Factorial Design and Optimization of Date Stone as A Natural Coagulant for

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Organic and Heavy Metals Removal from Industrial Wastewater

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- 24
- 25 GRAPHICAL ABSTRACT



26

28 Abstract

29 Several chemical coagulants previously utilize for wastewater treatment with significant 30 performance in removing heavy metals and other parameters. However, their cost effective and 31 the residual of toxic chemical precipitates that pose problems to human health and the 32 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 33 34 explore the performance of date stones as a natural coagulant in iron and steel plant wastewater 35 treatment and to optimize the operating parameters to assess the feasibility of using date stones in 36 the wastewater treatment sector. Response Surface Methodology (RSM), a statistical experimental 37 design, was used to improve the COD, TSS, NH₃-N, and heavy metals removal efficiency using 38 1.4 g/200 mL date stones as control parameters, as well as pH and settling time. At pH 8, the most 39 significant removal efficiency for COD, NH₃-N, Fe, Mn, Al, Cu, and Ni was 61, 63, 93, 96.5, 40 51, and 86 %, respectively. The quadratic models for the parameters chosen were found to be 41 significant with low probability (<0.001), except for NH₃-N (0.004), Fe (0.0042), and Ni (0.0025). 42 The study's results revealed the potential of utilizing date stones as a natural coagulant for the 43 treatment of iron and steel industrial wastewater.

44

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

47 **1. Introduction**

48 In recent times, water consumption has increased due to industrialization, urbanization, and 49 population growth (Ali & Tien Seng, 2018), and, accordingly, wastewater from the various 50 activities of industrialization and urbanization is also increasing, making access to clean and safe 51 water a critical issue (Abujazar, Fatihah, Kabeel, Sharil, & Abu Amr, 2018). Inappropriate 52 mistreatment or untreated wastewater containing contaminants such as suspended solids, 53 pathogens, nutrients, and heavy metals are hurtful and hazardous to the environment and lead to 54 numerous pollution problems (M. Y. D. Alazaiza et al., 2022; Mukherjee, Mandal, Ganguly, & 55 Chatterjee, 2016). Furthermore, leading to waterborne diseases, which affect human health and are 56 responsible for about 80% of the world's diseases (Lundqvist, Mandava, Lungu-Mitea, Lai, & 57 Ahrens, 2019; Ugwu, Umuokoro, Echiegu, Ugwuishiwu, & Enweremadu, 2017); therefore, the 58 best way to combat freshwater scarcity and waterborne diseases is to treat and reuse wastewater 59 (Abujazar, Fatihah, Lotfy, Kabeel, & Sharil, 2018).

60 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 61 62 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, 63 64 Datta, Joshi, & Pathak, 2000). Huge quantities of industrial effluents are produced daily all over 65 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 66 67 (Muralimohan, Palanisamy, & Vimaladevi, 2014; Tobajas, Alicia M. Polo, Mohedano, & Rodriguez, 2014). 68

69 Sometimes, wastewater contains heavy metals. These wastewaters containing heavy metals 70 mainly come from anthropogenic sources such as farms or mining that do not use environmentally 71 friendly techniques or from natural disasters such as earthquakes, storms, and volcanoes that 72 introduce toxic substances into the wastewater (Ahmed, Aktar, Zaman, Jahan, & Bari, 2020; Helen 73 Kalavathy & Miranda, 2010; Nath, Mishra, & Pande, 2019). Heavy metals such as arsenic (As), 74 lead (Pb), copper (Cu), cadmium (Cd), nickel, zinc (Zn), and chromium (Cr) are highly toxic. Even 75 at low concentrations, they are considered the most critical harmful wastes in freshwater reservoirs 76 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).

81 Consequently, effort must be made to eliminate environmental toxic substances from 82 bodies of water. Each industrial wastewater treatment procedure produces treatment outcomes, but 83 the results vary. However, most of these systems employed in the detoxification process have 84 several serious drawbacks operating and maintenance expenses, collateral harm, and complicated 85 treatment processes (M. Alazaiza et al., 2022; Ali & Tien Seng, 2018). The production of 86 secondary waste characterizes conventional treatment processes after the treatment process, such 87 as toxic sludge, which endangers human health and the environment.

