

Phenol and substituted phenols AOPs remediation

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Abstract

The oxidation of phenol and two substituted species (4-nitrophenol and 4-chlorophenol) has been carried out by means of the O_3 , UV-vis, $O_3 + UV\text{-vis}$, $TiO_2 + UV\text{-vis}$, $O_3 + UV\text{-vis} + TiO_2$ and $O_3 + TiO_2$ systems. From UV-vis experiments, the quantum yield of these organics has been calculated (0.018, 0.005 and 0.017 mol per Einstein for phenol, 4-nitrophenol and 4-chlorophenol, respectively). Broadly speaking, the addition of titania powder results in a slight inhibition of the parent compound degradation rate, although a positive effect is experienced when measuring the chemical oxygen demand (COD) and total organic carbon (TOC) removals. Amongst the technologies investigated, those combining ozone and radiation show the best efficiency in terms of phenols elimination and also COD and TOC decay rates. A simple economy analysis of the processes illustrates how the combinations $O_3 + UV\text{-vis}$ and $O_3 + UV\text{-vis} + TiO_2$ are the most attractive technologies, although some additional considerations have to be taken into account.

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1. Introduction

Phenol and substituted phenols show toxicity values from moderate to highly toxic depending on the number, position and substitution nature. Some of the most toxic members of this class of compounds are the chlorinated and nitro-substituted phenols that are used as pesticides and antibacterials (dinoseb, creosote, chlorinated phenol, *p*-nitrophenol).

The principal use of the monochlorinated phenols is as intermediates in the synthesis of the higher chlorinated congeners and certain dyes and pesticides. The chief use of 2,4-DCP is as an intermediate in the production of 2,4-D and other herbicides.

The main route of entry of 2-, 3- and 4-CP and 2,4-DCP into the aquatic environment is likely attributable to discharges from plants manufacturing the compounds or from plants using the compounds as intermediates in the production of higher chlorinated phenols and other products, such as phenoxy herbicides.

Indirect sources include discharges from paper mills, where they are formed as by-products of the bleaching process, as a result of the disinfection of sewage, industrial wastes and drinking water with chlorine, and from the microbial breakdown of agricultural herbicides such as 2,4-D and subsequent run-off/leaching of the products.

Use of various nitrophenols includes the synthesis of aminophenol, nitroaniline and other dyestuff intermediates, photochemicals and leather preservatives. Nitrophenolic compounds are thus released into the environment through their wide use in the transformation industry. The great concern in phenol-type compounds has been considered by the US Environmental Protection Agency as persistent, bio-accumulative and toxic (PBT) chemicals [1].

Available technologies to deal with phenolic compounds include the use of the so-called advanced oxidation processes (AOPs). These processes are based on the generation of the highly reactive hydroxyl radical capable of unselectively react with most of organic and inorganic substances present in drinking water and wastewaters. The main drawback of these technologies relies on the economy of the process and, in some cases, on the low mineralization level achieved,

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Nomenclature

C_i	concentration of species “ i ” (mol L^{-1})
C_{O_3}	ozone concentration in the aqueous phase (mol L^{-1})
$C_{\text{O}_3 \text{ inlet}}$	ozone concentration at the reactor gas inlet (mol L^{-1})
$C_{\text{O}_3 \text{ outlet}}$	ozone concentration at the reactor gas outlet (mol L^{-1})
E	electricity consumption (kWh)
I_0	incident photon flux by reactor volume unit ($\text{Einstein L}^{-1} \text{ s}^{-1}$)
L	effective optical path (cm)
Q_g	gas flow rate (L s^{-1})
t	time (s or min)
V	reaction volume
Z_{global}	overall ozone uptake (dimensionless)

Greek letters

ε	extinction coefficient ($\text{M}^{-1} \text{ cm}^{-1}$)
ϕ	photochemical reaction quantum yield (mol per Einstein)
Ψ_i	apparent stoichiometric coefficient of species i ($\text{mol O}_3 \text{ mol}^{-1} i$)

involving the need of a final polishing stage (i.e. adsorption, membrane usage, etc.).

In this study, six different oxidation technologies have been tested for the degradation of three model phenolic compounds, for instance, phenol, 4-chlorophenol and 4-nitrophenol.

Although a lot of work has been carried out focused on the oxidation of phenol-type compounds by means of AOPs [2–8], some drawbacks/lacks can be found in the literature. For instance, most of the related literature reports on the efficiency of the technology to remove the parent/target compound. Few works have simultaneously measured the evolution of the mineralization level and the evolution of the chemical oxygen demand (COD). Additionally, the majority of ozone-based works describe the performance of the process in terms of contaminant depletion levels with no attention paid to the wastage or not of the oxidising agent. Moreover, comparative studies are normally conducted by either using only one model compound and several systems or one oxidation system and several substances from the same family. This work tries to accomplish a comparative study by completing an investigation on different technologies and three model compounds. The systems investigated were single ozonation, UV–vis radiation, $\text{O}_3 + \text{UV–vis}$, $\text{TiO}_2 + \text{UV–vis}$, $\text{O}_3 + \text{UV–vis} + \text{TiO}_2$ and $\text{O}_3 + \text{TiO}_2$. Mineralization levels (as total organic carbon (TOC)) and chemical oxygen demand decrease were monitored to assess the extent of the oxidation. Also, the concentration of free chloride

and nitrate was measured when oxidising chlorophenol and nitrophenol, respectively. Finally, a rough estimation of operating costs associated to individual AOPs is presented.

2. Experimental

A 1-L capacity tubular borosilicate glass photoreactor (450 mm long, 80 mm diameter) was used in all the experiments (see Fig. 1). The reactor walls were covered by aluminium foil and an insulating material to avoid release of radiation and heat. Degradation of the phenols studied was carried out at atmospheric pressure in 0.9 L of aqueous solutions containing approximately 200 mg L^{-1} of the organic compound. Solutions of each organic were prepared with no buffer, so initial pH was governed by the different $\text{p}K_{\text{a}}$ s of phenols.

In the case of O_3 -based processes, an ozone–oxygen mixture was continuously bubbled into the solution through a diffuser placed at the bottom of the reactor. Ozone was produced from pure oxygen by using a Sander Laboratory Ozone Generator. The gas flow rate was kept constant at 51 L h^{-1} having an average ozone inlet concentration of 5 mg L^{-1} . The dissolved ozone in solution was determined by the indigo method [9].

