Assessing the Environmental Safety of Wastewater Post-treatment by Advanced Oxidation Processes: A Species Sensitivity Distribution Approach

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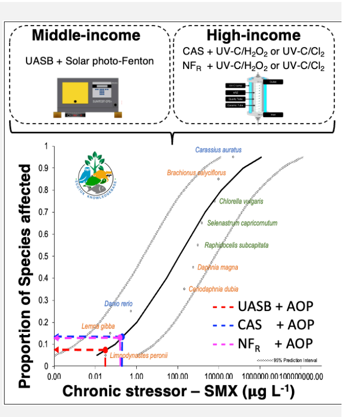

This study evaluates the effectiveness of advanced oxidation technologies (AOTs) in removing contaminants of emerging concern (CECs) and their potential ecological risks in municipal wastewater. Diclofenac and sulfamethoxazole were used as target CECs, and their removals were investigated in (i) upflow anaerobic sludge blanket (UASB) effluent from a middle-income country, (ii) conventional activated sludge (CAS) effluent, (iii) and nanofiltration retentate (NF_R) from a high-income country. Solar photo-Fenton was used for UASB effluent, while UV/H_2O_2 and UV/Chlorine were applied for CAS and NF_R. Species sensitivity distributions were constructed to assess the potential acute and chronic effects of residual CECs to aquatic and terrestrial organisms. CECs only pose a potential threat to freshwater organisms under poor dilution capacity (9x) (7.5%-12.5%). AOP-treated matrices presented no risk to tested terrestrial organisms (crops), indicating its potential for safety for agricultural reuse.

Introduction

Contaminants of emerging concern (CECs) in municipal secondary effluents (MSEs) pose a threat to environmental and human health. Advanced oxidation technologies (AOTs) are strategies to address this concern by removing CECs and controlling their toxicity. Thus, this study explores the application of AOTs in wastewater treatment scenarios reflecting different economic settings. Upflow anaerobic sludge blanket (UASB) systems, prevalent in low- and middle-income countries, such as Brazil, due to their low operational costs [1], were studied alongside conventional activated sludge (CAS), the dominant technology in high-income countries. Additionally, nanofiltration, an advanced separation method used in high-income countries for CEC removal from MSE, was also investigated for the nanofiltration retentate (NF_R) stream in which CECs remains a concern [2]. AOTs were employed to further reduce CECs in these treatment streams.
However, solely evaluating CEC removal efficiency overlooks potential risks from residual CECs [3]. Hence, the integration of toxicity data from multiple studies and endpoints through a probabilistic approach such as the species sensitivity distribution (SSD) compiles and integrates endpoints from diverse organisms and extrapolates individual and population-level responses to the community level by the estimation of a hazardous concentration to 5% (HC_5) as a threshold value for the protection of 95% of tested species [4]. Therefore, this study proposes a framework to assess potential risks of AOTs-treated wastewaters by using the SSD approach for both aquatic (wastewater discharge) and terrestrial (agricultural reuse) species.

Material and Methods

UASB effluents from southeast Brazil were used to represent middle-income countries. Solar photo-Fenton (SPF) with intermittent additions of Fe^{2+} at natural pH was employed for CEC removal [5]. In contrast, CAS and NF_R effluents from Portugal, representing high-income countries, were treated by UV-C/H_2O_2 and UV-C/Chlorine under continuous flow (retention time of 3.4 min) using a tube-in-tube membrane photoreactor for CEC removal [6].
Among CECs analyzed via AOTs performance, two target CECs, diclofenac (DCF) and sulfamethoxazole (SMX), were selected for a thorough evaluation of potential risks using toxicity data gathered over the past 20 years (2003-2023). Data were obtained from the USEPA ECOTOX Knowledgebase. Separate databases were created for acute and chronic effects to (i) freshwater aquatic organisms (relevant for discharge) and (ii) terrestrial organisms (relevant for agricultural reuse). The USEPA SSD generator was used to construct and customize separate SSDs curves (acute, chronic, aquatic, or terrestrial organisms). Dilution factors (DFs) corresponding to optimal dilution (DF 90), good dilution (DF 64), regular dilution (DF 27), and poor dilution (DF 9) were considered according to the National Water Agency of Brazil, to simulate potential scenarios for wastewater discharge.

