

## Effects of an electric or magnetic field on the radiolytic degradation of two biorefractory contaminants

Shu-Juan Zhang<sup>a</sup>, Han-Qing Yu<sup>a,\*</sup>, Qian-Rong Li<sup>b</sup>, Hao Yin<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

<sup>b</sup> Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China

Received 22 August 2004; received in revised form 13 November 2004; accepted 24 November 2004

Available online 28 December 2004

### Abstract

Effects of an electric or magnetic field on the radiolytic degradation of two biorefractory contaminants, Acid Orange 7 (AO7) and nitrobenzene (NB), were evaluated in this work. A continuous DC electric current with a low density ( $\sim 2.8\text{--}5.6\text{ mA cm}^{-2}$ ) applied during the radiolytic degradation of AO7 and NB solutions only led to slight enhancement in their degradation rate constants, but altered significantly the degradation mechanisms. On the other hand, application of a magnetic field (0.4 T) in irradiation processes slightly enhanced the degradation kinetics without leading to any change in degradation mechanisms.

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**Keywords:** Radiolytic degradation; Electric field; Magnetic field; Kinetics; Mechanism

### 1. Introduction

Over the past century, conventional biological processes have played an incomparable role in the treatment of waters and wastewaters. However, they are not efficient for the remediation of waters rich in biorefractory contaminants, such as Acid Orange 7 (AO7) and nitrobenzene (NB), two typically biorefractory compounds widely present in effluents from chemical industries. Consequently, intense efforts have been made to find efficient and cost-effective treatment methods for such effluents. AO7, due to its high production yield and wide presence in effluents, is frequently chosen as the model for azo dyes, while the significance of NB in industries makes it an important target in degradation research.

Both oxidative and reductive methods have been employed for the treatment of AO7/NB-laden wastewaters. The reduction of AO7 by elemental iron ( $\text{Fe}^0$ ) led to the formation of

sulfanilic acid and 1-amino-2-naphthol [1,2]. Direct reduction of NB by  $\text{Fe}^0$  to anilines was used as an in situ remediation for NB-rich waters [3,4]. Advanced oxidation processes based on the generation of highly reactive and oxidizing hydroxyl radicals either catalytically or non-catalytically, such as photocatalysis, Fenton's reaction, sonolysis, wet air oxidation and ionizing radiation, as well as various combinations of them have been employed for the mineralization of azo dyes [5–9] and NB [10–18].

Among the methods above, ionizing radiation has proven to be a promising approach because of its several unique advantages. First, it can work at ambient temperatures and normal pressures. Secondly, it needs no additional chemicals and consequently does not lead to further pollution. Thirdly, complete mineralization of contaminants can be achieved providing that sufficient irradiation dose is supplied. However, the energy required to realize complete mineralization of organic contaminants, especially those with aromatic structures, is so large that ionizing radiation loses its advantages in terms of operational costs. Therefore, it might be more reasonable to employ ionizing radiation with the combination of other methods. Synergistic effects on contaminant

\* Corresponding author. Tel.: +86 551 3607592; fax: +86 551 3601592.  
E-mail address: hqyu@ustc.edu.cn (H.-Q. Yu).

destruction have been achieved through combinations of radiation with conventional treatment methods, such as combination of  $\gamma$ -ray irradiation with ozonation [19] and combination of electron beam irradiation with biotransformation [20].

Both electric current and magnetic field are environmentally friendly energies. The effects of them on the radiolytic degradation of biorefractory contaminants, to our knowledge, have not been investigated yet. Therefore, in this work we focus our efforts on the evaluation of the effects of an electric or magnetic field on the radiolytic degradation of AO7 and NB, two model biorefractory contaminants in industrial effluents.

## 2. Experimental

### 2.1. Materials

AO7, NB, ethyl acetate (EA),  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{NaClO}_4$ , anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), all purchased from Shanghai Chemical Reagent Company, were of analytical reagent grade. Methanol was chromatographic purity grade. Except that EA was redistilled before use, the other reagents were used without further purification.

### 2.2. Sample preparation

Throughout the experiments, the samples were prepared with water doubly distilled using a quartz distillatory, and were contained in 250 mL Pyrex glass vials. All solutions were in equilibrium with ambient atmosphere. The pH of all solutions was in the range of 6.0–7.0 without any adjustment. No additional salts were dosed to AO7 solutions, whereas all NB solutions were kept at an identical ionic strength by addition of  $\text{NaClO}_4$ .