88 The shortcomings of the industrial wastewater treatment process include that it has limited 89 capabilities in the treatment process, is capable of leakage, is affected by the weather, and is not 90 treated thoroughly. Concerted efforts have been made in the field of research and development to 91 utilize new plant species and components that can be used as natural coagulants, such as date 92 kernel powder, which is convenient, easy to operate, simple in design, economically inexpensive, 93 and does not produce secondary results. Several studies recently reported the effectiveness of 94 different types of natural coagulants for wastewater treatment. Rifi et al., (2022) utilized Moringa 95 *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 96 97 wastewater. Iber, Okomoda, Rozaimah, & Kasan, (2021) reviewed the performance of chitosan as 98 a natural coagulant for aquaculture wastewater treatment. Besharati Fard et al., (2021) utilized 99 Lallemantia mucilage as a natural coagulant for the treatment of saline oily wastewater. 100 Satisfactory removal for COD was reported in this study. However, the performance of natural 101 coagulants for heavy metals removal from industrial wastewater was not well documented.

102 The effectiveness of date stones as a natural coagulant for organic removal from industrial 103 wastewater and their performance for heavy metals removal from industrial wastewater are 104 evaluated and discussed in this paper. The proper experimental settings and the statistical 105 relationship between variables and response for employing date stones as a natural plant-based 106 coagulant for industrial wastewater treatment are investigated.

4

107 **2. Materials and Methods**

108 Raw industrial wastewater was obtained from Karabuk iron and steel factory, Karabuk, Turkey. 109 The wastewater samples were collected from the discharge point of the factory and later on 110 transported to the laboratory in a cool box within one hour of the collection; if not used 111 immediately, the samples were kept at 25°C in the dark until.

112 **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.

119



- 120
- 121 **Figure 1.** Date stone and powder.
- 122

123 2.2 Analytical Study

- 124 The characterization parameters and strategies utilized are shown in Table 1. During the tests, the
- 125 pH of the samples was adjusted with a 1 N H2SO4/NaOH solution (Hanson, 2015).

126 **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

127

128 **2.3 Experimental Procedure**

129 The coagulation-flocculation process was simulated using Orbital shaker (Type: PSU-10i, 130 no:010144-1404-0228, Latvia), and three 500 mL beakers were used to test the effect of the 131 coagulant dose. Each beaker held 200 mL of sample. The timing and speed for rapid and slow 132 mixing were set using the shaker apparatus's automated controller. In this investigation, the 133 coagulation-flocculation technique included 5 minutes of rapid mixing at 200 rpm, 15 minutes of 134 slow mixing at 90 rpm, and 60 minutes of settling for farther testing for removal efficiency of 135 COD, TSS, ammonia-nitrogen NH₃-N, and heavy metals (Manganese "Mn," Iron "Fe", Zinc "Zn", 136 Aluminum "Al" and Nickel "Ni", Throughout this step of the test, the starting pH (8) of the sample 137 was kept uncorrected. Coagulation was tested on the removal efficiency of COD, and NH₃-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:

143 Removal efficiency(%) =
$$\left[1 - \left(\frac{c_f}{c_i}\right)\right] * 100$$

(1)

- 144 where C_i and C_f correspond to the initial and final values of each parameter
- 145 The characterization of the iron and steel industry wastewater used for these experiments is listed
- 146 in Table 2.
- 147
- 148

Industrial	wastewater	Units	results
parameters			
pН			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

 \mathcal{A}

149 **Table 2.** Characteristic of industrial (iron and steel factory) wastewater.

150 **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.

156
$$Y = f(X_1, X_2 X_3 \dots X_k) \pm \varepsilon$$

157 Where $x_1, x_2, x_3 \dots x_k$ are the input variables that might influence the result and \mathcal{E} is the 158 random error.

(2)

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).

$$_{163} \qquad Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X^2_j + \sum_i \sum_{(3)$$

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 (\mathbb{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.

173 CCD and RSM were used in this section to optimize and assess the relationship between 174 the two independent factors: (1) dosage of a date stone, (2) and pH, as shown in Table 3.

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

175 **Table 3.** Independent variables of the CCD design.

