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Wet air oxidation (WAO) as a precursor to biological treatment of substituted phenols: Refractory nature of the WAO intermediates

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Abstract

Wet air oxidation (WAO) was investigated as a suitable precursor for the biological treatment of industrial wastewaters that contained high concentrations of phenol, *o*-cresol or 2-chlorophenol. Two hours WAO semi-batch experiments were conducted at 2 and 9 bar of oxygen partial pressure (P_{O_2}) and at 215, 240 and 265 °C with total organic carbon (TOC) abatement up to 86%. The influence of hydroxyl-, methyl- and chloride ring substitution on the oxidation mechanism of aromatic compounds was established. Also, the readily biodegradable COD fraction (%COD_{RB}) of the WAO effluents was found by respirometric techniques. The maximum %COD_{RB} was 24% for phenol WAO at 265 °C and 9 bar of P_{O_2}, 10% for *o*-cresol WAO at 265 °C and 9 bar of P_{O_2} and 19% for 2-chlorophenol WAO at 215 °C and 2 bar of P_{O_2}. These results allow comparison of whether or not the WAO effluents were suitable for a conventional activated sludge plant with non-acclimated biomass. Also, the results were compared to those obtained from a previous study for the same model compounds but using catalytic WAO (CWAO) with activated carbon (AC) as a catalyst [1]. This comparison allows us to establish whether or not the WAO effluents were less biodegradable or had more refractory intermediates than CWAO effluents.

Keywords: Substituted phenols; Wet air oxidation; Biodegradability

1. Introduction

In the world's consumer-based economy, chemistry plays an essential role in our attempt to feed the world's population, to find new sources of energy, to maintain humankind, to improve health, to eliminate sickness, to provide substitutes for rare raw materials, to design necessary materials for new information and communication technologies and to monitor and to protect our environment. As a result, over fourteen million different molecular compounds have been synthesised during the last century and about one hundred thousand can be found in the market. Only a small fraction of them are found in nature [2]. This increasing design of new materials has produced new sources of pollution, which have often turned to be toxic, persistent and difficult to eliminate from aquatic systems.

A critical issue associated with this rapid industrial and technological development is sustainable wastewater management. Environmental concern is nowadays expressed by more and more stringent governmental regulations imposing lower pollutant discharge limits. So, for many industrial sectors, pollution prevention, waste minimisation and reuse are being increasingly integrated into their environmental policies. Thus, the challenges faced by chemical and related industries are to design efficient and cheap remediation processes and minimisation strategies for water pollution problems.

Nowadays, several technologies are available and have shown to be effective in treating a variety of refractory and complex effluents. These technologies can be mapped, according to Hancock [3], for their applicability with effluent COD concentration (measured as TOC) and effluent flow rate ($m^3 h^{-1}$). Fenton-like processes benefit from using H_2O_2 as a liquid oxidant and a homogeneous or heterogeneous catalyst to enhance the oxidation conditions. Advanced oxidation processes (AOP) such as ozonation, photocatalysis and electrochemical oxidation (among many others), utilise electron beams, UV light or

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ultrasound pulses to obtain high oxidation rate through the generation of free OH radicals (mainly hydroxyl radicals). Incineration is an appropriate technology for effluents having TOC > 100 g l^{-1}, but it has an extremely high energetic cost and it is not environmental friendly due to the dust dissemination to the atmosphere and to the related problems associated with dioxins production [4]. Another alternative is the recovery of organics, but it requires additional energy costs for the facilities construction and operation.

Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) use temperature and pressures over 120 °C and 10 bar and air or oxygen as oxidant, being particularly useful for toxic organic wastewater [4,5]. Depending on the reaction conditions two objectives can be achieved: (a) complete mineralisation of organics to CO_2 and H_2O or (b) only an increase of the effluent biodegradability by adjusting the conversion of toxic organic matter to the formation of biodegradable by-products such as carboxylic acids [6].