### 2.3. Irradiation experiments

A  $^{60}\text{Co}$ - $\gamma$ -source with an activity of about 60 kCi ( $2.22 \times 10^{15}$  Bq) was used for irradiation. The dose rates varied with the distance between  $^{60}\text{Co}$  column and sampling sites, and were determined using Fricke dosimetry [21]. The sample solutions were irradiated at certain dose rates and sampled at given time intervals.

Fig. 1 shows schematically the setup for electro-irradiation experiments. Kryptols from dry batteries were used as anode and cathode. The current density was maintained constant by means of a DC power supply. For the investigation on magnetic effect, the solutions were sandwiched between two permanent magnets ( $8.5 \text{ cm} \times 6.5 \text{ cm} \times 2.0 \text{ cm}$ ) which were arranged in parallel (S–N//S–N, S and N refer to south and north magnetic poles, respectively) as illustrated in Fig. 2. All experiments were conducted in duplicate or triplicate at ambient temperatures.

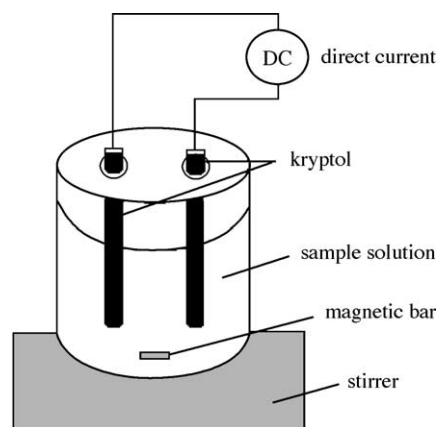


Fig. 1. Schematic diagram of the setup for generating an electric field.

### 2.4. Analytical approach

Quantitative determination of AO7 and NB was carried out by using an HPLC (HPLC-1100, Agilent Co.) with a Hypersil-ODS inverse phase column under  $30^\circ\text{C}$  oven temperature with an isocratic elution and detected at 254 nm. The mobile phase for AO7 determination was composed of 60% methanol and 40% phosphate buffer of  $33 \text{ mmol L}^{-1}$  (pH 7.0) and that for NB determination was of 60% methanol and 40% doubly distilled water.

GC–MS analyses were performed to identify the degradation products. Before subjecting to analysis, the 80 mL irradiated sample solutions were extracted triply with 20 mL redistilled EA. The resulting organic phases were decanted, and were then dehydrated by  $\text{MgSO}_4$  for 24 h. Thereafter, the organic phases were concentrated and then stored for GC–MS analysis. A GC system (Agilent 6890) with a  $30 \text{ m} \times 0.25 \text{ mm}$  DB-5 capillary column coupled to an MS (Micromass Co.) through an EI interface was used. Helium was used as the carrier gas. Sample analysis, exact mass measurement, and elemental composition determination were performed using the OpenLynx software within MassLynx. The compounds were identified by comparing with NIST library spectra.

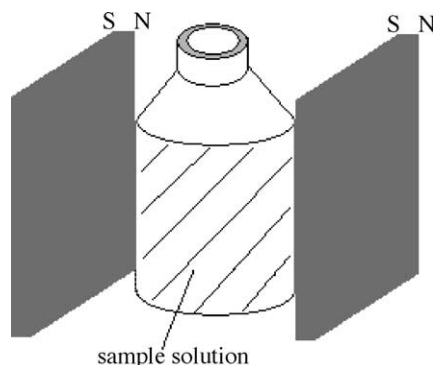


Fig. 2. Schematic diagram of the setup for generating a magnetic field.

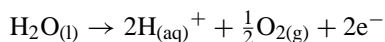
### 3. Technical background

Irradiation of water with ionizing radiation, e.g.,  $\gamma$ -rays, leads to the formation of a suite of species, including hydroxyl radicals ( $\bullet\text{OH}$ ), hydrated electrons ( $e_{\text{aq}}^-$ ), hydrogen atoms ( $\text{H}\bullet$ ), and small amounts of  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ , in which  $\bullet\text{OH}$  and  $e_{\text{aq}}^-$  account together for  $\sim 90\%$  of the total radical yield under neutral conditions [22]. The initial reactive species are generated in isolated volume elements in the directions of  $\gamma$ -rays called “spurs”. Only the fraction of species that escape into the bulk solution contributes to the degradation of substrates. The remaining species recombine as the spurs expand through diffusion, which is called as “cage effect”.

