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ORIGINAL RESEARCH ARTICLE

Assessment of Advanced Treatment Techniques for COD Removal from Industrial Wastewater in Baiji Refinery Using Chemical Coagulation, Ozonation, and UV/O_3 Technology

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ABSTRACT

Chemical Oxygen Demand (COD) is considered one of the most important parameters that indicates the presence of organic pollution in industrial wastewaters. Refinery wastes represent complex heterogeneous, structurally, oily liquid that contains a very high load of organics. This study aims to assess the efficiency of refinery wastewater treatment by three methods, namely coagulation, ozonation, and a UV/O_3 hybrid system, and to determine the optimum operational conditions of each technique at the Baiji oil refinery complex.

The study started by applying a coagulation process using two types of chemicals, namely $Al_2(SO_4)_3$ and $FeCl_3$ at varying pH to evaluate the effect of conditions on COD removal. The second process was ozonation with a range of concentrations and finally the UV/O_3 system for enhancing the advanced oxidation of steel. The standard methods of measurement as approved by the labs of Baiji Refinery and Tikrit University were followed for each procedure. The two-way ANOVA was used to find out the high coefficient factors affecting removal efficiency.

The results demonstrated that chemical coagulation alone gives removal rates of 44–62%. The efficiency increased when the procedure was coupled with ozonation to reach 67–81%. The UV/O_3 going system was the best, with removal efficiencies of 92–97%, which confirms the important role of the •OH hydroxyl radicals in destroying the complex organics. The statistical analysis indicates that the type of process was the most influential factor affecting the removal efficiency and that the coagulant did not have any statistically important effect. It could be concluded that the integrated system Coagulation + O_3 + UV/O_3 is a promising solution to treat high organic load refinery effluents. It is also recommended to optimize UV reactor design and O_3 dosage to ensure a higher efficiency and lower energy consumption. Further studies should be conducted to assess the optimum level of this system and to perform an economic feasibility study to scale them up in Iraqi refineries.

Keywords: COD, oil refinery wastewater, chemical coagulation, flocculation, (AOPs), industrial water treatment.

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1. Introduction

One of the most challenging environmental and industrial tasks is that oil refineries wastewater treatment due to high contents of hydrocarbons, oils, and heavy metals. Refinery effluents are the most complicated types of industrial wastewaters to be controlled and treated. According to Lawan et al [18], petroleum refinery wastewater is particularly challenging due to the presence of emulsified oils, phenols, sulfides, and a high load of non-biodegradable organic pollutants. These characteristics limit the performance of traditional biological and physical-chemical treatments, highlighting the need for integrated and advanced oxidation-based processes [18]. According to recent studies, for the reasons of containing hazardous recalcitrant organic pollutants that are resistant to biodegradation, conventional treatment approaches are usually not efficient. In response, integrated advanced solutions combining physical, chemical, and oxidative processes . [2]

The Chemical Oxygen Demand parameter is considered a critical index for assessing the extent of organic pollution in industrial wastewater samples, whether biodegradable or not. Biochemical and chemical oxygen consumed increases with water contaminants, metabolization, and oxidation rates. Elevated values of Chemical Oxygen Demand are associated with severe environmental issues, as they deplete the degree of dissolved oxygen and aquatic systems. This deviation can result in microbial life endangerment and ecological imbalance. It has been established that typical advanced oxidation processes are required to generate potent reactive species, for instance, Rafieyan et al [3] demonstrated that catalytic ozonation processes (e.g., O_3/H_2O_2 or $O_3/S_2O_8^{2-}$) achieve significant synergistic effects in degrading refractory organic compounds and reducing COD, particularly in complex effluents like those from gas refineries [3]. with an exemplar being hydroxyl radicals, to disintegrate the highly stable organic bonds that are not affected by regular treatment dyes [4].

Laboratory examinations confirm that the COD content in the Baiji oil refinery effluent is relatively large, including 823 mg/L of untreated refinery effluent. The sample is accompanied by significant levels of oils, chlorides, and heavy metals. Accordingly, that designates a highly multistage, precisely designed treatment system is required. It is relevant to point out that previous studies state that the wastewater of petroleum refineries always requires synergy of techniques, coagulation, ozonation, and UV processing, to ensure fairly safe and efficient pollutant removal. That being said, the substantial lack of literature relates to integrated systems combining chemical coagulation and ozonation and UV-based advanced oxidation [5].

