

# Use of Fenton's Reagent for Removal of Pesticides from Industrial Wastewater

K. Barbusiński<sup>1,2</sup>, K. Filipek<sup>2</sup>

<sup>1</sup> Institute of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-101 Gliwice, Poland

<sup>2</sup> Department of Water Protection, Central Mining Institute, 40-166 Katowice, Poland

Received: December 15, 2000

Accepted: February 19, 2001

## Abstract

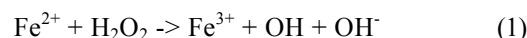
The process of pesticide ( $\gamma$ -HCH and inactive isomers  $\alpha$ - and  $\beta$ -HCH, DDT, DMDT, fenitrothion and chlorfenvinphos) removal from industrial wastewater using Fenton's reaction has been analysed. Most of the pesticides were completely degraded at  $\text{H}_2\text{O}_2$  concentration of  $2.5 \text{ g/dm}^3$ ; however, only at  $5 \text{ g/dm}^3$  were all the examined pesticides completely removed and the results repeatable. The most effective process was for fenitrothion (from 98.5 to 100%) and chlorfenvinphos (from 97.1 to 100%), whereas organochlorine pesticides were removed with efficiency of more than 90%. The optimum ratio of  $[\text{Fe}^{2+}]$  to  $[\text{H}_2\text{O}_2]$  was from 1:3 to 1:2 while the optimum pH was from 3.0 to 3.5. Tests based upon a bioluminescent bacteria *Vibrio fischeri* NRRL B-11177, at optimized Fenton's reaction parameters, show the reduction of toxicity to non-toxic levels.

**Keywords:** Fenton's reaction, chemical oxidation, pesticides, toxicity

## Introduction

The process of pesticide removal from industrial wastewater is of great importance because of well known pesticide resistance to microbial degradation, and its ability of cumulation in the environment as well as possible carcinogenic and mutagenic properties. One of the possible methods of their degradation and removal is chemical oxidation, especially advanced oxidation processes (AOPs) using e.g.  $\text{O}_3/\text{H}_2\text{O}_2$  (Peroxone),  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{TiO}_2/\text{UV}$  and Fenton reactions [1-4]. These processes involve the *in situ* formation of highly reactive hydroxyl radicals (OH), which react quickly and non-selectively with almost all-organic pollutants [5].

Fenton's reaction [6] is one of the most effective methods of oxidation of organic pollutants, that are oxidatively degraded by hydroxyl radicals generated from  $\text{H}_2\text{O}_2$  in the presence of  $\text{Fe}^{2+}$  as a catalyst [7]:



When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Equation 1). With ferric salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and hydrogen peroxide (Equation 2) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide [7, 8]:



The efficiency of Fenton's process depends on  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations and pH of the reaction. According to a previous researcher's report, pH value should be in the range of 3 to 5 [7, 9-11].

Fenton's reagent was found to be very effective in treating various industrial wastewater components, including aromatic and aliphatic compounds [10, 12-16],

a wide variety of dyes [9, 17, 18], as well as many other substances, including pesticides [19, 20]. Fenton's reagent has been applied in the decomposition of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-j-triazine], which is a potential carcinogenic compound relatively resistant to conventional oxidation methods such as ozonation or chlorine dioxide action and of a high persistence in the environment [20, 21].

The aim of the present study is to determine the efficiency of Fenton's reaction in the process of pesticide removal from wastewater produced by a chemical factory located in southern Poland. Various organochlorine pesticides and their derivatives, i.e.  $\gamma$ -HCH (Lindan) and its inactive isomers ( $\alpha$ - and  $\beta$ -HCH), DDT, DMDT (Methoxychlor) as well as organophosphorous pesticides, i.e. fenitrothion and chlorfenvinphos were the subject of experiments.

## Materials and Methods

### Wastewater

Presence of the pesticides in wastewater was both due to production of the pest control products and leaching out from the toxic solid wastes dump located in the area of the factory. Pesticide concentrations and other measured parameters in the wastewater are presented in Table 1.

