




Article

The Synergistic Power of Rosehip Seed Powder and Aluminum Chloride in Steel Industry Wastewater Treatment

Mohammed Shadi S. Abujazar ¹, Sakine Ugurlu Karaagaç ², Salem S. Abu Amr ³, Motasem Y. D. Alazaiza ^{4,*} , Ahmed Albahnasawi ⁵ , and Dia Eddin Nassani ⁶ 

- ¹ Al-Aqsa Community Intermediate College, Al-Aqsa University, Gaza 4051, Palestine; ms.abujazar@alaqsa.edu.ps or shadiabujazar@gmail.com
- ² Department of Environmental Engineering, Faculty of Engineering, Karabuk University, Karabuk 78050, Turkey; sakineugurlu@karabuk.edu.tr
- ³ International College of Engineering and Management, 111 St, Seeb, P.O. Box 2511, Muscat 111, Oman; salem.s@icem.edu.om
- ⁴ Department of Civil and Environmental Engineering, College of Engineering (COE), A'Sharqiyah University (ASU), Ibra 400, Oman
- ⁵ Department of Environmental Engineering, Gebze Technical University, Kocaeli 41400, Turkey; ahmedalbahnasawi@gmail.com
- ⁶ Department of Civil Engineering, Hasan Kalyoncu University, Gaziantep 27500, Turkey; diaeddin.nassani@hku.edu.tr
- * Correspondence: my.azaiza@gmail.com

Abstract: This study investigates the efficiency of a hybrid coagulation–flocculation process for the treatment of industrial wastewater from the steel industry. The novel method combines a natural coagulant, processed Rosehip Seed Powder (RSP), with a chemical coagulant, aluminum chloride (AlCl₃), across varying concentrations and pH levels. The study simulated the pH 8 conditions of iron and steel industrial wastewater and examined the removal of heavy metals, total suspended solids (TSS), chemical oxygen demand (COD), and ammonia–nitrogen (NH₃-N). At pH 8, the optimal coagulant dosage was determined to be 0.75:0.75 (g/g) of RSP/AlCl₃ powder, resulting in high removal efficiencies across several parameters: 88.29% for COD, 91.85% for color, 99% for TSS, 93.11% for NH₃-N, 94.3% for Mn, 98.5% for Fe, 96.7% for Zn, and 99.3% for Ni. The pH optimization demonstrated high removal efficiencies without pH adjudication. The removal of heavy metals at pH 8 demonstrated high efficiencies, with Mn, Fe, Zn, and Al achieving 99.00%, 90.6%, 95.73%, and 92.3%, respectively. These results suggest that no pH adjustment is required when using RSP/AlCl₃ for the treatment of iron and steel industry wastewater through the coagulation method.

Keywords: heavy metal removal; natural coagulant; hybrid RSP/AlCl₃; optimum dosage; industrial wastewater



Citation: Abujazar, M.S.S.; Karaagaç, S.U.; Amr, S.S.A.; Alazaiza, M.Y.D.; Albahnasawi, A.; Nassani, D.E. The Synergistic Power of Rosehip Seed Powder and Aluminum Chloride in Steel Industry Wastewater Treatment. *Water* **2024**, *16*, 2770. <https://doi.org/10.3390/w16192770>

Academic Editor: Laura Bulgariu

Received: 6 September 2024

Revised: 25 September 2024

Accepted: 26 September 2024

Published: 29 September 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Industrial processes, particularly within the iron and steel (IS) sector, have historically generated substantial quantities of wastewater characterized by a complex matrix of contaminants, including heavy metals, organic compounds, and suspended solids [1,2]. The efficient treatment of such industrial effluents is paramount, not only to meet regulatory requirements but also to mitigate environmental impacts and ensure the sustainability of water resources [3,4]. In this context, coagulation and flocculation processes have emerged as essential techniques for industrial wastewater treatment, offering the potential to enhance treatment efficiency [5,6]. Other methods commonly used in wastewater treatment include sedimentation, biological processes such as activated sludge or biological filters, chemical oxidation or reduction, membrane filtration (such as ultrafiltration or reverse osmosis), and advanced oxidation processes (AOPs) like ozone or UV treatment. Each

method has advantages and applications depending on the specific contaminants and treatment goals.

Wastewater generated by the iron and steel (IS) industries poses a significant environmental challenge due to its complex composition and potential for severe ecological impacts. This industrial effluent often contains elevated concentrations of heavy metals, including iron (Fe), zinc (Zn), manganese (Mn), aluminum (Al), and nickel (Ni). In addition to these metallic elements, the effluent typically contains substantial concentrations of organic compounds, suspended particles, and other pollutants. These complex mixtures pose significant environmental risks, as improper handling can lead to detrimental effects on ecosystems and public health. To ensure the removal of both metal ions and organic impurities, addressing this diverse range of pollutants requires an efficient and effective treatment approach [7]. When discharged without proper treatment, these contaminants can pollute natural water bodies, disrupt aquatic ecosystems, and pose serious health risks to humans and wildlife. Heavy metals can accumulate in aquatic organisms, entering the food chain and resulting in bioaccumulation, which has far-reaching consequences [8].

To mitigate these environmental hazards, effective treatment methods are essential to propose. Coagulation and flocculation processes have emerged as vital tools for removing impurities from industrial wastewater, particularly from the IS industry [9]. Coagulation and flocculation have been recognized as essential processes in wastewater treatment. Coagulants destabilize colloidal particles and microorganisms, enabling their aggregation into larger flocs. Subsequent flocculation promotes the formation of larger, settleable particles that can be easily separated from the treated water. In this regard, the coagulation–flocculation process relies on the suitable selection of coagulants and the optimization of operational parameters to achieve desirable removal efficiencies [5].

While the coagulation–flocculation process is a well-established approach, a pressing need exists to enhance its efficiency and environmental compatibility. Conventional chemical coagulants, such as aluminum salts, are effective but may introduce additional chemical residues into the treated water and require additional treatment steps [10]. Furthermore, the increasing focus on sustainability has driven the exploration of eco-friendly coagulant alternatives [11]. One promising method is the utilization of natural coagulants derived from plant sources, which possess inherent advantages, including biodegradability and low environmental impacts [12]. Among these natural coagulants, plant-based coagulants stand out due to their rich composition of bioactive compounds and their coagulation potential [13]. However, the practical application of these compounds alone in wastewater treatment has limitations, prompting the investigation of hybrid coagulation approaches that combine the strengths of both natural and chemical coagulants [14].

Conventional coagulants like aluminum chloride (AlCl_3) have been widely employed due to their proven efficacy in destabilizing colloidal particles and microorganisms [15]. Nevertheless, concerns regarding the environmental footprint and the generation of residual sludge have prompted the search for alternative coagulants with improved sustainability profiles [16]. Natural coagulants derived from plant materials have gained attention for their potential to address these concerns [17]. RSP, obtained from RS, is one such natural coagulant. Studies have highlighted its coagulation potential attributed to its unique composition, including tannins, pectin, and polysaccharides, which facilitate the bridging and adsorption mechanisms during coagulation–flocculation [12].

Moreover, recent research has demonstrated that the synergistic combination of natural and chemical coagulants can yield superior treatment outcomes [18]. The hybrid coagulation approach capitalizes on each coagulant type's strengths while mitigating its weaknesses [19]. In the context of natural coagulants and AlCl_3 , this hybrid strategy aims to enhance removal efficiencies and reduce the environmental impact of the treatment process. Abu Amr et al. [12] explored the use of a hybrid coagulant, combining date stone powder (DSP) and aluminum chloride (AlCl_3), to effectively remove heavy metals from industrial wastewater. Traditional chemical coagulants, though effective, produce toxic sludge, making natural alternatives like DSP more appealing due to their sustainability,

cost-effectiveness, and safety [20]. The study optimized the DSP/AlCl₃ dosage (7:1 g/g) and pH, achieving high removal efficiencies for contaminants such as COD, TSS, and heavy metals at pH 8 without needing pH adjustment. The results highlight the method's potential as a viable, eco-friendly alternative, though further research is needed to assess scalability. Despite the promise of hybrid coagulation, there remains a research gap in understanding the optimal conditions and mechanisms governing the synergy between natural coagulants and AlCl₃ [21]. Furthermore, few studies have been conducted on how pH influences the hybrid coagulation process or the capacity of RSP to buffer pH changes during treatment. Further investigation is needed to understand the impact of pH fluctuations on the overall effectiveness of the coagulation process and to determine whether RSP can serve as a stabilizing agent to maintain optimal pH levels during treatment. Such insights are crucial for optimizing the procedure to enhance pollution removal and treatment efficacy.

