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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.

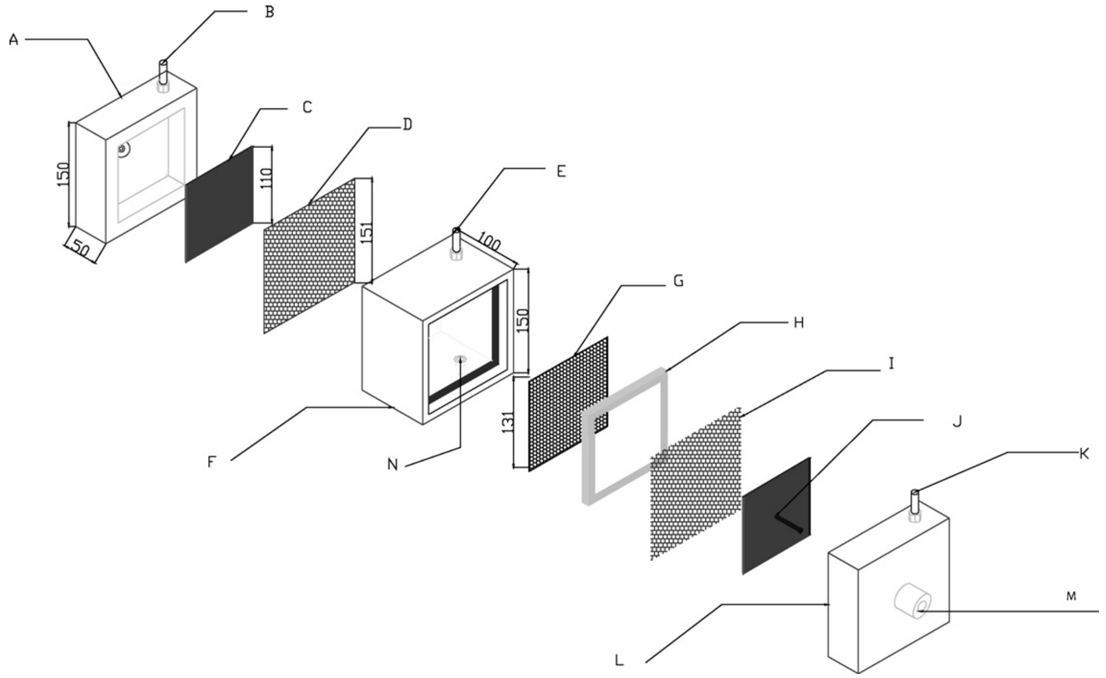

Fig. 1. Three-compartment electrochemical cell, operating in batch mode. Legend: (A) anode chamber; (B) oxygen outlet; (C) anode; (D) cationic membrane; (E) gas exit; (F) central chamber, containing the titania sponge; (N) oxygen inlet; (G) plastic grid for porous mass support in the assemblage stage; (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).

- The perm-selective *Neosepta* membranes (Tokuyama Soda, Japan), anionic (AFN) and cationic (ACS): exchange capacity (meq g^{-1}) = 1.5–2.5; average specific electrical resistance ($\Omega\ m^2$) = 2.0×10^{-4}; thickness (mm) = 0.15–0.20.
- The used power supply by *Eutron* (Italy) BV140; operational ranges: 0–100 V, 0–1 A.

The membranes were located in inverse order with respect to a dialysis cell. As a consequence, neither the inorganic nor the organic ionic species could get into the anodic or cathodic chambers from the treated solution, whereas ionic species (e.g. H^+, OH^-) could reach the treated solution in the central compartment from the electrode compartments. Additionally, the central compartment was saturated with oxygen recycled from the anodic chamber to boost the oxidation process. Conversely, the other product of electrolysis, pure hydrogen, might eventually be stored.

