Factorial Design and Optimization of Date Stone as A Natural Coagulant for Organic and Heavy Metals Removal from Industrial Wastewater

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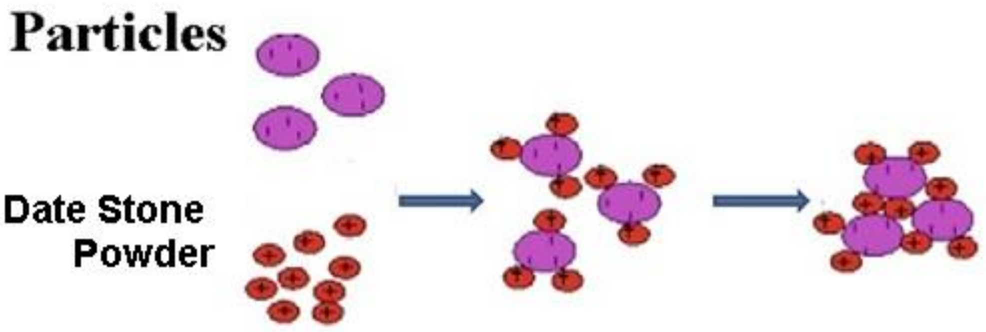
GRAPHICAL ABSTRACT



Abstract

Several chemical coagulants previously utilize for wastewater treatment with significant performance in removing heavy metals and other parameters. However, their cost effective and the residual of toxic chemical precipitates that pose problems to human health and the environment. Therefore, using plant-based natural coagulants is considered as an alternative technique which is non-toxic, biodegradable and environmentally friendly. This research aims to explore the performance of date stones as a natural coagulant in iron and steel plant wastewater treatment and to optimize the operating parameters to assess the feasibility of using date stones in the wastewater treatment sector. Response Surface Methodology (RSM), a statistical experimental design, was used to improve the COD, TSS, NH_3-N, and heavy metals removal efficiency using 1.4 g/200 mL date stones as control parameters, as well as pH and settling time. At pH 8, the most significant removal efficiency for COD, NH_3-N, Fe, Mn, Al, Cu, and Ni was 61, 63, 93, 93, 96.5, 51, and 86 %, respectively. The quadratic models for the parameters chosen were found to be significant with low probability (<0.001), except for NH_3-N (0.004), Fe (0.0042), and Ni (0.0025). The study's results revealed the potential of utilizing date stones as a natural coagulant for the treatment of iron and steel industrial wastewater.

Keywords: Industrial Wastewater, Natural coagulant, Date Stone, Treatment, Removal Efficiency, Heavy Metals, Factorial Design and Optimization.

1. Introduction

In recent times, water consumption has increased due to industrialization, urbanization, and population growth (Ali & Tien Seng, 2018), and, accordingly, wastewater from the various activities of industrialization and urbanization is also increasing, making access to clean and safe water a critical issue (Abujazar, Fatihah, Kabeel, Sharil, & Abu Amr, 2018). Inappropriate mistreatment or untreated wastewater containing contaminants such as suspended solids, pathogens, nutrients, and heavy metals are hurtful and hazardous to the environment and lead to numerous pollution problems (M. Y. D. Alazaiza et al., 2022; Mukherjee, Mandal, Ganguly, & Chatterjee, 2016). Furthermore, leading to waterborne diseases, which affect human health and are responsible for about 80% of the world's diseases (Lundqvist, Mandava, Lungu-Mitea, Lai, & Ahrens, 2019; Ugwu, Umuokoro, Echiegu, Ugwuishiwu, & Enweremadu, 2017); therefore, the best way to combat freshwater scarcity and waterborne diseases is to treat and reuse wastewater (Abujazar, Fatihah, Lotfy, Kabeel, & Sharil, 2018).

The production of effluents in different industrial processes has posed several environmental risks as a result of rapid industrialization (Mahmood et al., 2019). Water and soil contamination can result from indiscriminate dumping of these effluents. Besides, the effects on abiotic components such as soil and water substantially impact living organisms' health (Chhonkar, Datta, Joshi, & Pathak, 2000). Huge quantities of industrial effluents are produced daily all over the world. Industrial wastewater is rich in chemical dyes, sodium salts of organic acids, and lignin and has a significant concentration of COD, oils, detergents, fats, and suspended solids (Muralimohan, Palanisamy, & Vimaladevi, 2014; Tobajas, Alicia M. Polo, Mohedano, & Rodriguez, 2014).

Sometimes, wastewater contains heavy metals. These wastewaters containing heavy metals mainly come from anthropogenic sources such as farms or mining that do not use environmentally friendly techniques or from natural disasters such as earthquakes, storms, and volcanoes that introduce toxic substances into the wastewater (Ahmed, Aktar, Zaman, Jahan, & Bari, 2020; Helen Kalavathy & Miranda, 2010; Nath, Mishra, & Pande, 2019). Heavy metals such as arsenic (As), lead (Pb), copper (Cu), cadmium (Cd), nickel, zinc (Zn), and chromium (Cr) are highly toxic. Even at low concentrations, they are considered the most critical harmful wastes in freshwater reservoirs because they are harmful, non-biodegradable, and inherently long-lived (Azimi, Azari, Rezakazemi, & Ansarpour, 2017; Nath et al., 2019; Vikashni, Matakite, Kanayathu, & and Subramanium, 2012). As much as chemical usage continues on its current trend, removing these poisons from the environment will be challenging (Abujazar, Karaağaç, Abu Amr, Alazaiza, & Bashir, 2022).

Consequently, effort must be made to eliminate environmental toxic substances from bodies of water. Each industrial wastewater treatment procedure produces treatment outcomes, but the results vary. However, most of these systems employed in the detoxification process have several serious drawbacks operating and maintenance expenses, collateral harm, and complicated treatment processes (M. Alazaiza et al., 2022; Ali & Tien Seng, 2018). The production of secondary waste characterizes conventional treatment processes after the treatment process, such as toxic sludge, which endangers human health and the environment.