This study addresses the research gap by systematically evaluating the effectiveness of a hybrid coagulation–flocculation process using RSP and AlCl₃ for treating IS industry wastewater. This study assesses key parameters—COD, TSS, NH₃-N, and heavy metals (Mn, Fe, Zn, Al, and Ni)—across various pH conditions. The research highlights the potential of RSP to mitigate the environmental impact of conventional chemical coagulants and optimizes coagulant dosages and pH ranges for maximum removal efficiencies.

2. Materials and Methods

2.1. Steel and Iron (IS) Industry Wastewater Collection and Characterization

Wastewater from the Karabuk Iron and Steel Factory in Karabuk City, Turkey, served as the main experimental medium for this study. To gather wastewater, grab samples had to be taken straight from the source, without any dilution. The samples were promptly kept in a refrigerated environment at a controlled temperature of 4 °C to maintain their purity and integrity. Until they were used in tests at the Department of Environmental Engineering, Faculty of Engineering, Karabuk University, Turkey, the samples were kept under these conditions. Table 1, presented herein, presents comprehensive insights into the compositional characteristics of the wastewater utilized in the experimental investigations. These details offer a valuable snapshot of the wastewater's composition as essential reference data for the study's analytical and treatment processes.

Table 1. Characteristics of wastewater.

Industrial Wastewater Parameters	Units	Results
pH	--	8
Color	Pt-Co	865.6
TSS	mg/L	110
COD	mg/L	840.24
NH ₃ -N	mg/L	42.8
Manganese "Mn"	mg/L	6.27
Iron "Fe"	mg/L	5.30
Zinc "Zn"	mg/L	5.44
Aluminum "Al"	mg/L	0.38
Nickel "Ni"	mg/L	0.15

Furthermore, it is pertinent to note that the pH levels of the wastewater samples were actively controlled and regulated throughout the experimentation phase. This pH regulation was meticulously carried out by judiciously applying a 1 N H₂SO₄/NaOH solution. This control mechanism ensured that the pH conditions remained consistent and conducive to the study's specific objectives, thereby maintaining the experimental rigor and integrity essential to the research outcomes.

2.2. RSP Coagulant Preparation

High-quality RSs were carefully selected from a forest near Karabuk University in Turkey. The seeds underwent a rigorous preparation process to ensure their suitability for the study. Initially, any adhering flesh from the RSs was meticulously removed through a thorough rinsing procedure utilizing distilled water. Subsequently, the cleaned seeds were subjected to a precise drying process to achieve optimal dryness. Initially, they were allowed to air-dry at ambient room temperature, followed by a more controlled drying phase. During this phase, the seeds were placed in an oven for 8 h, maintaining a constant temperature of 50 ± 1 °C. This meticulous drying regimen guaranteed the complete elimination of moisture, rendering the seeds ideal for further processing. The next stage involved manually de-husking the dried RSs, followed by a finely detailed grinding process utilizing a laboratory mortar. This process effectively reduced the seeds into fine particles. For the final refinement, a specialized grinder, specifically the Retsch RS 200, was employed to further process the crushed rosehip seed stones. This step yielded a consistent and homogeneous powder characterized as RSP. The resulting powder, with its uniform and delicate texture, served as a natural coagulant of choice for the wastewater treatment procedures conducted in this study. This naturally derived coagulant was instrumental in facilitating the coagulation–flocculation process, contributing to the study’s research objectives and enhancing the eco-friendly approach to wastewater treatment (refer to Figure 1 for a visual representation).



Figure 1. Rosehip seeds and powder.

2.3. Chemicals

It is important to emphasize that all chemicals used in this research were of top analytical grade, ensuring maximum precision and reliability in the experimental processes. In particular, Sigma-Aldrich Chemical Co., a renowned and trustworthy supplier situated in St. Louis, MI, USA, provided the following chemicals: 98% sulfuric acid (H_2SO_4), 95% pellets sodium hydroxide (NaOH), and 99% aluminum chloride ($AlCl_3$). The use of such high-quality chemicals guaranteed strict adherence to scientific standards, reinforcing the

accuracy and dependability of the experimental results, and lending credibility to the study's findings.

2.4. Experiment Procedures

An orbital shaker (model: PSU-10i, Serial No.: 010144-1404-0228, made in Latvia) was used to precisely conduct the coagulation–flocculation studies. Rosehip coagulant (1 g/L), as previously studied by [22], was combined with different amounts of aluminum chloride (AlCl_3) (0.5, 1, 1.5, 2, and 2.5 g) and mixed with 1 L of wastewater from the iron–steel industry to systematically evaluate the effects of coagulant dosage. To ensure precision and uniformity throughout the testing, 500 mL beakers were carefully selected as experimental vessels. The parameters guiding the experimental design were thoughtfully determined through a comprehensive review of the literature. Within each experimental trial, a volume of 200 mL of the sample was meticulously transferred into a 500 mL beaker, which was then securely positioned on the shaker plate.

The coagulation process was initiated with a rapid mixing phase, characterized by a stirring speed of 200 revolutions per minute (rpm), maintained for 5 min. Subsequently, this was followed by a gentler and more prolonged mixing phase, operating at a speed of 90 rpm for 30 min as discussed by [23]. Following these mixing steps, the beakers were allowed to undergo a settling phase lasting 30 min. Whatman circle ashless/white ribbon filter paper was chosen for filtration to guarantee the efficient removal of impurities and produce a cleared sample. A clean, transparent sample was obtained through this painstaking procedure, and it was subsequently put through a thorough battery of tests. Several important characteristics were assessed in these tests, such as the concentrations of heavy metals like iron (Fe), manganese (Mn), aluminum (Al), nickel (Ni), and zinc (Zn), as well as (TSS), ($\text{NH}_3\text{-N}$), and (COD). Because this was the starting pH of the wastewater collected from the iron–steel (IS) industry, all evaluations were conducted at this natural pH of 8. An exhaustive and methodical evaluation of the coagulation–flocculation process's effectiveness in treating industrial wastewater was made possible by this scientific approach.

In this study, a synergistic approach was employed, combining a hybrid natural coagulant, specifically processed RSP, with a chemical coagulant, AlCl_3 , across a range of concentrations. The pH level was additionally recognized as a pivotal factor in the experimental design. To comprehensively assess the treatment efficiency, each unique combination of the natural and chemical coagulants at their optimal concentrations was subjected to varying pH conditions, spanning from a low of 4 to a high of 11. This extensive pH adjustment was meticulously executed utilizing 0.1 N solutions of both NaOH and H_2SO_4 . By systematically varying the pH within this broad spectrum, the study aimed to elucidate the influence of pH on the coagulation process, particularly in the context of the hybrid coagulant system. This rigorous and well-structured experimental approach allowed for a detailed exploration of the interaction between coagulant types, concentrations, and pH levels, ultimately contributing to a comprehensive understanding of the coagulation–flocculation process's efficiency in treating industrial wastewater.

2.5. Analytical Methods

The efficacy of the combination coagulation–flocculation technique was assessed in detail by the examination of multiple critical parameters, such as COD, $\text{NH}_3\text{-N}$, TSS, and the amounts of heavy metals including Fe, Mn, Zn, Al, and Ni included in the wastewater, which had a pH of 8 initially. Table 2 outlines the standard procedures for the examination of water and wastewater, which were adhered to for measuring all chemical and physical parameters. A 1 N sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) solution was used to carefully monitor and modify the pH levels of the samples during the experiment, guaranteeing exact conditions for reliable results (Veli et al. [21]). To ensure the accuracy and reliability of the analytical results, all chemical and physical parameters were subjected to rigorous measurement processes in strict accordance with the standard methods for

the examination of water and wastewater, as outlined in the specifications provided in Table 2. These standardized analytical methods are well established in environmental engineering and provide a robust framework for obtaining precise and consistent data. Throughout the experiments, the pH of the wastewater samples was actively monitored and regulated to maintain the desired pH conditions. This was expertly achieved by meticulously using a 1 N H₂SO₄/NaOH solution, ensuring that the pH levels remained within the predefined range suitable for the experimental objectives. This pH control mechanism further exemplifies the dedication to maintaining the integrity and reliability of the experimental procedures and data generated in this study, reaffirming the scientific rigor underpinning the research.

