Exploring electrochemical treatment of synthetic and real urine matrices for paracetamol removal using boron-doped diamond

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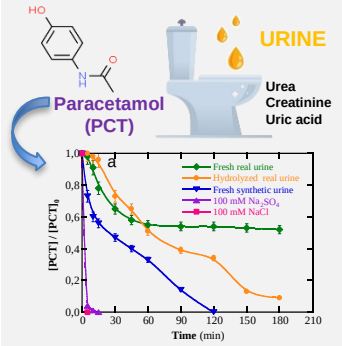
R. J. A. Felisardo[1,2], *E. Brillas*[3], *T. H. Boyer*[2] , *S. Garcia-Segura*[2], *E. B. Cavalcanti*[1,4] *(1) Graduate Program in Process Engineering, Tiradentes University, 300 Murilo Dantas Avenue, 49032-490 Aracaju, SE, Brazil, raulfelisardo.eng@gmail.com. (2) Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment. School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287, United States. (3) Departament de Ci`encia de Materials i Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franqu`es 1-11, 08028 Barcelona, Spain. (4) Institute of Technology and Research. 300 Murilo Dantas Avenue, 49032-490 Aracaju, SE, Brazil.*



This study makes a significant contribution to the understanding and development of effective treatment strategies for pharmaceutical-contaminated effluents. By investigating the effectiveness of electrochemical oxidation of paracetamol (PCT) in different urine matrices, together with the mineralization of organic components present in the effluent, the study offers important insights into drug removal under realistic conditions. The role of current density and different PCT concentrations were investigated in an electrochemical system with Boron-Doped Diamond (BDD) electrodes. This comprehensive approach sheds light on the complex interactions between electrochemical processes and urine composition.

Introduction

The increasing detection of pharmaceutical substances in aquatic environments is a global concern, driven notably by the COVID-19 pandemic. Paracetamol (PCT), widely used in COVID-19 treatment, presents a significant challenge due to its ubiquity and potential environmental impact [1]. Urgent action is required to prevent the accumulation of such drugs in water bodies, with human excretions, including urine, being a notable source [2]. In this context, electrochemical oxidation (EO) emerges as a promising technology due to its high efficiency in mineralizing refractory organic compounds and its suitability for decentralized systems [3]. This study focuses on EO's efficacy in degrading PCT across different urine matrices: synthetic fresh urine, fresh real urine, and hydrolyzed real urine. It explores the electrochemical process performance under varying concentrations and current densities, while also examining the degradation of organic components such as urea, creatinine, and uric acid. The insights generated by this research significantly advance our understanding of effective treatment strategies for complex effluents, providing valuable information on the simultaneous degradation of paracetamol and organic components in urine.

Material and Methods

The composition of synthetic urine included 3,333.34 mg L^{-1} Urea, 166.67 mg L^{-1} Creatinine, 50 mg L^{-1} Uric acid, 5,844 mg L^{-1} NaCl, 2,130 mg L^{-1} Na2SO4, and 2,340 mg L^{-1} Na_2HPO_4. In this matrix, paracetamol concentrations of 2.5, 5, 10, 20, and 40 mg L^{-1} were introduced based on the therapeutic dose of the drug in adults of 1 to 4 g day^{-1}, and the possible amount of unchanged drug excreted in urine (2%). Human urine acquisition followed an ethically approved protocol by the Institutional Review Board of Arizona State University. The electrolytic system consisted of an undivided cylindrical glass cell containing 250 mL of solution. The anode was a BDD plate while the cathode was a stainless steel plate. All trials were conducted at ambient conditions with a temperature of 25 ± 2 ºC and under galvanostatic conditions at a constant current density (j) of 6, 12, 24, and 48 mA cm^{-2} provided by a TENMA® 72-2710 power supply. Analytical methods included analyses on High-Performance Liquid Chromatography (Waters e2695 system), UV-Vis spectrophotometer (HACH DR6000), and Total Organic Carbon (Shimadzu TOC-L carbon analyzer).

Results and Discussion

Evaluating the effect of PCT concentration and current density on fresh synthetic urine with a natural pH of 7.56, it was found that an increase in current density led to a faster removal of PCT, possibly due to the accelerated production of oxidants BDD($^{\bullet}$OH) and HClO. The decrease in pH to final acidic values close to 4.9 confirmed the predominance of HClO as the active chlorine species. A deeper analysis revealed an increase in the oxidation capacity of the electrode as the drug concentration increased. For instance, at a current density of 24 mA cm^{-2}, a higher amount of drug was removed with increasing drug concentration. However, a progressive decline in the degradation rate at higher PCT concentrations was observed, attributed to various factors including mass transport limitations, competitive reactions, and electrode fouling. As PCT was degraded in urine, a complex matrix containing other organic compounds such as urea, creatinine, and uric acid,

these constituents may also influence the degradation kinetics.

