

REMEDIATION OF DIURON-CONTAMINATED WATER BY ADVANCED OXIDATION PROCESSES

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Abstract

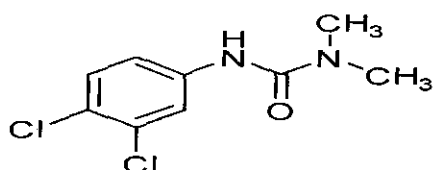
Water contamination with diuron (a substituted phenylurea compound widely used as a systemic herbicide and antifouling biocide) is a problem of general concern since this compound is commonly toxic and highly persistent in the environment. Among the advanced oxidation processes (AOPs) which are currently recognized as effective techniques in water treatment are heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton. Therefore, the remediation of diuron-contaminated water (1mg/L) by TiO₂ was studied using a solar simulator under different conditions such as pH, photocatalyst concentrations and addition of several electron acceptors beside molecular oxygen. The effect of combined TiO₂/photo-Fenton process was studied as well. The degradation rates were found to be strongly influenced by all the above parameters. The efficiency of the degradation rate for decomposition of diuron increased with the increase in reaction pH from 5 to 9 and a further increase in pH (11) led to a decrease in the degradation. It has been observed that the degradation rate for diuron pesticide increases with the increase in photocatalyst TiO₂ concentration up to 1g/L. The decrease of total organic carbon (TOC) as a result of mineralization of diuron was clearly enhanced with TiO₂ plus peroxydisulphate (10mM) compared to TiO₂ alone, and TiO₂ plus hydrogen peroxide (20mM). The combined solar TiO₂/photo-Fenton process was the most effective method for the decomposition and mineralisation of diuron from water. Eight kinds of intermediate products were identified by GC-MS analysis during the decomposition of diuron. **Keywords:** Diuron, Photo-Fenton, Titanium dioxide, hydroxyl radicals.

INTRODUCTION

The Green revolution's heavy reliance on pesticides has created different environmental problems. The majority of pesticides after deliberate or inadvertent release enter the soil and water, where they are either broken down to simpler forms or remain unaltered for a long time because of their persistent nature, posing a great threat to the ecosystem (Alexander, 1981).

Diuron, *N*-(3,4-dichlorophenyl)-*N,N*-dimethyl-urea, as a widely used herbicide and antifouling biocide belongs to the phenylamide family and the subclass of phenylurea. It has been used to control a wide variety of annual and perennial broadleaf and grassy weeds on many agricultural crops, non-crop areas such as roads, garden paths and railway lines as well as its use as antifouling paint biocide (Tomlin, 1997; Giacomazzi and Cochet, 2004). The world production of diuron is around 14 000 to 16 000 tons per year (European Commission, 2000).

Because of its extremely slow breakdown in water, diuron is highly persistent in the environment (Madhum and Freed, 1987). Its wide use leads to pollution of water by soil leaching and agricultural runoffs. It has been detected in aquatic environment in France (IFEN, 1998), Portugal (de Almeida Azevedo *et al.*, 2000), the United Kingdom (Thomas *et al.*, 2001), Germany (Lamoree *et al.*, 2002), Japan (Okamura *et al.*, 2003) and the United States (Sapozhnikova *et al.*, 2007). Diuron was included in 17 safe and effective antifouling compounds assessed by the Shipbuilding Research Association of Japan (Yonehara, 2000). In contrast, the European Water Framework Directive includes diuron as a priority substance that represents a significant risk to or through the European aquatic environment (European Commission, 2001). The U. S. Environmental Protection Agency (2005) also reported diuron on the list of substances considered as contaminants of drinking water since 1998. Thus, diuron indirectly possesses a significant amount of toxicity and could be a potential poisoning contaminant of surface and groundwater. The structure formula of this herbicide is shown in scheme 1.



Scheme 1. Chemical structure of diuron.

Consequently, the efficient disposal of diuron residues has become of immediate importance in a world faced with increasing pollution. The most promising approach in remediation of diuron-contaminated water is advanced oxidation processes (AOPs) [Farré *et al.*, 2007; Maldonado *et al.*, 2007]. AOPs are characterised by the production of free OH radicals ($\cdot\text{OH}$), which are able to oxidise and mineralise almost any organic molecule, yielding CO_2 , H_2O and corresponding mineral acids (Macounova *et al.*, 2003). Due to the reactivity of free hydroxyl radicals, their attack is unselective, which is useful for the treatment of wastewater containing many different pollutants. It is also well known that several AOPs can be performed with solar irradiation, as the sun provides photons with the wavelength required for these processes (Malato *et al.*, 2002). In the near future, advanced oxidation processes (AOPs) may become the

