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Journal of Photochemistry and Photobiology A: Chemistry 153 (2002) 229–236

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photo-oxidative degradation of insecticide dichlorovos by a combined semiconductors and organic sensitizers in aqueous media

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Received 22 March 2002; received in revised form 21 May 2002; accepted 10 June 2002

Abstract

Organophosphorus insecticide dichlorovos (DDVP) can be photodegraded into chloride ion, water, carbon dioxide and other compounds in an aqueous solution containing semiconductor powder suspensions, using ultraviolet light. Thermostatic photolytic photocell (35 ml) is used. The rate of this photodegradation has been measured by monitoring concentration of Cl^- ion, pH, conductivity of the solution and change in the absorption spectra of compound during irradiation. The effect of various parameters, including semiconductors (TiO_2, ZnO, TiO_2/V_xS_y), organic sensitizers (*p*-nitrophenol, hydroquinone, riboflavine), H_2O_2 concentrations and radiation sources (UV, visible and sunlight), has been studied and new experimental optimized conditions have been established.

According to the experimental and kinetic results, the photocatalytic degradation reaction is followed up first order, and possible mechanisms are suggested.

Keywords: Dichlorovos; Sensitizers; Semiconductors

1. Introduction

Insecticides are considered cumulative and toxic compounds. Their presence as contaminates in aquatic environments may cause serious problems to human beings and other organisms [1–5]. Dichlorovos (DDVP), as an organophosphorous insecticide, is used widely for crop protection mainly in greenhouses and for controlling parasites and insects in houses, aircraft, and outdoor areas (as aerosols, liquidsprays) [6]. LD_{50} of DDVP for mouse 87 mg/kg, rabbit 205 mg/kg and man 400 mg/kg [6,7]. Consequently, it becomes necessary to remove the residues of this toxic compound from matrices such as water by devising an efficient and economic purification method.

Recently, the so-called "advanced oxidation processes" have become a promising method of aquatic detoxification [8–10]. Of these, heterogeneous photocatalysis, which involves electron–hole pair formation initiated by gap excitation of semiconductor particles, has great potential as a technique to dispose off environmentally harmful or carcinogenic compounds at a semiconductor–water interface [11–13]. For instance, toxic organophosphorous insecticides are liable to photocatalyzed-decomposition, ultimately becoming completely mineralized products, over illuminated semiconductor suspensions [14]. Lu et al. [15] have investigated several factors affecting the photocatalytic degradation of DDVP using a glass photoreactor coated with TiO_2 and 20 W black-light tungsten fluorescent tube. They found that the activation energy was 28.4 kJ mol^{-1} and the quantum yield for the destruction of DDVP was 2.67%. Grätzel et al. [16] have described a complete mineralization of 4-nitrophenyltriethylphosphate on Nb-doped TiO_2. Harad et al. [17] have shown that efficient degradation of DDVP and Trichlorofon occurred by using Pt/TiO_2 photocatalyst and H_2O addition and that these are mineralized into non-toxic products of Cl^-, PO_4^{3-}, H^+ and CO_2.

This study describes the photodegradation of DDVP using (TiO_2, ZnO, V_xS_y/TiO_2) aqueous dispersions combined with organic sensitizers. The effect of various parameters (sensitizers, concentration, temperature, different light sources and semiconductors) on this photo-oxidation reaction is investigated. Moreover, photodegradation of DDVP in TiO_2/sensitizer system under solar exposure is observed. The possible mechanisms are proposed.

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PII: S1010-6030(02)00235-6

2. Experimental

2.1. Materials

DDVP used in this experiment was supplied by BDH (99% purity). The molecular formula is

$$Cl_2C{=}CHOP({=}O)(OCH_3)_2$$

TiO_2 (anatase and rutile) of Fluka, with BET surface area of 18.11 $m^2\,g^{-1}$ ($E_{bg} = -3.29$ eV) and 14 $m^2\,g^{-1}$ ($E_{bg} = -3.05$ eV), respectively, were used. ZnO (99% purity) was supplied by Ventron GmbH. A 5% V_xS_y/TiO_2 with BET surface area of 44.9 $m^2\,g^{-1}$ was prepared in this laboratory according to the procedure described elsewhere [18].