176 Chemical oxygen demand (COD), ammonia-nitrogen (NH₃-N), manganese (Mn), iron (Fe), Copper (Cu), aluminum (Al), and nickel (Ni) removal efficiencies of effluent wastewater 177 178 were examined and regarded as dependent variables (response). The process's performance was 179 assessed by measuring the removal efficiencies for the parameters mentioned above. Each 180 independent variable was adjusted across three levels between 1 and +1 at the given ranges 181 (Tizaoui, Bouselmi, Mansouri, & Ghrabi, 2007). The total number of experiments achieved for the 182 two factors was 13 (=2k+2k5), where k is the number of factors (k=2). Table 4 shows the specifics 183 of the coagulation exponential design matrix.

184 **Table 4. Summary for the experimental matrix of the amount of date stone powder and**

Run	Туре	Factor 1(date stone dosage)/	Factor 2 (PH)
		200 mL	
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

185 **pH number for each experiment.**

186 **3. Results and Discussion**

187 3.1 Characterization of Date Stone Powder Imaging using Scanning Electron Microscopy
 188 (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).

196

a

b)





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

199 **3.2 Fourier Transformed Infrared (FTIR) Analysis**

200 The corresponding Infrared (IR) spectrum using Fourier Transform Infrared (FTIR) Spectroscopy 201 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 202 203 highlight its main functional groups. To ease the analysis of the IR spectrum obtained for date 204 stone powder, the bands' range- where its functional groups could possibly highlight within the 205 range of wavelength peaks. The observed peaks in the 300-2500 cm⁻¹ range might indicate the 206 existence of solid amine salts (N-H) that are involved in the bridging mechanism used by particles 207 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 208 209 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 210 between 1200-1000 cm⁻¹ shows the N-H aliphatic amine. 211



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 stonepowder.

		Factors		Respo	nses					
Run	Туре	A: Da	te B: pH	COD	NH3-N	Fe	Mn	Ai	Cu	Ni
		stone								
		dosage								
		(g)			-	•	•	•	•	-
			$\langle \rangle$	al %	al %	al %	al %	al %	al %	al %
				nov:	nova	nov	nova	nova	nova	nova
				Reı	Reı	Reı	Reı	Reı	Reı	Reı
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

216 The process of adding date stone powder to the wastewater solution was carried out in 217 different quantities with a change in the experimental conditions, and the results of the removal 218 efficiencies ranged between 6.4% and 70.6% for COD, 24.3% to 97.7% for NH3-N, 89.0% to 219 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 220 Cu, and 80.7% to 90.7%, for Ni. The results indicate that the efficiency of date stone powder in 221 the processing process is extensive in removing **Fe** and **NH**₃-N, while the treatment rate was weak 222 in Ai and Cu; this is due to the cohesion of the molecules of these elements with each other, which 223 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 R² for COD, NH₃-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 R² value close to 1 indicates a worthy acceptance between the expected and calculated outcomes results.

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232

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

		Sum of		Mean	F		
%	Source	Squares	DF	Square	Value	Prob > F	
val	Model	5046.96	5	1009.39	65.31	< 0.0001	significant
emo	А	4961.86	1	4961.86	321.03	< 0.0001	
Dr	В	27.68	1	27.68	1.79	0.2227	
CO	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	5			
	Sum of		Mean	F		
Source	Squares	DF	Square	Value	Prob > F	X /
Model	7298.16	5	1459.63	9.93	0.0044	significant
А	60.76	1	60.76	0.41	0.5408	/
В	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 Day 12.12	D2. 0.9761	Maam. 52 00				

Std. Dev. 12.13, R²: 0.8764, Mean: 53.20

		Sum of		Mean	F		
	Source	Squares	DF	Square	Value	Prob > F	
	Model	66.30	5	13.26	10.11	0.0042	significant
	А	29.18	1	29.18	22.25	0.0022	
	В	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			
7	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, N	Mean:93.26				
le		Sum of		Mean	F		
mov:	Source	Squares	DF	Square	Value	Prob > F	
rel	Model	159.82	5	31.96	22.43	0.0004	significant

NH₃-N Removal %

Fe removal %

Mn

А	1.37	1	1.37	0.96	0.3593	
В	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				V /
Std. Dev. 1.19	R ² : 0.9412, N	Mean: 90.41	l			

