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Influence of activated carbons on the kinetics and mechanisms of aromatic molecules ozonation

T. Merle^a, J.S. Pic^{a,*}, M.H. Manero^b, S. Mathé^a, H. Debellefontaine^a

^a Université de Toulouse, LISBP, UMR INSA/CNRS 5504 & UMR INSA/INRA 792, 135 Avenue de Rangueil, 31077 Toulouse Cedex 4, France

^b Université de Toulouse, LGC, UMR CNRS 5503, IUT GCGP, 137 Avenue de Rangueil, 31077 Toulouse Cedex 4, France

A B S T R A C T

Companies have been looking for new methods for treating toxic or refractory wastewaters; which can mainly be used prior to or after or in connexion with biological treatment processes.

This paper compares conventional ozone oxidation with activated carbon (AC) promoted ozone oxidation, which helps developing a mechanism involving HO• radical. For a compound which is quite easy to oxidise, like 2,4-dichlorophenol (2,4-DCP) conventional ozonation is efficient enough to remove the initial molecule. The mechanism involved mainly consists of an electrophilic attack on the aromatic ring, which is activated by the donor effect of the –OH group, then followed by a 1,3 dipolar cycloaddition (Criegee mechanism) that leads to aliphatic species, mainly carboxylic acids. Yet, the addition of AC, through the presence of HO• radical, enhances the removal of these species which are more refractory.

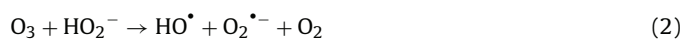
For a refractory compound like nitrobenzene (NB), with a de-activated aromatic ring because of the attractive effect of –NO₂, conventional ozonation is inefficient. On the contrary, this molecule can be quite easily removed with AC promoted oxidation and it is found that the mechanism (electrophilic attack followed by a 1,3 dipolar cycloaddition) is quite similar to the one corresponding to conventional ozonation, but with less selectivity.

For both molecules, a mass balance has established that the by-products accounting for more than 75% of the remaining COD can be quantified. A significant part is composed of carboxylic acids (acetic, oxalic, etc.), which could afterwards be easily removed in an industrial wastewater treatment process followed by a final biological treatment step.

1. Introduction

Wastewater is often treated by biological routes with good removal efficiencies; however, toxic organic compounds cannot be reliably eliminated by these bioprocesses. Additional treatments, such as adsorption or chemical oxidation, must be used for non-biodegradable molecules removal. Ozone is frequently used since it is a powerful oxidizing agent. The reactivity of the ozone molecule with unsaturated organics follows two main mechanisms [1,2]: electrophilic substitution and 1,3 dipolar cycloaddition, known as the "Criegee mechanism". In the particular case of aromatic compounds, the substituents of the aromatic ring play a major role in the actual mechanism. Yet all these reaction pathways are selective and unfortunately some organic compounds cannot be oxidised with a single ozonation step. In these cases, the use of advanced oxidation processes can be the best solution [3–6].

Ozone decomposition in water is a well-known phenomenon. It can be described thanks to a cyclic mechanism involving several radical species and acido–basic equilibria [7]. Hydroxide ions and hydrogen peroxide strongly participate in the initiation steps of this cycle (Eqs. (1) and (2)):



The kinetics of the first reaction is quite slow (second order constant $k_1 = 70 \text{ L mol}^{-1} \text{ s}^{-1}$) whereas the kinetic constant for the second reaction is much larger ($k_2 = 2.8 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$), thus hydrogen peroxide strongly enhances radicals production from ozone [8]. The kinetics of ozone decomposition into HO• radical are generally well described with a simple first order law according to dissolved ozone concentration [9]. The value of the corresponding kinetic constant (k_c) depends, among other parameters, on the pH of the solution, on hydrogen peroxide concentration or on the presence of catalytic materials.

In previous papers, we showed that ozone decomposition could be obtained through activated carbons (AC) [10–12] or zeolite

* Corresponding author. Tel.: +33 561 559 747; fax: +33 561 559 760.
E-mail address: jean-stephane.pic@insa-toulouse.fr (J.S. Pic).

