Degradation of Micropollutants in WWTP Effluent by Recycled Sludge and its Performance on CPC Reactor

J.H.F. Jesus1,2 , K.V.L. Lima² , A.Ruíz-Delgado3,5, A.M. París-Reche3,4, S. Malato3,5, A. Aguera3,4, R. F. P. Nogueira² .

(1) University of São Paulo (USP), Institute of Chemistry, São Paulo, Brazil (2) São Paulo State University (UNESP), Institute of Chemistry, Araraquara, Brazil (3) Solar Energy Research Center (CIESOL), Ctra. de Sacramento s/n, Almería, Spain (4) University of Almería (UAL), Department of Chemistry and Physics, Almería, Spain and (5) Plataforma Solar de Almería-CIEMAT, Ctra. Senés km 4, Tabernas, Almería.

This study evaluated the efficiency of the solar photo-Fenton process for degrading microcontaminants originally present in an effluent from a WWTP in Brazil by using a low cost, efficient, longwave UV/visible-light responsive catalyst based on sludge (SLC-600) previously characterized. From the 175 target microcontaminants, 48 compounds were quantified in the effluent, with a total concentration of 147 μ g L⁻¹. After 140 min (accumulated UVA dose 170 kJ $m²$), 43% of degradation was achieved, highlighting the efficiency of the process in a real effluent. The total concentration of the microcontaminants was reduced to 84 μ g L⁻¹, while around 25 compounds were completely degraded (< LQ). This study can provide valuable information on the use of SLC-600, a residue-based catalyst, as an alternative to micropollutants degradation and its use in large scale in a compound parabolic collector (CPC) reactor.

Introduction

Contaminants of emerging concern (CECs) are compounds in use worldwide that came up as an environment concern due to their adverse ecological and toxicological effects on aquatic organisms. Since they are not efficiently removed after conventional treatment in the WWTPs, they are released into aqueous environment, making domestic sewage one of the main sources of CECs [1-3].

Advanced oxidation processes (AOPs) are useful to degrade CECs in wastewater. Among AOPs, photo-Fenton processes exhibit effective economic advantages when performed under natural solar irradiation, due to the cyclic oxidation and photoreduction of iron under sunlight, becoming a trend in post-treatment of wastewater, [4].

In a recent study [5], a low cost, efficient, longwave UV/visible-light responsive catalyst prepared from WWTP sludge was properly characterized and tested for use as a solar photo-Fenton catalyst in wastewater treatment. Here, it was evaluated its application as a tertiary treatment in the matter of removal of CECs present in effluent form urban wastewater and its use in large scale in a compound parabolic collector (CPC) reactor.

Material and Methods

The use of the solar photo-Fenton process as a tertiary treatment was evaluated based on the decay of the concentration of the target microcontaminants present in the effluent from a WWTP by using a previously studied low-cost material, SLC-600 [5]. The previously optimized experimental conditions are as follows: 0.5 g L⁻¹ of SLC-600, 10 mmol L⁻¹ $H₂O₂$ at pH 3.5. The degradation experiments were performed in a glass photoreactor (5.5 cm height and 9.5 cm diameter) with a capacity of 300 mL, at 32 °C, under magnetic stirring and solar irradiation , in batch mode (solar dose after 140 min: 170 kJ m $^{-2}$, measured in the UVA). The analysis of the raw effluent and after photo-Fenton samples was carried out using a UHPLC-QqQ-MS/MS.

POSTER Journal: NONE

Posteriorly, solar photo-Fenton experiments were carried out in a compound parabolic collector (CPCs) at Plataforma Solar de Almería (Irradiated surface (Ai) : 0.224 m², Irradiated volume: 2.5 L, Total Volume (VT): 10 L, Flow rate: 22 L min-1). Sulfamethoxazole (SMX) was chosen as a CEC model in demineralized water (DW) and natural water (NW). Radiation intensity was measured with a UV radiometer titled 37º according to PSA coordinates.

Results and Discussion

Among the AOPs that can be applied as tertiary treatment, the solar photo-Fenton process is an efficient possibility to degrade microcontaminants in WWTP effluents..

Thus, the efficiency of the solar photo-Fenton process using SLC-600 for degrading microcontaminants in a real effluent was evaluated in bench scale. These assays can contribute to the elucidation of oxidation mechanisms and degradation kinetics of microcontaminants, the generation of transformation products, deconjugation reactions during the treatment as well as matrix effect.

