

## PHOTOCATALYTIC DEGRADATION OF HERBICIDE MECOPROP SENSITIZED BY COLLOIDAL TiO<sub>2</sub> NANOPARTICLES

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### Abstract

Photocatalytic degradation of pollutants on semiconductor nanoparticles attracts a great research interest. So far TiO<sub>2</sub> has been a photocatalyst of choice. Colloidal TiO<sub>2</sub> nanoparticles (mean particle diameter 4.5 nm) were synthesized in Institut of Nuclear Sciences, Vinča, Belgrade, by controlled hydrolysis of titanium(IV) chloride. In this study herbicide mecoprop ((RS-2-(4-chloro-*o*-tolylxy)propionic acid) was chosen as a model compound of an organic waste photodegradable substance in water in view of its wide use all over the world. The objective was to estimate the efficiency of colloidal TiO<sub>2</sub>/UV system by potentiometric titrations of chloride produced during the mecoprop photooxidation, because the photodegradation of the aromatic ring with chlorine as substituent takes place simultaneously with chlorine evolution. It was estimated that its complete degradation of, for example, 2.70 mmol dm<sup>-3</sup> of mecoprop (higher than acute toxicity for fishes) was achieved after about 15 h of illumination. The effects of the initial mecoprop concentration were investigated and it was concluded that the rate of mecoprop decomposition can be described in terms of the Langmuir-Hinshelwood kinetic model.

### Introduction

Environmental photochemistry using semiconductor nanoparticles is part of a general group of chemical remediation methods known as Advanced Oxidation Processes (AOPs). These methods are based on the almost total oxidation of organic and inorganic water pollutants by means of heterogeneous photocatalysis (1-3). So far TiO<sub>2</sub> nanoparticles in view of its high photocatalytic activities and potential for use in environmental purification (4-6) has been a photocatalyst of choice. In this study herbicide mecoprop ((RS-2-(4-chloro-*o*-tolylxy)propionic acid, C<sub>10</sub>H<sub>11</sub>ClO<sub>3</sub>) was chosen as a model compound of an organic waste photodegradable substance in water because of its wide use all over the world. As reported in the literature (7) it is one of the herbicides that is most often found in drinking water. The aim of this work was to follow the efficiency of colloidal TiO<sub>2</sub>/UV system towards the decomposition of mecoprop present in water at low concentration. On the basis of these measurements the kinetics of the photocatalytic degradation of the mentioned pesticide was studied. Potentionetric monitoring of chloride generated during the process was used for these purposes.

### Methods

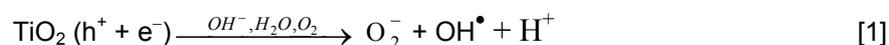
The herbicide mecoprop (98% purity), was obtained from the Chemical Factory "Župa" Kruševac, Serbia and Montenegro. The commercial product was purified by conventional recrystallization method from water-ethanol (1:1) solution, and its purity was confirmed by NMR spectroscopy. Colloidal TiO<sub>2</sub> nanoparticles (mean particle diameter 4.5 nm) were synthesized in Institut of Nuclear Sciences, Vinča, Belgrade, by controlled hydrolysis of titanium(IV) chloride (Fluka) (8). The solution of TiCl<sub>4</sub>, cooled to -20 °C, was added drop wise to water at 0 °C and kept at this temperature for several hours. The solution contains ~ 0.1 mol dm<sup>-3</sup> TiO<sub>2</sub> at pH 1.7. Adjustment of pH was made with dialysis against water at 4 °C, until pH 3. This step is important because of elimination of low-weight titanium hydroxide aggregates which are present at pH 1.7. At pH 3 concentration of low-weight aggregates is 5% of total concentration of Ti(IV) (8). Particle size was determined using a transmission electron microscope, JOEL CXII. The final concentration of TiO<sub>2</sub> was determined spectrophotometrically, from concentration of the peroxide complex obtained after dissolving the nanoparticles in concentrated H<sub>2</sub>SO<sub>4</sub>. This solution was appropriately diluted to obtain solution of lower content of TiO<sub>2</sub> (2 mg cm<sup>-3</sup>). In all experiments doubly-distilled water was used. All other chemicals were used without further purification.

