

## Electrochemical Processes and Apparatuses for the Abatement of Acid Orange 7 in Water

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We have studied the electrochemical treatment of aqueous solutions contaminated by Acid Orange 7 (AO7) by electro-Fenton process (EF). The main objective was to evaluate how the electrochemical route affects the performances of the degradation process. EF process was carried out in a number of very different reactors: conventional bench scale electrochemical cell, microfluidic electrochemical reactor, microbial fuel cell and stack for reverse electro dialysis processes. The utilisation of micro devices allowed to work without the addition of a supporting electrolyte and improved the performances of EF. Microbial fuel cell did not need the supply of electric energy but our device required very long treatment times. Reverse electro dialysis processes did not need electric energy and gave more reasonable treatment times.

### 1. Introduction

Wastewater treatment technology is undergoing a transformation due to more restrictive regulations governing the discharge and disposal of hazardous pollutants (Comninellis et al., 2010). Electrochemical based technologies are very promising methods for treating wastewaters containing organic and inorganic pollutants resistant to biological processes or toxic for microorganisms (Comninellis et al., 2010, Martínez-Huitle and Brillas, 2009). These methods have numerous advantages including the utilisation of a green reagent such as the electron, very high removal of numerous recalcitrant pollutants, efficient disinfection, high flexibility and no necessity to transport or stock chemical oxidants or reductants. On the other hand, a wide utilisation of such methods is likely to be limited by: (i) the cost of electric energy necessary to drive electrode reactions; (ii) the cost of the supporting electrolyte for waste waters with nonadequate conductivity and (iii), for some applications, by the cost of electrodes. In order to overcome some of these drawbacks, some innovative solutions were proposed in the last years such as the utilisation of micro reactors (Scialdone et al., 2010; Scialdone et al., 2013a) to avoid the utilization of supporting electrolytes and to increase the current efficiencies for the electrochemical processes controlled by mass transport stages, such as direct oxidation processes or electro-Fenton (EF). To avoid the supply of electric energy to the system, both the utilization of microbial fuel cells (Feng et al., 2010b) or reverse electro dialysis processes was proposed (Cusick et al., 2012; Scialdone et al., 2012; Scialdone et al., 2013b).

In this paper the performances of many electrochemical processes were evaluated and compared in the frame of the treatment of wastewaters contaminated by a model dye, Acid Orange 7 (AO7) which is a 2-naphthol Orange. Very large amounts of synthetic dyes are discharged in the environment from industrial effluents (Brillas et al., 2009). A loss of 1 - 2 % in production and 1 - 10 % in use are estimated. Due to their large-scale production and extensive application, synthetic dyes can cause considerable pollution and are serious health-risk factors. The majority of these compounds consumed at industrial scale are azo (–N=N–) derivatives that represent more than 50 % of the all dyes used in textile industries.

Since dyes usually have high stability under sunlight and resistance to microbial attack and temperature, most of these compounds are not degradable in conventional wastewater treatment plants.

Electrochemical methods are considered to be among the more efficient Advanced Oxidation Processes (AOPs) for the removal of dyes. The azo dye Acid Orange 7 (AO7, also called Orange II, is widely used in paperboard industries, for coloration, and in wool textile dyeing. Its removal by electrochemical techniques was previously studied in detail (Fernandes et al., 2004; Ozcan et al., 2009; Hammami et al., 2008).

The treatment of wastewaters contaminated by AO7 was here carried out by EF route driven by electrolysis processes in conventional and microfluidic reactors, by microbial fuel cell and reverse electro-dialysis processes.

EF is based on the electro-generation of hydrogen peroxide in aqueous solution by two-electron reduction of dissolved oxygen (eq. (1)) on a cathode such as mercury pool, compact graphite, carbon felt, activated carbon fiber and carbon-polytetrafluoroethylene-O<sub>2</sub> diffusion cathode (ADE) (Martinez-Huitile and Brillas, 2009):



The oxidizing power of H<sub>2</sub>O<sub>2</sub> is enhanced in the presence of Fe<sup>2+</sup> ion *via* classical Fenton's reaction (Eq. (2)) which leads to the production of hydroxyl radicals. Reaction (2) is propagated through the continuous electro-generation of Fe<sup>2+</sup> by reduction of Fe<sup>3+</sup> formed by reaction (3).



