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Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst

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Abstract

Continuous catalytic wet air oxidation (CWAO) was investigated as a suitable precursor for the biological treatment of industrial wastewater that contained phenols (phenol, *o*-cresol, 2-chlorophenol and *p*-nitrophenol), aniline, sulfolane, nitrobenzene or sodium dodecylbenzene sulfonate (DBS). Seventy-two-hour tests were carried out in a fixed bed reactor in trickle flow regime, using a commercial activated carbon (AC) as catalyst. The temperature and total pressure were 140 °C and 13.1 bar, respectively. The influence of hydroxyl-, methyl-, chloride-, nitro-, sulfo- and sulfonic-substituents on the oxidation mechanism of aromatic compounds, the occurrence of oxidative coupling reactions over the AC, and the catalytic activity (in terms of substrate elimination) were established. The results show that the AC without any supported active metal behaves bifunctionally as adsorbent and catalyst, and is active enough to oxidate phenol, *o*-cresol, 2-chlorophenol and DBS, giving conversions between 30 and 55% at the conditions tested. The selectivity to the production of carbon dioxide was considerable with total organic carbon (TOC) abatement between 15 and 50%. The chemical oxygen demand (COD) reduction was between 12 and 45%. In turn, aniline, sulfolane, *p*-nitrophenol and nitrobenzene conversions were below 5% and there was almost no TOC abatement or COD reduction, which shows the refractory nature of these compounds.

Keywords: Activated carbon; Substituted phenols; Dodecylbenzene sulfonate; Oxidation; Trickle bed

1. Introduction

Fresh and unfrozen water on the Earth constitutes only 0.65% of the hydrosphere, which is mostly groundwater (0.62%). Only 0.03% is surface water in lakes, rivers, soil and the atmosphere [1]. When it is used, water becomes contaminated with a wide variety of substances. For instance chemical industries generated in the EU 5.8 million tons of hazardous wastewater composed by aromatic compounds. From these quantities, 23% are phenol-like wastewater [2]. Given these large quantities of contaminated water, effective wastewater treatment processes are becoming mandatory.

In recent years, catalytic wet air oxidation (CWAO) has been increasingly focused on the treatment of biologically refractory organic compounds because it can operate at mild temperature and pressure conditions, which has a positive effect on the economics of the treatment. Unfortunately, the lack of stable and active catalysts is a serious drawback, which prevents a wider industrial implementation [3–5].

Because of its unique properties, activated carbon (AC) has been extensively used not only as an adsorbent but also as a catalyst support or even a direct catalyst [6]. In particular, AC has often been used as a support for active metals dedicated to CWAO [7–12]. It is also well known that

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AC alone can perform as a true catalyst for several reactions [13,14]. However, the potential of AC, in the absence of an active metal, as direct catalytic material for CWAO has only been recently proved for the destruction of phenol and other bioxenotic organic compounds [15–17]. It is noticeable that it performs better than other supported catalysts based on transition metals [4]. This better performance could be due to the phenol adsorption capacity of the AC that may enhance the oxidation environment conditions. Nevertheless, the performance of different ACs can be significantly different [18], which strongly suggests that not only adsorption but also other specific characteristics of the ACs affect their behaviour in CWAO. In all the above studies using AC [13,15–18], the only compound tested was phenol and less attention was devoted to other reluctant organic compounds, even using metal supported catalyst [9–12].

The present paper aims to demonstrate the feasibility of conducting CWAO in a continuous fixed bed reactor using AC as catalyst. Besides phenol, several model compounds were selected such as *o*-cresol, 2-chlorophenol, *p*-nitrophenol, aniline, sulfolane, nitrobenzene and sodium dodecylbenzene sulfonate (DBS). DBS was chosen as a representative of the linear alkylbenzene sulfonate (LAS) family. The tests were conducted at 140 °C and 13.1 bar of air, corresponding to 2 bar of oxygen partial pressure, in a fixed bed reactor operating in trickle flow regime. The performance was tested for 3 days so that the evolution of the catalytic activity could be checked. The AC used were further characterised to highlight the role of AC in the reaction mechanism.

2. Experimental

2.1. Materials

Aldrich provided analytical grade phenol, *o*-cresol, 2-chlorophenol, *p*-nitrophenol, aniline, sulfolane, nitrobenzene and DBS. Table 1 summarises the molecular weight, pK_a, solubility and purity of the model compounds. Deionised water was used to prepare all the solutions. Feed concentrations were taken as 5 g/l for all the model compounds. To prepare high performance liquid chromatography (HPLC) mobile phases, HPLC grade methanol (Aldrich) and ultra-pure water (Millipore Direct-Q system) were used. The synthetic air used as oxidant in CWAO experiments has a purity of 99.995% (Carburos Metálicos, Spain).

The AC used as catalyst was supplied by Merck (reference #102518) in the form of 2.5 mm pellets. Table 2 shows some of the characteristics of this AC. Prior to use, AC was crushed and sieved. Then, the particle size chosen was 25–50 mesh (0.7–0.3 mm) to optimise both pressure drop and internal mass transfer limitations, according to the work done by Stüber et al. [19]. Later, this fraction was washed to remove all the fines and finally dried overnight at 105 °C, cooled and stored under inert atmosphere until it was used.

Table 1
Molecular weight (MW), pK_a [50] and solubility [51] of the model compounds

Compound	MW	pK_a	Solubility (g/l at 20 °C)	Purity[a] (%)
Aniline	93.13	4.63	34	99.5
Phenol	94.11	9.89	90	99.0
o-Cresol	108.14	10.20	20	99.0
Sulfolane	120.17	12.90	1266	99.0
Nitrobenzene	123.11	3.98	1.9	99.0
2-Chlorophenol	128.56	8.48	15.5	99.0
p-Nitrophenol	139.11	7.15	16	98.0
DBS	348.48	7[b]	10	98.0

[a] As received from Sigma–Aldrich Corporation, Spain.
[b] Experimental pH value of 5 g/l DBS solution.

