

RESEARCH ARTICLE

HEAVY METAL REMOVAL FROM INDUSTRIAL WASTEWATER USING PINECONE SEED POWDER AND ALUMINUM CHLORIDE-BASED HYBRID NATURAL/CHEMICAL COAGULATION

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ABSTRACT

This study presents an innovative strategy that combines Pinecone Seed powder (PSP) with aluminum chloride ($AlCl_3$) to remove heavy metals from industrial wastewater. The objective was to fine-tune the utilization of PSP and $AlCl_3$, considering their quantities and the pH level, to ascertain the optimal conditions for the removal of heavy metal. The results show that a PSP/ $AlCl_3$ dose ratio of 3:1 (g/g) was the best, yielding outstanding remediation efficiency across a wide range of parameters, including COD, color, TSS, NH_3 -N, and heavy metals. Significantly, these efficiencies soared to 86.47%, 91.85%, 99.00%, 93.62%, 93.36%, 98.49%, 92.17%, 73.68%, and 93.3%, respectively, while maintaining a pH of 8. Interestingly, the investigation identified that refining the pH level led to extraordinary efficiency enhancements, notably obviating the necessity for pH adjustment. At pH 8, the removal efficiencies stood as follows: 86.78% for COD, 91.55% for color, 99% for TSS, 93.28% for NH_3 -N, 98.52% for Mn, 95.15% for Fe, 89.42% for Zn, 99.00% for Al, and 92.53% for Ni. This inquiry underscores the effectiveness and sustainability of the amalgamated PSP/ $AlCl_3$ coagulation technique for heavy metal removal from industrial wastewater. Extensive exploration remains imperative to gauge its scalability and potential constraints in full-scale implementation.

KEYWORDS

Coagulation; heavy metals; combined PSP/ $AlCl_3$; wastewater treatment

1. INTRODUCTION

The growth of socioeconomic behavior and the expansion of people, combined with the constricted availability of water due to climate change and human actions, have given rise to conflicts regarding the allocation of water resources (Yuan et al., 2023; Zuo et al., 2023; Morán-Valencia et al., 2023). Consequently, the task of managing water resources has grown increasingly intricate. The fast increase of industries contributed to a substantial effect in the worldwide spending of water (Ke et al., 2022). Notably, this industrial advancement has predominantly driven the expansion of chemical sectors, leading to an upsurge in water pollution problems across nations (Issakhov et al., 2023). The release of wastewater from these chemical industries constitutes a substantial origin of water contamination. Although industrial effluents usually undergo some treatment, their attributes differ based on the specific production methods and raw materials. Generally, these effluents consist of suspended solids ranging from 300 to 400 mg/L (Ifeanyi et al., 2012). Furthermore, specific industries discharge highly polluted wastewater containing organic contaminants and heavy metals (Mao et al., 2022).

Various technologies have been devised to tackle this challenge, and notably, the coagulation-flocculation method has surfaced as the prevalent and economically viable strategy for treating wastewater (Metin and Çifçi, 2023). Other alternative technologies encompass adsorption membrane filtration, ion exchange (Chakraborty et al., 2022) advanced oxidation processes and more (Tan et al., 2022; Elmoutez et al.,

2023; Lanzetta et al., 2023). Hence, a pressing need exists to formulate efficient techniques to immobilize or eliminate heavy metals, aiming to curtail their adverse impacts (Ifeanyi et al., 2012). The coagulation-flocculation procedures have captured substantial technical attention owing to their impressive efficiency, cost-effectiveness, simplicity of deployment, and the diverse array of coagulants accessible (Abujazar et al., 2023). Numerous industries, including textiles, iron and steel, chemicals, pharmaceuticals, and petrochemicals, use different methods in wastewater treatment (Ejimofo et al., 2020).

There are numerous uses for coagulation-flocculation procedures in wastewater treatment that use strongly positively charged metallic coagulants such ferric sulfate, aluminum sulfate, and ferric chloride (Pang et al., 2011; Abujazar et al., 2022; Abujazar et al., 2022). Nonetheless, this strategy has certain drawbacks, such as the high cost of importing chemicals, the production of a large amount of sludge, and variations in the pH level of the effluent water (Abujazar et al., 2022).

