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Factorial design and optimization of pinecone seed powder as a natural coagulant for organic and heavy metals removal from industrial wastewater

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ABSTRACT

Various chemical coagulants have previously been used for wastewater treatment with substantial efficacy in eliminating heavy metals and other criteria. However, their economic effectiveness and the remnant of harmful chemical precipitates that pose hazards to human health and the environment. As a result, utilizing plant-based natural coagulants is seen as an alternative non-toxic, biodegradable, and ecologically beneficial strategy. This study aims to investigate the performance of pinecone seed powder as a natural coagulant in iron and steel factory wastewater treatment, as well as to optimize the operating parameters to determine the feasibility of employing pinecone seed powder in wastewater treatment. Using 0.6 g/200 mL pinecone as a controlling factor, pH, and settling time, the response surface methodology, a statistical experimental design was utilized to increase the chemical oxygen demand (COD), ammoniacal nitrogen (NH_3–N), and heavy metals removal efficiency. COD, NH_3–N, Fe, Mn, Ai, Cu, and Ni removal efficiencies at pH 8 were 76%, 44%, 88%, 93%, 87%, 50%, and 92%, respectively. Except for Fe (0.0170), Mn (0.0021), and Cu (0.001), the quadratic models for the parameters specified were determined to be significant with a low probability.

Keywords: Heavy metals; Industrial wastewater; Natural coagulant; Pinecone seed powder; Removal; Wastewater treatment

1. Introduction

Water is an essential component of daily life. Water is used for cleaning, agriculture, and industry [1] and all of these uses generate wastewater. The industrial revolution and modernization in many aspects of life are increasing wastewater output [2]. Simultaneously, freshwater resources are rapidly depleting, and by 2050, several countries and

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over 1.5 billion people in 39 countries may face water scarcity [3,4].

Although the industrial revolution benefits economic progress, appropriate management and disposal of industrial wastewater is critical for ecosystem quality [5]. Heavy metal and organic chemical-containing effluent is common in iron and steel production [6]. Heavy metal-tainted wastewater reaches the environment, putting human health and the ecosystem at risk [7]. Heavy metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) are non-biodegradable and may cause cancer [8–11], Heavy metal pollution is a long-term health danger to both human health and the environment, and it may cause major health concerns to living things [12].

Consequently, recovering usable water from wastewater is critical for the world's long-term sustainability. As a result, wastewater treatment is critical for the world's long-term sustainability [13,14]. Depending on the type of wastewater, different wastewater treatment plants use different approaches, such as physical, chemical, and biological treatments or a combination of these methods. These methods, however, have significant limitations, such as incomplete removal, high energy consumption, and the production of toxic sludge [15–25]. Physicochemical techniques, such as coagulation–flocculation, have been shown to reduce pollution and generate clean water for reuse while remaining simple and cost-effective [26,27].

Coagulants are often inorganic, synthetic, or naturally organic [28,29]. Numerous recent studies have emphasized the significance of natural coagulants [30,31]. Plant-based materials can act as coagulants, performing some coagulation mechanisms, such as charge neutralization in colloidal particles and polymer bridging [32,33]. However, they still have several drawbacks, including cost savings, using a biodegradable natural ingredient, less sludge generation, and avoiding pH changes in treated water [34]. Several studies have lately reported on the efficacy of several forms of natural coagulants in wastewater treatment. Rifi et al. [35] used *Moringa oleifera* as a natural coagulant to remediate agricultural wastewater from the olive oil industry. The study found that turbidity and chemical oxygen demand (COD) levels in agricultural wastewater were significantly reduced. Iber et al. [36] investigated the effectiveness of chitosan as a natural coagulant for aquaculture wastewater treatment. Fard et al. [37] used *Lallemantia mucilage* as a natural coagulant to treat saline and oily wastewater. This investigation found satisfactory elimination of COD. However, the effectiveness of natural coagulants for heavy metals removal from industrial wastewater was not thoroughly studied.

This paper assesses and reviews the usefulness of pinecone powder as a natural plant-based coagulant for organic removal from industrial wastewater and its performance for heavy metal removal from industrial wastewater. The optimal experimental conditions and the statistical relationship between factors and response for using pinecone powder as a plant-based natural coagulant for industrial wastewater purification/treatment are assessed.

