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Photodegradation of fenitrothion in water under direct and indirect conditions

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ABSTRACT

Photodegradation kinetics of the insecticide fenitrothion (O, O-dimethyl O-4-nitro-m-tolyl phosphorothioate) at 5ppm level in water was carried out under direct and indirect photolysis (nitrate addition). The rate of loss of fenitrothion concentration with irradiation time using solar simulator was measured by HPLC. Loss of dissolved organic carbon (DOC) and inorganic ions (sulfate and nitrite) formation rates were analyzed to confirm the photodegradation kinetics of fenitrothion using solar simulator followed by a total organic carbon (TOC) analyzer and ion chromatography. The results showed that the degradation rate of fenitrothion under indirect photolysis was faster than direct photolysis. The faster degradation rate of fenitrothion under indirect photolysis was attributed to the presence of nitrate which generates OH radicals and subsequently accelerates the degradation. This study reflected the significant influence of indirect photolysis in fenitrothion degradation kinetics.

Keywords: Photodegradation, Fenitrothion, Water, Direct photolysis, Indirect photolysis.

INTRODUCTION

It is known that pesticides have a significant role in modern agriculture because of their efficient action in plant protection (Tomlin, 1995). Among them, organophosphorous insecticides have been widely used as an alternative to organochlorine compounds for pest control. However, most of them are highly toxic, can exhibit chemical stability and resistance to biodegradation and, because of the probability being discharged into aquatic systems, great attention has to be paid to their degradation, to diminish their harmful effects on the environment (Topalov, *et al.*, 2003).

Pesticides in contaminated natural water can undergo transformation by different degradation processes such as microbial, and photochemical processes (Durand *et al.*, 1992; El-Dib and Abou-Waly, 1998 and Mansour *et al.*, 1999) and the formed metabolites were sometimes more toxic than the parent compound (Amoros *et al.*, 2000). Photochemical transformation is one of the main abiotic degradation pathways occurring in natural waters and one of the factors controlling the fate of pesticides in the environment (Durand *et al.*, 1991; Castillo *et al.*, 1997 and Mansour *et al.*, 1999). Phototransformation of pesticides proceeds with different pathways through direct and indirect photolysis. Direct photolysis can occur if the concerned pesticide absorbs UV-Visible light (eq.1), while indirect photolysis of the pesticide compound can be induced by chemical components in the aquatic environment such as dissolved organic matter, nitrate, hydrogen peroxide and iron species (eq.2) (Torrents *et al.*, 1997; Vialation and Richard, 2002 and Southworth and Voelker, 2003).

Pesticides + light ⟶ degradation products (Direct photolysis) (1)
Photooxidants + pesticides ⟶ degradation products (Indirect photolysis) (2)

Fenitrothion, as an organophosphothionate insecticide, is a contact insecticide and selective acaricide, also used as a vector control agent for malaria in public health programs (Sarikaya *et al.*, 2004).

Fenitrothion is known for its acute toxicity toward nontarget organisms and, after application, different types of degradations affect this pesticide, such as photolysis, hydrolysis and biological degradation (Lacrote and Barcelo, 1994). In addition, for fenitrothion, many of the phototransformation products, such as fenitrooxon, 3-methyl-4-nitrophenol and s-methylfenitrothion, may be even more toxic than the parent compound (Eto, 1974 and Amoros *et al.*, 2000). There is lack of information about the comparative degradation studies of fenitrothion in water under direct and indirect photolysis.

On the basis of the previous information, we attempt in this study to compare the degradation kinetic of fenitrothion in aqueous media under both direct and indirect photolysis.

MATERIALS AND METHODS

Chemicals

Fenitrothion (O, O-dimethyl O-4-nitro-m-tolyl phosphorothioate) 98.5 % purity, was obtained from Kanto Chemicals Company, Japan. Solvents grade, methanol, acetone, acetonitrile, and dichloromethane were obtained from (Nacalai Tesuque, Inc, Japan). The stock solution of fenitrothion (100 ppm) was prepared by making the appropriate dilution in methanol and stored in a refrigerator at 4 °C. Working standard solutions of fenitrothion were prepared by making appropriate dilutions in MilliQ water and storing in a refrigerator at 4 °C. A nitrate stock solution (10 mM) was prepared by making appropriate dilutions in MilliQ water.