Table 2. Characterization parameters and methods.

Parameters	Method
pH	pH meter
Color (Pt-Co)	SM 2120 C
TSS (mg/L)	SM 2540 D
COD (mg/L)	ASTM D1252-A
NH ₃ -N (mg/L)	TS EN ISO 11732
Manganese "Mn" (mg/L)	TS EN ISO 11885
Iron "Fe" (mg/L)	TS EN ISO 11885
Zinc "Zn" (mg/L)	TS EN ISO 11885
Aluminum "Al" (mg/L)	TS EN ISO 11885
Nickel "Ni" (mg/L)	TS EN ISO 11885

To determine the removal of efficiency of various investigated parameters, Equation (1) was employed. This formula accounts for the final concentration of the wastewater after treatment as well as the initial concentration of the raw industrial wastewater sample.

$$\text{Percentage Removal (\%)} = \left[1 - \left(\frac{C_i - C_f}{C_i} \right) \right] * 100 \quad (1)$$

where C_i was the concentration before treatment (influent), and C_f was the concentration after treatment of each parameter (effluent).

3. Results and Discussion

3.1. RSP/AlCl₃ Dosage Effects

The influence of various dosages of the hybrid coagulant was examined in order to evaluate the efficacy of hybrid coagulation in the treatment of wastewater. Several studies were conducted employing different dosages of aluminum chloride (AlCl₃) at doses of 0.5 g, 1 g, 1.5 g, 2 g, and 2.5 g in conjunction with an ideal concentration of Rosehip Seed Powder (RSP) coagulant (1 g/L) [4]. A single liter of wastewater gathered from the iron and steel sector was used to prepare these mixes. An orbital shaker was used to stir the mixes under the precise circumstances indicated in Section 2.3 to guarantee homogeneity. The goal was to determine the hybrid coagulant dosage that would produce the best removal efficiency during the treatment. As previously observed by [24], it is essential to acknowledge that the surface charge of the coagulant plays a substantial role in influencing coagulation performance, chiefly due to its mass. Therefore, a critical facet of this investigation involves the economic optimization of the coagulant dosage, the determination of the requisite mass for potential scale-up, and the subsequent design of large-scale equipment.

The research outcomes yielded intriguing insights into the influence of varying RSP/AlCl₃ dosages on the removal efficiencies of key parameters in the industrial wastewater treatment process. Most notably, it was evident that changes in RSP/AlCl₃ dosages had negligible effects on the removal efficiencies of TSS, color, and NH₃-N, as these parameters consistently maintained high removal rates, specifically 100%, 90%, and 95%, respectively, across all investigated RSP/AlCl₃ dosages. However, the influence of RSP/AlCl₃ dosages

on COD removal was markedly distinct. The COD removal efficiency exhibited notable sensitivity to RSP/ AlCl_3 dosage variations. At a 1.0/0.5 RSP/ AlCl_3 dosage, the COD removal efficiency stood at approximately 70%. Remarkably, as the RSP/ AlCl_3 dosage increased to 1.0/1.0, the COD removal efficiency significantly improved, reaching 90%. However, the subsequent escalation of AlCl_3 dosage resulted in a sharp decline in COD removal efficiency, plummeting to approximately 65%. This intriguing pattern in COD removal underscores the complex interplay between RSP and AlCl_3 dosages and their impact on treatment efficacy. The initial enhancement in COD removal with an increased RSP/ AlCl_3 dosage suggests that the hybrid coagulant system effectively targeted the organic pollutants responsible for COD. Nonetheless, as AlCl_3 dosage continued to rise, it seemingly led to counter-stabilization effects, causing a reduction in COD removal efficiency. This phenomenon aligns with the findings reported by [25].

Adsorption-bridging mechanisms are the main driving force behind the coagulation process that uses the hybrid coagulant. Through charge neutralization—which successfully neutralizes the charges of suspended particles and promotes their aggregation—the Rosehip Seed Powder (RSP) component is crucial in this situation. In contrast, when aluminum chloride (AlCl_3) is added to a water sample, it causes a hydrolysis reaction that results in positively charged species that further encourage coagulation by generating flocs. This dual-action process increases the overall coagulation efficiency by fusing the hydrolytic activity of AlCl_3 with the charge-neutralizing qualities of RSP [26]. Charge neutralization, also known as electrostatic interaction, and sweep coagulation, also known as co-precipitation, are the two main mechanisms via which the coagulation process is generally considered to function. The process of charge neutralization entails balancing the electrical charges of suspended particles, which causes them to aggregate and eventually separate from the solution. On the other hand, sweep coagulation describes the action of coagulants creating precipitates that move through the water and pick up suspended particles. These mechanisms, which have a wealth of literature supporting them, are essential for improving the effectiveness of water treatment [27]. The coagulation process mediated by RSP can be elucidated through the charge neutralization mechanism, whereby the electrical charges of the coagulant and the suspended particles are balanced. Conversely, in the case of sweep coagulation, when AlCl_3 is dosed into the water sample, it undergoes a hydrolysis reaction, instigating a cascade of chemical transformations. These mechanisms collectively contribute to the coagulation process by facilitating the aggregation and subsequent removal of impurities from the water sample [28].

Examining the impact of different hybrid coagulant dosages on the elimination of COD, color, TSS, and $\text{NH}_3\text{-N}$ from wastewater coming from the iron–steel (IS) sector was the goal of this study. These experiments were conducted at an initial pH of 8, and Figure 2 shows the visual representation of the results. With a hybrid coagulant dosage of 1:1 (g/g), the highest removal efficiency was recorded, with removal rates of 88.29% for COD, 91.85% for color, 99.00% for TSS, and 93.11% for $\text{NH}_3\text{-N}$. To put things in perspective, these results were contrasted with the removal efficiencies obtained via RSP alone, as shown in a prior study. This comparison demonstrates how well the hybrid coagulant performs in terms of improving the treatment efficiency for several important wastewater characteristics [12].

The findings demonstrated that utilizing the hybrid coagulant led to an enhancement in removal efficiency ranging from 2.2% to 14.2%, contingent upon the specific parameter being considered, as illustrated in Figure 3. Notably, the efficacy of color removal exhibited a substantial improvement of 8.3% when utilizing a hybrid dosage of 1:1 (g/g) compared to RSP alone. Furthermore, the effectiveness of $\text{NH}_3\text{-N}$ removal displayed a significant increase of 14.2% with the exact hybrid dosage, underscoring the notable improvement achieved through hybrid coagulation in this context. On the other hand, when using the same 1:1 (g/g) hybrid coagulant dosage, the improvement in COD elimination was just 2.2% higher. This implies that the dosage of the hybrid coagulant affects $\text{NH}_3\text{-N}$ pollutants more strongly than COD elimination. Notably, removal effectiveness dropped when the hybrid coagulant dosage was increased above the 1:1 (g/g) ratio. This decrease suggests

that there may have been a coagulant overload throughout the treatment, which could have reduced efficacy.