2. Materials and methods

Karabuk iron and steel factory's raw industrial effluent was collected in Karabuk, Turkey coordinate 41°12′19.68″N 32°39′24.44″E. The wastewater samples were collected at the discharge point, transferred to the laboratory in a cool box within 1 h of collection, and utilized immediately; not used directly, the samples were maintained at 25°C in a dark room.

2.1. Preparation of pinecones powder

Pinecones were obtained from the yard of Karabuk University in Turkey to remove clinging and undesirable portions. The pinecones were rinsed with distilled water. The pinecones were dried at ambient temperature, then in a 50°C oven for approximately 8 h. These have been done to make smashing the pinecones simpler. The crushed pinecones were ground into powder using a (Retsch RS 200) grinder to be employed as a coagulant in the studies, as illustrated in Fig. 1.

Fig. 1. Pinecones and powder.

2.2. Experimental procedure

An orbital shaker (PSU-10i, No.: 010144-1404-0228, Latvia) and three 500 mL beakers were used to model the coagulation–flocculation process, with the influence of coagulant dosage taken into consideration. Each beaker contained 200 mL of sample. The automated controller of the shaker device was used to set the time and speed for fast and progressive mixing. In this investigation, the coagulation–flocculation process includes 5 min of rapid mixing at 200 rpm, 15 min of slow mixing at 90 rpm, and 60 min of settling for additional testing for COD, ammoniacal nitrogen (NH_3–N), and heavy metal removal efficiency (manganese Mn, iron Fe, zinc Zn, aluminum Al, and nickel Ni). The sample's initial pH (8) was left uncorrected throughout this experiment, and coagulation was evaluated depending on the removal efficiencies of COD, and NH_3–N.

The optimum pinecone powder dose determined in the previous experiment was assessed regarding the effect of pH (varying from 5 to 10) on removal efficiency for the specified parameters. Before adding the coagulant, the pH was adjusted using 1 M HCl and 1 M NaOH. Industrial wastewater samples were forcefully agitated prior to coagulation; removal efficiency is estimated as bellow:

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

where C_i and C_f refer to the initial and the final levels of each parameter.

The characterization of the iron and steel industry wastewater used for these experiments is listed in Table 1.

2.3. Factorial design and optimization

For statistical trial design and data analysis based on central composite design (CCD) and response surface (RSM), the Design-Expert Software (version 6.0.7) was used. The RSM is a mathematical and statistical approach frequently used in experimental designs to determine the optimal process parameter levels [38,39]; Eq. (2) describes the correlation and interaction between the input parameters process and their response.

Table 1
Characteristic of industrial (iron and steel factory) 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

$$Y = f\left(X_1, X_2 X_3 .....X_k\right) \pm \varepsilon \tag{2}$$

where X_1, X_2, X_3, …, X_k are the input variables that might influence the result, and ε is the random error.

The Design-Expert Software presented various designs based on the design parameters. The designs' ability to estimate higher-order terms varies. The majority of designs are only appropriate for the quadratic model. The equation represents the second-order model (3).

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} X_i X_j + e_i \tag{3}$$

where Y represents the response, X_i and X_j represents the variables, b represents the regression coefficient, k represents the number of factors studied and optimized in the experiment, and e represents the random error.

RSM aims to discover an approximation function for anticipating future responses and factor values that maximize the response function. One primary assumption is that the independent variables are continuous and controlled by low-error trials. As a result, the challenge is finding a good approximation for the exact functional link between the independent variables and the response surface [39].

Analysis of variance (ANOVA) was utilized to improve the three treatment choices for graphical data analysis to determine the interaction between the process components and the results. The coefficient of determination (R^2) value was used to reflect the quality of the fit polynomial model, and its statistical significance was validated using the F-test in the same application. The P-value (probability) with a 95% confidence level was used to analyze model terms.

CCD and RSM were used to optimize and examine the association between the two crucial independent variables: (1) pinecone powder dose and (2) pH, as shown in Table 2.

As dependent variables, the removal efficiencies of COD, NH_3–N, manganese (Mn), iron (Fe), zinc (Zn), aluminum (Al), and nickel (Ni) in effluent wastewater were investigated (response). The process's performance was evaluated using the efficiency of COD and NH_3–N removal. The removal efficiencies for the parameters mentioned above were used to evaluate the process's performance. Each independent variable was adjusted over three levels ranging from 1 to +1 at the specified ranges based on the literature [40]; yielding a total of 13 trials (=2k + 2k5) for the two factors (k = 2). Table 3 shows the specifics of the coagulation process's exponential design matrix.

