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Mineralization of Substituted Aromatic Compounds by Ozonation Catalyzed by Cerium Oxide and a Cerium Oxide-activated Carbon Composite

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Abstract Cerium oxide (Ce–O) and a novel cerium oxide-activated carbon composite (AC_0–Ce–O) were tested in the ozonation of three selected aromatic compounds: benzenesulfonic acid, sulfanilic acid and aniline. The catalysts performance was compared to that obtained with the commercial activated carbon. All the tested materials enhanced the mineralization of the selected compounds. Generally, best results were achieved with the AC_0–Ce–O composite.

Keywords Catalytic ozonation · Cerium oxide · Activated carbon · Benzenesulfonic acid · Sulfanilic acid · Aniline

1 Introduction

Ozonation and several catalytic ozonation processes have been widely studied in the scope of wastewater treatment. Heterogeneous catalytic ozonation, which is one of the most attractive alternatives, aims to enhance the removal of recalcitrant compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst [1].

Different supported and unsupported catalysts have been tested in the ozonation of several organic compounds [1]. Among the studied materials, activated carbon (AC) has been found to be a promising alternative to the treatment of wastewater containing dyes or other organic contaminants [2–4]. The application of cerium-based catalysts in several processes, including wet air oxidation reactions [5, 6], has been extensively studied. However, only a few studies have reported the use of cerium-containing catalysts for the ozonation of organic compounds [7, 8].

In a previous work [8], we prepared a cerium oxide/activated carbon composite for the application in catalytic ozonation reactions. The results obtained showed that cerium oxide catalysts are effective ozonation catalysts for the removal of carboxylic acids (oxalic and oxamic acids). Experiments in the presence of the radical scavenger *tert*-butanol, supported the involvement of hydroxyl radicals ($HO^\bullet$) in the oxidation mechanism. It was suggested that cerium oxide promotes the decomposition of ozone into $HO^\bullet$ radicals, which are the main oxidant species responsible for the oxidation of the compounds in the liquid phase. A strong synergic effect was observed between activated carbon and cerium oxide in the prepared composite. In this case, the reaction mechanism is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation [4] and also liquid bulk reactions involving $HO^\bullet$ radicals. It is assumed that the existence of delocalized π electrons on the basal planes of the activated carbon contributes to the formation of Ce(III) species, which are active for the decomposition of O_3 into $HO^\bullet$ radicals.

In the present publication, the study of the catalytic activity of cerium oxide and the cerium oxide/activated

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carbon composite was extended to the ozonation of three selected aromatic compounds containing sulfonic and/or amine substituents. Sulfonated aromatic compounds as well as aromatic amines constitute a group of pollutants particularly difficult to eliminate from wastewater streams. Many of those, formed during the reduction of sulfonated azo dyes, are not susceptible to anaerobic or aerobic biodegradation and thus conventional biological treatments fail to mineralize these compounds [9]. Some intermediates and final oxidation by-products of this class of pollutants are usually quite refractory to ozonation. Therefore, it is important to develop new catalysts capable of enhancing the mineralization of such compounds.

Benzenesulfonic acid, sulfanilic acid and aniline were used as model pollutants in the present study. The most refractory intermediates were followed along the experiments. In order to evaluate the performance of the composite, experimental results obtained with the activated carbon used in its preparation were included.

2 Experimental

2.1 Materials

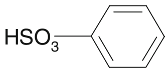
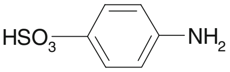
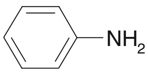
Benzenesulfonic acid (BSA), sulfanilic acid (SA) and aniline were obtained from Sigma-Aldrich and used as received. Some properties of these compounds are presented in Table 1.

Cerium oxide (sample Ce–O) was prepared by precipitation, according to the procedure described by Imamura et al. [5], using aqueous solutions of cerium (III) nitrate, $Ce(NO_3)_3 \cdot 6H_2O$. In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca. 15 g/100 mL H_2O) under continuous stirring. The resultant precipitate was thoroughly washed with distilled water, dried at 100 °C for 24 h and calcinated in air (50 cm^3 min^{-1}, measured at room T and P) at 450 °C for 3 h. A composite of activated carbon and cerium oxide (sample AC_0–Ce–O) was prepared by a similar procedure as for sample Ce–O, where a given amount of activated carbon was dispersed in the nitrate solution before addition of NaOH. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was used as received. After precipitation, the suspension was shaked for 5 h at room temperature. Then, it was filtered and thoroughly washed and dried in an oven for 24 h at 100 °C. This material was calcinated at 450 °C for 3 h under a flow of N_2 (50 cm^3 min^{-1}, measured at room T and P). The catalysts were sieved to a particle size of 100–300 μm prior to reaction studies.

The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. As reference, the BET surface areas (S_{BET}) of the samples were calculated. XRD spectra were recorded on a Philips X'Pert MPD diffractometer (Cu $K\alpha = 0.15406$ nm) and XPS was performed with a VG Scientific ESCALAB 200A spectrometer. XPS data corresponding to Ce 3d spectra was fitted using the software XPSpeak.

