KINETICS OF PHOTOCATALYTIC REMOVAL OF 2-AMINO-5-CHLOROPYRIDINE FROM WATER

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Titanium dioxide sensitized photocatalytic degradation of a pyridine pesticide analogue, 2-amino-5-chloropyridine, was investigated by monitoring the pyridine moiety degradation, as well as by monitoring the chloride generated in the process. Effect of the initial substrate concentration on the rate of its degradation is reported. Here we show that the kinetics of both reactions are of the zero-order in the entire investigated concentration range. The Langmuir-Hinshelwood kinetic model successfully described the influence of the initial substrate concentration on the rate of the pyridine moiety degradation. It was found that dechlorination of the substrate takes place by direct photolysis. The differences in the kinetics of pyridine moiety degradation and dechlorination were explained on the basis of the electrostatic potential for the investigated compound.

INTRODUCTION

Pollution of waterstreams by different organic pollutants, among which pesticides are very common, represents a serious environmental problem. Several conventional methods of water treatment exist, and as such have found certain practical applications. They are, however, either slow or non-destructive for some more persistent organic pollutants. Advanced oxidation processes have emerged in the past years as an efficient method for degradation of organic pollutants. Among these processes, photocatalytic degradation with titanium dioxide as catalyst and ultraviolet (UV) illumination has proven to be an efficient method for mineralization of organic compounds (1-6), and as such can be deemed suitable for treatment of water and wastewater. Namely, during this process, organic carbon and hydrogen are transformed to carbon dioxide and water, while covalently bound halo-

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gens, nitrogen, sulphur and phosphorus are transformed to halides, ammonium/nitrite/nitrate, sulphate and phosphate, respectively. It is also important to point out the biological and chemical inertness, non-toxicity and low cost of titanium dioxide, which make it a good choice of semiconductor in heterogeneous photocatalysis. Most frequently used type of titanium dioxide to these purposes is Degussa P25, which was used as photocatalyst in this work, too.

When TiO_2 is illuminated by UV radiation, formation of electron–hole pairs occurs (Eq. 1) (7):

$$TiO_2 \xrightarrow{\quad h\nu \quad} TiO_2\ (e^- + h^+) \qquad\qquad [1]$$
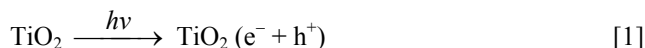
Although a number of possible decomposition pathways can be envisioned, in the reaction between photogenerated holes, water molecules and hydroxyl ions adsorbed on the TiO_2 surface, formation of hydroxyl radicals (Eq. 2), a strong oxidizing agent ($E = +2.8$ V), capable of mineralizing organic compounds, is generally accepted as predominant in oxygenated aqueous solutions.

$$2h^+ + H_2O\ (ads.) + OH^-\ (ads.) \rightarrow 2\ OH^\bullet\ (ads.) + H^+ \qquad\qquad [2]$$
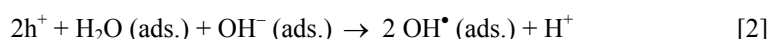
To prevent the electron–hole recombination, it is necessary for the illumination to take place in the presence of an electron acceptor. For this purpose, illumination is most often carried out in an oxygen stream.

Several pesticides contain in their structure the pyridine moiety and chlorine (8). Since their photodegradation, to the best of our knowledge, has not been studied in detail, in this work, the kinetics of photocatalytic degradation of an analogue of the pyridine pesticides, 2-amino-5-chloropyridine, were studied by spectrophotometry and potentiometry. The effect of initial pollutant concentration was studied as well, by applying both methods. From the obtained results Langmuir-Hinshelwood parameters were calculated.

EXPERIMENTAL

Chemicals and solutions

All chemicals used in the investigation were reagent grade and were used without further purification. 2-amino-5-chloropyridine was purchased from Merck. TiO_2 used as photocatalyst was Degussa P25 (predominantly anatase, 50 $m^2\ g^{-1}$, non-porous). In all experiments doubly distilled water was used.

For the investigation of the effect of the initial substrate concentration on the rate of degradation, a stock solution of the substrate ($c \sim 2.5$ mmol dm^{-3}) was prepared, which was further appropriately diluted to prepare solutions of lower concentration.

