

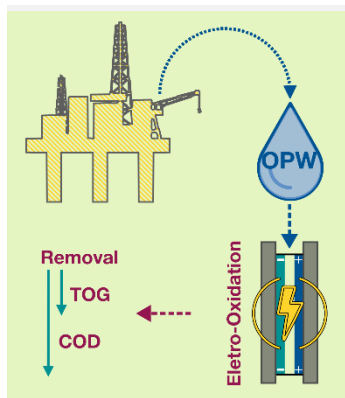
Oilfield Produced Water Treatment: Exploring Electro-Oxidation Principles, Challenges, and Future Research Prospects

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Managing oilfield produced water in the petroleum industry is a persistent challenge. Electro-oxidation process is a versatile approach for removing a wide range of contaminants from water, especially those challenging to treat conventionally. This study comprehensively overviews electro-oxidation technology for oilfield produced water treatment. Electrogenerated active species play a central role in organic compound oxidation, where selecting the most suitable electrode material remains challenging. Active materials show higher affinity for chloride, generating more active species, while non-active materials exhibit greater degradation potential via hydroxyl radicals. Different studies show the challenging process of treating oilfield produced water due to its complex matrix, making it difficult to determine the main parameters in the treatment process. However, it was shown that current density and initial pollutant concentration are the most influential parameters.

Introduction

One of the main environmental problems in the oil and gas industry is waste generation, mainly process-derived Oilfield Produced Water (OPW). The OPW properties may differ, depending on the age and localization of the production field. Hence, several pollutants are found in OPW samples, such as metals, organic contaminants, saturated and unsaturated hydrocarbons, microorganisms, radioactive materials, and suspended/dissolved solids that give rise to salinity values that often exceed that of seawater [1].

Current physical and chemical methods, commonly used to treat OPW samples, in some cases, fail to remove recalcitrant compounds (mainly Water-Soluble Organics (WSO)), not allowing reach zero discharge conditions to be achieved [2].

An innovative way to remove WSO from OPW samples is through advanced oxidation processes (AOPs) such as Electrochemical Oxidation (EO), which displays several advantages, including ease of operation, no use of chemicals, no sludge formation, low-temperature requirements, and simple equipment, all of which are essential factors for offshore applications [3].

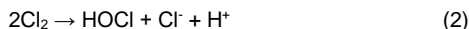
The degradation of organic compounds through the EO process could follow direct or indirect mechanisms. In direct routes, degradation occurs at the electrode surface, while in the indirect route, active species are electrogenerated (e.g. hydroxyl radicals, chlorine radicals), interacting directly with organic molecules in the bulk solution. In the case of OPW, the indirect method will be the main responsible for organics degradation, mainly by chlorine radicals [2].

Many factors could influence the EO such as anode

material, oxidizable content, reaction rate, process time, electrolyte, current density (CD), pH, temperature, flow rate, inter-electrode gap, and cell geometry [4]. However, the analysis of the parameters becomes difficult when just a few studies in the literature relate to the EO of real OPW samples, where most of these studies are associated with lab-scale tests. Therefore, this study comprehensively overviews the electro-oxidation technology for oilfield-produced water treatment.

State of the Art

As stated before, the indirect oxidation pathway is the main responsible for organics degradation in OPW, since its high salinity provides high concentrations of chlorine compounds. Chlorine radicals are formed through direct oxidation of chloride anions at the anode (reaction 1) which mostly generates hypochlorous acid (HOCl) and chloride ions (Cl⁻) (reaction 2). The HOCl could dissociate in ClO⁻ and H⁺ (reaction 3). In this case, the pH is an important factor, where at pH ≤ 3, Cl₂ is the predominant active chlorine species, whereas, for pH ranges between 3 – 8 and pH ≥ 8, the dominant species are HOCl and ClO⁻, respectively [5].



However, the interaction between the chlorine active species dissolved/suspended organics is hindered by their difficult oxidizing nature and the low oxidizing potential of such species, even at acid pH [6]. Hence, the high concentration of chlorine ions will induce the

degradation by their radicals. However, the generation of hydroxyl radicals could improve the degradation of the organic and is preferred for the molecules' oxidation due to their higher oxidation power. The high chlorine concentration could lead to the possible formation of toxic molecules (e.g. chlorates and perchlorates) originating from the oxidation of HClO with hydroxyl radicals [2].

Electrode composition is of utmost importance to take advantage of electrogenerated active species. Regarding the anode, active anodes (lower potential window) are preferable for the generation of chlorine active species, showing high affinity with hydroxyl radicals, also hindering the formation of toxic chlorine molecules. On the other hand, non-active anodes (higher potential window) generate readily available hydroxyl radicals, due to their low affinity with such molecules [7]. The cathode could also influence the EO efficiency making better use of the applied electric power and also improving the degradation of organic molecules since the reduction reaction at the cathode could degrade halogenated molecules and polycyclic aromatics hydrocarbons. In addition, electrogenerated chlorates and perchlorate molecules could also be remediated by H₂O₂ generation at the cathode [7].

In OPW treatment, higher current density values may not always enhance efficiency beyond a certain point, while longer treatment times are often required for complete mineralization. High NaCl concentrations and alkaline conditions can lead to the formation of polymeric films in the electrode surface, decreasing removal efficiencies. The

presence of sulfates, however, can benefit EO processes by enhancing current efficiency and mitigating film formation [2].

The literature regarding the EO of OPW samples showed related patterns for different treatment procedures. As an example, EO treatment of OPW samples from PETROBRAS Plant – Rio Grande do Norte was evaluated by three studies in batch and recirculation modes using BDD and Ti/Pt electrodes [8]. The results obtained by the authors showed COD removals of 46.5% and 57.5% for Ti/Pt and BDD anodes, respectively, at 30 mA·cm⁻² and 10 h of reaction time. In contrast, Campos et al. [9] obtained higher removal rates, reaching 50% and 90% at 30 mA·cm⁻² and 2 h for Ti/Pt and BDD anodes, respectively. The discrepancy in results could be attributed to differing initial COD concentrations, 1588 mg·L⁻¹ for Rocha et al. [8] and 4600 mg·L⁻¹ for Campos et al. [9]. In the recirculation treatment mode of OPW samples, both Santos et al. [10] and Campos et al. [9] observed increasing COD removal with higher current density, with BDD electrodes showing superior performance.

The OPW treatment by EO is a challenge since its composition changes concerning field location, reservoir age, and other parameters. Initial pollutant concentration, electrode material, and current densities were shown to be the most influential parameters for the pollutant's degradation by COD monitoring. Hence, samples with extremely high salt concentrations (>100 g·L⁻¹) and higher current densities are needed leading to a better performance of active anodes (fresh, brine) [11].

Conclusions

The recalcitrant compounds found in OPW samples could be removed through EO processes. The indirect method is mainly responsible for the degradation of the organic molecules present in OPW mainly due to their high salinity, leading to the formation of chlorine radicals, showing higher oxidation capacity at acidic pH medium. Electrode composition plays a crucial role in generating active species, with active anodes favoring chlorine generation and non-active anodes producing hydroxyl radicals. The cathode enhances EO efficiency by degrading organic molecules and remediating chlorates and perchlorates. Literature on EO treatment of OPW samples demonstrates variable outcomes influenced by initial COD concentrations and electrode types. Further research is needed to optimize EO for diverse OPW compositions and conditions.

Acknowledgments

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