Thermal analysis of sample AC_0–Ce–O, carried on in a Mettler TA 4000 thermal analyser under a flow of air, revealed a cerium oxide average content of 45% wt. Samples Ce–O and AC_0–Ce–O have BET surface areas of 72 and 583 m^2/g, respectively. The selected activated carbon has a BET surface area of 909 m^2/g. The complete characterization of this material is reported elsewhere [10]. According to the XRD results, the dominant diffraction peaks observed for both samples are those characteristic of cerianite (CeO_2). The presence of the Ce(IV)/Ce(III) redox couple on the surface of the prepared cerium oxide-containing catalysts was evidenced by XPS analysis. Additional detailed information on the characterization of the CeO_2 based materials is reported elsewhere [8].

Table 1 Properties of the selected aromatic compounds

		M (g/mol)	pKa
Benzenesulfonic acid (BSA)		158.2	−2.36
Sulfanilic acid (SA)		173.2	2.92*
Aniline		93.1	4.64*

* pKa corresponding to the group NH_3^+

2.2 Kinetic Experiments

The removal of BSA, SA and aniline from aqueous solutions was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket. For comparative purposes, ozonation experiments in the absence of catalyst were performed in the same system, under identical experimental conditions. In each experiment the reactor was filled with 700 mL of 1 mM solution at the natural pH of the compound. In the adsorption and catalytic ozonation experiments, 350 mg of catalyst (100–300 μm) were introduced in the reactor. The temperature of the reactor was maintained at 25 °C and the inlet concentration of ozone was 50 g/Nm^3. Additional experimental conditions and procedures are reported elsewhere [4].

The concentrations of the initial aromatic compounds and detected intermediates, including nitrates, were followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was an YMC Hydrosphere C18 column (250 mm × 4.6 mm) working at room temperature. SA, aniline and the respective degradation compounds were analysed under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2.0. In the case of BSA, HPLC measurements were done under isocratic elution with a mixture of water, NaH_2PO_4 and *o*-phosphoric acid at pH 2.8. Ammonium ion concentration was measured with a WTW NH500 ammonia-selective electrode. The degree of mineralization was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

3 Results and Discussion

The mineralization of benzenesulfonic acid, sulfanilic acid and aniline was studied by ozonation catalyzed by cerium oxide and activated carbon–cerium oxide composite materials, at the natural pH of each solution. For comparative purposes, the results obtained with the same activated carbon used in the preparation of the composite are also presented. The results obtained with each organic compound are presented separately in this section.

3.1 Benzenesulfonic Acid

The ozonation of BSA catalyzed by Ce–O and AC_0–Ce–O was carried out at pH 3.0, which is the natural pH of the solution. The experimental results obtained in terms of TOC and BSA concentrations are depicted in Fig. 1. In order to facilitate the evaluation of the catalytic activities and the comparison between the different catalysts in the degradation of the reactant, the curves corresponding to BSA decay were fitted by a first order kinetic model. The respective apparent first order rate constants are presented in Table 2.

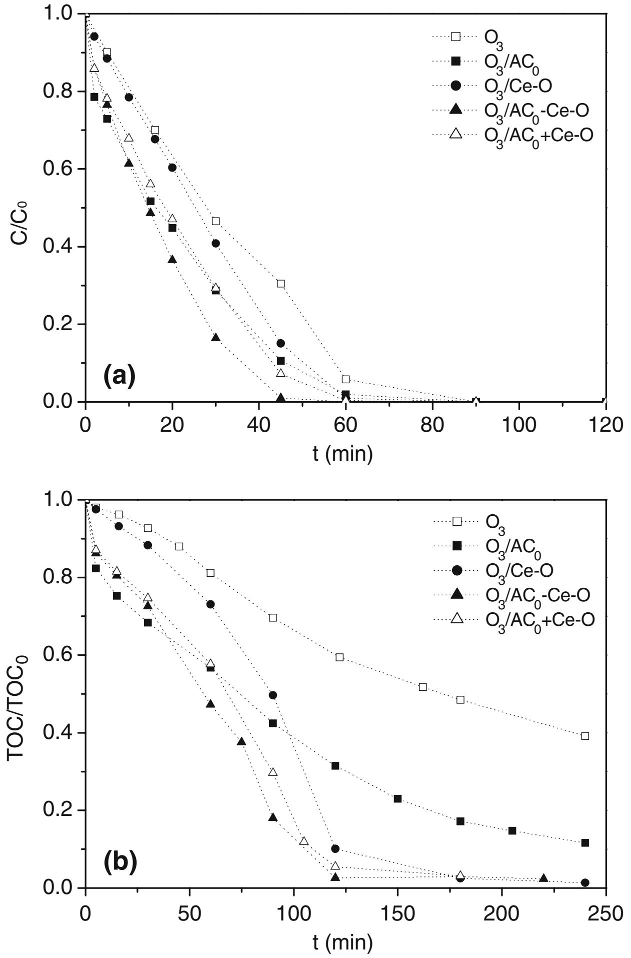


Fig. 1 Evolution of the dimensionless BSA (**a**) and TOC (**b**) concentrations during non-catalytic and catalytic ozonation of BSA (C_0 = 1 mM, pHi = 3.0, catalyst = 0.5 g/L)