When the UV–vis radiation was required, the aqueous solution was irradiated with a high pressure mercury lamp (Heraeus, TQ 718 700 W) immersed in a quartz well placed in the middle of the reactor. The lamp bandwidth was in the range 238–579 nm. The three main wavelengths emitted were 254, 313 and 366 nm with an incident radiation of 0.142, 0.189 and $0.331 \text{ Einstein L}^{-1} \text{ h}^{-1}$. Hydrogen peroxide actinometry experiments confirmed the I_0 radiation value at 254 nm ($0.139 \text{ Einstein L}^{-1} \text{ h}^{-1}$) with a radiation pathway of $L = 3 \text{ cm}$.

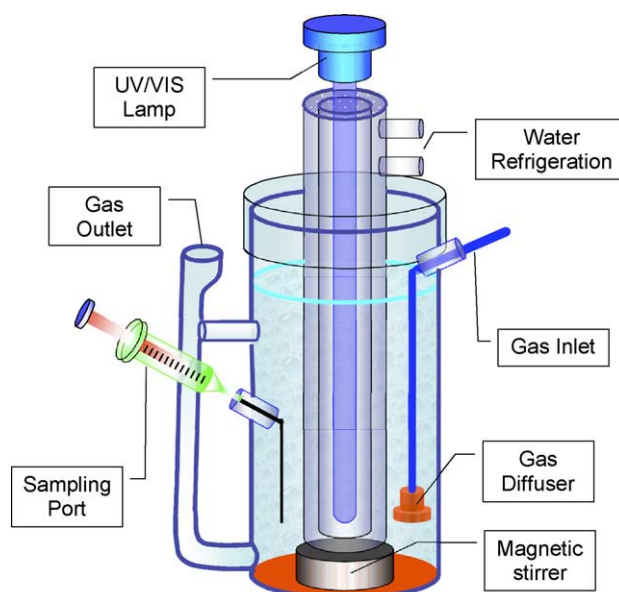


Fig. 1. Experimental set-up.

When TiO_2 was added, the solid was maintained in suspension by magnetic stirring with a concentration of 1.5 g L^{-1} in all the experiments. Prior to the analysis, the solid was removed from samples by a 5415D Eppendorf Centrifuge and further filtration through Millex-HA filters (Millipore, $0.45 \mu\text{m}$).

Phenol, 4-nitrophenol and 4-chlorophenol were purchased from Sigma–Aldrich and used as received. Organic solvents were HPLC grade obtained from Panreac.

A commercial TiO_2 Degussa P25 (70% anatase and 30% rutile) was used as a catalyst with an average particle size of 30 nm and BET surface area of $50 \text{ m}^2 \text{ g}^{-1}$.

Organics were analysed by high-performance liquid chromatography (Hewlett Packard Series 1100) with a Kromasil C18 column and a UV–vis detector. A 30:70, v/v, aqueous solution of acetonitrile and water was used as the eluting solvent.

In order to assess the degree of mineralization, total organic carbon was determined by ICP (Thermo Finnigan). COD was analysed in a Dr. Lange photometer, the method based on the dichromate standard procedure.

The chloride ion concentration accumulated in the solution was determined by standard volumetric titration with AgNO_3 (suitable method for chloride concentrations $\geq 20 \text{ mg L}^{-1}$). Nitrate concentration was determined by a spectrophotometric method measuring the absorbance at 410 nm of a yellow complex formed with brucine sulfanilic acid.

The pH of the reaction media was followed by means of a Radiometer Copenhagen pH-meter (HPM82).

3. Results and discussion

3.1. Phenol oxidation

The efficiency of the different oxidation systems investigated is illustrated in Fig. 2A. This plot shows the dimensionless remaining concentration of phenol versus time for a period of 2 h. From this figure, the following considerations can be inferred. Firstly, there is no appreciable adsorption of the parent compound onto the TiO_2 surface. For instance, according to literature data [10], the maximum adsorption capacity of phenol onto titania P-25 is $Q_{\text{max}} = 3.28 \times 10^{-6} \text{ mol g}^{-1}$. Therefore, any observable catalytic effect of the solid cannot be attributed to a simple adsorption process of the different phenols tested.

By only considering the processes in the absence of ozone, the presence of titania powder involves a negative effect on the phenol degradation profiles if compared to the non-catalysed photolysis. Based on literature data [10], the optimum catalyst dosage varies (even for the same photocatalyst P-25) from 0.15 to 2.5 g L^{-1} . Thus, Esplugas et al. [11] experienced a continuous improvement of the phenol photocatalytic degradation when increasing the TiO_2 concentration from 0.05 to 0.5 g L^{-1} , achieving, thereafter, a constant value in

