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Heterogeneous photocatalytic degradation of nitrophenols

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Abstract

The photocatalytic degradation of 2-, 3- and 4-nitrophenol has been investigated in oxygenated aqueous suspensions containing TiO_2. The organic reaction intermediates have been determined by high performance liquid chromatography.

The results indicate the complete mineralisation of the substrates and the formation of both nitrate and ammonium ions. The degradation pathways involve a rapid opening of the aromatic ring followed by a slower oxidation of the aliphatic compounds. The hydroxyl radicals are responsible for the primary attack of the nitrophenols with formation of dihydroxynitrobenzenes. The ring hydroxylation occurs in the positions activated by the contemporaneous presence of phenolic and nitro groups. The presence of ammonium ions confirms that reduction pathways are also operating.

Keywords: Photocatalytic degradation; Nitrophenols; Titanium dioxide

1. Introduction

The pollution of drinking water reservoirs and aquatic environment by chemicals is a dramatic problem of these last years. Nitrophenols are some of the most refractory substances present in industrial wastewaters because of their high stability and solubility in water. They are considered priority toxic pollutants by the United States Environmental Protection Agency [1] and the maximum allowed concentrations range from 1 to 20 ppb [2]. Nitrophenols are involved in the synthesis of many products and appear in the degradation of pesticides like parathion [3] and nitrofen [4].

The purification of wastewaters contaminated with these pollutants is very difficult since they are resistant to the traditional treatment techniques. A long periods of incubation is required for the microbial degradation of 4-nitrophenol [5].

Nitrophenols exposed to polychromatic light undergo photolysis in aqueous solutions [4,6] but the quantum yields are generally very low also if the solutions are irradiated with UV light [7–9]. The photochemical transformation of the nitrophenols results more efficient in the presence of nitrite or nitrate ions [10] due to the highly reactive hydroxyl radicals formed by excitation of NO_2^- and NO_3^-. Ultrasonic irradiation for the elimination of aqueous 4-nitrophenol has been also investigated [11].

Aqueous solutions of nitrophenols have been successfully degraded in the dark in the presence of the Fenton reagent ($FeCl_2/H_2O_2$) [12,13] and best results have been obtained if the solutions were illuminated during the treatment [13–15].

Heterogeneous photocatalysis is an alternative promising method for eliminating organic compounds from water [16–18]. Differently from the traditional methods, the photocatalytic processes often allow the complete mineralisation of the organic pollutants with the absence of dangerous residual intermediate compounds. Many works have investigated the photocatalytic degradation of the three isomeric nitrophenols in aqueous dispersions containing TiO_2 [19–28] or ZnO [8,20,22]. The papers have been principally concerned with the kinetics of degradation of the nitrophenols, studying the effects of pollutant concentration [19,21,25], pH [21,25], temperature [25], catalyst loading [21,25–27] and composition of the gas phase [21,25]. Only few papers have reported a certain identification of the main reaction intermediates obtained during the photodegradation of nitrophenols [7–10,14,23]. Radiolytic techniques have been employed to elucidate the radical reaction mechanisms [29].

In this paper, we have studied the photocatalytic degradation of aqueous solutions of 2-, 3- and 4-nitrophenol in the presence of aerated TiO_2 suspensions in order to establish the possible reaction pathways leading to the mineralisation

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of these compounds. Particular attention has been addressed to the identification and mechanistic formation of the primary attack intermediates whose presence has been only tentatively proposed in similar experiments.

2. Experimental details

2.1. Reagents

Reagent grade chemicals were purchased from BDH and were used without further purification. Some compounds were synthesised according to literature methods and used as standards for high performance liquid chromatographic analysis.

Nitrohydroquinone was obtained by Elbs persulphate oxidation of 2-nitrophenol [30]. 3-Nitrocatechol was prepared by nitration of catechol with nitric acid in ether [31]. After reaction, 3-nitrocatechol was separated from catechol by selective extraction with ether.

Degussa P25 titanium dioxide (BET area $= 50\,m^2\,g^{-1}$) was used as the photocatalyst.

2.2. Photoreactivity experiments

A 0.5 l batch cylindrical Pyrex reactor was used. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases, for sampling and for pH and temperature measurements. A 125 W medium pressure Hg lamp (Helios Italquartz) was immersed within the inner part of the photoreactor. The IR component of the incident beam as well as any radiation below 300 nm was eliminated by the circulation of cooling water through a Pyrex jacket surrounding the lamp. The photon flux transmitted ($10.5\,mW\,cm^{-2}$) was measured by using a radiometer (UVX Digital) leaned against the external wall of the photoreactor containing only pure water.

