

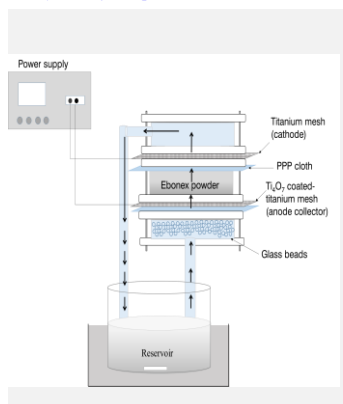
A Study of the Performance of a Packed Bed Anode in an Electrochemical Flow Reactor for the Treatment of Simulated Textile Wastewater.

POSTER

Ph.D. Student: N

Journal: CEJ

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The electro-oxidation process (EO) utilizing anodes based on a mixture of sub-stoichiometric titanium oxides constitutes a versatile and sustainable choice for addressing the challenges posed by textile effluent treatment and reuse. In this work, the EO of a simulated textile wastewater (STW) was studied using a full recycle up-flow tubular reactor with a packed bed anode (UFR-PBA) under galvanostatic conditions. About 5.5 g of Ebonex® powder were packed around the anode collector. Under the operating conditions tested, increasing temperature and current led to improvements in the RB5 and DOC removals and specific energy consumption. Undiluted STW could be significantly discoloured and partially mineralized. Ongoing research involves analyzing the effect of the additives present in the wastewater on EO, monitoring ionic species and assessing toxicity of the treated STW. Integrating the UFR-PBA with other Advanced Oxidation Technologies (AOT) emerges as a promising approach to enhance wastewater treatment.

Introduction

The development of highly efficient treatment methods to treat dyeing process wastewater, characterized by high contents of dyes, salts, among other chemicals, and produce treated wastewater of a quality suitable for discharge or, if possible, reuse, is crucial. Electrochemical Advanced Oxidation Technologies (EAOT), EO offers numerous advantages over traditional treatment approaches: it facilitates effluent mineralization, requires no additional reagents, avoids solid waste generation, features a modular design, and can easily integrate with other treatment techniques [1]. This makes electrooxidation a versatile and sustainable choice for addressing the challenges posed by textile effluent treatment and reuse. However, there is still a need for considerable efforts to enhance the cost-effectiveness of EO processes [2]. The traditional stirred three-electrode batch electrochemical cell typically employs 2D electrodes with limited surface area, this results in low current efficiency and high consumption of energy. Alternatively, systems that use 3D electrodes, such as, bed-based ones, constitutes an interesting approach to increase the efficiency of mass transfer and energy consumption [3].

In this work, the EO of a simulated textile wastewater was studied using a full recycle up-flow tubular reactor with a packed bed anode. The commercially available ceramics based on a mixture of sub-stoichiometric titanium oxides (Ti_nO_{2n-1}, 4 ≤ n ≤ 10), known as Magnéli phases (Ebonex®) have gained interest as promising working electrodes for the electrochemical degradation of diverse organic pollutants mainly due to their high electrical conductivity, chemical stability in a wide range of media, high oxygen evolution potential, and relatively low manufacturing costs [4]. The study aimed to investigate the impact of the applied current and temperature on the dye removal, as well as on the dissolved organic carbon (DOC) reduction and specific energy consumption.

Material and Methods

To prepare the STW, a methodology similar to that outlined in the work of Hanel et al. [5] was followed. This process led to the preparation of a wastewater sample representative of the dyeing process of cotton fiber with Reactive Black 5 (RB5) dye in local dyeing industries. The RB5 and auxiliary products were provided by a local textile industry.

The EO experiments were conducted in an UFR-PBA specifically designed for testing particulate anodes, using a power supply under galvanostatic conditions. The system consisted in a three-electrode cell setup, using a SCE as reference, a Ti mesh and a Pt/Ti mesh (30 × 30 mm) as cathode and anode collector, respectively. The electrical contact was attained by contacting each mesh to a Ti wire. Anode and cathode potential were measured against a SCE located at the reactor entrance. 5.5g of Ebonex® powder (500-350 μm), provided by QuanVerge Inc., were packed around the anode collector with the aid of two polypropylene cloths. The initial pH was adjusted to 3. The EO experiments were carried out at either 3 or 7 mA, 20°C or 70°C with liquid fully recirculated at flow rate of 0.2 L/h. Samples were withdrawn from the reservoir and analyzed immediately by UV-Vis spectroscopy and DOC. The total (cumulated) volume reduction was always less than 10%. The UV-Vis spectra of the samples were recorded using a Shimadzu UV-3600 Plus (Japan) spectrophotometer. The absorbance at 590 nm was correlated with RB5 concentration. DOC was measured in a Shimadzu TOC-VCPN analyzer. The specific energy consumption (SEC), i.e. the amount of energy consumed per unit mass of organic load removed during the electrooxidation process, was estimated as:

$$SEC = \int_0^t \frac{E_{cell} \cdot i}{V \cdot W} dt$$

where E_{cell} is the voltage difference between anode and cathode, i is the applied current (A), t is the electro-oxidation time (h), W is the removed DOC (g/L) and V is the volume of the treated solution.

