

THE REMOVAL OF IMAZETHAPYR HERBICIE FROM WATER USING TITANIUM DIOXIDE COUPLED TO UV LIGHT

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ABSTRACT

The TiO₂ coupled to UV light was used to removal imazethapyr in aqueous solution was investigated. TiO₂ was used as Millennium PC500 (100% anatase). Experiments were investigated in order to assess the influence of various parameters, such as adsorption, initial pesticide concentration and initial amount of catalyst on the photocatalytic process. It has been found that imazethapyr is rapidly degraded with a half-order kinetic. In respect to Langmuir-Hinshelwood model, the photocatalytic reaction is favored at high pesticide concentrations.

Keywords: Imazethapyr, Titanium dioxide, PC500 Millennium

1. INTRODUCTION

Imazethapyr [5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] belongs to a class of chemicals known as imidazolinones [1-3]. This class of herbicides has a very specific mode of action inhibiting certain plant systems, but they do not interact in animals [1].

Imazethapyr is an amphoteric herbicide, having a carboxylic acid and a basic pyridine functional group [4]. Its structure is shown in Figure 1.

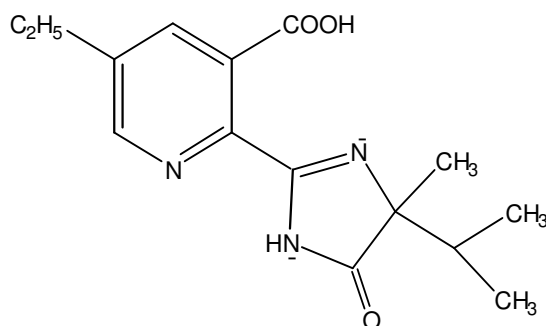


Fig. 1 The chemical structure of imazethapyr

Several reports indicate that Imazethapyr does not adsorb strongly to soil [5, 6] and may persist excessively and interfere with next cultures. Furthermore, it is sufficiently soluble to reach and contaminate the aquifers. Imazethapyr can then be considered as a potential pollutant of water.

TiO₂ photocatalysis has been widely established, in the last two decades, as an alternative physical-chemical process for decontamination of polluted waters. The use of UV energy and semiconductor photocatalysts such as TiO₂ either in suspension [7-9] or immobilized [10-12] can degrade or mineralize completely organic pollutants such as herbicides.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and reagents

Imazethapyr [5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] (99.9% purity) was purchased from Riedel-de-Haen.

All the other reagents used in this study were at least of analytical grade.

Herbicide solutions were prepared with water from a Millipore Waters Milli-Q water purification system.

The powder catalyst was Millennium PC500 titania (>99.5% anatase; surface area = 340 m²/g; mean size = 5 to 10 nm).

2.2. Irradiation experiments

The degradation experiments in aqueous pesticide solutions were carried out using a simple kind of reactor. This reactor was placed in front of a magnetic stirring plate and on an HPK 125W Philips lamp, at a fixed distance of 3 cm. In order to eliminate the short wavelengths able to induce photochemical degradations, an 0-52 filter was used to cut-off irradiation light below 340 nm. In these conditions, the lamp spectrum had a maximum of light emission at 365 nm.

A radio-meter Biollach Scientific model CX-365, was used to measure the light flux of all the experiments.

2.3. Samples preparation

Pesticide solutions were prepared by dissolving a suitable mass of imazethapyr in purified water. Titanium dioxide was added to 20 ml of this solution to make a 0.6 g/l suspension of the catalyst just prior to the experimental treatment.

The mixture constituted of pesticide solution and catalyst was stirred in the dark for 30 min before being irradiated.

During the adsorption step of imazethapyr on TiO₂ and during the irradiation, aliquots of the aqueous suspensions were collected at regular times and filtered through 0.45 nylon filters (Millipore) in order to remove TiO₂ particles.

2.4. Analytical determinations

HPLC-UV analyses were performed using an HPLC (Varian Prostar) equipped with a UV detector and a Column Hypersyl BDS C18 (125 mm x 4 mm, particle size 5 μm). Isocratic elution conditions were applied, the mobile phase composition and wavelength were H₂O / Methanol at a ratio 65/35 at 255 nm, the pH of water was set up at 2.8 using H₃PO₄ acid. The flow rate was 1ml/min and the injection volume 50 μl.

Under these conditions, the retention time for imazethapyr was 9.4 min. Its calibration was calculated on the basis of the peak areas obtained with standardized samples analyzed under the same HPLC conditions.

3. RESULTS AND DISCUSSION

3.1. Preliminary study of Imazethapyr adsorption to TiO₂

A series of experiments were carried out in the dark to study the adsorption kinetic and the isotherm adsorption of imazethapyr on TiO₂-PC500 surface.

