Asian Journal of Chemistry Vol. 21, No. 3 (2009), 2270-2282

Photodegradation of 2,4-Dichlorophenoxy Acetic Acid on TiO_2, ZnO and Fe_2O_3 by Sunlight

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The photocatalytic degradation of 2,4-dichlorophenoxy acetic acid (2,4-D) in aqueous solution containing a suspension of titanium dioxide (TiO_2), zinc oxide (ZnO) and ferric oxide (Fe_2O_3) was studied under sunlight or concentrated sunlight. As expected, in the presence of TiO_2 and ZnO irradiated by concentrated sunlight, the rate of photodegradation of 2,4-dichlorophenoxy acetic acid was seen to be faster than that irradiated by direct sunlight. Its degradation was not observed in the absence of catalyst and in the dark. TiO_2 and ZnO which possess more higher band gap energy than that of Fe_2O_3 are effective photosensitizer for the degradation of this pesticide under concentrated sunlight. The band gap energy of reddish brown Fe_2O_3 (2.2 eV) is lower than that of colourless TiO_2 (3.2 eV) and ZnO (3.2 eV). Fe_2O_3 absorbs more longer wavelength of the sunlight than others, but it is not successful as a catalyst under visible light. The results of all UV absorbtion spectroscopy and HPLC analysis regarding products illuminated showed that the complete degradations of 2,4-dichlorophenoxy acetic acid containing ZnO and TiO_2 were observed nearly 99 and 85 % only in 45 min under concentrated sunlight.

Key Words: 2,4-Dichlorophenoxy acetic acid, Photocatalytic degradation, Titanium dioxide, Zinc oxide, Ferric oxide, Concentrated sunlight.

INTRODUCTION

Due to the world-wide general application of intensive agricultural methods during the last few decades and to the large-scale development of the agrochemical industry, most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions[1]. Especially, pollutants include chlorinated organic compounds which are resistant to chemical, photochemical and biological degradation in the environment, making disposal, particularly of contaminated water, difficult[2]. Pesticides are identified as toxic, with very low concentrations of them in general being allowed a maximum permissible concentration for a particular pesticides of 0.1-0.5 pbb for the total load of all plaguicides[1].

2,4-Dichlorophenoxy acetic acid (2,4-D) is one of the most commonly used herbicides in controlling broadleaf weeds and other vegetation. World-wide 2,4-D and different salt derivatives and ester forms are used to contol broadleaf weeds in a variety of places including home lawns, cereal and grain crops, commercial areas, commercial turf, rights-of-way and forest[2-4]. This widespread use of 2,4-D leads to a certain environmental impact, because depending on the climatic conditions, the type of formulation used and the nature of the soil, this herbicide is easily spread within the environment[3,5]. Chemical structure of 2,4-D is shown in Fig. 1.

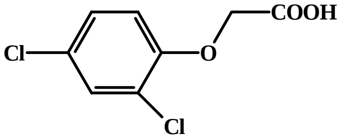


Fig. 1. Chemical structure of 2,4-dichlorophenoxy acetic acid (2,4-D)

The herbicide 2,4-D is widely used for spraying weeds. World Wealth Organization has given the recommended[6] maximum concentration of 2,4-D in drinking water as 0.1 mg L^{-1}. The elimination of 2,4-D from aqueous solutions has been investigated using microbial, chemical and photochemical processes with varying success[7-9]. Heterogeneous photocatalysis is an alternative promising method for eliminating organic compounds from water.

Differently from the traditional methods, the photocatalytic processes often allow the complete mineralization of the organic pollutants with the absence of dangereous residual intermediate compounds[10].

Extensive studies of photocatalytic degradation of 2,4-D in the absence of catalyst[11] and on semiconductors materials under light[6,12-14] have been reported.

Absorption of light by TiO_2 promotes an electron (e^-) from the valance band to the conduction band, creating a positive holes (h^+) in the valence band (vb). Most often, oxygen play the role of electon trap[15]. In aerated aqueous suspension, oxygen is reduced to superoxide anion radical ($O_2^{\bullet -}$) by electrons promoted in the conduction band (cb).

