

Applicability of solar photo-Fenton process to the remediation of water polluted with pesticides.Hiroshi Sakugawa¹, Nahed Hasan², Emmanuel F. Olasehinde^{1,3}, Kazuhiko Takeda¹, Hiroaki Kondo¹¹Department of Environmental Dynamics and Management, Graduate School of Biosphere Science, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan²Pesticide Department, Faculty of Agriculture, Kafr El-Sheikh University, Egypt³Chemistry Department, Federal University of Technology, Akure, Nigeria.hsakuga@hiroshima-u.ac.jp

Abstract: The applicability of solar photo-Fenton process to the degradation of three pesticides in pure and natural waters was investigated in Fe(III)/H₂O₂/UV-Vis and Fe(III)/H₂O₂ UV-Vis oxidation systems at pH 2.8 and 7.2. The pesticides concentrations were determined by HPLC analysis. Furthermore, total mineralization of the pesticides in these systems was evaluated by monitoring the decreases in DOC concentrations with solar simulator irradiation time by TOC analysis. The results obtained indicate that the spontaneous degradation due to solar illumination by Fe³⁺/H₂O₂/UV-Vis system is more effective than Fe²⁺/H₂O₂/UV-Vis system in Milli-Q water and river water at pH 2.8. This great enhancement in the pesticides degradation rate in the photo-Fenton reaction system Fe³⁺/H₂O₂/UV-Vis compared to Fe²⁺/H₂O₂/UV-Vis systems at pH 2.8 is due to the higher rate of ·OH generation in this system in Milli-Q water and river water (4.01 and 5.26 uM/min) compared to Fe²⁺/H₂O₂/UV-Vis systems 2.44 and 2.90 uM/min. respectively. At both pH values, the order of pesticides degradation was diuron > fenitrothion > fenarimol which seems to be related with their solubility. Results obtained from this study makes it plausible to apply the photo-Fenton process to the remediation of water polluted with toxic pesticides.

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1. Introduction

The herbicide diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] has been used worldwide for more than 40 years, and is often detected in surface waters (Tomlin 1997). Fungicide fenarimol (a-(2-chlorophenyl) a-(4-chlorophenyl)-5-pyrimidine-methanol) is commonly used in the form of a spray for treating mildew. However, it is known that it is photo chemically unstable (Worthing, 1983). Organophosphorus (OP) insecticides fenitrothion

(O,O-dimethylO-(3-methyl-4-nitrophenyl) phosphorothioate) has become one of the most widely used chemicals for pest controls (Tucker and Thompson 1987). Fenitrothion could cause contamination of water and injury to plants or animals that were not the targets of the pesticide application. Because of intensive use of these three pesticides in agriculture, relatively high levels of these pesticides and their degradation products are found in groundwater and surface water (Bucheli *et al.* 1997; Aaron and Oturan 2001). Such chemicals are included in several priority lists of pollutants in Japan and other countries, owing to their widespread use and relatively high toxicity.

The powerful oxidizing ability of Fe³⁺/H₂O₂ system is due to "Fenton" type thermal reactions which generate hydroxyl radicals (·OH). The

contributing photochemical reactions include: photo reduction of Fe(OH)²⁺, which gives ·OH; photodecomposition of Fe³⁺ complexes of starting material and/or intermediate degradation products containing -OH or -CO₂H groups; and an unknown Fe³⁺-sensitized reaction (Sun and Pignatello, 1993). The way to generate ·OH is by well-known reactions of hydrogen peroxide (H₂O₂) with Fe²⁺ and Fe³⁺ salts (Pignatello, 1992). The applications of Fe²⁺/H₂O₂ (Fenton reaction) and Fe³⁺/H₂O₂ (Fenton like reaction) systems to hazardous pesticides have been reviewed (Pignatello, 1992 and Sun and Pignatello, 1993).

