Abatement of pharmaceuticals and disinfection of hospital wastewater by LED photo-Fenton

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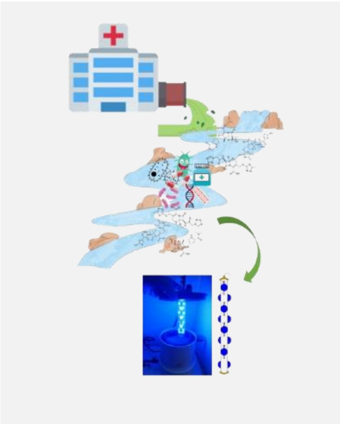

Hospitals produce complex wastewater (HWW) containing pharmaceuticals, pathogens and antibiotic resistance genes. However, these wastewaters are commonlly discharged in the sewage system in Brazil to be treated in Wastewater Treatment Plants (WWTP) which may contribute to the spread of antimicrobial resistance. The LED photo-Fenton (PF) process is an effective solution to remove contaminants from HWW. This study evaluated the degradation of ten pharmaceuticals commonly found in HWW by LEDs PF (450 nm). A duty Cycle (Dcy) 70% provided comparable results to 100% for HWW treatment, offering cost savings and extended LED lifespan. The LED photo-Fenton process at an acidic pH (2.8) and near-neutral pH removed approximately 65% and 48% removal of global contaminants of emerging concern (CECs), respectively. Disinfection efficacy was higher at acidic pH (5.6 and 6.8 log removal of *E. coli* and total coliforms, respectively) compared to near-neutral pH (4.5 log removal of both).

Introduction

Hospital wastewater (HWW) contains a mix of persistent chemicals, organic matter, detergents, disinfectants, drugs, and other contaminants. It hosts multi-resistant bacteria and it is more toxic than domestic sewage, showing 5 to 15 times higher toxicity to certain organisms than domestic sewage [1]. The concentration of antibiotics and antibiotic-resistant bacteria and genes in HWW is 5 to 10 times greater than in domestic sewage [2].

Globally, common practice involves discharging untreated HWW into municipal sewage systems [3]. However, this poses challenges, as biological reactors in these systems are not designed to degrade pharmaceutical drugs [4,5], compromising the overall treatment process. This also contributes to the selection and spread of antibiotic resistance bacteria (ARB) and antibiotic resistance genes (ARG) to the environment [3].

The photo-Fenton (PF) process is efficient to remove contaminants from HWW [6,7]. Alternative irradiation sources like sunlight and LEDs are currently being explored for this process to enhance sustainability and reduce costs [8,9]. In this context, this study evaluates the use of a novel LED system for photo-Fenton treatment of HWW, aiming to remove contaminants and achieve disinfection.

Material and Methods

The Degradation experiments were conducted in HWW sampled in a hospital in Brazil. HWW was filtered (20 µm) and fortified with target compounds (100 µg L^{-1}) including Sulfamethoxazole (SMX, >99%), Trimethoprim (TMP, 98%); acetaminophen (ACE, 99%), ciprofloxacin (CIP, 98%), caffeine (CAF, 99%), carbamazepine (CBZ, >99%) were purchased from *Sigma-Aldrich, and* losartan potassium (LP, 99%) were purchased from *Ichemical*. Experiments were carried out using a bench-scale photoreactor equipped with a borosilicate vessel (900 mL) and housing LEDs with a peak emission at 450 nm and a total power of 14.4 W placed in the center. Hydrogen peroxide (H_2O_2, 35% P.A. Neon) and ferrous ions ($FeSO_4.7H_2O$, P.A synth) were added at concentrations of 50 mg L^{-1} and 20 mg L^{-1}, respectively.

For PF, the pH was adjusted to approximately 2.8 before reactions using H_2SO_4 (0.1 mol L^{-1}; 98% P.A. CRQ). pH was monitored throughout reactions, and aliquots of 1.9 mL were sampled at the beginning and after 5, 15, 30, 60, and 90 minutes to monitor the contaminants concentrations. All aliquots were kept at a 95:5 ratio (sample: acetonitrile), filtered through a PVDF membrane (0.22 µm), and stored in vials (1.5 mL) in the refrigerator until injection into chromatographic analysis.

