, it was added at once to the pollutant solution, just before reactor pressurization and heating. Oxidative regeneration was carried out during 8 h after temperature stabilization. Solution samples were regularly taken in the tank for analysis (see Section 2.2).

2.3.2. Stirred autoclave experiments

Oxidation tests were performed in a stirred (800 rpm) autoclave reactor. They also followed successive adsorption and oxidation cycles – but adsorption step was here achieved at the reaction temperature (150°C) under inert atmosphere. Two hundred milliliter of 1 g/L phenol solution and 1 g of catalyst were left 3 h under nitrogen for adsorption equilibration. Then a liquid sample was taken to get initial concentration of oxidation step. Subsequently, hydrogen peroxide was injected into phenol solution, before air was continuously fed at a flow rate of 40 L/h to ensure a constant oxygen partial pressure. Total pressure was set to 20 bar by means of a pressure regulating valve. During the oxidation (4 h), liquid samples were periodically withdrawn for analysis.

3. Results and discussion

3.1. Adsorption–oxidation cycles in fixed bed

3.1.1. Selection of oxidation conditions

Operating conditions for PP-CWAO regeneration were chosen from a preliminary study performed on bare

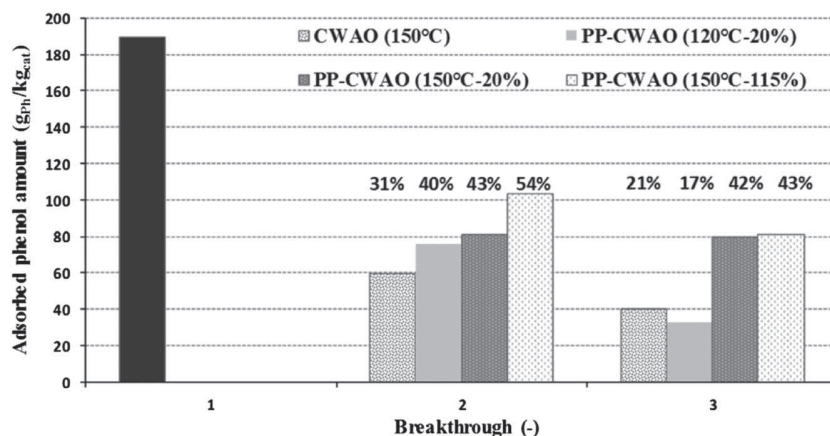


Figure 1. Evolution of adsorbed phenol amount onto bare AC (0.5 g/L of phenol in feed, in feed, $T = 25^\circ\text{C}$) during adsorption–oxidation cycles using different regeneration temperatures and H_2O_2 amounts (as percentage of stoichiometric amount in PP-CWAO). Numbers above the bars indicate the corresponding regeneration yield.

AC. Two parameters were investigated: temperature (120°C or 150°C) and H_2O_2 amount (20% or 115% of the required stoichiometric amount).

Figure 1 reports the adsorption capacity of the AC measured during successive cycles according to the applied oxidation conditions. First, oxidation at 150°C in the presence of hydrogen peroxide yielded a better recovery of adsorption capacity, clearly observed in the third cycle. This could be related to enhanced phenol degradation during PP-CWAO.

Nonetheless, the addition of H_2O_2 did not help to significantly reduce the temperature of the oxidative regeneration, since the same treatment performed at 120°C finally gave a lower efficacy than conventional CWAO at 150°C . Actually, residual TOC in the liquid phase

(Figure 2) was similar at 120°C or 150°C with hydrogen peroxide (about 140 mg/L after oxidation 1 and between 300 and 350 mg/L after oxidation 3). However, this came with a lower desorption peak at 120°C ; therefore there was probably more remaining pollutant on AC, leading to a lower phenol uptake in the following adsorption steps.

On the other hand, increasing hydrogen peroxide dosage from 20% to 115%, albeit beneficial for the first recycle, did not seem to have a noteworthy effect afterwards. An additional cycle performed with the highest hydrogen peroxide concentration only led to 29% of regeneration efficiency, indicating a further degradation of AC properties. Furthermore, AC pellets undergone a partial disintegration under H_2O_2 excess (some powder being observed along with higher residual TOC values in solution); so this condition should be proscribed for catalyst stability.

Thus, according to these preliminary results, a temperature of 150°C and the lowest amount of H_2O_2 were applied for the subsequent experiments using metal impregnated AC.

