Application of experimental design techniques for the optimization and the robustness study of photocatalytic degradation of emerging contaminants in water

Masho H. Belay[a], Elisa Robotti[a], Maria Cristina Paganini[e], Claudio Medana[b], Federica Dal Bello[b], Marcello Manfredi[c,d], Sara Timo[a,d], Paola Calza[e], Emilio Marengo[a]

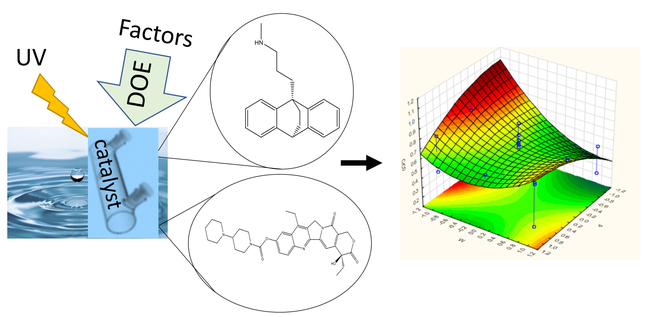
[a] Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale Michel 11, 15121 Alessandria, Italy; [b] Department of Molecular Biotechnology and Health Sciences, University of Turin, Via Nizza 52, 10126 Torino, Italy; [c] Department of Translational Medicine, University of Piemonte Orientale, Via Solaroli 17, 28100 Novara, Italy; [d] Center for Translational Research on Autoimmune and Allergic Diseases, University of Piemonte Orientale, Corso Trieste 15/A, 28100 Novara, Italy; [e] Department of Chemistry, University of Turin, Via Giuria 7, 10124 Torino, Italy. E-mail: masho.belay@uniupo.it.

INTRODUCTION

- Recently, great attention has been given to the spread of emerging contaminants in the environment and the development of removal strategies.
- In this context, we present a work that is part of the results obtained within the AQUAlity project (H2020-MSCA-ITN-2017 - Project N. 765860), which is devoted to developing an interdisciplinary cross-sectoral approach to effectively address the removal of contaminants of emerging concern from water.
- The current study focused on the photocatalytic degradation of two emerging contaminants of concern: maprotiline (an antidepressant) and irinotecan (anticancer drug).
- Experimental design techniques were applied to achieve two main goals: the optimization of the procedure and the identification of the robustness region around the nominal conditions.

EXPERIMENTAL

- Photocatalytic degradation under UV irradiation was performed using Philips Actinic BL TL-D lamps (290–400 nm range, 90±2 W m^{-2}) with a maximum emission at 365 nm, using Ce doped ZnO photocatalyst for maprotiline and Ce/Cu co-doped ZnO for irinotecan.



- The optimization involved 5 parameters: UV power (W), distance of the solution from the UV lamps (d), pH, concentration of the catalyst (K) and concentration of the contaminant. The levels are shown below.

Level	d (cm)	W (W m^{-2})	K (mg L^{-1})	MAP (mg L^{-1})	pH
-1	10	30	50.0	1.0	5.00
0	30	60	100.0	5.0	7.00
1	50	90	150.0	9.0	9.00

- For both molecules, a fractional factorial design (2^{5-2}) was adopted with the addition of a star design and at least 4 replicates at the center of the domain, and the experiments were evaluated at a fixed degradation time close to the half-time calculated at the center of the experimental domain.
- The target molecules and their degradation products were identified and quantified using UHPLC-HRMS with Orbitrap Q-Exactive Plus for maprotiline and Orbitrap Fusion for irinotecan.
- For each target molecule, as well as the signals for some of the identified degradation products, the ratio of the concentration at the fixed degradation time to the initial concentration (C/Co) was modelled with respect to the studied factors.

RESULTS

Maprotiline degradation using Ce doped ZnO

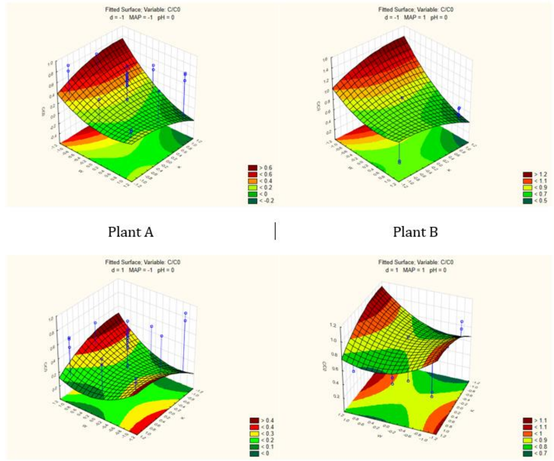
(Note: Results for irinotecan are not shown here)

- Kinetic study: Half-time of 4.71 min (R^2=0.9955)
- A very good model was obtained with R^2 = 0.9715.

$$Y = 0.631 + 0.319*MAP - 0.109*W - 0.128*pH - 0.067*d^2 + 0.136*W^2 - 0.076*K^2 - 0.070*MAP^2 + 0.148*(d*W) - 0.128*(W*K) + 0.037*(MAP*pH).$$

- A grid search algorithm was used to identify the best overall conditions and to test the system's behavior when some constraints are present, and four distinct scenarios were identified given as A, B, C and D in the table below.

Conditions	D	W	K	MAP	pH	Y pred
Global optimum	-1	1	1	-1	1	-0.32
Plant A	-1	**1**	**1**	-1	0	-0.15
Plant B	-1	1	1	1	0	0.48
Plant C	1	-0.6	-1	-1	0	0.14
Plant D	1	-0.6	-1	1	0	0.68



- Among the four scenarios identified, response surfaces revealed that **Plant C** provided with the best results that have more practical and economic implications: (i) Medium to high UV irradiance and low levels of the catalyst, and (ii) Medium UV irradiance and low to high catalyst levels. Furthermore, very small variations of UV irradiance and amount of catalyst are tolerable.

ACKNOWLEDGMENT

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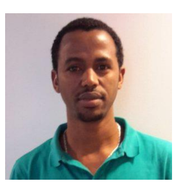

Masho H. Belay