most widely used water treatment technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability (Pera-Titus *et al.*, 2004). Among AOPs, heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton are of special interest since sunlight can be used for them (Malato *et al.*, 2002; Bahnemann, 2004). Photo-Fenton reaction offers high reaction yields with a low treatment cost, mainly because of the possibility of using solar light as photon source and the environmental compatibility of its reactants (Bauer and Fallmann, 1997). The Fenton reagent, consisting of H₂O₂ and ferrous iron, has been shown to be effective in the degradation of a wide spectrum of organic and inorganic pollutants through the formation of OH radicals (Pignatello *et al.*, 2006). Titanium dioxide has also turned out to be the semiconductor with the highest photocatalytic activity, being non-toxic, stable to photocorrosion, low cost and suitable to work using sunlight as energy source (Hermann *et al.*, 1999). It has been suggested that the hydroxyl radicals ([•]OH) and superoxide radical anions (O₂^{•-}) are the primary oxidizing species in the photocatalytic oxidation process using UV/TiO₂ (Hoffman *et al.*, 1995). To our knowledge no information has been published on the combined TiO₂/photo-Fenton for the degradation of diuron.

The purpose of the present work is to study the photodegradation of diuron in water by TiO₂ using a solar simulator under different conditions such as pH, photocatalyst concentrations, addition of several electron acceptors beside molecular oxygen. The combined effect of TiO₂/photo-Fenton process was also studied to improve the efficiency and extend the optimum pH range for this process towards neutral conditions. The intermediate products formed during the photodegradation of diuron were identified.

MATERIALS AND METHODS

1. Chemicals

Diuron 99% and hydrogen peroxide (30%) were obtained from Cica-reagent, Kanto Chemical Co. Inc., Tokyo, Japan, while 3,4-Dichlorophenyl urea and 3,4-Dichlorophenyl isocyanate were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Pesticide quality solvents of acetone, ethyl acetate, acetonitrile, and dichloromethane were obtained from Nacalai Tesuque, Inc, Japan. Ferric chloride (FeCl₃ · 6H₂O) (99%) was obtained from Katayama Chemicals, Japan. Titanium dioxide Degussa P25 contains 75% anatase and 25% rutile with a specific BET surface area of 50 m²g⁻¹ and a primary particle size of 20 nm was a gift from Evonik Degussa

Japan Co., Ltd. Sodium peroxydisulfate 99% was purchased from Merck KGaA, Darmstadt, Germany.

2. Photodegradation experiments

River water was collected from the Kurose River at the Ochiai site (next to water treatment facility that serves the city of Higashi Hiroshima), and then water samples were filtered through a glass fiber filter (GC-50, diameter: 47 mm; pore size: 0.5 μm , Advantec) before used. After filtration of water sample, water quality parameters, such as DOC, anions (Cl^- , NO_2^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , K^+ , and NH_4^+) were analyzed by TOC-VCSH (Shimadzu Co. Japan), Dionex ion chromatography (DX-500) and a Yokogawa IC-7000 Series II ion chromatographic analyzer, respectively. The chemical composition for this water is given in Table 1.

Table 1. Chemical composition of the Kurose river water collected for photocatalytic degradation of diuron pesticide.

Analytical item	Concentration level
NO_3^-	101.79 μM
NO_2^-	8.83 μM
Cl^-	2683.38 μM
SO_4^{2-}	1825.95 μM
NH_4^+	531.77 μM
Na^+	729.09 μM
K^+	194.24 μM
DOC	4.095 mgCl^{-1}
pH	6.9

Irradiations were carried out 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 several pesticide compounds. The wavelength range varies from 300 to 800 nm, which represents radiation very close to natural sunlight (Durand *et al.*, 1991).

For irradiation experiment, a solution containing the required amount of diuron (1mg/l) and Degussa P25 in a quartz glass cell (60 ml) was stirred and bubbled with molecular oxygen for 15 min. in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HCl or NaOH.

The initial time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. During irradiation, the solution in the quartz cell was well mixed with a stirring bar and the temperature was kept at 20°C. The solution from the irradiated samples was removed at regular intervals for HPLC analysis. These experiments were conducted in triplicates and the results representing the mean values. The relative standard deviations ranged from 4 to 9%.

3. HPLC system

After illumination, the sample solution was filtered through a 0.45µm Ekicrodisc syringe filter. The progress in the degradation of diuron was followed with HPLC system consisting of a PU-2089 plus pump (Jasco, Japan), a Rheodyne injection valve (Cotati, CA, USA) with a 50 µL sample loop and a UV-VIS detector (SPD-10A, Shimadzu) interfaced with a C-R6A Chromatopac integrator (Shimadzu, Japan) was used. 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 UV detector wavelength was 254 nm for the diuron and 260 nm for 2-nitrobenzaldehyde which was used to normalize the results of the present study to a clear sky, noon conditions of Higashi-Hiroshima city (34°N) on 7th of October calculated by (Takeda *et al.*, 2005) because the power of the solar simulator is slightly changed by time. Under these conditions, the retention time for diuron was 7.1 min. Its calibration was calculated on the basis of the peak areas obtained with standardized samples analysed under the same HPLC conditions.