Positive holes react with hydroxyl ion (HO^-) or water (H_2O) leading to the formation of hydroxyl radicals ($HO^\bullet$) which are known to be efficient oxidizer. It has also been suggested that direct oxidation of the substrate by positive hole (h^+) can occur[15-17]. Okomato *et al.*[18] suggested that hydroxyl radicals were formed not only *via* holes and water but also *via* electrons and oxygen. According to Okomato *et al.*[18] the mechanism for photocatalytic reaction in the presence of titanium dioxide is shown in following equations:

$$MO_x + h\nu \longrightarrow MO_x\ (e^-/h^+) \rightarrow e^-\ (cb) + h^-\ (vb) \quad (1)$$

$$OH^- + h^+ \longrightarrow {}^\bullet OH \quad (2)$$

$$H_2O + h^+ \longrightarrow {}^\bullet OH + H^+ \quad (3)$$

$$O_2 + e^-_{cb} \longrightarrow O_2^{\bullet -} \quad (4)$$

$$2O_2^{\bullet -} + H^+ \longrightarrow 2{}^\bullet OH + O_2 \quad (5)$$

$$2O_2^{\bullet -} + H^+ \longrightarrow HO^{\bullet}_2 \qquad pH = 4.88 \qquad (6)$$

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \qquad (7)$$

$$2O_2^{\bullet -} + H^+ \longrightarrow HO^{\bullet}_2 \qquad (8)$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow HO^{\bullet} + HO^- + O_2 \qquad (9)$$

$$H_2O_2 + e^-_{cb} \longrightarrow HO^{\bullet} + HO^- \qquad (10)$$

$$\text{Organic pollutant} + {}^{\bullet}OH \longrightarrow \text{Photoproduct} \qquad (11)$$

Zinc oxide and ferric oxide are know to be photoactive oxides under solar irradiation and their photodegradation mechanisms have been proven[6,19] to be similar to that of TiO_2.

The aim of the present work is the study of the photodegradation of 2,4-D in the presence of titanium dioxide (TiO_2), zinc oxide (ZnO) and ferric oxide (Fe_2O_3) irradiated with direct sunlight and concentrated sunlight and a comparison of the photooxidative degradation capacities of these metal oxides (MO_x) under sunlight and concentrated sunlight is studied.

EXPERIMENTAL

2,4-Dichlorophenoxyacetic acid (2,4-D) was provided by Fluka (purity greater than 99 %) TiO_2, ZnO, Fe_2O_3 was provided by P25 Degussa (AG Frankfurt, Germany), Merck, Surechem, respectively. Ultra pure distilled water (Human Power-I, Scholar-UV, Pure Water System) was used for the preparation of all solutions.

Light sources and reactors: Irradiation was accomplished using direct sunlight or concentrated sunlight. Concentrated sunlight experiments were performed at Fix Focus FF 3.5-HTC GmbH (Germany) instrument which has special focus for sunlight. Technical specifications; reflective surface area 3.68 m^2, usable reflector area 2.66 m^2 covered with a reflective aluminized polymer film, focal length 0.65 m, automatic photocell focus of sunlight on X-direction, manual focus on Y-direction. Aluminized PVC polymer film, with a 40 mm thick layer of alumina[19] and 0.91 g cm^{-3}.

The measuring of intensity of the direct sunlight was obtained by using Apply Black and White Piranometer during the spring-fall period. It was approx. 375 W/m^2. The reaction carried out in a pyrex reactor with water-cooling system. Its temperature was maintained always 15 ± 1 ºC by cryostat. Photodegradation studies were repetitively performed at 2 dissimilar concentrations and submitted to as average values. Photocatalytic experiments were carried out with 0.2 g of the metal oxide suspended in 100 mL of 5×10^{-4} M or 1×10^{-3} M of 2,4-D solution. The initial pH of the 2,4-D (5×10^{-4} M) was 4.0 without catalyst, 4.0 with TiO_2, 5.5 with ZnO and 4.0 with Fe_2O_3. The mixture was illuminated for 1 h under sunlight and concentrated sunlight. The reaction was also carried out in the absence and the presence of the metal oxides under dark conditions in order to compare.

Analyses: Prior to making spectroscopic measurements, all of aqueous solution samples were filtered with blue ribbon filter paper in order to remove suspended particles. The absorption spectra of 2,4-D solutions were measured using a Specord

S600 UV-Vis spectrophotometer. HPLC analyses were performed in the Institute of Hifzisihha in Izmir. HPLC was used as Dionex LC system with an UV dedector. Altima 5 µm 250 mm × 4.6 mm C18 type column was used. Acetonitrile: water (1:1) was used as eluent.

RESULTS AND DISCUSSION

Irradiations under direct sunlight: Absorption spectrum of 2,4-D in two different concentrations (5×10^{-4} M and 1×10^{-3} M) are shown in Fig. 2. The degradation of 2,4-D were studied under 3 different experimental conditions (i) under direct sunlight illumination in the absence of semiconductors, (ii) under sunlight illumination in the presence of semiconductors, (iii) in the dark with semiconductors. The experiments showed that the photocatalytic degradation of 2,4-D (5×10^{-4} M) in the presence of the TiO_2 and ZnO were much more efficient than that of Fe_2O_3 and without catalyst. The degradation was also faster with TiO_2 than with ZnO in Fig. 3.