Previous research has emphasized the effectiveness of hybrid systems combining photocatalysis and ozonation. Tetteh et al [6] compared TiO_2 and zeolite-based photocatalysts for COD and sulfate removal from refinery wastewater and found that optimized UV-based AOPs can achieve over 90% efficiency under controlled operating conditions [6]. These findings support the potential of integrated systems for enhanced pollutant degradation.

There is very little information on the synergies of those three methods in equal spheres working together, and most studies have neglected the capabilities of Coagulation–O_3–UV systems and have focused on one treatment method. Therefore, this study aims to evaluate the effectiveness of three advanced treatments techniques, chemical coagulation, ozonation, and UV irradiation techniques, when implemented alone and together for organic contaminant removal from industrial Baiji refinery wastewater. These objectives will together help understand the optimum operating conditions for the three techniques and the interactive mechanisms between them.

2. Materials and Methods

This study employed a comprehensive experimental methodology to evaluate the efficiency of three treatment technologies in removing the chemical oxygen demand (COD) from the industrial wastewater of the Baiji Refinery in Salah al-Din Governorate. Samples were collected from a single source to ensure accurate representation of the characteristics of the oily wastewater. They were then stored in sterile containers and transported directly to the Water Testing Laboratory at the College of Engineering, Tikrit University, for the required analyses. The initial properties of the sample were measured before any treatment, revealing an initial COD concentration of 823 mg/L, reflecting a high level of organic pollution that necessitates the application of a multi-stage treatment system. The materials used in the study included two main coagulants in the chemical coagulation stage: aluminum sulfate ($Al_2(SO_4)_3$ and ferric chloride ($FeCl_3$). An ozone generator equipped with an oxygen cylinder and an ultraviolet (UV) radiation system were also used, which were subsequently incorporated into advanced oxidation systems. All measurements were performed according to standard procedures at the Baiji Refinery and Tikrit University laboratories to ensure the reliability of the results.

Chemical coagulation was carried out using different doses of Alum and $FeCl_3$ to determine the optimal operating conditions for organic matter removal, adjusting the pH value according to the nature of each coagulant. Six doses of each coagulant were used at concentrations of 30, 50, 80, 110, 140, and 170 ppm to evaluate the effect of increasing the dose on COD removal efficiency and to determine the optimal dose of both aluminum sulfate and ferric chloride. The samples were mixed at specific mixing speeds to ensure the coagulant reacts with the pollutants, followed by a precipitation stage and collection of the clear samples for COD measurement.

To activate advanced oxidation processes, UV/O_3 technology was applied, which relies on the synergistic reaction between ozone and ultraviolet radiation to generate hydroxyl radicals (•OH) that are highly effective in breaking down complex organic compounds. This stage involved exposing the coagulated water to constant doses of ozone while the ultraviolet (UV) irradiation system was in operation, with COD changes monitored to assess system efficiency.

The chemical oxygen demand (COD) of all samples at different treatment stages was measured using the Closed Reflux Colorimetric (5220D) method, as approved by the APHA, AWWA, and WPCF (1995) manual. This technique involves the oxidation of organic compounds by dichromates in a heated acidic medium within closed tubes, followed by spectral absorption measurements of the resulting solution to accurately determine the COD concentration. This method is ideal for analyzing oily wastewater due to its sensitivity and ability to handle the complex composition of such water. A two-way ANOVA statistical analysis was performed to determine the effect of both the coagulant type and the treatment method on COD removal efficiency. The results showed that the treatment method was the most influential factor, while the effect of the coagulant type was not significant, reflecting the role of advanced treatments compared to the coagulation stage alone.

3. Results

3.1. Effect of coagulation on COD removal efficiency

3.1.1. Effect of pH Value

The removal efficiency of organic matter, measured by Chemical Oxygen Demand had been assessed at various pH values utilizing two coagulants: Aluminum sulfate (Al2 S O 4)3) and ferric chloride (FeCl3), both at a fixed variable of 1mL/L. The corresponding averages of removal efficiency using Al2 (SO 4)3 and FeCl3 were approximately equal with the mean being 49.34 ± 0.87% with FeCl3 the mean efficiency was 49.67 ± 4.22%. Descriptive analysis showed that removal efficiency was extremely variable in the case of FeCl3 with the range recorded as 11.95%. with the range of removal efficiency in the utilization of $Al_2 (SO_4)_3$ being 2.51% Thereby, suggesting that for the purpose of the pH spectrum, aluminum sulfate has to behave more consistently and to be more predictable for the situation. A similar observation was made by Odhaib et al [7] in a study on textile effluents, where both $FeCl_3$ and Alum showed optimal COD removal at higher pH values (around 11), although $FeCl_3$ exhibited more performance fluctuation depending on the wastewater matrix. This supports the idea that coagulant behavior across pH ranges can differ significantly based on pollutant characteristics [7] Finally, Two-way ANOVA analysis showed that there is effect for both pH level as the P value is less than 0.0001 and the interaction between pH and coagulants with the P value being less than 0.0001 However, the use of a coagulant is not statically important, and these outcomes are provided by the situation.