### Experimental Procedure

The following parameters of Fenton's reaction were examined and optimized:  $H_2O_2$  concentration,  $[Fe^{2+}]$ :  $[H_2O_2]$  ratio, and pH. The procedure was as follows: wastewater was put into reactors of 2 dm<sup>3</sup> volume, and then acidified with  $H_2SO_4$ , if necessary, as Fenton's reaction is only effective in acidic pH range. Hence, when the initial pH of wastewater was above 5.0, the samples were

acidified to the selected value, in the pH range of 2.5-4.0, in order to estimate the pH effect on pesticide removal. After that, the various doses of 30%  $H_2O_2$  and solid  $FeSO_4 \cdot 7H_2O$  were added with continuous magnetic stirring. Within two hours the wastewater was neutralized with 5% solution of CaO up to about pH 7. After sedimentation, pesticide concentration, COD, BOD<sub>5</sub> and residual  $H_2O_2$  were determined in the clear solution. Dewatering properties of chemical sediment were also estimated. At optimal parameters of Fenton's reaction, toxicity was measured using a bioluminescent bacteria *Vibrio fischeri* NRRL B-11177.

COD, BOD<sub>5</sub> and toxicity tests were made after total removal of residual  $H_2O_2$ , using  $Na_2SO_3$ , as even very low concentration of hydrogen peroxide resulted in inhibition of vital activity of bioluminescent bacteria *Vibrio Fischeri* NRRL B-11177 used as toxicity indicators. Hydrogen peroxide may also inhibit physiological activity of microbial populations used in BOD tests. The residual  $H_2O_2$  also increased the COD value since it acts as a reductant, especially in the chromate-based analysis of COD. Talinli and Anderson [22] investigated the reducing effect of  $H_2O_2$  on  $K_2Cr_2O_7$  and they show linear relationships between concentrations of  $H_2O_2$  and COD.

### Analytical Methods

#### Pesticides

The pesticides were analysed chromatographically with the external standard. The GC 6000 Vega Series 2 chromatograph with ECD detector and the capilar column Rtx-5 (30 m x 0.53 mm x 1.5  $\mu$ m) was applied with nitrogen as a carrier gas. The concentrations of the standards solutions were from 0.01 to 0.0035  $\mu$ g/cm<sup>3</sup> for  $\alpha$ ,  $\beta$  and  $\gamma$ -HCH, while 0.02 to 0.07  $\mu$ g/cm<sup>3</sup> for fenitrothion, chlorfenvinphos, DDT and DMDT. 0.5  $\mu$ l samples of the standards and the examined solutions were injected into the column.

Table 1. Pesticide concentrations and values of other measured parameters in wastewater.

Pesticide	Unit	Range	Series					Average	Standard deviation
			I	II	III	IV	V		
$\alpha$ -HCH	$\mu$ g/dm <sup>3</sup>	46.4 – 53.7	52.3	51.0	53.7	51.6	46.4	51.0	2.76
$\beta$ -HCH	$\mu$ g/dm <sup>3</sup>	9.5 – 34.1	24.5	9.5	23.7	29.5	34.1	24.3	9.25
$\gamma$ -HCH	$\mu$ g/dm <sup>3</sup>	54.3 – 62.4	57.1	56.7	62.4	56.8	54.3	57.5	2.98
DDT	$\mu$ g/dm <sup>3</sup>	0.0 – 46.9	20.9	0.0	46.9	3.91	8.8	16.1	18.90
DMDT	$\mu$ g/dm <sup>3</sup>	7.0 – 91.8	89.7	7.0	68.8	11.8	91.8	53.8	41.57
Fenitrothion	$\mu$ g/dm <sup>3</sup>	44.4 – 377.1	173.2	61.9	44.4	133.2	377.1	158.0	133.22
Chlorfenvinphos	$\mu$ g/dm <sup>3</sup>	30.2 – 312.8	87.3	30.2	130.1	312.8	139.1	139.9	105.82
COD	mg/dm <sup>3</sup>	124 – 366	124	265	180.3	233.6	366	233.8	91.34
BOD <sub>5</sub>	mg/dm <sup>3</sup>	37.2 – 49.5	37.2	41.4	37.8	40.1	49.5	41.2	4.94
BOD <sub>5</sub> /COD	–	0.13 – 0.30	0.30	0.16	0.21	0.17	0.13	0.19	0.066
pH	–	2.0 – 8.5	3.2	7.0	6.7	8.5	2.0	5.5	2.75

COD, BOD<sub>5</sub>, pH, Residual H<sub>2</sub>O<sub>2</sub>, Capillary Suction Time

COD (closed reflux, titrimetric method No. 5220C) and BOD<sub>5</sub> (Method No. 5210B) were determined in accordance with Standard Methods, APHA [23], while pH was measured by pH-meter (pH-196, WTW Germany). Concentration of residual H<sub>2</sub>O<sub>2</sub> was analyzed by iodometric method. In order to estimate filterability of chemical sludge (after neutralization with CaO), the capillary suction time (CST) was measured using Method 2710 G of APHA [23].