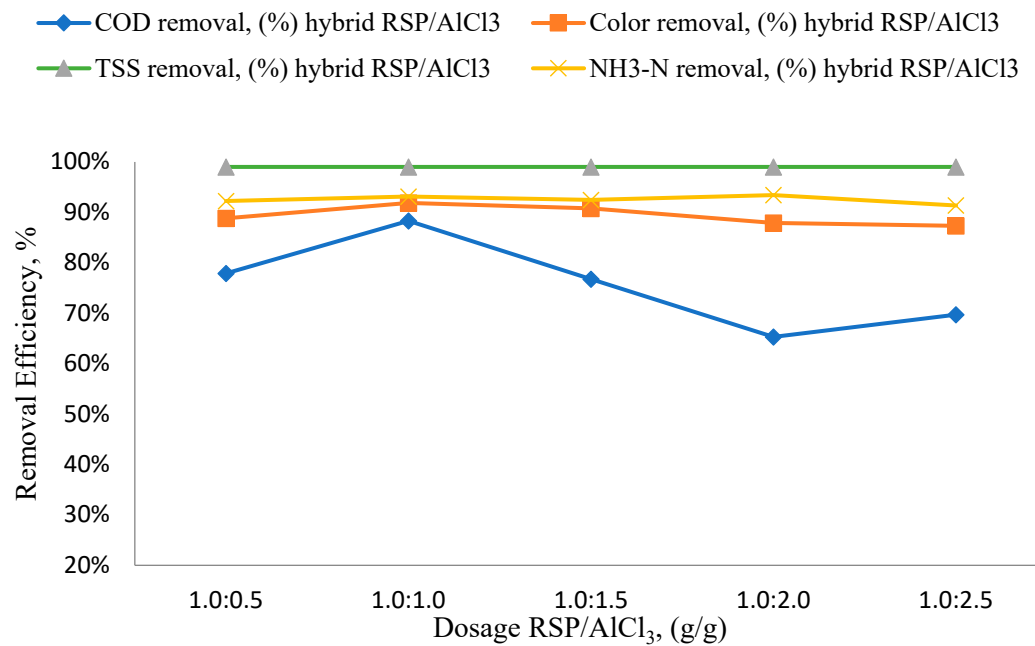


Figure 2. Impact of AlCl₃/RSP hybrid coagulant dosage on COD, color, TSS, and NH₃-N elimination (pH: 8).

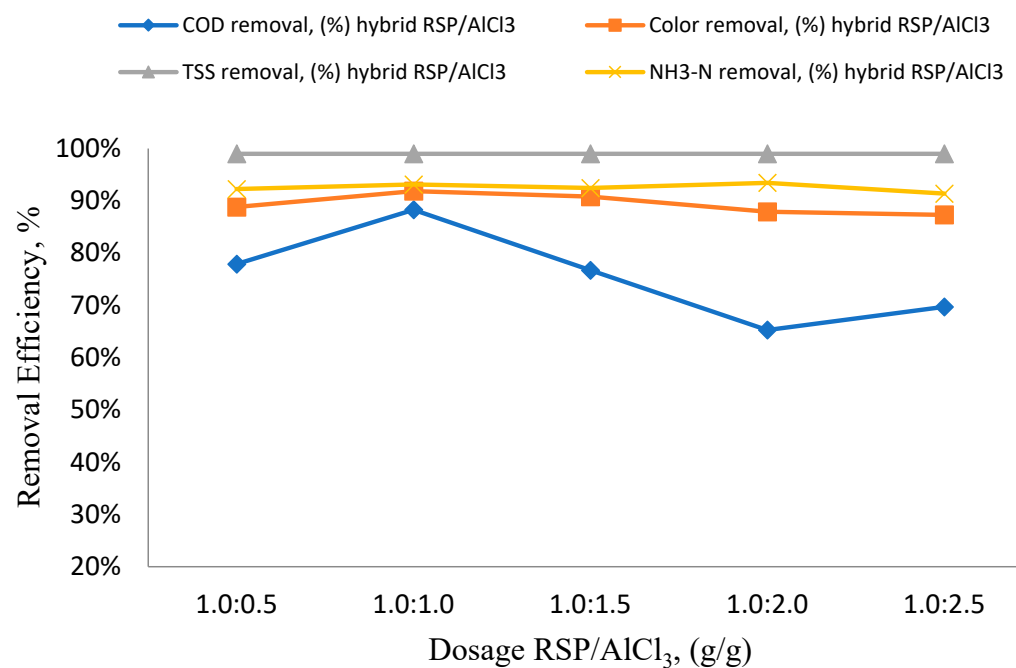


Figure 3. Comparison of the effects of RSP and RSP/AlCl₃ dosages on the removal of COD, color, TSS, and NH₃-N (pH: 8).

In general, it is important to remember that the quantity of adsorption sites that are available for bridging colloidal particles gradually decreases as the dose of AlCl₃ increases. This decrease happens because of AlCl₃'s propensity to coat the natural coagulant's surface and reduce the number of sites that can be used for efficient bridging. This result causes a considerable drop in total removal efficiency, as seen in Figure 2 and validated by another study [29,30].

Figure 4 provides a visual representation of the optimal dosage of the hybrid coagulant identified in our study, which was determined to be 1:1 (g/g). This ratio achieved the highest levels of efficiency in removing various contaminants from wastewater. The removal efficiencies at this optimal dosage were as follows: 94.3% for manganese (Mn), 98.5% for iron (Fe), 96.7% for zinc (Zn), 73.7% for aluminum (Al), and 99.3% for nickel (Ni). Figure 4 highlights the effectiveness of the 1:1 (g/g) coagulant dosage in addressing a range of contaminants, demonstrating that this ratio is particularly effective in optimizing the removal process. The substantial removal efficiencies achieved for each contaminant underscore the efficacy of the hybrid coagulant at this specific dosage. This study's findings revealed an interesting trend in the context of varying RSP/AlCl₃/dosages and their influence on the removal efficiencies of specific heavy metals, including Mn, Fe, Al, Ni, and Zn. Remarkably, for manganese, iron, aluminum, and nickel, RSP/AlCl₃ dosage alterations had no discernible effects on their removal efficiencies. These removal rates remained relatively consistent across the investigated range of dosages, highlighting the robustness and reliability of the hybrid coagulation process for these elements. Conversely, the removal efficiency of zinc (Zn) exhibited sensitivity to variations in RSP/AlCl₃ dosages. Specifically, as the RSP/AlCl₃ dosage increased from 1:1 to 1:2 (g/g), the Zn removal efficiency experienced a notable decline, decreasing from an impressive 96% to a reduced but still considerable 61%. This distinct behavior observed in Zn removal emphasizes the nuanced interplay between coagulant dosages and the removal of specific heavy metals. While the hybrid coagulant system remained highly effective in removing Mn, Fe, Al, and Ni across the range of dosages, Zn removal efficiency was notably affected by higher RSP/AlCl₃ dosages. This observation provides valuable insights into the selective removal of heavy metals. It underscores the importance of optimizing dosages for each target pollutant, contributing to a more tailored and efficient industrial wastewater treatment process.

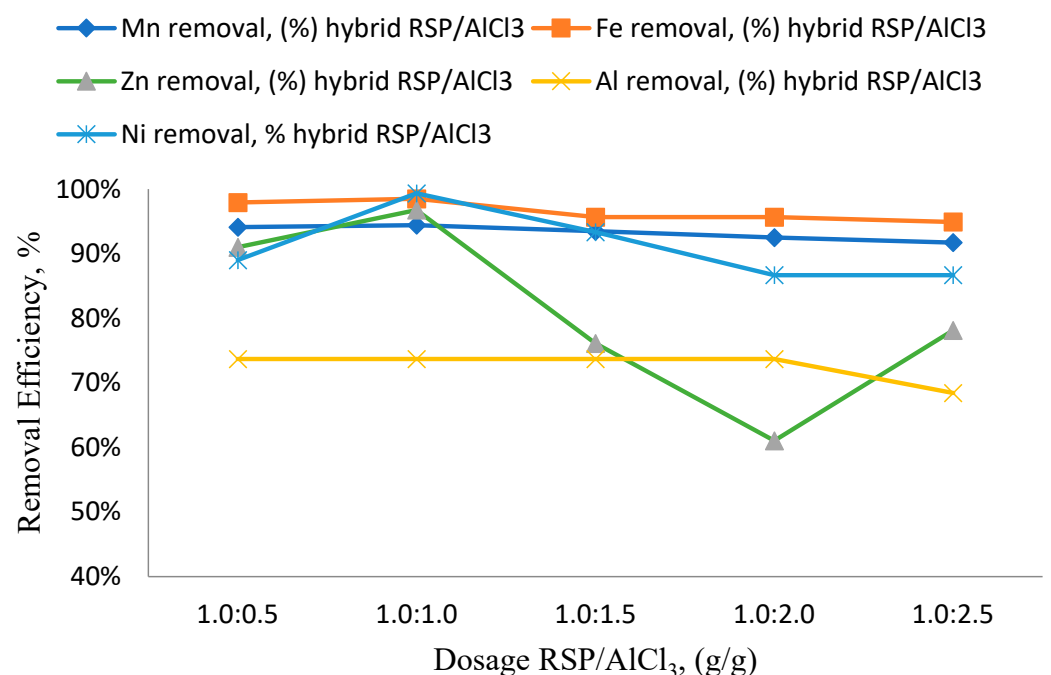


Figure 4. Impact of RSP/AlCl₃ hybrid coagulant dosage on the removal of heavy metals Fe, Mn, Al, Zn, and Ni (pH: 8).

