Efficient photolytic systems for the degradation of pharmaceuticals in effluents
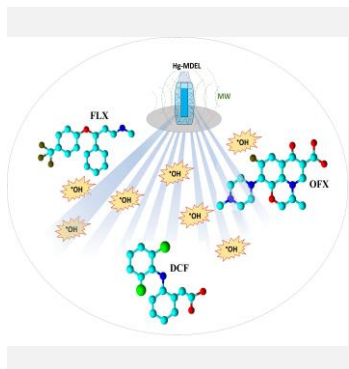
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A mixture of fluoxetine (FLX), ofloxacin (OFX), sulfamethoxazole (SMZ), and diclofenac sodium (DCF), prepared in domestic effluent was subjected to photochemical degradation. A microwave discharge electrodeless lamp (MDEL) was used as a reactor and the pH, microwave power, degradation time, and matrix type were investigated under a $3^3 \times 2^1$ multilevel design. Among the parameters investigated, only pH showed no significant effect on the degradation of the pollutants. The lowest degradation observed was 81% of OFX in 1.5 min, while > 95% removal was achieved for FLX and DCF. To monitor the pollutants quantitatively, 3D spectrofluorimetry coupled with parallel factor analysis (PARAFAC) was successfully applied. Thus, the MDEL reactor proved to be very efficient for the degradation of pharmaceuticals and PARAFAC to be advantageous.

Introduction

The environmental remediation of emerging contaminants in water and effluents has been one of the major challenges facing the scientific community [1]. In this sense, new advanced oxidation technologies with the potential to generate high amounts of oxidizing agents, such as hydroxyl radicals, have been developed [2]. The use of reactors based on microwave discharge electrodeless lamp (MDEL) has shown high potential for this application. These systems are efficient at producing high concentrations of hydroxyl radicals, achieving surprising results for the degradation of emerging pollutants [3,4]. However, its application has been carried out on synthetic samples that do not appropriately represent natural matrices. In these samples, natural interferents are non-existent, and therefore, the real difficulties of degradation identified in matrices such as natural waters and effluents are disregarded. In this work, the use of a mercury vapor MDEL reactor (Hg-MDEL) to degrade a mixture of FLX, OFX, SMZ, and DCF, prepared domestic effluent was investigated.

Material and Methods

Individual samples or mixtures of FLX, OFX, and DCF were prepared in a domestic effluent matrix. 10 mL of the sample was added to the Hg-MDEL reactor [3] and irradiated for up to 1.5 min. The influence of pH, microwave power, and matrix as investigated on degradation using a $3^3 \times 2^1$ multilevel design. The optimization parameters were pH (4, 6, and 8), degradation time (0.5, 1, and 1.5 min), microwave power (100, 250, and 400W), and matrix (ultrapure water and effluent). Analysis was performed using a spectrofluorimeter RF-5301pc (Shimadzu, Tokyo, Japan) to obtain the Excitation Emission Matrice (EEM). EEM was obtained by scanning $\lambda_{exc.}$ = 220-262 nm and $\lambda_{em.}$ = 275-325 nm for FLX and $\lambda_{exc.}$ = 245-305 nm and $\lambda_{em.}$ = 330-465 nm for OFX/DCF. The matrix data was treated by parallel factor analysis (PARAFAC). A calibration curve was constructed using PARAFAC and figures of merit were calculated. Hydroxyl radical (•OH) probe assays were carried out by monitoring 7-hydroxycoumarin (7HC) produced from the reaction between coumarin (COU) and hydroxyl radicals [1].

Results and Discussion

Fig.1 shows the EEM of effluent fortified with the FLX (a), OFX (b), DCF (c), and SMZ (d) standards.
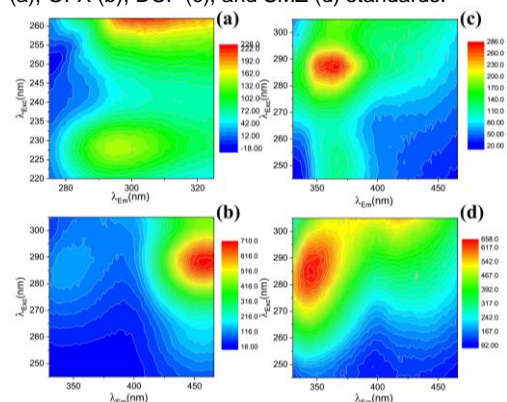

Fig. 1. EEM of effluent fortified with FLX (a), OFX (b), DCF (c) and SMZ (d) standards.

