

UV- and UV/Fe(III)-enhanced ozonation of nitrobenzene in aqueous solution

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Abstract

The degradation of nitrobenzene, a recalcitrant compound, using the combination of ozone with UV radiation and UV + Fe(III) has been carried out in a 21 L reactor and compared with results obtained from single ozonation. Whereas TOC elimination was not improved by using UV radiation, the addition of Fe(III) (O₃/UV/Fe(III)) enhanced the mineralization rate. The principal effect of Fe(III) on the photolytic ozonation is attributed to the photodecarboxilation of ferric ion complexes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aromatic compounds are widely used in explosives, pesticides and dyes production. Many of them, nitrobenzene and nitrophenols included, are considered to be highly toxic. Nitrobenzene (C₆H₅NO₂, NB) has been detected in different industrial effluents, mainly plastic processing, inorganic synthesis, paper, pesticides and in the explosives industry [1]. It shows a high toxicity, with a maximum allowed concentration of 1 ppm [2]. Recently, the US EPA has included it in a reduced list of drinking water contaminant to be assessed over the next 5 years for possible future regulation [3]. NB is resistant to oxidation by biological treatment, therefore chemical oxidation is needed [4]. In order to destroy this organic compound in wastewaters, oxidation processes involving hydroxyl radicals (OH•) may be adequate.

Both ozone and ozone combined with UV radiation have shown to be appropriate techniques for the removal of different pollutants from water. It seems that this type of processes combined with biological treatment is one of the most promising alternatives [5]. The oxidation of nitroaromatic hydrocarbons, however, has been the subject of few research studies [4,6–9]. The aim of this work was to study the degradation of nitrobenzene in aqueous solutions by

means of the advanced oxidation process O₃/UV and the UV + Fe(III)-enhanced ozonation process.

In the O₃/UV process, aqueous systems saturated with ozone are irradiated with UV light of 254 nm in a reactor suited for such heterogeneous media. The extinction coefficient of O₃ at 254 nm is 3600 M⁻¹ cm⁻¹, much higher than that of H₂O₂ [10]. Initially, H₂O₂ is produced practically stoichiometric with regard to ozone [11]:



Hydrogen peroxide presents photolysis reactions at the same time, which lead to the production of OH• radicals:



The H₂O₂ produced can dissociate into peroxianion, which reacts with the ozone forming O₃⁻ and HO₂•, and the latter can, at the same time, give O₂⁻. These species react through a radical mechanism. The radical species generated in this process can interact with the organic pollutants and degrade them. Some authors have studied the efficiency of this process in the degradation of some aromatic compounds [6,12–14].

The addition of iron ion (Fe³⁺ or Fe²⁺) has been reported to accelerate the UV-enhanced ozonation of several pollutants [15,16]. Fe(III) is considered to increase the number of hydroxyl radicals through the reduction of O₃ with the Fe²⁺ generated by the photoreduction of Fe³⁺ [15]. Nevertheless, this is not considered to be the only mechanism involved in the effect of Fe³⁺. Abe and Tanaka [16] also

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Nomenclature

<i>C</i>	Concentration (mol L^{-1})
COD	Chemical Oxygen Demand ($\text{mg O}_2 \text{ L}^{-1}$)
NB	Nitrobenzene
TOC	Total Organic Carbon (mg C L^{-1})

Subscripts

<i>o</i>	initial condition for the aqueous solution
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reported that the UV photodegradation of Fe^{3+} complex with aliphatic intermediate was found to be another mechanism besides the OH formation involved in the effect of Fe^{3+} .

2. Materials and methods*2.1. Chemicals*

Reagent grade nitrobenzene (98%) supplied by PROBUS and millipore water (Milli-Q Millipore system with a $18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) were used in all the experiments. For HPLC analysis, acetonitrile (99.8%, isocratic grade for HPLC), supplied by MERCK was used. Other reagents were iron trichloride (98%, PROBUS), phosphoric acid (85%, PROBUS), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, reagent grade, MERCK), uranyl nitrate (98%, PANREAC), oxalic acid (99.5%, PANREAC) and potassium permanganate (99%, PROBUS).

2.2. Installation

A 21 L pilot-scale plant, made of PVC, is used in batch operation (Fig. 1). Liquid recirculates through a centrifugal stainless steel pump at a flowrate of 300 L h^{-1} . Ozone was generated by a SANDER 301.19 unit ozonizer fed by oxygen with a maximum ozone production of 30 g h^{-1} at $400 \text{ L h}^{-1} \text{ O}_2$ flow. Gas–liquid contact was ensured with a venturi-type chlorine injector, together with a special design for the storage tank that helps contact. The lamp is a monochromatic (254 nm) UV705 (Trojan Technologies), with a nominal power of 26 W.