Unbuffered solutions of nitrophenols were prepared by dissolving the pure compounds in water. The concentrations ranged from 0.1 to 1 mM. The amount of photocatalyst was $0.4\,g\,l^{-1}$ for all the runs. The reacting mixtures were magnetically stirred and oxygen was continuously bubbled into the suspensions before and during the irradiation. The temperature inside the reactor was about 313 K.

Samples for analysis (10 ml) were whithdrawn at fixed intervals from the reaction mixture. The catalyst was separated from the solution by filtration through a 0.45 μm cellulose acetate membrane (HA, Millipore).

2.3. Analytical procedures

Qualitative and quantitative determinations of the initial substrates and reaction intermediates were carried out by high performance liquid chromatography (HPLC) by using a Varian 9010 chromatograph equipped with a Perkin-Elmer C 18 column. A mixture of methanol and an aqueous solution (5 mM) of phosphoric acid, 35:65 v/v, was used as eluant. The products were identified by comparison with standards. The detection wavelength was 210 nm.

The mineralisation of the substrate was monitored by determining the total organic carbon (TOC) with a Carlo Erba TCM 480 analyser.

The inorganic nitrogen species were determined by ion chromatography using a Metrhom 761 Compact IC instrument. For anion analysis a Metrosep Anion Dual 1 column was used and a $NaHCO_3/Na_2CO_3$ eluent (2.5 mM in each component). A Metrosep Cation 1–2 column was used for ammonium analysis with a 4 mM tartaric acid/1 mM dipicolinic acid eluent. A flow rate of $0.5\,ml\,min^{-1}$ was maintained during the analyses.

3. Results

Fig. 1 shows the photocatalytic disappearance of the three isomeric nitrophenols as a function of the irradiation time. The progress of the reactions was followed from the decrease in the substrate HPLC peak.

The degradation results substantially confirm those obtained in previous investigations [19,21]. The photocatalytic reactions exhibited pseudo-first-order kinetics with respect to the organic concentration. The rate constants were determined by linear regression of the data over the first 75 min of reaction. Table 1 lists the values of the rate constants obtained at three different concentrations of 2-, 3- and 4-nitrophenol.

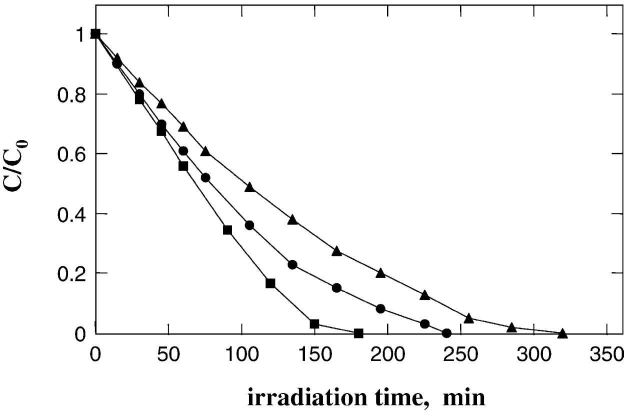


Fig. 1. Photocatalytic degradation of nitrophenols (0.5 mM) on TiO_2 ($4\,g\,l^{-1}$): (■) 4-nitrophenol, (▲) 3-nitrophenol, (●) 2-nitrophenol.

Table 1
Values of the rate constants, k (in min^{-1}) as a function of the initial concentrations of nitrophenols

Concentration (mM)	2-Nitrophenol	3-Nitrophenol	4-Nitrophenol
0.3	1.0×10^{-2}	8.7×10^{-3}	1.2×10^{-2}
0.5	6.3×10^{-3}	5.3×10^{-3}	7.1×10^{-3}
1	2.7×10^{-3}	2.5×10^{-3}	4.4×10^{-3}

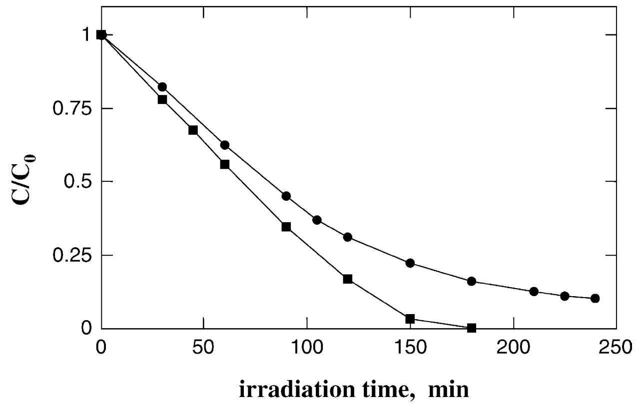


Fig. 2. Photocatalytic degradation of 4-nitrophenol (0.5 mM) and relative variation of the total organic carbon: (■) 4-nitrophenol, (●) TOC.