Thus, when analyzing the effect of current density on the degradation of these organic compounds, it was observed that for creatinine, there was little variation in removal regardless of the applied current density, with a consistent reduction of about 46-50% after 180 minutes of electrolysis. On the other hand, urea and uric acid showed a clear increase in degradation rate with higher current density. Urea exhibited a greater reduction, reaching up to 46% at j = 48 mA cm^{-2}, while uric acid completely disappeared in shorter times at higher current densities. Regarding the mineralization process, when considering fresh synthetic urine with 2.5 mg L^{-1} of PCT at different current density values, a progressive increase in the percentage of TOC removal was observed with the increase in j. However, this parameter was only 4.6 times higher when going from 6 to 48 mA cm^{-2}, despite an 8-fold increase in current, indicating that the greater parasitic reactions of the mentioned oxidants consumed part of their extra generation, decreasing the effective oxidation capacity of the system. The limited TOC reduction efficiency achieved at j = 48 mA cm^{-2}, reaching a maximum of about 30%, can be attributed to the partial oxidation of creatinine and urea, which persist in the final solution. This observation is particularly significant considering that urea alone represents more than 85% of the organic load in urine.

Based on these observations, the study compared PCT degradation in different aqueous matrices. Results indicated that while complete PCT degradation was achieved in 5 and 15 minutes in NaCl and Na_2SO_4 solutions, respectively, it took 120 minutes of electrolysis to achieve the same percentage in synthetic fresh urine. Regarding real urine matrices, fresh real urine exhibited significantly lower reduction, with a final degradation of 48% after 180 minutes of electrolysis. Conversely, hydrolyzed real urine showed substantial degradation, reaching 91% compound removal. Comparison of TOC removal results also demonstrated a similar trend, with synthetic fresh urine showing greater mineralization efficacy compared to fresh and hydrolyzed real urine. These findings underscore the importance of considering the complexity of real urine samples when evaluating the effectiveness of electrochemical treatment processes.

Evaluating the fate of nitrogen species released during the oxidation of nitrogen-containing compounds in contaminated synthetic fresh urine, a significant gradual accumulation of NH_3 was observed, reaching 356 mg L^{-1}, primarily produced from the oxidation of urea [4], and to a lesser extent, PCT and uric acid [5]. Much lower contents of 15.2 and 9.1 mg L^{-1} were determined for NO_3^- and NO_2^-, respectively, originating from the mineralization of uric acid [5] and creatinine [6]. The temporal course of final linear aliphatic carboxylic acids generated during the cleavage of organic compounds in synthetic fresh urine under the same conditions was determined. High levels of acetic acid, up to 348 mg L^{-1}, and fumaric acid, up to 78 mg L^{-1}, were continuously accumulated, while tartaric acid, malic acid, oxalic acid, and oxamic acid were produced and removed to a lesser extent. A general removal could be observed for the last two acids, which are final intermediates directly mineralized to CO_2. In addition to the slow removal of creatinine and urea, the formation of persistent carboxylic acids, especially acetic and fumaric acids, makes total remediation of contaminated synthetic fresh urine with BDD EO very challenging.

Conclusions

The study showed that EO with BDD effectively removes PTC in fresh synthetic urine, but less efficiently at higher drug concentrations and lower current densities. Uric acid was completely removed, while partial degradation to creatinine and urea was observed. However, TOC removal efficiency in fresh synthetic urine increased with increasing j, albeit with loss of oxidizing power due to increased parallel consumption of oxidizing agents by non-oxidizing parasitic reactions. Comparing the degradation of PCT in different matrices, it was observed that the greatest degradation occurred in the synthetic matrix, followed by hydrolyzed real urine and fresh real urian. Treatment of fresh synthetic urine with 2.5 mgL^{-1} PCT resulted in the detection of large accumulations of NH_3 and lower concentrations of NO_3^- and NO_2^- anions. The persistence of final carboxylic acids, along with the slow reduction of creatinine and urea, indicates challenges in the overall mineralization of EO contaminated fresh synthetic urine with BDD. These findings underscore the complex nature of remediation in real-world settings and highlight the importance of considering multiple factors in developing effective treatment strategies.

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