Based on the experimental results presented in Figure 1, one can see that with the increase in the pH value, the removal efficiency of COD increased from 4 to 7. The removal peak for both coagulants was observed at pH = 7, and after that, a sharp drop can be recognized for the values below 8. This pattern can be explained by taking into account the changes in hydroxide species, formed during the coagulation. In near neutral condition:

(pH 6–7) bivalent hydroxides: Al $(OH)_2^+$ and $Fe(OH)_2^+$ are formed. They are highly effective in adsorption of the pollutants and neutralization of colloidal charges, which leads to better floc formation. In an acidic condition (pH= 8), less reactive precipitates are formed: $Al(OH)_3(s)$ and $Fe(OH)_3(s)$ and they not as effective in coagulation.

It can be concluded that both coagulants were similar in their removal capabilities, regarding COD, however, $Al_2(SO_4)_3$ was more consistent, while $FeCl_3$ presented a greater fluctuation especially while the solution was in alkaline conditions. It can be presumed that in the higher pH level there are formed less reactive oxidized species or ineffective precipitate. Therefore, the transmission of the optimal settings for coagulation regarding the pH of the solution: pH = 7 for $Al_2(SO_4)_3$ and pH = 5 for $FeCl_3$. This is where the highest COD removal efficiencies were observed. Comparable trends were noted by Erkan (2019), who found that ceramic industry wastewater responded best to alum at pH 5, achieving over 95% COD removal. This highlights the role of effluent type in determining optimal pH for coagulation and confirms that acidic to neutral pH may be more effective in systems with high inorganic content [8]. The results can be corroborated with the opinion that coagulation is largely dependent on the type of the coagulant but one must have a profound knowledge of underlying chemical reactions.

The results closely mirror those presented by Monira & Pramanik [9] that alum effectively optimized coagulation efficiency to a noticeable extent by employing electrostatic charge neutralization and efficient floc formation at fairly neutral pH, with pH 6–7 being especially effective. Shewa & Dagnew[10] reiterated this finding by noting that $FeCl_3$ operates at maximum efficiency as a coagulant, achieving the 64% total COD removal at pH 5. The results are considerably different from Tırınk [11] who noted the 99.6% removal of some pollutants at pH of 3. The disparity can be traced back to the fact that the wastewater of different kinds contains various pollutants. In the case of the refinery wastewater, the pollutants are more complex organic compounds and hydroxides forming efficient flocs in less acidic conditions. As such, it is important to remember that optimal coagulation conditions are usually highly specific and should not be generalized. This finding is echoed in research by Guvenc & Guven[12], where coagulation efficiency in food industry wastewater was also strongly dependent on pH. Both $Al_2(SO_4)_3$ and $FeCl_3$ showed significant variability in COD removal at different pH levels, further emphasizing that optimization must be matrix-specific[12].

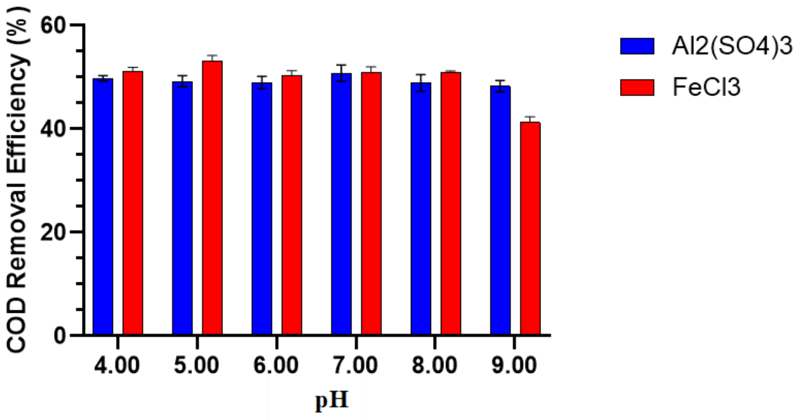

Figure 1. Effect of pH and coagulant type on COD removal efficiency

(Bars represent mean ± standard deviation of three replicates per treatment)