The cell was operated batch-wise with no stirring of the central compartment, under galvanostatic conditions. The temperature of the anolyte and catholyte was controlled by continuous flow of the corresponding rinse solution cooled outside the cell in a rinse tank. A concentrated Na_2SO_4 solution (10 g l^{-1}) was used both as anolyte and catholyte in order to minimize the Ohmic losses. The operating temperature range was 25–30 °C. Synthetic organics solutions were prepared by using pure grade (Aldrich) phenol, "Reactive Blue-4" (1-amino-4-[3-(4,6-dichlorotriazin-2-ylamino)-4-sulphophenyl-amino] anthraquinone-2-sulphonic acid), and ranitidine hydrochloride (*N*-(2-{[5-(dimethylamino)methyl]-2-furanyl}-methylthioethyl)-*N*′-methyl-2-nitro-1,1′-ethane diamine·HCl) and in distilled water, with addition of sodium sulphate or chloride (Fluka) as electrolytes. Each of these organics was selected to prove specific features of the proposed reactor: discolouration, C.O.D. abatement, specific reaction mechanism, respectively. The oxidation runs were carried out independently for each target pollutant in a supporting electrolyte.

The residual concentration of organics was analyzed during the electro-oxidation runs by means of UV–vis spectrophotometry (CARY 500 Scan single ray spectrophotometer) 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. Finally, the determination of the colour index was performed via the Orbeco-Hellige water analysis system (model 975-MP).

3. Results and discussion

The colour intensity is indeed a preliminary and easy-to-follow parameter to assess the level of conversion of some organics. A bio-refractory dye molecule was actually tested for this purpose, characterized by an intense colour even in very diluted solutions (order of magnitude of ppm): Reactive Blue-4.

The progressive decay of the colour of the solution (Fig. 2) can be provisionally related with the decay of concentration of the original molecule. The contribution of the decolouration due to absorption on the porous mass can be eliminated by a previous saturation of the material with the solution itself.

The behaviour of the colour index (inlet graph in Fig. 2) corresponds to the behaviour of the absorption peak during electrolysis.

The observed non-linearity of the decay is related to different factors such as: diffusion limitations, order of reaction higher than 1, the variation of the ionic strength of the solution (and corresponding conductivity) during the electrolysis. In particular, the variation of the electric resistance of the solution is due to the continuous income of ions from cathode and anode chambers, which is in turn responsible for the decay in the cell potential during the runs. At the end of runs the pH value of the treated solution is equal to the starting value, even if a considerable gradient of ions (H^+, OH^-) thoughout the reactor during the electrolysis is to be expected. The control of the temperature (carried out by means of indirect cooling of the anolyte and catholyte solutions) was mandatory for the stability of the anionic membrane that showed rapid degradation at temperatures higher than 35 °C. This correspond to an evidence of significant radicals generation which may easily react with polymers [17] as membranes.

A determination of the mineralization of carbon towards CO_2 was also carried out in the system by monitoring the C.O.D. parameter (Fig. 3) for the case of phenol solution. From the plotted data, an average energetic consumption for mineralization of 40 g C.O.D. l^{-1}/kWh could be estimated based on the first hour of treatment.

The fall of cell potential (inner graph in Fig. 3) is due to the decrease of the electrical resistance in the central chamber, deriving from the, above-mentioned, continuous inlet of ions from the catholyte and anolyte.

To have a confirmation that the oxidizing agent corresponds to radicals generated from water that react in homogeneous

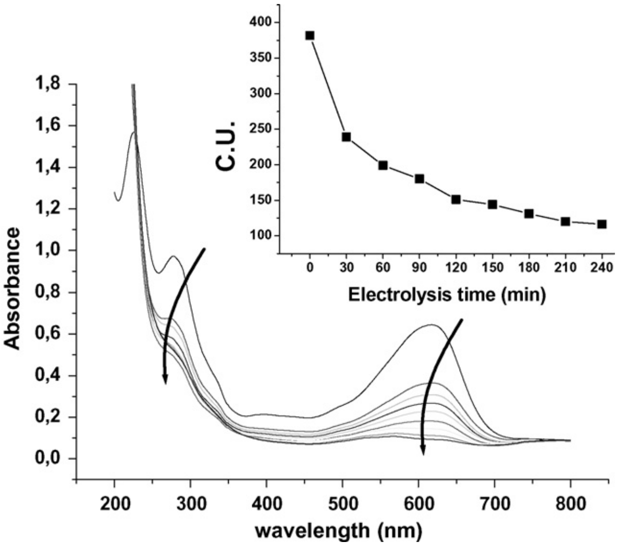

Fig. 2. Spectra of dye Reactive Blue-4 solution with starting concentration of 25 ppmw and sodium sulphate 0.02 N during the electrolysis, the narrow indicates the effect of time; imposed current: 0.25 A. In the small graph the behaviour of the colour of the solution in the Platinum-Cobalt Colour Unit (C.U.) scale for the same run.