Table 2 First order apparent rate constants of non-catalytic and catalytic ozonation of BSA, SA and aniline

	BSA		SA		Aniline	
	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
O_3	0.027	0.990	0.111	0.986	0.184	0.982
O_3/AC_0	0.046	0.983	0.145	0.990	0.268	0.990
O_3/Ce–O	0.029	0.984	0.128	0.991	0.204	0.982
O_3/AC_0–Ce–O	0.057	0.980	0.151	0.985	0.256	0.982

Under the experimental conditions used in this work, the conversion of BSA was enhanced by all the materials tested, which is confirmed by the calculated apparent first order rate constants. During the ozonation in the presence of activated carbon this enhanced effect is sometimes attributed to the adsorption capacity of this material. Nevertheless, the catalytic role played by activated carbon cannot be discarded [11]. In the case of the cerium oxide, the enhanced effect must be attributed mainly to a catalytic effect because BSA adsorption on this material is negligible (less than 8% of the initial concentration after 3 h). Based on our previous work [8], these results are due to the formation of $HO^{\bullet}$ radicals that are responsible for the enhanced oxidation of BSA. It has been found that the elimination of BSA is hardly accomplished only by molecular ozone attack [11]. The substituent $-HSO_3$ is a strongly deactivating group since it decreases the electron density of the ring at the *ortho-* and *para-* positions through a resonance withdrawing effect. Hence these sites are less nucleophilic and, therefore, less prone to electrophilic attack by molecular ozone. According to Fig. 1 and Table 2, there is a significant difference between the results obtained with samples AC_0 and AC_0–Ce–O. Even though the latter sample has a significantly lower surface area (583 m^2/g vs. 909 m^2/g), the catalytic effect in the elimination of BSA is more pronounced. This behaviour was attributed to the presence of cerium oxide. In order to understand the nature of the observed effect, another experiment using a physical mixture of activated carbon and cerium oxide (in the same proportion as in sample AC_0–Ce–O) was carried out. In fact, a slight synergic effect was also observed in this experiment. Nevertheless, this effect was enhanced in the CeO2-activated carbon composite, showing that an intimate mixture between cerium oxide and activated carbon is a benefit for the ozonation of BSA. Both Ce–O and AC_0–Ce–O have a remarkable effect in terms of TOC removal leading to nearly complete mineralization of the compounds in solution after 2 h. The combination of cerium oxide and activated carbon has an important synergic effect in the mineralization of BSA.

According to the chromatograms obtained by HPLC, many intermediates arise from the ozonation of BSA but, under the experimental conditions used, their identification was not always possible to accomplish. In this work we were interested in identifying final oxidation products, which are usually saturated compounds quite refractory to oxidation. Oxalic acid was identified as one of the main reaction intermediates that persisted in solution throughout single ozonation, and was monitored during the reaction period. This particular carboxylic acid is known to be one of the most common final oxidation products of a large number of organic compounds in aqueous solutions. It is a small chain carboxylic acid, highly refractory to ozonation. The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04\ M^{-1}\ s^{-1}$ [12]) explain why such compounds always accumulate as final products when organic aqueous solutes are ozonized in water. The compounds of low reactivity towards ozone may be oxidized by secondary oxidants such as hydroxyl radicals $HO^{\bullet}$ produced during the decomposition of ozone in aqueous solution. A few catalysts have been reported to enhance the ozonation of oxalic acid in aqueous solution. Among them, activated carbon was shown to be an effective catalyst for the mineralization of this particular compound [4, 13]. In a previous work [8], cerium oxide-containing catalysts were also found to be highly active for the mineralization of this compound.

As can be observed in Fig. 2, the evolution of oxalic acid concentration in the presence of cerium oxide catalysts is quite different from that corresponding to single ozonation and activated carbon catalyzed ozonation. In the former case the ozonation leads to faster and total disappearance of oxalic acid.

After 180 min of single ozonation, oxalic acid concentration in solution represents ca. 36% of the measured TOC. In the presence of AC_0 the concentration of oxalic acid is lower and represents ca. 21% of the TOC in solution. In both cases there are other unidentified organic products responsible for the remaining TOC. On the other hand, the ozonation of BSA catalyzed by Ce–O or AC_0–Ce–O results in the total elimination of oxalic acid formed and in the practically complete mineralization of the organic compounds in solution (see Fig. 1b). The mineralization of BSA is accompanied by the release of the sulphur moiety which is, at least partially, converted into SO_4^{2-} [11].

