Influence of H_2O_2 and Fe(III) in the photodegradation of nitrobenzene

Miguel Rodríguez[a,b], Andreas Kirchner[c], Sandra Contreras[a], Esther Chamarro[a], Santiago Esplugas[a,*]

[a] *Departamento de Ingeniería Química y Metalúrgica de la Universidad de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Spain*
[b] *Facultad de Ingeniería de la Universidad de Los Andes, Mérida Venezuela*
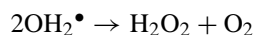[c] *Universidad de Leoben, Leoben, Austria*
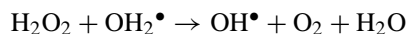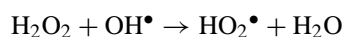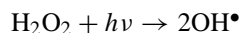
Abstract

The influence of H_2O_2 and Fe(III) in the degradation of nitrobenzene in aqueous solutions combined with UV radiation has been studied. A major efficiency is achieved when UV is combined with H_2O_2 or Fe(III). Likewise, H_2O_2 and Fe(III) concentration has an important effect on the degradation. Nitrophenol isomers are detected as the major intermediate products. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Ultraviolet radiation; Photochemical decomposition; Nitrobenzene; Hydrogen peroxide; Iron trichloride

1. Introduction

Aromatic compounds are widely used in explosives, pesticides and dyeings production. A lot of them, nitrobenzene and nitrophenols included are considered to be highly toxic. Nitrobenzene is resistant to oxidation by biological treatment, therefore, a chemical oxidation is needed [1]. Treatment of wastewater by chemical oxidation is an effective method to destroy pollutants. Reactions that produce hydroxyl radicals in solution at low temperature have an especial interest on the destruction of toxic organic compounds [2–4].

The combination of hydrogen peroxide and UV radiation is one of the easiest ways to produce hydroxyl radicals. The absorption of UV photons by hydrogen peroxide dissociate it into hydroxyl radicals which react rapidly and non-selectively with most organic compounds by H-abstraction or by addition to C–C unsaturated bonds. Main reactions that occur in the dissociation of hydrogen peroxide in the presence of UV radiation are [5]:

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O$$

$$H_2O_2 + OH_2^\bullet \rightarrow OH^\bullet + O_2 + H_2O$$

$$2OH_2^\bullet \rightarrow H_2O_2 + O_2$$

Otherwise, although the iron complexes species formation as a probably degradation cause is under discussion, Fe(III) solutions in presence of UV radiation constitutes a source of hydroxyl radical according to the reaction [4]:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^\bullet + H^+$$
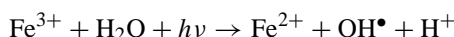
Additionally iron ions may give complexes with degradation compounds of nitrobenzene, which are able to be degraded by the UV radiation.

In the degradation of organic compounds, two ways are possible: complete mineralisation of the pollutant to CO_2 and H_2O, or obtaining more degradable intermediates. In the first case and in the degradation using UV/H_2O_2, it may be evaluated that at least 14.5 mol of H_2O_2 are needed in order to convert all the organic carbon and the hydrogen in CO_2 and H_2O, respectively. In order to save reagents, it could be interesting to explore the second possibility; degradation of nitrobenzene to nitrophenol isomers, followed by the conversion of them to more degradable products.

2. Materials and methods

2.1. Installation

The experiments were done in a tubular photoreactor, whose scheme is shown in Fig. 1. The photoreactor capacity is 5 l. It is equipped with four germicides low pressure mercury lamps, placed parallel to its axis. These lamps emit radiation basically at 253.7 nm and they are cooled by air.
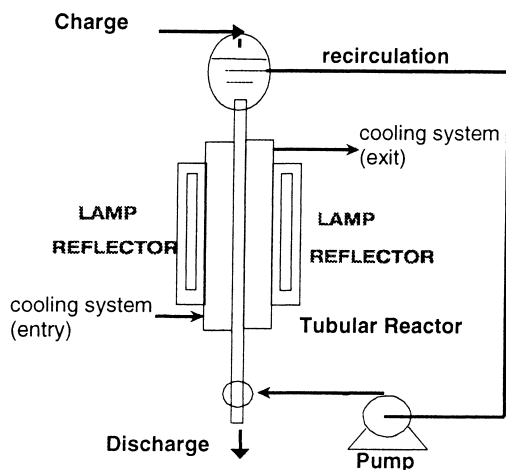
Fig. 1. Scheme of the pilot plant.

