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Chemical Engineering Journal 132 (2007) 105–115

Chemical Engineering Journal

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Catalytic wet air oxidation of substituted phenols: Temperature and pressure effect on the pollutant removal, the catalyst preservation and the biodegradability enhancement

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Received 31 July 2006; received in revised form 15 January 2007; accepted 17 January 2007

Abstract

The influence of temperature (140 and 160 °C) and oxygen partial pressure (2 and 9 bar) on the continuous catalytic wet air oxidation (CWAO) over activated carbon (AC) has been investigated for the removal of phenol, *o*-cresol and 2-chlorophenol in aqueous solutions. Seventy-two-hour tests were performed in a fixed bed reactor in trickle flow regime. A commercial AC was employed as catalyst. The pollutant elimination effectiveness, the distribution of major reaction products and the AC behaviour were studied for each compound. Also, respirometric screening tests were completed to the effluents before and after each CWAO experiment to assess the biodegradability enhancement. The results show that pollutant disappearance, chemical oxygen demand (COD) removal, total organic carbon (TOC) abatement and biodegradability enhancement (fraction of COD readily biodegradable, $\%\mathrm{COD}_{\mathrm{RB}}$) were very sensitive to temperature but rather independent of the oxygen partial pressure (P_{O_2}). On the contrary, AC catalyst preservation was strongly influenced by both temperature and pressure. For instance, for phenol CWAO at 2 bar of P_{O_2}, as temperature increased from 140 to 160 °C, phenol conversion increased from 45% to 78%, COD removal from 33% to 65%, TOC abatement from 21% to 62% and $\%\mathrm{COD}_{\mathrm{RB}}$ from 4% to 36%. Similar behaviour was found for the other model compounds tested, although the level of refractoriness was rather different.

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Keywords: Activated carbon; Substituted phenols; Wet air oxidation; Biodegradability enhancement

1. Introduction

The importance of phenolic industrial effluents, besides their potential toxicity, is outlined by the high quantities that are eventually disposed. For instance, phenol, *o*-cresol and 2-chlorophenol are recognised toxic substances listed in the 2000 OECD List of High Production Volume Chemicals [1].

Biological treatment of these compounds usually has low removal efficiency. For instance, microbial toxicity studies with *Daphnia magna* showed that these compounds are toxics [2,3]. Among many others, catalytic wet air oxidation (CWAO) is a technique for treating this kind of hazardous wastewater that is not amenable to biological treatment. At the proper operating conditions, CWAO is able to generate an effluent suitable to be discharged into a municipal biological wastewater treatment plant (WWTP). However, the catalyst choice is indeed the core in the CWAO performance. Recently, several studies have demonstrated that activated carbon (AC) alone can successfully perform as a true catalyst [4] for several reactions, including CWAO of phenol, *o*-cresol, 2-chlorophenol and other bioxenotic organic compounds [5–8]. Nevertheless, the performance of different ACs can significantly differ [9], which strongly suggests that different characteristics of the ACs affect their behaviour as catalyst. Hence, a depth inspection of the CWAO performance is needed for each AC chosen as catalyst and for each substrate in order to properly design a successful treatment plant.

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doi:10.1016/j.cej.2007.01.025

This study deals with an integrated treatment of substituted phenols based on CWAO followed by biological treatment. The main objective is that the CWAO effluent becomes a regular fraction of the total influent to a municipal biological WWTP without causing adverse effects over the efficiency and operation of the conventional sewage sludge process. To design such integrated chemical–biological systems, the substrate degradation extent and the knowledge of physical, chemical and biological properties of the main reaction intermediates occurring in the CWAO step are key points [10]. Thus, the appropriate CWAO conditions for each specific case can be assessed.

Several CWAO tests were done using phenol, *o*-cresol and 2-chlorophenol as target pollutants. CWAO was continuously conducted in a trickle bed reactor using a commercial AC as catalyst. Two temperatures, 140 and 160 °C, and two oxygen partial pressures (P_{O_2}), 2 and 9 bar, were studied. The aims are to determine the effect of varying temperature and pressure on the substrate removal and the biodegradability enhancement (i.e. fraction of chemical oxygen demand (COD) readily biodegradable (%COD_{RB}) of the CWAO effluents) and on the AC preservation.

Another article presents a detailed study of the biodegradability, toxicity and inhibition characteristics of the main intermediates detected in the effluents coming from CWAO of a high-strength *o*-cresol wastewater. In addition, the results of a pilot scale study for an integrated CWAO-biological WWTP for the treatment of this wastewater are presented [11].

2. Experimental

2.1. Materials

Aldrich provided analytical grade phenol, *o*-cresol and 2-chlorophenol. Table S1 in supporting information summarises some physic-chemical characteristics of the model compounds. Feed concentration was always 5 g l^{-1}. However, in terms of COD concentration, the initial concentrations were 10.8 g COD l^{-1} for phenol, 9.5 g COD l^{-1} for *o*-cresol and 7.5 g COD l^{-1} for 2-chlorophenol. These concentrations were chosen to check the feasibility of using CWAO as an effective pre-treatment before a biological WWTP, according to the technology map drawn by Hancock [12].

The AC used as catalyst was supplied by Merck (reference #102518) in the form of 2.5 mm pellets. Prior to use, AC was crushed and sieved. Then, the chosen particle size was in the range 0.7–0.3 mm in order to minimise mass transfer limitations according to Stüber et al. [13]. The characteristics of this AC, prior to use, can be found elsewhere [6].

2.2. Experimental set-up and procedures for CWAO experiments

A complete scheme of the CWAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [6,7,9].

CWAO experiments were done in a trickle bed reactor in down-flow co-current for 72 h. The experiments were run at 140 and 160 °C and synthetic air was used as oxidant to guarantee a P_{O_2} of 2 and 9 bar at each temperature. Typically, 7.0 g of AC was loaded into the reactor. In all the experiments, the liquid flow rate was set to give a space time of 0.12 h, i.e. a liquid weight hourly space velocity of 8.2 h^{-1}, giving a value of 57.4 ml h^{-1}. The air flow rate was kept constant at 2.4 STP ml s^{-1} in all the experiments, which is well beyond the stoichiometric oxygen uptake needed. Liquid samples were periodically withdrawn and analysed to determine target compound destruction (X), COD reduction (X_{COD}), TOC abatement (X_{TOC}), distribution of partial oxidation products, and biodegradability enhancement, measured as %COD_{RB}.

