

# New Photochemical and Electrochemical Methods for the Degradation of Pesticides in Aqueous media. Environmental Applications\*

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The development of new electrochemical and photochemical methods for the decontamination of natural water containing significant concentrations of aromatic pesticides is described. The electrochemical method is based on the electro-Fenton process, i.e. the simultaneous reduction of  $O_2$  and  $Fe^{3+}$  ions. Hydroxyl ( $OH\cdot$ ) radicals are electrosynthesized in aqueous solutions, followed by complete mineralization of the initial pollutants. The photochemical methods involve either a direct photodegradation reaction of pesticides by UV light, or indirect photodegradation processes including  $H_2O_2$  photolysis or photo-Fenton reagents ( $H_2O_2/Fe^{3+}$ ). Examples of the application of these methods to chlorophenoxy acid herbicides and four aromatic pesticides (bendiocarb, pirimiphos-methyl, coumatetralyl, chlorophacinon) in aqueous media are given. Environmental applications are also presented. The performances of electrochemical and photochemical methods are compared.

**Key Words:** electro-Fenton method; photo-Fenton method; pesticides; water treatment.

## Introduction

During recent years, owing to the widespread use of pesticides in agriculture, the amounts of these compounds in aqueous media have increased significantly. Therefore, pesticides constitute major pollutants of the aquatic environment, and their presence is of concern because of their potential toxicity towards animals and humans; they are only partially eliminated by biological and chemical degradation. Presently, several hundred pesticides of various chemical natures are used worldwide for agricultural and non-agricultural purposes. Many of these pesticides are utilized in amounts over 50000 kg/year; for instance, malathion is

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consumed at a rate of about  $25 \times 10^6$  kg/year worldwide and  $2 \times 10^6$  kg/year in Mediterranean countries alone, and about  $90 \times 10^6$  kg of atrazine are spread annually worldwide<sup>1</sup>. As a consequence, relatively high pesticide contamination levels are found in groundwaters and surface waters: 0.1-0.3  $\mu\text{g/L}$  in US groundwaters, and 0.03-0.5  $\mu\text{g/L}$  in European groundwaters. To protect the quality of drinking and surface waters, priority lists of pesticides discharged in the aquatic environment have been established by the European Community, with very drastic tolerance limits<sup>2</sup>. Therefore, there is an increasing interest in the development of simple, cheap and rapid methods for the destruction of organic pesticides in water.

Direct and indirect photochemical reactions have been applied extensively in recent years for the degradation of pesticides. Direct photodecomposition processes can be used whenever organic pesticides absorb light sufficiently in the UV region (250-300 nm)<sup>3-5</sup>. However, several factors often limit the efficiency of these photoprocesses in aquatic environments: the transparency of natural waters, pesticide molar extinction coefficient and water solubility, solar light absorption and pH value of water, which may shift the pesticide absorption maximum and produce significant effects on photohydrolysis kinetics. For example, in the case of the direct photolysis of aromatic pesticides, the conversion yield has been shown to range from 18 to 99.5% for reaction times of 40-70 min, according to the molecular structure of compounds and the nature of the solvent<sup>3-4</sup>. Generally, the degradation efficiency of pesticides and other organic pollutants can be improved using indirect photochemical processes. In most indirect photochemical methods, UV irradiation of pesticide aqueous solutions is performed in the presence of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$  or  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ <sup>6-11</sup>. Typically, these technologies are based on the use of advanced oxidation processes (AOPs), in which very oxidizing reactive free radicals, mainly  $\text{OH}\cdot$  species, are generated in aqueous solutions and produce rapid photodegradation of organic pollutants. For instance, Mazellier *et al.*<sup>9</sup> have found that, upon solar irradiation of diuron, an aromatic dimethylurea herbicide, in the presence of  $\text{Fe}^{3+}$ , 90% of the diuron disappeared within 2h.

Until now, electrochemical methods have seldom been applied to the degradation of pesticides. Recently, electrochemical reductive dechlorination<sup>12-13</sup> and the electro-Fenton reaction<sup>14-15</sup> have been used successfully for the destruction of chlorophenoxy acid herbicides.

In this work, we present and compare new electrochemical and photochemical methods that we have developed, for the decontamination of natural waters containing significant amounts of pesticides. The electrochemical method is based on the electro-Fenton process, i.e. the simultaneous reduction of oxygen and ferric ions. Hydroxyl radicals ( $\text{OH}\cdot$ ) are electrosynthesized in aqueous solutions and can react rapidly with aromatic pesticides, leading to a polyhydroxylation reaction, followed by complete mineralization of the initial pollutants. We applied this method to selected pesticides, including chlorophenoxy acid herbicides<sup>14</sup>, carbamate and organophosphate insecticides, and coumarin and indanedione rodenticides. The photochemical methods involve either a direct photodegradation of pesticides, or indirect photodegradation processes resulting from UV irradiation of  $\text{H}_2\text{O}_2$  alone or in the presence of  $\text{Fe(III)}$ ; the latter process, corresponding to the formation of  $\text{OH}\cdot$  radicals, has been called the photo-Fenton reaction<sup>6-9</sup>. Examples of applications of these various photochemical methods to selected aromatic pesticides are given. Monitoring the disappearance of pesticides and the formation of reaction products as a function of time was performed by high performance liquid chromatography (HPLC). The environmental interest of these methods for water treatment is discussed. The performances of the electrochemical and photochemical methods are compared.