For the kinetic study, a pesticide solution (20 ml, 69 μmol/l) with 12 mg of PC500, was magnetically stirred in the dark for 60 min. Samples of 0.5 ml were collected at different time intervals, filtered and analyzed by HPLC. The results of this experiments show that the adsorption equilibrium is rapidly attained (20 min).

For the isotherm adsorption study, 20 ml of herbicide solutions (14.5, 30.3, 69.2 μmol/l) and 12 mg of PC500 were magnetically stirred in the dark for 30 min. The results fitted to Langmuir adsorption model described by equation (1):

$$Y = n K_{ads} C_{eq} / (1 + K_{ads} C_{eq}) \quad (1)$$

where:

Y is the amount of imazethapyr adsorbed by 1g of TiO_2 .

C_{eq} is the concentration of imazethapyr present in solution when the equilibrium of adsorption is reached.

K_{ads} is the Langmuir adsorption constant.

The linear form of this equation is: $1/Y = 1/(n K_{ads} C_{eq}) + 1/n$

The linear fit of Langmuir equation applied to the adsorption of imazethapyr by PC500 Millennium is presented in Figure 2.

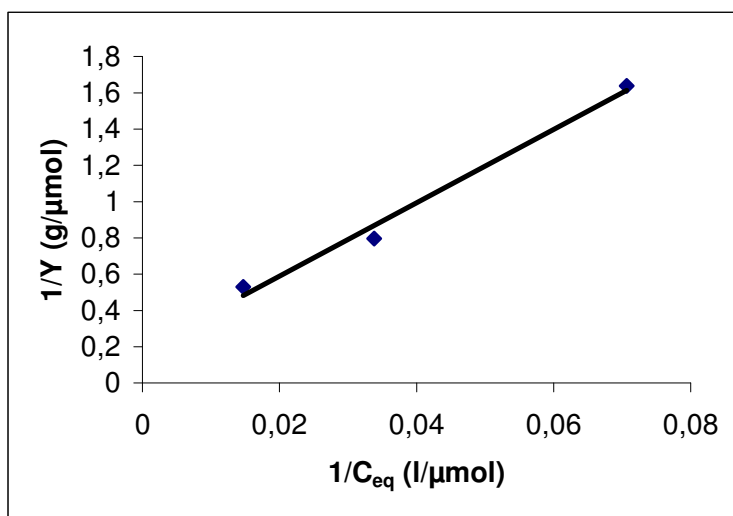


Fig. 2 Linear transformation of Langmuir isotherm relative to the adsorption of imazethapyr by PC500-TiO₂

The adsorption parameters (K_{ads} and n) in addition to the linear regression coefficient (r^2) are reported in Table 1.

Table 1: adsorption parameters of imazethapyr adsorption to PC500

K_{ads} (l/ μmol)	$9.164 \cdot 10^{-3}$
n ($\mu\text{mol/g}$)	5.40
r^2	0.9881

3.2. Imazethapyr removal

No obvious degradation of imazethapyr in darkness at room temperature (pH = 5) was observed within 48 h indicating that no hydrolytic processes of the pesticide during the course of the experiments will be observed.

Also, several blank experiments without catalyst, at the same concentrations as the photocatalytic experiments, were performed to guarantee that under these conditions the system was working in a pure photocatalytic regime.

During photocatalytic degradation, several intermediates are formed and can influence the determination of kinetics due to possible competition between adsorption and degradation. Therefore, calculations were done for an interval time where the intermediates effects may be considered as negligible.

3.2.1. Degradation kinetic order

Generally, photocatalytic degradation of organic compounds follows a first-order kinetic law [9]. In our case, to determine the kinetic order of the photocatalytic reactions, the rate r of the herbicide disappearance as a function of the concentration at the adsorption equilibrium according to equation (2) was calculated:

$$r = -dC/dt = k_{ap} C_{eq}^n \quad (2)$$

where:

k_{ap} is the apparent rate constant.

r was calculated for each catalyst as $r = \Delta C / \Delta t$.

The $\log r = \log k_{ap} + n \log C_{eq}$ plot (Figure 3) gives a straight line of which slope is equal to the kinetic order.

