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Bio-refractory organics degradation over semiconductor foam under a superimposed electric field

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Abstract

The production of oxidizing agents (mainly $OH^\bullet$ radicals) by heterogeneous catalytic reaction between a semiconductor and water under a superimposed electric field was assessed in a three-compartment electrochemical cell for the abatement of non-biodegradable toxic organic compounds. The performance of a batch-operated reactor was comparable with other advanced oxidation reactors, from both the abatement kinetics and energy consumption points of view, with no formation of chlorinated intermediates in the presence of chloride ions. 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 pollutants.

Keywords: Electrochemical reactor; Hydroxyl radicals; Hydrogen peroxide; Metal oxide semiconductor; Ranitidine spin-trap

1. Introduction

Electrochemical oxidation was proved to be an environmental friendly and economically viable abatement method for bio-refractory organics molecules [1,2] as well as for the disinfection of waste waters [3].

In the direct electro-oxidation process strong oxidants are generated from the dissociative adsorption of water over anodic surfaces: superior oxides MO_{x+1} in the case of conductive metal oxide anodes and hydroxyl radicals $OH^\bullet$ in the case of semiconductor anodes. Afterwards, organic molecules react with these oxidants at the electrode surface.

In indirect, or mediated, electro-oxidation the abatement kinetics are generally enhanced by the occurrence of homogeneous oxidation pathways promoted by oxidizing species (persulphates, hydrogen peroxide, ...) which are generated over the anode and get dissolved in the solution. Particularly, in the presence of chloride ions, very frequent in waste waters, the generation of hypochlorous ions is rather easy. This generally brings about the oxidation of organic molecules to chloro-organic compounds [4], whose discharge limits in surface water basins are often even more restrictive than original pollutant molecules.

The present investigation is aimed at developing an electrochemical system for producing radicals able to oxidize organic pollutants and simultaneously avoid the generation of hypochlorous ions.

A three-compartment electrochemical cell configuration was adopted for this purpose, where the treated solution, fed to the central compartment, does not get in contact with the electrodes.

In the central compartment a semiconductor porous mass is placed, to occupy the great majority of the compartment volume. This mass, when the current is fed to the cell becomes charged and acts as bipolar electrode. This kind of electrode configuration has found some important applications in industry as: the manufacture of sodium chlorate, recovery of ions, electrosynthesis, electrowinning, etc. [5–11]. Pletcher [12] pointed out that in addition to the simplicity of electrical connection, the bipolar cell has the advantage that it produces the equivalent amount of reacted matter to monopolar cell using a lower current and a higher voltage, since the current is used many time and this can be more economic way of using power.

In the three-compartment cell described in details in the next section, the electrolysis current (I), that crosses the central compartment, is divided in an ionic current (i_i) passing thought the electrolyte and an electronic current (i_e) passing thought

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porous mass. In porous bipolar electrodes this last current contribution is generally of low intensity and just sufficient to compensate the de-polarization actions of the environment [13,14]. In particular, the current in a semiconductor materials is due to migration of generated positive "hole" (h^+) at the valence band and electron (e^-) in the conduction band. Both current carriers can modify the polarization state of adsorbed water for which semiconductor surfaces exhibit a strong interaction. This leads to electronic excitation of water molecules that dissociate into radicals [15], which eventually can react with dissolved organics or generate secondary oxidizing agents.

2. Experimental

2.1. Electrochemical cell configuration and experimental procedures

The three-compartment electrochemical cell employed in this investigation is depicted in Fig. 1.

A 1 kg porous titania sponge was located in the central compartment and kept separated from the anodic and cathodic compartments by means of perm-selective ionic membranes in order to avoid any mixing between the treated solution (1 l in the central compartment) and the electrode rinse solutions. The titania porous mass 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%). The pore diameter distribution (200–1000 μm) 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 titanium oxide was found to be 5 h at 500 °C under slight air flow. XRD analysis confirmed the formation of a thin and highly crystalline anatase layer.