3.2 Sulfanilic Acid

The oxidation of SA was carried out at pH 3.3. The results obtained in non-catalytic and catalytic ozonation are depicted in Fig. 3. In a previous work [11], SA was found to be easily oxidized by ozone. In fact, as it can be

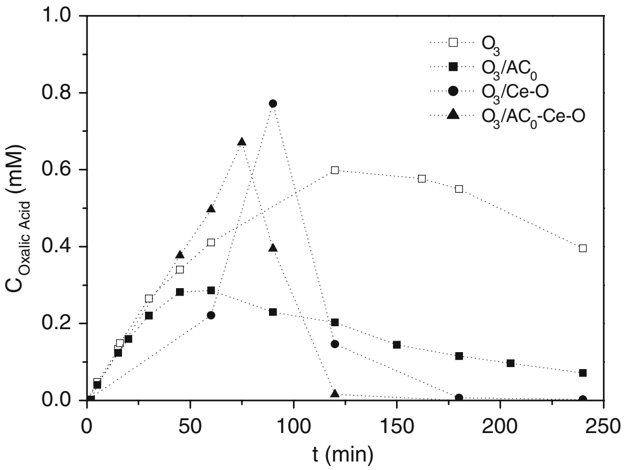


Fig. 2 Evolution of oxalic acid concentrations during non-catalytic and catalytic ozonation of BSA ($C_0 = 1$ mM, pHi = 3.0, catalyst = 0.5 g/L)

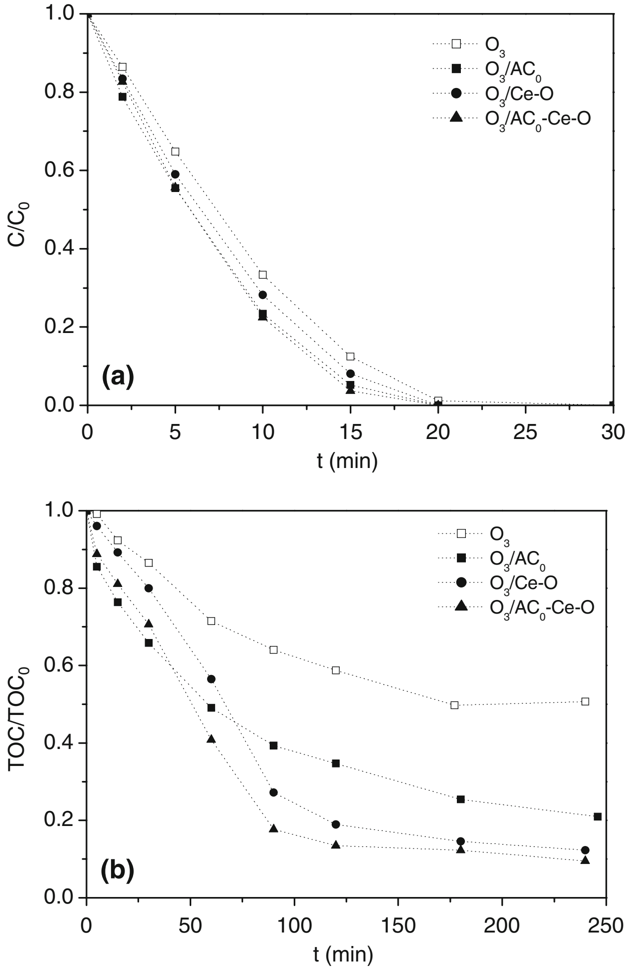


Fig. 3 Evolution of the dimensionless SA (**a**) and TOC (**b**) concentrations during non-catalytic and catalytic ozonation of SA ($C_0 = 1$ mM, pHi = 3.3, catalyst = 0.5 g/L)

observed in Fig. 3a, the complete removal of SA from solution occurs in approximately 20 min.

The addition of the Ce–O catalyst to the ozonation process slightly enhanced the elimination of SA, which can be confirmed by the apparent first order rate constants listed in Table 2. It should be pointed out that the amount of SA adsorbed on Ce–O after 3 h, represents less than 6% of the initial concentration. The catalytic activity of this material is evidenced especially when analyzing the TOC removal attained during the catalytic ozonation of SA. The composite material AC_0–Ce–O also presents an enhanced effect both in the elimination of SA and in the mineralization of the dissolved organic compounds. In fact, the best results in TOC removal are obtained with this catalyst. After 120 min of reaction, the removal of TOC achieved with sample AC_0–Ce–O was 87% against 41% and 65% obtained with single ozonation and ozonation in the presence of activated carbon, respectively. Similarly to what was explained for BSA, the observed enhanced catalytic effect results from a cooperative action between activated carbon and cerium oxide. The former is thought to be able to promote the reduction of Ce(IV) to Ce(III), thus increasing the redox properties of the latter [8].

According to the apparent first order rate constants listed in Table 2, SA is less refractory to oxidation than BSA. The presence of the strong activating group -NH_2, increases the aromatic ring electron density through a resonance donating effect. The resonance allows electron density to be positioned at the *ortho-* and *para-* positions. Therefore, sulfanilic acid is susceptible of being attacked by molecular ozone preferentially at those sites. Nonetheless, higher TOC removals are attained for solutions of BSA (cf. Figs. 1b and 3b), since almost complete mineralization of BSA is achieved in the presence of the cerium oxide catalysts. This must be related to the characteristics of the intermediates formed, which are expected to be more refractory in the case of SA. Actually, during the ozonation of sulfanilic acid, oxalic acid and oxamic acid are formed and the latter is an extremely recalcitrant carboxylic acid [4, 14]. These compounds are usually refractory to molecular ozone attack, but react more effectively with oxygenated radicals in the solution or on the catalysts surface [4].

The two mentioned carboxylic acids were found to be responsible for the greatest fraction of TOC in solution at longer reaction times. The concentrations of oxamic and oxalic acids were followed and the results obtained are depicted in Fig. 4.

