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Degradation of the herbicide isoproturon by a photocatalytic process[☆]



Dégradation de l'herbicide isoproturon par un procédé photocatalytique

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ABSTRACT

In this study, the adsorption and photocatalytic degradation of isoproturon (one of the most widely used herbicides in agriculture) was investigated in an annular photoreactor packed with a TiO₂ photocatalyst. The results highlighted that the monolayer Langmuir adsorption isotherm model was well obeyed. The isoproturon adsorption equilibrium constant was determined experimentally. The codegradation of isoproturon and of other copollutants such as salicylic acid and phenol occurred, demonstrating that within the catalyst, the same type of sites can be involved in the adsorption of the two pollutants. The heat of adsorption fell in the range of 20 to 50 °C and was found to be ~43 kJ/mol. As expected, the adsorption constant K_a decreased with increasing the fluid flow due to the temperature rise. The kinetics of the photocatalytic degradation of isoproturon revealed a first-order reaction for initial concentrations between 3 and 43 ppm. In our experimental conditions, no by-products were detected and total disappearance of isoproturon was observed.

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1. Introduction

The pollution of ground or surface water has been a major environmental problem for many years. Most of these organic pollutants come from pesticides used in agriculture. The diversity of these compounds, as well as the lack of knowledge about their toxicity to human health, are important factors favoring the study of means for their elimination.

Various remediation processes already exist, such as chlorination or treatment on activated carbon. However, those processes do not allow satisfactory elimination of all

chemical species: chlorination induces the production of toxic by-products [1,2], and adsorption on activated carbon results in pollutant transfer and not in pollutant elimination [3]. An ideal treatment method for pesticide wastes would be a non-selective one that could achieve rapid and complete degradation into inorganic products and could be suitable for small-scale treatment units [4]. Among the so-called advanced oxidation processes (AOPs), photocatalytic methods in the presence of artificial or solar light, like heterogeneous photocatalysis (TiO₂/UV-A), have been proven to be effective for the degradation of various contaminants found in industrial or domestic wastewaters [5].

In the present study, the photocatalytic decomposition and mineralization of pollutants was studied with a TiO₂/UV system. The pollutant used is an herbicide (isoproturon) that is widely used in the treatment of cereal crops in particular. Its elimination was then compared with that of atrazine, another pesticide that is commonly studied in

[☆] Thematic issue dedicated to François Garin.

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the laboratory. The influence of experimental conditions such as flow rate, temperature and the presence of other pollutants in the treated solution was also investigated.

2. Photocatalysis principle

A photochemical reaction is characterized by an activation related to the absorption of at least one photon by a molecule. The range of wavelengths generally used in photochemistry is in the UV/visible region (wavelength 200 to 700 nm). However, this is not always sufficient for suitable pollutant remediation. Thus, oxidants such as O_3 , H_2O_2 and/or a catalyst are often used.

Semiconductors are characterized by a certain non-stoichiometry, unlike oxides such as MgO or Al_2O_3 , which are insulators. Indeed, their electronic structure is characterized by a filled valence band and an empty conduction band. If a photon provides an energy $h\nu$ equal to or higher than the gap band energy, an electron of the valence band moves to the conduction band as shown in Fig. 1. As a consequence, this leads to the appearance of a positive hole in the valence band and of a negative charge in the conduction band. Thus, the catalyst becomes very reactive while also gaining redox capacity [6,7].

The most commonly used semiconductor is TiO_2 , due to its performance, stability, low cost and resistance to corrosive conditions. Its gap energy is 3.2 eV, which corresponds to 308 kJ/mol. The exposure of this material to an UV irradiation emitted at 365 nm is sufficient to supply this amount of energy. TiO_2 can be used for the degradation of most organic pollutants, such as alkenes, olefin hydrocarbons, aliphatic compounds, phenols, chlorinated organic compounds [8], pesticides, and herbicides [9].

Two types of photocatalytic decomposition can take place:

- by direct reaction on the created electron-hole after the absorption of photons: $h^+R_{ad} \rightarrow R_{ad}^+$;
- by reaction with OH^\bullet radicals generated on the surface of the catalyst: $OH^\bullet + RH_{ad} \rightarrow R_{ad}^\bullet + H_2O$.

These radicals can be generated via several pathways:

- interfacial charge transfer with H_2O and/or OH^- :
 - $h^+ + H_2O_{ad} \rightarrow OH^\bullet + H^+$,
 - $h^+ + OH_{ad}^- \rightarrow OH^\bullet$;
- hydrogen peroxide action:
 - hydrogen peroxide is formed using oxygen present in the medium according to the following pathway (O_2 is indeed the principal acceptor of e^- in the medium):

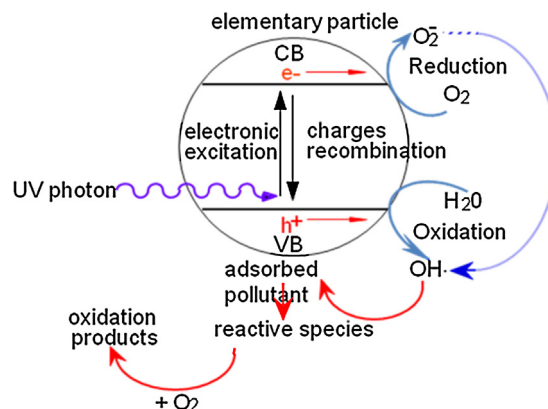
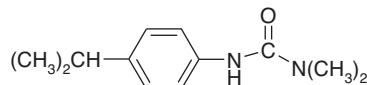


Fig. 1. The principle of the photocatalytic process.

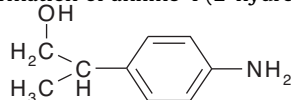
- $e^- + O_2 \rightarrow O_2^-$,
- $O_2^- + H^+ \rightarrow HO_2^\bullet$,
- $HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$,
- $O_2^- + HO_2^\bullet \rightarrow HO_2^- + O_2$,
- $HO_2^- + H^+ \rightarrow H_2O_2$,
- then, hydrogen peroxide is broken up to yield OH^\bullet radicals:
 - $e^- + H_2O_2 \rightarrow OH^\bullet + OH^-$,
 - $H_2O_2 + O_2^- \rightarrow OH^\bullet + OH^- + O_2$.

3. Elimination of isoproturon

Isoproturon, or 3-(4-isopropylphenyl)-1,1-dimethylurea, is one of the most-used herbicides in the world, in particular on cereal crops. It can be absorbed by plants, mainly by their roots. It acts primarily on annual graminaceous weeds. Its developed formula is:

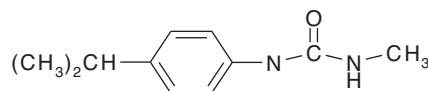


Isoproturon's LD50 toxicity for rats is 1,826 mg/kg (oral) or >2,000 mg/kg (skin); these values are rather low. In spite of its substantial use, it is only found in relatively small quantities in ground or surface water. This is because it can be hydrolyzed or biodegraded in the natural environment. Indeed, enzymatic and microbial action can lead to the formation of aniline 4 (2-hydroxyisopropyl):

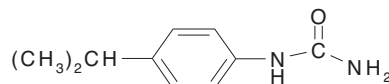


Isoproturon can also be photodegraded to yield:

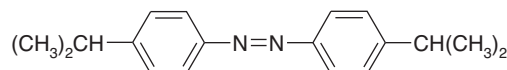
3(4-isopropylphenyl)-1-methylurea



3(4-isopropylphenyl)-urea



and 4-4'-diisopropyl-azobenzene



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