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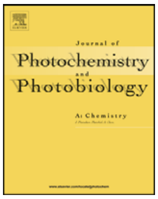

The photocatalytic degradation of dichlorvos under solar irradiation

Petruta Oancea*, Tatiana Oncescu

Department of Physical Chemistry, University of Bucharest, Bd. Regina Elisabeta No. 4-12, 030018 Bucharest, Romania

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ABSTRACT

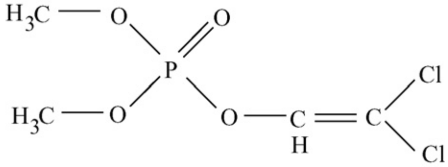
The photocatalytic degradation of the organophosphorous pesticide dichlorvos (DDVP) in suspended TiO_2 was studied under solar irradiation. It is completely oxidized following a pseudo-first-order kinetic with a characteristic half-life time $t_{1/2}$. The mineralization product formation followed the same kinetic order, Cl^- ion being totally released, whereas ${PO_4}^{3-}$ only partially, due to formation of phosphate organic stable intermediates.

Starting from various initial DDVP concentrations we used Langmuir–Hinshelwood equation to calculate K_{ad} the adsorption–desorption equilibrium constant, k_r the rate of the oxidation reaction and $t^*_{1/2}$ the corresponding half-life time. The variation of $t^*_{1/2}$ and $t_{1/2}$ versus DDVP concentration suggests that there is no competition between the parent pollutant and its oxidation byproducts for the $^\bullet OH$ radical consumption. The addition of low concentration of H_2O_2 enhanced the oxidation effect on DDVP degradation.

1. Introduction

Heterogeneous catalysis which involves semiconductors developed in the last 10–15 years due to its potential applications to environmental problems [1–4].

Detoxification of dichlorvos (2,2-dichlorvynil dimethyl phosphate, see structure), a soluble pesticide contaminates the surface and even the ground waters:



A suitable method for the aquatic environment detoxification is the “advanced oxidation process” (AOP) [1,5–7] using photocatalysis in the presence of semiconductors. TiO_2 was studied by many authors, because it is suited to solar irradiation [8–10]. Fig. 1 shows the absorption spectrum of TiO_2 [11] located in UV range 200–400 nm, with an absorption maximum of about 254 nm. The majority UV wavelengths which reach the Earth are situated between 300 and 400 nm (UVA) and are absorbed by TiO_2.

Clearly the degradation of DDVP under solar irradiation in the presence of suspended TiO_2 will need a longer exposure time in comparison to the irradiation with a low-pressure Hg lamp which emits predominantly at $\lambda = 254$ nm. Prolonged irradiation time is not a problem; solar light being an economic energy source and in addition, a non-pollutant. Mak and Hung [12] studied DDVP photocatalytic degradation at pH 4–5 in illuminated TiO_2 suspension by a 450 W Xenon lamp and by solar light. Zhao et al. [13] followed the evolution of the same organophosphorous pesticide using thin films of TiO_2. Naman et al. [14] studied dichlorvos photodegradation under UV irradiation of a Hg lamp and on solar irradiation too. They monitored the dechlorination of DDVP and found a very low efficiency of 2.9% after 7 h exposure to sun ($I_0 = 1.425 \times 10^{-8}$ einstein s^{-1}). But these authors did not offer any analysis of the only one experiment under solar irradiation. Thus we decided to reinvestigate this subject.

Before the presentation of our results it is suitable to remember that by irradiation of a semiconductor with wavelengths of energy $h\nu \geq E_g$ (band gap), an electron e^- is propulsed in the conduction band CB, remaining a positive hole h^+ in the valence band VB; both the electron and the hole migrate towards the particle surface. After the absorption of UV light corresponding to $E_g = 3.2$ eV in the case of TiO_2 (anatase) its start the primary processes [4,15–16]:

$$TiO_2 \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \quad \text{charge separation} \qquad (1)$$

$$h^+_{VB} + H_2O_{ads} \rightarrow {}^\bullet OH_{ads} + H^+_{ads} \qquad (2)$$

$$e^-_{CB} + O_{2ads} \rightarrow O^{\bullet -}_{2ads} \xrightarrow{e^-} O^{\bullet 2-}_{2ads} \qquad (3)$$

in which are generated the oxidative species $^\bullet OH$ and O_2^{-}. These ones are immediately involved in secondary processes in which

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* Corresponding author. Tel.: +40 13143508/2274; fax: +40 13159249.
E-mail address: petrutaoancea73@yahoo.com (P. Oancea).

