HYDROXYL RADICAL FORMATION RATE AND ITS ROLE IN DIURON DEGRADATION VIA FENTON'S REAGENT IN WATER

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Abstract

Hydroxyl radical ($^{\bullet}$OH) is one of the most powerful oxidative agents. A recent application of this radical is its use in decontamination of polluted water by toxic organic substances like pesticides. Chemically, this radical is produced by the use of a mixture of (Fe^{2+}/H_2O_2), called Fenton's reagent. In this work hydroxyl radical formation rates under different oxidation systems i.e., $Fe^{2+}/H_2O_2/UV$-Vis, $Fe^{3+}/H_2O_2/UV$-Vis, $Fe^{2+}/H_2O_2/Dark$, $Fe^{3+}/H_2O_2/Dark$, Fe^{2+}/UV-Vis, Fe^{3+}/UV-Vis, $Fe^{2+}/Dark$, $Fe^{3+}/Dark$, H_2O_2/UV-Vis and $H_2O_2/Dark$ were determined after addition of benzene as a chemical probe to MilliQ water in a reaction cell. Phenol produced by the reaction between $^{\bullet}$OH and the benzene added to the water sample was determined by HPLC as a function of time to quantify the $^{\bullet}$OH formation rate in the presence and absence of simulated sunlight. Degradation and mineralization of diuron (1mg/L) in some of these effective systems were evaluated as well. Results demonstrated that $Fe^{2+}/H_2O_2/UV$-Vis (Photo-Fenton reaction) is likely to be the most important source of $^{\bullet}$OH due to the higher rate of $^{\bullet}$OH generation in this system (107.2 µM min^{-1}) compared to 58.71 µM min^{-1} with $Fe^{3+}/H_2O_2/UV$-Vis (Photo-Fenton like reaction), and 6.73 µM min^{-1} with $Fe^{2+}/H_2O_2/Dark$ (Fenton reaction). Consequently, photo-Fenton reaction was the most effective method for diuron degradation, dechlorination and mineralization in water since complete degradation, total conversion of the initial diuron chloride content and 85% total organic carbon (TOC) mineralization were achieved after 180, 240 and 540 min of irradiation time at pH 2.8, respectively.

Keywords: Diuron, Fenton reaction, MilliQ water, hydroxyl radical formation rate.

INTRODUCTION

Phenylurea derivatives are reported to be among the most widely used herbicides in agriculture nowadays (Barbash *et al.,* 2001). Accordingly, their residues were shown prominently in surface or runoff waters (Mazellier *et al.,* 2007). Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is one of the most popular substituted phenylurea herbicides used to control a wide variety of annual and perennial broadleaf and grassy weeds. It is used on many agricultural crops, but is more widely applied for long-term pre-emergence weed control in non-crop areas (Tomlin, 2003), especially along railway lines (Schweinsberg *et al.,* 1999). Diuron is used as algicide in paints

and coatings as well (Gerecke *et al.,* 2001). Its wide use leads to pollution of water by soil leaching and agricultural runoffs. Because of its extremely slow breakdown in water, diuron is highly persistent in the environment (Madhum and Freed, 1987). It was considered as priority hazardous substance by the Water Framework Directive of the European Commission, and included in Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001, in which a list of priority substances in the field of water policy is established.

The negative impact of diuron on ecosystems and human health requires more positive efforts for the development of efficient and environmentally friendly technologies for water treatment. Advanced oxidation processes (AOPs), which are based on *in situ* generation of a powerful non-specific oxidizing agent, the hydroxyl radical ($^{\bullet}$OH), provide a convenient method for the treatment of pesticide wastes (Pignatello *et al.,* 2006). Oxidation methods like Fenton reaction, which generate hydroxyl radicals, are promising methods for treating polluted water. The Fenton system consists of a mixture of ferrous salt and hydrogen peroxide, namely Fenton's reagent. If ferrous is replaced by ferric iron it is called Fenton-like reagent. It can be described as the generation of $^{\bullet}$OH through catalytic decomposition of hydrogen peroxide by a transition metal such as ferrous iron. In spite of this, environmental applications of this oxidation system are relatively recent because of its advantages in comparison to other oxidation processes, like the fact that, hydrogen peroxide is environmentally friendly, since it slowly decomposes into oxygen and water and it considers as one of the cheapest oxidizers that are normally used in water treatment, has high oxidizing power, easy to handle, water-soluble and does not produce toxic by-products or color (Rodríguez, 2003). Besides that, the abundance, lack of toxicity, and ease of removal from water makes Fe^{2+} the most commonly used transition metal for Fenton process applications (Safarzadeh-Amiri *et al.,* 1996). Using solar energy as a photon source, the system activity can be greatly increased (Lee and Yoon, 2004). Hydroxyl radicals thus formed react with organic pollutants leading to their mineralization into CO_2, water and inorganic ions. They are effective in attacking a wide range of organic compounds (Balci *et al.,* 2009).