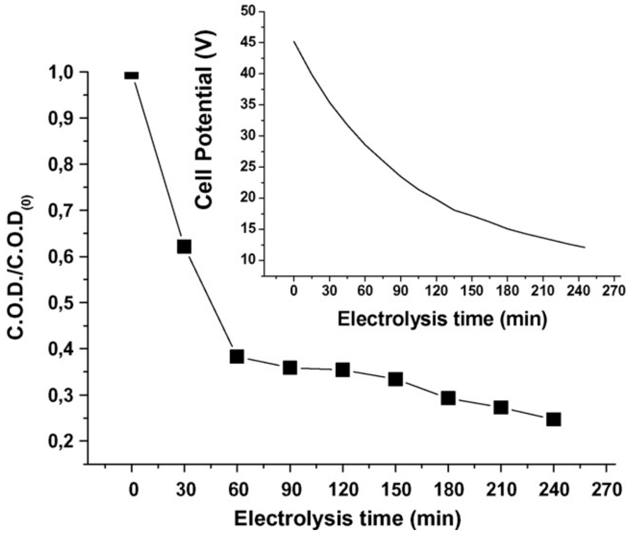

Fig. 3. Normalized behaviour of C.O.D. parameter during electrolysis for Phenol solution with starting concentration equal to 100 ppmw (C.O.D.: 690 mg l^{-1}) and sodium sulphate 0.02 N, imposed current: 0.25 A. In the small graph the corresponding behaviour of cell potential.

phase, a run with organics-free distilled water was performed and the generation of hydrogen peroxide (a common end-process product of chemistry of water radicals) was monitored.

Hydrogen peroxide formation was indeed noticed as plotted in Fig. 4. The behaviour of the concentration of hydrogen peroxide seems to be related to a complex kinetics mechanism conformed for a set of in-series and parallel reactions, mainly between radicals species, that create and react away hydrogen peroxides [18,19].

It is generally accepted that the hydroxyl radicals represent the most important agent in the advanced oxidation processes [20]. To try to determine the hydroxyl radicals generation in the reactor, a spin-trap was used. For this purpose, runs with distilled water in presence of the antacid drug ranitidine (Aldrich) were performed.

The selection of this drug is based on one of its distinctive properties. It is indeed used to prevent the stress-induced gastric lesions that are mainly caused by oxidative damage due to hydroxyl radicals, for which ranitidine is very powerful hydroxyl radicals scavenger (as other H_2-receptor antagonist drugs) with a rate constant equal to $7.5 \times 10^9\ M^{-1}\ s^{-1}$ [21]. For this property, ranitidine was also proposed for radio-protective application [22]. In addition, the drug was checked to have much less effective oxidation kinetics with superoxide anions and hydrogen peroxide, that allow minimize the error in the determination of the role of $OH^{\bullet}$ in the oxidation of ranitidine [23]. The results of electrolysis of diluted solution of ranitidine for two different imposed current densities are shown in Fig. 5. Conversely, the corresponding evolution of cell potential is plotted in Fig. 6. From these data it can be concluded that the kinetics of degradation increase with the imposed current density more than linearly, since by increasing the imposed current the electric field is also increased (under galvanostatic conditions) and an effect of the electric field on both the generation of radicals at polarized layer and the polarization state and reactivity of organic molecules is very likely. The enhancement of the electric field also boosts the tendency of