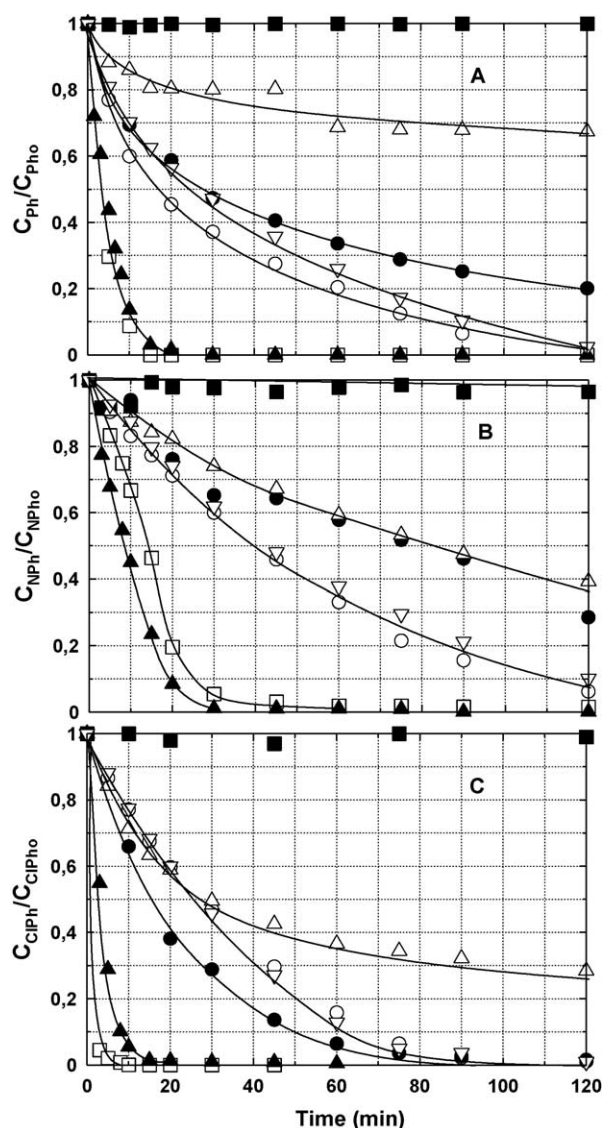


Fig. 2. AOPs removal of phenols. Experimental conditions: $T_0 = 20^\circ\text{C}$, $C_{\text{O}_3 \text{ inlet}} = 10^{-4} \text{ M}$, $Q_g = 50 \text{ L h}^{-1}$, $C_{\text{TiO}_2} = 1.5 \text{ g L}^{-1}$. (A) Phenol: $C_{\text{phenol}} = 2.1 \times 10^{-3} \text{ M}$, $\text{pH}_0 = 6.2$. (B) *p*-Nitrophenol: $C_{\text{nitrophenol}} = 1.4 \times 10^{-3} \text{ M}$, $\text{pH}_0 = 4.7$. (C) *p*-Chlorophenol: $C_{\text{chlorophenol}} = 1.6 \times 10^{-3} \text{ M}$, $\text{pH}_0 = 5.1$. Symbols: (○) O_3 ; (●) UV–vis; (□) $\text{O}_3/\text{UV–vis}$; (■) adsorption; (△) $\text{TiO}_2/\text{UV–vis}$; (▲) $\text{O}_3/\text{TiO}_2/\text{UV–vis}$; (▽) O_3/TiO_2 .

the process effectiveness. Similar results were also reported by Chen and Ray [10] who claimed a gradual positive effect of TiO_2 concentration up to a value of 1.5 g L^{-1} . Nevertheless, at the sight of results obtained in this study, it seems that phenol is mainly degraded by the UV radiation emitted by the lamp. Addition of 1.5 g L^{-1} of titania is likely overdosed in this particular reactor, and the excess of the catalyst leads to a shielding effect on the UV penetrating light.

Additionally, it has to be pointed out that adsorption of organics in photocatalytic processes is a key step to achieve an acceptable degradation rate of the contaminants. Thus, first degradation intermediates might be strongly

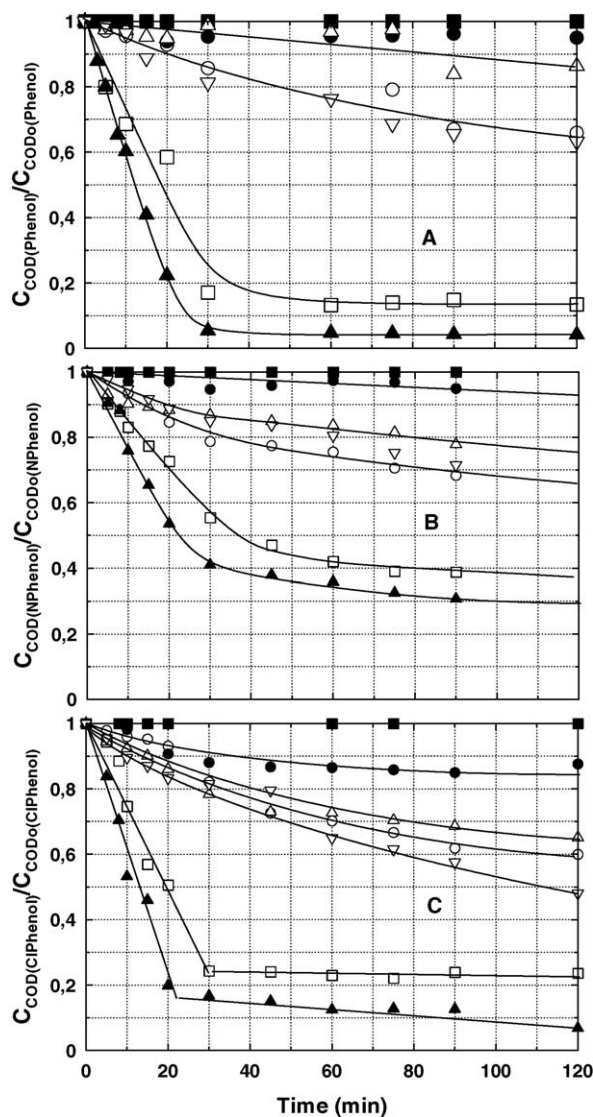


Fig. 3. AOPs removal of phenols. Evolution of normalized COD. Experimental conditions and symbols as in Fig. 2. (A) $C_{\text{COD}_0(\text{phenol})} = 550$ ppm, (B) $C_{\text{COD}_0(\text{nitrophenol})} = 407$ ppm and (C) $C_{\text{COD}_0(\text{chlorophenol})} = 417$ ppm.

adsorbed onto TiO_2 as reported for the case of 4-chlorocatechol with a Q_{max} 25 times higher than the parent compound 4-chlorophenol [12]. Hence, the catalytic effect of added TiO_2 can be positively appreciated by measuring other more general parameters like COD and/or TOC. The latter effect was experienced in this study for the photocatalysis of phenol (also on the substituted phenols analysed next on the manuscript) where a slight improvement was observed in terms of COD (Fig. 3A) and TOC (Fig. 4A) elimination.

Since in the absence of TiO_2 , none of the compounds studied is appreciably degraded by the visible light emitted by the lamp (i.e. the quantum yield of 4-nitrophenol under visible light is 3×10^{-5} at pH 5.5 [13]), it can be postulated that phenols are mainly degraded by the radiation emitted at 254 nm in the UV spectrum. Thus, the photolysis rate of a substance

