Abatement of Acid Orange 7 in macro and micro reactors. Effect of the electrocatalytic route

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ABSTRACT

The electrochemical treatment of aqueous solutions contaminated by Acid Orange 7 (AO7) was widely studied with the main objective to evaluate as the electrocatalytic route affects the performances of the degradation process in macro and microfluidic cells. Direct anodic oxidation (EO), electro-Fenton (EF), electro-generation of active chlorine (IOAC) and coupled processes were investigated in macro and microfluidic reactors in order to select more effective conditions for the treatment of such compound. The effect of numerous operative parameters (such as nature of the electrode materials, coupling of processes, flow rate, current density and inter-electrode distance) on the performances of the process was studied in detail. It was found that the catalytic route affects strongly the performances of the process in terms of removal of color, abatement of AO7 and COD and nature of by-products. Furthermore, different operative conditions were required to optimize the various electrocatalytic routes. The utilization of micro devices allowed to work without the addition of a supporting electrolyte and improved the performances of EO and EF that are kinetically controlled by mass transfer processes. On the other hand, the performances of IOAC did not depend on the adopted reactor.

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1. Introduction

Very large amounts of synthetic dyes are discharged in the environment from industrial effluents [1]. 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 nonaesthetic pollution and are serious health-risk factors [2]. Dyes are commonly classified from their chromophore group. 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, although antraquinone, indigoide, triphenylmethyl, xanthene, sulfur and phtalocyanine derivatives are frequently utilized [3].

Since dyes usually present high stability under sunlight and resistance to microbial attack and temperature, most of these compounds are not degradable in conventional wastewater treatment plants. The research of powerful and practical treatments to decolorize and degrade dyeing wastewaters to decrease their environmental impact has then attracted increasing interest over the past two decades. Electrochemical methods are considered to be among the more efficient Advanced Oxidation Processes (AOPs) for the removal of dyes [2]. The main electrochemical procedures utilized for the remediation of dyestuffs wastewaters are electrocoagulation (EC), direct electrochemical oxidation (EO) with different anodes, indirect electro-oxidation with active chlorine (IOAC) and Electro-Fenton (EF) [2]. The azo dye Acid Orange 7 (AO7), also called Orange II ($C_{16}H_{11}N_2NaO_4S$), was often chosen as model compound to evaluate promising approaches because, being a simple molecule, it is very useful as test and since it is widely used in paperboard industries, for coloration, and in wool textile dyeing.

The electrochemical oxidation of aqueous solutions of AO7 was previously investigated by various authors [4–10]. Fernandes et al. studied the electrochemical oxidation at BDD anodes both in the absence and in the presence of chlorides. An almost complete colour removal and very high COD removal were obtained. In the presence of KCl a faster colour removal was achieved as a consequence of active chlorine formation [4]. A detailed study on the effect of the supporting electrolyte on the oxidation of AO7 at BDD anode was carried out by Zhang et al. [6]. Peralta-Hernandez et al. compared the performances of hydrogen peroxide based processes (direct photolysis, electro-Fenton process and photoelectro-Fenton process) [7]. Electro-Fenton process (EF) was, in particular, studied in detail by various authors [7–10]. Oturan and co-authors studied in detail the nature of intermediates and by-products [8]. Garcia-Segura et al. [10] studied the abatement of monoazo, diazo and triazo dyes by EF in the presence of a gas diffusion cathode and a BDD anode.

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According to the literature, the performances of the electrochemical treatment of dyes are likely to strongly depend on the adopted electrocatalytic route [2]. However, in spite of the numerous papers devoted to the electrochemical treatment of azo dyes, comparisons of various electrocatalytic routes under similar and optimized operative conditions were not usually carried out. In this paper, the possible utilization of more promising electrocatalytic routes for the treatment of aqueous solutions of Acid Orange 7 chosen as a model compound (namely, direct electrochemical oxidation, indirect oxidation with active chlorine and electro-Fenton) used alone or in a combined way was widely and systematically studied to evaluate as the electrocatalytic route affects the degradation process. Both conventional cells and microfluidic apparatus were used in order to select more effective electrochemical conditions for the treatment of such compound.

Thus, recently it has been demonstrated that the electrochemical abatement of organic pollutants in water by both anodic direct oxidation and electro-Fenton process can strongly benefit from the utilization of microfluidic electrochemical reactors (i.e. cells with a distance between the cathode and the anode of tens or hundreds of micrometers) [11–13]. Very small distances between electrodes lead from one side to a drastic reduction of ohmic resistances [11–14] (allowing to operate with lower cell voltages and without supporting electrolyte) and on the other side to increase the abatement of organic pollutants [12,13]. These aspects are of particular relevance for the treatment of dyes. Indeed, real textile effluents often present quite low conductibility that imposes the addition of a costly supporting electrolyte [15] or the utilization of a microfluidic reactor to achieve reasonable cell voltages. In this paper a systematic comparison between conventional cell and micro reactors for various electrocatalytic route (namely, direct anodic oxidation, electro-Fenton, oxidation by electrogenerated active chlorine) and coupled approach was carried out for the first tine.