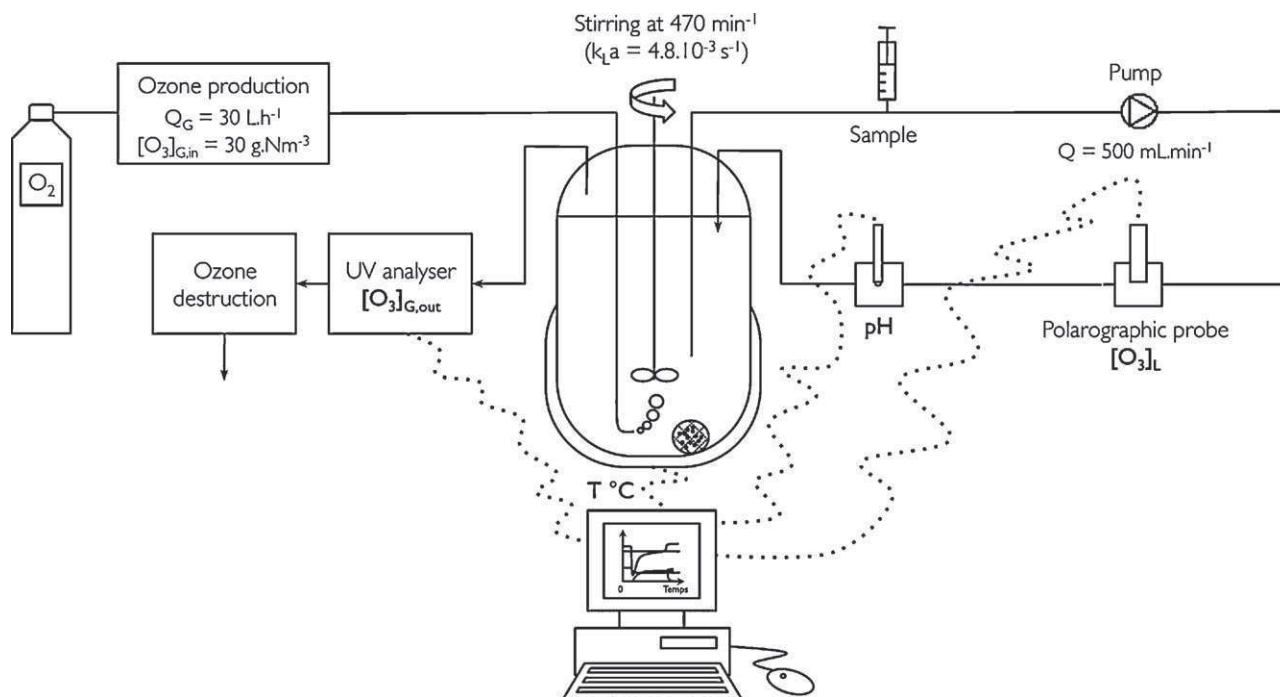
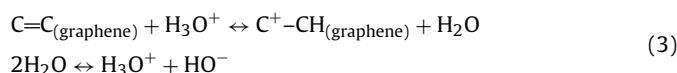


Fig. 1. Experimental set-up.

[13,14]. In particular, some authors assume that the formation of HO^\bullet radicals from activated carbons is due to their surface basicities [15]. Indeed, the basic-oxygen-containing functional groups and/or delocalised π electrons of the graphene layers of AC can act as Lewis bases and form electron donor-acceptor complexes with H_2O molecules (Eq. (3)). The hydroxide ion which is released will then initiate ozone decomposition



The present work studies the influence of AC on the oxidation by ozone of two bio-recalcitrant compounds: nitrobenzene and 2,4-dichlorophenol. The process efficiency is expressed as molecule removal rate, reaction mechanisms, by-products quantification and mass balance calculations.

2. Materials and methods

Oxidation runs were performed in a 2L well stirred semi-batch reactor fed with ozonated oxygen (30Lh^{-1} , 30g m^{-3}) through a pipe placed below the stirrer. Ozone concentration was measured in the liquid phase (polarographic probe Orbisphere model 410/probe 31330.15xx) as well as in the gas inlet and outlet (UV absorbance analyser Trailgaz UVOZON TLG 200). In most experiments pH was not controlled.

Two microporous activated carbons (supplied by PICA Corp., France) called F-22 and S-23 were used with 1g L^{-1} amounts. Their specific areas and mean pore diameter are, respectively $1000\text{m}^2\text{g}^{-1} - 0.9\text{nm}$ and $1300\text{m}^2\text{g}^{-1} - 1.7\text{nm}$.