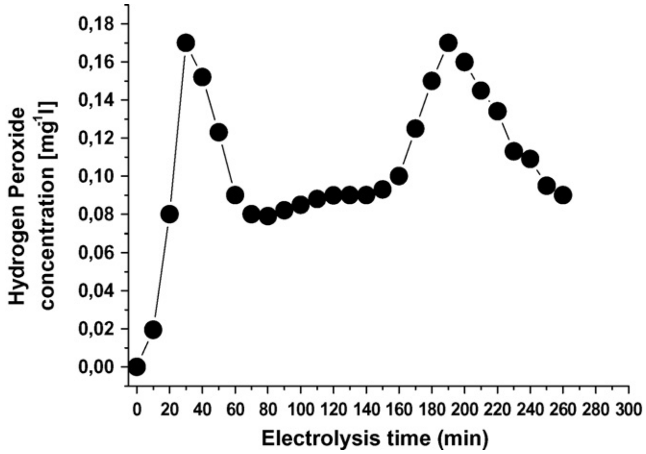

Fig. 4. Concentration evolution of hydrogen peroxide in the cell during electrolysis of distilled water. Imposed current: 0.25 A.

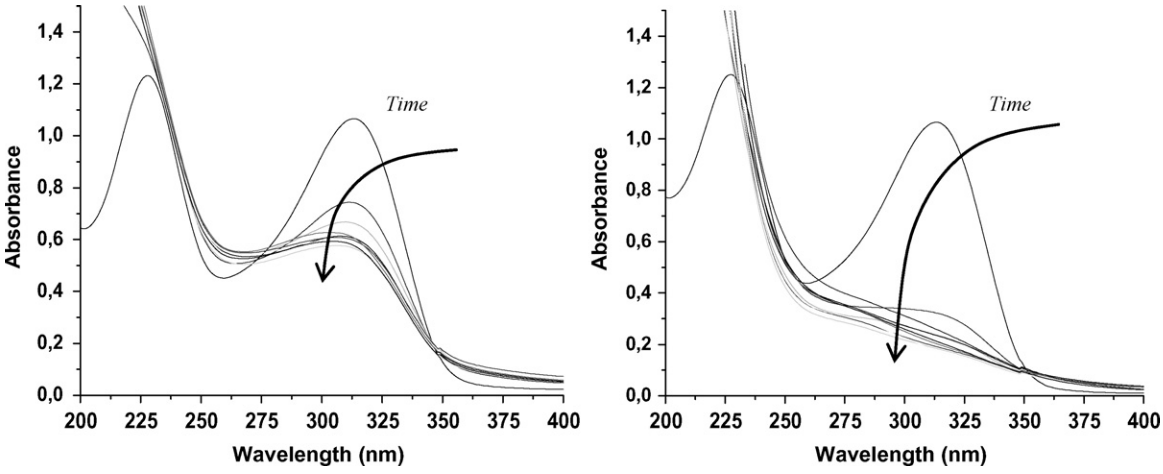

Fig. 5. Spectra of ranitidine hydrochloride solution with starting concentration of 25 ppmw in distilled water during the electrolysis (samples every 20 min); imposed current: 0.25 A at the left and 0.5 A at the right.

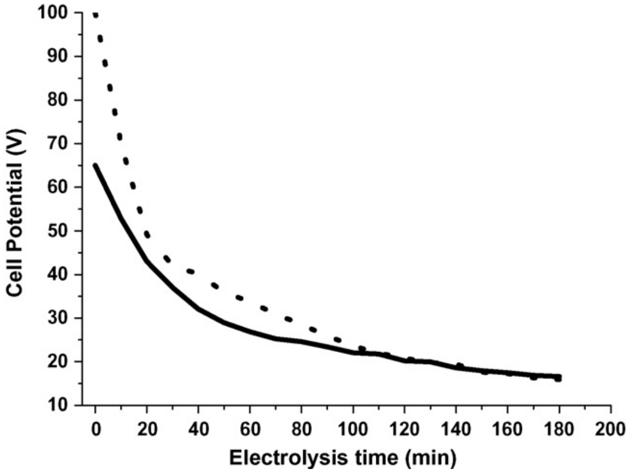

Fig. 6. Cell potential behaviour of runs with ranitidine; imposed current: 0.5 A (doted curve) and 0.25 A (continuous curve).

electrically excited organics molecules to enter the reaction zone, the diffusion layer (electrostriction phenomena [24]).

The primary oxidation products of ranitidine can be various: e.g. ranitidine N-oxide, desmethyl ranitidine and ranitidine S-oxide. Despite this, the electrophilic addition to the furanyl group is expected to be the faster reaction due to π-electron-rich compound properties. The decay of the absorption band at 312 nm can in fact be related to the reaction of $OH^{\bullet}$ with this group as schematized in Fig. 7 [25].