Fig. 2 shows the variation of the total organic carbon during the degradation of 4-nitrophenol. The initial rate of mineralisation was not much different from the rate of disappearance of the substrate but 4-nitrophenol totally disappeared within 3 h, while the complete removal of TOC occurred after more than 6 h.

Nitrite ions appeared in the early stages of the degradation process of the nitrophenols. The nitrite concentration increased rapidly until a maximum value but disappeared with subsequent irradiation. Fig. 3 shows the evolution of the nitrogen containing inorganic species during the photodegradation of a solution of 3-nitrophenol. Nitrate accumulated throughout the reaction period and reached approximately 70–75% of the corresponding quantity of initial organic nitrogen. Ammonium ions accounted for the remaining nitrogen species.

pH decreased as the photocatalytic transformation of the nitrophenols proceeded, due to the formation of HNO_3. Fig. 4 shows the variation of pH observed during the degradation of a 1 mM solution of 2-nitrophenol. Similar results were obtained with the other two isomers.

Chromatographic analysis of the solutions after different irradiation times revealed the presence of several intermediates. Fig. 5 shows the HPLC chromatogram of a 1 mM solution of 3-nitrophenol irradiated for 195 min. Products A, B and C were identified as 4-nitrocathecol, nitrohydroquinone and 3-nitrocathecol, respectively. In the case of the other two isomers the main intermediates were: nitrohydroquinone and 3-nitrocathecol for 2-nitrophenol, hydroquinone and 4-nitrocathecol for 4-nitrophenol. Unidentified organic species are likely to be aliphatic compounds.

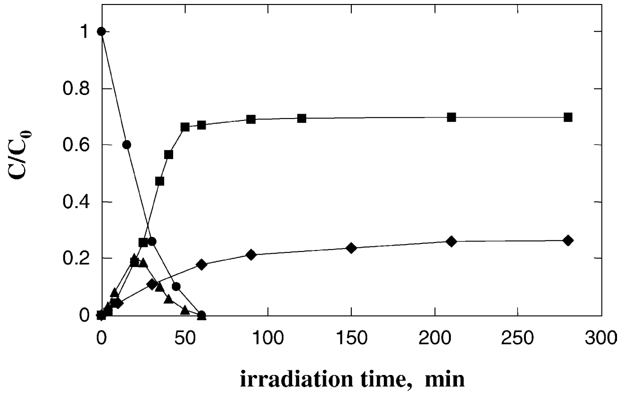


Fig. 3. Photocatalytic degradation of 3-nitrophenol (0.1 mM) and time evolution of the nitrogen containing inorganic species: (●) 3-nitrophenol, (■) $NO_3{}^-$, (▲) $NO_2{}^-$, (◆) $NH_4{}^+$.

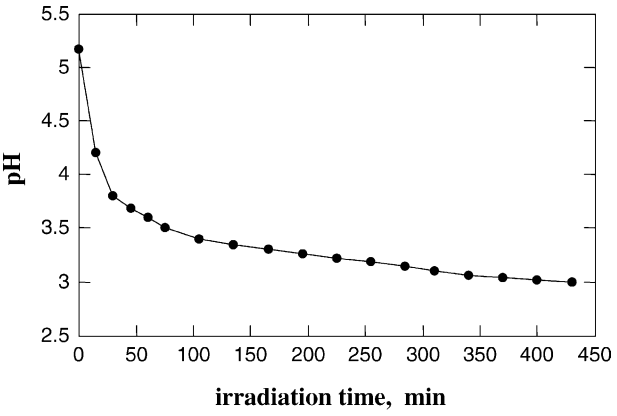


Fig. 4. Variation of pH during the photocatalytic degradation of 2-nitrophenol (1 mM).