Experiments were repeated to check reproducibility of results and the agreement (within ±5%) between successive experiments was excellent. The data reported in this work are the arithmetic average of the results derived from three repeated CWAO experiments.

According to the oxidation pathways proposed in the literature for each model compound [14–19], a set of reported oxidation intermediates was checked. Target compounds, quinone-like compounds, condensation products and organic acids were separated by HPLC. The analysis was done in a C18 reverse phase column (Hypersil ODS, Agilent Technologies) with a gradient mixture of ultra-pure water and methanol. A HPLC chromatogram from a standard calibration mixture is shown in the supporting information section (Figure S1). In addition, 4-hydroxybenzoic acid (4-HB), its isomer salicylic acid (2-HB) and resorcinol were also calibrated. Other possible intermediates such as methyl- and chlorinated-quinones were also checked. However, these latter intermediates were not detected in any CWAO sample, therefore, they were neither included in the sample chromatogram (Figure S1, supporting information section) nor in the results section.

COD and total organic carbon (TOC) analysis were measured following the standard methods 5220D and 5310B [20], respectively.

The AC used in each CWAO test was collected and dried overnight at 105 °C under N_2 atmosphere. Then, the used AC was subjected to several analysis such as thermogravimetric analysis (TGA), nitrogen adsorption isotherms at 77 K to determine its textural properties, and mass change estimation (M_{AC}) by drying at 400 °C as described elsewhere [6,7].

2.3. Experimental set-up for respirometric experiments

The respirometer used for the biodegradability screening tests corresponds to a LFS type, in which dissolved oxygen concentration (S_O) is measured in the liquid-phase (L), which is static (S) and continuously aerated (F) [21]. The pH was maintained at 7.5 ± 0.5 and the temperature was set at 31 ± 0.5 °C. The biomass used as seed culture came from a municipal biological WWTP (Tarragona, Catalonia, Spain). The biomass was starved overnight to ensure endogenous conditions before each respirometric experiment. The presence of 20 mg l^{-1} of 1-allyl-2-thiourea (ATU) avoided nitrification interference. The average concentration of volatile suspended solids (VSS) in the respirometric tests was 3400 ± 300 mg VSS l^{-1}.

All the respirometric data presented in this work corresponds to the arithmetic average of the results derived from two repeated experiments. The reproducibility of the respirometric results and the match (within 10%) between successive respirometric experiments was excellent.

2.4. Determination of readily biodegradable COD fraction of the CWAO effluents

In any wastewater, the total biodegradable COD (COD_{TB}) is the sum of the readily (COD_{RB}) and the slowly biodegradable COD (COD_{SB}) fractions, in accordance to the original bi-substrate model proposed in the 1980s by Dold et al. [22]. The determination of COD_{TB} requires a combination of several techniques and experiments [23,24] but, specifically the COD_{SB} determination is extremely time-consuming, whereas the available methods for COD_{RB} determination mostly lies in fast respirometric experiments [25]. Therefore, the COD_{RB} can be used as a fast method to characterize the biodegradability of a specific wastewater. Here, respirometry is used as a screening test to compare the biodegradability enhancement reached with different CWAO conditions in comparison to the initial target effluents.

The procedure used in this study was originally proposed by Ekama et al. [26]. To assess the biodegradability of the treated and non-treated effluents, a $20\,\text{mg COD}\,\text{l}^{-1}$ (COD_{added}) pulse of either the CWAO effluent or the target compound solution was added inside the respirometer. Then, the oxygen uptake rate (OUR) profile and the oxygen consumption (OC) are obtained solving the dissolved oxygen (S_O) balance in the liquid phase of the respirometer. More information about the OUR and OC calculation can be found elsewhere [21].

Because respirometry is used in this study as simple and fast screening tool, the concentrations used in the tests were chosen taking into account two items. First, the use of low load to feed ratios leads to short-term experiments, as the substrate is rapidly assimilated and no significant biomass growth occurs [27]. Also, the organic matter storage by the heterotrophic biomass and the subsequent intracellular consumption of COD is avoided [23,28]. Second, the following biological treatment of the CWAO effluent is assumed to be done in a continuous stirred tank reactor (CSTR). Assuming that the reactor is well mixed, the compositions in the bioreactor will be everywhere uniform and the composition of the effluent will be the same that the mixture within the tank. This composition must be below the discharge limits if the biological treatment is working efficiently, consequently, the concentration of the compounds will be low.

Once the OC is obtained from the respirometric tests, the COD_{RB} can be calculated using the heterotrophic yield coefficient (Y_H) as follows [25,29,30]:

$$COD_{RB} = \frac{OC}{1 - Y_H} \qquad (1)$$

The biological COD removal is a process where part of the substrate is directly used for new biomass growth and the rest is oxidized for energy production. In this context, Y_H represents the fraction of substrate used for production of new biomass. This coefficient can be also calculated using respirometric techniques, with a similar protocol than that used by Strotmann et al. [29].

The COD_{RB} fraction of CWAO effluents is then calculated according to

$$\%COD_{RB} = \frac{COD_{RB}}{COD_{added}} \times 100 \qquad (2)$$

3. Results and discussion

In this study, the influence of temperature and pressure variations in the CWAO effluent biodegradability and composition was checked against several phenolic compounds. Liquid flow rate, i.e. space time, was fixed to a selected value assuring a distribution of intermediates where the quinone-like fraction was minimised and the carboxylic acids fraction maximised, though mineralisation of the target pollutants was not complete. This selection was made according to the results obtained in a previous work [31] where several space times were tested at several temperatures and pressures for phenol CWAO. That work demonstrated at 140 °C and 2 bar of P_{O_2} that a low space time, i.e. high liquid flow rates, gives a low *p*-benzoquinone concentration, acceptable concentrations of carboxylic acids, and enough phenol elimination.

Also, it must be noted that several simultaneous reactions occur when using AC as catalyst in CWAO. There is not only the expected oxidation of the target compound and its intermediates, but also the AC oxidation/burning and the oxidative coupling (or irreversible adsorption) of the compounds over the AC, which occur to some extent. Additionally, the physical adsorption of the substrate and the partial oxidation products is also happening at the same time. Therefore, the use of AC as catalyst in CWAO increases even more the already intrinsic complexity of wet oxidation. These parallel reactions and adsorption processes cannot be uncoupled and studied separately. Therefore, only global information can be taken from the effluent (Section 3.1) and used AC characterisation (Section 3.2) attempting to establish the contribution of each one in the biodegradability enhancement (Section 3.3).

