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Complete Destruction of *p*-Nitrophenol in Aqueous Medium by Electro-Fenton Method

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An indirect electrochemical method, which is very efficient for the degradation of organic pollutants in water, is described. The method, named electro-Fenton, is based on electrocatalytical generation of Fenton's reagent to produce hydroxyl radicals, which are very active toward organic compounds. An industrial pollutant, *p*-nitrophenol (PNP), was chosen for this study and was eventually mineralized. The major intermediary degradation products such as hydroquinone, benzoquinone, 4-nitrocatechol, 1,2,4-trihydroxybenzene and 3,4,5-trihydroxynitrobenzene were unequivocally identified by HPLC and GC-MS methods. The rate constants of the hydroxylation reactions were determined. The mineralization of the initial pollutant and the intermediates formed during electro-Fenton treatment was followed by total organic carbon (TOC) analyses. Dependence of mineralization on the amount of electrical energy consumed is shown by the relative decrease of TOC values. A mineralization reaction mechanism is proposed.

Introduction

Pollution of water and the environment by toxic and nonbiodegradable organic materials of industrial or agricultural origin, like pesticides, brings about very serious health hazards for all living species of the nature. The enormous diversity of pollutants of different chemical composition excludes the possibility of using an universal treatment method and led to the development of special treatment methods for water decontamination. Among the methods for water treatment are ozonation (*1*−*3*), UV-photodegradation using UV/H_2O_2, UV/TiO_2, and UV/H_2O_2/Fe^{3+} systems (*4*−*6*) and sensitized sunlight (*7, 8*). These so-called advanced oxidation processes (AOPs) (*9, 10*) have attracted an increasing scientific and technique attention during the last two decades. Their applicability has been experimentally verified by the oxidation of some model pollutants (*11, 12*). In recent years another wastewater treatment method, using electrochemically generated hydroxyl radicals, has been investigated (*13, 14*). Efficiency of the electrochemical techniques in water treatment was also demonstrated in heterogeneous electro-oxidation (*15, 16*) and indirect electro-reduction (*17*−*19*) studies. Since electrochemical techniques are more environmentally friendly than the chemical methods used in polluted water treatment, there is a need of improvement of such techniques.

Nitrophenols are among the most common organics of toxic persistent pollutants in industrial and agricultural wastewater (*20*−*22*). They are considered to be hazardous wastes and priority toxic pollutants by U. S. Environmental Protection Agency (EPA) (*23a*). They are present in industrial effluents of chemical plants producing pesticides, explosives, dyestuffs, and products for leather treatment and in the agricultural irrigation effluents. Moreover, they were also found in rainwater, in Germany, in concentrations up to 170 nM which are formed in the troposphere by the interaction of monoaromatic chemicals with nitrogen oxides and ozone (*23b*).

Purification of wastewater polluted with *p*-nitrophenol (PNP) is a very difficult task. The presence of a nitro group in the aromatic ring enhances the stability to chemical and biological degradation. These pollutants are unaffected by aerobic biodegradation (*24*), while the anaerobic degradation produces nitroso and hydroxylamines compounds which are known as carcinogenic (*25*). The kinetics of *p*-nitrophenol (PNP) ozonolysis depends on the pH of the medium and on partial pressure of ozone (*26*). The direct photolysis is very slow and inefficient (*27*), while the photolysis using UV+H_2O_2 (*28*), UV+H_2O_2+Fe^{3+} (photo-Fenton) (*29, 30*) or UV+H_2O_2+TiO_2 in suspension as catalyst (photo catalysis) (*31, 32*) brings satisfactory results, but they necessitate addition of chemicals.

The destruction of PNP in aqueous medium by electro-Fenton method, presented in this study, is a scientific effort to develop an environmentally friendly and efficient method for water treatment. This method is based on the oxidation of the substrate by hydroxyl radicals generated in situ in an electrochemically induced Fenton reaction. The Fenton's reagent (mixture of $H_2O_2 + Fe^{2+}$) to produce hydroxyl radicals is formed in a catalytic manner by electrochemistry.

Experimental Section

Chemicals and Standard Materials. *p*-Nitrophenol (Sigma, reagent grade, CAS: 100-02-7) and 4-nitrocatechol (Acros, reagent grade, CAS: 3316-09-4) were used without further purification. Hydroquinone (CAS: 123-31-9), benzoquinone (CAS: 106-51-4), 1,2,4-trihydroxybenzene (CAS: 533-73-3), 4-nitropyrogallol (3,4,5 trihydroxynitrobenzene, CAS: 87-66-1), iron(III) chloride hexahydrate (CAS: 10025-77-1) and salicylic acid (CAS: 69-72-7) were purchased in the highest purity available from Aldrich. All these chemicals were used without any further purification. Deionized water used for the preparation of solutions and HPLC eluents was obtained from a Milllipore Milli RO6 system, with a conductivity lower than 4×10^{-6} S.cm^{-1}. Methanol (chromanorm grade, CAS: 67-56-1), acetic acid (chromanorm grade, CAS: 64-19-7), and ethyl acetate (pestinorm grade, CAS: 141-78-6) were supplied by Prolabo. The pressurized oxygen gas (99.99%) to saturate the solutions was obtained from Carboxyque.