The experimental set up is shown in Fig. 1 and detailed physical properties of the activated carbons are listed in Table 1.

Nitrobenzene and 2,4-dichlorophenol were chosen to prepare synthetic polluted water. The initial concentrations of the two pollutants were 250mg L^{-1} , i.e. $1879\mu\text{mol L}^{-1}$ for nitrobenzene and $1534\mu\text{mol L}^{-1}$ for 2,4-dichlorophenol. The concentrations of the pollutants and oxidation products (purchased from Acros Chemicals) were determined by High Performance Liquid Chromatography using a HP 1050 series chromatograph equipped with a Diode Array Detector (Agilent Technologies HP 1200) and a C-18 column (EQUISORB ODS2 $5\mu\text{m}$). Samples were first passed through a $0.45\mu\text{m}$ filter before analyses in order to remove undissolved compounds. Table 2 lists the different chemicals which were monitored and gives their maximum absorbance wavelengths (λ) and kinetic diameters (σ). The chemical oxygen demand (COD) of the solutions was measured by Hanna Instrument test tubes (COD MR Reagent).

Table 1
Characteristics of the activated carbons.

	S-23	F-22
Specific area (m^2g^{-1})	1374	1005
Microporous volume (cm^3g^{-1})	0.56	0.38
Mesoporous volume (cm^3g^{-1})	0.05	0.10
Mean pore diameter (\AA)	17.00	9.00
Granular diameter (mm)	1.46	1.00

matography using a HP 1050 series chromatograph equipped with a Diode Array Detector (Agilent Technologies HP 1200) and a C-18 column (EQUISORB ODS2 $5\mu\text{m}$). Samples were first passed through a $0.45\mu\text{m}$ filter before analyses in order to remove undissolved compounds. Table 2 lists the different chemicals which were monitored and gives their maximum absorbance wavelengths (λ) and kinetic diameters (σ). The chemical oxygen demand (COD) of the solutions was measured by Hanna Instrument test tubes (COD MR Reagent).

3. Results and discussions

3.1. Ozone decomposition with or without activated carbon

The decomposition rate of ozone was studied according to increasing concentrations of activated carbon F-22 and S-23. The kinetic constant of ozone decomposition k_C was calculated through the mass balance for ozone dissolved in water (Eq. (4)). It was compared to results without materials and plotted in Fig. 2. The measurement method as well as the reference value obtained without AC, $1.1 \times 10^{-3}\text{s}^{-1}$, are described by Lopez-Lopez et al. [16]

$$k_C = \frac{Q_G([O_3]_{G,in} - [O]_{G,out}^\infty)}{[O_3]_L^\infty V_L} \quad (4)$$

with Q_G : volumetric gas flow rate (m^3s^{-1}); $[O_3]_{G,in}$: ozone concentration in inlet gas (g m^{-3}); $[O]_{G,out}^\infty$: ozone concentration in outlet gas at steady state (g m^{-3}); $[O_3]_L^\infty$: ozone concentration in water at steady state (g m^{-3}); V_L : liquid volume in the reactor (m^3).

Table 2
Molecules characteristics of nitrobenzene, 2,4-dichlorophenol and ozonation by-products.

Molecule name	λ (nm)	σ (Å)	Stoichiometric ratio COD/molecule (mg O ₂ mg ⁻¹)
Nitrobenzene (NB)	267	5.9	1.951
o-Nitrophenol (o-NP)	274	8.1	1.612
m-Nitrophenol (m-NP)	274	8.1	1.612
p-Nitrophenol (p-NP)	317	6.7	1.612
2,4-Dichlorophenol (2,4-DCP)	286	–	1.178
3,5-Dichlorocatechol (3,5-DCC)	202	–	0.447
4,6-Dichlororesorcinol (4,6-DCR)	202	–	0.447
4-Chlorocatechol (4-CC)	202	–	0.537
2-Chlorohydroquinone (2-CHQ)	202	–	0.537
2-Chlorobenzoquinone (2-CBQ)	254	–	0.673
Catechol (C)	202	–	0.644
Oxalic acid (OA)	202	–	0.177
Acetic acid (AA)	202	–	1.066