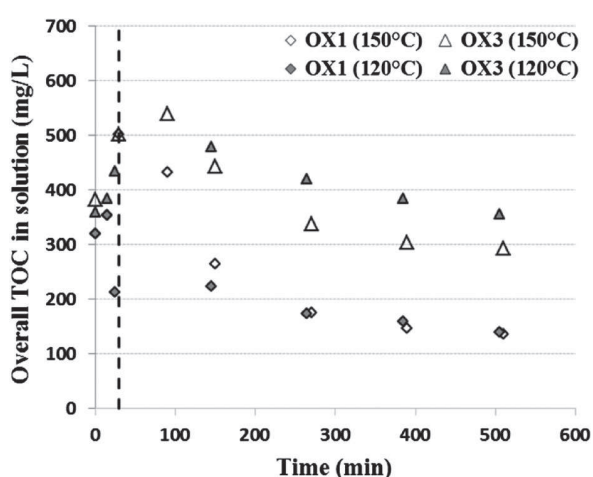


Figure 2. Evolution of TOC in solution during first and third peroxide-promoted oxidations on bare activated carbon at 120°C and 150°C (oxidation conditions in fixed bed: $C_0 = 0.5$ g/L, $m_{\text{AC}} = 7.0$ – 7.4 g, $V_L = 350$ mL, $n_{\text{H}_2\text{O}_2} = 44$ mmol, $P_{\text{O}_2} = 9.5$ bar, $Q_L = 1$ L/h, $Q_{\text{air}} = 30$ NL/h). Dashed line delineates the heating period.

3.1.2. Comparison of AC-based catalysts

3.1.2.1. Evolution of adsorption capacity. In addition to the assessment of AC, Fe/AC and Cu/AC in peroxide-promoted oxidation, another test was performed with bare AC using 6 mmol of dissolved iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), equivalent to the amount impregnated onto Fe/AC. To avoid reactor corrosion, pH was not lowered to the classical range used for Fenton oxidation (between 2 and 3) and most of added iron got precipitated at the pH value of phenol solution (ca. 5). However this precipitate could be a more accessible iron source than that deposited onto AC. Indeed, Bach et al. [14] and Chiu et al. [15]

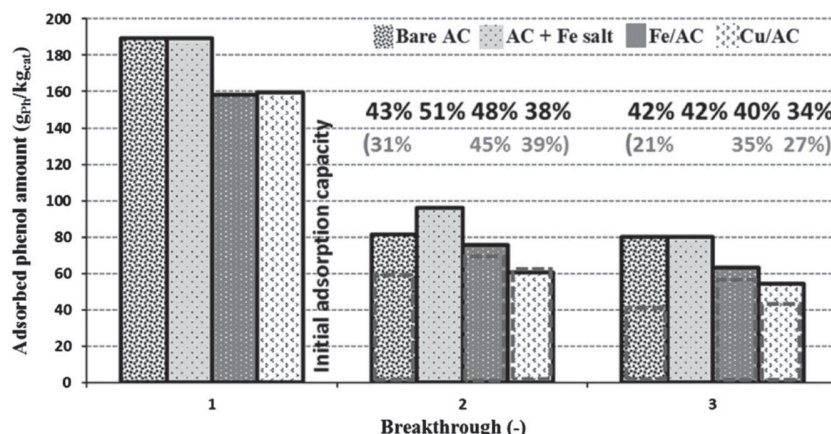


Figure 3. Evolution of adsorbed phenol amount onto bare and metal loaded ACs (0.5 g/L of phenol in feed, $T = 25^\circ\text{C}$) during adsorption-oxidation cycles using PP-CWAO. Dashed bars and regeneration yields in brackets show the results for classical CWAO.

reported high regeneration yield of ACs (exhausted with ethylene glycol or phenol) by heterogeneous Fenton oxidation using non-supported iron oxide nanoparticles: up

to 90% of the original adsorption capacity could be retained after four cycles.

Figure 3 compares the evolution of the adsorption capacity of bare AC treated by PP-CWAO with and without the addition of iron salt to that of metal-loaded carbons. Results relative to CWAO treatment are also recalled to analyze the effect of H_2O_2 addition for the different catalysts.

Addition of iron salt (AC+Fe salt) improved the regeneration yield of bare AC during the second cycle, but this positive effect vanished in the next cycle, due to porosity blockage by the iron precipitate. After the experimental campaign, the AC particles indeed showed a reddish color as the result of iron oxide deposition onto the solid surface.

