

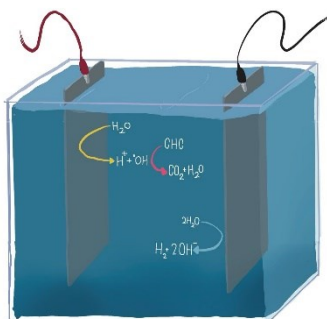
Effect of Voltage on the Electrochemical Advanced Oxidation for Efficient Synthetic Produced Water Treatment

POSTER

Post-doctoral
researcher: Y

Journal: Chemical
Engineering Journal

D.G. Della Rocca¹, L.P. Cesconeto¹, S. E. Weschenfelder², L.P. Mazur¹, R.A. Peralta³, R.F.P.M. Moreira¹ (1) Laboratory of Energy and Environment – LEMA, Department of Chemical and Food Engineering, Federal University of Santa Catarina, Florianópolis, Brazil, danigierdellarocca@gmail.com. (2) Petrobras Research Center – CENPES, Av. Horácio Macedo, 950 - Cidade Universitária, Rio de Janeiro, Brazil. (3) Bioinorganic and Crystallography Laboratory, Department of Chemistry, Federal University of Santa Catarina, Florianópolis, Brazil.



Oilfield produced water generated from oil and gas exploration is a complex effluent containing various contaminants necessitating advanced treatment methods for disposal. While traditional treatments are well developed, challenges remain in effectively removing stable emulsions and small oil droplets. In particular, electrochemical oxidation (EO) emerge as a promising solution. This study investigates the impact of applied voltage on EO process to treat synthetic produced water, using active and non-active electrodes. The non-active electrode - Ti/SnO₂ demonstrated the highest oxidation rate to remove cyclohexanecarboxylic from saline water. Increasing voltage to 4 V resulted in notable COD removal (56%) after 2 h of reaction. Moreover, pH increased with voltage, attributed to hydrogen evolution reactions. Conductivity remained unaffected due to the high initial salinity. Thus, these findings suggest a promising potential of EO for treating high salinity produced water.

Introduction

Produced water (PW) is a byproduct of the oil and gas extraction and production process, formed by the combination of formation water with injection water. This effluent is produced in large volumes and exhibits a complex composition, containing elevated concentrations of salts, inorganic ions, metals, as well as several classes of dispersed and soluble organic compounds, which are counted in the total oil and grease content (TOG). Given these intricate characteristics, the treatment of PW necessitates advanced solutions, frequently employing a combination of various separation technologies to enable either reuse or appropriate disposal [1]. However, traditional treatment of PW in offshore may present difficulties on treating stable emulsions, small oil droplets, and water-soluble organics, which not always can be removed by these treatments [1,2].

Recently, various advanced treatment techniques, including electrochemical oxidation (EO) techniques, are being studied on a laboratory scale and optimistic results have been reported. In particular, electrochemical advanced oxidation processes are efficient in reducing oil and grease (O&G) in PW [3]. Nevertheless, there is no consensus about the optimal operating conditions to remove dissolved oily compounds in high salinity wastewater.

Therefore, the present study aims to investigate the effect of the applied voltage to the electrodes on the soluble organic compounds removal by monitoring the chemical oxygen demand (COD) using electrochemical advanced oxidation process.

Material and Methods

The tests were conducted with Ti/IrO₂ + Ta₂O₅, Ti/IrO₂ + RuO₂ or Ti/SnO₂ as anode and Ti/Pt cathode of the same size (100×100×2 mm) with a distance between them of 0.5 cm. Both electrodes were supplied by Hebei Chaochuang Metal Mesh Co., Ltd. The reactor consisted of a rectangular vessel (Minihua Store, 25×10×8 cm), in which the plate electrodes were centered in the middle of the reactor and two magnetic stirrers (one on each side) guaranteed the homogenization of the solution.

The synthetic PW was prepared (2 L) to simulate real offshore PW. The solution was prepared with 500 mg·L⁻¹ of cyclohexanecarboxylic acid (CHC), 100 g·L⁻¹ of NaCl, and 2 g·L⁻¹ of NaOH (basic pH was used to guarantee completely solubilization of the naphthenic acid), and distilled water. The solution was led stirring for 18 h, then the pH was adjusted to pH 7 (similar to real PW characteristics). The tests were carried out at room temperature and initial conductivity was close to 132 mS·cm⁻¹.

The solution was added to the reactor and the electric clips were connected. The electric output was 2 V, 3 V or 4V, adjusted in the power supply Hikari (HF-3205S). For the Ti/SnO₂, when 2 V were applied the current was too low and could be measured, for this reason this data is not presented. The reaction was accomplished for 2 h, and the COD, pH, and conductivity were monitored. For the COD analysis, samples were diluted 1:5 and chlorine was precipitated as described by Tsonis (1993) [4], in order to avoid the interference of chloride ions.