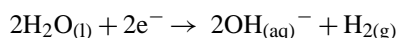
As a powerful oxidant, the hydroxyl radical adds to unsaturated bonds at rates near the diffusion-controlled limit and readily abstracts H from C–H bonds. In contrast,  $e_{\text{aq}}^-$  acts as a nucleophile in its reactions with organic molecules of more positive reduction potentials. The hydrogen atom is the conjugate acid of  $e_{\text{aq}}^-$ , and it is the major reducing species in acidic solution.  $\text{H}\bullet$  reacts with organic compounds by abstracting H from saturated molecules and by adding to centers of unsaturation. In this respect it resembles  $\bullet\text{OH}$ , although the latter is more reactive and less selective in abstraction reactions [23].

Electrochemical method, similar to ionizing radiation, is also a clean approach that reactive species are generated or consumed within the electrodes. For example, the electrolysis of water generates oxygen and hydrogen gases in anode and cathode, respectively, with reactive oxygen and hydrogen atoms as the intermediates [24]. The electrode reactions of water with neutral electrolytes can be described as follows:

Anode reaction:



Cathode reaction:



Nevertheless, the electrochemical treatment has some disadvantages, e.g., it is expensive in comparison with some other methods. Introduction of a low density of DC electric current to irradiated solutions might be able to make full use of the advantages of both electrochemical and radiolytic methods and accordingly to overcome their shortcomings.

A prolonged lifetime of radicals was observed in a magnetic field due to enhanced singlet–triplet transitions in the spin state of radicals [25]. By maintaining the radicals in the

triplet state, the recombination of radicals in spurs might be abated. Consequently, the utilization efficiency of radicals generated from water radiolysis could be increased. In other words, the presence of a magnetic field might be beneficial to the radiolytic degradation of aqueous contaminants.

### 4. Results and discussion

The effects of an electric or magnetic field on the radiolytic degradation of AO7 and NB were evaluated in terms of both degradation kinetics and mechanisms.

The concentrations of AO7 and NB ( $C$ ) both decayed exponentially with irradiation time ( $t$ ) in the presence or absence of an electric or magnetic field. The profile of  $\ln C \sim t$  showed a good linearity, demonstrating that their degradation kinetics was pseudo first-order. The first-order degradation rate constants ( $k_1$ ) were estimated from the slopes of  $\ln C \sim t$ . Typically, the regression coefficients were larger than 0.990 for the 7-data points determined within 2.5 h for AO7 or 5 h for NB irradiation.

As presented in Table 1, taking the contributions of direct electrolysis of AO7 and NB into account, the introduction of a DC current exerted no significant effect on the radiolytic kinetics of the substrates. However, drastic effects of a DC current on the degradation mechanisms of AO7 or NB were observed.

Fig. 3 shows the GC chromatograms of the EA extracts from the irradiated AO7 solutions. For the extracts obtained from electro-irradiated solution (Sample A), several peaks were observed, whereas no peaks in the GC chromatogram of the extracts from the directly irradiated solution (Sample B), except the one marked with an asterisk which was from an inner reference, cyclohexanone. This result implies that the degradation products in Sample B were nonvolatile or were of low extractability to organic solvents. Through MS analysis, the products in Sample A were identified as *p*-benzoquinone, diacetyl phthalate and nitrobenzene, as summarized in Table 2. These three compounds were oxidation products [7], but none of them were detected in the directly irradiated solution. The introduction of a DC current to the AO7 solution led to the electrolysis of  $\text{H}_2\text{O}$  into  $\text{H}_2$  and  $\text{O}_2$  on cathode and anode respectively with hydrogen and oxygen atoms as intermediates. Observable gas bubbles were released from the carbon electrodes. It is likely that the combined role of reductive hydrogen atoms with the oxidative

Table 1

The  $k_1$  values of AO7 and NB in direct radiolysis and in the presence of an electric or magnetic field (initial concentration of contaminants:  $[\text{AO7}]_0 = 350 \text{ mg L}^{-1}$ ,  $[\text{NB}]_0 = 120 \text{ mg L}^{-1}$ , dose rate:  $55 \text{ Gy min}^{-1}$ )