Hydroxyl radical ($^{\bullet}$OH) plays an important role in the degradation of organic compounds in water (Andreozzi *et al.,* 2003), due to its high reactivity with organic compounds in the aqueous phase (Buxton *et al.,* 1988). The non-selective nature of hydroxyl radical makes it useful for degradation of a broad range of pollutants leading finally to the mineral end-products (Lindsey and Tarr, 2000). The effectiveness of $^{\bullet}$OH in the degradation of organic compounds depends on its steady-state concentration (Nakatani *et al.,* 2004).

Accordingly, the aim of the present study is to determine the formation rate of $^{•}$OH under different oxidation systems in order to understand its role in the degradation of pollutants, and to compare the efficiency of different Fenton systems to find the best removal performance for the degradation and mineralization of diuron from water.

MATERIALS AND METHODS

1. Chemicals

All chemicals and solvents used were of analytical reagent grade and were used as received. Diuron 99% and hydrogen peroxide (30%) were obtained from Cica-reagent, Kanto Chemical Co. Inc., Tokyo, Japan. Acetonitrile and benzene were purchased from Nacalai Tesque Inc., Japan (HPLC grade, >99.5%). Commercial phenol standard stock solution (100 mg L^{-1} of phenol) was purchased from Sigma–Aldrich Japan. Ferric chloride (FeCl$_3$ · 6H$_2$O) (99%) was obtained from Katayama Chemicals, Japan. Ferrous sulfate (FeSO$_4$ · 7H$_2$O) (99%) was obtained from Nacalai Tesque Inc., Japan. 2-nitrobenzaldehyde was purchased from Tokyo Kasei Kogyo. All solutions were prepared with ultra-pure water (Milli-Q water, >18 MΩ cm^{-1}, Millipore Japan).

2. Determination of OH radical formation rate

Hydroxyl radical formation rates under different oxidation systems i.e., $Fe^{2+}/H_2O_2/UV$-Vis, $Fe^{3+}/H_2O_2/UV$-Vis, $Fe^{2+}/H_2O_2/Dark$, $Fe^{3+}/H_2O_2/Dark$, Fe^{2+}/UV-Vis, Fe^{3+}/UV-Vis, $Fe^{2+}/Dark$, $Fe^{3+}/Dark$, H_2O_2/UV-Vis and $H_2O_2/Dark$ were determined after addition of benzene as a chemical probe to MilliQ water in a reaction cell. Phenol produced by the reaction between $^{•}$OH and the benzene added to the water sample was determined by HPLC as a function of time to quantify the $^{•}$OH formation rate in the presence and absence of simulated sunlight. At the beginning of each experiment, an aliquot of aqueous benzene stock solution (2 × 10^{-2} M) was added to MilliQ water giving a benzene concentration of 1.2 mM. The solution was then spiked with Fenton's reagent (e.g., Fe^{2+} or Fe^{3+} and H_2O_2), agitated to mix the solution, transferred to a quartz cell (60 ml) and irradiated using a solar simulator (Oriel, Model 81160-1000) unit equipped with a 300 W Xenon lamp (ozone free, Oriel Model 81160) and special glass filters restricting the transmission of wavelengths below 300 nm were used. This Xenon lamp has been demonstrated to be equivalent to natural sunlight for conducting aqueous photolysis studies for certain pesticide compounds. The wavelength range varies from 300 to 800 nm, which represents radiation very close to natural sunlight (Durand *et al.*, 1991).

Due to the high concentration of Fe^{2+} or Fe^{3+} (0.2 mM) and H_2O_2 (20 mM) under Fenton reaction conditions, diluted solution (100 times) was employed to measure the $^{\bullet}OH$ formation rates in MilliQ water. The initial pH of the diluted solution was adjusted to 2.8 with hydrochloric acid in all experiments (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. All the experimental conditions of the oxidation systems that carried out in the absence of simulated sunlight were the same as in its presence.

The concentration of phenol, which was produced by the reaction of benzene with $^{\bullet}OH$, was measured as a function of time under the conditions where a high concentration of benzene is added to water sample. Determination of phenol was performed using HPLC system (Faust and Allen, 1993), consisting of a PU-2089 plus pump (Jasco, Japan), a Rheodyne injection valve (Cotati, CA, USA) with a 50 μL sample loop. The column was an Ultron VX-ODS (Suplecosil LC-18, particle size 5 μm; Supelco) 250 mm × 4.6 mm I.D. A guard column (Suplecosil LC-18, 5 μm, 10 mm × 4.6 mm I.D.) was fitted in the front of the analytical column. A mixture of acetonitrile and MilliQ water (40/60, v/v) was used as a mobile phase at a flow rate of 1 ml min^{-1}. The fluorescence detector (Shimadzu, $RF-10A_{XL}$) was operated at 270 nm for excitation and 298 nm for emission. Analytical signals were recorded by an integrator (Shimadzu, CR-6A). The detection limit of phenol using this HPLC system was 2×10^{-9} M.