During the discussion, the CWAO conditions will use the following nomenclature: 140-2 will refer to 140 °C and 2 bar of P_{O_2}, 160-9 equals to 160 °C and 9 bar of P_{O_2} and so on.

3.1. Target pollutant disappearance and reaction intermediates

The steady-state conversions (X, X_{COD} and X_{TOC}) are listed in Table 1. As expected, temperature has a strong influence on the conversions. For *o*-cresol, at 2 bar, X goes from 33% to 83%, X_{COD} from 15% to 53% and X_{TOC} from 14% to 47% as temperature increases from 140 to 160 °C. In turn, P_{O_2} has a weaker effect on the overall conversions. For *o*-cresol, at 160 °C, X goes from 83% to 90%, X_{COD} from 53% to 64% and X_{TOC} from 47% to 46% as pressure increases from 2 to 9 bar. The same trends are found for the other compounds. However, a detailed inspection of Table 1 shows an exception in the effect of P_{O_2}. For *o*-cresol at 140 °C, as P_{O_2} increases from 2 to 9 bar, X changes from 33%

Table 1
Final conversions for CWAO tests

Compound	P_{O_2} (bar)	140 °C			160 °C		
		X (%)	X_{COD} (%)	X_{TOC} (%)	X (%)	X_{COD} (%)	X_{TOC} (%)
Phenol	9	58	42	32	62	58	52
	2	45	33	21	78	65	62
o-Cresol	9	97	42	40	90	64	46
	2	33	15	14	83	53	47
2-Chlorophenol	9	60	51	49	80	58	56
	2	55	48	47	75	70	69

Data from 140-2 bar are from Ref. [6].

to 97%. This exception could be caused by a strong modification in the AC catalytic activity as discussed later.

Because of the presence of partially oxidized products, X_{COD} is lower than the respective X. The higher the difference between X and X_{COD}, the higher the amount of partially oxidized products in the liquid effluent. For example, the differences between X and X_{COD} at 140-2 are 18% for *o*-cresol, 12% for phenol and only 7% for 2-chlorophenol. This suggests that 2-chlorophenol undergoes deeper oxidation towards carbon dioxide than phenol or *o*-cresol. The difference between X and X_{TOC}, which directly gives the selectivity towards carbon dioxide, also confirms this fact. The carbon dioxide selectivity increases as X and X_{TOC} get closer. Hence, in 140-2 tests, the differences were 19% for *o*-cresol, 24% for phenol and 8% for 2-chlorophenol. These values indicated that complete mineralisation reaction pathway clearly depends on the substituent involved, too.

As far as X in steady state is concerned, for CWAO tests performed at 140-2, the reactivity order, according to Table 1, is 2-chlorophenol > phenol > *o*-cresol, whereas in the case of 140-9 tests the reactivity order is *o*-cresol > 2-chlorophenol ≈ phenol. For 160-2 the reactivity order is *o*-cresol > phenol ≈ 2-chlorophenol. Finally for 160-9 test, the reactivity order is *o*-cresol > 2-chlorophenol > phenol. However, with the exception of phenol 140-9 test, it must be noticed that the steady state is not clearly achieved for 9 bar tests (Figs. 1 and 2, discussed later). This can be caused by the continuous loss of AC due to oxidation side reactions discussed later, which cannot be prevented at these severe conditions. Also, this loss in AC weight could explain the slight decrease in X observed for *o*-cresol test at 160-9 compared to the X at 140-9.

From these results it seems that two different reaction mechanisms could exist to explain the first oxygen radical attack to the target phenolic compound. In the nucleophilic aromatic substitution mechanism, the chloride group (–Cl) is strongly activating and the hydroxyl and methyl groups (–OH and –CH_3), in that order, are deactivating. De et al. [16] proposed this mechanism for the oxidation of phenol and 2-chlorophenol with hydrogen peroxide. Therefore, these compounds are expected to be eliminated in the order 2-chlorophenol > phenol > *o*-cresol, which closely matches with the experimental results obtained at 140-2.

On the contrary, for an electrophilic aromatic substitution, the mechanism passes through the benzenium cation or a sigma complex, so that the activating groups in the nucleophilic substitution should help to refuse the electrophilic substitution in

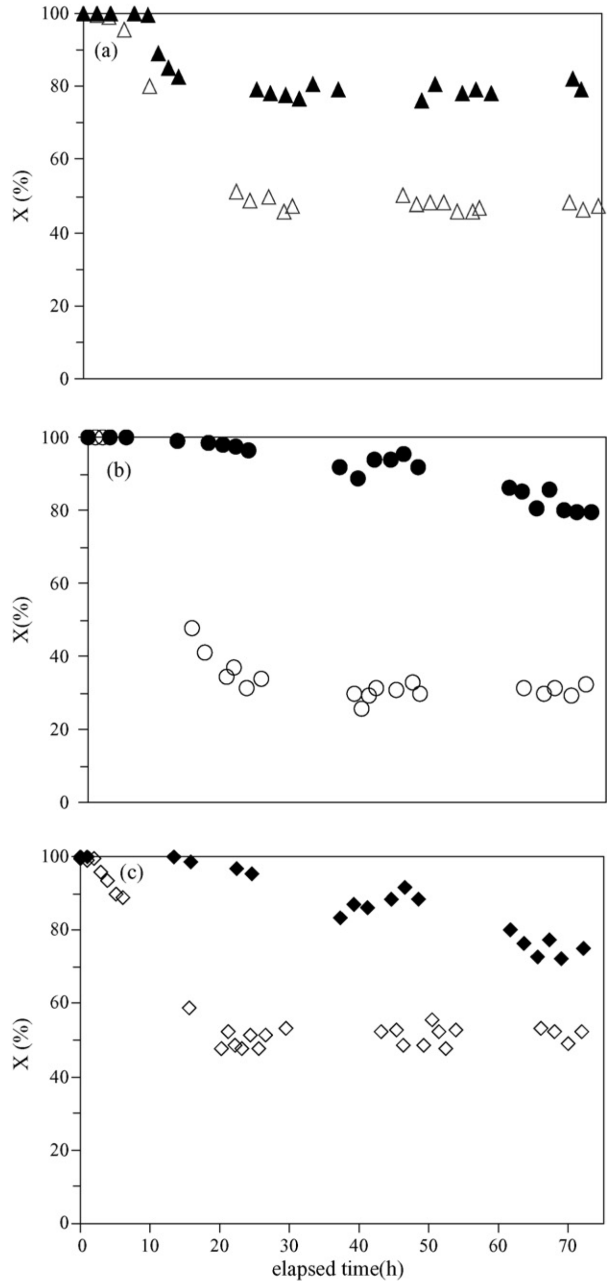

Fig. 1. Conversion evolution in 72 h tests at 2 bar of O_2 partial pressure and 140 °C (open symbols) and 160 °C (full symbols). Symbols indicate experimental data ((a) phenol; (b) *o*-cresol; (c) 2-chlorophenol). Data at 140-2 are from Ref. [6].

