

Catalytic and non-catalytic wet air oxidation of sodium dodecylbenzene sulfonate: Kinetics and biodegradability enhancement

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Abstract

Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) were investigated as suitable precursors for the biological treatment of industrial wastewater containing sodium dodecylbenzene sulfonate (DBS). Two hours WAO semi-batch experiments were conducted at 15 bar of oxygen partial pressure (P_{O_2}) and at 180, 200 and 220 °C. It was found that the highest temperature provides appreciable total organic carbon (TOC) and chemical oxygen demand (COD) abatement of about 42 and 47%, correspondingly. Based on the main identified intermediates (acetic acid and sulfobenzoic acid) a reaction pathway for DBS and a kinetic model in WAO were proposed. In the case of CWAO experiments, seventy-two hours tests were done in a fixed bed reactor in continuous trickle flow regime, using a commercial activated carbon (AC) as catalyst. The temperature and P_{O_2} were 140–160 °C and 2–9 bar, respectively. The influence of the operating conditions on the DBS oxidation, the occurrence of oxidative coupling reactions over the AC, and the catalytic activity (in terms of substrate removal) were established. The results show that the AC without any supported active metal behaves bi-functional as adsorbent and catalyst, giving TOC conversions up to 52% at 160 °C and 2 bar of P_{O_2} , which were comparable to those obtained in WAO experiments. Respirometric tests were completed before and after CWAO and to the main intermediates identified through the WAO and CWAO oxidation route. Then, the readily biodegradable COD (COD_{RB}) of the CWAO and WAO effluents were found. Taking into account these results it was possible to compare whether or not the CWAO or WAO effluents were suitable for a conventional activated sludge plant inoculated with non adapted culture.

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1. Introduction

Sodium dodecylbenzene sulfonate (DBS), a member of the linear alkylbenzene sulfonates (LAS) family [1,2] is used as detergent, as dispersant, and as anionic surfactant.

Although LAS in wastewater has been successfully treated by conventional biological wastewater treatment plant (WWTP) at low concentrations [3,4], it has a biologically inhibitory effect at high concentration such as those from detergent manufacturing wastewater streams which can have a COD of up to 50 g l⁻¹ [5]. Highly concentrated LAS wastewater results also in other problems in the WWTP, such as foaming and oxygen mass

transfer limitations in the aeration basin and poor sludge settling, making necessary the LAS neutralization and increased retention times. Moreover, a large fraction of LAS is adsorbed into the sludge, so LAS is eliminated from the WWTP during the removal of the excess sludge instead of being a true biodegradation [4,6]. Therefore, other type of treatment is needed for highly concentrated LAS industrial effluents.

This study aims to compare both WAO and CWAO as precursors for the biological treatment of industrial wastewater containing DBS. First, a kinetic model was developed based on the generalized kinetic model suggested by Li et al. [7]. The model attempted to understand the reaction pathway and identify the major intermediates occurring during WAO subjected to modifications in the temperature and the residence time as the major dominant factors in the oxidation. Second, the kinetic model was validated by comparing with experimen-

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tal WAO data in order to achieve better understanding of the reaction process and to provide information for predictive reactor performance and cost effective scale-up in an aided reactor design. Third, several CWAO test using activate carbon (AC) as catalyst were performed in order to reduce the temperature and pressure and to control the reaction intermediates with the aim of producing a more biodegradable effluent than in WAO. The AC performance was tested for 5 days so that the evolution of the catalytic activity could be continuously checked. The used AC were further characterised to highlight the role of AC into the DBS reaction mechanism. Finally, the biodegradability enhancement between both processes was compared by using respirometry to get the biodegradability of each CWAO effluent and by using the intermediates distribution of WAO effluents.

2. Experimental

2.1. Materials

Aldrich provided technical grade DBS. Deionised water was used to prepare all the solutions. The synthetic air used as oxidant in CWAO and WAO experiments has a purity of 99.995% (Carbueros Metálicos, Spain and BOC gases, UK).

The AC used as catalyst was purchased from Merck (reference #102518) in the form of 2.5 mm pellets. Prior to use, AC was crushed and sieved. Then, the particle size chosen was 25–50 mesh (0.7–0.3 mm). This AC is manufactured from wood and was characterised in a previous study [8] giving a BET surface area of $1481 \text{ m}^2 \text{ g}^{-1}$, a micropore volume of $0.34 \text{ cm}^3 \text{ g}^{-1}$, a BJH cumulative surface area of $304 \text{ m}^2 \text{ g}^{-1}$, a pH_{PZC} of 8.05 and a maximum adsorption capacity for DBS of $1028 \text{ mg}_{\text{DBS}} \text{ g}_{\text{AC}}^{-1}$ at 25°C .