Experiment	$k_1$ ( $\text{min}^{-1}$ )	
	AO7	NB
Direct radiolysis	$0.0183 \pm 0.0003$	$0.0093 \pm 0.0005$
Radiolysis with a DC electric current ( $2.8 \text{ mA cm}^{-2}$ )	$0.0228 \pm 0.0009$ (0.0042 <sup>a</sup> )	$0.0121 \pm 0.0011$ (0.0024 <sup>a</sup> )
Radiolysis in a magnetic field (0.4 T)	$0.0194 \pm 0.0003$	$0.0098 \pm 0.0005$

<sup>a</sup> The  $k_1$  values in direct electrolysis.

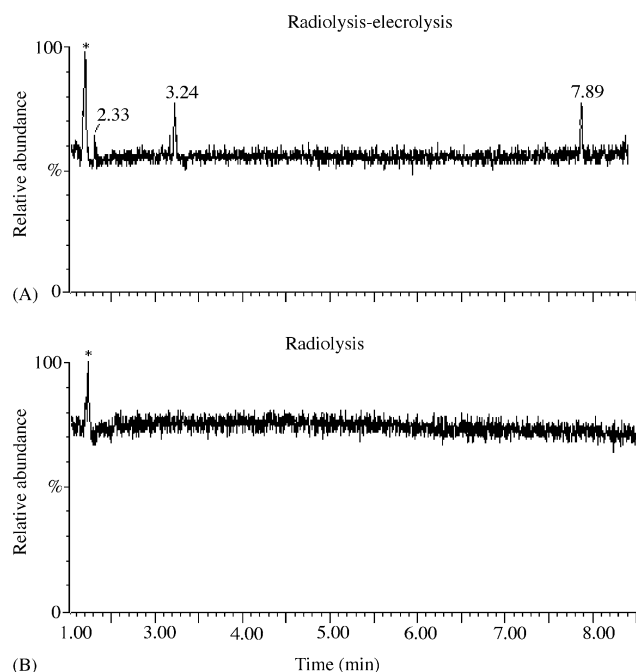


Fig. 3. The GC chromatograms of the extracts from Samples A and B ( $t = 3$  h, dose rate =  $55 \text{ Gy min}^{-1}$ ).

species led to the formation of *p*-benzoquinone, diacetyl phthalate and nitrobenzene. The role of hydrogen atoms, which were produced from water electrolysis (the yield of hydrogen atom in water radiolysis is rather low), might be a key factor in preventing AO7 from being rapidly oxidized to products of low volatility or of low extractability to organic solvents. However, further efforts are needed for the better understanding of the degradation mechanisms.

The degradation products of NB solutions irradiated in the presence and absence of an electric field provided powerful support for the interpretation about the electric effects given above. Fig. 4 shows the GC chromatograms of the EA extracts from irradiated NB solutions. Both the extracts obtained from electro-irradiated solution (Sample C) and from the directly irradiated solution (Sample D) present several peaks in the GC chromatograms. The products identified from these chromatograms are summarized in Table 3. For the directly irradiated solution, oxidizing radicals  $\bullet\text{OH}$  played the dominant role in the degradation of NB. As a result, the products were almost identical to those obtained from highly oxidative conditions as presented in our previous work [26]. The same radicals were generated from water radiolysis in the presence of a

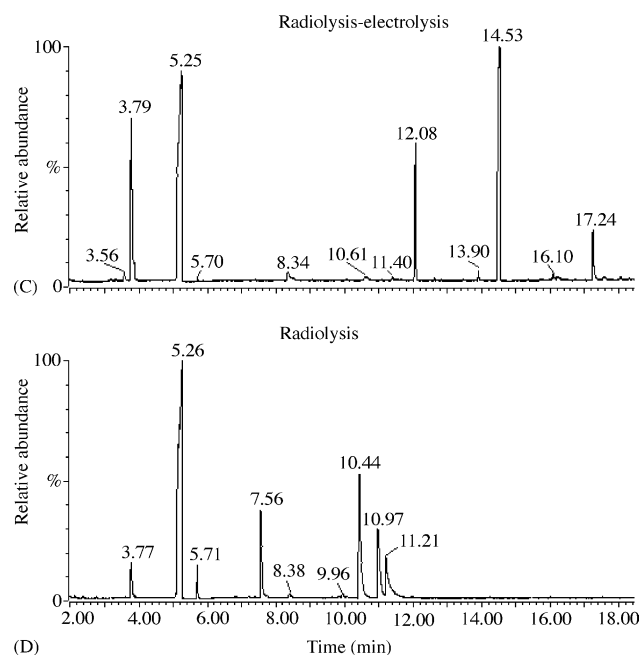
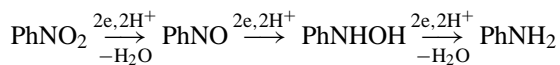