## Experimental

### Chemicals

2-(4-chloro-2-methylphenoxy)propionic acid (MCP) was obtained from Lancaster, while 2,4-dichlorophenoxyacetic acid (2,4-D), 2-(4-chloro-phenoxy)-2-methyl-propionic acid (CPMP), 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and chlorophenols used as standard, as well as solvents (methanol, acetic acid) were purchased in the highest purity available from Aldrich. Distilled water was utilized. Bendiocarb (2,3-isopropylidendioxy-phenyl-N-methylcarbamate), pirimiphos-methyl [O-(2-diethylamino-6-methylpyrimidin-4-yl)-O,O-dimethylphosphorothioat], coumatetralyl [(4-hydroxy-3-(1,2,3,4-tetrahydro-1-naphthyl)coumarin)], and chlorophacinon ([2-[2-(4-chlorophenyl)-2-phenyl-acetyl]indan-1,3-dion] were used as received.

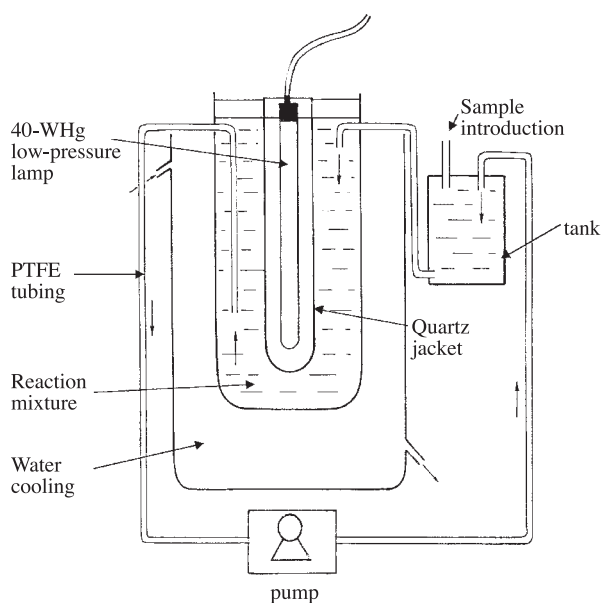
### Electrochemical Procedure

Electrolyses were performed with an EG& G potentiostat/galvanostat (model 273A, Princeton Applied Research) and were carried out in a 150 mL three-electrode electrochemical cell. The working electrode was a 10 cm<sup>2</sup> piece of carbon felt (Carbone Lorraine). The counter-electrode was a 1 cm<sup>2</sup> Pt sheet (Radiometer), which was placed in the anodic compartment separated from the cathodic compartment by a glass frit (porosity: 5). A saturated calomel electrode (SCE, Radiometer) was used as the reference electrode.

Prior to the electrolysis, oxygen was bubbled for 5 min and then 12.6 mg of Fe(III) chloride salt was introduced ( $[Fe^{3+}] = 1 \text{ mM}$ ); the solution was stirred magnetically and the oxygen was bubbled through the solution during the electrolysis. The cathode potential was maintained at  $-0.5V$  vs SCE. This potential permits the simultaneous reduction of both O<sub>2</sub> and Fe<sup>3+</sup>. Under these conditions, the current remained constant (60 mA) during the electrolysis, allowing the production of a constant amount of OH<sup>-</sup> radicals. The quantity of charge passed through the solution was measured continuously by the EG& G potentiostat/galvanostat.

### Photochemical Procedure

All photochemical experiments were carried out at room temperature in a laboratory-made photoreactor, including a 350 mL hollow cylindrical quartz tube. A 40 W low pressure mercury lamp (Heraeus) was positioned within the inner part of the photoreactor, and cooling water was circulated through a Pyrex jacket surrounding the tube (Figure 1). The reaction mixture was continuously pumped through the photoreactor with a peristaltic pump (Heidolph, type 523.030) by means of PTFE tubing; sample and reagent were introduced into a tank. Three different reaction systems were used.



**Figure 1.** Experimental set-up of the photochemical reactor.

In the case of direct irradiation, an aqueous solution of pesticide was used. The initial concentration was 0.85 mM for bendiocarb, 0.1 mM for primiphos-methyl, 0.5 mM for coumatetrlyl and 0.2 mM for chlorophacinon. Samples were withdrawn over time and analyzed in a HPLC (Gilson) apparatus equipped with an UV detector set to 280 nm and a RP-C18 Hypersil column.

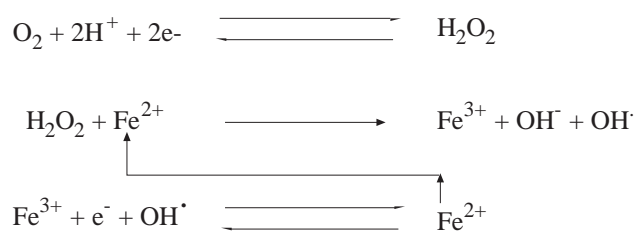
For  $\text{H}_2\text{O}_2$  photolysis, the concentration of  $\text{H}_2\text{O}_2$  was four times that of the pesticide. In the case of the photo-Fenton reaction, the solution contained (in addition to  $\text{H}_2\text{O}_2$ ) an  $\text{FeCl}_3$  concentration twice that of the pesticide under study.