Photodegradation Experiments

In the photodegradation experiments, a solar simulator (Oriel, Model 81160-1000) unit equipped with a 300 W Xenon lamp and special glass filters restricting the transmission of wavelengths below 300 nm was used. This Xenon lamp has been demonstrated to be equivalent to natural sunlight for conducting aqueous photolysis studies for several pesticide compounds. The wavelength ranged from 300 to 800nm, which represents radiation very close to natural sunlight (Durand *et al.*, 1991). As fenitrothion has a limited solubility in water (14 mg / l), a water-methanol solution was employed (Durand *et al.*, 1992). The water samples were filtered through a glass fiber filter (GC-50, diameter: 47 mm; pore size: 0.5µm, Advantec) before they were used. MilliQ water samples were spiked with fenitrothion at a concentration of 5 ppm, In the case of indirect photolysis; nitrate was added to the MilliQ water samples at a level of 200 µM. This nitrate concentration was selected to be similar to that found in the river water samples. The irradiation of the samples was carried out in a quartz glass cell (60 ml) containing the desired amount of fenitrothion. During the irradiation period the solution in the quartz cell was well mixed using a stirring bar and the temperature was kept at 20 °C.

HPLC system

The irradiated samples were analyzed directly by the HPLC system, which consists of a pump (LC-10Ai, Shimadzu), a sample injector (Rheodyne Model 1296, sample size 50 µl) and a UV-VIS detector (SPD-10A, Shimadzu). The column was an Ultron VX-ODS (Suplecosil LC-18, particle size 5 µm; Supelco) 250 mm X 4.6 mm I.D. A guard column (Suplecosil LC- 18, 5 µm, 10 mm X 4.6 mm I.D.) was fitted in the front of the analytical column. A mixture of acetonitrile (HPLC grade) and

MilliQ water (60:40) was used as the mobile phase under the isocratic elution mode. The flow rate was set at 1.0 ml / min. The UV detector wavelength was 220 nm for the fenitrothion (Kiso *et al.*, 1996).

Determination of kinetics parameters

In order to determine the degradation kinetics, the collected data for fenitrothion at intervals time of irradiation was plotted on semi-log paper to calculate the degradation rate constant (slope), K, that obeyed to the first order equation:

$$C_t = C_o e^{-kt}$$

Where C_t represents the concentration of the pesticide at time t, C_o represents the initial concentration, and k is the degradation rate constant. When the concentration falls to 50 % of its initial amount, the half-life ($t_{1/2}$) can be determined by $t_{1/2}$=0.693/k, according to the method described by Daley and O'Malley, 1974 and Derbalah *et al.*, 2004.

Determination of dissolved organic carbon (DOC)

Loss in DOC analysis was measured by Shimadzu TOC 5000 A total organic carbon (TOC) analyzer. Four points calibration curve was constructed for each measurement using potassium phthalate standards prepared in MilliQ water. The standard and samples were acidified using hydrochloric acid (HCl). All DOC concentrations reported are the average of 3 injections from each sample.

