

Photocatalytic removal of the herbicide clopyralid from water

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Abstract: The stability of the herbicide clopyralid (3,6-dichloro-2-pyridinecarboxylic acid) was studied under different experimental conditions of pH, illumination and initial substrate concentration. It was found that in the pH interval from 1.0 to 9.0 in the presence/absence of daylight, clopyralid solutions were stable for at least a period of two months. The kinetics of the photocatalytic degradation of clopyralid in aqueous suspensions of TiO₂ (Degussa P25) under UV and visible light, as well as of direct photolysis using the same radiation sources, were also investigated. It was found that the rate of photocatalytic degradation in the presence of UV light was more than five times higher compared to direct photolysis, whereas in the presence of visible light, the corresponding rates of photocatalytic/photolytic degradation were much lower (more than 15 times). The reaction in the investigation concentration range is zero-order with respect to the degradation of the clopyralid pyridine moiety, with a reaction rate of $3.4 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ and an adsorption coefficient of the substrate of $2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$.

Keywords: clopyralid, photocatalytic degradation, TiO₂ Degussa P25, photolysis, water treatment.

INTRODUCTION

Clopyralid (3,6-dichloro-2-pyridinecarboxylic acid, CAS No. 1702-17-6, C₆H₃Cl₂NO₂, $M_r = 192.00 \text{ g mol}^{-1}$) is a systemic herbicide from the chemical class of pyridine compounds, *i.e.*, pesticides of picolinic acid. It was registered by the U. S. Environmental Protection Agency (EPA) for the control of weeds and woody plants in lawns, turf, pastures, rights-of-way and various crops, such as wheat, barley and oats. This substance is absorbed by the leaves and the roots of the weed and moves rapidly through the plant. It affects plant cell respiration and growth. The acidic form of clopyralid¹ and especially three clopyralid salts, *i.e.*, triethylamine, triisopropylamine and monoethanolamine, are very soluble in wa-

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ter and very mobile in soil, thus having the potential to leach to ground water and contaminate surface water.² Clopyralid is formulated in the form of concentrated solutions. In Serbia it is commercially available as Lontrel 100, Pikogal, Piralid 100 and Hemoklop 100-SL, which contain 100 g dm⁻³ of clopyralid. It is also sold in combination with other herbicides, such as triclopyr, (4-chloro-2-methylphenoxy)acetic acid (MCPA) and (2,4-dichlorophenoxy)acetic acid (2,4-D).³ Clopyralid is by its structure and mode of action similar to the herbicide picloram.³

Efficiency is certainly a very important characteristic of pesticides but their degradability is equally, if not more, important because of their potential to contaminate water courses. For this reason, special attention has recently been paid to the degradation of pesticides as a means of water decontamination. A promising way to perform the mineralization of this type of substance is the application of an advanced oxidation process (AOP). Heterogeneous photocatalysis with titanium dioxide as a semiconductor is one of the most popular treatment technologies for eliminating a number of pesticides from water based on AOPs, as can be seen from the large amount of information available in the literature.^{4–10} Continuing on previously initiated investigations of the kinetics and mechanism of photocatalytic degradation of compounds which in their structures contain chlorinated pyridine moiety, such as 3-amino-2-chloropyridine and 2-amino-5-chloropyridine^{11–13} as model compounds for pyridine containing pesticides, the aim of this work was to study the kinetics of the photocatalytic degradation of the herbicide clopyralid from the mentioned group of compounds. The kinetics of photocatalytic degradation under UV light was compared to that of direct photolysis, as well as to the kinetics under visible irradiation in the presence and absence of TiO₂. The effect of the initial concentration of pesticide was also investigated.

EXPERIMENTAL

Chemicals and solutions

All chemicals used in the investigation were of reagent grade and were used without further purification. Clopyralid, 99.4 %, PESTANAL[®], analytical standard, was purchased from Riedel-de Haën. Britton–Robinson (BR) buffers were prepared using hydrochloric acid, 35 %, p.a., and phosphoric acid, 85 %, p.a., both purchased from Lachema, Neratovice; acetic acid, 99.5 %, p.a., from Polskie Odczynniki Chemiczne S. A., Gliwice; boric acid, 99.8 %, p. a., from Kemika, Zagreb; while sodium hydroxide, p.a., was purchased from ZorkaPharm, Šabac. All solutions were made using doubly distilled water. Acetonitrile, 99.8 % (J. T. Baker, Deventer) was used as a component of the mobile phase for HPLC analyses.

