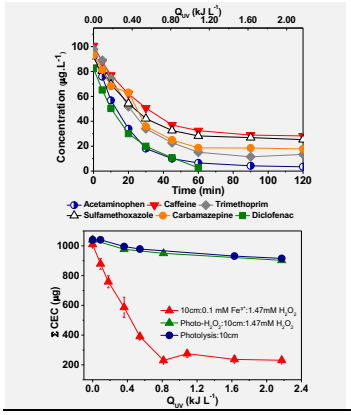
Removal of contaminants of emerging concern, disinfection, and antibiotic-resistant bacteria in UASB system effluent at natural pH by modified solar photo-Fenton with Fe^{3+}-EDDS

ORAL
Ph.D. Student: N
Journal: YES

F. Rodrigues-Silva[1], *E.P. Costa*[1], *M.C.V.M. Starling*[1], *C. C. Amorim*[1]. *(1) Research Group on Environmental Applications of Advanced Oxidation Processes, the Federal University of Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, Minas Gerais, 31270-901, Brazil, camila@desa.ufmg.br*



This study aims to evalute the efficiency of modified solar photo-Fenton with the Fe^{3+}:EDDS chelating agent as a post-treatment for a municipal secondary effluent (MSE) from an upflow anaerobic sludge blanket reactor (UASB), followed by a trickling filter (TF). Treatment efficacy was assessed by the removal of contaminants of emerging concern (CECs), disinfection by total coliforms (TC), *E. coli*, and total heterotrophic bacteria (THB), and the removal of antibiotic-resistant bacteria (ARB). Solar photo-Fenton achieved the highest removal of CECs (86% for CECs, 2.47±0.78 logs for TC and 2.53 logs for *E. coli*) compared to photoperoxidation (14% for CECs, 3.58 logs for TC and 3.35 logs for *E. coli*). Sulfamethoxazole + trimethoprim and azithromycin ARB were entirely removed by both processes. Thus, modified solar photo-Fenton with Fe^{3+}:EDDS proved efficient for CEC removal, disinfection and ARB elimination in UASB+TF MSE.

Introduction

Contaminants of emerging concern (CECs), such as pesticides, hormones, pharmaceutical drugs, and antibiotic-resistant bacteria (ARB), are continuously released into environment due to their insufficient removal by conventional wastewater treatment processes [1]. Therefore, there is a critical need for technologies to remove CECs, especially in municipal secondary effluents (MSE). Advanced oxidation technologies (AOTs), like solar photo-Fenton, are indicated for treating environmental matrices such as MSE. Current research on removing CECs from MSE via solar photo-Fenton post-treatment mainly focuses on effluents from conventional activated sludge (CAS) systems. However alternative wastewater treatment systems like upflow anaerobic sludge blanket (UASB) reactors are gaining traction in low- and middle-income countries, particularly in Brazil [2]. Hence, investigating the efficiency of photo-Fenton for treating MSE from UASB system is crucial.

Giving the high potential of AOTs for advanced wastewater treatment using low-cost options like open photoreactors (*e.g.,* raceway pond reactor - RPR) and the abundant solar light availability in tropical low- or middle-income countries, this work proposes applying modified photo-Fenton at neutral pH with the complexing agent Fe^{3}+:EDDS (1:2) for the removal of CECs, disinfection, and elimination of ARB in MSE from a UASB system followed by a biological trickling filter.

Material and Methods

The removal of six target CECs, namely acetaminophen (ACE), caffeine (CAF), carbamazepine (CBZ), diclofenac (DCF), sulfamethoxazole (SMX), and trimethoprim (TMP), was evaluated in UASB + TF MSE. Each CEC was spiked the MSE at an initial concentration of 100 µg L^{-1}. The influence of CEC spiking on disinfection and ARB removal was also assessed. CEC quantification followed high-performance liquid chromatography as described by Rodrigues-Silva et al. [3]. Disinfection for total coliforms (TC) and *Escherichia coli* was evaluated using the Colilert method (IDEXX®) following USEPA guidelines. Similar, the removal of ARB was assessed by plating method using non-selective agar medium enriched with SMX + TMP (350 mg L^{-1} + 350 mg L^{-1}) and azithromycin (AZM, 1,000 mg L^{-1}) using selective media targeting bacteria resistant to SMX/TMP and AZM. Total heterotrophic bacteria (THB) were evaluated as the control in the non-enriched media. The photo-Fenton process was conducted at bench scale in a solar chamber simulator (Atlas – SunTest CPS+) with 30 mg L^{-1} of H_2O_2 and 5.5 mg L^{-1} of total iron (Fe_{total}), at natural pH (7.5 - 8.5). Iron source was a mixture of $Fe_2(SO_4)_3.5H_2O$ and the chelating agent EDDS. The treatment time was up to 120 minutes and accumulated ultraviolet energy (Q_{UV}) was determined.