Electrochemistry. A potentiostat-galvanostat EG&G, model 273A, was used for electrolyses and for measurements of consumed electrical charge. Electrolyses were carried out in a divided three-electrode electrochemical cell (Figure 1). The working electrode (WE) was a 15 cm^2 carbon felt (Carbon-Lorraine), and the counter electrode (CE) was a platinum

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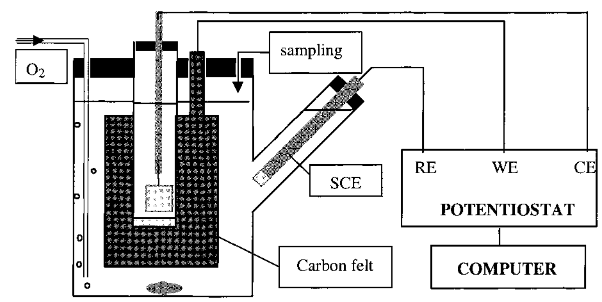


FIGURE 1. Schematic setup of the electrochemical cell used for electrolysis. R: reference electrode; WE: working electrode; CE: counter electrode.

grid (Goodfellow), placed in the anodic compartment containing a 0.01 M aqueous HCl solution. The anodic compartment was separated from the cathodic compartment by a glass frit of porosity 5. The reference electrode (RE) was a saturated calomel electrode (SCE), from Radiometer. The RE and WE were placed in the cathodic compartment, which has a volume of 150 cm^3. The electrolyzer is also equipped with a magnetic stirrer.

High Performance Liquid Chromatography. Progress of all reactions and product distribution was monitored by high performance liquid chromatography (HPLC). Analyses was achieved by a Gilson HPLC system equipped with a model 118 UV/Vis detector and a reverse phase hypersil C-18 column (250 mm × 4,6 mm i. d., 5 μm particle size). The column was eluted with a mixture water-methanol-acetic acid 65:33:2 v/v with a flow rate of 0.5 mL/min. The detection was performed by UV absorption at 280 nm.

Gas Chromatography−Mass Spectrometry. The decay of PNP and evolution of its hydroxylated derivatives were also monitored by gas chromatography−mass spectrometry (GC-MS). Analyses were performed on a Carlo Erba Instrument (QMD 1000). The GC column used was a Quadrex fused-silica capillary column (30 m × 0.53 mm ID × 0.25 μm film) with a 80% methyl-20% phenyl polysiloxane stationary phase. The temperature of the injector was kept at 250 °C. Electron impact (EI) mode at 70 eV was used.

Total Organic Carbon (TOC) Analysis. TOC analysis of initial and electro-Fenton treated aqueous PNP solutions were carried out by Analytik Jena Laboratory using an IDC Micro N/C TOC analyzer equipped with an automatic sample injector and a platinum based catalyst. The carrier gas was pure oxygen at a rate of 12 dm^3/h. The detector was an infrared NDIR. The samples were acidified to $pH < 4.0$ before to be sent to Jena Analytic Laboratory GmbH for analysis.

Procedure. All the solutions were prepared with water at mM concentrations. The solutions prepared for electrolysis were adjusted to pH 2.0 by addition of concentrated HCl, a catalytic amount of ferric chloride (to reach 0.5 mM Fe^{3+}) was added, and then they were saturated with oxygen by bubbling oxygen for 5 min before starting the electrolysis. The working electrode potential was adjusted at −0.5 V/ECS; the electric current (mA) and the amount of electrical charge (C) were continuously checked and registered during the electrolysis.

The kinetic study was done by carrying out a competition reaction between the substrate and salicylic acid as internal standard, for which the absolute rate constant of reaction with hydroxyl radicals is well-known (*33*). Hydroxyl radicals were formed in situ by electrochemistry in the presence of substrate (1.0 mM) and salicylic acid (1.0 mM). Concentration change of substrate and reference (salicylic acid) during the electrolysis was continuously followed by HPLC analysis. Also the relative rate constants of hydroxylation of substrates have determined by comparison with those of salicylic acid. For the kinetic study, the process was stopped after 5 coulombs have passed through the electrolysis cell, while for the experiments aimed to destroy the PNP, the electrolyses were carried up to 1500 C. The reaction mixtures were sampled continuously. Volume of the samples injected to HPLC was 20 μL.