Metal-loaded catalysts exhibited a slightly reduced initial phenol uptake with respect to bare AC (by about 16%), as the consequence of their lower surface area

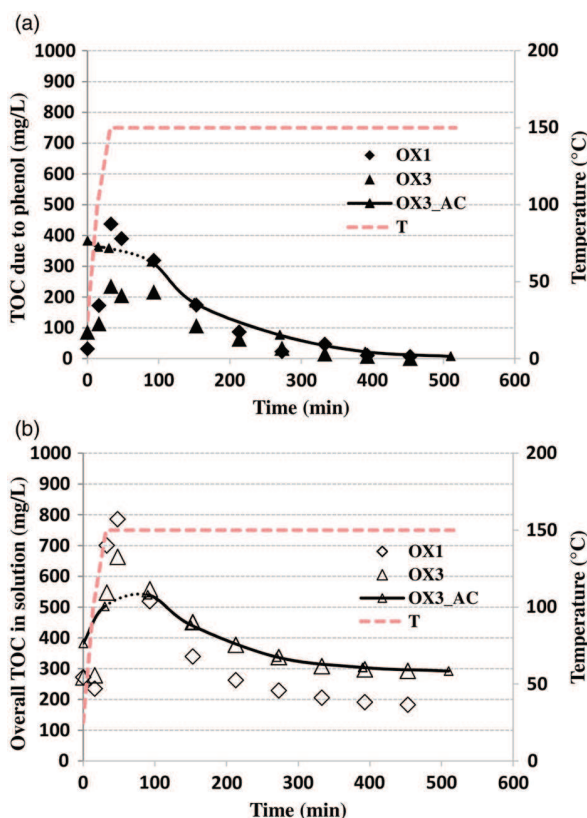


Figure 4. Evolution of (a) TOC due to phenol and (b) TOC in solution during first and third peroxide-promoted oxidations on bare AC in the presence of iron salt (large symbols, $n_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} = 6 \text{ mmol}$), under fixed bed conditions ($T = 150^\circ\text{C}$). Line with small symbols shows the results of third peroxide-promoted oxidation on bare AC.

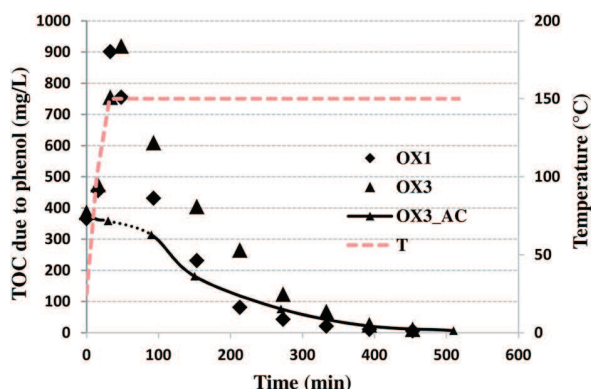


Figure 5. Evolution of TOC due to phenol during first and third peroxide-promoted oxidations on Fe/AC (large symbols) under fixed bed conditions ($T = 150^\circ\text{C}$). Line with small symbols recalls the results of third peroxide-promoted oxidation on bare AC.

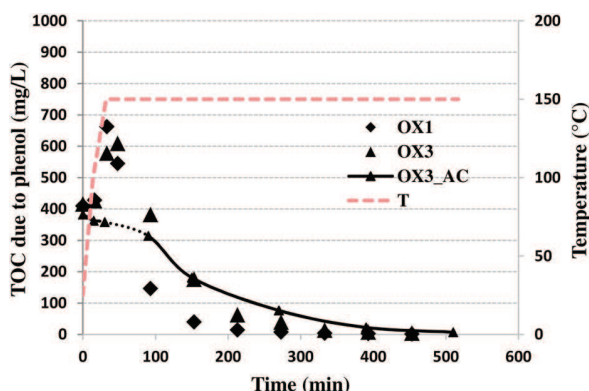


Figure 6. Evolution of TOC due to phenol during first and third peroxide-promoted oxidations on Cu/AC (large symbols) under fixed bed conditions ($T=150^{\circ}\text{C}$). Line with small symbols recalls the results of third peroxide-promoted oxidation on bare AC.

