Removal of pharmaceuticals by LED photo-Fenton in hospital wastewater, using a LTPE followed by HPLC-MS determination

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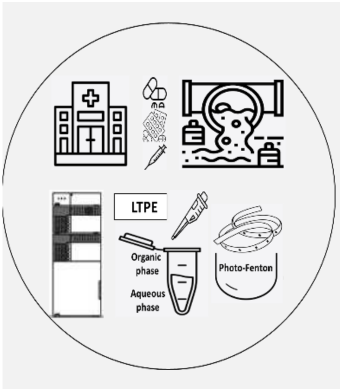

Raw hospital wastewater (RHW) is a potential source of contaminants of emerging concern (CECs). Thus, it is crucial to develop an efficient system to remove them before their discharge in the domestic sewage system. In this context, a LED photo-Fenton reactor was used to remove six pharmaceutical compounds (sulfamethoxazole, trimethoprim, acetaminophen, caffeine, carbamazepine, and losartan). As RHW is a complex matrix, careful sample preparation is required to eliminate interferences. Low-temperature partitioning extraction (LTPE) was used to perform a clean-up in samples considering a simple and low-cost alternative to guarantee sample clean-up. Photo-Fenton promoted a CECs removal up to levels below the method quantification limits for all selected compounds. In addition, the LTPE demonstrated to be satisfactory for the extraction of the selected CECs from RHW.

Introduction

Raw hospital wastewater (RHW) is often mixed with domestic sewage without previous treatment. This type of effluent contains pharmaceutical compounds in concentrations up to 2 to 150 times higher than domestic effluent [1]. Thus, inadequate disposal of RHW can accelerate the spread of these compounds as well as antibiotic-resistant bacteria (ARBs) and antibiotic-resistance genes (ARGs). Hence, the dissemination of ARBs and ARGs corresponds to a public health threat and impact worldwide [2] considering the spread of contaminants of emerging concern (CECs). In addition, as conventional wastewater treatment plants (WWTP) are not designed to remove these compounds, global strategies to mitigate this problem are necessary. Currently, several studies show that technologies based on advanced oxidative processes (AOPs) may be a promissory alternative for the removal of CECs from complex matrices such as sewage and RHW. The photo-Fenton process is widely used for this purpose [3]. However, enhancing the sustainability and cost-benefit of photo-Fenton are required to assess the removal of CECs. Thus, in the present work, photo-Fenton was applied to remove CEC from RHW using a LED-reactor.

High-performance liquid chromatography coupled to mass spectrometry (HPLC-MS) is vastly used to determine the residual CECs from photo-Fenton applied in complex matrices as RHW. Therefore, to quantify CECs it is crucial to carry out a clean-up and often pre-concentrate samples. Solid phase extraction (SPE) is a conventional procedure used to extract organic compounds. However, suspended solids, including microorganisms and colloids from complex matrices (i.e. RHW), are eliminated by the filtration process in this method, since these particles may clog up the SPE cartridges. Nevertheless, this operation may result in losses of target compounds adsorbed on suspended solids or filters [4]. Hence, whole samples should be considered in the extraction of compounds. In this context, the low-temperature partitioning extraction (LTPE) has a simple, low cost and sustainable alternative for CECs extraction [4,5,6].

Thus, the objective of this study was to assess the removal of some selected CECs in RHW by photobioreactors lightened with low intensity LED applying photo-Fenton process. In addition, this study evaluated the performance of an analytical mutiresidue method based on LTPE procedure followed by HPLC-MS for the extraction of CEC from whole RHW samples.

Material and Methods

The photo-Fenton process was carried out in RHW. Six CECs were targeted: Sulfamethoxazole (SMX), trimethoprim (TMP), acetaminophen (ACE), caffeine (CAF), carbamazepine (CBZ) and losartan (LOR). LED photoreactor used in this study (900 mL of volume) is shown in Figure 1.

H_2O_2 (35% v/v) and $FeSO_4.7H_2O$ were added at 50 mg L^{-1} and 20 mg^{-1}, respectively. The pH values were previously adjusted to 2.8 before photo-Fenton process that was performed in duplicate.

Aliquots of 600 µL were collected in triplicate before and after the photo-Fenton process. The samples were prepared by LTPE procedure (Figure 2) [6]. Then, 100 µL of the extract was transferred to insert in vial and stored at -20 °C prior to HPLC-MS.

The quantification of CECs was performed by HPLC-MS with triple quadruple mass analyzer (LCMS-8040, Shimadzu) by multiple reaction monitoring (MRM) in positive electrospray ionization (+ESI) mode. Nine concentrations levels (1.0; 2.5; 5.0; 10.0; 25.0; 50.0; 75.0; 100 and 125.0) of standard solution were injected in triplicates for analytical curve construction. The recovery rate and matrix effect was assessed using the modified methodology proposed by Barros et al. 2019 [5].

Figure 1. Photoreactor used in the experiments. LED: peak emission at 450 nm and a total power of 14.4 W.

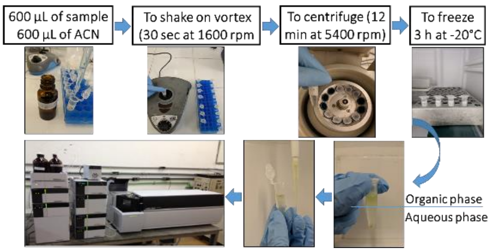

Figure 2. Scheme of LTPE procedure.

Results and Discussion

The initial concentration of CECs in RHW varied between 1.46 µg L^{-1} (TMP) to 183.02 µg L^{-1} (CAF). After the applied photo-Fenton process, the concentrations were below the method quantification limit (< 1.0 µg L^{-1}) for all target compounds, as shown in Table 1. The coefficient of determination (R^2) was higher than 0.99 for all CECs. The factor of matrix effect (FME) ranged between 0.85 to 2.15. Values of FME < 1 and FME > 1 indicate supression and accentuation of signal, respectively. Thus, matrix effect must be considered in analysis performed in HPLC-MS [5,6]. The recovery values obtained in this study ranged from 35.8 (TMP) to 130.7% (CAF) and the relative standard deviation (RSD%) values were below than 20% . Selectivity (retention time, RT), linearity (regression equations and R^2), FME and recovery are shown in Table 1 and confirm the feasibility of using LTPE for the extraction of CECs from RHW.

Table 1. Selectivity, linearity, recovery of the selected CECs.

CECs	RT[a] (min)	Regression Equations	R^2	FME[b]	Recovery (%)	RHW (µg L^{-1})	Treated RHW (µg L^{-1})
ACE	1.1	y = 4467.2x + 4465.2	0.9993	1.65	73.1	124.9	<1.0
CAF	1.5	y = 6691.6x + 721.58	0.9992	2.15	130.7	183.0	<1.0
CBZ	3.7	y = 101828x + 182826	0.9985	1.22	60.3	<1.0	<1.0
LOR	4.2	y = 38580x + 34507	0.9975	0.85	42.3	9.2	<1.0
SMX	3.4	y = 14520x - 740.48	0.9993	1.32	44.4	3.1	<1.0
TMP	1.8	y = 36220 + 81903	0.9953	0.87	35.8	1.5	<1.0

[a] RT = retention time; [b] FME = factor correction of matrix effect.

Conclusions

The LTPE demonstrated to be a promising alternative to extract all target CECs from complex matrix assessed in this study. In addition, the LED photo-Fenton reactor applied to treat the raw hospital wastewater was efficient to removal the selected CECs.

Acknowledgments

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