The shortcomings of the industrial wastewater treatment process include that it has limited capabilities in the treatment process, is capable of leakage, is affected by the weather, and is not treated thoroughly. Concerted efforts have been made in the field of research and development to utilize new plant species and components that can be used as natural coagulants, such as date kernel powder, which is convenient, easy to operate, simple in design, economically inexpensive, and does not produce secondary results. Several studies recently reported the effectiveness of different types of natural coagulants for wastewater treatment. Rifi et al., (2022) utilized *Moringa oleifera* as a natural coagulant for treating the agricultural wastewater produced from olive oil industry. The study reported significant removal for turbidity and COD from agricultural wastewater. Iber, Okomoda, Rozaimah, & Kasan, (2021) reviewed the performance of chitosan as a natural coagulant for aquaculture wastewater treatment. Besharati Fard et al., (2021) utilized *Lallemantia mucilage* as a natural coagulant for the treatment of saline oily wastewater. Satisfactory removal for COD was reported in this study. However, the performance of natural coagulants for heavy metals removal from industrial wastewater was not well documented.

The effectiveness of date stones as a natural coagulant for organic removal from industrial wastewater and their performance for heavy metals removal from industrial wastewater are evaluated and discussed in this paper. The proper experimental settings and the statistical relationship between variables and response for employing date stones as a natural plant-based coagulant for industrial wastewater treatment are investigated.

2. Materials and Methods

Raw industrial wastewater was obtained from Karabuk iron and steel factory, Karabuk, Turkey. The wastewater samples were collected from the discharge point of the factory and later on transported to the laboratory in a cool box within one hour of the collection; if not used immediately, the samples were kept at 25°C in the dark until.

2.1 Preparation of Date Stone Powder

Date stones Figure 1 were obtained from a household Gaza strip, Palestine, and transferred to Karabuk University, Turkey. To remove sticking pieces, the date stone was cleaned with distilled water. The stones were dried under atmospheric temperature first and then inside an oven for about eight (8) hours at 50°C. to make the date stones easy to crush. The crushing of the date stones was carried out for size reduction using a (Retsch RS 200) grinder to obtain powder form for the experiments.

Figure 1. Date stone and powder.

2.2 Analytical Study

The characterization parameters and strategies utilized are shown in Table 1. During the tests, the pH of the samples was adjusted with a 1 N H_2SO_4/NaOH solution (Hanson, 2015).

Table 1. 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
Ammonia-nitrogen 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

2.3 Experimental Procedure

The coagulation-flocculation process was simulated using Orbital shaker (Type: PSU-10i, no:010144-1404-0228, Latvia), and three 500 mL beakers were used to test the effect of the coagulant dose. Each beaker held 200 mL of sample. The timing and speed for rapid and slow mixing were set using the shaker apparatus's automated controller. In this investigation, the coagulation-flocculation technique included 5 minutes of rapid mixing at 200 rpm, 15 minutes of slow mixing at 90 rpm, and 60 minutes of settling for farther testing for removal efficiency of COD, TSS, ammonia-nitrogen NH_3-N, and heavy metals (Manganese "Mn," Iron "Fe", Zinc "Zn", Aluminum "Al" and Nickel "Ni", Throughout this step of the test, the starting pH (8) of the sample was kept uncorrected. Coagulation was tested on the removal efficiency of COD, and NH_3-N.

The optimal date stone powder dosage found in the prior experiment was next examined to see how pH (ranging from 5-10) affected efficient removal for the desired parameters. Before adding the coagulant, the pH was adjusted using 1M of HCl solution and 1M of NaOH solution. To reduce the potential of solids settling, industrial wastewater samples were vigorously shaken prior to coagulation; efficiency removal is computed as follows:

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

where C_i and C_f correspond to the initial and final values of each parameter

The characterization of the iron and steel industry wastewater used for these experiments is listed in Table 2**.**

Table 2. 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
Ammonia-nitrogen 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

2.4 Factorial design and optimization

The Design Expert Software (version 6.0.7) was used for statistical trial design and data analysis based on CCD and response surface RSM. The RSM is a mathematical and statistical approach that is often used for experimental designs to discover the optimal process parameter levels (Ghafari, Aziz, & Bashir, 2010; Yi, Su, Qi, Su, & Wan, 2010), the following equation (2) describes the correlation and interaction between the input parameters process and their response.

$$\boldsymbol{Y} = \boldsymbol{f}\,(X_1, X_2 X_3 \ldots\ldots X_k) \pm \varepsilon \qquad (2)$$

Where x_1, x_2, x_3 …..x_k are the input variables that might influence the result and $\mathcal{E}$ is the random error.

Depending on the number of design parameters, the Design Expert program presented numerous designs. The Design Expert Software showed a variety of designs based on several design factors. The designs' ability to estimate higher-order words differs. The majority of designs are only appropriate for the quadratic model. The equation represents the second-order model (3).

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

where Y represents the response, X_i and X_j represent the variables, the regression coefficient, k is the number of components evaluated and optimized in the experiment, and e represents the random error.

For graphical analyses of the data to determine the interaction between the process factors and the responses, analysis of variance (ANOVA) was performed to optimize the three treatment techniques. The coefficient of determination (R^2) value was used to describe 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 evaluate model terms.

CCD and RSM were used in this section to optimize and assess the relationship between the two independent factors: (1) dosage of a date stone, (2) and pH, as shown in Table 3.

Table 3. Independent variables of the CCD design.

Level of Value	A:Date stone (g)	B: pH
-1	0.6	7.5
0	1	5.38
+1	1.4	9

Chemical oxygen demand (COD), ammonia-nitrogen (NH_3-N), manganese (Mn), iron (Fe), Copper (Cu), aluminum (Al), and nickel (Ni) removal efficiencies of effluent wastewater were examined and regarded as dependent variables (response). The process's performance was assessed by measuring the removal efficiencies for the parameters mentioned above. Each independent variable was adjusted across three levels between 1 and +1 at the given ranges (Tizaoui, Bouselmi, Mansouri, & Ghrabi, 2007). The total number of experiments achieved for the two factors was 13 (=2k+2k5), where k is the number of factors (k=2). **Table 4** shows the specifics of the coagulation exponential design matrix.