It has recently been discovered that the oxidizing power of Fenton-type systems is greatly enhanced by irradiation with UV or UV-Vis light, and this technique has proved to be very powerful in destroying persistent pesticides such as methyl parathion, endosulfan, methamidofos,

Oxamyl and alachlor (Haag and Yao, 1992; Sun and Pignatello, 1993; Penuela and Barcelo, 1996). The majority of sunlight is visible light; therefore it must be of importance in the environmental field utilizing visible light to degrade pollutants (Xie *et al.*, 2000). Although the Fe³⁺ ion is known to absorb weakly in the solar UV region (290–400nm), the absorption spectra of its hydrated and other complexed ion species are shifted toward the visible

region (Knight and Sylva, 1975), which might make their use in sunlight possible (Larson et al., 1991). Moreover, in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system, the rate of free radical production and, consequently, the rate of contaminant removal, are significantly accelerated by the effective reduction of Fe^{3+} to Fe^{2+} . In addition, in other cases, formation of organic Fe^{3+} complexes also accelerates H_2O_2 decomposition (Rivas et al., 2002). This means that the use of Fe^{3+} instead of Fe^{2+} in the Fenton reaction contributes to the economy of the process since the reduction step of the sludge produced is avoided. In this sense, direct reutilization of the catalyst, Fe^{3+} , (after acid re-dissolution) can be accomplished with the subsequent savings in chemicals (reducing agent) (Rivas et al., 2002).

However, as regards pesticide elimination using the Fenton reaction, many of the studies conducted up till now employed pesticide concentrations at mg L^{-1} levels in water, which is not close to the actual environmental concentrations of the pesticides in water (Pignatello, 1992; Huston and Pignatello, 1999). In this paper we describe an indirect photochemical method for ecological treatment of pure water and natural river water contaminated by organic pollutants. This method is based on

An *in situ* and catalytic production of Fenton's reagents, a mixture of H_2O_2 and ferrous iron Fe^{2+} or ferric iron Fe^{3+} to produce $\cdot\text{OH}$. $\cdot\text{OH}$ efficiently reacts with organic compounds, leading to their degradation, as reported by Oturan (2000). Therefore using $\cdot\text{OH}$ to degrade industrial and agricultural organic pollutants looks very promising. Indeed, $\cdot\text{OH}$ are very powerful oxidizing agents that are able to degrade most organic compounds, leading to mineral end-products such as CO_2 and H_2O (Guivarch, et al., 2003).

2. Material and Methods

2.1. Chemical

Fenarimol (99.8% purity) was obtained from Riedel Seelze Germany. Diuron, ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (99% purity) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (99% purity) were obtained from Katayama Chemicals, and 30% H_2O_2 was obtained from Kanto Chemicals Company, Japan. Fenitrothion (98.5% purity) was obtained from Kanto Chemicals Company, Japan. Benzene, acetonitrile and phenol (99.5% purity) were obtained from Nacalai Tesque, Japan, and methanol was obtained from Wako Chemical Company, Japan. Due to the low solubility of pesticides in water, a stock solution of 100 mg of each one was prepared by making appropriate dilutions from diuron and fenarimol in acetonitrile but fenitrothion in methanol and stored in a refrigerator at 4°C. Working standard solutions of pesticides were prepared by making appropriate

dilutions with Milli-Q water, and were stored in a refrigerator at 4°C.

2.2. Irradiation and degradation experiments

In the photo-degradation experiments, a solar simulator (Oriel, Model 81160-1000) unit equipped with a 300W Xenon lamp (O_3 free) and special glass filters (Oriel, AM0 and AM1.0) restricting the transmission of wave lengths below 300 nm was used. River water samples were collected from the Kurose River at near the Higashi-Hiroshima campus of Hiroshima University in August, 2008 and were filtered through a glass fiber filter (GC-50, diameter: 47mm, nominal rating: 0.5µm, Advantec) before use. The solutions were prepared by addition of the desired amount of each pesticide (5mg L^{-1}) to either filtered river or Milli-Q water, and after that, the mixtures were carefully agitated. Then, freshly prepared $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or FeCl_3 at Fe concentration of 50 mg L^{-1} was added, and finally, H_2O_2 to a final concentration of 10 mM was added (Malato et al., 2002; Maldonado et al., 2007). Ferric chloride was used as a source of Fe catalyst because this salt remains unchanged before and after oxidation and this made the study of the reaction and the future engineering scale-up simpler, as the system remains homogeneous (Murphy et al., 1989). The initial pH of the solution was adjusted to 2.8 and 7.2 with 1M hydrochloric acid (HCl) or sodium hydroxide (NaOH) respectively for experiments (Pignatello, 1992; Huston and Pignatello, 1999). During the irradiation, the solution in the quartz cell (60 ml) was mixed well using a magnetic stirrer and the temperature was kept constant at 20°C. Solutions from the irradiated samples were removed at regular intervals for HPLC analysis to monitor the rate of photolysis of pesticides.