(cf. Table 1). During the subsequent cycles, they never exceeded the adsorption capacity of the original AC, their regeneration efficiency being similar or even slightly lower in the case of Cu/AC. Compared to the results of simple CWAO treatment (dashed bars in Figure 3), the addition of hydrogen peroxide did not appear as beneficial for these catalysts as it was for bare AC.

3.1.2.2. Concentration profiles during oxidation steps.

Similarly to adsorption, the oxidation efficiency of the catalysts mainly dropped between cycles 1 and 2 and was not significantly modified afterwards. Therefore only the results of first and third oxidations are shown in Figures 4–6 for bare AC with *ex situ* iron, Fe/AC and Cu/AC, respectively. The profiles measured with bare AC at the last cycle are also given on these figures for comparison purpose.

In the presence of iron salt (Figure 4(a)), the oxidation started with a much lower phenol concentration than that introduced in the liquid tank (0.5 g/L equivalent to 380 mg/L of TOC), because the concomitant addition of H_2O_2 quickly initiated a Fenton-like mechanism.

Phenol concentrations in the third cycle were always lower than that observed without added iron, but this was not the case for overall TOC in solution (Figure 4 (b)). Thus the effect of Fenton oxidation should be probably more pronounced during the heating period than afterwards, due to the oxidation and precipitation of ferrous ions. With or without addition of iron salt, TOC concentration plateaued far from complete mineralization after 8 h of oxidation.

Phenol concentration profiles observed with Fe/AC (Figure 5) displayed a much higher desorption peak, hydrogen peroxide being introduced after 30 min in

this case. Conversion of the pollutant occurred then much faster than on the original AC, yielding similar values in solution at the end of the oxidation step. Same trend was observed for mineralization yield (see Figure S3 in Supplementary Information). This enhanced oxidation could be also the result of the multi-step introduction of peroxide hydrogen, optimizing the production and effective use of hydroxyl radicals by reduction of scavenging reactions. Nonetheless this higher oxidation rate did not result into a better regeneration of Fe/AC, as shown in Figure 3.

Finally, Cu/AC (Figure 6) appeared as a very efficient catalyst, as it achieved complete phenol conversion within 200 min. Moreover, at the end of the third oxidation overall TOC concentration reached 60 vs. 290 mg/L for bare AC (see Figure S4). As abovementioned, Cu/AC was also the best catalyst in CWAO [20], but its oxidation performance seemed to be further improved by the addition of H_2O_2 . Indeed, the remaining COD in solution after 8 h of CWAO was about 300 mg/L, which should account for a higher content of organic matter than in the present case, with COD/TOC ratio expected lower than 3 (initial value for phenol solution). Liou and Chen [27] also concluded that copper oxide deposited onto AC was able to accelerate the decomposition of hydrogen peroxide with respect to the non-impregnated AC. This could be also the result of homogeneous reactions involving dissolved copper, as significant leaching was observed with this catalyst (see Section 3.1.2.3).

To evaluate the decomposition efficiency of H_2O_2 by the investigated systems, its residual concentration was measured at the end of the oxidation steps. Seven percent of the initial H_2O_2 amount was measured with bare AC after the first oxidation, as compared to 10% for Cu/AC. This could be the result of the different procedures for co-oxidant addition: the progressive injection of H_2O_2 in the latter case allowed maintaining a higher residual value and a better utilization for TOC removal. After the third oxidation, the final concentration of H_2O_2 increased to 23% of the initial value for the non-impregnated AC due to its lowered activity, but it remained unchanged for Cu/AC.

3.1.2.3. Characterization of used catalysts.

To better understand the observed phenomena, the catalysts were characterized at the end of the adsorption–oxidation cycles. Resulting textural properties and metal leaching are summarized in Table 2 for both classical and PP-CWAO treatment.

Hydrogen peroxide helped to preserve the textural properties of bare AC; a twofold increase in residual Brunauer–Emmett–Teller equation (BET) surface area and

Table 2. Surface properties and metal loss of the used catalysts after three adsorption–oxidation cycles in the case of CWAO and PP-CWAO regeneration (with 20% H₂O₂ dosage).

