Global NEST Journal, **28** (3), 08458
Available online: 18/05/2026

Mechanistic Optimization of $FeSO_4$ for Synthetic Petroleum Wastewater Treatment

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Abstract

The presented work investigates the performance of ferrous sulfate ($FeSO_4$) in treating contaminated seawater with petroleum hydrocarbons. Synthetic water containing 0.1% (v/v) oil was subjected to varying $FeSO_4$ dosage, pH and reaction time under controlled conditions. The effects of the operating conditions were evaluated based on removing chemical oxygen demand (COD), color and the final pH effluent. COD and color removal reached to 64.8% and 96.8% respectively using 16.7g/60ml $FeSO_4.7H_2O$ (≈3350 mg/L Fe^{2+}) at 120 min reaction time. At this optimum, the settled sludge volume was 13-17% of the treated sample and residual iron in the supernatant was 12-18 mg/L, within marine discharge limits. The COD reduction stabilized, indicating coagulation equilibrium, however, the first 30 min shows rapid color removal. The $FeSO_4$ concentration when increased, resulted in reduction of pH due to Fe^{2+} hydrolysis, which in turn promoted floc formation through neutralization and coagulation. Statistical analysis (ANOVA)confirmed that dosage, pH, and reaction time significantly affected removal efficiencies ($p < 0.05$). From the results it can be confirmed that $FeSO_4$ is an efficient and low cost treatment for petroleum wastewater. It offers substantial pollution reduction and has potential compatibility with subsequent oxidation and/or biological treatment processes. Taken together, these findings show that $FeSO_4$ offers a practical and cost effective alternative for pre-treatment of Petroleum affected seawater under saline conditions, and that its use could enhance the overall efficiency of subsequent AOP or biological processes. The approach used is particularly feasible for contained coastal applications and as a rapid response for near shore oil spills. Unlike prior studies for freshwater or low salinity refinery wastewater, this work gives saline-specific benchmark for $FeSO_4$ dosage, pH shift, kinetics, amount of sludge production and residual iron-critical parameters for coastal oil spill treatment.

Keywords: Petroleum wastewater; Treatment; Removal efficiency; Contaminated marine water.

OPEN ACCESS

Received: 23/02/2026,

Accepted: 09/05/2026,

Available online: 18/05/2026

https://doi.org/10.30955/gnj.08458

Graphical abstract

1. Introduction

The extraction and refining of crude oil, as well as downstream petrochemical processes, produce vast amounts of crude oil-rich and suspended solids, oil, greases, and trace metal-contaminated wastewater (Abdelhamid *et al.*, 2024). The effluents are in the form of stable oil-water emulsions with their chemical complexity and stability rendering them hard to treat by the conventional methods (Cavallini *et al.*, 2015) Disposal of such wastewater in an under-treated state may cause acute intoxication, depletion of oxygen, and the ability of recalcitrant organics to accumulate in the bodies of water and the soil (Muftah *et al.*, 2016, Metin and Cifci, 2023) Such environmental risks can only be exacerbated in environmentally sensitive coastal areas like the Arabian Gulf where the salinity is high and the hydrodynamic dispersion is low (Giwa *et al.*, 2013). Thus, the development of effective and environmentally sound treatment strategies is a pending task for regulatory compliance and the environment protection, particularly in high salinity coastal waters where conventional coagulant behavior is altered (Zueva *et al.*, 2020; Zhao *et al.*, 2020).

Traditional treatment processes such as gravity separation, dissolved air flotation, and biodegradation, are often ineffective for petroleum-based wastewaters due to high salinity, variable organic loads, and pH variation (Zueva *et al.*, 2020). In addition to catalytic and chemical approaches, biological treatment has also captured consideration to be a sustainable option for treating petroleum wastewater. Another recently published critical review by (Ali *et al.*, 2025) investigated the potential of aerobic/anaerobic and hybrid configurations which are designed to improve biodegradability, supporting biogas recovery. The work highlighted that, microbial processes can be very effective while conditions are well controlled. However, they remain sensitive to fluctuations in salinity, organic load and the presence of toxic hydrocarbons. It was also noted in the review about the growing role of membrane bioreactors, microbial fuel cells, enzymatic pathways and data driven monitoring in improving process liability. The analysis showed that the biological treatment alone might struggle with stability and complexity of the emulsions present in the petroleum wastewater, unless supported by suitable pretreatment. These findings further emphasized the need for a robust process, such as ferrous based coagulation for reduction in suspended and colloidal hydrocarbons before the application of Biological or AOP techniques.