2.2. Experimental set-up and procedures

CWAO experiments were carried out in a trickle bed system in downflow co-current. The reactor containing the AC packed bed consists of a titanium tube (20 cm long and 1.1 cm i.d.), which is placed in a controlled temperature oven (±1 °C). Typically, 7.0 g of AC was loaded into the reactor. The liquid flow rate was set to give a space-time of 0.12 h, i.e. a liquid weight hourly space velocity (WHLV) of 8.2 h^{-1}. Synthetic air was used as oxidant at a total pressure of 13.1 bar corresponding to an oxygen partial pressure of 2 bar. The air flow rate was kept constant at 2.4 ml s^{-1} in standard conditions, which is well beyond the stoichiometric oxygen uptake needed. The experiments were run at 140 °C for 72 h. Liquid samples were periodically withdrawn and then analysed to determine substrate conversion (X), COD reduction (X_{COD}) and TOC abatement (X_{TOC}).

The same experiment was conducted twice to check the reproducibility of results and the match (within ±5%) between successive experiments was excellent. The data reported in the paper are the arithmetic average of the results derived from repeated CWAO experiments.

Sample concentrations of substituted phenols and sulfolane were immediately determined by gas chromatography (GC 6890, Agilent Technologies). The chromatograph was equipped with an HP-5 capillary column (5% phenyl-methyl-siloxane, 30 m × 0.32 mm i.d. × 0.25 μm film thickness). The same analytical protocol served to quantify substituted phenols and sulfolane. An isothermal (40 °C) program was applied for the first 6.3 min, then the temperature was increased by 20 °C/min for 3 min, and finally the heating rate was changed to 30 °C/min until the temperature reached 120 °C, which was maintained constant for 1 min. After that, a ramp of 30 °C/min was applied to reach 140 °C, which was kept constant for 1 min. The last sequence increased the temperature from 140 to 180 °C at a heating rate of 10 °C/min. The FID detector was maintained at 300 °C and the injector was kept at 250 °C.

Sample concentrations of *p*-nitrophenol, nitrobenzene, aniline and DBS were immediately determined by HPLC (model 1100 Agilent Technologies). The analysis was performed with a C18 reverse phase column (Hypersil ODS, Agilent Technologies) and a mobile phase of methanol and water consisting of 35:65 (v/v) for *p*-nitrophenol and of 50:50 (v/v) for nitrobenzene. The flow rate was 1 ml/min. The wavelength in the diode array detector was 254 nm. For aniline, the mobile phase used was a mixture of acetonitrile and water (60:40, v/v), with a flow rate of 1 ml/min and a wavelength of 280 nm in the detector. The mobile phase was acidified to pH equal to 1.5 with concentrated sulphuric acid.

Finally for DBS, a method described by Matthijs and De Henau [20] and Patterson et al. [21] was adapted by using an acetonitrile–water–sodium perchlorate mobile phase to separate the DBS from its reaction products. Two mobile phases were used. Solution A was a mixture of acetonitrile and water with a proportion of 70:30 (v/v), whereas, solution B was only water. Sodium perchlorate was added to both mobile phases at a concentration of 0.15 M. Again a flow rate of 1 ml/min and a wavelength of 225 nm were used.

COD was measured with the standard method 5220D [22], whereas TOC was quantified with the method 5310B [22]. The CO_2 selectivity was calculated by balance between the initial and final TOC values in the experimental samples.

The results are compared in terms of conversion, i.e. model compound destruction. The general expression used is

$$X(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 is the inlet concentration and C_e the concentration in the effluent. Eq. (1) can also be used to calculate both X_{COD} and X_{TOC} in a similar way.

The classical phenol oxidation scheme proposed in the literature [23] was investigated in the phenol experiments by checking the presence of the reported intermediates. Hence, samples were subjected to a deeper analysis by HPLC to determine oxidation intermediates such as quinone-like products and organic acids. The analysis was carried out using a C18 reverse phase column (Hypersil ODS, Agilent Technologies) and a mixture of water and methanol. The gradient starts from 100% of water and goes to 50:50 (v/v) of water:methanol B at 8 min. It remains isocratic until the end. Both mobile phases were acidified to pH equal to 1.5 with concentrated sulphuric acid.

Table 2
Physical characteristics of the AC

Source	Wood
Ash (%)	4.5
BET surface area (m^2/g)	1481
Micropore volume ($cm^3\ g^{-1}$)	0.3428
BJH cumulative surface area[a] (m^2/g)	304
pH_{PZC}	8.05

[a] Between 17 and 3000 Å.

A complete scheme of the CWAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [15,18,24].

2.3. Characterisation of the activated carbon

AC adsorption isotherms for the various target compounds were obtained at 20 °C (±2 °C) in oxic conditions following a standard protocol [25,26]. The pH in the point of zero charge (pH_{PZC}) for the AC was determined according to Nouri et al. [27].

At the end of the CWAO test, the AC used was carefully collected and dried at 105 °C overnight under an inert atmosphere to remove the excess water. Then, the AC was divided into three parts. The first one was dried at 400 °C under nitrogen atmosphere to remove any physisorbed compound. This temperature was selected because all the compounds seem to be completely desorbed but AC does not undergo major reactions. Subsequently, the AC was weighed to measure the weight change (W_{AC}).

The second part (approx. 25 mg) was subjected to thermogravimetric analysis (TGA). The analysis was carried in a Thermobalance Perkin-Elmer model TGA7, TCA7. The sample was heated from 100 to 900 °C under nitrogen flow at a heating rate of 10 °C/min.

Finally, the last part (between 20 and 30 mg) was used to determine textural properties by nitrogen adsorption isotherms at 77 K in a Micromeritcs instrument model ASAP 2010. For such studies, samples were outgased at 120 °C under vacuum for 24 h. The textural properties such as surface area, micropore volume and cumulative surface area were calculated by applying different model methods, i.e. BET, Harkins and Jura *t*-plot and Barret–Joyer–Halenda (BJH), which are included with the Micromeritics software.

3. Results and discussion

The results and discussion are divided into two sections. In the first, the CWAO performance is discussed by means of X, X_{COD} and X_{TOC}. Also, the reactivity order and the reaction mechanisms are examined. In the second section, the relation between AC behaviour and the reactivity order is investigated, using adsorption isotherm data, AC weight change, TGA and data from N_2 adsorption isotherms.