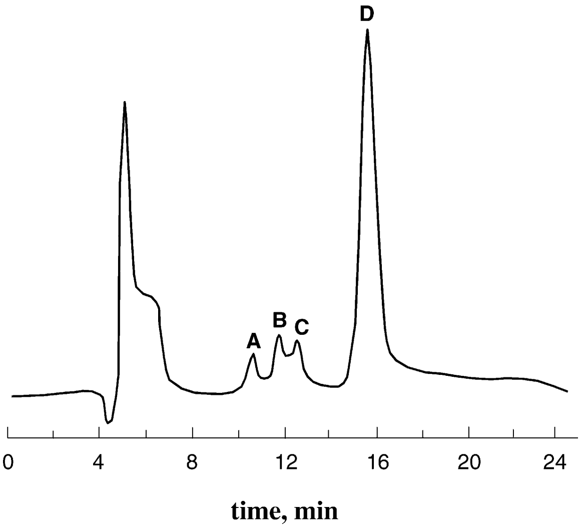


Fig. 5. HPLC chromatogram of a solution of 3-nitrophenol (1 mM) after 195 min of irradiation: (A) 4-nitrocathecol; (B) nitrohydroquinone; (C) 3-nitrocathecol; (D) 3-nitrophenol.

Table 2
Dihydroxynitrobenzenes identified in the photocatalytic degradation of nitrophenols

2-Nitrophenol	3-Nitrocatechol (1,2-dihydroxy-3-nitrobenzene) Nitrohydroquinone (1,4-dihydroxy-2-nitrobenzene)
3-Nitrophenol	3-Nitrocatechol (1,2-dihydroxy-3-nitrobenzene) 4-Nitrocatechol (1,2-dihydroxy-4-nitrobenzene) Nitrohydroquinone (1,4-dihydroxy-2-nitrobenzene)
4-Nitrophenol	4-Nitrocatechol (1,2-dihydroxy-4-nitrobenzene)

The dihydroxynitrobenzene intermediates formed during the photocatalytic degradation of the three nitrophenols are reported in Table 2.

4. Discussion

Irradiation of TiO_2 with photons having ultraband gap energy causes the promotion of valence band electrons to the conduction band of the semiconductor and the creation of positive holes in the valence band:

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}. \quad (1)$$

The electrons and holes thus separated migrate to the surface of the particles where they can either recombine or participate in interfacial oxidation and reduction reactions.

In aerated aqueous solutions, the photocatalytic oxidation of an organic pollutant has been attributed to the reaction of the positive holes with adsorbed water or hydroxyl groups, followed by the formation of hydroxyl radicals ($^\bullet OH$) which then react with the pollutant [32]:

$$H_2O + h^+_{vb} \rightarrow {}^\bullet OH + H^+ \quad (2)$$

$$OH^- + h^+_{vb} \rightarrow {}^\bullet OH. \quad (3)$$

According to Okamoto et al. [33] oxygen is the primary acceptor of the conduction band electrons with formation of $^\bullet O_2{}^-$:

$$O_2 + e^-_{cb} \rightarrow {}^\bullet O_2{}^-. \quad (4)$$

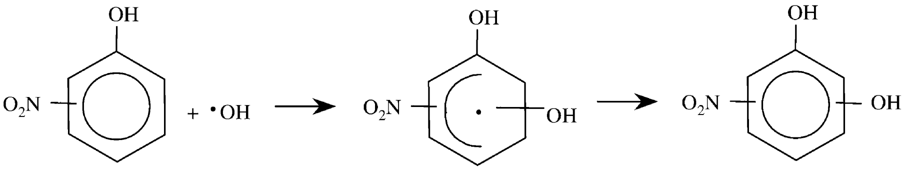
The superoxide species is unstable and reactive. Hydroxyl radicals can be also generated by the following chain reactions:

$$^\bullet O_2{}^- + H_2O \rightarrow OH^- + {}^\bullet HO_2 \quad (5)$$

$$^\bullet HO_2 + {}^\bullet HO_2 \rightarrow H_2O_2 + O_2 \quad (6)$$

$$H_2O_2 + {}^\bullet O_2{}^- \rightarrow {}^\bullet OH + OH^- + O_2. \quad (7)$$

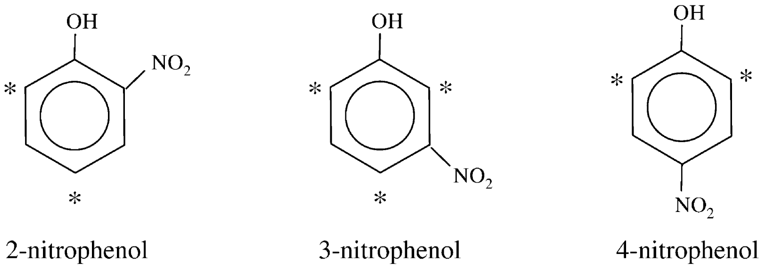
The photodegradation of the nitrophenols seems to occur in two steps: a rapid one destroying the aromatic group, followed by a much slower oxidation of the aliphatic chains. The hydroxylation of the aromatic ring is the most important process. The first stage of the photodegradation implies the addition of $^\bullet OH$ to the benzene ring to yield dihydroxynitrobenzene isomers [10,19,23,28], through formation of dihydroxynitrocyclohexadienyl radicals:



(8)

The hydroxyl radicals are also indicated as the actual oxidants in the degradation of aerated aqueous solutions of 2- and 4-nitrophenol by means of the Fenton reaction [12,13].