To eliminate these shortcomings and expand the water reuse opportunities, treatment methods such as membrane filtration, adsorption, and other types of oxidation have been recommended (Moussa *et al.*, 2017). Among the higher oxidation processes (AOPs) or to say the least; the Fenton process, the photo Fenton process and the TiO_2 based process are all capable of degrading refractory hydrocarbon to simple intermediates. Nevertheless, they are limited in their large scale use due to their high operating costs and energy requirement (Ganiyu *et al.*, 2020). A previous review by (Ali *et al.*, 2024) discussed these AOP technologies in detail, including Fenton, Photo Fenton, Electro Fenton, Ozonation, TiO_2 assisted photocatalysis and persulfate. It pointed out their potential, as well as, operational constraint. In contrast to this, chemical coagulation is a treatment method that is less expensive and more mass based and can be employed as a mandatory pretreatment method. It also possesses the advantage of destabilizing emulsified and colloidal particles, elimination of colors and boost of the effectiveness of subsequent biological or oxidative treatment (Liang Z *et al.*, 2009). There is a need to optimize the nature of the coagulant used and the environmental terms in order to minimize the dosage of the coagulant used and the amount of sludge formed whilst retaining high removal efficiency.

Ferrous sulfate heptahydrate ($FeSO_4$ $7H_2O$) was found to be an effective and very low-cost coagulant of a very wide range of industrial effluent. This is caused by the neutralization of charges and hydrolysis of Fe^{2+} ions to $Fe(OH)_2$ and further to $Fe(OH)_3$ which are effective adsorbents and bridging agents of suspended material (Zueva *et al.*, 2020). At acidic pH, Fe^{2+} may further be involved in a redox reaction to produce hydroxyl radicals, which leads to partial oxidation of dissolved organics (Ganiyu *et al.*, 2020). $FeSO_4$ does not have disadvantages of high sludge production, poor color removal, and incompatibility with other coagulants in a combined system, compared to other iron-based coagulants ($FeSO_4/TiO_2$/Photo-Fenton systems). Other studies had a 60-70% COD and more than 90% color removal in refinery and a produced water under optimized conditions of acidic water (Zueva *et al.*, 2020). These assertions put the $FeSO_4$ to be a viable pretreatment agent and which could potentially enhance the overall performance of the combination coagulation-oxidation system.

The present study investigates the efficiency of $FeSO_4$ for treating petroleum contaminated seawater under controlled laboratory conditions. The effect of $FeSO_4$ dosage on COD and color removal were evaluated. The influence of pH and contact time variation for targeted parameters removal was identified and discussed. Moreover, the influence of the experimental conditions on the final pH were evaluated to assess the applicability of the final effluent discharge and reuse options. A key contribution of this work is a systematic parametric evaluation of $FeSO_4$ specifically for a saline, petroleum contaminated matrix. Unlike most previous studies that used freshwater or low-salinity refinery effluent (Zueva *et al.*, 2020; Cavallini *et al.*, 2015), this study provides the following advances: (i) quantitative data on the interplay between $FeSO_4$ dosage, pH shifts due to Fe^{2+} hydrolysis in seawater, and the kinetics of rapid color removal (92.4% in 30 min) versus slower COD reduction (stabilizing after 120 min); (ii) demonstration that the optimal Fe^{2+} dos (≈3350 mg/L) is substantially higher than in fresh water systems due to ionic competition from Na^+, Mg^{2+}, and Ca^{2+}; (iii) reporting of sludge volume (13-17% by volume) and residual iron (12-18 mg/L) to assess practical feasibility; and (iv) explicit linkage to near-shore oil spill response and contained coastal effluents. This investigation contributes to the broader goal of optimizing low-cost, iron-based treatment strategies for industrial effluents in arid coastal environments, supporting sustainable wastewater reuse and discharge compliance.