It has been shown that the performances of EF process strongly depend on cathode material and on the adopted cell (Martinez-Huitile and Brillas, 2009).

## 2. Experimental

### 2.1 Conventional electrochemical cell

Electrolyses in macro-scale were performed in batch mode in a cylindrical, undivided 50 mL tank glass cell under vigorous stirring by a magnetic stirrer. Compressed air was bubbled continuously at 0.35 L/min into the aqueous solution by a diffuser. The inter-electrode distance was about 2 cm.

A two-compartment electrolysis cell was also used. The catholyte (75 mL) was separated from the anolyte (75 mL) by an anionic membrane Selemion. The inter-electrode gap was about 5 cm. Electrolyses were carried out at room temperature (with electrodes having geometric area of 5 cm<sup>2</sup>) and they were driven by an Amel 2053 potentiostat/galvanostat operated under galvanostatic mode.

### 2.2 Microfluidic electrochemical reactor

The micro reactor consists of a commercial undivided filter press flow cell ElectroCell AB, equipped with one or more polytetrafluoroethylene (PTFE) spacers, with a distance between electrodes of 120 μm (using a single spacer). Spacers sheets were cut to define the working area (A = 5 cm<sup>2</sup>). For each tested operating condition at least 3 samples of 1 mL solution were analysed to be sure that the steady state conditions were achieved. Experiments in the micro reactor were performed under a continuous mode with a single passage of the solution inside the cell, using a syringe pump (New Era Pump Systems, Inc.) to feed the solutions with a flow rate between 0.05 and 0.4 mL/min and without the addition of a gaseous stream to the solution. Electrolyses were performed at room temperature and they were driven by an Amel 2053 potentiostat/galvanostat operated under galvanostatic mode.

### 2.3 Microbial fuel cell

*G. sulfurreducens* bacterial strain was obtained from DSMZ, Germany, and cultured as reported in the literature (Bond and Lovley, 2003). In particular, the culture was maintained on acetate-iron hydroxide medium and sub-cultured on acetate-fumarate medium.

The two-chamber microbial fuel cells (MFC) were custom made. Each chamber had a working volume of 50 mL, where a hand cut 6.25 cm<sup>2</sup> carbon felt electrode was immersed. The two chambers were separated by a Nafion membrane. An external 4Ω resistor and a multimeter in order to measure voltage and current were used. The anolyte consisted of a medium as described on Bond and Lovley, 2003; both the description of the catholyte and the analytical procedures are reported on section 2.5.

The assembled MFC were mounted on a magnetic stirrer, which also maintained constant temperature at 30 °C throughout the experiments. The headspace of the MFC was continuously flushed with sterile N<sub>2</sub>/CO<sub>2</sub> 80/20 w/w gas mixture. After 30 min of flushing, 5 mL of cell suspension were added to the MFC filled with 45 mL of acetate medium. The electron acceptor was not added to promote the respiration of the

electrode. Every 3 days, the spent medium was replaced with the fresh one in order to promote the growth of the culture as electroactive biofilm.

#### 2.4 Reverse electro dialysis (RED) process

A custom made lab scale stack was used (Scialdone et al., 2013b). The RED stack consists of two electrodic chambers (10 cm x 10 cm x 2 mm) and it contained a carbon felt cathode and a titanium meshes coated with Ru-Ir or Ir-Ta anode (geometric surface area 10 cm x 10 cm, Magneto). The stack, assembled between the anode and cathode chambers, consists of 39 anion- and 40 cation-exchange membranes (Fuji), gasket integrated with spacers (Deukum, 0.28 mm thickness) and two external membranes to separate electrodic compartments and side ones, creating 40 pairs of alternating high concentrated (HC) and low concentrated (LC) chambers. Two external anionic membranes (Selemion) were also used.

The HC solution entered from the cell next to the anode chamber and flowed in parallel through the 40 HC cells in the stack, while the LC stream entered in the RED stack near the cathode and flowed in parallel through the 40 LC cells in the stack. Two peristaltic pumps (General Control SpA) continuously fed the HC and LC solutions at a flow rate of 190 mL/min. The two electrodic solutions were continuously recirculated to the electrodic compartments and to two different reservoirs, by two peristaltic pumps (General Control SpA) with a flow rate of 75 mL/min (Scialdone et al., 2013b). The cathodic electrolytic solution was fed with air for the treatment of AO7.

