



Continuous heterogeneous Fenton type process intensified by subsequent hydrodynamic cavitation for dye pollution abatement

Stefania Napoleone¹, Gabriel Salierno¹, María Agustina Maisterrena¹, Miryan Cassanello^{1,2*},
Lucila Doumic³, María Alejandra Ayude³

1 Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Industrias. Buenos Aires, Argentina; 2 CONICET-Universidad de Buenos Aires, Instituto de Tecnología de Alimentos y Procesos Químicos – ITAPROQ, Buenos Aires, Argentina; 3 División Catalizadores y Superficies, INTEMA, Juan B. Justo 4302, B7608FDQ, Mar del Plata, Argentina

**Corresponding author E-Mail: miryan@di.fcen.uba.ar*

1. Introduction

Advanced Oxidation Processes (AOPs) have been extensively tested for abatement of highly toxic and biocide contaminants [1]. Among them, the heterogeneous Fenton type (HFT) process poses many advantages related to the catalyst separation and reuse and negligible generation of sludge. Most of the works aimed at developing suitable catalysts and optimizing conditions of HFT processes have been carried out in batch mode [2]. Although results from batch experiments yield valuable information related to catalyst activity, it is difficult to properly test the catalyst stability. The continuous heterogeneous Fenton type (CHFT) process performed in a fixed bed reactor allows the treatment of large volumes of wastewaters with straightforward separation and recovery of the catalyst. Naturally, the catalysts should be particularly stable for a dedicated process carried out in a fixed bed reactor. Prussian blue, a mixed valence iron compound (ferric hexacyanoferrate– $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) is a good candidate particularly for its very low solubility in water. The suitability of Prussian blue nanoparticles (PBNP) supported on γ -alumina for the catalytic peroxidation of the model dye Orange G (OG) in batch operation has been shown in previous contributions [3, 4].

The aim of this work was to study the capability of a fixed bed reactor formed by PBNP/ γ - Al_2O_3 spheres for the continuous discoloration and mineralization of an OG solution. The influence of the flow rate, oxidant concentration and temperature was explored. Moreover, since hydrodynamic cavitation (HC) has been proposed as an excellent method for intensifying AOPs, and particularly HFT processes [5], it was applied in this case for intensifying the process efficiency. Thus, under certain conditions in which the output might still contained significant amount of reactive organic species (ROS), the liquid was collected and subjected to HC for optimizing the efficiency of the method.

2. Methods

The catalyst was prepared as described in [4] by synthesizing PBNP and immediately adsorbing them onto γ - Al_2O_3 spheres of 2.5 mm mean diameter. The catalysts beads were then packed in a 24 mm internal diameter glass column. The catalyst bed (20g of 0.4%w PBNP/ γ - Al_2O_3) had 80 mm length and was located above a 10 mm length section containing 3mm glass beads. The reactor and a coil located before the entrance were immersed in a thermostatic bath with regulated temperature. The reactor temperature was determined by a thermocouple located in the upper part of the bed.

The liquid flowed upwards to ensure complete catalyst wetting. Even if oxygen may evolve due to hydrogen peroxide decomposition, no visible bubbles were produced. The reactor was fed from a reservoir containing

the liquid, which was a 0.02mM aqueous solution of dye mixed with different concentrations of hydrogen peroxide. The reservoir was kept in the dark at ambient temperature. The flow rate was regulated with a peristaltic pump. The liquid passed through the heating coil before entering the reactor. The dye and oxidant concentrations at the reactor outlet were determined every 20 minutes for at least one hour. Steady state was generally attained after 10-20 minutes. Several liquid flow rates, oxidant concentrations and temperatures were examined. For given conditions, the residual total organic carbon (TOC) and the distribution of organic acids formed were assessed. In addition, iron concentration in the outlet was measured to quantify the extent of iron leaching.

