Exploring the efficiency of AOPs based on hydroxyl and sulfate radicals in Brines treatment: challenges and opportunities

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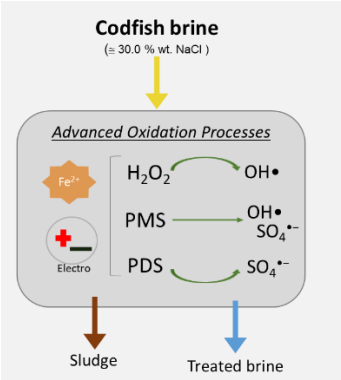

This study investigated the efficiency of sulfate ($SO_4^{\bullet-}$) and hydroxyl (OH•) radicals in reducing the total organic carbon (TOC) concentrations in high-saline wastewater from a Portuguese codfish industry. Fenton and electro-Fenton (EF) processes, using hydrogen peroxide (H_2O_2), peroxymonosulfate (PMS), and peroxydisulfate (PDS) as oxidative precursors, were employed. The results showed EF outperformed Fenton, with PMS exhibiting the highest TOC reduction efficiency (70 %) under the following conditions: treatment time of 10 min, current density of 429 $A \cdot m^{-2}$, and 62.5 mM of PMS. Conversely, the Fenton process yielded TOC removals below 45 %. These results provide valuable insights and suggestions for enhancing advanced oxidation processes in the treatment of high-saline wastewaters.

Introduction

During various industrial production processes (e.g., textile, codfish, tannery, petrochemical industries, among others), high-saline wastewaters, commonly referred to as brines, are an inevitable generated. These brines typically have high concentrations of salt (NaCl) along with high concentration of organic matter [1]. As environmental concerns increase and regulatory standards become more stringent, different approaches for managing brine effluents are being considered [2]. Advanced oxidation processes (AOPs), like electrooxidation and Fenton, have been efficiently applied in the treatment of a wide range of wastewaters with recalcitrant pollutants [3]. AOPs can be classified based on the radicals produced (*in situ*). When hydrogen peroxide (H_2O_2) is used as the oxidant to generate hydroxyl radicals (OH• - E◦ = 2.8V) it is called Hydroxyl Radical Based (HR-AOP). Alternatively, the use of peroxymonosulfate (PMS) or peroxydisulfate (PDS) leads to the production of sulfate radicals ($SO_4^{\bullet-}$ - E◦ = 2.5–3.1V), hence the process is named Sulfate Radical Based (SR-AOP) [4]. Until recently, the prevailing consensus held that chloride (Cl^-) ions hindered AOPs efficiency, limiting their applicability in treating saline wastewaters [5]. However, recent studies suggest that the AOP/Cl^- system may actually enhance pollutant removal efficiencies [6,7]. This research focuses on assessing the effectiveness of $SO_4^{\bullet-}$ and OH• radicals in reducing total organic carbon (TOC) concentrations from a real high-saline industrial wastewater. The study employed Fenton and electro-Fenton (EF) processes using as oxidative radicals' precursors H_2O_2, PMS and PDS.

Material and Methods

A composite sample of real contaminated brine (CcB) was provided by a Portuguese codfish industry with approx. 30.0 % wt. NaCl and 5650 mg/L of TOC. The efficiency of three oxidative systems (Fe^{2+}/H_2O_2, Fe^{2+}/PMS, and Fe^{2+}/PDS) were tested using both Fenton and electro-Fenton processes, with the latter employing iron electrodes. The central composite experimental design was adopted, and the tested independent variables were: (i) current density (126 – 429 $A \cdot m^{-2}$), (ii) treatment time (EF: 5.0 – 15.0 min, Fenton: 5.0 – 40.0 min), catalyst concentration (Fenton: 2.5 – 12 mM) and (iii) precursors concentration (H_2O_2 and PDS: 50 – 200 mM, PMS 25 – 100 mM). TOC removal was the variable used for assessing treatment efficiencies. In the Fenton process, $FeSO_4$ was used as catalyst. PMS and PDS were supplied in the form of $KHSO_5$ and $K_2S_2O_8$, respectively. The natural pH of the raw CcB was slightly acidic (pH ≅ 6) and, thus, suitable for the SR-AOP. However, to conduct the HR-AOPs, there was a need to reduce the initial pH to approximately 3. All experiments were carried out at room temperature.

Results and Discussion

Table ***1*** summarizes the maximum TOC removal achieved for each AOP studied, with values ranging between 21 and 70 %. Across all oxidative systems, EF demonstrated better efficiency compared to Fenton, likely due to the continuous activation of precursors facilitated by the sacrificial iron anode supply. In terms of oxidative effectiveness, the

sequence was observed as PMS > PDS > H_2O_2. The superior performance of PMS can be attributed to its decomposition, which generates not only $SO_4^{\bullet-}$ but also OH•, two potent oxidants that have proven to be effective in TOC removal from the codfish brine. Furthermore, chlorine ions have played an important role in these treatments, particularly in SR-AOP, as they enhance the activation of sulfate radicals. For instance, Li et al. [7] observed that in the presence of Cl^-, the radicals $SO_4^{\bullet-}$ and OH• react rapidly with it to generate reactive chlorine species, resulting in the promotion of pollutants oxidation.

Table 1. *The influence of AOPs on TOC removal in brine solutions derived from codfish processing.*

	Oxidative System					
	Fe^{2+}/H_2O_2		Fe^{2+}/PMS		Fe^{2+}/PDS	
	Electro-Fenton	**Fenton**	**Electro-Fenton**	**Fenton**	**Electro-Fenton**	**Fenton**
Oxidant [mM]	125	125	62.5	62.5	125	125
Fe^{2+} [mM]	-	12	-	12	-	12
Current density [$A \cdot m^{-2}$]	429	-	429	-	429	-
Treatment time [min]	10	23	10	23	10	23
TOC removal	51 %	36 %	70 %	44 %	57 %	21 %

SR-AOPs with PMS showed distinct advantages, including higher TOC removal efficiency, lower PMS concentration requirements compared to PDS and H_2O_2, and the absence of the need for additional chemicals for pH adjustment.

Conclusions

Three oxidative systems were studied (H_2O_2, PMS, and PDS) with both EF and Fenton processes to treat high organic load codfish brine. The EF process consistently achieved TOC removals exceeding 50 %, irrespective of the precursor used. PMS showed to be the best oxidative radical precursor for reducing the brine's organic load. Chlorine ions may have played an important role in enhancing process efficiencies by promoting the formation of oxidative radicals. However, further investigation warranted to validate this assertion and to assess the formation of potential hazardous by-products. This research serves as groundwork for advancing the comprehension of oxidation processes in high-saline wastewaters.

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