### Toxicity

The ToxAlert® 10 instrument (Merck) was used to determine wastewater toxicity. The ToxAlert® 10 system is a screening tool designed to provide a rapid and simple test for determining acute biological toxicity. It is based upon a freeze-dried bioluminescent bacteria *Vibrio fischeri* NRRL B-17177. These bacteria are commonly used in Microtox test [24]. Bioluminescence is directly linked to the vitality, and metabolic status of the cell. A toxic substance will cause changes in the cellular state - cell wall, cell membrane, the electron transport system, enzymes, and cytoplasmic constituents - which are rapidly reflected in a decrease in bioluminescence.

## Results and Discussion

### Optimal Conditions

The optimum concentration of H<sub>2</sub>O<sub>2</sub>, sufficient for pesticide removal was determined to be between 2.5 and 5.0 g/dm<sup>3</sup>. The range of concentrations, however, was not precisely determined for all the pesticides. It was most likely due to the relatively high variability in their concentrations in the examined wastewater. This was especially apparent for fenitrothion, chlorfenvinphos, DDT and DMDT (Table 1).

A dose of 2.5 g/dm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> was sufficient to remove most of the examined pesticides; however, at a dose of 5 g/dm<sup>3</sup> the stable results of removal were achieved for all the pesticides. It is worth adding that a dose higher than 5 g/dm<sup>3</sup> did not cause any improvement (see example of an  $\gamma$ -HCH in Fig. 1). Moreover, for chlorfenvinphos and DMDT at a dose of 20 g/dm<sup>3</sup> a decrease of efficiency was observed (Fig. 1), in accordance with a known opinion [10] that at the high excess of H<sub>2</sub>O<sub>2</sub> it may behave as an OH<sup>•</sup> radical scavenger. The other clear result of our experiments was that pH should be in a range of 3.0 - 3.5 and at the more acidified solution (pH less than 3.0) no visible improvement of efficiency was observed.

Experiments concerning the optimization of Fe<sup>2+</sup> concentrations show that the best results were achieved at a [Fe<sup>2+</sup>]:[H<sub>2</sub>O<sub>2</sub>] ratio of 1:3 - 1:2. Some of the examples are shown in Fig. 2, where the influence of a Fe<sup>2+</sup> concentration on the removal of an  $\gamma$ -HCH and DDT is shown. A diminishing efficiency of Fenton's reaction at a [Fe<sup>2+</sup>]:[H<sub>2</sub>O<sub>2</sub>] ratio 1:1.33 (i.e. an increase of ferrous ions) was in accordance with other report results [10, 19,

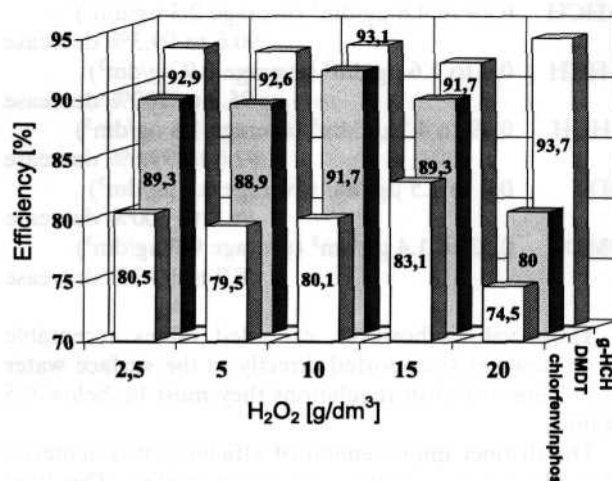


Fig. 1. The efficiency of chlorfenvinphos, DMDT and  $\gamma$ -HCH removal vs. H<sub>2</sub>O<sub>2</sub> dose.

