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Effect of inorganic ions on the photocatalytic treatment of agro-industrial wastewaters containing imazalil

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ABSTRACT

In this work we studied the elimination, mineralization and detoxification of wastewaters from banana postharvest industries, contaminated with the fungicide imazalil, by means of heterogeneous advanced oxidation processes. We compared the activity of the commercial photocatalyst Evonik P25 and the lab-made EST-1023t in the degradation of imazalil in deionized water and in industrial wastewater. Results show an important negative water-matrix effect for wastewater treatment at acidic pH values due, mainly, to the presence of ions adsorbed onto the TiO_2 photocatalyst surface. At pH 7 only bicarbonate anions and bacteria hindered the degradation and mineralization of imazalil. Mineralization of imazalil was completely inhibited by dissolved aluminium in concentrations as low as 5 mg L^{-1}.

1. Introduction

In order to prevent the appearance of postharvest diseases during the transportation and storage of fruits, it is necessary to employ fungicides. Water contaminated with these substances is normally disposed into the sewage system and thus produces a negative environmental impact. Legislations have been established by many countries to control fungicide MRLs (maximum residual levels) in fruits [1,2], as well as fungicide MCLs (maximum contaminant levels) in wastewater [3].

In this study, wastewater samples from a banana producer were analyzed. This producer employs imazalil as postharvest fungicide in order to prevent banana crown rot. In addition, a considerable amount of aluminium sulphate is added to the process to flocculate the dirt particles washed away from the fruit and thus delay the renewal of wash-water [4]. Calcium hydroxide is also added to increase water pH to prevent corrosion of the washing machinery.

Conventional wastewater treatment plants, based on biological treatments, are unable to eliminate certain substances such as fungicides due to the low biodegradability of these pollutants [5,6]. Advanced oxidation techniques, including heterogeneous TiO_2-based photocatalysis, have proved to be an efficient alternative for the degradation of fungicides, including imazalil [7–10]. This technique is based on the production by the photocatalyst of highly reactive oxidizing agents, such as hydroxyl radicals (${}^{\bullet}OH$). However, the presence of inorganic ions in the water matrix has been shown to greatly influence the removal efficiency of target pollutants [11–15].

The objective of this study is the optimization of the removal of imazalil from an industrial wastewater effluent by means of heterogeneous photocatalysis. For this purpose, two TiO_2-based photocatalysts, commercial Evonik P25 and the lab-made EST-1023t photocatalyst, were tested. Both photocatalysts have proven to be efficient in the degradation and mineralization of imazalil in deionized water [10].

The effects of the most abundant ions (Cl^-, $SO_4{}^{2-}$, $HCO_3{}^-$, Al^{3+} and Ca^{2+}) in the collected wastewater were also studied on an individual basis.

2. Materials and methods

2.1. Reagents/chemicals

The photocatalysts used in the experiments and their properties are shown in Table 1.

The imazalil used was the commercial Fruitgard-IS-7.5. pH was adjusted with diluted H_2SO_4 or HCl and NaOH or $Ca(OH)_2$.

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Table 1
Characteristics of the different photocatalysts used in this work [9].

Catalyst	Specific surface area ($m^2 g^{-1}$)	Anatase/Rutile ratio (%)	Crystallite size (nm)		Band gap (eV)	pH_{pzc}	Particle size (μm)
			Anatase	Rutile			
Evonik P25	52	80/20	22.0	25.0	3.18	6.5	3.9
EST-1023t	13.51	70–80/30–20	62.3	96.1	2.96	6.2	30.1

To study the effect of various inorganic ions, sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) and calcium sulphate ($CaSO_4 \cdot 2H_2O$), from Panreac, were used.

2.2. Analytical determinations

Concentrations of imazalil at different reaction times were HPLC measured according to [10].

Total organic carbon (TOC) and inorganic carbon (IC) were measured using a TOC Shimadzu V-CSN.

Analysis of intermediates was performed with a Varian System consisting of a 212-LC Binary Gradient LC/MS Chromatography Pump fitted with a Prostar 410 HPLC Autosampler and a 320–MS LC/MS/MS system (triple quadrupole) equipped with an electrospray ionization (ESI) interface, according to [10]. Solid-phase extraction using Waters Sep-Pak C18 (500 mg) cartridges was applied to the samples to reduce the salting out effect before chromatographic analysis [16].