2.2. Experimental set-up and procedure for WAO and CWAO

WAO experiments were done in a 0.5-l working volume stainless steel high-pressure reactor (Autoclave engineers, USA). In a typical semi-batch experiment, 500 ml of the solution with DBS concentrations of 1 g l^{-1} were introduced into the reactor. Experiments were done at temperatures from 180 to 220°C and an oxygen partial pressure (P_{O_2}) of 15 bar was maintained in all the experiments. At the end of the experiments, the temperature dropped to ambient conditions and the reactor content was collected for analysis to determine remaining chemical oxygen demand (Y_{COD}) and total organic carbon (Y_{TOC}).

CWAO set-up description can be found elsewhere [8]. Typically, 7.0 g of AC was loaded into the reactor. Synthetic air was used as oxidant to ensure a P_{O_2} of 2 and 9 bar at each temperature. The experiments were run at 140 and 160°C for 72 h. DBS feed concentration was taken as 5 g l^{-1} . Liquid samples were periodically withdrawn and then analysed to determine Y_{COD} and Y_{TOC} .

In both cases, the same experiment WAO or CWAO was conducted twice to check the reproducibility of results. The match (within $\pm 5\%$) between repeated experiments was excellent. The

data reported in this study are the arithmetic average of the results derived from repeated experiments.

2.3. AC characterization

At the end of the CWAO test, the AC used was carefully collected and dried at 105°C overnight under an N_2 atmosphere to remove excess water. Then, the AC (between 15 and 20 mg) was used to determine textural properties by nitrogen adsorption isotherms at 77 K in a Micromeritics instrument model ASAP 2010. The textural properties such as surface area, micropore volume and cumulative surface area were calculated by applying different model methods i.e. BET, Harkins and Jura t -plot and Barret–Joyer–Halenda (BJH) which are included with the Micromeritics software. Finally, the remaining used AC was dried at 400°C under nitrogen atmosphere to remove any physisorbed compound. Subsequently, the AC was weighed to measure the weight change (W_{AC}).

2.4. Analytical procedures

Sample concentrations of DBS were immediately determined by HPLC (Agilent 1100 or Varian Prostar). The analysis method was adapted from Matthijs and De Henau [9] and Patterson [5] and was performed with a C18 reverse phase column (Agilent-Hypersil ODS or Thermo-ThermoHypersil ODS), using an acetonitrile-water (70:30) mobile phase to separate the DBS from its reaction products. Sodium perchlorate was added to both mobile phases in a concentration of 0.15 M. A flowrate of 1 ml min^{-1} and a wavelength of 225 nm were used. Identification and quantification of several carboxylic acids were done with different methods. 4-Sulfobenzoic acid was quantified with two mobile phases at flow rate 1 ml min^{-1} : solution A containing a mixture of acetonitrile and water (20:80) and solution B containing just water; again sodium perchlorate was added to both mobile phases at a concentration of 0.15 M.

For other acidic intermediates (glyoxilic, oxalic, formic, 4-hydroxybenzoic sulfonic, malonic, acetic, succinic, fumaric, benzene sulfonic and propionic acids), the analysis was done using a mixture of ultra-pure water (A): methanol (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 pH equal to 1.5 with concentrated sulphuric acid.

COD was measured with the standard method 5220D, TOC was quantified with the method 5310B and volatile suspended solids (VSS) with method 2540E [10]. The CO_2 selectivity was calculated by a mass balance between the initial and final TOC values in the experimental samples.

The results are compared in terms of remaining COD and TOC in the effluents, the general expression used is:

$$Y(\%) = \left(\frac{C_e}{C_0} \right) 100 \quad (1)$$

where C_0 is the inlet concentration and C_e is the concentration in the effluent.

2.5. Experimental set-up and procedure for respirometric tests

The description of the respirometer used in this study to measure biodegradability enhancement can be found elsewhere [11,12].

The respirometer was inoculated with biomass from the urban WWTP of Tarragona (Catalonia, Spain) with an average value of VSS of $2100 \pm 320 \text{ mg l}^{-1}$.

The biodegradability of the CWAO effluents was estimated by adding a substrate pulse of 8 mg COD l^{-1} ($\text{COD}_{\text{added}}$). Then, the oxygen uptake rate (OUR) profile is obtained solving the oxygen balance in the liquid phase of the respirometer. The biodegradation parameter used to compare OUR profiles obtained in each experiment is the area under the OUR profile or oxygen consumption (OC). More information about the OUR calculation can be found elsewhere [11].