Catalyst label	CWAO				PP-CWAO			
	BET surface area (m ² /g)	Micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)	Metal loss (%)	BET surface area (m ² /g)	Micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)	Metal loss (%)
Bare AC	220	0.09	0.15		441	0.17	0.17	
AC + Fe salt	–	–	–		175	0.06	0.14	
Fe/AC	571	0.22	0.19	nd	501	0.19	0.17	24
Cu/AC	391	0.15	0.14	25	407	0.14	0.15	37

Note: nd = not detected.

microporous volume was observed when 20% of the stoichiometric amount was added. For the highest H₂O₂ concentration (115%), the surface area of aged carbon further increased to 600 m²/g, and the mesoporous volume (0.21 cm³/g) exceeded that of the original AC. This evolution suggests an enlargement of the smallest pores. The co-oxidant should partly oxidize phenol oligomers chemisorbed on the carbon surface or increase the acidity of the AC surface inhibiting oxidative coupling. As a result, regeneration efficiency was enhanced.

Conversely, the addition of iron salt had a negative effect, leading to a significant loss of microporosity (and mesoporosity in a much lower extent), even worse than observed after CWAO. This phenomenon was clearly related to iron precipitation on AC during oxidation.

For Fe/AC and Cu/AC, hydrogen peroxide addition did not improve the residual microporosity. This should explain the much lower effect observed on the evolution of their adsorption capacity. The mesoporous volume of these catalysts was unchanged or slightly increased after the oxidative treatments. It is noticeable that metal loading on the one hand and sub-stoichiometric addition of hydrogen peroxide on the other hand yielded similar surface properties of the catalysts after use, but their combination did not show any additional effect.

Elemental analyses of liquid samples by inductively coupled plasma atomic emission spectroscopy (ICP-AES) indicated a significant increase in metal leaching for Fe/AC and Cu/AC in the presence of H₂O₂. This would indicate that carboxylic acids like oxalic acid were formed in higher amounts with the co-oxidant and yielded soluble organometallic complexes. Indeed a much lower pH than that measured (around 3–4) would be otherwise necessary to dissolve Fe₂O₃. Corresponding dissolved iron species were probably weakly active for pollutant mineralization.

The catalysts were also examined after use by TEM and XRD analysis (Figures S5 and S6). Nanoparticles of ca. 20 nm were measured on aged Fe/AC, but the addition of H₂O₂ led to an increased crystallinity of the

metal deposit. Larger individual particles (20–50 nm) and more aggregates were observed for Cu/AC, probably as the result of the lower stability of copper oxide.

Finally, in order to evaluate the amount of adsorbed compounds, 0.5 g of bare AC and Cu/AC collected after the adsorption–oxidation cycles were contacted three times with 30 mL of methanol during 24 h at room temperature. The extracts were analyzed by liquid chromatography coupled to UV and mass spectroscopy. Oligomers such as phenoxyphenol were not found, probably because they were too strongly chemisorbed on the AC surface. The main identified compound was 4-hydroxybenzoic acid, as previously observed in CWAO [20]. Although it is known to compete with phenol for adsorption onto ACs [34], the measured quantities (6.0 and 2.3 mg/g for AC and Cu/AC, respectively) could not explain the significant loss in adsorption capacity of the catalysts. Note that these adsorbed amounts were very similar to those obtained after CWAO regeneration, while this reaction intermediate was not detected in final solutions in the presence of H₂O₂.

3.2. PP-CWAO in stirred autoclave

Successive oxidations in the presence of sub-stoichiometric H₂O₂ amount were also performed on bare AC, Fe/AC and Cu/AC using a solid to liquid ratio of 1/200 (vs. 1/50 in the adsorption–oxidation cycles operated in fixed bed).

Time-concentration profiles of phenol measured in the liquid phase after preliminary adsorption are presented in Figure 7(a–c), where they are compared to those obtained during classical CWAO. These results confirmed that hydrogen peroxide addition accelerated phenol oxidation for the three catalysts, as previously observed during the oxidative regeneration in fixed bed.

The concentration drop was prominent during the first minutes following the oxidant injection and it was nearly equivalent for bare AC and Fe/AC (around 0.2 g/L).

