

## Photocatalytic process for energy recovery in wastewater decontamination

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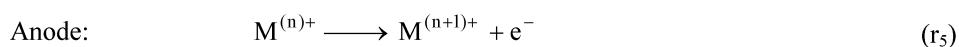
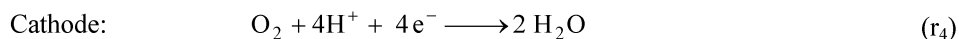
The contemporary removal of formic acid (FA) from aqueous solution and electricity generation is studied by means of the combination of a photocatalytic reactor and an electrochemical cell. The proposed system relies on the capability of  $\text{Cu}^{2+}$  ions to reduce in presence of  $\text{TiO}_2$ , (solar) UV radiations and a sacrificial organic agent. In the anodic solution of the combined photoreactor-cell,  $\text{Cu}^0$  is oxidized to  $\text{Cu}^{2+}$  due to the cell work and the latter is reduced again to the lowest oxidation state as a result of the photocatalytic process. The use of different sacrificial agents such as formic acid (FA) and glycerol (GLY) is investigated.

### 1. Introduction

During last decade increasing concerns for  $\text{CO}_2$  emissions from fossil fuel combustion stimulated the search for new way of producing energy from renewable substances (biomasses) and to recover it from the treatment of wastewaters (Venkata Mohan et al., 2008; Tilche and Galatola, 2008). Among the others, microbial fuel cells gained a great attention in the Scientific Community due to their capability to use the catalytic activities of microorganisms to oxidize organic and inorganic matter and generate current (Feng et al., 2008; Kim et al., 2007; Logan, 2005). The same aim may be reached through an alternative non-biological system in which the oxidation of an organic species is exploited to generate electricity. This is made possible by the use of an electrochemical cell combined with a photocatalytic reactor. This process enables in presence of  $\text{TiO}_2$  particles, solar-UV radiation and in absence of oxygen, the contemporary oxidation of an organic substrate, which is the sacrificial agent, ( $r_2$ ) and the reduction of a metal ion in the solution ( $r_3$ ):



One way of assembling this type of device is that of considering an electrochemical cell in which the couple ( $M^{(n+1)+}/M^{n+}$ ) is used for anodic compartment and an  $O_2$  electrode for the cathode. Reactions occurring during cell working are:



The cathodic reaction consumes hydrogen ions when the cell works. This means that hydrogen ions have to migrate from the anodic compartment through the membrane to replenish them.

Once the cell was discharged, in the anodic solution the concentration of the species  $M^{n+}$  is increased through the reduction of  $M^{(n+1)+}$  ions ( $r_3$ ) and the contemporary oxidation of sacrificial agent ( $r_2$ ) by submitting it to a photocatalytic process.

The overall device can be seen as a system to which oxygen, an organic species and a UV radiation are fed whose outputs are electricity and the oxidized organic species. In the present work, a device as that described above is adopted with an anode based on the system  $Cu^{2+}/Cu^0$ . Sacrificial photocatalytic processes in presence of  $Cu^{2+}$  ions have been extensively investigated in the past (Vinu and Madras, 2008; Kyung et al, 2005) and recently also by the authors (Canterino et al., 2008). The use of different sacrificial agents such as formic acid and glycerol is investigated.

## 2. Experimental

Experiments were carried out using a photocatalytic reactor and a modified electrochemical H-shaped cell (Fig. 1). The latter consists in two compartments with the anode made by an electrode of metallic copper and a solution containing cupric sulfate. The cathode was an  $O_2$  electrode that had an inert wire coated with a finely divided layer of platinum inserted in an aqueous solution in which an air stream was bubbled. The anode and cathode were connected through a Nafion117 membrane. An UV high-pressure lamp was used in a photocatalytic reactor or in the anodic compartment of the photoelectrochemical cell. An helium stream was continuously fed to the reacting solutions - to prevent the dissolution of atmospheric oxygen - during the photocatalytic reduction of dissolved  $Cu^{2+}$  ions in presence of an organic compound as sacrificial agent.

The concentration of  $Cu^{2+}$  ions during the experiments was measured by means of a photometric method using an analytical kit based on oxalic acid bis-cyclohexylidene hydrazide (cuprizone), purchased by Macherey-Nagel. Formic acid (FA) and glycerol (GLY) were used as sacrificial agents. The concentrations of FA and GLY at different reaction times were evaluated by HPLC analysis. For this purpose, the HPLC apparatus equipped with a UV-VIS detector ( $\lambda = 215$  nm) and a Phenomenex Rezex column was used. The Open Circuit Voltage (OCV) and cell voltage ( $E_{cell}$ ) were measured by a digital multimeter ISO-tech IDM101.

