Removal of Ketoprofen in Wastewater Effluent by *Constructed Wetland* Combined with Photoelectro-Fenton Process in near-neutral pH

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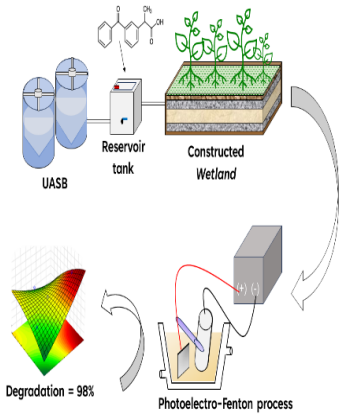

This study aimed to evaluate the efficiency of removing the anti-inflammatory drug ketoprofen (KET) from real wastewater effluent from a sewage treatment plant (WWTP) using a constructed vertical flow wetland (VF-CW) combined with the photoelectro-Fenton process (PEF) at pH 6.0. The electrochemical device consisted of a platinum anode and a carbon-PTFE air diffusion cathode, with a 4 W fluorescent tube lamp as the radiation source. A 2^4 factorial experimental design, with triplicates at the central point, was applied to investigate four independent variables influencing the process, under the following conditions: j = 10 to 100 mA cm^{-2}; Fe^{3+} concentration = 3 to 15 mg L^{-1}; Fe^{3+}:citrate molar ratio = 1:0.5 to 1:5.5; and reaction time = 10 to 90 minutes. The combined VF-CW and photoelectro-Fenton process showed good performance in KET degradation, reaching 98%, and for the toxicity removal in *Artemia sp*. (TU < 0.4). This highlights that Nature-Based Solutions, coupled with advanced technologies, are promising methods for water treatment for reuse.

Introduction

Emerging contaminants are considered an environmental concern due to their persistent nature and the ability to affect water quality, ecosystems, and human health [1]. Non-steroidal anti-inflammatory drugs (NSAIDs), such as ketoprofen (KET), are examples of medications that frequently appear in the environment due to their prolonged use in healthcare [2].

As conventional wastewater treatment plants are not designed to effectively remove pharmaceutical residues, they become bioavailable contaminants in aquatic ecosystems [3]. Studies have show that 11.0 ng L^{-1} of KET was found in surface waters in Beijing [4], and 56.5 ng L^{-1} in the effluent of a sewage treatment plant in Portugal [5].

Constructed *wetlands* (CWs) and advanced oxidative processes (AOPs) have been used separately for wastewater treatment [6,7]. Therefore, hybrid processes, such as CW combined with AOPs are still poorly studied. There are still no reports in the literature about combined processes between CW and photoelectro-Fenton (PEF) process for effluent treatment.

The objective of this study was to evaluate the removal efficiency of KET and toxicity through a constructed vertical flow wetland (VF-CW) combined with PEF process at pH 6.0.

Material and Methods

In a reservoir tank located at the Wastewater Treatment Plant (WWTP) in Campo Grande - MS, Brazil, a solution of KET was applied to 300 L of effluent, with a final concentration of 25 mg L^{-1}. This effluent was used for irrigation of the VF-CW. Effluent samples were collected at the outlet of the VF-CW after eight hours and subjected to treatment by the PEF process. For this, Fe^{3+}, sodium citrate, and Na_2SO_4 were added to 100 mL of the collected sample, and the pH was adjusted to 6.0. The electrochemical device consisted of a platinum anode and a carbon-PTFE air diffusion cathode, confined to an area of 3cm^2. A fluorescent lamp (Philips TL/4W/08 with λ_{max} = 360 nm) was used as the radiation source. A 2^4 factorial experimental design, with triplicates at the central point, was applied to investigate the variables influencing KET degradation. The ranges of values studied were: (i) j = 10 to 100 mA cm^{-2}; (ii) [Fe^{3+}] = 3 to 15 mg L^{-1}; (iii) Fe^{3+}:citrate molar ratio = 1:0.5 to 1:5.5; and (iv) reaction time = 10 to 90 minutes. The optimized conditions of the 2^4 factorial design were applied to the EF and PEF processes. UVA and AO were used as "blanks". The KET concentration was monitored by high-performance liquid chromatography (HPLC). Mineralization was monitored by injecting the sample into a SHIMADZU® TOC total organic carbon analyzer. The toxicity of degradation products was evaluated using the bioindicator *Artemia sp*. [8].

Results and Discussion

Based on the percentages of degradation and mineralization of the drug, the optimal experiment demonstrated 98% degradation of KET and 47% organic matter mineralization in 90 minutes of reaction (j = 10 mA cm^{-2}; Fe^{3+} = 15 mg L^{-1}; Fe^{3+}:citrate molar ratio 1:0.5) at a significance level of 95%.

The results indicate antagonistic effects in the interaction between the initial concentration of Fe^{3+} and the Fe^{3+}:citrate molar ratio, as well as between current density and Fe^{3+} concentration. The Pareto chart (Fig. 1) for mineralization emphasizes the statistical significance ($p > 0.05$) of the independent variables, Fe^{3+}:citrate molar ratio and time, as well as the interactions between current density and Fe^{3+}:citrate ratio, and [Fe^{3+}] and Fe^{3+}:citrate ratio.