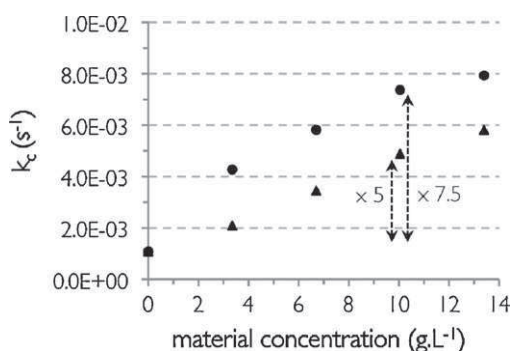


Fig. 2. Ozone decomposition constant versus activated carbons concentration (pH 7, [O₃]₀ = 30 g N m³, 25 °C) S-23 (▲) and F-22 (●).

The k_c constant evolution is proportional to the material concentration, in accordance with the results of Guiza et al. [17]. With 10 g_{AC} L⁻¹, the decomposition rate is multiplied by 5 for S-23 and by 7.5 for F-22.

This phenomenon can be explained either by the AC physical structure and also by the AC chemical composition which both influence the reactivity of the catalyst. The experimental measurements of surface groups according to Boehm method [18] showed that both AC have basic sites on their surfaces: 157 μequiv. g⁻¹ for F-22 and 306 μequiv. g⁻¹ for S-23. These sites can enhance the decomposition of ozone by the reaction with chromene and pyrone groups, as shown in Fig. 3 [2]. Then, hydrogen peroxide provided by this reaction can react with remaining ozone to give hydroxyl radicals as explained in Section 1.

Moreover, material porosity is an important factor for the diffusion of ozone molecules to the active sites. Even if F-22 has a lower external specific area than that of S-23, it has a greater mesoporous volume, so the diffusion in F-22 is probably easier than in

S-23, which has a microporous structure, and as a consequence the decomposition of ozone can be superior with F-22 than with S-23.

3.2. NB and 2,4-DCP ozonation

Fig. 4 shows NB and 2,4-DCP ozonation removal rate, with and without AC. First, it can be observed that none of the two media had any beneficial effect on 2,4-DCP oxidation rate. Indeed, 2,4-DCP is totally removed after only 1 h single or combined oxidation process. On the other hand, the presence of activated carbon allows a lower ozone consumption: it is lowered by 31% with F-22 AC and by 11% with S-23 AC. Concerning NB, the presence of activated carbon slightly enhances the oxidation rate: a total removal occurs after 3.5 h single ozonation whereas only 2.5 h treatment are necessary with AC. The performances of the two media are quite similar, ozone consumption is reduced by 4% with F-22 and by 12% with S-23.

The difference of reactivity with ozone itself can be easily explained by the molecules mesomery. Indeed ozone direct pathways, Criegee addition or electrophilic attack, are improved when the aromatic ring is strongly activated. The –NO₂ substituent of NB is a deactivating group whereas the –OH substituent of 2,4-DCP is an activating group. Also the –Cl group is a deactivating group since ozone reacts faster with phenol than with 4-chlorophenol (4-CP). However, Benitez et al. [19] showed that the more phenol is substituted with –Cl groups, the faster ozone oxidation occurs. Thus 2,3,4,6-tetrachlorophenol is more quickly oxidised than phenol. A strong substitution on the aromatic ring probably changes the reaction mechanism, for example nucleophilic substitution onto –Cl groups could take place [15]. These statements explain the faster ozonation rate for 2,4-DCP than that of NB.

In the presence of activated carbon, NB oxidation kinetics is enhanced whereas when 2,4-DCP is used the removal is not any faster. Single adsorption cannot explain this behaviour since the

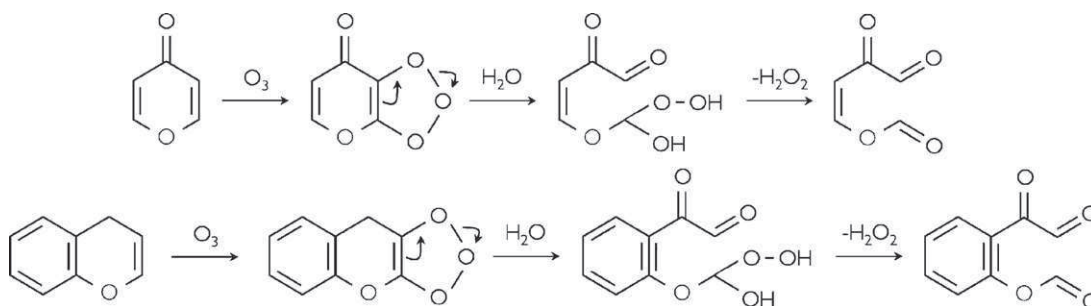


Fig. 3. Basic group (chromene up and pyrone down) reaction with ozone, leading to hydrogen peroxide.