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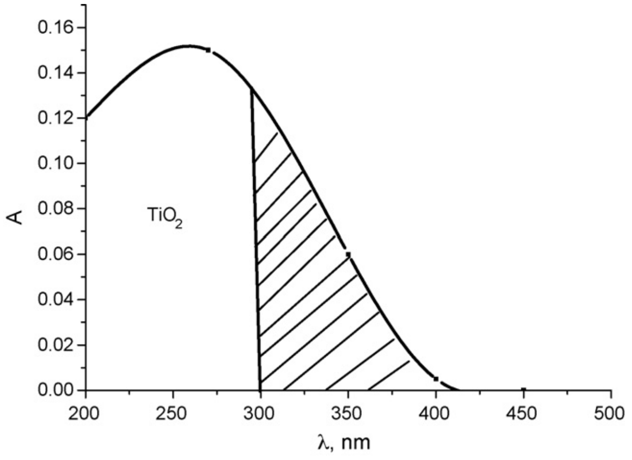

Fig. 1. The absorption spectrum of TiO_2 [11].

the pollutant RH adsorbed on the TiO_2 surface is oxidized:

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad (4)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow\rightarrow\rightarrow CO_2 \quad (5)$$

In acidic solution, the following process takes also place:

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \quad (6)$$

$HO_2^{\cdot}$ being another oxidative species involved in the following processes in which it forms H_2O_2:

$$HO^{\bullet}_{2ads} + H^{+}_{ads} \rightarrow H_2O_{2ads} \quad (7)$$

$$HO^{\bullet}_{2ads} + HO^{\bullet}_{2ads} \rightarrow H_2O_{2ads} \quad (8)$$

$$H_2O_{2ads} + e^{-}_{ads} \rightarrow {}^{\bullet}OH_{ads} + OH^{-}_{ads} \quad (9)$$

$$H_2O_{2ads} + O^{\bullet -}_{2ads} \rightarrow {}^{\bullet}OH_{ads} + OH^{-}_{ads} + O_{2ads} \quad (10)$$

$$H_2O_{2ads} + {}^{\bullet}OH_{ads} \rightarrow HO_2^{\bullet} + H_2O \quad (11)$$

Thus, the presence of H_2O_2 enhanced the effect of the primary $^{\bullet}OH$ radicals.

2. Experimental

2.1. Materials

Substances used:

- Dichlorvos (DDVP) Riedel de Haen, 98% purity, with a density of 1.412 g/mL.
- TiO_2 (anatase) Merck with a specific area of 8–11 m^2/g.
- Malachite green Chemapol, used as colour reagent for $PO_4{}^{3-}$ determination.
- J acid (6-amino-1-naphtol-3-sulphonic acid) Sigma, used for DDVP concentration determination.
- Acetonylacetone Sigma, used for the determination of formaldehyde concentration.
- H_2SO_4 Merck used to adjust the pH to a value of 4 in order to minimize DDVP hydrolysis [17].

2.2. Methods

DDVP samples (20 mL) in aqueous suspensions of TiO_2 (6.02×10^{-5} g/mL) were exposed to solar light. Another set of samples was exposed to an artificial source, the medium pressure Hg lamp of 228 W, filtered for 360–380 nm with a Jena transmission filter. The incident photonic flow was determined in both cases by ferrioxalate actinometry [18]. We found a value of 8.2×10^{-7} einstein s^{-1} for the solar light and of 6.5×10^{-6} enstein s^{-1} for the medium pressure Hg lamp. DDVP degradation was monitored spectrophotometrically using J acid according to Shivare and Gupta [19] measuring the absorbance at $\lambda = 470$ nm. Malachit green was used for $PO_4{}^{3-}$ determination, measuring the absorbance at $\lambda = 600$ nm [20]. The presence of formaldehyde as unstable intermediate was put into evidence by yellow colour of the formed complex with acetonylacetone measuring the absorbance at $\lambda = 412$ nm [21]. For the absorbance measurements Unicam α Helios spectrophotometer was used. The pH of the solution was measured with a Radiometer pH-meter with glass electrode E11M001 and Cl^- ion was determined with a selective chloride electrode ISE25Cl.