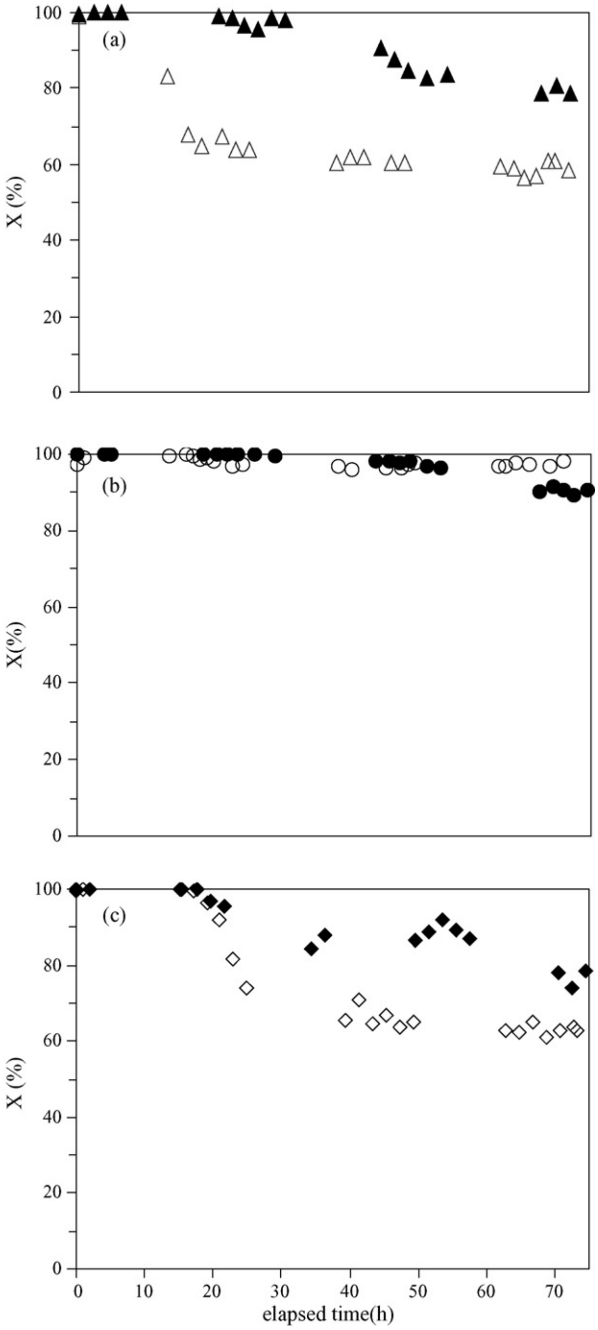

Fig. 2. Conversion evolution in 72 h tests at 9 bar of partial O_2 pressure and 140 °C (open symbols) and 160 °C (full symbols) bar. Symbols indicate experimental data ((a) phenol; (b) *o*-cresol; (c) 2-chlorophenol).

the aromatic ring. Hence, the compounds are expected to be destroyed in a reverse order: *o*-cresol > phenol > 2-chlorophenol, which better fits the experimental results at 160-2, 160-9 and 140-9.

In the present conditions, the AC could be envisaged as a promoter in the generation of oxygen radicals similar to those coming from hydrogen peroxide and ozone [17]. Therefore, it is possible that the molecular oxygen to subsequently form anions and radicals, which respectively behave as nucleophiles and electrophiles in the reaction media. Regardless the reactive species involved in the oxidation, the addition rate of a nucleophile or an electrophile to the aromatic ring depends on the stabilisation of the benzonium carbanion or the sigma complex, respectively. Therefore, seems to be reasonable the hypothesis that a nucleophilic or an electrophilic aromatic substitution could be the first step in the reaction mechanism. However, the reactivity order is only a qualitative statement and the different steady-state reactivity orders above listed could be largely affected by the temperature (activation energy effect), changes in the AC performance, as later discussed, competition with the other organic compounds for the available oxygen radicals, and even adsorption over the AC surface.

The full conversion profiles throughout the CWAO tests are shown in Figs. 1–4. As previously found [6], three different zones could be distinguished in all the profiles after the start-up of the experiment. Firstly, an adsorption-dominating period resulted in an apparent total conversion. Secondly, when the breakthrough front progressively approaches to the end of the AC bed, a sudden fall in conversion is monitored. Finally, once the bed is pseudo-equilibrated, the compound conversion almost attains steady state. The evolution of X_{COD} and X_{TOC} for phenol, 2-chlorophenol and *o*-cresol (Figs. 3 and 4) follows the same trends described for *X*. In despite of this characteristic shape, the starting transient period does not significantly influence the steady state reached, although some of the changes in the AC occurs during this period.

Regarding to the reaction intermediates, the theoretical chemical oxygen demand ($\mathrm{COD_{Th}}$) of each one was calculated from the obtained HPLC concentration [32]. The partial oxidation products have been grouped into carboxylic acids, quinone-like products, condensation products, non-identified products and, remaining target compound. Later, the contribution of each group was compared to the total experimental COD analytically measured. The results are summarised in Fig. 5 for phenol (Fig. 5a), *o*-cresol (Fig. 5b) and 2-chlorophenol (Fig. 5c).