Standard curves have been prepared for quantitative determination of PNP and intermediary products formed during electro-Fenton process. Standard solutions containing authentic expected products were used for qualitative identification of the intermediates in the electrolysis mixture. Identification was achieved by comparison of retention times and also by using them as internal reference, directly injected into samples taken from the electrolysis.

Preparation of samples for qualitative identification of the reaction products present in the electrolyzed solutions was carried out as follows: first the reaction time was chosen, so that the HPLC chromatogram will show an optimum presence of the relevant peak(s) that should be identified; then the reaction mixture was extracted 3 times with ethyl acetate. The extract was dried over anhydrous sodium sulfate, filtered, and concentrated in a rotavapor to 2 mL, and 1−2 μL was injected in the capillary column. The GC-MS temperature program was as follows: the temperature was held at 50 °C for 5 min and then increased at a rate of 5 °C/min up to a temperature of 250 °C which was maintained for 15 min.

Results and Discussions

Hydroxyl Radical Production. At the cathodic potential of −0.50 V/SCE applied to carbon felt WE, reduction of the molecular oxygen, dissolved in the aqueous solution, takes place. In the acidified medium, this reduction leads to the formation of hydrogen peroxide, H_2O_2, (*34*):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E° = 0.69\ \mathrm{V/NHE} \tag{1}$$

Hydrogen peroxide formed electrochemically at the WE surface diffuses into solution and reacts with ferrous ions present in solution, according to Fenton's reaction:

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O + \mathbf{OH^{\cdot}} \tag{2}$$

Ferric ions produced above are also reducible on the WE at the same applied potential to reduce molecular oxygen:

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E° = 0.77\ \mathrm{V/NHE} \tag{3}$$

Ferrous ions consumed by Fenton's reaction in homogeneous medium are regenerated in this way electrochemically on the cathode (eq 3). On the other hand, molecular oxygen necessary to form H_2O_2 (eq 1) which participated in the hydroxyl radical formation (eq 2) is also produced at anodic compartment by simply oxidation of water:

$$H_2O \rightleftharpoons 1/2O_2 + 2H^+ + 2e^- \quad E° = 1.23\ \mathrm{V/NHE} \tag{4}$$

The sum of the above cathodic and anodic processes (by elimination of the electrons) gives the overall equation

$$1/2O_2 + H_2O \rightarrow 2\mathbf{OH^{\cdot}} \tag{5}$$

which clearly shows the catalytic character of the electro-Fenton method (*19*).

Analyses of Degradation Products. The HPLC chromatograms (Figure 2) of the samples, taken from the electrochemical reactor during the electro-Fenton process, shows the disappearance of PNP and formation of its degradation products peaks, which also disappear after reaching a maximum concentration. By comparison of the retention times (t_R, in min) of the peaks in the above

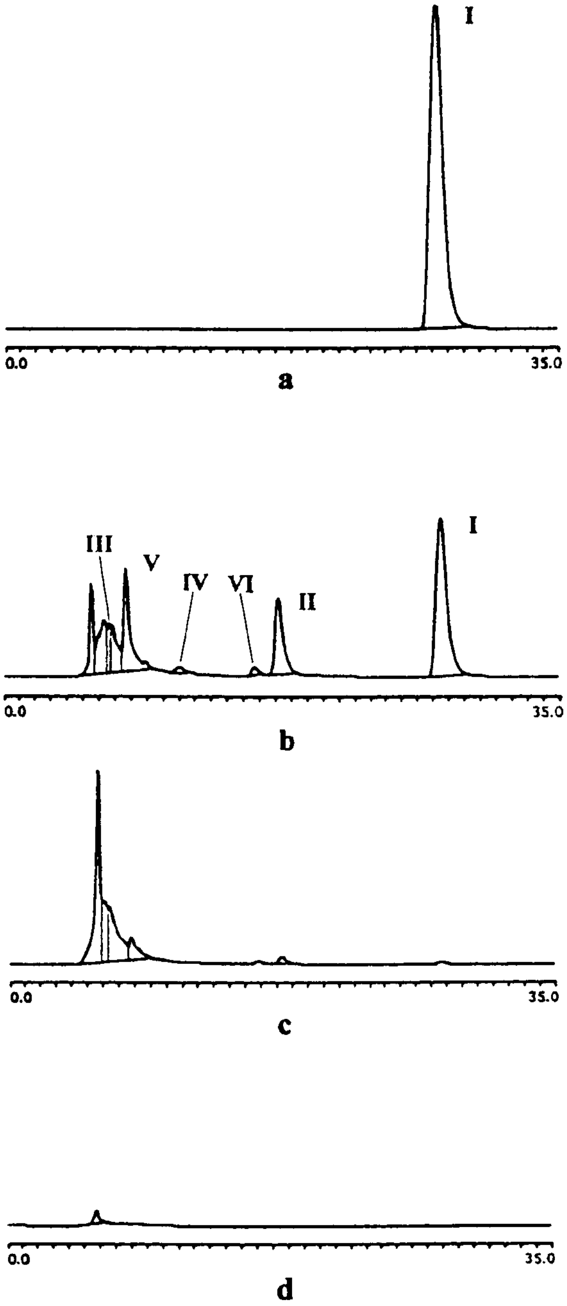
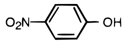
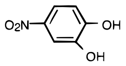
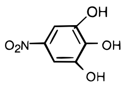
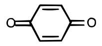
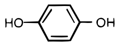
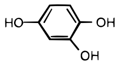