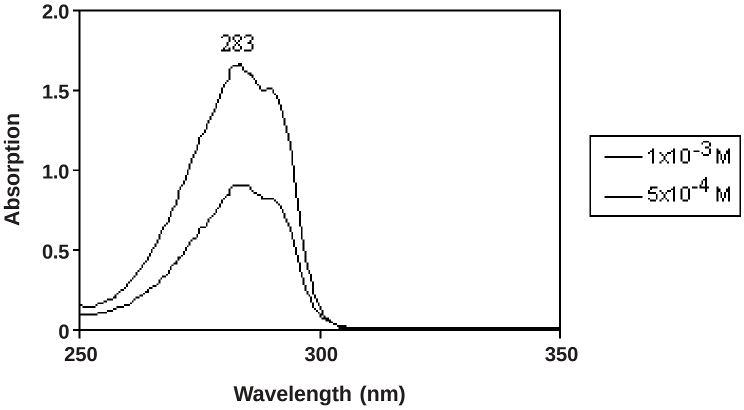
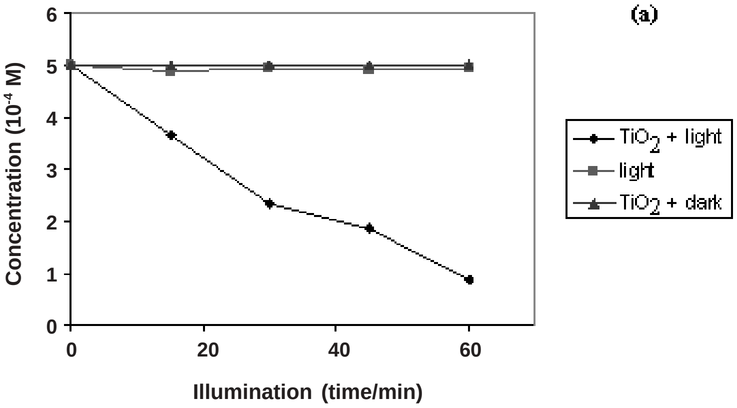


Fig. 2. Absorption spectra of 2,4-D in water (at pH: 4 and in 2 different concentrations)



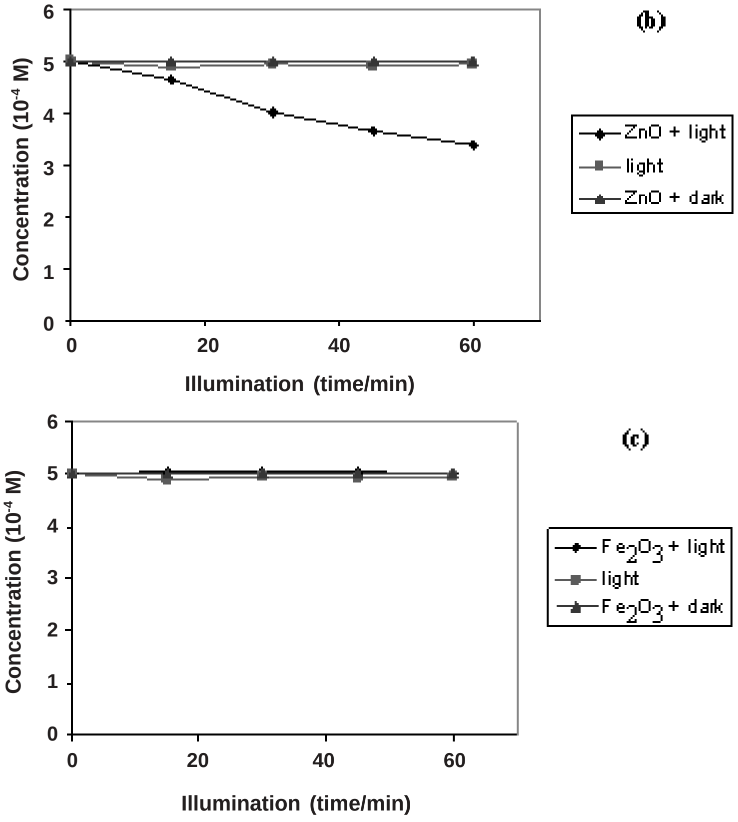
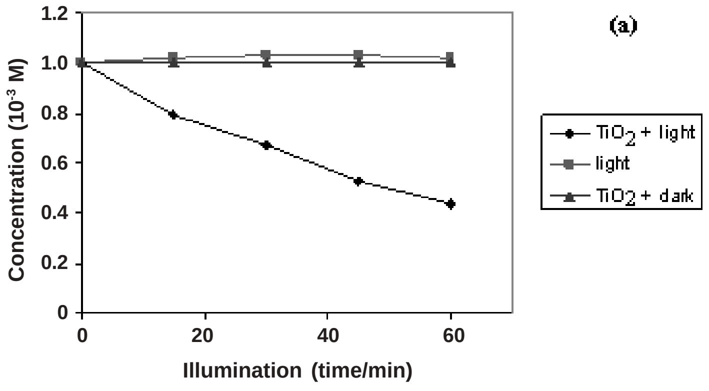