2.3. Experimental

Before the experiments were carried out, actinometry experiments based on the photochemical decomposition of oxalic acid in the presence of uranyl ion [17,18] were performed to determine the amount of radiation emitted by the lamps and transferred into the reactor. It was found that the flux of radiation entering the reactor was $25.4 \mu\text{einstein s}^{-1}$.

The reactor was charged with 21 L of a 100 ppm ($0.813 \text{ mmol L}^{-1}$) NB aqueous solution. The pH of reaction solution was allowed to evolve freely or adjusted adding borax or phosphoric acid solutions. The recirculation flowrate was 250 L h^{-1} . All experiments were performed at temperature $21\text{--}25^\circ\text{C}$. Gas flowrate was set at 400 L h^{-1} with an ozone production of 7.4 g h^{-1} .

2.4. Analytical methods

Nitrobenzene concentration was determined by reversed-phase HPLC. A Waters HPLC apparatus (photodiode array

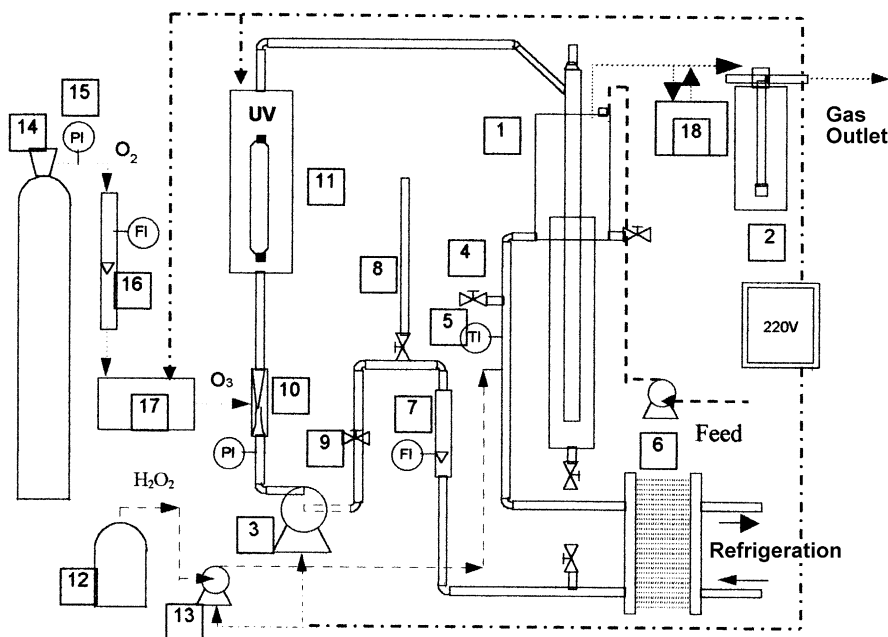


Fig. 1. Scheme of the experimental installation.

detector 996, autosampler 717, controller 600) with a Millennium Software was used. The column was a Spherisorb ODS2, 5 μ , 25 cm \times 0.46 cm. The mobile phase was a mixture of water, acetonitrile and phosphoric acid (60:40:0.5%) isocratically delivered by a pump at a flowrate of 1 mL min⁻¹. The wavelength of the UV absorbance detector was 267.3 nm [7,19]. Under these conditions, retention time was 14.8 min.

3. Results and discussion

3.1. Photolytic ozonation of NB

Three experiments in the range 3–9 were performed to test the effect of pH in the photolytic ozonation of aqueous solutions of NB. The pH is an important variable in ozonation processes due to the catalytic action of the hydroxyl ion in the ozone decomposition [20]. One experiment was set at pH 3 acidified with H₃PO₄, one at pH 9 buffered with borax (0.01 M Na₂B₄O₇) and one at free pH (leaving the pH to evolve freely from 6 to 3). The ozone production was set at 7.4 g h⁻¹ and temperature at 25–27°C. The diminution of the normalized concentration of NB with time is shown in Fig. 2.