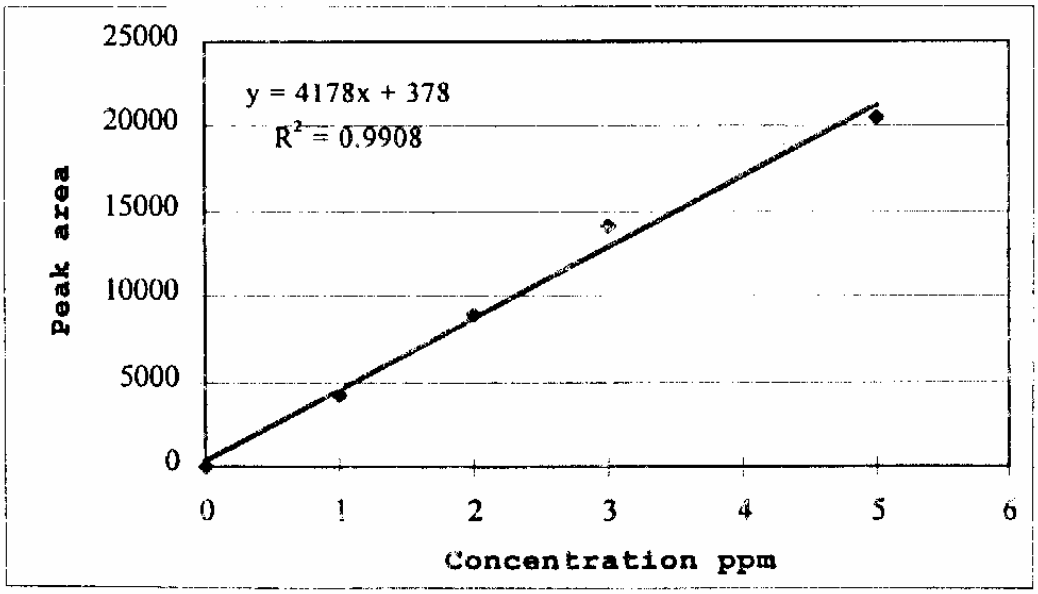

Figure (1): Standard curve of dissolved organic carbon using TOC analyzer.

Ion chromatography analysis

Ion chromatograph (Dionex 4000) equipped with conductivity detector was using for measuring sulfate ion. Samples were injected directly after irradiation in solar simulator. Standard solution of sulfate ion (sodium sulfate) and nitrite ion were prepared in MilliQ water. Each solution was analyzed in ion chromatograph and from the results standard curves were obtained. Sample concentration was determined by measuring peak hight and using standard curve.

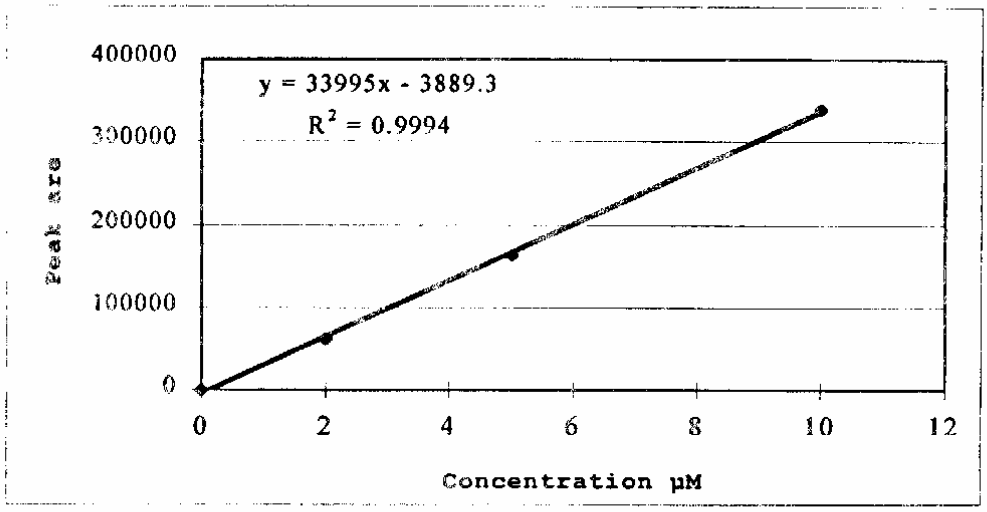

Figure (2): Standard curve of sulfate ion using ion chromatography.