Following experiments were carried out to find the most effective procedures for decomposition of pesticides by the photo Fenton reaction.

- Exp. 1 Milli-Q water + H_2O_2 + Fe^{2+} (pH 7.2)
- Exp. 2 River water + H_2O_2 + Fe^{2+} (pH 7.2)
- Exp. 3 Milli-Q water + H_2O_2 + Fe^{3+} (pH 7.2)
- Exp. 4 River water + H_2O_2 + Fe^{3+} (pH 7.2)
- Exp. 5 Milli-Q water + H_2O_2 + Fe^{2+} (pH 2.8)
- Exp. 6 River water + H_2O_2 + Fe^{2+} (pH 2.8)
- Exp. 7 Milli-Q water + H_2O_2 + Fe^{3+} (pH 2.8)
- Exp. 8 River water + H_2O_2 + Fe^{3+} (pH 2.8)

2.3. Analytical methods

The irradiated samples were analyzed by high-performance liquid chromatography (HPLC) system equipped with a pump (LC-10AD, Shimadzu), column temperature at 40°C (CTO-10A, Shimadzu) a sample injector (Rheodyne Model 7725, sample loop size 50µl) and a UV-Vis detector (SPD-10A, Shimadzu). A Supelcosil LC-18 (Supelco, particle

size 5 μ m) 250mm length \times 4.6mm ID column was used. A guard column (Supelcosil LC-18, 5 μ m, 20mm length \times 4.0mm ID) was fitted before the analytical column. A mixture of acetonitrile and Milli-Q water (60 : 40) was used as the mobile phase. The flow rate was maintained at 1.1ml min⁻¹ and the UV detector wavelength for diuron, fenarimol and fenitrothion was 254, 220 and 220 nm, respectively (Mateus et al., 2002).

The losses in DOC with irradiation time were estimated by TOC 5000-A (Shimadzu Company, Japan) for an initial pesticides concentration of (5 ppm). After irradiation, water samples were acidified with HCl and then injected directly into the TOC analyzer, which was calibrated with standard solutions of hydrogen potassium phthalate.

2.4. Measurement of OH formation rate

Hydroxyl radicals were quantified by trapping with added benzene, and measuring the product phenol an HPLC (Faust and Allen, 1993), using a mobile phase of 60 : 40 CH₃CN : H₂O, a Supelcosil LC-18 column (5 μ m particle size, 250mm \times 4.6mm) and a fluorescence detector operating at excitation and emission wavelengths of 270 and 298 nm, respectively. The flow rate was maintained at 1.0 ml min⁻¹. At the beginning of each experiment, an aliquot of aqueous benzene stock solution (20 mM) was added to either pure or filtered river water to give an initial benzene concentration, [benzene]₀, of 1.2 mM. The solution was then spiked with Fe³⁺ or Fe²⁺ and H₂O₂, agitated to mix the solution, transferred to a quartz cell (60 ml) and irradiated using a solar simulator to determine the formation rate of OH in both pure and river water samples. The initial pH of the diluted solution was adjusted to 7.2 or 2.8 in experiments (Pignatello, 1992; Huston and Pignatello, 1999). During the irradiation, the solution in the quartz cell (60 ml) was mixed well with a stirring bar and the temperature was kept at 20°C. Solutions were removed at regular intervals from the irradiated samples for HPLC analysis. The total concentration of \cdot OH produced by the photoreaction in a given time period, [\cdot OH]_{total}, was determined as follows:

$$[\cdot\text{OH}]_{\text{total}} = [\text{phenol}] / (Y_{\text{phenol}})(F_{\text{Benzene,OH}}) \quad (1)$$

Where the phenol concentration [Phenol] is measured as function of irradiation time, F_{benzene, OH} is the fraction of \cdot OH that reacts with benzene (in competition with other \cdot OH scavengers), and Y_{phenol} is the yield of phenol formed per benzene molecule oxidized by \cdot OH.