The attack of the electrophilic radical $^\bullet OH$ occurs at the ring positions activated by the presence of the two substituents. The phenolic –OH group is electron-donating for the electrophilic aromatic substitution, while the $–NO_2$ group is electron-withdrawing. The electron-donating substituents increase the electron density at the *ortho* and *para* positions while the electron-withdrawing substituents are strongly deactivating and *meta* directing. When both the substituents (–OH and $–NO_2$) are present, the electrophilic attack will occur preferentially in *ortho* and *para* positions with respect to the –OH group [34]. The activated positions in the ring of the three nitrophenols are shown below:

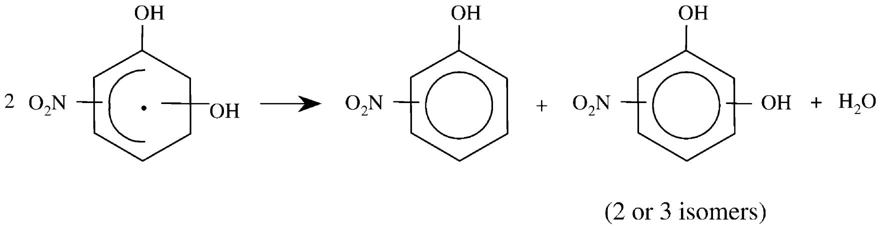


In the presence of 2- or 3-nitrophenol the $^\bullet OH$ radicals may enter in the *ortho* and *para* positions to form respectively 3-nitrocatechol and nitrohydroquinone or 3-nitrocatechol, 4-nitrocatechol and nitrohydroquinone. In the case of 4-nitrophenol only 4-nitrocatechol can be obtained. The examination of Table 2 reveals that the attack of the $^\bullet OH$ radicals follows the expected pattern of the electrophilic substitution.

It is not possible to distinguish whether the actual reaction occurs on the semiconducting surface or in solution. According to Turchi and Ollis [32], there are four possible mechanisms of $^\bullet OH$ attack to an organic reactant: an adsorbed $^\bullet OH$ radical may attack an adjacent adsorbed (i) or solution-phase molecule (ii), or the radical may diffuse away from its surface formation site and later react with an adsorbed (iii) or solution-phase molecule (iv). The kind of intermediates found in this work suggests that the reaction between hydroxyl radicals and nitrophenols mainly occurs in the solution phase, probably very close to the surface of the catalyst particles. Indeed, the distribution of the electronic density of the nitrophenol molecules is surely modified by the adsorption on the photocatalyst surface and consequently the presence of all the observed intermediates cannot be explained by taking into account only photoreactions involving adsorbed species. On the other hand, the same dihydroxynitrobenzenes of Table 2 were obtained by Alif and Boule [10] which studied the homogeneous phototransformation of the three nitrophenols induced by excitation of nitrite and nitrate ions. In that case the hydroxyl radicals were generated by photolysis of nitrite and nitrate ions. It should be mentioned that reactions among adsorbed species could play a major role in the degradation process after the occurrence of the first steps, due to an enhanced ability of the more hydroxylated species to be adsorbed.

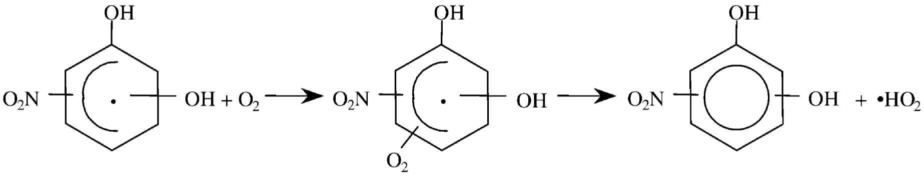
4-Nitrocatechol was identified during the photodegradation of 4-nitrophenol with TiO_2 suspensions [23] and this same intermediate was obtained by means of the Fenton reaction [12]. 3-Nitrocatechol, 4-nitrocatechol and nitrohydroquinone were found during the photocatalytic transformation of 3-nitrophenol in the presence of a suspension of ZnO [8] whereas 3-nitrocatechol and nitrohydroquinone were produced during the direct phototransformation of 2-nitrophenol in aqueous solutions [9]. The formation of dihydroxynitrobenzene isomers as intermediate compounds has been also verified by gas chromatographic and mass spectrometric analyses [19].