Table 2
Independent variables of the CCD

Level of value	A: pinecone powder (g)	B: pH
–1	0.2	7.5
0	0.6	5.38
+1	1.0	9

3. Results and discussion

3.1. Characterization of pinecone powder imaging using scanning electron microscopy

The morphological surface structure of pinecone powder was investigated before and after the coagulation technique. Fig. 2a shows a condensed crystalline brick-shaped structure of pinecone powder. The structure served as a site of attachment for suspended particles and cations [41]. The coagulant aggregated the particles, resulting in larger flocs that sank readily, as seen in Fig. 2b. Consequently, scanning electron microscopy pictures of pinecones indicated that bridging might be necessary for the pinecone's outstanding coagulation properties [41,42].

3.2. Fourier-transform infrared analysis

The matching infrared (IR) spectrum was obtained using Fourier-transform infrared (FTIR) spectroscopy, as shown in Fig. 3, to investigate further the presence of the main potential functional groups in the powdered pinecone. The FTIR analysis sufficed for simplifying and maybe stressing the major functional groups. To investigate the IR spectra produced for pinecone, the band's range—where its functional groups may be emphasized within the range of wavelength peaks—was chosen. The presence of solid amine salts (N–H) in the 3,000–2,500 cm^{-1} range may indicate the presence of solid amine salts during the coagulation process. It may aid in the removal of ammonia and organics from wastewater.

The peak between 1,750–1,650 cm^{-1} demonstrates the C–N connection, while the one between 1,650–1,550 cm^{-1} confirms either a primary amine N–H or the aromatic C=C. The peak in the green region between 1,300–1,250 cm^{-1} suggests an aromatic ester C–O bond, whereas the one between 1,200–1,000 cm^{-1} indicates an N–H aliphatic amine [43,44].

Adding pinecone powder to the wastewater solution was done in different quantities, changing the experimental conditions. Therefore, the removal results ranged from 57.0% to 81.2% for COD removal, 26.0% to 57.4% for NH_3–N removal, and 89.0% to 97.0% for Fe removal. The removal ratio for Mn is 84.7% to 96.0%, the removal ratio for Ai is 69.0% to 90.2%, the removal ratio for Cu is 15.8% to 64.0%, and the removal ratio for Ni is 58.0% to 92.0%. According to the findings, pinecone powder has high effectiveness in removing COD and Fe throughout the processing procedure, while the treatment rate in NH_3–N was low; this was attributed to the cohesiveness of these elements' molecules, which resulted in poorer treatment efficiency, as seen in Table 4.

Table 3
Summary for the experimental matrix of the amount of pinecone powder and pH number for each experiment

Run	Type	Factor 1(pinecone powder dosage)/200 mL	Factor 2 (pH)
SP1	Fact	1.00	9.00
SP2	Axial	0.03	7.50
SP3	Center	0.60	7.50
SP4	Axial	0.60	9.62
SP5	Center	0.60	7.50
SP6	Fact	1.00	6.00
SP7	Center	0.60	7.50
SP8	Center	0.60	7.50
SP9	Center	0.60	7.50
SP10	Axial	1.17	7.50
SP11	Axial	0.60	5.38
SP12	Fact	0.20	9.00
SP13	Fact	0.20	6.00

3.3. Variance analysis

Table 5 displays the regression parameters of the projected response area exponential models as well as additional statistical parameters for ANOVA for COD, NH_3–N, Fe, Mn, Ai, Cu, and Ni. The table below shows that all models were significant at the 5% confidence level based on P value. The values of the R^2 (coefficients of determination) found in this investigation were for me (COD, NH_3–N, Fe, Mn, Ai, Cu and Ni). R^2: 0.93, 0.96, 0.81, 0.90, 0.91, 0.89, 0.93, which is more than 0.80 to properly suit the model, a value

