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Solar photocatalytic oxidation of Triclosan with TiO_2 immobilized on volcanic porous stones on a CPC pilot scale reactor

Sandra Martínez[a], Julio C. Morales-Mejía[a,b], Perla P. Hernández[a], Lauro Santiago[a], Rafael Almanza[a]*

[a]Universidad Nacional Autonoma de Mexico, Instituto de Ingenieria. Av. Universidad 3000, Universidad Nacional Autonóma de México, 04510, Coyoacan. México, DF
[b]Universidad Nacional Autónoma de México, Facultad de Estudios Superiores Cuautitlán. Av. 1o de mayo s/n, Santa María las Torres, Cuautitlán Izcalli, 54740, México, México

Abstract

Triclosan (TCS) has been used as an antimicrobial agent for more than 30 years and is present in effluents from wastewater treatment plants, in receiving rivers, in tap water and even in groundwater. This compound is resistant to conventional water treatment processes and has been classified as endocrine disruptor and emerging concern pollutant by several organizations. For this reason it is essential to find an efficient process that allows its degradation to non-toxic substances. In this study, TiO_2 was immobilized by forming thick TiO_2 films on volcanic meso-porous stones, creating a photocatalyst that fills a Pyrex® CPC reactor (packed bed reactor type CPC). This reactor is used to remove aqueous Triclosan from water. Films structure and composition is determined experimentally. Efficiency of the organic molecule removal is being related with initial conditions. Films present a very high mechanical stability, excellent adhesion on stones and photocatalytic activity. Reactor, packed with covered stones, presents a reasonable pressure drop. One of the main goals is to have the reactor in operation without any solid – liquid separation step (which is quite expensive energy – demanding) and to employ locally available and inexpensive packing material for the reactor, reaching high cleaning of polluted water.

Keywords: TiO_2 photocatalysis, Triclosan, EDC, Tezontle, porous stones, CPC, Solar

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* Corresponding author. Tel.: 00-5255-56233689; fax: +52 (55) 56233600 x 8051.
E-mail address: ras@pumas.iingen.unam.mx.

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1. Introduction

1.1 General background.

Among the decontamination techniques, the photocatalytic processes have received an increasing attention in the last decades [1-3] because they are potentially able to completely mineralize many organic compounds present in aqueous wastes [4-6]. Heterogeneous photocatalysis is a process based on the excitation of a semiconductor by light of energy equal to or higher than the band gap one (E_{gap}). This excitation generates electron-hole pairs which can give rise to redox reactions with species adsorbed on the catalyst surface [7]. Among the various semiconductors, TiO_2 is the most suitable photocatalyst because of its high activity, photo-stability and availability. TiO_2 exists in three principal crystallographic forms (anatase, brookite and rutile [8]) but only the anatase and rutile form are photocatalytically active. A key technology for the practical application of photocatalysis to environmental problems is the immobilization of TiO_2 as thin film on a solid substrate because this allows an operation without a nanoscopic filtration system for the recovery of the catalyst, since such systems are difficult to assemble and a have a high cost. TiO_2 can be deposited on suitable substrates such as silica, soda lime and Pyrex glasses, Quartz, Si wafers, stainless steel, etc. The TiO_2 films have found applications in photocatalysis, protective anti-reflection coatings, solar cells, lithium batteries and sensors [8]. TiO_2 films have been often prepared by expensive methods as pulsed laser deposition, reactive evaporation and chemical vapor deposition [7]. Low cost preparation methods are the sol-gel processes including dip or spin-coating as the final step of preparation. Furthermore, the interest in the use of sol-gel method is due to other advantages: good homogeneity, ease of composition control, low processing temperature and good optical properties. In particular, the sol-gel processes is efficient in producing thin, transparent, multicomponent oxide layers of many compositions on various substrates, including glass [9].

