Removal of Heavy Metals from Industrial (Petroleum-Based) Wastewater Using Tertiary Treatment by Coagulation, Ozonation, and Ultraviolet (UV) Irradiation

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Abstract

Industrial petroleum wastewater poses significant environmental challenges due to its high concentrations of toxic heavy metals, including chromium (Cr) and cobalt (Co). These metals are non-biodegradable, bioaccumulative, and hazardous to both ecosystems and human health. This study aimed to evaluate the effectiveness of an integrated tertiary treatment process—comprising chemical coagulation, ozonation, and ultraviolet (UV) irradiation—for the removal of heavy metals from real refinery wastewater, with a focus on optimizing operational conditions. Wastewater samples were collected from the Baiji Oil Refinery in Iraq. The treatment process involved three sequential stages: (1) coagulation using either ferric chloride ($FeCl_3$) or aluminum sulfate ($Al_2(SO_4)_3$), (2) ozonation with varying doses (600–1800 mg/L), and (3) combined UV/O_3 advanced oxidation. Parameters such as pH, coagulant dose, ozone concentration, and UV intensity were systematically varied. The concentrations of heavy metals were analyzed using atomic absorption spectroscopy, and the data were statistically analyzed using two-way ANOVA. The results demonstrated that the optimal pH for coagulation was in the neutral-to-slightly alkaline range (6–8). $FeCl_3$ consistently outperformed $Al_2(SO_4)_3$ in removing Cr and Co across different conditions. An ozone dose of 1200 mg/L yielded the highest removal efficiency without inducing metal re-solubilization. The combined UV/O_3 treatment significantly enhanced removal, reducing Cr and Co concentrations to below regulatory discharge limits. The best chromium removal was achieved using $Al_2(SO_4)_3$ under high UV intensity (0.001 ppm), while optimal cobalt removal occurred with $FeCl_3$ under similar UV conditions (0.01 ppm). The integrated treatment system proved highly effective in removing Cr and Co from petroleum-based wastewater. Optimizing pH, coagulant dose, ozone levels, and UV intensity is crucial for maximizing removal efficiency. The findings support the potential application of this tertiary treatment approach as a scalable, eco-friendly solution for industrial wastewater remediation.

Keywords: Heavy metals, Industrial wastewater, Coagulation, Ozonation, UV irradiation.

Introduction

Industrial wastewater represents one of the most critical environmental challenges in the modern era due to its complex composition of organic and inorganic pollutants. Among these, heavy metals stand out for their high toxicity, persistence, and bioaccumulative potential in living organisms. Elements such as lead chromium (Cr) and cobalt (Co) are particularly hazardous due to their adverse effects on human health and aquatic life, even at trace concentrations [9]. These metals typically exist in dissolved or colloidal forms in industrial effluents, making them difficult to remove through conventional treatment techniques.

In refinery wastewater, heavy metals originate from various sources, including raw materials,

added chemicals, equipment corrosion, and processing residues. Analytical studies have shown that refinery effluents often contain heavy metals at concentrations ranging from 10 to 100 µg/L, necessitating the use of specialized, highly effective treatment technologies [10]. Additionally, such wastewater is characterized by a low biodegradability index (BOD_5 /COD < 0.2), which severely limits the effectiveness of biological treatment systems [1].

While several methods are available for treating heavy metals—such as chemical precipitation, adsorption, and membrane filtration—their efficiency often falls short due to the complexity of the wastewater matrix. As a result, there has been a growing interest in integrated or hybrid advanced treatment systems that combine multiple technologies to enhance overall removal efficiency [8]. Among these, a triple-treatment approach—involving chemical coagulation, ozonation, and ultraviolet (UV) radiation—has emerged as a promising solution for the simultaneous removal of heavy metals and a broad spectrum of organic pollutants [4].

Coagulation involves adding chemical coagulants, such as ferric chloride or aluminum sulfate, to destabilize and remove colloidal particles and associated metals. Ozonation, on the other hand, targets the oxidation of complex organic structures, while UV radiation enhances the production of hydroxyl radicals and promotes oxidative reactions, especially when combined with ozone [2]. Studies have shown that the sequence of treatment processes, ozone dosage, and pH levels play a significant role in improving removal efficiency, particularly in highly polluted environments such as Baiji Refinery [12].

Although many studies have examined these treatment techniques individually, there remains a lack of integrated research evaluating the performance of their combined use under semi-industrial conditions, especially for heavy metal removal from petroleum refinery wastewater. Furthermore, the influence of operational variables such as pH, coagulant dosage, and UV exposure time in a combined treatment framework requires systematic investigation and optimization [6].