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 irradiated solutions at regular intervals after filtration. TOC of the sample solution was measured with a Shimadzu TOC-VCSH analyzer based on CO₂ quantification by non-dispersive infrared analysis after high-temperature catalytic combustion and calibrated with standard solutions of potassium phthalate.

5. Identification of diuron photoproducts

In order to identify the photoproducts of diuron, MilliQ water samples were spiked at 10 mg/l levels of diuron and irradiated for 2 hours in the quartz glass cell, then subjected to solid phase extraction followed by GC-MS analysis. The intermediate products of the photodegradation of diuron were extracted by solid phase extraction

(OASIS 60 mg Waters cartridges, Milford, MA, USA). The irradiated water samples were passed through the cartridges at a flow rate of about 10 ml/min. Air vacuum was employed to eliminate the water residues from the cartridges. A mixture of dichloromethane and ethyl acetate (1/1, v/v) was used to elute the intermediate products. This solution was concentrated under nitrogen flow for the by-products analysis. The GC-MS was performed using a GC (HP 6890 series) equipped with a mass selective detector MSD (HP 5973). The system was equipped with a TC-5 capillary column (30 m long \times 0.25 mm i.d., film thickness 0.25 μ m), splitless injection, and used helium as carrier gas (1 ml/min). The GC oven temperature was programmed to initially hold at 50°C for 3 min, to increase from 50 to 275°C at a rate of 5°C/min and to hold at 275°C for 15 min. The injector and interface temperature were kept at 250°C. Mass spectra were obtained by the electron-impact (EI) mode at 70 eV, using the full scan mode.

RESULTS AND DISCUSSION

1. Photolysis of diuron

Irradiation of diuron solution in the absence of TiO₂ and Fenton reagents under the same irradiation conditions as for photocatalysis shows that photolytic decomposition of the herbicide occurs at low rates (Fig. 1). This indicates that photochemical processes are scarcely responsible for the observed fast degradation when the solution was irradiated in the presence of titania and Fenton reagents. The photolysis of diuron showed approximately similar results within the pH range studied. It is evident that the pH had a slight effect on the degradation of diuron.

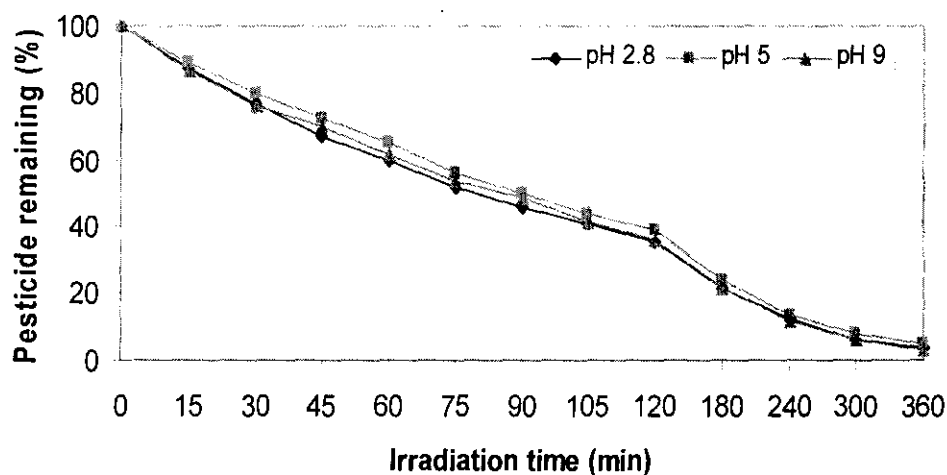


Figure 1. Influence of solution pH on photolysis of diuron (1mg/l).

2. Effect of catalyst concentration

The influence of the catalyst concentration on the degradation rate of diuron was investigated using different concentrations of Degussa P25 varying from 0.25 to 1 g/l. Fig. 2 Shows that diuron degradation rate as a function of catalyst concentration increased with the increase in catalyst concentration. The best result for photocatalytic degradation for diuron was obtained at 1g/l. However, it has been observed that above a certain concentration, the reaction rate levels off and becomes independent of the catalyst concentration. The increase in the rates is likely due to the increase in the total surface area (or number of active sites) available for photocatalytic reaction as the dosage of TiO₂ increased. However, when TiO₂ was overdosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which embedded the positive effect coming from the dosage increment and therefore the overall performance reduced (Wong and Chu, 2003). Therefore, in any given application, the optimum catalyst concentration has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons (Muneer *et al.*, 2005).