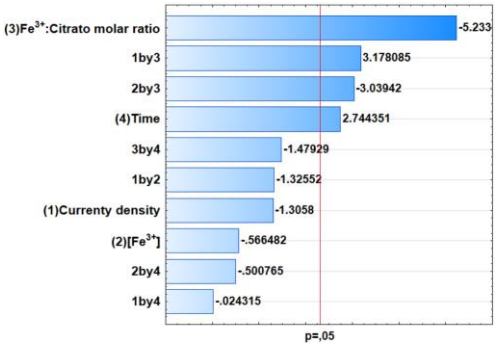

Figure 1. Pareto Chart for mineralization.

After the 2^4 factorial experimental design with SW-KET, the optimized conditions were applied to the EF and PEF processes (Fig. 2). UVA and AO were used as "blanks".

The toxicity of the treated SW-KET effluent was evaluated using the bioindicator *Artemia sp*. Table 1 presents the results obtained for Artemia sp., with toxicity levels expressed in toxic units (TUs).

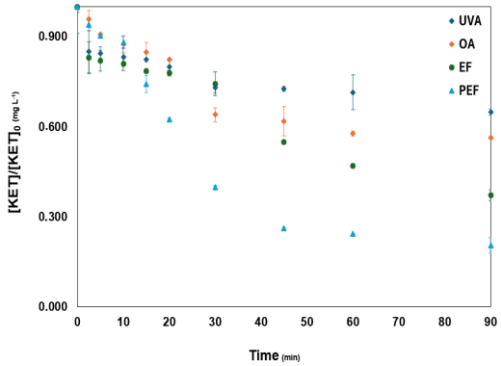

Figure 2. Degradation of KET in SW-KET effluent by AOPs.

Table 1. Toxicity of SW-KET effluent after treatments with AOPs.

	Toxicity Unit (TU)	Toxicity classification
UVA	0.51	Mild acute toxicity
OA	0.55	Mild acute toxicity
EF	0.32	No acute toxicity
PEF	0.19	No acute toxicity

The results confirm that the PEF process was more efficient in degrading KET and removing toxic substances, making the effluent non-toxic (TU < 0.4).

Conclusions

The photoelectro-Fenton process combined with CW-VF proved to be effective in degrading KET, exhibiting optimal performance under conditions of j = 10 mA cm^{-2}; [Fe^{3+}] = 15 mg L^{-1}; molar ratio = 1:0.5, within 90 minutes of reaction. Treatment of the effluent from the sewage treatment plant at pH 6.0 resulted in nearly complete degradation of KET, reaching 98%, as well as in the removal of toxicity to the bioindicator *Artemia sp.* This highlights that Nature-Based Solutions, coupled with advanced technologies, are promising methods for water treatment for reuse.

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References

[1] ROUT, P.R.; ZHANG, T.C.; BHUNIA, P.; SURAMPALLI, R.Y. *Science of The Total Environment*. 753 (2021) 141990.
[2] KOLTSAKIDOU, A.; KATSILOULIS, C.; EVGENIDOU; LAMBROPOULOU, D. A. *Science of The Total Environment*. 689 (2019) 245.
[3] KUMAR, M.; SRIDHARAN, S.; SAWARKAR, A.D.; SHAKEEL, A.; ANERAO, P.; MANNINA, G.; SHARMA, P.; PANDEY, A. *Science of The Total Environment*. 859 (2023) 160031.
[4] LU, G.; PIAO, H.; GAI, N.; SHAO, P.; ZHENG, Y.; JIAO, X.; RAO, Z.; YANG, Y. *Archives of Environmental Contamination and Toxicology*. 76 (2019) 255.
[5] PAIGA, P.; CORREIA, M.; FERNANDES, M.J.; SILVA, A.; CARVALHO, M.; VIEIRA, J.; JORGE, S.; SILVA, J.G.; FREIRE, C.; DELERUE-MATOS, C. *Science of The Total Environment*. 648 (2019) 582.
[6] ÁVILA, C.; GARCÍA-GALÁN, M.J.; UGGETTI, E.; MONTEMURRO, N.; GARCÍA-VARA, M.; PÉREZ, S.; GARCÍA, J.; POSTIGO, C. *Journal Of Hazardous Materials*, 412 (2021) 125231.
[7] MARTÍNEZ-PACHÓN, D.; ECHEVERRY-GALLEGO, R.A.; SERNA-GALVIS, E.A.; VILLARREAL, J.M.; BOTERO-COY, A.M.; HERNÁNDEZ, F.; TORRES-PALMA, R.A.; MONCAYO-LASSO, A. *Science of the Total Environment* 772 (2021) 144890.
[8] MESARIC, T.; GAMBARDELLA, C.; MILIVOJEVIC, T.; FAIMALI, M.; DROBNE, D.; FALUGI, C.; MAKOVEC, D.; JEMEC, A.; SEPCIC, K. *Aquat Toxicol*, 163 (2015) 121.