

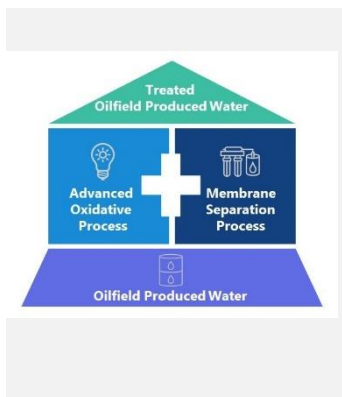
The Use of Advanced Oxidative Processes Combined with Membranes in Oilfield Produced Water Treatment: State of The Art

ORAL/POSTER

Ph.D. Student: Y/N

Journal: NONE

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Oilfield produced water is a wastewater from oil and gas production, with a complex composition and large volume generated. Therefore, properly managing of this wastewater is essential for its disposal into the environment or reuse as reinjection water. The use of membranes proves to be a promising method in oilfield produced water treatment, and interest in integrating methods has been increasing as a strategy for antifouling and maintaining long-term filtration performance. In this context, this work briefly reviews the combined use of advanced oxidative processes and membrane separation in oilfield produced water treatment as an alternative to mitigate the negative effects of membrane fouling during filtration.

Introduction

Oilfield produced water (OPW) is the primary wastewater stream generated in oil and gas production due to the natural presence of water in underground formations and water injected during oil extraction. The OPW composition is a complex mixture of organic and inorganic compounds, consisting mainly of benzene, toluene, aromatic hydrocarbons, phenols, organic acids, salts, and chemical compounds added during oil production. Thus, it is evident that proper management of this complex wastewater is a critical point in the oil and gas industry, and the OPW treatment economically and effectively is of academic and commercial interest [1].

In this sense, membrane separation processes (MSP) have been gaining importance in OPW treatment. MSP removes very small particles (less than 10 μm) and soluble compounds without adding chemicals or changing temperature. However, due to the OPW characteristics, the literature consensus is that fouling is the major challenge to consolidate MSPs as a method in OPW treatment, resulting in severe declined permeate flux and process performance [2].

Fouling mitigation is increasingly the focus of research efforts. Studies suggest that the combination of other processes and MSP is the key to fouling mitigation. The advanced oxidation process (AOP) is a potential method to mitigate membrane fouling in OPW treatment. Among the advantages of AOPs is the ability to degrade a wide range of organic compounds present in OPW without necessarily needing to add chemicals or thermal exchange and requiring relatively simple equipment [1, 3].

This work aims to provide a brief review of the applications of AOPs alongside MSPs in OPW treatment. This review intends to provide the state of the art in using AOPs as pretreatment to mitigate fouling in membranes and improve OPW filtration performance.

State of the Art

Research articles have evaluated the use of AOP as an antifouling strategy and indicate that this process is a promising pretreatment technique for subsequent membrane filtration. The choice to use AOPs is based on their ability to degrade a wide range of organic compounds. The hydroxyl radicals ($\bullet\text{OH}$) generated during the oxidative process are highly reactive and have a high oxidation potential. Most AOPs use strong oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), semiconductor solids, ultraviolet (UV), and catalysts [3]. Using the Scopus platform as the database and the keywords "produced water" AND membrane AND "advanced oxidation process" around 80 scientific articles are found considering the last five years (2019-2024). AOPs proposed as pretreatment for MSP in OPW filtration include ozonation, peroxidation, Fenton, photocatalysis, and electrooxidation.

O_3 is a powerful oxidant widely used to degrade organic contaminants, particularly effective for treating large volumes of effluents. In the case of Fenton, the reaction occurs in an acidic medium combining H_2O_2 and ferrous ions (Fe^{2+}), forming hydroxyl radicals ($\bullet\text{OH}$). Titanium dioxide (TiO_2) associated with UV light is the most common example of photocatalytic degradation. This process is capable of degrading a wide range of organic compounds through the oxidation of organic matter by hydroxyl radicals and superoxide anions produced by the process. In electrooxidation, electron transfer occurs between the OPW and the electrode by applying an electric current, causing the oxidation of organic compounds. Most AOPs can be combined with UV to increase the decomposition of oxidative agents' kinetics [4].

In a study conducted by Ferreira et al. (2021) [5], the

photoperoxidation process performed better results than ozonation in oil and grease (O&G) removal and microfiltration membrane (0.1 μm , ceramic) fouling reduction. The results showed 86% O&G removal from the OPW after 2 hours of photoperoxidation treatment, reflecting a 200% increase in permeate flux compared to untreated OPW.

Dai et al. (2019) [6] evaluated using H_2O_2 as a pretreatment for ultrafiltration (60 kDa, polyethersulfone hollow fiber). Using H_2O_2 in OPW increased ultrafiltration operation time by up to 20 h without interruptions for membrane cleaning. The process's H_2O_2 concentration and the pH of OPW were the critical factors in the treatment. The increase in the H_2O_2 concentration may not necessarily promote an increase in the O&G degradation, probably due to competitive reactions capable of eliminating the available $\bullet\text{OH}$ [5].

Another proposed alternative is to investigate the fabrication of specific membranes designed for the AOP by coating the membrane surfaces with electroconductive materials (such as graphene oxide) or photocatalytic compounds (such as TiO_2/UV) to create self-cleaning membranes capable of maintaining an efficient process in OPW treatment. Karkooti et al. (2020) [7] showed that

increasing the applied voltage (from 3 V to 9 V) significantly improves the antifouling property of electrooxidation membranes in OPW permeation.

The anti-fouling property of membranes coated with electroconductors can be justified by the modified electrostatic interactions and electrochemical reactions on the membrane surface. Applying an electrical potential can generate a repulsive force between the membrane surface and solutes. Additionally, when an electrochemical reaction occurs on the membrane surface, hydroxyl radicals can attack solutes near the membrane surface, decreasing hydrophobic interaction or complete compound degradation [7].

In summary, the studies show that AOPs improve the membrane process performance in OPW treatment. Probably, the positive result is a consequence of O&G degradation. Despite the effectiveness of AOPs, the relationship between the most appropriate AOPs type and the applied operational conditions according to the OPW composition it is not very clear in the literature. Therefore, further research is needed to better understand the combination of processes in the treatment of OPW.

Conclusions

The AOPs discussed in this study are an alternative antifouling method in MSP for OPW treatment. AOP can be applied as a pretreatment before OPW filtration or as a hybrid process to obtain self-cleaning membranes. However, it is still an emerging technique that requires further in-depth studies.

Acknowledgments

The authors thank Petrobras SA (Process: 2023/00226 0) for the financial support and UFSC for all the infrastructure.

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