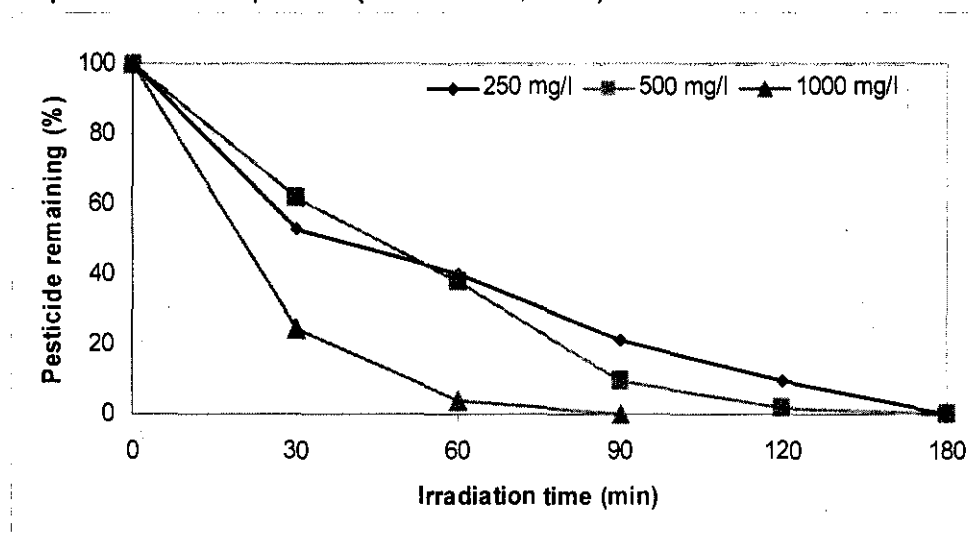
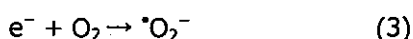
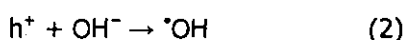
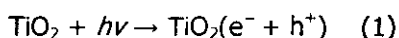


Figure 2. Influence of the photocatalyst Degussa P25 concentration on the degradation of diuron (1mg/l) at pH 9.

3. pH effect

The degradation rate for the decomposition of diuron as a function of reaction pH is shown in Fig.3. The efficiency of the degradation rate for decomposition of diuron increased with the increase in reaction pH from 5 to 9 and a further increase to pH 11 led to a decrease in the degradation. A rate of enhancement of about 1.698 times was observed as the pH increased from pH 5 to pH 9. This increment is likely due to the increase in hydroxyl ions in the solution, a matter critical for determining the concentration of hydroxyl radicals ($\cdot\text{OH}$) in a UV photolysis process (Sun and

Pignatello, 1995) or an oxidation process (Chu and Ma, 2000). An increased amount of OH^- at an elevated pH level could enhance the generation of free radicals through photo-oxidation by holes (h^+) on TiO_2 valence band which may react with surface-bound H_2O or OH^- to produce the hydroxyl radical, as indicated in Eq. (1) and (2), since the hydroxyl free radical is likely the dominant oxidizing species in the photocatalytic process (Chu and Wong, 2004). Whereas the electron (e^-) on TiO_2 conduction band is picked up by oxygen to generate superoxide radical anion ($^{\cdot}\text{O}_2^-$) as indicated in Eq. (3).



However, above a certain OH^- concentration present in the solution, unfavorable electrical forces are generated i.e. repulsion occurs between the negatively charged surface of the catalyst and OH^- . Consequently, the degradation efficiency decreases at higher pH. Another reason for this behavior could be attributed to the fact that when the concentration of OH^- is higher in the solution, it prevents the penetration of UV light from reaching the catalyst surface (Qamar *et al.*, 2006).

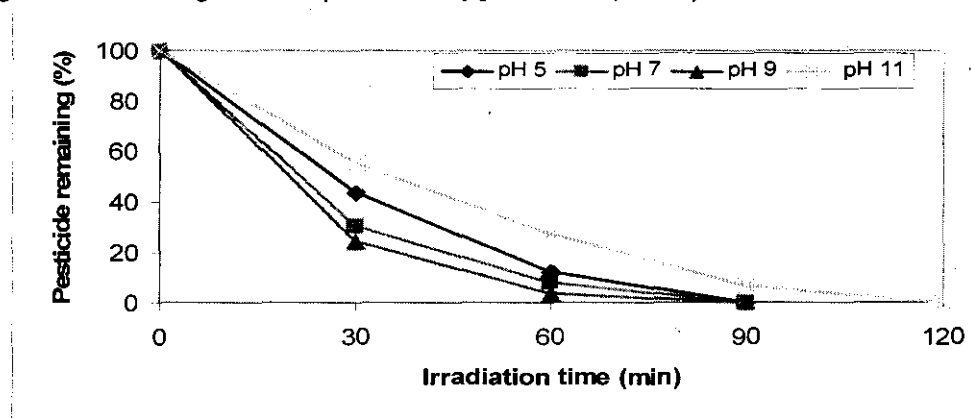
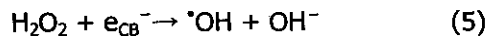