2. Methods and Materials

2.1. *Sample preparation*

A batch of synthetic petroleum wastewater (PWW), cloning oil contaminated marine effluent was prepared, mixing crude oil with seawater (0.1% (v/v) oil/seawater). This mixture was selected to replicate the dilution typically encountered in off shore discharge, including accidental spill (Tahraoui H *et al.*, 2024, Giwa *et al.*, 2013, El Naas *et al.*, 2013). A local petroleum facility was contacted to obtain the crude oil required for sample preparation, characterized by its presence of high aromatic hydrocarbon content and density of approx. 0.87 g/cm^3 at 25°C. Some 12 liters of seawater was obtained from coastal region in Batinah, filtered through a 0.45 µm membrane for removing suspended solids before use. To achieve homogenous emulsion, the mixture was vigorously agitated, using a magnetic stirrer at 1000 rpm for 10 min. This approach reproduces the physiochemical characteristics of petroleum wastewater discharged from offshore oil production facilities (Abdelhamid *et al.*, 2024). The average initial COD of 24,000 mg/L, color intensity of 9225 Pt-Co units, and pH of 7.1 were recorded from the resulting synthetic wastewater. These values were consistent with the range reported from refinery and produced waters (Cavallini *et al.*, 2015, Metin and Cifci, 2023).

2.2. *Experimental Procedure*

Experiments regarding coagulation flocculation were performed using mechanical shaking method simulating homogenous mixing conditions during treatment. 60 mL of prepared synthetic sample was filled in a 150 mL Erlenmeyer flask, and placed on an orbital shaker (VELP Scientifica SKI 4, ITALY). A pre-weighed amount of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was added to achieve the targeted dosage levels (0.25, 0.5, 0.75, 1.0, and 1.25g per 60mL, corresponding to 4.2,8.3,12.5,16.7, and 20.8 g/L, respectively). For clarity, all dosages are also reported in the standard unit of mg Fe^{2+}/L (e.g. 16.7 g/L $FeSO_4$ ≈ 3350 mg/L Fe^{2+}). The mixtures, were shaken at a steady speed of 150 rpm to ensure uniform dispersion of Fe^{2+} ions and to reach a stable emulsion prior to treatment. The purpose was to have effective contact amongst the coagulant and the petroleum constituents. The shaking duration varied between 30 and 150 min to evaluate the impact of contact time on the efficiency of pollutant removal. Once the shaking was over, the samples were kept for 30 min under latent conditions to expedite floc sedimentation. The supernatant, was carefully withdrawn and examined for chemical oxygen demand (COD), color and pH following (APHA, 2017) standards. The initial physicochemical characteristics of the prepared sample of PWW were found to be, COD to be 24,200mg/L, color to be 9,225 Pt Co units and pH to be 7.1 respectively. This represented highly contaminated conditions, consistent with the reported values for offshore and refinery produced wastewater (El Naas *et al.*, 2013, Zhao *et al.*, 2020). The experiments were performed at temperature (25 ± 1° C) to ensure reproducibility. The supernatant samples collected at fixed intervals of (30, 60, 90, 120 and 150 min) were analysed for residual pollutants. The design parameters selected were based on optimization ranges reported in similar coagulation studies for oily wastewater (Muftah *et al.*, 2016, Luo *et al.*, 2022).

The effect of dosage was examined using $FeSO_4{\cdot}7H_2O$ at 0.25g, 0.5g, 0.75g, 1.0g and 1.25g/60mL (4.2-20.8 g/L). The range was selected to decide the optimal coagulant dosage to maximize pollutant removal, and minimizing residual iron and sludge formation. A fresh solution was prepared before each run, to prevent oxidation of Fe^{2+} to Fe^{3+} in air (Tony *et al.*, 2012). Initial tests established that a dosage of 1g/60mL (equivalent to ≈ 3350 mg/L Fe^{2+}) gave the highest removal efficiency for both COD and color. Beyond this dosage a decline in performance was observed, consistent with charge reversal and restabilization of colloidal particles as reported in prior work by (Metin and Cifci, 2023, Moussa *et al.*, 2017). The pH was tracked continuously during treatment, using a calibrated pH meter (Hanna Instruments HI 5221), and no external pH adjustment was performed unless otherwise specified.

2.2.1. Mixing Protocol

To ensure proper coagulation and flocculation, a two-stage mixing method was applied. Rapid mixing at 150 rpm for 5 min (velocity gradient G ≈ 20-30 s-1) was done to disperse the coagulant. Followed by slow mixing at 60 rpm for 25 min (G ≈ 20-30 s-1) to promote floc growth. The samples were then allowed to settle inactively for 30 min. This protocol follows standard jar-test practices for iron coagulation (Liang *et al.*, 2009; Tahraoui *et al.*, 2024).