The $^{\bullet}OH$ formation rate (R_{OH}) was determined as follows:

$$R_{OH} = \frac{R_{phenol}}{Y_{phenol} \times F_{benzene,OH}}$$

Where R_{phenol} is the photoformation rate of phenol in water samples (M s^{-1}), Y_{phenol} is the yield of phenol formed per benzene oxidized by $^{\bullet}OH$ (mean ± standard deviation = 0.75 ± 0.07, Arakaki and Faust, 1998), and $F_{benzene,OH}$ is the fraction of $^{\bullet}OH$ that reacts with benzene and it was assumed to be 1.00 in this study. It is worth to note that actual $F_{benzene,OH}$ may be a little lower than 1.00 due to possible reactions of $^{\bullet}OH$ with other scavengers such as H_2O_2 and Fe used for the Fenton reagents. Moreover, the effect of other chemical species occurring in the experimental aquatic systems for the Fenton reactions in the present study on $^{\bullet}OH$ scavenging is very limited compared with that of benzene and, for practical purposes, it can be assumed that $F_{benzene,OH}$ = 1.00.

The irradiation light intensity for each day of photochemical experiment was determined by using 2-nitrobenzaldehyde (2-NB) as a chemical actinometer (Kuhn et

al., 2004), using the same reaction cell which used for the determination of $^{\bullet}OH$. The 2-NB photolysis rate constant ($J_{2\text{-NB}}$) was determined by HPLC with a UV detector set at an absorbance wavelength of 260 nm. The column, mobile phase and flow rate were the same as for the determination of $^{\bullet}OH$. The degradation rates of 2-NB ($J_{2\text{-NB}}$) obtained in the present study ranged from 0.0090 to 0.0093 s^{-1}. In this study, the $^{\bullet}OH$ photoformation rates were normalized to $J_{2\text{-NB}}$ = 0.0093 s^{-1}, which was determined at noon, under clear-sky conditions in Higashi-Hiroshima city (34°N) on 7th of October (Takeda et al., 2005). It must be recognized that the photochemical reaction depends on both the light intensity and the wavelength of the light source. However, this normalization using 2-NB photolysis rate constant enables a comparison to be made between data, and a quantitative discussion on the contribution from each $^{\bullet}OH$ source.

3. Degradation experiments

A solution containing the required amount of diuron (1mg/l) in MilliQ water was carefully agitated. Then, freshly prepared ferrous sulfate ($FeSO_4 \cdot 7H_2O$) at Fe concentration of 0.2 mM was added, and H_2O_2 at a final concentration of 20 mM was finally added, to account the degradation of diuron with photo-Fenton reaction ($Fe^{2+}/H_2O_2/UV\text{-Vis}$). The pH of the reaction mixture was adjusted to 2.8 by adding a dilute aqueous solution of hydrochloric acid. Another experiment was carried out using ferric chloride ($FeCl_3 \cdot 6H_2O$) at the above-mentioned concentration of Fe and H_2O_2 to account for the degradation of diuron with photo-Fenton like reaction ($Fe^{3+}/H_2O_2/UV\text{-}Vis$). During the irradiation using a solar simulator, the solution in the quartz cell was well mixed with a stirring bar and the temperature was kept at $20°C$. In addition, to account for any possible degradation of diuron under dark conditions, one experiment was carried out in the absence of light, with Fenton reaction (Fe^{2+}/H_2O_2). The solution from the treated samples was removed at regular intervals and filtered through a 0.45µm Ekicrodisc syringe filter for HPLC analysis under the same conditions as mentioned in $^{\bullet}OH$ determination except using a UV-VIS detector (SPD-10A, Shimadzu) at 254 nm wavelength, the retention time for diuron was 7.1 min. The detection limit of diuron under these conditions was 3 µg L^{-1}. Its calibration was calculated on the basis of the peak areas obtained with standardized samples analysed under the same HPLC conditions. These experiments were conducted in triplicates and the results representing the mean values. The relative standard deviations ranged from 3 to 7%.