Table 4. Summary for the experimental matrix of the amount of date stone powder and pH number for each experiment.

Run	Type	Factor 1(date stone dosage)/ 200 mL	Factor 2 (PH)
SD1	Center	1.00 g	7.50
SD2	Axial	1.57 g	7.50
SD3	fact	0.60 g	9.00
SD4	Axial	1.00 g	5.38
SD5	Axial	1.00 g	9.62
SD6	Center	1.00 g	7.50
SD7	fact	1.40 g	9.00
SD8	Axial	0.43 g	7.50
SD9	Fact	1.40 g	6.00
SD10	Fact	0.60 g	6.00

3. Results and Discussion

3.1 Characterization of Date Stone Powder Imaging using Scanning Electron Microscopy (SEM)

The morphological surface structure of date stone powder was studied before and after the coagulation procedure. Date stone powder has a condensed crystalline brick-shaped structure, as shown in Figure 2 (a). The structure functioned as an attachment point for suspended particles and cations (Salehizadeh & Shojaosadati, 2001). Figure 2 (b) shows how the coagulant aggregated the particles, resulting in the creation of bigger flocs that sank readily. As a result, SEM pictures of date stone powder revealed that bridging may be to blame for date stone powder's outstanding coagulation capabilities (He, Li, Chen, & Lun, 2002; Salehizadeh & Shojaosadati, 2001).

a) b)

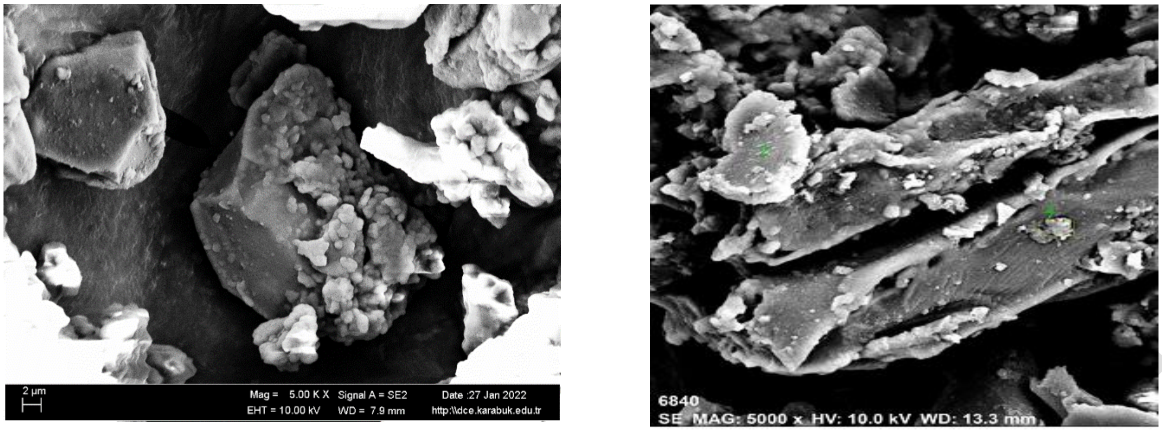


Figure 2. Scanning electron microscopy image (2 µm) of date stone powder (a) before (b) after the coagulation procedure.

3.2 Fourier Transformed Infrared (FTIR) Analysis

The corresponding Infrared (IR) spectrum using Fourier Transform Infrared (FTIR) Spectroscopy was generated to investigate further the existence of the powdered date stone's main possible functional groups. As shown in Figure 3, FTIR analysis was adequately done to simplify and highlight its main functional groups. To ease the analysis of the IR spectrum obtained for date stone powder, the bands' range- where its functional groups could possibly highlight within the range of wavelength peaks. The observed peaks in the 300-2500 cm^{-1} range might indicate the existence of solid amine salts (N-H) that are involved in the bridging mechanism used by particles during the coagulation-flocculation and may contribute to the increase of ammonia and organic removal from wastewater. The peak between 1750-1650 cm^{-1} shows the C-N link, whereas the ones from (1650-1550) cm^{-1} either confirm a primary amine N-H or the aromatic C=C. The peak between a green region of 1300-1250) cm^{-1} 1 indicates an aromatic ester C-O bond, while the one between 1200-1000 cm^{-1} shows the N-H aliphatic amine.

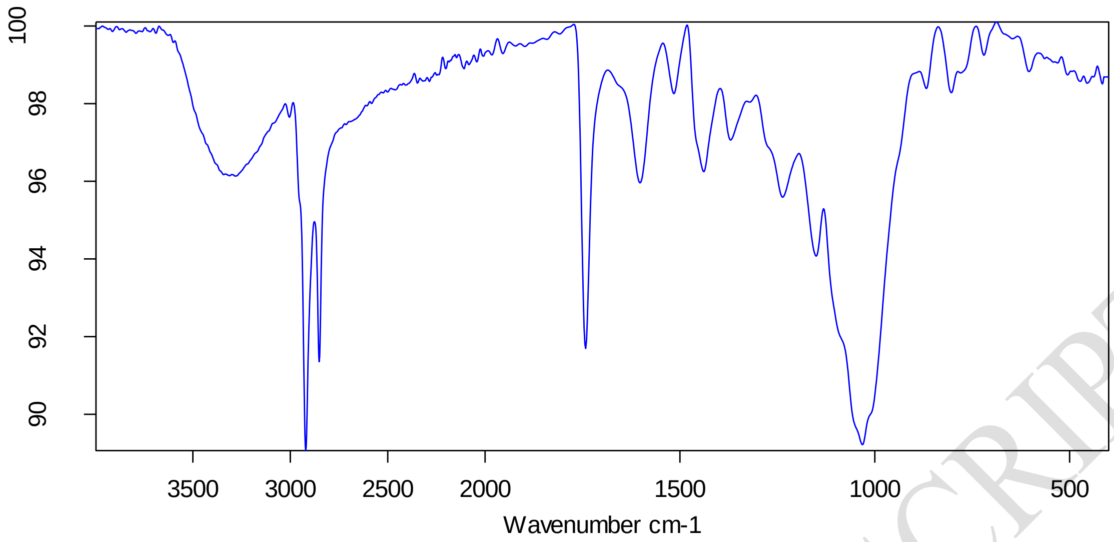


Figure 3. Fourier transformed infrared (FTIR) spectroscopy curve for date stone powder.