2.2.2. Control experiments

Two control experiments were performed in triplicate: (A) synthetic petroleum wastewater without $FeSO_4$, subjected to the same mixing and settling procedure to quantify natural settling or wall adsorption. (B) $FeSO_4$ (16.7 g/L) added to deionized water to measure any background COD contribution from residual ferrous iron. Control A gave <5% COD reduction and <3% color reduction, confirming observed removals are due to coagulation. Control B showed negligible COD (<10 mg/L) after 0.45 µm filtration.

2.3. *Analytical Study*

Performance of all experiments carried out was in accordance with (APHA 2017), Standard Methods for Examination of Water and Wastewater. A calibrated digital pH meter with standard buffer solution (4, 7 and 10) was used for measurements. As for COD the closed reflux titrimetric method (Method 5220 C) was used. Samples were digested for 2 hours at 150oC in an HACH COD reactor, followed by titration using ferrous ammonium sulphate. Spectrophotometric quantification was done for color using Platinum-Cobalt method (Method 2120 C) at 455 nm, with results presented in Pt-Co units. Method detection limits were 5 mg/L for COD and 2 Pt-Co units for color. Prior to COD analysis all supernatant samples were filtered through 0.45 µm syringe filters to remove $Fe(OH)_3$ flocs that could otherwise cause positive interference (Metin & Cifci, 2023). All reagents were of analytical grade. Blank tests (deionized water) and method blanks (reagents without sample) were run with each batch. Data represents the mean of three replicates; relative standard deviations were <3% for COD and <2% for color.

Statistical analysis was performed using Minitab 19 (Minitab Inc., State College, PA, USA). One-way analysis of variance (ANOVA) followed by Tukey's post-hoc test was employed to determine the significance of differences between mean removal efficiencies under varying experimental conditions. A p-value of less than 0.05 was considered statistically significant.

3. Results and Discussion

3.1. *Effect of $FeSO_4$ dosage*

Dosages of 0.25, 0.5, 0.75, 1.0 and 1.25g/60mL (4.2 – 20.8 g/L of $FeSO_4.7H_2O$ were selected to check the impact of COD and color removal from the petroleum contaminated seawater, while keeping controlled shaking conditions (**Figure 1**). A nonlinear trend was exhibited in removal efficiency of COD, reaching to a maximum of 64.8% reduction, accomplished at a dosage of 1.0g/60 mL $FeSO_4$. At lower dosages of 0.25-0.5 g/60 mL, the removal efficiency ranged from 44.6% to 56%, mainly due to the neutralization of negatively charged oil and colloidal organic matter by Fe^{2+} ions. As the dosage was increased from 0.75 to 1.0g/60 mL, it resulted in sweep flocculation and directed to the enmeshment of suspended and dissolved organic constituents. However, when the dosage was further increased to 1.25g/60 mL, the impact was reduced reduction in COD removal to 39%. This suggests an overdosing effect with excess Fe^{2+}/Fe^{3+} ions inducing charge reversal and redispersion of already formed flocs, contributing to soluble residuals which elevate apparent COD (Lukasiewicz *et al.*, 2025). Bell-shaped COD removal patterns have been earlier compared and documented for refinery wastewater and leachate treatment (Aziz & Ramli, 2014), confirming the need for dosage optimization. Color removal efficiency increased with $FeSO_4$ dosage, reaching 96.8% at 1.0g/60mL. It remained above 90% at 1.25g/ml. This improvement is attributed to charged neutralization and sweep coagulation, occurring due to amorphous $Fe(OH)_2$ and $Fe(OH)_3$ precipitates effectively capturing chromophoric and aromatic compounds. (Aziz & Ramli, 2014; Nurul *et al.*, 2021) reported similar high decolorization efficiencies being >90%, in oily and industrial wastewater treated with $FeSO_4$ under acidic conditions. This contemplated performance highlights strong affinity of $FeSO_4$ for visible organic pollutants, promoting its application as a pretreatment step for petroleum wastewater.