4. Mineralisation

The progress of mineralisation for an initial diuron concentration of 3 mgC l-1 MilliQ water was monitored by measuring the total organic carbon (TOC) in treated solutions at regular intervals after filtration and acidification by hydrochloric acid (1% HCl 2mM). TOC of the sample solution was measured with a Shimadzu TOC-VCSH

analyzer according to the thermal catalytic oxidation principle. Platinum was used as catalyst in order to carry out the combustion reaction at 680°C. The carrier gas was oxygen with a flow rate of 150 ml min^{-1}. The detection was carried out by using non-dispersive infrared (NDIR) detector. Calibration of the analyzer was achieved with potassium hydrogen phthalate standards.

5. Evolution of chloride ion

Chloride ion released into treated solutions during photo-Fenton reaction experiment was determined using Dionex DX-500 ion chromatography (IC) system (Dionex, Idstein, Germany), equipped with a gradient pump (GP-40) and a Dionex Ion Pac AS11 (250×4 mm) anion exchange column for chromatographic separation provided with a guard column AG11 (50×4 mm) and coupled with a conductivity detector CD-20 to measure anions. Samples were introduced through an auto sampler AS-3500 in a 100 µl injection loop fitted with Rheodyne injector in a 2 ml min^{-1} of flow rate. The Peaknet chromatography workstation was used for instrument control, data collection and data processing.

RESULTS AND DISCUSSION

1. Hydroxyl radical formation rate

Data in Table (1) revealed that photo-Fenton reaction is likely to be the most important source of $^{\bullet}$OH due to the higher rate of $^{\bullet}$OH generation in this system (107.2 µM min^{-1}) compared to 58.71 µM min^{-1} with photo-Fenton like reaction, and 6.73 µM min^{-1} with Fenton reaction. In addition to the photo-Fenton reactions, iron photo-assisted systems (Fe^{2+}/UV-Vis & Fe^{3+}/UV-Vis) and the direct photolysis of hydrogen peroxide (H$_2$O$_2$/UV-Vis) are important sources for $^{\bullet}$OH formation in water representing 31.30, 26.54 and 19.61 µM min^{-1}, respectively.

Table 1. Calculated hydroxyl radical formation rates under different oxidation systems in MilliQ water in the presence and absence of simulated sunlight.

| Degradation system	Generation rate of $^{\bullet}$OH (µM min^{-1})
Fe^{2+}/H$_2$O$_2$/UV-Vis	107.2 ± 4.2
Fe^{3+}/H$_2$O$_2$/UV-Vis	58.71 ± 2.1
Fe^{2+}/H$_2$O$_2$/Dark	6.730 ± 0.5
Fe^{3+}/H$_2$O$_2$/Dark	5.233 ± 0.3
Fe^{2+}/ UV-Vis	31.30 ± 2.8
Fe^{3+}/ UV-Vis	26.54 ± 1.9
Fe^{2+}/ Dark	0.078±0.004
Fe^{3+}/ Dark	0.045±0.002
H$_2$O$_2$/UV-Vis	19.61 ± 1.1
H$_2$O$_2$/Dark	5.125 ± 0.4

The hydroxyl radicals are now generated by the Fenton's reagent, the initiation step in this mechanism is the generation of $^{\bullet}OH$ by the reaction of hydrogen peroxide and ferrous iron (Fe^{2+}), according to Walling, (1975):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$
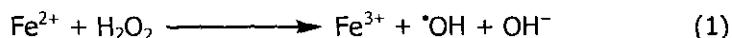
Then, these hydroxyl radicals formed react rapidly and nonselectively with most organic compounds by three types of reactions: additions on a double bond, abstraction of a hydrogen atom or electron transfer (Buxton et al., 1988; Haag and Yao, 1992), and cause their chemical decomposition:

$$\text{Organic compounds} + {}^{\bullet}OH \longrightarrow \text{Degradation products} \qquad (2)$$
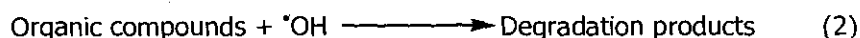
Furthermore, the Fe^{3+} formed, which is present in the aqueous solution, undergoes spontaneous hydrolysis with water to form $Fe(OH)^{2+}$, which considers as one of the most photosensitive species, and such a complex is capable of producing hydroxyl radicals directly through the photo-sensitization reaction (Benkelberg and Warneck, 1995):

$$Fe(OH)^{2+} \xrightarrow{\quad h\nu \quad} Fe^{2+} + {}^{\bullet}OH \qquad (3)$$
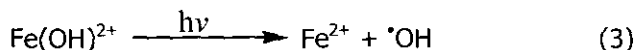
Among the AOPs, the iron photo-assisted system has received special attention as a potential water treatment process because it can provide an efficient and less expensive treatment method in comparison with photo-Fenton and H_2O_2/UV processes (Mazellier et al., 1997).