From Fig. 5 in phenol tests, the carboxylic acids fraction roughly increased, with the severity of the CWAO. However, at 160-9, this fraction is lower than at 160-2. On the contrary, the quinone-like fraction behaviour was opposite to that of carboxylic acids, also increasing at 160-9 demonstrating that most severe conditions does not mean always a higher mineralisation. At 160-2, formic, acetic and propionic acids were 87% of the COD in form of carboxylic acids (35% over the total effluent composition), whereas *p*-benzoquinone and catechol were 81% of the COD in form of quinone-like products (7% over the total effluent composition). At 160-9, *p*-benzoquinone and catechol were the 81% of the COD in form of quinone-like products (27% over the total effluent composition), whereas the COD from carboxylic acids were mainly composed of acetic, maleic, succinic and 4-HB acids, accounting for 89% of the COD in form of carboxylic acids (22% over the total effluent composition). At 140 °C the COD in form of carboxylic acids was composed mainly by acetic and propionic acid, being 95% at 2 bar of $P_{\mathrm{O_2}}$, and 51% at 9 bar of $P_{\mathrm{O_2}}$ of the remaining COD in form of carboxylic acids (14% at 2 bar and 16% at 9 bar compared to the total effluent composition). The quinone-like fraction was mainly catechol for both $P_{\mathrm{O_2}}$, being its concentration always double than the concentration of hydroquinone

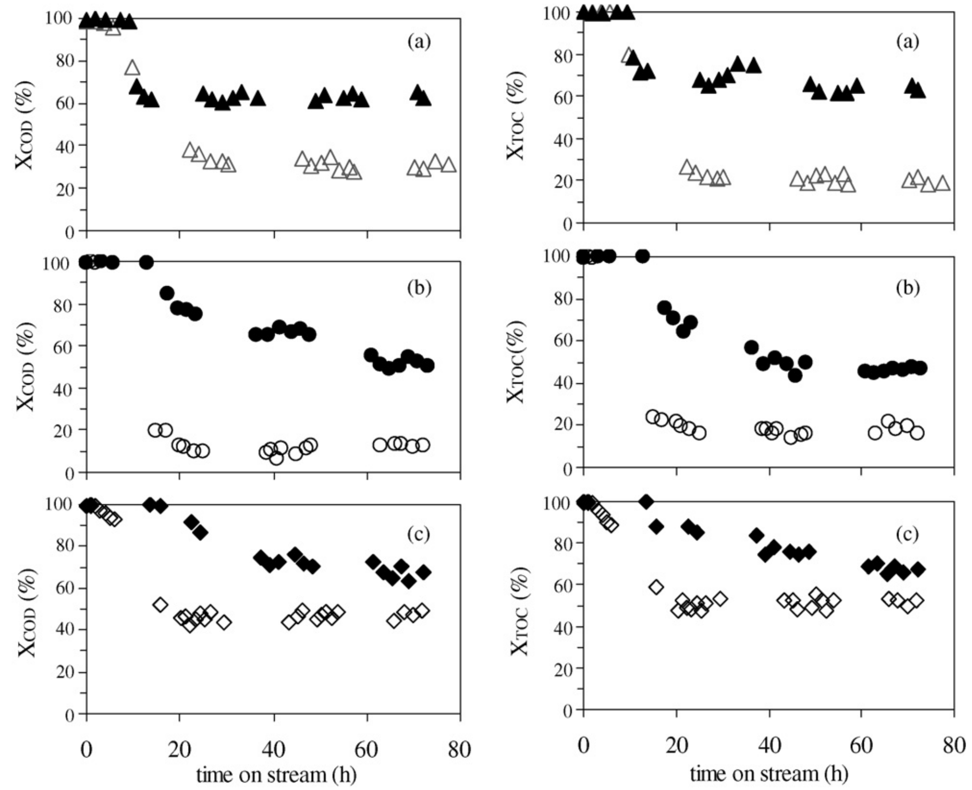

Fig. 3. X_{COD} and X_{TOC} profiles at 2 bar for (a) phenol; (b) *o*-cresol; (c) 2-chlorophenol and empty symbols indicates CWAO test at 140 °C, filled symbols indicates CWAO tests at 160 °C. Data at 140-2 are from Ref. [6].

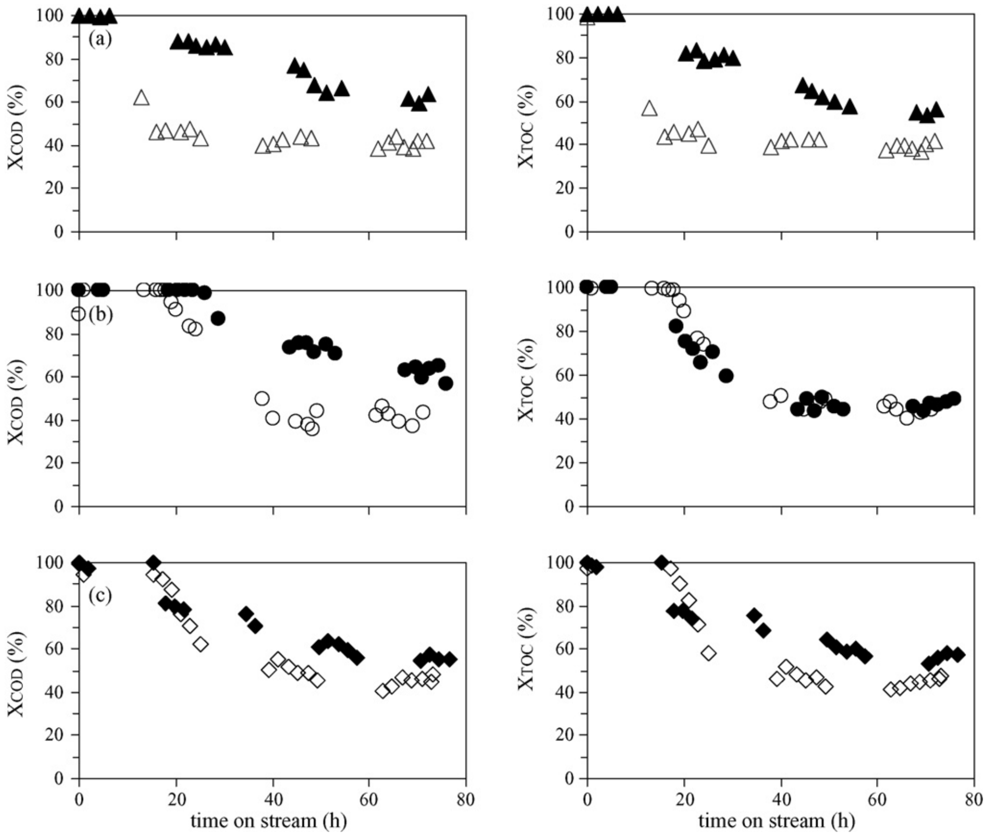

Fig. 4. X_{COD} and X_{TOC} profiles at 9 bar for (a) phenol; (b) *o*-cresol; (c) 2-chlorophenol and empty symbols indicates CWAO test at 140 °C, filled symbols indicates CWAO tests at 160 °C.

