

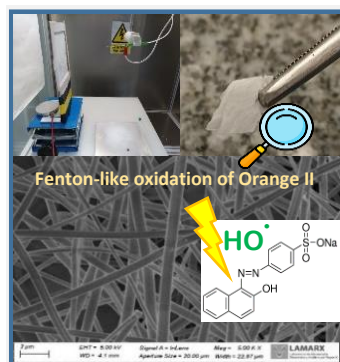
## Electrospun Fe-Doped Silica Membrane for the Fenton-like Oxidation of Orange II

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Electrospun Fe-doped silica membrane was developed through the combination of the sol-gel synthesis with solvent evaporation-induced self-assembly (EISA) (TEOS: ethanol: P123: PVP: H<sub>2</sub>O: HCl molar ratio of 1: 15: 0.012: 2.75\*10<sup>-5</sup>: 2: 0.01) and the electrospinning technique. The Fe was incorporated through the incipient wetness impregnation method. The obtained catalyst (membrane flakes of 260 m<sup>2</sup>/g with 3 % Fe) was tested in the Fenton-like oxidation of a probe molecule, the azo-dye Orange II (batch reactor, 100 mg/L OII, H<sub>2</sub>O<sub>2</sub> stoichiometric dose, 240 min, 25-60°C). The catalyst achieved complete discoloration and an outstanding mineralization level (60 %) at the highest temperature tested, with iron leaching below discharge limits (up to 4.5 ppm).

### Introduction

Textile industries generate large quantities of highly colored wastewater containing a wide range of persistent contaminants. Azo dyes constitute the most important group (> 60%) among various textile dyes [1]. The commonly used physicochemical treatments for color removal only achieve phase transfer, without fundamentally solving the problem. In this context, this study proposes the development of an innovative, active, easily recoverable, and reusable material for the Fenton-like oxidation of a model pollutant from the textile industry, the azo-dye Orange II (OII). The Fenton-like process promotes the removal and/or modification of recalcitrant compounds into more biodegradable and less toxic products, based on the generation of strongly oxidizing species. The use of appropriate catalysts allows moderating the operating conditions and increasing the efficiency, reducing time and costs. In order to achieve this, materials with specific properties must be designed, including a highly porous structure, high surface area, high density and dispersion of active sites, structural stability, and long-lasting activity. In line with these requirements, the design of a catalytic material is proposed through the combination of the sol-gel synthesis with solvent evaporation-induced self-assembly (EISA) and the electrospinning technique to obtain a nanostructured mesoporous silica ceramic membrane doped with Fe. The sol-gel/EISA synthesis allows the obtention of mesoporous structures with high surface area and a great dispersion of active sites on the surface [2]. The electrospinning technique enables the production of materials with high interconnected porosity at low cost, with high production speed, and simplicity in equipment design [3].

### Material and Methods

The following procedure was employed: (1) Preparation of a homogeneous and electrospinnable sol-gel precursor, (2) Electrospinning under appropriate conditions, (3) Thermal treatment. Pluronic P123 was used as a structure-directing agent to generate ordered mesoporosity, TEOS as the SiO<sub>2</sub> precursor, ethanol as a common solvent, and polyvinylpyrrolidone (PVP, Mw 1,300 kDa) to increase viscosity. The H<sub>2</sub>O/HCl solution was added dropwise to initiate a 30-minute pre-hydrolysis at room temperature. Then, the hydrolysis/condensation reaction continued at 80°C under reflux for 3 hours. The molar ratio TEOS: ethanol: P123: PVP: H<sub>2</sub>O: HCl was set at 1: 15: 0.012: 2.75\*10<sup>-5</sup>: 2: 0.01. According to previous studies, the H<sub>2</sub>O:TEOS:HCl ratio chosen favors fiber formation [4].

The electrospinning conditions were set at: 23°C, 50 % relative humidity, 1 mL/h sol flow, 14 kV and 15 cm distance to the collector plate.

The obtained membrane was then dried at 60°C for 1 hour and calcined at 550°C (2°C/min) for 3 hours. After calcination, it was doped with Fe(III) using the incipient wetness impregnation method, employing ethanol and an iron nitrate salt (calcination at 350°C, 3°C/min, 3 h).