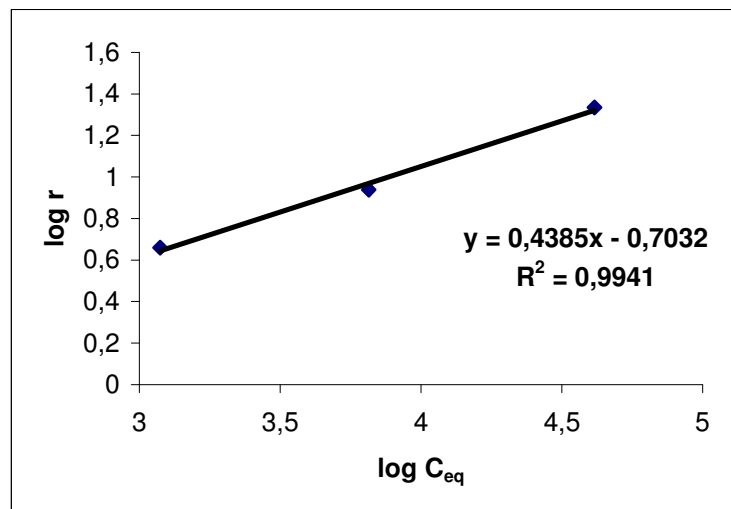


Fig. 3 log-log of the initial rate of photocatalytic degradation of imazethapyr as a function of its initial concentration by PC500

The slope obtained for imazethapyr is near to 1/2. The reaction followed a half-order kinetic according to the equation $-dC/dt = k_{ap} \sqrt{C_{eq}}$ indicating a dissociative

adsorption [13]. Such a result could be explained by the fact that imazethapyr is a weak acid whose pKa of the carboxylic acid is 3.8. As the pH of the irradiated solutions is 5 the protonated and deprotonated forms are present in solution.

The associative and dissociative adsorptions may coexist on TiO₂ surface. In the dark, adsorption is essentially associative but is preferentially dissociative under illuminated Titania.

3.2.2. Langmuir Hinshelwood constants

In spite of the fact that some authors believe that the Langmuir-Hinshelwood model is not sufficient to describe and represent the whole catalytic process, this model is widely used because it enables one to correlate the degradation rate to the instantaneous concentration according to the expression:

$$r = k \frac{(K_{LH} C_{eq})^n}{1 + (K_{LH} C_{eq})^n} \quad (3)$$

where:

- r is the initial rate of photocatalytic degradation,
- k is the true rate constant,
- K_{LH} is the Langmuir-Hinshelwood adsorption constant,
- C_{eq} is the initial concentration after adsorption step,
- n is the kinetic order.

And the linear form of equation (3) is:

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{k(K_{LH} C_{eq})^n} \quad (4)$$

Figure 4 presents the linear forms of Langmuir-Hinshelwood model for imazethapyr in presence of PC500.

k and K_{LH} constants were calculated:

- ✖ $k = 17.153 \cdot 10^{-2} \mu\text{mol l}^{-1} \text{min}^{-1}$
- ✖ $K_{LH} = 7.31 \cdot 10^{-4} \text{l} \mu\text{mol}^{-1}$

K_{ads} obtained in the preceding section (Table 1) was found slightly different to K_{LH} calculated in this part ($K_{LH}/K_{ads} \approx 11$). This difference can be neglected if we compare it to the results of other studies [13] where this difference was found to be much more important.

The difference obtained in our case, can be attributed to the inexactitude of Langmuir and Langmuir-Hinshelwood alignments. Thus, we can conclude that K_{LH} reflects the adsorption affinity of imazethapyr on the surface of PC500.

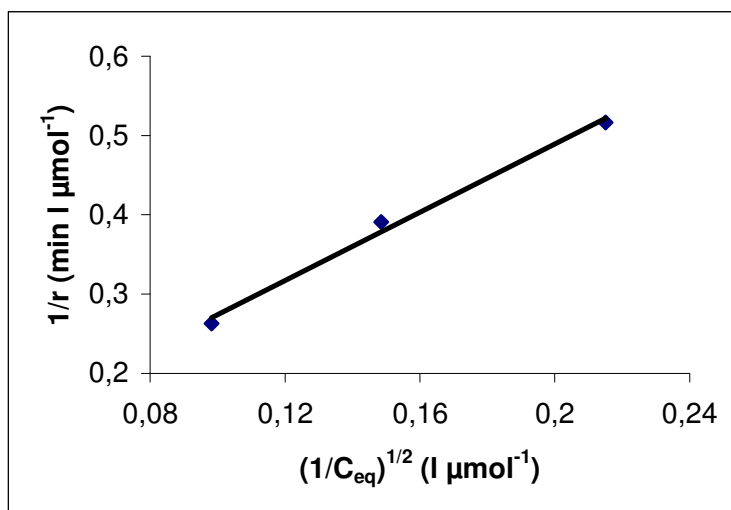


Fig. 4 Linearization of Langmuir-Hinshelwood isotherm: reciprocal of the initial rate as a function of the reciprocal of the initial concentration of imazethapyr

4. CONCLUSION

The removal of imazethapyr in aqueous solutions was studied using powder TiO_2 as semiconductor photocatalyst.

It appears first, that adsorption is an essential factor in the photocatalytic degradation of this herbicide and second that the kinetic order of imazethapyr degradation is a half order indicating a dissociative adsorption of the pesticide on the catalyst surface.

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