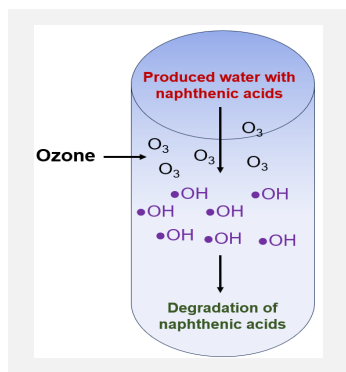


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This study investigated how pH and salt concentration affect the oxidation of cyclohexanecarboxylic acid (CHCA) in synthetic produced water (80 L) using the ozonation process on a pilot-scale. Under highly alkaline conditions (pH = 12), CHCA underwent near-complete degradation within 200 min, with its concentration reaching nearly zero ($C/C_0 \approx 0$), while at pH = 10, its degradation was approximately 60% ($C/C_0 \approx 0.4$). The strongly alkaline environment favored oxidation due to indirect reactions with hydroxyl radicals formed in the presence of ozone. Adding a high concentration of sodium chloride (100 g/L) to the synthetic effluent slightly decreased the degradation of CHCA compared to effluent without added salt. The Cl^- anion reacted with $\cdot OH$, reducing the oxidation of CHCA and increasing the rate of ozone self-decay in the presence of salt.

Introduction

The oil and grease content in oilfield produced water (OPW) can vary depending on the location of the oil production field, as it is closely related to the nature of the oil. Oil and grease content levels can exceed 500 mg/L and the organic composition can be categorized into two groups: dispersed oil and water-soluble organic compounds. Among the soluble, naphthenic acids are particularly noteworthy [1].

Advanced oxidative processes (AOPs) offer innovative solutions that have not yet been fully embraced by the oil industry. The key advantage of AOPs lies in their high reactivity, allowing them to effectively break down a wide range of organic compounds by generating hydroxyl radicals ($\cdot OH$) and other reactive species. This enables the mineralization of recalcitrant organic compounds into carbon dioxide and water. As a powerful oxidant, ozone (O_3) makes ozonation a particularly effective method for treating large volumes of effluents. Furthermore, the process requires minimal space, a critical advantage in offshore applications [2].

This pilot-scale study explores how pH and salt levels affect ozonation's ability to oxidate these contaminants, paving the way for a more efficient environmentally friendly treatment process for offshore produced water.

Material and Methods

The produced water was synthesized by combining cyclohexanecarboxylic acid (500 mg/L) and sodium chloride (100 g/L) in 80 L of distilled water. Sodium hydroxide (0.05 M) was added to the solution that was stirred for 24 h to ensure complete dissolution

of the CHCA. The pH was regulated with hydrochloric acid (1 M) and sodium hydroxide (0.05 M).

The pilot-scale experimental system (Fig. 1) included an 80-liter reactor with liquid inlet and outlet at the base, and a degassing outlet at the top. A centrifugal pump circulated the synthetic OPW solution through a 3/4" stainless steel pipe at a flow rate of 21 L/min. Ozone was generated (Brazil Ozônio BRO3 Plus 4) from concentrated oxygen and directly injected into a venturi located in the pipeline at a rate of 3 NL/min with a concentration of 74 mg/L in the gas phase. After ozone injection, the mixture passed through a 0.2 m long kenics-type static mixer before returning to the reactor.

This study monitored the oxidation of CHCA over time within the reactor for pH 10 and 12 and with the presence and absence of salt (NaCl). CHCA quantification was performed according to the procedure described in detail by Carvalho Neto [1]. Briefly, samples of 50 mL were extracted using a liquid-liquid extraction procedure with n-heptane as the solvent. The absorbance of the solvent at a specific wavelength (1708 cm^{-1}) was measured in FTIR spectrophotometer using a sealed cell with ZnSe window. A pre-established calibration curve was then used to convert the absorbance values into the mass concentration of CHCA [1].