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3. Results and Discussion

3.1. Pesticides degradation by photo-Fenton reaction at pH 7.2.

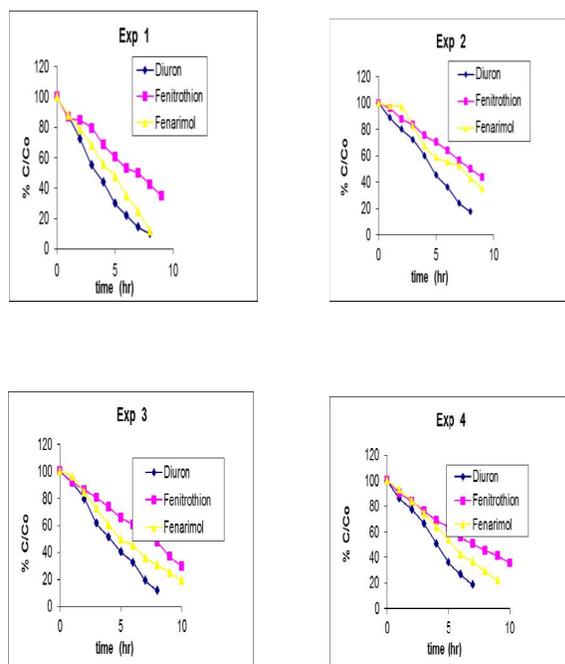
The results of photolysis experiments with the three pesticides, diuron, fenarimol and fenitrothion, at pH 7.2 are shown in Fig. 1. The results obtained indicate that the spontaneous degradation due to solar illumination by Fe³⁺/H₂O₂/UV-Vis system is more effective than Fe²⁺/H₂O₂/UV-Vis system in Milli-Q water and river water. The order of pesticides degradation was diuron > fenitrothion > fenarimol, the order seems to be related with pesticides solubility. Fenarimol was the least reactive pesticide with photo-Fenton treatment.

In the case of Fe²⁺/H₂O₂/UV-Vis system, the results in Milli-Q water show that near complete degradation of diuron (85.66%) was achieved within 7 hr, in comparison to 57.73% and 88.22% for fenarimol and fenitrothion, respectively within 8 hr. (Fig 1 Exp 1). However, degradation in river water obtained was 82.46% for diuron within 8hr., 56.25% and 65.03% for fenitrothion and fenarimol, respectively within 9hr (Fig 1 Exp 2). The chemical composition of the river water sample is given in Table 1.

Table 1. Chemical composition of river water collected in the Kurose river

Site	pH	Cl ⁻ (μM)	SO ₄ ²⁻ (μM)	NO ₂ ⁻ (μM)	NO ₃ ⁻ (μM)	DOC (mg/L)	H ₂ O ₂ (nM)
Kurose							
Bunka	7.7	498	302	7.9	133	4.4	41
Center							

Moreover, As also shown in Figure 1, the results of photolysis experiments with the three pesticides by Fe³⁺/H₂O₂/UV–Vis system in Milli-Q water showed that near complete degradation of diuron (88.41%) was achieved within 8 hr., in comparison to only 70.23% and 81.06% within 10 hr. for fenarimol and fenitrothion, respectively, (Fig 1 Exp 3). However, degradation in river water for diuron was 81.5% within 7 hr., in comparison to 64.38% within 9 hr. for fenarimol and 64.38% for fenitrothion within 10 hr. (Fig 1 Exp 4).

**Figure 1:** Pesticides degradation by photo-Fenton reaction at pH 7.2

As shown in Table 2, for Fe²⁺/H₂O₂/UV–Vis system, the half-lives for diuron, fenarimol and fenitrothion were 2.37, 6.17 and 2.9 hr. in Milli-Q water, respectively and 3.22, 7.58 and 5.81 hr. for river water, respectively. However, for Fe³⁺/H₂O₂/UV–Vis system, the half-lives for diuron, fenarimol and fenitrothion in Milli-Q water were 2.68, 5.49 and 3.82 hr. respectively and 2.88, 6.83 and 4.13 hr. in river water, respectively.

Table 2: Half-lives for the three pesticides treated with Fe²⁺ or Fe³⁺ and H₂O₂ at pH 7.2

Compound	Milli-Q water (hr)		River water (hr)	
	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
Diuron	2.37	2.68	3.22	2.88
Fenarimol	6.17	5.49	7.58	6.83
Fenitrothion	2.90	3.82	5.81	4.13

Pesticide added: 5mg L⁻¹, H₂O₂ added: 10mM, Fe²⁺ or Fe³⁺ added: 50mg L⁻¹. Light conditions were normalized to sun light intensity of clear sky midday on May 1 at 34°N

The increased degradation rate of the pesticides in Milli-Q water compared to the river water could be as a result of higher steady state concentration of hydroxyl radicals in Milli-Q water system compared to the river water system. This is expected because the steady state concentration of hydroxyl radicals is a function of the photo-formation rate and the scavenging rate. Although, it is expected that the photo-formation rate of hydroxyl radicals in river water should be higher than that of the Milli-Q water because of the OH radical sources such as NO₂⁻, NO₃⁻, DOM etc that are initially present in the river water samples. However, it is also known that river water samples contain some natural scavengers such as Cl⁻, HCO₃⁻, CO₃²⁻, DOM, etc which react with the photo-formed OH radicals. Hence the steady state concentrations of the OH radicals in Milli-Q water system was higher than that of the river water samples which accounts for the higher degradation rate of the pesticides observed in the Milli-Q water system compared to the river water system.