Stock solutions with 1.0 and 3.0 mol m⁻³ of clopyralid were prepared and protected from the sunlight. For the investigations of the influence of pH on the kinetics of photodegradation, 0.10 mol m⁻³ solutions of clopyralid were prepared by measuring 5.00 cm³ of 1.0 mol m⁻³ stock solution into 50.00 cm³ volumetric flasks. Then, 25.0 cm³ of BR buffer of appropriate pH were added to each flask and the solutions were made up to mark with doubly distilled water. For the investigation of the effect of the initial clopyralid concentration, stock solutions were further diluted to prepare lower concentration solutions. Standard solutions for the construction of the calibration curves (3.1×10⁻³–5.0×10⁻² mol m⁻³) for spectrophotometric and HPLC determinations were prepared by measuring the necessary volumes of stock solutions into 10.00 cm³ volumetric flasks.

Degussa P25 TiO₂ (75 % anatase and 25 % rutile form, 50±15 m² g⁻¹, about 20 nm, non-porous) was used as the photocatalyst.

Photodegradation procedure

For the investigation of the stability of clopyralid solutions at various pH values, experiments were performed at 25±2 °C, either exposed to daylight or in the dark during the spring months of 2007.

The photocatalytic reaction was carried out in a cell (sample volume 20.0 cm³, continuously flushed with O₂) made of Pyrex glass, with a plain window on which the light beam was focused, equipped with a magnetic stirring bar and a water circulating jacket. Aqueous suspensions of TiO₂ Degussa P25, containing 1.0 mol m⁻³ herbicide (except for the study of the effect of initial substrate concentration), were sonicated for 15 min before illumination, to make the particles of the photocatalyst uniform. The thus obtained suspension was thermostated at 40±1 °C in a stream of O₂ and then irradiated. Irradiation in the UV range was performed using a 125-W medium-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm), with an appropriate concave mirror. Irradiation in the visible range was performed using a 50-W halogen lamp (Philips) and a 400-nm cut-off filter. During irradiation, the mixture was stirred at a constant speed. All the experiments in the presence of photocatalyst were carried out using 2 mg cm⁻³ TiO₂.

Direct photolysis experiments were performed under the same conditions, but without catalyst addition.

Analytical procedure

For the spectrophotometric determination of the effect of pH on the stability of the clopyralid solutions under daylight and in the dark, 5.00 cm³ aliquots of the samples were taken and diluted to 10.00 cm³ with doubly distilled water. For the blank, 2.0 cm³ aliquots of BR buffer of the appropriate pH value were taken and diluted to 10.00 cm³ with doubly distilled water.

For the spectrophotometric monitoring of the degradation of the substrate, aliquots of 0.50 cm³ of the reaction mixture were taken at regular time intervals, then 5.0 cm³ of 0.1 mol dm⁻³ HCl were added, and the solution diluted to 10.00 cm³ with doubly distilled water. The suspensions containing the photocatalyst were filtered through Millipore (Milex-GV, 0.22 µm) membrane filters and the spectra were recorded in the wavelength region from 200 to 400 nm on a Secomam Anthelie Advanced 2 spectrophotometer in 1 cm quartz cells. The kinetics of the degradation of the pyridine moiety was monitored at 225 nm.

For the HPLC determinations, the samples were prepared in the same way as for the spectrophotometric measurements. After that, 20 µl of the sample were injected and analyzed on an Agilent Technologies 1100 Series liquid chromatograph, with a UV/VIS DAD set at 225 nm and with an Eclips XDB-C18 column (150 mm×4.6 mm, particle size 5 µm). The mobile phase (flow rate 1.0 cm³ min⁻¹) was a mixture of acetonitrile and water acidified with 0.1 % phosphoric acid (3:7, v/v). For the 3D HPLC measurements of the potentially formed intermediates, 1.00 cm³ aliquots of the reaction mixture were taken at regular time intervals without subsequent dilution.

RESULTS AND DISCUSSION

Since it was to be expected that the degradation of clopyralid would be accompanied by changes in pH, because of both the disappearance of clopyralid (p*K* 2.0)¹ and the formation of hydrochloric acid and, presumably, nitrate/ammonium (due to the presence of chlorine and nitrogen in the molecule), it was also necessary to investigate the effect of pH on the spectral pattern (Fig. 1). As can be seen, in the investigated pH range, certain changes in the shape of the spec-

trum occurred, and a spectrum with a well defined maximum at 225 nm was obtained at pH 1.0. Hence, this pH value was adjusted in the spectrophotometric monitoring of the kinetics of clopyralid photodegradation.