The effect of numerous operative parameters, including the nature of the electrode materials, flow rate, current density, and the inter-electrode distance, on the performances of the process was also systematically studied to determine more proper operative conditions.

2. Experimental

2.1. Electrolyses

Electrolyses in macro-scale were performed in batch mode in a cylindrical, undivided tank glass cell under vigorous stirring performed by a magnetic stirrer with 50 mL of solution. For EF experiments, compressed air was fed (0.35 L min^{-1}) to the water solution by a diffuser or directly inside the Air Diffusion Electrode (ADE). The inter-electrode gap was about 2 cm. Experiments in the micro reactor were performed in 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 flow rate between 0.05 and 0.4 mL/min and without addition of a gaseous stream to the solution. The micro reactor consists in a commercial undivided filter press flow cell ElectroCell AB, equipped with one or more polytetrafluoroethylene (PTFE) spacers with the following nominal distances between electrodes: 50 (using one spacer), 75 (using two spacers of 50 and 25 μm), 120 (with a single spacer) and 240 μm (using two spacers of 120 μm). Spacers were cut to define the working surface (A = 5 cm^2). For each tested operative condition at least 3 samples of 1 mL were analyzed to be sure that steady state conditions were achieved.

Electrolyses were driven by an Amel 2053 potentiostat/galvanostat operated in galvanostatic mode. Electrolyses were usually performed at room temperature with an initial

AO7 concentration of 0.43 mM. Na$_2$SO$_4$ (0.035 M) was used as supporting electrolyte for experiments carried out in the macro device. FeSO$_4$ (0.5 mM) was used as catalyst for EF processes.

2.2. Analyses

The concentration of H$_2$O$_2$ was determined from the light absorption of the Ti(IV)—H$_2$O$_2$ colored complex at λ = 409 nm, using O$_5$STi·H$_2$SO$_4$ from Fluka. 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 color was monitored from the decay of the absorbance (A) at λ = 482 nm for AO7 [10]. 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 and of some byproducts 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 μ, 4.6 mm × 250 mm, from Alltech, which was thermostated at 25 °C. Injection volumes were 30 μL. The column was eluted at isocratic mode with a mixture of a buffer solution, containing HK$_2$PO$_4$ (99 + % ACS reagents, Aldrich) and H$_3$PO$_4$ at pH 2.5, methanol (≥99.9% for HPLC, Aldrich), 1-pentanol (ACS reagent, ≥99%, Aldrich), 65:30:5 (v/v) with a flow rate of 1 mL min^{-1}. Detection was performed at 280 nm.

Carboxylic acids were identified and quantified using the same system by a Preavail Organic Acid 5 μ column, 4.6 mm × 250 mm, from Grace with a 100% of the same buffer solution. The detection was performed at 210 nm with a flow rate of 1 mL min^{-1}. Calibration curves were obtained by using the pure standards of the related carboxylic acids. The eventual presence of chlorinated products was evaluated by HPLC/MS thermo TSQ Quantum Access, Type ESI, negative Polarity Q1 MS, fitted with a Zic-Hilic column 5 μ, 2.1 mm × 150 mm, from Merck. The column was eluted with a mixture of a buffer solution, containing CH$_3$CN (99+% ACS reagents, Fluka) and 10 mM of Ammonium Acetate (99+% ACS reagents, Aldrich) at pH 5, 90:10 (v/v).

The thickness of the stagnant layer in the adopted conditions was estimated trough a typical limiting-current essay using the redox couple hexacyanoferrate(II)/hexacyanoferrate(III) focusing on the oxidation reaction and using the value 6.631 × 10^{-10} m^2 s^{-1} for the diffusivity of ferry-cyanide ion [16]. The mass transfer coefficient of AO7 k_m was estimated as the ratio between its diffusivity D (assumed to be about 10^{-9} m^2 s^{-1}) and the thickness of the stagnant layer.

The color removal X was computed by Eq. (1) [10] while the current efficiency CE for the removal of COD was defined by Eqs. (2) and (3) [11,13] for a macro and a micro cell, respectively.

$$\text{Color removal} = \frac{(A^0 - A^f)}{A^0} \qquad (1)$$

$$CE = \frac{nFVCOD^0X}{(i_{app}At)} \qquad (2)$$

$$CE = \frac{nFCOD^0X\Phi_V}{(i_{app}A)} \qquad (3)$$

where A° and A^f are the absorbance at initial time and time t at λ = 482 nm, n is the number of electrons, F the Faraday constant (96487 C mol^{-1}), i_{app} the applied current density, V the volume of the cell and Φ_V the volumetric flow rate. Similarly, for generation of H$_2$O$_2$ in micro-device, $CE = 2F[\text{H}_2\text{O}_2]\Phi_V/(i_{app}A)$.