Cercek and Ebert [29] suggested that the dihydroxynitrocyclohexadienyl radical formed between •OH and 4-nitrophenol, disproportionates into 4-nitrophenol and 4-nitrocatechol. Alif and Boule [10] generalised this mechanism to the other nitrophenols, hypothesising that the corresponding dihydroxynitrocyclohexadienyl radicals of 2- and 3-nitrophenol disproportionate into two and three dihydroxynitrobenzene isomers, respectively:



(9)

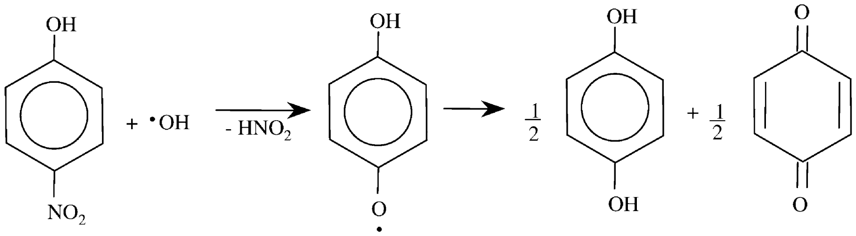
The dihydroxynitrobenzenes could be also formed by trapping of the cyclohexadienyl radicals with O_2, followed by elimination of $•HO_2$ [11,22]:



(10)

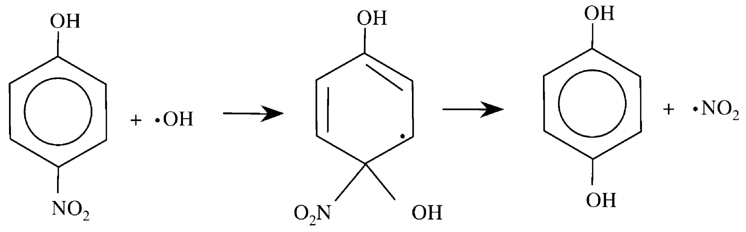
Hydroquinone was produced during the photodegradation of 4-nitrophenol. This result is in agreement with previous studies by Dieckmann and Gray [23], that identified hydroquinone as the primary product of the phototransformation of 4-nitrophenol via photocatalysis or by γ-radiolysis. Hydroquinone was also the main organic compound produced by UV irradiation [7]. Wang et al. identified hydroquinone and 1,4-benzoquinone for 4-nitrophenol but did not detect any intermediates for 2- and 3-nitrophenols [26].

The nitrogroup in nitroaromatics is a very good leaving group which can be easily eliminated, favouring the electrophilic substitution of the •OH radicals at the *para* position with respect to the hydroxyl group [6,23]. Suarez et al. [35] reported that the •OH radicals eliminate nitrous acid from 4-nitrophenol to yield 1,4-benzosemiquinone as an intermediate, which subsequently disproportionates into hydroquinone and 1,4-benzoquinone:



(11)

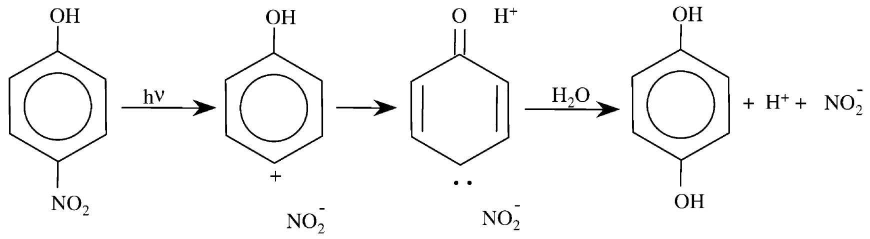
The possibility also exists of a direct attack of the hydroxyl radicals at the position carrying the nitrogroup with resultant hydroquinone formation.



(12)

Analogous reaction pathways could occur in the case of 2- and 3-nitrophenol but we did not elaborate any mechanistic hypothesis for the denitration of nitrophenols and dihydroxynitrobenzenes.