Accordingly, this study aims to assess the efficiency of an integrated coagulation–ozone–UV treatment system in removing four key heavy metals—Cr, Co, Ni, and Pb—from real refinery wastewater. It also seeks to determine the optimal operating conditions and evaluate the effect of process sequencing on removal performance, ultimately providing a scalable and efficient treatment model for industrial applications in similar contexts [9].

Material and Methods

1. Wastewater Sample Collection

The industrial wastewater used in this study was obtained from Baiji Oil Refinery, located in Salah Al-Din Governorate, Iraq. The samples were collected from the effluent of the treatment units before discharge, representing real refinery wastewater with high organic and inorganic pollutant loads, particularly heavy metals. The samples were stored in clean polyethylene containers and preserved at 4°C to prevent chemical and biological changes before testing.

2. Chemicals and Reagents

The main chemicals used for the coagulation process were:

- Ferric chloride ($FeCl_3$)
- Aluminum sulfate ($Al_2 (SO_4)_3$)

All chemicals were of analytical grade. For COD analysis, standard digestion solutions were used, and all glassware was thoroughly cleaned and rinsed with deionized water before each use.

3. Instrumentation

- The experimental work employed the following instruments and devices:
- Jar test apparatus for coagulation experiments
- Ozone generator to produce O_3 at controlled flow rates
- UV lamps (254 nm) for photolysis and advanced oxidation
- Atomic Absorption Spectrophotometer (AAS) for heavy metal concentration measurement (Cr, Co)
- COD Reactor and Colorimeter (DR/870) for COD analysis
- pH meter for pH adjustment and monitoring
- Infrared Analyzer for oil and grease measurement (Infra CAL2)
- Conductivity meter for TDS analysis

4. Experimental Procedure

4.1 Coagulation Process

Coagulation experiments were performed using a jar test apparatus, where the coagulant ($FeCl_3$ or $Al_2(SO_4)_3$) was added at various dosages (ranging from 20 to 100 mg/L) to the wastewater samples. The pH was adjusted to specific values (4, 6, 8, and 10) using HCl or NaOH. The rapid mixing phase lasted for 1 minute at 120 rpm, followed by slow mixing for 20 minutes at 30 rpm. The samples were then allowed to settle for 30 minutes before being analyzed for residual heavy metals and turbidity.

4.2 Ozonation Process

After coagulation, the supernatant was ozonated. Ozone gas was introduced into the samples using porous diffusers, and the contact time ranged from 10 to 30 minutes. The ozone dosage was controlled by the generator and measured indirectly by changes in pollutant concentrations.

4.3 UV/O_3 Combined Treatment

In the third stage, the samples previously treated with coagulation and ozonation were

exposed to UV radiation in a transparent glass chamber fitted with UV lamps. This stage lasted 20–30 minutes depending on the experimental setup. The combined effect of UV and ozone was expected to enhance the formation of hydroxyl radicals ($•OH$), further oxidizing residual pollutants including heavy metals.

5. Analytical Methods

- Heavy metals (Cr, Co) were measured using Atomic Absorption Spectroscopy (AAS) in accordance with standard methods.
- Chemical Oxygen Demand (COD) was analyzed by the closed reflux colorimetric method.
- Turbidity was measured using a turbidity meter.
- All tests were repeated three times to ensure reproducibility, and average values were reported.

Results and Discussion

1- Effect of pH on Chromium (Cr) Concentration after Coagulation Treatment

Figure 1 illustrates the relationship between pH values and the removal efficiency of chromium from industrial wastewater using two different coagulants: aluminum sulfate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$). The experimental results clearly demonstrate that chromium removal efficiency varies significantly with changes in pH, highlighting the critical influence of pH on coagulation behavior and chromium precipitation.

The data revealed that the lowest residual chromium concentrations were observed at pH 6 and 7, where concentrations dropped to 3.2 ppm with $FeCl_3$ and 2.8 ppm with $Al_2(SO_4)_3$, indicating effective removal under near-neutral conditions. In contrast, under acidic conditions (pH = 4), the chromium concentrations were notably higher—4.7 ppm with $Al_2(SO_4)_3$ and 4.6 ppm with $FeCl_3$ —suggesting that coagulation

efficiency was significantly reduced in acidic environments.

In the alkaline range (pH = 9), the results showed a decrease in chromium concentration to 4.4 ppm with $Al_2(SO_4)_3$ and 3.4 ppm with $FeCl_3$. Although this indicates an improvement compared to acidic conditions, it still does not match the removal efficiency observed at near-neutral pH levels. This trend follows a U-shaped pattern, with removal efficiency decreasing at both acidic and strongly alkaline pH, while achieving optimal performance in the neutral to slightly alkaline range (pH 6–7).