## Results and Discussion

### Electrochemical Method (Electro-Fenton Reaction)

#### *Principle*

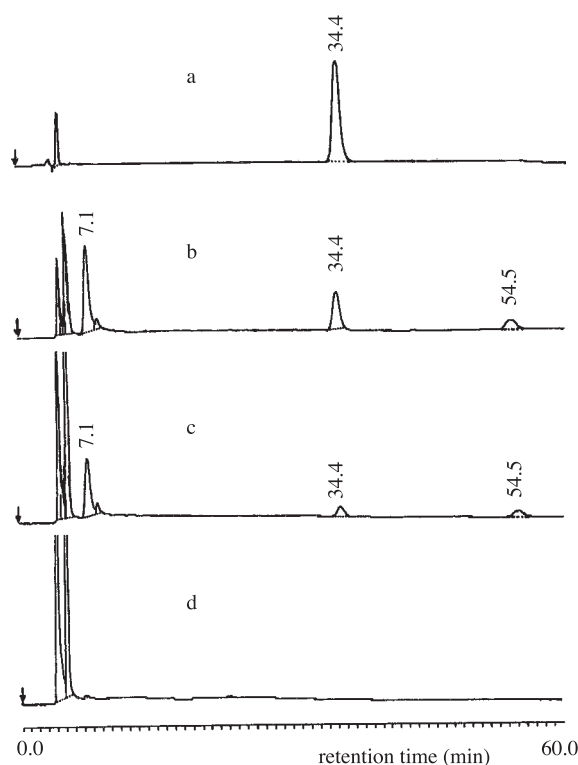
The production of  $\text{OH}\cdot$  radicals is a two step process: (1) electrochemical reduction of dioxygen into  $\text{O}_2^-$  and formation of  $\text{H}_2\text{O}_2$  in the acidic medium; (2) reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  ions yielding  $\text{OH}\cdot$  radicals (electro-Fenton reaction)<sup>14-15</sup> (Scheme 1). In these conditions,  $\text{Fe}^{3+}$  ions are electrochemically reduced to  $\text{Fe}^{2+}$  ions ( $\text{Fe}^{3+}/\text{Fe}^{2+}$  electrocatalytic system).



**Scheme 1.**  $\text{OH}\cdot$  radical production, based on the electrochemical Fenton reaction<sup>14</sup>.

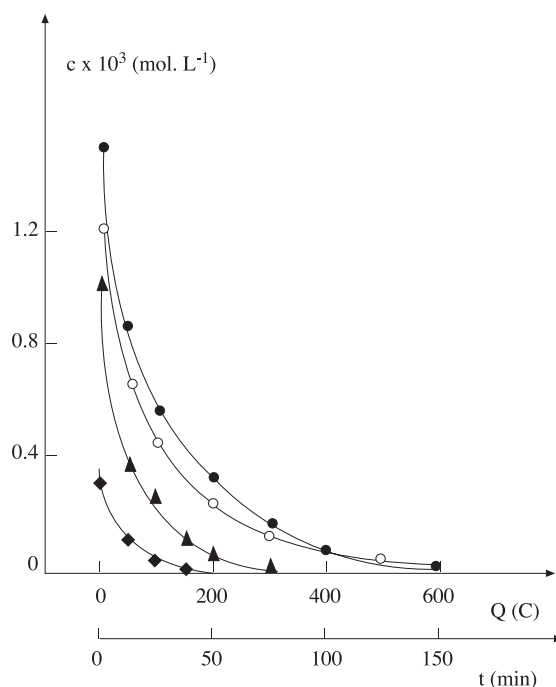
***Application to Degradation of Chlorophenoxy Acid Herbicides***

HPLC analysis allowed us to monitor the disappearance of chlorophenoxy acid herbicides and the formation and/or destruction of reaction products during the electrolysis. A typical example of HPLC study is provided in Figure 2, which presents chromatograms recorded at different coulombic charges in the case of the electrolysis of 2,4,5-T<sup>14</sup>. The HPLC limit of detection was  $10^{-6}$ M for 2,4,5-T in our working conditions. GC-MS analysis permitted the identification of reaction products, which correspond to hydroxylated derivatives of the initial molecules<sup>14</sup>.

