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Biodegradability enhancement of phenolic compounds by Hydrogen Peroxide Promoted Catalytic Wet Air Oxidation

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Abstract

The aim of this work is to study the viability of the H_2O_2 Promoted Catalytic Wet Air Oxidation (PP-CWAO) process, using activated carbon (AC) as catalyst, to increase the biodegradability of phenolic aqueous solutions. Seventy-two hours experiments were performed in a trickle bed reactor at 140 °C and 2 bar of oxygen partial pressure. Feed concentrations, in terms of theoretical chemical oxygen demand (ThCOD), were $11.8\ \mathrm{g\ COD\ l^{-1}}$ for phenol, $12.6\ \mathrm{g\ COD\ l^{-1}}$ for *o*-cresol and $8.0\ \mathrm{g\ COD\ l^{-1}}$ for *p*-nitrophenol. Air was used as main oxidant and 20% of the stoichiometric amount of H_2O_2 needed for pollutant complete mineralisation was added as oxidation promoter. Adding H_2O_2 to the CWAO process not only increases pollutant removal but also leads to higher mineralisation of the remaining oxidation products. For instance, removal of phenol, *o*-cresol and *p*-nitrophenol increase from 45, 33 and 15% in the CWAO process to 64, 64 and 49% in the PP-CWAO process. In addition, the PP-CWAO process leads to better biodegradability enhancements, when compared to CWAO, as demonstrated by the respirometric tests. However, it is still necessary to improve the oxidation step in order to assure more biodegradable effluents that could be combined with a subsequent biological wastewater plant.

Keywords: Activated carbon; Biodegradability; CWAO; Hydrogen peroxide; Phenolic compounds; Respirometry

1. Introduction

The importance of phenolic industrial effluents, besides from their potential toxicity, is outlined by the high quantities that are eventually disposed. For instance, phenol, *o*-cresol and *p*-nitrophenol are recognised toxic substances listed in the 2004 OECD List of High Production Volume Chemicals [1] and also, each year 1.3 tonnes of phenolic compounds are rejected by the European countries, being 28,000 of them corresponding to Spanish wastes [2]. Biological treatment of these compounds usually has low removal efficiency. Moreover, microbial toxicity studies with Daphnia Magna showed that these compounds are toxic [3,4].

Wet Air Oxidation (WAO) and Wet Peroxide Oxidation (WPO) are technologies, among many others, for treating this kind of hazardous wastewater that is not amenable to biological treatment. Both processes could be suitable to generate an effluent to be discharged into a municipal biological Wastewater Treatment Plant (WWTP) as part of the total influent, according to the technology map drawn by Hancock [5]. The WPO process has an oxidation efficiency comparable to that obtained when using oxygen as the sole oxidant, as in the WAO [6]. However, WAO requires both higher temperatures (200–325 °C) and pressures (50–150 bar) that increase investing and running costs. The use of a catalyst in WAO would help to softer those operating conditions.

The implementation of the Catalytic Wet Air Oxidation (CWAO) process has become an attractive technique to successfully deal with organic wastewater that is either too concentrated or too poorly biodegradable as to be biologically restored. However, in the case of the Catalytic Wet Peroxide Oxidation (CWPO) process, the homogeneous catalyst must be

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removed before biological treatment or before final disposal; and in the case of CWAO process, the catalyst choice is the core for an efficient and cost competitive performance.

Recently, several studies have demonstrated that activated carbon (AC) alone can successfully perform as a true catalyst for several reactions [7], including CWAO of phenol, *o*-cresol, 2-chlorophenol and other bioxenotic organic compounds [8].

Nowadays chemical oxidation processes are focussed on giving partially oxidised effluents containing readily biodegradable compounds that allow its combination with a biological treatment. Coupling chemical pre-oxidation with biological post-treatment would be beneficial since it can lead to increased treatment efficiencies [9]. Therefore, determining the effluent biodegradability is a key point for the eventual application of any wastewater process.

The main objective of this research is to integrate the benefits of CWAO (with AC as catalyst) and CWPO in an intensified process, named here Hydrogen Peroxide Promoted Catalytic Wet Air Oxidation (PP-CWAO), to give and effluent that could be later biologically treated. Principal advantages of using these promising processes should be, on one hand, the decrease of conventional WAO and WPO process costs, keeping high conversion of pollutant in industrial wastewater, and on the other hand, the use of a low cost catalyst, non-modified activated carbon, which avoids leaching problems associated to heterogeneous processes using metal-based catalysts.