Alif et al. [7] suggested that hydroquinone can be formed through a heterolytic photohydrolysis of 4-nitrophenol, with formation of HNO_2:



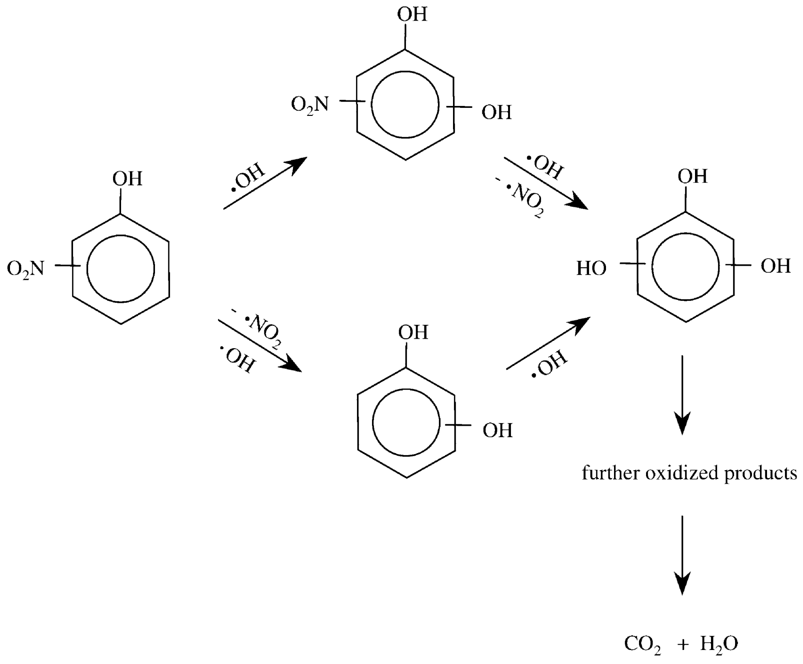
(13)

Anyway, the contribution of direct photolysis appears to be modest in the overall degradation process, due to the slow degradation of 4-nitrophenol in the absence of TiO_2 (only 3–5% of substrate was decomposed after 5 h of irradiation).

Further reactions of the primary intermediates with $^{\bullet}$OH radicals lead to benzene ring cleavage and formation of oxygenated aliphatic compounds. In the case of 4-nitrophenol, probably both hydroquinone and 4-nitrocatechol react before with $^{\bullet}$OH to form 1,2,4-trihydroxybenzene. This intermediate was detected only under not much oxidising conditions, i.e. by direct photocatalysis in absence of oxygen or by sensitised photocatalysis [23] and during the degradation of 4-nitrophenol by means of the Fenton reaction [14]. As suggested by Dieckmann and Gray [23], the ring cleavage in the presence of oxygen is so rapid such that no detectable amount of 1,2,4-trihydroxybenzene accumulates in the system.

Scheme 1 shows the reaction pathways proposed for the photocatalytic degradation of the nitrophenols.

$^{\bullet}$OH is the reaction initiator, yielding hydroxylated products through hydrogen abstraction and subsequent $^{\bullet}$OH addition or substitution to the formed radicals [23,24]. Oxygen, most likely, participates in the secondary phase of the



Scheme 1. Pathways proposed for the photocatalytic degradation of the nitrophenols.

oxidation and further degradation steps lead to mineralisation into carbon dioxide and nitric acid.

The aromatic intermediates detected in this work are similar to those observed in the γ-radiolysis or homogeneous photodegradation experiments confirming that the hydroxyl radical oxidation is the major reaction pathway [7–10,35].

The formation of inorganic nitrogen species is the result of the denitration of the nitrophenols. Nitrite is the main product formed at short reaction times. Results of radiation chemistry studies confirm that $^{\bullet}$OH reacts rapidly with 4-nitrophenol to produce 4-nitrocatechol, benzoquinone and NO_2^- [29,35]. The nitrite concentration quickly reaches a maximum and then decreases rapidly and vanishes, as already reported in previous investigations [23,26,28]. The fast disappearance of nitrite ions is in agreement with the results of Hori et al. [36], who found that nitrite is rapidly oxidised to nitrate by $^{\bullet}$OH radicals produced during the irradiation of aqueous suspensions of various semiconductor powders. Similar results were found by Kiwi for the degradation of 2- and 4-nitrophenol in the presence of H_2O_2 [13].

The addition of $^{\bullet}$OH radicals to the aromatic ring to yield dihydroxynitrobenzenes is a preferred process in comparison with the $^{\bullet}$OH-induced denitration (at $pH = 5$, only about 15% of the $^{\bullet}$OH radicals attack 4-nitrophenol to produce nitrite whereas the remaining $^{\bullet}$OH radicals react to form 4-nitrocatechol [11,34]). This justifies the low initial amount of nitrate ions found in the early stages of the degradation process due to the slow reaction of denitration of the aromatic ring.