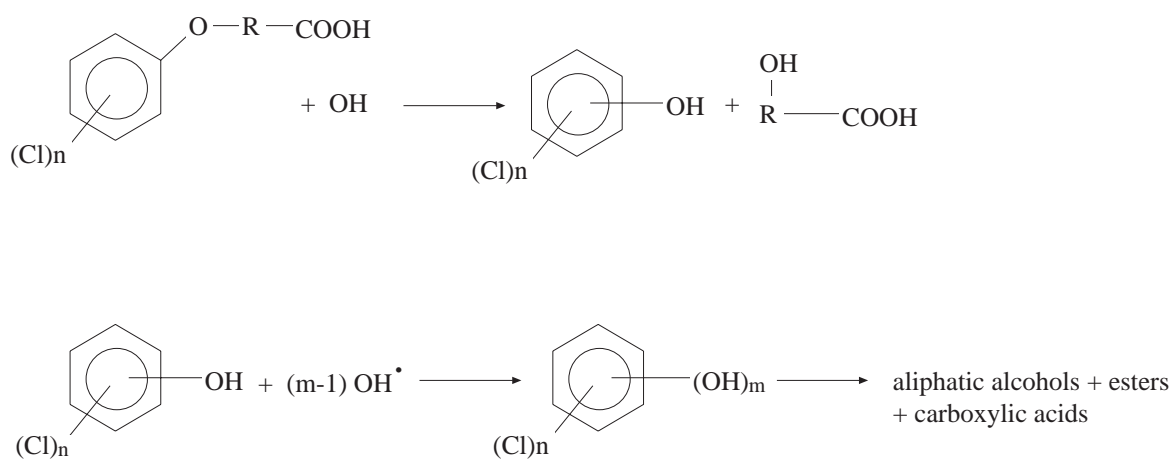


**Figure 2.** HPLC chromatograms recorded for the electrolysis of 2,4,5-Trichlorophenoxy acid ( $3.1 \times 10^{-4}$  M) at different coulombic charges  $Q =$  (a) 0 C; (b) 50 C; (c) 150 C; (d) 200 C<sup>14</sup>. The peaks at 7.1 min, 34.4 min and 54.5 min correspond to the 2,4,5-T dihydroxy derivative, 2,4,5-T and the 2,4,5-T monohydroxy derivative, respectively.

Kinetic and mechanistic studies of the electrochemical degradation of chlorophenoxy acids were performed in aqueous solution. Figure 3 shows the evolution of the chlorophenoxy acid herbicide concentration (measured by HPLC) with coulombic charge and electrolysis time. In all cases, kinetic curves are characterized by a relatively rapid and regular decrease in the herbicide concentration during electrolysis. The final herbicide concentrations were not detectable by HPLC, indicating that they were smaller than about  $10^{-6}$  M, a value which has to be compared to the allowable minimum concentrations of  $2 \times 10^{-7}$  to  $7 \times 10^{-6}$  M in industrial waters and  $5 \times 10^{-10}$  M in drinking water. It can also be seen that the reaction rate is enhanced by the number of chlorine substituents on the aromatic ring. The mechanism of addition of  $\text{OH}\cdot$  radicals on the chlorophenoxy acid aromatic moiety and further degradation reactions (Scheme 2) was confirmed by the kinetic data and product distribution results<sup>14</sup>.



**Figure 3.** Kinetics of degradation of (-●-): 2-(4-chloro-2-methylphenoxy propionic acid (CMPP); (-○-): 2-(4-chlorophenoxy)-2-methylpropionic acid (CPMP); (-▲-): 2,4-dichlorophenoxyacetic acid (2,4-D); (-◆-): 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Electrolysis current: 60 mA. Initial concentrations: 1.50 mM for CMPP; 1.20 mM for CPMP; 1.00 mM for 2,4-D; 0.30 mM for 2,4,5-T.



**Scheme 2.** Mechanism of the addition reaction of OH<sup>•</sup> radicals on the chlorophenoxy acid aromatic moiety and further reactions in aqueous media<sup>14,15</sup>. n = number of substituents (1 ≤ n ≤ 3). m = number of hydroxy groups (m < 4).

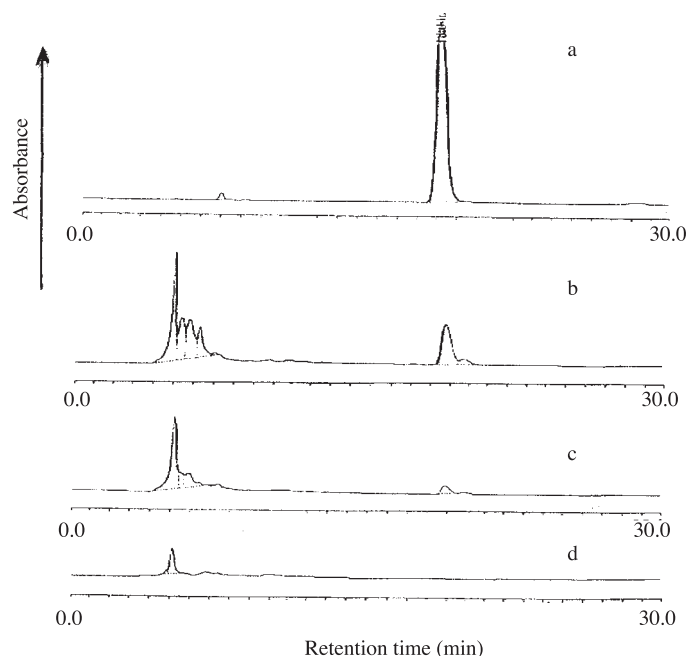
### Application to Degradation of Aromatic Pesticides

Using the same electrochemical method, we also investigated the addition reaction of OH<sup>•</sup> radicals on four aromatic pesticides (bendiocarb, pirimiphos-methyl, coumatetralyl, chlorophacinon) in aqueous media.