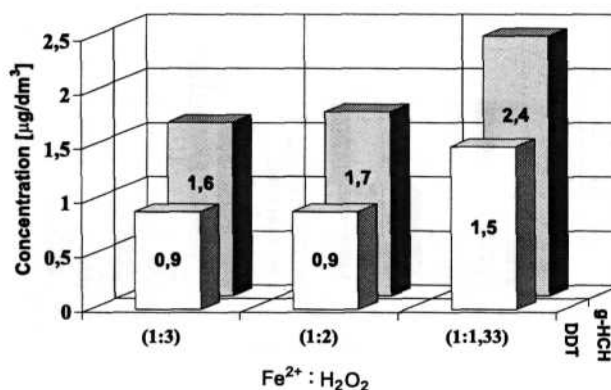
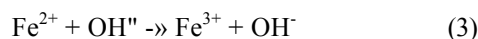


Fig. 2. Influence of [Fe<sup>2+</sup>]:[H<sub>2</sub>O<sub>2</sub>] ratio on efficiency of removal of DDT and  $\gamma$ -HCH.

25]. These phenomena could be explained by an observation that in the absence of organic substrates, excessive ferrous ions are the dominant hydroxyl radical's scavenger through the following reaction [10, 26]:



The best removal results were achieved for the organophosphorous pesticides, i.e. fenitrothion (from 98.5 to 100%; average value 3.2 µg/dm<sup>3</sup>) and chlorfenvinphos (from 97.1 to 100%; average value 2.1 µg/dm<sup>3</sup>). The sum of final concentration of fenitrothion and chlorfenvinphos, at optimal conditions, did not exceed the acceptable in Poland normalized values (10 µg/dm<sup>3</sup>). The efficiency of organochlorine pesticides removal was also very high. At optimal conditions (pH = 3.0 - 3.5, Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub> = 1:3), and at the dose of H<sub>2</sub>O<sub>2</sub> = 5.0 g/dm<sup>3</sup>, the final concentrations of pesticides and removal efficiency were as follows:

$\alpha$ -HCH	0.49 to 4.8 $\mu\text{g}/\text{dm}^3$ (average 2.3 $\mu\text{g}/\text{dm}^3$ ) 90.6 to 99.3% decrease
$\beta$ -HCH	0.0 to 1.6 $\mu\text{g}/\text{dm}^3$ (average 0.9 $\mu\text{g}/\text{dm}^3$ ) 95.3 to 100% decrease
$\gamma$ -HCH	0.39 to 4.2 $\mu\text{g}/\text{dm}^3$ (average 1.8 $\mu\text{g}/\text{dm}^3$ ) 92.6 to 99.6% decrease
DDT	0.0 to 1.5 $\mu\text{g}/\text{dm}^3$ (average 0.4 $\mu\text{g}/\text{dm}^3$ ) 96.8 to 100% decrease
DMDT	0.23 to 1.4 $\mu\text{g}/\text{dm}^3$ (average 0.9 $\mu\text{g}/\text{dm}^3$ ) 88.9 to 99.2% decrease

These values, however, exceeded values acceptable for wastewater transported directly to the surface water (according to Polish regulations they must be below 0.5  $\mu\text{g}/\text{dm}^3$ ).

The distinct improvement of efficiency was achieved when the reagents were added step-by-step. The final concentrations of the pesticides for the processes with a single and a distributed (step-by-step) dosage are presented in Figure 3. It is easy to notice that the final concentration of the pesticides in the latter case was several times lower than in the former one.

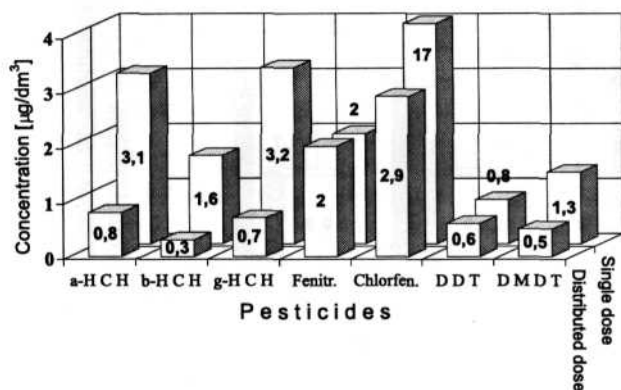


Fig. 3. The pesticide concentrations after Fenton's reaction with a single and a distributed dosage of the reagents.