Photodegradation procedure

For the irradiation experiments, 20.0 cm^3 of the investigated compound solution were measured into a double-walled photochemical cell made of Pyrex glass with a plain window

(on which the light beam was focused), equipped with a magnetic stirring bar. Then 40 mg of TiO$_2$ were added, the suspension was sonicated for 15 minutes before illumination, to make the particles uniform and then thermostated at 40.0 ± 0.5°C in a stream of oxygen. A 125 W Phillips HPL-N mercury lamp, with the highest emission intensity in the UV region at 365 nm, was used as the irradiation source. During irradiation, the mixture was stirred at a constant speed.

Analytical procedure

For spectrophotometric determinations during degradation of the investigated compound in the presence of TiO$_2$, as well as for direct photolysis experiments, aliquots of 0.2 cm^3 of the reaction mixture were taken at regular time intervals and diluted to 10 cm^3 with doubly distilled water. For photocatalytic degradation experiments, the solutions were filtered through membrane filters (Millex-GV, 0.22 μm), to separate the TiO$_2$ particles, and their spectra were recorded on a spectrophotometer (Secomam Anthelie Advanced 2) in the wavelength range from 200 to 400 nm. Spectra of the solutions obtained from direct photolysis experiments were recorded in the same way, without filtration of the samples. Kinetics of the degradation were monitored at 239 nm.

Concentration changes of the chloride generated during the degradation were monitored by a chloride ion-selective electrode (Mettler Toledo Me-51340400) coupled to a saturated calomel electrode (Iskra K401) via a potassium nitrate electrolytic bridge and connected to a pH-meter (Radiometer PHM62). Since, according to the manufacturer's declaration TiO$_2$ contains chloride, calibration of the chloride electrode was carried out in the presence of the same amount of TiO$_2$ used in the experiments and at the same temperature. KNO$_3$ was added to keep the ionic strength of the solution constant throughout the experiment.

RESULTS AND DISCUSSION

Degradation of the pyridine moiety. It was found that in the range from 200 to 400 nm UV spectra of the investigated compound have two distinct absorption maxima (239 and 304 nm). The value of the molar absorption coefficient for the absorption maximum at 239 nm is significantly higher than for the absorption maximum at 304 nm. Because of that, kinetics of the pyridine moiety photocatalytic degradation were monitored at 239 nm.

It was found that, under the applied experimental conditions, the concentration of the pyridine moiety decreased linearly with the irradiation time during the first 90 minutes of irradiation. The linear regression correlation coefficients (r) varied in the range 0.981 – 0.998 (Table 1).

The deviation from linearity found for high conversions, as well as for higher substrate concentrations is presumably due to the accumulation and growing influence of the intermediates in the reaction mixture. Namely, as will be seen in the second part of the paper, the dominating process in the initial period is the evolution of chloride, which is known to inhibit the photodegradation reaction because of its tendency to adsorb on the surface of titanium dioxide (9).

Table 1. Effect of the initial concentration (c_0) of 2-amino-5-chloropyridine on the photodegradation rate in the presence of TiO_2

Pyridine moiety degradation				Chloride evolution			
c_0 (mmol dm^{-3})	$10^6 r_0$ [§]	r [†]	$t_{1/2}$ [‡]	c_0 (mmol dm^{-3})	$10^4 r_0$ [§]	r [†]	$t_{1/2}$ [‡]
0.5	6.2	0.998	41.4	0.5	1.1	0.997	2.3
1.0	7.3	0.990	71.7	1.0	1.2	0.991	4.1
2.1	7.5	0.995	139	2.0	1.0	0.997	9.6
2.5	7.6	0.981	164	2.5	1.2	0.998	10.8

[§] initial decomposition rate (mol dm^{-3} min^{-1}); [†] linear regression coefficient; [‡] half-life, (min).

Since the rate of pyridine moiety photodestruction in the irradiated suspensions could be satisfactorily described by formal zero-order kinetics, the kinetic behaviour of the substrate was subsequently characterized by initial decomposition rates (r_0) obtained through linear regression fits to the kinetic curves. As can be seen from Table 1, in the investigated concentration range, the initial decomposition rate changes only slightly with increasing concentration, i.e. the reaction is practically of the zero-order. This is in agreement with the Langmuir-Hinshelwood kinetic model, used to describe reactions that take place on the surface of semiconductors (3).