The comprehensive trend aligns closely with prior research on Fe based coagulants. Ferrous sulfate effectively removes the turbidity and color in refinery effluents, and similar behavior was observed in systems where Fe^{2+} oxidized in situ to Fe^{3+} (Nurul *et al.*, 2021) achieving around 65% COD reduction and above 90% color removal using $FeSO_4$ in palm oil mill effluent, confirming it applicability across various oily wastewater types. (Matilainen *et al.*, 2010) reviewed further and emphasized that acidic operating range (pH 4 to 5.5) is ideal for $FeSO_4$ coagulation. This balances high removal efficiency with minimal sludge generation. It was also observed in this study that pH reduced from 7.1 (raw) to 4.8 (1 g/60mL). This results from hydrolysis of Fe^{2+}, where proton release accompanies the formation of $Fe(OH)_2$ and $Fe(OH)_3$ precipitation, lowering the alkalinity of the sample (Eq. 1). The optimum pH range observed in this study, also corresponds well to the previously reported studies favorable for iron based coagulation (Matilainen *et al.*, 2010, Knap *et al.*, 2023). The decline in COD removal at 20.8 g/L (1.25 g/60 mL) was statistically significant ($p = 0.008$, Tukey's HSD), confirming a genuine overdosing effect, rather than random variability. Although the optimal $FeSO_4$ dosage (16.7 g/L) appears high as compared to municipal wastewater treatment, it is consistent with reported values for high-strength industrial effluents (COD > 20,000 mg/L). For example, Zueva *et al.* (2020) used $FeSO_4$ dosage up to 10 g/L for refinery wastewater, and Nurul et al, (2021) applied 8 g/L for palm oil mill effluent with initial COD of ≈50,000 mg/L.

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2(s) + 2H^+ \tag{1}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3(s) \tag{2}$$

The most favorable pH range observed (4.5 to 5.5) falls within the acidic range previously identified as appropriate for coagulation with iron salts (Knap *et al.*, 2023).

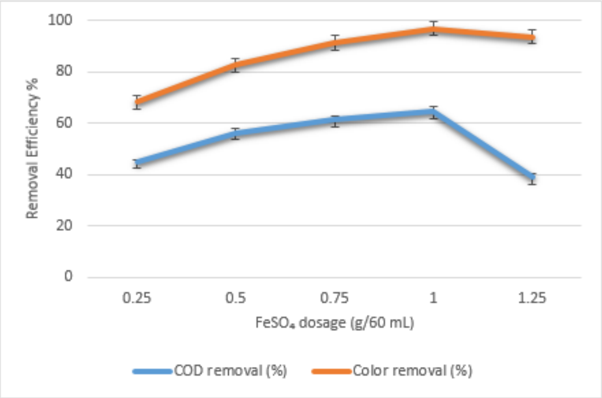

Figure 1. Effect of $FeSO_4$ dosage (g/L $FeSO_4.7H_2O$) on COD and Color removal. Experimental conditions: natural sample pH 7.1 rapid mixing 150 rpm for 5 min, slow mixing 60 rpm for 25 min, settling 30 min, total reaction time 60 min

3.2. *Effect of pH*

Keeping the pH range from 3 to 11, influence of $FeSO_4$ performance was observed, while maintaining the optimum dosage of 1.0g/60mL (**Figure 2**). Under these conditions 64.8% COD removal, 96.8% color removal and a final pH of 4.8 was achieved. This optimal state reflects a balance between sufficient Fe^{2+} availability for hydrolysis and floc formation, whereas, preventing excess Fe^{2+} leading to radical scavenging/secondary pollution. The high color removal efficiency of 96.8% indicates strong coagulation between Fe^{2+} ions and aromatic hydrocarbons, responsible for coloration. COD removal, although remained lower at 64.8%. reason being soluble organic fractions are less responsive to coagulation mechanisms. This pattern agrees with (Cavallini *et al.*, 2015) who noted Fe^{2+} selectively targeting hydrophobic and colloidal petroleum fractions while leaving soluble organics being partially untreated. (Yaghoobian *et al.*, 2022) observed that acidification from pH 7.1 to 4.8 supports Fe^{2+} hydrolysis and H^+ generation being consistent with iron hydrolytic acidification. Maintaining pH between 4 and 5 enhances the solubility of Fe ions and promotes efficient floc formation (Moussa *et al.*, 2017). Conversely by lowering pH beyond this range reduced COD removal to 39%, showing the risk of overdosing.

These results are consistent with prior studies on petroleum and oily wastewater treatment. Giwa *et al.* (2013) reported 62% COD and 95% color removal from refinery wastewater at similar $FeSO_4$ dosages and acidic conditions. (Zueva *et al.*, 2020) also observed 60 to 70 % COD reduction using Fe^{2+} based coagulation, noting their role to be as a precursor for Fenton oxidation. All in all, the findings demonstrate that $FeSO_4$ alone, without auxiliary oxidants such as H_2O_2 or TiO_2, can serve as an effective pretreatment step for petroleum contaminated seawater, particularly for fast color removal and initial pollutant reduction.