Sample toxicity was determined with the MultiTox® *Vibrio fischeri* toxicity test following standard UNE-EN-ISO 11348-3:1998, using an Optocomp I luminometer from MGM Instruments.

Ion Chromatography was used to determine ion concentrations in solution. For this purpose, a DIONEX Ionic Chromatograph equipped with a GP50 gradient pump, ED50 electrochemical detector and an IonPac AS11-HC column (4 × 250 mm) for anions or an IonPac CS12A column (2 × 250 mm) for cations were employed, using a flow rate of 1 mL min^{-1} and aqueous NaOH (30 mM) or 20 mM metasulphonic acid as eluent for anions and cations, respectively.

The FTIR (Fourier Transform Infrared) determinations followed the procedure described in [10].

For dissolved aluminium determinations, a GFAAS (AA 240z Zeeman) graphite furnace atomizer (Varian GTA120) and longitudinal Zeeman-effect background correction were used. A Varian hollow cathode lamp (HCL) was used with wavelength of 396.2 nm. Atomization was held for 2.8 s at 2500 °C. The flowrate of the inert gas (argon) was 0.3 L min^{-1}. This flow was stopped during atomization. The detection and quantification limits for aluminium were 0.35 μg L^{-1} and 1.06 μg L^{-1}, respectively. The adjusted R^2 was 0.9998.

Total suspended solids were measured following standard EN-872, BOD_5 was measured following ISO 5815:1989 using Velp Scientifica BOD Sensor System 10, and COD was determined according to standard ISO 6060:1989 using Velp Scientifica Eco6 Thermoreactor for digestion.

Heterotrophic bacteria were determined using the Heterotrophic Plate Count (HPC) method and R2A as culture media following Standard Methods (9215 C APHA) with incubation at 28 °C for 7 days.

3. Experimental conditions

Degradation tests were performed in 250 mL Pyrex glass batch reactors, filled with 200 mL of the pollutant aqueous solution and 1 g L^{-1} of photocatalyst. Aeration was maintained with an aquarium pump (EOLO AC3000 model: 2.5 W power, 2 L min^{-1} output and pressure >0.02 MPa) and a constant stirring of 450 rpm. A 60 W Philips Solarium HB175 equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) and with an average irradiation power of about 9 mW was used as UV source in the photodegradation and mineralization studies. The lamp was turned on after establishing the adsorption equilibrium. Samples were taken to monitor the reaction in time intervals of 15 min during the first hour and 30 min thereafter. The samples were filtered using 0.45 μm syringe filters before analysis. The experimental setup is shown in Scheme 1.

The photocatalytic process was studied for initial imazalil concentrations of 50 mg L^{-1}. Studies were carried out in deionized water, in the wastewater sample and, finally, in the presence of each of the main ions found in the wastewater sample to evaluate the interference of each ion on the photocatalytic treatment.

Suspended solids and flocs in wastewater were left to settle and the supernatant, free of turbidity, was filtered through 0.45 μm filters for the experimental assays. In order to evaluate the possible effect of bacteria in the photocatalytic treatment, assays were also performed without the filtering stage.

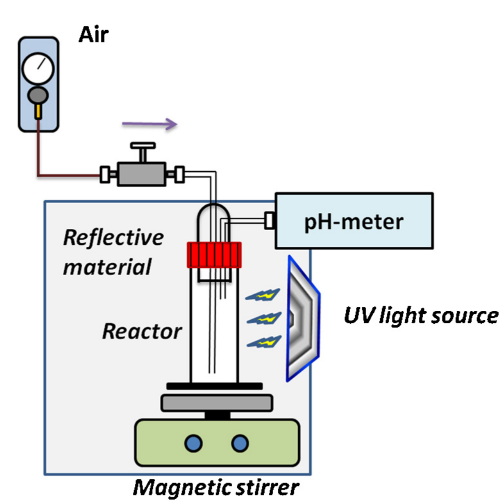
The data presented in this work were subjected to statistical treatment. The standard errors shown in the Figures were calculated using 95% confidence limits.

4. Results and discussion

4.1. Characterization of industrial water sample

The banana producer that provided wastewater for this study processes 10,000 tn yr^{-1} of banana and generates 63 m^3 $week^{-1}$ wastewater containing imazalil.

The mean main parameters found in the wastewater samples from this company and the MCLs for wastewater disposal [17] and reuse in irrigation [18] in the particular case of Spain are listed in Table 2.



Scheme 1. Experimental setup.