Owing to the difficulties mentioned above, using natural coagulants instead of inorganic chemicals in coagulation operations has become a practical method for handling a variety of industrial effluent (Owodunni and Ismail, 2021). Several studies have been directed toward the use of natural coagulants that could be extracted from plants to solve the global water crisis. Recent studies have underscored the importance of natural coagulants like dates seeds, water hyacinth, moringa seeds, locust bean seeds, olive seeds, rosehip seeds, and other substances (Abujazar et al., 203; Sciban et al., 2005; Yongabi, 2010; Karaağaç et al., 2022; Abujazar et

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al., 2022; Abujazar et al., 2022; Madrona et al., 2017). All of these natural coagulants have shown a high performance in wastewater treatment.

Moreover, natural coagulants stand as environmentally friendly options that do not impose harm on ecosystems. Furthermore, bio-coagulants exhibit greater cost-effectiveness than chemical coagulants, which is considered as easy treatment method (Yang et al., 2019). There is a concentrated effort to develop an effective organic-inorganic hybrid strategy that enhances the performance of the inorganic coagulant because natural coagulants are superior to inorganic chemical agents, which interact with the inorganic coagulant chemically or physically (El-Gaayda et al., 2021; Iloamaeke and Julius, 2019). This hybrid framework elevates floc aggregation capacity by introducing innovative natural polymeric materials (Owodunni et al., 2023; Shabanizadeh and Taghavijeloudar, 2023).

Aligned with this view, the current investigation evaluated the efficacy of a hybrid coagulation process combining natural and chemical wastewater treatment agents. The primary goal was to identify the optimal pH and dosage requirements necessary to achieve the most optimal performance of the recently developed Pinecone Seed Powder and Aluminum Chloride based hybrid natural/chemical coagulation (PSP/AlCl₃) in the coagulation process. This endeavor aimed to produce high-quality treated water for reuse in an iron and steel factory. The methodology involved the incorporation of PSP as a natural coagulant, capitalizing on its inherent coagulation properties, and the use of AlCl₃ as a chemical coagulant. The study aimed to optimize the combined effects and increase the efficiency of treating iron wastewater by utilizing the synergy formed by these coagulants. In addition to evaluating the performance of the hybrid coagulant, a comparative analysis was conducted between the application of PSP alone and the hybrid approach involving PSP/AlCl₃. This comparative assessment focused on assessing pollutant and heavy metal removal efficacy.

2. MATERIALS AND METHODS

2.1 Source of Wastewater and Sample Collection

Wastewater samples were collected from the industrial factory in Karabuk City, Turkey. The grab sampling method was used to collect the samples without any dilution, where the samples were stored in a refrigerator at 4°C after collection to avoid any change in samples characteristics. Comprehensive details regarding the wastewater's composition can be found in Table 1. 1 N H₂SO₄/NaOH solution was used for pH monitoring during samples test.

Table 1: Characteristics Of Raw Wastewater		
Industrial wastewater parameters	results	Unit
pH	8	--
Color	865.6	Pt-Co
TSS	110	mg/L
COD	840.24	mg/L
NH ₃ -N	42.8	mg/L
Manganese	6.27	mg/L
Iron	5.30	mg/L
Zinc	5.44	mg/L
Aluminum	0.38	mg/L
Nickel	0.15	mg/L

2.2 Pinecone Seed Powder (PSP) Natural Coagulant Preparation

Carefully selected Pinecone Seeds were gathered from a forest near Karabuk University in Turkey. To ensure their purity, these seeds underwent a meticulous rinsing process using distilled water, eliminating any adhering flesh. For complete desiccation, the seeds were initially air-dried at room temperature and then subjected to an eight-hour drying period in an oven, maintained at a constant temperature of 50 ± 1°C. Following the manual removal of husks, the seeds were finely ground with the assistance of a laboratory mortar, resulting in finely divided particles. This pulverized material was refined using a grinder (specifically, the Retsch RS 200) to yield a consistent and homogeneous powder called Pinecone Seed Powder (PSP). This uniformly textured PSP was employed as a natural coagulant in the wastewater treatment process detailed in the study (refer to Fig.1 for an illustration).