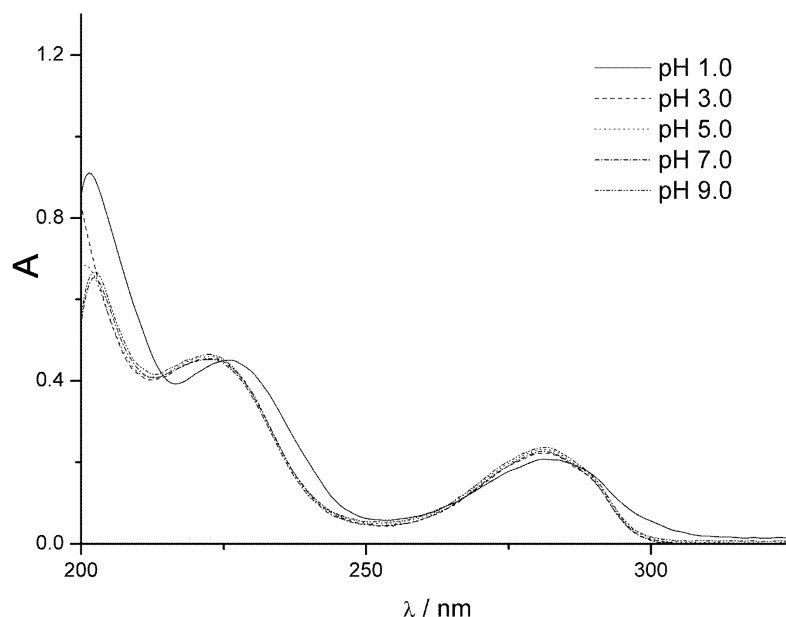


Fig. 1. The influence of pH on the shape of the absorption spectra of a $5 \times 10^{-2} \text{ mol m}^{-3}$ clopyralid solution.

To investigate the stability of clopyralid solution (0.10 mol m^{-3}) experiments were performed in the presence and absence of daylight in the pH interval 1.0–9.0 during the spring months of 2007. On the basis of the obtained results, it can be concluded that in none of the cases did degradation of the substrate occur in the period of two months, which indicates its stability under the given experimental conditions. This is an indicator of the even greater importance of studying the efficiency of the process of the photocatalytic degradation of clopyralid.

As can be seen from Fig. 1, the optimal wavelength for monitoring the kinetic of the photocatalytic degradation of clopyralid by the HPLC method was 225 nm. It was found that the peak with a retention time (t_r) at 3.2 min, corresponding to clopyralid, had disappeared completely after 240 minutes of illumination, indicating that in this period complete degradation of the parent compound had occurred (Fig. 2, curve 2). On the basis of these measurements, it was found that the reaction is of zero-order with $k_a = 4.61 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ (linear regression coefficient, $r = 0.997$). The kinetic curve obtained by the spectrophotometric monitoring of the photocatalytic degradation of clopyralid is shown in Fig. 2 (curve 1). The difference in the presented kinetic curves, *i.e.*, the lower rate

of degradation of clopyralid obtained by spectrophotometric monitoring ($k_a = 4.11 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$; $r = 0.998$), suggests the presence of intermediates with a pyridine moiety, which absorbs at the same wavelength as the substrate. The small difference in the kinetic curves indicates a low concentration of the intermediates.