Thereafter the concentration profiles followed first-order kinetic trend for both catalysts, whose apparent constant was higher in the presence of H₂O₂. For Fe/AC it varied between 1.2·10^{−2} and 6.9·10^{−3} min^{−1} from

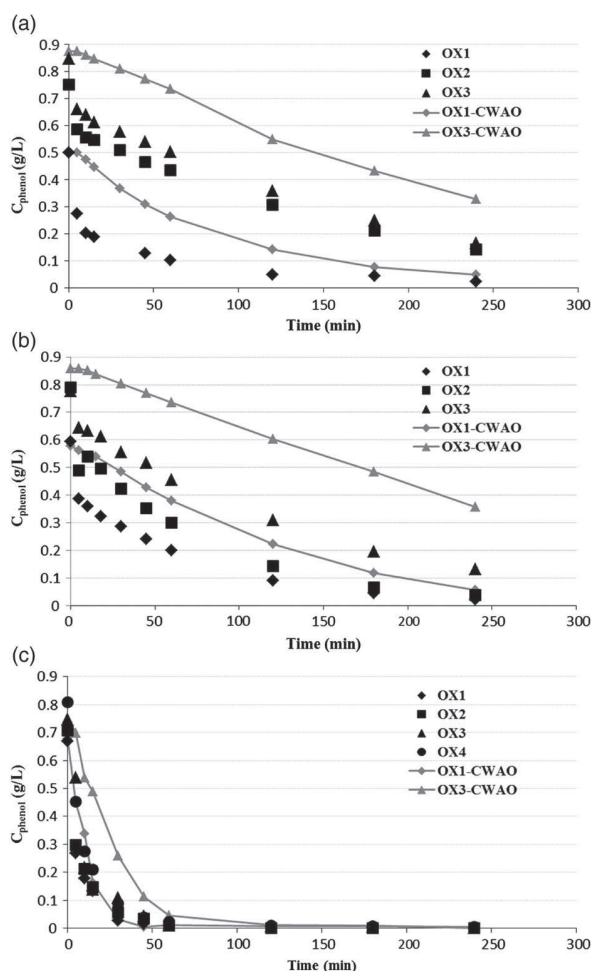


Figure 7. Evolution of phenol concentration during successive PP-CWAO on (a) bare AC, (b) Fe/AC and (c) Cu/AC (oxidation conditions in autoclave: $C_0 = 1$ g/L prior to adsorption step, $m_{\text{cat}} = 1$ g, $V_L = 200$ mL, $n_{\text{H}_2\text{O}_2} = 6$ mmol, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 3.3$ bar, $Q_{\text{air}} = 30$ NL/h). Lines show the results of oxidations 1 and 3 for classical CWAO.

oxidation 1 to 3, as compared to $9.5 \cdot 10^{-3}$ and $3.6 \cdot 10^{-3}$ min^{-1} without hydrogen peroxide. For bare AC, the effect was slightly lower, with 10–40% improvement of

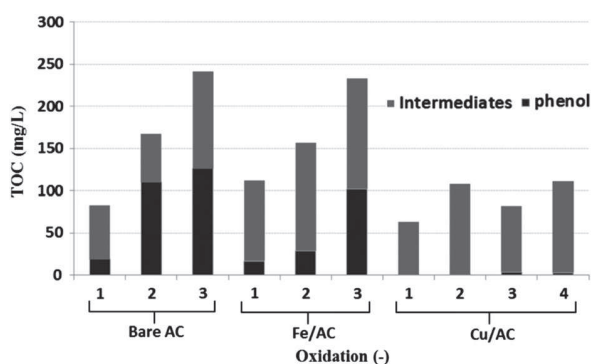


Figure 8. Residual TOC in solution after 4 h of PP-CWAO on the different catalysts under autoclave conditions.

the apparent rate constant. Nonetheless, bare AC and Fe/AC exhibited very similar profiles during the third oxidation.

Complete phenol degradation was only achieved on Cu/AC, within 1 h when H_2O_2 was added (vs. 2 h otherwise). This performance could be maintained over four oxidation cycles, as also confirmed by the remaining TOC in solution (Figure 8). Part of its catalytic activity being due to dissolved copper contribution [20], it is remarkable that no significant deactivation was observed in PP-CWAO owing to the higher metal loss. Residual TOC was almost constituted by reaction intermediates with Cu/AC, while the contribution of phenol reached up to 50% for bare AC and Fe/AC after the third oxidation. With respect to CWAO alone (cf. Figure S7), a rather similar evolution of the remaining organic pollution was observed in the presence of H_2O_2 , but associated to lower values (considering a COD/TOC ratio below 3).

The significantly better mineralization yield achieved on Cu/AC was consistent with the oxidation step results during the fixed bed operation (cf. Figure S4). It confirmed that the homogeneous reaction, implying leached copper, dissolved oxygen and hydrogen peroxide, was much more efficient to remove the pollutants in solution than on the carbon surface, so that the apparent activity and stability of the catalyst assessed from liquid phase monitoring could not presume upon the recovery of its adsorption properties.