Results and Discussion

As can be observed in Table 1, 2 V and 3 V were ineffective for COD removal with Ti/IrO₂ + Ta₂O₅

anode, since very low current density (CD) ($< 1 \text{ mA cm}^{-2}$) was achieved. At the same time, for $\text{Ti/IrO}_2 + \text{RuO}_2$ anode, for the 2 V test, a very low DC was obtained, but a higher CD was observed when 3V were applied (17 mA cm^{-2}). However, this value was not enough to overcome the electronic resistance and promote an adequate pollutant removal. This is because organic substrates with high redox potential (such as naphthenic acids) require a higher potential, normally higher than the oxygen evolution (OER), to favor the direct electrochemical oxidation or the generation of oxidative radicals (such as $\cdot\text{OH}$) for indirect oxidation. Therefore, an electrode material needs to have a high OER overpotential to avoid oxygen production, as SnO_2 [5]. Moreover, although Ti/SnO_2 electrode demonstrated a lower CD in 3 V, when compared to $\text{Ti/IrO}_2 + \text{RuO}_2$ anode, its removal rate was three times higher (36% versus 8%). This result is correlated to the fact that Ti/SnO_2 is a non-active electrode, whereas $\text{Ti/IrO}_2 + \text{RuO}_2$ is an active one [5]. Non-active anodes present low $\cdot\text{OH}$ adsorption enthalpy, unlike active electrodes. Therefore, in these anodes $\cdot\text{OH}$ weakly physisorbs, thus, normally enhancing the obtained mineralization rates [5]. On the other hand, a further increase to 4 V ($38 - 48 \text{ mA cm}^{-2}$), caused an increase on COD removal for all anodes, varying from 25-56% after 2 h of reaction. This is correlated to the non-linear behavior of the current density (CD) with the applied voltage, as can be noticed in Table 1. Therefore, it can be

concluded that for the studied system, a voltage close to 4 V would be the minimum to start to observe considerable effects from the electro-oxidation reactions.

Once again, Ti/SnO_2 presented the highest oxidation rate, followed in descending order by $\text{Ti/IrO}_2 + \text{RuO}_2$ and $\text{Ti/IrO}_2 + \text{Ta}_2\text{O}_5$, respectively. Demonstrating, again Ti/SnO_2 showed a higher electrocatalytic efficiency.

At the same time, it is important to point out that with a voltage increase, the final pH of the reactions increased as well, achieving up to 9.25. This fact is correlated to the hydrogen evolution reactions, which generate OH^- anions, liberating them to the aqueous media [6]. As expected, the application of low voltage and low current density, led to ineffective reaction, not causing a pH modification.

Moreover, conductivity was not affected by any of the studied conditions, due to the extremely high initial salinity content (100 g L^{-1} of NaCl).

Thus, these preliminary results indicated that the electrochemical advanced oxidation process appears to be a promising technique for the treatment of PW, however should be investigated in details. The benefits of these technologies should be better explored, since no chemicals and reduced footprint are required to degrade pollutants in PW. Additionally, the possibility to use renewable energy to electrochemical advanced oxidation technology is other attractive advantage.

Table 1. Characteristics from the synthetic PW before and after EO treatment for 2 hours of reaction.

Electrode	Voltage (V)	Current density ($\text{mA}\cdot\text{cm}^{-2}$)	pH		Conductivity ($\text{mS}\cdot\text{cm}^{-1}$)		COD removal (%)
			Initial	Final	Initial	Final	
$\text{Ti/IrO}_2 + \text{Ta}_2\text{O}_5$	2	0.13 ± 0.01	7.04	6.82	132	122	~0
	3	0.39 ± 0.05	6.62	6.86	134	125	1
	4	38 ± 2	7.04	9.25	131	124	25
$\text{Ti/IrO}_2 + \text{RuO}_2$	2	0.4 ± 0.2	7.04	7.26	136	124	~0
	3	17 ± 1	7.08	8.54	131	125	8
	4	48 ± 3	6.92	8.74	132	129	33
Ti/SnO_2	3	10 ± 1	7.04	8.61	129	120	36
	4	46 ± 1	6.94	8.98	132	125	56

Conclusions

This study shows that EO appears is a promising technique for treating PW. The increase in the applied voltage, and consequently, the current density of the system led to higher removal rates, achieving up to 56% COD removal after 2 hours, being the Ti/SnO_2 the anode with the best removal results. Although, further studies are needed to achieve higher degradation levels. The pH raised considerably when 4 V were applied, indicating the formation of by products with alkaline character, which is a point of attention for its final discharge.

Acknowledgments

We would like to thank PETROBRAS [2023/00226 0] for financial support and LEMA-UFSC for the infrastructure.

References

- [1] Ghafoori et al., *Separation and Purification Technology*, 289 (2022) 120652.
- [2] Liu et al., *Science of The Total Environment*, 775 (2021) 145485.
- [3] Khorram et al., *Chemosphere*, 338 (2023) 139565.
- [4] Tsonis, S.P., *Transactions on Ecology and the Environment*, 2 (1993) 723.
- [5] Zuo et al., *Nature reviews materials*, 8 (2023), 472.
- [6] Espinoza-Montero et al, *Molecules*, 25, (2020), 5550.