2.6. Kinetic modeling

Generalized Kinetic Model (GKM) was established following the GKM suggested by Li et al. [7]. For engineering purposes, it is sufficient to quantify the global reaction rate by identifying the major WAO pathways [7]. As a result, key intermediates, which were considered to be rate controlling, were selected in this study. The model equations were solved by a program done in C language. The least square method was used in conjunction with the Excel[®] solver function to calculate rate constants (k_i).

Several assumptions were considered for kinetic modelling: first order was assumed for the organic concentration term [7]. Due to the large amount of water present in the system, the water concentration was excluded from the model. In addition, since an excess oxygen was maintained at a constant partial pressure in the reactor, oxygen concentration in the aqueous phase was considered unchanged throughout the experiments [13]. Finally, all concentration terms are expressed by means of the calculated TOC concentration.

GKM is based on a simplified reaction scheme involving the formation and destruction of rate controlling intermediates. Low molecular weight carboxylic acids such as glyoxylic, oxalic, formic, propionic and acetic acids are well known refractory intermediates for WAO, being acetic acid the most refractory one [7,14–16]. Therefore, acetic acid can be regarded as the

only representative of the rate controlling intermediate (Group B) in the GKM [7].

Three groups are included in the reaction pathway of GKM. Group A comprises the DBS. Group B is represented by acetic acid. Group C includes end products such as carbon dioxide and water.

The final equations used in the model are expressed as:

$$[A] = [A_0]e^{-(k_1+k_2)t} \quad (2)$$

$$[B] = [B_0]e^{-k_3t} + \left(\frac{k_2[A_0]}{(k_1+k_2-k_3)} \right) [e^{-k_3t} - e^{-(k_1+k_2)t}] \quad (3)$$

$$\frac{[A+B]}{[A]_0} = \left(\frac{k_2}{(k_1+k_2-k_3)} \right) e^{-k_3t} + \left(\frac{(k_1-k_3)}{(k_1+k_2-k_3)} \right) e^{-(k_1+k_2)t} \quad (4)$$

The value of k_1 was determined from the initial reaction rate of the WAO experiment of DBS. Foussard's equation [17] of acetic acid was used to determine k_3 , whereas k_2 value was calculated by linear square method. The result of GKM for DBS was evaluated against experimental TOC removal as well as quantified acetic acid concentration.

3. Results and discussion

The results and discussion are divided into three sections. In the first one, the WAO and CWAO performance is discussed by means of Y_{COD} and Y_{TOC} . Also, the reaction mechanisms and intermediates are examined. In the second section, the kinetic model is stated. Finally, in the last section, both processes are compared in terms of biodegradability enhancement.

During the discussion, the WAO and CWAO conditions will use the following nomenclature: 180–15 will refer to 180 °C and 15 bar of P_{O_2} , 160–9 equals to 160 °C and 9 bar of P_{O_2} and so on.

3.1. DBS disappearance: WAO against CWAO

Fig. 1 shows the Y_{COD} and Y_{TOC} at 180, 200 and 220 °C for different reaction times in WAO at 15 bar of P_{O_2} . As expected, an increase in temperature gives a higher TOC abatement and COD removal. For instance, a TOC reduction of 19, 34 and 47% were

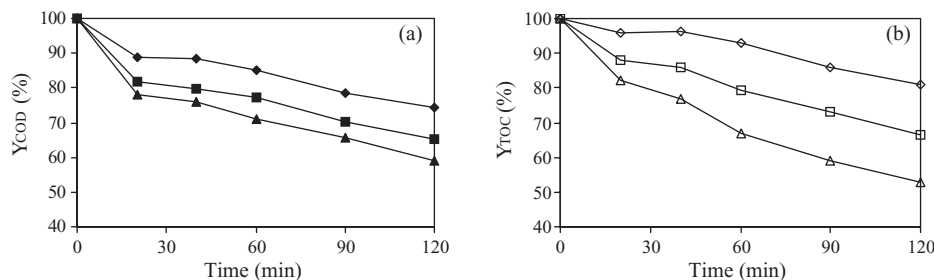


Fig. 1. Remaining COD (a-filled symbols) and remaining TOC (b-empty symbols) during WAO at 15 bar of P_{O_2} of DBS at different temperatures. Symbols indicate experimental data ((▲ or △) 180 °C, (■ or □) 200 °C and (◆ or ◇) 220 °C). Lines show trends.