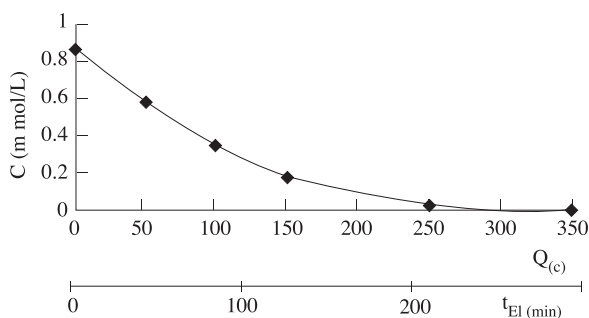
Although the mechanism is not yet fully elucidated, it should include several successive and competitive steps, as shown in Scheme 3 for bendiocarb.

The disappearance of the aromatic pesticides and the formation and/or destruction of reaction products during electrolysis were monitored by HPLC analysis. Typical examples of chromatograms obtained at various coulombic charges during the galvanostatic electrolysis of a 0.85 mM bendiocarb aqueous solution are presented in Figure 4. It can be seen that the peak at a retention time of 13.3 min (corresponding to bendiocarb) decreases with increasing coulombic charges, whereas at retention times ranging from about 3.5 to 4.5 min, several peaks appear, probably due to bendiocarb polyhydroxylated derivatives and/or degradation aliphatic products.

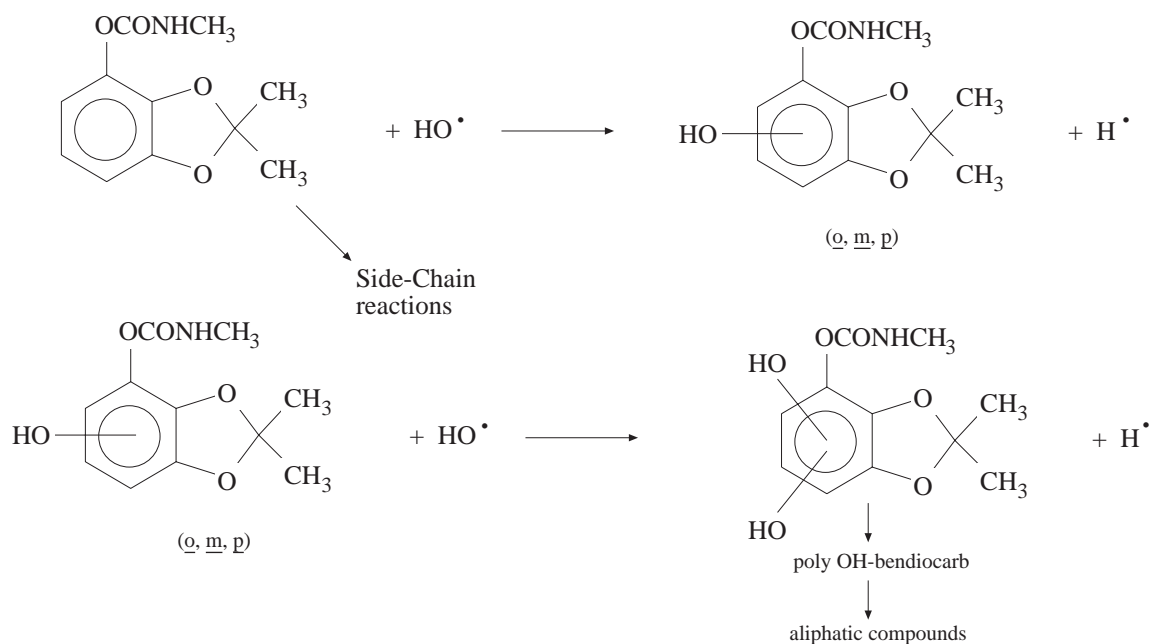
The kinetics of the degradation of aromatic pesticides in aqueous solution were characterized by a regular and exponential decrease in pesticide concentration with coulombic charge and electrolysis time. As can be seen in Figure 5, the total disappearance of the initial bendiocarb concentration (0.85 mM) occurs within 290 min for a coulombic charge of 350 C.



**Figure 4.** HPLC chromatograms recorded for the electrolysis of 0.85 mM bendiocarb at coulombic charges  $Q =$  (a) 0 C; (b) 150 C; (c) 250 C; (d) 750 C. Electrolysis current 20 mA.



**Figure 5.** Kinetic of degradation of 0.85 mM bendiocarb in aqueous solution. Electrolysis current: 20 mA.



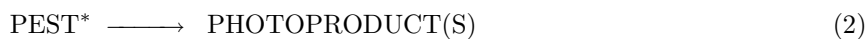
**Scheme 3.** Proposed mechanism of the addition reaction of OH<sup>•</sup> radicals on the bendiocarb aromatic moiety and further reactions in aqueous media.