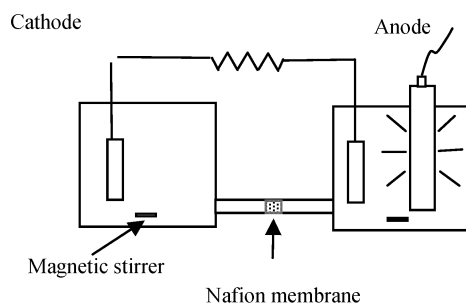


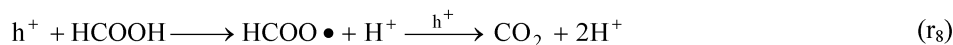
Fig. 1 Photoelectrochemical cell

### 3. Results and discussion

#### 3.1 Formic acid as a sacrificial agent

For a cell of this type in which the concentration of  $\text{Cu}^{2+}$  and FA in the anodic solution are equal to 1.85 mmol/L and 3.0 mmol/L, respectively, with an air stream fed to the cathode at a pressure of 1 atm, the pH of both the compartment being equal to 2.0, an OCV of 590 mV is measured. When the electrodes are connected through an external circuit in which a resistor of 4600  $\Omega$  is present a cell voltage of 275 mV is observed.

If the lamp is switched on and the system behaviour followed against the time, the data reported in the fig. 2 are collected. As a result of the photocatalytic process  $\text{Cu}^{2+}$  ions were reduced to  $\text{Cu}^0$  - which remained suspended in the solution- while FA was oxidized. Reactions occurring during this step in the anodic solution, along with the reaction  $r_1$ , are:



In the first 50 minutes, a rapid oxidation of FA is observed until an almost complete disappearance of  $\text{Cu}^{2+}$  ions in the solution is achieved, according to reactions  $r_7$  and  $r_8$ . Although the contemporary oxidation of  $\text{Cu}^0$  ( $r_9$ )



is occurring during this phase (since the cell is working), the concentration of  $\text{Cu}^{2+}$  decreases being the last reaction slower than  $\text{Cu}^{2+}$  photoreduction. This results into a cell voltage increase. Once cupric ions had disappeared (their concentration being below the detection limit of the method, 0.01 mg/L) a very weak reactivity is shown by FA whose concentration slowly continues to decrease when the cell voltage reached an almost constant value (440 mV).

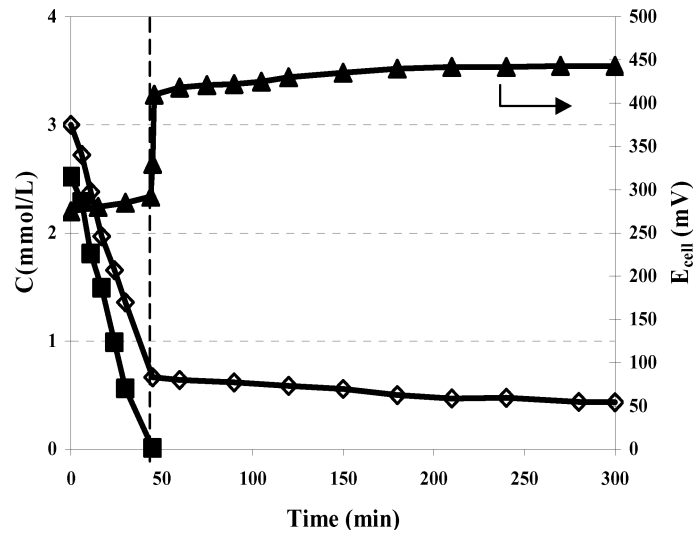
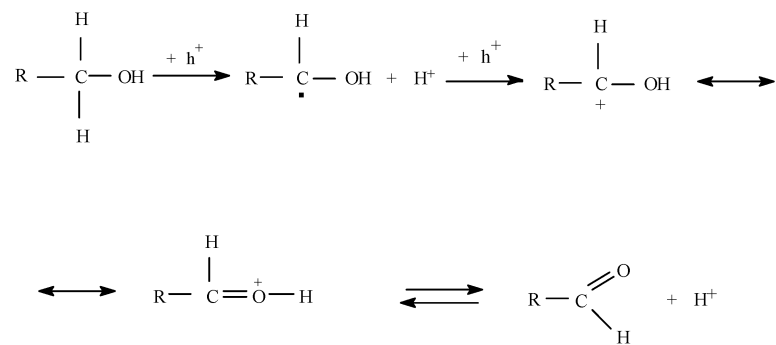


Fig.2 Charging process in electrochemical cell  $\diamond$ : FA;  $\blacksquare$ :  $\text{Cu}^{2+}$  ions;  $\blacktriangle$ :  $E_{\text{cell}}$ .