For high liquid velocities, i.e., low residence time in the reactor, hydrogen peroxide was not completely consumed and the remaining concentration of reactive oxygen species (ROS) would probably be significant. Hence, the output was collected and subjected to hydrodynamic cavitation to intensify the process. A vortex diode type cavitator provided by Vivira Process Technology S.A. was used. Experiments in the cavitation unit were performed at 40°C and 3.5bar pressure through the vortex diode valve. Further discoloration, TOC removal extent and distribution of organic acids were determined periodically during the subsequent 60 minutes to analyse the effect of HC on the output.

3. Results and discussion

Experiments were conducted in the fixed bed reactor at different operating conditions. Figure 1 illustrates the influence of the liquid residence time on the relative concentration of OG and hydrogen peroxide. As expected, an increase in oxidant concentration and/or temperature promoted OG conversion. Although temperature also affected hydrogen peroxide decomposition, the effect on OG conversion was significantly larger. Hence, an increase in temperature enhanced the efficiency of oxidant consumption for dye discoloration. Iron leaching was generally low, representing an hourly loss of around 0.1% of the iron load.

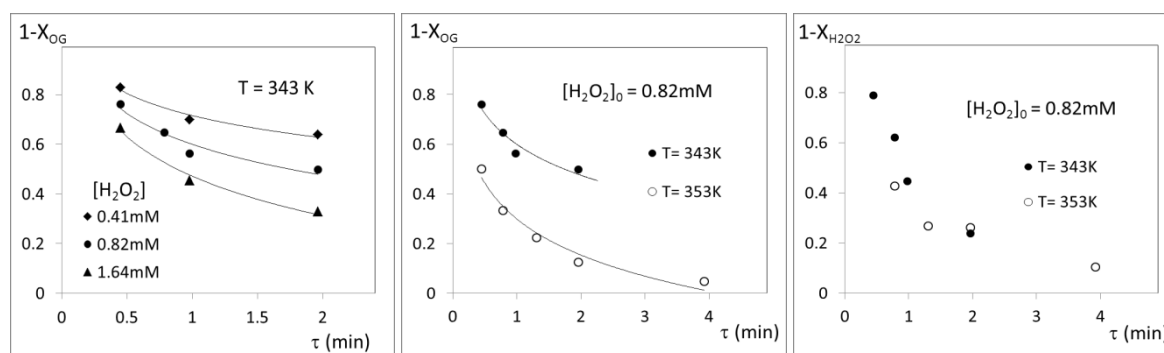


Figure 1. Left: relative concentration of OG attained at 343 K under steady state, as a function of the liquid residence time, for different oxidant initial concentrations; middle: relative concentration of OG vs liquid residence time obtained with a given oxidant concentration at two temperatures; right: influence of temperature on hydrogen peroxide decomposition

The outlet solution from experiments conducted at a liquid residence time of 30s was collected for several hours and subjected to HC. Complete discoloration was attained very fast, HC was continued for 60 minutes to investigate the effect on mineralization and organic acids distribution. Further results focusing on TOC removal and improvements arising from the hybrid CHFT-HC process over the CHFT will be presented in the conference.

References

- [1] R. Dewil, D. Mantzavinos, I. Poulios, M.A. Rodrigo, J. Environ. Manage. 195 (2017) 93–99
- [2] C. di Luca, P. Massa, J. Grau, S. Marchetti, R. Fenoglio, P. Haure, App. Cat. B: Environ. 237 (2018) 1110–1123
- [3] L. Doumic, G. Salierno, P. Haure, M.C. Cassanello, M.A. Ayude, Catal. Today, 240, 67-72
- [4] L. Doumic, G. Salierno, C. Ramos, P. Haure, M.C. Cassanello, M.A. Ayude, RSC Adv. 6 (2016) 46625–46633
- [5] M. Cai, J. Su, Y. Zhu, X. Wei, M. Jin, H. Zhang, C. Dong, Z. Wei, Ultrasonic Sonochemistry 28 (2016) 302–310