The photocatalytic activity of Titanium Dioxide thick films on porous stones was evaluated by using the photocatalytic degradation of Triclosan or Irgasan, an Emerging Concern Pollutant belonging to the Endocrine Disrupting Compounds (EDC). Irgasan, 5-chloro-2-(2, 4-dichlorophenoxy) phenol, was elected as the contaminant to degrade because it is widely used all around the world in common life products., like deodorants, soaps, creams, cosmetics, sun cream, and as an additive on plastics that gives them the property to be anti-bacterial. The term EDC refers to any chemical compound that, once incorporated into an organism, interferes with the endocrine system, somehow altering or disrupting the normal functions of this system. This is to say that it affects the hormonal balance, both qualitatively and quantitatively [10, 11]. Triclosan is presented in Fig. 1.

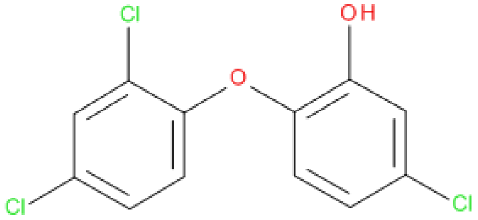

Fig. 1. Triclosan molecule.

Triclosan molecule is not polar because of the symmetrical arrangement of Cl and OH ions (Fig. 1), what causes a very low solubility in water; despite this fact, Triclosan has been found in water and wastewater in several places and samples: river water, drinking water, wastewater, soils, and human bodies [14, 15].

Tezontle is a mesoporous volcanic stone widely present in Mexico. It can be either red or black-colored, in agreement on its chemical composition. Its main composition is SiO_2, and Fe, Na and Ca compounds. It is chemically stable and mechanically resistant. Abrasive forces can easily damage its structure. Then, Tezontle can be used on fixed bed reactors, but it cannot be proposed as an element on expanded or mobile bed reactors, either biological or physicochemical. The deposition of TiO_2 on Tezontle is considered advantageous over flat supports for films because this stone might increase the porosity of Titania films.

2. Materials and Methods

Chemicals: Titanium ter-butoxide (Reagent grade, 97 %), Acetyl Acetone (Reagent Plus, >99 %), ethanol (Absolute grade), isopropanol (Analytical grade), tetraethyl ortho silicate (Reagent grade, 98%) were bought to Sigma Aldrich and used without any further purification. Concentrated Hydrochloric acid (Reagent grade, 36 %) was from Backer. Triclosan was from Fluka (Irgasan, Reagent grade). Red and porous Tezontle was from a non-technical grade since it is widely distributed as a construction material on Civil Engineering. Aqueous solutions of Triclosan were done in a solution of ethanol in water (10 % v/v). Ethanol is an organic molecule that competes with Triclosan for active sites of the Catalyst. Despite this, absorbance of ethanol does not overlap with Triclosan.

Thick TiO_2 films on porous Tezontle stones. Tezontle stones were selected by average size by a grid set, what allowed selecting stones with aerodynamic diameter between 7 and 9.8 mm. The average size of selected stones is 1 cm. Tezontle raw stones were washed with distillated water, rinsed and dried (105 °C, 2 hours); then, they were covered by 1 SiO_2 layers by the sol – gel method [12, 13] at 400° C during 4 hours (Sola Basic – Lindberg oven). Once films were cool, the stones were covered by 3 TiO_2 layers, each one sintered at 605° C and 3 hours. The molar ratios of the precursors are: 1:50 : 0.5 (tetraethyl orthosilicate : ethanol : hydrochloric acid) and 1 : 62.5 : 0.06 : 0.04 : 8.8 (titanium terbutoxide : ethanol : acetylacetone : hydro¬chloric acid : water).