4. Conclusion

Addition of a sub-stoichiometric amount of hydrogen peroxide accelerated the degradation of phenol during CWAO on AC, and helped to preserve the catalyst porosity and its adsorption capacity. The improvement of regeneration efficiency was much less pronounced in case of metal loaded carbon: despite metal deposit and co-oxidant should play similar role for oligomer inhibition/removal, their combination showed no additive effect. The presence of unsupported metal (through ferrous salt addition or copper leaching in the case of Cu/AC) was no more beneficial for the recovery of textural properties although it could significantly enhance phenol conversion and mineralization in solution.

This contradiction between oxidation and re-adsorption results is quite unexpected and shows that the two mechanisms are certainly connected, but not fully transposable. The catalytic activity does not only depend upon the amount of adsorbed reactant, and the knowledge of the liquid phase concentrations does not provide information on the catalyst/adsorbent surface.

Further work will investigate the potential of iron-impregnated AC as catalyst in advanced oxidation-based treatments at ambient conditions, such as photo-Fenton oxidation and ozonation.

Acknowledgements

The authors would like to thank J.L. Labat (LGC Toulouse) for the implementation of experimental setup, M.L. Pern, G. Raimbeaux, M.L. de Solan Bethmale and C. Rey-Rouch (LGC Toulouse) for their help on the characterization techniques. They also acknowledge P. Alphonse (CIRIMAT Toulouse) for XRD analyses.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors are grateful to the French-Algerian cooperation PHC 'Tassili'-CMEP program (11 MDU 833) for financial support.