3.1. Model compound disappearance

Fig. 1(a) shows the conversion evolution for a 72 h test at 140 °C and 2 bar of oxygen partial pressure. As previously found [18], three different zones can be distinguished in all the cases. Firstly, after starting an adsorption-dominating period results in an apparent total conversion. Secondly, a continuous fall in conversion is observed when the AC bed progressively undergoes both adsorption and oxidation of the model compound. Finally, once the bed is saturated, true conversion almost attains steady state.

The adsorption-dominating period lasts for about 8 h in the case of phenol, 5 h for *o*-cresol, 7 h for 2-chlorophenol, 7 h for DBS, 4 h for aniline and 1–2 h for sulfolane. The duration of the adsorption-dominating period fairly agrees with the respective adsorption capacity and bed loading. The saturation times according to the flow rate and adsorption capacity calculated from the Freundlich equation at 20 °C (Section 3.2) are 10 h for phenol, 11 h for *o*-cresol, 16 h for 2-chlorophenol, 25 h for DBS, 12 h for aniline and 5 h for sulfolane, assuming a constant concentration through the bed. The difference between the experimental and theoretical saturation times could be due to this assumption but also to the fact that the adsorption capacity decreases as the temperature increases [28,29]. It must be noted that adsorption isotherms were obtained at 20 °C while the experiments were done at 140 °C.

Another factor that could influence the adsorption capacity is the pH. Fig. 1(b) shows the pH profiles throughout the test. At the start the pH is between 6.7 and 6.8, close to neutrality, which confirms the absence of the compound in the effluent. Then the pH begins to decrease during the transient state and reaches a steady state value. This decrease is caused by the formation of organic acids (or hydrochloric acid, in the case of 2-chlorophenol) as oxidation by-products. The adsorption period occurs at pHs above 5 and a decrease in adsorption capacity has been reported above this pH for several substituted phenols. These compounds can be in undissociated and ionised forms, above a pH of 5 and it is well known that ionised forms of species adsorb less effectively onto AC than their undissociated forms do [26]. However, as shown in Table 2, the $\mathrm{pH_{PZC}}$ of this AC is 8.05, therefore the AC surface is positively charged during the adsorption period and during the rest of the test; therefore, the AC surface would exhibit a high affinity for anions or ionised forms of parent compounds.

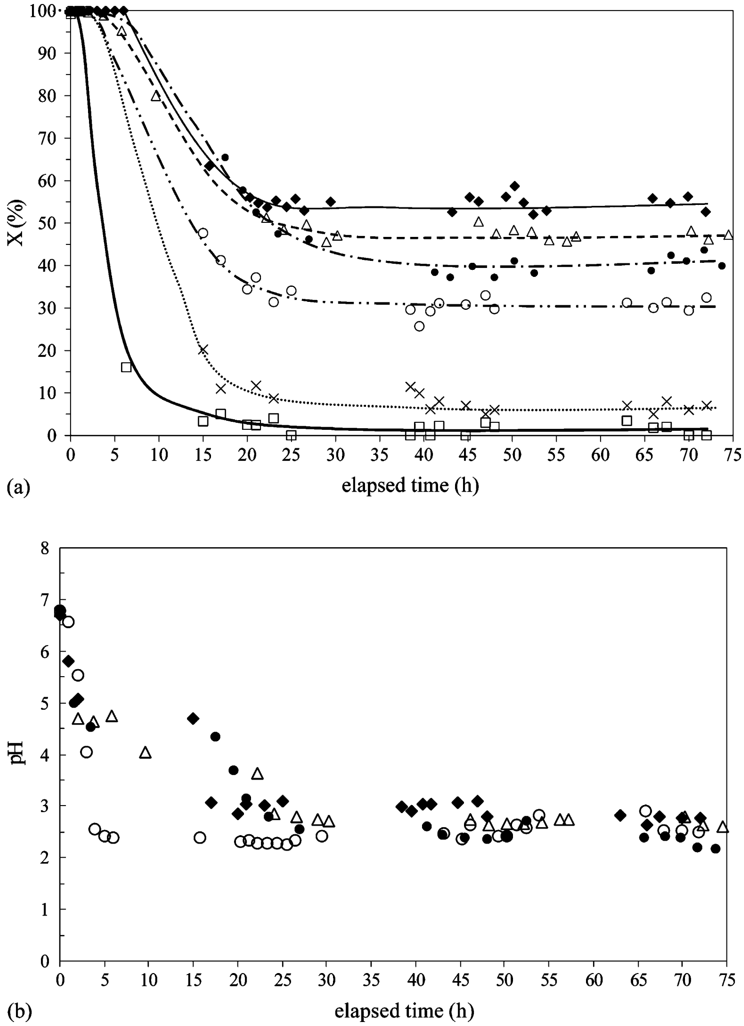
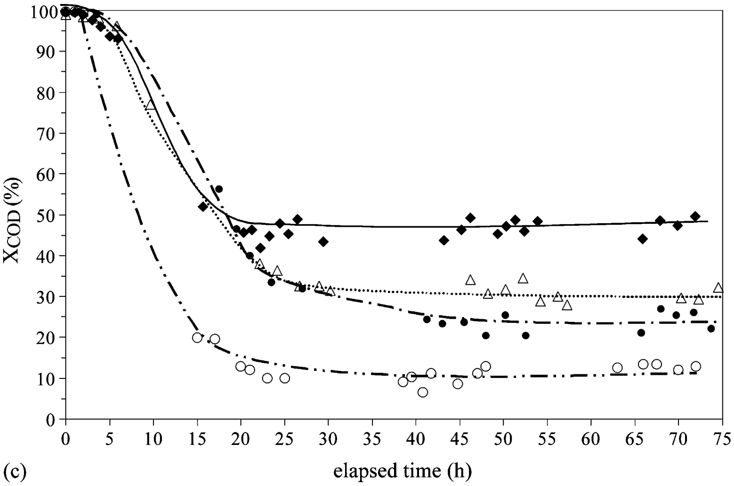


Fig. 1. Conversion (a), pH (b), COD reduction (c) and TOC abatement (d) profiles at 140 °C and 2 bar of partial O_2 pressure. Symbols indicate experimental data are: (◆) 2-chlorophenol, (△) phenol, (●) DBS, (○) *o*-cresol, (×) aniline and (□) sulfolane. Lines only show tendencies are: (—) 2-chlorophenol, (- -) phenol, (– –) DBS, (– · · –) *o*-cresol, (···) aniline and (—) sulfolane.



