



PHOTOSENSITIZED OXIDATION OF DICHLORVOS BY H₂O₂

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abstract: Dichlorvos (DDVP), is a toxic pesticide which contaminates the surface and even the ground waters. In this paper was studied the photosensitized degradation of dichlorvos (DDVP) in presence of H₂O₂ under UV irradiation. It was established a pseudo-first order kinetics in respect to DDVP degradation, Cl⁻ release and PO₄⁻³ liberation and calculated their rate constants. It was also showed the role of H₂O₂ concentration.

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Introduction

Photochemical methods for removing of the toxic organic pollutants, which have been discharged into the aquatic environment, are being applied in an ever increasing number of cases. Since the late 1960s, many studies have indicated that the UV/H₂O₂ process is able to oxidize a wide variety of organic pollutant in aqueous solutions.

Many studies have been carried out on the UV/H₂O₂ – induced destruction of aromatic pollutants, such as benzene, toluene, chlorobenzene, phenol [1,2], non-halogenated aliphatics [3] and halogenated aliphatic [e.g. trichloroethylene (TCE), perchlorethylene (PCE) [4,5].

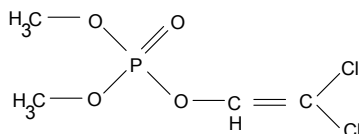
Generally, the effectiveness of homogeneous light-driven oxidation processes is associated with very reactive species, such as hydroxyl •OH radicals, which are generated under irradiation:



But sometime the intermediates are resistant to further oxidation (3) so that the destruction of pollutants doesn't lead to complete mineralization. The hydroxyl radicals attack organic compounds non-selectively with rate constants ranging 10⁶ to 10¹⁰ M⁻¹s⁻¹. Dichlorvos (2,2 dichlorovinyl-*o,o*-dimethyl phosphate) was commercially manufactured in 1961 and it is used for insect control in food storage areas, greenhouses and barns [6]. It is also used for

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controlling parasites and insects in houses, aircraft and outdoor areas (as aerosols, liquid sprays):



In this study, the photolytic degradation of dichlorvos in aqueous solution by advanced oxidation process (AOP) using H_2O_2 has been investigated.

Experimental

In our experiments the following substances were used:

- dichlorvos (DDVP) Riedel de Haen, 98% purity, with a density of 1.412 g/mL
- malachite green Chemapol, used as colour reagent for PO_4^{3-} determination.
- J acid (6-amino-1-naphthol-3-sulphonic acid) Sigma, used for indirect DDVP concentration determination.
- H_2SO_4 Merck used to adjust the *pH* to a value of 4 in order to minimize DDVP hydrolysis [7].

DDVP samples were exposed to low pressure Hg lamp which emitted predominantly $\lambda=254$ nm. The incident photonic flow was determined by ferrioxalate actinometry [8]. We found a value of 1.92×10^{-6} einstein s^{-1} .

DDVP degradation was monitored spectrophotometrically using J acid according to Shivare and Gupta [9] measuring the absorbance at $\lambda=470$ nm.

Malachit green was used as colour reagent for PO_4^{3-} determination, measuring the absorbance at $\lambda=600$ nm [10].

For the absorbance measurements we used an Unicam α Helios spectrophotometer.

The *pH* of the solution was measured at a Radiometer *pH*-meter using a glass electrode E11M001 and Cl^- ion was determined using a selective chloride electrode ISE25Cl.

Results and discussion

Both hydrogen peroxide and dichlorvos are weakly absorbing compounds in the UV range. For example, at $\lambda=254$ nm the molar absorption coefficients are $\epsilon=18.4 \text{ M}^{-1}\text{cm}^{-1}$ [11] and $\epsilon=20 \text{ M}^{-1}\text{cm}^{-1}$ for hydrogen peroxide and dichlorvos, respectively (Fig. 1).