	Sum of		Mean	F		
Source	Squares	DF	Square	Value	Prob > F	
Model	616.14	5	123.23	5.99	0.0181	significant
А	0.65	1	0.65	0.032	0.8636	
В	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				

Al removal %

Std. Dev. 4.54, R²: 0.8105, Mean 87.16

		Sum of		Mean	F		
	Source	Squares	DF	Square	Value	$\mathbf{Prob} > \mathbf{F}$	
	Model	1608.41	5	321.68	16.47	0.0010	significant
	А	743.85	1	743.85	38.08	0.0005	
. •	В	284.92	1	284.92	14.58	0.0066	
al %	A2	151.78	1	151.78	7.77	0.0270	
mov	B2	370.98	1	370.98	18.99	0.0033	
u re	AB	110.80	1	110.80	5.67	0.0488	
Ü	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 55.2		26			
Z		Sum of		Mean	F		

Source	Squares	DF	Square	Value	Prob > F	
Model	148.77	5	29.75	12.01	0.0025	significant
А	4.83	1	4.83	1.95	0.2052	
В	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	, Mean87.1	13			/

234 **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, NH₃-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.

240 The Design Expert 6.0.7 program was used to investigate the interaction linkages between 241 independent factors and the responses of specific models using 3D surface response and contour 242 plots, as illustrated in Error! Reference source not found. (a-g). The largest percent of NH₃-N 243 and COD removal is 82.2% and 66.5 %; respectively, when the dose of ground date stones is 1.4 244 g, and the level is 9.0 as well as for Fe, Mn, Ai, Cu, and Ni, the removal percentage is 97.2% and 245 94.9%, 98.24%, 67.6%, and 90.8%, respectively. These response charts indicate that the amount 246 of treatment needed is determined by the ratios of these elements in the wastewater and the 247 experimental settings (pH level). The effectiveness of date stone powder's coagulation in removing 248 COD and NH3-N varied. Determining the ideal coagulant dose is crucial to ensure that the 249 treatment process runs at its best while lowering material costs and sludge formation. The ability 250 of date stone powder's natural polyphenols to adsorb metal ions and organic impurities improved 251 the elimination of organic pollutants (Palma, Freer, & Baeza, 2003). The action of electric double 252 layers produced by carboxylic, phenolic, and amino groups may be responsible for the

253 improvement in organic and ammonia elimination (Schofield, Mbugua, & Pell, 2001). The 254 efficiency of the targeted parameters' elimination decreased when date stone doses more than 7 g 255 were utilized. The wastewater's colloids and particles were better able to bridge one another thanks 256 to date stone's positively charged primary amino groups, which also enhanced the flocculation 257 process (Mangrich, Doumer, Mallmannn, & Wolf, 2014). High molecular weight date stone 258 powder is not hydrolyzed in wastewater. A larger dose of date stone causes a significant volume 259 of powder to precipitate quickly, which may lessen the efficiency of flocculation (Kim, Silva, Kim, 260 & Jung, 2010).







Figure 4. Normal probability plots for a (COD), b (NH₃-N), c(Fe),d (Mn), e (Ai), f(Cu) and g(Ni) removals.

g)

- ----



e)

f)

19



3.5 Optimization Operational Conditions

Figure 5. Response surface Plots for a(COD), b(NH₃-N), c(Fe), d(Mn),e (Ai), f(Cu) and g(Ni) removals.

280 Work was done to determine the optimal value for treating the presence of COD and NH₃-N, Fe,

281 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

283 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 NH₃-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. Experm	ent		61	63	93	93	96.5	51	86	

4. Conclusion

In this study, the percentage of COD, NH₃-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, NH₃-N, Fe, Mn, Al, Cu and Ni from effluent at pH 8, with percentages 61, 63, 93, 93, 96.5, 51 and 86 %, respectively.

301 Due to the organic structure of date stones powder, the pH of industrial effluent remained 302 unchanged after its addition. Consequently, no pH adjustment was necessary throughout the 303 treatment process when date stone powder was used as a coagulant.

304

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318 The authors declare the following financial interests/personal relationships which may be considered 319 as potential competing interests:

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- 322 323
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