Performance of Combined FeSO4 / TiO2 Based AOP for Treating Petroleum Wastewater

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Abstract

Globally the oil and gas industry generates an estimated several billion barrels of produced water annually.
Oman being a major oil producer, generates a substantial volume of produced water.
The quantity is specially high because the mature oil fields require enhanced oil recovery techniques, which typically results in increased water production.
The PWW contains a variety of pollutants including oil residues, heavy metals, radioactive materials, and a range of dissolved inorganic and organic compounds.
The produced water is highly saline, often more so than sea water, and contains chemicals used during drilling and extraction, such as biocides, scale inhibitors, and corrosion inhibitors, making it a challenging waste stream to manage.

Methods and Materials

FeSO4 can be used initially in the reactor to cause coagulation and flocculation of suspended solids, oils and greases.
By aggregating these contaminants into larger particles, FeSO4 makes them easier to separate from the water phase, significantly clearing the water of turbidity and bulk pollutants.
After the initial clearing of larger particles and some organic contaminants, the treated water can be exposed to UV light in the presence of TiO2.
When exposed to TiO2 and UV light, this could localize the reaction, enhancing the degradation efficiency of persistent compounds.
Iron from FeSO4 can react with peroxide radicals and water to generate additional hydroxyl radicals under UV light, potentially enhancing the photocatalytic process driven by TiO2.

Contaminant	Removal Efficiency (%)	Treatment Process
Total Suspended Solids	90-99	Primary clarification, filtration
Oil and Grease	95-99	Skimming, floating, biological treatment
BOD	85-99	Aerobic biological treatment
COD	50-90	Biological treatment, Advanced oxidation
TDS	50-95	Reverse osmosis, Distillation
Heavy Metals	90-99	Chemical precipitation, ion exchange
VOC's	80-99	Air stripping, carbon adsorption

Table 1. Removal efficiencies of various treatment processes.

Introduction

Petroleum wastewater, also known as produced water is a significant by product of oil and gas extraction processes, pose various challenges globally and particularly in oil-rich regions like Oman.
From the complicated oil and gas production activities, the petroleum wastewaters have now come to be amongst the most important environmental challenges of the treatment. Some parts of this waste contain a wide variety of pollutants, high organic compounds level, heavy metals, and many other toxins, all of which infer huge damage to the environment and human health if not controlled effectively.
It is characterized by high levels of organic compounds, inorganic salts, hydrocarbons, and potentially production chemicals, making it one of the most complex industrial wastewaters to manage.

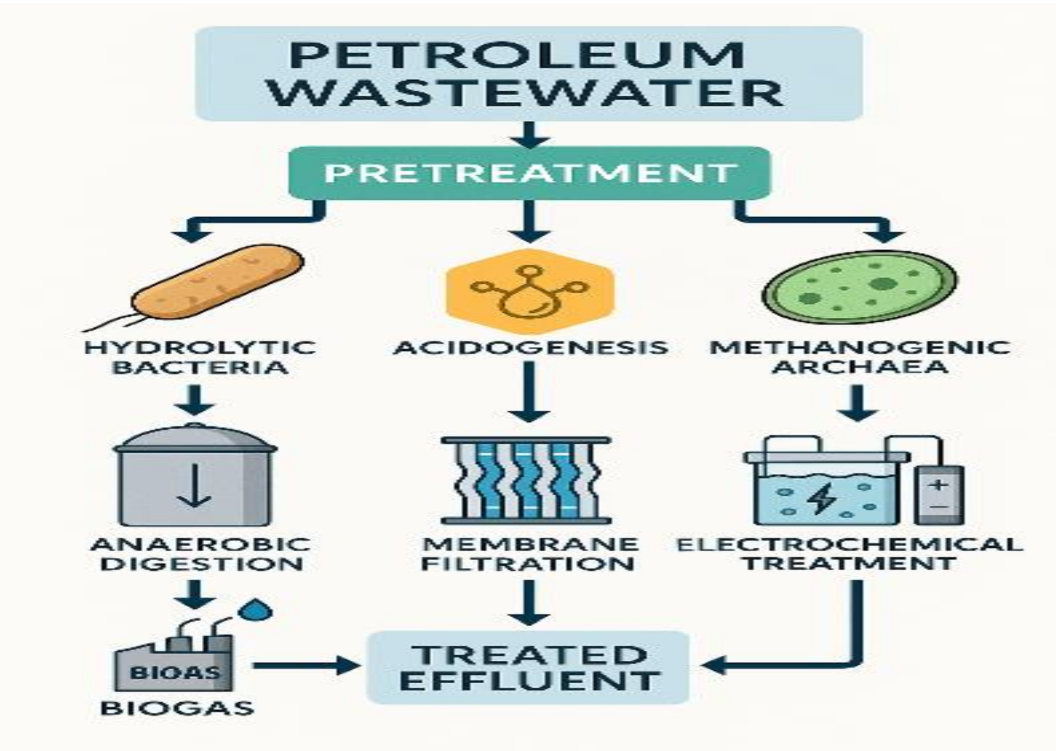
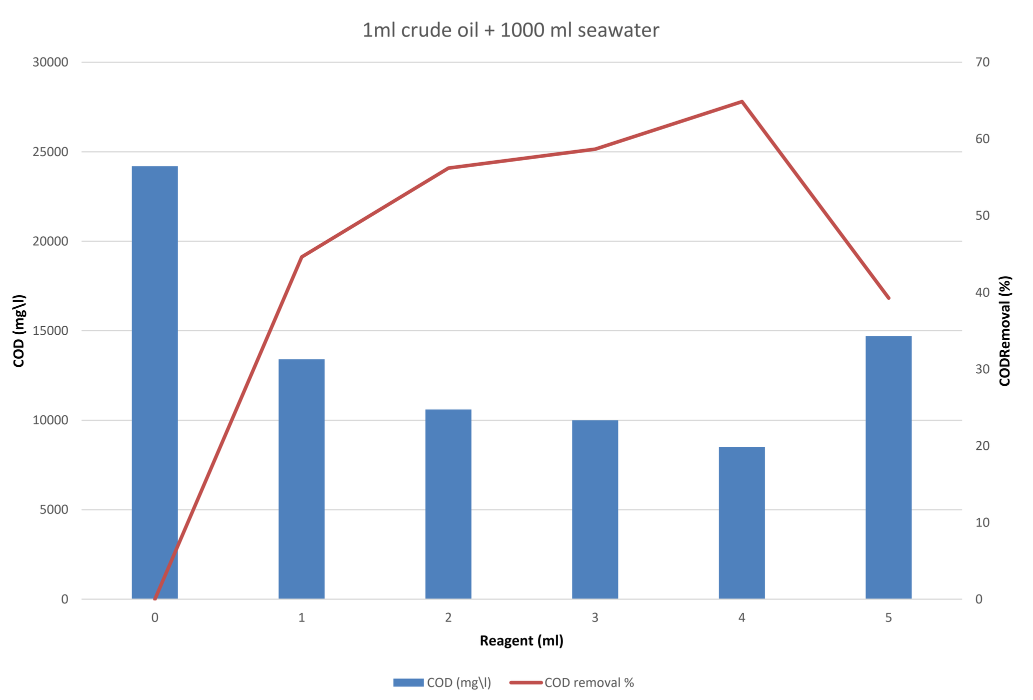