As complete mineralisation would be excessively costly, the interest is to integrate (C)WAO with a following biological process. In this way, a core study integrating WAO with biotreatment was done by Mantzavinos et al. [7], by Otal et al. [8] and by Patterson et al. [9]. These authors concluded that the overall reactor space time required during the integrated treatment is almost an order of magnitude less than that for a direct biological treatment of polyethylene glycol, *p*-coumaric acid and a mixture of linear alkylbenzene sulfonates, thus making the integrated process an attractive option.

Finally, Donlagic and Levec [10] reported that CWAO yields products more biodegradable than WAO as a pre-treatment step, therefore, it is important to assess the potential products of incomplete oxidation prior to implementing the WAO or CWAO technology as pre-treatment step for wastewater, which requires additional treatment, before entering to a conventional biological treatment plant [5,11].

Few works examine the relationship between the intermediates formed in the WAO or CWAO processes and the following biodegradation step. For example, Santos et al. [12,13] used the Microtox® EC50 values of the intermediates that appeared in the oxidation of phenol to predict the toxicity of the CWAO effluent in its posterior biological oxidation. Thomsen and Kilen [14] studied the intermediates in the WAO of quinoline and their toxicity using a test of nitrification inhibition. Suárez-Ojeda et al. [15] use respirometry to establish the biodegradability, toxicity and inhibitory properties of several intermediates from a high-strength *o*-cresol wastewater treated by CWAO with activated carbon as catalyst [15]. Finally, Hsu et al. [16] showed that biodegradability (expressed as BOD_5/COD) of ozonised phenolic solutions was strongly dependent on the accumulation and type of intermediates.

The present study aims to demonstrate the feasibility of using WAO as pre-treatment for biological remediation of industrial wastewaters containing phenolic compounds such as phenol, *o*-cresol or 2-chlorophenol. Two hours WAO semi-batch experiments were conducted at 2 and 9 bar of oxygen partial pressure (P_{O_2}) and at 215, 240 and 265 °C. The biodegradability characterisation has been made using respirometric techniques. The results of this study are compared to those obtained for the same model compounds, but using CWAO with activated carbon as pre-treatment technique [1] at 140 and 160 °C, and two oxygen partial pressures (P_{O_2}), 2 and 9 bar. This comparison allows us to establish whether or not the WAO effluents are less biodegradable or has more refractory intermediates than CWAO effluents.

2. Experimental

2.1. Materials

Aldrich provided analytical grade phenol, *o*-cresol and 2-chlorophenol. Deionised water was used to prepare all the solutions. HPLC (high performance liquid chromatography) grade methanol (Aldrich) and ultra-pure water (ELGA SP1 195 R.O.) were used to prepare HPLC mobile phases. The synthetic air used as oxidant had a purity of 99.995% (BOC gases, UK).

Phenol and *o*-cresol feed concentrations were taken as 5 g l^{-1}, whereas for 2-chlorophenol, the feed concentration was taken as 0.5 g l^{-1} to avoid corrosion problems in the reactor vessel [17]. In terms of Chemical Oxygen Demand (COD), the initial feed concentrations were 10.8 g COD l^{-1} for phenol, 9.5 g COD l^{-1} for *o*-cresol and 0.75 g COD l^{-1} for 2-chlorophenol.

2.2. Experimental set-up and procedures for WAO experiments

WAO experiments were performed in a 1 l working volume stainless steel high-pressure reactor (Autoclave engineers, USA). In each semi-batch experiment, 500 ml of the solution were introduced into the reactor. Then, the reactor was heated to the desired temperature with nitrogen. As soon as the set temperature was reached, defined as time zero, air was continuously fed into the reactor while being stirred at 1000 rpm. Samples were withdrawn every 30 min. After the total reaction time (120 min), the airflow was shut off and the reactor was depressurised (through the relief valve) to a pressure above the vapour pressure at the reaction temperature. Most of the air was removed stopping the oxidation while no evaporation of the liquid phase occurred. As soon as the temperature dropped to ambient conditions, the autoclave was opened and the reactor contents collected for analysis.