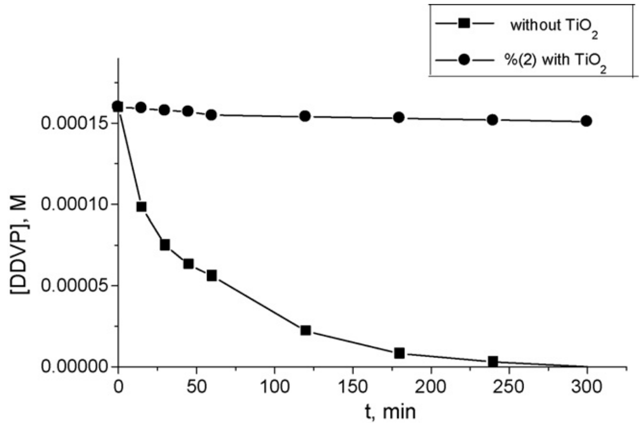

Fig. 2. DDVP degradation in the presence and absence of TiO_2, $[DDVP] = 1.6 \times 10^{-4}$; $[TiO_2] = 6.02 \times 10^{-5}$ g/mL.

3. Results and discussion

We confirmed only *qualitatively* some observations of Mak and Hung [12], the amount of TiO_2 as well as the DDVP concentration being different from ours. In addition they did not calculate any rate constants and did not measure the initial photon flow I_0 of the sunlight so it was not possible to compare quantitatively the two sets of results. Fig. 2 shows the behavior of DDVP under solar irradiation, in the absence and presence of TiO_2, which revealed the contribution of photocatalysis.

DDVP does not absorb in the spectral range 300–400 nm (Fig. 3), therefore its concentration was practically unchanged.

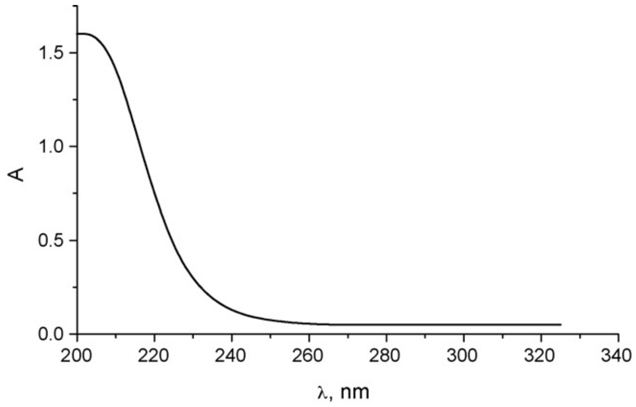

Fig. 3. The absorption spectrum of DDVP (1.6×10^{-4} M); $l = 1$ cm.

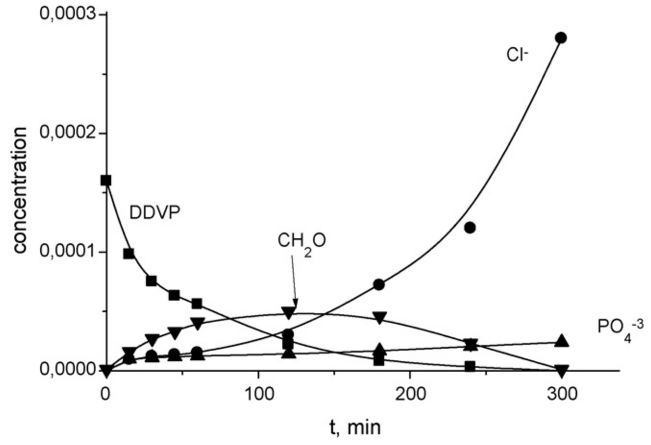

Fig. 4. The kinetic curves of DDVP degradation and Cl^-, PO_4^{3-} release.