FIGURE 2. Evolution of HPLC chromatograms during the electro-Fenton treatment of a PNP solution (C_0 = 4 mM) in water, as a function of electrical charge Q (coulombs). (a) 0 C, (b) 400 C, (c) 800 C and (d) 1500 C.

chromatograms, with retention times of authentic samples expected to be the PNP degradation products (which were also used as internal standards), it was possible to identify five major decomposition products II–VI. Retention times and chemical structure of these compounds are given in Table 1.

Their identification was confirmed by GC-MS. Results are given in Table 2. For unambiguous identification of the reaction products, their GC-MS spectra were compared with spectra of standard compounds performed with the same apparatus in identical experimental conditions.

TABLE 1. HPLC Identification of PNP Degradation Products Formed by the Reaction with Electrochemically Generated OH· Radicals

HPLC peak no	retention time t_R (min)	identification	chemical structure
I	28.0	p-nitrophenol	
II	17.1	p-nitrocatechol	
VI	15.9	4-nitropyrogallol	
IV	10.1	benzoquinone	
V	7.7	hydroquinone	
III	6.7	1,2,4-trihydroxybenzene	

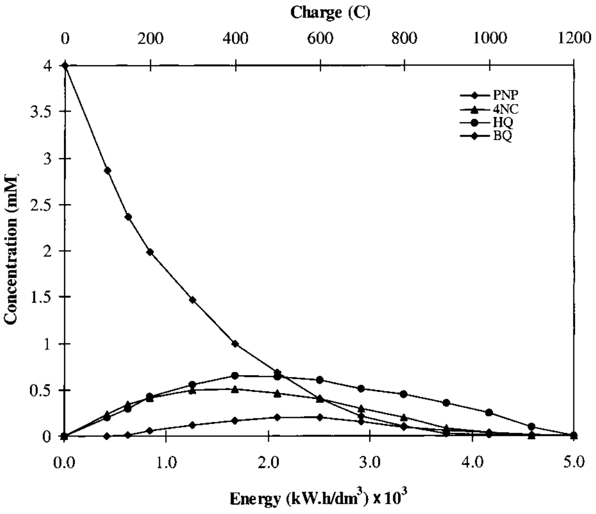


FIGURE 3. Concentration change of PNP (C_0 = 4.0 mM, V = 0.125 dm^3) and some of its degradation products during the electro-Fenton treatment as function of charge (higher scale) and electrical energy consumed (lower scale). 4-NC: *p*-nitrocatechol, HQ: hydroquinone, BQ: benzoquinone.

Change of concentrations of PNP and some of its hydroxylated derivatives is shown in the Figure 3 as a function of charge (C) and of electrical energy (kW.h/dm^3). Figures 2 and 3 show that the rapid degradation of PNP is accompanied by the appearance of aromatic intermediates such as *p*-nitrocatechol and hydroquinone. Concentrations of these intermediates reach to a maximum steady state value at around 500 C, for an aqueous solution containing initially 4 mM PNP, and then decrease until disappearance. The decrease of *p*-nitrocatechol is accompanied by the increase of 1,2,4-trihydroxybenzene. The evolution of benzoquinone follows that of hydroquinone. At 1200 C the PNP and its degradation intermediates have completely disappeared.

Determination of Rate Constants. Since the solution was continuously saturated with molecular oxygen, the production rate, therefore the concentration, of hydrogen peroxide is stable. Ferrous ion concentration was also steady due to its cathodic regeneration during the electro-Fenton process. The electrolysis current was remained constant accordingly these suggestions. Hydroxyl radicals are very short-lived species. Their concentration may be considered in a quasi-stationary state. In these conditions the hydroxylation of PNP is a pseudo first-order reaction. So, the rate constant of hydroxylation reaction

$$\mathrm{PNP} + \mathrm{OH}^{\cdot} \rightarrow \text{products} \tag{6}$$

TABLE 2. GC-MS Data for the Reaction Mixture after Passing 400 C during the Electro-Fenton Treatment of the PNP Solution with Initial Concentration $C_0 = 4$ mM

retention time (min)	molecular weight (*m/z*)	mass of predominant ions in fragmentation pattern	product identification
3.84	108	108 (M^+), 80, 54, 37	benzoquinone
12.85	110	110 (M^+), 81, 63, 53, 39	hydroquinone
14.89	126	126 (M^+), 108, 97, 80, 69, 63, 52, 38	1,2,3-trihydroxybenzene
16.55	139	139 (M^+), 123, 109, 93, 81, 65, 53, 39	*p*-nitrophenol
18.08	155	155 (M^+), 137, 125, 109, 81, 53, 36	*p*-nitrocatechol