Each sample was analysed to determine target compound destruction (X), total organic carbon (TOC) removal (X_{TOC}) and biodegradability enhancement as the readily biodegradable COD percentage ($\%COD_{RB}$). Experiments were performed at 215, 240 and 265 °C and total pressure from 30 to 93 bar depending on the oxygen partial pressure (P_{O_2}) selected for the experiment (2 or 9 bar).

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

The composition of the effluents was determined by HPLC (Varian Prostar). The analysis was performed using a C18 reverse phase column (Thermo-ThermoHypersil ODS) and a mixture of ultra-pure water (phase A) and methanol (phase B). The gradient started from 100% of A and progressively changes to 50:50 (v/v) of A:B in 25 min, then it remained isocratic until minute 37. Both mobile phases were acidified to a pH of 2 with concentrated sulfuric acid. According to several oxidation pathways proposed in the literature for each model compound [18–23], a set of reported oxidation intermediates was checked and used for HPLC calibration. 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 WAO sample, therefore, they were not taken into account.

COD was measured with the standard method 5220D [24], whereas TOC was quantified with a Shimadzu TOC-V CSH analyser based on combustion and subsequent non-dispersive infrared (NDIR) CO_2 detector. The CO_2 selectivity was inferred from a mass balance between the initial and final TOC values in the experimental samples.

A complete scheme of the WAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [11,25,26].

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 is continuously aerated (F) [27]. In all respirometric tests, the pH was maintained at 7.5 ± 0.5 and the temperature was set at $31 \pm 0.5\,^{\circ}C$. The biomass used as seed culture came from a municipal biological wastewater treatment plant (WWTP) (Tarragona, Catalonia, Spain) and was starved overnight to ensure endogenous conditions before each respirometric experiment. The addition of $20\,mg\,l^{-1}$ of 1-allyl-2-thiourea (ATU) avoids nitrification interference. The average concentration of volatile suspended solids (VSS) was $3400 \pm 300\,mg\,VSS\,l^{-1}$.

2.4. Determination of readily biodegradable COD fraction of the WAO 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 80's by Dold et al. [28]. The determination of COD_{TB} requires a combination of several techniques and experiments [29,30] but, specifically the COD_{SB} determination is extremely time-consuming, whereas the available methods for COD_{RB} determination mostly lies in fast respirometric experiments [31]. Therefore, the COD_{RB} can be used as a fast method to characterise the biodegradability of a specific wastewater. Here, respirometry is used as a screening test to compare the biodegradability enhancement reached with different WAO conditions in comparison to the initial target effluents.

The procedure used in this study was originally proposed by Ekama et al. [32]. To assess the biodegradability of the treated and non-treated effluents, a $20\,mg\,COD\,l^{-1}$ (COD_{added}) pulse of either the WAO effluent or the target compound solution was added to the respirometer. Then, the Oxygen Uptake Rate (OUR) profile and the Oxygen Consumption (OC) are obtained solving the S_O balance in the liquid phase of the respirometer. More information about the OUR and OC calculation can be found elsewhere [27].

Because respirometry is used in this study as a simple and fast screening tool [15], the concentrations used in the tests were chosen taking into account two points. 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 [33]. Second, the subsequent biological treatment of the WAO effluent is assumed to be performed 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 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 [31,34,35]:

$$COD_{RB} = \frac{OC}{1 - Y_H} \tag{2}$$

The biological COD removal is a process where part of the substrate is directly used for new biomass growth and the rest is oxidised 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. [34].

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

$$\%COD_{RB} = \frac{COD_{RB}}{COD_{added}} \times 100 \tag{3}$$

All the respirometric data presented correspond to the arithmetic average of the results derived from two repeated experiments. The reproducibility of the results and the match (within ±5%) between successive experiments was excellent.