Fig. 3. Degradation of 2,4-D (5×10^{-4} M) illuminated in 1 h in the absence and presence of catalyst under direct sunlight and dark conditions, (a) TiO_2, (b) ZnO (c) Fe_2O_3

The high concentration of 2,4-D (1×10^{-3} M) were used that degradation was observed with TiO_2, but no degradation was observed with Fe_2O_3, ZnO and without catalyst (Fig. 4).



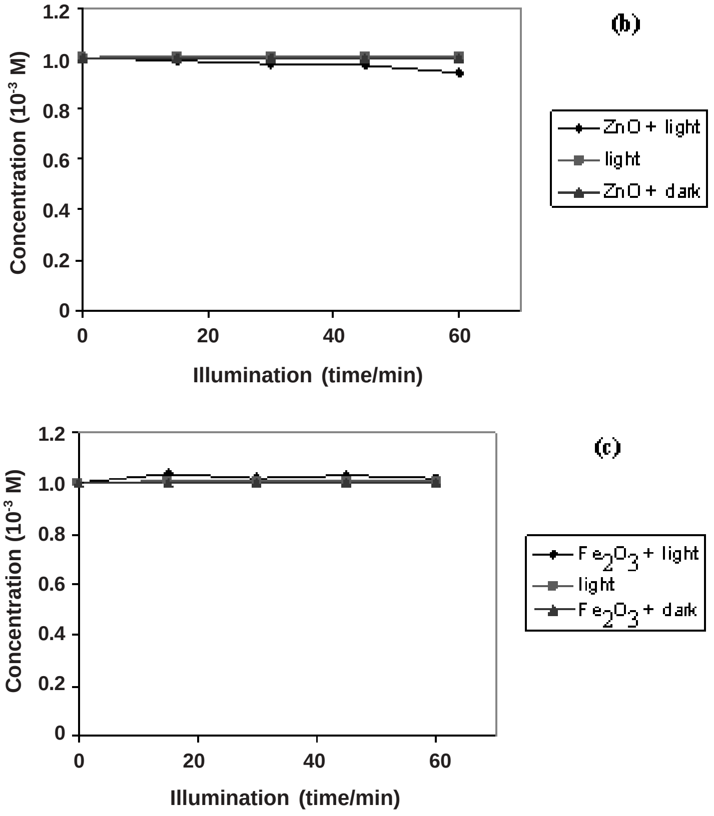


Fig. 4. Degradation of 2,4-D (1×10^{-3} M) illuminated in 1 h with and without catalyst under direct sunlight and dark conditions, (a) TiO_2, (b) ZnO, (c) Fe_2O_3

As it was shown in Fig. 5, any rate of its degradation was not observed in the presence of each selected catalyst in dark conditions, similarly, only using direct sunlight was also not enough to decompose pesticide samples in 1 h. Influence of catalysts on the photodegradation of 2,4-D (5×10^{-4}) by direct sunlight illumination after 1 h in the presence of Fe_2O_3, ZnO and TiO_2 is shown in Fig. 5 (Table-1).

Influence of catalysts on the photodegradation of 2,4-D (1×10^{-3}) by direct sunlight illumination after 1 h in the presence of Fe_2O_3, ZnO and TiO_2 is shown in Fig. 6 (Table-2).

TABLE-1
RATIO OF DEGRADATION OF 2,4-DICHLOROPHENOXY ACETIC ACID (5×10^{-4} M) AFTER 1 h IRRADIATION UNDER DIRECT SUNLIGHT

Type of catalyst	Degradation extent of 2,4-D (%)
TiO_2	85.50
ZnO	35.00
Fe_2O_3	3.20