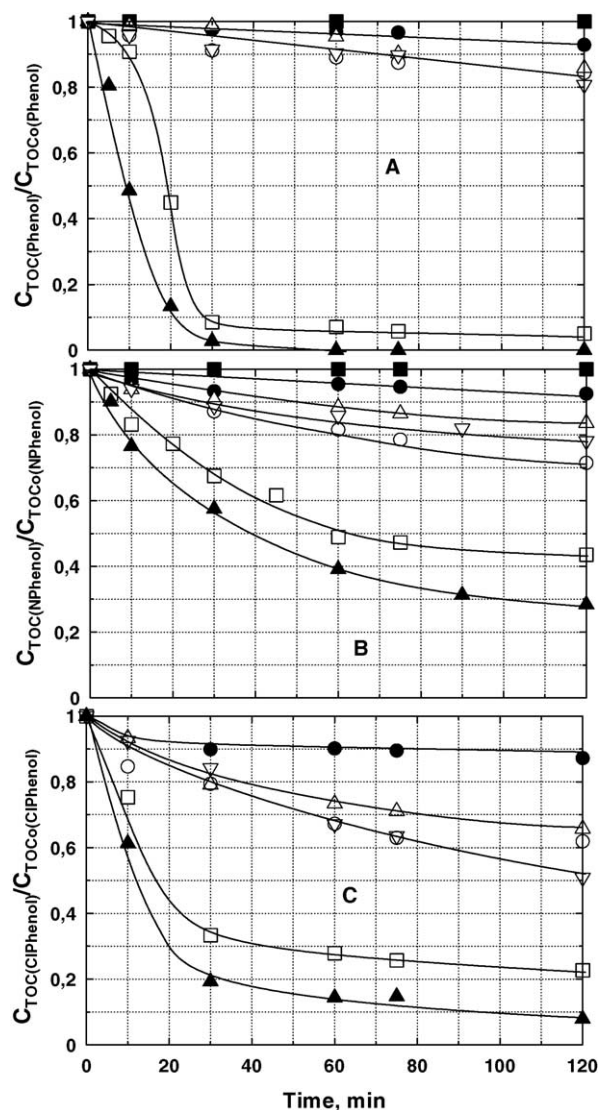


Fig. 4. AOPs removal of phenols. Evolution of normalized TOC. Experimental conditions and symbols as in Fig. 2. (A) $C_{\text{TOC}_0(\text{phenol})} = 140$ ppm, (B) $C_{\text{TOC}_0(\text{nitrophenol})} = 102$ ppm and (C) $C_{\text{TOC}_0(\text{chlorophenol})} = 113$ ppm.

under a specific wavelength can be calculated as [14]:

$$-\frac{dC_i}{dt} = \phi_i F_i I_0 \left[1 - \exp\left(-2.303L \sum_j \varepsilon_j C_j\right) \right] \quad (1)$$

$$\text{being } F_i = \frac{\varepsilon_i C_i}{\sum_j \varepsilon_j C_j}$$

where ϕ_i , ε_i , I_0 and L stand for the quantum yield and extinction coefficient of compound “ i ”, the incident photon flux by reactor volume unit and the effective optical path in the reactor, respectively. Additionally, if only the beginning of the photolysis process is considered, it can also be assumed that almost all radiation is absorbed by the parent compound “ i ” and that no other generated intermediates “ j ” compete for

Table 1

Determination of the quantum yield for phenol, 4-nitrophenol and 4-chlorophenol by Eq. (4) (experimental data corresponding to the first 10 min of photolysis)

Compound	Extinction coefficient ($M^{-1} cm^{-1}$)	Slope	R^2	Quantum yield (mol per Einstein)
Phenol	516	7.95×10^{-7}	0.998	0.018
4-Nitrophenol	1167	2.28×10^{-7}	0.999	0.005
4-Chlorophenol	180	7.26×10^{-7}	0.997	0.017

the absorption of photons. In the latter case, it follows that $\varepsilon_i C_i \approx \varepsilon_j C_j$ and $F_i \approx 1$. Consequently, the analytical integration of (1) leads to:

$$C_{i0} - C_i - \frac{1}{\xi} \ln \left[\frac{1 - \exp(-\xi C_{i0})}{1 - \exp(-\xi C_i)} \right] = \phi_i I_0 t \quad (2)$$

where $\xi = 2.303 \varepsilon_i L$.

As a consequence, a plot of the left side member of (2) versus time at the beginning of the process should give a straight line of slope $\phi_i I_0$. Once I_0 and L are known by actinometry experiments, the quantum yield of the species “*i*” can be calculated. Values of ε_{phenol} , $\varepsilon_{nitrophenol}$ and $\varepsilon_{chlorophenol}$ determined at 254 nm were 516, 1167 and $180 M^{-1} cm^{-1}$, respectively. Results are displayed in Table 1.

The quantum yield obtained for the case of phenol (0.018 mol per Einstein) is of the same order as previously reported values by other authors (i.e. Rodríguez et al. found a value of 0.011 ± 0.002 mol per Einstein [15]). A similar ϕ has also been reported for the case of 2-nitrophenol, a value of 1.3×10^{-3} was given by Alif et al. [16], close to the value of 5.3×10^{-3} found in this study for the isomer 4-nitrophenol.

Bubbling of ozone into the reaction media significantly enhances the phenol depletion rate, especially when combined with the UV-vis radiation (Fig. 2A). For the latter cases, no appreciable differences were observed regarding the parent compound oxidation rate, either in the presence or absence

of titania. Also, a significant decrease of COD and TOC was experienced in the systems combining UV-vis radiation and ozone (Figs. 3 and 4). Hence, a fast 85% (UV-vis/ O_3) and 95% (UV-vis/ O_3/TiO_2) COD conversions were attained in the first 30 min of reaction compared to values below 20% for the rest of systems used. The evolution of intermediates corroborates the high efficiency of the systems containing radiation and ozone. Thus, as an example, Fig. 5 depicts the evolution of some of the main intermediates formed along the reaction period corresponding to the oxidation systems: O_3 , $O_3 + TiO_2$ and $O_3 + UV-vis$. From this figure, two main conclusions can be drawn. On one hand, in the absence of radiation, intermediates are detected from the beginning of the process up to a reaction period above 120 min, while if radiation is applied, almost all the by-products identified disappear after just 30 min of reaction. Additionally, on the other hand, in the absence of radiation, some of the intermediates (mainly oxalic acid) accumulate in the reaction media which is not the case when the system $O_3 + UV-vis$ is employed. Similar results were observed for the rest of phenols studied in this work (results not shown) although in the case of nitrophenol, oxalic acid accumulated in the liquid even in the presence of UV radiation in combination with ozone.