3. Results and discussion

The results and discussion are divided into two sections. In the first, the WAO performance is discussed by means of X and X_{TOC}. Also, the reactivity order, the detected intermediates and the reaction mechanisms are examined. In the second section, the determination of the biodegradability of WAO effluents is presented.

During the discussion, the WAO conditions will use the following nomenclature: 215-2 will refer to 215 °C and 2 bar of P_{O_2}, 265-9 equals to 265 °C and 9 bar of P_{O_2} and so on.

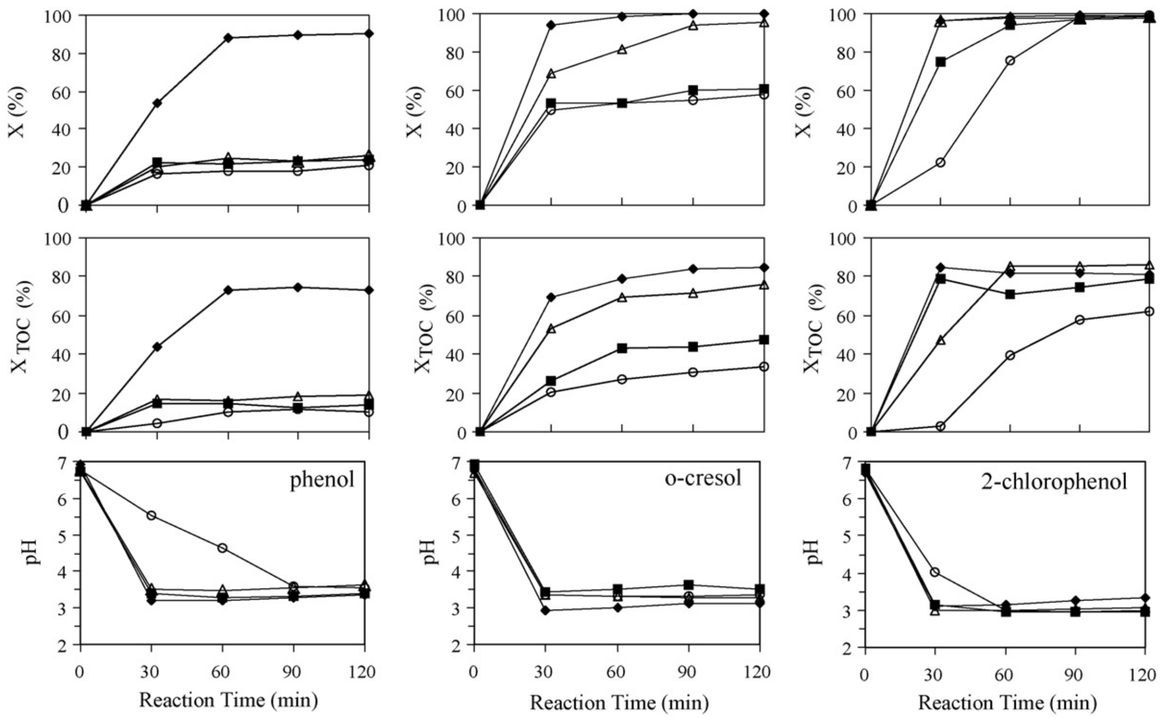

Fig. 1. Conversion (1st row), TOC abatement (2nd row) and pH (3rd row) profiles for phenol (left), *o*-cresol (centre) and 2-chlorophenol (right) at different conditions. Symbols indicate experimental data {(♦): 265-9; (△): 265-2; (■): 240-2 and (○): 215-2}. Lines only show tendencies.

3.1. Model compound disappearance and intermediates distribution

Fig. 1 shows the X, X_{TOC} and pH profiles for phenol, *o*-cresol and 2-chlorophenol tests at the four conditions of temperature and $P_{\mathrm{O_2}}$ tested. Table 1 summarises all the results obtained in this work. At the end of the tests at 265-9, X are between 90 and 100% for all compounds. At 265-2, X is close to 98% for 2-chlorophenol, 95% for *o*-cresol and 26% for phenol. At 240-2, X is close to 98% for 2-chlorophenol, 61% for *o*-cresol and 26% for phenol. Finally, at 215-2, X is close to 98% for 2-chlorophenol, 58% for *o*-cresol and 21% for phenol.