Table 5. Summary of an experimental matrix for coagulation of wastewater using date stone powder.

		Factors		**Responses**						
Run	**Type**	**A: Date stone dosage (g)**	**B: pH**	**COD**	**NH_3-N**	**Fe**	**Mn**	**Ai**	**Cu**	**Ni**
				Removal %	**Removal %**	**Removal %**	**Removal %**	**Removal %**	**Removal %**	**Removal %**
1	Center	5.00	7.50	35.8	28.0	92.0	92.5	92.8	63.2	90.7
2	Axial	7.85	7.50	6.4	64.0	95.9	92.3	87.1	63.2	88.0
3	Fact	3.00	9.00	65.3	65.7	96.7	93.8	93.7	47.4	87.0
4	Axial	5.00	5.38	44.2	58.2	94.3	83.4	74.8	34.2	81.0
5	Axial	5.00	9.62	41.2	24.3	94.0	94.7	93.9	60.5	86.0
6	Center	5.00	7.50	41.2	34.1	92.0	91.7	82.5	60.5	90.0
7	Fact	7.00	9.00	9.1	64.7	96.0	88.9	78.3	60.5	80.7
8	Center	5.00	7.50	35.8	28.0	92.0	92.5	92.8	63.2	90.7
9	Center	5.00	7.50	35.8	28.0	92.0	92.5	92.8	63.2	90.7

10	Axial	2.15	7.50	67.9	93.0	90.0	90.2	89.1	42.1	89.3
11	Fact	7.00	6.00	14.5	97.7	96.7	87.9	91.3	65.8	85.0
12	Fact	3.00	6.00	70.6	77.8	89.0	82.6	70.7	31.6	83.0
13	Center	5.00	7.50	35.8	28.0	92.0	92.5	92.8	63.2	90.7

The process of adding date stone powder to the wastewater solution was carried out in different quantities with a change in the experimental conditions, and the results of the removal efficiencies ranged between 6.4% and 70.6% for **COD,** 24.3% to 97.7% for **NH_3-N,** 89.0 % to 96.7% for **Fe,** 82.6% to 94.7% for **Mn,** 70.7% to 93.9% for **Ai,** ranges from 31.6% to 65.8%, for **Cu, and** 80.7% to 90.7%, for **Ni.** The results indicate that the efficiency of date stone powder in the processing process is extensive in removing **Fe** and **NH_3**-N, while the treatment rate was weak in **Ai** and **Cu**; this is due to the cohesion of the molecules of these elements with each other, which gave a lower treatment efficiency. As shown in Table 5.

3.3 Analysis of variance

Table 6 depicts the modules' analysis of variance and the statistical relationship between the variables and responses. The findings in the table below reveal that all simulations were weighty at the 5% confidence level based on the value of **P. (Prob).** The values of the R^2 for COD, NH_3-N, Fe, Mn, Al, CU and Ni, were: 0.9790, 0.8764, 0.8784, 0.9412, 0.9216, 0.8105 and 0.8956, respectively, which is more than 0.80 in order to fit the model well, and R^2 value close to 1 indicates a worthy acceptance between the expected and calculated outcomes results.

Table 6. Analysis of Variance (ANOVA) for parameters removal.

	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
COD removal %	Model	5046.96	5	1009.39	65.31	< 0.0001	significant
	A	4961.86	1	4961.86	321.03	< 0.0001	
	B	27.68	1	27.68	1.79	0.2227	
	A2	0.088	1	0.088	5.724E-003	0.9418	

	B2	56.94	1	56.94	3.68	0.0964	
	AB	0.000	1	0.000	0.000	1.0000	
	Residual	108.19	7	15.46			
	Lack of Fit	85.36	3	28.45	4.99	0.0774	not significant
	Pure Error	22.83	4	5.71			
	Cor Total	5155.15	12				

Std. Dev. 3.93 R^2: 0.9790, Mean:38.75

	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
NH_3-N Removal %	Model	7298.16	5	1459.63	9.93	0.0044	significant
	A	60.76	1	60.76	0.41	0.5408	
	B	1081.24	1	1081.24	7.35	0.0301	
	A2	5759.35	1	5759.35	39.17	0.0004	
	B2	715.29	1	715.29	4.86	0.0632	
	AB	108.10	1	108.10	0.74	0.4196	
	Residual	1029.36	7	147.05			
	Lack of Fit	999.84	3	333.28	45.16	0.0015	significant
	Pure Error	29.52	4	7.38			
	Cor Total	8327.52	12				

Std. Dev. 12.13, R^2: 0.8764, Mean: 53.20

	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Fe removal %	Model	66.30	5	13.26	10.11	0.0042	significant
	A	29.18	1	29.18	22.25	0.0022	
	B	5.50	1	5.50	4.20	0.0797	
	A2	3.66	1	3.66	2.79	0.1388	
	B2	12.24	1	12.24	9.33	0.0184	
	AB	17.23	1	17.23	13.14	0.0085	
	Residual	9.18	7	1.31			
	Lack of Fit	9.18	3	3.06			
	Pure Error	0.000	4	0.000			
	Cor Total	75.48	12				

Std. Dev. 1.15 R^2:0.8784, Mean:93.26

	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Mn removal	Model	159.82	5	31.96	22.43	0.0004	significant