In a second sponge, deposits of two different metals (Sn and Cu) were placed onto the titanium sponge surface to verify the influence of varying the free carrier density in the activity of the semiconductor surface. The deposition of Sn and subsequent oxidation to obtain the oxide (SnO_2) was accomplished via a technique described in the literature [16]. The titanium foam was rapidly taken out of the packaging (to minimize the self-oxidation with air) completely immersed in an isopropyl alcohol solution containing $SnCl_4{\cdot}5H_2O + SbCl_3$ (0.1 and 0.01%, w/w, respectively of the titanium foam substrate). Some drops of hydrochloric acid were added to the solution. All reagents were purchased from Aldrich. The alcohol was slowly evaporated by heating it in air at 80 °C to allow progressive metals absorption onto the foam substrate. A second thermal process was then accomplished at 500 °C in an electric oven with forced air flow for the formation of the surface titanium oxide and SnO_2 crystals (n-type semiconductor). An analogous parallel procedure was followed for the deposition of copper, where the coating solution consist in a dissolved CuCl (final target: 0.1%, w/w, of the titanium foam substrate) in slightly acidified isopropyl alcohol. A second heat treatment at 500 °C lead to the formation of mix of cuprous oxides Cu_xO crystals ($x = 1$ or 2 p-type semiconductors).

The other prevalent cell features are listed hereafter:

- The housing was made of plexiglas.
- The electrodes were an iridium–tantalum mixed oxides deposited on titanium anode (DSA® electrode from DeNora, Italy) and a stainless steel cathode.

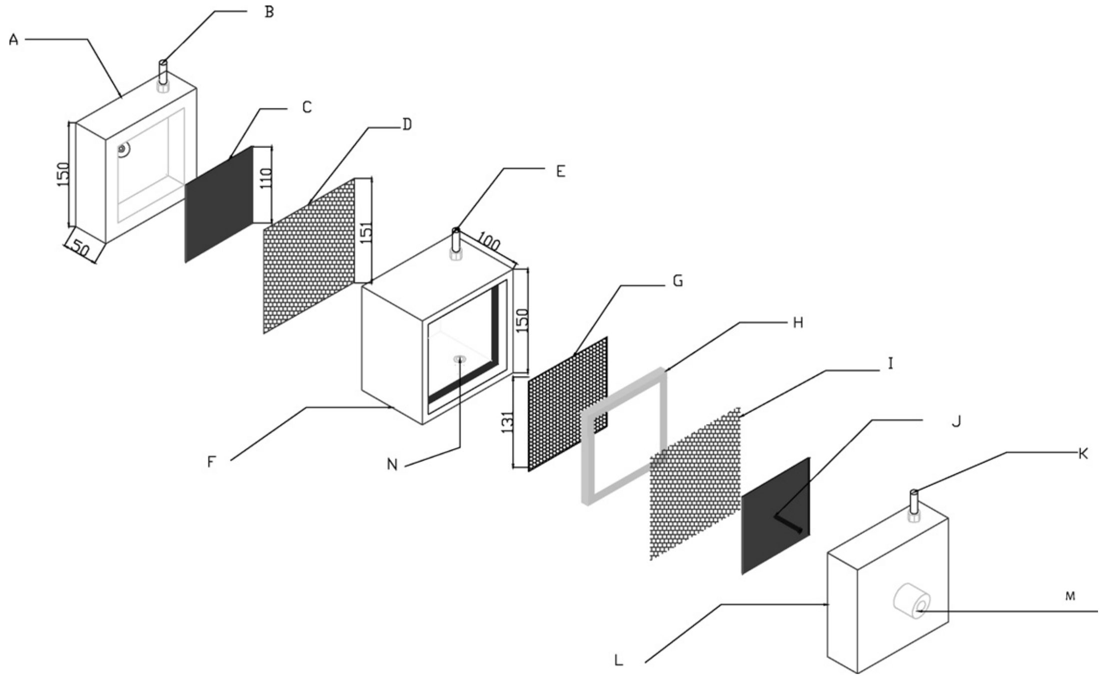

Fig. 1. Three-compartment electrochemical cell, operating in batch mode. Legend: (A) anode chamber; (B) oxygen outlet; (C) anode; (D) cationic membrane; (E) gas exit; (F) central chamber, containing the titania sponge; (N) oxygen inlet; (G) plastic grid for porous mass support in the assemblage stage; (H) support of plastic grid; (I) anionic membrane; (J) cathode; (K) hydrogen outlet; (L) cathodic chamber; (M) connection to a power supply (all dimensions are in millimetres).