As expected, X_{TOC} is lower than the respective X because of the presence of partially oxidised products. It should be pointed out that the higher the difference between X and X_{TOC}, the higher the amount of partially oxidised products in the liquid effluent and the lower the selectivity to CO_2. For instance, the differences between X and X_{TOC} at the end of the tests at 265-9 are 17% for phenol, 15% for *o*-cresol, and 12% for 2-chlorophenol. At the end of the tests, as far as X is concerned, the experimental reactivity order is 2-chlorophenol ≥ *o*-cresol > phenol.

Table 1
X and X_{TOC} in WAO

T (°C)–$P_{\mathrm{O_2}}$ (bar)	215-2		240-2		265-2		265-9	
Compound	X	X_{TOC}	X	X_{TOC}	X	X_{TOC}	X	X_{TOC}
WAO								
Phenol	21	12	24	13	26	14	90	73
o-Cresol	57	33	61	47	95	76	100	85
2-Chlorophenol	99	62	98	79	97	81	99	86

Compared to the results obtained in a previous work with CWAO using activated carbon as catalyst [1] several trends can be drawn. First, for 2-chlorophenol the X and X_{TOC} obtained with WAO are always higher than those obtained with CWAO.

In the case of phenol, in general the X or X_{TOC} obtained with CWAO are higher than those achieved with WAO, however, with WAO at 265-9, the attained X or X_{TOC} are the highest of all.

Finally, for *o*-cresol, the X or X_{TOC} varies depending on the process. For instance, the highest X is obtained with CWAO at 140-9 and 160-9 and at 265-9 and 265-2 in WAO. However, in the case of X_{TOC}, with WAO at 265-2 and 265-9, the X_{TOC} is higher than either X_{TOC} obtained with CWAO, therefore the mineralisation degree obtained with WAO at 265-2 and 265-9 is higher than with CWAO at 140-9 and 160-9.

The phenols' oxidation mechanism is a very complex reaction network, which is not yet fully understood. It has been reported that the WAO 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 [21]. For the free radical mechanism, the phenol oxidation must be characterised by an induction period followed by a fast reaction phase typical of radical mechanism. In this study no induction period was observed, probably because this appears before 30 min, when the first sample is taken, however, it should be pointed out that profile obtained for 2-chlorophenol at 215-2 exhibits a light "S" shape, which could serve to confirm the occurrence of some induction period.

The ease with which phenols form aryloxy radicals is related to the half-wave oxidation potentials (HWP); the lower the HWP, the easier the oxidation is [36]. The HWP of the model compounds are ordered as follows: *o*-cresol ≥ 2-chlorophenol > phenol [36]. Therefore, for a free radical mechanism, the reactivity order should follow the same order as the HWP. Moreover, as explained by Joglekar et al. [21], the ease of phenols' oxidation, by electrophilic substitution, increases as the steric crowding in the *ortho*-positions and the electron-releasing properties of substituents in the *ortho*- and the *para*-positions increase. Hence, the reactivity order found in this study is close to the reactivity order found by Joglekar et al. [21] and to the HWP order discussed earlier, because the methyl group is an electron-releasing group, whereas the hydroxyl and chloride (–OH and –Cl) are electron-withdrawing substituents.

Turning to pH, at the start the pH has the value of the initial solution according to the pK_a values of each model compound (phenol: 9.89; *o*-cresol: 10.20 and 2-chlorophenol: 8.48, values taken from [37]). Then the pH begins to decrease, which is caused by the formation of organic acids, and chlorhydric acid from 2-chlorophenol, as oxidation by-products, as confirmed by the HPLC analysis.