Figure 1: Pinecone Seed and powder

2.3 Chemicals

All the chemicals used in this study were procured from Sigma-Aldrich Chemical Co. (St Louis, MO, USA).

2.4 Coagulation Experiments

Orbital shaker was used to conduct coagulation flocculation experiments. To evaluate the impact of hybrid coagulant, (3 g/L) dosage of pinecone seed (Karaağaç et al., 2022) was combined with several dosages of (AlCl₃) (0.5, 1, 1.5, 2, and 2.5 g). These dosages were mixed with one liter of raw wastewater in 500 ml beakers. After that, 200 ml of the sample was slowly poured in a 500 ml beaker on the shaker plate.

Samples were mixed gently at a rate of 200 rpm for 5 minutes, followed by more soft mixing of 90 rpm for 30 minutes. The beakers were then left to settle for half an hour. Using Whatman filter paper, contaminants were removed to produce a clear sample. The effectiveness of the different parameters, such as COD, TSS, NH₃-N, and the presence of heavy metals, was then assessed using this treated sample. The initial pH of the wastewater sample taken from the iron and steel industry was 8, which is also the pH at which these studies were carried out. A hybrid technique was used in this work, integrating a chemical coagulant AlCl₃ and a natural coagulant (processed PSP) at varying doses.

Additionally, the pH level was recognized as a pivotal variable. For each combination of the natural and chemical coagulants at their respective optimal concentrations, the pH was modulated to a spectrum of values from 4 to 11. This pH modulation was accomplished using either 0.1 N NaOH or H₂SO₄. For each combination of the natural and chemical coagulants at their respective optimal concentrations, the pH was modulated to a spectrum of values from 4 to 11. This pH modulation was accomplished using either 0.1 N NaOH or H₂SO₄.

2.5 Analytical Methods

The effectiveness of the hybrid coagulation/flocculation process was assessed by analyzing several crucial parameters, including COD, TSS, NH₃-N, and the concentration of heavy metals present in the original pH (8) of the raw wastewater. All tests were measured using analytical techniques followed the Standard Method of Water and Wastewater, as detailed in Table 2. Throughout the experimentation, the pH levels of the samples were meticulously controlled using a 1 N H₂SO₄/NaOH solution (Veli et al., 2021).

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
Mn (mg/L)	TS EN ISO 11885
Fe (mg/L)	TS EN ISO 11885
Zn (mg/L)	TS EN ISO 11885
Al (mg/L)	TS EN ISO 11885
Ni (mg/L)	TS EN ISO 11885

To calculate the removal efficiency, Equation 1 was used. This formula considers both the initial concentration of the untreated industrial

wastewater sample and the industrial wastewater's concentration after treatment.

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

where C_i was the initial concentration before treatment, and C_f was the final concentration after treatment of each parameter

3. RESULTS AND DISCUSSION

3.1 Effect of PSP/ AlCl_3 Dosages

To comprehensively assess the impact of hybrid coagulation on treatment efficiency, several dosages of the hybrid coagulant were applied during wastewater treatment. This series of experiments involved the utilization of the best dosage of Pinecone Seed Powder coagulant (3 g/L) combined with varying quantities of AlCl_3 as mentioned earlier, all incorporated into 1 liter of raw wastewater (Abujazar et al., 2022). These mixtures were vigorously agitated on the shaker, employing the conditions detailed in section 2.3 to pinpoint the dosage that yields the highest removal efficiency. As underscored it is crucial to recognize that the surface charge of the coagulant can significantly influence coagulation performance, mainly because of its mass (Ramavandi and Farjadfar, 2014).