In addition, the effect of lamp intensity was also assessed via pulse-width modulation (PWM) at Duty cycles (Dcy) of 30%, 50%, 70%, and 100%. The most effective DCy value was subsequently applied at natural pH. Iron availability at natural pH was guaranteed by using the intermittent iron addition strategy. Briefly, iron was added at times 0, 5, 15 and 25 min at concentrations of 10, 5, 5, and 5 mg L^{-1}.

Results and Discussion

Degradation profiles were similar for all DCy (30%, 50%, 70%, and 100%) (Fig. 1). A significant difference was detected between Dcy 30% and 50%, 50% and 70% ($p < 0.001$), and 30% and 100% ($p < 0.05$). Notably, the 50% DCy achieved 60% of global removal after 60 min, while the 70% DCy required 15 min to reach a similar removal. A 70% DCy had the potential to effectively reduce contaminants, producing similar results to the 100% Dcy while extending LED's lifespan.

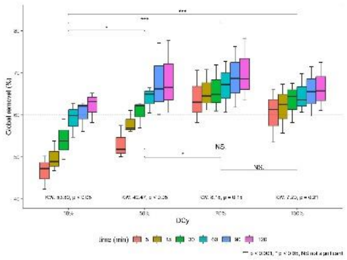

Figure 1. Global removal of CEC by PF in HWW at DCy 30%, 50%, 70%, and 100%, pH 2.8, after 120 minutes (n = 3). NS (not significant difference), KW (Kruskal-wallis test).

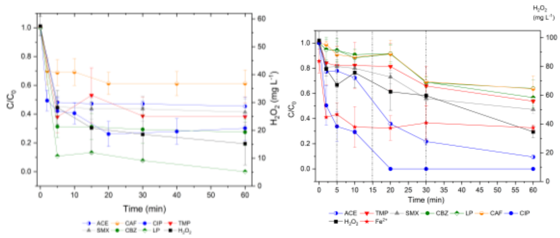

Figure 2. Degradation of CEC by PF in HWW, DCy 70%, after 60 minutes a) at pH 2.8 and b) natural pH. (n=2).

Treatment at acidic pH (2.8), exhibited higher removal rates (65%) for most compounds compared to natural pH (48%) (Fig. 2). Disinfection effectiveness was notably higher under acidic pH conditions, achieving a 5.6 and 6.8 log removal of *E. coli* and total coliforms, respectively, compared to 4.5 log removal at natural pH.

It is important to highlight that treatments performed under both pH comply with legal standards for effluent discharge into the sanitary sewage system in Minas Gerais- Brazil (pH 6.0 - 10.0 and dissolved iron concentration below 15 mg L^{-1}, VMP T-187/6) [10] (Table 1). In addition, turbidity, nitrite, and nitrate were reduced. Although Chemical Oxygen Demand (COD) removal is apparently higher in the treatment at natural pH compared to pH 2.8, there is no significant difference between these values (p = 0.46).

Table 1. Physicochemical properties of the raw and filtered HWW, and HWW treated by LED PF process at acidic (2.8) natural pH

Parameter	Raw HWW	Filtered 20 µm	Treated at pH 2.8	Treated at natural pH
pH	7.23±0.15	6.96±0.10	6.14^{a}	6.04±0.16
Total dissolved iron (mg L^{-1})	1.375±0.007^{b}	-	13.14±0.48^{b}	5.55±0.27^{b}
Turbidity	76.65±0.64	16.0±0.3^{b}	3.89±0.1^{b}	9.5±0.2^{b}
COD (mg O_2 L^{-1})	430.6±16.3^{b}	304.7±13.4^{b}	285.0±6.2^{b}	270.9±8.4^{b}
NO_2^- (mg L^{-1})	0.2455±0.002^{b}	0.233±0.003^{b}	0.084±0.002^{b}	0.154±0.01^{b}
NO_3^- (mg L^{-1})	58.4±6.9^{b}	55.8±1.6^{b}	25.1±2.6^{b}	39.1±2.6^{b}

[a] pH adjusted at the end; [b]filtered sample (0.45 µm).

Conclusions

This study presents that the novel LED reactor is capable of effectively removing pharmaceutical drugs commonly detected in HWW, which represent significant environmental and health concerns. Results demonstrate that the LED photo-Fenton process at a 70% DCy is promising to improve the removal of emerging contaminants while reducing operating costs and an extended LED lifespan.

Acknowledgments

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