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Photocatalysis as a pre-treatment prior to a biological degradation of cyproconazole

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ABSTRACT

The feasibility of coupling photocatalysis and a biological treatment (*Pseudomonas fluorescens*) to remove a fungicide, cyproconazole, in pure water was examined. Photocatalytic elimination of 85 10^{-3} g L^{-1} cyproconazole was almost complete after 500 minutes irradiation. In view of a subsequent biological treatment, the residual organic content should be significant and hence 255 minutes irradiation time was chosen, leading to 85.8% elimination yield, 38.5% mineralisation and 51.6% oxidation. COD on TOC ratio decreased during photocatalysis indicating a favourable trend, which however was not confirmed by a decrease of the toxicity, since the EC_{50} values were 61% and 64% initially and after 255 minutes irradiation. In addition, the presence of by-products from photocatalysis after *P. fluorescens* culture, showing their non-biodegradability, was also in disfavour of a coupling of the two operations. Therefore in the considered experimental conditions, photocatalysis prior to biological treatment with *P. fluorescens* is not really relevant to treat water containing cyproconazole.

1. Introduction

The worldwide general application of intensive agricultural methods and the large-scale development of the agrochemical industry involve a large accumulation of pesticides in continental and marine natural waters. Effluents arising from agricultural activities (unused treatment solution, spray, machine and container washing) contribute to water resource pollution and the pesticide concentrations can reach levels superior to the French legislation (0.1 μg L^{-1}) for instance [1].

Physical techniques can be used to remove recalcitrant pollutants [2,3]. Among them, adsorption, flocculation, electro-flocculation, reverse osmosis, ultrafiltration and coagulation have been applied. The main drawback is the need of expensive regeneration and post-treatment processes, because of the non destructive characteristic of these processes. Indeed, the pollutant is only transferred to another phase [4–6].

Advanced oxidative processes (AOP) can also be used to remove pesticides [7,8]. Among AOP, heterogeneous photocatalysis appears as an interesting technique for the treatment of endogenous organic pollutions [9–11]. TiO_2, the most used catalyst [10,12–14], was activated under UV irradiation ($\lambda < 390$ nm), allowing the generation of highly reactive free radicals $^{\bullet}OH$ from water or hydroxide ions. When used in suspension [10,12,15,16] a separation of the photocatalyst from the irradiated effluent is needed, while its deposit on an appropriate support [13,17] allows to avoid this drawback. Recently, in order to degrade recalcitrant compounds such as pesticides and reduce operational costs, several studies recommend integrating processes, more especially the coupling of AOP and biological treatment [18,19]. Photocatalysis constitutes a pre-treatment in order to increase the biodegradability of the effluent degrading pesticides and/or to reduce toxicity [17]. The knowledge concerning the reaction pathway and the photocatalytic kinetic degradation have to be improved in view of a better knowledge with respect to the operating conditions of the integrated process (irradiation time, mineralisation yield, etc.).

Cyproconazole, of the azole fungicides group, is a widely used fungicide; 2423 t are annually consumed in France, in agriculture, on foliage and in cereal cultivation [20]. As a consequence of pesticide use in the urban area, azole fungicides were monitored (from the μg L^{-1} to ng L^{-1} level) in effluents of wastewater treatment plant [21]. Among the several works dealing with the photocatalytic elimination of pesticides containing nitrogen rings [22–25], only few concerned cyproconazole [20,26] and proposed a possible pathway for its photocatalytic degradation [20]. A hydroxyl radical attack occurs on the phenyl ring, the methyl groups and the C1 carbon of the molecule; there is a partial transformation of the triazole moiety into NH_4^+ and NO_3^- and a complete release of the chlorine atoms as chloride ions [20]. The potential formation of cyanuric acid [20], a non toxic [27] and biodegradable compound [17,28,29], as well as the low mineralisation rates [26] indicate a significant residual organic carbon while the cyproconazole is almost totally degraded. Our previous works [20] suggest that this pollutant was an interesting candidate to test an

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integrated process coupling photocatalysis and biological process and was therefore considered in this work.

The aim of this study was to investigate the possible formation of more biodegradable by-products during photocatalysis if compared to the parent compound (cyproconazole) and to determine the optimal irradiation time for the coupling of these two operations. In addition, for an identification of the reaction pathway occurring during possible biodegradation, pure cultures of selected microorganisms were considered. In this aim, a strain belonging to the *Pseudomonas* genus was selected, the most widely used for an environmental purpose [30]. In this genus *Pseudomonas fluorescens* was considered owing to their safety, while they found numerous applications in xenobiotic bioremediation [31].

2. Experimental procedure

2.1. Chemicals

Technical grade cyproconazole (purity 96.9%) was used for experiments (Fig. 1). Analytical-standard cyproconazole (purity 99.8%) was obtained from Aldrich, and used without further purification, for HPLC calibration. The solubility of cyproconazole in water (298 K) is equal to 140 10^{-3} g L^{-1} and the Kow is 2.91. Analytical-grade organic solvents were used for HPLC-UV analysis. The water used during experiments was obtained after purification using reverse osmosis ($Cl^- = 0.05\ 10^{-3}$ g L^{-1}, $NO_3^- = 0.07\ 10^{-3}$ g L^{-1}).

2.2. Photocatalyst characteristics

The powdered photocatalyst was PC-500 Titania from Millennium Inorganic Chemicals (Thann, France) (anatase >99%). TiO_2 was fixed on non-woven paper by using an aqueous dispersion of colloidal SiO_2-like binder and zeolite-like adsorbent (mass TiO_2/SiO_2 ratio of 1).