The organic sensitizers, riboflavine, *p*-nitrophenol, other sensitizers and chemicals used were analytically pure grade obtained from recognized suppliers. Oxygen (99.9%) and nitrogen (99%) gasses were locally produced.

2.2. Photochemical reactor and procedures

A 150 W medium-pressure mercury lamp ($\lambda_{max} = 365$ nm) supplied by PHYWE Ltd. was used as light source. A Pyrex photoreactor (cylindrical shape, volume 35 ml) equipped with a slice window (diameter 3 cm) surrounded by a thermostatically controlled water jacket was used. The operation and arrangement of the whole laboratory system are given elsewhere [19].

A known amount of a certain photocatalyst was added to an aqueous solution of dichlorovos (with initial concentration of 1.25×10^{-4} M, unless otherwise noted) in a photoreactor cell. The reaction mixture was magnetically stirred, and the resulting suspended solution was irradiated with a medium-pressure mercury lamp, while bubbling oxygen of flow rate of 20 ml min^{-1} was passed through the solution. Several samples were withdrawn at different irradiation time intervals and immediately centrifuged to remove photocatalyst particles. These samples were analyzed for final photodegradation products, using ion chromatograph (Metrohm 690) equipped with an electroconductivity detector for measuring the quantity of Cl^- ion formation, UV–visible spectrometer (Philips PW8800), gas chromatograph (Varian Vesta 6500), conductometer (WtW LF 191) and pH meter (Philips PW942). Classical qualitative analytical methods were also used to identify the final ions.

Experiments under sunlight were carried out in glass flasks containing an aqueous solution of 1.25×10^{-4} M DDVP and 0.0606 mg l^{-1} $TiO_{2\,anatase}$ with and without riboflavine as sensitizer. These experiments were conducted on sunny days between 9.00 a.m. and 4.00 p.m.

3. Results and discussion

3.1. Preliminary studies

Preliminary experiments showed that the destruction of DDVP (1.25×10^{-4} m) in the presence of TiO_2 (60.6 ppm) and oxygen flowing (20 ml min^{-1}) did not occur in the absence of UV-light ($\lambda = 365$ nm). No promising results were observed by using tungsten (500 and 1000 W) lamps during 3 h illumination under similar conditions.

When the same concentrations of DDVP was illuminated with UV-150 W in the presence of TiO_2 (60.6 ppm) in oxygen atmosphere, an increase in the formation of Cl^- ions and conductivity, but a decrease in pH were observed. This indicates that photodegradation of DDVP occurs better under UV-150 W illumination than that of two visible sources according to intensity [20].

Figs. 1 and 2 show that the concentration of Cl^- ions and conductivity increases with time but the pH decreases (Fig. 3), indicating that the dechlorination of DDVP occurs for formation of acidic products (i.e., HCl, H_2PO_4). The effect of flow rate of oxygen bubbling was found to be in important factor on the rate of dechlorination of DDVP (1.25×10^{-4} M) under similar condition.

Fig. 4 shows that the highest concentration of Cl^- ions is obtained at the flow rate of 20 ml min^{-1} after irradiation

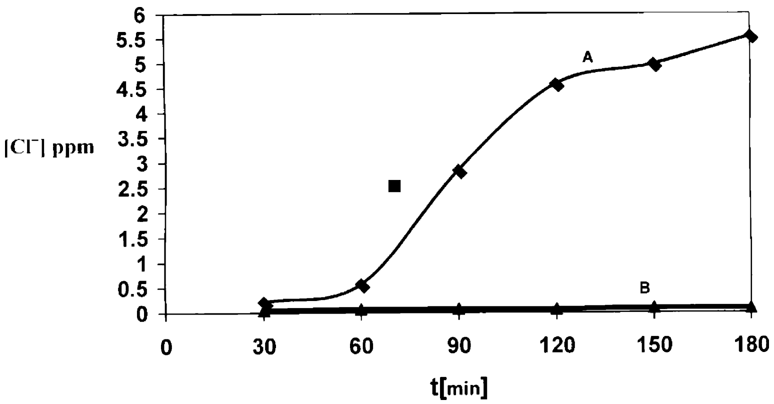


Fig. 1. Formation of Cl^- ion with time of irradiation (A) using UV-light and (B) in dark.