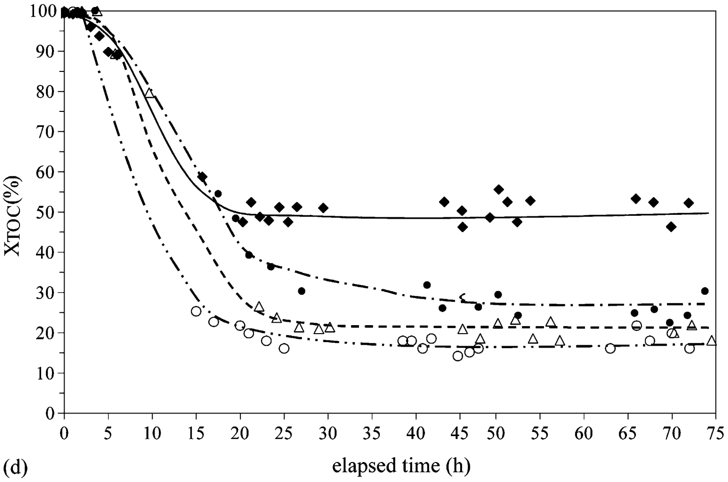


Fig. 1. (*Continued*).

Adsorption isotherms were obtained without adjusting the pH, i.e. the solution pH was provided according to the pK_a values of each compound (Table 1). In accordance with the values, the model compounds are of an acid nature, thus, the solutions pH was below the pH$_{PZC}$, and the electrostatic forces would increase the adsorption capacity. For these reasons, the pH does not seem to be determinant in the adsorption capacity decrease observed in the CWAO test.

The transient period lasts between 10 and 20 h depending on the compound. In this period, the conversion goes from apparently 100% to the steady state value, and the oxidation reaction continues, producing reaction intermediates that are adsorbed onto AC. These intermediates could compete with the compound for the active sites until a balance between them is attained, which finally results in the steady state conversion.

The steady state period corresponds to the last 30 or 40 h in each test, depending on the compound. The steady state values of X are 55% for 2-chlorophenol, 45% for phenol, 38% for DBS, 33% for *o*-cresol, 6% for aniline, 5% for sulfolane and practically no conversion for nitrobenzene and *p*-nitrophenol. The results permit to distinguish two groups. The first one with high reactivity includes phenol, 2-chlorophenol, *o*-cresol and DBS, while the second one with low reactivity, includes aniline, *p*-nitrophenol, sulfolane and nitrobenzene. For this latter group, no further study was made. Thus, the following discussion will not refer to the analyses of these compounds.

Fig. 1(c) and (d) show the evolution of X_{COD} and X_{TOC} for phenol, 2-chlorophenol, *o*-cresol and DBS. The same tendencies described for Fig. 1(a) can be drawn in these cases. At steady state, X_{COD} is close to 48% for 2-chlorophenol, 30% for phenol, 25% for DBS and 15% for *o*-cresol. For X_{TOC}, the values in the steady state are 47% for 2-chlorophenol, 21% for phenol, 24% for DBS and 14% for *o*-cresol.

In the case of phenol, the detailed HPLC analyses showed that the main partial oxidation products were light carboxylic acids such as oxalic, acetic and formic acids. Malonic, maleic, and fumaric acids were detected in trace amounts. Finally, measurable amounts of hydroquinone, catechol and benzoquinones were also observed. No other possible intermediates were detected. All the intermediates detected are reported in the reaction pathway described by Devlin and Harris [23] and have also been found in previous research, using the same reactor and operating conditions [30]. The presence of these intermediates thus suggests a consecutive-parallel reaction pathway, which agrees with the simplified reaction pathway proposed by Eftaxias et al. [31].

Because of the presence of partially oxidised products, X_{COD} is obviously lower than the respective X. It should be pointed out that the higher the difference between X and X_{COD}, the higher the amount of partially oxidised products in the liquid effluent. Hence, the differences in the tests are 18% for *o*-cresol, 15% for phenol, 13% for DBS, and only about 7% for 2-chlorophenol. This demonstrates that 2-chlorophenol undergoes deeper oxidation. This can also be confirmed by the difference between X and X_{TOC}, which gives the selectivity towards carbon dioxide. This selectivity increases as X and X_{TOC} become closer. Thus, the differences are 9% for 2-chlorophenol, 24% for phenol, 14% for DBS and 17% for *o*-cresol. These values indicate that complete mineralisation also depends on the substituent involved.

As found, the oxidation depends on the properties of the compound. As far as X is concerned, the experimental reactivity order is 2-chlorophenol > phenol > DBS > *o*-cresol > aniline, sulfolane. This reactivity order can be explained by nucleophilic aromatic substitution mechanism [32]. The substituents can be classified by their capacity to stabilise the sigma complex, i.e., the benzonium carbanion. The substituents are strongly deactivating if they withdraw electrons and strongly activating if they releases electrons.

Hence, the sulfonic and chloride groups ($-SO_3H$ and $-Cl$) are strongly activating and the hydroxyl, methyl, dodecyl, sulfo and amino groups ($-OH$, $-CH_3$, $CH_3(CH_2)_5CH(CH_2)_4CH_3$, $-SO_2$, and $-NH_2$) are deactivating for the nucleophilic aromatic substitution. Therefore, these compounds are expected to be destroyed in the order 2-chlorophenol > phenol > DBS > *o*-cresol > aniline and sulfolane, which matches the experimental results. De et al. [33] also propose this mechanism for the oxidation of phenol and 2-chlorophenol with hydrogen peroxide, which shows many similarities with the present case. At the selected temperature, the unique function of AC can be the generation of anions and oxygen radicals similar to those that occur in the oxidation with hydrogen peroxide or ozone. Then, the oxidation reaction should evolve in solution. As De et al. propose [33], whatever reactive species are involved, the rate at which they are added to the aromatic ring depends on the stabilisation of the sigma complex. Therefore, the proposal of a nucleophilic aromatic substitution as the reaction mechanism seems to be a reasonable explanation of the reactivity order found.