From a chemical perspective, this behavior is attributed to the solubility of chromium hydroxide $(Cr(OH)_3)$, which reaches its minimum under moderately alkaline conditions, allowing for effective precipitation as stable and easily settleable compounds. Under strongly acidic conditions, chromium remains predominantly in its soluble ionic form, reducing its tendency to precipitate.

Comparing the two coagulants, $FeCl_3$ exhibited more stable removal performance across the tested pH range, with a relatively consistent decline in chromium concentration and fewer fluctuations. In contrast, $Al_2(SO_4)_3$ showed slightly more variability, indicating that ferric chloride forms more stable complexes with chromium ions, making it a more effective choice under varying pH conditions.

These findings clearly emphasize the importance of precise pH control as a key parameter influencing chromium removal efficiency. The results confirm that operating within the neutral-to-mildly alkaline pH range (6–8) yields the highest chromium removal performance using chemical coagulation techniques.
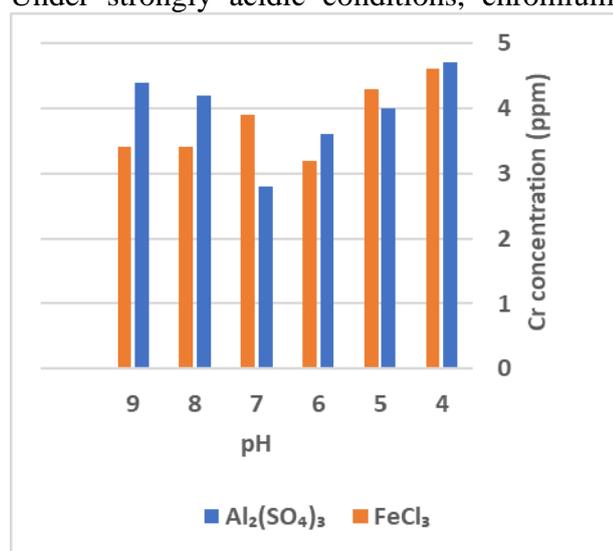

Figure 1: Effect of pH value on residual chromium (Cr) concentration after coagulation treatment

2- Effect of pH on Cobalt (Co) Concentration

Figure 2 illustrates the influence of varying pH levels on the residual cobalt concentration in industrial wastewater after coagulation using two different coagulants: aluminum sulfate $(Al_2(SO_4)_3)$ and ferric chloride $(FeCl_3)$. The results reveal that cobalt removal efficiency is significantly affected by pH changes. When using $Al_2(SO_4)_3$, the lowest residual concentration of cobalt was recorded at pH 7.0, reaching 0.40 ppm, while the highest concentration was observed at pH 5.0, with 0.80 ppm. These findings suggest that cobalt removal improves under near-neutral

pH conditions when aluminum sulfate is applied.

In contrast, when $FeCl_3$ was used as the coagulant, the highest residual cobalt concentrations were noted at pH 9.0 (0.89 ppm) and pH 7.0 (0.81 ppm), whereas the lowest values were recorded at pH 5.0 (0.65 ppm) and pH 4.0 (0.67 ppm). This indicates that the removal efficiency of $FeCl_3$ decreases noticeably in alkaline conditions, unlike $Al_2(SO_4)_3$, which performs better in neutral to slightly alkaline environments (pH 7–8).

These findings suggest that cobalt removal efficiency is influenced by the interaction between coagulant type and pH, with $Al_2(SO_4)_3$ showing relatively better performance under neutral conditions, while $FeCl_3$ exhibits variable behavior possibly due to the formation of different coordination complexes with cobalt under varying pH conditions.

This behavior can be chemically explained by differences in precipitation reactions and ion exchange mechanisms between cobalt ions and coagulants, as well as the stability of the resulting hydroxide species such as $Co(OH)_2$, whose solubility varies significantly with pH.

From a statistical standpoint, a two-way ANOVA revealed that there was no statistically significant effect at the 95% confidence level for either pH (P = 0.1807) or coagulant type (P = 0.5432). Furthermore, the interaction between the two factors was also not significant (P = 0.5579). This indicates that the observed differences in cobalt concentration after treatment may not be directly attributed to the tested variables, but rather fall within the bounds of natural variability or reflect nonlinear or interactive effects not captured by the model.
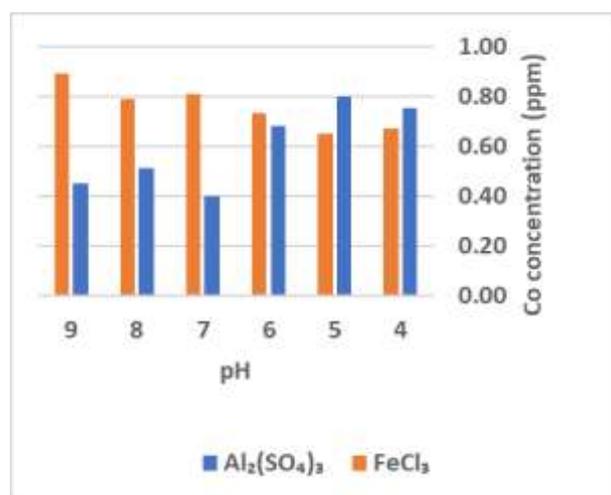