Table 3: ·OH photo-formation rates in photo-Fenton solutions at pH 7.2 (μM/Min)

Degradation system	Milli-Q water	River water
Sample + Fe ²⁺ + UV	0.036	0.016
Sample + H ₂ O ₂ + UV	1.57	0.74
Sample + Fe ³⁺ + UV	0.0014	0.33
Sample + Fe ²⁺ + H ₂ O ₂ + UV	0.71	0.67
Sample + Fe ³⁺ + H ₂ O ₂ + UV	1.03	0.65

3.2. Pesticides degradation by photo-Fenton reaction at pH 2.8

The results of photolysis experiments with the three pesticides treated by Fe²⁺/H₂O₂/UV–Vis system and Fe³⁺/H₂O₂/UV–Vis system at pH 2.8 in Milli-Q water and river water are shown in Fig. 2. Also, the order of pesticides was diuron > fenitrothion > fenarimol. In the case of Fe²⁺/H₂O₂/UV–Vis system, the results in Milli-Q water showed that the degradation of diuron, fenarimol and fenitrothion within 8 hr. was 98.01%, 75.7 and 78.1%, respectively (Fig 2 Exp 5), but in river water, degradation of diuron, fenarimol and fenitrothion within 7 hr., was 98.43, 73.28 and 83.39% respectively (Fig 2 Exp 6).

Also, the results of photolysis experiments with

the three pesticides by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system indicated that the three pesticides were successfully degraded. The results in Milli-Q water showed that near complete degradation of diuron (95.84%) was achieved within 2hr., in comparison to 67.21% and 71.25% within 7 hr for fenarimol and fenitrothion, respectively (Fig 2, Exp7). However, in river water, the degradation of diuron was 90.89% within 4 hr, but 78.88 and 80.01% within 7 hr for fenarimol and fenitrothion, respectively (Fig 2, Exp 8). The results presented indicate that the degradation of the pesticides was higher in river water compared to the Milli-Q water in both $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems.

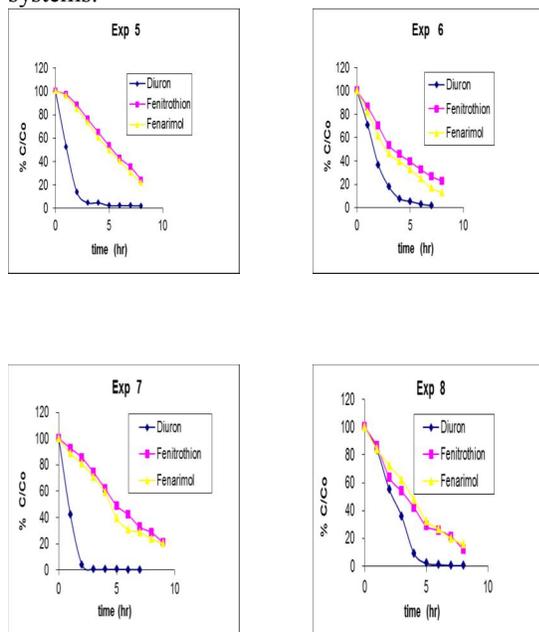


Figure2: Pesticides degradation by photo-Fenton reaction at pH 2.8

Furthermore, at pH 2.8, the half-lives for diuron, fenarimol and fenitrothion in Milli-Q water and river water for both photo-Fenton systems are presented in Table 4.