#### 2.5 Chemicals and analytical procedures

The cathode compartments and the undivided conventional or microfluidic cells were filled with an aqueous solution with an initial AO7 concentration of 0.43 mM at a pH of 3 obtained by addition of sulfuric acid (Sigma Aldrich). 35 mM Na<sub>2</sub>SO<sub>4</sub> (Janssen Chimica) and 0.5 mM FeSO<sub>4</sub> (Fluka) were used as supporting electrolyte (for experiments performed in the macro-devices) and catalyst, respectively. Compact graphite (Carbon Lorraine) or carbon felt (The Electrosynthesis Co.) and Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> (ElectroCell AB) were used as cathode and anode, respectively.

The chemical oxygen demand (COD), a routinely measure that determines the quantity of oxygen required to oxidize the organic matter in a sample, under specific conditions of oxidizing agent, temperature and time, was evaluated using Merck cell tests. The removal of colour was monitored from the decay of the absorbance (A) at  $\lambda = 482$  nm wavelength for AO7. An Avantes Optic Spectrophotometer (DH-2000) was used. The total organic carbon (TOC) was analyzed by a TOC analyzer Shimadzu VCSN ASI TOC-5000 A. The degradation of AO7 was monitored by high-performance liquid chromatography (HPLC) using a Hewlett Packard 1100 system, equipped with UV-Vis detector, and fitted with a Platinum EPS C18 column 100A 5 $\mu$ , 4.6mm $\times$ 250mm, from Alltech, which was thermostated at 25 °C. Injection volumes were 30  $\mu$ L (Scialdone et al., 2014).

The color removal  $X$  and the current efficiency  $CE$  were computed according to the literature (Scialdone et al., 2011).

Power production during experiments was determined by measuring the cell potential using a fixed external resistance (1 or 4  $\Omega$ ) and the current intensity by a multimeter Simpson. Power density (P) was computed by the ratio between the delivered power and the geometric area of the electrode.

### 3. Results and discussion

First electrolyses were carried out in a conventional undivided cell equipped with a cheap compact graphite cathode (Table 1, entry 1). Quite high and fast abatement of the colour was achieved. Thus, after about 3.5 h, 95 % of the colour was removed but a very low abatement of COD occurred as a result of the formation of several by-products (Scialdone et al., 2014). After a quite long time and a quite high amount of charge passed (24 times the theoretical charge necessary for the complete oxidation of AO7 with a process with a current efficiency of 100 %), only a partial removal of COD (40 %) was obtained as a result of the strong stability of carboxylic acids formed during the process (Scialdone et al., 2014).

When the compact graphite was replaced with a carbon felt cathode, a significantly higher abatement of COD was achieved (Table 1, entry 2). Indeed, carbon felt presents a three-dimensional structure with dramatically higher surface with respect to the geometric one, thus allowing a more efficient EF process. When the electrolyses were repeated in a divided cell, faster abatements of COD were achieved (see as an example, data reported in Table 1, entry 3, with compact graphite cathode). This is probably due to the

fact that, in undivided cell, a part of the hydrogen peroxide generated at the cathode is consumed by anodic oxidation at the anode. However, the utilisation of the divided cell gave drastically higher energetic consumptions as a result of the presence of the separator.

Table 1: Effect of electrochemical routes and apparatuses on the abatement of AO7 by EF

Entry	System	Electrode	I [A/m <sup>2</sup> ] (and $\Delta V$ [Volt]) <sup>a</sup>	P [W/m <sup>2</sup> ] <sup>a</sup>	Q/Q <sup>th</sup> <sup>b</sup>	Nominal time <sup>c</sup> [h]	Abatement of colour [%]	Abatement of COD [%]
1	Undiv. cell	Graphite	100 (4.1)	410 <sup>e</sup>	3.5	3.5	95	12
					24	24	100	42
2	Undiv. cell	Carbon felt	100 (3.7)	370 <sup>e</sup>	24	24	100	72
3	Div. cell	Graphite	100 (7.0)	700 <sup>e</sup>	2.8	2.8	98	30
4	Micro cell <sup>d</sup>	Graphite	20 (2.9)	58 <sup>e</sup>	1.7	8.3	100	76
5	MFC	Carbon felt	0.46	0.016 <sup>f</sup>	1.8	540	98	n.d.
			(0.035)					
6	RED	Carbon felt	6.2 (0.08)	0.5 <sup>f</sup>	1.1	20	100	58

Experiments performed in different systems with carbon felt or compact graphite as cathode and Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> or carbon felt (for MFC) as anode. The aqueous solution in the cathodic compartment or in the undivided cells contained an initial AO7 concentration of 0.43 mM at a pH value of 3, obtained by addition of H<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich), 35 mM Na<sub>2</sub>SO<sub>4</sub> (Janssen Chimica) as supporting electrolyte and 0.5 mM FeSO<sub>4</sub> as catalyst for electro-Fenton process.