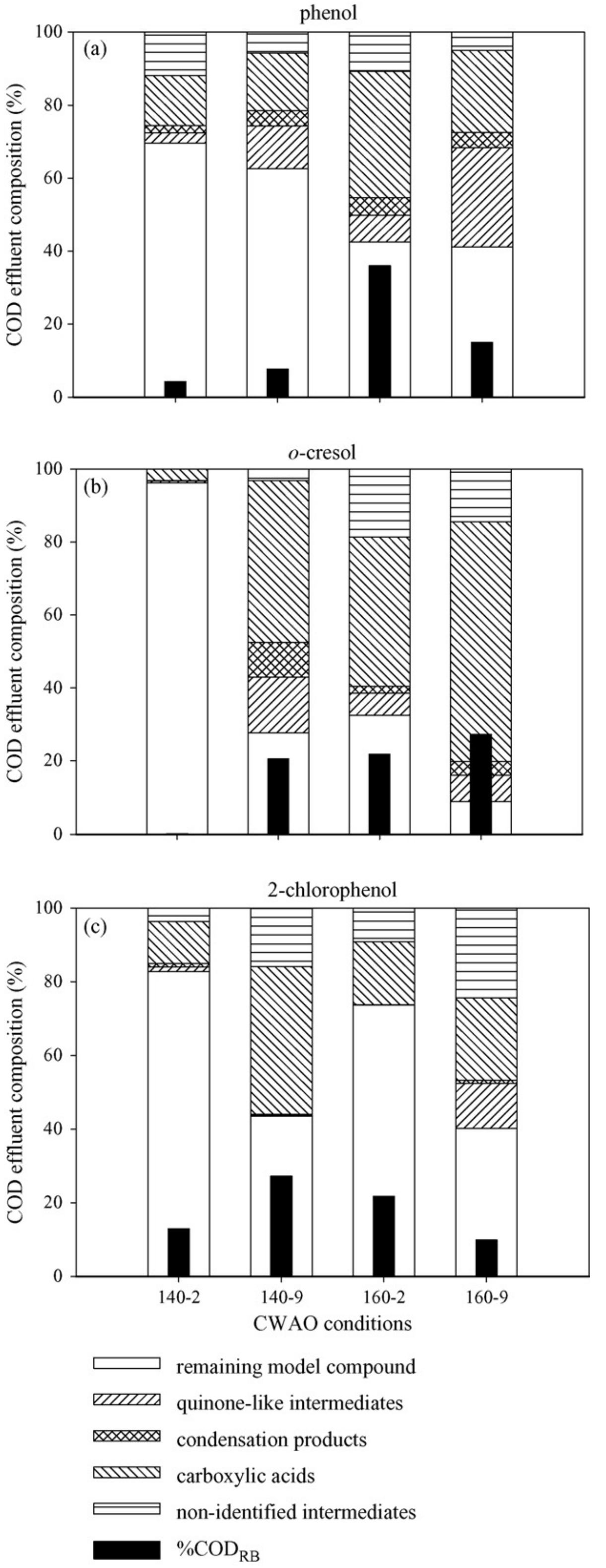

Fig. 5. Intermediates distribution and %COD$_{RB}$ obtained by respirometric test for phenol (a), *o*-cresol (b) and 2-chlorophenol (c) for each CWAO effluent.

and *p*-benzoquinone together. Overall, phenol CWAO at 160-2 seems to progress enough to oxidize most of the organics to formic, acetic and propionic acids. However, at 160-9, the acids are of larger molecular weight and the quinone-like products are also in higher proportion, indicating that the reaction conditions were not suitable or that the AC activity loss is too high (Section 3.2). Similar trends can be withdrawn for 140 °C and both P_{O_2}, although in those cases the reaction conditions were not sufficient to transform phenol into more amenable intermediates.

For *o*-cresol and 2-chlorophenol similar conclusions can be drawn from Fig. 5 than those previously described for phenol. However, several remarks should be pointed out. For *o*-cresol, at 140-9 and 160-2, the products distribution are similar, indicating that these reaction conditions were severe enough to oxidize the *o*-cresol but not sufficient to yield significant changes in the selectivity towards carboxylic acids. At 140-2 bar, the reaction conditions were not sufficient to transform *o*-cresol into more suitable intermediates. Also, during *o*-cresol CWAO, it must be noticed that glyoxilic acid and resorcinol were detected in considerable amounts, which were not detected during phenol CWAO. The presence of these compounds suggests a different reaction pathway between phenol and *o*-cresol. Finally, from Fig. 5c, 2-chlorophenol undergoes a high degree of mineralisation, as a result of the high conversion and the low occurrence of partial oxidation products, which also agrees with the higher X_{TOC} measured (Table 1).

3.2. AC performance

The AC characterisation presented in this section takes into account the changes in weight and in textural properties undergone by the AC after its use in CWAO tests. It must be noted that, during the CWAO tests, the AC is suffering, at the same time, two processes: burning and/or surface oxidation and oxidative coupling reactions with irreversible adsorption over the AC surface. These processes could affect the AC performance and help to explain some trends for the effect of temperature and P_{O_2} over the disappearance of the target compounds.

The M_{AC}, calculated as the relative difference between the final and the original weight of the loaded AC dried at 400 °C, will serve to quantify which process, oxidative coupling or AC oxidation prevails, as oxidative coupling renders a gain in AC weight whereas AC oxidation results in a decrease of AC weight. The total weight loss (TWL) was calculated after TGA up to 900 °C and will assess the extent of oxidative coupling reactions giving irreversible adsorption of phenolics on the AC. Thus, the greater the TWL is, the higher the development of oxidative coupling reactions. Finally, when the M_{AC} and TWL do not allow to clearly distinguishing which process dominates, the textural properties, i.e. surface area, micropore volume and macro- and meso-pore cumulative area surface, could help to highlight the situation.