Table 4: Half-lives for the three pesticides treated with Fe^{2+} or Fe^{3+} and H_2O_2 at pH 2.8

Compound	Milli-Q water (hr)		River water (hr)	
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
Diuron	1.41	0.87	1.13	0.83
Fenarimol	3.96	3.97	3.69	2.75
Fenitrothion	3.65	3.57	2.74	2.89

Pesticide added: 5mg L^{-1} , H_2O_2 added: 10mM , Fe^{2+} or Fe^{3+} added: 50mg L^{-1} , Light conditions were normalized to sun light intensity of clear sky midday on May 1 at 34°N

From these results, it is evident that the degradation of the pesticides in both photo-Fenton

systems at pH 2.8 was higher in river water than in the Milli-Q water. This could also be attributed to higher OH radicals generation rate in the river water than in the Milli-Q water in the both systems (Table 5). This high rate of $\cdot\text{OH}$ formation in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system in river water can firstly be attributed to the presence of extra Fe (0.04 ppm) as a natural component of the Kurose River water (ICP analysis). It can also be attributed to the presence of NO_3^- ($133\ \mu\text{M}$), and dissolved organic matter DOC ($4.4\ \text{mg L}^{-1}$) in river water samples (Table 1). This extra Fe, NO_3^- (Eq. (8) (Mack and Bolton, 1999) and dissolved organic matter (Eq. (9) (Fukushima et al., 1998) in river water samples leads to the generation of additional $\cdot\text{OH}$ under light conditions (Southworth and Voelker, 2003).

In addition, the retarding effects of Cl^- ($498\ \mu\text{M}$) and SO_4^{2-} ($302\ \mu\text{M}$) present in the river water (Table 1) (Pignatello, 1992) on the rate of $\cdot\text{OH}$ formation are considered to be negligible due to the very high amounts of $\cdot\text{OH}$ generated in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system. We note that dissolved organic matter such as humic substances is known to scavenge $\cdot\text{OH}$, but is also able to generate $\cdot\text{OH}$ in the presence of light (Sakkas et al., 2002). Moreover, it is known that the photochemical properties of humic substance result from complex phenomena and depend on many factors, such as the type of structure (fulvic acid or humic acid) and the origin of each substance. Therefore, the type and origin of dissolved organic matter can have different influences on the photoprocess (Sakkas et al., 2002).

Although the rate of $\cdot\text{OH}$ formation in river water was higher than that in pure water (Table 5), the rate of pesticides degradation in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system in natural water was slightly slower than in pure water. This may be attributed to the intense competition between the degradable portion of dissolved organic matter in the water body and pesticides for $\cdot\text{OH}$ to react with during the early stage of the reaction (Epling and Lin, 2002; Sakkas et al., 2002). There is competition between humic substances (that co-exist in river waters) and pesticides to absorb light, since humic substances are known to absorb sunlight energy, which reduces the direct photolysis rate of pesticides (Epling and Lin, 2002; Sakkas et al., 2002).

In the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ system at pH 2.8, the degradation rate of diuron in Milli-Q water and in River water was much slower after a 3 hr period of irradiation. Furthermore, the degradation of the pesticides in $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ system was much slower after the first 2 hrs for Milli-Q water and 4 hr for river water. This is plausible because the scavenging rate of OH radicals with the photodegradation products of diuron increases which

reduces the concentration of OH radicals available for the reaction with the diuron.

Table 5: OH photo-formation rates in photo-Fenton solutions at pH 2.8 ($\mu\text{M}/\text{Min}$)

Degradation system	Milli-Q water	River water
Sample + Fe^{2+} + UV	1.76	1.13
Sample + H_2O_2 + UV	0.82	0.77
Sample + Fe^{3+} + UV	1.57	1.12
Sample + Fe^{2+} + H_2O_2 + UV	2.44	2.90
Sample + Fe^{3+} H_2O_2 + UV	4.006	5.26

3.3. Total mineralization of synthetic mixture

An important measure of the success of an AOP is the extent of mineralization of target compounds to CO_2 and inorganic ions because it signifies the overall destruction of possible toxic intermediates in addition to the parent compound itself (Huston and Pignatello, 1999).

The effect of different contaminated water sample's pH (7.2 and 2.8) on total mineralization of synthetic mixture of diuron, fenarimol and fenitrothion in the photo-Fenton systems in pure and natural water is shown in Fig 3a and 3b. The results indicate that the DOC removal is highest under acid condition, pH 2.8 (Fig 3a), it declines remarkably with the increase of pH 7.2 (Fig 3b). DOC is decrease in the concentration with increase in irradiation time. The mineralization rate of synthetic mixture in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system was much faster than in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system. Furthermore, the rate was slightly faster in natural water than pure water. These results are consistent with the $\cdot\text{OH}$ formation rate data presented in Tables 3 and 5.