Best results are achieved at free pH and the reaction seems to be slightly inhibited at pH 9, although differences in the studied range are rather small. Experiments carried out with single ozonation (not shown) gave similar results. As the ozone decomposition into hydroxyl radicals increases with pH, these results would suggest that the direct ozonation may be the main pathway for NB degradation. However, if the concentration of ozone in the outlet gas vs. time is represented (Fig. 3), it can be observed that the ozone concentration decreases with pH, leading to the conclusion that hydroxyl radical formation by ozone decomposition is favored by pH, but this higher radical production is not translated into an increase in the degradation rate of this compound. This could be explained by the withdrawing character of the nitro group, which depletes the aromatic ring of electron density. The mechanism of the OH[•] radical

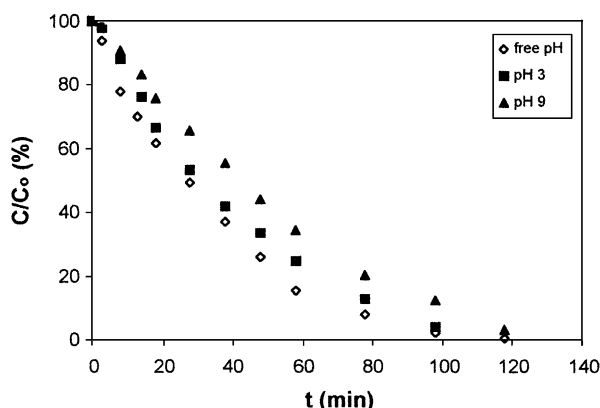


Fig. 2. Effect of pH in the photolytic ozonation of NB.

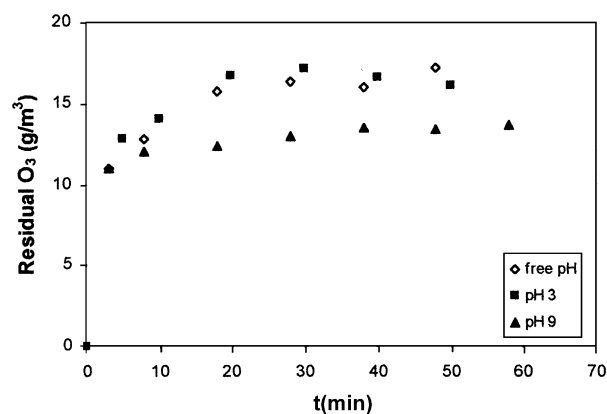


Fig. 3. Effect of pH in the ozone concentration in the residual gas in the combination O₃/UV.

on aromatic compounds is analogous to an electrophilic substitution, and this kind of substitution is retarded by electron-accepting substituents [4].

3.2. UV + Fe(III)-enhanced ozonation of NB

In previous studies [21], the degradation of NB by the combination UV/Fe(III) in a lab scale installation was investigated, finding that the NB degradation rate by the photolysis process was considerably improved by the addition of Fe(III). In this study, the effect of the addition of Fe(III) to the O₃/UV combination has been tested. Three experiments with 7.4 g h⁻¹ ozone production at free pH under UV irradiation were carried out by adding Fe(III) (as FeCl₃) at 3:1, 1:1 and 0.1:1 Fe(III)/NB molar ratio. The diminution of the normalized NB concentration is represented in Fig. 4, where it can be seen that the effect is rather inhibitory. But significant differences are observed with regard to TOC diminution (Fig. 5), where the addition of ferric ion improves the mineralization rate considerably. Small amounts of ferric ion are enough to observe its catalytic effect.

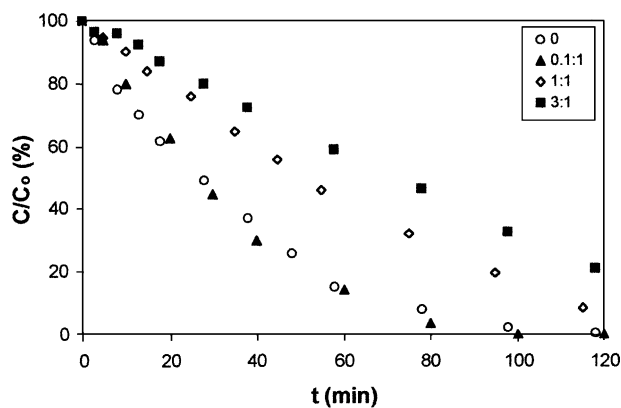


Fig. 4. Influence of the addition of Fe(III) in the combination O₃/UV/Fe(III) — Decrease of the normalized NB concentration.

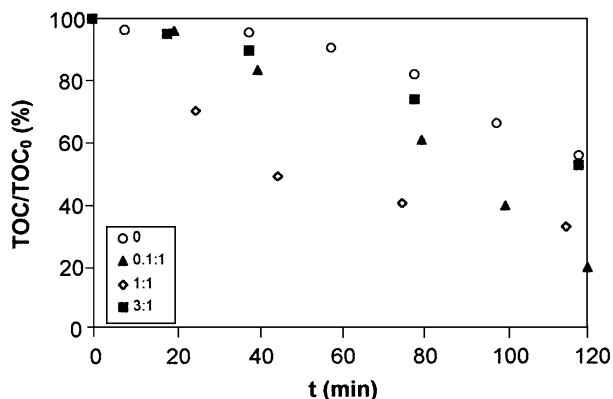


Fig. 5. Influence of the addition of Fe(III) in the combination O₃/UV/Fe(III) — Decrease of TOC.