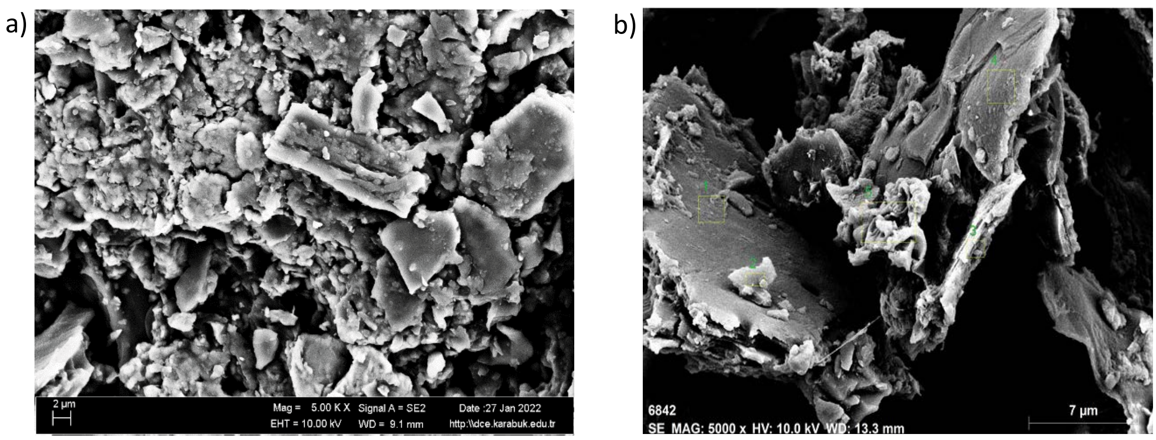

Fig. 2. Microscopic image (2 µm) for pinecones powder (a) before and (b) after coagulation process observed by scanning electron microscopy.

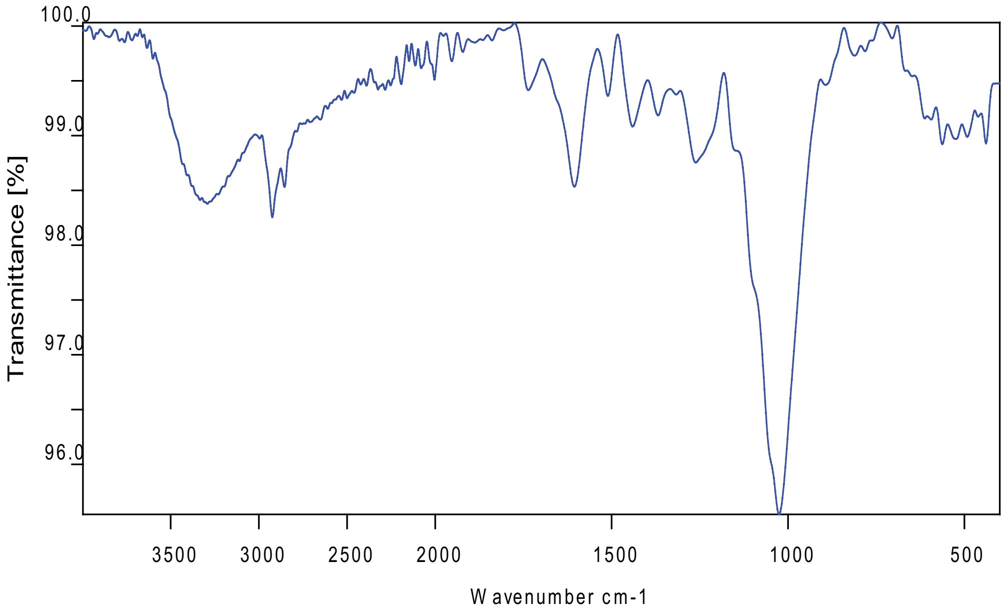

Fig. 3. Fourier-transform infrared (FTIR) spectroscopy curve for pinecone powder.

Table 4
Summary of an experimental matrix for coagulation of wastewater using pinecone powder

Run	Type	Factors		Responses						
		A: pinecone dosage	*B*: pH	COD	NH_3–N	Fe	Mn	Ai	Cu	Ni
		g		Removal %	Removal %	Removal %	Removal %	Removal %	Removal %	Removal %
1	Fact	1.00	9.00	60	30	97	96	86.5	55.3	80
2	Axial	0.03	7.50	81.2	52.5	86	90	85	36.8	88.6
3	Center	0.60	7.50	71	39.2	93	92.2	89.3	60.5	89.3
4	Axial	0.60	9.62	65.2	26	96	95	88.8	47.4	93
5	Center	0.60	7.50	71	34.3	93.5	89	89	60	89
6	Fact	1.00	6.00	73	51.8	91	86.4	76.5	15.8	80
7	Center	0.60	7.50	70	39.2	93	92.2	89.3	64	89.3
8	Center	0.60	7.50	71	39.2	93	92.2	89.3	60.5	89.3
9	Center	0.60	7.50	70	39.2	93	92.2	89.3	60.5	89.3
10	Axial	1.17	7.50	57	57.4	92	90	90.2	51	58
11	Axial	0.60	5.38	73.2	31.5	82	85.6	73.8	21.1	94
12	Fact	0.20	9.00	78.6	48	90	96	87.7	57	92
13	Fact	0.20	6.00	78.6	26.6	89	84.7	69	36.8	90