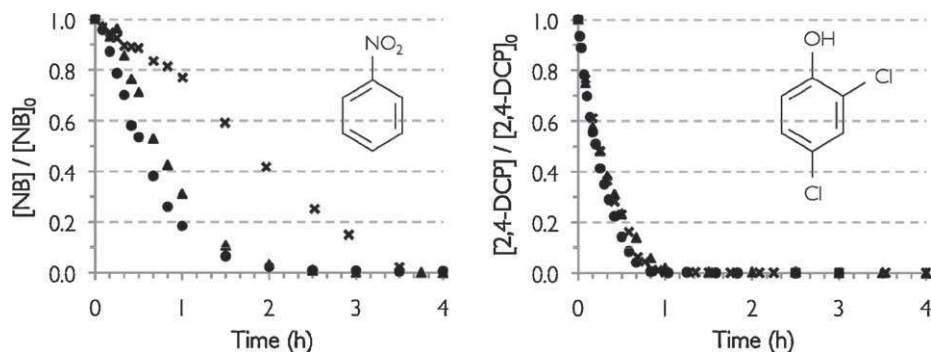


Fig. 4. NB and 2,4-DCP removal by single ozonation (x) and combined ozonation with S-23 (▲) and with F-22 (●).

adsorption kinetics is relatively slow for both molecules [12]. Thus the difference in NB removal rate is clearly attributed to a catalytic effect of activated carbon. Indeed, NB is rather refractory to direct ozonation, so radical oxidation with CA being less selective, clearly enhances the oxidation kinetics. For 2,4-DCP, direct ozonation kinetics is faster and thus is not improved through the radical mechanism. Finally, for both molecules, the radical route probably leads to a better yield for the oxidizing agent resulting in a reduced ozone global consumption.

3.2.1. Oxidation mechanisms of NB

Ortho-nitrophenol (o-NP), meta-nitrophenol (m-NP), para-nitrophenol (p-NP) and acetic acid, which are four NB ozonation by-products, were quantified using HPLC. o-NP and m-NP were equally produced with maximum concentrations reaching 14–22 μmolL^{-1} after 30 min experiment. The corresponding curves are not showed here for lack of space. p-NP concentration was twice higher with 40 μmolL^{-1} after 1 h experiment. At last about 1330 μmolL^{-1} acetic acid were formed after 1.5 h experiment (Fig. 5). The presence of meta-nitrophenol can be explained by NB resonance. Indeed, the $-\text{NO}_2$ substituent linked to the aromatic

ring is meta directing and deactivating for an electrophilic attack. The simultaneous presence of o-NP and p-NP in the solution can be attributed either to another mechanism or to a low selectivity in the position of the electrophilic attack. This can occur when the stability of the o, m and p-transition states are very close [15]. However, after 1 h experiment, the amount of nitrophenols only accounts for 10% of the oxidised NB. Thus the electrophilic attack is not the only pathway in NB ozonation and the Criegee reaction occurs too. Indeed carboxylic acids such as acetic (Fig. 5) or oxalic acids are produced. Unfortunately the quantification of oxalic acid was unsuccessful because of interferences with nitrates, also produced. Finally, a pathway for NB direct ozonation is suggested in Fig. 6.

The addition of activated carbons slightly improved the removal rates for the four by-products. Hence, the radical route increases reaction rates without much changing the nature of the by-products. The reason why radical efficiency is higher is probably due to less selectivity.