This observation is in agreement with Feigenbrugel et al. [22] which determined a molar extinction coefficient ε less than $1\,M^{-1}\,cm^{-1}$ in this spectral range. They determined also ε at $\lambda = 240$ nm and found a value $\sim 20\,M^{-1}cm^{-1}$, near our value (in the limit of the experimental error) measured at $\lambda = 254$ nm and namely $\varepsilon = \sim 24\,M^{-1}\,cm^{-1}$ [23]. In contrast TiO_2 absorbs in this spectral range (see Fig. 1) so that the reactions (1–11) take place on its surface and DDVP is oxidized by $^{\bullet}OH$ radicals.

3.1. Kinetics

In a set of kinetic experiments, samples of DDVP (1.6×10^{-4} M) in aqueous suspended TiO_2 (6.06×10^{-5} g/mL) at pH 4 under solar irradiation, were monitored in respect to the pollutant degradation, as well as the formation of its mineralization products Cl^- and PO_4^{3-} ions, as the kinetic curves shown in Fig. 4.

It indicates that after 300 m exposure to solar light, DDVP is practically degraded, Cl^- ions are released in high proportion (95%) whereas PO_4^{3-} ions are eliminated in proportion of 25%. Therefore, PO_4^{3-} is stoked in phosphate organic compounds which limit the total mineralization of the pollutant. Our experiments evidenced also the formation and disappearance of formaldehyde as an unstable intermediate which of course is oxidized to formic acid, another resistant compound to oxidation as shown in [24]. These kinetic curves (Fig. 4) were linearized by the kinetic equation of the pseudo-first-order reaction in respect to DDVP degradation as well as to the mineralization product formation, exemplified in Fig. 5 for $[DDVP] = 1.6 \times 10^{-4}$ M.

The photocatalytic reaction rate of most organic compound is described by pseudo-first-order kinetics which is rationalized in terms of the Langmuir–Hinshelwood model, modified to accommodate reactions occurring at a solid–liquid interface [25–27].

From the slopes of the linear plots were calculated the pseudo-first-order rate constants $k_{\rm I}$ with the following values: $k_{\rm I}^{\rm DDVP} = 1.35 \times 10^{-2}\,\rm min^{-1}$; $k_{\rm I}^{\rm Cl^-} = 6.96 \times 10^{-3}\,\rm min^{-1}$ and $k_{\rm I}^{\rm PO_4^{-3}} = 4.26 \times 10^{-4}\,\rm min^{-1}$.

In another set of experiments we studied comparatively the photocatalytic degradation of dichlorvos under solar and artificial UV irradiation, TiO_2 and DDVP concentrations being the same as before. Fig. 6 presents the kinetic aspect of DDVP evolution during the irradiation.

Under Hg lamp irradiation, DDVP is completely degraded before 200 m ($k_{\rm I}^{\rm DDVP} = 3.33 \times 10^{-2}\,\rm min^{-1}$), whereas under solar exposure, a prolonged irradiation time is necessary, about 300 m. This result is due mainly to the different initial photon flow of both light sources: 8.2×10^{-7} einstein s^{-1} for the solar incident light and 6.5×10^{-6} einstein s^{-1} for the medium pressure Hg lamp. Of course, if solar rays will be focused on the reaction cell (photoreactor), AOP method applied for water detoxification may be a competitive one, because it does not need any electrical energy consumption.