The coagulation process facilitated by this hybrid coagulant primarily engages in adsorption bridging mechanisms. Pinecone Seed Powder (PSP) operates through charge neutralization as its coagulation mechanism (Gheraout, 2020). In the PSP coagulation process context, a charge neutralization mechanism elucidates its function. Conversely, the AlCl_3 coagulant, as part of the remove coagulation mechanism, undergoes hydrolysis upon introduction into the water sample.

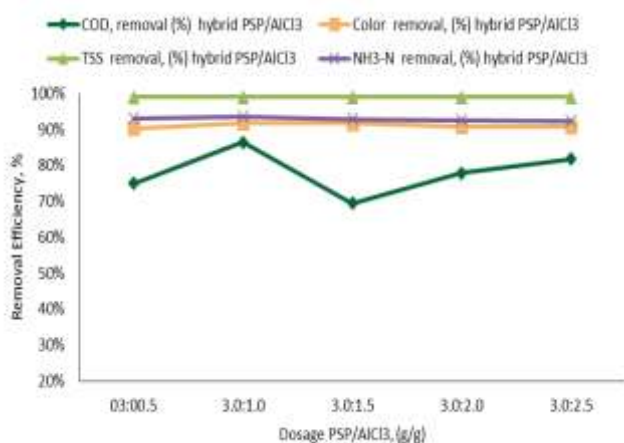


Figure 2: Impact of PSP/ AlCl_3 dose on the removal of different parameters at pH = 8

Figure 2 shows that high removal efficiencies were achieved at pH = 8 where the maximum removal were 86.47% for COD, 91.85% for color, 99.00% for TSS, and 93.62% for $\text{NH}_3\text{-N}$, respectively. These exceptional efficiencies were attained with PSP/ AlCl_3 dosage of 3:1 (g/g), using pH of 8. In a comparison to the removal efficiency achieved when using only PSP, as reported in it was evident that the hybrid coagulant has a notable improvement in removal, increasing from 3.1% to 9.7%, contingent upon the specific parameter, as depicted in Fig. 3. Particularly noteworthy was the substantial 8.3% improvement in color removal efficiency achieved with a hybrid dosage of 3:1 (g/g), in contrast to using PSP alone (Hamza and Ramadan, 2023).

Similarly, the efficacy of COD reduction exhibited a noticeable rise of 3.1% using the same PSP/ AlCl_3 dosage, again compared to the use of PSP in isolation. Conversely, the boost in $\text{NH}_3\text{-N}$ removal was relatively higher, registering an impressive 9.7% increase when employing the PSP/ AlCl_3 dosage of 3:1 (g/g). This implies that the impact of the hybrid dosage was notably more pronounced on $\text{NH}_3\text{-N}$ removal when compared to COD removal. It is worth noting that exceeding the PSP/ AlCl_3 coagulant dosage of 3:1 (g/g) resulted in a reduction in removal efficiency, attributed to an overloading of the coagulant. Since AlCl_3 covers the surface of the natural coagulant, increasing the dosage generally decreases the number of adsorption sites accessible for colloidal particle bridging. Removal effectiveness is decreased by this phenomenon as elucidated in Fig. 2 (Aghyani, 2023; Izquierdo et al., 2023; Asadi-Ghalhari et al., 2023).

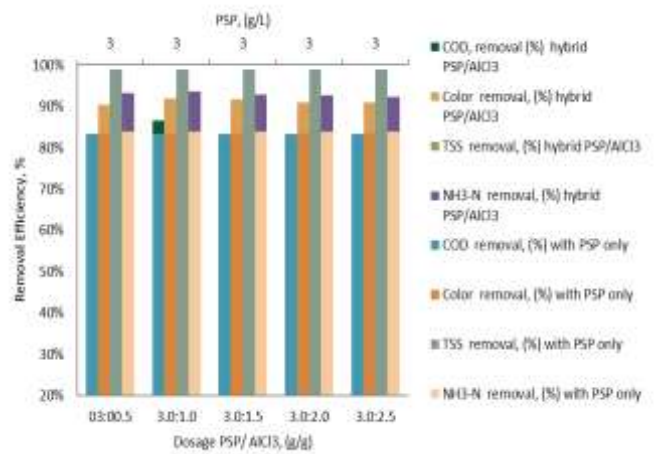


Figure 3: PSP and PSP/ AlCl_3 effect on the removal of different parameters at pH=8

Figure 4 illustrates the suggested optimal PSP/ AlCl_3 coagulant dosage of 3:1 (g/g), which yielded the most substantial removal effectiveness: 93.36% for Mn, 98.49% for Fe, 92.17% for Zn, 73.68% for Al, and 93.3% for Ni, respectively.