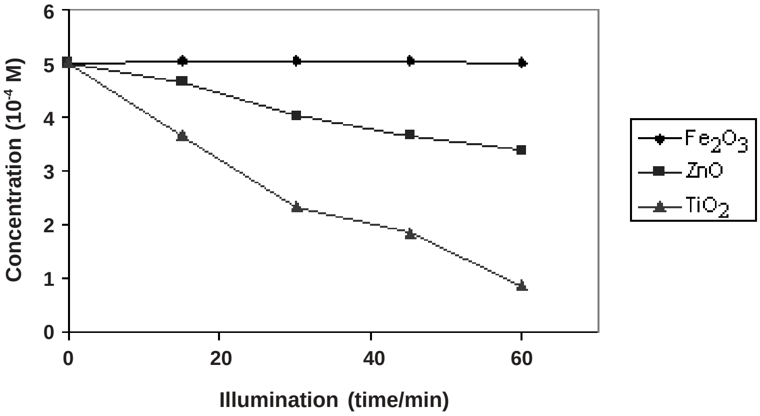


Fig. 5. Effect of catalyst on degradation of 5 × 10^{-4} M concentration of 2,4-D under direct sunlight (catalyst = 2 g/L)

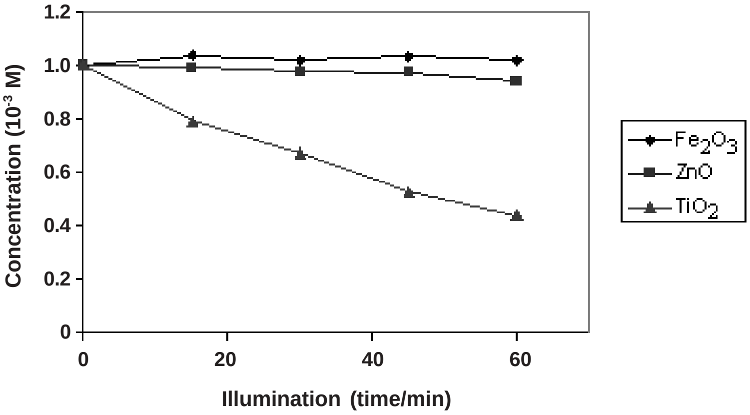


Fig. 6. Effect of catalyst on degradation of 1 × 10^{-3} M concentration of 2,4-D under direct sunlight (the catalyst = 2 g/L)

TABLE-2
RATIO OF DEGRADATION OF 2,4-DICHLOROPHENOXY ACETIC ACID (1 × 10^{-3} M) AFTER 1 h IRRADIATION UNDER DIRECT SUNLIGHT

Type of catalyst	Degradation extent of 2,4-D (%)
TiO_2	60.00
ZnO	10.00
Fe_2O_3	0.00

Irradiations under concentrated sunlight: The degradation of 2,4-D were studied under 3 different experimental conditions (i) under concentrated sunlight illumination in the absence of semiconductors, (ii) under concentrated illumination in the presence of semiconductors, (iii) in the dark with semiconductors. The experiments showed that the photocatalytic degradation of 2,4-D (5 × 10^{-4} M) in the presence of the TiO_2 and ZnO, was more efficient than Fe_2O_3 and without catalyst for 5 × 10^{-4} M 2,4-D in Fig. 7 and for 1 × 10^{-3} M 2,4-D in Fig. 8. 2,4-D (5 × 10^{-4} M) was almost completely degraded in 45 min with ZnO and TiO_2. Also the degradation is nearly equal with TiO_2 and with ZnO in Figs. 9 and 10. The photoactivity of ZnO was also as reactive as TiO_2 under concentrated sunlight for this pestiside compound like phenol compounds[19].