TABLE 3. Rate Constants for Hydroxylation Reactions of PNP and Its Hydroxylated Derivatives by OH· Radicals

substrate (S)	rate constant ($L.mol^{-1}.s^{-1}$) for S + $OH^\bullet$ → products
p-nitrophenol	$(1.2 \pm 0.2) \times 10^{10}$
p-nitrocatechol	$(1.0 \pm 0.2) \times 10^{10}$
hydroquinone	$(1.6 \pm 0.5) \times 10^{10}$
1,2,4-trihydroxybenzene	$(8.6 \pm 0.3) \times 10^{9}$

might be comparatively determined taking the salicylic acid (SA) reaction as standard. In fact, salicylic acid hydroxylation was chosen because its hydroxylation rate constant ($2.2 \times 10^{10}\ M^{-1}\ s^{-1}$) is well-established (*33*).

$$\mathrm{SA} + \mathrm{OH}^{\cdot} \rightarrow \text{products} \qquad (7)$$

Assuming that there are no side reactions of PNP and our reference compound (SA), other than their reaction with hydroxyl radicals, the rates of these processes are given by

$$-\mathrm{d[PNP]/dt} = k_{\mathrm{PNP}}[\mathrm{OH}\cdot][\mathrm{PNP}]$$

$$-\mathrm{d[SA]/dt} = k_{\mathrm{SA}}[\mathrm{OH}\cdot][\mathrm{SA}]$$

which can be integrated and combined to give the following equation

$$\ln([\mathrm{PNP}]_0/[\mathrm{PNP}]_t) = (k_{\mathrm{PNP}}/k_{\mathrm{SA}}) \times \ln([\mathrm{SA}]_0/[\mathrm{SA}]_t) \qquad (8)$$

where the subscripts 0 and t indicate concentration at the beginning of the experiment and at time t, respectively. A plot of $\ln([\mathrm{PNP}]_0/[\mathrm{PNP}]_t)$ vs $\ln([\mathrm{SA}]_0/[\mathrm{SA}]_t)$ thus yields the rate constant ratio, therefore k_{PNP}. Equation 8 was also used to determine the rate constants of *p*-nitrocatechol, hydroquinone and 1,2,4-trihydroxybenzene with OH· radical (Table 3).

Total Organic Carbon (TOC) Measurement. The variation of TOC values found in the samples taken at different times of electro-Fenton process shows their dependence on the charge (C) passed or electrical energy consumed ($kW.h/dm^3$). Figure 4 illustrates these results during the electro-Fenton treatment of a 1.0 mM PNP solution. It also proves that the disappearance of peaks on HPLC chromatograms not only due to the formation of aliphatics, which cannot be detected by the UV detector of HPLC, but this is a result of the mineralization process which takes place during the electro-Fenton treatment. Mineralization rate is higher at the beginning of the electrolysis, but diminishes with the decrease of concentration of compounds in the reaction mixture and with change in their structure, from aromatics to aliphatics by ring opening reactions, which are more resistant to mineralization. Under above conditions, the mineralization process reached a ratio of 95% at 800 C passed, which is equivalent to $3 \times 10^{-3}\ kW.h/dm^3$. The continuation of the process beyond this point resulted in a nonsignificant reduction of the TOC value. At this stage, organics present in solution are probably carboxylic acids, which resist to mineralization, although their biodegradation should be in principle possible. The decrease in mineralization rate may be influenced by the competition with

$$\mathrm{OH}^{\bullet} + \mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-}$$

when the concentration of organic matter decrease. In fact, this reaction has a highly rate constant; $k = 4.3 \times 10^{8}\ M^{-1}\ s^{-1}$ (*38*).

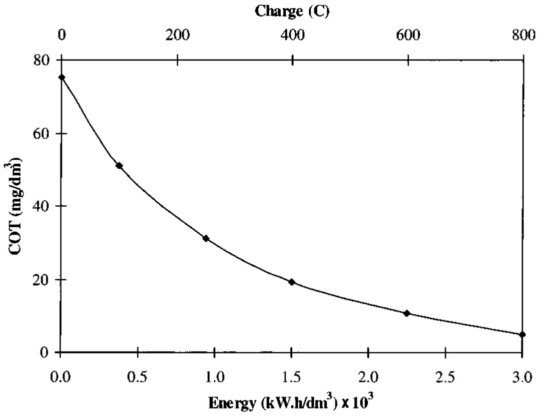
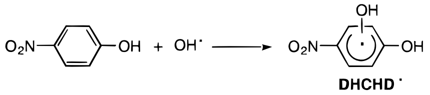


FIGURE 4. Decrease of TOC value in the reaction mixture during the electro-Fenton treatment of a PNP aqueous solution (with initial concentration $C_0 = 1.0$ mM, $V = 0.125\ dm^3$) as function of charge (C) and energy ($kW.h/dm^3$).