The nominal power is 15 W each one. The reaction zone consists of a cylindrical quartz tube, 100 cm in longitude, with an exterior diameter of 2.2 cm and an interior diameter of 1.85 cm. It is mounted within a quartz tube with a longitude of 48 cm, exterior diameter of 5.4 cm and interior diameter of 5.0 cm. Air circulates in the tubular space between the two tubes. The exit zone was designed to maintain a constant level by means of a spillway.

2.2. Reagents

Nitrobenzene (98%, PROBUS), H_2O_2 (33% p.a., PROBUS), $FeCl_3$ (98%, PROBUS), uranyl nitrate (98%, PANREAC), oxalic acid (99.5%, PANREAC), 2-nitrophenol (>99%, MERCK), 4-nitrophenol (>99%, MERCK), potassium permanganate (99%, PROBUS), acetonitrile (99.8%, isocratic grade for HPLC, MERCK), phosphoric acid (85%, PROBUS) and millipore water (Milli-Q Millipore system with a 18 $M\Omega \, cm^{-1}$ resistivity).

2.3. Analytical methods

Nitrobenzene concentration was determined by reverse-phase high performance liquid chromatography (HPLC). A Waters HPLC apparatus (photodiode array detector 996, autosampler 717, controller 600) using a Millennium Software was used. The reverse-phase column used was a Spherisorb ODS2. The mobile phase was a mixture of water, acetonitrile and phosphoric acid (60:40:0.5%) isocratically delivered by a pump at a flow rate of 1 ml min^{-1}. The wavelength of the UV absorbance detector was 267.3 nm [6,7]. Under these conditions, retention time was 14.5 min.

3. Experimental

Before the experiments were carried out, actinometry experiments based on the photochemical decomposition of oxalic acid in the presence of uranyl ion [8,9] were performed to determine the flux of radiation entering the reactor. For pH in the range of 3 and 7, and oxalic acid conversions lower than 20%, the reaction that takes place is:

$$UO^{2+} + H_2C_2O_4 \rightarrow UO^{2+} + CO + CO_2 + H_2O$$

For $\lambda = 254$ nm, the quantum yield of this system is equal to 0.6 mol Einstein^{-1}. It was found that the flux of radiation entering the reactor was 10.4 μEinstein s^{-1}.

The reactor was always charged with 2.5 l of an aqueous nitrobenzene solution, initial concentration 50 ppm (0.407 mmol l^{-1}) and initial pH (not buffered) between 6–6.5. H_2O_2–nitrobenzene and Fe(III)–nitrobenzene molar ratios were 1:1, 3:1 and 6:1. All experiments were carried out in a batch operation, with a recirculation flow rate of 100 l h^{-1}

4. Results and discussion

4.1. Calculation of quantum yield (Φ)

One initial experiment using UV radiation alone (Fig. 2, symbolised with points) and with an initial concentration of 50 ppm of nitrobenzene was made to evaluate the quantum yield for nitrobenzene degradation. The quantum yield is the number of molecules that react divided for the number of absorbed photons. It may be evaluated through the slope of the compound degradation rate at initial irradiation time and the absorption radiation rate. It is important to take into account that photoproducts from nitrobenzene absorb radiation and, in consequence, determination of quantum yield must be done at low conversions of nitrobenzene. At 253.7 nm, the absorbance of the aqueous solution was 5.2 cm^{-1}, and according to the geometry of the reactor and the actinometric result, the quantum yield at initial time was evaluated to be equal to $(6\pm0.5)\times10^{-3}$ mol Einstein^{-1}. This value is consistent with the one given by Beltrán [10], which was $(7\pm0.6)\times10^{-3}$ mol Einstein^{-1}.

4.2. Nitrobenzene oxidation by UV/H_2O_2 combination

To determine the influence of hydrogen peroxide in nitrobenzene photodegradation, experiments at different molar H_2O_2:nitrobenzene ratios were carried out.