A global mass balance was performed through two COD estimations. The actual COD was measured, and the part of COD due to NB was calculated from NB concentration. The difference between

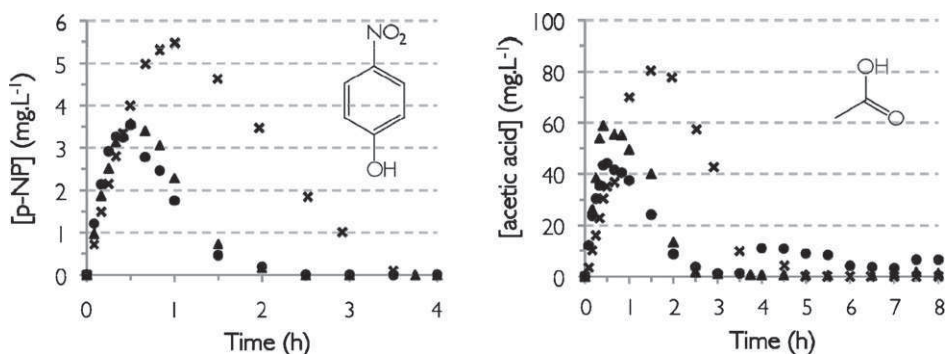


Fig. 5. NB ozonation by-products versus time: single ozonation (x), ozonation with S-23 (▲) and with F-22 (●).

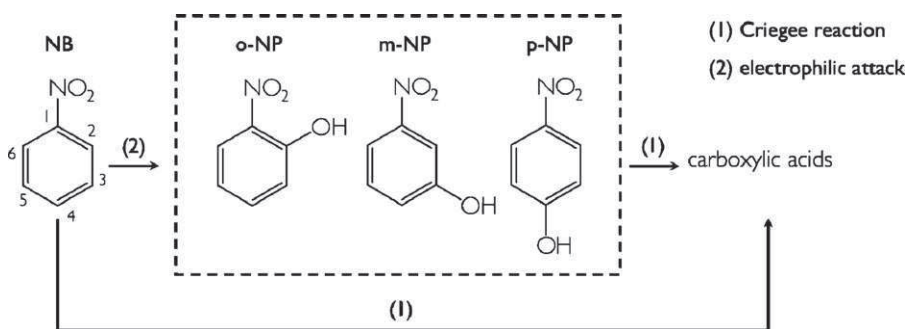


Fig. 6. Suggested reaction pathway for nitrobenzene direct ozonation.

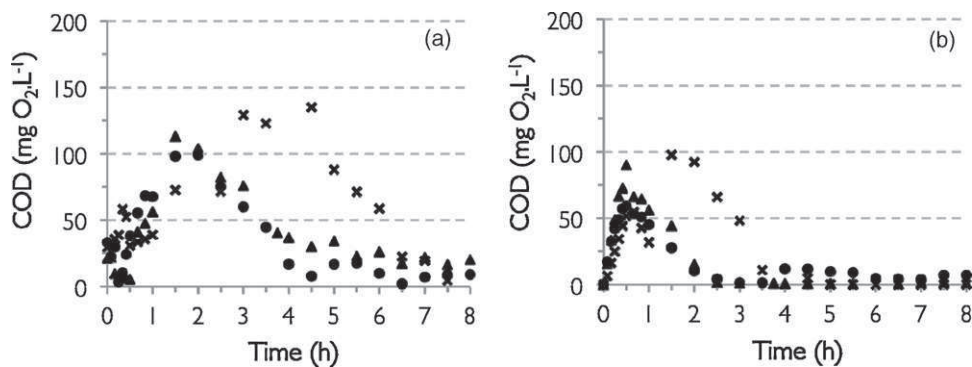


Fig. 7. Evolution of nitrobenzene by-products COD, estimated from (a) actual COD and NB concentration and (b) by-products concentration: single ozonation (✕), ozonation with S-23 (▲), ozonation with F-22 (●).