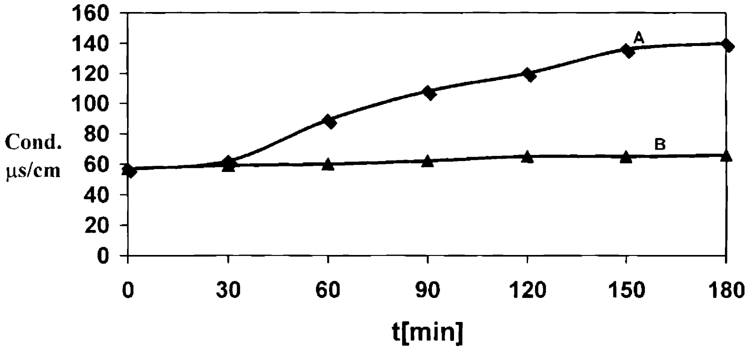


Fig. 2. Change in conductivity of DDVP solution with time of irradiation (A) using UV-light and (B) in dark.

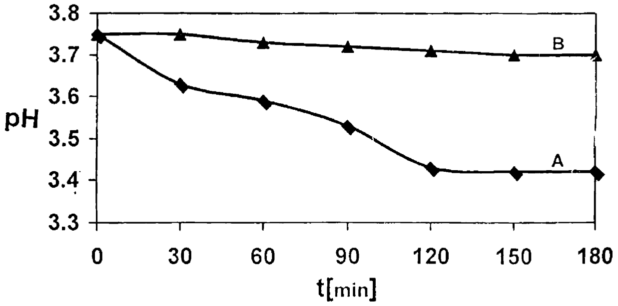


Fig. 3. Change in pH with time of irradiation (A) using UV-light and (B) in dark.

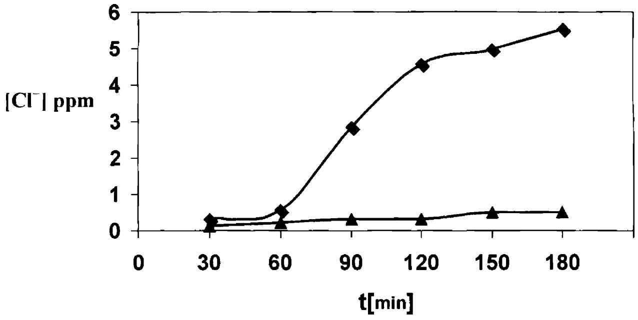


Fig. 5. Formation of Cl^- ion with time of irradiation using (■) oxygen and (▲) nitrogen flowing at 20 ml min^{-1}.

under UV-light for 3 h. Above this flow rate, dechlorination of DDVP gradually decreases. This may be attributed to the competition of such compounds significantly with O_2 on the adsorbed sites of TiO_2 surface, thus decreasing the formation of hydroxyl radical as a powerful oxidizing agent, which is responsible for the photomineralization of DDVP in aqueous solution under similar conditions. However, in a nitrogen atmosphere (20 ml min^{-1}), dechlorination of DDVP is completely suppressed (Fig. 5), because nitrogen molecules cannot react with photoelectrons generated in conducting band (CB) on the TiO_2 surface. Therefore, UV-light and oxygen bubbling at 20 ml min^{-1} were used throughout.

3.2. Effect of adding H_2O_2 on photodegradation of DDVP

Many researchers have shown that the addition of H_2O_2 to the photodegradation process in the presence of semiconductor would increase the efficiency of the process [21–24]. This is because H_2O_2 as an efficient electron acceptor increases the generation of more OH radicals when reacting

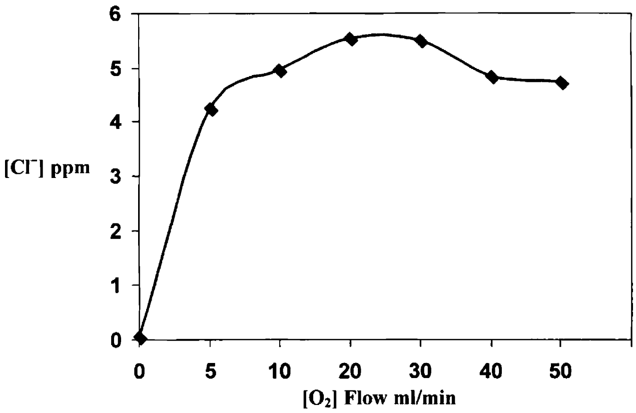


Fig. 4. Formation of Cl^- ion with oxygen flow rate using UV-light at 180 min.