of R^2 close to one indicates significant agreement between predicted and computed results. Typical terms were omitted from the analysis (they were unimportant), and six quadratic models were retained in Table 6 despite their small influence.

3.4. Treatment efficiency

The selected model is proven equivalent to the existing system using Design-Expert 6.0.7 software by delivering typical protection graphs for diagnostics and standardized residuals. Probability graphs produced by Design-Expert 6.0.7 software were used to evaluate the models. Fig. 4 depicts the probability plots of the standardized residuals for COD, NH_3–N, Fe, Mn, Al, Cu, and Ni. As a result, it may be stated that the reactions of some models to data are regularly distributed.

The Design-Expert 6.0.7 program was used to investigate the interaction relationships between independent components and the responses of specific models using 3D surface response and contour plots, as shown in Fig. 5a–g, and reveals that when the dosage of powdered pinecone

Table 5
ANOVA for parameter removal

	Source	Sum of squares	DF	Mean square	F-value	Prob. > F	
COD removal %	Model	542.81	3	180.94	43.50	<0.0001	Significant
	A	426.67	1	426.67	102.57	<0.0001	
	B	73.89	1	73.89	17.76	0.0023	
	AB	42.25	1	42.25	10.16	0.0111	
	Residual	37.44	9	4.16			
	Pure error	1.20	4	0.30			
	Cor. total	580.25	12				
	Std. Dev.: 2.04; R^2: 0.9355; Mean: 70.75; C.V.: 2.88						
NH_3–N removal %	Model	1,201.96	5	240.39	40.90	<0.0001	Significant
	A	24.96	1	24.96	4.25	0.0783	
	B	8.36	1	8.36	1.42	0.2719	
	A^2	410.05	1	410.05	69.76	<0.0001	
	B^2	204.55	1	204.55	34.80	0.0006	
	AB	466.56	1	466.56	79.37	<0.0001	
	Residual	41.15	7	5.88			
	Pure error	19.21	4	4.80			
	Cor. total	1,243.11	12				
	Std. Dev.: 2.42; R^2: 0.9669; Mean: 39.61; C.V.: 6.12						
Fe removal %	Model	157.09	5	31.42	6.14	0.0170	Significant
	A	38.22	1	38.22	7.47	0.0292	
	B	89.77	1	89.77	17.54	0.0041	
	A^2	12.91	1	12.91	2.52	0.1562	
	B^2	12.91	1	12.91	2.52	0.1562	
	AB	6.25	1	6.25	1.22	0.3057	
	Residual	35.83	7	5.12			
	Pure error	0.20	4	0.050			
	Cor. total	192.92	12				
	Std. Dev.: 2.26; R^2: 0.8148; Mean: 91.42; C.V.: 2.47						
Mn removal %	Model	153.51	5	30.70	12.82	0.0021	Significant
	A	0.39	1	0.39	0.16	0.6970	
	B	148.55	1	148.55	62.04	0.0001	
	A^2	2.60	1	2.60	1.08	0.3324	
	B^2	1.53	1	1.53	0.64	0.4500	
	AB	0.89	1	0.89	0.37	0.5614	
	Residual	16.76	7	2.39			
	Lack of fit	8.53	3	2.84	1.38	0.3694	Not significant
	Pure error	8.23	4	2.06			
	Cor. total	170.27	12				
	Std. Dev.: 1.55; R^2: 0.9016; Mean: 90.96; C.V.: 1.69						
Ai removal %	Model	549.25	5	109.85	15.87	0.0011	Significant
	A	25.10	1	25.10	3.63	0.0986	
	B	318.52	1	318.52	46.02	0.0003	
	A^2	26.38	1	26.38	3.81	0.0918	
	B^2	177.04	1	177.04	25.58	0.0015	
	AB	16.83	1	16.83	2.43	0.1628	
	Residual	48.44	7	6.92			
	Pure error	0.092	4	0.023			
	Cor. total	597.70	12				
	Std. Dev.: 2.63; R^2: 0.9189; Mean: 84.97; C.V.: 3.09						