In a previous work [4], oxamic acid was found to be highly refractory to single ozonation. On the other hand, the ozonation catalyzed by activated carbon enhanced the mineralization of oxamic acid at low pH. As expected, during the oxidation of sulfanilic acid at pH 3.3, the presence of activated carbon enabled the decrease of oxamic acid concentration in solution. Higher concentrations of oxamic acid were detected along time during the ozonation of SA catalyzed by Ce–O or AC_0–Ce–O. Similarly to the observations during the ozonation of BSA, the curves of oxalic acid concentrations detected in the cerium oxide catalyzed ozonation follow a different pattern from those of single ozonation and ozonation in the presence of activated carbon. Sample Ce–O leads to almost complete removal of oxalic acid after 3 h, and in the case of sample AC_0–Ce–O, after the same reaction time, no oxalic acid was detected in solution. In this case, the amount of oxamic acid detected represents 66% of the TOC in solution, which means that only a relatively small fraction of TOC is due to unidentified products.

The mineralization of SA is accompanied by the conversion of its initial nitrogen and sulphur moieties into inorganic ions. Both ammonium NH_4^+ and nitrate NO_3^- ions were detected and quantified during the ozonation of

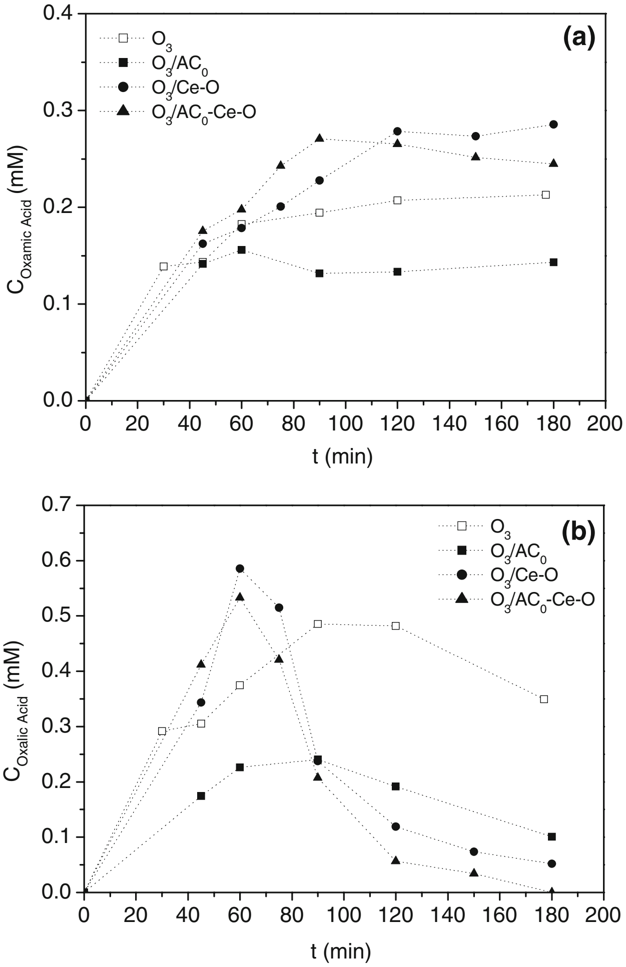


Fig. 4 Evolution of oxamic (**a**) and oxalic (**b**) acids concentrations during non-catalytic and catalytic ozonation of SA (C_0 = 1 mM, pHi = 3.3, catalyst = 0.5 g/L)

SA. Figure 5 depicts the evolution of the concentrations of NO_3^- during non-catalytic and catalytic ozonation. The concentrations of NH_4^+ found after 180 min of reaction are listed in Table 3, together with the nitrogen balance in solution at that time.

It was observed that the concentrations of NO_3^- were always lower whenever the ozonation of SA was carried out in the presence of activated carbon-containing materials. This might be due to the formation of different N-containing intermediates and to the adsorption of some of those intermediates on the activated carbon. Moreover, the ozonation of such compounds in the presence of activated carbon may follow a route that does not lead to the potential formation of NO_3^-, as was reported for the catalytic ozonation of oxamic acid [4].

Regarding the formation of NH_4^+, no major differences were observed for the different catalytic systems studied. In a previous work [11], it was reported that there was a fast accumulation of NH_4^+, coincident with the disappearance of SA, probably due to the quick conversion of N-containing products in the early stage of the ozonation process. Several reasons can explain the fact that the nitrogen balance is not closed. The presence of unidentified nitrogen-containing species, especially in the cases of single ozonation and activated carbon catalytic ozonation must be taken into account. In the presence of activated carbon materials, the adsorption of the initial compound and the possible adsorption of nitrogenated oxidation by-products may also be considered. Additionally it is possible that the catalytic ozonation of SA may lead to the formation of gaseous nitrogen compounds, such as N_2 or nitrogen oxides.