In the absence of radiation, by comparing the systems O_3 and O_3/TiO_2 , once more the addition of titania involves a certain deceleration of phenol removal, which is also accompanied by a lower ozone consumption. In this sense, the

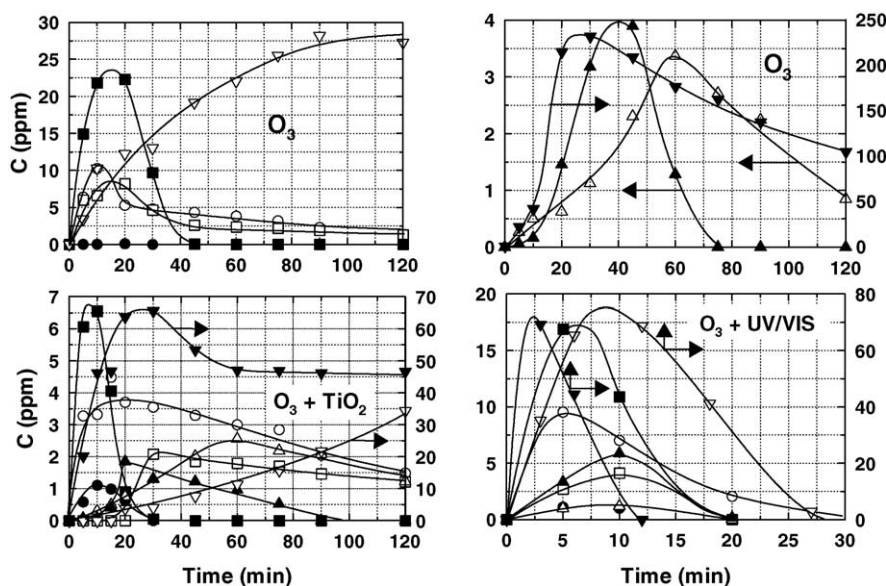


Fig. 5. AOPs removal of phenol. Intermediate evolution. Experimental conditions as in Fig. 2. Symbols: (○) hydroquinone; (●) resorcinol; (□) benzoquinone; (■) catechol; (△) maleic acid; (▲) fumaric acid; (▽) oxalic acid; (▼) glyoxilic acid.

overall ozone uptake, Z_{global} (i.e. ratio moles of O_3 absorbed per mol of O_3 fed), is defined as:

$$Z_{\text{global}} = \frac{C_{\text{O}_3 \text{ inlet}} Q_{\text{g}} t - \int_0^t C_{\text{O}_3 \text{ outlet}} Q_{\text{g}} dt - C_{\text{O}_3} V}{C_{\text{O}_3 \text{ inlet}} Q_{\text{g}} t} \quad (3)$$

where $C_{\text{O}_3 \text{ inlet}}$, $C_{\text{O}_3 \text{ outlet}}$ and C_{O_3} refer to ozone concentrations at the reactor inlet, outlet and dissolved in the liquid, respectively, Q_{g} the gas flow rate, V the reaction volume and t stands for the reaction time.

As seen in Fig. 6A(1), for the single ozonation experiment (although the concentration of dissolved ozone accumulated in the liquid was the highest of the series), practically all the oxidant fed was consumed in the degradation of phenol and intermediates (at least for the first 80 min of reaction). No ozone at the gas outlet or dissolved was detected when combining $\text{O}_3/\text{TiO}_2/\text{UV-vis}$ leading to a 100% of ozone uptake. Contrarily, the run conducted in the absence of TiO_2 ($\text{O}_3/\text{UV-vis}$) or in the absence of radiation (O_3/TiO_2) was characterised for a lower ozone uptake of the order of 70% in the $\text{UV-vis}/\text{O}_3$ system (after roughly 40 min) and a constant decrease of this parameter in the TiO_2/O_3 system with a value of hardly 43% after 120 min of reaction. As inferred from the previous calculations, there is not a direct relation between ozone uptake and reacted phenol.

To assess the effectiveness of the different oxidising systems used in the presence of ozone, a deeper analysis has

to be conducted. As stated previously, Z_{global} gives values of ozone consumption taken as a whole; however, a high value of Z_{global} does not necessarily mean a high efficiency of the oxidants used/fed to the reactor. A more accurate parameter to estimate the efficacy of the ozone uptake is the apparent stoichiometry coefficient referred to the degradation of the parent compound (Ψ_{phenol}), COD (Ψ_{COD}) or TOC (Ψ_{TOC}). This parameter is expressed by Eq. (4):

$$\Psi_i = \frac{\left[C_{\text{O}_3 \text{ inlet}} Q_{\text{g}} t - \int_0^t C_{\text{O}_3 \text{ outlet}} Q_{\text{g}} dt - C_{\text{O}_3} V \right]_i - \left[C_{\text{O}_3 \text{ inlet}} Q_{\text{g}} t - \int_0^t C_{\text{O}_3 \text{ outlet}} Q_{\text{g}} dt - C_{\text{O}_3} V \right]_{\text{water}}}{(C_{i0} - C_i)V} \quad (4)$$

where the first term in the numerator denotes the ozone consumed when oxidising the compound “ i ” and the second term accounts for the ozone decomposed/accumulated when ozonating ultrapure water. By conducting this subtraction, the whole numerator would consider only the moles of O_3 that really disappear due to the presence of phenol and not to other parallel effects like O_3 decomposition in the system pipes, existence of dead times, etc. Additionally, the denominator of (4) represents the moles of “ i ” degraded (phenol, COD or TOC) from the initial conditions (subscript “0”) to time t .