The obtained samples were characterized by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), Transmission Electron Microscopy (TEM), and N<sub>2</sub> adsorption/desorption.

Oxidation experiments were conducted in a thermostated batch reactor using 250 mL of 100 mg/L OII (Biopack 95 %) and 1 g/L of catalyst load in the form of flakes, at temperatures of 25, 40, 50, 60°C, for 240 minutes. The pH was maintained at

3±0.2. The reaction started with the addition of the stoichiometric dose of H<sub>2</sub>O<sub>2</sub> for complete mineralization (H<sub>2</sub>O<sub>2</sub>:OII molar ratio of 42:1). Samples were taken periodically to determine H<sub>2</sub>O<sub>2</sub>, leached Fe and total organic carbon (TOC). OII was evaluated at 485 nm (SHIMADZU UV-1800 spectrophotometer). H<sub>2</sub>O<sub>2</sub> was determined by a Glycemia enzymatic test (Wiener Lab). Total organic carbon (TOC) was determined in a TOC analyser (Shimadzu, TOC-VCPN). Total Fe leached in the supernatant was measured using a commercial kit (FerroVer, Hach).

## Results and Discussion

The obtained membrane showed a BET surface area of 260 m<sup>2</sup>/g, with a hybrid Type II/IV isotherm (Fig. 1), with an H4 hysteresis loop, indicating the presence of mesopores resulting from the addition of P123. The sample displayed a broad pore size distribution, with meso ( $V_{MP}$  of 0.1 cm<sup>3</sup>/g) and micropores ( $V_{MP}$  of 0.05 cm<sup>3</sup>/g,  $\alpha$ -plot method). SEM images (see Graphical Abstract) displayed randomly arranged fibers in a non-woven network, while TEM images showed fibers with a disordered porous structure. While the sample exhibited mesoporosity, the interference of the electric field and the rapid solvent evaporation during electrospinning could have had a negative effect on the formation of an ordered mesoporous structure. EDS measurements

showed an iron weight percentage of 3 %.

According to the results obtained from the oxidation tests (see table 1), the membrane resulted catalytically active in the Fenton-like oxidation of OII, but in order to obtain complete discoloration and high mineralization levels, high temperatures must be employed. An outstanding mineralization level of 60 % was obtained at the highest temperature, but this condition also promoted iron leaching (4.5 ppm). While this falls below the maximum admitted for sewage discharge in the Argentinian region, it will lead to long-term deactivation.

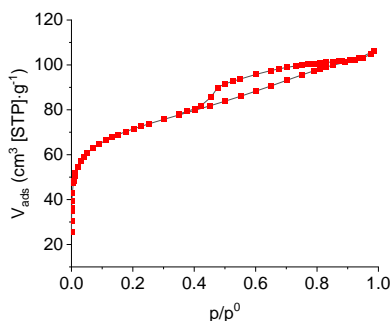


Figure 1. Adsorption-desorption isotherm (N<sub>2</sub> at 77 K).

Table 1. Results of the Fenton-like oxidation of OII with the Fe doped electrospun silica membrane

Temperature (°C)	OII Conversion (%)	TOC Conversion (%)	H <sub>2</sub> O <sub>2</sub> Conversion (%)	Fe leached (mg/L)
25	44.1 ± 4.1	6.5 ± 1.1	11.8 ± 3.1	0.9 ± 0.3
40	100	15.0 ± 6.1	20.3 ± 3.3	1.1 ± 0.1
50	100	42.7 ± 7.2	43.8 ± 3.6	2.4 ± 1.5
60	100	59.9 ± 4.9	64.2 ± 6.1	4.5 ± 0.4

## Conclusions

The material displayed remarkable activity in the Fenton-like oxidation of OII, achieving complete discoloration and mineralization levels up to approximately 60%, under the most drastic operating conditions (60°C). However, the material also exhibited Fe leaching (up to 4.5 ppm). Therefore, current efforts are focused on the optimization of the membrane synthesis to incorporate iron into the precursor sol, anchoring it in the host structure during the synthesis of mesoporous silica, creating a strong interaction between the metal and the matrix, enhancing the stability of the catalyst.

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## References

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