Fenton's reaction was very effective for the other organic component's destruction. The efficiency of COD removal was changed from 58.7 to 87.1% as a result of its application. The COD values in the purified wastewater were in the range of 10.8-74.5  $\text{mg O}_2/\text{dm}^3$ , which is well below acceptable Polish values for wastewater transported directly to surface water (150  $\text{mg O}_2/\text{dm}^3$ ). The positive side-effect of Fenton's reaction was also an increase of wastewater biodegradability that has been evaluated by measuring the  $\text{BOD}_5/\text{COD}$  ratio. The  $\text{BOD}_5/\text{COD}$  ratio in wastewater not treated by Fenton's reaction was ca. 0.13-0.30, which made their biological decomposition practically impossible. The application of Fenton's reaction, at the  $[\text{H}_2\text{O}_2] = 1.0 \text{ g}/\text{dm}^3$ , changed the ratio to the range of 0.38-0.50. At these conditions, however, the efficiency of pesticide removal was not satisfactory. The increase of a hydrogen peroxide dose was followed by a very efficient degradation of pesticides and decrease of a  $\text{BOD}_5/\text{COD}$  ratio. The decrease in

$\text{BOD}_5/\text{COD}$  ratio observed under severe conditions (high dose of  $\text{H}_2\text{O}_2$ ) was due to the faster  $\text{BOD}_5$  decrease in comparison with COD changes. This result suggests the chemical oxidant ( $\text{H}_2\text{O}_2$ ) in Fenton's reaction was largely decomposed to react with biodegradable compounds. Similar effects were also observed by other research groups [27-29]. For example, Gilbert [27] found that partial oxidation of aromatic and EDTA-containing industrial wastewater with Fenton's reagent led to a highly biodegradable effluent, but further oxidation led to lower  $\text{BOD}/\text{COD}$  ratios.

### Toxicity

The increase in  $\text{BOD}_5/\text{COD}$  ratio observed after oxidation with lower doses of  $\text{H}_2\text{O}_2$  shows that the treatment by Fenton's reagent can lead to wastewater containing organics that are considerably more biodegradable than those contained in raw wastewater (prior to oxidation). The increase in  $\text{BOD}_5/\text{COD}$  ratio can also indicate that significant concentrations of toxic products are not formed. In described experiments raw wastewater inhibited vital functions of the bioluminescent bacteria *Vibrio fischeri* in 90%. In the experiments when Fenton's reagent was used at the optimal range (2.5 - 5.0  $\text{g H}_2\text{O}_2/\text{dm}^3$ ;  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  ratio 1:3 - 1:2; pH = 3.0 - 3.5), toxicity was completely reduced.

On the basis of literature data on degradation of pesticides and their derivatives [12, 30-32] one may assume that in oxidation reactions with  $\text{OH}^-$  radicals no stable toxic intermediate products are formed. Generally, pesticides are oxidized to  $\text{CO}_2$ ; however, carboxylate anions, as formates, acetates or oxalates are formed as intermediate, non-toxic products [30]. Pesticides containing halogen, sulphur or phosphorous heteroatoms are quantitatively oxidized by Fenton's reagent to form chlorides, sulphates and phosphates [32]. This suggests that Fenton's process may also be applied to treat the examined wastewater in an integrated chemical-biological oxidation system. In these systems wastewater that is toxic, inhibitory or refractory to biological cultures can be chemically pretreated to produce biogenic intermediates.

### Neutralization with CaO

The necessary doses of lime (CaO) used to neutralise wastewater after Fenton's reaction are dependent on a  $\text{H}_2\text{O}_2$  dose,  $\text{Fe}^{2+}$  concentration and an initial pH of a reaction system. Generally, a decrease in initial pH of Fenton's reaction, increase of  $\text{H}_2\text{O}_2$  dose and increase of a  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$  ratio are followed by increasing doses of CaO used to neutralization. Thus, an increase of hydrogen peroxide dose from 2.5 to 5.0  $\text{g}/\text{dm}^3$  caused an increase of a CaO dose from 3.7 to 6.3  $\text{g}/\text{dm}^3$ . When initial pH was changed from 4.0 to 2.5, the amount of CaO was increased for about 0.4 to 1.5  $\text{g}/\text{dm}^3$  in relation to the  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$  ratio. The necessary doses of CaO required for Fenton's reaction neutralization are shown in Figure 4 ( $[\text{H}_2\text{O}_2] = 5.0 \text{ g}/\text{dm}^3$ , pH 3.0 and 3.5). It is worth noting that at the  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$  ratio above 1:2, the amount of CaO, necessary to neutralise pH of solution was rapidly