2. Methods

2.1. Materials

Aldrich provided analytical grade phenol, *o*-cresol and *p*-nitrophenol. Deionised water was used to prepare all the solutions. Feed concentrations were taken always as 5 g l^{-1}. However, in terms of theoretical chemical oxygen demand (ThCOD), the initial concentrations were 11.8 g COD l^{-1} for phenol, 12.6 g COD l^{-1} for *o*-cresol and 8.0 g COD l^{-1} for *p*-nitrophenol. These concentrations were chosen to check the feasibility of using CWAO and PP-CWAO as an effective pre-treatments before a biological WWTP. 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 the experiments was 99.995% pure (Carburos Metálicos, Spain). Hydrogen peroxide used in the PP-CWAO process was bought from Panreac as a 30% (w/v) aqueous solution. 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 to get the fraction between 25 and 50 mesh (0.7–0.3 mm) that was used in the experiments. Some characteristics of this AC can be found elsewhere [10].

2.2. Experimental set-up and procedure for oxidation tests

CWAO and PP-CWAO experiments were performed in a trickle bed reactor for 72 h in continuous mode. The air flow rate was adjusted to guarantee excess oxygen. 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}. Total operating pressure was selected to provide a oxygen partial pressure (p_{O_2}) of 2 bar while temperature was set to 140 °C. Usually 7.0 g of AC were used as catalytic material. For the PP-CWAO tests, according to previous studies [11], 20% of the stoichiometric amount of H_2O_2 needed for complete mineralisation of each model compound was directly added in the feed tank. Some experiments were performed under N_2 atmosphere, instead of air, in order to discriminate the beneficial effect of using H_2O_2 as the only oxidant or in combination with O_2. A more detailed description of the reaction system and operating procedures can be found elsewhere [10–11]. Liquid samples were periodically withdrawn and analysed to determine target compound conversion (i.e. percentage of organic compound destruction) (X), COD reduction (X_{COD}), total organic carbon (TOC) abatement (X_{TOC}) and biodegradability enhancement, measured as percentage of readily biodegradable COD ($\%COD_{RB}$).

Characterisation of the liquid samples was done by HPLC using a method previously developed [10]; all calibration curves were performed by means of external standards. COD and TOC were measured following the standard methods 5220D and 5310B, respectively [12]. Residual H_2O_2 is not present in the effluent stream after oxidation process at 140 °C.

The AC used in each CWAO and PP-CWAO test was collected and dried overnight at 105 °C under N_2 atmosphere. Then, the used AC was subjected to thermogravimetric analysis (TGA) 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 in order to determine the total weight loss (TWL) suffered by the used AC after the reaction. The TWL allows assessing the extent of oxidative coupling reactions giving irreversible adsorption of phenols on the AC surface.

2.3. Experimental set-up and procedure for respirometric tests

Biodegradation parameters of the effluents were determined by respirometric tests [13,14]. These tests used a LFS respirometer [15] in which the oxygen solved in the liquid phase (So) is monitored. When a substrate pulse is added, microorganisms consume the So while metabolising the substrate. Then, the oxygen balance in the liquid phase is solved and the oxygen uptake rate (OUR) and the oxygen consumption (OC) are obtained as indicators of the biodegradability, toxicity or inhibitory effect of the studied substrate. More detailed information about the OUR and the OC calculation can be found in literature [13,15]. All respirometric tests were done with a pulse of 20 mg COD l^{-1} (COD_{added}) from each CWAO or PP-CWAO effluent. This concentration was selected taking into account that the biological treatment of the CWAO or PP-CWAO effluents would be done in a continuous stirred tank reactor (CSTR), therefore, the concentration in the bioreactor must be the same as in its effluent, which must be below the discharge limits. The respirometer temperature was fixed at 30 ± 0.5 °C using a thermostatic bath, the biomass had an average concentration of volatile suspended solids (VSS) of 2100 ± 320 mg VSS l^{-1} and the pH was kept at 7.5 ± 0.5. The activated sludge used in this respirometric determination came from a municipal biological WWTP in Tarragona (Catalonia, Spain), which was not adapted to metabolise phenolic compounds.

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, the heterotrophic yield coefficient (Y_H) represents the fraction of substrate used for production of new biomass. This coefficient can be calculated using respirometric techniques, with a similar protocol than that used by Strotmann et al. [16].