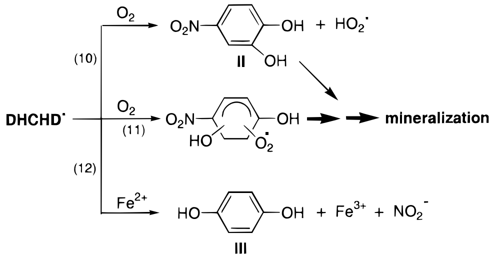
Mineralization Mechanism. The reaction mechanism of hydroxyl radicals with the aromatic compounds is well-known (*34*–*36*). It consists of an electrophilic addition to the aromatic ring with the formation of a hydroxylated radical, dihydroxycyclohexadienyl (DHCHD) radical in case of PNP:



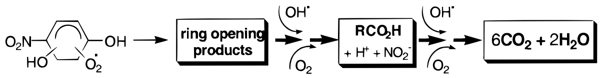
(9)

This radical may undergo different reactions according to the nature of reaction medium. In an anaerobic medium it may dimerize and/or disproportionate (*37*, *38*) leading to formation of a biphenyl compound and a phenol one, respectively. In the oxidative medium this radical will undergo hydroxylation reactions (*34*, *39*, *40*). Analysis of the intermediates and monitoring of the TOC values during the electro-Fenton process helped to understand the possible pathways of reaction of DHCHD· in the presence of O_2 and ferric ions. The mesomeric electron-donor character of hydroxyl group on the benzene ring favors the electrophilic attack of hydroxyl radicals on ortho- and para-positions. Electrophilic attack of hydroxyl radical on ortho-position of PNP leads to the formation of *p*-nitrocatechol (Scheme 1, reaction 10). Formation of hydroquinone (reaction 12) might be explained by an *ipso* attack of the hydroxyl radical (at para-position of OH group) with a simultaneous leave of the nitro group. The continuous decrease of TOC value since the

SCHEME 1. Evolution of DHCHD Radical in Oxidative Medium Leading to the Formation of Compounds II and III



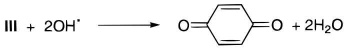
SCHEME 2. Proposed Mineralization Pathway for PNP Following the Electrophilic Addition of OH· Radical



beginning of electro-Fenton process might be explained by partial mineralization of this radical (reaction 11).

The mineralization pathway includes the opening of the aromatic ring followed by successive oxidations of the aliphatic products up to CO_2 and H_2O (Scheme 2), by hydroxyl radicals in the presence of molecular oxygen (*6*, *17*, *19*, *40*). The nitrite ion NO_2^- liberated by reaction 12 and by mineralization process (Scheme 2) is subsequently oxidized into nitrate ion NO_3^-. Ion chromatography (Dionex 100) analyses show that 85−90% of nitrogen initially containing in PNP was recovered as nitrate ion at the end of process.

Benzoquinone (compound IV) appears in the reaction mixture when hydroquinone reaches to a concentration of 0.2−0.3 mM (Figures 2 and 3). It is well-known that hydroquinone is very easily oxidized into benzoquinone (*41*) thus it is probably formed by reaction of hydroxyl radicals (eq 13) which are also powerful oxidizing agents ($E^0_{OH^\bullet,H^+/H_2O}$ = 2.72 V/NHE):



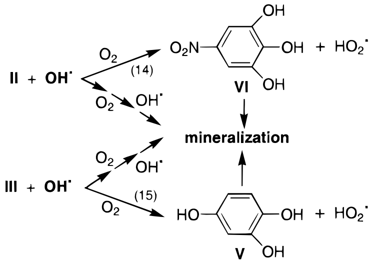
(13)

The values of the kinetic constants (Table 3) show that the reactivity of the compounds II and III versus hydroxyl radicals is comparable to that of PNP. However, their hydroxylation starts to compete with of PNP when their concentrations reach to a sufficient value. Scheme 3 shows the possible reactions of these compounds with OH· radicals.