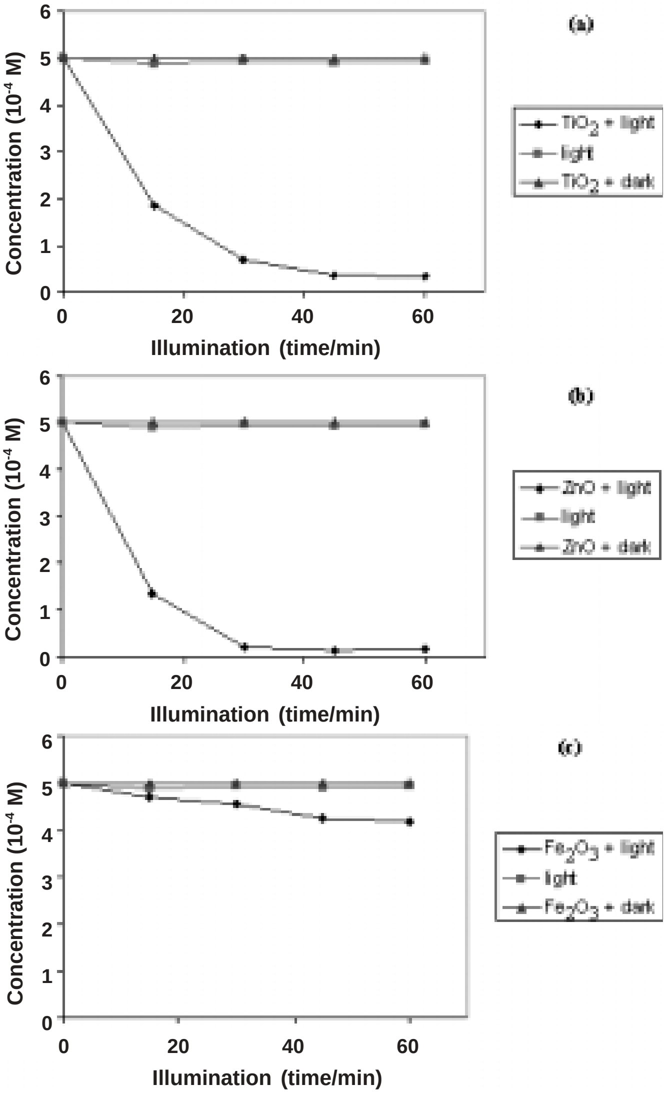


Fig. 7. Degradation of 2,4-D illuminated (5 × 10^{-4} M) in 1 h in the absence and presence of catalyst under concentrated sunlight and in dark conditions; (a) TiO_2 (b) ZnO (c) Fe_2O_3

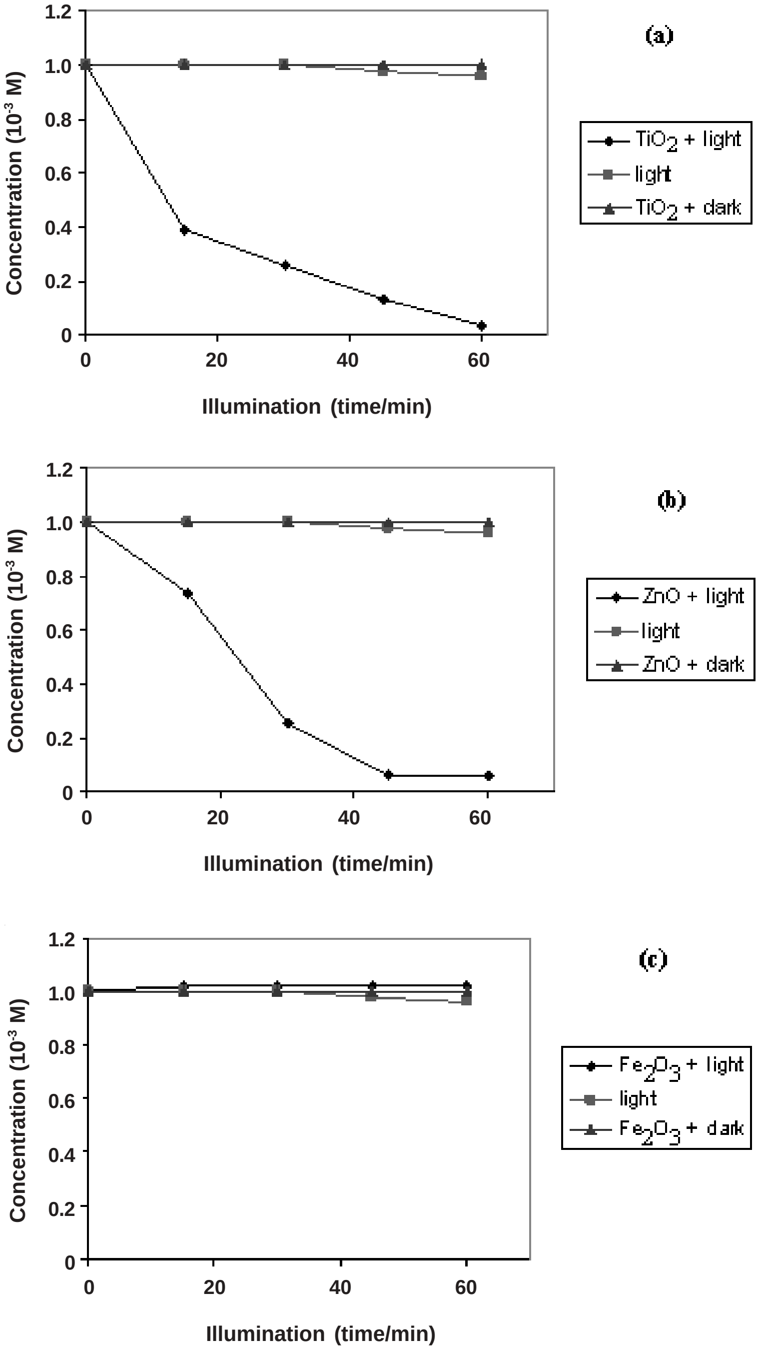


Fig. 8. Degradation of 2,4-D illuminated (1×10^{-3} M) in 1 h in the absence and presence of catalyst under concentrated sunlight and dark conditions (a) TiO_2, (b) ZnO, (c) Fe_2O_3

