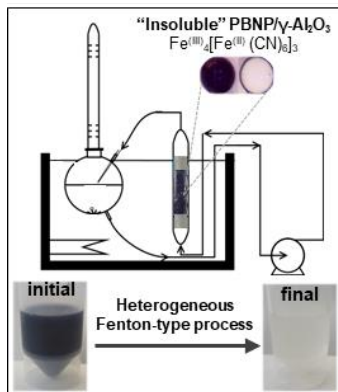


## Prussian Blue-Alumina as Stable Fenton-type Catalysts in Textile Dyeing Wastewater Treatment

POSTER  
Ph.D. Student: N  
Journal: CEJ

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The feasibility to treat a synthetic cotton-textile dyeing wastewater (STW) containing Reactive Black 5 (RB5) by Heterogeneous Fenton-type (HTF) oxidation using a promising PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was investigated. The influence of initial oxidant concentration on the process and the effect of NaCl and other auxiliary products on the oxidation and catalyst stability were studied. With  $[\text{H}_2\text{O}_2]_0 = 11 \text{ mmol/L}$ , the STW was completely discolored, oxidant was fully depleted and the treated solution was not toxic. The catalyst showed to be stable along 8 cycles of 270 min. The NaCl did not affect the oxidant consumption rate, but exhibited a negative effect on RB5 oxidation rate and Dissolved Organic Carbon (DOC) removal. Other additives present in STW contributed to decrease both, oxidant consumption and discoloration rates, and had a deleterious effect on DOC removal.

### Introduction

Textile wastewater exhibits intense color, high salts content and biological recalcitrant character, which brings difficulties to physico-chemical and biological treatment methods. Particularly, applying Advanced Oxidation Technologies (AOTs) as pretreatment that yields a wastewater conditioned for subsequent biological treatment may be optimal, improving the overall efficiency and effectiveness of the treatment process [1]. Among the AOTs, the HFT process stands out due to its advantages regarding catalyst separation and reuse, negligible generation of sludge, and its independence from external energy sources. Operating the HFT process continuously enables the treatment of large volumes of wastewater, and can be easily coupled with a subsequent AOT and/or biological treatment. However, it is essential that the catalysts exhibit stability to sustain the desired reaction efficiently. A previously developed and studied catalyst based on "insoluble" Prussian blue nanoparticles supported on  $\gamma$ -alumina spheres (PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$ ) showed to be active and highly stable in the peroxidation of a model dye in batch and continuous operations [2, 3]. However, it is recognized that salts and specific auxiliary products found in textile dyeing wastewater can pose challenges to the process.

In this study, the feasibility to treat a STW by HFT oxidation using the promising PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was investigated. The influence of initial oxidant concentration on the process was assessed. The effect of NaCl and other additives on the oxidation and catalyst stability was disclosed. The toxicity of the treated solutions was evaluated.

### Material and Methods

The STW was prepared by mixing the dye reactive

black (RB5) and the additives (humectant, detergent, NaCl,  $\text{Na}_2\text{CO}_3$  and softener) taking into account the dyeing process and the percentage of fixation on cotton fibres, following a methodology based on [4]. The RB5 and additives were provided by a local textile industry. STW was characterized in terms of UV-vis spectrum, pH, conductivity, DOC and toxicity. The HFT experiments were carried out using a liquid batch-recycle reactor schematically shown in the Graphical Illustration. The reactor was a 11 mm ID glass column containing 2g of randomly packed PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$ . The "insoluble" PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was prepared as described in [2]. The system was submerged inside a thermostatic bath to maintain the temperature at 70°C. 175 mL of STW, RB5 or RB5 with NaCl aqueous solutions were introduced into the reservoir to start each test. Initial pH was adjusted to 3.  $\text{H}_2\text{O}_2$  was added and allowed for mixing. The initial sample was collected, and the liquid flow (0.1 L/h) through the reactor was initiated by means of a peristaltic pump. Liquid samples were periodically taken out from the reservoir and analyzed at once in terms of pH, UV-Vis spectrum, RB5,  $\text{H}_2\text{O}_2$  and DOC concentrations. Stability was tested by reusing the catalytic bed.

Analytical techniques:  $\text{H}_2\text{O}_2$  concentration was determined by a Glycemia enzymatic test (Wiener Lab). Color after 1:40 dilution was visually assessed. Shimadzu UV-1800 spectrophotometer was used to obtain the UV-Vis spectra between 190 and 800 nm. The absorbance at 590 nm was correlated with RB5 concentration. DOC was measured in a Shimadzu TOC-VCPN analyzer. Toxicity was determined considering the inhibition of the microbial respiratory activity (%) by using a closed respirometer.

