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Electrochemical enhanced photocatalysis to the 2,4,6 Tribromophenol flame retardant degradation

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ABSTRACT

This study investigates the photoassisted processes, namely direct photolysis (DP), heterogeneous photocatalysis (HP) and photoelectrolysis (PEC), in 2,4,6-Tribromophenol (TBP) abatement, mineralization and debromination. Electric energy per order (E_{EO}), degradation kinetic (k'), half-life time ($t_{1/2}$) and toxicity were also evaluated. The results showed that the direct photolysis process is an important TBP debromination and oxidation pathway. However, the DP process leads to higher by-product formation, presenting phytotoxicity and genotoxicity. The hydroxyl radical based processes (HP and PEC) showed higher mineralization and also decreased toxicity. This indicates that hydroxyl radicals based processes represent a chief route for diminishing the overall environmental impact of TBP.

1. Introduction

Many synthesized compounds are used nowadays as flame retardant in consumer products. In fact, these substances are incorporated in materials used in common household items such as computers, electronic devices, polyurethane foams, textiles and others [1]. Some brominated flame retardants (BFR) are not chemically bound to the plastic or textiles matrix. Therefore, they may spread out or leach from their product applications into the environment [2]. Organobromine might pose high risks to both humans and wildlife, since BFR are persistent and may accumulate in the environment. In fact, numerous research reports have indicated high levels of BFR not only in water, atmosphere, indoor air, soil and sewage sludge, but also in tissue, blood and milk in humans [3,4] and wildlife [5,6]. Chronic effects and endocrine disrupting activity provided evidence for estrogenic and androgenic features [7], immunotoxicity, thyroid function disruption [8], behavioral modification and gastrointestinal lesions [2].

One of the most common substances applied as flame retardant is the 2,4,6-Tribromophenol (TBP), currently used as an antiseptic and germicidal agent, a fungicide in wood treatment processes and a monomer for the synthesis of other substances. In addition, TBP is also generated by the photolytic degradation of some BFR [9]. Although most BFR present anthropogenic origin, bromophenols were found to be biosynthesized in marine biota [10]. Additionally, TBP is one of the most volatile flame retardants, being detected in indoor air [11].

Many degradative processes have been studied to reduce the potential pollution and related health issues. The biological degradation is included on these studies. However this process requires long period of treatment and an appropriate bacterial metabolism [12]. Photodecomposition represents a potent mechanism of debromination and elimination of the brominated species in the environment. The UV radiation is capable of interacting with the molecule structure releasing bromine. The photoreactivity of bromophenols rises with the degree of bromination. In this way, the TBP molecule may be debrominated by photodecomposition, but requires a deep UV environment [13], resulting mainly in harmful organic by-products. The stable C–Br bond in bromophenols is responsible for their toxicity and persistence, meaning that, breaking the C–Br bond and debromination are crucial for toxicity reduction. The difficulty to destroy, in environmental conditions, the C–Br in TBP is associated to the strong bond energy of the C–Br bond (349.4 ± 1 0.5 kJ mol^{-1}) [14].

Advanced oxidation process (AOP) is a method of organic contaminant degradation, which involves generation and interaction among the transitional radical species, especially hydroxyl radical ($HO^{\cdot}$). The $HO^{\cdot}$ has a high oxidative potential, enabling mineraliza-

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tion. The photocatalytic process is one of the most promising technologies for abatement of contaminants of emerging concern. They promote a high degradation rate and a non-selective oxidation, even to recalcitrant compounds.

Although some studies reported an effective abatement and debromination of TBP by heterogeneous photocatalysis (HP) over Fe-doped $ZnIn_2S_4$ [14], much less information is available concerning the portion degraded by direct photolysis (DP). Gao et al. [14] showed that 95% TBP was removed by Fe-$ZnIn_2S_4$ under visible irradiation, but the debromination efficiency was low. The results did not meet the intended purpose of decreasing the toxicity of TBP, by destroying the C–Br bond and also by reducing the generation of toxic by-products [15]. In fact, debromination and mineralization are important mechanisms, and both should be efficient to reduce the toxicity.

The high degree of recombination of photogenerated electrons and holes (e^-/h^+), causing a low photocatalytic activity, limits the application of a single semiconductor photocatalyst. When a higher mineralization rate is demanded, the employment of a doped catalyst and the application of a current density between electrodes are important processes that can result in complementary phenomena [16]. The photoactive catalyst may be a thin doped-layer-coating on a conductive support, resulting in less recombination of the photogenerated pairs e^-/h^+, with a consequent improvement in photocatalytic activity [17,18]. Besides, the HP may be electrochemically assisted, resulting in a photoelectrolysis (PEC) process. PEC have been studied to the degradation of organic contaminants, presenting effective results [19].

This work is focused on the verification and comparison of three photoassisted methods (DP, HP and PEC) aiming at TBP removal, mineralization and debromination. The DP, HP and PEC processes were separately evaluated, providing important information about complementary and synergic phenomena. For comparison purposes, electric energy per order (E_{EO}), degradation kinetic (k') and half-life time ($t_{1/2}$) were also evaluated, as well as the phytotoxicity and genotoxicity to the *Lactuca sativa* (lettuce) and *Allium cepa* (onion) organisms.