As Table 2 shows, M_{AC} was either positive (i.e. the AC weight increased) or negative (i.e. the AC weight decreased) depending on the compound and the operating conditions. In the less severe CWAO conditions, for 140-2, the M_{AC} was always positive. For 140-9 and 160-2, the M_{AC} was positive for phenol and *o*-cresol

Table 2
M_{AC}, textural characterisation and TWL during TGA at the end of CWAO tests

Compound	P_{O_2} (bar)	M_{AC} (%)[a]	BET surface area ($m^2\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)	BJH cumulative area surface ($m^2\,g^{-1}$)	TWL (%)
140 °C						
Original AC	–	–	1481	0.343	304	8
Phenol	9	3.6	284	0.003	191	21
	2	7.1	122	0.003	96	12
o-Cresol	9	19.3	122	0.002	75	25
	2	17.0	24	0.001	2	24
2-Chlorophenol	9	−38.9	201	0.008	148	20
	2	26.2	169	0.002	120	30
160 °C						
Phenol	9	−57.4	280	0.003	253	2
	2	7.4	243	0.007	131	16
o-Cresol	9	−62.3	109	0.004	83	22
	2	54.2	77	0.003	52	15
2-Chlorophenol	9	−52.6	260	0.006	153	22
	2	−16.5	474	0.004	315	25

Data for original AC are from Ref. [6].
[a] Dried at 400 °C.

whereas it was negative for 2-chlorophenol. Finally for the most severe oxidative condition, 160-9, the M_{AC} was always negative.

M_{AC} evolution was previously studied for 240 h during continuous phenol CWAO in a trickle bed reactor, at 140 °C and 9 bar of P_{O_2} [9]. It was observed that, from the start-up, the AC weight firstly, near 24 h, underwent an increase, then reached a maximum and later decreased to values far below the original weight, resulting in a ultimate catalyst loss by direct AC oxidation/burning, 33% after 96 h at the reported conditions. The early increase was due to the irreversible deposition of phenolic polymers by oxidative coupling. AC oxidation was the responsible of the subsequent decrease. When the P_{O_2} was decreased to 2 bar, the AC weight always increased in the same period, so oxidative coupling governed the AC weight evolution.

As mentioned, the increase in AC weight could be attributed to the deposition of polymeric compounds produced by oxidative coupling reactions over the AC [33,34]. Moreover, Cooney and Xi [35] demonstrated that, at low pH, oxidative coupling reactions can be accelerated by the presence of a substituent on the phenol molecule. According to Cooney and Xi [35], oxidative coupling reactions follow the order *o*-cresol > 2-chlorophenol > phenol. However, for 140-2, where AC oxidation should be less important, the observed order in M_{AC} is 2-chlorophenol > *o*-cresol > phenol, which differs from that predicted [35], although easiness of the further polymeric chain oxidation could balance this effect. In any case, the occurrence of oxidative coupling is expected to affect the subsequent AC performance.

Regarding to the TWL shown in Table 2 after 72 h on stream, it must be noted that the original AC gives a 8% TWL and the difference with the used ACs can be assumed to be mainly due to chemisorbed polymers. At 140-2 for phenol test, the TWL is fairly smaller (12%) than at 140-9 (21%), however the M_{AC}, as above noticed, is slightly higher (7.1%) than at 140-9 (3.6%). This indicates that although oxidative coupling is higher at 9 bar, the resulting gain in weight is also offset by the greater burning of AC. For *o*-cresol and 2-chlorophenol, at 140-2, the TWL are respectively 24% and 30%, which reveals a higher extent of oxidative coupling than that occurring for phenol, as predicted. In this case, oxidative coupling compensates any AC burning consequently giving exceedingly positive M_{AC} values. From the textural characterisation, it must be noted that all the used ACs show a dramatic decrease of surface area. The AC used in *o*-cresol test at 140-2 display the highest surface area loss (BET surface area of 24 $m^2\,g^{-1}$ and BJH cumulative area surface of 2 $m^2\,g^{-1}$). Taking into account that oxidative coupling is the main responsible for the surface area loss, this is an additional sign of the occurrence of oxidative coupling.

For the tests at 140-9, all the used ACs show comparable TWL, revealing a similar oxidative coupling degree, despite the completely different M_{AC}. This latter is slightly positive for phenol (3.6%), moderately positive for *o*-cresol (19.3%), and largely negative for 2-chlorophenol (−38.9%). Therefore, the increase of P_{O_2} renders an unacceptable AC loss for 2-chlorophenol, which probably is the reason that explains the unchanged conversion achieved for this compound at both 140-2 and 140-9 CWAO conditions. In general terms, textural properties of the used ACs rather correlate with the level of oxidative coupling estimated.

From Table 2, at 160 °C, the used ACs show similar trends in function of the target compound and the pressure. Nevertheless, while the TWL are in the same order of magnitude than at 140 °C, i.e. similar oxidative coupling is assumed, the M_{AC} measured is mostly negative, demonstrating a high AC loss by burning. This more significant AC burning is expected as the operating temperature is higher. Unfortunately, the determination of AC loss in function of the temperature cannot be completed for AC alone as its burning is one order of magnitude higher in absence of any organic compound [9]. It is believed that the organic compound adsorbs onto the AC surface, thus preventing the AC from being more deeply oxidized as the adsorbed compounds compete for the oxidizing species. Anyway, it must be noticed the unexpectedly high positive M_{AC} obtained for *o*-cresol at 160-2, which agrees with the low BET surface area but disagrees with the TWL measured. No evident explanation exists for this value, although it could be speculated that oxidative coupling early occurred into the pores entrance, mostly blocking their availability for subsequent adsorption. As it can be seen in Table 2, the micropore volume after use is almost negligible when compared to that original.

In general terms, the textural properties also changed according to the compound and the operating conditions. The lowest surface area and micropore volume seems to correspond to the less severe CWAO condition (140-2), regardless the model compounds considered.

On the other hand, for the rest of conditions, the textural properties vary with each compound and CWAO conditions, for example, the maximum in micropore volume occurs for phenol at 160-2, for *o*-cresol at 160-9 and for 2-chlorophenol at 140-9. Although the microporosity is almost eliminated after AC use in CWAO test, it seems that a maximum in the remaining microporosity, which also should correlate with mesopore availability, corresponds to a higher progression in the oxidation reaction for all model compounds and vice versa. In fact, from Fig. 1, the maximum proportion of carboxylic acids occurred in the CWAO experiments at 160-2 for phenol, at 160-9 for *o*-cresol and at 140-9 for 2-chlorophenol, the same conditions giving maximum microporosity.

3.3. CWAO effluents biodegradability

At this point, the intermediates distribution will be correlated with the measured biodegradability of each CWAO effluent in order to find the best condition in the CWAO, which could permit a successful coupling with a municipal WWTP by integrating the CWAO effluents in the regular wastewater management of the total influent to the WWTP.

As the Y_H is necessary to calculate the $\%COD_{RB}$ (Eq. (2)), an average Y_H was estimated using the data obtained from several respirometric tests (data not shown) performed at different concentrations of acetic and propionic acid, which were the major carboxylic acids detected in all the CWAO effluents, giving a Y_H value of 0.71 ± 0.02 mg COD mg^{-1} COD [11]. The Y_H obtained in this study was in the range of the values reported in the literature (0.61–0.87 mg COD mg^{-1} COD) [29].