Once the OC is obtained from the respirometric tests, the COD_{RB} can be calculated using the Y_H as follows [16,17]:

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

Then, the COD_{RB} fraction of CWAO effluents is calculated according to:

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

3. Results

The results and discussion are divided into two sections. In the first one, the performance of each process is discussed by means of the organics removal (X, X_{COD} and X_{TOC}) and AC behaviour. In the second section, the biodegradability enhancement of the effluents is presented.

Several simultaneous reactions occur when using AC as catalyst in CWAO or PP-CWAO. There is not only the expected oxidation of the target compound and its intermediates, but also two parallel reactions of the AC are occurring to some extent: on one hand, AC oxidation/burning and, on the other hand, oxidative coupling reactions (or irreversible adsorption) of the phenolic compounds over the AC. Besides, physical adsorption of the substrate and of the partial oxidation products is also happening at the same time. Therefore, the use of AC as catalyst in CWAO or PP-CWAO increases even more the already high intrinsic complexity of wet oxidation processes. These parallel reactions and adsorption processes cannot be uncoupled and studied separately. Thus, only global information can be taken from the effluent and the AC characterisation (Section 3.1), attempting to establish the contribution of each one in the biodegrability enhancement (Section 3.2).

3.1. Model compounds removal: CWAO and PP-CWAO comparison

Fig. 1 shows the X, X_{COD} and X_{TOC} profiles obtained from CWAO and PP-CWAO tests of phenol, *o*-cresol and *p*-nitrophenol, at 2 bar of p_{O_2} and 140 °C. As previously observed [10,11,18], when using AC as catalyst in CWAO or PP-CWAO, three different zones can be distinguished in the conversion profiles obtained from the effluent characterisation. First, after the start-up, an adsorption-dominating period results in an apparent total conversion. Secondly, as the run proceeds, the adsorption-equilibration zone progresses throughout the