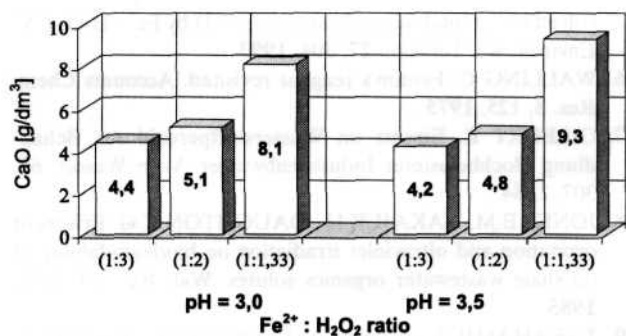


Fig. 4. CaO concentrations in relation to a Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub> ratio.

growing. On the other hand, the sludge thickening after a neutralisation reaction was an effective yet very quick process.

#### Sludge Dewatering Properties

In the examined experiments, in contrast to organic sediments of activated sludge type, it was not a problem to obtain mineralized, biologically stable and non-odorous sludge. The crucial advantage was their ability to easy and effective dewatering. The capillary suction time (CST) gives useful information about sludge tendency to dewatering: low CST values indicate a faster dewatering and contrariwise. All the examined sludges, formed after neutralization with CaO, possessed low values of CST, changing from 10 to 12 seconds. They were thus very sensitive to dewatering.

The ferric hydroxide sludge, an additional product of Fenton's reaction, was formed in a low amount, up to 3-5% of total sludge volume after neutralization with CaO. Its stability and dewaterability were not determined.

#### Conclusions

The examined Fenton's reaction was found to be very efficient for removing pesticides from industrial wastewater. The best removal efficiency was achieved for fenitrothion (from 98.5 to 100%) and chlorfenvinphos (from 97.1 to 100%). The organochlorine pesticides were destroyed with efficiency of more than 90%. However, regardless of the applied doses of reagents, the determined minimum of the residue pesticides concentration has never been exceeded. This refers mainly to the organochlorine pesticides. For individual pesticides a dose of H<sub>2</sub>O<sub>2</sub> = 2.5 g/dm<sup>3</sup> was in most cases sufficient and caused the maximum removal effects. However, a dose of 5.0 g/dm<sup>3</sup> led to the best results for all the examined pesticides. It was discovered that the best effects were achieved for a Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub> ratio 1:3 to 1:2 and at pH 3.0 to 3.5. At described conditions, Fenton oxidation completely eliminated high toxicity of raw wastewater towards bioluminescent bacteria *Vibrio fischeri*.

#### Acknowledgements

The authors wish to thank Mr C. Gierczak and Mr A. Kaczmarczyk from the "Organika-Azot" chemical factory for their technical and analytical assistance.