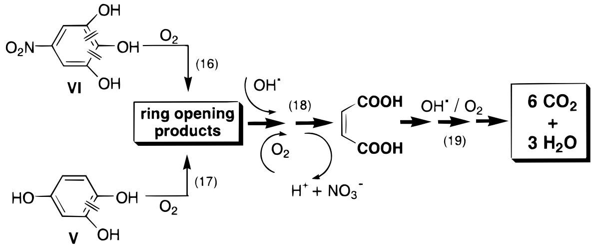
Pelizzetti et al. (*32*) have already studied the photocatalytic degradation of PNP on irradiated TiO_2. Their degradative process yields hydroquinone and 4-aminophenol as well as other dihydroxynitrobenzene derivatives. Our experimental conditions are oxidative; therefore, we could not detect 4-aminophenol which should have resulted from a reductive ($6e^- + 6H^+$) transformation of nitro group ($Ar-NO_2$) into the corresponding amine ($Ar-NH_2$) (*41*).

Formation of compound VI (3,4,5-trihydroxynitrobenzene or 4-nitropyrogallol) by hydroxylation of PNP during the photo-Fenton process is already described (*30*). A peak of t_R = 15.9 min found on HPLC chromatogram was attributed to compound VI by comparison with an authentic standard. To confirm reaction 14, an electrolysis of compound II was performed separately; compound VI (identified by comparison with authentic products) appears as the major formed product. This is not mentioned in Table 2, because its identification leaves some problems remaining: first it is not accumulated with a significant concentration due to its rapid degradation (cf. Figure 2), and second its extraction from water is difficult because of its rather high polarity.

SCHEME 3. Hydroxylation Reaction Pathways for *p*-Nitrocatechol and Hydroquinone



SCHEME 4. Proposed Mineralization Pathway for Compounds V and VI



It is to be mentioned that, in the compound V and VI, the C−C bonds between the adjacent hydroxyl groups are destabilized due to the strong electrophilic effect of hydroxyl and nitro groups. Consequently these bonds easily undergo oxidative ring opening reactions leading to aliphatic compounds. Scheme 4 shows a plausible mineralization pathway of compounds V and VI. It can also be seen that the compound VI has two C−C bonds predisposed to oxidative rupture while the compound V has only one. This leads to the rate of mineralization of VI (Scheme 4, reaction 16) to be faster than those of V (reaction 17) and explains the fact that the presence of VI in the reaction mixture is in a lower concentration than V. The products of the ring opening reaction might be alcohols, aldehydes or ketones (from quinones) which will be oxidized to carboxylic acids (Scheme 2 and reaction 18) and then mineralized to CO_2 and H_2O (reaction 19).

To identify the major carboxylic acid formed from oxidative cleavage of hydroxylated aromatic compounds, the experiments with compounds V and VI were performed separately. Ion chromatographic analyses revealed the maleic acid as the major byproduct of these reactions. The presence of fumaric and oxalic acids in a very small concentration has also been identified. Maleic acid concentration reaches a maximum value of 0.2 mM at 200 C, in the conditions of Figure 3, and then slowly decreases. These observations are in agreement with previous studies (*42*−*45*) in which the maleic acid has been identified as major oxidation product by advanced oxidation processes with different organic substrates. Concerning mineralization of carboxylic acids, Stephan et al. (*46*) recently proposed a mineralization reaction pathways induced by hydroxyl radicals.

Finally the overall mineralization reaction of PNP could be summarized as follows:

$$O_2N\text{-}(C_6H_4)\text{-}OH + 28OH^\cdot \xrightarrow{\text{electrical energy}} 6CO_2 + 16H_2O + H^+ + NO_3^-$$

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Literature Cited

(1) Bühler, R. E.; Staehelin, J.; Hoigné, J. *J. Phys. Chem.* **1984**, *88*, 2560−2564.