Upon comparing these findings with the removal efficiencies achieved using RSP as a standalone coagulant, as reported in [12], the data demonstrate that the application of the hybrid coagulant led to notable increases in removal efficiency, which varied from 6.1% to 10% based on the particular parameter assessed. Significant improvements were seen in the elimination of zinc (Zn), manganese (Mn), and iron (Fe) when comparing the efficacy of the

ideal hybrid dosage of 1:1 (g/g) with the use of RSP alone. In particular, a rate of 94.4% was attained by an astounding 10% improvement in Mn removal efficiency. In a similar vein, the removal efficiencies of Zn and Fe also increased by around 7% to 98.49% and 96.76%, respectively. These results highlight the hybrid coagulant dosage's significant beneficial effects on the elimination of pollutants containing Mn, Fe, and Zn. When compared to RSP alone, the hybrid coagulant's improved removal efficiencies show how effective it is in greatly increasing the removal of these components.

Conversely, the enhancements in removal efficiency seen for manganese (Mn), iron (Fe), and zinc (Zn) were significantly greater than those for nickel (Ni) and aluminum (Al). Even while the improvements in the elimination of Ni and Al were not as significant, they nevertheless showed a modestly favorable effect of the hybrid coagulant dose on these metals. Nevertheless, no additional gains in the removal efficiencies of Fe, Mn, Al, Zn, or Ni were found when other hybrid doses were examined. The finding that the ideal hybrid dosage of 1:1 (g/g) is the most effective for maximizing the elimination of these pollutants is supported by the absence of any further benefits. These data suggest that the removal efficiencies for aluminum (Al) and nickel (Ni) were not significantly improved by employing various hybrid doses in comparison to RSP alone. But the particular hybrid dosage of 1:1 (g/g) led to a significant improvement in these components' elimination efficiency. This result emphasizes that the best removal efficiencies of manganese (Mn), iron (Fe), and zinc (Zn) can be obtained by using a dosage of 1:1 (g/g). According to the findings, the elimination of Mn, Fe, and Zn pollutants is efficiently targeted by this specific dosage combination, which considerably improves the overall efficacy of therapy.

3.2. Effects of Different RSP/AlCl₃ Hybrid Natural and Chemical Coagulant Ratios on Particular Parameters

The efficacy of different hybrid coagulant concentrations in the coagulation–flocculation process was comprehensively examined in this study. The concentration ratios that were looked at included intermediate values like 0.75:0.75, 1:1, 1.25:1.25, 1.5:1.5, and 1.75:1.75, and they varied from 0.5:0.5 to 2:2 (g/g). A distinct pattern became evident, indicating that removal efficiency improved in tandem with an increase in the hybrid coagulant concentration ratio. According to this study, most of the concentration ratios that were examined produced favorable outcomes, significantly improving the removal of NH₃-N, color, TSS, and COD. This suggests that using the hybrid coagulant at larger doses often produced better results when treating these pollutants. Figure 5 shows the remarkable removal efficiencies that were obtained from this investigation: 87.4% for COD, 92.4% for color, 96.8% for NH₃-N, and 99.0% for TSS at the hybrid coagulant concentration ratio of 0.75:0.75 (g/g). These outcomes unequivocally show how successful the adsorption-bridging mechanism used in the therapy procedure was. The mechanism's successful implementation is shown by the high efficiencies obtained at this concentration ratio, highlighting its crucial role in improving the coagulation–flocculation process's overall performance.

In particular, this study focused on the removal of manganese (Mn), iron (Fe), zinc (Zn), aluminum (Al), and nickel (Ni) at a pH of 8. It also examined the effectiveness of a hybrid coagulant that combined RSP and aluminum chloride (AlCl₃) in treating wastewater from iron and steel (IS) companies. The results, as illustrated in Figure 6, suggest that a decrease in the removal efficiency of these heavy metals was caused by an increase in the dosage of the hybrid coagulant. A dosage ratio of 2.25:0.75 (g/g) produced the best removal efficiency, which led to significant removal rates of 99.8% for Fe, 97.4% for Mn, 99.0% for Al, 87.5% for Zn, and 93.3% for Ni. Charge reversal is a phenomenon that can be brought about by using a high dosage of the hybrid RSP/AlCl₃ coagulant, as seen in Figure 6. The particles become stabilized because of this process, which lowers the effectiveness of heavy metal removal. To avoid this charge reversal and ensure efficient contamination clearance, it is imperative that the coagulant dosage be properly optimized.

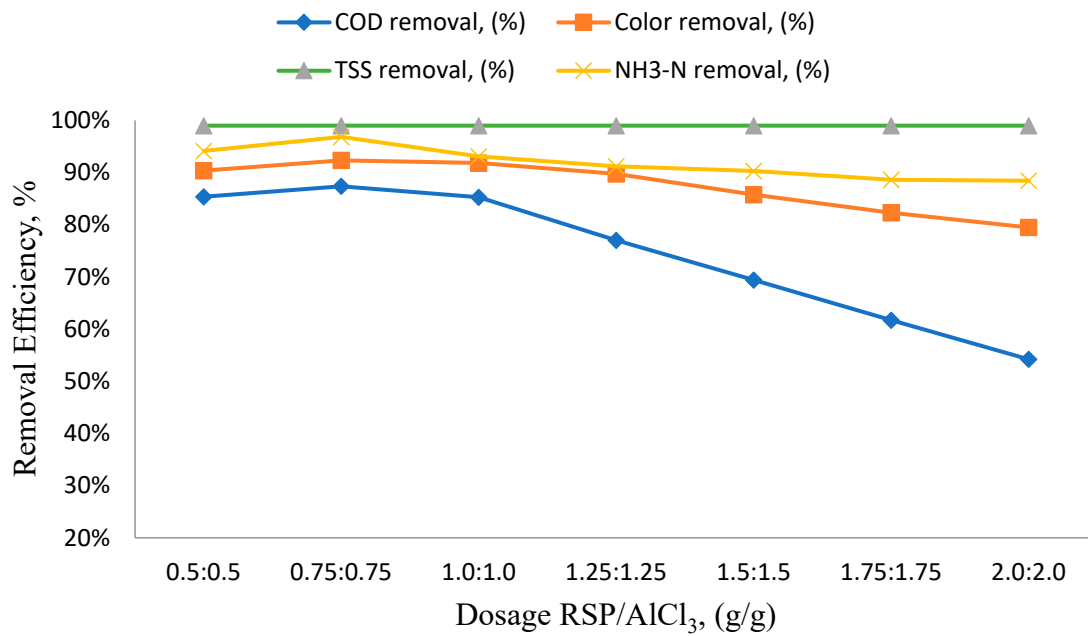


Figure 5. Impact of RSP/AlCl₃ hybrid coagulant dose concentration on the removal of COD, color, TSS, and NH₃-N (pH: 8).