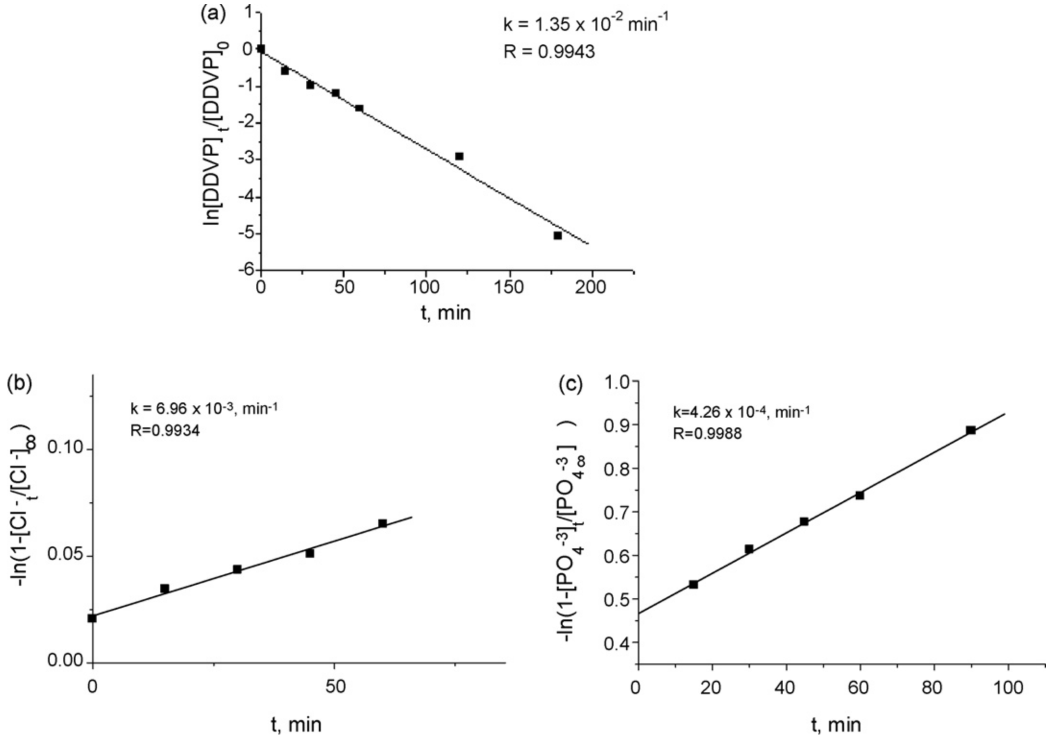

Fig. 5. The pseudo-first-order kinetic of (a) DDVP degradation; (b) Cl^- release and (c) PO_4^{3-} elimination.

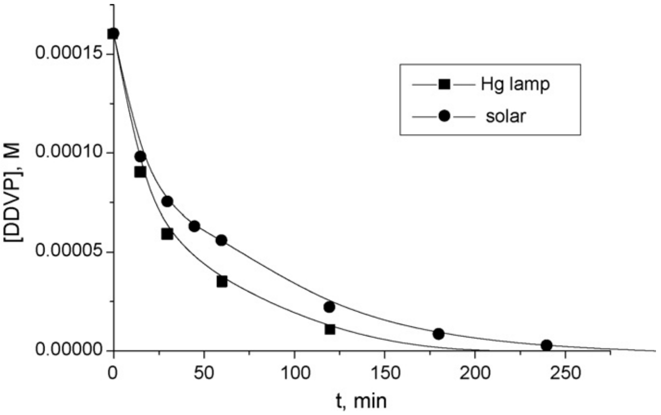

Fig. 6. Comparison between the DDVP degradation by solar and Hg lamp irradiation.

3.2. *The influence of H_2O_2*

In order to facilitate the oxidation of DDVP under solar irradiation we added from the beginning H_2O_2 in the samples, in two different concentrations (see Fig. 7).

Indeed, the presence of H_2O_2 increases the DDVP degradation rate. This result was expected since H_2O_2 is a good electron acceptor generating $^{\bullet}$OH radicals according to Eqs. (9) and (10). Thus, the rate constant k_1^{DDVP} has a double value of $2.64 \times 10^{-2}\,\mathrm{min}^{-1}$ in the presence of H_2O_2 (1.32×10^{-3} M) than that obtained in its absence, namely $1.35 \times 10^{-2}\,\mathrm{min}^{-1}$. Fig. 7 indicates also that at higher H_2O_2 concentration (2.8×10^{-2} M) the degradation rate of DDVP diminishes (over a certain concentration H_2O_2 acts as scavenger of $^{\bullet}$OH radical according to the reaction (11)). In consequence the effect of H_2O_2 on the DDVP oxidation is dependent to the ratio $[H_2O_2]/[P]$, [P] being the pollutant concentration, as also other authors [28] evidenced at the acetone degradation.