The reconstructed spectra applying PARAFAC are shown in Fig. 2. The components C1, C2, C3, and C4 were recovered from the samples prepared in effluent, confirming that PARAFAC could separate and identify the analytes. So, a calibration curve was previously constructed and the figures of merit were:

LOD = 109.4 µg L^{-1}, LOQ = 331.7 µg L^{-1} and R^2 = 0.998 for FLX, LOD = 0.5 µg L^{-1}, LOQ = 1.6 µg L^{-1} and R^2 = 0.999 for OFX, LOD = 1.2 µg L^{-1}, LOQ = 3.7 µg L^{-1} and R^2 = 0.997 for DCF. The SMZ curve was not completed in this study.
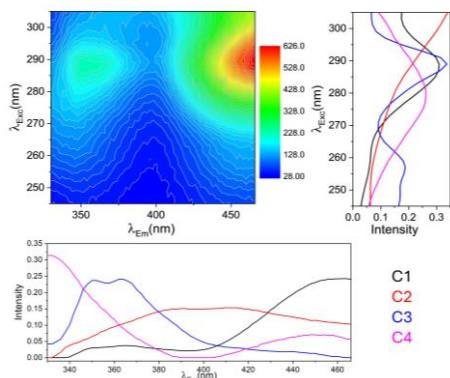

Fig 2. EEM spectra of the sample prepared in domestic effluent.

The experimental design results showed that pH did not influence the degradation efficiency of the drugs, bringing advantages to the process, since it does not require pH adjustment in application stage. At the same time, the higher levels of time, matrix purity and microwave power were favorable to degradation. The effluent matrix hinders the degradation, which is expected due to the presence of natural interferents. Analyses of Total Carbon (TC), Inorganic Carbon (IC), Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) found concentrations of TC = 23.88 mg L^{-1}, IC = 11.81 mg L^{-1} and TOC = 12.07 mg L^{-1} and COD = 80.18 mg L^{-1} on effluent. Removal was >99, 99 and 96% for FLX, OFX, and DCF, respectively, after 1.5 min for the individually fortified samples (Fig. 3a). When applied as a mixture in the effluent, only the degradation of OFX decreased to 81% (Fig. 3b), confirming the interference of the matrix in the OFX degradation. The formation of 7HC, which is a product of the reaction of COU with hydroxyl radicals formed from the photolysis of water was confirmed (Fig. 3c). The higher PL intensity of the sample in water confirms a greater amount of 7HC, degraded after 0.25 min due to the excess of hydroxyl radicals produced.
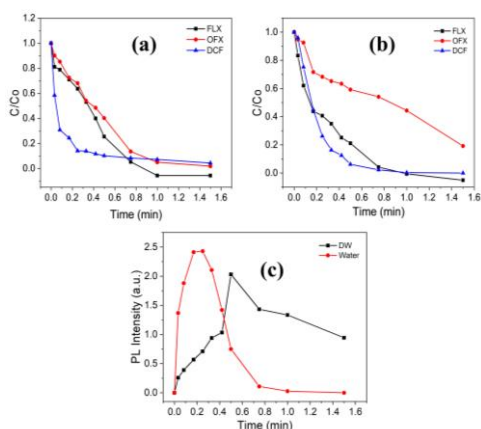

Fig. 3. Individual degradation profile (a), mixture (b), and hydroxyl radical probe assays (c).

The kinetic constants calculated revealed that in the mixture, the degradation of FLX and DCF is favored (Table 1). The k values increase by 68% for FLX and 40% for DCF. On the other hand, the k value decreases by 66% for OFX, confirming that the matrix has a positive effect on the degradation of FLX and DCF and a negative effect for OFX. These results suggest that hydroxyl radicals may follow a preferential degradation mechanism for FLX/DCF.

Table 1: Pseudo-first order kinetic constants for the degradation of drugs in the effluent matrix.

Sample	k(min^{-1}) /R^2 (individual)	k(min^{-1}) /R^2 (mixture)
FLX	1.18 / 0.969	3.73 / 0.941
OFX	1.72 / 0.984	0.96 / 0.937
DCF	3.41 / 0.849	5.71 / 0.990

Conclusions
The Hg-MDEL reactor showed high efficiency for the degradation of the mixture of FLX, OFX, and DCF in effluents presented in environmentally relevant concentrations. Even in the presence of interferents naturally present in effluents, the degradation of FLX, OFX, and DCF was > 95% after only 1.5 min. Thus, the system showed great potential for environmental degradation of emerging pollutants in complex environmental matrices.

References
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