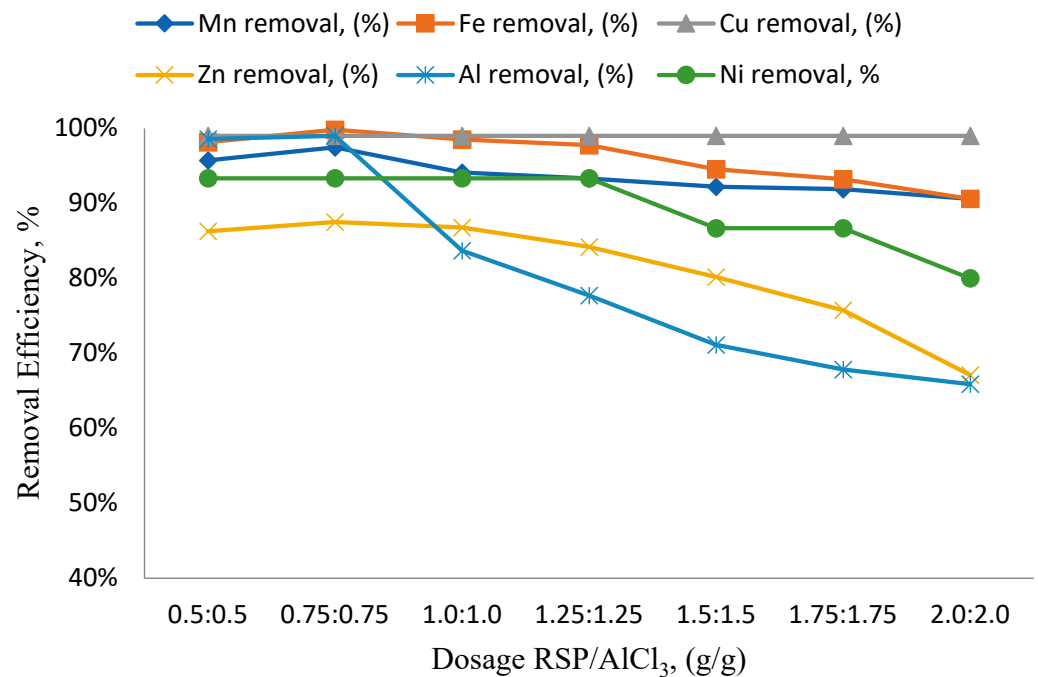


Figure 6. Impact of PSP/AlCl₃ hybrid coagulant dose concentration on the removal of Mn, Fe, Zn, Al, and Ni (pH: 8).

Therefore, this study identified the optimum hybrid RSP/AlCl₃ concentration as 0.75:0.75 (g/g). At this concentration, the removal efficiency for heavy metals exhibited a positive trend. Increasing the dosage beyond this point reduced removal efficiency due to the charge reversal phenomenon. This highlights the critical role of dosage optimization in effectively removing heavy metals from IS factory wastewater.

3.3. The Impact of pH Variation on the Efficiency of Removing Specific Parameters

The impact of pH on the coagulation process was rigorously examined by adjusting the pH levels of the wastewater across a comprehensive range spanning from pH 5 to pH 10.

To preserve the original composition of the industrial wastewater sample, as indicated in Table 2, the coagulation tests were carried out at room temperature. An RSP and AlCl_3 hybrid mixture was used in the studies, with a constant coagulant dose of 0.75:0.75 (g/g). Adjustments were carefully made using a 1 N $\text{H}_2\text{SO}_4/\text{NaOH}$ solution to provide exact pH control throughout the testing. The role of pH in the coagulation process is crucial, particularly in relation to the mechanisms of sweep-floc formation and adsorption-bridging. In this context, the polymer acts as a bridging agent, connecting the contaminants to the surface of AlCl_3 . This interaction facilitates the effective precipitation of the contaminants, enhancing the overall coagulation efficiency. The pH level significantly influences these mechanisms by affecting the charge characteristics of the coagulants and contaminants, thereby impacting the efficacy of the coagulation process.

This study revealed that the coagulation process achieved its highest efficiency within a pH range of 7 to 8. Notably, at a pH of 8, the process demonstrated its peak performance, with removal efficiencies reaching 89.8% for COD, 92.9% for color, 99% for total suspended solids (TSS), and 74.3% for $\text{NH}_3\text{-N}$. The removal rates for COD and $\text{NH}_3\text{-N}$ showed a consistent increase with rising pH levels, peaking at this optimal pH. However, deviations beyond this optimal pH range led to a reduction in the removal efficiencies for COD and $\text{NH}_3\text{-N}$. This decline is attributed to the increased adsorption capacity of particles under neutral electric charges, as particles become less effective at bridging and precipitating contaminants when pH levels slightly exceed the optimal range. This phenomenon is consistent with observations reported in previous studies, highlighting the importance of maintaining pH within the optimal range for effective coagulation [31].

Additionally, it was discovered that the cations in the wastewater played a critical role in enhancing the coagulation process. By neutralizing and stabilizing the negative charges connected to the coagulant's functional groups, they made a substantial contribution. More interactions between the cations and the RSP particles are made possible by this neutralization, which encourages more efficient flocculation and coagulation [32]. Remarkably, it was noted that when RSP was employed as the coagulant, there was no imperative requirement for pH adjustment throughout the treatment process, as delineated in Figure 7. This finding underscores the self-sufficient pH buffering properties of RSP, rendering additional pH modification unnecessary during the treatment course.

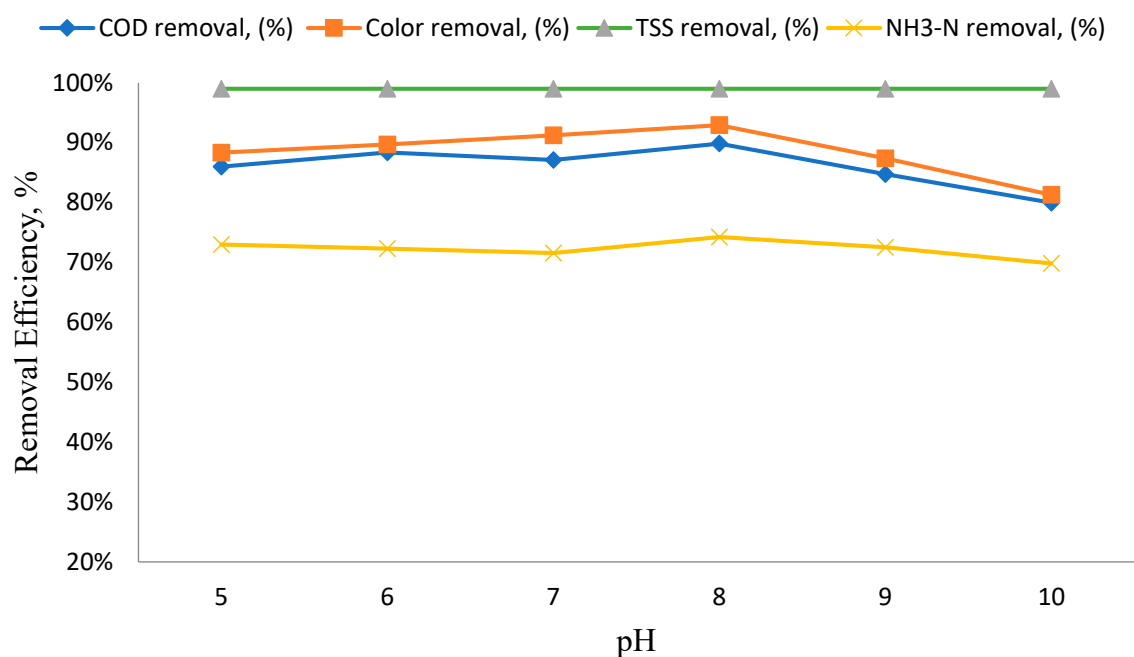


Figure 7. Impact of pH on the removal of COD, TSS, and ammonia–nitrogen ($\text{NH}_3\text{-N}$).

On the other hand, it was amply shown that pH 8 was found to be the ideal pH for the coagulation process. The use of the hybrid RSP/AlCl₃ coagulant significantly increased removal efficiency at this pH level. Specifically, utilizing the RSP/AlCl₃ coagulant, the removal efficiencies at pH 8 for Fe, Mn, Al, Zn, and Ni were 92.7%, 90.6%, 95.00%, and 92.3%, respectively. These results are graphically represented in Figure 8. This achievement can be partially attributed to the organic content of RSP, which was crucial in preserving the pH stability of the industrial effluent. Because RSP can naturally buffer pH, using the RSP/AlCl₃ coagulant during the treatment process decreased the need for external pH modifications. Fundamentally, the inherent properties of RSP expedited the entire treatment procedure by aiding in the effective elimination of contaminants and maintaining the proper pH balance for coagulation.