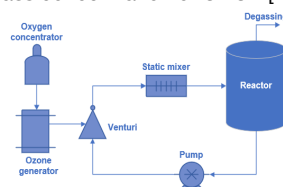


Figure 1. Pilot-scale experimental scheme.

Results and Discussion

Although the solubility of ozone in water is favored in acidic solutions, for pH = 12 the oxidation efficiency was higher than at pH = 10 (Fig. 2). This can be explained by the dissociation into ions of this naphthenic acid in alkaline environments ($pK_a \approx 4.5$), i.e., ozone molecules could generate more $\cdot\text{OH}$ under the induction of hydroxide ions [3]. At a highly alkaline condition (pH = 12), CHCA underwent near-complete degradation within 200 min, with its concentration reaching nearly zero ($C/C_0 \approx 0$), while at pH = 10 this degradation was approximately 60% ($C/C_0 \approx 0.4$).

Ozonation can occur through two main mechanisms: direct and indirect. Direct ozonation reactions are selective but slow due to the limited reactivity of ozone with pollutants at low pH values. This is because protons (H^+) readily react with ozone, consuming it and forming water (H_2O) and oxygen (O_2). In contrast, under alkaline conditions, ozonation becomes more efficient due to the prevalence of indirect reactions. These reactions involve highly reactive free radicals, particularly $\cdot\text{OH}$, generated by the decomposition of ozone in water. The high reactivity of $\cdot\text{OH}$ allowed for the degradation of CHCA [2]

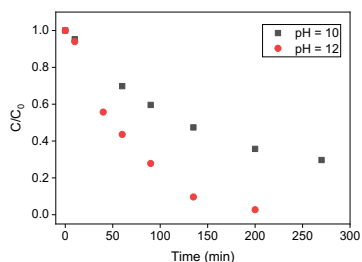


Figure 2. Effect of pH on the ozonation of CHCA (with addition of 100 g/L NaCl).

The presence of electrolytes can favor the solubility of ozone in water. However, the presence of inorganic anions, such as chlorides (Cl^-), can hinder the mineralization of organic compounds during ozonation [4].

The addition of a high concentration of sodium chloride (100 g/L) to the synthetic OPW slightly decreased the degradation of CHCA (Fig. 3).

The reaction between Cl^- and $\cdot\text{OH}$ can lead to the formation of $\text{ClOH}\cdot^-$, which subsequently breaks

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down into Cl^- and $\cdot\text{OH}$. In the presence of an excess of Cl^- , $\text{ClOH}\cdot^-$ can combine with Cl^- to produce $\text{Cl}_2\cdot^-$, which has a lower reduction potential (2.0 V) compared to $\cdot\text{OH}$'s (2.8 V) (Equations 1-2). This ultimately hinders the effective removal and mineralization of organic compounds [5].

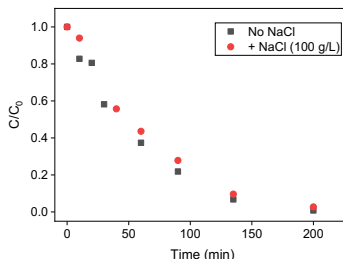
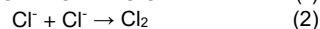
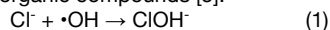


Figure 3. Effect of salt on the ozonation of CHCA at pH 12.

An additional theory suggests that the rate of ozone self-decay may increase in the presence of salts. This slight elevation could potentially be attributed to the interaction between O_3 and chloride ions [4].

Conclusions

This study unveiled the potential of ozonation as a technique for removing organic compounds from OPW. The influence of pH on the ozonation of CHCA revealed that a strongly alkaline environment favored oxidation, attributed to indirect reaction with $\cdot\text{OH}$ formed in the presence of O_3 . The presence of NaCl slightly reduced the degradation efficiency of CHCA, as the Cl^- anion reacted with $\cdot\text{OH}$, thereby decreasing CHCA degradation and also increasing the rate of ozone self-decay under the presence of salt.

Acknowledgments

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