3.3. *Langmuir–Hinshelwood equation*

In order to verify if DDVP oxidation in the absence of H_2O_2 is a surface reaction, we tested the Langmuir–Hinshelwood equation [29,30]:

$$r_0 = -\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{k_{\mathrm{r}} K_{\mathrm{ad}} c_0}{1 + K_{\mathrm{ad}} c_0} \tag{12}$$

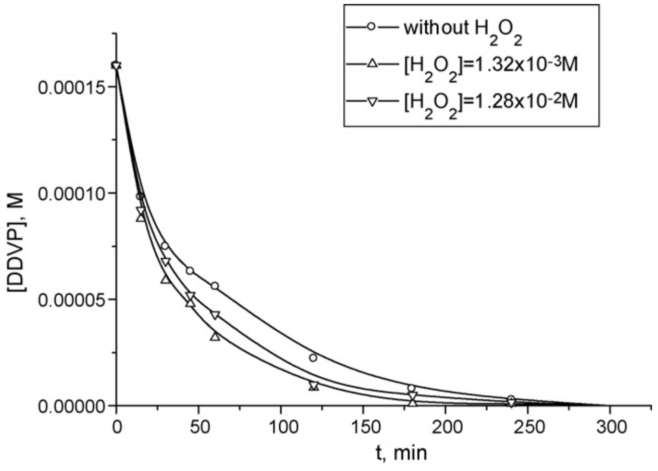

Fig. 7. The degradation of DDVP in the absence and presence of H_2O_2 at two different concentrations under solar irradiation.

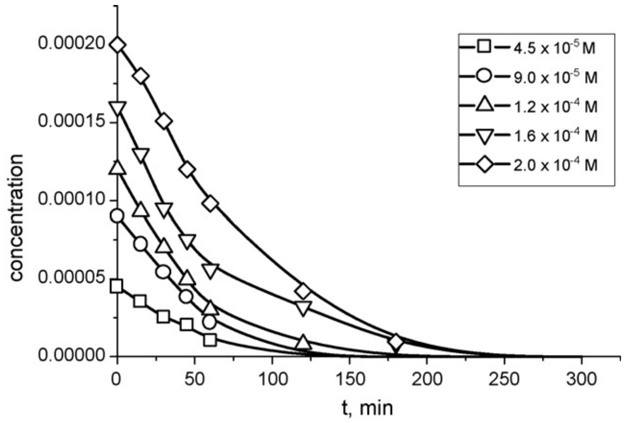

Fig. 8. DDVP photocatalytic degradation at different initial concentration, $[TiO_2] = 6.02 \times 10^{-5}$ g/mL.

in which r_0 is the initial rate of DDVP degradation, c_0 its initial concentration, K_{ad} the equilibrium constant of DDVP adsorption on TiO_2 particles and k_{r} the reaction rate of pollutant oxidation which reflects the limiting reaction rate at maximum coverage for the experimental conditions [1]. In this aim we carried out experiments at five different initial concentrations of DDVP (Fig. 8).

The values r_0 were independently obtained from these curves by the linear fit, using only the experimental points during the first minutes of illumination.

Eq. (12) is linearized by its reciprocal expression (13):

$$\frac{1}{r_0} = \frac{1}{k_{\mathrm{r}}} + \frac{1}{k_{\mathrm{r}} K_{\mathrm{ad}} c_0} \tag{13}$$

With our experimental data we plotted Eq. (13) in Fig. 9.

The linearity obtained attests that the reaction occurs at TiO_2 surface. From the intersection of this straight line with the ordinate results $1/k_{\mathrm{r}}$ and hence the value of the reaction rate $k_{\mathrm{r}} = (1.10 \pm 0.08) \times 10^{-5}\,\mathrm{M\,min}^{-1}$. From the slope of this line we calculated the adsorption equilibrium constant $K_{\mathrm{ad}} = (1.200 \pm 0.011) \times 10^{3}\,\mathrm{M}^{-1}$. Chan et al. [31] integrated Eq. (12) in order to calculate the reaction time t^*:

$$t^* = \frac{1}{k_r K_{\mathrm{ad}}} \ln\frac{c}{c_0} + \frac{1}{k_r}(c_0 - c) \tag{14}$$