Thus, it can be concluded that the active $^{\bullet}OH$ is generated through three possible sources: the original Fe^{2+}/H_2O_2 reaction (Eq.1), Fe^{3+} sensitization (Eq. 3), and photolysis of hydrogen peroxide (Eq. 4) (Benitez et al., 2007).

$$H_2O_2 \xrightarrow{\quad h\nu \quad} 2\,{}^{\bullet}OH \qquad (4)$$
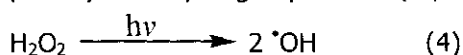
3.2. Diuron degradation

As shown in Fig. 1, the degradation of diuron is faster with photo-Fenton reaction than with photo-Fenton like reaction at equimolar iron concentration of 0.2 mM. The complete disappearance of diuron needs 180 and 240 min with photo-Fenton reaction and photo-Fenton like reaction, respectively. On the other hand, under dark conditions diuron decomposition was found to be markedly slower and does not go to completion because in the dark, the reaction in (Eq.1) is retarded after complete conversion of Fe^{2+} to Fe^{3+}.

These findings suggest an increasing contribution of the photo-Fenton system in diuron degradation due to an additional generation of $^{\bullet}OH$. When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Eq. 1). With ferric salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and

hydrogen peroxide (Eq. 5) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide (Kiwi *et al.,* 1993):

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (5)$$

Moreover, Fe^{3+} has a lower activity than Fe^{2+} and may complex with the organic pollutants or their degradation products, producing weaker oxidants than $^{\bullet}OH$ (Sun and Pignatello, 1993). UV irradiation attacks and decomposes organic molecules by bond cleavage, although it occurs usually at very slow rates (Yue, 1993). Additionally, the presence of hydrogen peroxide increases substantially the rate of the oxidation, due to the generation of hydroxyl radicals, which react with organic compounds (Haag and Yao, 1992).
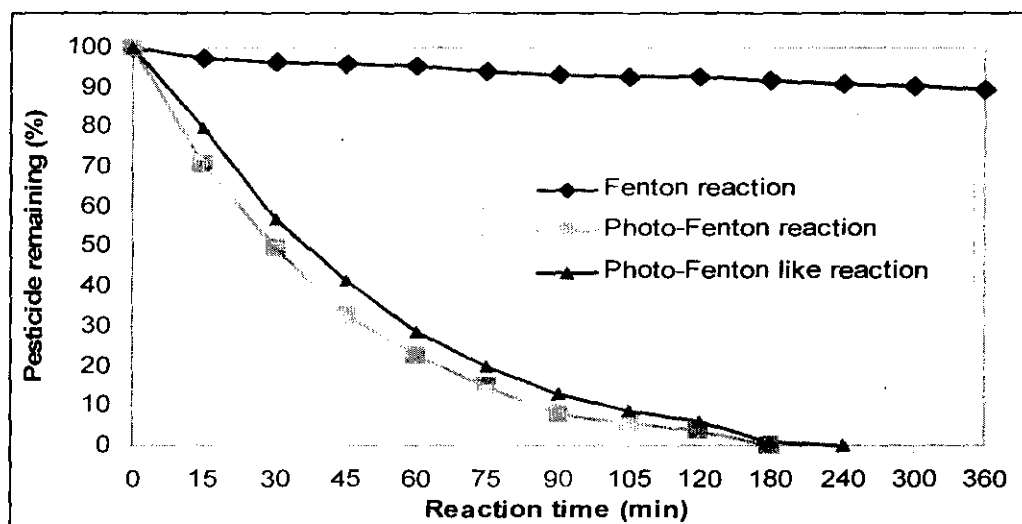

Fig. 1. Effect of Fenton and photo-Fenton reactions on the degradation of diuron
(1mg/L) at pH 2.8.

3. Total organic carbon mineralisation

As it can be seen from Fig. 2, a high mineralization of diuron (85%) was reached by $Fe^{2+}/H_2O_2/UV$-Vis system compared to (78%) by $Fe^{3+}/H_2O_2/UV$-Vis system after 540 min of irradiation time, which could be explained by increasing the production of hydroxyl radicals and therefore, the mineralization grade also increases. However, Fenton reaction shows very poor mineralization rate (2%) after 540 min of treatment. Consequently, illumination was necessary to reach high degrees of mineralisation.