#### References

- SCOTT J.P., OLLIS D.F. Integration of chemical and biological oxidation processes for water treatment: review and recommendations. *Environ. Prog.* **14**, 88, **1995**.
- HUSTON P.L., PIGNATELLO J.J. Reduction of perchloroalkanes by ferrioxalate-generated carboxylate radical preceding mineralization by the photo-Fenton reaction. *Environ. Sci. Technol.* **30**, 3457, **1996**.
- PROUSEK J. Advanced oxidation processes for water treatment - chemical processes. *Chem. Listy.* **90**, 229, **1996 a**.
- PROUSEK J. Advanced oxidation processes for water treatment - photochemical processes. *Chem. Listy.* **90**, 307, **1996 b**.
- BAUER R., FALLMANN H. The photo-Fenton oxidation - a cheap and efficient wastewater treatment method. *Res. Chem. Intermed.* **23**, 341, **1997**.
- FENTON H. J.H. Oxidation of tartaric acid in presence of iron. *J. Chem. Soc.* **65**, 899, **1894**.
- BISHOP D.F., STERN G., FLEISCHMAN M, MAR SHALL L. S. Hydrogen peroxide catalytic oxidation of refractory organics in municipal waste waters. *Ind. Eng. Chem. Proc. Des. Dev.* **7**, 110, **1968**.
- KIWI J., PULGARIN C, PERINGER P., GRATZEL M. Beneficial effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in wastewater treatment. *Appl. Catal. B: Environmental.* **3**, 85, **1993**.
- KUO W.G. Decolorizing dye wastewater with Fenton's reagent. *Wat. Res.* **26**, 881, **1992**.
- TANG W.Z., HUANG C.P. 2,4-dichlorophenol oxidation kinetics by Fenton's reagent. *Environ. Technol.* **17**, 1371, **1996**.
- BARBUSINSKI K, KOSCIELNIAK H. Degradation of industrial contaminants by Fenton's reaction (in Polish). *Chemia i Inżynieria Ekologiczna.* **4**, 153, **1997**.
- SEDLAK D.L., ANDREN A.W. Oxidation of chlorobenzene with Fenton's reagent. *Environ. Sci. Technol.* **25**, 777, **1991**.
- LIPCZYNSKA-KOCHANY E. Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction. *Chemosphere.* **22**, 529, **1991**.
- HAGG W.R., YAO C.C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol.* **26**, 1005, **1992**.
- PIGNATELLO J.J, HUANG L.Q. Degradation of polychlorinated dibenzo-*p*-dioxin and dibenzofuran contaminants in 2,4,5-T by photoassisted iron-catalyzed hydrogen peroxide. *Wat. Res.* **27**, 1731, **1993**.
- KOYAMA O, KAMAGATA Y, NAKAMURA K. Degradation of chlorinated aromatics by Fenton oxidation and methanogenic digester sludge. *Wat. Res.* **28**, 895, **1994**.
- LIN S.H., PENG C.F. A continuous Fenton's process for treatment of textile wastewater. *Environ. Technol.* **16**, 693, **1995**.
- LIN S.H, CHEN M.L. Purification of textile wastewater effluents by a combined Fenton process and ion exchange. *Desalination.* **109**, 121, **1997**,

19. LU M.C., ROAM G.D, CHEN J.N., HUANG C.P. Photocatalytic oxidation of dichlorvos in the presence of hydrogen peroxide and ferrous ion. *Wat. Sci. Technol.* **30**, 29, **1994**.
20. ARNOLD S.M., HICKEY W.J., HARRIS R.F. Degradation of atrazine by Fenton's reagent: condition optimization and product quantification. *Environ. Sci. Technol.* **29**, 2083, **1995**.
21. BELTRAN F.J., OVEJERO G., ACEDO B. Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. *Wat. Res.* **27**, 1013, **1993**.
22. TALINLI I., ANDERSON G.K. Interference of hydrogen peroxide on the standard COD test. *Wat. Res.* **26**, 107, **1992**.
23. APHA. Standard Methods for the Examination of Water and Wastewater, 18th edn. American Public Health Association, Washington, DC, **1992**.
24. BULICH A.A., TUNG K., SCHEIBNER G. The luminescent bacteria toxicity test: its potential as an in vitro alternative. *Jour. of Bioluminescence and Chemiluminescence.* **5**, 71, **1990**.
25. SUN Y., PIGNATELLO J.J. Photochemical reactions involved in the total mineralization of 2,4-D by  $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ . *Environ. Sci. Technol.* **27**, 304, **1993**.
26. WALLING C. Fenton's reagent revisited. *Accounts Chem. Res.* **8**, 125, **1975**.
27. GILBERT E. Einsatz von Wasserstoffperoxid zur Behandlung Hochbelasteter Industrieabwasser. *Vom Wasser.* **62**, 307, **1984**.
28. JONES B.M., SAKAJI R.H, DAUGHTON C.G. Effects of ozonation and ultraviolet irradiation on biodegradability of oil shale wastewater organics solutes. *Wat. Res.* **19**, 1421, **1985**.
29. TAKAHASHI N., NAKAI N.T., SATOH Y., KATOH Y. Variation of biodegradability of nitrogenous organic compounds by ozonation. *Wat. Res.* **28**, 1563, **1994**.
30. WHITE-STEVENS R. Pesticides in the environment, vol. 1. Marcel-Dekker, Inc., New York. **1971**.
31. OLLIS D.F., PELIZZETTI E., SERPONE N. Destruction of water contaminants. *Environ. Sci. Technol.* **25**, 1523, **1991**.
32. PIGNATELLO J.J. Dark and photoassisted  $\text{Fe}^{3+}$  - catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* **26**, 944, **1992**.