	A	1.37	1	1.37	0.96	0.3593	
	B	98.60	1	98.60	69.18	< 0.0001	
	A2	6.92	1	6.92	4.86	0.0634	
	B2	30.17	1	30.17	21.17	0.0025	
	AB	25.95	1	25.95	18.21	0.0037	
	Residual	9.98	7	1.43			
	Lack of Fit	9.52	3	3.17	27.86	0.0039	significant
	Pure Error	0.46	4	0.11			
	Cor Total	169.80	12				
	Std. Dev. 1.19	R^2: 0.9412, Mean: 90.41					
Al removal %	**Source**	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
	Model	616.14	5	123.23	5.99	0.0181	significant
	A	0.65	1	0.65	0.032	0.8636	
	B	170.78	1	170.78	8.30	0.0236	
	A2	27.61	1	27.61	1.34	0.2848	
	B2	104.53	1	104.53	5.08	0.0589	
	AB	324.53	1	324.53	15.77	0.0054	
	Residual	144.09	7	20.58			
	Lack of Fit	59.31	3	19.77	0.93	0.5028	not significant
	Pure Error	84.78	4	21.19			
	Cor Total	760.22	12				
	Std. Dev. 4.54,	R^2: 0.8105, Mean 87.16					
Cu removal %	**Source**	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
	Model	1608.41	5	321.68	16.47	0.0010	significant
	A	743.85	1	743.85	38.08	0.0005	
	B	284.92	1	284.92	14.58	0.0066	
	A2	151.78	1	151.78	7.77	0.0270	
	B2	370.98	1	370.98	18.99	0.0033	
	AB	110.80	1	110.80	5.67	0.0488	
	Residual	136.75	7	19.54			
	Lack of Fit	131.21	3	43.74	31.58	0.0030	significant
	Pure Error	5.54	4	1.39			
	Cor Total	1745.15	12				
	Std. Dev. 4.42	R^2: 0.9216, Mean 55.26					
Ni		**Sum of**		**Mean**	**F**		

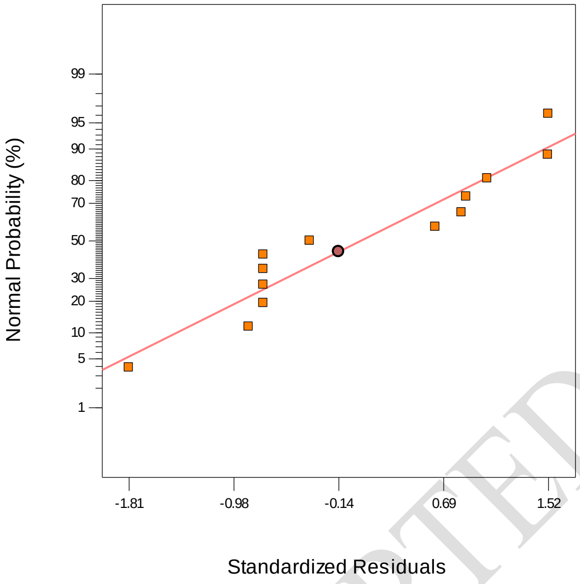
Source	Squares	DF	Square	Value	Prob > F	
Model	148.77	5	29.75	12.01	0.0025	significant
A	4.83	1	4.83	1.95	0.2052	
B	5.67	1	5.67	2.29	0.1740	
A2	15.13	1	15.13	6.11	0.0427	
B2	114.57	1	114.57	46.24	0.0003	
AB	17.36	1	17.36	7.01	0.0331	
Residual	17.35	7	2.48			
Lack of Fit	16.99	3	5.66	63.72	0.0008	significant
Pure Error	0.36	4	0.089			
Cor Total	166.12	12				
Std. Dev. 1.57	R^2: 0.8956, Mean87.13					

3.4 Treatment Effectiveness

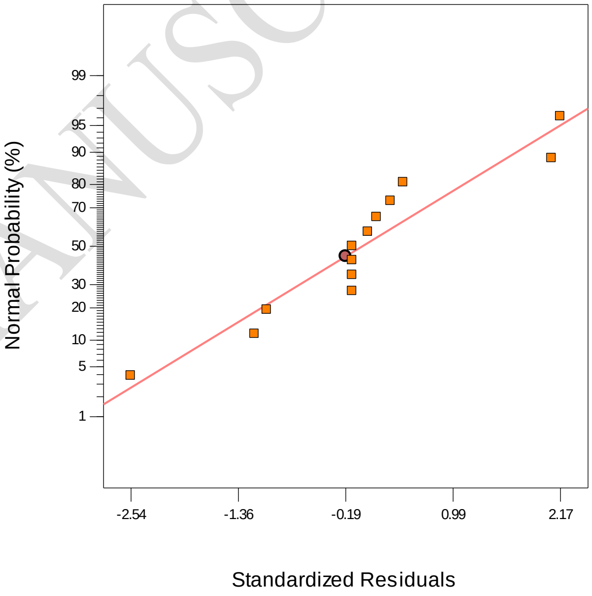
The selected model is equivalent to the existing system using Design Expert 6.0.7 software by delivering typical protection graphs for diagnostics and standardized residuals. Probability graphs produced by Design Expert 6.0.7software were used to evaluate the models. The standardized residuals probability plots for COD, NH_3-N, Fe, Mn, Al, Cu, and Ni are shown in Figure 4 (a-g). 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 linkages between independent factors and the responses of specific models using 3D surface response and contour plots, as illustrated in **Error! Reference source not found.** (a-g). The largest percent of NH_3-N and COD removal is 82.2% and 66.5 %; respectively, when the dose of ground date stones is 1.4 g, and the level is 9.0 as well as for Fe, Mn, Ai, Cu, and Ni, the removal percentage is 97.2% and 94 .9%, 98.24%, 67.6%, and 90.8%, respectively. These response charts indicate that the amount of treatment needed is determined by the ratios of these elements in the wastewater and the experimental settings (pH level). The effectiveness of date stone powder's coagulation in removing COD and NH3-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 date stone powder's natural polyphenols to adsorb metal ions and organic impurities improved the elimination of organic pollutants (Palma, Freer, & Baeza, 2003). The action of electric double layers produced by carboxylic, phenolic, and amino groups may be responsible for the improvement in organic and ammonia elimination (Schofield, Mbugua, & Pell, 2001). The efficiency of the targeted parameters' elimination decreased when date stone doses more than 7 g were utilized. The wastewater's colloids and particles were better able to bridge one another thanks to date stone's positively charged primary amino groups, which also enhanced the flocculation process (Mangrich, Doumer, Mallmannn, & Wolf, 2014). High molecular weight date stone powder is not hydrolyzed in wastewater. A larger dose of date stone causes a significant volume of powder to precipitate quickly, which may lessen the efficiency of flocculation (Kim, Silva, Kim, & Jung, 2010).