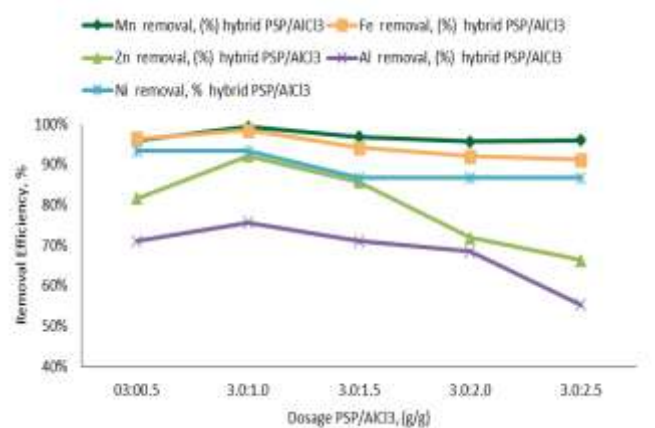


Figure 4: Impact of PSP/ AlCl_3 dose on heavy metal removal at pH= 8

When comparing these findings with the behavior of PSP only, as documented in (Hamza, Ramadan, 2023) it becomes evident that the PSP/ AlCl_3 coagulant engendered an appreciable increase in removal efficiency, spanning a range from 2.5% to 13%, contingent upon the specific parameter, as delineated in Fig. 5. In particular, when assessing the performance of the recommended hybrid dosage of 3:1 (g/g) in comparison to PSP mono coagulant application, substantive augmentations were discerned in the removal efficiencies of Mn, Al, and Ni. Notably, Mn removal efficiency exhibited a remarkable augmentation of 13.2%, surmounting 94.1%, while Ni removal efficiency experienced an ascent of 9%, attaining 93.3%. Al removal efficiency showcased an elevation of 14%, reaching 88.42%. This signifies a significant affirmative influence of the hybrid dosage on the removal of Mn and Ni, leading to elevated removal efficiencies for these metallic elements.

In contrast, the improvement in removal efficiency for Zn and Fe were quite more moderate. The removal of Fe displayed a moderate enhancement of 3.6%, while Zn removal was rose by 0.94%. Although these improvements were less pronounced than those observed for Al, Mn, and Ni, they still denoted a slightly beneficial effect of the PSP/ AlCl_3 dosage on removing these metallic constituents. Notably, the removal efficiencies of Mn, Fe, Zn, Al, and Ni did not exhibit any enhancements when applying hybrid dosages other than the recommended optimum dosage of 3:1 (g/g). This underscores the efficacy of the 3:1 (g/g) PSP/ AlCl_3 dosage as the most effective. It implies that for alternative hybrid dosages, the removal efficiencies for Fe and Zn did not experience enhancement compared to using PSP in isolation. However, the precise hybrid dosage of 3:1 (g/g) culminated in noteworthy enhancements in the removal efficiencies of these metallic elements. This accentuates that the 3:1 (g/g) hybrid dosage is definitively established as the optimal dosage, effectively targeting the removal of Fe and Zn contaminants and ending in improved effluents.