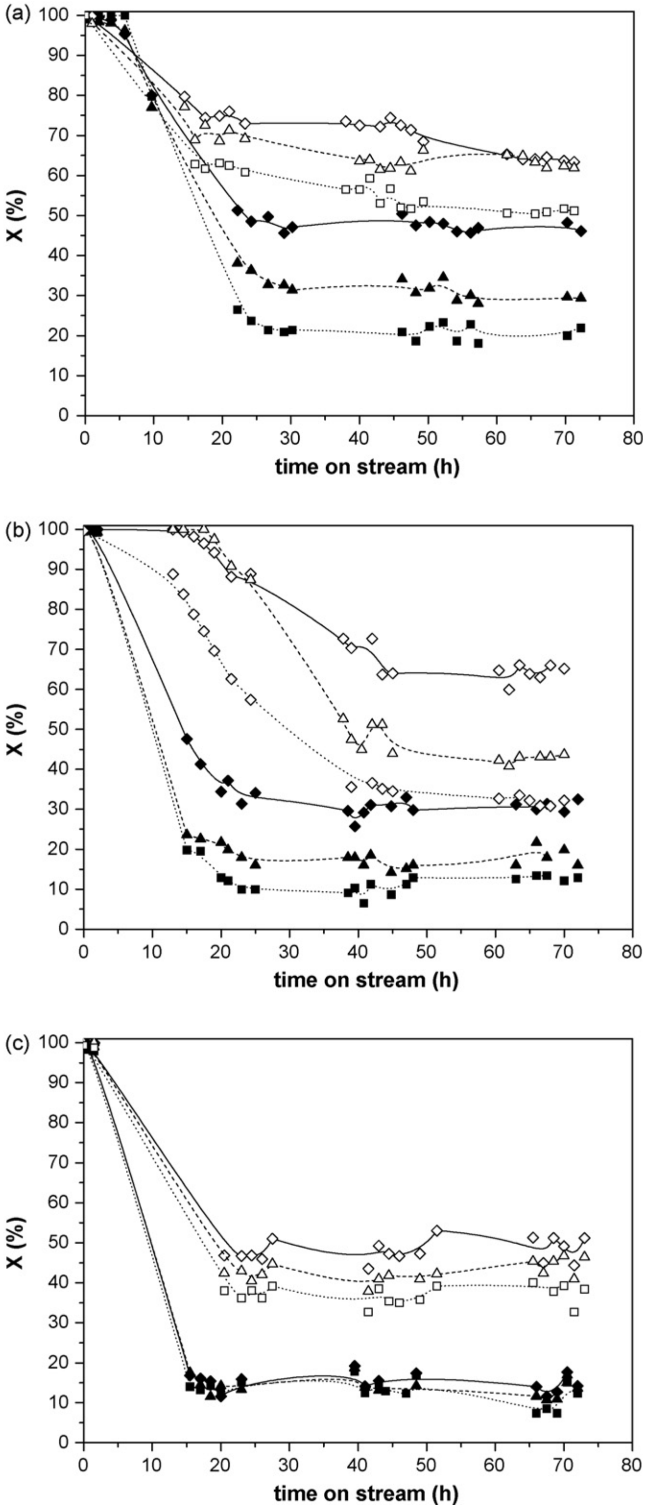

Fig. 1. CWAO (solid symbols) and PP-CWAO (open symbols): (a) phenol, (b) *o*-cresol and (c) *p*-nitrophenol. Symbols: (◆) X, (▲) X_{COD} and (■) X_{TOC}.

Table 1
Steady-state results for X, X_{COD}, X_{TOC} and TWL of phenolic compounds treated by CWAO and PP-CWAO

Target pollutant	CWAO				PP-CWAO			
	X (%)	X_{COD} (%)	X_{TOC} (%)	TWL (%)	X (%)	X_{COD} (%)	X_{TOC} (%)	TWL (%)
Phenol	45	30	21	12	64	63	51	26
o-Cresol	33	15	14	24	64	43	32	24
p-Nitrophenol	15	13	11	23	49	45	38	20

catalytic bed resulting in a rapid conversion fall. Finally, conversion almost attains steady state.

As it could be expected, the use of H_2O_2 as oxidation promoter leads to a remarkable raise in the conversions. For example, in the case of *p*-nitrophenol, X goes from just 15 to 49% (Table 1). In addition, the beneficial effect of using a stronger oxidant in the reaction media leads to an improvement in the oxidation performance also in terms of pollutant mineralisation (i.e. higher X_{TOC}), leading to more oxidised intermediate products. As it would be discussed in the next section, this higher mineralisation should have an impact in increasing the effluents biodegradability.

Because of the presence of partially oxidised products, X_{COD} should be equal or lower than the respective X. The higher the difference between X and X_{COD} is, the higher the amount of partially oxidised products in the liquid effluent. In the case of phenol oxidation, the PP-CWAO gives closer values of X and X_{COD}, that clearly indicates a higher degree of mineralisation (Table 1). The difference between X and X_{TOC}, which directly gives the selectivity towards carbon dioxide as X and X_{TOC} get closer, also corroborate for phenol, the higher degree of mineralisation in PP-CWAO than in CWAO. In the case of *o*-cresol and *p*-nitrophenol, although higher conversions were achieved, the opposite effect was observed when comparing X to X_{COD} and X to X_{TOC}, showing a higher occurrence of partially oxidised reaction products, as it will be discussed later on.

Regardless the use of H_2O_2 in the reaction and as far as X is concerned, the experimental reactivity order is phenol = *o*-cresol > *p*-nitrophenol. This reactivity order can be explained by the nucleophilic aromatic substitution mechanism [10]. In this mechanism, the substituents can be classified by their capacity to stabilise the benzonium carbanion. The substituents are strongly deactivating if they withdraw electrons and strongly activating if they release electrons. Hence, the hydroxyl group (–OH) is activating and the methyl and nitro groups (–CH_3 and –NO_2) are weakly or strongly deactivating groups, respectively, for the nucleophilic aromatic substitution. Therefore, these compounds are expected to be destroyed in the order phenol > *o*-cresol > *p*-nitrophenol, which closely matches the experimental results.

The TWL shown in Table 1 was measured from TGA up to 900 °C and can be used to assess the extent of oxidative coupling reactions giving irreversible adsorption of phenols over the AC. Thus, the greater the TWL is, the higher the development of oxidative coupling reactions and therefore the higher the loss in catalytic activity. It must be noted that the AC, before being used in any oxidation process, gives a TWL of 8%; therefore the difference with the used AC can be assumed to be mainly be due to oxidative coupling reactions, as stated before. From Table 1, the TWL in PP-CWAO for phenol is twice that obtained for the process not using H_2O_2, so the loss of AC surface by oxidative coupling seems to be greater in PP-CWAO than in CWAO. As it could be expected and as previously found when using higher amounts of H_2O_2 [11], this loss of catalytic surface affects the conversions profiles and can lead to a decrease in the steady state conversions. On the contrary, the TWL for *o*-cresol and *p*-nitrophenol did not change whether H_2O_2 was used or not in the oxidation process. Therefore, it has to be assumed that H_2O_2 was mainly used to oxidise the substituted phenols and did not influence the formation of carbonaceous deposits on the AC surface at the present conditions.