(Continued)

Table 5

	Source	Sum of squares	DF	Mean square	*F*-value	Prob. > *F*	
Cu removal %	Model	2,714.15	5	542.83	12.19	0.0024	Significant
	A	0.96	1	0.96	0.021	0.8876	
	B	1,172.44	1	1,172.44	26.32	0.0014	
	A^2	451.68	1	451.68	10.14	0.0154	
	B^2	1,160.00	1	1,160.00	26.04	0.0014	
	AB	93.27	1	93.27	2.09	0.1911	
	Residual	311.83	7	44.55			
	Pure error	10.61	4	2.65			
	Cor. total	3,025.98	12				
	Std. Dev.: 6.67; R^2: 0.8969; Mean: 48.21; C.V.: 13.85						
Ni removal %	Model	1,013.02	5	202.60	21.07	0.0004	Significant
	A	534.14	1	534.14	55.55	0.0001	
	B	0.043	1	0.043	4.461E-003	0.9486	
	A^2	385.67	1	385.67	40.11	0.0004	
	B^2	48.39	1	48.39	5.03	0.0598	
	AB	1.00	1	1.00	0.10	0.7565	
	Residual	67.31	7	9.62			
	Pure error	0.089	4	0.022			
	Cor. total	1,080.32	12				
	Std. Dev.: 3.1; R^2: 0.9377; Mean: 86.31; C.V.: 3.58						

Table 6
Optimal response results from model prediction and laboratory

Pinecone (g)	pH	COD	NH_3–N	Fe	Mn	Ai	Cu	Ni	Desirability
0.24	8.83	77.3	46.4	90.9	94.6	89.4	51.5	93.1	0.793
Exp. Lab		76	44	88	93	87	50	92	

powder is 0.6 g/200 mL. The pH level is 9.0, and the percentages of COD and NH_3–N removed were 78% and 44%, respectively. In contrast, the removal percentage of Fe, Mn, Ai, Cu, and Ni was 90.9%, 94.9%, 89.4%, 51.5%, and 93.1%, respectively. These response charts indicate that the quantity of treatment required is determined by the amounts of these constituents in the wastewater and the experimental settings (pH level).

The effectiveness of pinecone seeds powder's coagulation in removing COD and NH_3–N varied. Determining the ideal coagulant dose is crucial to ensure that the treatment process runs at its best while lowering material costs and sludge formation. The ability of pinecone seeds powder's natural polyphenols to adsorb metal ions and organic impurities improved the elimination of organic pollutants [45]. The action of electric double layers produced by carboxylic, phenolic, and amino groups may be responsible for improving organic and ammonia elimination [46]. The targeted parameters' elimination efficiency decreased when pinecone seed powder doses of more than 7 g were utilized. The wastewater's colloids and particles could better bridge one another thanks to pinecone seeds powder's positively charged primary amino groups, which enhanced the flocculation process [47]. High molecular weight pinecone seeds powder is not hydrolyzed in wastewater. A larger dose of pinecone seeds powder causes a significant powder volume to precipitate quickly, which may lessen flocculation efficiency [48].

3.5. Optimization operational conditions

Using the Design-Expert 6.0.7 program, work was done to establish the ideal value for handling the presence of COD and NH_3–N, Fe, Mn, Ai, Cu, and Ni in wastewater. As a result, the experimental conditions for each case (pH concentration and dose of crushed pinecone) were calculated, and the answers were found to be the optimal limits in obtaining the maximum treatment value. Individual preferences are combined into a single value, which the computer then seeks to optimize depending on the response objective. Consequently, the best-operating conditions and per cent removal efficiency, as indicated in Table 6, were identified.

According to Table 6, it is projected to remove 77.3%, 46.4%, 90.9%, 94.9%, 89.4%, 51.5%, and 93.1% of COD and NH_3–N, Fe, Mn, Ai, Cu, and Ni based on optimal operating conditions (pinecone powder 0.24 g, pH 8.83). An experiment was conducted in the laboratory to validate the correctness of the ideal outcomes, revealing that the experiment's findings matched the projected response value.