In the case of phenol samples, the main partial oxidation products were light carboxylic acids such as oxalic, acetic and succinic acids in concentration between 110 and 665 mg l^{-1}. Malonic, maleic, fumaric (maleic acid isomer), 4-hydroxybenzoic (4-HB) and 2-hydroxybenzoic (2-HB) acids were detected in amounts between 5 and 100 mg l^{-1}. Finally, hydroquinone and catechol were detected in concentrations up to 350 mg l^{-1}, whereas *p*-benzoquinone was detected in concentration as low as 8 mg l^{-1}. No other possible intermediates were detected.

The presence of 4-HB and 2-HB suggests a reaction pathway where either phenol or dihydric-phenols (hydroquinone and catechol) can be destroyed via two routes. The first one leading to the formation of benzoquinones and the second one could proceed through the reaction of phenol with malonic acid to form 4-HB and/or 2-HB and acetic acid as Fig. 2 shows. To the best of our knowledge this second route has not been reported in the case of un-catalysed oxidation of phenol. Only two previous works have reported the presence of 4-HB as a reaction intermediate but both were concerned with the CWAO of phenol with activated carbon as catalyst [38,39].

For *o*-cresol samples, oxalic and succinic acids were the main light carboxylic acids, appearing in concentrations up to 400 mg l^{-1}. Other acids like malonic, acetic, maleic, fumaric and 4-HB acids were detected in concentrations below 50 mg l^{-1}. Neither formic acid nor 2-HB acid were detected. The quinone-like intermediates, such as hydroquinone and catechol, were measured in amounts below 35 mg l^{-1} whereas *p*-benzoquinone concentrations were found almost at trace levels. Finally, phenol was detected as a reaction intermediate of *o*-cresol WAO in amounts up to 100 mg l^{-1}. The absence of 2-HB as an intermediate in *o*-cresol WAO suggests that direct oxidation of the methyl-side chain, which could lead to 2-HB formation, does not occur under the tested conditions.

Finally, in the case of the 2-chlorophenol samples, oxalic and succinic acids were detected again as main light carboxylic acids in concentrations up to 350 mg l^{-1}. The other acidic intermediates detected were malonic and acetic acids, but in amounts below 40 mg l^{-1}. Hydroquinone, catechol and *p*-benzoquinone were not detected and phenol was measured in concentrations as low as 10 mg l^{-1}. In turn, chloride ions were detected in amounts between 5 and 100 mg l^{-1}. If total dechlorination occurs and no other chlorinated intermediates are formed, the maximum concentration of free chloride ions should be around 140 mg l^{-1}. These results indicate that other non-identified chlorinated intermediates should be in the effluents from 2-chlorophenol WAO, as the chloride ions concentration is below the maximum expected.

3.2. WAO effluents biodegradability

Biodegradability respirometric tests were conducted with each WAO effluent following the procedure explained in Section 2.4. Biodegradability of WAO effluents will be compared to that obtained for the same model compounds, but using CWAO with activated carbon as catalyst [1] in order to establish whether or not the WAO effluents are less biodegradable or have more refractory intermediates than CWAO effluents. Also, the results will be explained using the biodegradability information of each major intermediate detected by HPLC as explained by Suárez-Ojeda et al. [15]. According to [15], the CWAO major intermediates can be classified as readily biodegradable compounds (fumaric, propionic, acetic, succinic and formic acids), inert intermediates with no biodegradability but without toxic or inhibitory effect over the biomass (oxalic, maleic, malonic, 4-HB and 2-HB acids), toxic (hydroquinone and *p*-benzoquinone), and finally, inhibitory intermediates (catechol) for the biodegradation.

Fig. 3a shows the results of %$\mathrm{COD_{RB}}$ obtained for phenol oxidation in the semi-batch WAO experiments (at 120 min of reaction time). Fig. 3b and in Fig. 3c display the same information for *o*-cresol and 2-chlorophenol, respectively. The measured %$\mathrm{COD_{RB}}$ of the initial model compounds was always 0%, therefore, the values of Fig. 3 directly represents the biodegradability enhancement owing to the treatment.

