Advanced electrochemical process as alternative for the abatement of multicontaminats from membrane brines

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The membrane separation process (MSP) has been used successfully to remove pharmaceuticals active compounds (PhACs) from water and wastewater. However, the brine was the main drawback of the processes. With the aim of proposing a solution to this problem, it was proposed in this work, the use of electrochemical advanced oxidation (EAOPs) for the abatement of PhACs present in the membrane brine. The results indicated that anodic oxidation (AO) or electro-Fenton (EF) leads to the PhACs degradation, with EF presenting better results. As mineralization was lower, analysis showed generation of low molecular weight organic acids, mainly propionic and isovaleric acids. It means that the treated brine by EF or AO have a higher degradability than the untreated ones.

Introduction

The expansion of analytical equipment has facilitated the identification and enhancement of the capacity to detect and quantify contaminants of emerging concern (CEC) in water and effluents. These compounds have been found to exert effects on the ecosystem and, consequently, on human health that are not yet fully understood. Furthermore, conventional techniques are unable to remove them effectively [1]. These compounds have been identified at concentrations ranging from mg L^{-1} to ng L^{-1} and wastewater treatment plants.

An alternative approach to the removal of these CEC could be the implementation of a hybrid process, which involves the combination of two technologies. The initial stage of the process involves the utilization of the nanofiltration technique to generate a solution with a low concentration of CEC, designated as the permeate, and another solution with a high concentration of CEC, designated as the concentrate [2]. One of the most significant drawbacks of membrane processes is the generation of a concentrate. This can be mitigated through the use of the electro-Fenton (EF) or anodic oxidation (AO) process, which facilitate the formation of highly oxidizing compounds, primarily the hydroxyl radical (HO). This enables the degradation of CEC, thereby enhancing the biodegradability of the effluent [3].

The objective of this study was to investigate the efficacy of an integrated process based on advanced technologies for the elimination of atenolol (ATN), prednisone (PRED), rosuvastatin (ROSU), and sulfamethoxazole (SMX) from a solution obtained from a wastewater sample.

Material and Methods

Nanofiltration (NF) process was employed to remove atenolol (ATN), prednisone (PRED), rosuvastatin (ROSU), and sulfamethoxazole (SMX) from wastewater, resulting in the production of contaminant-free water and a concentrated stream, which is subsequently subjected to EAOPs.

The concentration process was carried out using 0.036 m^2 of NF270 (DuPont - FilmTec, USA). The NF experimental runs were performed on a Lab-Unit M20 plate and frame filtration unit (Alfa Laval, Denmark) in total concentration mode.

The NF feed solutions consisted of an ATN, PRED, ROSU, and SMX mixture, ranging from 3.8 to 7.2 mg L^{-1} of each compound diluted in deionized water. The pH was adjusted to 7.0 ± 0.2 with 0.1 M hydrochloric acid.

A gas diffusion electrode (GDE, DURA-gdl ST400LC, Sainergy Tech) supported on a copper mesh was used as cathode and a DSA® (DeNora) was used as anode for the optimization of hydrogen peroxide (H_2O_2) generation. The electrodes have a geometrical surface area of 0.785 cm^2 and was assembled with a gap of 1 cm. An Autolab potentiostat/galvanoastat was used as a power supply. Whereas an air pump was used as air source being the flow rate controlled using a rotameter.

To optimize the generation of H_2O_2, the central composite design (CCD) was used as a tool to plan the experiments (Statistica 14.0.1 software). The boundary conditions involved two independent numerical variables: the air flow rate (Q_{air}) and the applied current density (*j*).

For the EF process, it was added 0.5 mmol L^{-1} of $FeSO_4$ at time = 0 min in the optimized H_2O_2 system.

Tests using only H_2O_2 or anodic oxidation were also carried out.

The H_2O_2 concentration was determined using titanium (IV) oxysulfate method. The ATN, PRED, ROSU, and SMX decay were monitored in a Shimadzu HPLC-LC20A with a diode array detector (DAD) SPD-20AV using a C18 collum. For the generation of the low molecular weight carboxylic acids the HPLC was assembled with a roa-organic acid H^+ exclusion column (8%, 100 x 4.6 mm, Allcrom Rezex). The carboxylic acids analyzed were citric, formic, acetic, propionic, butyric and isovaleric.

Results and Discussion

The results of NF operated in concentration mode showed that PRED and ROSU had high concentration values at the end of the process (Table 1). The brine is a known problem from the membrane processes that need a friendly discharge. In order to reduce the environmental impact of discharging the NF brine, it was proposed the use of EAPOs to the abatement of PhAC content in the brine.

Table 1. PhACs concentration values in the NF brine.

Compound	Concentration (mg L^{-1})
ATN	15.43
PRED	23.50
ROSU	104.39
SMX	14.32

For that, the H_2O_2 generation was optimized as presented in Figure 1. This process demonstrated that a high concentration of H_2O_2 was achieved with a Q_{air} = 0.4 L min^{-1} and j = 10 mA cm^{-2}.

In Figure 2 it is noted that the degradation values are higher for EF than those observed for AO. This was attributed to the homogeneous $HO^{\bullet}$ formation that can be transported in the solution increasing the PhAC oxidation [3].

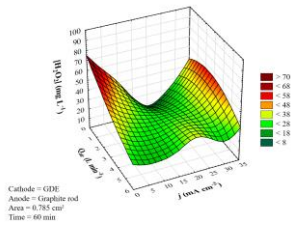

Figure 1. Surface response for the optimization of H_2O_2 concentration using CCD.

The mineralization values were less than 11% for EF process which indicate the formation transformation products, such as low molecular weight organic acids [4].

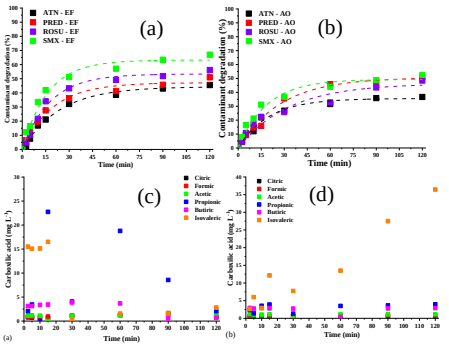

Figure 2. Degradation values obtained in (a) EF process and (b) AO process. Carboxylic acid concentration generation using (c) EF process and (d) AO process.

A high concentration of propionic and isovaleric acids was observed in all the processes and this indicates that, despite the low mineralization, the treated brine by EF or AO has a higher degradability than the untreated brine.

Conclusions

It was proposed EAOPs as electro-Fenton (EF) and anodic oxidation (AO) as suitable process to eliminate the PhAC from the membrane brines. The results indicate that using EF process, degradation up to 40% for all compounds are found. As low mineralization was found, the formation of transformation products like the low molecular weight organic acids were a possibility. The results indicates that the biodegradability of the treated brine was higher than that the initial ones, thus solving the most significant environmental issue associated with the brine from membrane treatment processes.

Acknowledgments

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