Adding H_2O_2 to the CWAO not only has a promoting effect that leads to higher organic removals. It also shows a synergic effect that makes the process more efficient than what could be expected from the isolated contribution of small amounts of H_2O_2 to the CWAO over AC. This synergic effect can be observed in Fig. 2 where X and X_{TOC} of each phenolic compound studied are compared for the conventional CWAO process (AC-O2-00) and adding 20% H_2O_2 under N_2 atmosphere (AC-N2-20) or air (AC-O2-20). Fig. 2 also shows the predicted conversions that could be expected in the PP-CWAO process if the effect of a small amount of H_2O_2 could just be added to the results obtained from the process using only oxygen from air as oxidant (AC-N2-20 + AC-O2-00). As it can be seen in Fig. 2a, the predicted conversions for phenol and *p*-nitrophenol are higher than those actually obtained in the PP-CWAO. However, if TOC reductions are considered (Fig. 2b), the promoted process gives always better results than expected, e.g. 17% higher TOC removal than the predicted for phenol oxidation. The higher TOC reductions obtained show a preferential use of the oxygen radicals to degrade partial oxidation products rather than the parent phenolic compound. The explanation of this preferential use should have into account that since hydrogen peroxide is already present in the liquid stream when it enters the reactor bed, mass transfer problems related to using gaseous oxidants such as air are avoided. Therefore, the availability of oxidant to react with a phenolic molecule is higher than in the non-promoted process. Consequently, the amount of partially oxidised products appearing in the reaction media should also be higher, facilitating their oxidation by the oxygen radicals once they are formed and solved in the reaction solution.

Regarding to the reaction intermediates, Fig. 3 summarises the results for the effluents characterisation in terms of fraction of COD, in both processes: CWAO (AC-O2-00) and PP-CWAO

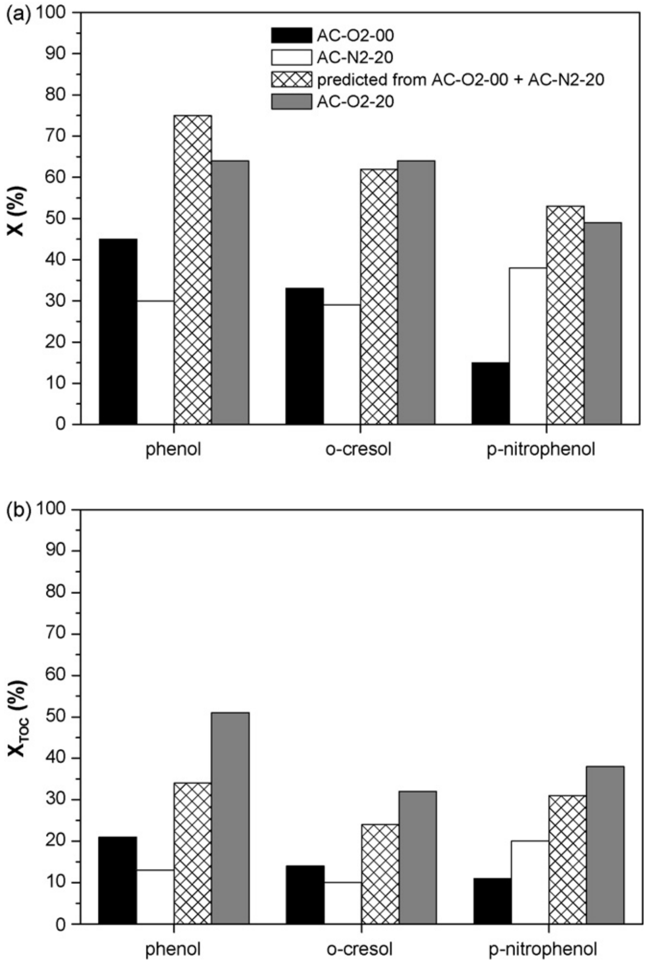

Fig. 2. Promoting and synergic effect of H_2O_2 in the CWAO: (a) conversion of initial model compound and (b) TOC conversion.