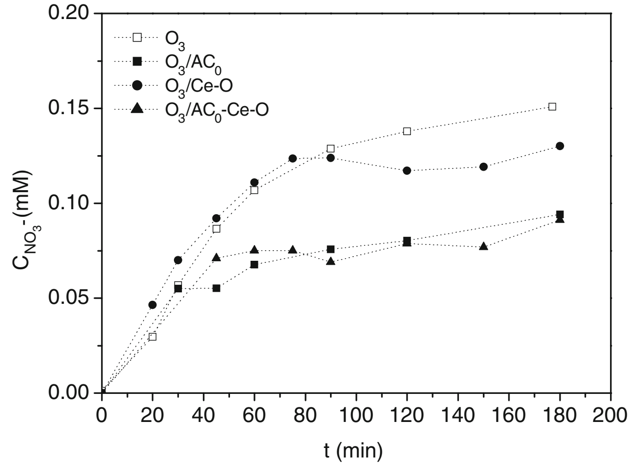


Fig. 5 Evolution of NO_3^- concentration during non-catalytic and catalytic ozonation of SA (C_0 = 1 mM, pHi = 3.3, catalyst = 0.5 g/L)

Table 3 Balance of nitrogen-containing species resultant from the oxidation of SA (Ci = 1 mM, *t* = 180 min)

System	NO_3^- (mM)	NH_4^+ (mM)	Oxamic acid (mM)	N-total (mM)
O_3	0.151	0.414	0.213	0.778
O_3/AC_0	0.094	0.416	0.143	0.653
O_3/Ce–O	0.130	0.455	0.286	0.871
O_3/AC_0–Ce–O	0.091	0.457	0.245	0.793

3.3 Aniline

Ozonation is an efficient process for the degradation of compounds containing either an activated aromatic ring or double bonds, as ozone selectively attacks these chemical structures. The amino group ($-NH_2$) is electron donating and thus, it activates the aromatic ring by increasing its electronic density. Aromatic compounds, such as aniline, have a higher delocalisation of electrons and exhibit advanced reactivity towards ozone. In a previous work [15], aniline was found to be easily oxidized by single ozonation in a wide range of solution pH. In the present work, the ozonation of aniline was studied starting from a 1 mM aqueous solution at the natural pH, which is 6.4. Catalytic ozonation experiments were carried out using samples AC_0, Ce–O and AC_0–Ce–O. Both aniline and TOC decay were followed during 180 min and the obtained experimental data is depicted in Fig. 6. The curves corresponding to aniline decay were fitted by a first order kinetic model. The respective apparent rate constants obtained are presented in Table 2.

Ozonation enables a fast decay of aniline concentration and, under the selected experimental conditions, the elimination of this compound from aqueous solution is achieved in less than 20 min. The simultaneous use of ozone and activated carbon improves the rate of aniline removal, which is explained by a sum of contributions of direct and indirect ozonation and adsorption on activated carbon. At pH 6.4, aniline is present in solution in its molecular form. It adsorbs on the AC through dispersive interactions between the free electrons of the AC surface and the electrons of the aromatic ring [16]. Thus, adsorption of aniline on activated carbon accounts for part of its removal from the solution. On the other hand, adsorption of aniline on Ce–O was found to be negligible and the elimination of aniline during Ce–O catalytic ozonation is not noticeably enhanced. However, when analyzing the TOC removal curves, the conclusions withdrawn are quite different. Sample Ce–O has a significant catalytic effect in the mineralization of the solution. Best results are achieved with sample AC_0–Ce–O, which allows attaining an even higher mineralization degree than activated carbon after, 90 min. Consequently, the role of these catalysts, as well as that of activated carbon, in the ozonation of organic compounds becomes crucial in the mineralization of the oxidation by-products.

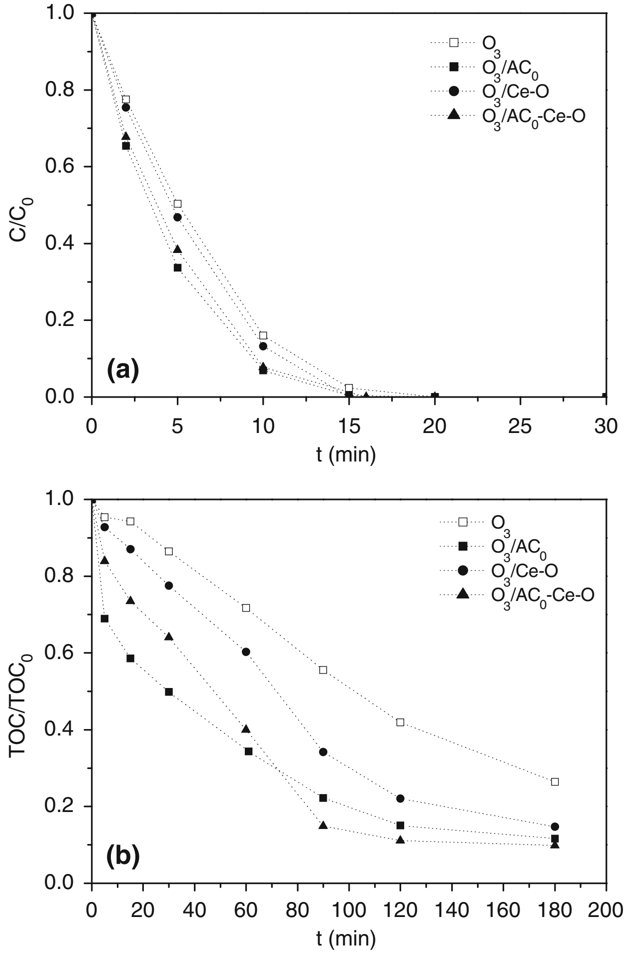


Fig. 6 Evolution of the dimensionless aniline (**a**) and TOC (**b**) concentrations during non-catalytic and catalytic ozonation of aniline (C_0 = 1 mM, pHi = 6.4, catalyst = 0.5 g/L)