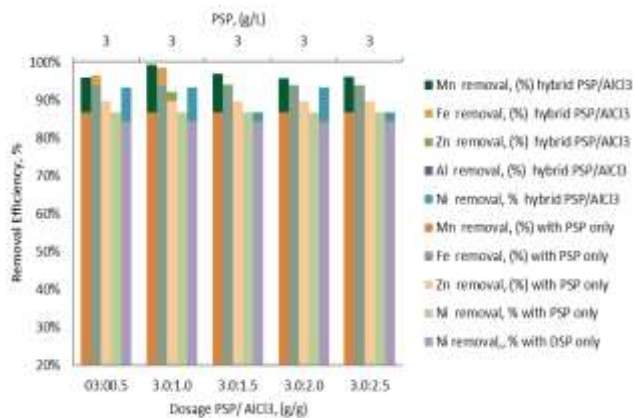


Figure 5: PSP and PSP/ AlCl_3 doses effect on heavy metals removal at pH=8

3.2 Impact of PSP/ AlCl_3 ratio on Removal Efficiency

Several concentration ratios, including 1.5:0.5, 2.25:0.75, 3/1, 3.75:0.125, 4.5:1.5, 3.25:1.75, and 6:2 (g/g) were used in this study. It was noted that the application of PSP/ AlCl_3 exhibited a marked and positive correlation between removal efficiency and the concentration ratio of the PSP/ AlCl_3 coagulant.

Overall, a substantial portion of the distinct concentration ratios for the PSP/ AlCl_3 coagulant demonstrated better performance in removal. Specifically, using the concentration ratio of 2.25:0.75 (g/g), yielded notably favorable results, achieving removal efficiencies of 88.0% for COD, 93.75% for color, 99% for TSS, and 94.08% for $\text{NH}_3\text{-N}$, as represented in Fig. 6. These results substantiate the operation of an efficient adsorption-bridging mechanism within the hybrid coagulation process, where the increased concentration of the hybrid coagulant is correlated with improved removal efficiencies for the evaluated parameters.

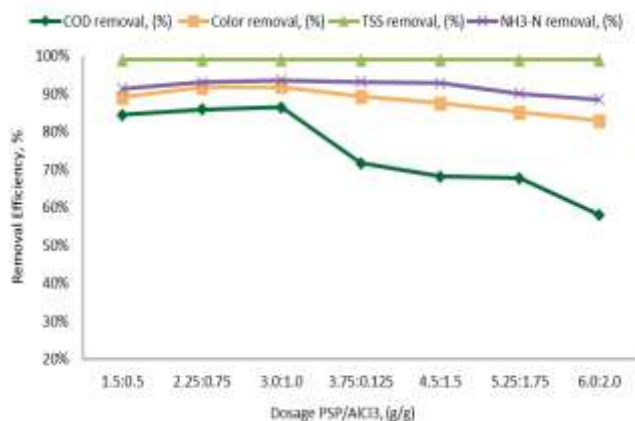


Figure 6: Impact of PSP/ AlCl_3 doses on the removal of different parameters at pH=8

The investigation delved into the effectiveness of the PSP/ AlCl_3 coagulant, combining PSP and AlCl_3 for wastewater treatment. This analysis emphasized removing heavy metals while maintaining a pH level of 8. The findings presented in Fig. 7 illuminate an intriguing trend: the removal effectiveness of these heavy metals exhibit a reducing pattern as the dosage of the AlCl_3 coagulant escalates.

Notably, most remarkable removal efficiencies, notable in their magnitude, were seen at a specific dose ratio of 3:1 (g/g). These figures are noteworthy, with Mn exhibiting an astounding removal efficiency of 99.52%, Fe reaching a substantial 94.15%, Zn attaining 88.42%, Al achieving a commendable 99.00%, and Ni recording a noteworthy 93.33% removal efficiency. The discernible reduction in removal efficiencies with an excessive dosage of the hybrid PSP/ AlCl_3 coagulant can be attributed to a phenomenon known as charge reversal. This results in the destabilization of particles within the wastewater. An excessive coagulant concentration introduces an excess of oppositely charged ions, which neutralize the charges on the suspended particles. This charge neutralization causes the particles to repel rather than agglomerate,

ultimately diminishing their removal efficiency.