The complete mineralisation of diuron was not achieved after 540 min, although diuron was completely degraded after 180 and 240 min in the treated solution with photo-Fenton reaction and photo-Fenton like reaction, respectively. This difference indicates that persistent intermediate products were produced during the

photo-Fenton processes (Katsumata *et al.*, 2005). It is likely that diuron, a phenylurea herbicide, will generate urea as stable intermediate. This urea could account for the remaining TOC. Urea is non-toxic and it can be easily metabolized by microorganisms (Gernjak, 2006).
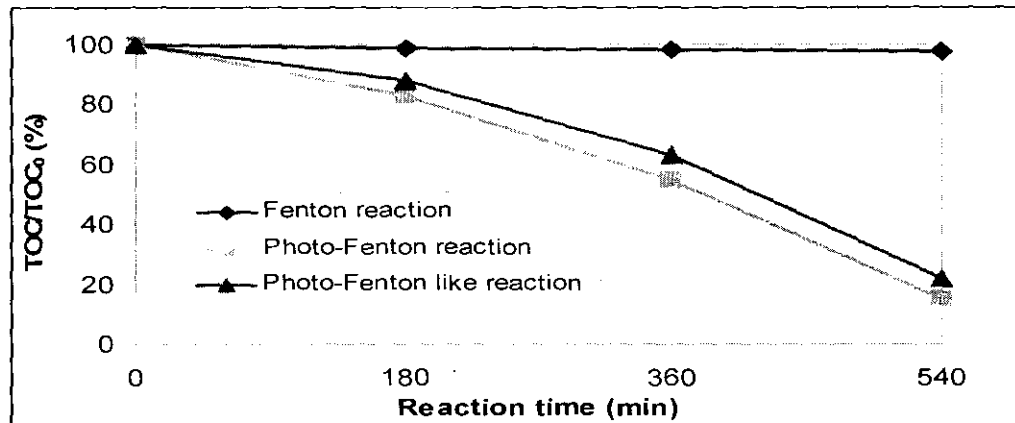

Fig. 2. Mineralisation of diuron herbicide (3mgC/L) by Fenton and photo-Fenton reactions at pH 2.8.

4. Chloride ion evolution

The release of chloride ion from diuron degradation during photo-Fenton reaction was investigated. The concentration of chloride ion quickly increased with increasing the reaction time, suggesting a fast degradation and dechlorination (Fig. 3). The total amount of chloride ion produced after 240 min of irradiation time was reached the value of 8.58×10^{-6} mol L^{-1} (100% conversion of the initial diuron chloride content). This means that the residual TOC after 540 min of irradiation time did not correspond to any chlorinated compounds. These results are in agreement with those obtained by Malato *et al.*, (2003).
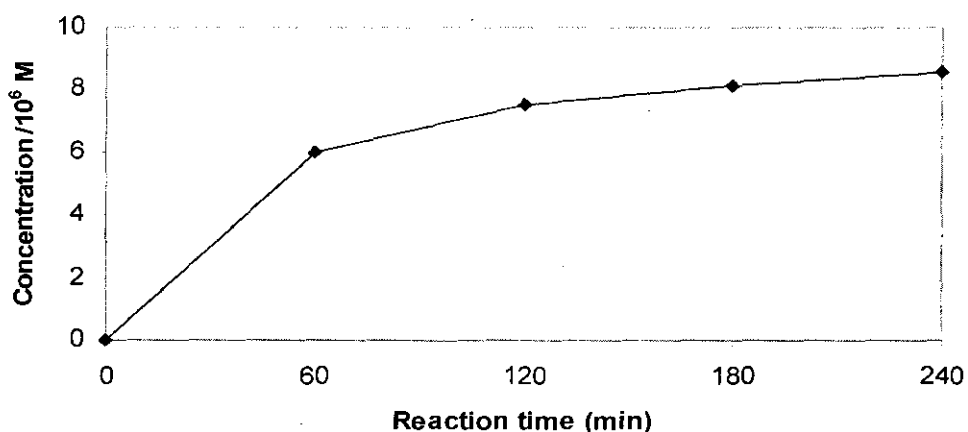
Fig. 3. Time evolution of chloride ion concentration during treatment of diuron
(1mg/L) by photo-Fenton reaction at pH 2.8.

CONCLUSION

In this study, photo-Fenton system reveals increases in the decomposition,
dechlorination and mineralisation levels of the diuron herbicide, due to the additional
generation of hydroxyl radicals through several reactions. Major advantages of the
photo-Fenton system include its reagents which are environmentally friendly, and
usage of sunlight instead of artificial light would significantly lower the costs of the
process particularly in areas, where solar irradiation is highly available making this
process industrially applicable. On the other hand, a major disadvantage of this
process is the pH dependence since the optimum pH around 3, which is far from
neutral pH of natural waters.

ACKNOWLEDGMENT

REFERENCES

1. Andreozzi, R., M., Raffaele and P. Nicklas. 2003. Pharmaceuticals in STP effluents
    and their solar photodegradation in aquatic environment. Chemosphere, 50:
    1319-1330.