3.1.2. Effect of Coagulant Concentration

The role of aluminium sulphate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$) were evaluated in terms of their effect on organic matter removal in terms of COD as a function of coagulant dosage under previously determined optimal pH conditions. From the descriptive analysis, the average of COD removal efficiency with alum ($Al_2(SO_4)_3$) was slightly higher than with $FeCl_3$ [52.27 ± 3.02% vs. 50.17 ± 4.36%]. In contrast, $FeCl_3$, had a mean with a high variability about the mean, (range = 11.95%) while alum (range= 8.17%) showed more consistency about its mean indicating that $FeCl_3$ does not perform the same at every dosage. These findings are in line with Odhaib et al [7], who showed that increasing $FeCl_3$ dosage from 10 to 30 mg/L in textile effluent improved COD removal up to 46%, but beyond that, no significant gains were observed. Alum exhibited more predictable behavior, with optimal performance at 30 mg/L. This suggests that overdosing can lead to diminishing returns, especially with Fe-based coagulants [7].

Two-way ANOVA results showed that the dosage factor (P = 0.0477) and the interaction between the dosage and coagulant type (P = 0.0113) had significant effects on COD removal efficiency. Conversely, the type of coagulant alone showed no significant effect (P = 0.0939). This implies that the specific organic contaminants in the wastewater matrix determine the coagulant action on the coagulation and flocculation system response.

As can be seen in Figure 2, removal efficiency increased with dosage up to 110 ppm for $Al_2(SO_4)_3$ and 50 ppm for $FeCl_3$. Except for these aspects, decreased efficiency was detected in the higher dose ranges (140–170 ppm), showing that the maximum reducing dose had been exceeded. This phenomenon of "charge reversal" due to overdosage has been quantitatively demonstrated by Abdollahzadeh[13], where increasing $FeCl_3$ from 1000 mg/L to 3000 mg/L initially boosted COD removal to 80%, but caused undesirable pH drops and elevated TDS. This highlights the importance of optimizing coagulant concentration not only for efficiency but also for effluent quality[13]. This reduction is typically ascribed to charge reversal as too many positive charges cause re-stabilisation of colloidal particles, preventing aggregation and sedimentation and subsequently lowing the flocculation efficiency.

Our findings coincide with the findings of Shewa & Dagnew[10] found that 64% TCOD was removed from complex organic compound wastewater at the optimal dosage of $FeCl_3$ (0.5 mM). Higher than this ideal level caused medium saturation and the development of nonreactive sediments, which in view resulted in low performance. Similarly, Briseño-Peña et al. Paris et al found in their research on pharmaceutical industrial wastewater that overdosing of oxidants or coagulants reduced the removal efficiency due to the re-stabilization of colloidal particles which is the similar re-stabilization phenomenon we have been observed in our high-dosage experiments.

In the case of alum revealed that a higher coagulant concentration improved COD removal efficiency above 96%, but after a certain point, it resulted in surface saturation that resulted in a decrease in efficiency. However, in textile wastewater, Tırınk[11] observed the best dye removal with the addition of $FeCl_3$ at 400 mg/L, which is distinct from the results of the current study. The reason for the difference is that textile and petroleum wastewater are quite different in nature, and less dosage is necessary for petroleum wastewater due to the higher size, polarity, and concentration of the pollutants.

Additionally, Erkan [8] applied statistical optimization (RSM) in ceramic wastewater and found that alum dosage of 3.3 g/L at pH 5 removed over 95% COD, but higher dosages caused sludge handling issues and no further removal benefits. This reinforces the principle of identifying a precise dose-response curve to avoid overdosing and resource waste [8]. Such differences highlight the necessity for disclosing optimal coagulant dose values, not merely in terms of chemical nature of the coagulants but also based on characteristics of the pollutants in the effluent to be treated.

This study suggests the following from a practical perspective:

- $Al_2(SO_4)_3$ at pH =7 (110 ppm)
- $FeCl_3$ at pH =5 (50 ppm)

as the best coagulation conditions to treat petroleum refinery wastewater of high organic loads.