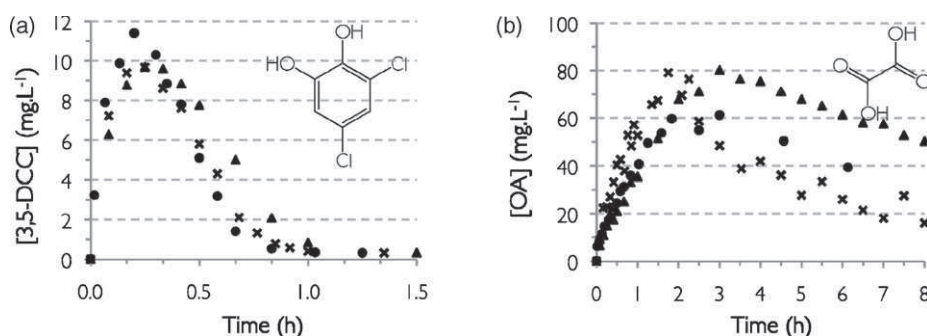


Fig. 8. 2,4-DCP oxidation by-products versus time: single ozonation (✕), ozonation with S-23 (▲), with F-22 (●).

the two values stands for the actual by-products COD, plotted in Fig. 7a [3]. Alongside this experiment, a theoretical COD value for the by-products was calculated from the measured by-products concentrations, as showed in Fig. 7b. The actual COD was higher than the theoretical COD, which indicates that about 25% of the by-products were not quantified. Again it should be pointed out that the monitoring of oxalic acid was unsuccessful.

For a single ozonation, 130 mg_{COD} L⁻¹ of by-products were detected after 4 h experiment whereas only 30 mgL⁻¹ were observed in the AC/ozone combined process. Thus, the addition of AC greatly enhances the oxidation rates of the by-products com-

pared to those in single ozonation. This also explains the gain in global ozone consumption and clearly justifies the interest of a radical route for NB oxidation.

3.2.2. Oxidation mechanisms of 2,4-DCP

Eight 2,4-DCP ozonation by-products, listed in Table 2, were monitored. Fig. 8 shows the results for two of them: an intermediate aromatic species (3,5-DCC) and a final product (oxalic acid). The aromatic intermediates reached their maximum concentrations between 15 and 30 min experiment. The resultant values were: 3,5-DCC (56 μmol L⁻¹), 4,6-DCR (2 μmol L⁻¹), 4-CC (14 μmol L⁻¹),

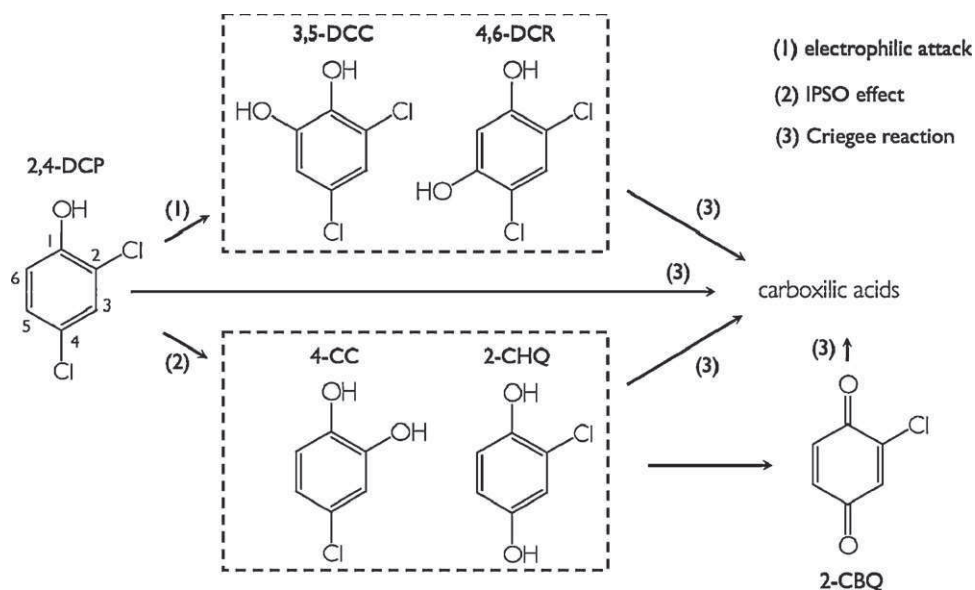


Fig. 9. Suggested reaction pathway for 2,4-dichlorophenol direct ozonation.