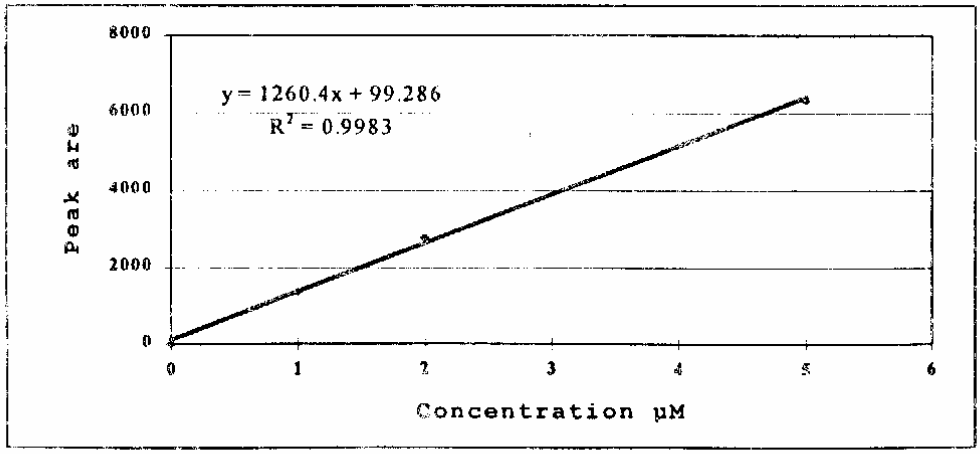

Figure (3): Standard curve of nitrate ion using ion chromatography.

RESULTS AND DISCUSSION

Degradation kinetics of fenitrothion

The photodegradation kinetics of fenitrothion at a concentration level of 5 mg / L in pure water-methanol solution under both direct and indirect photolysis was investigated by monitoring the loss in fenitrothion concentration with irradiation time using HPLC analysis. Samples were withdrawn at 0, 2, 4, 6, 8, 10 and 12 hours after starting the irradiation. The results in Table (1) showed that the photodegradation rate of fenitrothion in pure water under direct photolysis was (0.09 h^{-1} n=3) slower than that of indirect photolysis which was (0.13 h^{-1} n=3) and subsequently resulted in a shorter half life of fenitrothion under indirect photolysis (5.33 h) than direct photolysis (7.70 h).

Table 1: Degradation rate constant and half life of fenitrothion in pure water under direct and indirect photolysis

Type of sample	Degradation rate constant (h^{-1})	Half life $t_{1/2}$ (h)
MilliQ water	0.09 (n=3)	7.70 (n=3)
MilliQ water + No_3	0.13 (n=3)	5.33 (n=3)

Fenitrothion was found to be more rapidly photodegraded in pure water under indirect photolysis compared to direct photolysis. This result was consistent with those found by Torrents *et al.* (1997) who reported that, where the hydroxyl radical was readily formed, and then faster degradation of atrazine was observed compared to direct photolysis in distilled water in the presence of the nitrate. Therefore, the differences in the degradation rate of fenitrothion between the two aqueous media are attributed mainly to the presence of nitrate under indirect photolysis, which accelerates the degradation rate of fenitrothion compared with direct photolysis.

Dissolved organic carbon losses

To confirm the role of indirect photolysis in fenitrothion degradation, the loss in DOC concentration with irradiation times was determined. Fig (4) showed that the loss rate of fentrothion under indirect photolysis was faster than direct photolysis. Furthermore, the loss rate of fenitrothion in the first 8 hr. slightly changed under both direct and indirect photolysis. Then, it became faster under indirect photolysis comparing with direct photolysis. The difference in the two systems was due to the reason reported previously.