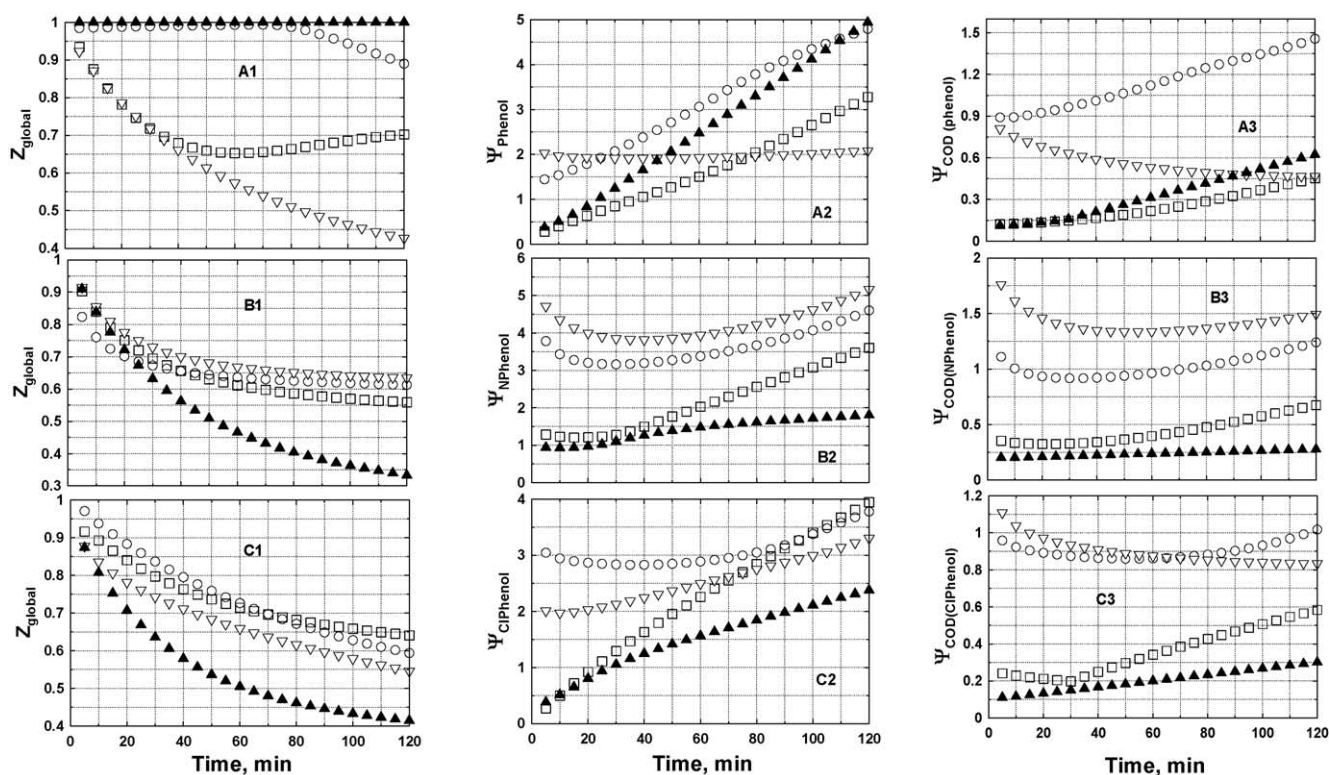


Fig. 6. (1) Evolution of the overall ozone uptake, (2) evolution of the apparent stoichiometric coefficient related to the parent compound and (3) evolution of the apparent stoichiometric coefficient related to the chemical oxygen demand. Experimental conditions and symbols as in Fig. 2.

Fig. 6A(2) depicts the apparent stoichiometric factor related to phenol removal under different systems. From this figure, an important aspect is noticed. Hence, although the single ozonation is slightly more effective than the TiO₂ catalytic ozonation (in terms of phenol removal), the specific O₃ consumption leads to opposite results. Thus, an average value of 2 mol O₃ mol⁻¹ phenol is experienced for the catalytic ozonation, similar to the reported value of the direct phenol ozonation (true stoichiometric coefficient [17]), while an increasing value of this parameter was obtained for the single ozonation reaching a value close to 5 after 2 h of treatment. The apparent stoichiometric coefficient calculated for the O₃/TiO₂/UV-vis and O₃/UV-vis systems also presents an analogous upwards trend from the beginning, although in those cases, the parent compound completely disappears in the first 15–20 min of reaction with a Ψ_{phenol} average value of 0.5 up to this moment.

Correspondingly, the effectiveness of ozone when considering the COD removal also does follow an opposite tendency when comparing the catalytic and non-catalytic ozonation experiments. $\Psi_{\text{COD(phenol)}}$ values of 0.46 and 1.46 were calculated after 120 min, respectively, indicating the activity of TiO₂ as an heterogeneous catalyst in phenol ozonation processes. When combining O₃ and UV-vis radiation in the presence or absence of TiO₂, an abrupt COD decay was experienced in the first 30 min of reaction with $\Psi_{\text{COD(phenol)}}$ values of roughly 0.15 up to this moment. $\Psi_{\text{COD(phenol)}}$ then starts to increase.

The degree of mineralization (TOC profiles) was also studied in terms of ozone utilization observing the same results as in Fig. 6A(2) (results not shown), that is, an increasing value of $\Psi_{\text{TOC(phenol)}}$ for the single ozonation (5.5 after 120 min), a relatively constant value for the O₃/TiO₂ system (approximately 2) and a low value in the range 0.15–0.20 when combining ozone and radiation and for the first 30 min, when the major fraction of TOC decrease is experienced.

3.2. Substituted phenol oxidation: the case of 4-nitrophenol and 4-chlorophenol

The presence of hetero-atoms in the phenol molecule might change the reactivity of the former species depending on the nature of the hetero-atom and its position. Consequently, the effect of the *para* substitution of a nitro group and a chloride group was therefore studied. These groups with an electron withdrawing character (positive Hammett constant) diminish the electron density of the aromatic ring [18] complicating, therefore, the electrophilic attack of oxidising agents (i.e. ozone).

3.2.1. 4-Nitrophenol

The evolution of the dimensionless concentration of nitrophenol with time under the different systems studied is displayed in Fig. 2B. According to this figure and by comparing the results obtained for the case of phenol oxidation, a first important difference is noticed. Hence, the presence

of titania in the photolysis process does not influence the nitrophenol degradation rate even though the concentration of the latter was as high as 1.5 g L⁻¹ (as in the case of phenol). Once more, although the elimination of the parent compound shows a similar profile in the photolytic and photocatalytic processes, the efficiency on the COD removal was positively affected by the addition of TiO₂ (Fig. 3B).

Analogously, the ozonolysis of *p*-nitrophenol is not affected by the addition of titania powder. The small differences found in the analysis of COD (Fig. 3B) or TOC (Fig. 4B) cannot lead to any conclusive statement on the catalytic activity of TiO₂ in the presence of ozone.

If UV-vis radiation is used in combination with O₃, a drastic improvement of the process is observed, also accompanied of a slight catalytic effect if TiO₂ is added to the reaction media. Broadly speaking, regardless of the system studied, the oxidation rate (except for the TiO₂/O₃ system) decreases if compared to the degradation kinetics of phenol, corroborating the negative effect of the nitro group.

For those technologies based on the use of ozone, the overall O₃ uptake can be calculated according to expression (3). Thus, contrarily to the oxidation of phenol, the system O₃/TiO₂/UV-vis is shown as the less ozone-consuming process (Fig. 6B(1)) gradually decreasing throughout the whole reaction period ($\approx 30\%$ ozone uptake at 120 min). The rest of systems studied exhibit a comparable behaviour, Z_{global} continuously diminishing up to a steady-state average value of 55–65% after 50 min.

The specific ozone consumption (apparent stoichiometric factor) ranges in the interval 3–4.5 mol O₃ mol⁻¹ nitrophenol for the single ozonation and 3.8–5 mol O₃ mol⁻¹ nitrophenol for the catalytic ozonation. These values are somewhat higher than the stoichiometric coefficient of the molecular reaction between O₃ and the organic molecule previously reported to be one [19].