2. Arakaki, T. and B.C. Faust. 1998. Sources, sinks, and mechanisms of hydroxyl
    radical (•OH) photoproduction and consumption in authentic acidic continental
    cloud waters from Whiteface Mountain, New York: The role of the Fe(r) (r = II,
    III) photochemical cycle. J. Geophys. Res. 103: 3487-3504.

3. Balci, B., N. Oturan, R. Cherrier and M.A. Oturan., 2009. Degradation of atrazine in aqueous medium by electrocatalytically generated hydroxyl radicals. A kinetic and mechanistic study. Water research, 43: 1924 – 1934.

4. Barbash, J.E., G.P. Thelin, D.W. Kolpin and R.J. Gilliom. 2001. Major herbicides in ground water: results from the national water quality assessment. J. Environ. Qual., 30: 831–845.

5. Benitez, F.J., F.J. Real, J.L. Acero, C. Garcia and E.M. Llanos. 2007. Kinetics of phenylurea herbicides oxidation by Fenton and photo-Fenton processes. J. Chem. Technol. Biotechnol., 82: 65–73.

6. Benkelberg, H. and P. Warneck. 1995. Photodecomposition of iron (III) hydroxo and sulfate complexes in aqueous solution. Wavelength dependence of OH and SO4- quantum yields. J. Phys. Chem., 99: 5214-5221.

7. Buxton, G.V., C.L. Greestock, W.P. Helman and A.B. Ross. 1988. Critical review of rate constants for oxidation of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/ •O-) in aqueous solutions. J. Phys. Chem. Ref. Data, 17: 513-886.

8. Durand, G., N. De Bertrand, D. Barcelo. 1991. Applications of thermospary liquid chromatography-mass spectrometry in photochemical studies of pesticides in water. J. Chromatogr. A, 554: 233–250.

9. Faust, B.C., J.M. Allen. 1993. Aqueous-phase photochemical formation of hydroxyl radical in authentic cloudwaters and fogwaters, Environ. Sci. Technol., 27: 1221–1224.

10. Gerecke, A.C., S. Canonica, S.R. Muller, M. Scharer and R.P. Schwarzenbach. 2001. Quantification of dissolved natural organic matter (DOM) mediated phototransformation of phenylurea herbicides in lakes. Environ. Sci. Technol., 35: 3915–3923.

11. Gernjak, W. 2006. Solar photo-Fenton treatment of EU priority substances – process parameters and control strategies. Ph. D. Dissertation, University of natural resources and applied life sciences, Vienna.

12. Haag, W.R. and D.C.C. Yao. 1992. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ. Sci. Technol., 26: 1005-1013.

13. Huston, P.L. and J.J. Pignatello. 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. Water Res., 33: 1238–1246.

14. Katsumata, H., S. Kaneco, T. Suzuki, K. Ohta and Y. Yobiko. 2005. Degradation of linuron in aqueous solution by the photo-Fenton reaction. Chem. Eng. J., 108: 269–276.

15. Kiwi, J., C. Pulgarin, P. Peringer and M. Gratzel. 1993. Beneficial effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in wastewater treatment. Appl. Catal. B: Environmental, 3: 85-99.

16. Kuhn, H.J., S.E. Braslavsky and R. Schmidt. 2004. Chemical actinometry (IUPAC Technical Report). Pure Appl. Chem., 76: 2105-2146.

17. Lee, C. and J. Yoon. 2004. Temperature dependence of hydroxyl radical formation in the hv/Fe3/H2O2 and Fe3/H2O2 systems. Chemosphere, 56: 923–934.

18. Lindsey, M.E. and M.A. Tarr. 2000. Inhibited hydroxyl radical degradation of aromatic hydrocarbons in the presence of dissolved fulvic acid. Water Research, 34: 2385-2389.

19. Madhum, Y.A. and V.H. Freed. 1987. Degradation of the herbicides bromacil, diuron and chlortoluron in soil. Chemosphere, 16:1003–1011.

20. Malato, S., J. Caceres, A.R. Fernandez-Alba, L. Piedra, M.D. Hernando, A. Aguera and J. Vial. 2003. Photocatalytic treatment of diuron by solar photocatalysis: evaluation of main intermediates and toxicity. Environ. Sci. Technol., 37: 2516–2524.

21. Mazellier, P., C. Busset, A. Delmont and J. De Laat. 2007. A comparison of fenuron degradation by hydroxyl and carbonate radicals in aqueous solution. Water research, 41: 4585 – 4594.

22. Mazellier, P., G. Mailhot and M. Bolte. 1997. Photochemical behavior of the Iron(III)/2,6-dimethylphenol system. New J. Chem., 21: 389-397.

23. Nakatani, N., N. Hashimoto, H. Sakugawa, In: R.J. Hill, J. Leventhal, Z. Aizenshtat, M.J. Baedecker, G. Claypool, R. Eganhouse, M. Goldhaber, K. Peters and (Eds.), 2004. Geochemical Investigations in Earth and Space Science: A Tribute to Issac R. Kaplan, Elsevier B.V, The Netherlands, p. 233.