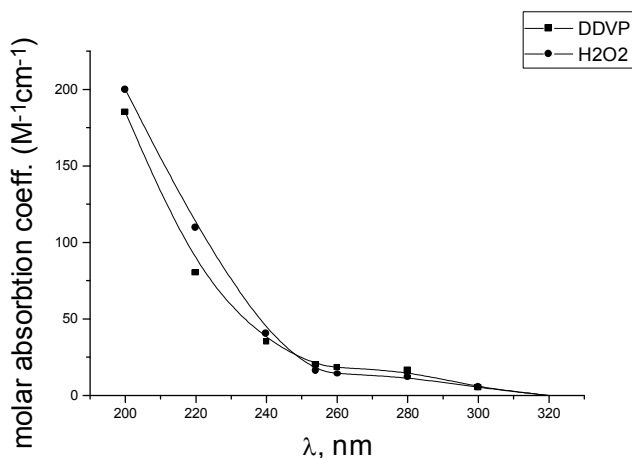


Fig. 1 Spectral distribution of molar absorption coefficients of H₂O₂ and DDVP.

DDVP does not react with H₂O₂ in the dark. Only by irradiation with UV its degradation takes place according to (1) – (3) processes.

A solution of 1.6×10^{-4} M of Dichlorvos at pH=4 was prepared and irradiated with UV light in the presence of H₂O₂. The rate constant of DDVP degradation was monitored by its concentration decreasing. Fig. 2 shows the photochemical behaviour of this solution in which H₂O₂ was present in a concentration of 3.36×10^{-3} M.

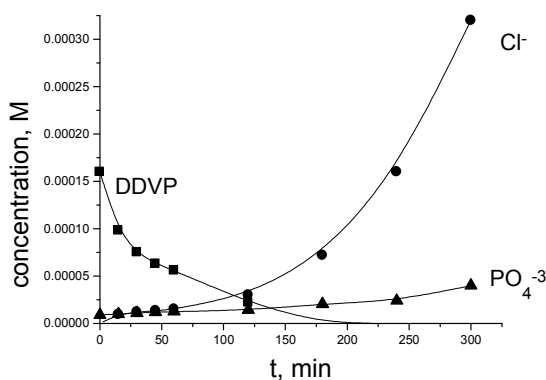


Fig. 2 The kinetic curves of DDVP degradation and Cl⁻, PO₄⁻³ release

It indicates that after 300 minutes exposure to UV light, DDVP is earlier degraded, Cl⁻ ions released in proportion of 100% whereas PO₄⁻³ ions are eliminated only 25%. Therefore PO₄⁻³ is stoked in phosphate organic compounds which limit the total mineralization of the pollutant.

These kinetic curves were linearized by the kinetic equation of the pseudo-first-order reaction in respect to DDVP degradation as well as to the mineralization products formation, exemplified for $[\text{DDVP}]/[\text{H}_2\text{O}_2] = 1/20$ in Fig. 3.