Figure 2: Effect of pH on residual cobalt (Co) concentration using $Al_2(SO_4)_3$ and $FeCl_3$ as coagulants.

3- Effect of Coagulant Dosage on Chromium (Cr) Concentration

Figure 3 illustrates the effect of varying doses of chemical coagulants—aluminum sulfate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$)—on the residual concentration of chromium in industrial wastewater following coagulation treatment. The results indicate that chromium's response to treatment varied depending on both the coagulant type and the applied dosage. When using $Al_2(SO_4)_3$, the residual chromium concentration ranged from 3.8 to 4.7 ppm, whereas with $FeCl_3$ it ranged from 2.5 to 4.5 ppm. Notably, the lowest chromium concentration (2.5 ppm) was observed at a $FeCl_3$ dose of 50 ppm,

highlighting the effectiveness of this coagulant at that dosage. For $Al_2(SO_4)_3$, performance was less consistent, with the best results observed at 80 and 110 ppm doses, both of which yielded 3.8 ppm of residual chromium.

These findings suggest that removal efficiency is strongly influenced by the balance between the added coagulant dose and operational conditions, particularly pH and the ionic composition of the treated water. This variability can be explained by the fact that increasing the coagulant dose promotes the formation of greater amounts of metal hydroxide precipitates (e.g., $Fe(OH)_3$ and $Al(OH)_3$), which are highly effective at adsorbing and capturing chromium ions via co-precipitation mechanisms. However, excessive dosing may result in the formation of soluble complexes between chromium and excess coagulant, or may redissolve the formed precipitates, causing slight fluctuations in removal efficiency, as observed at specific dosages.

Overall, $FeCl_3$ exhibited more stable and consistent performance compared to $Al_2(SO_4)_3$, maintaining relatively low chromium concentrations across most dosages, reflecting its chemical stability and superior ability to form stable precipitates under coagulation conditions. In contrast, $Al_2(SO_4)_3$ exhibited less uniform performance, with sudden increases in chromium concentration at 30 and 50 ppm, likely due to interactions with other operational factors or the characteristics of the treated water.

These observations are consistent with the findings of Kowalik-Klimczak (2025), who reported that chemical coagulation is among the most effective techniques for chromium removal from industrial wastewater, provided that the coagulant dose is precisely controlled [5]. The study emphasized that optimal dosing promotes the formation of dense, efficient flocs for heavy metal removal, whereas overdosing can have adverse effects, diminishing treatment efficiency.

Based on the above, the results of this experiment underscore the importance of optimizing coagulant dosage according to the specific characteristics of industrial wastewater. The findings also highlight the superior performance of $FeCl_3$ as a preferred coagulant for chromium removal under the laboratory conditions of this study. Moreover, the residual chromium concentrations remained below the environmental discharge limit of 5 ppm, supporting the potential applicability of this treatment approach in real industrial scenarios.
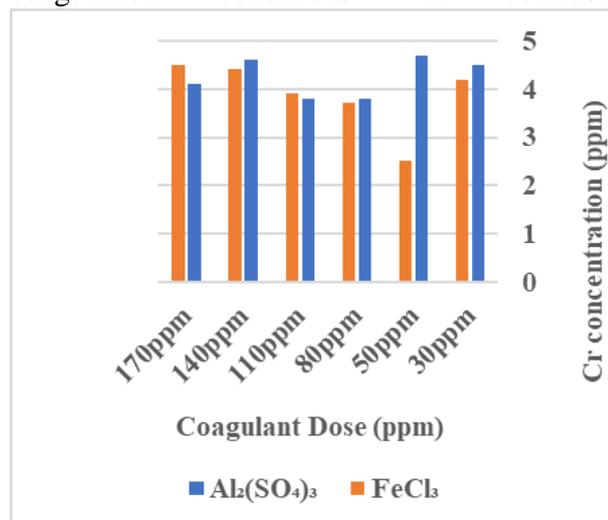

Figure 3: Effect of coagulant dosage ($Al_2(SO_4)_3$ and $FeCl_3$) on residual chromium (Cr) concentration in industrial wastewater after coagulation.