## Photochemical methods

### Principle

Three distinct photochemical methods can be considered for pesticide degradation in aqueous media.

Direct photolysis of pesticides is a two-step process in which UV light (250-350 nm) was used for irradiation:



with PEST = pesticide in the ground state; PEST\* = pesticide in the electronic excited state.

A third step, which is competitive with step (2) may occur :



with X = solvent, pesticide or other molecule present in the solution.

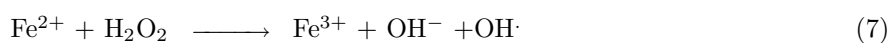
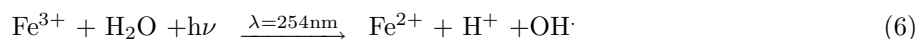
The second, the indirect photochemical method, is based on the photolysis of H<sub>2</sub>O<sub>2</sub> by UV light. It leads to formation of OH<sup>•</sup> radicals which react subsequently with pesticides:





This method presents several advantages such as the use of a cheap, easy-to-handle and infinitely hydro-soluble oxidant ( $\text{H}_2\text{O}_2$ ), and of a simple photoreactor set-up. Moreover, no product has to be separated since the reagent in excess (hydrogen peroxide) is rapidly transformed into non-toxic compounds. However, some drawbacks include the low molar absorption coefficient of  $\text{H}_2\text{O}_2$  and a weak quantum yield of  $\text{OH}\cdot$  production at 254 nm.

The third, the indirect methods, is based on the photo-Fenton reaction which takes place in the presence of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$  ions :



It has also several advantages, such as the use of an economical oxidant and of a catalytic system; it constitutes a fast, efficient and clean method. Indeed, the added Fe(III) concentrations were rather small (in the mM range), well below the allowable minimum limit of this pollutant; in addition, the Fe(II) and Fe(III) ions could be easily eliminated by neutralizing the aqueous medium to be treated.

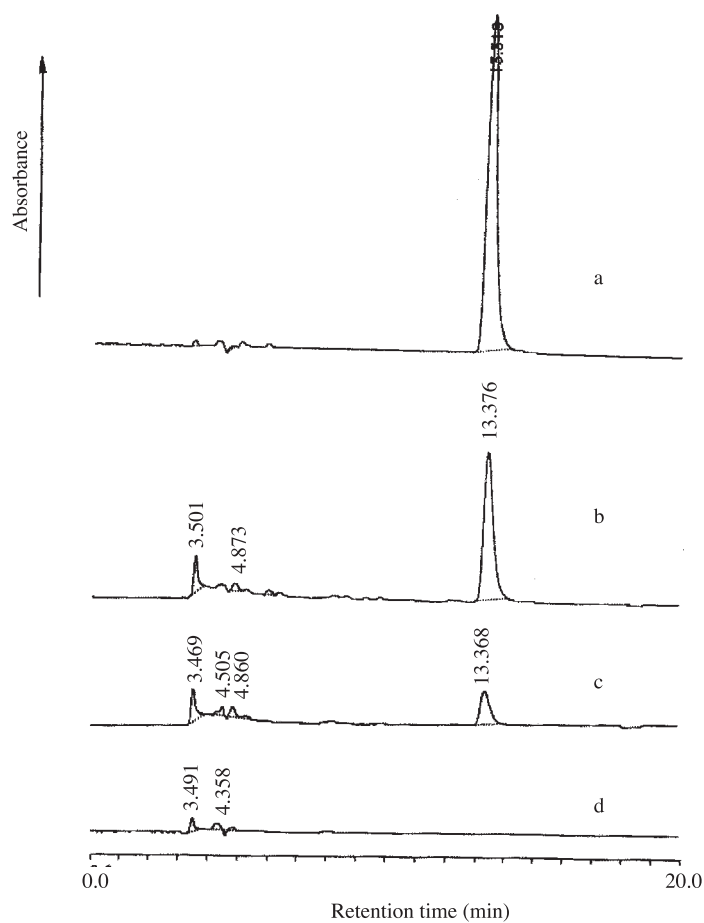
### ***Application to Photodegradation of Aromatic Pesticides***

The disappearance of the aromatic pesticides and formation and/or destruction of photoproducts during direct and indirect photolysis reactions were followed by HPLC analysis. Typical examples of chromatograms recorded at various irradiation times for the direct photolysis and photo-Fenton reaction of a 0.5 mM bendiocarb aqueous solution are shown in Figures 6 and 7, respectively.