For phenol WAO effluents (Fig. 3a), there was a very low %$\mathrm{COD_{RB}}$ at 215-2, 240-2 and 265-2, probably because the low concentration of carboxylic acids and the high remaining phe-

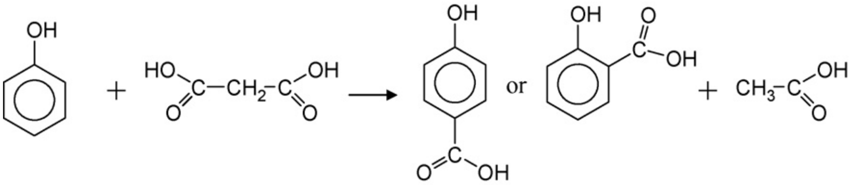

Fig. 2. Reaction network proposed for 4-HB/2-HB formation from non-catalytic WAO of phenol.

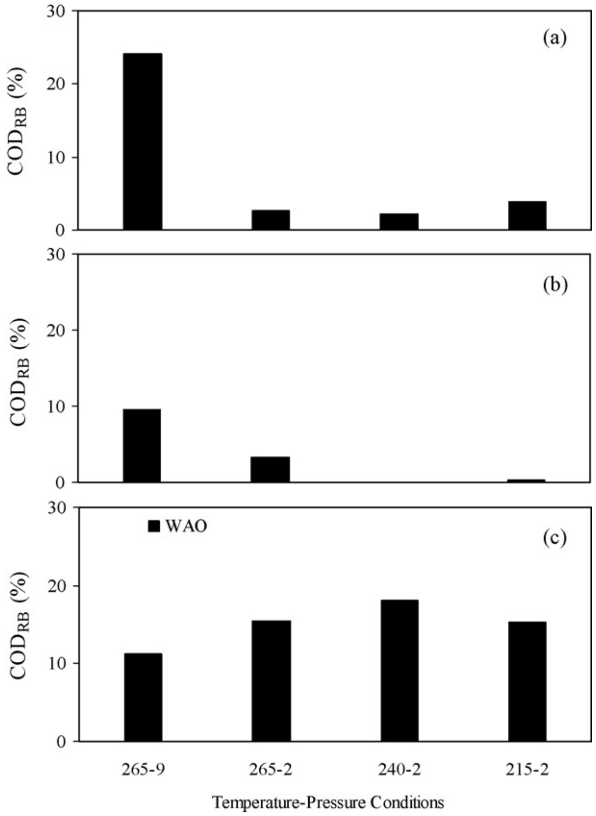

Fig. 3. Readily biodegradable COD fraction of phenol (a), *o*-cresol (b) and 2-chlorophenol (c) effluents from WAO.

nol concentration. The maximum $\%COD_{RB}$ (24%) for WAO tests occurred at 265-9. At this condition, the sum in concentration of readily biodegradable acids showed a maximum, representing 27% of the total COD, whereas the sum in concentration of possible toxic/inhibitory intermediates (catechol, hydroquinone and *p*-benzoquinone) showed a low value (5% of the total COD). Comparing the phenol WAO results with those obtained with phenol in CWAO [1], in general, the $\%COD_{RB}$ is higher in CWAO than in WAO. Those differences in biodegradability could be explained by the differences in the intermediate distribution in both treatments. In WAO the readily biodegradable intermediates were in lower proportion and the possible toxic/inhibitory intermediates were in higher proportion than in CWAO [1], which explains the better biodegradability enhancement when using CWAO.