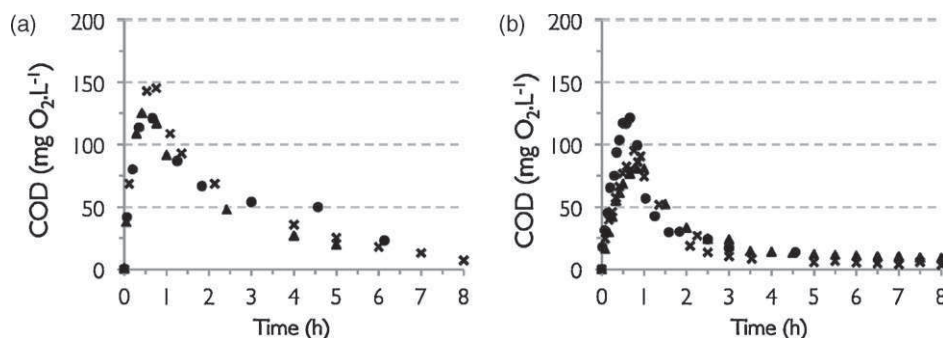


Fig. 10. 2,4-DCP by-products COD removal, estimated from (a) actual COD and 2,4-DCP concentration and (b) by-products concentration: single ozonation (✕), ozonation with S-23 (▲), with F-22 (●).

2-CHQ ($76 \mu\text{mol L}^{-1}$) and catechol ($118 \mu\text{mol L}^{-1}$). The first two molecules are generated through the electrophilic attack of ozone on 2,4-DCP. The amount of 3,5-DCC is higher because the $-\text{OH}$ group activates the aromatic ring in position 6 while the $-\text{Cl}$ group has a smaller influence on position 5. Then, the two mono-chlorinated compounds are probably formed through the electrophilic substitution (called the "ipso effect") of ozone on the $-\text{Cl}$ group position. The difference in the concentration of these two species was not explained. At last the presence of catechol cannot be easily explained, but however, it is certainly obtained after several elementary steps. Finally, the aromatic molecules are opened following the Criegee reaction, and carboxylic acids are formed. Up to $1000 \mu\text{mol L}^{-1}$ acetic acid was generated in the first 30 min and was subsequently totally removed after about 2 h. On the other hand, oxalic acid was continuously formed during the 2 h and reached $889 \mu\text{mol L}^{-1}$ before slowly being removed from the solution until the level of $222 \mu\text{mol L}^{-1}$ recorded after 8 h experiment. Finally a pathway for 2,4-DCP ozonation is proposed in Fig. 9.

The addition of activated carbons had no noticeable effect on the removal of 2,4-DCP and its by-products. Yet, there seems to be a slight increase in oxalic acid production in the presence of S-23 media. This may be due to the production of dissolved organic species (either oxalic acid or other ones such as formic, acetic or glyoxylic acids) resulting from the oxidation of the AC itself but this hypothesis still has not been verified. Nevertheless, this difference is not really significant, as oxalic acid amounts to very little in the global mass balance (Fig. 10). Whatever the oxidation route, about 150 mg L^{-1} COD was generated after 1 h experiment, followed by a slow decrease during the 7 remaining hours. Thus, the radical route does not improve 2,4-DCP oxidation, the direct ozonation kinetics is too fast to be enhanced by activated carbons, at least for the AC concentrations (1 g L^{-1}) used in this study.

4. Conclusions

The feasibility and interest of adding activated carbon to ozonation process was studied in this paper, in order to develop a hybrid process (combining at the same time and in the same device adsorption and oxidation) for refractory molecules treatment. The results showed the ability of the activated carbons to decompose molecular ozone and to create radical species, which were much more efficient for oxidation as they are non-selective. For organic pollutants which are easy to oxidise by ozone, like 2,4-dichlorophenol, the removal rate was not significantly enhanced, but a smaller ozone consumption was noticed. For organic pollutants much more refractory to ozone oxidation, like nitrobenzene, the development of a radical route dramatically increased the removal rate and the ozonation kinetics became faster.

In addition, the analysis of by-products obtained during oxidation enabled an understanding of the major steps in the oxidation

mechanisms of the various molecules. Classical mechanisms of electrophilic substitution and dipolar cycloaddition explained most of the sub-products formations. The same by-products have been found with or without AC, but the reaction rates are enhanced by the presence of activated carbon.

Finally, considering the ability of HO^\bullet radicals to remove an extremely wide range of refractory organics, including trace pollutants and emerging compounds, it appears that this AOP process, coupling activated carbon and ozonation, could be a good candidate for an additional treatment after biological treatment, above all for strongly refractory to ozone molecules oxidation.

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