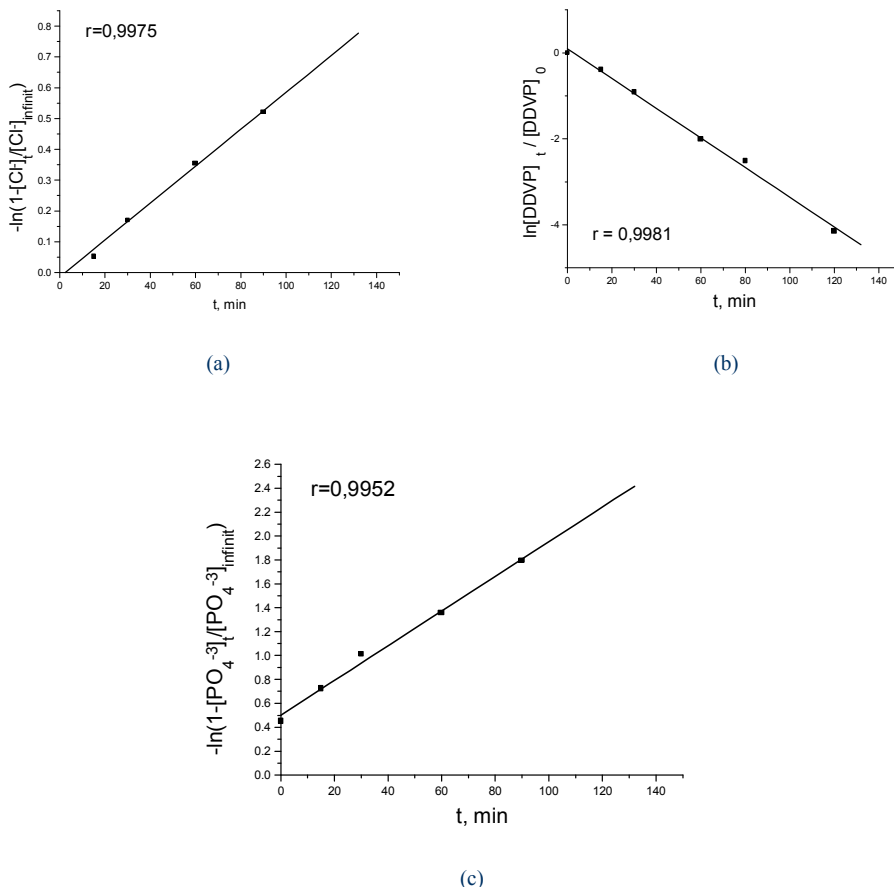


Fig. 3 The pseudo-first-order kinetic in respect to:
a) DDVP degradation b) CF^- ion release and c) PO_4^{3-} ion liberation.

From the slopes of the linear plots were calculated the pseudo-first-order rate constants k_1 with the following values: $k_{\text{DDVP}} = 2.25 \times 10^{-4} \text{ s}^{-1}$; $k_{\text{Cl}^-} = 1.16 \times 10^{-4} \text{ s}^{-1}$; $k_{\text{PO}_4^{3-}} = 7.1 \times 10^{-5} \text{ s}^{-1}$.

The rate constant of dichlorvos degradation sensitized by the UV photolysis of H_2O_2 depends on the hydrogen peroxide concentration. The dependence of the rate constant versus DDVP/hydrogen peroxide concentration ratio is presented in Fig. 4.

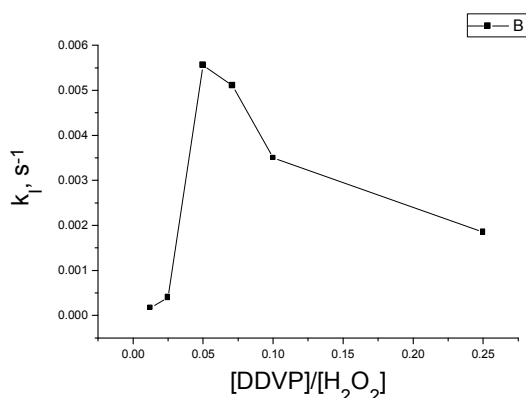
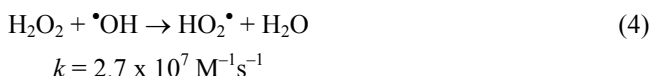


Fig. 4 The rate constant versus $[DDVP]/[H_2O_2]$

The optimum range of this ratio seems to be of about 1:14. At very low concentration, H₂O₂ absorbs only a small fraction of the incident light and the rate constant of dichlorvos is also low. At higher concentrations, H₂O₂ becomes a strong scavenger for •OH radicals:



generating HO₂• radicals which reacts rapidly with the hydroxyl radical according to:



Under such conditions H₂O₂ competes with DDVP for •OH radicals consumption and hence the rate constant of dichlorvos degradation decreases. In consequence the effect of H₂O₂ on the DDVP oxidation is dependent to the ratio $[H_2O_2]/[P]$, [P] being the pollutant concentration, as also other authors [12] evidenced at the acetone degradation.

Conclusion

In this paper was optimized the H₂O₂ concentration for a convenient efficiency of DDVP degradation.

Then kinetic of this degradation was followed experimentally in respect to the pollutant as well as the mineralization products and their pseudo-first order rate constant calculated.

Our results showed that the byproducts resulted from DDVP oxidation did not mineralize totally in solution.

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