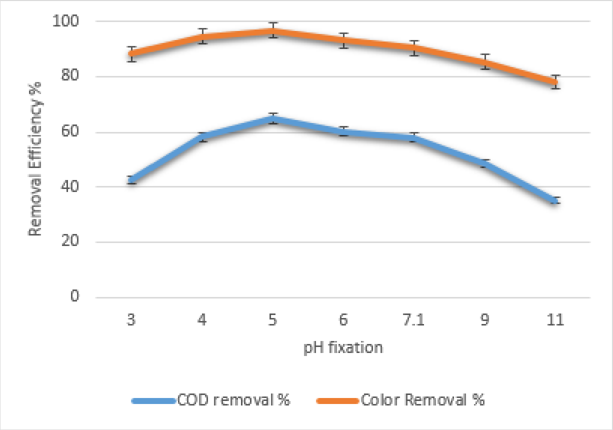

Figure 2. Effect of initial pH on COD and color removal. Experimental conditions: $FeSO_4$ dosage 16.7g/L (1.0g/60mL), mixing as described in Figure 1, reaction time 60 min

3.3. *Effect of Reaction Time*

The time dependent behavior of $FeSO_4$ (16.7 g/L, 1.0 g/60 mL), was analyzed to evaluate COD and color removal as a function treatment duration (**Figure 3**). Experimental results show that COD decreased from 10,900 mg/L at 30 min to 7,900 mg/L at 150 min, corresponding to the removal efficiencies of 54.9 to 67.4%. A faster response was observed for color removal, achieving 92.4% within 30 min, and stabilizing at around 97% at 120 min. The accelerated decolorization suggests that Fe^{2+} quickly destabilizes hydrocarbons, whereas COD represents both particulate and dissolved organics. This requires longer retention to reach equilibrium. After 120 min, COD removal became stable, implying that the system has attained coagulation equilibrium and further spent time did not specifically increase the removal. This trend aligns with work done by (Cavallini *et al.*, 2015) who also observed limited COD reduction after the early flocculation stage, due to the endurance of soluble hydrocarbons. Likely, (Giwa *et al.*, 2013) also reported COD and color removal to be 65% and 95% respectively, for iron based coagulation of refinery wastewater. At the optimum dosage, reduction of pH to about 4.8 likely enhanced flocculation by increasing the solubility and reactivity of Fe presence (Lukasiewicz *et al.*, 2025). Excessive Fe^{2+} however can seek reactive radicals and cause restabilization of floc, as documented by (Oturan *et al.*, 2014) in Fenton related systems. The almost stable COD and color removal after 120min shaking can thus confirm as the optimum contact time for $FeSO_4$ based treatment.

The results validate the earlier studies reporting 60-70% of COD removal with ferrous coagulation at acidic pH (Zueva *et al.*, 2020) and extend them to a high-salinity (≈35 g/L) seawater matrix where ionic strength partially screens electrostatic interactions but still allows effective floc formation.

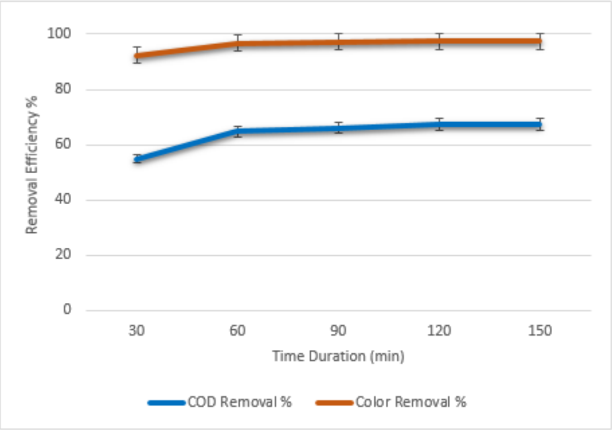

Figure 3: Effect of reaction time on COD and Color removal. Experimental Conditions: FeSO$_4$ dosage 16.7 g/L (1.0g/60mL), mixing as described in Figure 1, initial pH 7.1 reaction time 60 min

3.4. *Statistical Validation*

In order to establish the significance of the experimental results, a triplicate set of the experimental data concerning COD and color removal were analyzed using one-way analysis of variance (ANOVA). The experiment examined the effects of the key variables, which included; FeSO$_4$ dosage, initial pH and reaction time. The above results summarized in **Table 1**, confirm that all the three factors had statistically significant effect on the two response variables ($p < 0.05$). As an example, the F-value of dosage effect on COD removal was 24.6 ($p = 0.0002$) which was much greater than the critical value of 4.07 ($p = 0.0004$). Post-hoc comparisons made using the Tukey HSD test, revealed that the removal of the COD at the highest dosage was statistically significant overdosing effect, not due to chance variation in the experiment. In the same way, the fast color removal time of the first 30 minutes has been found to be significantly different than the plateau time of the first 120 minutes ($p = 0.05$), which will support the discussion of kinetic behavior.