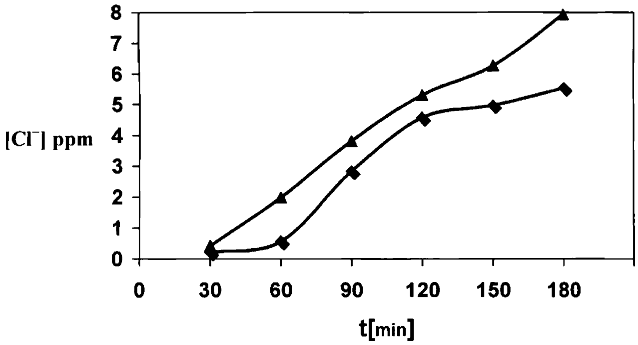


Fig. 6. Formation of Cl^- ion with time of irradiation (▲) in the presence of H_2O_2 and (■) in the absence of H_2O_2.

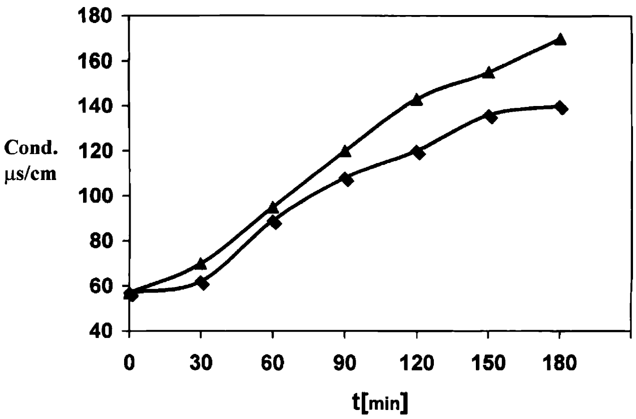


Fig. 7. Change of conductivity of DDVP solution with time of irradiation (▲) in the presence of H_2O_2 and (■) in the absence of H_2O_2.

with conduction band electrons ($H_2O_2+e_{cb} \rightarrow OH^-+OH^{\bullet}$) on the surface of semiconductors, resulting in more destruction of most organic pollutants [22]. Fig. 6 shows a comparison of photodegradation of DDVP (1.25×10^{-4} M) with and without H_2O_2 addition in the presence of TiO_2 (66.6 ppm) and O_2 flowing as a function of irradiation time. A high dechlorination rate is observed, and the percentage of Cl^- ion liberated increased to about 89.4% with H_2O_2 (5×10^{-5} M), compared with 62.4% without H_2O_2 addition during a 3 h irradiation time.

Conductivity of the solution (Fig. 7) also increases 1.5-fold by the addition of H_2O_2. Results show that the pH of irradiated solution (figure not shown) during 3 h decreases markedly. These results are in good agreement with those reported by other workers for photocatalytic degradation of such insecticides [25,26].

3.3. Effect of concentration of TiO_2

Fig. 8 shows the optimum concentration of $TiO_{2\,\mathrm{anatase}}$ which gives a maximum concentration of Cl^- ion at $0.0606\,g\,l^{-1}$ (60.6 ppm) through the photodegradation of DDVP (1.25×10^{-4} M) in the presence of O_2 flowing ($20\,ml\,min^{-1}$) during a 3 h irradiation time. Above this concentration, the light scattering becomes more effective, and this decreases the photo-intensity usually absorbed by TiO_2, thereby decreasing the rate of photodegradation after $0.061\,g\,l^{-1}$ concentration of TiO_2. Our findings are in harmony with those of other researchers who used a semiconductor system for photo-oxidation of such pesticides [13,27–29].

This reaction scheme is far too complicated because of different secondary reactions, as the encounter reaction in liquid is very crude and there are uncertainties due to the "Cage effect" from the different fragments produced and the solvent.