## Results and Discussion

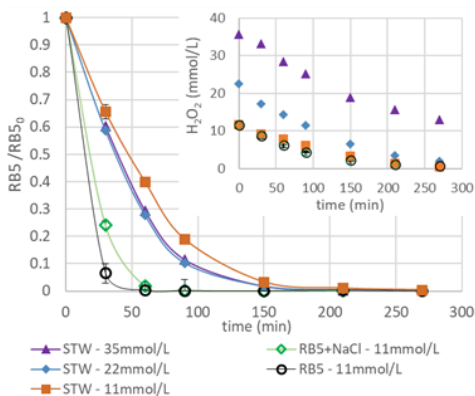
The STW has a moderate organic load (DOC=131 mg/L) and RB5 concentration of 135 mg/L. It presents a conductivity of 16 mS/cm, 10 g/L of Cl<sup>-</sup>, a basic pH of 8.5 and a blue-black colour with a maximum absorbance peak at 590 nm. Wastewater colour remains visible after a dilution 1:40. Toxicity of raw STW is negligible since there is no inhibition of microbial respiratory activity (4.5±1.8%).

The STW oxidation was conducted using different initial H<sub>2</sub>O<sub>2</sub> concentrations. The results, depicted in Figure 1 as solid symbols, show that there was a slight improvement in discoloration rate when the oxidant dose was increased from 11 to 22 mmol/L. No further improvement was observed for a higher dose. In all cases, mineralization was negligible in the conditions and reaction time studied. H<sub>2</sub>O<sub>2</sub> was completely consumed along the studied reaction time (Figure 1 - inset) only with 11 mmol/L.

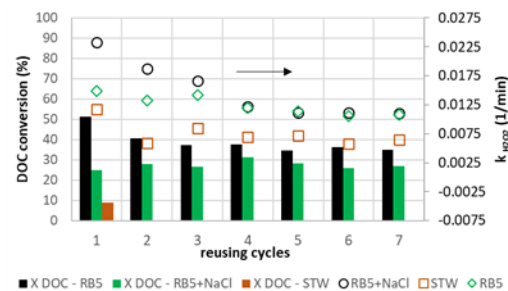
The catalytic bed showed to be stable along 8 cycles of 270 min with [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 11 mmol/L. In all cases, the STW was completely discolored within 210 min and oxidant was fully depleted. For all cycles, oxidant consumption rate followed a pseudo first order kinetic with respect to the oxidant concentration (R<sup>2</sup>>0.981). Apparent kinetic constant values (k<sub>H<sub>2</sub>O<sub>2</sub></sub>) decreased during the first cycles of use and then stabilized (Figure 2). The profiles shown in Figure 1 correspond to the 7th reusing cycle (8th use). The treated STW showed no inhibition of microbial respiratory activity (2.0±0.9%) demonstrating its lack of toxicity.

Aiming to elucidate the influence of NaCl and other additives on the HFT oxidation of STW and on catalyst stability, the process was performed using RB5 and RB5+NaCl aqueous solutions (containing the same concentrations as in the STW). Oxidant consumption rate was faster for these solutions. The NaCl did not affect the oxidant consumption rate, from the 4th cycle onwards, but exhibited a negative effect on RB5 oxidation rate and DOC removal (Figures 1 and 2). The other auxiliary products

contributed to decrease both, oxidant consumption and discoloration rates, and had a deleterious effect on DOC removal, which was negligible for the STW. The high content of inorganic ions (Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) induces the OH• scavenger reactions. Surfactants and other organic additives may also compete with the dye for the HO• radicals [5]. Catalyst demonstrated its stability in all cases.



**Figure 1.** Temporal profiles of normalized RB5 concentration and H<sub>2</sub>O<sub>2</sub> (inset) for the HFT oxidation of RB5, RB5 + NaCl with 11 mmol/L of H<sub>2</sub>O<sub>2</sub> and STW with 11, 22 and 35 mmol/L of H<sub>2</sub>O<sub>2</sub>.



**Figure 2.** DOC conversion at the end of each reaction cycle (bars) and pseudo-first order kinetic constant for H<sub>2</sub>O<sub>2</sub> consumption (symbols) for RB5, RB5 + NaCl and STW.

## Conclusions

The PBNP/γ-Al<sub>2</sub>O<sub>3</sub> demonstrated to be stable in the HFT treatment of a STW. Completely uncolored and no toxic solutions were obtained. The presence of salts and additives used in the dyeing bath negatively affect the process efficiency, especially regarding DOC removal. The combination with other AOTs which promote mineralization and/or with a subsequent biological process may arise as a good treatment strategy.

## Acknowledgments

The authors gratefully acknowledge financial support from National University of Mar del Plata, CONICET (PIP 1220200102822CO, PIBAA 28720210100663CO), ANPCyT (PICT-2018-00575, PICT-2021-CAT-I-00086, PICT-2020-03170).

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