Similar trends can be drawn for *o*-cresol WAO effluents. There was no biodegradability at 215-2 and 240-2 because the remaining *o*-cresol concentration was the highest and the readily biodegradable intermediates (acetic, succinic and fumaric) concentrations were very low. The $\%COD_{RB}$ was 10 and 3% at 265-9 and 265-2, respectively. At 265-9, the proportion of readily biodegradable acids is not the highest one, but the non-identified intermediates (data not shown) lie in the retention times of carboxylic acids, probably being some other type of readily biodegradable intermediate. Comparing the *o*-cresol WAO results with those obtained with *o*-cresol in CWAO [1], in general, the $\%COD_{RB}$ is higher again in CWAO than in WAO. These differences in the biodegradability enhancement could be again explained by the difference in the distribution of the intermediates between both treatments as for phenol. Nevertheless, it could be also related to the fact that TOC abatement is higher for *o*-cresol WAO than in CWAO treatment, which means a high mineralisation leaving the WAO effluents without biodegradable intermediates.

Therefore, for phenol and *o*-cresol wastewater the CWAO pre-treatment seems to be a better option in terms of biodegradability enhancement than WAO pre-treatment. Instead, for 2-chlorophenol WAO the $\%COD_{RB}$ obtained were comparable to those obtained with CWAO ranging from 10 to 27% [1]. Hence, both WAO and CWAO are suitable technologies for 2-chlorophenol treatment, in terms of biodegradability enhancement and *X*. Therefore, the final selection of the treatment should be based on technical and economic feasibility.

It must be noted that, the $\%COD_{RB}$ of the WAO effluents obtained in this work were in the range of other industrial wastewaters treated biologically in WWTPs. For example, Arslan and Ayberk [40] 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. Ubay Çokgór et al. [35] reported the $\%COD_{RB}$ for several untreated industrial wastewaters: textile (15%), tannery (16%) and meat processing (13%). Moreover, Suárez-Ojeda et al. [15] demonstrated that a high-strength *o*-cresol wastewater pre-treated by CWAO with a $\%COD_{RB}$ of 22% can be efficiently treated in a biological WWTP without causing undesirable effects over the biomass. Therefore, it can be concluded that if the effluents have $\%COD_{RB}$ around 10%, then they could be treated in a biological WWTP, because as far as it is known, the rest of the organic matter should be slowly biodegradable COD without adverse effects on the sewage sludge, as demonstrated by Suárez-Ojeda et al. [15].

In this way, the WAO effluents obtained at 265-9 seem to be the only candidates for a further biological treatment, whereas the effluents obtained at 2 bar do not have enough biodegradability with the exception of 2-chlorophenol. This suggests that only more severe temperature and pressure WAO conditions could assure effluents not endangering a subsequent biological treatment.

4. Conclusions

Several WAO tests were performed with 2-chlorophenol, phenol, and *o*-cresol, as target compounds in order to establish if the WAO effluents were suitable for a WWTP. Substrate conversions were between 21 and 100%. Reactivities in the order 2-chlorophenol ≥ *o*-cresol > phenol were experimentally found.

The presence of 4-HB and 2-HB could suggest the occurrence of a side reaction pathway of phenol removal through the condensation of phenol with malonic acid. In the case of *o*-cresol, the absence of 2-HB as intermediate suggests that direct oxidation of the methyl-side chain did not occur.

Although 2-chlorophenol completely disappears, the chloride concentration is lower than the maximum expected, indicating that other non-identified chlorinated intermediates should be in the effluents from 2-chlorophenol WAO. Also, phenol concentrations were below 10 mg l^{-1} suggesting an alternative reaction pathway for 2-chlorophenol degradation.

The differences in biodegradability between WAO and CWAO effluents could be explained by the differences in the intermediate distribution in both treatments. In general, in WAO the readily biodegradable intermediates were in lower proportion and the possible toxic/inhibitory intermediates were in higher concentration than in CWAO; this latter renders a better biodegradability enhancement.

However, for 2-chlorophenol, both WAO and CWAO are suitable technologies, in terms of biodegradability enhancement and therefore, the final selection of the treatment should be based on technical and economic feasibility.

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