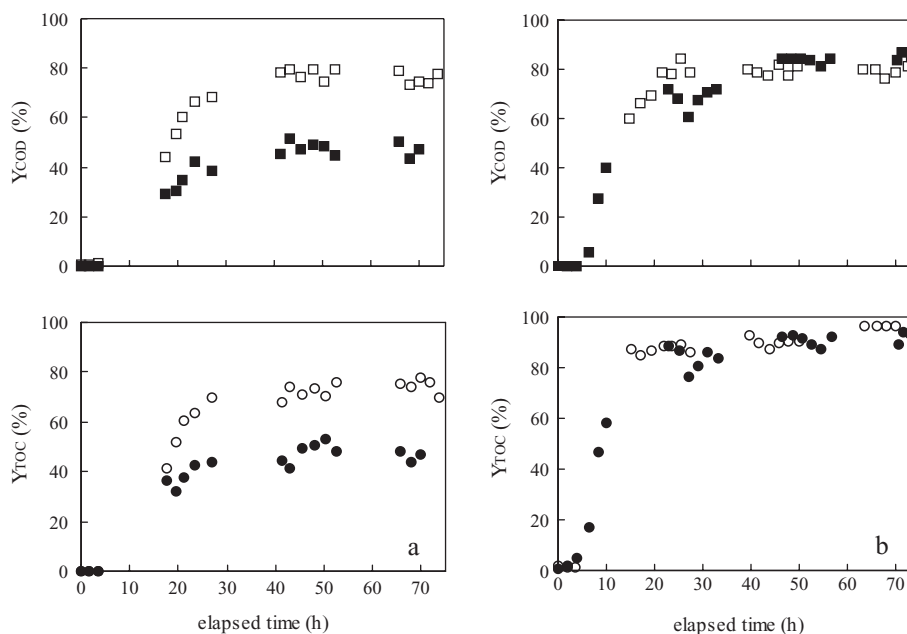


Fig. 2. Remaining COD and remaining TOC profiles during CWAO at 2 bar of P_{O_2} (a) and at 9 bar of P_{O_2} (b). Filled symbols correspond to 160 °C whereas empty symbols correspond to 140 °C.

obtained at 180–15, 200–15 and 220–15, respectively. However, complete degradation of TOC and COD was not achieved. In addition, the oxidation of DBS in WAO system takes place in two periods. The initial fast reduction stage, which appears to occur from 0 to 20 min, is followed by a slow reaction stage (Fig. 1). There are two parallel routes which can destroy the detergent nature of the original molecule: a random scission of alkyl side chain and an attack of the aromatic ring followed by removal of the sulfonic group. Since the aromatic ring is more difficult to attack, it is expected that the initial step can be related to the oxidation of dodecyl-chain to short-chain alkyl aromatic groups such as 4-sulfobenzoic acid, sulfobenzaldehyde, alkylsulfo-benzoic carboxylic acid and alkylsulfo-benzaldehyde which are relatively stable for further oxidation under given conditions [5,18]. Because short-chain carboxylic acids and other carboxylic acids may be refractory intermediates in WAO systems [14–16], the slow oxidation step after the initial one may be explained by the accumulation of these kind of intermediates during the WAO of DBS.

For CWAO tests, Fig. 2 shows the Y_{COD} and Y_{TOC} evolution in 72-h tests at 140 °C (empty symbols) and 160 °C (filled symbols). Fig. 2a corresponds to the results at 2 bar of P_{O_2} , whereas the results for 9 bar of P_{O_2} are in Fig. 2b. As previously found [8,19], three different zones can be distinguished in all the cases. Firstly, after starting, an adsorption dominating period results in an apparent total COD and TOC removal. In a previous work [8], the DBS adsorption capacity of the AC used in the CWAO tests were established as $1028 \pm 44 \text{ mg g AC}^{-1}$, therefore, taking into account the liquid flow (57 ml h^{-1}), the weight of the catalytic bed (7 g) and the feed concentration in the CWAO experiments (5000 mg l^{-1}), the time needed to saturate the AC bed could be calculated, giving a value of 25 h. Secondly, a continuous rise in Y_{COD} and Y_{TOC} is observed when the AC bed progressively

undergoes both adsorption and oxidation of the DBS. Finally, after 25 h, once the bed is equilibrated with DBS, the remaining COD and TOC almost attain steady state. In the steady state period, which corresponds to the last 30–40 h in each CWAO test, the steady state values of COD reduction are 25% at 140–2, 55% at 160–2, 16% at 140–9 and 14% at 160–9. Similar trends can be drawn for TOC removal.