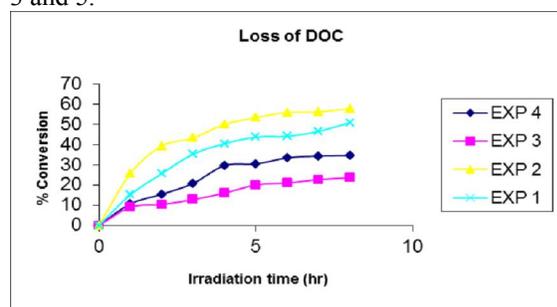


Figure 3a: Loss of DOC at pH 7.2

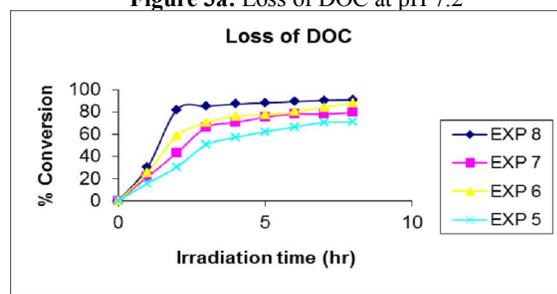


Figure 3b: Loss of DOC at pH 2.8

After 2h of irradiation, the mixture mineralization rate of the remaining in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system was much slower than that achieved during the first 2h. This is due to the low concentration of pesticides remaining after 2h of irradiation, which emphasized that all pesticides decompose giving rise to by-products, which could also be competitive on photo-Fenton for treating all the pesticides tested. Moreover the parent compounds disappear very quickly by photo-Fenton (El-Morsi et al., 2002).

Therefore, at pH 2.8 (Fig 3a) near-complete mineralization of mixture (90.8 and 79.4%) were achieved in river water after 8h of irradiation in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system respectively, while 88.2 and 71.0% of the compound were achieved in pure water after 8h of irradiation in the tow system respectively. On the other hand, at pH 7.2 (Fig 3b) slow mineralization of mixture (57.9 and 34.5%) were achieved in river water after 8h of irradiation in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ -Vis system respectively, while 50.9 and 23.6% of the compound were achieved in pure water after 8h of irradiation in the tow system respectively.

Several processes and technologies are available today for the treatment of wastewater. The wastewater treatment techniques most frequently used can be classified as physical, biological and chemical. However, very often wastewater containing pesticides cannot be treated by biological techniques because of they are toxic to the microorganisms, it is well known that pesticides are resistant to microbial degradation, and therefore its ability of accumulation in the environment as well as possible carcinogenic and mutagenic properties is conceivable.

In natural waters $\cdot\text{OH}$ is generated by a number of mechanisms (e.g. photolysis of nitrate) and trace organic pollutants may be degraded there (Mabury and Crosby, 1994); however, the natural generation of $\cdot\text{OH}$ is slow and much of it is scavenged by dissolved organic matter which is often abundant compared to the pollutant.

One of the possible methods of their degradation and removal is chemical oxidation, using Fenton reactions. The efficiency of Fenton's process depends on H_2O_2 and Fe^{2+} concentrations and pH of the reaction. The photo-Fenton reaction is optimum at pH 2.8 (Pignatello, 1992), higher or lower pH values hamper the development of photo-Fenton and electro-Fenton processes. Where approximately half of the Fe^{3+} is present as Fe^{3+} ion and half as $\text{Fe}(\text{OH})^{2+}$ ion, the photo-active species. Below this pH the concentration of $\text{Fe}(\text{OH})^{2+}$ declines and at higher pH the Fe^{3+} precipitates as oxyhydroxides.

The results reflect the superiority of the

$\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system at pH 2.8 over the other systems for removal of pesticides from water.

As commented above, the iron concentration used during photo-Fenton treatment is such that it does not require separation previous to water disposal or Fe^{3+} catalyst can be removed by raising the pH of the solution, which reduces operating costs. H_2O_2 is considered to be a "clean" reagent, has to be evaluated to find out which treatment is more economical since it is consumed in oxidation of the pollutant and quickly decomposes to form only H_2O and O_2 as products.

3.4 Removal of pollutant from wastewater with pesticides by photo-Fenton photochemical decomposition

Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions (Grover and Cessna 1991). Three different pesticides were selected diuron, fenarimol and fenitrothion for the following two main reasons: they have three different structures that are representative of a wide range of modern pesticides (containing different heteroatom and bonding structures) and they have different solubility in water (42mg L^{-1} , 14 mg L^{-1} and 14mg L^{-1} at 25°C respectively) and transport in the environment, seriously threatening all surface and groundwater.