The hydrogen peroxide effect is shown in Fig. 2, where variation of pollutant concentration (in %) versus irradiation time is represented. It can be seen, that a H_2O_2–UV combination is more effective that UV alone. The greater the H_2O_2 concentration is, the greater is the degradation obtained. Nitrobenzene is attacked either by UV photons flow or hydroxyl radicals generated in H_2O_2-photolysis. When the H_2O_2 concentration is increased, more hydroxyl radicals are available to attack the aromatic ring. Bibliography indicates that hydrogen peroxide may act as an 'scavenger'.
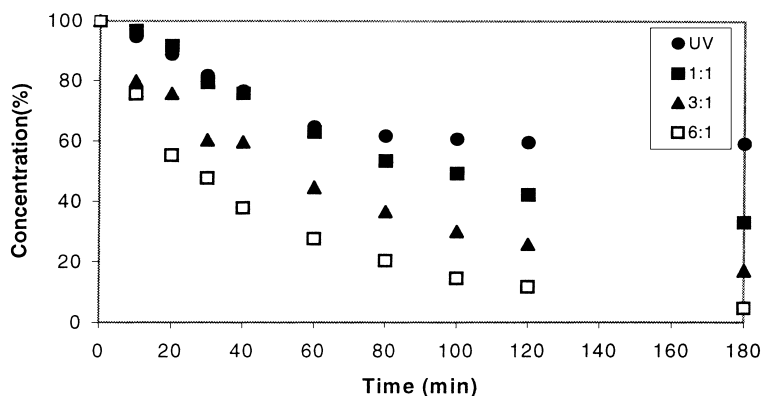
Fig. 2. Influence of H_2O_2 concentration in the photodegradation of nitrobenzene.

This would have given an optimal value for the hydrogen peroxide/nitrobenzene ratio. But in our experiments we do not see this effect, because of the low ratios used in the experiments.

4.3. Nitrobenzene oxidation by UV/Fe(III) combination

To determine the influence of Fe(III) in nitrobenzene photodegradation, experiments at different molar Fe(III): nitrobenzene ratios were carried out. The Fe(III) effect is illustrated in Fig. 3, where the variation of nitrobenzene concentration (in %) versus irradiation time is represented. As in the previous case, the Fe(III)/UV combination effectiveness is greater than with UV radiation. It can also be seen that the major percentage of degradation is obtained during the first 60 min. Initial pH of the solutions was 2.8 and during the experimentation, it was not appreciate any precipitate of iron hydroxides. The absorbance at 253.7 nm of a 100 ppm aqueous solution of $FeCl_3$ is $4.19\,cm^{-1}$.

In Figs. 4 and 5, the comparison of the two studied combinations in 1:1 and 3:1 molar ratio, respectively, is represented.

Under our experimental conditions ([Fe(III)$_0$]$>1.0\times10^{-4}$ mol l^{-1} and pH around 2.8), Fe(OH)$^{2+}$ is the predominant monomeric Fe(III) aqua-complex, as reported by Mazellier [11], due to the following equilibria:

$$Fe^{3+} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+$$
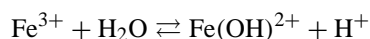
Fe(III) species undergo a photoredox process giving rise to Fe(II) and OH$^\bullet$ radicals according to [12]:

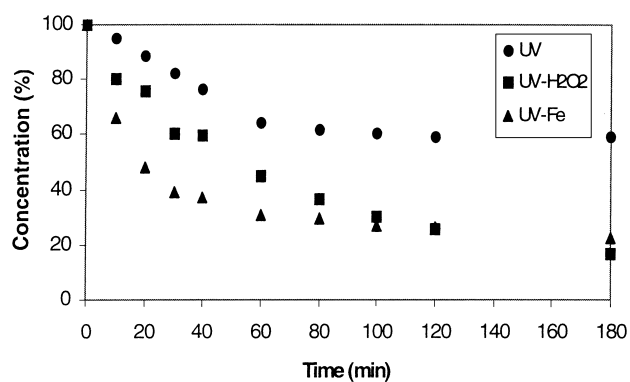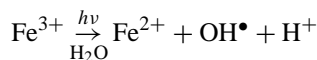$$Fe^{3+} \xrightarrow[H_2O]{h\nu} Fe^{2+} + OH^\bullet + H^+$$

Fig. 4. Efficiency of mixtures (UV/H_2O_2, UV/Fe(III)) in relation 3:1.
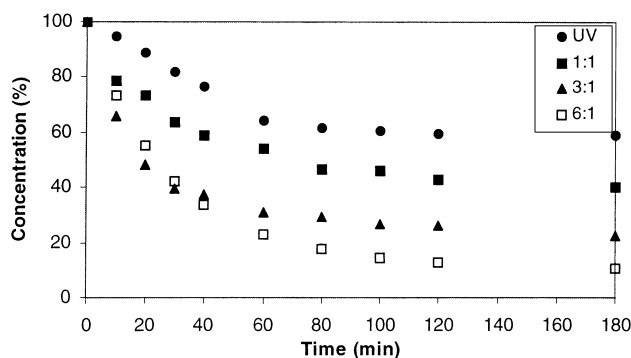