Table 1. Summary of one-way ANOVA results for COD and Color removal

Factor	Response Variable	F-Static	p-value	Significance (p<0.05)
FeSO$_4$ Dosage	COD Removal	24.6	0.0002	Significant
FeSO$_4$ Dosage	Color Removal	18.2	0.0011	Significant
Initial pH	COD Removal	31.5	< 0.0001	Significant
Initial pH	Color Removal	22.8	0.0003	Significant
Reaction Time	COD Removal	15.9	0.0024	Significant
Reaction Time	Color Removal	45.7	< 0.0001	Significant

Degrees of freedom for each factor were 4 (dosage), 3 (pH), and 4 (time). Tukey's post-hoc comparisons showed that COD removal at 16.7 g/L FeSO$_4$ was significantly higher than at 4.2 g/L ($p = 0.001$) and at 20.8 g/L ($p = 0.008$).

3.5. *Sludge production and residual iron*

For practical application, the amount of generated sludge and residual iron in the treated effluent are important. At the optimum dosage (16.7 g/L FeSO$_4$), the settled sludge volume was 8-10 mL per 60 mL of treated wastewater (≈13-17% by volume). The supernatant contained total residual iron of 12-18 mg/L as measured by ICP-OES, which falls within the marine discharge limits, enforced by several Gulf countries (El-Naas *et al.*, 2013). No additional iron removal step would be required before further biological or oxidative treatment.

3.6. *Influence of Salinity on coagulation*

The seawater used in this study had a salinity of approximately 35 g/L. High ionic strength compresses the electrical double layer around oil droplets, reducing the zeta potential and thereby lowering the coagulant demand required for charge neutralization (Zueva *et al.*, 2020). However, excessive salinity also screens the electrostatic bridging necessary for floc growth, which explains why our optimal Fe^{2+} dose (≈3350 mg/L) is higher than typical doses for low-salinity refinery water (≈500-1000 mg/L; Cavallini *et al.*, 2015). The presence of Cl$^-$ ions forming weak FeCl$^+$ complexes, slightly alters the hydrolysis pathway, affecting floc morphology (Stumm & Morgan, 1996). This highlights the need for site specific optimization when treating petroleum contaminated marine waters.

3.7. *Limitations of the current optimization approach*

The study used a one factor at a time (OFAT) experimental design. Being useful for initial screening, OFAT cannot capture interaction effects between variables (e.g. dosage x pH, time x salinity). Future work shall employ response surface methodology (RSM) or central composite design to identify optimal and interaction effects (Tahraoui *et al.*, 2024). Additionally, continuous flow studies are needed to assess long term performance and sludge handling.

3.8. *Mechanistic insights into FeSO$_4$ coagulation in seawater*

The observed performance is explained by several interacting mechanisms, such as the high ionic strength seawater (≈35 g/L) compressing the electrical double layer around oil droplets, reducing the zeta potential, thereby lowering the coagulant demand required for charge neutralization (Zueva *et al.*, 2020). However, excessive salinity also screens the electrostatic bridging necessary for floc growth, which explains why our optimal Fe^{2+} dose (≈3350 mg/L) is higher than typical doses for freshwater systems (≈500-1000 mg/L; Cavallini *et al.*, 2015). The presence of Cl$^-$ ions can work for weak FeCl$^+$ complexes, slightly altering the hydrolysis pathway and possibly affecting floc morphology (Stumm & Morgan, 1996).

Secondly, the rapid color removal (92.4% within 30 min) is attributed to adsorption of aromatic, chromophoric hydrocarbons onto freshly precipitated amorphous $Fe(OH)_2$ and $Fe(OH)_3$. These flocs have high surface area and strong affinity for π-electron rich compounds. In contrast, COD removal is slower because it includes not only the adsorbed aromatic fraction but also soluble aliphatic hydrocarbons and oxygenated intermediates that are less efficiently removed by coagulation alone (Metin & Cifci, 2023).