The oxidation of aniline leads to the fast formation of intermediates that stay in solution for further mineralization. In these work two classes of intermediates were identified: primary aromatic oxidation by-products, *ortho*- and *para*-aminophenol, and final oxidation products, oxalic and oxamic acids. Additionally inorganic ions, NO_3^- and NH_4^+, were also quantified. The formation of *ortho*- and *para*-aminophenol results from the hydroxylation of the aromatic ring in the *ortho* and *para* positions, respectively. After 15–20 min of reaction none of these products is present in solution. Though nitrobenzene was not followed in these reactions, it is known that this is also one of the primary intermediates of the oxidation of aniline [15]. Other aromatic compounds such as coloured condensation products are also formed in the early stages of aniline oxidation reactions but are further eliminated [17]. For longer reaction times, mainly saturated aliphatic compounds are expected to be found in solution. Under the experimental conditions used, oxamic and oxalic acids were identified as two of the carboxylic acids formed during the ozonation of aniline. The concentrations measured along time are depicted in Fig. 7.

The evolutions of oxamic acid concentrations in the different processes are similar to those obtained in the ozonation of SA, i.e., lower concentrations of oxamic acid were found in the ozonation catalyzed by activated carbon. On the contrary, the removal of oxalic acid is favoured by the presence of AC_0–Ce–O which, according to TOC data (Fig. 6b), enhances the degree of mineralization. After 180 min of reaction, the concentrations of these two carboxylic acids are responsible for a significant fraction of the TOC in solution. In non-catalytic ozonation and ozonation in the presence of activated carbon they represent, respectively, 42% and 45% of the measured TOC. In the case of the cerium-containing catalysts, the residual concentrations of oxamic and oxalic acids account for 82% of the measured TOC for sample Ce–O while for sample AC_0–Ce–O they represent 97% of the measured TOC. In

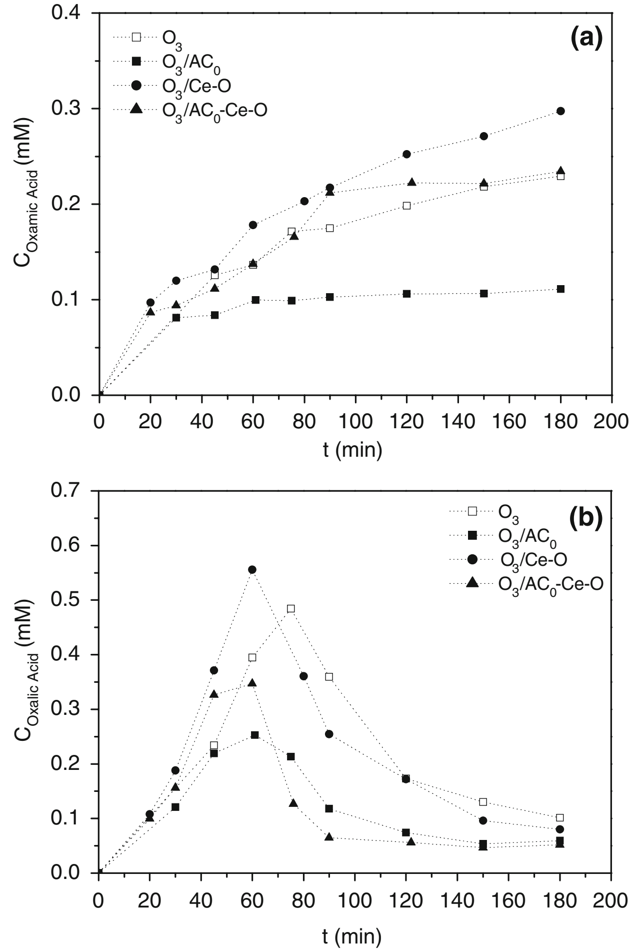


Fig. 7 Evolution of oxamic (**a**) and oxalic (**b**) acids concentrations during non-catalytic and catalytic ozonation of aniline ($C_0 = 1$ mM, pHi = 6.4, catalyst = 0.5 g/L)

the latter case, oxalic and oxamic acids are, certainly the major final oxidation by-products of organic nature. This observation reinforces the high effectiveness of the cerium oxide-activated carbon composite as ozonation catalyst.

During the ozonation, the nitrogen moiety of the aniline molecule is partially converted into inorganic nitrogen species, such as NH_4^+ and NO_3^-. The concentrations of NO_3^- detected in non-catalytic and catalytic ozonation of aniline are shown in Fig. 8. The concentrations of NH_4^+ measured after 180 min of reaction are listed in Table 4, together with the nitrogen balance corresponding to the species present in solution.