(AC-O2-20). The theoretical COD of each identified intermediate was calculated using the empirical correlations from Baker et al. [19] and then grouped into remaining model compound, phenol (from *o*-cresol oxidation), quinone-like compounds (catechol, hydroquinone and *p*-benzoquinone), condensation products (4 hydroxybenzoic acid and salicylic acid), carboxylic acids (oxalic, formic, malonic, acetic, maleic, succinic, fumaric and propionic acids) and non-identified products. Then, the contribution of each group was compared to the experimental remaining COD obtained in the CWAO and PP-CWAO effluents. As it can be observed from Fig. 3, in all the cases, the biggest part of the remaining COD corresponds to the remaining model compound. Regarding to the quinone-like fraction, it is noticeable that it only appeared in significant amounts in the phenol tests, being negligible for *o*-cresol and *p*-nitrophenol tests. The carboxylic acids fraction is higher in the PP-CWAO processes than in the CWAO process for *o*-cresol and *p*-nitrophenol, but the opposite is found in the case of phenol. Moreover, the intermediates occurrence in phenol PP-CWAO tests is lower than in phenol CWAO (approximately, 10 and 20% of the effluent COD, respectively), which confirms the higher degree of mineralisation achieved with PP-CWAO for phenol. In the case of *o*-cresol, the intermediates for the CWAO process represent less than 4% of the effluent COD, due to the low conversion achieved, but, observing the PP-CWAO process, the intermediates occurrence increase to 30% of the effluent COD, being phenol one of these intermediates (20% of the effluent COD). Finally, for *p*-nitrophenol, both the intermediates occurrence and distribution were similar, although a higher COD removal was achieved when using H_2O_2 in the reaction media.

3.2. Biodegradability enhancement

Once the biodegradability parameters (OUR and OC) are obtained by respirometry, the fraction of readily biodegradable COD (%COD_{RB}) of an effluent can be calculated as explained in Section 2.3. The total biodegradable COD (COD_{TB}) fraction of an effluent is the sum of the readily (COD_{RB}) and the slowly (COD_{SB}) biodegradable fractions, therefore COD_{RB} is always lower than COD_{TB}. Determination of COD_{SB} requires long term experiments in a biological pilot plant configuration, which would be extremely time-consuming. Therefore, COD_{RB} can be used as a fast method to compare the biodegradability enhancement reached in an effluent from different oxidation treatments with respect to the initial phenol, *o*-cresol and *p*-nitrophenol solutions, which have an experimentally determined 0% of COD_{RB}.

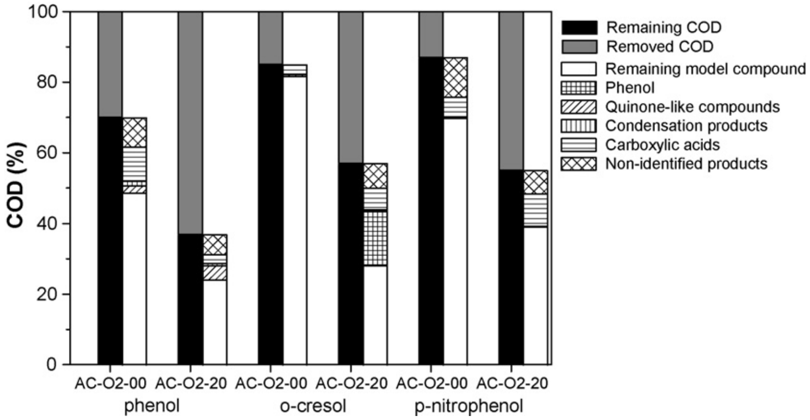

Fig. 3. Distribution of oxidation products in the CWAO and PP-CWAO effluents using phenol, *o*-cresol or *p*-nitrophenol as target pollutants.

