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Assessment of a hybrid technology for liquid fuel dimethyl aminoethyl azide wastewater treatment

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ABSTRACT

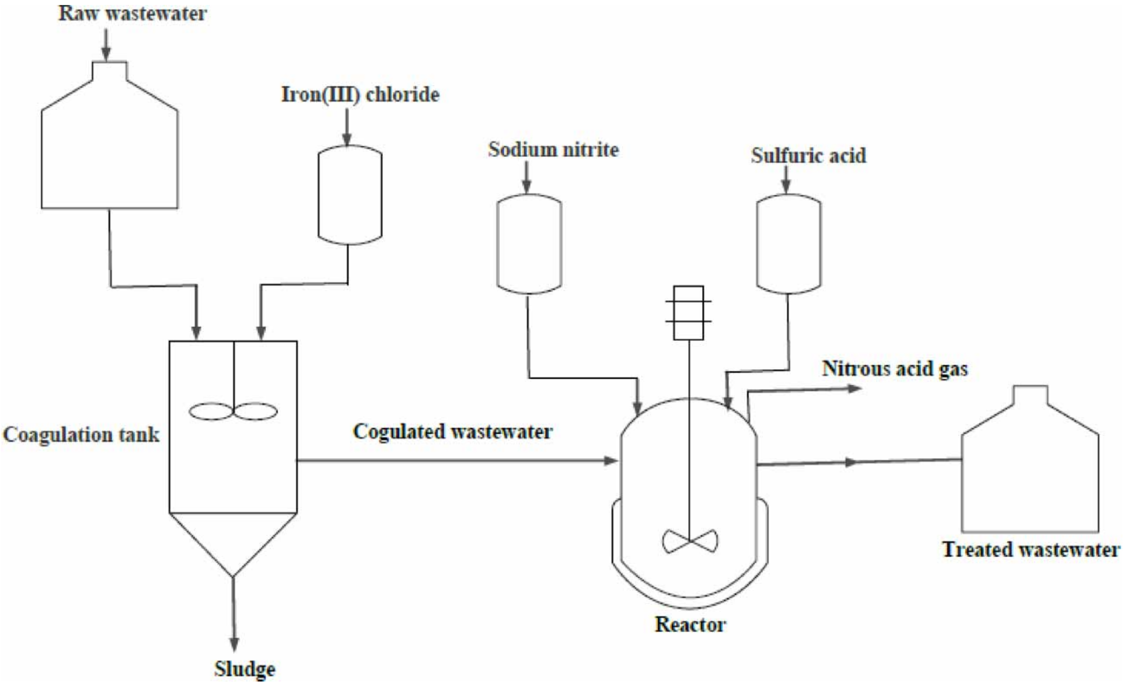
Dimethyl aminoethyl azide (DMAZ) is a liquid fuel in the space industry. Although this fuel is non-carcinogenic, its wastewater suffers from some hazardous pollutants, such as sodium azide (NaN_3). A hybrid process of coagulation–flocculation and chemical reaction with nitrous acid was applied for the wastewater treatment. The Taguchi method was used for the process optimization. Coagulant concentration, rapid mixing intensity, duration time, CAMP number and settlement time were found to be effective parameters for the efficiency of the former process. Turbidity and total suspended solids (TSS) of the wastewater were used to track the removal efficiency in the first stage. The complete removal efficiency was achieved. In the latter process, NaN_3 was removed using a reaction with nitrous acid. pH of the wastewater was optimized as the controlling factor in the second process. Biochemical oxygen demand (BOD), chemical oxygen demand (COD) and NaN_3 removals of 98.9, 98.2 and 96.3% were obtained under the optimum conditions, respectively. As a result, a reduction of 91.9% in turbidity, 98.5% in TSS, 98.5% in BOD, 98.1% in COD and 96.7% in NaN_3 concentration were observed in the output of the wastewater.

Key words: chemical reaction with nitrous acid, coagulation–flocculation process, DMAZ wastewater treatment, sodium azide removal

HIGHLIGHTS

- A hybrid process of coagulation–flocculation and chemical reaction was used for DMAZ wastewater treatment.
- The conditional optimization for overall processes was performed by the Taguchi method.
- Optimal removal of TSS and turbidity was found with $FeCl_3$ dosage, rapid mixing time, gradient velocity, CAMP number and sedimentation rate.
- The overall hybrid process has good and suitable performance.