A much better utilization coefficient is obtained when the UV-vis radiation is applied with values in the proximity of 1 mol O₃ mol⁻¹ nitrophenol before nitrophenol has completely disappeared (up to 30 min of reaction).

In terms of COD specific O₃ uptake, the system O₃/TiO₂/UV-vis shows a relatively constant pattern in the proximity of 0.25 mol O₃ mol⁻¹ COD (nitrophenol) experiencing higher values with the systems O₃/UV-vis (0.3–0.7), O₃ (≈ 0.75) and O₃/TiO₂ (≈ 1.5). It has to be pointed out that regardless of the process, the effectiveness of the different oxidising technologies at the time of COD removal (measured as ozone consumed) is lower than results obtained for the case of phenol, likely due to: on one hand, the higher refractory nature of nitrophenol and first intermediates, and on the other hand, to a potential scavenging nature of nitrates over hydroxyl radicals in solution [20]. In this sense, the presence of the latter species has been demonstrated by the corresponding analysis (Fig. 7). From the previous analysis, it can be observed how for the best of cases, only the 45% of the stoichiometric amount is detected in the liquid, even when the TOC decrease is even higher than the corresponding

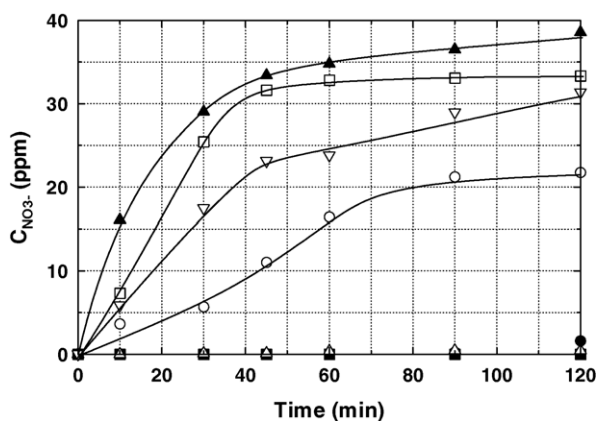


Fig. 7. AOPs removal of 4-nitrophenol. Evolution of free nitrates in solution. Experimental conditions and symbols as in Fig. 2.

60%. This might be due to the presence of other nitrogen containing species like nitrites or ammonia [21].

3.2.2. 4-Chlorophenol

Results corresponding to chlorophenol destruction are displayed in Fig. 2C. Once more, from photolysis and photocatalytic profiles in the absence of ozone, two divergent trends are observed. On one hand, a negative effect, after TiO₂ addition, on the parent compound removal rate, and on the other hand, a positive influence on COD elimination. The former detrimental fact, i.e. TiO₂ in excess, has been previously reported in the photocatalytic decomposition of 2-chlorophenol [22]. Additionally, it is also inferred from Fig. 2 that the chlorinated phenol is the most photosensitive compound among the three compounds studied, with a half-life of approximately 15 min in comparison to roughly 30 min for phenol and 80 min for nitrophenol. In this sense, it has to be realized that the simple photolysis is even more effective than the use of ozone alone or in combination with titania.

As expected, the pair O₃/radiation leads to the best results either in chlorophenol removal COD or TOC elimination.

The parameters reflecting the ozone uptake present similar tendencies than those observed in the case of nitrophenol, that is, a continuous decrease in Z_{global} with the lowest values for the O₃/TiO₂/UV-vis system, a relatively stable value of $\Psi_{\text{chlorophenol}}$ and Ψ_{COD} for the O₃ and O₃/TiO₂ systems (in the range ≈ 2 –3.5 and 0.8–1.0, respectively) and minimum values for the same parameters when the UV-vis radiation is present (notice that chlorophenol disappears in just 5–10 min).

The effectiveness of the different systems is also corroborated by the presence of dissolved chlorine in the reaction media (Fig. 8). As observed, the stoichiometric amount of chlorine is obtained after 120 min of reaction when radiation and ozone are used together. It is also noticeable the high dechlorination efficiency of the TiO₂/O₃ process and especially the TiO₂ photocatalysis, where (after 2 h) a 70% of

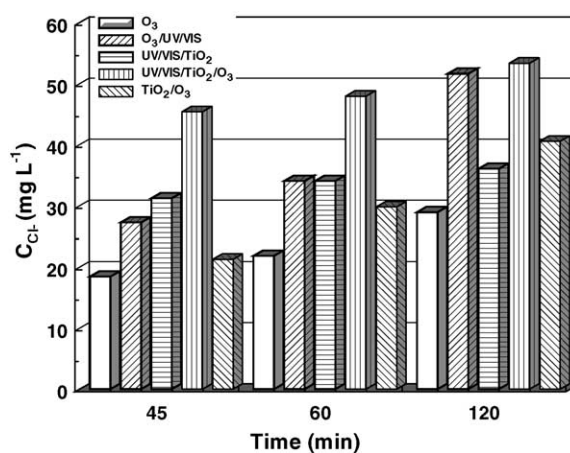


Fig. 8. AOPs removal of 4-chlorophenol. Evolution of free chloride in solution. Experimental conditions as in Fig. 2.

chlorophenol conversion results in approximately a 63% of Cl⁻ release.

3.3. Further considerations

As inferred from the results previously presented, in general, in spite of the electron withdrawing character and regardless of the system used, the chloro-substitution on the phenol molecule increases the oxidation rate of the organic. Contrarily, the nitro group, also with a positive Hammett constant follows a more logical trend slowing down the efficiency of the different processes studied in this work. Nevertheless, it has to be pointed out that other factors play an important role in this type of reactions. Amongst them, the distribution between the ionic and molecular forms of phenols, the water–octanol partition coefficient (when titania is used as heterogeneous catalyst), the scavenging character of anions released throughout the oxidation, etc.

Evaluating the best technology to be applied is primarily a matter of the economy of the process and feasibility of scaling up. In this sense, at the moment, technologies based on the use of titania powder seem to be far away of being applied at industrial scale. Obviously, many factors contribute to account for all the investments and operating costs; however, some simple “figures of merits” have been used to give priority to the use of one or another technology. Among them the electrical energy per order (EEO) considers the energy required to remove the compound oxidised to a pre-specified degree (usually 90% removal). For that purpose, a general first-order rate is used, which is obtained from experimental data. Nevertheless, fitting of data to simple first-order kinetics is not always the best option, and in some cases, distinct kinetics law apply. As a consequence, to gain an insight into the economic aspects of the different technologies, other methodologies seem to be most appropriate.