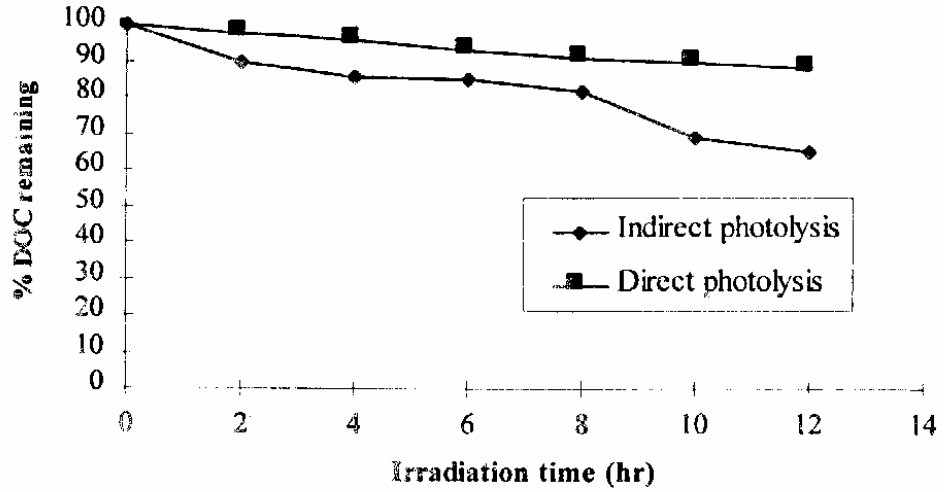

Figure (4): Losses of DOC concentration of fenitrothion under direct and indirect photolysis.

Sulfate ion formation rate.

In Fig (5) the formation rate of sulfate ion was determined to estimate the degradation kinetics of fenitrothion under both direct and indirect photolysis. The results showed that, the formation rate of sulfate ion under indirect photolysis was faster than that of direct photolysis. As shown in Fig. (4), indicated that there was no a great difference between the degradation rate of fenitrothion under direct and indirect photolysis. This may be due slight adsorption of nitrate ion in visible region and most of solar light located in the visible range of the light.

The present work reflects more details on what can happen in samples similar to real environmental condition, since the photolysis was conducted in water spiked with nitrate instead of only organic solvent or pure water, as reported previously by Greenhalgh and Marshall, (1976); Mikami *et al.*, (1985); Durand *et al.*, (1992) and Durand *et al.*, (1994). Moreover, the photodegradation was conducted using low concentration (5 mgl^{-1}), so in this way, the behavior of fenitrothion was more closely to the degradation kinetics in the real environmental situation compared to previous studies (Greenhalgh and Marshall, 1976; Mikami *et al.*, 1985; Durand *et al.*, 1992; Durand *et al.*, 1994; Kerzhentsev *et al.*, 1996 and Castillo *et al.*, 1997).

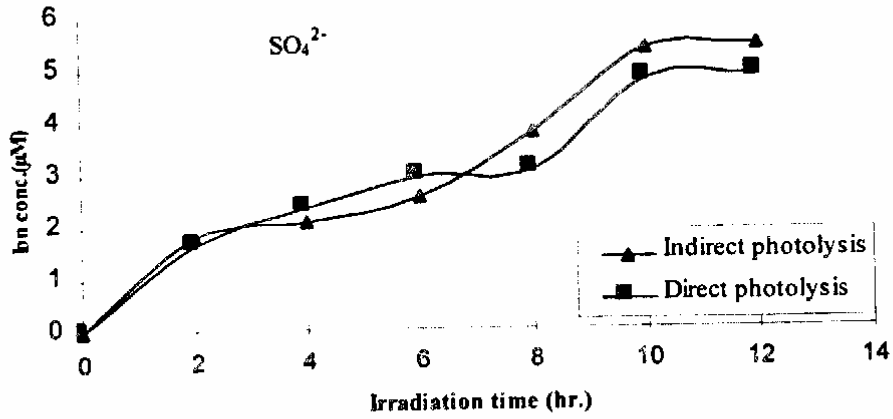

Figure (5): Sulfate ion formation rate due to photodegradation of fenitrothion under direct and indirect photolysis.

Nitrite ion formation rate

Fig (6) showed that, the formation rate of nitrite ion was faster under indirect photolysis than direct photolysis. As shown in Fig (6), the formation rate of nitrite in first 2hr. was almost the same under both direct and indirect photolysis. However, after that there is a marked difference in the formation rate of nitrite ion between direct and indirect photolysis. The differences between direct and indirect photolysis were attributed mainly to presence of nitrate as reported previously.