Fig. 4. The GC chromatograms of the extracts Samples C and D ( $t = 3$  h, dose rate =  $55 \text{ Gy min}^{-1}$ ).

DC current, but the degradation products were substantially different, implying that new active species were produced directly from water electrolysis or from the interaction between the initial species generated from the radiolysis and electrolysis of water.

The electrochemical reduction of refractory organics, including NB, has been studied extensively [24]. A variety of products have been reported as the result of electrochemical reduction of NB, including phenylhydroxylamine (PhNHOH), aniline (PhNH<sub>2</sub>), azoxybenzene (Ph–N=N(O)–Ph) and azobenzene (Ph–N=N–Ph) [27]. A schematic description of the reaction steps was outlined as successive 2e steps [24]:



In our previous work on the reductive radiolysis of NB aqueous solutions [26], all of the products mentioned above were observed. This provides support for the successive 2e steps mechanisms proposed.

As shown in Table 3, both oxidative and reductive products were observed in the combined radiolysis and electrolysis of

Table 2

Products of an irradiated AO7 solution in the presence of a DC current of density of  $2.8 \text{ mA cm}^{-2}$  (Sample A)

RT <sup>a</sup>	MI <sup>b</sup>	BP <sup>c</sup>	Main fragments	Formula	Compound
2.33	108	108	82, 54	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	<i>p</i> -Benzoquinone
3.24	123	77	93, 51	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> N	Nitrobenzene
7.89	223	149	205, 167, 104, 76	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	Diacetyl phthalate

<sup>a</sup> Retention time in the GC chromatogram in units of min.

<sup>b</sup> Molecular ion.

<sup>c</sup> Base peak in the MS spectra.

Table 3

Products of an irradiated NB solution in the presence of a DC current of density of 5.6 mA cm<sup>-2</sup> (Sample C) and those of the directly irradiated solution (Sample D)

RT	MI	BP	Main fragments	Formula	Compound
Sample C					
3.56	119	119	91, 64	C <sub>7</sub> H <sub>5</sub> ON	4-Hydroxy-benzonitrile
3.79	93	93	66	C <sub>6</sub> H <sub>7</sub> N	Aniline
5.25	123	77	93, 65, 51	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> N	Nitrobenzene
5.70	139	139	122, 109, 92, 81	C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> N	<i>o</i> -Nitrophenol
8.34	121	121	96, 66	C <sub>7</sub> H <sub>7</sub> ON	<i>n</i> -Phenyl-formamide
10.61	139	139	93, 81, 65	C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> N	<i>m</i> -Nitrophenol
11.40	139	139	109, 93, 81, 65	C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> N	<i>p</i> -Nitrophenol
12.08	182	77	152, 105, 51	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub>	Azobenzene
13.90	198	198	170, 121, 93, 77	C <sub>12</sub> H <sub>10</sub> ON <sub>2</sub>	2-Phenylazophenol
14.53	198	77	169, 141, 105, 91	C <sub>12</sub> H <sub>10</sub> ON <sub>2</sub>	Azoxybenzene
16.10	214	107	196, 52	C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> N <sub>2</sub>	Nitrosobenzene dimer
17.24	214	214	167, 139, 115	C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> N <sub>2</sub>	2-Nitro- <i>n</i> -phenyl-benzenamine
Sample D					
3.77	94	94	66, 39	C <sub>6</sub> H <sub>6</sub> O	Phenol
5.26	123	77	93, 65, 51	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> N	Nitrobenzene
5.71	139	139	122, 109, 92, 81	C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> N	<i>o</i> -Nitrophenol
7.56	155	155	107, 93, 79, 52	C <sub>6</sub> H <sub>5</sub> O <sub>4</sub> N	4-Nitrocatechol
8.38	121	121	96, 66	C <sub>7</sub> H <sub>7</sub> ON	<i>n</i> -Phenyl-formamide
9.96	168	168	122, 92, 76, 75,	C <sub>6</sub> H <sub>4</sub> O <sub>4</sub> N <sub>2</sub>	1,3-Dinitrobenzene
10.44	139	139	93, 81, 65	C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> N	<i>m</i> -Nitrophenol
10.97	155	155	125, 97, 81, 52	C <sub>6</sub> H <sub>5</sub> O <sub>4</sub> N	2-Nitrohydroquinone
11.21	139	139	109, 93, 81, 65	C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> N	<i>p</i> -Nitrophenol

