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Photocatalytic removal of s-triazines: Evaluation of operational parameters

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ABSTRACT

The photocatalytic degradation of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and simazine (2-chloro-4,6-diethylamino-1,3,5-triazine) herbicides widely used in agriculture has been investigated. Experimental design methodology was used to assess the influence of pH and TiO_2 concentration and the efficiency of the process. The results indicated that in the experimental domain investigated TiO_2 concentration was the most significant factor in contrast to the scarce influence shown by the initial pH. The mechanism of atrazine and simazine photocatalytic degradation was studied under the experimental conditions determined as optimal. No full mineralization of atrazine or simazine was achieved. The main intermediates occurring during the reaction were identified by high performance liquid chromatography (HPLC). Based on the concentration profile of intermediates formed during the treatment a degradation pathway is proposed for each herbicide. The toxicity along the reaction was monitored by means of luminescence bioassays using *Vibrio fischeri*. The inhibition percentage decreases with the irradiation times what can be associated with the formation of highly hydroxylated intermediates.

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and simazine (2-chloro-4,6-diethylamino-1,3,5-triazine) are some of the herbicides most widely used over the last 30 years for selective broad-leaved and grassy weeds control on a variety of crops such as corn, sugarcane, and pineapple [1]. Due to their relatively high persistence and mobility in soils these s-triazines can contaminate surface and ground waters where, in addition to their direct toxic effects, their phytotoxicity may constitute a major environmental problem. It has been probed that many zooplankton species show a reduction in reproduction and growth when their ecosystems are exposed to triazines [2].

In general, s-triazines are not readily biodegradable and rather resistant to conventional treatment methods therefore difficulting detoxification water processes. Concerns about the widespread water pollution and the repeatedly presence of atrazine and simazine residues in drinking water have led to bans or severe restrictions for their use in many countries. In the EU both herbicides are included in the list of priority substances given in the Directives 2000/60/EC and 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy [3].

Heterogeneous photocatalysis with titanium dioxide has been demonstrated as a good alternative to the conventional methods for the treatment of effluents contaminated with a variety of pesticides [4,5]. Previous studies have shown that photocatalytic degradation of triazine herbicides takes place by several steps leading to formation of cyanuric acid (trihydroxy s-triazine) as final stable product [6–11]. The high stability of the s-triazine ring prevents a further degradation to achieve the full mineralization even upon addition to the solution of an oxidant such as peroxydisulphate [7]. The majority of research done to study the influence of reaction parameters on the efficiency of the photocatalytic degradation of triazines has been carried out by univariate approaches (one variable is changed at time maintaining the others constant). An interesting alternative to this methodology is the experimental factorial design, a statistical tool that allows the simultaneous change of several variables [12,13]. To the best of our knowledge, only Héquet et al. [8] have reported a multivariate analysis on atrazine photocatalytic degradation, but no similar studies have been described for simazine.

The present work focuses on the photocatalytic degradation of atrazine and simazine in water using suspended TiO_2. The main aspects investigated have been: (i) the optimization of the degradation procedure by means of a factorial design of experiments studying the simultaneous effect of pH and TiO_2 concentration on the herbicide degradation rate, (ii) the identification of intermediate products in order to establish a tentative reaction pathway for both triazines and clarify some dissimilarities found in the literature and (iii) the evaluation of the toxicity along the pho-

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tocatalytic reactions by means of luminescence bioassays using *Vibrio fischeri*.

2. Materials and methods

2.1. Chemicals

Table 1 displays the chemical structure, nomenclature and acronyms of the organics according to the nomenclature developed by Cook and Hütter [14] and Nélieu et al. [15] to identify s-triazine compounds. All were of analytical grade and used as received. Atrazine 99% (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), simazine 99.5% (2-chloro-4,6-diethylamino-s-triazine), desisopropyl-atrazine 95% (2-chloro-4-ethylamino-6-amino-s-triazine), desethyl-atrazine 99% (2-chloro-4-amino-6-isopropyl-amino-s-triazine), hydroxy-atrazine 96% (2-hydroxy-4-ethyl-amino-6-isopropylamino-s-triazine), desisopropyl-2-hydroxy-atrazine 95% (2-hydroxy-4-ethylamino-6-amino-s-triazine) and hydroxy-simazine 99.5% (2-hydroxy-4,6-diethylamino-s-triazine) were purchased from Riedel-de Häen. The standard desethyl-2-hydroxy-atrazine 99% (2-hydroxy-4-amino-6-isopropylamino-s-triazine) was obtained from Fluka. Standards cyanuric acid 98% (2,4,6-trihydroxy-s-triazine) and desethyl-desisopropyl-atrazine 95% (2-chloro-4,6-diamino-s-triazine) were acquired from Aldrich. Ammeline 95% (2-hydroxy-4,6-diamino-1,3,5-triazine) and ammelide (2,4-dihydroxy-6-amino-1,3,5-triazine) were purchased from ABCR. All standard solutions were prepared using organic-free deionized water (Milli-Q). Titanium dioxide P-25 supplied by Degussa was used as photocatalyst. It is a non-porous solid for which a BET surface area of 50 m^2 and mean particle size of ca. 30 nm were measured. It contains anatase and rutile crystalline phases in a ratio 4:1. In all experiments initial concentrations of 25 and 5 mg L^{-1} were set for atrazine and simazine, respectively.