Electro-active surface area were calculated by determining double layer capacitances (apparent capacitance) from cyclic voltammetry (CV) analyses conducted in STW by implementing the same reactor configuration used for the EO experiments [1,4].

Results and Discussion

The STW has a moderate organic load (DOC=131 mg/L) and a RB5 concentration of 135 mg/L. It presents a conductivity of 16 mS/cm, 10 g/L of Cl⁻, a pH of 8.5 and a blue-black colour. Wastewater colour remains visible after a dilution 1:40.

Voltammograms for textile wastewater and blank electrolyte solutions at pH 3 were similar, indicating that the direct electron transfer didn't occur (not shown). Electro-active surface area was 245 cm², as calculated from voltammetry experiments (not shown).

Figure 1 shows that by increasing the current, the RB5 removal significantly improved, attaining 72.6% at 3 mA and 96.5% at 7mA at the end of the treatment conducted at 20°C. This increase in current also resulted in higher DOC removal rates, rising from 4% at 3 mA to 23.8% at 7 mA. These trends are likely attributed to the higher production of hydroxyl radicals and electroactive chlorine species.

Temperature may play a crucial role in the mediated electrooxidation (EO) process. Higher temperatures promote faster reaction kinetics and enhanced mass transfer, thereby improving the effectiveness of the EO process as they facilitate better interaction between contaminants and the oxidizing species produced during EO. However, higher temperatures can also promote scavenger reactions. In our setup, an increase in temperature correlated with a decrease in cell voltage. As depicted in Figure 1, the initial degradation rate of RB5 was enhanced with higher temperatures. For a given electrical charge, higher temperatures led to increased initial DOC removal rate, especially at 3 mA (not explicitly shown). This improvement was also reflected in the calculated SEC values (Table 1). This highlights the positive effect of temperature on the efficiency of the EO process in our specific setup at 3 mA. Varying the recirculation flow rate from 0.6 L/h to 1.8 L/h showed no significant change in DOC removal.

Conclusions

The EO implemented in a UFR-PBA almost completely discoloured and partially mineralized the STW. Increasing current and temperature led to improvements in the oxidation and the process efficiency. However, challenges arise due to the presence of salts and additives in the STW. In particular, the high chlorine ion content in STW may trigger the formation of harmful compounds. To address this concern, ongoing research involves analyzing the effect of the additives present in the wastewater on EO, monitoring ionic species and assessing toxicity of the treated STW. Integrating the UFR-PBA with other AOT emerges as a promising approach to enhance wastewater treatment.

Acknowledgments

The authors gratefully acknowledge financial support from the National University of Mar del Plata, the CONICET (PIP 1220200102822CO) and the ANPCyT (PICT-2021-CAT-I-00086, PICT-2020-SERIEA-03170).

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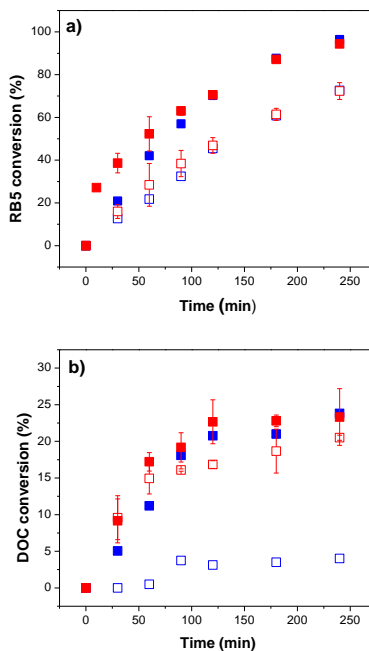


Figure 1. (a) RB5 and (b) DOC conversions as a function of time for EO experiments conducted in the UFR-PBA at 3 mA (empty symbols) and 7 mA (solid symbols). Blue and red symbols correspond to 20°C and 70°C, respectively. Conditions: pH₀ = 3.0±0.3, liquid flow rate = 0.6 L/h.

All the experiments presented here were conducted with the same powder load, which displayed excellent stability through fourteen cycles of 4-hour reaction, indicating the robustness of the treatment system.

Table 1. SEC values (kWh/gDOC)

	20°C	70°C
3 mA	0.36	0.07
7mA	0.28	0.20