However, the phenol oxidation mechanism is extremely complex and is not yet fully understood. It has been reported that the oxidation of phenol and some substituted phenols in aqueous solution by molecular oxygen is an electrophilic reaction that follows a heterogeneous–homogeneous free radical chain mechanism, where the limiting step is the reaction between the aryloxy radical and oxygen [34–36]. In this case, the easiness of oxidation to the corresponding radicals could be inferred from the half-wave potentials (HWP) of each compound [37]. The HWP refers to the relative oxidation potentials of irreversible phenol oxidations, obtained by polarographic analysis. Actually, thermodynamic redox potentials should be used for comparing oxidation rates, but these can only be measured for reversible systems and most monohydric phenol oxidations are practically irreversible because the initially formed aryloxy radicals undergo further fast reactions. Therefore, thermodynamic redox potentials for such systems cannot be determined experimentally. Nevertheless, it has been shown that polarographic HWP for irreversible systems are similar, at least in their sequence, to the actual redox potentials, so the HWP has usually been taken as a measure of oxidability of phenols [37].

Table 3
Half-wave oxidation potentials [37]

Compound	$E_{1/2}$ (mV)
o-Cresol	556
2-Chlorophenol	625
p-Nitrophenol	924
Phenol	1004
Aniline	1135

The facility with which phenols can be oxidised (i.e. the formation of aryloxy radicals) increases as the steric crowding in *ortho*-positions and the electron-releasing properties of substituents in *ortho*- and *para*-positions increase. Table 3 shows the HWP of the model compounds [37]. The lower the HWP, the easier the oxidation. Therefore, for the free radical mechanism, the reactivity order should be *o*-cresol > 2-chlorophenol > *p*-nitrophenol > phenol > aniline, which does not match the reactivity order found in this study. This suggests that the presence of AC as catalyst probably modifies the classical reaction mechanism.

3.2. Activated carbon performance

Fig. 2 shows the adsorption isotherms at 20 °C. These isotherms come from equilibration for 4 h and were obtained in oxic conditions, i.e. the solution was always in contact with air. Thus, some degree of oxidative coupling could take place during the process as a result of the presence of dissolved oxygen [38]. Anyway, according to the literature [39], this effect should only be relevant for long exposures (over 12 h) between the phenols and the AC, which is not the case.

These adsorption isotherms were later fitted to the Freundlich equation:

$$q = kc^{1/n} \quad (2)$$

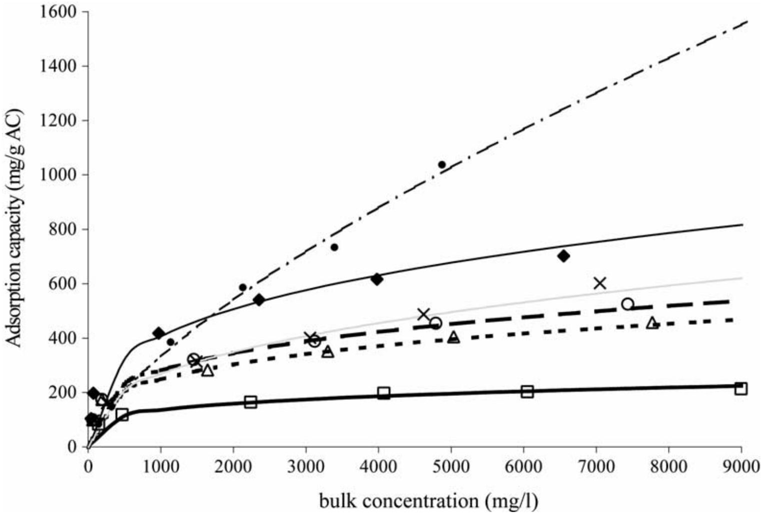


Fig. 2. Adsorption isotherms of selected model compounds. Symbols indicate experimental data are: (◆) 2-chlorophenol, (△) phenol, (●) DBS, (○) *o*-cresol, (×) aniline and (□) sulfolane, whereas lines correspond to the Freundlich model are: (—) 2-chlorophenol, (– –) phenol, (- - -) *o*-cresol, (- - · – · - -) DBS, (···) aniline and (—) sulfolane.

where c is the compound concentration in bulk solution (mg l^{-1}) and q the amount of substrate adsorbed in milligram per gram of AC. This empirical equation assumes that the adsorbent has a heterogeneous surface composed by different classes of adsorption sites, so as $1/n$ values are closer to 0 indicates heterogeneous adsorption, and $1/n$ values close to 1 indicates homogeneous adsorption. Table 4 lists the parameters obtained by fitting and the adsorption capacity calculated at 5000 ppm for each compound. In Table 4, the $1/n$ values are below 1, indicating a favourable adsorption onto the surface [40]. Also, it must be noted that the larger molecule (DBS, Table 1) has $1/n$ value of 0.7 being close to a homogeneous adsorption. On contrary, aniline and phenol have more or less the same molecular weight but aniline has two unpaired electrons which could increase the possibility for heterogeneous adsorption and therefore decreases its adsorption capacity onto the AC.

The adsorption capacity follows the order DBS > 2-chlorophenol > aniline > *o*-cresol > phenol > sulfolane. It is evident that the higher the solubility in water (Table 1), the lower the adsorption capacity. Also, the bigger the molecule, the higher the adsorption capacity, which agrees with the results of Daifullah and Girgis [41]. In their study, the adsorption capacity of substituted phenols is a direct function of the molecular dimension of the sorbate and an inverse function of its solubility. The same direct correlation between solubility and adsorption capacity was found by García-Araya et al. [42] for phenolic acids. Comparing the reactivity order obtained with the adsorption capacity, it can be concluded that the adsorption phenomena do not explain the CWAO performance for the different compounds tested.