(2) Staehelin, J.; Bühler, R. E.; Hoigné, J. *J. Phys. Chem.* **1984**, *88*, 5999−6004.
(3) Sanchez, L.; Peral, J.; Doménech, X. *Appl. Catal. B: Env.* **1998**, *19*, 59−65.
(4) Legrini, O.; Oliveros, E.; Braun A. *Chem. Rev.* **1993**, *93*, 671−698.
(5) Acher, A.; Ficher, E.; Turnheim, R.; Manor, Y. *Water Res.* **1997**, *6*, 1398−1404.
(6) Ruppert, G.; Bauer, R.; Heisler, G.; Novalic, S. *Chemosphere* **1993**, *27*, 1339−1347.
(7) Acher, A. J.; Dunkelblum, E. *J. Agric. Food. Chem.* **1979**, *27*, 1164−1167.
(8) Acher, A. J. *Water Sci. Technol.* **1984**, *17*, 623−632.
(9) Alloway, B.; Ayres, D. *Chemical Principles of Environmental Pollution*, 1st ed.; Blackie Academic & Professional: London, 1993.
(10) Prousek, J. *Chem. Listy* **1996**, *90*, 229−237.
(11) Pelizzetti, E.; Minero, C.; Pramauro, E. In *Chemical Reactor Technology for Environmentally Safe Reactors and Products*; de Lasa, H., Ed.; Kluwer Academic Publications: The Netherlands, 1993; pp 577−608.
(12) Bahnemann, D.; Cunningham, J.; Fox, M. A.; Pelizzetti, E.; Serpone, N. In *Aquatic and surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 261−317.
(13) Simonsson, D. *Chem. Soc. Rev.* **1997**, *26*, 181−189.
(14) Hsiao, Y.-L.; Nobe, K. *J. Appl. Electrochem.* **1993**, *23*, 943−946.
(15) Tahar, N. B.; Savall, A. *J. Electrochem. Soc.* **1998**, *145*, 3427−3434.
(16) Comninellis, Ch.; Pulgarin, *C. J. Appl. Electrochem.* **1991**, *21*, 703−708.
(17) Brillas, E.; Sauleda, R.; Casado, J. *J. Electrochem. Soc.* **1998**, *145*, 3427−3434.
(18) Oturan, M. A.; Aaron, J. J.; Oturan, N.; Pinson, J. *Pestic. Sci.* **1999**, *55*, 558−562.
(19) Oturan, M. A. *J. Appl. Electrochem.* **2000**, *30*, 477−484.
(20) Nagakawa, M.; Crosby, J. *J. Agric. Food Chem.* **1974**, *22*, 849.
(21) *List of Worldwide Hazardous Chemical and Pollutants, The Forum for Scientific Excellence*; J. B. Lippincot Co., Ed.; New York, 1990.
(22) Megharaj, M.; Pearson, H. W.; Vekateswarlu, K. *Arch. Environ. Contam. Toxicol.* **1991**, *21*, 578−585.
(23) (a) U. S. Environmental Protection Agency, *4-nitrophenol, Health and Environmental Effects Profile* No. 135, Washington DC, 1980. (b) Rippen, G.; Zietz, E.; Franck, R. *Environ. Technol. Lett.* **1986**, *8*, 475−482.
(24) Ishag, M. I. O.; Moseley P. G. N. *Tetrahedron* **1977**, *33*, 3141−3144.
(25) O'Connor, O. A.; Young, L. Y. *Environ. Toxicol. Chem.* **1989**, *8*, 853−862.
(26) Beltran, F. J.; Gomez-Serrano, V.; Duran, A. *Water Res.* **1992**, *26*, 9−17.
(27) Chow, Y. L. Photochemistry of nitro and nitroso compounds. In *The Chemistry of Functional Group*; Patai, S., Ed.; J. Wiley & Sons: Chichester, 1982; Supplement F, pp 181−291.
(28) Lipczynska-Kochany, E. *Environ. Technol.* **1991**, *12*, 87−92.
(29) Lipczynska-Kochany, E. *Chemosphere* **1992**, *24*, 1369−1380.
(30) Kiwi, J.; Pulgarin, C.; Peringer, P. *Appl. Catal. B: Env.* **1994**, *3*, 335−350.
(31) Balcioglu, I. A.; Inel, Y. *J. Environ. Sci. Health* **1996**, *A(31)*, 123−138.
(32) Maurino, V.; Minero, C.; Pelizzetti, P.; Piccinini, P.; Serpone, N.; Hidaka, H. *J. Photochem. Phorbiol. A* **1997**, *109*, 171−176.
(33) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513−759.
(34) Oturan, M. A.; Pinson, J. *J. Phys. Chem.* **1995**, *99*, 13948−13954.
(35) Eberhardt, M. K. *J. Phys. Chem.* **1977**, *81*, 1051−1057.
(36) Raghavan, N. V.; Steenken, S. *J. Am. Chem. Soc* **1980**, *102*, 3495−3499.
(37) Eberhardt, M. K. *J. Phys. Chem.* **1974**, *78*, 1795−1797.
(38) Chen, R.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 2399−2406.
(39) Merga, G.; Schuchmann, H.-P.; Madhava Rao, B. S.; von Sonntag, C. J. *Chem Soc., Perkin Trans. 2* **1996**, 1097−1103.
(40) Sun, Y.; Pignatello, J. J. *Environ. Sci. Technol.* **1993**, *27*, 304−310.
(41) Hoare, J. P. In *Standard Potentials in Aqueous Solutions*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker Inc.: New York, 1985.
(42) Brillas, E.; Mur, E.; Sauleda, L.; Sanchez, L.; Peral, J.; Domènech, X.; Casado, J. *Appl. Catal. B: Env.* **1998**, *16*, 31−42.
(43) Comninellis, Ch.; Pulgarin, C. *J. Appl. Electrochem.* **1993**, *23*, 108−112.
(44) Belhadj Tahar, B.; Saval, A. *J. Appl. Electrochem.* **1999**, *29*, 277−283.
(45) Huston, P. L.; Pigratello, J. J. *Water Res.* **1999**, *33*, 1238−1246.
(46) Stephan, M. I.; Bolton, J. R. *Environ. Sci. Technol.* **1998**, *32*, 1588−1595.

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