### 3.2 Glycerol as a sacrificial agent

There is a great interest to identify other organic species that can oxidize during the photoreduction of cupric ions and in particular mainly those whose presence has been documented in common wastewater. The choice of the species to be included in the investigation was performed on the basis of literature suggestions (Foster et al., 1995) Following these criteria, glycerol, a by-product in biodiesel production process, was selected as a possible sacrificial agent. This species is characterized by the presence in its structure of alcoholic groups. A possible mechanism capable of explaining the reactivity of alcohols after the irradiation of  $\text{TiO}_2$  is depicted in the following:



In figure 3 the concentration-time plots recorded when GLY is used as sacrificial agent in the photoreactor are shown. Due to the presence in this molecule of different groups capable to oxidize, more than one  $\text{Cu}^{2+}$  ion reduces for each GLY molecule.

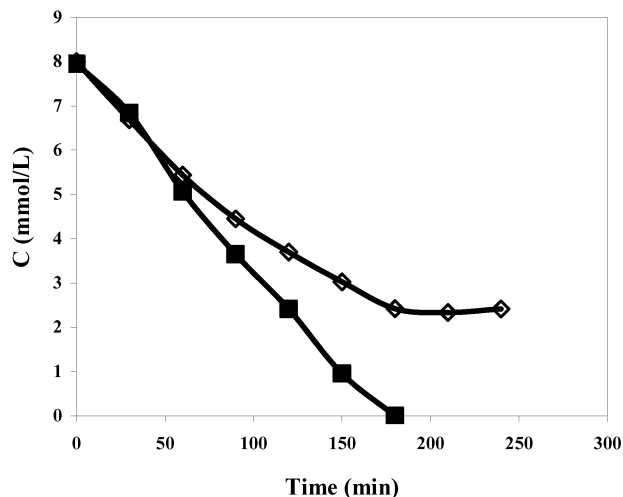


Fig. 3  $Cu^{2+}$  reduction in presence of glycerol  $\diamond$ : GLY;  $\blacksquare$ :  $Cu^{2+}$  ions.

In Fig. 4 the data collected in an experiment carried out in the photoelectrochemical cell in presence of GLY in the anodic solution without the addition of cupric sulphate are shown.

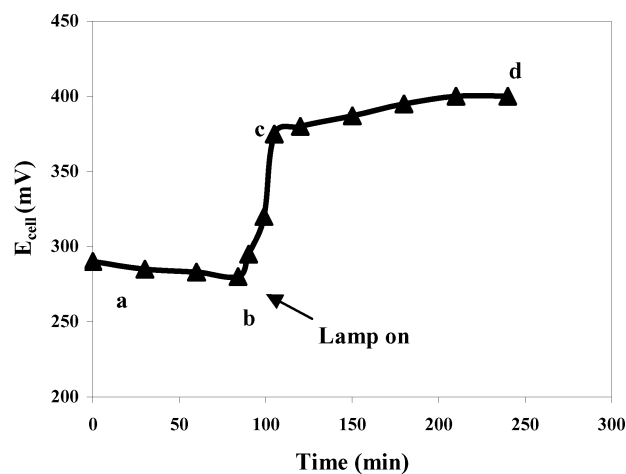


Fig. 4 Cell voltage changes in charging process of photoelectrochemical cell in presence of GLY.  $[GLY]=1.0$  mM;  $[Cu^{2+}]_0=0$  mM

The first part (a-b) of the curve in Fig. 4 represents the discharge of the cell when the external circuit is closed ( $R_{est}=4600 \Omega$ ). After 80 minutes, the lamp was switched on and a charging process started with a sharp increase of  $E_{cell}$  (curve b-c) due to a fast reduction of  $Cu^{2+}$  to  $Cu^0$  whereas GLY is consuming. Then the charging process

became slow, (c-d) due to very low concentration of  $\text{Cu}^{2+}$  present, until it stops. In this phase  $\text{Cu}^{2+}$  ions available for the process are only those generated by the cell working.

#### 4. Conclusions

The results of the present work indicate that it is possible to combine a photocatalytic reactor and an electrochemical cell to achieve a contemporary removal of an organic pollutant from an aqueous solution and generate electricity. This is made possible by the exploitation of the capability of  $\text{Cu}^{2+}$  ions to reduce in presence of  $\text{TiO}_2$ , (solar) UV radiation and a sacrificial organic agent. The possibility to use different sacrificial agents ranging (formic acid and glycerol) has been proved in present investigation.

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