Two different behaviours can be extracted from Fig. 2. At 2 bar, an increase in temperature leads to a remarkable increase in the COD and TOC removal. However, when the P_{O_2} changes to 9 bar, the removal of COD and TOC are much lower than in the case of 2 bar. At 9 bar of P_{O_2} , a high quantity of foam was observed in the sample port and also in the reactor outlet. This non expected behaviour can be explained according to changes in the hydrodynamic operation as follows: At 9 bar of P_{O_2} , the liquid flow pattern is laminar in the pipes before the reactor but the gas flow pattern is turbulent. Consequently, when the aqueous DBS solution is mixed with the turbulent air flow, a non-flowing foam phase is developed, causing a dramatic change in the reactor operating mode and performance. At 2 bar of P_{O_2} , both flow patterns are laminar and foam formation was not observed.

Comparing both WAO and CWAO processes, the use of AC as catalyst allows to reduce the temperature and pressure maintaining the removal of COD and TOC. For instance, in WAO at 220–15, the Y_{TOC} is 53% (Fig. 1) whereas in CWAO at 160–2, the Y_{TOC} is 48% (Fig. 2). However, it should be pointed out, the hugely different time scales needed to achieve the same removal levels in both processes, 120 min for WAO (non steady state) and 30 h for CWAO (steady state).

Regarding to reaction intermediates, the formation of organic acids as oxidation by-products in both processes was confirmed by HPLC analysis and pH of the effluent. The pH was left uncontrolled during all the experiments, but when DBS was subjected

Table 1
Original bed loading, W_{AC} and textural characterization at the end of the CWAO tests

	Condition			
	140-2	160-2	140-9	160-9
Loaded AC (g)	7.01	7.03	7.00	7.00
W_{AC} (%) ^a	17.2	−46.7	6.0	−43.1
BET surface area (m ² /g)	285	308	10	70
Micropore Volume (cm ³ g ^{−1})	0.006	0.014	0.001	0.002
BJH cumulative area surface (cm ² /g) ^b	148	185	8	49

^a Dried at 400 °C.

^b Between 17 and 3000 Å.

to WAO the pH decreased significantly from 7.3 to 3.7, 3.6 and 3.3 after 120 min at 180–15, 200–15 and 220–15, respectively. In the case of CWAO experiments, the steady state pH was between 2.9 and 2.3. This decrease is caused by the formation of organic acids as reaction intermediates as confirmed by HPLC analysis.

In WAO experiments, quantification of 4-sulfobenzoic acid and short-chain carboxylic acids (formic and acetic acid) was done by means of HPLC using external standards. In order to calculate the contribution of each intermediate to the experimental COD, the theoretical oxygen demand (COD_{Th}) of each oxidation product was calculated using the empirical correlations obtained by Baker et al. [20] and the obtained HPLC concentration. The same procedure was applied to calculate the contribution of the intermediates to the experimental TOC, but using in this case the combustion reaction of each intermediate.

A greater concentration of 4-sulfobenzoic acid was observed at higher temperatures. Especially during the initial oxidation step, concentration of 4-sulfobenzoic acid increases significantly, which is a consistent result as those of TOC and COD. Therefore, it can be expected that oxidation of initial DBS to short-chain sulfobenzene group via decarboxylation of alkyl side chain is the major route of WAO for DBS. Accumulation of acetic acid during oxidation increased with time and temperature. However, formic acid was variable and identified at very low concentration. Since formic acid is more reactive than acetic acid and oxidizes to carbon dioxide and water at temperatures as low as 150 °C in WAO system, formic acid may react with other oxidation intermediates or undergo further oxidation [16].

From the above results, 4-sulfobenzoic acid (representative of sulfo-aromatic group) and acetic acid (representative of short-chain carboxylic acids) could be regarded as major intermediates during WAO of DBS. Moreover, it is expected that there are three successive reaction steps for degradation of DBS in WAO system; decarboxylation of alkyl-side chain, aromatic ring cleavage including desulfonation and conversion of short-chain carboxylic acids to CO₂ and H₂O. Sulfo-aromatic groups such as 4-sulfobenzoic acid can be produced at the end of decarboxylation step, whereas short-chain carboxylic acids such as acetic acid may be generated during alkyl chain random scission and after aromatic ring cleavage. Furthermore, it was seen that the content of 4-sulfobenzoic acid tends to increase with time under any given conditions. Besides the peak of 4-sulfobenzoic acid, other peaks were also seen at low retention times and they also are likely to accumulate as intermediates. These unknown compounds are suspected to be refractory sulfonated aromatics

such as sulfophenylcarboxylic acids, sulfophenylaldehydes, sulfophenyldialdehydes and carboxylsulfophenylaldehydes. The above results suggest a consecutive-parallel reaction pathway, which agrees with the reaction pathway proposed previously by Patterson et al. [5].