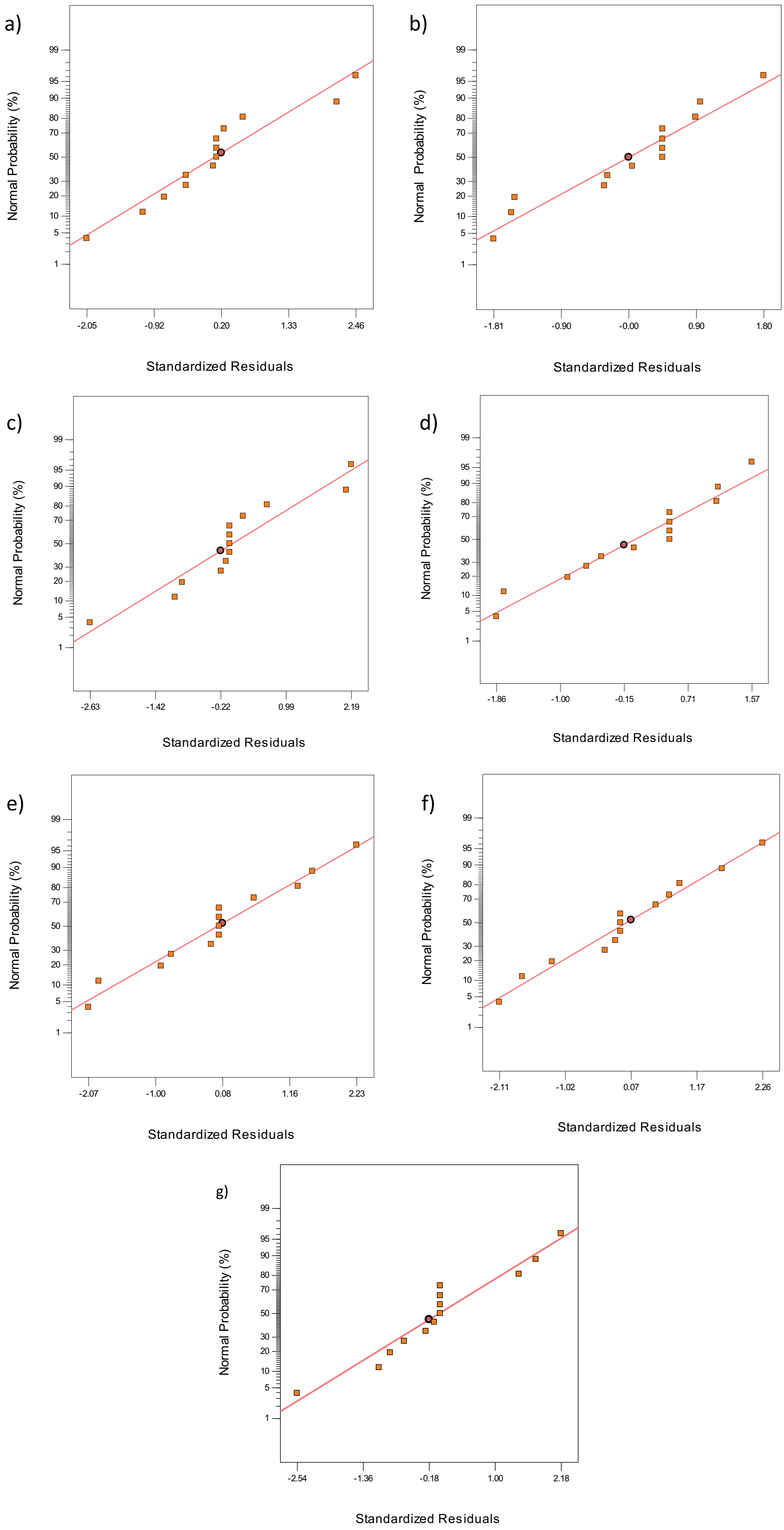

Fig. 4. Normal probability plots for a (COD), b (NH_3–N), c (Fe), d (Mn), e (Ai), f (Cu) and g (Ni) removals.