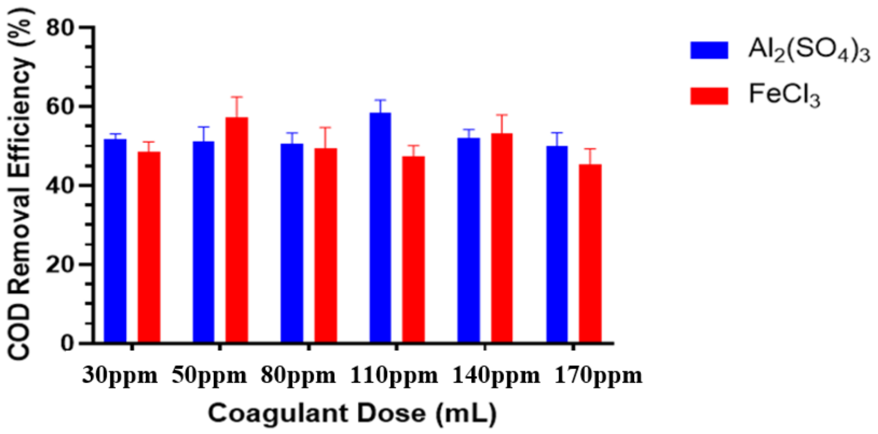

Figure 2. Effect of coagulant dosage on COD removal efficiency

(Bars represent the mean ± standard deviation of three replicates for each dosage).

3.2. Effect of ozone treatment after coagulation

The application of ozone on chemically coagulated wastewater was studied in order to increase the removal of organic pollutants, based on COD parameters. In this phase, Aluminum sulfate ($Al_2(SO_4)_3$) and Ferric chloride ($FeCl_3$) were applied as coagulants. As indicated in the results, the ozonation step was effective, improving the COD removal by an average of 64.58 ± 4.25% for $Al_2(SO_4)_3$ and 68.00 ± 10.51% for $FeCl_3$.

Statistical analysis using two-way ANOVA indicated that all the three factors, i.e., concentration of ozone, type of coagulant and their interaction produced a significant effect on the COD removal efficiencies ($P < 0.05$). Our experimental data showed that removal efficiency (71–81%) increased sharply when the ozone dose was increased from 600 to 1200 mg/L. Increasing the dose again to 1800 mg/L resulted in a significant drop in performance (57–62%). Similar trends in optimal ozone dose have been reported in dairy industry wastewater treatment. Güneş [14] showed that ozonation after coagulation-flocculation significantly enhanced COD removal up to 65%, with peak efficiency at around 1200 mg/L ozone. Beyond this dose, treatment efficiency plateaued or declined, likely due to saturation effects and resistant intermediate formation [14]. This change indicates that 1200 mg/L is the ideal level of ozone, maximizing the volume of •OH produced as a signal byproduct that causes only partial oxidation.

It is possible that at 1800 mg/L the efficiency began to decline due to the accumulation of intermediate oxidation products that can be more difficult to degrade. Another possibility of limiting oxidation is fragmentation of complex organic molecules into smaller compounds which are less reactive to ozone or hydroxyl radicals. However, $FeCl_3$ had a greater average removal efficiency than $Al_2(SO_4)_3$ ($P = 0.0168$) when comparing coagulants. The better performance is probably the result of the catalytic action of the ferrous ions (Fe^{2+}) released during the coagulation, which is favorable for the Fenton-like reactions and thus accelerates the generation of hydroxyl radicals and oxidation efficiency. This catalytically driven enhancement is corroborated by Barrera-Diaz & González-Rivas [15], who demonstrated that the integration of Fe-based electrocoagulation and ozonation led to an 88% COD removal within just 12 minutes in mixed industrial effluent, underscoring the efficiency of Fe ions in generating hydroxyl radicals under oxidative conditions [15].

These results are in accordance with the ones reported by Shewa & Dagnew[10] that the pairing of $FeCl_3$ coagulation/and after treatments such as biological filtration resulted in higher organic matter elimination and carbon recovery, with 80% TCOD reduction in highly loaded industrial wastewaters (2025). In a similar vein, Monira & Pramanik [9] confirmed better removal of fats and oils with the introduction of oxidizing agents such as ozonised and dissolved air flotation after coagulation, further suggesting an environment close to actual refinery effluents.

On the contrary, the results are different from those of [16], who recorded a decreasing trend in COD removal efficiency as the oxidant dose increased for food industry wastewater. This was explained by the presence of stable intermediate oxidation product buildup, consistent with the trend noted in this study at 1800 mg/L ozone. These byproducts are often more persistent due to their low biodegradability and oxidizability, causing a decrease in overall treatment efficiency.