Consequently, it becomes apparent that an optimal balance must be struck in coagulant dosage to ensure optimal removal of heavy metals. The investigation's findings substantiate the selection of a specific hybrid PSP/ AlCl_3 concentration of 3:1 (g/g) as the most efficacious. This specific dosage achieved the highest removal efficiencies for heavy metals while steering clear of the diminishing returns associated with excessive coagulant dosages. It is worth noting that this optimal dosage strategy demonstrates the potential for an enhanced heavy metal removal process, addressing the intricacies of charge interactions within the wastewater treatment framework.

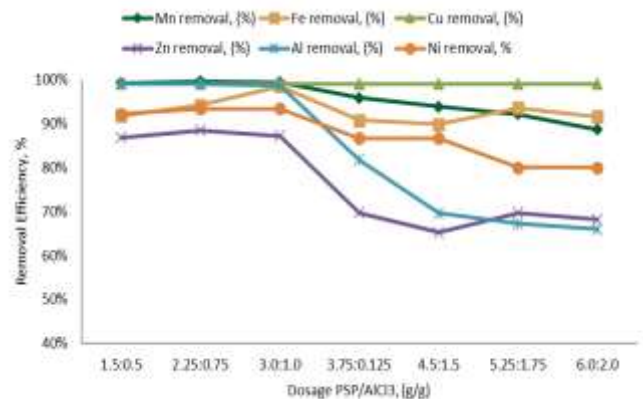


Figure 7: Impact of PSP/ AlCl_3 on heavy metal removal at pH=8

3.3 Impact Of Different pH On Removal Efficiency

Examining pH's influence on the coagulation process entailed a meticulous exploration involving adjustments to the pH levels of the wastewater, covering the range from pH 5 to 10. A consistent coagulant dosage of 3:1 (g/g) of PSP/ AlCl_3 was controlled.

The role of pH in the coagulation process is of substantial significance, invoking intricate mechanisms such as adsorption-bridging and sweep-floc generation. These mechanisms leverage the polymer as a bridging agent that facilitates the interaction between pollutants and the surface of AlCl_3 , ultimately promoting precipitation. The study revealed a pivotal pH range for optimal coagulation performance, notably from pH 7 to 8. At a precise pH value of 8, the removal efficiency demonstrated its zenith, with remarkable values of 86.78% for COD, 91.55% for color, 99% for TSS, and 93.28% for $\text{NH}_3\text{-N}$ removal. As the pH levels ascended within this range, the removal of COD and $\text{NH}_3\text{-N}$ exhibited progressive improvement, culminating in their maximum achievable removal efficiencies (El Gaayda et al., 2023).

An intriguing observation was the minimal need for pH change during the treatment when PSP was the coagulant, as explicitly demonstrated in Fig. 8. This observation underscores the versatility and suitability of PSP as a coagulant, effectively adapting to the pH conditions of industrial wastewater without necessitating external pH adjustments. It indicates the intrinsic charge-neutralizing capabilities of PSP particles and their adeptness at interacting with cations in the wastewater, thereby enhancing the coagulation process (Ting et al., 2022).

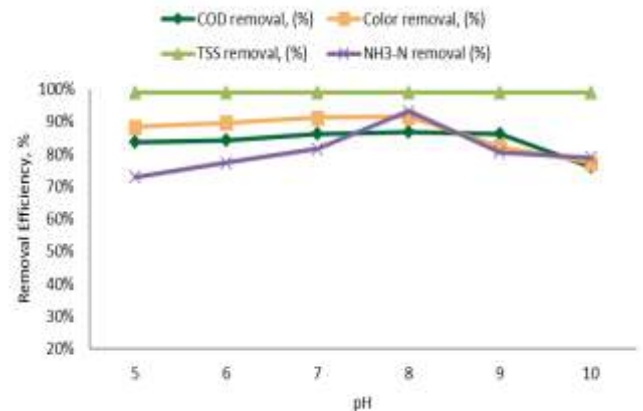


Figure 8: Impact of pH on COD, TSS, and $\text{NH}_3\text{-N}$ removal.