4- Effect of Coagulant Dosage on Cobalt (Co) Concentration

Figure 4 illustrates the effect of coagulant dosage on the residual concentration of cobalt (Co) in industrial wastewater using two types of chemical coagulants: aluminum sulfate ($Al_2 (SO_4)_3$) and ferric chloride ($FeCl_3$). The results show that the residual cobalt concentration did not follow a linear trend with increasing dosage, but rather fluctuated within a limited range, suggesting that interacting operational factors influenced removal efficiency.

When $Al_2 (SO_4)_3$ was used, cobalt concentration decreased from 0.66 ppm at a 30 ppm dose to a minimum of 0.40 ppm at 50 ppm, then gradually increased, reaching 0.83 ppm at the highest tested dose (170 ppm). This pattern may indicate partial re-dissolution of previously formed precipitates at higher coagulant dosages. In contrast, $FeCl_3$ exhibited a more stable removal trend, with residual cobalt concentrations remaining within a narrow range of 0.30–0.40 ppm, and the lowest value observed at a 110 ppm dose.

These results suggest that $FeCl_3$ offers greater stability in precipitate formation under the applied operating conditions compared to $Al_2 (SO_4)_3$, which displayed greater sensitivity to dosage changes. This behavior can be attributed to $FeCl_3$'s ability to generate more stable hydroxide flocs in slightly acidic environments. At the same time, $Al_2 (SO_4)_3$ tends to show performance fluctuations, especially when the optimal dosage is exceeded—leading to re-flocculation or secondary dissolution of metal hydroxides.

Overall, the results indicate that a dosage range of 50–110 ppm is optimal for achieving effective cobalt removal without causing secondary increases in residual concentrations.

From a statistical perspective, the two-way ANOVA analysis (Appendix 11-C) revealed no statistically significant effect ($P>0.05$) for either the coagulant dosage (P = 0.7328) or the coagulant type (P = 0.6891). The interaction effect between the two factors was also not significant (P = 0.5423), indicating that the observed variations in cobalt concentration were not statistically attributable to their interaction. Nonetheless, the numerical differences observed across treatments provide valuable operational insight, helping to define the most efficient dosage range for each coagulant type.

These findings align with those of Kowalik-Klimczak (2025), who reported that excessive coagulant dosages may form soluble complexes with heavy metal ions, thereby reducing overall removal efficiency [5]. Therefore, the design of coagulation processes for cobalt removal must consider dosage optimization, balancing precipitate stability with the goal of minimizing residual metal concentrations.
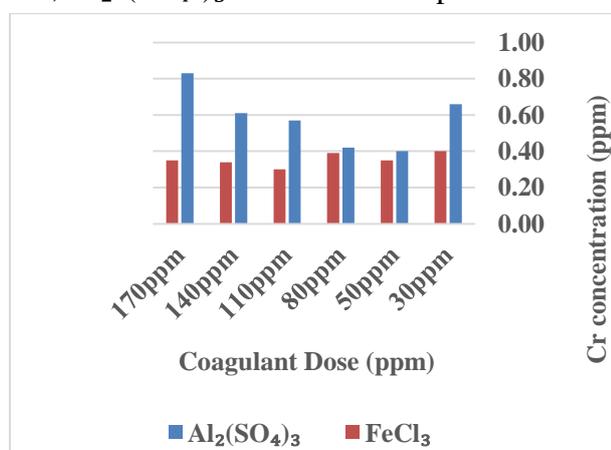

Figure 4: Effect of coagulant dosage on cobalt (Co) concentration using $Al_2 (SO_4)_3$ and $FeCl_3$.

5- Effect of Ozone (O₃) Dosage After Coagulation on Chromium (Cr) Removal Efficiency

Figure 5 illustrates the effect of varying ozone doses (600, 1200, and 1800 mg/L) on the residual concentration of chromium (Cr) in industrial wastewater treated with prior chemical coagulation using aluminum sulfate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$). The results show that the lowest residual chromium concentrations were observed at the lowest ozone dose (600 mg/L), reaching 3.1 ppm with $Al_2(SO_4)_3$ and 4.0 ppm with $FeCl_3$. These values indicate moderate removal efficiency, although not sufficient for complete removal, suggesting that this ozone dose alone was inadequate to achieve full chromium precipitation.