A)

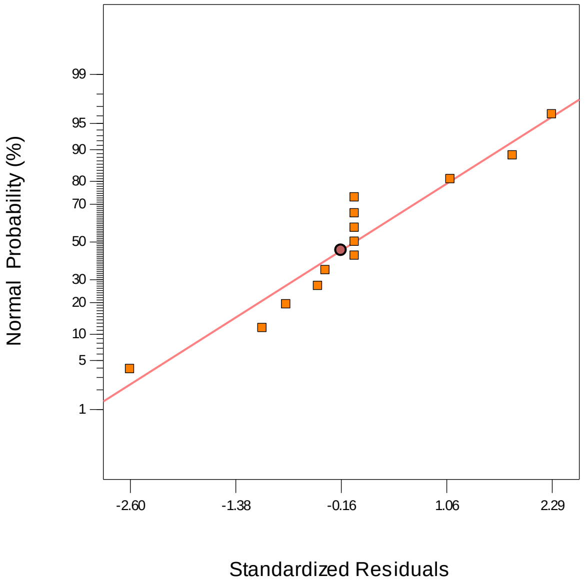


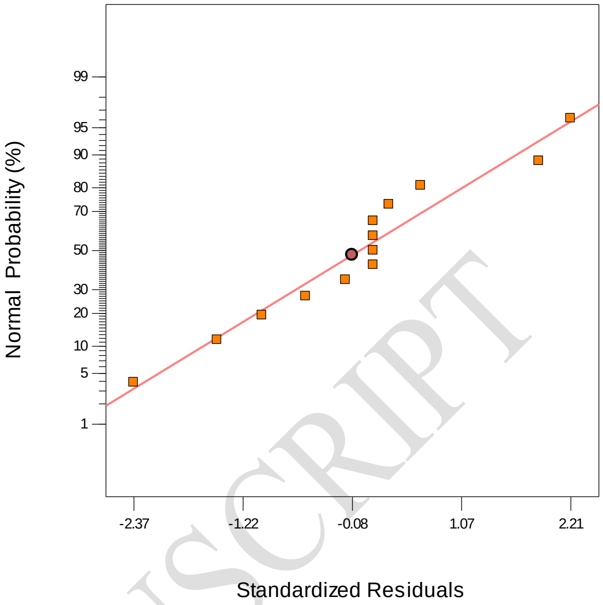
b)



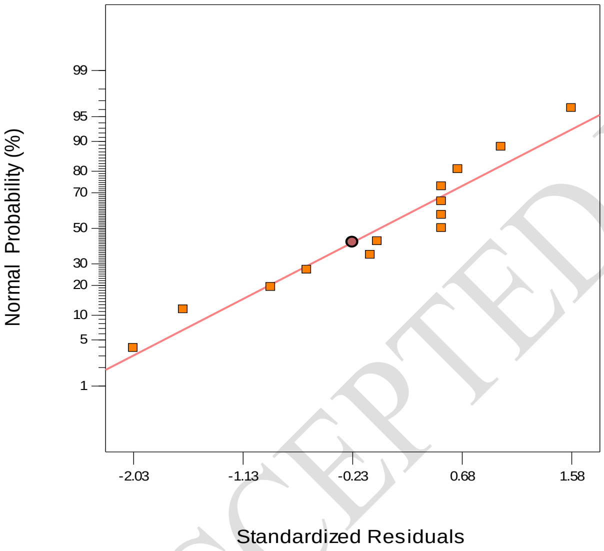
c)

d)

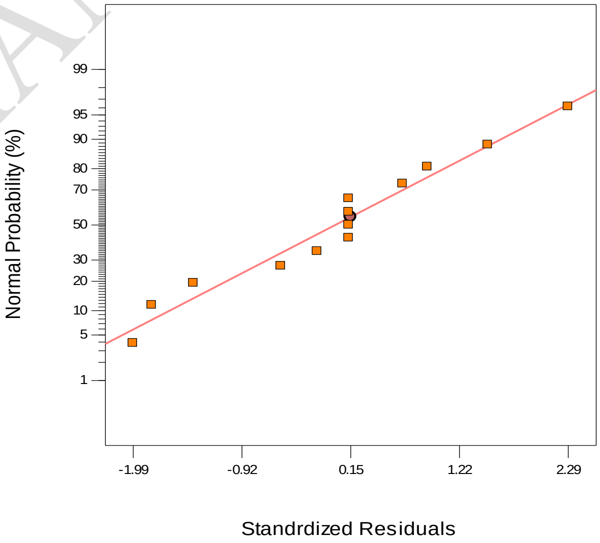

Normal Probability (%)
99
95
90
80
70
50
30
20
10
5
1
-2.60
-1.38
-0.16
1.06
2.29
Standardized Residuals


Normal Probability (%)
99
95
90
80
70
50
30
20
10
5
1
-2.37
-1.22
-0.08
1.07
2.21
Standardized Residuals

e)


Normal Probability (%)
99
95
90
80
70
50
30
20
10
5
1
-2.03
-1.13
-0.23
0.68
1.58
Standardized Residuals

f)


Normal Probability (%)
99
95
90
80
70
50
30
20
10
5
1
-1.99
-0.92
0.15
1.22
2.29
Standrdized Residuals

g)