Photocatalytic reactors. There were 2 photocatalytic reactors for this works. The first one (Fig. 2), used for the preliminary bench tests, consisted on a Pyrex pipe (external diameter: 25 mm; wall thickness: 1.5 mm) thermo-molded to a U shape (30 cm long), and placed inside a CPC reactor (Concentration ratio, C = 1). The linear part of the U shaped pipe was filled with TiO_2 covered stones, and a fine grid was used to retain them inside. This reactor was placed inside a Solar simulator (Atlas X++, Atlas Corp.) and operated in batch mode. Triclosan solution was pumped (Little Giant, P-AAA submergible pump, 2.4 L/min for actual operation) from a small reservoir to the CPC collector (Total water volume: 1 L; irradiated volume: 0.081 L, residence time in CPC reactor: 2 seconds, CPC collector area: 0.05 m^2, stones porosity: 70 %). The second reactor was a CPC collector that held 5 Pyrex pipes (1900 mm long; external diameter: 22.22 mm; wall thickness: 1.5 mm) connected in series. This pilot scale CPC photocatalytic reactor was packed with 2.4 kg of covered TiO2 stones that were distributed only inside the Pyrex pipes. A pump had water flowing from a holding tank trough reactor cyclically. Total water volume is 21 L, the irradiated water volume is 2.09 L, and CPC collector aperture area is 1.71 m^2 (Fig. 3).

Fig. 2. Bench scale photocatalytic reactor.

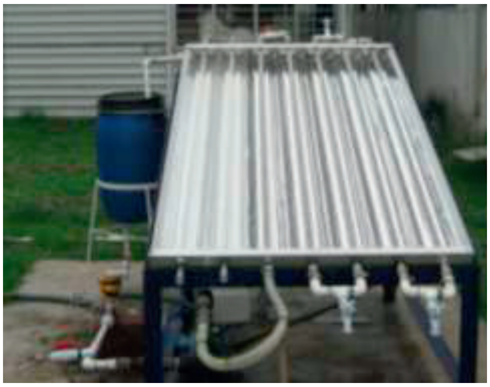

Fig. 3. Pilot scale photocatalytic reactor

Automatic acquisition of experimental data. Special software for acquiring data was developed on LabView platform. It integrates and records temperatures at inlet and outlet ports, flow, pressures (inlet and outlet) during the desired time and time intervals. The acquired data are converted to MS Excel format (.xls) and stored.

Pressure, flow and temperature were measured and converted to a signal that could be read and stored on a PC. For this goal, temperature sensors, Pressure transducers and a magnetic flow meter were linked to a National Instrument acquisition card (NI-USB-6216, 16 channels on analogue mode, 16 channels on digital mode). The data acquisition process was programmed with LabView software. For these experiments, surface temperature was not recorded. The signals produced by sensors and transducers are derived, first, to a block of low – pass filters in order to suppress frequencies of electrical noise. After, signals were sent to the acquisition cards (analogue mode), then to the PC with the help of the PC program. Once data were received by PC, they were stored.

3. Results

3.1 The catalyst

The porous stones that were covered by TiO_2 precursor conforms a very porous film (Fig. 4). Here, it is evident that Tezontle continues being a material with very high porosity when the TiO_2 film was deposited. This high porosity increases surface area of the films, what leads to have higher photocatalytic oxidation rates and efficiencies than smooth catalysts.

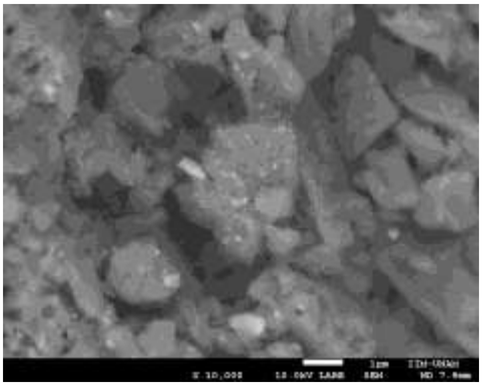

Fig. 4. FESEM image of a porous Tezontle stone covered by 3 TiO_2 layers.

3.2 Photocatalytic oxidation of Triclosan.

The bench scale photocatalytic reactor presented a good performance. Table 1 resumes the efficiencies for 2 sets of tests: the first one, with a fixed initial concentration of sodium persulfate and acidic, neutral and basic initial pH; the second, with neutral pH, and 3 different concentrations of persulfate. For all these tests, 30 W/m^2 was set as the UVA irradiance at the solar simulator.