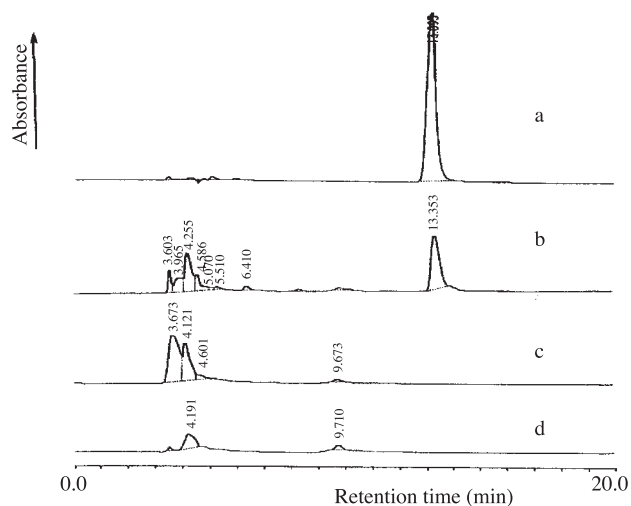
The kinetics of the photodegradation of aromatic pesticides in aqueous solution exhibit a regular and exponential decrease in pesticide concentration with photolysis time. In Figure 8, we compared the kinetics of direct photolysis,  $\text{H}_2\text{O}_2$  photolysis and photo-Fenton reaction of a 0.5 mM bendiocarb aqueous solution. As can be seen, the photoreaction rate was dramatically enhanced in the presence of  $\text{H}_2\text{O}_2$  and of  $\text{H}_2\text{O}_2 + \text{Fe}^{3+}$ .

### **Environmental Applications of the Electrochemical and Photochemical Methods**

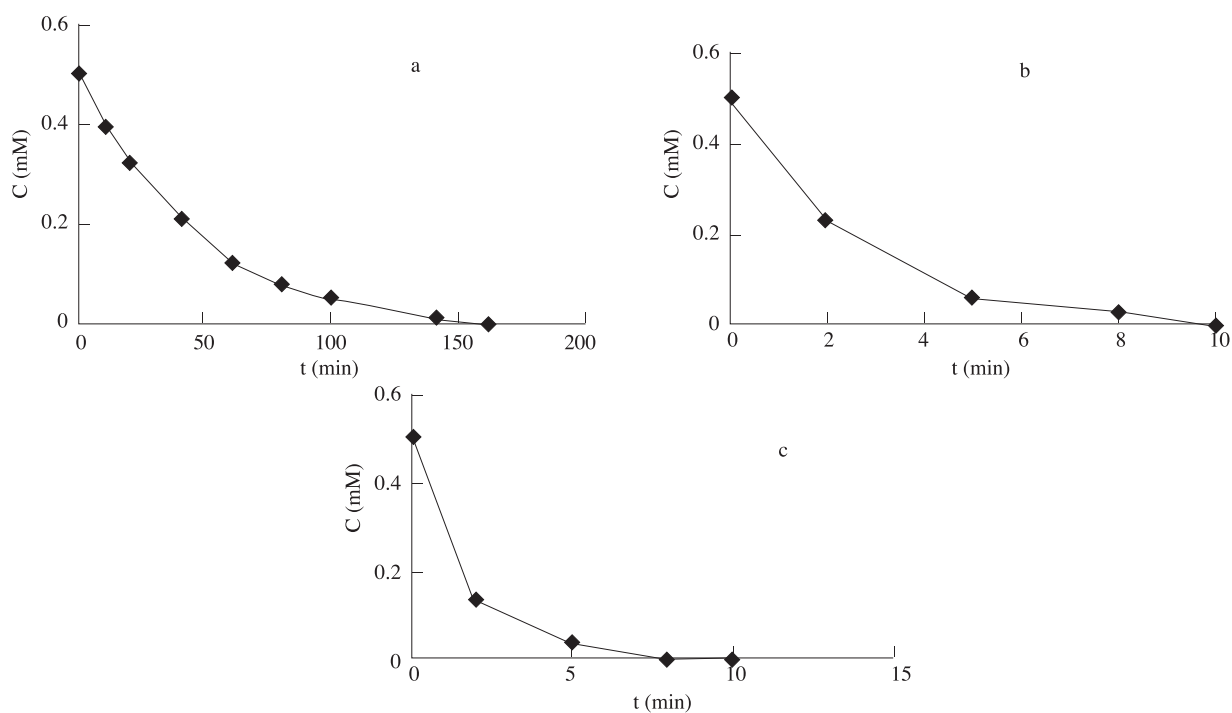
We found that it was possible to apply  $\text{H}_2\text{O}_2$  photolysis, the photo-Fenton reaction and electro-Fenton reaction to remediation of natural water containing millimolar concentration of toxic, persistent aromatic pesticides. It is expected that pesticides will be transformed into biodegradable compounds and mineralized into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , by using these methods for an appropriate duration. Indirect photochemical and electrochemical methods can be considered very efficient and much cleaner techniques than chemical ones for improving the quality of water resources and eliminating aromatic pesticide traces dissolved or dispersed in water.



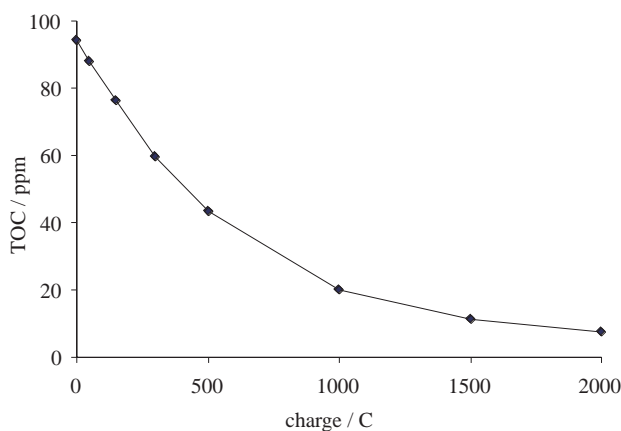
**Figure 6.** HPLC chromatograms recorded for the direct photolysis of 0.5 mM bendiocarb in aqueous solution at irradiation times  $t_{irr}$  = (a) 0 min; (b) 40 min; (c) 100 min; (d) 200 min.