NB. In this case, the reductive products were predominated. However, in a control experiment with only electrolysis under given conditions, no products were detected by GC–MS analysis, demonstrating that the low density DC current applied was not sufficient to degrade NB effectively, but that it posed a significant effect on the radiolytic degradation of NB.

The presence of a magnetic field only led to a slight increase in the degradation rate constants of AO7 and NB as shown in Table 1. The slight enhancement might be associated with prolonged lifetime of radicals in the magnetic field by the singlet–triplet transitions in the spin state of radicals [25]. By maintaining the radicals in the triplet state, the magnetic field modifies the ratio between “cage” and “escape” processes for the benefit of the latter. In other words, the depletion of radicals due to random recombination in the cage is reduced by the magnetic field. Consequently, an increased fraction of radicals from water radiolysis could make contributions to the degradation of AO7 or NB. However, no effect of magnetic field on degradation mechanisms was found in the radiolysis of AO7 or NB.

## 5. Conclusions

The introduction of a DC current of low density or a magnetic field to irradiated AO7 and NB solutions slightly increased the degradation rate constants of AO7 and NB with no change in kinetic model. Active species formed from water electrolysis, or from the interaction between the initial species from the radiolysis and electrolysis of water might

be responsible for the enhanced degradation efficiency in the presence of an electric field. The magnetic effect on the radiolytic degradation of AO7 and NB might be associated with an enhanced escaping capability of radicals from spurs to the bulk solution. No magnetic effect on the degradation mechanisms of AO7 and NB was observed, whereas significant effects on the degradation mechanisms were observed in the presence of a DC current.

## Acknowledgment

The authors wish to thank the Jiangsu Key Laboratory of Environmental Science & Engineering, China, for the financial support of this study (Grant No. KJS03072).

## References

- [1] J.S. Cao, L.P. Wei, Q.G. Huang, L.S. Wang, S.K. Han, Reducing degradation of azo dye by zero-valent iron in aqueous solution, *Chemosphere* 38 (3) (1999) 565–571.
- [2] S. Nam, P.G. Tratnyek, Reduction of dyes with zero-valent iron, *Water Res.* 34 (6) (2000) 1837–1845.
- [3] A. Agrawal, P.G. Tratnyek, Reduction of nitro aromatic compounds by zero-valent iron metal, *Environ. Sci. Technol.* 30 (1) (1996) 153–160.
- [4] M.M. Scherer, K.M. Johnson, J.C. Westall, P.G. Tratnyek, Mass transport effects on the kinetics of nitrobenzene reduction by iron metal, *Environ. Sci. Technol.* 35 (13) (2001) 2804–2811.
- [5] C. Bauer, P. Jacques, A. Kalt, Photooxidation of an azo dyes induced by visible light incident on the surface of TiO<sub>2</sub>, *J. Photochem. Photobiol. A: Chem.* 140 (1) (2001) 87–92.