Because it is well known that phenolic compounds can undergo coupling reactions, the changes in the AC weight and AC surface area during oxidation should shed some light on the loss of AC catalytic activity and the influence of oxidative coupling on CWAO. Table 5 shows the W_{AC} and textural properties for the used AC from each experiment.

As Table 5 shows, W_{AC} was positive (i.e. the AC weight increased) for all model compounds at the end of the test, which is in reasonable agreement with the observations of Fortuny et al. [18] for phenol CWAO. These observations can be extended to the rest of compounds tested in this study. The W_{AC} has previously been studied [15,18] for phenol CWAO, with the same reactor and a range of conditions (temperature, pressure and space-time) that includes those used here. W_{AC} turned out to be positive or negative depending on the elapsed time and the operating conditions [15,18]. At 140 °C and 9 bar of oxygen partial pressure, it was observed that AC weight increases in the first 24 h, then reaches a maximum and finally decreases to values below the original one. Furthermore, after 10 days of experiment and at lower oxygen partial pressures, the AC weight increases [15].

Many studies have shown that this positive W_{AC} can be attributed to the deposition of polymeric compounds

Table 4
Parameters of the Freundlich equation and adsorption capacity at 5000 ppm

Compound	q^a (mg/g AC)	k (mg/g AC) $(l\ mg^{-1})^{1/n}$	$1/n$
Sulfolane	188 ± 11	25 ± 1	0.24 ± 0.01
Phenol	395 ± 20	34 ± 1	0.29 ± 0.02
o-Cresol	451 ± 16	37 ± 1	0.29 ± 0.02
Aniline	496 ± 32	19 ± 1	0.38 ± 0.01
2-Chlorophenol	674 ± 35	44 ± 1	0.32 ± 0.01
DBS	1028 ± 44	3 ± 1	0.70 ± 0.01

Correlation factor (R^2) are over 0.98.

[a] At 5000 ppm in the bulk solution.

Table 5
Original bed loading, W_{AC} and textural characterisation at the end of the CWAO test

Compound	Phenol	*o*-Cresol	2-Chlorophenol	DBS
Loaded AC (g)	7.60	7.30	6.90	7.01
W_{AC} (%)[a]	3.61	6.09	7.84	6.16
BET surface area (m^2/g)	122	24	169	285
Micropore volume (cm^3 g^{-1})	0.003	0.001	0.004	0.006
BJH cumulative area surface (cm^2/g)[b]	96	2	120	148

[a] Dried at 400 °C.

[b] Between 17 and 3000 Å.

produced by oxidative coupling reactions over the AC [43–46]. Cooney and Xi [26] demonstrated that, at low pHs, oxidative coupling reactions can be accelerated by the presence of a substituent in the phenol molecule. They postulated that oxidative coupling reactions occur simultaneously with the oxidation reaction and these coupling reactions probably block the active sites in AC, and decrease its catalytic activity. According to Cooney and Xi [26], oxidative coupling reactions follow the order *o*-cresol > 2-chlorophenol > phenol, which except for 2-chlorophenol is similar to the W_{AC} presented in Table 5.

A minimum AC weight gain (i.e. a minimum of oxidative coupling reactions), must correspond to a maximum of X, since oxidative coupling is expected to block the active sites and diminishes the superficial area (as Table 5 shows) and, therefore, the catalytic activity. However, as can be seen in

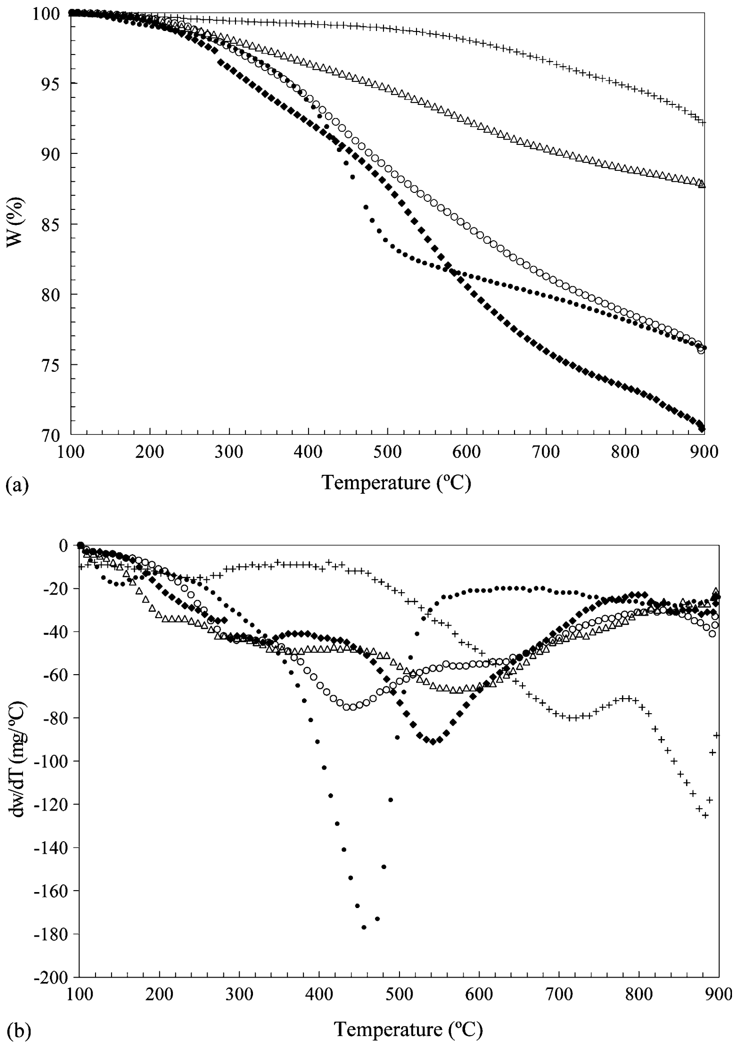


Fig. 3. TGA data (a) and first derivative of TGA data (b) of original and used AC after being tested in 72 h CWAO experiments. (+) Virgin AC, (◆) 2-chlorophenol, (△) phenol, (●) DBS, and (○) *o*-cresol.

