COMPARATIVE TREATMENT OF REPRESENTATIVE ACTIVE PHARMACEUTICAL INGREDIENTS IN FRESH URINE THROUGH THREE ADVANCED OXIDATION PROCESSES

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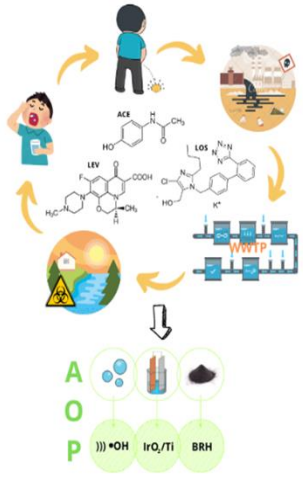

After consumption, many active pharmaceutical ingredients (API), are excreted through urine, thus becoming a primary source of contamination. In this work, the elimination of three representative APIs (i.e., acetaminophen (ACE), losartan (LOS), and levofloxacin (LEV)) in synthetic urine, was evaluated through three advance oxidation processes (AOP), considering the effects of relevant operational parameters, matrix, and chemical structure of the pharmaceuticals. Sonochemical, electrochemical, and carbocatalysis (using peroxymonosulfate (PMS)) were the evaluated processes. Considering the most favorable process per API, it was found that the APIs degradation by the electrochemical system was strongly affected by the matrix, while PMS acting alone removed 100% of LEV at only 1 min of treatment. The carbocatalytic process (a carbonaceous material (BRH) with PMS) efficiently degraded ACE (~90% in 30 min) via a non-radical route. In turn, LOS was degraded (~42%) by high-frequency ultrasound through the radical route.

Introduction

APIs are excreted as metabolites or in unaltered forms mainly in the urine after being consumed [1]. The urine is discharged into the sewage system (where APIs are diluted to ng/L or µg/L levels). These sewage systems enter water treatment plants, where the APIs remain; thus, reaching natural water sources (rivers, lakes, etc.). The APIs may be bioaccumulated and cause toxic effects on the environmental species (e.g., feminization in fish, endocrine disruption, antibiotic-resistant bacteria proliferation, among others) [2,3].

There is an evident need for research about alternatives to limit the discharge of APIs into the environment. Thus, in this work, the treatment of API in primary pollution sources such as urine is proposed. The main objective was to study the efficacy of sonochemical, electrochemical, and carbocatalytic AOPs for the elimination of three representative APIs (ACE, LOS, and LEV) in simulated fresh urine. The effects of relevant operational parameters in each process were evaluated. Also, the influence of the urine matrix and the elucidation of the main routes of action of the processes were assessed.

Material and Methods

ACE, LOS, and LEV at a concentration of 66.15 µM were used. Experiments were performed in fresh synthetic urine (SU) prepared in distilled water (DW) and adjusted to pH 6.5 ± 0.1. For the sonochemical system, a Meinhardt high-frequency ultrasound equipment was used, evaluating the frequency variation (582 kHz and 1144 kHz) and power (40% and 80% amplitude). In the electrochemical process, experiments were carried out using an IrO_2 anode and a Ti cathode, studying the effects of supporting electrolyte type (NaCl 0.1M or Na_2SO_4 0.1M), the influence of the current (10-20mA) and the concentration of NaCl (0.1M-0.01M). The carbocatalytic process was evaluated using a material obtained from rice husk (BRH), testing the change in PMS concentration (100-500µM). Action routes of the processes were elucidated by using a scavenger of radicals (methanol at 6.6mM). HPLC was employed to determine the evolution of the APIs.

Results and Discussion

- **Electrochemical system (EC)**

Initially, the process action was evaluated in DW for treating ACE. In this system, at a current of 20 mA, a removal of 3.92% was obtained with Na_2SO_4 0.1 M, while the degradation was 44.43% with NaCl 0.1 M after 5 min of treatment, which gives an idea about possible routes of action associated with reactive chlorine species [4]. Regarding the effect of parameters, when decreasing the concentration of NaCl 0.1M to 0.01M, the removal decreased up to 16.88%, and using a current of 10 mA with NaCl

0.1M, the removal decreased up to 32.75%, which can be associated with a limited production of the degrading agents [4]. In the experiments in the urine matrix, it was observed that ACE removal, represented by the Rho value (ρ), was inhibited, which denotes the detrimental effects of the urine matrix (Figure 1).

- **Ultrasound (US) and carbocatalysis processes (CB)**

The results for the US and CB systems for the treatment of ACE, LOS, and LEV by US and BC are shown in Figure 2. The differences observed for the three APIs suggested a strong influence of the chemical structure of the pollutants on the degradation by these two AOPs. The US involved the attacks of radicals (which was evidenced using methanol) and allowed a differentiated degradation as a function of the hydrophobicity of pollutants. In this process, the higher removal of LOS can be related to the higher hydrophobicity (LogP ≈ 5.0), compared to ACE (LogP ≈ 0.5) and LEV (LogP ≈ 0.0-0.1) [5].

In the CB system, from the use of the methanol, it was found that the removal involved non-radical degradation routes. The degradation was mainly due to adsorption on the carbonaceous material in the case of ACE, and an important direct action of PMS in the case of LEV; in addition to the possible participation of other reactive species such as $^1O_2$ and HOCl [6]. In the case of LOS, low removal was observed, which may be associated with the low reactivity of this chemical structure to PMS or non-radical species (e.g., singlet oxygen), and low adsorption on the carbonaceous material. Table 1 summarizes the removal percentages obtained for each API by the sonochemical and carbocatalytic processes.

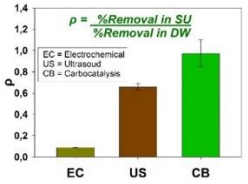

Figure 1. Effects of matrix on the degradation of ACE.

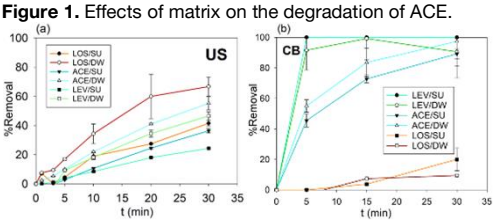

Figure 2. Removal of ACE, LOS, and LEV by (a) US at 582 kHz and 80% power, and (b) CB at BRH 0.2 g/L and PMS 500 µM.

Table 1. Degradation percentage of the APIs by AOP in urine after 30 minutes of treatment.

AOP	ACE	LOS	LEV
Ultrasound (582kHz)	36.40	41.54	24.33
Carbocatalysis (BRH/PMS)	89.19	11.66	100[a]

[a] Removal value after 1 minute of treatment.

Conclusions

The urine matrix significantly affected the API degradation by the EC system, whereas, the degradation of the pollutants by the CB and US AOPs was less influenced by the matrix. The API degradation involved the radical route through ($HO^•$) in the US and non-radical routes (adsorption, $^1O_2$, and HOCl) in the CB. Additionally, it was evidenced that the removal of APIs was influenced by their respective chemical structures being particular in each tested process.

Acknowledgments

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