- [6] J. Fernandez, J. Bandara, A. Lopez, P. Buffat, J. Kiwi, Photoassisted Fenton degradation of nonbiodegradable azo dye in Fe-free solutions mediated by cation transfer membranes, *Langmuir* 15 (1) (1999) 185–192.
- [7] I.I. Raffainer, P.R. von Rohr, Promoted wet oxidation of the azo dye Orange II under mild conditions, *Ind. Eng. Chem. Res.* 40 (4) (2001) 1083–1089.
- [8] M. Hosono, H. Arai, M. Aizawa, L. Yamamoto, K. Shimizu, Decoloration and degradation of azo dye in aqueous solution supersaturated with oxygen by irradiation of high energy electron beam, *Int. J. Appl. Radiat. Isot.* 44 (1993) 199–204.
- [9] J.M. Joseph, H. Destailats, H.-M. Hung, M.R. Hoffmann, The sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions, *J. Phys. Chem. A* 104 (2) (2000) 301–307.
- [10] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation of nitrobenzene using titanium dioxide and concentrated solar radiation: chemical effects and scaleup, *Water Res.* 37 (6) (2003) 1223–1230.
- [11] E. Chamarro, A. Marco, S. Esplugas, Use of fenton reagent to improve organic chemical biodegradability, *Water Res.* 35 (4) (2001) 1047–1051.
- [12] R.W. Matthews, D.F. Sangster, Production of isomeric nitrophenols in radiolysis of aqueous nitrobenzene solution, *J. Phys. Chem.* 71 (12) (1967) 4056–4062.
- [13] J.H. Fendler, G.L. Gasowski, Radiation-induced hydroxylation of nitrobenzene in dilute aqueous solution, *J. Org. Chem.* 33 (5) (1968) 1865–1868.
- [14] Y. Maham, G.R. Freeman, Effect of solvent structure on electron reactivity: 1-propanol/water mixtures, *J. Phys. Chem.* 89 (20) (1985) 4347–4352.
- [15] J. Kuruc, M.K. Sahoo, J. Locaj, M. Dutta, Radiation degradation of waste waters. I. Reverse phase-high performance liquid chromatography and multicomponent UV–vis analysis of gamma-irradiated aqueous solutions of nitrobenzene, *J. Radioanal. Nucl. Chem. Art.* 183 (1) (1994) 99–107.
- [16] T.W. Marin, J.A. Cline, K. Takahashi, D.M. Bartels, C.D. Jonah, Pulse radiolysis of supercritical water. 2. Reaction of nitrobenzene with hydrated electrons and hydroxyl radicals, *J. Phys. Chem.* 106 (51) (2002) 12270–12279.
- [17] M. Rodríguez, A. Kirchner, S. Contreras, E. Chamarro, S. Esplugas, Influence of H<sub>2</sub>O<sub>2</sub> and Fe(III) in the photodegradation of nitrobenzene, *J. Photochem. Photobiol. A: Chem.* 133 (12) (2000) 123–127.
- [18] H.M. Hung, F.H. Lind, M.R. Hoffmann, Kinetics and mechanism of the enhanced reductive degradation of nitrobenzene by elemental iron in the presence of ultrasound, *Environ. Sci. Technol.* 34 (9) (2000) 1758–1763.
- [19] A. Sakumoto, T. Miyata, Treatment of waste water by a combined technique of radiation and conventional method, *Radiat. Phys. Chem.* 24 (1) (1984) 99–115.
- [20] J.S. Zhao, O.P. Ward, P. Lubicki, J.D. Cross, P. Huck, Process for degradation of nitrobenzene: combining electron beam irradiation with biotransformation, *Biotechnol. Bioeng.* 73 (4) (2001) 306–312.
- [21] ASTM, Standard Method for Using the Fricke Dosimeter to Measure Absorbed Dose in Water, E1026-84, ASTM, Philadelphia, 1984.
- [22] N.V. Klassen, Primary Products in Irradiation Chemistry, VCH Publishers, New York, 1987.
- [23] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\bullet\text{OH}/\text{O}^-$ ) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [24] M.M. Baizer, H. Lund, Organic electrochemistry—an introduction and a guide, 2nd ed., Marcel Dekker, Inc., New York, 1983.
- [25] A.P. Chiriac, I. Neamtu, C.I. Simionescu, Aspects regarding the grafting of some lignosulfonates with acrylamide under a magnetic field, *Die Angewandte Makromolekulare Chemie* 273 (75) (1999) 75–85.
- [26] S.H. Feng, S.J. Zhang, H.Q. Yu, Q.R. Li, Radiation-induced degradation of nitrobenzene in aqueous solutions, *Chem. Lett.* 32 (8) (2003) 718–719.
- [27] M.C.F. Oliveira, Study of the hypophosphate effect on the electrochemical reduction of nitrobenzene on Ni, *Electrochim. Acta* 48 (13) (2003) 1829–1835.