In contrast, Mehdipoor et al [17] observed lower COD reductions (~34–48%) in rubber industry wastewater after ozonation post-coagulation, indicating that ozone effectiveness varies greatly with effluent type and organic complexity. This supports the current study's findings that petrochemical effluents respond more favorably to controlled oxidative treatment [17]. The findings of this comparative study highlight the catalytically advantageous nature of $FeCl_3$ over that of $Al_2(SO_4)_3$ in initiating advanced oxidation process via Fenton-type mechanisms. Results of the experiments conclusively show that accurately controlling the concentration of ozone after coagulation is a key factor contributing to COD removal from petrochemical industrial effluent.

As coming out the statistical and chemical interpretation, the next conclusions were reached:

- The best COD removal occurs at an ozone concentration of 1200 mg/L after coagulation.
- This stage was the only point where $FeCl_3$ had an advantage over $Al_2(SO_4)_3$, most likely caused by the ability of $FeCl_3$ to promote further catalytic reactions.

An upper limit of ozone above which no further improvement in treatment is feasible, and where treatment efficiency may actually decline due to the production of refractory oxidation byproducts is observed as shown in figure 3.

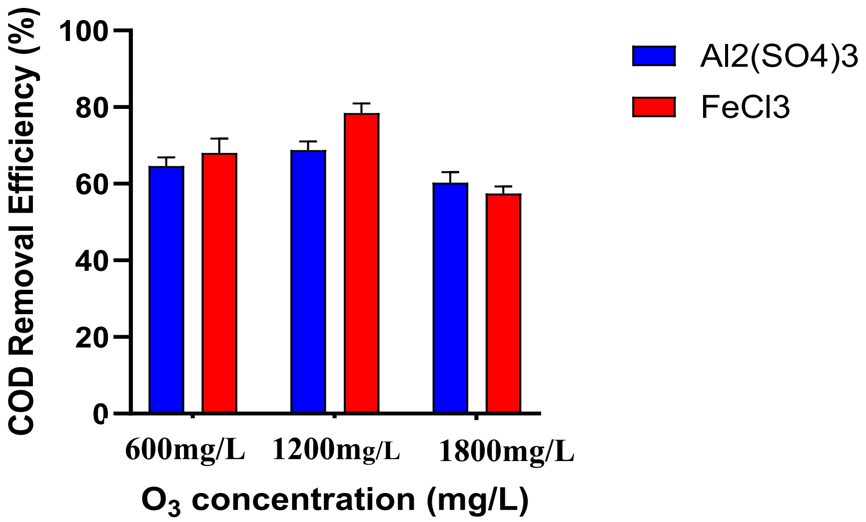

Figure 3. Effect of post-coagulation ozone concentration on COD removal efficiency

(Bars represent the mean ± standard deviation of three replicates for each concentration)

3.3. The combined effect of ozone and ultraviolet radiation after coagulation

Based on the experimental results, a significant enhancement in the removal of organic pollutants was found with chemical coagulation followed by ozone and ultraviolet radiation (UV/O_3). All conditions exhibited average COD removal efficiencies of higher than 92% [92.75 ± 0.98% using $Al_2(SO_4)_3$ based coagulant, and

93.43 ± 4.11% using $FeCl_3$ based ones], reflecting a remarkable performance of both coagulants with negligible difference between them.

Two-way factorial ANOVA analysis indicated a statistically significant interaction of number of UV lamps and coagulant type ($P = 0.029$) (Table 6). When taken individually, neither factor demonstrated statistically significant influence ($P > 0.05$), indicating that UV/O_3 system performance is likely controlled interactively by both coagulant type and UV dose and not by either factor separately.

The significant enhancement of COD removal achieved while simultaneous CLR irradiation after ozonation can be mainly ascribed to the extremely high production of hydroxyl radical (•OH). The formation of these radicals is through photolysis of ozone $\lambda = 254$ nm, leading to one of the strongest oxidant species in aqueous systems. They can degrade huge organic molecules into smaller biodegradable, water soluble molecules. Additionally, residual ferric ions (Fe^{3+}/Fe^{2+}) present in the solution from the previous step of coagulation probably favored this step through photo-Fenton-like reactions that might explain the slightly higher removal capacity obtained with $FeCl_3$ than with $Al_2(SO_4)_3$ at this stage.

The average efficiency with two UV lamps was about 2% higher than with one lamp (not statistically significant $P = 0.1414$). This means that the system reached a limit on radiative saturation, so that improving light emission after a certain threshold will not improve oxidation efficiency, presumably because of a limitation of ozone or oxidizable organic compounds.