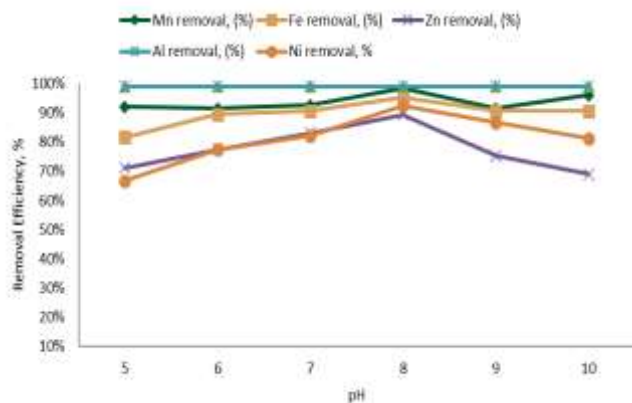


Figure 9: Impact of pH on heavy metal removal

Conversely, the investigation emphasized that the best pH condition for the coagulation achieved at pH 8, demonstrating that applying PSP/AlCl₃ coagulant significantly enhanced removal efficiencies. Precisely, under the pH condition of 8, the reductions achieved for Mn, Fe, Zn, Al, and Ni through the utilization of PSP/AlCl₃ manifested as follows: 98.52% for Mn, 95.15% for Fe, 89.42% for Zn, 99.00% for Al, and 92.53% for Ni, as visually delineated in Fig. 9. The organic composition inherent in PSP played a pivotal and multifaceted role in stabilizing the pH level within the industrial effluent. This intrinsic characteristic effectively obviated the need for pH adjustment during the treatment process when PSP/AlCl₃ served as the coagulant. It attests to the unique capacity of PSP to naturally modulate pH conditions within the wastewater, further enhancing its suitability as a coagulant for the treatment process.

4. CONCLUSION

The hybrid PSP/AlCl₃ coagulant has demonstrated significant promise as an effective solution for treating iron and steel mill wastewater. The empirical findings obtained in this study unequivocally emphasize the coagulation prowess of the hybrid PSP/AlCl₃ compound. The key takeaways from our research can be succinctly summarized as follows: The hybrid PSP/AlCl₃ coagulant exhibited remarkable efficiency in removing contaminants at a pH level of 8. Notably, it achieved impressive removal rates, including 86.47% for COD, 91.85% for color, 99.00% for TSS, and 93.62% for NH₃-N, thereby highlighting its efficacy in addressing a wide spectrum of pollutants. Moreover, the concentration of the hybrid coagulant was found to impact removal efficiency significantly. Specifically, the dosage of 3:1 (g/g) of hybrid PSP/AlCl₃ resulted in the highest removal efficiencies, with values such as 93.36% for Mn, 98.49% for Fe, 92.17% for Zn, 73.68% for Al, and 93.3% for Ni. This dosage optimization underscores the importance of precise coagulant dosing for optimal wastewater treatment outcomes.

Additionally, the study studied pH ranges from 5 to 10, revealing that the natural pH of the wastewater sample yielded the most favorable removal efficiencies. The coagulant was exceptionally effective at this pH level, achieving 86.78% for COD, 91.55% for color, 99% for TSS, and 93.28% for NH₃-N removal. Similarly, for crucial metals including Mn, Fe, Zn, Al, and Ni, the use of PSP/AlCl₃ resulted in substantial removal efficiencies, with values such as 98.52%, 95.15%, 89.42%, 99.00%, and 92.53%, respectively.

This natural pH compatibility is a noteworthy advantage, as it eliminates the need for pH adjustment during the wastewater treatment process, simplifying operational requirements. The hybrid PSP/AlCl₃ coagulant has demonstrated robust potential as an effective agent for wastewater treatment within the iron and steel industry. It has consistently delivered enhanced removal efficiencies across various contaminants and pH levels, making it a promising candidate for sustainable and efficient wastewater treatment processes. This research contributes to advancing wastewater treatment methods and underscores the practical applicability of the hybrid PSP/AlCl₃ coagulant in addressing the specific challenges posed by iron and steel mill effluents. Further exploration and application of this coagulant in real-world industrial settings are warranted to realize its environmental and economic benefits fully.

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