On the basis of the Langmuir-Hinshelwood kinetic model (10) transformed into equation [3],

$$t_{1/2} = \frac{0.693}{k_r K} + \frac{0.5 c_0}{k_r} \qquad [3]$$

where c_0 is the initial substrate concentration, k_r is the reaction rate constant, K is the equilibrium adsorption constant of the substrate, and $t_{1/2}$ is the reaction half-life. A linear plot of $t_{1/2}$ against c_0 was obtained (Fig. 1A), which revealed a good agreement with the Langmuir-Hinshelwood model ($r = 0.999$).

From the slope and the intercept of this plot it is possible to calculate the reaction rate, as well as the equilibrium adsorption constant. For the pyridine moiety degradation, it was found that $k_r = 8.0 \times 10^{-6}$ mol dm^{-3} min^{-1}, and $K = 1.1 \times 10^4$ dm^3 mol^{-1}. Since k_r and K depend on experimental conditions, their values reported from different laboratories are difficult to compare. However, the values obtained under our experimental conditions are within the range of those reported in the literature (4).

Chloride evolution. Since chloride is formed during photocatalytic degradation of the investigated compound, it was possible to monitor the kinetics of this reaction by direct potentiometry. It was found that the reaction of chloride evolution is significantly faster than the reaction of pyridine moiety degradation (Table 1). Namely, if the results for the lowest investigated concentration are compared, it can be seen that degradation of the pyridine moiety takes place in about two hours, while complete chloride elimination takes about seven minutes. This indicates that dechlorination of the substrate takes place in the initial phase of the reaction, with a negligible occurrence of pyridine moiety degradation, as indicated by the results of the spectrophotometric measurements. It can also be assumed that most likely no stable chlorinated intermediates are formed in the process, since chloride is quantitatively released in such a short time period.
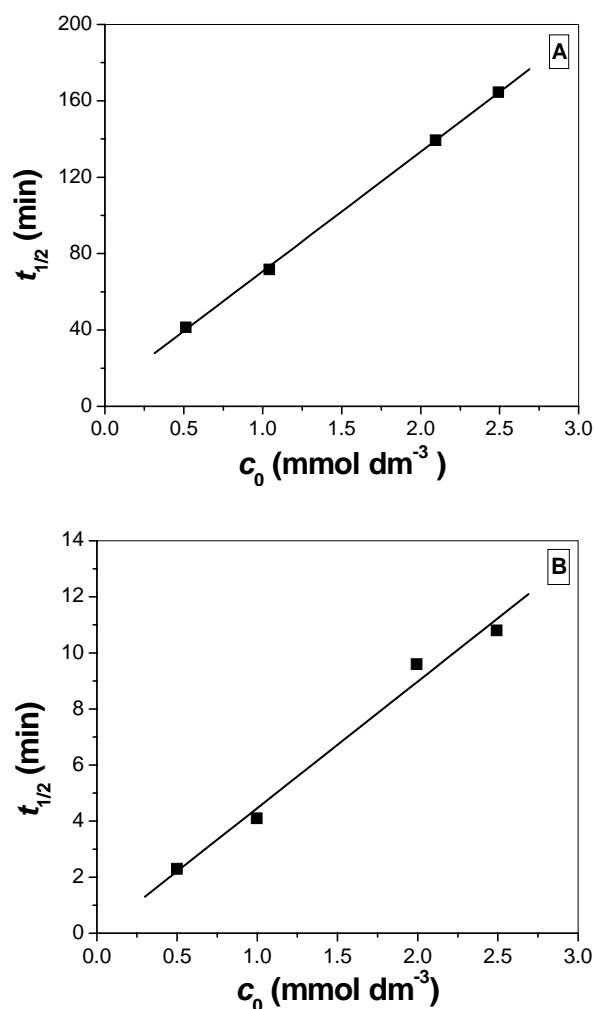
Fig. 1. Linearized Langmuir-Hinshelwood plot for 2-amino-5-chloropyridine photodegradation
(A) degradation of the pyridine moiety; (B) dechlorination

As in the case of pyridine moiety photodegradation, it was found that the kinetics of chloride evolution in the investigated concentration range are of zero-order (Table 1). However, if the Langmuir-Hinshelwood model is applied (Fig. 1B), a significantly higher reaction rate constant ($k_r = 1.1 \times 10^{-4}$ mol dm^{-3} min^{-1}, $r = 0.996$) is obtained. An intercept of a zero value also indicates that adsorption on the TiO$_2$ surface most likely does not play a role in the substrate dechlorination.