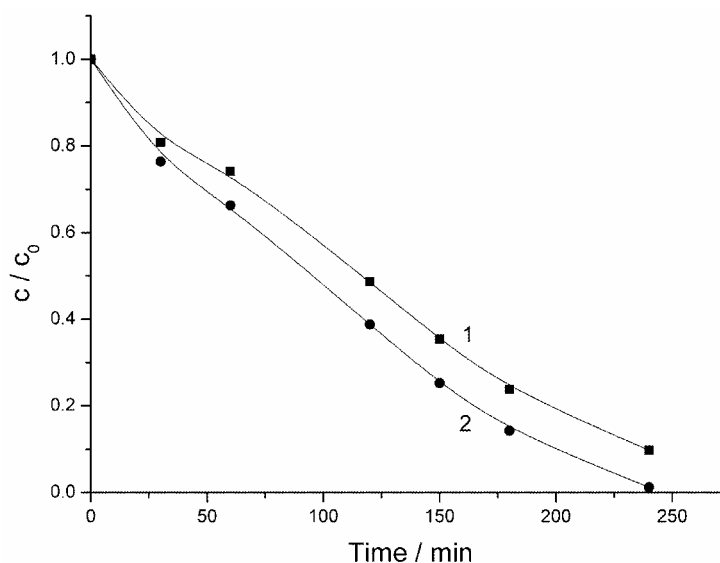


Fig. 2. Kinetics of the photocatalytic degradation of clopyralid (1.0 mol m^{-3}) in the presence of TiO_2 (2 mg cm^{-3}) under UV light: (1) spectrophotometry ($\lambda = 225 \text{ nm}$); (2); HPLC ($\lambda = 225 \text{ nm}$).

Since the concentration of intermediates during photodegradation was low, 3D chromatograms were recorded for aliquots of the reaction mixture without dilution. A 3D chromatogram taken after 180 min of irradiation is presented in Fig. 3, from which the presence of intermediates is visible. Similar chromatograms were also obtained for shorter irradiation times. On the basis of the spectra of the intermediates it can be supposed with great certainty that pyridine derivatives are in question. The formation of such a small number of these intermediates at low concentrations is a good indicator of the efficiency of the heterogeneous photocatalysis in the destruction of clopyralid.

To explore the photocatalytic activity of TiO_2 in the UV light region (Fig. 4, curve 4), the kinetics of degradation of clopyralid under UV light was compared to that under visible light (Fig. 4, curve 2). It can be said that the rate of clopyralid degradation in the former case was about 30 times higher (Table I).

To investigate the photodegradation efficiency of the catalyst, experiments were also performed under conditions of direct photolysis without TiO_2 using artificial UV radiation (Fig. 4, curve 3) and visible (Fig. 4, curve 1) light. The results of these experiments show that in this case too, clopyralid degradation occurred under UV irradiation, although at a significantly lower rate, *i.e.*, about five

times slower compared to photocatalytic degradation (Table I). Under the conditions of visible light, photolysis of the substrate was much slower. Therefore, the slower processes observed in both cases indicate that direct photolysis does not play a significant role in the overall photocatalytic degradation.

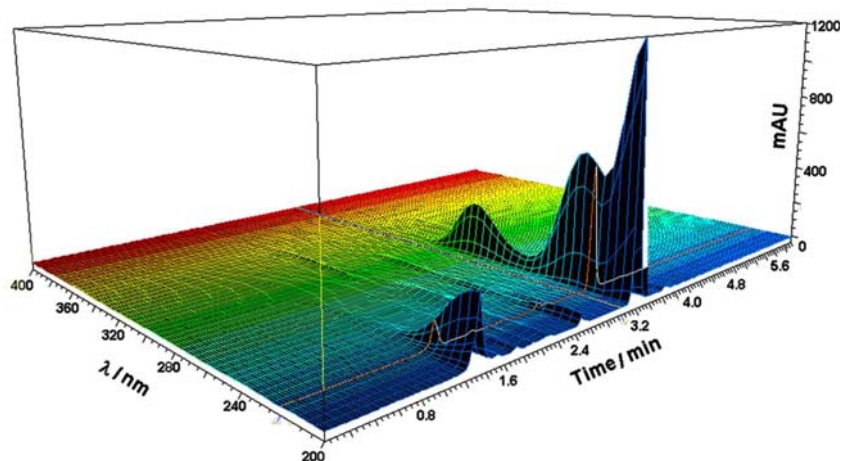


Fig. 3. The 3D chromatogram obtained after 180 min of photocatalytic degradation of clopyralid (1.0 mol m^{-3}) in the presence of TiO_2 (2 mg cm^{-3}) under UV light.