When the ozone dose was increased to 1200 mg/L, significant reductions in chromium concentrations were observed, reaching 1.9 ppm and 2.1 ppm for $Al_2(SO_4)_3$ and $FeCl_3$, respectively. This improvement reflects the enhanced oxidative reactions facilitated by ozone, which promote the formation of insoluble $Cr(OH)_3$ precipitates and thereby increase removal efficiency. However, a further increase in the ozone dose to 1800 mg/L resulted in an increase in residual chromium concentrations, with values of 2.8 ppm ($Al_2(SO_4)_3$) and 3.2 ppm

($FeCl_3$). This reversal is attributed to ozone's strong oxidative potential, which at high doses may re-oxidize trivalent chromium (Cr^{3+}) into the more soluble hexavalent form (Cr^{6+}), thereby increasing total dissolved chromium.

These findings suggest that the optimal ozone dose for chromium removal is 1200 mg/L, which strikes a balance between effective oxidation and preventing the re-dissolution of chromium species. Excessive ozone dosing appears to have an adverse effect, as intensified oxidative reactions may release previously precipitated chromium back into the aqueous phase. These outcomes are consistent with the conclusions of Mohanadevi & Dhanabalan (2025), who emphasized that high doses of oxidizing agents may lead to the transformation of precipitated chromium into its more soluble hexavalent form (Cr^{6+}), thereby reducing overall removal efficiency during advanced treatment stages [7].

Based on the above, it is recommended to apply a moderate ozone dosage (1200 mg/L) in combination with chemical coagulation to achieve optimal chromium removal performance, while avoiding overdosing to prevent adverse effects on treatment efficiency.
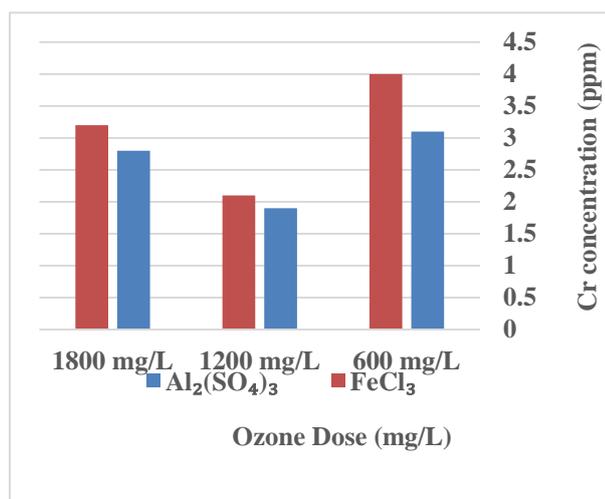

Figure 5: Effect of ozone (O_3) dosage on residual chromium (Cr) concentration in industrial wastewater after coagulation with aluminum sulfate and ferric chloride.

6- Effect of Ozone (O_3) Dosage After Coagulation on Cobalt (Co) Removal Efficiency

Figure 6 illustrates the effect of ozone (O_3) dosage on the residual concentration of cobalt (Co) in industrial wastewater following coagulation with either aluminum sulfate ($Al_2(SO_4)_3$) or ferric chloride ($FeCl_3$). The untreated raw sample had a cobalt concentration of 0.91 ppm. After ozonation, the concentration dropped to varying levels depending on both the ozone dose and the type of coagulant used.

When $Al_2(SO_4)_3$ was applied, the lowest cobalt concentration was achieved at an ozone dose of 1200 mg/L, reaching 0.22 ppm, while the concentrations at 600 mg/L and 1800 mg/L were 0.29 ppm and 0.26 ppm, respectively. In contrast, with $FeCl_3$, the residual cobalt concentrations were generally higher: 0.31 ppm at 600 mg/L, 0.28 ppm at 1200 mg/L, and 0.40 ppm at 1800 mg/L. These results indicate that cobalt removal did not follow a linear trend with increasing ozone dosage and varied depending on the coagulant type.

The data suggest that aluminum sulfate demonstrated relatively better performance in reducing cobalt concentration, particularly at the intermediate ozone dose (1200 mg/L). This behavior may be attributed to the fact that excessive ozone dosing can lead to over-oxidation of organic and inorganic compounds, potentially resulting in the release of previously bound cobalt due to complex degradation or destabilization of the formed precipitate equilibrium.

The Two-way ANOVA test results showed that the effect of ozone dose on cobalt concentration was not statistically significant, with F = 1.213 and P = 0.3472, which exceeds the conventional significance threshold of 0.05. Similarly, the effect of coagulant type was not statistically significant (F = 2.001, P = 0.2065). The interaction between the two factors (ozone dose × coagulant type) also lacked statistical significance (F = 3.156, P = 0.1178). Therefore, the observed variations in cobalt concentrations are considered descriptive rather than statistically conclusive, likely influenced by uncontrolled factors such as contact time or variations in water characteristics during treatment.