Results and Discussion

SPF treatment of UASB effluent followed by a biological trickling filter (UASB+ TF) achieved 83% of $\sum$CECs removal, compared to 65% removal for the effluent from UASB system alone. This difference is attributed to variations in organic and inorganic matter content between MSE produced by UASB+TF and UASB standalone systems. Notably, removal rates of target CECs in this study were comparable (Table 1), demonstrating the effectiveness of Fenton-based processes at natural pH without chelating agents, particularly for complex matrices such as UASB effluents (middle-income country) compared to CAS effluent.

Considering advances in technologies applied in municipal wastewater treatments in high-income countries, such as Portugal, a significant difference in efficiencies was observed between remaining concentrations of target CECs in MSE from CAS and NF_R. This is likely due to the complexity of these matrices and potential effects of radical scavengers [1]. For both wastewater matrices (CAS or NF_R), UV-C photolysis (3.3 kJ L^{-1}) achieved high (>95%) removal of CECs susceptible to photolysis, such as DCF and SMX, although lower treatment performance was observed for NF_R (67%-90%).

Comparing HC_5 values for target CECs with residual concentrations of CECs after treatment, it is clear that AOTs performed effectively in all matrices, as target CECs were below hazardous concentration to 5% of tested species (HC_5) for acute toxicity to freshwater organisms even without considering the dilution factor. This finding underscores the importance of evaluating chronic toxicity, even though residual concentrations fell below the HC_5 for acute toxicity in freshwater organisms without considering dilution. The chronic HC_5 values obtained for the tested species (Table 1) demonstrated that SMX still poses potential risk to freshwater aquatic organisms since concentrations must be inferior to 0.01 μg L^{-1} to protect 95% of the tested species. Considering DF 9, which represents the scenario of poor dilution capability, post-treatment of these matrices via AOTs for both middle- and high-income countries resulted in potential threat to 7.5% to 12.5% of the tested species as represented by the dashed lines in the Graphical Abstract. Furthermore, the lowest HC_5 value for terrestrial species in this study was also observed for SMX. Yet, AOTs could safeguard 95% protection of the tested terrestrial organisms for all post-treated matrices. As terrestrial organisms encompass main crops, these results indicate the safety of agricultural wastewater reuse with no potential risk for plant development.

Table 1. Residual concentrations of diclofenac and sulfamethoxazole after the application of AOPs and protective values for freshwater aquatic organisms ($HC5^a$) and terrestrial organisms ($HC5_b$)

Matrix + AOP	Diclofenac				Sulfamethoxazole			
	Residual conc. (μg L^{-1})	Removal (%)	HC_5^a (μg L^{-1})	HC_5^b (μg L^{-1})	Residual conc. (μg L^{-1})	Removal (%)	HC_5^a (μg L^{-1})	HC_5^b (μg L^{-1})
UASB-TF + SPF	0.2	44	0.04	190.6	0.21	36	0.01	2.3
UASB + SPF	0.3	44			0.27	43		
CAS + UV-C/H_2O_2	0.7	94			1.5	94		
CAS + UV-V/Chlorine	0.5	95			2.3	92		
NF_R + UV-C/H_2O_2	1.0	86			1.3	70		
NF_R + UV-V/Chlorine	1.1	87			0.9	74		

Conclusions

AOTs effectively remove CECs from MSEs even considering dissimilarities between middle- and high-income countries, yet potential chronic effects require further investigation. This study establishes a novel framework using species sensitivity distribution to assess the ecological risks of AOTs-treated wastewater considering its discharge or agricultural reuse risks based on ecotoxicity data. Comprehensive risk evaluation frameworks are essential to inform stricter regulations and promote environmental sustainability.

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