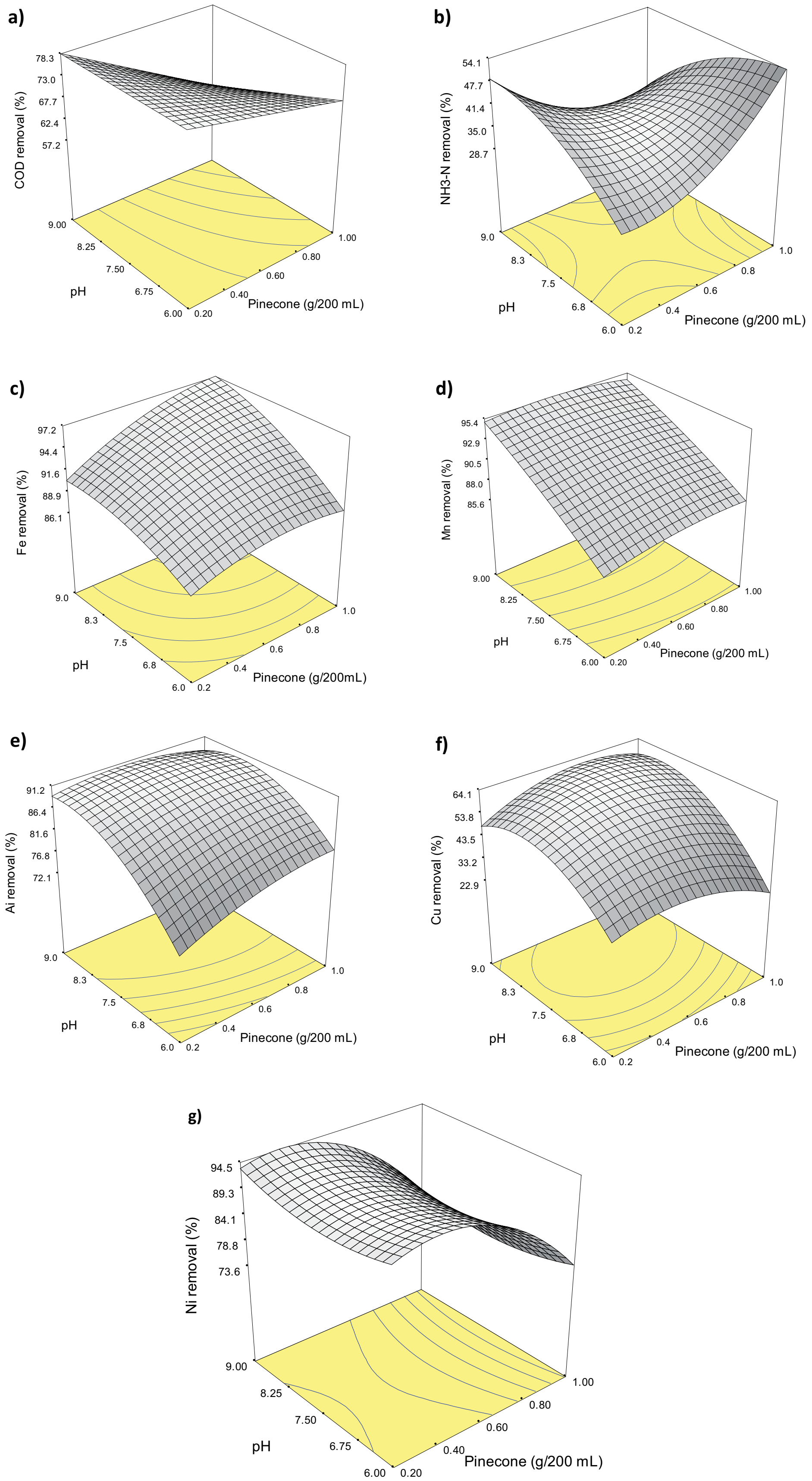

Fig. 5. Response surface plots for a (COD), b (NH_3–N), c (Fe), d (Mn), e (Ai), f (Cu) and g (Ni) removals.

4. Conclusion

The elimination of COD, total suspended solids (TSS), NH_3–N, Mn, Fe, Zn, Al, and Ni by pinecone seed powder showed substantial potential as a plant-based natural coagulant in iron and steel mill treatment. The experiment demonstrated that the powdered pinecone seeds had substantial coagulation properties. The specific findings of the research are as follows. The existence of various functional groups involved in the coagulation process was shown by FTIR investigation. The pinecone seeds powder eliminated a large proportion of COD, NH_3–N, Fe, Mn, Ai, Cu, and Ni from effluent at pH 8 at 0.6 g/200 mL, with percentages of 76%, 44%, 88%, 93%, 87%, 50%, and 92%, respectively.

Because of the organic nature of pinecone powder, the pH of the industrial effluent remained unaltered after its addition. As a result, when pinecone seeds powder was utilized as a coagulant, no pH modification was required during the treatment procedure.

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