The photochemical cell (sample volume 20 cm<sup>3</sup>) was made of pyrex glass with a plain window (on which the light beam was focused), with a magnetic stirring bar, a water circulating jacket, and opening for O<sub>2</sub> stream. The process was carried out at 40.0 ± 0.5 °C. Colloid was illuminated with a 125 W mercury lamp (Philips, HPL-N) using an appropriate concave mirror.

Concentration changes of chloride generated during the degradation were monitored by potentiometric titration, with the aid a silver electrode coupled *via* a suitable salt bridge to a saturated calomel electrode (Radiometer) and connected to a pH-meter (Radiometer PHM 62). The standard solution of silver nitrate (0.05 mol dm<sup>-3</sup>, standardized by using of standard solution of 0.005 mol dm<sup>-3</sup> of NaCl) was added discontinuously by a Radiometer ABU12 automatic piston burette. After transferring the illuminated sample to a 50 cm<sup>3</sup> beaker, the solution was mildly heated to reduce its volume to 10 cm<sup>3</sup>, and after the addition of 10 cm<sup>3</sup> of acetone to the reaction vessel, the reaction mixture titrated with standard silver nitrate solution. The titration end-point was determined from the derivative titration curve.

## Results and discussion

Published reaction mechanisms for oxidation of organic compounds over TiO<sub>2</sub> colloids in oxygenated aqueous solution involve reaction with OH radicals produced by the reaction of photogenerated holes with adsorbed water molecules or hydroxyl ions (9):



The resulting OH radical, being a very strong oxidizing agent (standard redox potential +2.8 V), can oxidize almost all organic compounds to CO<sub>2</sub> and H<sub>2</sub>O. Photoconversion of organic compounds containing halogens, sulfur, phosphorous, and nitrogen produces halides, sulfates, phosphates, as well as ammonium ions and nitrates/nitrites, respectively.

Results obtained by studying the photocatalytic decomposition of the various compounds with chlorine (10) show that the complete degradation gives carbon dioxide, water and hydrochloric acid. For this reason we decided to follow the photooxidation of mecoprop by potentiometric titrations of chloride produced as a function of illumination time. The time development of chloride released from different initial concentration of mecoprop during photocatalysis is shown in Fig. 1. As it was found in literature (10) the photodecomposition of the aromatic ring with chlorine as substituent takes place simultaneously with the HCl evolution. So, in our case the increases in percentages of chloride released (Fig. 1) can be used to calculate the rate of mecoprop aromatic ring decomposition. It is

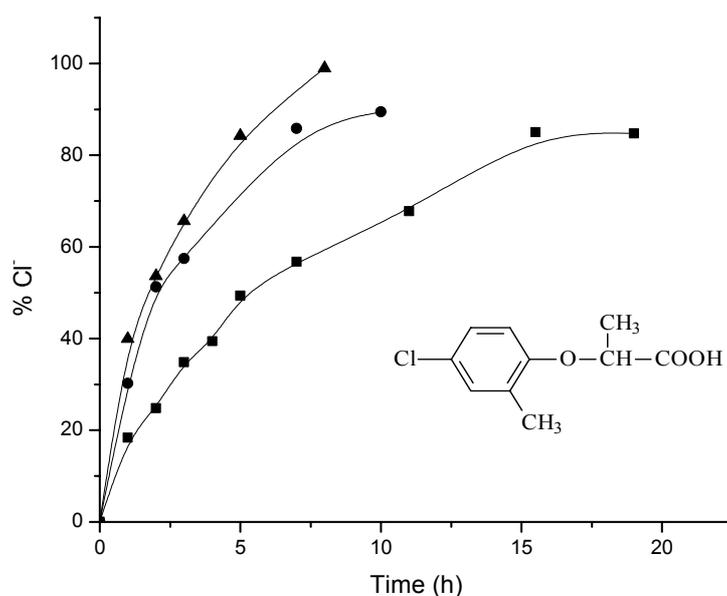


Fig. 1. Effect of initial concentrations of mecoprop (mmol dm<sup>-3</sup>): 2.70 (■), 1.35 (●), 0.9 (▲) on the percentages of chloride released, in the presence of TiO<sub>2</sub> (2 mg cm<sup>-3</sup>).

evident that the initial concentration has a pronounced effect on the degradation rate; at the same irradiation time, the percentages of chloride released is smaller if the initial mecoprop concentration is higher.