The concentrations of NO_3^- follow a similar trend to that observed in the oxidation of SA. Apparently, in the presence of Ce–O, slightly higher concentrations of NO_3^- are formed, comparatively to single ozonation, which might be related to a higher mineralization of the compounds present in solution. Similar reasons presented for SA may account for the fact that the nitrogen balance is not closed.

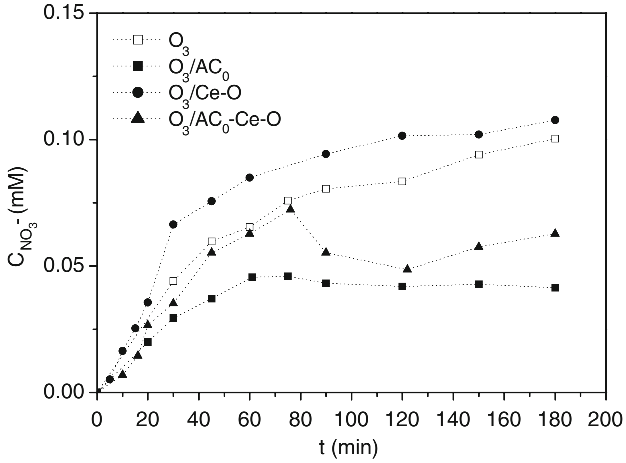


Fig. 8 Evolution of NO_3^- concentrations during non-catalytic and catalytic ozonation of aniline ($C_0 = 1$ mM, pHi = 6.4, catalyst = 0.5 g/L)

Table 4 Balance of nitrogen-containing species resultant from the oxidation of aniline (Ci = 1 mM, *t* = 180 min)

System	NO_3^- (mM)	NH_4^+ (mM)	Oxamic acid (mM)	N-total (mM)
O_3	0.100	0.492	0.229	0.821
O_3/AC_0	0.041	0.357	0.111	0.509
O_3/Ce–O	0.108	0.448	0.297	0.853
O_3/AC_0–Ce–O	0.063	0.370	0.234	0.667

3.4 Remarks on the Individual Catalysts Roles and Cooperative Effect in the AC_0–Ce–O Composite

In our previous work, the simultaneous use of ozone and activated carbon was shown to enhance the mineralization of several aromatic compounds [11, 15] as well as carboxylic acids [4], when compared to single ozonation and single adsorption, proving the existence of a catalytic reaction mechanism. It is generally accepted that the ozonation catalyzed by activated carbon involves both surface and bulk reactions between the organic solute and oxygenated radical species.

More recently, both CeO_2 and CeO_2-activated composite were found to be highly active catalysts for the ozonation of oxalic and oxamic acids [8]. Particularly in the case of oxalic acid, a strong synergic effect was observed in the prepared composite. Both cerium oxide and activated carbon are active ozonation catalyst. The first was shown to enhance the decomposition of ozone into highly reactive species in solution, such as $HO^\bullet$, which participate in the oxidation reaction mechanism. Activated carbon has a more complex role. It catalyzes the decomposition of ozone in the aqueous phase through the formation of surface oxygenated radical species as well as promoting the formation of $HO^\bullet$ in solution. The intimate mixture of cerium oxide and activated carbon is believed to promote the reduction of Ce(IV) to Ce(III) species, due to the existence of delocalized π electrons on the basal planes of the activated carbon. Therefore, the presence of the redox pair Ce(IV)/Ce(III) on the composite is believed to enhance its catalytic properties for the generation of $HO^{\bullet}$ radicals in the solution.

The synergic effect observed in the CeO_2-activated carbon composite for the mineralization of the selected aromatic compounds is thus attributed to a combination of heterogeneous catalytic reactions, occurring preferentially on the surface of the activated carbon, and homogeneous reactions between the solutes and $HO^{\bullet}$ radicals resultant from the catalytic decomposition of ozone, mainly on cerium oxide.

4 Conclusions

Both the CeO_2-containing catalysts studied were found to be highly effective in ozonation. Comparatively to the performance of the commercial activated carbon, an enhanced mineralization extent was achieved, particularly in the case of benzenesulfonic acid, where complete mineralization was attained after 2 h of reaction.

Catalytic and non-catalytic ozonation of sulfanilic acid and aniline results in the formation of extremely refractory final oxidation products, such as oxamic acid, which prevents attaining mineralization degrees greater than 90%, within the total time defined for the kinetic experiments.

In the case of benzenesulfonic acid, the synergic effect was shown to be stronger for the composite material than for the physical mixture of cerium oxide and activated carbon, suggesting that an intimate mixture of those two materials is highly effective for the ozonation of organic compounds. The intimate mixture of activated carbon and cerium oxide is believed to promote the existence of the redox pair Ce(IV)/Ce(III), which seems to be active for the generation of $HO^{\bullet}$ radicals in the solution.

The mechanism of the ozonation catalyzed by the CeO_2-activated carbon composite is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation, and also liquid bulk reactions involving $HO^{\bullet}$ radicals, resultant from the catalytic decomposition of ozone on the surface of the activated carbon and mainly in the presence of cerium oxide.

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