Based on these results, it can be concluded that while the individual effects of ozone dosage and coagulant type were not statistically significant at the 0.05 level, the lowest residual cobalt concentration was achieved using $Al_2(SO_4)_3$ at 1200 mg/L, suggesting that this combination represents a promising operational condition for minimizing cobalt without triggering re-release from precipitates or chemical complexes.
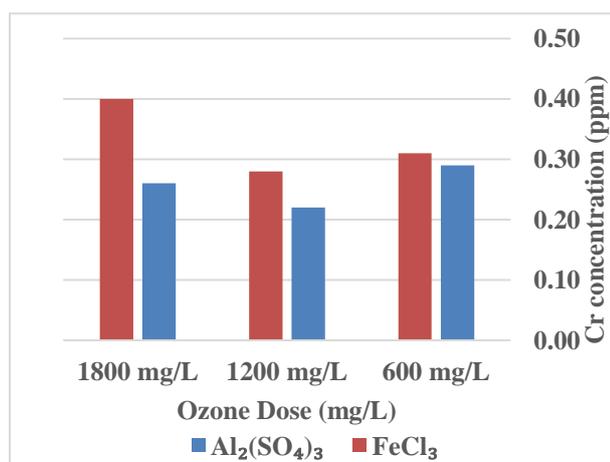

Figure 6: Effect of ozone (O_3) dosage on residual cobalt (Co) concentration using $Al_2(SO_4)_3$ and $FeCl_3$.

7- Effect of Combined UV and Ozone (UV + O_3) Treatment After Coagulation on Chromium (Cr) Removal Efficiency

Figure 7 presents the effect of combined ultraviolet (UV) irradiation and ozone (O_3) treatment on the concentration of chromium (Cr) in industrial wastewater following chemical coagulation using aluminum sulfate ($Al_2 (SO_4)_3$) and ferric chloride ($FeCl_3$). The results indicate that the integration of UV at an intensity of 10.62 mW/cm² with an ozone dose of 1200 mg/L led to residual chromium concentrations of 0.007 ppm with $Al_2 (SO_4)_3$ and 0.01 ppm with $FeCl_3$.

Upon increasing the UV intensity to 21.24 mW/cm², while maintaining the exact ozone dosage, a divergent trend was observed: chromium concentration decreased further to 0.001 ppm with $Al_2 (SO_4)_3$, whereas it increased to 0.064 ppm with $FeCl_3$. This contrast highlights the critical role of UV intensity in directing the oxidative reaction pathway. In the case of aluminum sulfate, the increased irradiation enhanced removal efficiency, suggesting the stability of coagulation products under advanced oxidation conditions. However, for ferric chloride, the higher UV intensity may have promoted partial oxidation of trivalent chromium (Cr^{3+}) to its hexavalent form (Cr^{6+}), which is more soluble and thus led to the re-release of chromium ions into the aqueous phase.

This behavior is attributed to the UV/O_3 system's ability to generate highly reactive hydroxyl radicals (•OH), which, despite their strong oxidative power, may sometimes oxidize heavy metals into chemically more stable but less precipitable forms, as is the case in the Cr^{3+} to Cr^{6+} transformation. This phenomenon aligns with the findings of Wada et al. (2005) and Azizi (2024), who noted that reaction parameters such as pH, ozone concentration, and UV intensity directly influence the equilibrium between different chromium species [11] [3].

Despite the observed variations, all residual concentrations remained below the environmental safety threshold (<0.1 ppm), indicating the effectiveness of the combined UV/O_3 system in reducing chromium to acceptable levels. Nonetheless, the results underscore the importance of precise operational control to avoid potential adverse effects of excessive oxidation, particularly when using coagulants that are highly reactive with ozone.
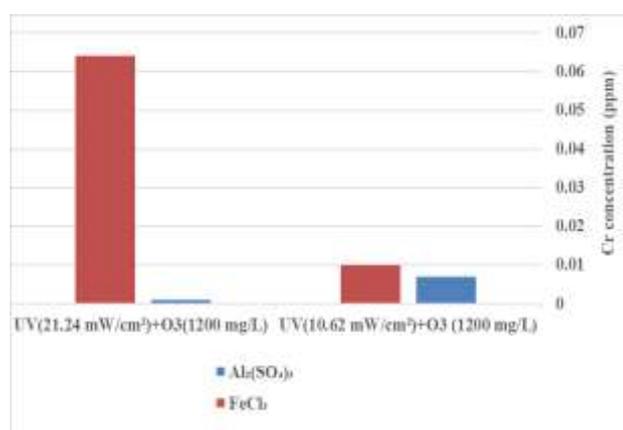

Figure 7: Effect of combined UV and ozone (O_3) treatment on chromium (Cr) concentration in industrial wastewater after coagulation using aluminum sulfate and ferric chloride.