Results and Discussion

The removal of CECs obtained for the post-treatment of UASB + TF MSE was similar to the degradation of CECs performed on CAS MSE [4]. DCF was the most susceptible to degradation by photolysis and AOPs, showing higher removal in shorter reaction times and lower accumulated irradiation energy as shown in Graphical Abstract. A

longer treatment time (48 min), with a Q_{UV} of 0.87 kJ L^{-1}, was required to achieve an 80% removal efficiency for CECs compared to results obtained under similar, and even more unfavorable, conditions with lower radiation penetration (due to a shallower reaction depth of 10 cm compared to 15 cm) [4]. Dissolved organic carbon present in UASB systems MSE compared to CAS MSE may affect oxidation reactions and result in different pathways and degradation rates [2]. There was rapid oxidant consumption at the beginning of treatment for both MSE spiked with CECs and without spiking. However, by the end, the total consumption of H_2O_2 was 94% and 74%, respectively (Figure 1).

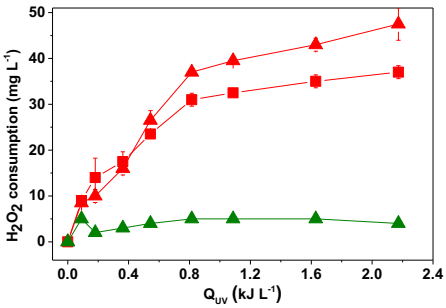


Figure 1. H2O2 consumption during photoperoxidation, and modified solar photo-Fenton at natural pH for UASB+TF MSE spiked with CECs, and UASB+TF non-spiked with CECs.

This difference is possibly related to relatively early iron precipitation in the non-spiked MSE compared to the spiked matrix. Iron precipitation only began after 60 for non-spiked MSE and 90 min of reaction for the spiked MSE (Figure 2).

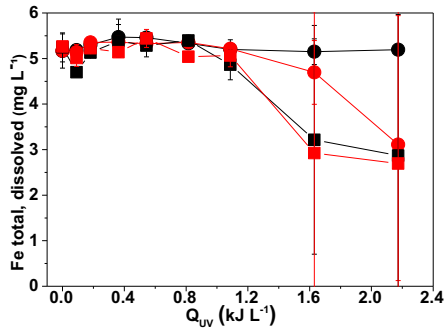


Figure 2. Total iron (black symbols) and dissolved iron (red symbols) during modified solar photo-Fenton at natural pH for UASB+TF MSE spiked with CECs, and UASB+TF non-spiked with CECs.

Regarding disinfection, photolysis was not efficient for the removal of TC. It also showed the least efficiency for TC, *E. coli*, THB, and ABR by the end of the 2-hour reaction period (2.3 kJ L^{-1}). Solar photoperoxidation was highly efficient in the disinfection process for TC (3.58 logs), *E. coli* (3.35 logs) THB (2.78 logs), and achieved total removal of ARB, showing the highest removal efficiencies and the shortest reaction time required required to achieve the complete ARB removal (30 min, 0.6 kJ L^{-1}). However, it is important to highlight that despite the high disinfection efficiency by photoperoxidation, the removal of CECs was limited to 14%.

Therefore, the application of modified solar photo-Fenton process at neutral pH with Fe^{3+}:EDDS complex (1:2) showed an 86% removal efficiency for the ΣCECs, 2.47±0.78 log removal of TC, 2.53 log removal for *E. coli*, and total removal of ARBs (SMX + TMP, and AZM) within a reaction time between 30 min (0.6 kJ L^{-1}) and 60 min (1.1 kJ L^{-1}).

Conclusions

High disinfection efficiency and removal of ARB were achieved by photoperoxidation. However, the modified solar solar photo-Fenton process at neutral pH exhibited the highest removal efficiency of CECs, making it a promising post-treatment option for UASB + TF MSE. This study demonstrates that modified solar photo-Fenton with Fe^{3+}-EDDS (1:2) effectively removes CECs and achieves disinfection similar to the results observed in studies using CAS MSE. Following this advanced treatment, the resulting MSE would be suitable for reuse applications such as irrigation due to its significantly lower concentrations of CECs and ARB compared to secondary effluent generated by the evaluated UASB system.

Acknowledgments

The foundation of Support and Research of the state of Minas Gerais (FAPEMIG) [grant number PPM 00489 17]; Coordination of Superior Level Staff Improvement (CAPES) [001]; and the National Council for Scientific and Technological Development (CNPq) [grant numbers, 436902/2018 4, 314642/2021 8] have supported this work.

References

[1] E.O. Marson, C.E.S. Paniagua, O. Gomes Junior, B.R. Gonçalves, V.M. Silva, I.A. Ricardo, M.C.V.M. Starling, C.C. Amorim, A.G. Trovó, *Science of the Total Environment*, 836 (2022) 150605.

[2] F. Rodrigues-Silva, M.C. Starling, C. Amorim, *Science of the Total Environment*, 850 (2022) 157940.

[3] *F. Rodrigues-Silva, M.C. Starling, D. Rodrigues, C. Amorim, Journal of Environmental Chemical Engineering, 11 (2023) 110675.*

[4] E.P.Costa, M. Roccamante, P. Plaza-Bolaños, I. Oller, A. Agüera, C.C. Amorim, S. Malato, *Science of the Total Environment,* 755 (2021) 142624.