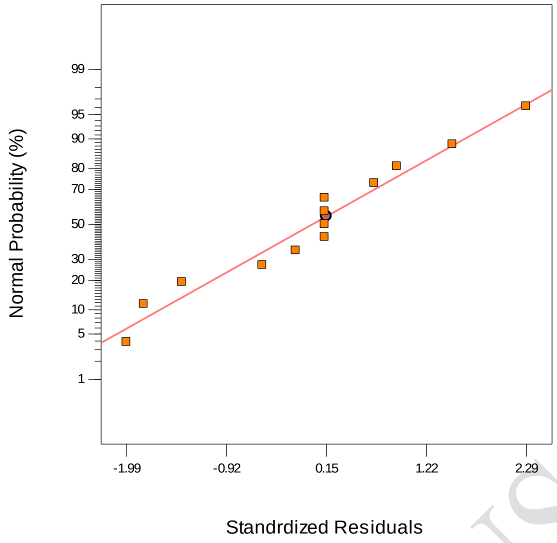
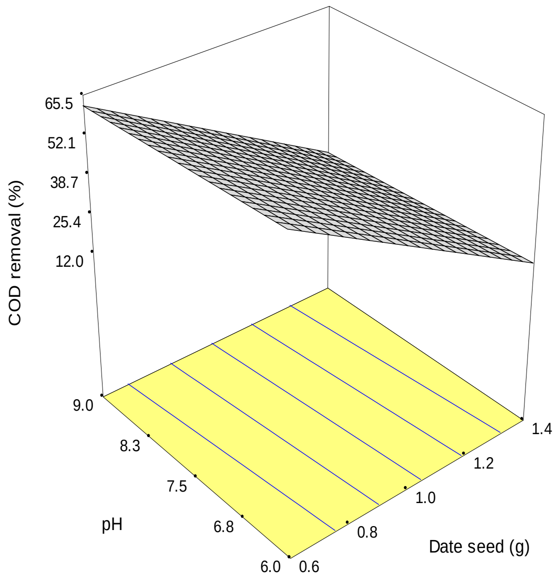
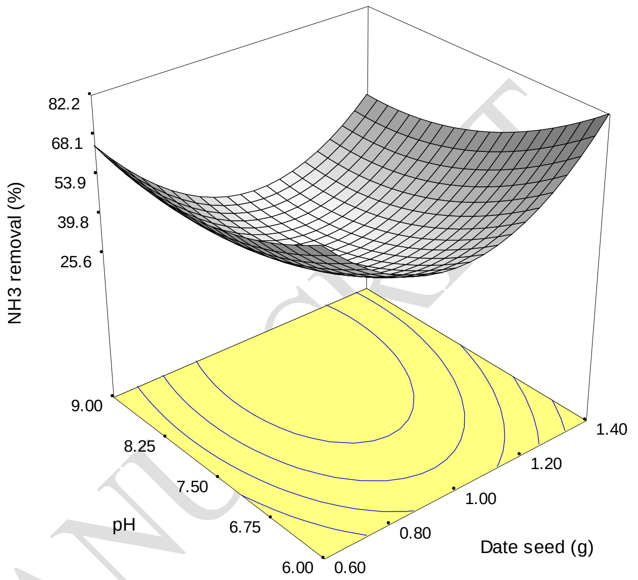


Figure 4. Normal probability plots for a (COD), b (NH_3-N), c(Fe),d (Mn), e (Ai), f(Cu) and g(Ni) removals.

a)

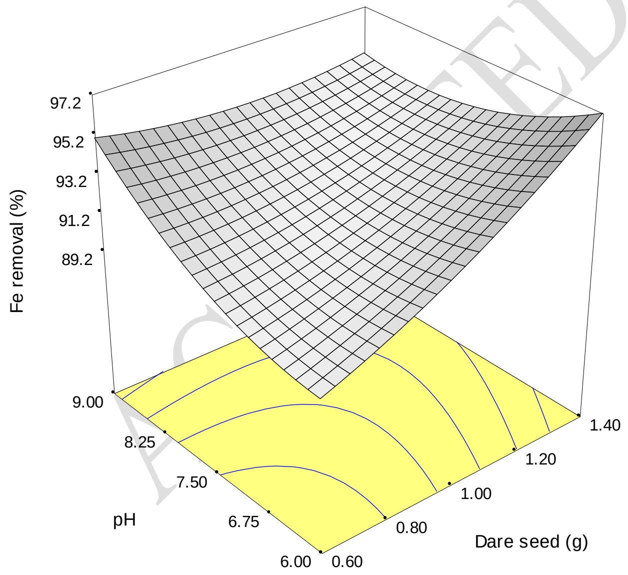
b)

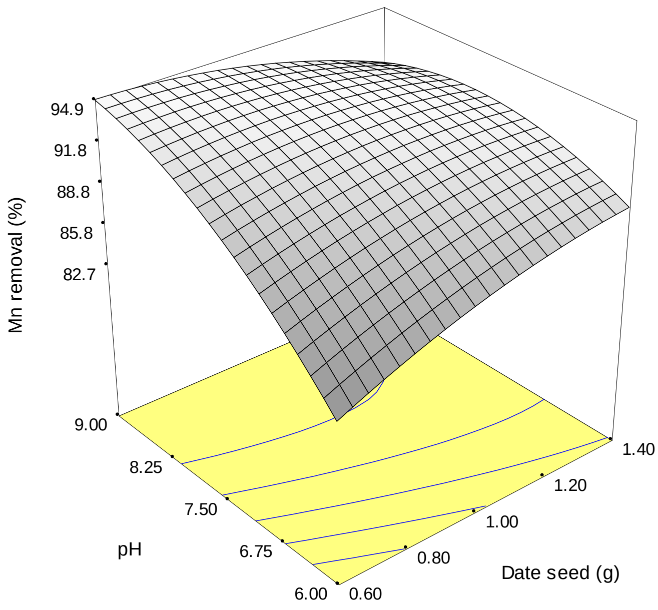

COD removal (%)
65.5
52.1
38.7
25.4
12.0
9.0
8.3
7.5
6.8
6.0
pH
0.6
0.8
1.0
1.2
1.4
Date seed (g)