Therefore, it can be concluded that:

- The UV/O_3 process after coagulation is the most effective among all treatment methods used.
- Removal efficiency exceeded 93% using either coagulant.
- Increasing the number of lamps (UV intensity) does not significantly improve efficiency, meaning that a single lamp (10.62 mW/cm^2) may suffice to reduce energy consumption while maintaining high efficiency. Supporting these findings, Hansson et al. (2015) observed that combining UV with ozone treatment at basic pH achieved 93% COD removal from highly recalcitrant wood-based industrial effluents. The study confirmed that the synergistic O_3/UV process significantly enhanced biodegradability and oxidation capacity, particularly when ozone photolysis was optimized to generate •OH radicals efficiently [19].

These results are closely in accordance with present industrial wastewater treatment research trends that strongly recommending high removal efficiency of the UV/O_3-based advance oxidation processes in terms of persistent organic pollutants. The study demonstrated a COD removal higher than 92% with both $FeCl_3$ and $Al_2(SO_4)_3$ which is higher than those achieved in many recent studies with comparable or alternative methods.

However, the primary oxidative species are likely to be hydroxyl radicals, which lead to ~90% COD removal in industrial wastewater using a combined H_2O_2–O_3 system. Likewise, hybrid ozone-based systems have resulted in substantial improvements in biodegradability and COD elimination in wastewaters from food and textile industries..

The >93% removal in this work is likely due to a number of interconnected factors, relative to others' processes:

- Ultraviolet light and ozone with chemical coagulation pre-treatment (removing turbidity and part of initial organic load which made UV/O_3 stage more efficient, ½)
- A previously unexplored significant synergistic interaction ($p = 0.034$) between coagulant type and UV intensity.

- Necessarily optimized the operational parameters such as ozone dose, contact time, and pH to generate the highest possible amount of hydroxyl radicals (•OH), the main species responsible for degrading refractory organics by breaking chemical bonds between the complex organics.

In contrast, filled with harsh actinobacteria and subjected to high stress conditions that demand alterations like codon usage optimization, Juret et al [20] find that UV/H_2O_2 systems can also result in 34% COD removal or less when treating wastewaters that contain particulary complex organics [20], demonstrating the necessity of choosing an oxidation strategy optimally suited for a given contamination profile as shown in figure 4.

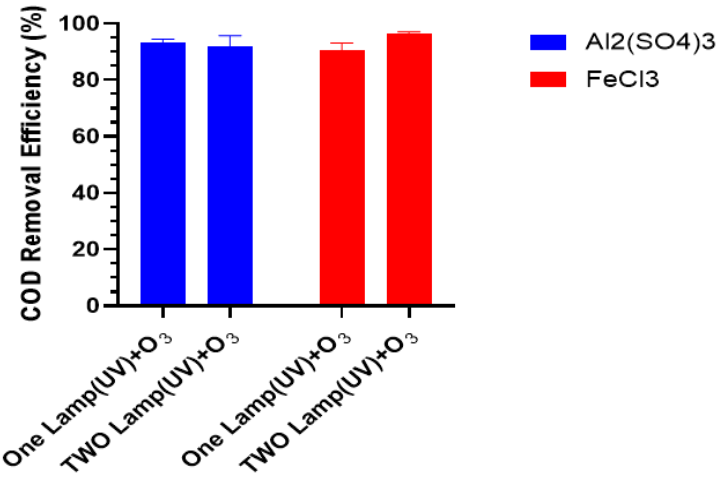

Figure 4. Effect of combining UV radiation with ozone on COD removal efficiency

(Bars represent the mean ± standard deviation of three replicates per treatment)

3.4. General Comparison of Treatment Methods and Overall Statistical Performance Evaluation of COD

Results of Two-way Anova analysis indicates that type of treatment method has a highly significant effect on COD removal efficiency ($P < 0.0001$). 03 most terms of total variance is contributed by type of treatment method. The kind of coagulant did not have a significant influence ($P = 0.6117$); therefore, aluminum sulfate and ferric chloride produced comparable final COD removal. Nonetheless, a statistically significant interaction was detected between coagulant type and treatment ($P < 0.0001$), indicating that each coagulant showed slight variations depending on the complementary treatment applied (ozonation and/or UV).

As seen in figure 5, the treatment stages showed a better removal efficiency of COD.