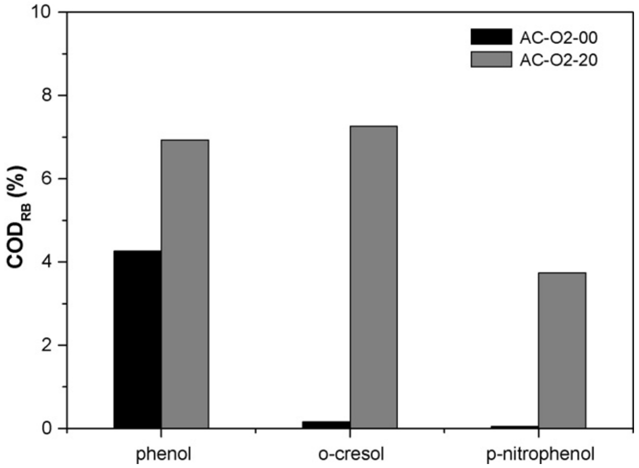

Fig. 4. Fraction of COD readily biodegradable from the respirometric tests performed to effluents from CWAO (AC-O2-00, (■)) and PP-CWAO (AC-O2-20, (▨)).

As 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 with acetic and propionic acid. Those acids were chosen due to its predominant occurrence in all CWAO and PP-CWAO effluents. The obtained Y_H value was 0.71 ± 0.02 mg COD mg^{-1} COD [14], which is in the range of the reported values in literature (0.61–0.87 mg COD mg^{-1} COD) [16]. Fig. 4 shows the %COD_{RB} obtained from the respirometric tests performed to each effluent coming from CWAO and PP-CWAO experiments.

Fig. 4 shows that PP-CWAO process gave more biodegradable effluents than CWAO, although the maximum %COD_{RB} was only 7.5% for *o*-cresol PP-CWAO. In the case of *o*-cresol and *p*-nitrophenol after CWAO, the operating conditions selected were not severe enough to transform the pollutant into an effluent with a higher biodegradability. In this way, Arslan and Ayberk [20] found a %COD_{RB} between 3 and 24% for wastewaters treated in the Izmit industrial and domestic WWTP that included pre-treated industrial wastewaters of various sectors such as tyre, drug or chemistry. The comparison of the values obtained in this work and the values presented by Arslan and Ayberk (2003) shows that the effluents obtained in this work are difficult to handle in a context of integrated management of these pre-treated effluents as part of the total influent to a WWTP. Probably, the %COD_{RB} would be higher if the remaining model compounds fraction is lowered. For example, from Fig. 2, there are almost 6% of carboxylic acids COD in the effluent of *p*-nitrophenol CWAO available for microorganism consumption, but a negligible experimental %COD_{RB} was obtained, probably because the 70% of the remaining COD is in form of *p*-nitrophenol, which can have a toxic effect over the biomass.

Therefore, it can be concluded that the selected conditions of temperature and p_{O_2} in both CWAO and PP-CWAO are not effective enough to produce a suitable effluent that could be safely sent to a municipal WWTP, despite having a fraction of readily biodegradable compounds up to 7.5%. Nevertheless, it has proved the potential of H_2O_2 as oxidation promoter for CWAO process, since higher pollutant conversions and higher biodegradability was obtained. Further insight on optimising the PP-CWAO conditions that could eventually produce biodegradable effluents is the ongoing research in our laboratory.

4. Conclusions

Preliminary tests in a trickle bed reactor at mild total pressure (i.e. 2 bar of p_{O_2}, 13.1 bar) and temperature (140 °C) conditions, using small amounts of hydrogen peroxide, confirm that AC can be included among the catalysts able to be used in the hydrogen peroxide promoted CWAO of phenolic compounds. The role of AC is to adsorb and concentrate the pollutants on its surface, where surface functional sites should be able to activate hydrogen peroxide and oxygen to form highly reactive radicals.

The PP-CWAO process leads to higher pollutant removal, COD and TOC conversions than the CWAO process. Although the improvement on the oxidation efficiency was not proportional to the amount of hydrogen peroxide added, a synergic effect was found when H_2O_2 is combined with O_2 which lead to higher mineralisation of the target pollutants. These results show that there should be a preferential use of the oxygen to degrade partially oxidised products rather than to oxidise the initial phenolic compounds.

PP-CWAO process also gives better biodegradability enhancement than CWAO, obtaining 7.3% COD_{RB} for *o*-cresol, 7% COD_{RB} for phenol and 3.7% COD_{RB} for *p*-nitrophenol effluents, at the conditions tested. Research ongoing in our lab is devoted to improve the oxidation step in order to assure more biodegradable effluents for a subsequent wastewater plant than those obtained in this work.

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