(a) Average values of the cell voltage and of current and power densities.

(b) Q is the charge passed. Q<sup>th</sup> (theoretical charge) is the charge necessary to mineralize all the initial AO7 concentration by a process with a current efficiency of 100 %.

(c) Nominal time for the treatment of 1 L solution of AO7 with an electrode having a geometric area of 100 cm<sup>2</sup>.

(d) No presence of supporting electrolyte.

(e) Supplied power density.

(f) Generated power density.

According to the literature, the utilization of an undivided microfluidic cell allows to increase the abatement of AO7 by working at quite low current densities and in the absence of the supporting electrolyte (Scialdone et al., 2013a). Indeed, as shown in Table 1 (entry 4), a quite high removal of colour and COD was achieved using a cheap cathode as the compact graphite, working at 20 A/m<sup>2</sup> in the absence of the supporting electrolyte. Despite of the significantly lower amount of alimented power, a higher abatement of COD was achieved after a relatively low amount of time and charge passed with respect to that obtained in conventional undivided cell (compare entries 1 and 4 in Table 1).

It was previously shown in the literature that the EF process can be sustained by MFC or RED processes. In particular, it has been shown that microbial fuel cells can be used for wastewater treatment (Fernando et al., 2012) and, also, for the removal of AO7 dye by EF (Feng et al., 2010), thus avoiding the necessity to supply energy to the system. The anode side contained electroactive biofilm (EAB), such as *G. sulfurreducens* in our MFC, that worked as biocatalysts using various organic substrates to produce electrons while the EF process took place at the cathode (Lovley et al., 2011).

As shown in Table 1 (entry 5), the utilization of a MFC allowed a very high removal of colour and the simultaneous generation of electric energy. However, very long times were necessary to achieve significant removal of colour as a result of the very low current densities generated by the MFC.

As an alternative, the EF process can be sustained by reverse electrodialysis (RED). RED is a clean, renewable energy with large global potential since the electricity is produced from supplies of aqueous solutions with different salt concentrations (Brauns, 2008; Pattle, 1954). In reverse electrodialysis, cation and anion conductive membranes are placed in an alternating way in order to produce dilute and concentrate compartments (Post et al., 2008). The salt concentration difference (salt gradient) between both compartments in the cell pair creates a Nernst potential across the cell pair, which causes an electrical current to flow through the electrical load connected to the electrodes (Veerman et al., 2010b). As recently proposed by Scialdone and co-authors, the electrochemical process in the RED stack can be

used to treat wastewaters contaminated by organic and inorganic pollutants, thus allowing the simultaneous generation of electric current and the treatment of waste waters contaminated by pollutants resistant to conventional biological processes. In particular, in our experiments, the cathodic processes allowed the EF removal of Acid Orange 7 (AO7) dye. As shown in Table 1 (entry 6), the abatement of AO7 and the simultaneous generation of electric energy was successfully achieved by RED. Quite interesting abatement of both colour and COD was achieved after reasonable times and charge passed. The process gave, in particular, drastically faster abatements of colour and higher current densities with respect to that achieved in a MFC.

#### 4. Conclusions

The electrochemical treatment of aqueous solutions contaminated by Acid Orange 7 (AO7) was carried out by electro-Fenton driven by electrolyses carried out in either conventional or microfluidic electrochemical reactor, by a microbial fuel cell (MFC) or by reverse electrodialysis (RED) process, using salinity gradients. The utilisation of micro devices allowed to work without the addition of a supporting electrolyte, with a cheap cathode as compact graphite, lower power densities and improved the removal of AO7 with respect to that achieved in conventional cells. The utilization of MFC or RED allowed to drive the EF removal of AO7 without the supply of electric energy. MFC required very long treatment times because of the very low current densities, while more reasonable treatment times were achieved with RED.

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