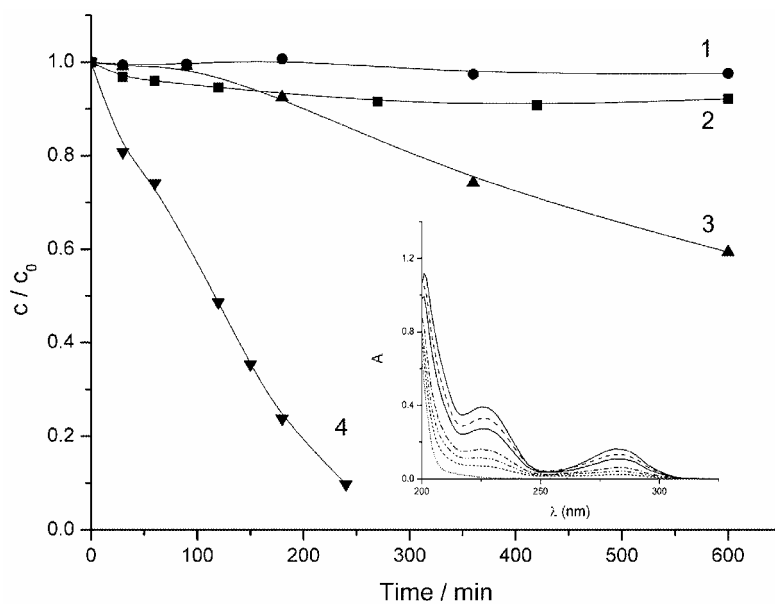


Fig. 4. Kinetic curves for the degradation of the pyridine moiety of clopyralid (1.0 mol m^{-3}) monitored by spectrophotometry: (1) direct photolysis, visible light; (2) TiO_2 (2 mg cm^{-3}), visible light; (3) direct photolysis, UV light; (4) TiO_2 (2 mg cm^{-3}), UV light. Insert represents the profiles of the UV spectrum during the photocatalytic degradation of clopyralid in the presence of TiO_2 under UV light.

TABLE I. Effect of various light sources on the degradation rate, R , of the pyridine moiety of clopyralid^a

	$R \times 10^6 / \text{mol dm}^{-3} \text{min}^{-1}$	
	Mercury lamp	Halogen lamp
TiO ₂ Degussa P25	3.76 ^b	0.13
Direct photolysis	0.68	0.04

^aDegradation rate calculated for time period of 600 min, except ^b240 min

On comparing the obtained results with those obtained in a study of the efficiency of the photocatalytic degradation of mecoprop¹⁴ under visible light, it can be concluded that the efficiency of clopyralid degradation is significantly lower. Namely, the efficiency of photocatalytic degradation of mecoprop under visible light was practically the same as in the direct photolysis by UV light, whereas with clopyralid, as already mentioned, the difference is very large (about five times, Fig. 4, curves 2 and 3). This confirms the supposition that the efficiency of TiO₂ as a photocatalyst under artificial visible light depends to a great extent of the type of substrate.¹⁵

The effect of the initial substrate concentration on the reaction kinetics was investigated in the concentration range 0.5–3.0 mol m⁻³ (Fig. 5). It was found that the substrate concentration decreased linearly with irradiation time, *i.e.*, the reaction was of zero-order (Table II), which is in agreement with the Langmuir–Hinshelwood (L–H) kinetic model.^{16,17} Since the rate of photodegradation in the irradiated suspensions could be satisfactorily described by formal zero-order kinetics (the linear correlation coefficients varied in the range of 0.997–0.999, Table II), the kinetic behavior of clopyralid was subsequently characterized by the initial decomposition rates obtained by linear regression fits (by the least squares method with simple weighting) to the curves $c(\text{substrate})$ vs. $t(\text{irradiation})$. The slopes of these plots were used to calculate the k_a values (the apparent zero-order reaction rate constant). It is worthy of mention that a significant deviation from linearity was found only for high conversions (>80 %).

On the basis of the L–H kinetic model¹⁷ transformed to Eq. (1):

$$t_{1/2} = \frac{0.693}{k_r K} + \frac{0.5c_0}{k_r} \quad (1)$$

where k_r is the reaction rate constant and K is the equilibrium adsorption constant of the substrate, a linear dependence ($r = 0.986$) of the half-life, $t_{1/2}$, against the initial substrate concentration, presented in the insert of Fig. 5, is obtained. The value for k_r determined from the line slope was $3.4 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ and for K from the intercept $2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$.

By comparing the results obtained for the photocatalytic degradation of clopyralid with those of the degradation of 3-amino-2-chloropyridine and 2-amino-5-chloropyridine,^{11–13} as model compounds for pyridine-containing pesticides,

it can be concluded that there is a significant difference between them. Namely, the rate of photocatalytic degradation of the pyridine moiety of clopyralid is about two times slower. This difference in the degradation rate is probably a consequence of the different substituents on the pyridine moiety, which influence the kinetics of photocatalytic degradation.