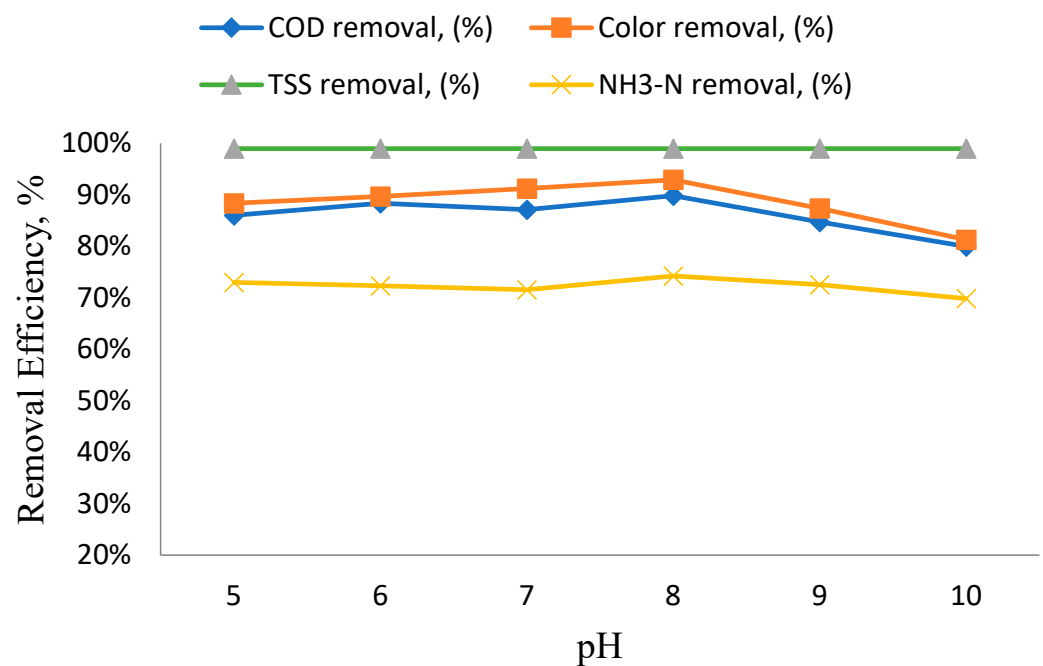


Figure 8. Impact of pH on Fe, Mn, Al, Zn, and Ni removal.

The results in Table 3 present a comparison of the performance of RSP alone, AlCl₃ alone, and the combined RSP/AlCl₃ process. Each process was evaluated based on its efficiency in removing COD, color, TSS, NH₃-N, Mn, Fe, Zn, and Ni. The removal efficiencies of both RSP- and AlCl₃-only processes were recorded slightly lower than those of the combined RSP/AlCl₃ process, which demonstrated the highest removal efficiencies for all parameters. This improvement in the combined process suggests synergistic effects between RSP and AlCl₃, potentially due to enhanced coagulation and flocculation processes. In summary, the combined RSP/AlCl₃ process showed enhanced performance in terms of COD and color removal, as well as the removal of various parameters including TSS, NH₃-N, and metal ions, compared to the individual processes. This suggests the synergistic effects of combining RSP and AlCl₃. In summary, the combined RSP/AlCl₃ process showed enhanced performance in terms of COD and color removal, as well as the removal of various parameters including TSS, NH₃-N, and metal ions, compared to the individual processes. This suggests the synergistic effects of combining RSP and AlCl₃.

Table 3. Comparison between the performance of AlCl₃ only and combined RSP/AlCl₃ for parameter removal.

Process	COD Removal (%)	Color Removal (%)	TSS Removal (%)	NH ₃ -N Removal (%)	Mn Removal (%)	Fe Removal (%)	Zn Removal (%)	Ni Removal (%)
RSP (1 g)	86.1%	82.9%	99.0%	79.0%	85.7%	90.7%	90.6%	78.0%
AlCl ₃ (1 g)	87.80%	84.00%	99.00%	88.60%	88.70%	91.50%	91.70%	88.80%
RSP/AlCl ₃ (0.75:0.75 g/g)	88.29%	91.85%	99.00%	93.11%	94.3%	98.5%	96.70%	99.30%

4. Conclusions

This study highlights the significant potential of a hybrid coagulation–flocculation process utilizing processed Rosehip Seed Powder (RSP) and aluminum chloride (AlCl₃) in treating industrial wastewater from the steel industry. Through extensive experimentation, it was determined that the optimal coagulant dosage is a 0.75:0.75 (g/g) ratio of RSP to AlCl₃, particularly effective under the pH 8 conditions typical of iron and steel industrial wastewater. This hybrid coagulant demonstrated high removal efficiencies across key parameters, with results showing 88.29% removal of COD, 91.85% for color, 99% for TSS, 93.11% for NH₃-N, and over 90% for heavy metals including Mn, Fe, Zn, and Ni. These findings are particularly significant as they suggest that no additional pH adjustment is necessary to achieve optimal pollutant removal. The high efficiency in removing heavy metals at pH 8—specifically, 94.3% for Mn, 98.5% for Fe, 96.7% for Zn, and 99.3% for Ni—emphasizes the efficacy of this hybrid approach. Furthermore, the results underscore the potential of integrating natural coagulants like RSP into conventional wastewater treatment methods, reducing reliance on chemical agents and contributing to more sustainable practices. The outcomes of this research not only demonstrate the viability of hybrid coagulation for the steel industry but also offer promising implications for future applications in other sectors where industrial effluents present significant environmental challenges.

Author Contributions: Conceptualization, M.S.S.A. and S.U.K.; methodology, S.S.A.A.; writing—original draft preparation, M.Y.D.A.; writing—review and editing, A.A. and D.E.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [Karabuk University] grant number [KBÜBAP-ABP-114] And The APC was funded by [Asharqiyah University].

Data Availability Statement: Dataset available on request from the authors.

Acknowledgments: The authors would like to express their sincere gratitude to all of the people and institutions whose kind assistance made this work possible. Particular gratitude is extended to the Scientific Research Projects Coordination Unit of Karabuk University in Turkey, which provided financing under the KBÜBAP-ABP-114 program. Furthermore, the assistance for this research is gratefully recognized by the Institute of International Education-Scholar Rescue Fund (IIE-SRF) in New York, NY, USA.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Abu Amr, S.S.A.; Abujazar, M.S.S.; Alazaiza, M.Y.D.; Albahnasawi, A.; Omer, F. Heavy metals removal from industrial wastewater using date seeds powder and aluminum chloride-based hybrid natural/chemical coagulation. *Desalin. Water Treat.* **2024**, *318*, 100392. [[CrossRef](#)]
2. Abujazar, M.S.S.; Karaagaç, S.U.; Abu Amr, S.S.; Alazaiza, M.Y.D.; Fatihah, S.; Bashir, M.J.K. Recent Advancements in Plant-Based Natural Coagulant Application in the Water and Wastewater Coagulation-Flocculation Process: Challenges and Future Perspectives. *Global Nest J.* **2022**, *24*, 687–705. [[CrossRef](#)]
3. Alazaiza, M.Y.D.; Alzghoul, T.M.; Amr, S.A.; Bangalore Ramu, M.; Nassani, D.E. Bibliometric Insights into Car Wash Wastewater Treatment Research: Trends and Perspectives. *Water* **2024**, *16*, 2034. [[CrossRef](#)]