2.2. Photocatalysis procedure

Photocatalytic reactions were carried out in a batch Pyrex reactor of 1 L effective solution volume. Irradiations were carried out using a 150 W medium pressure mercury lamp (Heraeus TQ-150), placed inside a Pyrex jacket and provided with a cooling tube through which an aqueous solution of copper sulphate (0.01 M) was circulated to prevent the overheating of the suspension and to cut off the radiation below 300 nm. The initial pH values of the herbicides solutions were adjusted with H_2SO_4 0.1 M or NaOH 0.1 M. Prior to irradiation, the suspension of triazine and catalyst was air saturated and equilibrated by magnetic stirring for 20 min in the dark to ensure complete equilibration of adsorption/desorption of the organic compound on the catalyst surface. Continuous air bubbling and stirring were maintained through the reaction. Aliquots were taken at time intervals, following filtration through 0.22 μm Nylon filters in order to remove the suspended TiO_2 particles before being analyzed.

2.3. Analysis

2.3.1. Liquid chromatography

High performance liquid chromatography (Varian Polaris Prostar 320) system equipped with UV–VIS detector was used to identify and quantify the products obtained in the photocatalytic reactions. The separation was performed using a Synergi 4 μ MAX-RP column. CEIT, CEET, ACIT and ACET were eluted with a gradient of aqueous phosphate buffer (pH 7)–acetonitrile (55:45, v/v) to (35:65, v/v), at a flow rate of 0.5 ml min^{-1} and detection at 210 nm. Elution of the other components, EOIT, EEOT, AOIT, AEOT, CAAT, OAAT, OOAT and OOOT were carried out with a gradient of aqueous phosphoric acid buffer (pH 3)–acetonitrile (95:5, v/v) to (40:60, v/v), at a flow rate of 0.8 ml min^{-1} and UV detection at 205 nm.

2.3.2. Toxicity measurements

The toxicity evaluation of samples was performed with a Microtox Model 550 Toxicity Analyzer. The analysis is based on the measurement of the ability of the sample to inhibit the natural bioluminescence of the marine bacterium *Vibrio fischeri* (strain NRLL no. B-11177). The bacteria were in freeze-dried form (acquired from Gomensoro) and activated prior to use by NaCl (2%) reconstitution solution. Samples were tested in solution containing 2% sodium chloride in six dilutions. After 15 min of incubation at 15 °C light emission was recorded and compared with a toxic-free control. The percentage of inhibition was obtained following the established protocol using the Microtox calculation program.

2.3.3. Factorial experimental design

Multivariate experimental design was carried out following the methodology of response surface [13]. The software Statgraphics Plus 5.0 was used to obtain the polynomial equations and the response surfaces.

3. Results and discussion

Preliminary experiments were done without either titanium dioxide or UV irradiation to evaluate the extent of adsorption and photolysis of the herbicides under our experimental conditions. Dark adsorption was negligible for both compounds as no significant variations in concentration were found after 6 h. On the contrary, photolysis was shown to occur to some extent. After a time period of 1 h, degradation percentages of 15% and 25% were respectively observed for atrazine and simazine. Our results are significantly different from those reported by Héquet et al. [8] who found a half-life time of 2.3 min for the photolytic atrazine degradation using a TQ 150-Z2 Heraeus lamp. Dissimilarities can be mainly due to the differences in the irradiation set-up as we employed a combination of Pyrex and copper sulphate solution as filtering system instead of the quartz filter they used. On the other hand, the photolysis extent found for simazine is in accordance with the results obtained by Chu et al. [10] who also report a significant dependence of the process with wavelength in the 254–350 nm range.

The kinetics of atrazine and simazine degradation was significantly enhanced by irradiation in the presence of titanium dioxide as catalyst following a pseudo-first order decay, in agreement with previous reports [6,9,10]. The effect of pH and titania concentration on the kinetics of the reaction were investigated by experimental design methodology as it allows to obtain the optimal conditions for the photocatalytic procedure from a minimum set of experiments. Based on preliminary experiments carried out in a wide domain of TiO_2 concentration from 0.05 to 3 g L^{-1} at the natural pH of the herbicide, a catalyst concentration ranging from 0.05 to 1.95 g L^{-1} and initial pH from 3 to 9 was selected for atrazine. For simazine, a TiO_2 concentration from 0.05 to 0.25 g L^{-1} and a pH interval 3–8 was fixed. Natural pH, i.e. 6.0 for atrazine and 5.5 for simazine, was chosen as central point in both cases.

In a first approach, a two-level factorial design consisting in four experiments (2^2) at the limits of the pH and TiO_2 intervals and three experiments at the central values of the two factors to determine the experimental error and any possible effects of curvature in the response surface were carried out. The analysis of the data obtained showed that the curvature was significant, indicating that a high-order model or response surface study was needed in order to uncover the behaviour of the significant factors [13]. Therefore, four experiments were performed in addition at the midpoints to

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