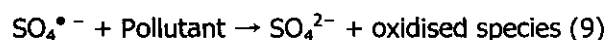
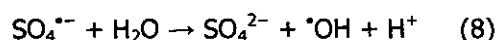
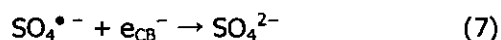
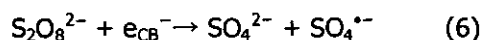
Figure 3. Influence of pH on the degradation of diuron (1mg/l) in the presence of Degussa P25 (1g L^{-1}).

4. Effect of electron acceptors

The degradation rate for diuron in the presence of hydrogen peroxide and sodium peroxydisulphate as electron acceptors is shown in Fig.4. The reaction rate increased with the addition of H_2O_2 (20 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (10 mM) to TiO_2 showing 1.233 and 2.224 times, respectively compared to that of sole photocatalysis with TiO_2 . The rate improvement at H_2O_2 addition is probably due to the direct photolysis of H_2O_2 by UV light that can generate $^{\cdot}\text{OH}$ radicals (Bolton and Cater, 1994), which are likely to be the dominant rate-improving mechanism in this process (Eq. (4-5)) where e^-_{CB} is the electron generated in the TiO_2 conduction band.



Addition of the two electron acceptors enhance the formation of hydroxyl radicals and also inhibit the electron/hole (e^-/h^+) pair recombination, which, in the absence of a proper electron acceptor or donor, is extremely efficient and represents the major energy wasting step thus limiting the achievable quantum yield. The peroxydisulphate reactions are expressed according to the following equations (6–9) (Yamazaki *et al.*, 2001; Haque and Muneer, 2003).



Obviously reactions 6 and 7 enhanced the photocatalytic reaction rate by avoiding e^-/h^+ recombination (the major cause of the low quantum yield of TiO_2 photocatalysis). This leaves a larger number of holes (h^+) able to produce $\cdot\text{OH}$. Photolysis of peroxydisulphate also produces two sulphate radical anions (Eq.10) (Pérez *et al.*, 2006).

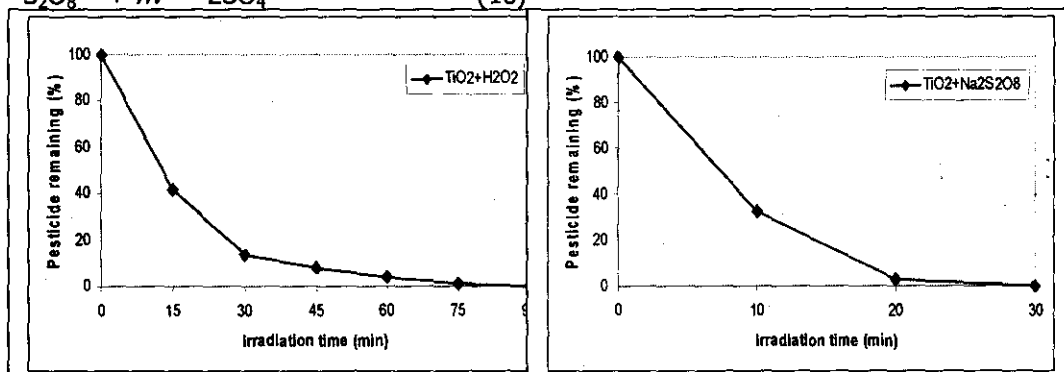
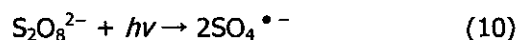


Figure 4. Effect of two electron acceptors H_2O_2 (20 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (10 mM) on the photocatalytic degradation of diuron (1mg/l) in the presence of Degussa P25 (1g L^{-1}) at pH 9.