In CWAO experiments, the reaction intermediates were also quantified by means of external standards. In order to compare with WAO experiments, the carboxylic acids COD_{Th} (calculated from HPLC results) contribution to the total experimental COD was calculated for each effluent of each CWAO test. As example, at 160–2 (which is the condition with the lowest Y_{COD} and Y_{TOC}) the majority of the remaining COD was in form of carboxylic acids (50%) and DBS (21%); the rest was in form of non-identified COD (27%), quinone-like products (1%) and condensation products (1%). Glyoxilic, formic, acetic, succinic, benzene sulfonic and propionic acids were 96% of the COD in form of carboxylic acids. In the case of 140–2, the effluent composition was mainly carboxylic acids (22%) and DBS (37%) whereas non-identified COD accounted for 39% and both quinone-like intermediates and condensation products were 1%.

The concentration of carboxylic acids in the effluent from 140 to 2 and 160 to 2 is higher than in WAO experiments at 220–15, which confirms a deeper oxidation reaction. In this case, no 4-sulfobenzoic acid was detected but benzene sulfonic and 4-hydroxybenzene sulfonic acids were quantified in concentrations up to 25 and 100 mg l^{−1}, respectively. Also, the short-chain carboxylic acids fraction roughly increases with the increase of temperature in CWAO, nevertheless, an increase in P_{O_2} up to 9 bar, led to an unfavourable behaviour, lowering the short-chain carboxylic acids fraction for 160–9 and 140–9 CWAO tests. As explained before, the drop in the reaction progress could be caused by the observed presence of a non-flowing foaming system which causes a poor reactor performance.

From CWAO results, at 160–2 and 140–2 the reaction seems to evolve enough to oxidise most of the organic matter to glyoxilic, formic, acetic and propionic acids, which are the latest intermediates before total mineralisation. However, at 160–9 and 140–9, the acids are in lower proportion but also were of high molecular weight (results not shown) indicating that the reaction was not progressing enough, probably because the non-flowing foaming system stopped the liquid flow in the TBR leaving the AC unprotected in front of side reactions such as oxidation and/or burning, preventing the DBS oxidation from progressing. This statement was confirmed in a previous work for CWAO control tests, with and without phenol in the liquid stream [21],

using the same CWAO reactor and range of operating conditions than those used in this work.

To confirm the previous statement, the changes in the AC weight and in the AC textural properties during oxidation have been studied and should shed some light on the AC catalytic activity. Also, the influence of oxidative coupling reactions on CWAO could be assessed, because oxidation of DBS and its intermediates occur in parallel with AC oxidation/burning and coupling reactions. Table 1 shows the W_{AC} and the textural properties for the used AC from each CWAO experiment.

As Table 1 shows, W_{AC} was positive (i.e. the AC weight increased) by the end of the 140-2 and 140-9 tests. However, the W_{AC} was negative at the end of 160-9 and 160-2 tests. W_{AC} has previously been studied [18,20] for phenol CWAO, with the same reactor and a range of conditions (temperature, pressure and space time) that includes those used here. W_{AC} turned out to be positive or negative depending on the elapsed time and the operating conditions [19,21]. For instance, Fortuny et al. [21] observed that AC weight increases in the first 24 h at 140-9, then reaches a maximum and finally decreases to values below the original one. Furthermore, after 10 days on stream and at lower oxygen partial pressures, the AC weight always increases [21].

Many studies have shown that this positive W_{AC} can be attributed to the deposition of polymeric compounds produced by oxidative coupling reactions over the AC [22–25]. Cooney and Xi [26] demonstrated that, oxidative coupling reactions can be accelerated by the presence of a substituent in the phenol molecule at low pH. They postulated that oxidative coupling reactions occur simultaneously with the oxidation reaction and these coupling reactions probably block the active sites in AC, and decrease its catalytic activity.

Following this idea, a minimum AC weight gain (i.e. a minimum of oxidative coupling reactions), must correspond to a maximum in COD and TOC removal, since oxidative coupling is expected to block the active sites and diminishes the superficial area (as Table 1 shows) and, therefore, the catalytic activity. As can be see it in Table 1, all textural properties (BET surface, Micropore volume and BJH cumulative area surface) decrease following the order 160-2 > 140-2 > 160-9 > 140-9, which in fact is the behaviour of COD and TOC removal as well as the increasing concentration of carboxylic acids in the CWAO effluents.