In the photocatalytic oxidation of organic substrate over  $\text{TiO}_2$  catalysts it has been repeatedly observed (9, 11, 12) that the dependence of the reaction rate on the initial solute concentration can be described by the Langmuir-Hinshelwood kinetic model (L-H). According to this model the rate of a surface reaction is:

$$R = -dc/dt = k_r K c_0 / (1 + K c_0) \quad [2]$$

where  $R$  is the rate of the surface reaction,  $k_r$  is the reaction rate constant,  $K$  is the equilibrium adsorption constant,  $c$  and  $c_0$  are the actual mecoprop aromatic ring concentration, as well as initial concentration of mecoprop. Integration of equation [2] yields the expression:

$$\ln(c_0 / c) + K(c_0 - c) = k_r K t \quad [3]$$

When  $c_0$  is very small equation [3] reduces to:

$$\ln(c_0 / c) = k_r K t = k_{ap} t \quad [4]$$

where  $k_{ap}$  is the apparent first-order reaction constant ( $k_{ap} = k_r K$ ).

On the basis of the results shown in Fig. 1 a linear dependence of  $\ln(c)$  with irradiation time was obtained for all three initial mecoprop concentrations (Fig. 2).

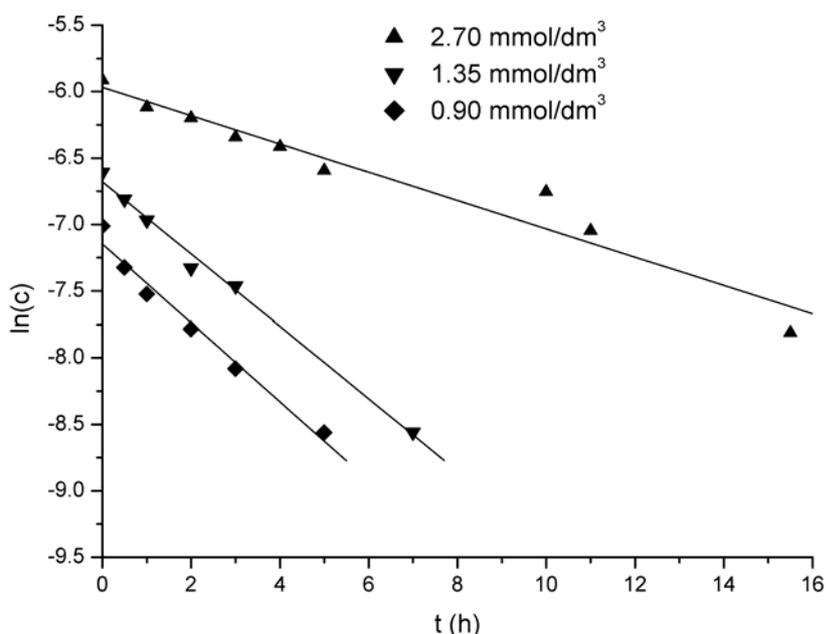


Fig. 2. The dependence of  $\ln(c)$  on irradiation time for all three initial mecoprop concentrations.

This suggests that equation [4] can be used as a good approximation in the range of examined initial concentrations. From the slopes of these plots we calculated the  $k_{ap}$  values (Table 1).

Table 1. Values of  $k_{ap}$  obtained for different initial concentrations of mecoprop

$c_0(\text{Mecoprop})$ (mmol $\text{dm}^{-3}$ )	$k_{ap} \cdot 10^3$ ( $\text{min}^{-1}$ )	Linear regression coefficient
0.90	4.90	0.9946
1.35	4.50	0.9982
2.70	1.83	0.9864

The  $k_{ap}$  values decrease with increasing mecoprop concentrations (Table 1), indicating thus that the reaction is not a simple first-order one but is combined (13). The extrapolation to  $c_0 = 0$  yielded  $k_{ap} = 6.66 \cdot 10^{-3} \text{ min}^{-1}$ .