Table 5, the BET surface area decreases according to the following order DBS > 2-chlorophenol > phenol > *o*-cresol, which is in fact the reactivity order obtained in the experiments with the exception of DBS. Thus, according to the present results, the oxidative coupling cannot explain by itself the reactivity order found.

In order to relate W_{AC} with X, the experimental results were fitted to a first-order kinetic model for substrate concentration assuming a plug-flow model for the trickle bed reactor [15]. Hence, the apparent kinetic constant, k_{ap}, for the compound disappearance can be estimated from:

$$k_{ap} = -\frac{Q_L}{W_{cat}} \ln\left(1 - \frac{X}{100}\right) \quad (3)$$

where Q_L is the volumetric flow rate (ml h^{-1}) and W_{cat} is the AC weight (g) in the packed bed at the start of the test. The calculated kinetic constants are 3.32 ± 0.04 ml h^{-1} g^{-1} for *o*-cresol, 3.92 ± 0.04 ml h^{-1} g^{-1} for DBS, 4.52 ± 0.05 ml h^{-1} g^{-1} for phenol and 7.31 ± 0.06 ml h^{-1} g^{-1} for 2-chlorophenol. The apparent kinetic constants suggest that the higher W_{AC} (i.e. the higher loss in surface area), the lower the conversion. Again, this is valid for phenol, *o*-cresol and DBS, but not for 2-chlorophenol, which simultaneously shows the highest conversion, the highest W_{AC} and the highest BET surface area.

TGA were performed to find out which kind of compounds could be responsible for the weight change and to evaluate the quantity of adsorbed products. Fig. 3(a) and (b) show the thermograms and their first derivatives (dw/dT) of the model compounds for virgin and used AC during the TGA performed between 100 and 900 °C under nitrogen flow. The virgin AC thermogram is a typical one showing an appreciable peak around 715 °C. This peak can be related to desorption of CO and CO_2 species coming from surface oxygen groups attached to AC. According to Figueiredo et al. [47], the surface species attached to the AC are desorbed at different temperatures. Thus, from 100 to 300 °C, the slow release of species is due to the decomposition of such carboxylic groups as CO_2, whereas, the zone between 300 and 900 °C can be assigned to the release of CO_2 due to the decomposition of lactones and CO from oxygen surface groups such as carboxyl, phenyl and ether groups.

Generally speaking, the thermograms have two zones. In the first one, between 200 and 300 °C, the species are slowly released; in the second one, between 300 and 800 °C, in which they are released continuously and rapidly. This second zone shows a marked peak, which depends on the compound used in the CWAO. The peak occurs at 577 °C for phenol, at 442 °C for *o*-cresol, at 542 °C for 2-chlorophenol and at 462 °C for DBS.

It is believed that the weight loss in the first zone coincides with the release of physisorbed model compounds and reaction intermediates, whereas, the weight loss in the second zone corresponds to the decomposition of chemisorbed species, including the cracking of polymers from oxidative coupling reactions [48,49].

Table 6
Total weight loss during the TGA of the virgin and used AC (%, w/w)

Virgin AC	Phenol	*o*-Cresol	2-Chlorophenol	DBS
8.0	12.2	24.2	29.8	24.1

The total weight loss (TWL) of each sample is summarised in Table 6 for all the CWAO tests and the virgin AC. It should be noted that the highest TWL is 29.8% for 2-chlorophenol CWAO, about three and a half times greater than that of the original AC, which was only 8%. The TWL in the AC used follows the order 2-chlorophenol > *o*-cresol > DBS > phenol. As expected, the same inverse relation exists between X and TWL and between X and surface area, but again the AC used in the 2-chlorophenol test is an exception.

The W_{AC} and the TWL for each compound follow a trend that does not match the one predicted from oxidative coupling [26], so again the oxidative coupling reaction does not explain the reactivity order obtained.

A satisfactory explanation for the reactivity order in this study is still lacking, as no definitive conclusions come out from the AC characterisation done. However, the results suggest that the reaction occurs in solution instead of over the AC surface, therefore the role of AC could only be the generation of oxygen radicals and/or anions.

4. Conclusions

Several CWAO were performed with 2-chlorophenol, phenol, DBS, *o*-cresol, aniline, sulfolane, *p*-nitrophenol and nitrobenzene as model compounds. The oxidation was conducted in mild conditions of air pressure (13.1 bar) and temperature (140 °C) in a fixed bed reactor operating in trickle flow regime. Conversions were between 30 and 55% for phenol, 2-chlorophenol, DBS and *o*-cresol. On the other hand, conversions were below 6% for aniline, *p*-nitrophenol, sulfolane and nitrobenzene.

The activated carbon without any active metal was shown to have a catalytic effect on the wet oxidation of phenol, *o*-cresol, 2-chlorophenol and DBS. In all cases, the oxidation was highly selective to CO_2.

The reactivity order 2-chlorophenol > phenol > DBS> *o*-cresol > aniline, sulfolane seems to correspond to a nucleophilic aromatic substitution mechanism. Other possible factors influencing the CWAO performance such as adsorption, oxidative coupling reactions, pore blockage, etc. have been studied without obtaining a satisfactory explanation for the reactivity order obtained in this study. In the case of phenol, a detailed HPLC analysis shows intermediates that have been reported previously, which suggests a consecutive-parallel reaction pathway.

The apparent kinetic constants suggest that the higher W_{AC} is the lower the conversion is. This is true for phenol, *o*-cresol and DBS but not for 2-chlorophenol, which has the highest conversion and highest W_{AC} simultaneously. The positive W_{AC} can be explained by the presence of adsorbed phenolic-based polymers on the AC produced by oxidative coupling reactions, as demonstrated by TGA results and nitrogen adsorption isotherms.