According to the behaviour of the W_{AC} and the textural properties it could be concluded that at 140-2, oxidative coupling reaction occurred in a bigger proportion than the AC oxidation/burning, because the weight gain is the highest one. However the BET surface area and BJH cumulative area surface are equivalent to those values obtained at 160-2. At 160-2, the AC oxidation/burning was greater than oxidative coupling reactions, because the loss in AC weight is the highest one, but the textural properties are the highest ones. At 140-9, the oxidative coupling reactions over the AC occurred in biggest proportion of all the tests because the textural properties are the lowest. However, the AC weight gain is almost negligible (just 6%). Finally at 160-9, the AC oxidation/burning is almost equivalent to that occurred at 160-2 but, the oxidative coupling reactions occurred in a higher degree than those occurred at 160-

Table 2
Calculated kinetic parameters from GKM fit

Parameter	Temperature			E (kJ/mol)
	180 °C	200 °C	220 °C	
k_1 (10^3 min^{-1})	1.77	4.92	9.29	77.3
k_2 (10^3 min^{-1})	2.00	6.4	9.9	74.7
k_3 (10^6 min^{-1})	0.575	3.99	23.9	173.1
Selectivity α (k_2/k_1)	1.13	1.30	1.07	–
SSE	0.0019	0.0017	0.0017	–

2, because the textural properties are lower than at 140-2 and at 160-2.

3.2. Kinetic modelling: GKM

Table 2 shows the kinetic parameters, for the three proposed reactions at the three tested temperatures in WAO experiments, estimated by fitting to the proposed reaction network. Fig. 3 depicts the predicted evolution of Y_{TOC} in WAO experiments.

The energies of activation for k_1 and k_2 were found to be 77.3 and 74.7 kJ mol⁻¹, respectively. The range of selectivity (α) was from 1.07 to 1.13, which indicates a higher tendency to form acetic acid. Model prediction has an excellent agreement with experimental data. Least square method was used to fit the data. The kinetic model was fitted to minimise the sum of squared errors (SSE). The SSE was 0.0019, 0.0017 and 0.0017 for 180, 200 and 220 °C, respectively. The activation energies for destruction of DBS are lower than the reported values for oxidation of alkyl or chlorinated substituted benzene rings but falls in the range of activation energies for phenol oxidation [27,28]. Nevertheless, these values cannot be directly compared as, to the best of our knowledge, there is no literature reporting

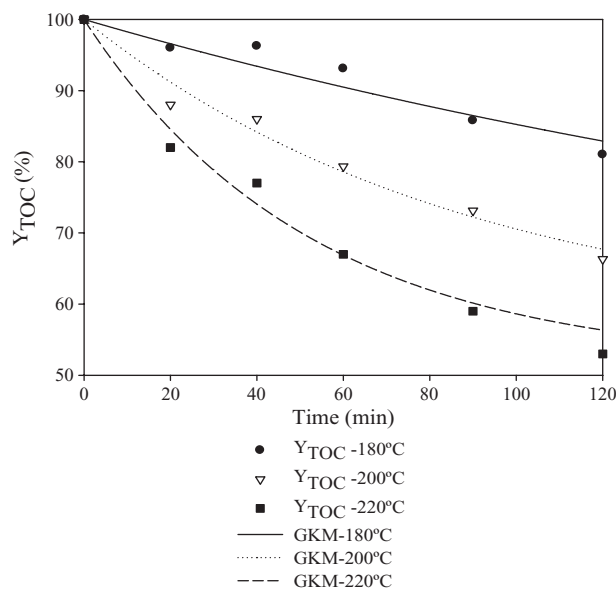


Fig. 3. GKM fit for Y_{TOC} in WAO of DBS at different temperatures. Symbols indicate experimental Y_{TOC} data (■) 180 °C, (▽) 200 °C and (●) 220 °C whereas lines indicates GKM model prediction (—) 180 °C, (· · ·) 200 °C and (---) 220 °C).

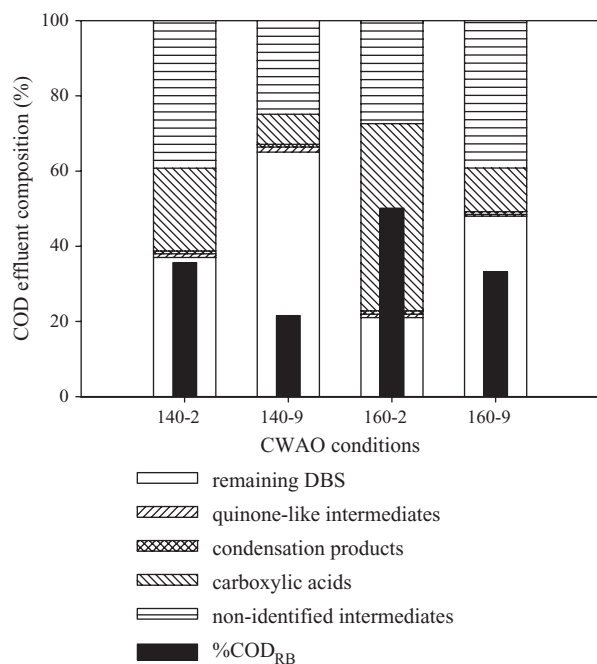


Fig. 4. COD_{Th} intermediates distribution (calculated from HPLC results) and biodegradability enhancement in CWAO effluents at the end of the tests.

any kinetic data for the oxidation of a benzene group with a sulfo-substituent.