A run performed with a tin- and copper-free anatase-lined Ti sponge were comparable. Tin and copper deposits can just be considered as dopant that allow just a few percent increase in conversion rate (<5% in any case).

As mentioned above, concentrated sodium sulphate was used as both catholyte and anolyte, the perm-selective anionic and cationic membranes permit the passing of sulphate and sodium ions, respectively, together with hydroxyl and hydronium (H_3O^+) ions. To estimate the influence of these ions on the electro-oxidation performance, anolyte and catholyte were changed into sulphuric acid and sodium hydroxide, respectively. The results obtained, not reported here, showed a negligible influence of this factor. This is an expected result since the electrochemical potential involved in the process are considerably below the potential for electrochemical interaction of Na^+ and SO_4^{2-} ions with the electrode surface. By analogy the addition of chloride salt (NaCl) to the treated solution, did not change neither the kinetics of abatement nor the oxidation product. As underlined in Section 1, this is absolutely different from what can be obtained by direct electro-oxidation, where the addition of chloride salt results in boosting the rate of generation of harmful chlorinated organic by-products [26,27].

4. Theoretical considerations

As mentioned in Section 1, the semiconductor porous mass acts as bipolar electrode.

When this material is dipped in water a layer of water dipoles becomes physisorbed spontaneously. Under an imposed electric field these dipoles vary their orientation and consequently their energy. In addition, the passing of the ionic current generates a field of ions, thereby producing a local gradient of charge concentration. The correspondingly generated potential in turn promotes the creation of a de-polarization current over the metallic mass, namely electronic current (i_e), that favours electron transfer from the mass to the accepting species in the solution.

As in other processes for $OH^{\bullet}$ radicals formation from water (generally classified on the grounds of the energy source), the reaction pathway here involves excitation, ionization and dissociation of water.

On these grounds, a likely $OH^{\bullet}$ generation pathway by analogy with the excited water model of Magee [28] is here proposed (Fig. 8).

The main steps of this process are:

a. Passivation of oxides with formation of superficial hydroxyl groups, as a consequence of the strong tendency of oxygen on the surface to react with a neighbouring H_2O molecule.
b. Adsorption of water dipoles (water can actually be considered like hydroxyl ion having a vacant level for a proton).
c. Proton transfer producing excited state of water.

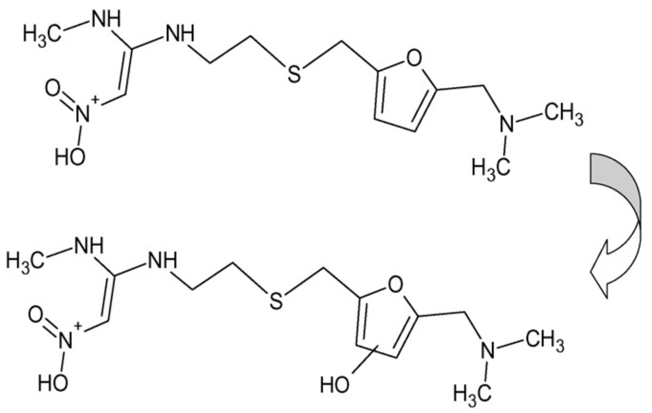

Fig. 7. Scheme of the first oxidation step of ranitidine.

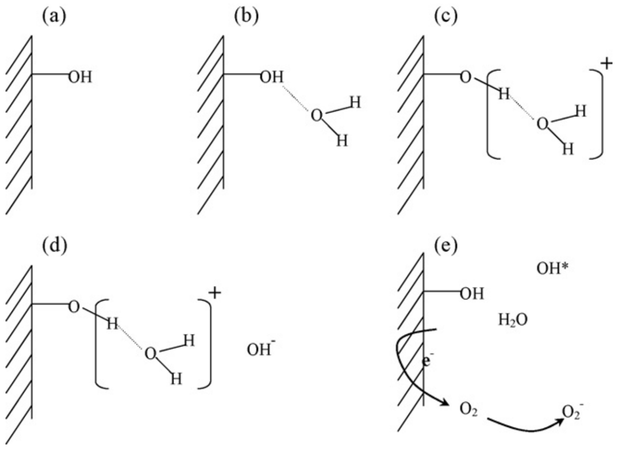

Fig. 8. Simplified scheme of generation of $OH^{\bullet}$ near to the interface.