Persulfate additions at the beginning of the tests increased removal efficiencies up to a limit of 59 % at neutral pH. When persulfate is not used, PCO efficiency dropped to 33.7 %. Then, persulfate did the difference on efficiencies but it becomes a water pollutant on treated water. Despite this, its usage is advantageous and, on several countries, sulfates are not considered on water discharges laws, then sulfates can be present on treated water at low concentrations.

Table 1. PCO of Triclosan with bench scale reactor

Fixed parameters	Independent variables	Triclosan removal (%)
Initial persulfate: 0.001 M	pH = 5	65.9
	pH = 7	58.5
	pH = 9	74.7
Initial pH: 7	$S_2O_7^{2-}$: 0 M	33.7
	$S_2O_7^{2-}$: 0.001 M	58.5
	$S_2O_7^{2-}$: 0.0001 M	59.0

3.3 Pilot scale photocatalytic reactor

With the CPC pilot reactor, 3 sets of tests were done, each by duplicate. In this case, persulfate was not used and initial pH was set neutral. Insolation times ranged from 1.5 to 2 hours. Main results are presented in Table 2.

Reaction kinetics is presented on Fig. 5 for solar PCO experiments. When time is used as a reference, the effect of variations on irradiance is not taken into account; on the other hand, it is much simpler to measure time than UV irradiance.

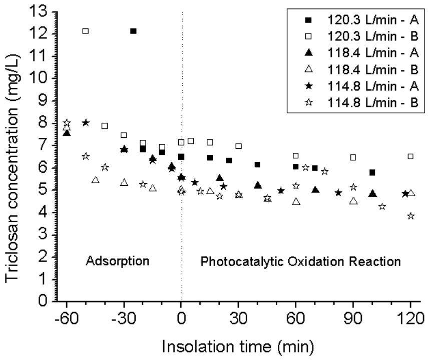

Fig. 5. Kinetics of solar PCO of Triclosan

Pressure drops on CPC pipes were determined and they are presented as relative pressure drop (pressure drop divided by initial pressure). It is presented on Fig. 6.

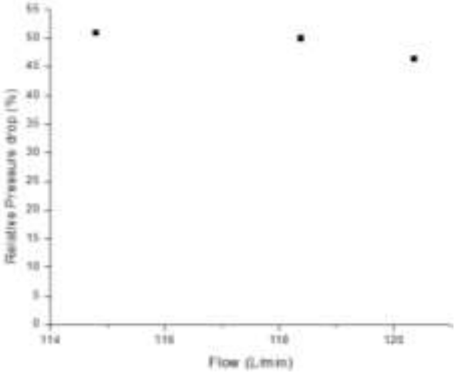

Figure 6. Relative pressure drop inside the CPC pipes packed with Tezontle

Table 2. PCO of Triclosan with CPC pilot scale reactor under sunlight.

Recirculation flow (L/min)	Initial Triclosan concentration (mg/L)	Average Triclosan removal, (%)
114.80	12.12	50.50
118.37	7.55	35.89
120.36	8.03	39.00

4. Conclusions

- Porous Tezontle stones were effectively covered with TiO_2 by Sol – gel method, with high adherence and homogeneity.
- TiO_2 particles on the thick films were nanosized and porous, mainly due to the high porosity of the stones.
- Tezontle porous structure is kept after sintering the thick TiO_2 layer, what allows reactors to work with important surface areas of supporting materials.
- The conditions for sintering the films were adequate to produce particles whose main crystalline phase is anatase, and the second, rutile; this phase combination is photocatalytically active.
- Tezontle stones were used as packing media on a CPC photocatalytic reactor, which removed Triclosan effectively.
- Triclosan was removed by a TiO_2 solar photocatalytic reactor, with Tezontle as immobilization media, with efficiencies up to 74 % when persulfate is used as a stronger electron acceptor.
- Pressure drop on Tezontle porous media is important and size of stones has to be modified in order to reduce pressure drop and pumping costs.

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