If equation [2] represents the reaction rate, a plot of initial data as  $1/R_0$  vs.  $1/c_0$  should be linear, because this equation can be transformed to:

$$\frac{1}{R_0} = \frac{1}{k_r} + \frac{1}{k_r K} \frac{1}{c_0} \quad [5]$$

Values for  $k_r$  and  $K$  can be calculated from the intercept ( $1/k_r$ ) and the slope ( $1/k_r K$ ). Such a plot for our experimental results is shown in Fig. 3.

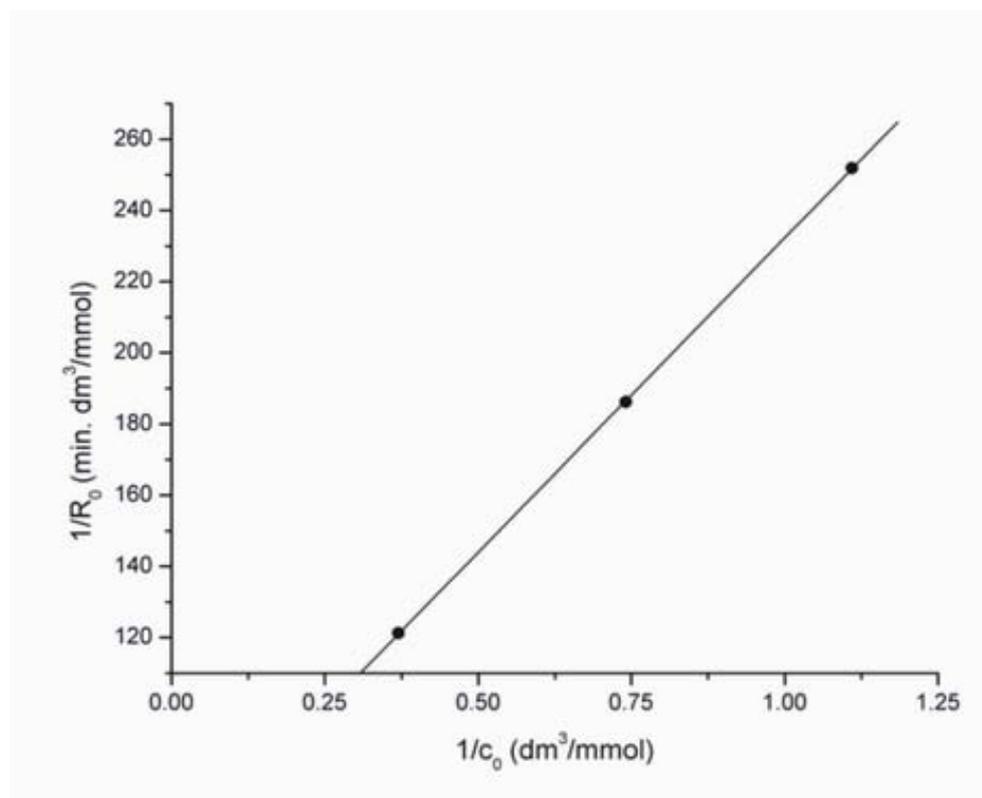


Fig. 3. Plot of the reciprocal of the initial rate of degradation ( $R_0$ ) against the reciprocal of initial mecoprop concentrations.

The initial rate ( $R_0$ ) was calculated on the basis of the changes in mecoprop aromatic ring concentration during the first 60 min of irradiation.

From the slope and intercept in Fig. 3 we found the values  $k_r = 1.80 \cdot 10^{-2} \text{ mmol dm}^{-3} \text{ min}^{-1}$  and  $K = 0.315 \text{ mmol}^{-1} \text{ dm}^3$ . It is evident that the value obtained for the product  $k_r K$  ( $5.65 \cdot 10^{-3} \text{ min}^{-1}$ ) is in agreement with the  $k_{ap}$  value extrapolated to the zero concentration.

### Conclusions

Our results obtained by studying mecoprop photodegradation by potentiometric titration of the chloride released showed that the L-H model is applicable for describing the oxidative photocatalytic processes on colloidal  $\text{TiO}_2$  surface. The obtained results give a good evidence for the possibility that such a process can be used for mecoprop removal from waste waters.

### Acknowledgments

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