Thirdly, a partial Fenton-like oxidation may occur even without external H_2O_2. Dissolved oxygen in seawater (≈6-8 mg/L) can slowly oxidize Fe^{2+} to Fe^{3+}, generating superoxide and hydroxyl radicals (Eq. 3). These radicals can attack dissolved organics, contributing to COD reduction beyond mere coagulation. However, the effect is limited because the radical yield from auto- oxidation is low as compared to classical Fenton systems (Ganiyu *et al.*, 2020)

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \quad (3)$$

Finally, the observed pH drop from 7.1 TO 4.8 is caused by proton release during Fe^{2+} hydrolysis (Eq. 1). This acidic condition is favorable for Fe^{2+} solubility and also for maintaining a positive surface charge on flocs, enhancing electrostatic attraction of negatively charged oil droplets (Knap-Baldyga and Zubrowska-Sudol, 2023). The combination of charge neutralization, sweep flocculation, and limited radical oxidation is self-explanatory for the overall removal profile.

4. Conclusion

This study demonstrates that, ferrous sulfate ($FeSO_4$) is an efficient and cost-effective coagulant for the pretreating petroleum-contaminated seawater. The systematic evaluation of $FeSO_4$ dosage, pH, and reaction time reveals that optimal treatment conditions occurred at 16.7g/L $FeSO_4.7H_2O$ (≈3350 mg/L Fe^{2+}), pH 4.8, and 120 min contact time. Under specified conditions, the system achieved 64.8% COD removal and 96.8% color removal, highlighting the strong coagulative and partial oxidative capacity of Fe^{2+} towards petroleum-derived organics. The hydrolysis of Fe^{2+} ions induced acidification facilitates floc formation through charge neutralization and sweep flocculation mechanisms. Whereas, color removal is nearly complete within 30 minutes, indicating rapid destabilization of hydrophobic and aromatic compounds. However, COD reduction progressed more gradually, stabilizing after 120 minutes. This difference underscores the selective affinity of Fe^{2+} for particulate and colloidal petroleum fractions compared to dissolved organics consistent with previous reports. A moderate decrease in COD removal efficiency at higher dosages confirmed that excessive Fe^{2+} may lead to charged reversal or contributes to secondary pollution, emphasizing the importance of dosage optimization. Statistical analysis (ANOVA) validated that the effects of dosage, pH and reaction time were significant ($p < 0.05$).

The main contribution of this work is a systematic and parametric evaluation of $FeSO_4$ for a saline (seawater) petroleum contaminated matrix – a scenario rarely studied despite its relevance to coastal spills. We provide quantitative benchmarks for optimal Fe^{2+} dosage (≈3350 mg/L), pH shift due to hydrolysis in seawater (from 7.1 to 4.8), and kinetic differentiation between rapid color removal (92.4% in 30 min) and slower COD reduction (stabilizing at 120 min). Additionally, we report sludge production (13–17% by volume) and residual iron (12–18 mg/L), which are essential for practical feasibility but often omitted. These findings advance the field by offering a saline-specific reference for pretreatment design. In terms of feasibility, while open-ocean application for large spills remains challenging due to logistics, the method is highly applicable for contained coastal industrial effluents, collected oily water from skimmers, and near-shore spills where containment and mixing are feasible. The overall findings affirm that $FeSO_4$ coagulation effectively removes chromophoric and colloidal pollutants from petroleum wastewater and can serve as a robust pretreatment step prior to advanced oxidation, photocatalysis, or biological treatment. Integrating $FeSO_4$ coagulation within hybrid treatment frameworks could thus enhance overall process efficiency, minimize reagent consumption, and support sustainable treatment strategies for petroleum-contaminated marine and industrial effluents. Future studies should focus on (i) continuous flow pilot trials, (ii) characterization and dewatering of Fe rich sludge; (iii) reusability of the sludge as a coagulant or Fenton catalyst; and (iv) multivariate optimization using RSM to capture interaction effects. The high coagulant dosage used in this study, while justified for high-strength wastewater, underscores the need for pilot-scale jar test validation and life cycle assessment of sludge management before full-scale application. This study is the first to systematically report $FeSO_4$ coagulation kinetics, sludge production and residual iron of petroleum contaminated seawater. This provides a realistic basis for coastal pretreatment applications.

5. Acknowledgement

The authors would like to thank KARABUK University for providing all in support for conducting the research and experimentation for this paper. The authors would also like to thank the International College of Engineering and Management (ICEM) for Internal research grant No. IRC/24–25/002.

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