Fe(III) species undergo a photoredox process with UV and near-UV light giving rise to Fe(II) and OH• radicals according to Eq. (3) [22,23]



where Fe(III) is mainly present as Fe(OH)²⁺ [24].

Besides this reaction, the initial oxidation of organic pollutants generates oxygenated intermediates (i.e. intermediates with carboxylic functional groups) which can react with Fe(III) and form complexes. These complexes are also photoactive and produce CO₂, organic radicals and ferrous ions on irradiation (Eq. (4)), contributing to the mineralization of these pollutants without the participation of hydroxyl radicals [22]:



In Figs. 6 and 7, the combinations O₃/UV and O₃/UV/Fe(III) are compared with single ozonation, with regard to TOC and COD decrease, respectively, for experiments performed at room temperature, free pH and a 7.4 g h⁻¹ ozone production. As for TOC diminution, no important differences are observed between single and photolytic ozonation, with a

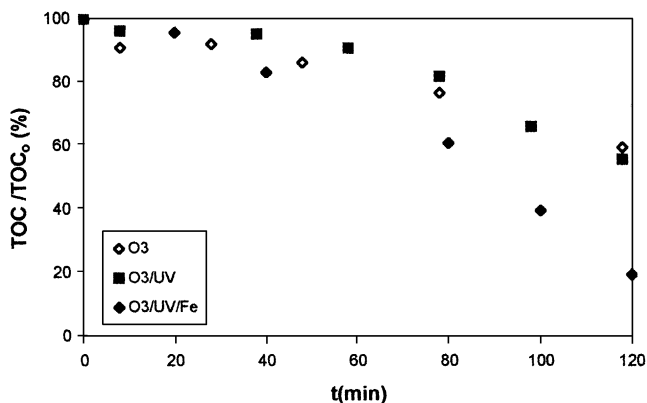


Fig. 6. TOC removal rate for the three oxidation processes.

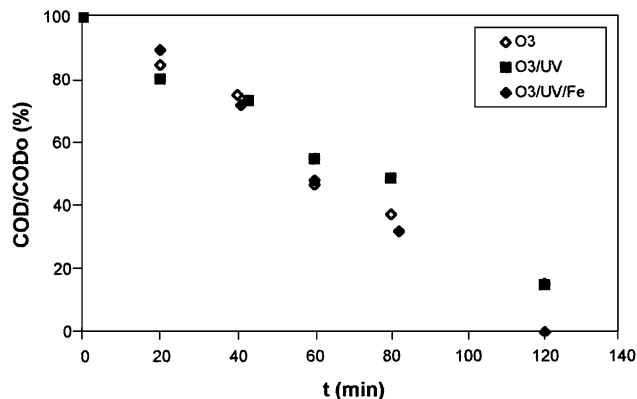


Fig. 7. COD diminution for the three oxidation processes.

40–45% of TOC diminution for both of them. This mineralization rate is greatly enhanced by the addition of ferric ion, achieving an 80% of mineralization with a 0.1:1 Fe(III)/NB molar ratio. Photodecarboxylation of ferric ion complexes (Eq. (4)), Fenton chemistry and photo-Fenton reaction of aqueous ferric ions with UV light (Eq. (3)) may account for this higher efficiency. As for COD diminution, differences are smaller, achieving an 85% of COD elimination after two hours with the single and photolytic ozonation and a 100% with the UV/Fe(III)-enhanced ozonation.

3.3. Intermediate products

The three nitrophenol isomers are identified by HPLC as the main intermediate products, as it has been reported by other authors [4,25]. With nitrophenols, mechanism would be similar to the ozonation of phenol [25 and references herein], leading to catechol, benzoquinone and hydroquinone, besides low molecular weight acids.

4. Conclusions

The principal conclusions extracted from the study of the oxidation of NB by the advanced oxidation processes O₃/UV and O₃/UV/Fe(III) are the following:

- The combination of ozone with UV radiation does not essentially improve the degradation and mineralization rate achieved by means of the single ozonation. The pH does not show a significant effect on the combination O₃/UV, although at basic pH the degradation rate is slightly inhibited, as was observed with single ozonation.
- The addition of Fe(III) accelerates the UV-enhanced ozonation of NB. The addition of ferric ion at low concentrations enhances the TOC removal rate, probably due to photodecarboxylation of ferric ion complexes, Fenton chemistry and photo-Fenton reaction of aqueous ferric ions with UV light.
- The three nitrophenols isomers were detected among the formed intermediates.

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