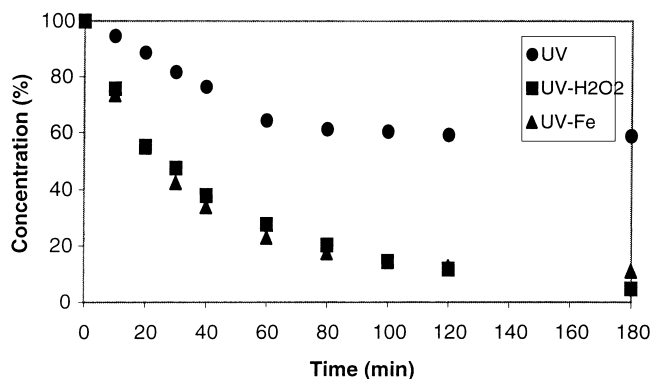Fig. 3. Influence of Fe(III) concentration in the photodegradation of nitrobenzene.

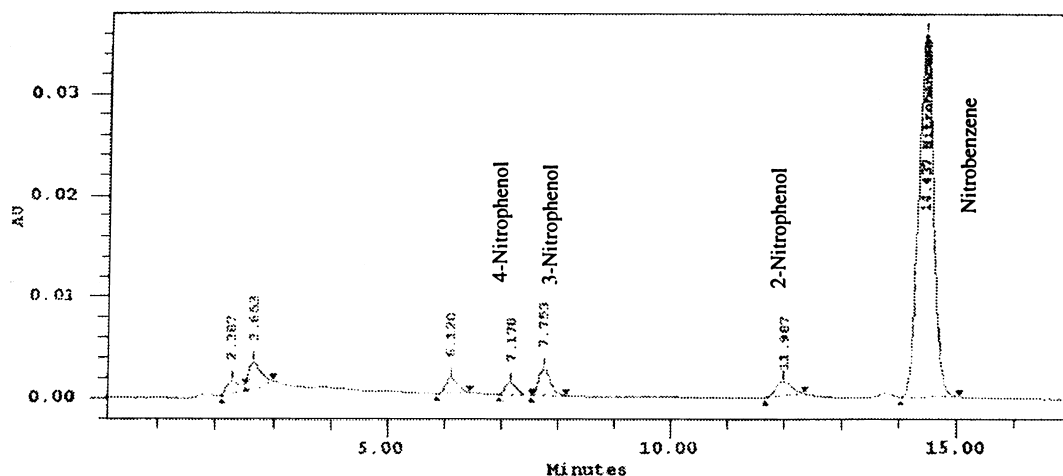Fig. 5. Efficiency of mixtures (UV/H_2O_2, UV/Fe(III)) in relation 6:1.

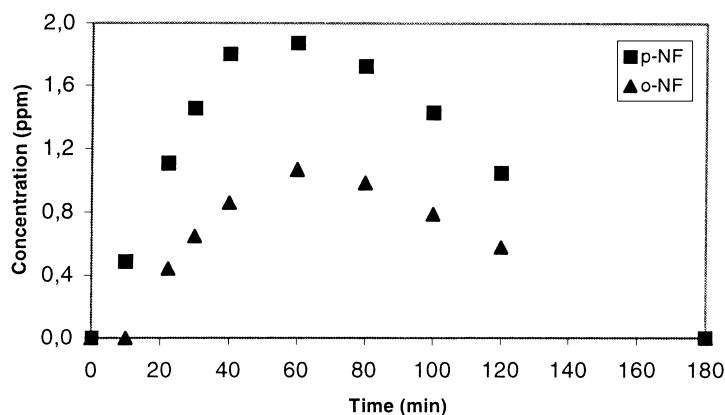Fig. 6. Chromatogram of the experiment H_2O_2–UV 6:1 at 60 min.

Fig. 7. Formation and degradation of intermediate products (ortho-, para-nitrophenol).

The redox potential of the couples Fe^{3+}/Fe^{2+} is 0.77 V (NHE). The simultaneous re-oxidation of Fe(II) into Fe(III) by oxygen as well as by appropriate products present in the solution confers an interesting catalytic aspect to the process [11]. Upon excitation of $Fe(OH)^{2+}$, $OH^\bullet$ radicals are the only oxidising species generated and these radicals are responsible for the degradation of NB.