5. Effect of the combined TiO_2 /photo-Fenton

Among the advantages of the photo-Fenton process are that Fe is abundant, nontoxic and is easily removed from water (Safarzadeh-Amiri *et al.*, 1996). In addition to that, hydrogen peroxide is easy to handle and environmentally friendly, since it slowly decomposes into oxygen and water (Benitez *et al.*, 2007). However, the disadvantage of the photo-Fenton reaction method is its sensitivity to pH. The main reason for the low reactivity at circumneutral pH is the precipitation of Fe(III) as hydrous oxyhydroxides $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ which inhibits the recycling of Fe(III)/Fe(II)

(Georgi *et al.*, 2007). The optimum pH for Fenton oxidations is usually reported in the acidic range near pH 3 (Pignatello *et al.*, 2006). However, water and soil may possess a high buffer capacity. Therefore, the necessity to acidify the reaction medium limits the applicability of the Fenton process in environmental technology (Georgi *et al.*, 2007).

Consequently, this study examines the applicability of the combined solar TiO_2 /photo-Fenton process with the aim of shortening the photo-Fenton treatment time in order to enhance the economical feasibility of the process and extending the optimum pH range for this process towards neutral conditions. As shown in Fig. 5, the combined solar TiO_2 /photo-Fenton process was the most effective method for the elimination of diuron herbicide from water since complete degradation was achieved after 20 min at pH 5. Therefore, it is a promising mean for increasing the efficiency of photo-Fenton and extending the optimum pH of this process towards neutral conditions.

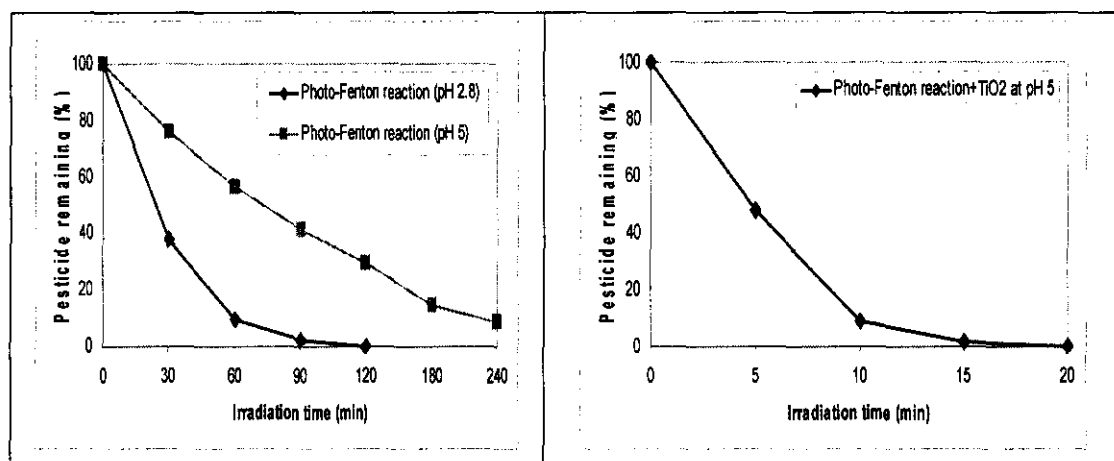


Figure 5. Effect of photo-Fenton process [Fe (0.9 mM) and H_2O_2 (20 mM)] on the degradation of diuron (1mg/l) at pH 2.8 and 5 (a), Effect of the combined TiO_2 (1g L^{-1})/photo-Fenton process [Fe (0.9 mM) and H_2O_2 (20 mM)] on the degradation of diuron (1mg/l) at pH 5 (b).

6. Diuron mineralization

As shown in Fig. 6, the combined solar photo-Fenton/ TiO_2 process was the most effective method for diuron mineralization (i.e., complete disappearance of TOC) since it achieved 99.8% evolution after 540 min of irradiation time. On the other hand, around 77, 83 and 91% of the initial TOC in diuron was mineralized by TiO_2 alone, TiO_2 plus hydrogen peroxide and TiO_2 plus peroxydisulphate, respectively after 540 min of irradiation time. The very slow degradation of TOC in phenylurea pesticides after 80–90% mineralisation (Muneer *et al.*, 1999; Parra *et al.*, 2002) and the very slow mineralisation of urea (Maletzky and Bauer, 1998), can be predicted by the formation of persistent intermediate compounds of diuron which are likely to be

present in the reaction system after the complete degradation of the tested herbicide (Konstantinou *et al.*, 2002; Katsumata *et al.*, 2005). Urea contains only 1 C atom and 2 N atoms, which could justify not only the remaining 10% of the initial TOC, but also the incomplete release of N (Pérez *et al.*, 2006). The complete mineralization of diuron has been described previously by (Maldonado *et al.*, 2007) in Eq. (11).