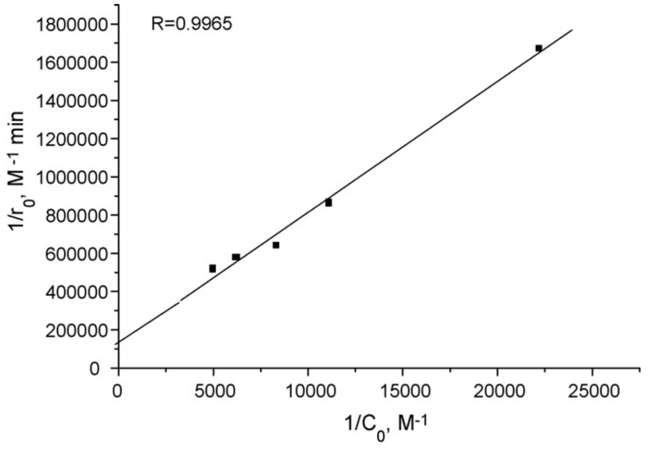

Fig. 9. The linearization of Langmuir–Hinshelwood equation, $[TiO_2] = 6.02 \times 10^{-5}$ g/mL.

Table 1
Pseudo-first-order rate constants k_I, half-live times $t_{1/2}$ and $t^*_{1/2}$ of DDVP photodegradation by solar irradiation at different initial concentrations

[DDVP] ($\times 10^4$ M)	k_I ($\times 10^2$ min^{-1})	$t_{1/2}$ (min)	$t^*_{1/2}$ (min)
0.45	1.91	28.9	50.5
0.9	1.80	36.7	53.4
1.2	1.76	38.5	55.4
1.6	1.35	42.6	58.0
2.0	1.28	52.1	60.6

which under the condition $c = c_0/2$ gives the half-life time $t^*_{1/2}$:

$$t^*_{1/2} = \frac{c_0}{2k_\mathrm{r}} + \frac{\ln 2}{k_\mathrm{r}K_\mathrm{ad}} \tag{15}$$

On the other hand, the half-life time $t_{1/2}$ may be calculated from the value of the pseudo-first-order rate constant $k_\mathrm{I}^\mathrm{DDVP}$ determined from our experiments, as follows:

$$t_{1/2} = \frac{\ln 2}{k_\mathrm{I}^\mathrm{DDVP}} \tag{16}$$

Chan et al. [31] which studied the photodegradation of 2-chlorphenol in suspended TiO_2 under 360 nm illumination and Lu et al. [7] who studied also DDVP degradation but on TiO_2 film (coated the inner wall of the photoreactor) obtained two *diverging* straight lines by plotting $t^*_{1/2}$ and $t_{1/2}$ versus DDVP initial concentration. They concluded that this behavior is due to the competition between the byproducts and the pattern pollutant for the $^\bullet$OH radical consumption, which manifests an inhibitor effect. This is the reason for which in their case, $t_{1/2} > t^*_{1/2}$.

We also calculated $t^*_{1/2}$, $t_{1/2}$, $k_\mathrm{I}^\mathrm{DDVP}$ and found the values summarized in Table 1.

The rate constants k_I were calculated from the slopes of the typical linear plot characteristic to the pseudo-first-order reaction as shown in Fig. 10.

In contrast to [31] and [7], we found that $t^*_{1/2}$ is higher than $t_{1/2}$ (see Table 1) which therefore suggests that the oxidation of DDVP under our experimental conditions occurs faster than predicted Langmuir–Hinshelwood theory, that is, $t_{1/2}$ is shortened. Indeed, the plot of $t^*_{1/2}$ and $t_{1/2}$ versus [DDVP], using the data from Table 1 gives two *convergent* straight-lines as shown in Fig. 11.