3.4. Effect of mixed semiconductor

A comparative study was carried out using 5% V_xS_y/TiO_2 (60.6 ppm) mixed semiconductor and $TiO_{2\,\mathrm{anatase}}$, ZnO, and $TiO_{2\,\mathrm{rutile}}$ as a single semiconductor. Fig. 9 shows that the percentage of Cl^- ion liberated increases as follows: 5% V_xS_y/TiO_2 (66.8%) > $TiO_{2\,\mathrm{anatase}}$ (62.4%) > ZnO (49.8%) > $TiO_{2\,\mathrm{rutile}}$ (21.7%).

It is worth noting that a high increase in the dechlorination of DDVP using 5% V_xS_y/TiO_2 may be due to the large surface area of this photocatalyst, which leads to an increase in the adsorbed oxygen molecules on its surface and forma-

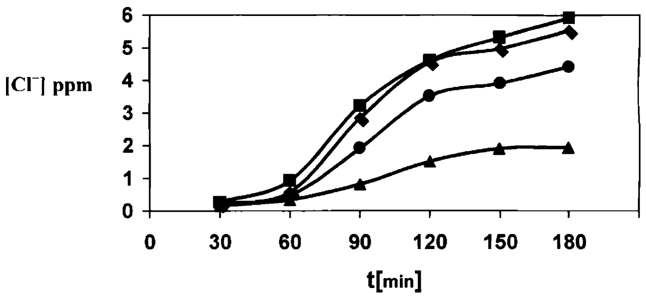


Fig. 9. Formation of Cl^- ion with time of irradiation using UV-light in the presence of (■) 5% V_xS_y/TiO_2 (60.6 ppm), (◆) $TiO_{2\mathrm{anatase}}$ (60.6 ppm), (●) ZnO (394 ppm) and (▲) $TiO_{2\mathrm{rutile}}$ with (60.6 ppm).

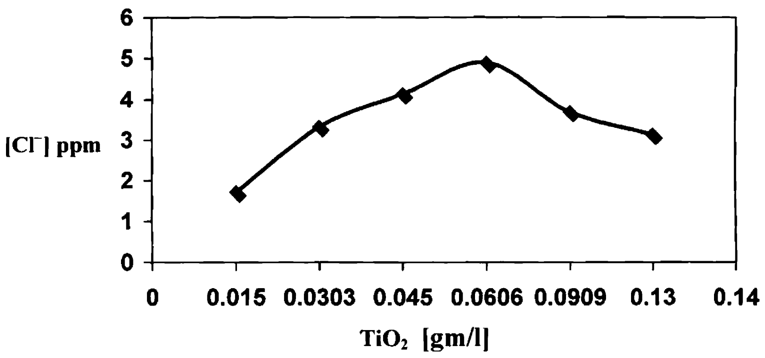


Fig. 8. Change in formation of Cl^- ion with concentration of $TiO_{2\,\mathrm{anatase}}$ using UV-light at 180 min irradiation at room temperature.

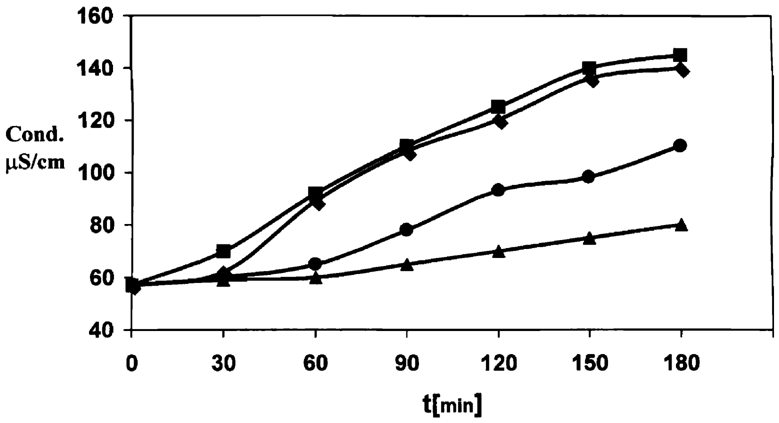


Fig. 10. Change in conductivity of DDVP solution with time using UV-light in the presence of (■) 5% V_xS_y/TiO_2 (60.6 ppm), (◆) $TiO_{2\,anatase}$ (60.6 ppm), (●) ZnO (394 ppm) and (▲) $TiO_{2\,rutile}$ with (60.6 ppm).

tion of more radical ions (O_3^-, O_2^-, O^-) that enhance the photo-oxidative degradation process of the DDVP molecule. Similarly, the conductivity of the solution during a 3 h irradiation also increases (Fig. 10) in the same order, indicating that V_xS_y/TiO_2 is more efficient than the other semiconductors investigated. These results agree well with other works that used different semiconductors (but not V_xS_y/TiO_2) for photocatalytic degradation of polluted molecules [11,18].