From the 175 target microcontaminants monitored,

48 compounds were quantified in the effluent, with a total concentration of 147 μ g L⁻¹. After 140 min (accumulated UVA dose 170 kJ $m⁻²$) of solar photo-Fenton, the total concentration of the microcontaminants decreased to 84 μ g L⁻¹, with total degradation of around 25 compounds (< LQ). This decrease in the total concentration of the micropollutants represents 43% of degradation (Figure 1), highlighting the efficiency of this catalyst in degrading micropollutants in a real effluent. Longer treatment time can be applied to achieve a higher conversion.

Figure 1: Degradation of the solar photo-Fenton process for degrading microcontaminants in effluent from WWTP in a lab reactor. Conditions: $[H_2O_2] = 10$ mmol L⁻¹; $[SLC-600] =$ 0.5 g L⁻¹; pH 3.5

To evaluate the possibility of using SLC-600 as a catalyst in a larger scale, experiments were carried out under sunlight in CPCs at PSA with SMX as a model compound. Figure 2 shows the degradation curve for photo-Fenton experiments with SMX in demineralized water (DW) and natural water (NW). At the end of the treatment (300 min), the concentration of SMX descreased from 20 mg L^{-1} to 4.5 and 5.5 mg L^{-1} in DW and NW, respectively, with TOC removal of 15% only in DW, similar to the previous study [5].

Figure 2: Degradation of SMX in a CPC reactor in DW and NW. Conditions: $[SMX]_0 = 20$ mg L⁻¹; $[H_2O_2] = 10$ mmol L⁻¹; [SLC-600] = 1.0 g L⁻¹; pH 3.5. The resulting average solar
UV irradiance was 43.7 W m⁻² (average accumulated Q_{uv} = 18.1 kJ L⁻¹ during 5 h of experiment).

As an additional way to assess the persistence of TPs during photo-Fenton process with SLC-600 in a CPC reactor, the identification of the main TPs generated during the treatment and their evolution as a function of the time was carried out in DW and NW. The TPs of SMX in DW showed similar behavior compared to TPs in NW. Most of the hydroxylated products were detected in DW and in NW, evidencing a similar pathway of degradation in both matrices. As SMX concentration decreases, TPs concentration increases, mostly in the beginning of the experiment. As the reaction proceeded, TPs concentration decreased, revealing their nonpersistence nature during photo-Fenton process in a CPC reactor, and the efficiency of SLC-600, that can be used as catalyst for degrading CECs in different matrices.

Conclusions

A previously studied catalyst, SLC-600, was applied in a solar photo-Fenton process aiming application in a tertiary treatment to degrade microcontaminants present in WWTP. After 140 min (accumulated UVA dose 170 kJ m⁻²), the total concentration of the CECs was reduced in 43%. SLC-600 was also tested in a large scale (CPC reactor), with SMX as a model compound maintaining the efficiency. TPs evolution showed their nonpersistence nature. The promising results highlight the capacity of SLC-600 use in photo-Fenton process as a complementary treatment in a large-scale.

Acknowledgments

The authors are grateful to the São Paulo State University (PROPe/UNESP), University of São Paulo (PRPI and IQ), São Paulo State Research Foundation (FAPESP), DAAE/Araraquara, the National Council for Scientific and Technological Development (CNPq) and the Coordination for the Improvement of Higher Education Personnel (CAPES, Finance Code 1). The authors also wish to thank the Grant PID2021-126400OB-C33 (AquaEnAgri) funded by MCIN/AEI/ 10.13039/501100011033 and, by "ERDF A way of making Europe" and the financial support by the Andalusian Government through the MODITRAGUA project (PROYEXCEL_00585).

References

[1] Marson, E.O., Paniagua, C.E.S., Gomes Júnior, O., Gonçalves, B.R., Silva, V.M., Ricardo, I.A., Maria, M.C., Amorim, C.C., Trovó, A.G.. Science of the Total Environment 836, 2022.

- **[2]** Martínez-Piernas, A.B., Plaza-Bolaños, P., Agüera, A., J Hazard Mater 412, 2021.
- **[3]** Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., N Biotechnol 32, 2015, 147.
- **[4]** Thomas, N., Dionysiou, D.D., Pillai, S.C., J Hazard Mater 404, 2021, 124082.

[5] de Jesus, J.H.F., Lima, K.V.L., Hammer, P., Nogueira, R.F.P., Chemical Engineering Journal 467, 2023, 143380.