

# PACKED-BED ELECTROCHEMICAL REACTOR FOR BIO-REFRACTORY ORGANICS DEGRADATION

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*Summary:* The production of oxidizing agents (mainly OH\* radicals) by heterogeneous reaction between a semiconductor and water under a superimposed electric field was assessed in a packed-bed electrochemical reactor. The performance was comparable with other advanced oxidation reactors, from both the abatement kinetics and energy consumption points of view, with no formation of chlorinated intermediates. The rate of radicals generation was found to depend on several factors: imposed current, electric field intensity and electrical resistivity of the phases involved. The innovative electro-oxidative treatment proposed seems to be particularly suitable for low conductivity solutions with low concentration of non-biodegradable toxic pollutants.

*Keywords:* Electrooxidation, bipolar electrode, tin oxide, waste water, pharmaceutical compounds

## Introduction

Electro-oxidative treatments have shown promise as environmental friendly and economically viable methods for the abatement of hardly-biodegradable organic molecules<sup>1</sup> and the disinfection<sup>2</sup> of some industrial waste waters (e.g. pharmaceutical industry).

The present communication concerns an innovative concept based on a electrochemical reactor where the possibility to produce oxidizing agents from water (mainly OH\* radicals) by heterogeneous catalytic reaction between a semiconductor and water under a superimposed electric field was assessed for the degradation of non biodegradable toxic organic compounds.

The superimposed potential gradient may induce ionization of the dissolved organic molecules, which may then interact either with the solvent or with the semiconductor surfaces. The electrolysis current that crosses the cell is divided into an ionic current passing through the electrolyte and an electronic current passing through porous mass<sup>3</sup>. These active surfaces hold superficial charges as a consequence of the occurrence of electrochemical reactions that take place at the metal oxide surfaces. The oxidizing agents are indeed formed at the interface between the semiconductor and the treated solution, where the interaction of the polarized surface and water generate high-energy "electron-initiated" chemical species (radical and ionic)<sup>4</sup> which may react with adsorbed organic species or diffuse into the aqueous phase and react with dissolved organics as in the case of photocatalysis<sup>5</sup>.

As a peculiar feature of this new electro-oxidative reactor, the energy required for OH\* generation comes from a superimposed electric field. This method may indeed provide alternative pathways, nearly equivalent from the energetic viewpoint, to the creation of oxidizing species compared to the more conventional photochemical oxidation process.

## Experimental

The reactor was made of acrylic where the semiconductor packed bed was disposed. The semiconductor was obtained by means of a thermal treatment of titanium sponges by Aldrich (particles radius: 2 to 12 mm) that are characterized by a high micro-porosity (50%) covered by a precursor solution of Sn and Sb chlorides, in order to obtain a deposit of SnO<sub>2</sub> doped by Sb oxides. The pore diameter distribution (200–1000 nm) exceeds the limiting diffusion layer thickness and promotes a good mass transfer and continuous ionic diffusion within the mass. The optimal thermal treatment for the generation of superficial oxides was found to be 5 h at 500 °C under slight air flow. XRD analysis confirmed the formation of a thin and highly crystalline layer.

The residual concentration of organics was analyzed during the electro-oxidation runs by means of UV–vis spectrophotometry on samples periodically withdrawn. The chemical oxygen demand (C.O.D.) was conversely measured with the standard digestion method. The hydrogen peroxide concentration in the bulk of the treated solution was monitored using iodometric titration.

## Result and discussions

The results obtained treating pharmaceutical compounds containing solutions (Diclofenac, Gemfibrozil, Carbamazepine, Sulfamethoxazole, Sotalol and Ranitidine) show a specific pollutant abatement per unit power about 2.5 g/kWh when starting from a concentration of 50 to 100 ppm, a comparable figure to those obtainable with the best direct anodic electro-oxidation processes with the advantage that chlorine is not produced when chloride salt is naturally contained in the treated solution, avoiding the risk of chloro-organics compounds synthesis as in the case of mediated

electrooxidation process<sup>6</sup>.

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