In this study, costs associated to the normal operation of the oxidising systems have been approximately evaluated by taking into account the electrical energy required to generate

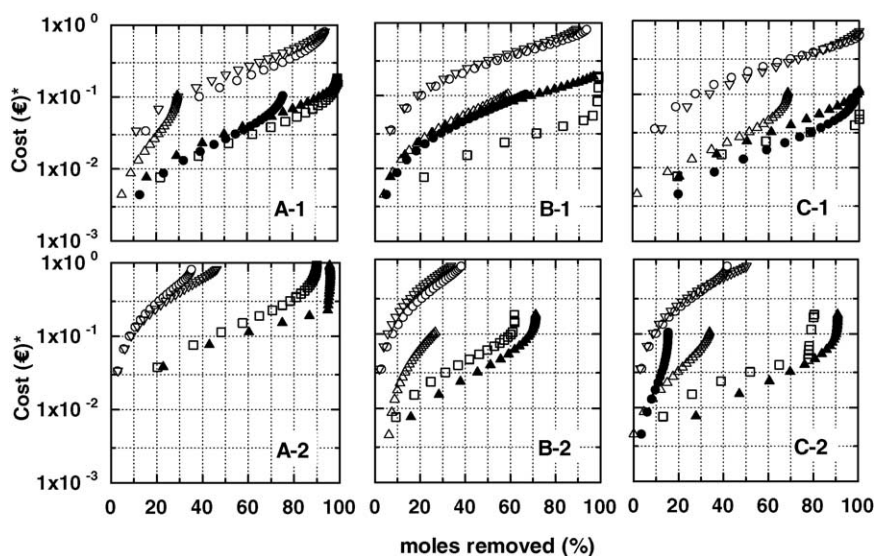


Fig. 9. AOPs removal of phenols. Comparative estimation of costs to treat 0.9 L of water. Experimental conditions and symbols as in Fig. 2. (1) refers to parent compound while (2) refers to COD.

the oxidants, consumables needed and the amount of the target parameter removed (i.e. phenol, COD or TOC). At this point, it has to be noted that the aim of this simplistic economic study is the direct comparison between technologies rather than a deep analysis of costs associated to the actual implementation of the processes (i.e. no investments and other factors are considered).

Thus, for the O_3 -based processes, according to the generator manufacturer, the dependence between O_3 production and current consumption is approximately:

$$O_3 \text{ (\% of the maximum mass flow-rate in g L}^{-1}\text{)} \\ = 186 \times \text{current consumption (A)}$$

The maximum mass flow-rate of the SANDER 301.7 ozonator from oxygen is 12 g h^{-1} . Consequently, from the experimental conditions applied in this work, the ozone fed to the reactor is $5 \times 10^{-3} \text{ g L}^{-1} \times 50 \text{ L h}^{-1} = 0.25 \text{ g h}^{-1}$, that is, a 2.08% of the maximum amount produced. Accordingly, the electricity used is $2.08/186 = 11.2 \text{ mA}$. The electricity usage is therefore $E_{O_3}(\text{kWh}) = 220 \text{ V} \times 11.3 \times 10^{-3} \times t \text{ (h)} \times 10^{-3}$.

Technologies using UV-vis radiation employ a TQ700 Heraeus UV-vis lamp with an input power of 700 W. Consequently, the energy requirements are $E_{UV\text{-vis}}(\text{kWh}) = 0.7 \times t \text{ (h)}$.

Cylinders containing oxygen have a cost of $\text{€}5.55 \text{ m}^{-3}$ O_2 (including taxes), having to add transport ($\text{€}17.5$ for a 10.6 m^3 cylinder) and cylinder rental ($\text{€}0.545/\text{day}$).

With the above data and considering cost associated to electricity of $\text{€}0.0753 \text{ (kWh)}^{-1}$ [23], an estimated comparative analysis of the economy of the different technologies can be conducted.

Fig. 9 shows the aforementioned comparison. As inferred from this plot, a general trend is observed in all graphs. Thus, as a rule of thumb, the combination of O_3 and UV-vis radiation results in the lowest operating costs, albeit some controversial points need to be addressed.

Thus, TiO_2 costs have not been considered as it is supposed that the catalyst can be reused and it is not considered as a consumable product. If the price of titania is to be included ($\text{€}0.05 \text{ g}^{-1}$), catalytic processes add an extra amount of $\text{€}0.0675$ which makes the $O_3/UV\text{-vis}$ process as the most economically attractive technology.

Oxygen price significantly increases the overall ozonation costs. By only considering the electrical requirements of the ozone generator, the single ozonation is by far the cheapest oxidising system. The photolysis costs are comparable to those obtained in the combination of O_3 and UV-vis radiation, although in the first case, a 100% degradation of the parent compound is not always achieved for the period of time considered. Additionally, if it is assumed that UV radiation is the main responsible of organics degradation, further savings can be achieved. In this sense, the TQ700 Heraeus lamp used in this study has an electricity input of 700 W with a radiant energy output at 254 nm of 18.6 W. Likely, similar results would have been obtained by using three monochromatic low Hg pressure TNN 15/32 Heraeus lamps, with an electricity consumption of 15 W (each) and an output radiation of 6 W.

Analogous results to those previously discussed were found when considering the COD removal; however, it has to be pointed out that only some of the technologies used are capable of attaining high levels of COD conversion.

Finally, it is worth to mention the shift of the cost profiles between the systems $O_3/UV\text{-vis}$ and $O_3/UV\text{-vis}/TiO_2$ depending on removal of the parent compound or COD. The

shift is undoubtedly due to the highest efficiency on COD elimination in the presence of titania.

4. Conclusions

From the previous study, the following conclusions can be drawn:

- The efficiency of the different methods tested shows the following trend (with some exceptions) if the parent compound is analysed: adsorption < TiO₂ + UV–vis < UV–vis < O₃ + TiO₂ ≈ O₃ < O₃ + UV–vis ≈ O₃ + UV–vis + TiO₂.
- In general, the presence of titania favours COD and TOC elimination even for those processes where the parent compound depletion rate is decelerated.
- With the exception of phenol oxidation, the system O₃ + UV–vis + TiO₂ is the less ozone-consuming technology.
- The presence of NO₃[−] and Cl[−] in the reaction media accounts up to a maximum of 45% in the first case and almost 100% for the second if compared to the maximum achievable concentration.
- A first approach to the economy of the different processes shows the O₃ + UV–vis and O₃ + UV–vis + TiO₂ methods as the most economically attractive. Nevertheless, further savings can be achieved by using air instead of oxygen, less powerful UV lamps, etc.

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