Figure 1. Integrated Treatment pathways for treating PWW.

Results

Varying $FeSO_4$ dosages (0–5 mL) (DF 20%) were tested to assess their impact on pH, COD (Chemical Oxygen Demand), and color removal.
The reaction intensifies with higher $FeSO_4$ doses, leading to greater H^+ accumulation.
While a mildly acidic pH (4.8–5.5) enhances coagulation by promoting $Fe(OH)_3$ floc formation, excessive acidity (pH < 4.5) can dissolve these flocs, reducing efficiency
The dosage fixed at 4ml, and the tests were performed for varying pH (3 to 11).
The best removal efficiencies were achieved at pH being 7, (64.9% removal).
Further experiments are being conducted with differing various parameters such as mixing time and rpm for further analysing the effects.
TiO2 will be used in the same way.

Figure 2 . Effect of FeSO4 on PWW.



Discussion

Seawater's high salinity (ionic strength) can compress the electrical double layer around oil droplets, enhancing coagulation, however, divalent ions (Ca^{2+}, Mg^{2+}) may compete with Fe^{2+} for binding sites, reducing $FeSO_4$ efficiency (Shi et al., 2017). Additionally, chloride ions (Cl^-) can form soluble $FeCl_2$ complexes at low pH, limiting floc formation. These interactions explain the need for higher $FeSO_4$ dosages (4 mL) compared to freshwater systems (typically 2–3 mL) (Zhou et al., 2011).
Aziz et al. (2020) reported 60–70% COD removal at pH 4–6 using $FeSO_4$ in oily wastewater (initial COD ~20,000 mg/L), consistent with this study's 64.8% at pH 4.8. Wang et al. (2019) noted reduced efficiency at pH < 4.5, corroborating the poor COD removal (39%) at pH 4.4 (5 mL $FeSO_4$). Zhou et al. (2011) achieved >95% color removal in refinery wastewater using $FeSO_4$ at pH 5–6, aligning with this study's 96.8% at pH 4.8. Shi et al. (2017) highlighted that seawater's ionic strength improves coagulation but necessitates higher coagulant doses, mirroring the requirement for 4 mL $FeSO_4$ here versus lower doses in freshwater.

Conclusions

4 mL $FeSO_4$ at pH 4.8 balances COD (64.8%) and color (96.8%) removal. Post-treatment pH adjustment is necessary to meet discharge standards (e.g., pH 6–9).
$FeSO_4$ introduces iron sludge, requiring disposal. High salinity complicates floc settling, necessitating clarifiers or dissolved air flotation.
$FeSO_4$ effectively removes oil contaminants from seawater via charge neutralization, with 4 mL identified as the optimal dosage. However, seawater's ionic composition and pH sensitivity necessitate careful process control.
Future work should explore $FeSO_4$-polysaccharide composites to enhance floc stability in saline environments.

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