24. Pignatello, J.J., E. Oliveros and A. Mackay. 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Environ. Sci. Technol., 36: 1–84.

25. Rodríguez, M. 2003. Fenton and UV-vis based advanced oxidation processes in wastewater treatment: Degradation, mineralization and biodegradability enhancement. Ph. D. Dissertation. Barcelona Univ., Spain.

26. Safarzadeh-Amiri, A., J.R. Bolton and S.R. Cater. 1996. The use of iron in advanced oxidation processes. J. Adv. Oxid. Technol., 1: 18–26.

27. Schweinsberg, F., W. Abke, K. Rieth, U. Rohmann and N. Zullei-Seibert. 1999. Herbicide use on railway tracks for safety reasons in Germany? Toxicol. Lett., 107: 201 –205.

28. Sun, Y. and J.J. Pignatello. 1993. Photochemical reactions involved in the total mineralization of 2,4-D by Fe3+/H2O2/UV. Environ. Sci. Technol., 27: 304–310.

29. Takeda, K., H. Shindo, N. Nakatani and H. Sakugawa, 2005. Photochemical formation of hydroxyl radicals from chemical species dissolved in river water. J. Jpn. Soc. Wat. Environ., 28: 509-513.

30. Tomlin, C.D.S. 2003. The Pesticide Manual, A World Compendium. 13th edition. British Crop Protection Council, Farnham and Cambridge, UK.

31. Walling, C. 1975. Fenton's reagent revisited. Accounts of Chemical Research, 8: 125-131.

32. Yue, P.L. 1993. Modelling of kinetics and reactors for water purification by photo-oxidation. Chem. Eng. Sci., 48: 1-11.

معدل تكوين الهيدروكسيل راديكال ودوره فى تحطم الدايرون بواسطة تفاعل فينتون

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يعتبر الهيدروكسيل راديكال ($OH^{\cdot}$) واحد من أقوى العوامل المؤكسدة وتشمل التطبيقات الحديثة له استخدامه فى معالجة المياه الملوثة بالمركبات العضوية السامة مثل المبيدات. وينتج الهيدروكسيل راديكال بطريقة كيميائية من تفاعل أيون الحديدوز مع فوق أكسيد الهيدروجين والذى يطلق عليه تفاعل فينتون. فى هذه الدراسة تم تقدير معدلات تكون الهيدروكسيل راديكال عند إستخدام أنظمة أكسدة مختلفة مثل:-

($Fe^{2+}/H_2O_2/UV$-Vis, $Fe^{3+}/H_2O_2/UV$-Vis, $Fe^{2+}/H_2O_2/Dark$, $Fe^{3+}/H_2O_2/Dark$, Fe^{2+}/UV-Vis, Fe^{3+}/UV-Vis, $Fe^{2+}/Dark$, $Fe^{3+}/Dark$, H_2O_2/UV-Vis, $H_2O_2/Dark$) وذلك بعد إضافة البنزين والذى يتفاعل مع الهيدروكسيل راديكال المتكون من التفاعلات السابقة كى ينتج الفينول والذى يتم تقديره بواسطة جهاز كروماتوجرافى السائل عالى الاداء HPLC كدالة للوقت كى نحسب معدل تكون الهيدروكسيل راديكال فى وجود وغياب ضوء الشمس. كذلك تم تقدير تحطم ومعدنة الدايرون (١مجم/لتر) بإستخدام بعض أنظمة الأكسدة الفعالة. أظهرت النتائج أن تفاعل فينتون فى وجود الضوء $Fe^{2+}/H_2O_2/UV$-Vis كان هو أهم مصدر للهيدروكسيل راديكال حيث أنه تكون بمعدل عالى (107.2 μM min^{-1}) مقارنة بمشابه فينتون فى وجود الضوء $Fe^{3+}/H_2O_2/UV$-Vis (58.71 μM min^{-1}) وتفاعل فينتون $Fe^{2+}/H_2O_2/Dark$ (6.73 μM min^{-1}) وبناء على ذلك كان تفاعل فينتون فى وجود الضوء هو أكثر هذه الأنظمة فعالية فى تحطم ونزع كلور ومعدنة الدايرون فى الماء حيث أن التحطم الكامل والتحول الكلى لمحتوى الدايرون الأولى من الكلور ومعدنة ٨٥% من الكربون العضوى الكلى قد تم إنجازهم بعد ١٨٠ و ٢٤٠ و ٥٤٠ دقيقة من التعرض للاشعاع الشمسى عند pH 2.8 على التوالى.