3.5. Effect of various sensitizers addition to semiconductors

It is proposed that the photosensitization of semiconductor by various dyes permits the expansion of the wavelength response of the photocatalysts to visible region, thereby enhancing their photocatalytic activity, i.e., increase in the rate of photodegradation of pesticides and other organic compounds [29].

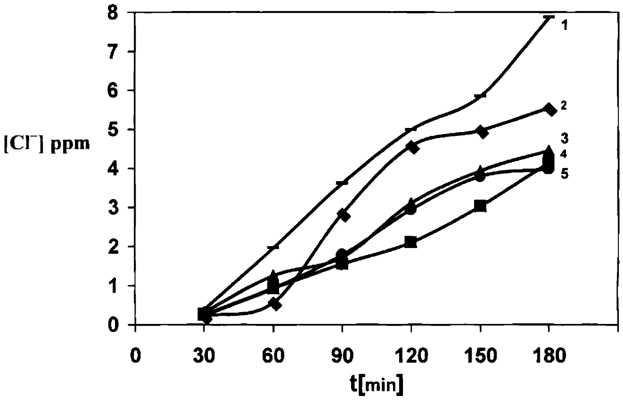


Fig. 11. Formation of Cl^- ion with time of irradiation in the presence of $TiO_{2\,anatase}$, and (—) riboflavine (15 mg), (▲) *p*-aminophenol (2 mg), (◆) hydroquinone (2 mg), (●) *p*-nitrophenol (2 mg) and (■) TiO only.

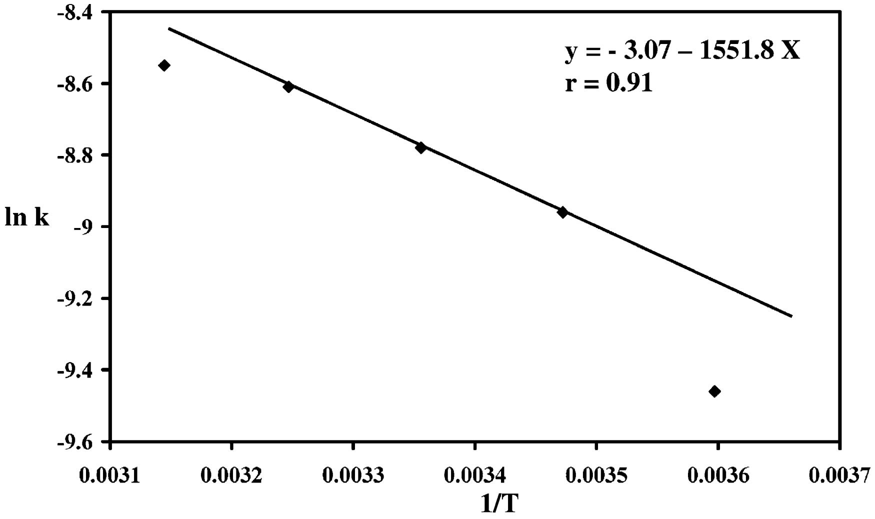


Fig. 12. Arrhenius plot of reaction rate constant versus 1/*T* at 215 nm.

Fig. 11 shows the addition of different sensitizers in the concentration range of 0.015–0.002 g per 35 ml to TiO_2 (60.6 ppm) for the photodegradation of DDVP (1.25×10^{-4} M) in oxygen flowing (20 ml min^{-1}), using an UV-150 W lamp. Results show that only riboflavine with TiO_2 increases markedly by the concentration of Cl^- ion liberated compared to the other sensitizers investigated. This may due to the absorption of new wavelength by riboflavine and TiO_2.