References

- [1] Pollard SJT, Fowler GD, Sollars CJ, et al. Low-cost adsorbents for waste and wastewater treatment: a review. *Sci Total Environ.* 1992;116(1-2):31-52.
- [2] Mishra VS, Mahajani VV, Joshi JB. Wet air oxidation. *Ind Eng Chem Res.* 1995;34:2-48.
- [3] Ahmaruzzaman MD. Adsorption of phenolic compounds on low-cost adsorbents: a review. *Adv Colloid Interface.* 2008;143(1-2):48-67.
- [4] Magne P, Walker PL. Phenol adsorption on activated carbons: application to regeneration of activated carbons polluted with phenol. *Carbon NY.* 1986;24:101-107.
- [5] Sheintuch M, Matatov-Meytal YI. Comparison of catalytic processes with other regeneration methods of activated carbon. *Catal Today.* 1999;53:73-80.
- [6] Suarez-Ojeda ME, Stuber F, Fortuny A, et al. Catalytic wet air oxidation of substituted phenols using activated carbon catalysts. *Appl Catal B.* 2005;58:105-114.
- [7] Quesada-Penate I, Julcour-Lebigue C, Jauregui-Haza UJ, et al. Degradation of paracetamol by catalytic wet air oxidation and sequential adsorption-catalytic wet air oxidation on activated carbons. *J Hazard Mater.* 2012;221:131-138.
- [8] Matatov-Meytal YI, Sheintuch M, Shter GE, et al. Optimal temperatures for catalytic regeneration of activated carbon. *Carbon NY.* 1997;35:1527-1531.
- [9] Valdés H, Sanchez-Polo M, Rivera-Utrilla J, et al. Effect of ozone treatment on surface properties of activated carbon. *Langmuir.* 2002;18:2111-2116.
- [10] Alvarez PM, Beltran FJ, Gomez-Serrano V, et al. Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol. *Water Res.* 2004;38:2155-2165.
- [11] Alvarez PM, Garcia-Araya JF, Beltran FJ, et al. Ozonation of activated carbons: effect on adsorption of selected phenolic compounds from aqueous solutions. *J Colloid Interf Sci.* 2005;283:503-512.
- [12] Horng RS, Tseng IC. Regeneration of granular activated carbon saturated with acetone and isopropyl alcohol via a recirculation process under H₂O₂/UV oxidation. *J Hazard Mater.* 2008;154:366-372.
- [13] Huling SG, Jones PK, Ela WP, et al. Fenton-driven chemical regeneration of MTBE-spent GAC. *Water Res.* 2005;39:2145-2153.
- [14] Bach A, Zelmanov G, Semiat R. Cold catalytic recovery of loaded activated carbon using iron oxide-based nanoparticles. *Water Res.* 2008;42:163-168.
- [15] Chiu CA, Hristovski K, Huling S, et al. In-situ regeneration of saturated granular activated carbon by an iron oxide nanocatalyst. *Water Res.* 2013;47:1596-1603.
- [16] Toledo LC, Silva ACB, Augusti R, et al. Application of Fenton's reagent to regenerate activated carbon saturated with organochloro compounds. *Chemosphere.* 2003;50:1049-1054.
- [17] Muranaka C, Julcour C, Wilhelm AM, et al. Regeneration of activated carbon by (photo)-Fenton oxidation. *Ind Eng Chem Res.* 2010;49:989-995.
- [18] Polaert I, Wilhelm AM, Delmas H. Phenol wastewater treatment by a two-step adsorption-oxidation process on activated carbon. *Chem Eng Sci.* 2002;57:1585-1590.
- [19] Delmas H, Creanga Manole C, Julcour C, et al. AD-OX: A sequential oxidative process for water treatment-adsorption and batch CWAO regeneration of activated carbon. *Chem Eng J.* 2009;152:189-194.
- [20] Benhamed I, Barthe L, Kessas R, et al. Effect of transition metal impregnation on oxidative regeneration of activated carbon by catalytic wet air oxidation. *Appl Catal B.* 2016;187:228-237.
- [21] Arena F, Di Chio R, Gumina B, et al. Recent advances on wet air oxidation catalysts for treatment of industrial wastewaters. *Inorg Chim Acta.* 2015;431:101-109.
- [22] Arena F, Giovenco R, Teresa T, et al. Activity and resistance to leaching of Cu-based catalysts. *Appl Catal B.* 2003;45:51-62.
- [23] Santiago M, Stüber F, Fortuny A, et al. Modified activated carbons for catalytic wet air oxidation of phenol. *Carbon NY.* 2005;43(10):2134-2145.
- [24] Wang JB, Fu WT, He X, et al. Catalytic wet air oxidation of phenol with functionalized carbon materials as catalysts: reaction mechanism and pathway. *J Environ Sci China.* 2014;26(8):1741-1749.
- [25] Rubalcaba A, Suarez-Ojeda M, Carrera J, et al. Biodegradability enhancement of phenolic compounds by hydrogen peroxide promoted catalytic wet air oxidation. *Catal Today.* 2007;124:191-197.
- [26] Quintanilla A, Casas JA, Rodriguez JJ. Hydrogen peroxide-promoted-CWAO of phenol with activated carbon. *Appl Catal B.* 2010;93:339-345.
- [27] Liou RM, Chen SH. CuO impregnated activated carbon for catalytic wet peroxide oxidation of phenol. *J Hazard Mater.* 2009;172:498-506.
- [28] Inchaurredo NS, Massa P, Fenoglio R, et al. Efficient catalytic wet peroxide oxidation of phenol at moderate temperature using a high-load supported copper catalyst. *Chem Eng J.* 2012;198-199:426-434.
- [29] Messele SA, Stüber F, Bengoa C, et al. Phenol degradation by heterogeneous Fenton-like reaction using Fe

- supported over activated carbon. *Proc Eng.* **2012**;42:1373–1377.
- [30] Nichela DA, Berkovic AM, Costante MR, et al. Nitrobenzene degradation in Fenton-like systems using Cu(II) as catalyst. comparison between Cu(II)- and Fe(III)-based systems. *Chem Eng J.* **2013**;228:1148–1157.
- [31] Yan Y, Wu X, Zhang H. Catalytic wet peroxide oxidation of phenol over Fe₂O₃/MCM-41 in a fixed bed reactor. *Sep Purif Technol.* **2016**;171:52–61.
- [32] Julcour-Lebigue C, Krou NJ, Andriantsiferana C, et al. Assessment and modeling of sequential process for water treatment adsorption and batch CWAO regeneration of activated carbon. *Ind Eng Chem Res.* **2012**;51:8867–8874.
- [33] Lindsey ME, Tarr MA. Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide. *Chemosphere.* **2000**;41:409–417.
- [34] Andriantsiferana C, Julcour-Lebigue C, Creanga-Manole C, et al. Competitive adsorption of p-hydroxybenzoic acid and phenol on activated carbon: experimental study and modeling. *J Environ Eng.* **2013**;139(3):402–409.