2. Experiments

2.1. Solution

The standard solution was prepared diluting 120 mg of 2,4,6-Tribromophenol (TBP) (Sigma Aldrich, 99%) in 2 L of distilled and deionized water. The pH was adjusted in 8 because the TBP is more water soluble in alkaline conditions [15]. Background solution was prepared adding 1 g L^{-1} of sodium sulfate (Na_2SO_4) (Sinthy, 99%) in distilled and deionized water. Initial solutions used in the experiments were prepared diluting 420 mL of standard solution in the background solution to a final volume of 5 L and final TBP concentration of 5 mg L^{-1}.

2.2. Catalysts

Two materials were used as catalysts. One (Fig. 1a) was a commercial mesh (rhomboid open area: 9 × 2 mm), prepared by thermal decomposition of titanium doped with ruthenium by De Nora do Brazil®, with a surface geometrical area of 475.2 cm^2. The other one (Fig. 1b) was a commercial TiO_2-Ti mesh (rhomboid open area: 23.5 × 10.5 mm), prepared by thermal decomposition of titanium by De Nora do Brazil®, with a surface geometrical area of 118 cm^2.

2.3. Reactional systems

The reactor used in the trials was a jacket borosilicate glass reactor with a capacity of 2 L connected to a 5 L reservoir. The reactor is connected to an ultra-thermostatic bath to keep at room temperature. 5 L of the initial solution was placed in the reservoir that feeds the reactor at an average flow rate of 1 L min^{-1} with the aid of a peristaltic pump.

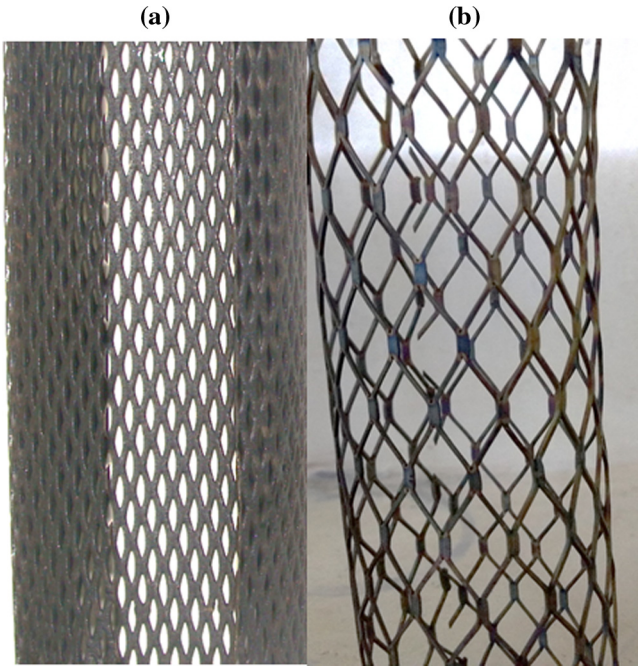

Fig. 1. Catalysts employed in HP and PEC processes. (a) (70%)TiO_2(30%)RuO_2-Ti and (b) TiO_2-Ti.

A first set of experiments, namely Heterogeneous Photocatalysis (HP), was achieved by irradiating the two catalysts with a 250 W high-pressure mercury vapor lamp (HPL-N) [20] without the glass bulb and inside a quartz tube. The catalysts were placed concentrically around the lamp, with a 5 mm gap provided by three rubber rings. The experimental set-up is shown in Fig. 2a.

A second set of experiments was performed aiming to enhance the HP process. A current density of 5 mA cm^{-2} (CEL P-6000) was applied between the catalysts. In these cases the (70%)TiO_2(30%)-RuO_2-Ti acts as anode, while TiO_2-Ti acts as cathode. The experimental set-up of Photoelectrolysis (PEC) is presented in Fig. 2b.

A third set of experiments was performed by irradiating the initial solution with the 250 W HPL-N lamp in the absence of both catalysts in order to establish the existence or not of a Direct Photolysis (DP) effect on the TBP. The experimental set-up is represented in Fig. 2c.

All experiments were repeated three times. The samples were collected at different treatment times until 140 min.

2.4. Analysis

2.4.1. Voltammetry experiments

Cyclic Voltammetry measurements were obtained using a conventional three-electrode cell in conjunction with a computer-controlled potentiostat/galvanostat Auto lab model PGCTAT 302N. (70%)TiO_2(30%)RuO_2-Ti with surface geometric area of 0.2 cm^2 was used as the working electrode, Ag/AgCl (saturated) as a reference electrode and platinum as the counter electrode.

2.4.2. UV irradiation

First, the photometric data of the 250 W HPL-N lamp in UV-C spectra were characterized using a spectrophotometer Princeton Acton Spectra Pro 2300 coupled to a photomultiplier. Then, the irradiance (E_e, in W m^{-2}) on the catalyst surface was measured by an Instrutherm MRUR-203 UV-C light meter, when background