Since the reaction rate constants are significantly higher than those found in the literature (1, 4, 11), it can be postulated that the rate limiting step in the reaction of chloride generation is not the reaction of hydroxyl radical formation on the surface of TiO$_2$,

which should be independent of the type of the substrate, but that it occurs by direct photolysis. Furthermore, upon illumination of the solution in the absence of TiO_2, it was found that the reaction of chloride generation takes place at an even higher rate than in its presence, which is not the case with the degradation of the pyridine moiety. The lower reaction rate of chloride elimination in the presence of titanium dioxide is probably a consequence of the opacity of the suspension and light scattering by titanium dioxide particles.

The observed behaviour of the investigated compound can further be described by considering its electrostatic potential (Fig. 2). Namely, calculation of electrostatic potential is helpful in the determination of the most likely way the substrate will interact with the catalyst surface. Under the applied experimental conditions (pH < 6), the surface of the TiO_2 particle is positively charged, and the most negative side of the organic substrate should easily approach the TiO_2 surface electrostatically. As can be seen, the most negative value of the electrostatic potential is on the pyridine nitrogen, which facilitates the approach of the substrate to the TiO_2 surface via this atom, causing the chlorine atom to be oriented toward the solution, away from the catalyst surface. As a consequence, pyridine moiety degradation and dechlorination take place by different kinetics.
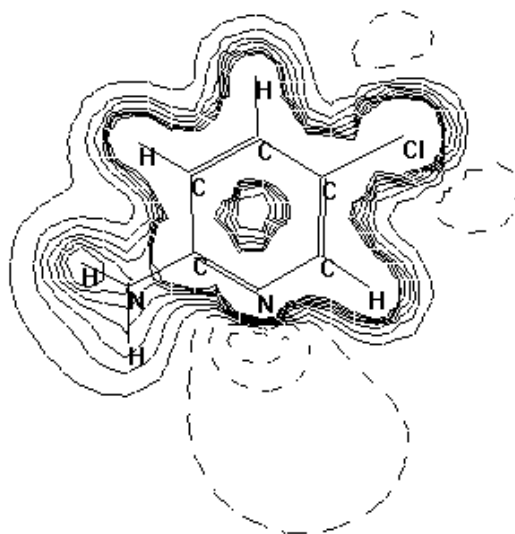

Fig. 2. Electrostatic potential for 2-amino-5-chloropyridine
(dotted lines electronegative, solid lines electropositive)

CONCLUSION

The investigation of 2-amino-5-chloropyridine photodegradation revealed the dechlorination of the initial compound takes place very quickly at the beginning of illumination, as well as that this reaction does not require the presence of titanium dioxide. However, for the degradation of the pyridine moiety, the presence of titanium dioxide is obli-

gatory. For both, the degradation of the pyridine moiety, as well as for dechlorination, zero-order kinetics were observed. It was found that the Langmuir-Hinshelwood kinetic model can be successfully used to describe the kinetics of the pyridine moiety degradation.

ACKNOWLEDGEMENTS

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КИНЕТИКА УКЛАЊАЊА 2-АМИНО-5-ХЛОРПИРИДИНА ИЗ ВОДЕ ПРИМЕНОМ ФОТОКАТАЛИЗЕ

Биљана Ф. Абрамовић, Весна Б. Андерлух, Анђелка С. Топалов и Ferenc F. Gaál

Испитивана је фотокаталитичка разградња 2-амино-5-хлорпиридина, једињења структурно сродног пиридинским пестицидима, уз примену титан(IV)-оксида као полупроводника, праћењем разградње пиридинског прстена, као и праћењем промене концентрације хлоридног јона који настаје у току разградње. Испитан је и утицај почетне концентрације супстрата на брзину разградње. У оба случаја је уочено да брзина реакције следи кинетику нултог реда у целом опсегу испитиваних концентрација. Лангмир-Хиншелвудов кинетички модел је успешно примењен за интерпретацију утицаја почетне концентрације супстрата на брзину разградње пиридинског прстена. Нађено је да се дехлоринација супстрата одвија при условима директне фотолизе. На основу вредности електростатичког потенцијала испитиваног једињења објашњене су разлике у кинетици разградње пиридинског прстена и дехлоринацији молекула.