To achieve levels of permitted pollutant concentration in treated wastewater, the combination of H_2O_2/UV is needed, because it is more effective that the combination of Fe(III)/UV. As it can be seen in Figs. 4 and 5, the effect of Fe(III) stops after 2 h of treatment, approximately.

4.4. Intermediate products

The presence of the three nitrophenol isomers was identified besides other by-products, as can be observed in the chromatogram (Fig. 6). These intermediates have been also reported by other authors [6,11]. The concentration of the ortho- and para-nitrophenol isomers versus time has been followed in the experiment H_2O_2–UV with a 6:1 molar ratio (Fig. 7). It was found that both of them reached a maximum of concentration at 60 min of treatment, which led to a total degradation in a 3 h treatment.

5. Conclusions

The combination of hydrogen peroxide or Fe(III) with UV radiation was found to be more effective than the application of only UV radiation in the degradation of the pollutant.

Among the studied combinations, the use of UV–H_2O_2 was the most effective one. In the range of 1–6 molar ratios of hydrogen peroxide/nitrobenzene, increasing the concentration of hydrogen peroxide more degradation was obtained.

Although 1 h of treatment was found to be sufficient to degrade the major part of nitrobenzene, it would be neces-

sary to continue the treatment during longer periods of time, to obtain a total degradation of nitrobenzene and the nitro-phenol isomers formed as intermediate products.

The fastest degradation occurred in the usage of the 6:1 molar ratio, which leads to a degradation velocity of $1.578\,\mathrm{mmol\,h^{-1}}$ for the H_2O_2–UV combination and $0.81\,\mathrm{mmol\,h^{-1}}$ in the case of Fe(III)–UV combination.

6. Nomenclature

NB   nitrobenzene
NF   nitrophenol

Greek letters
Φ quantum yield (mol Einstein^{-1})
λ wavelength (nm)

Subscript
o   initial conditions for the aqueous solution

Acknowledgements

References

[1] E. Lipczynska-Kochany, Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction, Chemosphere 22 (1991) 529–536.

[2] W.H. Glaze, G.R. Peyton, S. Lins, F.Y. Huang, J.L. Burleson, Destruction of pollutants in water with ozone in combination with ultraviolet radiation, Environ. Sci. Technol. 16 (1982) 454–461.

[3] S. Esplugas, P.L. Yue, M.I. Pervez, Degradation of 4-chlorophenol by photolytic oxidation, Wat. Res. 28 (1994) 1323–1328.

[4] W. Spacek, R. Bauer, Heterogeneous and homogeneous wastewater treatment — comparison between photodegradation with TiO_2 and the photo-Fenton reaction, Chemosphere 30 (1995) 477–484.

[5] F.J. Beltrán, M. González, P. Álvarez, Tratamiento de aguas mediante oxidación avanzada (II), Ingeniería Química 331 (1997) 161–168.

[6] E. Lipczynska-Kochany, Degradation of nitrobenzene and nitrophenols by means of advanced oxidation processes in a homogeneous phase: photolysis in the presence of hydrogen peroxide versus the Fenton reaction, Chemosphere 24 (1992) 1369–1380.

[7] E.L. Lin, L.W. Chang, M.K. Smith, F.B. Daniel, Separation and quantitation of nitrobenzenes and their reduction products nitroanilines and phenylenediamines by reversed-phase HPLC, J. Chromatogr. A 665 (1993) 331–335.

[8] D.H. Volman, J.R. Seed, The photochemistry of uranyl oxalate, J. Am. Chem. Soc. 86 (1964) 5095–5098.

[9] L.J. Heidt, G.W. Tregay, F.A. Middleton, Influence of the pH upon the photolysis of the uranyl oxalate actinometer system, J. Phys. Chem. 74 (1979) 1876–1882.

[10] F.J. Beltrán, J.M. Encinar, M.A. Alonso, Nitroaromatic hydrocarbon ozonation in water. 2. Combined ozonation with hydrogen peroxide or UV radiation., Ind. Eng. Chem. Res. 37 (1998) 32–40.

[11] P. Mazellier, M. Sarakha, M. Bolte, Primary mechanism for the iron(III) photoinduced degradation of 4-chlorophenol in aqueous solution, New J. Chem. 23 (2) (1999) 133–135.

[12] P. Mazellier, G. Mailhot, M. Bolte, Photochemical behaviour of the iron(III)/2,6-dimethylphenol system, New J. Chem. 21 (3) (1997) 389–397.