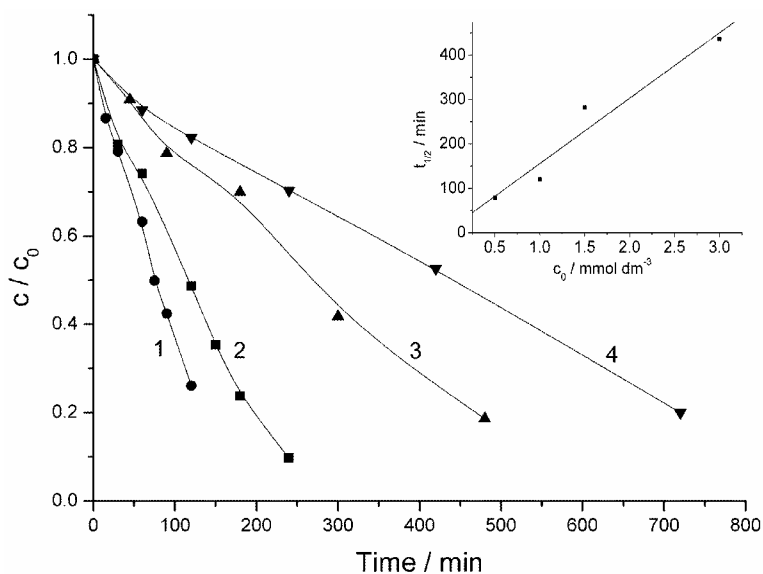


Fig. 5. Effect of the initial clopyralid concentration on its degradation in the presence of TiO_2 (2 mg cm^{-3}) under UV light: (1) 0.5; (2) 1.0; (3) 1.5; (4) 3.0. The inset represents the plot of $t_{1/2}$ against the initial clopyralid concentration.

TABLE II. Effect of the initial concentration, c_0 , of clopyralid on the rate of photocatalytic degradation of the pyridine moiety with UV light

$c_0 / \text{mol m}^{-3}$	$k_a \times 10^6 / \text{mol dm}^{-3} \text{ min}^{-1a}$	r	$t_{1/2} / \text{min}$
0.5	3.04	0.999	78.6
1.0	4.11	0.998	120
1.5	2.55	0.997	282
3.0	3.21	0.999	436

^aapparent zero-order rate constant

CONCLUSION

In the presence/absence of daylight at pH 1.0–9.0, clopyralid is stable for at least two months. The rate of photocatalytic degradation of clopyralid under UV light is about 30 times higher than that under visible light. A comparison of the results of the photocatalytic degradation of clopyralid in the presence of TiO_2 with those of direct photolysis obtained under the same irradiation with UV light shows that the substrate decomposition by direct photolysis is considerably slo-

wer (about five times). It was also found that the kinetics of the degradation of the parent substrate are of zero-order, with $k_a = 4.61 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ ($r = 0.997$). In the investigated concentration range, the reaction is of zero-order with respect to the degradation of the pyridine moiety clopyralid, with a reaction rate constant of $3.4 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ and adsorption coefficient of the substrate of $2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$.

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ИЗВОД

ФОТОКАТАЛИТИЧКО УКЛАЊАЊЕ ХЕРБИЦИДА КЛОПИРАЛИДА ИЗ ВОДЕ

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Испитана је стабилност хербицида клопиралида (3,6-дихлор-2-пиридинкарбоксилна киселина) при различитим експерименталним условима. При проучавању утицаја рН у интервалу од 1,0 до 9,0 у присуству и одсуству дневне светлости нађено је да је раствор клопиралида стабилан најмање у периоду од два месеца. Испитана је и кинетика фотокаталитичке разградње клопиралида у воденим суспензијама TiO₂ (Degussa P25) уз озрачивање UV и видљивом светлошћу, као и директне фотолизе применом истих извора зрачења. Нађено је да је брзина фотокаталитичке разградње у присуству UV светлости преко пет пута већа у поређењу са директном фотолизом, као и да је применом видљивог зрачења брзина разградње у оба случаја знатно нижа (преко 15 пута). При испитивању утицаја почетне концентрације клопиралида на брзину фоторазградње пиридинског прстена, нађено је да је реакција нултог реда са константом брзине од $3,4 \times 10^{-6} \text{ mol dm}^{-3} \text{ min}^{-1}$ и коефицијентом адсорпције супстрата $2,5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$.

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