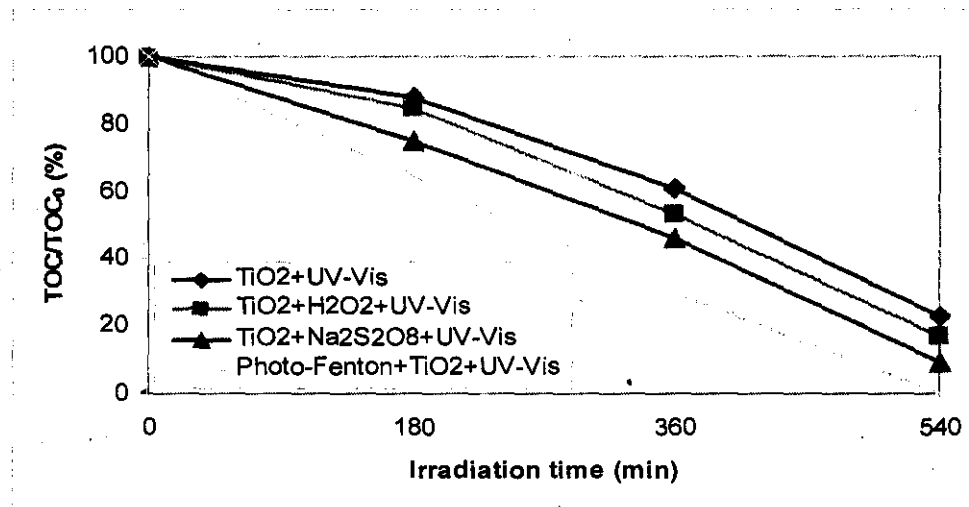
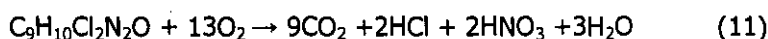


Figure 6. Mineralisation of 3mgC/L of diuron pesticide by TiO_2 alone (1g L^{-1}), with H_2O_2 (20 mM), with $\text{S}_2\text{O}_8^{2-}$ (10 mM) at pH 9 and combined TiO_2 (1g L^{-1})/photo-Fenton process at pH 5 [Fe (0.9 mM) and H_2O_2 (20 mM)].

7. Identification of diuron photoproducts

Eight products were identified by the molecular ion and mass fragmentation pattern and through comparison with NIST library data and also by comparing retention times and spectra with commercially available authentic standards. The structures of the main photoproducts are represented in Table 2. The similarities of these compounds to the NIST library data were more than 85%. In addition to these eight compounds, other degradation products would still possibly exist in the photocatalysis system but were not detected because of their low concentration, extraction efficiency and limited sensitivity in GC-MS. Based on the intermediate products listed in Table 2, it could be concluded that the first step in the degradation pathway of diuron was initiated by the attack on the aromatic ring by OH^\bullet radicals without dechlorination or alkyl chains. The next step involved a series of oxidation processes that eliminated alkyl groups and chlorine atoms. The last step involved oxidative opening of the aromatic ring, leading to small organic ions and inorganic species (Malato *et al.*, 2003). Moreover, during the photodegradation of diuron loss of the two methyl- and 3,4-dichlorophenyl groups are the dominant processes. At the same time, the organic radicals produced by photodissociation can also recombine

with each other, producing, for example, *N,N'*-dimethylurea, the most abundant component of the completely degraded mixture. This recombination process can also result in products of higher molecular mass, e.g. *N, N'*-bis(3,4-dichlorophenyl)urea (Lányi, 2003). 3,4-dichloroaniline and 3,4-dichlorophenyl isocyanate were proposed as the main degradation intermediates by (Salvestrini *et al.*, 2002; Farré *et al.*, 2006) in diuron. *N, N'*-dimethylurea was also identified as the main degradation product of diuron (Lányi, 2003). 3,4-Dichlorophenylurea and *N*-(3,4-dichlorophenyl) formamide were also detected as diuron degradation products by (Macounova *et al.*, 2003) and (Bouquet-Somrani *et al.*, 2000), respectively.

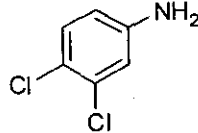
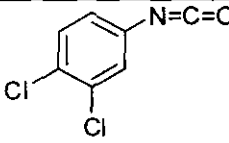
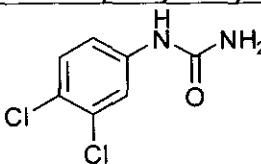
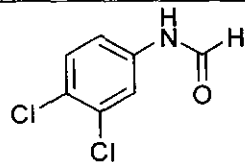
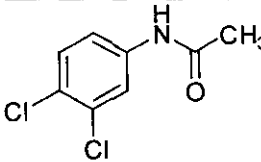
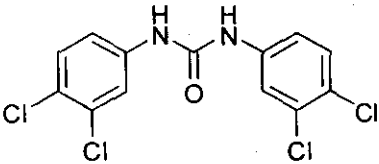
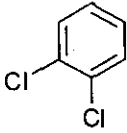
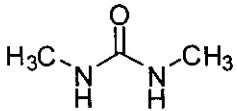
CONCLUSION