3.6. Photodegradation of DDVP under solar exposure

Photodegradation of DDVP (1.25×10^{-4} M) under sunlight radiation ($I_0 = 1.425 \times 10^{-8}$ einstein l^{-1} s^{-1}) was carried out in the presence of $TiO_{2\,\mathrm{anatase}}$ (60.6 ppm) and oxygen atmosphere (20 ml min^{-1}). After 7 h of solar irradiation, dechlorination of DDVP was low compared with that of UV-illumination, and the of Cl^- ion liberated was found to be 29%, while aqueous suspension of riboflavine sensitized $TiO_{2\,\mathrm{anatase}}$ was 33% (under similar experimental conditions). These values are approximately 2–2.5-fold less than that with UV-irradiation of the two systems. This lower activity is due to the absorption of a small function of solar energy by a combined TiO_2 and sensitizer.

3.7. Effect of temperature on photodegradation of DDVP

Photodegradation reactions for DDVP have been carried out by varying the reaction temperature from 278 to 318 K. Fig. 12 shows the Arrhenius plot between ln k of degradation and $1/T$. The data of activated energy E_a has been calculated from the change of optical density at three

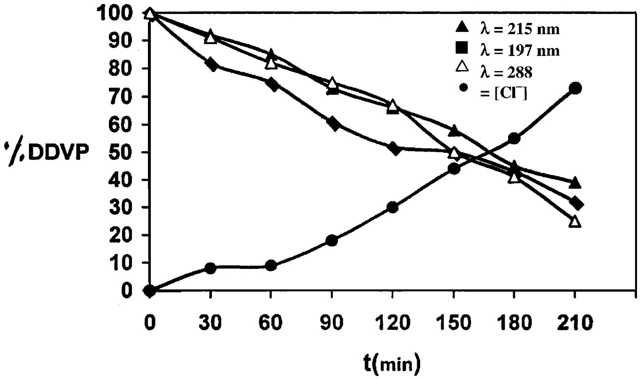


Fig. 13. Destruction of DDVP (1×10^{-4} M) and formation of Cl^- ion with irradiation time in the presence of TiO_2 (66.6 ppm) measured at different wavelengths.

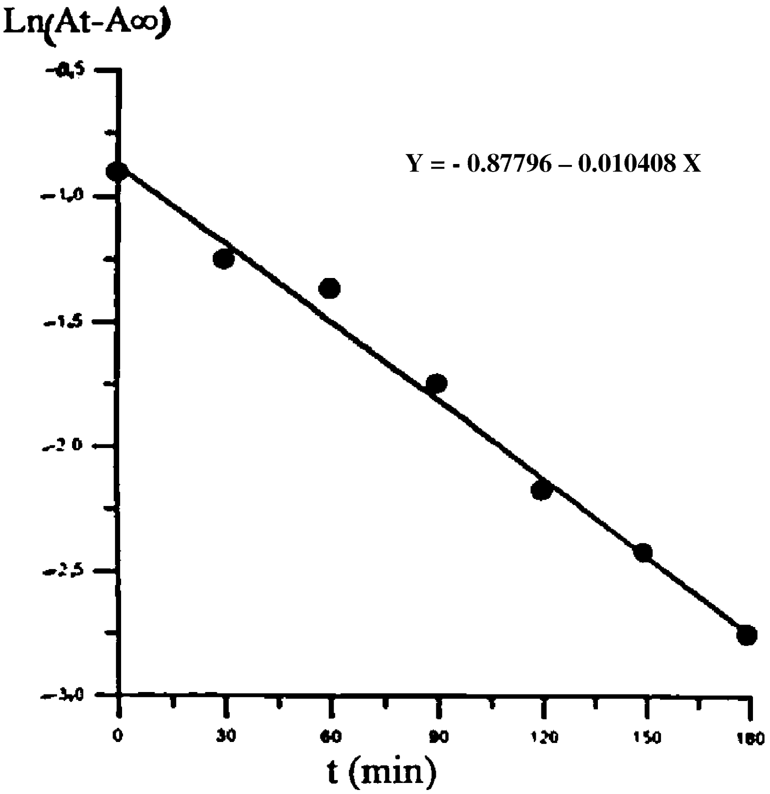


Fig. 14. Plot of $\ln(A_t - A_\infty)$ versus irradiation time. When the initial DDVP concentration is 1×10^{-4} M and TiO_2 loading is 60.6 ppm.