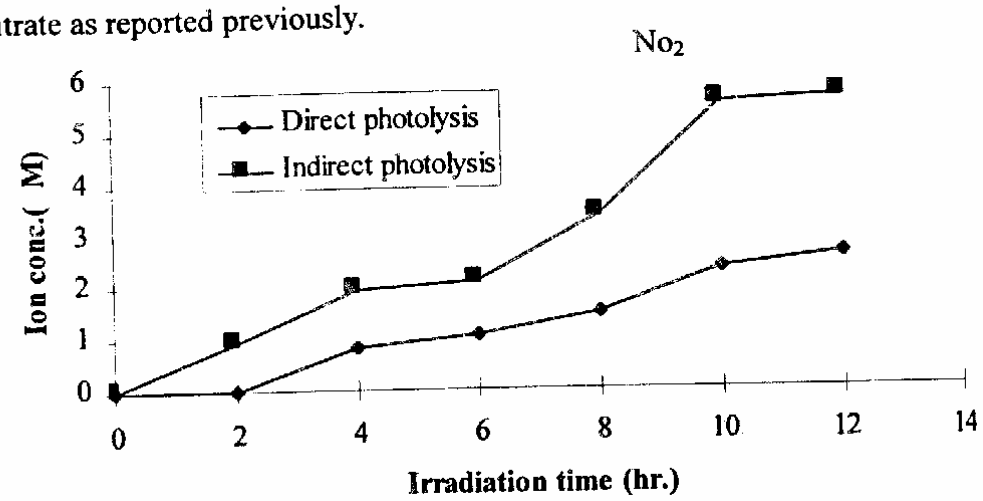

Figure (6): Nitrite ion formation rate due to fenitrothion degradation under direct and indirect photolysis.

The results of DOC losses and inorganic ions formation rate indicated that the influence of indirect photolysis in fenitrothion degradation as reported by Derbalah *et al.*, (2004). This influence clearly found in river water which contain many photo oxidant beside nitrate such as dissolved organic matter, ions, H_2O_2 and so on.

Spite of the significant was influence of indirect photolysis in fenitrothion degradation kinetics. The role of indirect photolysis in pesticides degradation kinetics assumed to be more significant due the presence of many photo oxidants other than nitrate (Dissolved organic matter , iron ions etc), which able to absorb the light in visible region comparing with nitrate (Malato, *et al.*, 2002).

Finally, extensive photodegradation studies of pesticides are needed for allowing the modeling of pesticides behavior after application, which in turn led to understand the kinetics of pesticides degradation as well as increasing our knowledge about the degradation products that can form under natural conditions, and enabling us to assess their risk.

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التحطم الضوئى لمبيد الفينتروثيون فى الماء تحت الظروف المباشره والغير مباشره

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تم دراسة ديناميكية التحطم الضوئى المباشر والغير المباشر (فى وجود النترات) لمبيد الفينتروثيون عند مستوى ٥ جزء فى المليون وذلك بقياس الانخفاض فى تركيز المبيدد مع وقت التعرض للضوء. وايضا تم دراسة ديناميكية التحطم الضوئى الكامل للمبيد الى عناصره الاولية وذلك بقياس الانخفاض فى تركيز الكربون العضوى وقياس معدل تكوين ايونات الكبريتات والنتريت مع وقت التعرض للضوء.

اظهرت النتائج ان معدل التحطم وكذلك معدل التحلل الكامل لمبيد الفينتروثيون تحت ظروف التحطم الضوئى غير المباشر كان اسرع منه تحت ظروف التحطم المباشر. سرعة التحطم للمبيد تحت ظروف التحلل الضوئى غير المباشر مقارنة بالتحلل الضوئى المباشر ترجع الى وجود النترات تحت ظروف التحلل الضوئى الغير مباشر و التى تمتص الضوء وتنتج اصول ايدروكسيل حرة ذات الطاقة العالية والتى تسرع بدورها من تحطم مبيد الفينتروثيون. وهذه النتائج تعكس الدور المؤثر للتحطم الضوئى الغير مباشر فى فهم ديناميكية التحطم لمبيد الفينتروثيون. وكذلك تسهم فى التعرف على مصير المبيدات فى البيئة المائية بعد تطبيقها.