2.3. Photoreactor

The irradiation of cyproconazole solutions was carried out in a closed loop step photoreactor, which consisted of several parts: a tank, a pump, a spillway at the top and steps [32]. The reactor was made of six regular steps of the same dimensions (depth/height/width: 6 cm/6 cm/25 cm) covered with the photocatalytic media (0.18 m^2; 72 cm × 25 cm corresponding to 3.2 g of TiO_2). Three UV lamps, Phillips PL-L24W/10/4P ($\lambda_{max} = 365$ nm) were placed at the inside of a cover; the incident photon flux was measured by actinometry at 38 ± 0.2 W m^{-2} at the surface of the liquid. In a typical experiment, 3 L of 85 10^{-3} g L^{-1} pesticide solution was introduced into the photoreactor. The solution was pumped into the tank at a flow rate of 24.6 L h^{-1}. At given time-intervals, samples were taken into the tank to evaluate the concentration of the target compound. The liquid flow on the photocatalytic media was a thin falling film of about 1 mm thickness. After reaching adsorption equilibrium in the dark (30 min), the UV light was turned on to irradiate the solution and the first sample was taken ($t = 0$).

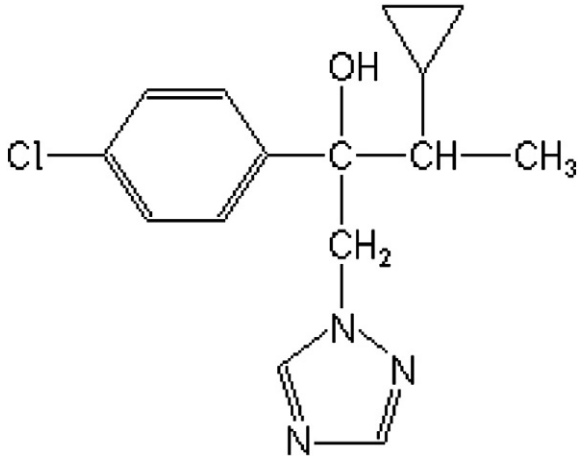

Fig. 1. Chemical structure of cyproconazole.

2.4. Biological treatment

A commercial strain of *P. fluorescens* Migula 1895 AL (DSMZ, Braunschweig, Germany) was used.

Stock cultures were maintained at −18 °C in the following medium (g L^{-1}): glycerol, 200, yeast extract, 15 and glucose, 10. Before culture, bacteria were reactivated by propagation during 24 h at 25 °C in Petri dishes containing the following agarose medium (g L^{-1}): casein pancreatic peptone, 5; yeast extract, 3; and bacteriological agar type E, 15. The pH of the propagation medium was adjusted to 7.0. To avoid any residual nutrient from the propagation medium, bacteria were collected at the surface of colonies and resuspended in a saline solution (9 g L^{-1} NaCl); after less than 4 h, 1 mL of this suspension (having an absorbance in the range 1–2) was used to inoculate culture media.

Cultures were carried out in duplicates at 30 °C in 250 ml Erlenmeyer flasks containing 100 mL of the considered medium (their compositions are collected in Table 1).

2.5. Analytical methods

2.5.1. Biodegradation

During culture, pH was monitored, as well as bacterial growth [34] turbidimetrically followed after periodical sampling at a wavelength of 600 nm, using a Thermospectronic Helios 8 spectrophotometer (Bioblock, Illkirch, France). The remaining analyses (cyproconazole, inorganic anions and ammonium concentrations, TOC, COD, toxicity) were then carried out after centrifugation of samples (20 min at 4000 rpm—Jouan C412, Saint-Herblain, France).

2.5.2. Photocatalysis

In a typical experiment, at scheduled times, 10 mL samples were taken from the photoreactor or the biological vessel and filtered through a Millipore filter (Millex®-HV—0.45 μm) to prevent particles entering the instruments (HPLC and ion chromatography columns or the TOC analyser).

The concentration of cyproconazole was measured by means of a high performance liquid chromatography (HPLC) and a diode array detector [20]. Acetonitrile/water mixture (60%/40%) was used as the mobile phase. Flow rate was set at 1 mL min^{-1}. Detection of cyproconazole was carried out at 197 nm.

The TOC was measured with a 1010 O.I. Analytical TOC analyser (College Station, TX, USA). COD was measured by means of a Nanocolor test CSB 160 (Macherey-Nagel, Düren, Germany).

Inorganic anions, namely nitrates, nitrites and chlorides, as well as organic anions, namely acetate, formate and oxalate were analysed by DIONEX DX-120 (Amsterdam, Netherlands) ion chromatography

Table 1
Composition of the solution for biological treatment.

M1	M2	M3
Mineral supplementation (g L^{-1}): KH_2PO_4, 3.4; $NaH_2PO_4 \cdot H_2O$, 3.4		
Trace elements (10^{-3} g L^{-1}) [33]: EDTA as chelating agent, 585; Mg, 25; Fe, 20; Ca, 18; Zn, 4.5; Mo, 2; Cu, 1.3		
Target compound: cyproconazole (85 10^{-3} g L^{-1}) or a photocatalysed solution of cyproconazole		
pH = 7 (adjusted with 1 mol L^{-1} NaOH)		
Without additive	5 g L^{-1} glucose	5 g L^{-1} glucose and 1 g L^{-1} ammonium chloride