**Figure 7.** HPLC chromatograms recorded for the photo-Fenton reaction of 0.5 mM bendiocarb in aqueous solution ( $[H_2O_2] = 2.0$  mM;  $[Fe^{3+}] = 1.0$  mM) at irradiation times  $t_{irr}$  = (a) 0 min; (b) 2 min; (c) 5 min; (d) 10 min.



**Figure 8.** Kinetics of photodegradation of 0.5 mM bendiocarb aqueous solution. (a) Direct photolysis; (b) Indirect photolysis (UV + H<sub>2</sub>O<sub>2</sub>); (c) Photo-Fenton reaction (UV + H<sub>2</sub>O<sub>2</sub> + Fe<sup>3+</sup>).



**Figure 9.** Total organic carbon (TOC) decay with total charge passed during mineralization of a 125 mL aqueous solution containing 1 mM (220 ppm) of 2,4-D<sup>15</sup>.

An example of environmental application of the electro-Fenton method to the treatment of a natural water sample fortified with 2 mM (440 ppm) of 2,4-D is given in Figure 9. As can be seen, the total organic carbon (TOC) decreases progressively with electrolysis time, leading to removal of more than 93% of the initial quantity of 2,4-D at 2000 C, corresponding to a TOC removal time of 550 min.

### Comparison of the Performances of Photochemical and Electrochemical Methods

In terms of rapidity, the photo-Fenton reaction was found to be much more rapid than the electro-Fenton reaction for the degradation of aromatic pesticides in aqueous solution. As far as cleanliness was concerned,

H<sub>2</sub>O<sub>2</sub> photolysis seemed cleaner than both the electro-Fenton and photo-Fenton reactions, because of the presence of significant concentrations of Fe<sup>3+</sup> and Fe<sup>2+</sup> species in the latter reactions. From the standpoint of simplicity, all photochemical and electrochemical methods considered in this work require relatively simple, cheap and easy-to-handle experimental devices for the degradation of pesticides in aqueous media. Finally, the photo-Fenton and electro-Fenton methods can be considered the more efficient techniques for obtaining high mineralization values within relatively short times.

## Conclusion

We can conclude from this study that it is possible to degrade efficiently several classes of pesticides in aqueous media, either by electrocatalyzed formation of Fenton reagent (H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>) or by indirect photolysis (H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>). In these indirect methods, we have demonstrated that very reactive OH· radicals were formed, leading to polyhydroxylation of aromatic rings, transformation into biodegradable products and rapid mineralization in CO<sub>2</sub> and H<sub>2</sub>O. In addition, these photochemical and electrochemical reactions can be monitored by simple analytical techniques, such as HPLC, GC-MS and TOC measurements. Indirect photochemical methods can be considered alternative approaches for decontaminating natural waters polluted by pesticides. Indeed, these novel water treatment techniques can be considered ecologically friendly, simple to handle and economical, since catalytic processes are generally involved and low concentrations of reagents are needed.

## References

1. D. Barcelo, **J. Chromatogr.**, **643** 117 (1993).
2. C. Tomlin, Ed., "**The Pesticides Manual**", 10<sup>th</sup> ed., British Crop Protection Council, Brackwell, UK, 1994.
3. A. Coly, J. J. Aaron, **Talanta**, **41**, 1475 (1994).
4. A. Coly, J. J. Aaron, **Anal. Chim. Acta**, **360**, 129 (1998).
5. L. Patria, N. Merlet, M. Dore, **Environ. Technol.**, **16**, 315 (1995).
6. R. Bauer, M. Fallmann, **Res. Chem. Intermed.**, **23**, 341 (1997).
7. Y. Sun, J. J. Pignatello, **Environ. Sci. Technol.**, **27**, 304 (1993).
8. R. A. Doong, W. H. Chang, **Chemosphere**, **37**, 2563 (1998).
9. P. Mazellier, M. Sarakha, M. Bolte, **Pestic. Sci.**, **49**, 259 (1997).
10. P. Mazellier, M. Sarakha, M. Bolte, **New J. Chem.**, **23**, 133 (1999).
11. C. Y. Kuo, S. L. Lo, **Chemosphere**, **38**, 2041 (1999).
12. A. Tsyganok, K. Otsuka, I. Yamanaka, V. Plekhanov, S. Kulikov, **Chem. Lett.**, **4**, 261 (1996).
13. D. C. Coumbex, D. J. Tucker, A. M. Bond, **J. Electroanal. Chem.**, **426**, 23 (1997).
14. M. A. Oturan, J. J. Aaron, N. Oturan, J. Pinson, **Pestic. Sci.**, **55**, 558 (1999).
15. M. A. Oturan, **J. Appl. Electrochem.**, **30**, 475 (2000).