4. Abujazar, M.S.S.; Karaağaç, S.U.; Abu Amr, S.S.; Fatihah, S.; Bashir, M.J.K.; Alazaiza, M.Y.D.; Ibrahim, E. The Effectiveness of Rosehip Seeds Powder as a Plant-Based Natural Coagulant for Sustainable Treatment of Steel Industries Wastewater. *Desalin. Water Treat.* **2022**, *270*, 44–51. [[CrossRef](#)]
5. Rivera, E.; Muñoz-Meneses, R.A.; Marín, L.; Mora, M.; Tabares, J.A.; Manotas-Albor, M.; Rodríguez, L.A.; Dios, J.E.; Mosquera-Vargas, E. Structural, Optical, and Magnetic Properties of Submicron Hematite ($\alpha\text{-Fe}_2\text{O}_3$) Particles Synthesized from Industrial Steel Waste. *Mater. Sci. Eng. B* **2023**, *288*, 116170. [[CrossRef](#)]
6. Bashir, M.J.K.; Sheen, O.S.; Ng, C.A.; Abujazar, M.S.S.; Alazaiza, M.Y.D.; Abu Amr, S.S. Advanced Treatment of Palm Oil Mill Effluent Using Thermally Activated Persulfate Oxidation. *Separations* **2022**, *9*, 171. [[CrossRef](#)]
7. Pratap, B.; Kumar, S.; Nand, S.; Azad, I.; Bharagava, R.N.; Romanholo Ferreira, L.F.; Dutta, V. Wastewater Generation and Treatment by Various Eco-Friendly Technologies: Possible Health Hazards and Further Reuse for Environmental Safety. *Chemosphere* **2023**, *313*, 137547. [[CrossRef](#)]
8. Gao, W.; Zhou, W.; Lyu, X.; Liu, X.; Su, H.; Li, C.; Wang, H. Comprehensive Utilization of Steel Slag: A Review. *Powder Technol.* **2023**, *422*, 118449. [[CrossRef](#)]
9. Ma, J.; Wu, G.; Zhang, R.; Xia, W.; Nie, Y.; Kong, Y.; Jia, B.; Li, S. Emulsified Oil Removal from Steel Rolling Oily Wastewater by Using Magnetic Chitosan-Based Flocculants: Flocculation Performance, Mechanism, and the Effect of Hydrophobic Monomer Ratio. *Sep. Purif. Technol.* **2023**, *304*, 122329. [[CrossRef](#)]
10. Patchaiyappan, A.; Sarangapani, S.; Saksakom, Y.A.; Devipriya, S.P. Feasibility Study of a Point of Use Technique for Water Treatment Using Plant-Based Coagulant and Isolation of a Bioactive Compound with Bactericidal Properties. *Sep. Sci. Technol.* **2020**, *55*, 112–122. [[CrossRef](#)]
11. Abdullayev, E.; Vakili, A.H.; Amr, S.S.A.; Karaağaç, S.U.; Alazaiza, M.Y.D. Navigating heavy metal removal: Insights into advanced treatment technologies for wastewater: A review. *Global Nest J.* **2024**, *260*, 06247. [[CrossRef](#)]
12. Abu Amr, S.S.; Abujazar, M.S.S.; Karaağaç, S.U.; Mahfud, R.; Alazaiza, M.Y.D.; Hamad, R.J.A. Application of Plant-Based Natural Coagulant for Sustainable Treatment of Steel and Iron Industrial Wastewater, Karabuk, Turkey. *Desalin. Water Treat.* **2023**, *287*, 39–45. [[CrossRef](#)]
13. Kristianto, H. Recent Advances on Magnetic Natural Coagulant: A Mini Review. *Environ. Technol. Rev.* **2021**, *10*, 255–270. [[CrossRef](#)]
14. Mehdinejad, M.H.; Bina, B. Application of Moringa Oleifera Coagulant Protein as Natural Coagulant Aid with Alum for Removal of Heavy Metals from Raw Water. *Desalin. Water Treat.* **2018**, *116*, 187–194. [[CrossRef](#)]
15. Leiviskä, T.; Santos, S.C.R. Purifying Water with Plant-Based Sustainable Solutions: Tannin Coagulants and Sorbents. *Groundw. Sustain. Dev.* **2023**, *23*, 101004. [[CrossRef](#)]
16. Badawi, A.K.; Salama, R.S.; Mostafa, M.M.M. Natural-Based Coagulants/Flocculants as Sustainable Market-Valued Products for Industrial Wastewater Treatment: A Review of Recent Developments. *RSC Adv.* **2023**, *13*, 19335–19355. [[CrossRef](#)]
17. Wang, D.; Chen, L.; Li, T.; Chang, X.; Ma, K.; You, W.; Tan, C. Successful Prediction for Coagulant Dosage and Effluent Turbidity of a Coagulation Process in a Drinking Water Treatment Plant Based on the Elman Neural Network and Random Forest Models. *Environ. Sci.* **2023**, *9*, 2263–2274. [[CrossRef](#)]
18. Elemile, O.O.; Eze, N.E.; Ogedengbe, K. Effectiveness of Moringa Oleifera and Blends of Both Alum and Moringa as Coagulant in the Treatment of Dairy Wastewater. *IOP Conf. Ser. Mater. Sci. Eng.* **2021**, *1036*, 012007. [[CrossRef](#)]
19. Fauzani, D.; Handajani, M.; Notodarmojo, S.; Helmy, Q.; Kardiansyah, T. The Synthesis and Use of Bio-Based Flocculant from Boehmeria Nivea in Coagulation-Flocculation and Direct Flocculation of Kaolin Suspension. **2023**. [[CrossRef](#)]
20. El Bouaidi, W.; Libralato, G.; Tazart, Z.; Enaime, G.; Douma, M.; Ounas, A.; Yaacoubi, A.; Lofrano, G.; Carotenuto, M.; Saviano, L.; et al. Nature-based Coagulants for Drinking Water Treatment: An Ecotoxicological Overview. *Water Environ. Res.* **2022**, *94*, e10782. [[CrossRef](#)]
21. Veli, S.; Arslan, A.; Isgoren, M.; Bingol, D.; Demiral, D. Experimental Design Approach to COD and Color Removal of Landfill Leachate by the Electrooxidation Process. *Environ. Chall.* **2021**, *5*, 100369. [[CrossRef](#)]
22. Zhang, H.; Ran, X.; Wu, X.; Zhang, D. Evaluation of electro-oxidation of biologically treated landfill leachate using response surface methodology. *J. Hazard. Mater.* **2011**, *188*, 261–268. [[CrossRef](#)] [[PubMed](#)]
23. Ramavandi, B.; Farjadfard, S. Removal of Chemical Oxygen Demand from Textile Wastewater Using a Natural Coagulant. *Korean J. Chem. Eng.* **2014**, *31*, 81–87. [[CrossRef](#)]
24. Shruthi Keerthi, D.; Mukunda Vani, M. Optimization Studies on Decolorization of Textile Wastewater Using Natural Coagulants. *Mater. Today Proc.* **2022**, *57*, 1546–1552. [[CrossRef](#)]
25. Owodunni, A.A.; Ismail, S. Revolutionary Technique for Sustainable Plant-Based Green Coagulants in Industrial Wastewater Treatment—A Review. *J. Water Process Eng.* **2021**, *42*, 102096. [[CrossRef](#)]
26. Ng, M.; Liu, S.; Chow, C.W.K.; Drikas, M.; Amal, R.; Lim, M. Understanding Effects of Water Characteristics on Natural Organic Matter Treatability by PACl and a Novel PACl-Chitosan Coagulants. *J. Hazard. Mater.* **2013**, *263*, 718–725. [[CrossRef](#)]
27. Silveira, J.E.; Zazo, J.A.; Pliego, G.; Bidóia, E.D.; Moraes, P.B. Electrochemical oxidation of landfill leachate in a flow reactor: Optimization using response surface methodology. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5831–5841. [[CrossRef](#)]
28. Karaağaç, S.U.; Abujazar, M.S.S.; Amr, S.S.A.; Fatihah, S.; Bashir, M.J.K.; Alazaiza, M.Y.D.; Ibrahim, E. The Potential Use of Olive Seeds Powder as Plant-Based Natural Coagulant for Sustainable Treatment of Industrial Wastewater. *Desalin. Water Treat.* **2022**, *270*, 44–51. [[CrossRef](#)]

29. Getahun, M.; Asaithambi, P.; Befekadu, A.; Alemayehu, E. Chemical oxygen demand removal from wet coffee processing wastewater using indigenous natural coagulants: Optimization through response surface methodology. *Desalination Water Treat.* **2024**, *317*, 100217. [[CrossRef](#)]
30. Besharati Fard, M.; Hamidi, D.; Alavi, J.; Jamshidian, R.; Pendashteh, A.; Mirbagheri, S.A. Saline Oily Wastewater Treatment Using Lallelantia Mucilage as a Natural Coagulant: Kinetic Study, Process Optimization, and Modeling. *Ind. Crops Prod.* **2021**, *163*, 113326. [[CrossRef](#)]
31. Schofield, P.; Mbugua, D.M.; Pell, A.N. Analysis of Condensed Tannins: A Review. *Anim. Feed. Sci. Technol.* **2001**, *91*, 21–40. [[CrossRef](#)]
32. Zainal, S.F.F.S.; Abdul Aziz, H.; Mohd Omar, F.; Alazaiza, M.Y.D. Sludge performance in coagulation-flocculation treatment for suspended solids removal from landfill leachate using Tin (IV) chloride and *Jatropha curcas*. *Int. J. Environ. Anal. Chem.* **2023**, *103*, 4716–4730. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.