NH3 removal (%)
82.2
68.1
53.9
39.8
25.6
9.00
8.25
7.50
6.75
6.00
pH
0.60
0.80
1.00
1.20
1.40
Date seed (g)

C)

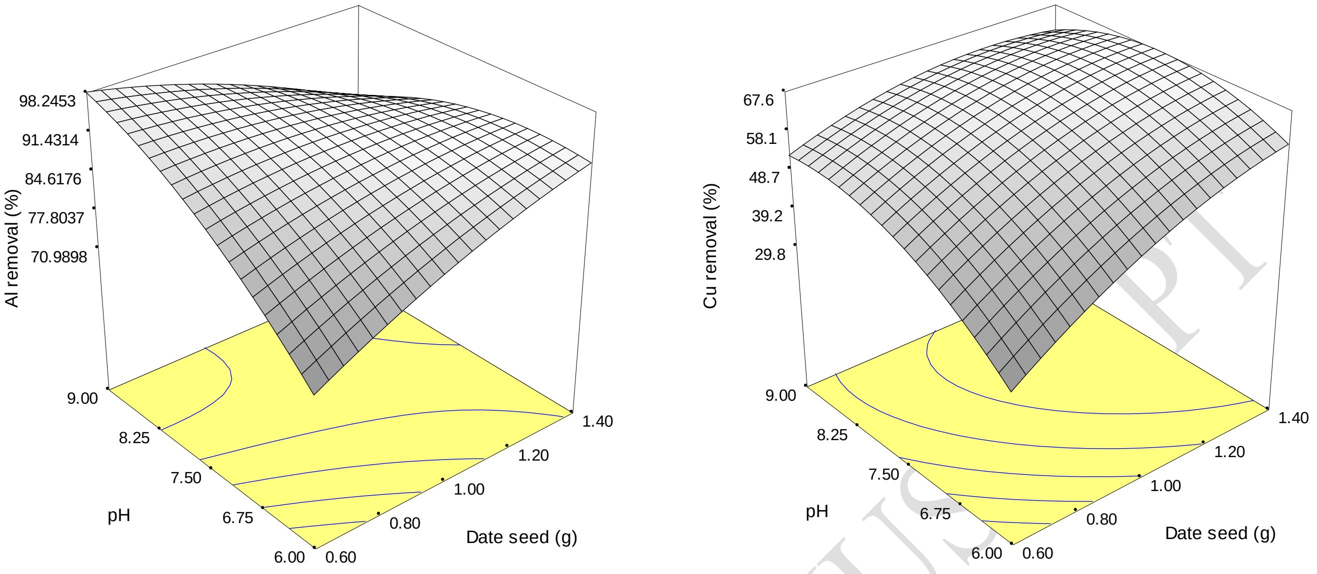
d)


Fe removal (%)
97.2
95.2
93.2
91.2
89.2
9.00
8.25
7.50
6.75
6.00
pH
0.60
0.80
1.00
1.20
1.40
Dare seed (g)

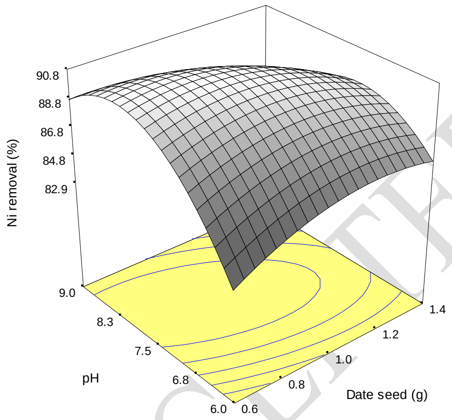

Mn removal (%)
94.9
91.8
88.8
85.8
82.7
9.00
8.25
7.50
6.75
6.00
pH
0.60
0.80
1.00
1.20
1.40
Date seed (g)

e)

f)



g)



3.5 Optimization Operational Conditions

Figure 5. Response surface Plots for a(COD), b(NH_3-N), c(Fe), d(Mn),e (Ai), f(Cu) and g(Ni) removals**.**

Work was done to determine the optimal value for treating the presence of COD and NH_3-N, Fe, Mn, Ai, Cu, Ni in wastewater using the Design Expert 6.0.7 program. Accordingly, the experimental conditions were determined for each case (pH concentration and dose of crushed date stones), and the answers were determined as the best limits in achieving the highest treatment value. The software combines individual desirability into a single value, which it then strives to optimize based on the response objective. As a consequence, the ideal operating conditions and efficiency removals were identified, as indicated in Table 6.

Table 7 shows, it is expected to remove 61%, 65%, 95%, 94%, 98%, 52%, 88% of COD and NH_3-N, Fe, Mn, Ai, Cu, Ni, respectively. Based on optimized operating conditions (date stone 0.6g, pH 9). an experiment was conducted in the laboratory to ensure the correctness of the optimal results. Moreover, it was found that the experiment's results correspond to the value of the expected response.

Table 7. Optimal response results from model prediction and laboratory.

	Date stone (g)	pH	COD removal (%)	NH_3-N removal	Fe removal (%)	Mn removal (%)	Ai removal (%)	Cu removal (%)	Ni removal (%)	Desirability
Prediced	0.6	9	61.8	65	95	94	98	52	88	0.923
Lab. Experment			61	63	93	93	96.5	51	86	

4. Conclusion

In this study, the percentage of COD, NH_3-N, Fe, Mn, Al, Cu and Ni removal by date stone powder showed significant promise as a plant-based natural coagulant in iron and steel factory treatment. The experiment proved the date stone's significant coagulation characteristics. The following are the particular findings of the studies. The FTIR analysis verified the presence of several functional groups that are involved in the coagulation process. At 1.4 g/200 mL, the date stone powder removed a high percentage of COD, NH_3-N, Fe, Mn, Al, Cu and Ni from effluent at pH 8, with percentages 61, 63, 93, 93, 96.5, 51 and 86 %, respectively.

Due to the organic structure of date stones powder, the pH of industrial effluent remained unchanged after its addition. Consequently, no pH adjustment was necessary throughout the treatment process when date stone powder was used as a coagulant.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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