- When only coagulation was performed, the removal efficiency (44-62%) was low, as coagulants predominantly act on larger, particulate organic molecules, leaving behind the smaller, dissolved organic ones.

- Coagulation and ozonation improve the efficiency to 67–81%.

This is because partial oxidation of dissolved organic matter improve settleability and removal efficiency.

- The combination of coagulation, ozonation, and UV treatment resulted in a marked improvement with more than 92–97% removal of COD. This was a consequence of the formation of high quantities of reactive hydroxyl radicals, whose action would completely oxidise the remaining complex organics.

A comparative study by Hansson et al [19] confirmed that combining ozone with UV light achieved up to 93% COD removal from highly resistant wood-based industrial wastewater, significantly outperforming ozone-only treatments. The improvement was attributed to the synergy of advanced oxidation and photolysis in producing hydroxyl radicals under basic pH conditions [19].

Based on the outcomes, UV/O_3 in conjunction with coagulation would effectively eliminate organic materials almost completely. Also, the difference between the two coagulants is not significant. Therefore, either of them can be effectively used in the first treatment step.

Using the dual-stage approach of COAGULATION + UV/O3 will be the most efficient configuration from an operation point of view using moderate intensity conditions with a removal of over 93% of COD and also meeting the discharge standards for the environment.

The current findings corroborate the study findings of Li et al [1] which also showed that the combination of coagulation and advanced oxidation has strong potential as one of the best treatment options for highly complex industrial wastewater. This conclusion is supported by Lafi et al [21], who demonstrated that combining coagulation with advanced oxidation (O_3/UV or H_2O_2/UV) resulted in up to 95% COD removal from olive mill wastewater, surpassing the performance of each method applied alone. The integration exploited both particle removal and radical oxidation, achieving superior overall efficiency [21].

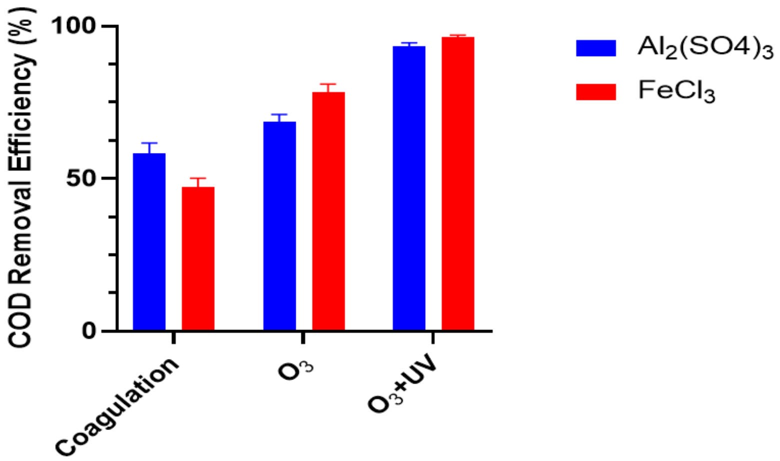

Figure 5. Overall comparison of the effect of treatment methods on COD removal efficiency (bars represent the mean ± standard deviation of three replicates for each treatment).

4. Conclusion

1. The use of chemical coagulation, whether with aluminum sulfate ($Al_2(SO_4)_3$) or ferric chloride ($FeCl_3$), proved reasonably effective in lowering the initial organic load. This step serves as a reliable pre-treatment that helps boost the efficiency of later stages in the wastewater treatment process.
2. Introducing ozonation right after coagulation led to a noticeable improvement in COD removal. This emphasizes ozone's value as a mid-stage treatment, capable of breaking down dissolved organic substances and making them more amenable to further degradation.
3. Among all the treatment setups tested, the combined UV/O_3 process delivered the most impressive results—achieving over 92% removal efficiency. This clearly points to the strength of hydroxyl radicals (•OH) in attacking and decomposing complex organic molecules, reinforcing the effectiveness of this advanced oxidation method compared to other approaches.
4. Based on the Two-way ANOVA results, the choice of treatment method had a statistically significant impact on COD removal rates, while the type of coagulant used did not. This suggests some flexibility in coagulant selection, provided that operational conditions are properly managed.

5. Taken together, the results indicate that a multi-step approach—blending coagulation, ozonation, and UV treatment—offers a practical and highly efficient way to handle complex refinery wastewater. This method not only performs well at the lab scale but also shows promise for broader industrial use, especially with further refinement aimed at reducing energy use and lowering operational costs.

Conflict of interest

The authors declare no conflict of interest

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