The first conclusion was that in our experimental condition (DDVP concentration ranging between 4.5×10^{-5} and 2×10^{-4} M) there is no competition between DDVP and its byproducts. On the other hand we observed that the two straight-lines converge to a point after which, they become divergent as Lu et al. [7] found using DDVP concentrations between 10^{-4} and 10^{-3} M (one order of magnitude higher than ones). In conclusion when $t^*_{1/2} < t_{1/2}$ (their case), the competition manifested as an inhibitor effect, whereas when $t^*_{1/2} < t_{1/2}$ (our case) there is no competition and manifested as a catalytic effect increasing the reaction rate of DDVP oxidation. Of course, when $t^*_{1/2} \approx t_{1/2}$ (intersection point) the reaction rate does not modify. In our experiments at a constant amount of suspended TiO_2 (6.06×10^{-5} g/mL) and under the constant incident solar photon flow of 8.2×10^{-7} einstein s^{-1}, the same quantity of $^\bullet$OH radicals will be constantly generated. If the DDVP initial concentration is lower (as in our case), an adequately small amount of the pollutant will be adsorbed on TiO_2 surface which is fast oxidized by the excess of $^\bullet$OH radicals. Under these circumstances also the byproducts appeared in small quantities on TiO_2 surface will be oxidized without competition. Fig. 11 shows that with the increasing of DDVP concentration the difference between $t^*_{1/2}$ and $t_{1/2}$ shortens because the same amount of $^\bullet$OH radicals is used to oxidize higher quantities of the pollutant and its byproducts. Therefore, at higher DDVP concentration when the two straight lines intersect (in our case 3.3×10^{-4} M), $t_{1/2}$ levels $t^*_{1/2}$ and they become divergent due to competition between the partners. We compared the position of the intersection point from Fig. 11 situated at some higher DDVP concentration that those we used in our experiments, to the intersection point obtained by Lu et al. [7], situated at lower concentration than those used in their experiments. Both points would have to coincide. Unfortunately it is not possible to control quantitatively this affirmation because the experimental conditions are quite different: irradiation source (solar versus artificial) characterized by different incident photon flow I_0 and TiO_2 state (powder versus film).

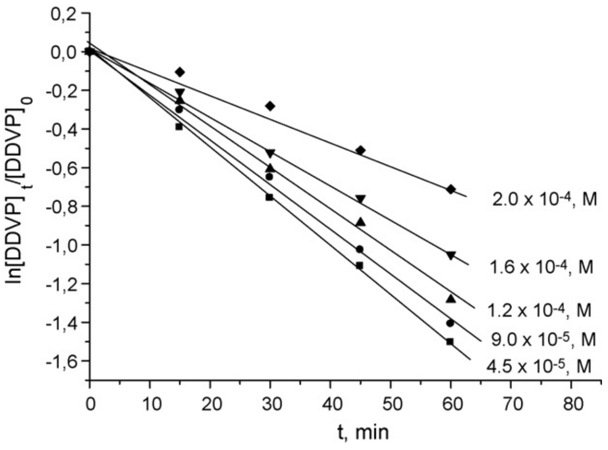

Fig. 10. The pseudo-first-order kinetic of DDVP degradation in different initial concentrations.

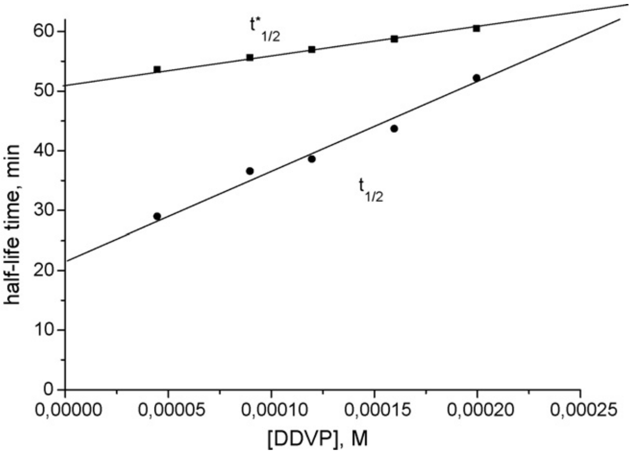

Fig. 11. Half-life profiles of observed and estimated, versus the initial concentration of DDVP.

4. Conclusions

The present paper brings new details regarding the DDVP degradation in aqueous suspended TiO_2 under solar irradiation.

The kinetic measurements refer to DDVP degradation as well as to the formation of its mineralization final products Cl^- and PO_4^{3-} ions. DDVP is completely oxidized and Cl^- ion is totally released in solution, whereas PO_4^{3-} only partially liberated being stocked in phosphate organic compounds as stable intermediate.

It was evidenced the presence of formaldehyde as unstable intermediate.

The experimental data verify the Langmuir–Hinshelwood equation on the assumption of no competitiveness between the pollutant and its byproducts in the reaction with $^{\bullet}$OH radical onto TiO_2 surface. This affirmation is also supported by the behavior of $t^{*}_{1/2}$ and $t_{1/2}$ with the variation of the DDVP initial concentration.

Solar irradiation may be a promising procedure for water detoxification, being an unpollutant and an economic method too.

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