Literature data show that the mass balance of the nitrogen containing inorganic species can be different according to the experimental conditions. Generally, nitrate does not account the total nitrogen available from the nitrophenols. Maurino et al. [28] reported that the quantity of nitrate ions reached approximately 70–80% of the total initial organic nitrogen whilst Augugliaro et al. [19] found 60–70% of nitrate at the end of the photodegradation runs. Wang et al. reported that nitrate was not more than 50% of the initial value of 2-nitrophenol at $pH = 7$ [26] and about 90% at $pH = 9$ [27]. The remaining percentages of inorganic nitrogen were usually due to the formation of ammonium ions [23,26,28].

The production of ammonium ions implies that, in the presence of oxygen, not only the oxidation but also the reduction of nitrophenols occurs. Maurino et al. [28] have reported that the direct reduction of the nitro group in nitrophenols can be an important degradation pathway, even in oxygenated solutions. This means that oxygen and nitrophenol compete for electrons as confirmed also by the presence of 4-aminophenol during the initial steps of degradation of 4-nitrophenol [28].

The reaction path leading to ammonia must involve the nitro group before it forms nitrate ions. Mahadavi et al. [38] have shown that the nitro group can be reduced to an amine group on the ring and then is released into the system as ammonia. pH appears the most important factor because the production of amine requires the presence of H^+. In basic solutions the concentration of H^+ is very small and this may hinder amine production as confirmed by the results obtained by Wang et al. at $pH = 9$ [27]. Similarly, Dieckmann and Gray [23] found that nitrate accounted for ca. 93% of the total denitration products of 4-nitrophenol at $pH = 8.5$, while ammonium ions only accounted for 7% of the total nitrogen.

As shown in Fig. 2, the continuous decrease of total organic carbon confirms the progressive mineralisation of the nitrophenols during the irradiation. The conversion into carbon dioxide is slower than the disappearance of the substrates, indicating that the intermediates are degraded less rapidly than the initial compounds. In particular, the fast removal of TOC observed in the beginning can be attributed to a rapid degradation of the cyclic intermediates while the final slowing down reflects a much slower mineralisation of the aliphatic intermediates originated by ring fission [13,22,28].

Table 1 shows that the rate of degradation of the three isomers decreased with increasing the substrate concentration. This behaviour is typical for the photocatalytic degradation of many organic compounds [17,37] and it has been attributed to the fact that the intermediate compounds deriving from the substrate oxidation compete with the same substrate for adsorption on the active sites. As already reported in previous investigation [19,21,25] the inverse dependence of the rate constants on the initial concentration of nitrophenol can be justified expressing the photodegradation rate by the Langmuir–Hinshelwood kinetics, hypothesising that the activation of the adsorbed organic molecule from radicals is the rate determining step.

The three isomers have revealed different photoreactivities in the order 4-nitrophenol > 2-nitrophenol > 3-nitrophenol [21], in agreement with the results of Dieckmann et al. [20]. Different orders of reactivity are reported in other works [19,26,28] but can be due to differences in the experimental conditions as the structure of the catalyst [19], the type of lamp [28], the pH [26] or the amount of oxygen present in the solution [19,28]. It is noteworthy that the photo-Fenton degradation of 4-nitrophenol proceeds faster than that of 2-nitrophenol [13].

As found previously [19–21], 3-nitrophenol was photooxidised with greater difficulty than 2- and 4-nitrophenol. The lower photoreactivity of this isomer has been previously attributed to a high stability of the surface species produced [19]. According to Dieckmann et al. [20], 4-nitrophenol and 2-nitrophenol have effective resonance structures whilst 3-nitrophenol, due to the position of the nitro group, cannot delocalise the charge. As a consequence, 4-nitrophenol and 2-nitrophenol are predicted to have fast degradation rate.

5. Conclusion

The photocatalytic degradation of 2-, 3- and 4-nitrophenol in oxygenated aqueous suspensions containing TiO_2 leads to the complete mineralisation of the substrates.

The formation of dihydroxynitrobenzene isomers, identified by HPLC, confirms that the hydroxyl radical oxidation is the major reaction pathway in the photocatalytic degradation of the three isomeric nitrophenols. Nitrite ions are formed in the early stages of the process, whereas nitrate and ammonium ions are present at the end of the degradation. The formation of ammonium ions implies that reductive pathways are also significant under the experimental conditions used in this work.

Acknowledgements

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