A previous report (Mateus et al., 1997) presented a spectroscopic study of the fungicide, fenarimol showing that the lowest excited singlet state, corresponding to an absorption between 280 and 330 nm, is localized on the pyrimidine ring and has n,p character. This overlaps with the solar emission spectrum and is expected to play a dominant role in the photo degradation processes of this fungicide under natural environmental conditions (Mateus et al., 1994).

Herbicides are able to reach surface waters either directly by the herbicidal control of aquatic weeds or indirectly via the discharge of agricultural drainage water from treated land and via runoff after application on hard surfaces (Leu et al., 2004; Vianello et al., 2005). Diuron is a phenylurea herbicide that has been widely used for the selective control of non-cultivated areas, annual weeds, and field crops (Tomlin, 1994). Indeed, partly because of its low solubility in water (40 mg/L at 20°C), diuron is persistent in surface soil (*the Koc* varying from 500 to 700) where it is prone to lateral movement via surface runoff and migration to both surface and groundwater (Field et al., 2003 and Prichard et al., 2005). Diuron can also disseminate by leaching after intensive rainfall, making it one of the main causes of groundwater pollution (Landry et al., 2006).

Widespread use of organophosphorus

compounds resulted in the release of their residues into natural water. Fenitrothion is considered to be a common river water pollutant, and is detected with high frequency in river water all over Japan (Numabe et al., 1992; Okumura and Nishikawa, 1995). Furthermore, fenitrothion residues in natural water undergo photo degradation, resulting in the release of many toxic metabolites, some more toxic than the parent compound, to aquatic organisms (Amoros et al., 2000).

Subsequently, the goal to clean up wastewater containing organic pesticides and its metabolites in natural water has led to a search for highly effective methods for their removal or decomposition into environmentally compatible compounds.

Production of $\cdot\text{OH}$ by Fenton reagent occurs by means of the addition of H_2O_2 to Fe^{2+} salts. The degradation rate of organic pollutants is strongly accelerated with photo-Fenton by irradiation with UV-Vis light. Under these conditions, the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and the occurrence of Fenton reactions due to the presence of H_2O_2 and iron may be considered a true catalyst. This is a simple way of producing $\cdot\text{OH}$, neither special reactants nor special apparatus being required. Iron is very abundant non-toxic element and H_2O_2 is easy to handle and environmentally safe. $\cdot\text{OH}$ can also be generated with a semiconductor that absorbs radiation when in contact with water. Detoxification of wastewater is today the most successful photochemical application of solar photons with several relevant facilities already in operation. (Malato et al., 2002).

It was observed that all the pesticides are degraded in a short time with photo-Fenton reaction. The three pesticides concentrations were decreased with irradiation time, with respect to the half-life and complete degradation. The results show that the degradation rate of pesticides was greatly enhanced by irradiation in a $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system relative to in systems with $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ system and at pH 2.8 relative to pH 7 in both Milli-Q water and river water.

4. Conclusions

Our results show that photo-Fenton is more efficient not only for pesticides degradation but also for TOC mineralization. The degradation of the pesticides resulting from the attack of $\cdot\text{OH}$ contributes to the reduction of the toxicity of the pesticides solution. The resulting compounds being biodegradable, a biological process can thus complete mineralization. The rapid and non-selective character of the Electro-Fenton process could be used for a wide range of organic pollutants. This process has some advantages compared with classical treatment

methods since it provides another possible approach using natural sunlight to the treatment of water contaminated with pesticides. By using the oxygen of air and the absence of an added chemical reagent, except a catalytic amount of an iron salt, it is an ecologically friendly process with low electrical energy consumption. Moreover, the use of sunlight, instead of artificial light, and direct current generator, instead of costly chemicals, for the photo-Fenton reaction would lower the costs of the process and non-polluting method. However, the disadvantage of this method is its sensitivity to pH, the need for acidification, the change in the working pH value from about 3 cause a precipitation of iron as hydroxide. In this study iron at very low concentrations enough for treating water containing pesticides. The removal of iron at this concentration would not be necessary before disposal. Results obtained from this study makes it plausible to apply the photo-Fenton process to the remediation of water polluted with toxic pesticides. Consequently it considered alternative approaches, clean and efficient technique for decontaminating natural waters

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