3.3. Biodegradability enhancement

In this section, the dependence of the intermediates distribution and the AC behaviour on the operational conditions in the CWAO will be correlated with the measured biodegradability of each CWAO effluent. The objective is to find the best condition in the biodegradability enhancement which permits a successful coupling with an urban WWTP.

The readily biodegradable COD (COD_{RB}) of each CWAO effluent can be estimated using the heterotrophic yield coefficient (Y_H), calculated in a previous work [12], and the OC obtained from the OUR profile in the respirometric tests.

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

$$\% \text{COD}_{\text{RB}} = \frac{\text{COD}_{\text{RB}}}{\text{COD}_{\text{added}}} 100 \quad (5)$$

Fig. 4 shows the %COD_{RB} and a detailed distribution of intermediates for each CWAO effluent. It should be pointed out that the biodegradability of the un-treated solution was zero. There was a lower OC at 140-9 and 160-9, probably because the high remaining DBS concentration could be inhibiting the biological consumption. The maximum %COD_{RB} (50%) occurred at a CWAO condition of 160-2. From Fig. 4, the carboxylic acids had a maximum concentration at this condition. At 140-2, the %COD_{RB} (36%) was lower than the previous case being the carboxylic acids in lower proportion than at 160-2. In addition, the proportion of non-identified compounds, which was very high, should be considered. From HPLC chromatograms,

at 140-9 and 160-9 the most of non-identified intermediates were in the retention times corresponding to quinone-like and aromatic compounds, probably being toxic or inhibitory intermediates [12]. On the contrary, at 160-2 and 140-2 most of the non-identified COD were in the retention times of carboxylic acids, which could be contributing to the effluent biodegradability. In fact, the values of COD_{RB} are always higher than the proportion of carboxylic acids, which could indicate that a non-identified intermediate or a non-detected co-metabolic effect was increasing the experimental OC in the respirometric tests [12].

Three different factors 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 this case, the maximum COD conversion and the maximum COD_{RB} were obtained at 160-2. Additionally, the AC conservation is clearly higher at 2 bar than at 9 bar. Based on these results, 160-2 should be an appropriated CWAO condition for DBS oxidation.

For WAO effluents no respirometry was made. Nevertheless, according to Suarez-Ojeda et al. [12] acetic acid is a readily biodegradable intermediate from the CWAO of several substituted phenols. Therefore, the WAO biodegradability enhancement should be lower than in the case of CWAO since acetic acid (the known readily biodegradable intermediate in WAO effluents) was in lower proportion in WAO experiments (12% at 220-15) than in CWAO experiments (15% at 160-2).

4. Conclusions

DBS can be efficiently destroyed by both WAO and CWAO. TOC reduction was between 19 and 47% for WAO experiments between 180 and 220 °C at 15 bar of P_{O_2} , whereas for CWAO experiments at 2 bar of P_{O_2} in the range of 140–160 °C, the TOC removal was between 24 and 52%. The AC without any active metal was shown to have a catalytic effect on the CWAO of DBS, which allows lowering the temperatures and pressures needed to maintain the same COD and TOC removals than in WAO.

Concerning to the biodegradability enhancement of the DBS solution, CWAO increased the COD_{RB} up to 50% compared to the un-treated solution. The CWAO was highly selective to short-chain carboxylic acids when using 2 bar of P_{O_2} . In turn, at 9 bar of P_{O_2} the development of a non-flowing foaming system causes a poor reactor performance.

Factors influencing the CWAO performance such as adsorption, oxidative coupling reactions or pore blockage have been studied obtaining a fairly satisfactory explanation for the DBS reaction mechanism in presence of AC. The positive W_{AC} can be explained by the presence of attached polymers on the AC surface, which are produced by oxidative coupling reactions, as demonstrated by nitrogen adsorption isotherms.

A generalised kinetic model correctly fits the Y_{TOC} experimental data. Although the model is based in the concentrations of DBS, acetic acid and end products (water and CO_2), the reaction scheme is enough to assess reactor design.

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