8- Effect of Combined UV and Ozone (UV + O$_3$) Treatment After Coagulation on Cobalt (Co) Removal Efficiency

Figure 8 illustrates the effect of combined ozone and ultraviolet (UV) irradiation treatment on cobalt (Co) concentration in industrial wastewater following chemical coagulation using two coagulants: aluminum sulfate (Al$_2$ (SO$_4$)$_3$) and ferric chloride (FeCl$_3$). The experiment was conducted using a fixed ozone dose of 1200 mg/L, while varying the UV intensity between two levels: low (10.62 mW/cm²) and high (21.24 mW/cm²).

The untreated sample initially contained 0.91 ppm of cobalt. Following treatment, the residual cobalt concentration decreased significantly. When Al$_2$ (SO$_4$)$_3$ was used, the cobalt concentration dropped to 0.03 ppm under low UV intensity but increased to 0.13 ppm at the higher intensity. Conversely, with FeCl$_3$, the residual cobalt concentration was 0.10 ppm at the lower UV intensity and decreased further to 0.01 ppm at the higher intensity. These values suggest a differential interaction between UV intensity and coagulant type, highlighting the influence of coagulant type on oxidation pathways and cobalt removal efficiency.

A Two-way ANOVA was conducted to evaluate the statistical significance of the effects of coagulant type and UV intensity, as well as their interaction, on cobalt concentration. The analysis revealed that both factors had statistically significant effects: the p-value for coagulant type was 0.0046, indicating a meaningful difference between the two coagulants, while the p-value for UV intensity was 0.0113, also significant. Most notably, the interaction between coagulant type and UV intensity showed a highly significant effect, with a p-value of 0.0019, suggesting that the combined effect of the two variables cannot be explained independently but instead emerges from their interaction.

The average cobalt concentration following treatment with FeCl$_3$ was approximately 0.08 ppm, whereas with Al$_2$ (SO$_4$)$_3$ it was about 0.055 ppm, indicating a slight advantage for FeCl$_3$ at this treatment stage. These findings suggest that increasing UV intensity enhances cobalt removal when FeCl$_3$ is used, likely due to the enhanced generation of hydroxyl radicals (•OH), which improve the system's capacity to oxidize cobalt into more easily precipitable or removable forms. In contrast, elevated UV intensity in the presence of Al$_2$ (SO$_4$)$_3$ may have promoted the oxidation of Co²⁺ to Co³⁺ , a more soluble species, leading to increased residual cobalt levels.

Therefore, it can be concluded that combining FeCl$_3$ with high-intensity UV irradiation represents the optimal configuration within this hybrid system for the efficient removal of cobalt from industrial wastewater.
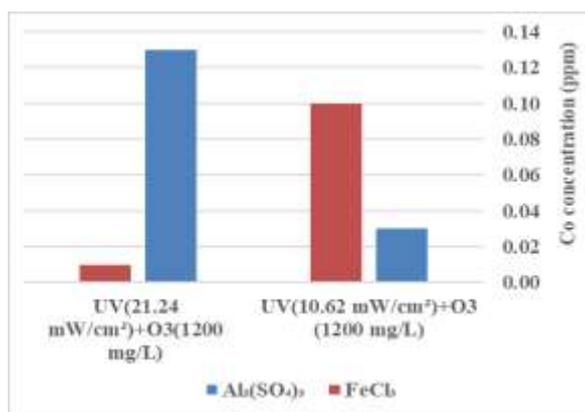
Figure 8: Effect of combined UV and ozone (UV + O_3) treatment on cobalt (Co) concentration using $Al_2 (SO_4)_3$ and $FeCl_3$

Conclusion

1. The integrated tertiary treatment system combining chemical coagulation, ozonation, and ultraviolet (UV) irradiation proved to be highly effective in removing heavy metals, specifically chromium (Cr) and cobalt (Co), from petroleum-based industrial wastewater.

2. Ferric chloride ($FeCl_3$) demonstrated superior and more stable performance in metal removal compared to aluminum sulfate ($Al_2 (SO_4)_3$), especially under varying pH levels and coagulant dosages, making it the preferred coagulant in most conditions.

3. The optimal pH range for maximum heavy metal removal efficiency was found to be between 6.0 and 8.0, which facilitates the formation of stable hydroxide precipitates and enhances coagulation effectiveness.

4. An ozone dosage of 1200 mg/L combined with UV irradiation at higher intensity significantly enhanced the oxidation of residual pollutants and reduced metal concentrations to below environmental discharge standards.

5. The findings support the applicability of this combined treatment approach as a scalable, environmentally friendly, and cost-effective solution for the advanced treatment of industrial wastewater in oil refinery settings.

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