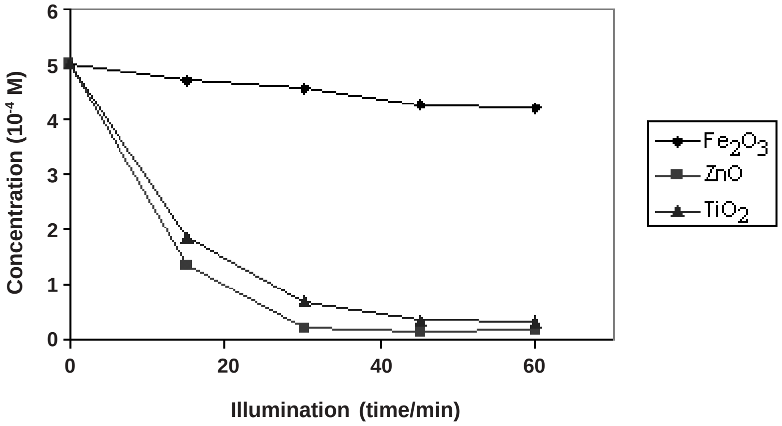


Fig. 9. Effect of catalyst on degradation of 5×10^{-4} M concentration of 2,4-D under concentrated sunlight (catalyst = 2 g/L)

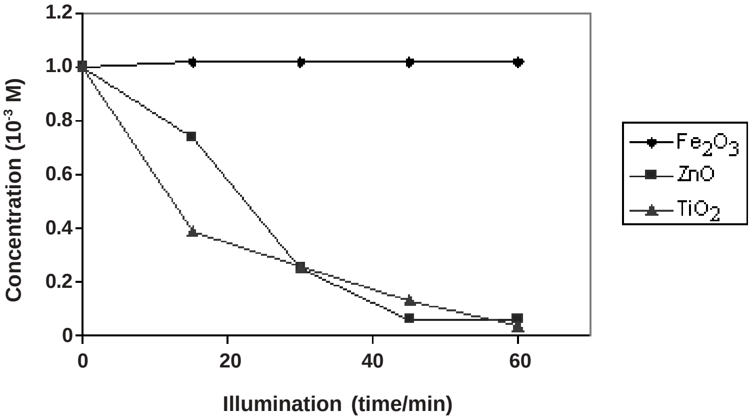


Fig. 10. Effect of catalyst on degradation of 1×10^{-3} M concentration of 2,4-D under concentrated sunlight (catalyst = 2 g/L)

Photodegradation of 2,4-D (5×10^{-4} M) by concentrated sunlight illumination within 1 h in the presence of Fe_2O_3, ZnO and TiO_2 is shown in Fig. 9 (Table-3).

TABLE-3
RATIO OF DEGRADATION OF 2,4-DICHLOROPHENOXY ACETIC ACID (5×10^{-4} M) AFTER 1 h IRRADIATION UNDER CONCENTRATED SUNLIGHT

Type of catalyst	Degradation extent of 2,4-D (%)
TiO_2	99.52
ZnO	100.00
Fe_2O_3	22.60

Photodegradation of 2,4-D (1×10^{-3} M) by concentrated sunlight illumination within 1 h in the presence of Fe_2O_3, ZnO and TiO_2 is shown in Fig. 10.

Amount of 2,4-D (5 × 10^{-4} M) in the initial solution and whole samples were analyzed by HPLC. HPLC chromatogram of an initial aqueous solution of 2,4-D is shown in Fig. 11. The 2,4-D characterized by a retention time to 6.92 min was identified. The ratio of photodegradation of 2,4-D over TiO_2, ZnO and Fe_2O_3 were identified by HPLC and by comparing the retention time of each peak with initial standard. The ratios of photocatalytic degradation of 2,4-D with different catalyst after 1 h irradiation under concentrated sunlight are reported in Table-4.