Fig. 5 also shows the $\%COD_{RB}$ of each 1 of the 12 CWAO effluents for phenol, *o*-cresol and 2-chlorophenol. The measured $\%COD_{RB}$ of the initial model compounds was 0% in all the cases. For phenol effluents, at 140-2 and 140-9, there was low biological degradation, probably because the still high remaining phenol concentration could be inhibiting it. The maximum $\%COD_{RB}$ (36%) appeared at a CWAO condition of 160-2. From Fig. 5, at these conditions, the carboxylic acids had a maximum concentration, whereas the concentration of possible toxic or inhibitory intermediates (catechol, hydroquinone and *p*-benzoquinone [36]) was low. At 160-9, the $\%COD_{RB}$ was lower (15%) than that of the previous case since the carboxylic acids were in lower proportion whereas the possible toxic/inhibitory intermediates were in higher proportion.

Similar tendencies can be drawn for *o*-cresol CWAO effluents. There was no biodegrability at 140-2 (Fig. 5b) because the remaining *o*-cresol concentration was the highest and the carboxylic acids concentration was almost negligible. For the rest of conditions, the $\%COD_{RB}$ was very similar, being 160-9 the condition which had the highest proportion of carboxylic acids and consequently the highest biodegradability, as reflected by the maximum $\%COD_{RB}$ (27%).

Finally for 2-chlorophenol, the lowest $\%COD_{RB}$ (10%) occurred at 160-9 (Fig. 5c), despite the significant concentration of carboxylic acids. In fact, this case was the only one with significant hydroquinone and *p*-benzoquinone amounts present as intermediates in the CWAO of 2-chlorophenol. Therefore, the possible toxic effect of these quinones could be a potential cause for the low biodegradability at this condition. In addition, the proportion of non-identified compounds, which was around 24%, should also be considered as potentially toxic candidates. From HPLC chromatograms, most of them were in the retention times of quinone-like and aromatic compounds, probably being toxic or, at least, inhibitory intermediates for the biological oxidation. The highest $\%COD_{RB}$ (27%) was obtained at 140-9 because there was the highest proportion of carboxylic acids and the lowest proportion of remaining 2-chlorophenol. However, the $\%COD_{RB}$ (22%) at 160-2 was very similar to that obtained at 140-9. From these results it can be concluded that the only important biodegradability enhancement for 2-chlorophenol occurred at 140-9 and at 160-2.

Three different features should be considered when selecting the most suitable CWAO condition: the maximum COD conversion obtained in the CWAO, the maximum $\%COD_{RB}$ and the catalyst preservation. In general, it could be concluded that the best CWAO condition for phenol, *o*-cresol and 2-chlorophenol is 160-2. At this condition, the X_{COD} was the highest one for phenol and 2-chlorophenol and just the second one for *o*-cresol. In addition, the catalyst preservation was clearly better at 2 bar than at 9 bar of P_{O_2}. Finally, the $\%COD_{RB}$ was the highest for phenol and almost the maximum for *o*-cresol and 2-chlorophenol.

Moreover, the $\%COD_{RB}$ of the effluents obtained at 160-2 (22–36%) were slightly higher than those obtained in the characterisation of other industrial wastewaters biologically treated in WWTPs. For instance, Arslan and Ayberk [37] found a $\%COD_{RB}$ between 3% and 24% for a wastewater that included raw domestic wastewater and pre-treated industrial wastewaters of various sectors such as tyre, drug or chemistry. In turn, Ubay Çokgör et al. [30] presented the $\%COD_{RB}$ for several untreated industrial wastewaters: textile (15%), tannery (16%) and meat processing (13%). Taking into account that the COD_{RB} is only a part of the COD_{TB} of a particular wastewater, this comparison shows that the effluents obtained at 160-2 could be efficiently managed and treated in a municipal WWTP if they only mean a properly selected part of the total influent to the WWTP. Further insight on biological depuration of the CWAO pre-treated effluents is provided in another article [11].

4. Conclusions

Several CWAO tests were done using phenol, *o*-cresol and 2-chlorophenol as target pollutants. CWAO was continuously conducted in a trickle bed reactor using a commercial AC as catalyst. Two temperatures, 140 and 160 °C, and two oxygen partial pressures (P_{O_2}), 2 and 9 bar, were studied.

Target pollutant disappearance, COD removal, TOC abatement, distribution of partial oxidation products and biodegradability enhancement were very sensitive to temperature but almost independent of the oxygen partial pressure (P_{O_2}). On the contrary, AC catalyst preservation was strongly influenced by both temperature and P_{O_2}.

The reactivity of the target pollutants was different depending on the operating conditions and catalyst behaviour. Two different reaction mechanisms, electrophilic or nucleophilic substitution, can explain the conversion achieved depending on the operating conditions. However, conversion is also affected by kinetics and catalyst performance and the prevalent mechanism cannot be sufficiently assessed. As both mechanisms are based in the presence of oxygen species, the AC could be envisaged as a promoter in the generation of oxygen radicals and anions, which respectively behaves as nucleophiles and electrophiles in the reaction media.

The best CWAO condition for the pre-treatment of phenol, *o*-cresol and 2-chlorophenol was 160-2. At this condition, the X_{COD} was the highest one for phenol and 2-chlorophenol and just the second one for *o*-cresol. In addition, the catalyst preservation was clearly better at 2 bar than at 9 bar of P_{O_2}. Finally, the %COD_{RB} was the highest for phenol and almost the maximum for *o*-cresol and 2-chlorophenol.

Acknowledgements

This work was funded by the Spanish Ministry of Science and Technology and FEDER (research grants REN2001/1589TECNO, REN2002/03565/TECNO and FIT-050000-2003-41) and the Catalan Government (research grant ITT01-4). We are indebted to the Rovira i Virgili University, the Departament d'Universitats, Recerca i Societat de la Informació (DURSI, Generalitat de Catalunya) and the Social European Fund for providing a fellowship to one of the authors. The authors are also grateful to TRISA for its collaboration in the TOC analyses. Also, we thank to Dr. M.A. Argudo Moya for his help to obtain N_2 adsorption isotherms and to Dr. F. Guirado for his help in the TGA. M.E. Suárez-Ojeda wants to express her deep acknowledgement to A. Rubalcaba, B. Larruy, M. Santiago and M. Baricot.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2007.01.025.

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