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References

[1] B. Lomborg, The Skeptical Environmentalist: Measuring the Real State of the World, Cambridge University Press, UK, 2001, Part III, Chapter 13.
[2] European Pollutant Emission Register, EU15 overview report of direct and indirect emissions to water in 2001. http://www.eper.eea.eu.int/eper/Emissions_member_state.asp?i=, 2004.
[3] S. Mishra, V.V. Mahajani, J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2.
[4] Y. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 37 (1998) 309.
[5] S.T. Kolaczkowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh, Chem. Eng. J. 73 (1999) 143.
[6] F. Rodríguez-Reinoso, Carbon 36 (1998) 159.
[7] X. Hu, L. Lei, H.P. Chu, P.L. Yue, Carbon 37 (1999) 631.
[8] J. Trawczynski, Carbon 41 (2003) 1515.
[9] P. Gallezot, N. Laurain, P. Isnard, Appl. Catal. B 9 (1996) 11.
[10] L. Oliviero, J. Barbier Jr., D. Duprez, A. Guerrero Ruiz, B. Bachiller-Baeza, I. Rodríguez Ramos, Appl. Catal. B 25 (2000) 267.
[11] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Appl. Catal. B 27 (2000) 217.
[12] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catal. Today 75 (2003) 23.
[13] R.W. Coughlin, Ind. Eng. Chem. Prod. Res. Dev. 8 (1969) 12.
[14] M.F.R. Pereira, J.J.M. Orfao, J.L. Figueiredo, Appl. Catal. A 19 (2000) 643.
[15] A. Fortuny, J. Font, A. Fabregat, Appl. Catal. B 19 (1998) 165.
[16] V. Tukac, J. Hanika, Collect. Czech. Chem. Commun. 61 (1996) 1010.
[17] A. Santos, P. Yustos, S. Gómis, F. García-Ochoa, Proceedings of the Ninth Mediterranean Congress of Chemical Engineering, Barcelona, November 2002, p. 91.
[18] A. Fortuny, C. Miró, J. Font, A. Fabregat, Catal. Today 48 (1999) 323.
[19] F. Stüber, I. Pollaert, H. Delmas, J. Font, A. Fortuny, A. Fabregat, J. Chem. Technol. Biotechnol. 76 (2001) 743.
[20] E. Matthijs, H. De Henau, Tenside Detergents 24 (1987) 193.
[21] D.A. Patterson, I.S. Metcalfe, F. Xiong, A.G. Livingstone, Ind. Eng. Chem. Res. 40 (2001) 5507.
[22] American Water Association (Ed.), Standard methods for the examination of water and wastewater, Washington American Public Health Association, Washington, 1999.
[23] H.R. Devlin, I.J. Harris, Ind. Eng. Chem. Fund. 23 (1984) 387.
[24] A. Fortuny, C. Ferrer, C. Bengoa, J. Font, A. Fabregat, Catal. Today 24 (1995) 79.
[25] T.M. Grant, C.D. King, Ind. Chem. Res. 29 (1990) 264.
[26] D. Cooney, Z. Xi, AIChE J. 40 (1994) 361.
[27] S. Nouri, F. Haghseresht, M. Lu, Adsorp. Sci. Technol. 20 (2002) 1.
[28] D. Do Duong, Adsorption Analysis: Equilibria and kinetics, Imperial College Press, London, 1998, Chapter 2.
[29] I. Polaert, A.M. Wilhelm, H. Delmas, Chem. Eng. Sci. 57 (2002) 1585.
[30] A. Eftaxias, Catalytic wet air oxidation of phenol in a trickle bed reactor: kinetics and reactor modelling, PhD Dissertation, Universitat Rovira i Virgili, Tarragona, Spain, 2001.
[31] A. Eftaxias, J. Font, A. Fortuny, J. Giralt, A. Fabregat, F. Stüber, Appl. Catal. B 33 (2001) 175.
[32] S. Weininger, F.R. Stermitz, Química Orgánica, Editorial Reverté, Barcelona, 1988, Chapters 15, 23 and 24.
[33] A.K. De, B. Chaudhuri, S. Bhattacharjee, J. Chem. Technol. Biotechnol. 74 (1999) 162.
[34] A. Pintar, J. Levec, Ind. Eng. Chem. Res. 33 (1994) 3070.
[35] A. Sadana, J.R. Katzer, J. Catal. 35 (1974) 140.
[36] H.S. Joglekar, S.D. Samant, J.B. Joshi, Water Res. 25 (1991) 135.
[37] S. Patai (Ed.), The Chemistry of the Hydroxyl Group, Interscience Publishers, New York, 1971, Chapter 10.
[38] R.D. Vidic, M.T. Suidan, Environ. Sci. Technol. 25 (1991) 1612.
[39] R.D. Vidic, M.T. Suidan, R.C. Brenner, Water Res. 28 (1994) 263.
[40] B. Okolo, C. Park, M.A. Keane, J. Colloid Interf. Sci. 226 (2000) 308.
[41] A.A.M. Daifullah, B.S. Girgis, Water Res. 32 (1997) 1169.
[42] J.F. García-Araya, F.J. Beltrán, P. Álvarez, F.J. Masa, Adsorption 9 (2002) 107.
[43] C.H. Tessmer, R.D. Vidic, L.J. Uranowski, Environ. Sci. Technol. 31 (1997) 1872.
[44] T.M. Grant, C.J. King, Ind. Eng. Chem. Res. 29 (1990) 264.
[45] N.S. Abuzaid, G.F. Nakhla, Environ. Sci. Technol. 28 (1994) 216.
[46] G.A. Sorial, M.T. Suidan, R.D. Vidic, S.W. Maloney, J. Environ. Eng. 119 (1993) 1026.
[47] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfao, Carbon 37 (1999) 1379.
[48] P.M. Álvarez, F.J. Beltrán, V. Gómez-Serrano, J. Jaramillo, E.M. Rodríguez, Water Res. 38 (2004) 2155.
[49] A.P. Terzyk, Adsorp. Sci. Technol. 21 (2003) 539.
[50] D. Lide (Ed.), CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data, CRC Press, Boca Raton, 2003.
[51] Sigma–Aldrich Corporation, Material safety data sheets, Spain, 2003.