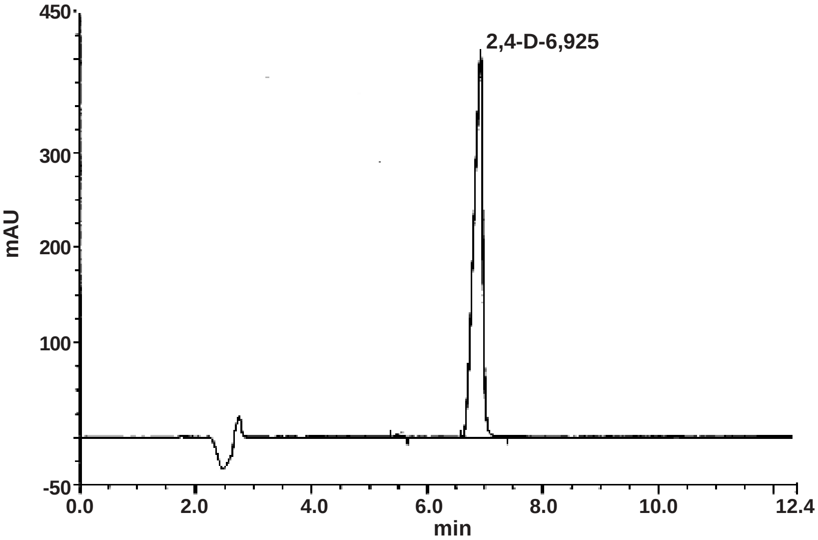


Fig. 11. HPLC chromatogram of an initial solution of 2,4-D (5 × 10^{-4} M)

TABLE-4
RATIO OF DEGRADATION OF 2,4-DICHLOROPHENOXY ACETIC ACID (1 × 10^{-3} M) AFTER 1 h IRRADIATION UNDER CONCENTRATED SUNLIGHT

Type of catalyst	Degradation extent of 2,4-D (%)
TiO_2	100.00
ZnO	99.20
Fe_2O_3	9.40

Conclusion

The degradation of 2,4-dichlorophenoxy acetic acid (2,4-D) were studied under different experimental conditions (i) under sunlight or concentrated sunlight illumination in the absence of semiconductors, (ii) under sunlight or concentrated sunlight illumination in the presence of semiconductors (iii) in the dark with semiconductors.

The results showed that the photocatalytic degradation of 2,4-D in the presence of the TiO_2 and ZnO, was much more efficient than Fe_2O_3 and without catalyst under illumination for 1 h. However, without catalyst, 2,4-D was rather resistant and the degradation of 2,4-D was not seriously observed under sunlight or concentrated sunlight or in the dark conditions after 1 h illumination. Under concentrated sunlight, the experiments showed that the photocatalytic degradation of 2,4-D (5×10^{-4} M or 1×10^{-3} M) in the presence of the TiO_2 and ZnO were especially much more efficient than Fe_2O_3. However, the ratio of photodegration of 2,4-D was decreased in the high concentration of 2,4-D. The whole degradation extents of 2,4-D solutions were determined by HPLC.

As a conclusion, HPLC analysis of ultimate solutions have proved that the almost complete degradation of 2,4-D containing ZnO and TiO_2 was quantitatively carried out under concentrated sunlight nearly 45 min.

The band gap energy of reddish brown Fe_2O_3 (2.2 eV) is lower than that of colourless TiO_2 (3.2 eV) and ZnO (3.2 eV)[19,20]. Fe_2O_3 absorbs more longer wavelength of the sunlight than others, but it is not very successful as a catalyst under visible light.

In the dark conditions, these selected catalyzers did not exhibit any catalytic effect; in contrast, the photodegradation efficiency was 85.50 % with TiO_2, 35.00 % with ZnO and 3.20 % with Fe_2O_3 in 1 h under direct sunlight and increased up to 99.52 % with TiO_2, 100.00 % with ZnO and 22.60 % with Fe_2O_3 for 2,4-D (5×10^{-4} M) under concentrated sunlight in 1 h.

As a final result, These semiconductor photocatalyzers are heterogen, cheap, easy withdrawn from an aqua media, so, they are functional. Under direct sunlight, the experiments showed that TiO_2 was more efficient than ZnO, however, the efficiency of ZnO was same as TiO_2 under concentrated sunlight; accordingly, ZnO is conspicuous and alternative catalyzer to be removed of 2,4-D pestiside in the aqua media.

ACKNOWLEDGEMENTS

The authors express their appreciation to Ege University Research Funds Office and Scientific and Technical Research Council of Turkey (TUBITAK) for financial support of this project. The authors are grateful to Prof Dr. Siddik Icli, Director of Solar Energy Institute and the Institute of Hifzisihha, Izmir for HPLC analysis. Thanks are also due to Selami Solmaz, Belgin Uluocak and Gülser Akbas and other workers in the water research laboratory and the pesticide research laboratory. One of the authors (OS) thanks TUBITAK for scholarship.

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(*Received*: 9 May 2008; *Accepted*: 20 November 2008) AJC-7055