d. Charge neutralization of the excited state with resonance charge transfer to the substrate and formation of primary hydroxyl radicals; by undergoing this initial reaction the newly formed hydroxyls can take part in a new chain of proton exchange reactions with a neighbouring water molecule.
e. Simultaneous conduction of negative charge through the surface to an acceptor in the solution (H^+, O_2) to complete the electric circuit.
f. Formation of secondary radicals.
g. Reaction of radicals with organics and scavengers.

The scheme in Fig. 8 is simplified since it considers only monomer water at the reactive interface from the different possible model for water clusters that can be assumed to form in adsorption process. The reaction can also involve two water molecules, one of which is remote and provides an H atom whilst the other reacts with the surface. In this case, the redox perturbation is transferred away from the initial site of excitation.

The additional energy required in step 4 can be supplied by the fluctuations of adsorbed water at the solid interface (molecular vibration) like thermal agitation that is likely to break up the whole local structure of water by modifying the state of polarization of the medium surrounding the ions in such way that a transfer process is favoured [29]. This vibration comes from continuous dipole orientation by both the imposed electric field [24] and generated field induced by the ions [30] resulting from the competition among:

(i) the tendency to maximize the number of hydrogen bonds,
(i) the nature of the molecular forces governing adsorption, and
(ii) the electrostatic requirement to minimize surface dipoles.

The whole dissociation process based on charge transfer has a particularly low energy of activation since the dominant kinetic parameter is the availability of a vacant orbital of the solute into which an electron can be transferred, i.e. the presence of electron acceptor like dissolved molecular oxygen [31].

According to the above arguments, the radicals formation rate resulting from the electron-transfer unimolecular reactions (for constant imposed current, electric field and electrical resistivity of the involved phases) can be written as (F is Faraday constant):

$$\frac{\partial[\mathrm{OH}^{\bullet}]}{\partial t} = \frac{\partial[\mathrm{O_2}^{\bullet -}]}{\partial t} = \frac{i_{\mathrm{e}}}{F} = k_0$$

The concentration of hydroxyl radicals is not constant, due principally to the aforementioned fluctuation of the electrical resistance of the solution in the central compartment and to the distribution of the electrolysis current into an ionic and an electronic one.

The maximum theoretical electronic current value (i_{e}), proportional to the kinetic constant (k_0), is related to the available couples of absorption sites for both hydroxyl and dissolved oxygen, that represent the necessary sites for the charge transfer process. The theoretical surface density of the adsorbed species can be calculated from the lattice parameters of the planes comprising the surface after taking into account the surface proportion of each plane [32].

The kinetic parameter (k_0) in the utilized electrochemical cell (batch mode) was not really constant due to the continuous changes in the resistivity of the treated solution and the corresponding electric field (in galvanostatic condition). These changes will be surely much less remarkable in a continuously operated reactor (nowadays in construction) where the residence time of the treated solution can be tuned in order to limit the increase of the electrical conductivity due to the continuous introduction of ions from anolyte and catholyte.

5. Conclusions

A new electrochemical reactor concept has been proved to be effective for the abatement of organic compounds by oxidation mediated by the *in situ* generated radical species (mainly $OH^{\bullet}$) over a semiconductor sponge under a superimposed electric field.

The electro-oxidative treatment can be regarded as very promising for low concentration of pollutants containing in low conductivity solution.

The operating conditions and the nature of the semiconductor have to be optimized for each specific pollutant considered, because the variety of geometric and electronic structures associated with different metal oxides surfaces is wide and implies changes in the water–metal oxide adsorption and charge transfer characteristics.

The energetic consumption for mineralization of dissolved organics in the reactor (40 g C.O.D. l^{-1}/kWh) demonstrates that the here-proposed system is a viable process in view of the high values of energetic consumption inferred by other advanced oxidation processes [18,32–37].

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