The combined solar TiO₂/photo-Fenton process has been found to be the most effective method for both degradation and mineralisation of diuron herbicide from water and is considered as a promising mean for increasing the efficiency of photo-Fenton reaction and extending the optimum pH range of this process towards neutral conditions. The addition of electron acceptors to the photocatalyst Degussa P25 enhanced the degradation rate of diuron. The analysis of the intermediate product formed during the photodegradation process could be a useful source of information on the degradation mechanism. Once photocatalysis is complete, the catalyst (TiO₂ and Fe) separation from solution must be undertaken. Furthermore, TiO₂ catalyst may be reused to reduce treatment cost. Usage of sunlight instead of artificial light for the advanced oxidation processes would significantly lower the costs of the process, and thus provides a major step towards industrial application particularly in areas, where solar irradiation is highly available making this process quite attractive.

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Table 2. Photoproducts obtained by degradation of diuron.

No.	Molecular weight (m/z)	Empirical Formula	Retention time (min)	Photoproduct
1	162	C ₆ H ₅ Cl ₂ N	23.085	 3,4-Dichloroaniline
2	188	C ₇ H ₃ Cl ₂ NO	19.761	 3,4-Dichlorophenyl isocyanate
3	204	C ₇ H ₆ Cl ₂ N ₂ O	23.607	 3,4-Dichlorophenyl urea
4	189	C ₇ H ₅ Cl ₂ NO	21.052	 N-(3,4-dichlorophenyl) formamide
5	203	C ₈ H ₇ Cl ₂ NO	22.046	 3,4-dichloroacetanilide
6	350	C ₁₃ H ₈ Cl ₄ N ₂ O	32.051	 N,N'-bis(3,4-dichlorophenyl)urea
7	147	C ₆ H ₄ Cl ₂	11.798	 Dichlorobenzene
8	88	C ₃ H ₈ N ₂ O	9.217	 N, N'- dimethyl urea

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معالجة المياه الملوثة بالدايرون بواسطة عمليات الأكسدة المتقدمة

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إن تلوث المياه بمبيد الدايرون والذي يستخدم على نطاق واسع فى مكافحة الحشائش والطحالب يعتبر مشكله كبيرة لكون هذا المركب سام و ذو ثبات عالى فى البيئه. من بين عمليات الاكسده المتقدمه المعروفه حالياً كتقنية فعالة لمعالجة المياه الملوثة هى استخدام ثانى أكسيد التيتانيوم وتفاعل فينتون . لذلك فقد تم دراسة معالجة المياه الملوثة بتركيز (١ مجم دايرون/ لترماء) بواسطة ثانى أكسيد التيتانيوم باستخدام محاكى لاشعة الشمس تحت ظروف مختلفه مثل الـ PH ، وجود تركيزات مختلفه من ثانى أكسيد التيتانيوم ، وإضافة مستقبلات الكترون عديده له (مثل فوق اكسيد الهيدوجين و البيروكسى داي سلفات) بجانب الاكسجين الجزيئى. كذلك تم دراسة تأثير خلط (ثانى أكسيد التيتانيوم مع مشابهه الفينتون فى وجود الضوء).

وجد أن معدلات التحطم تأثيرات بقوه بكل العوامل السابقه ، حيث إزداد معدل التحطم للدايرون بزيادة الـ PH من ٥ - ٩ بينما أدت زياده PH إلى ١١ إلى إنخفاض معدل التحطم. لوحظ كذلك أن معدل تحطم مبيد الدايرون ازداد بزيادة تركيز ثانى أكسيد التيتانيوم حتى ١ جم/لتر.

كما ازداد انخفاض الكربون العضوى الكلى الناتج من معدنة الدايرون بوضوح عند استخدام (ثانى أكسيد التيتانيوم + البيروكسى داي سلفات) مقارنة باستخدام (ثانى أكسيد التيتانيوم بمفرده) واستخدام (ثانى أكسيد التيتانيوم + فوق اكسيد الهيدوجين). أما عن تأثير خلط (ثانى أكسيد التيتانيوم مع مشابهه الفينتون فى وجود الضوء) فقد كانت هذه الطريقة هى أكثر الطرق فعالية لتحطم ومعدنة الدايرون فى الماء الملوث به. كذلك تم التعرف على ثمانية أنواع من نواتج تحطم الدايرون بواسطة جهاز الكروماتوجرافى الغاز المزود بمطياف الكتلة GC-MS.