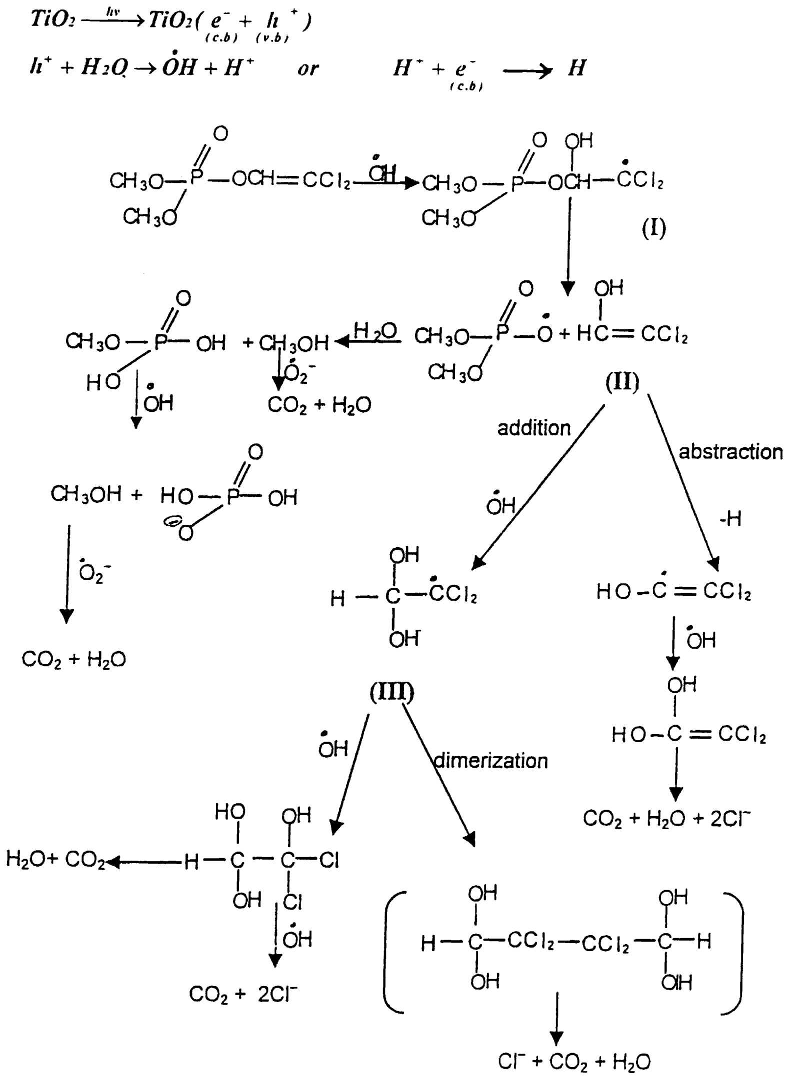
wavelengths 197, 219 and 288 nm as a function of the temperature. We found that the best data at 215 nm with value of $E_a = 12.88$ kJ/mol with less scattered; this reaction may be diffusion controlled and the fragments that are produced have considerable opportunity to react with each other or with the adjacent solvent before they move freely into the bulk of the solution to react with other entities (Cage effect).

Fig. 13 shows the destruction of DDVP measured at different wavelengths by UV–visible spectrophotometry and the formation of Cl^- ion measured by ion-selective electrode for initial concentration of 1×10^{-4} M of DDVP in the presence of TiO_2 and oxygen flowing. About 70% destruction occurred after irradiation for 3.5 h. The half-life ($t_{1/2}$) of this photodegradation process was about 67 min at room temperature.

3.8. Kinetic analysis and mechanism of photoreaction

Fig. 14 shows a straight line when the logarithm absorbance ($A_t - A_\infty$) is plotted versus irradiation time. This indicates a first-order reaction kinetic with specific rate constant of $1.73 \times 10^{-4}\ s^{-1}$. Accordingly, the calculated half-life of the reaction is 3998.8 s.

We can suggest that from the data already obtained and kinetic studies of the photo-oxidative degradation of DDVP in aqueous colloidal suspended of TiO_2 the following mechanism may be proposed:



3.9. Conclusions

Degradation of insecticides in water is very important owing to their accumulation in plant and animal cells. Research is on to find the best and easiest way of degradation of these molecules and soluble ions. Our research group is examining the application of degradation to industrial water. Thus the type of insecticides and the range of concentration in tap water have been studied.

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