GRAPHICAL ABSTRACT



UNITS AND SYMBOLS

A (mg)	Final weight of the filter
A_i ($mg{\cdot}L^{-1}$ or NTU)	Initial values of COD, BOD, TSS, turbidity and NaN_3
A_t ($mg{\cdot}L^{-1}$ or NTU)	Final values of COD, BOD, TSS, turbidity and NaN_3
ANOVA	Analysis of variance
B (mg)	Initial weight of the filter
BOD ($mg{\cdot}L^{-1}$)	Biochemical oxygen demand
C_i ($mg{\cdot}L^{-1}$)	Concentration of component i
COD ($mg{\cdot}L^{-1}$)	Chemical oxygen demand
DMAEC	Dimethyl aminoethyl chloride
DMAZ	Dimethyl aminoethyl azide
DOF	Degree of freedom
E (%)	Removal efficiency
G (s^{-1})	Velocity gradient
N (s^{-1})	Impeller speed
n	Number of repetitions
N_1 (s^{-1})	Impeller speed
N_P	Power number of the impeller
NaN_3	Sodium azide
NTU	Nephelometric turbidity unit
OA	Orthogonal array
P ($N{\cdot}m{\cdot}s^{-1}$)	Power requirement
Re	Reynolds number
S/N	Signal-to-noise ratio
t (s)	Slow mixing time
t_1 (s)	Coagulation time
t_2 (min)	Flocculation time
t_s (h)	Settlement time
TSS ($mg{\cdot}L^{-1}$)	Total suspended solids
V (m^3)	Volume of wastewater filtered
y_i	Result of each measurement

Greek symbols

λ_{max} (nm)	Maximum absorbance wavelength
μ ($N{\cdot}s{\cdot}m^{-2}$)	Dynamic viscosity
ρ ($kg{\cdot}m^{-3}$)	Wastewater density

1. INTRODUCTION

Chemical industries require a substantial amount of water for efficient operation and produce a significant amount of wastewater that usually does not meet the environmental regulations for direct discharge to surface or underground waters (Turunen *et al.* 2020). Discharge of such effluents without proper treatment on the one hand and limited water supplies, on the other hand, are big challenges for the environment (Osode & Okoh 2009).

The most important goal of wastewater treatment is to reduce or eliminate existing pollution so that refined wastewater can be drained or reused without any consequences. A wastewater treatment plant consists of some processing units with several options and its process design depends on the properties of raw wastewater and the quality requirements for the treated wastewater. For this purpose, sufficient knowledge of the amount and degree of raw wastewater pollution is essential (Valta *et al.* 2017; Baharvand & Mansouri Daneshvar 2019). The new liquid fuel, dimethyl aminoethyl azide (DMAZ), also follows this rule.

DMAZ is a new non-carcinogenic and relatively non-toxic liquid fuel that is used in space programs. It has desirable energetic and safe environmental properties (Guseinov *et al.* 2018). The fuel is synthesized from the reaction between 2-dimethyl aminoethyl chloride and sodium azide in an aqueous solution. In this reaction, DMAZ is separated and purified as an organic phase (Azizi *et al.* 2018). However, a part of the product, byproducts and unused raw materials remain in the reaction solution, which is interpreted as the wastewater in the DMAZ production unit and is high in biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), turbidity and toxic chemicals.

The wastewater is considered toxic and hazardous because of the presence of sodium azide (Bhat *et al.* 2012). Hence, the wastewater should be treated. Chemical treatment methods are the best option for treating this type of wastewater. These methods are used to affect the complete breakdown of hazardous waste into non-toxic gases or, more frequently, to modify the chemical properties of the waste. Accordingly, sodium azide can be chemically degraded using the reaction with nitrous acid (Denisaev *et al.* 2013). The presence of DMAZ, other organic azide compounds and also byproducts reduce the BOD and COD levels. The most effective factor of this reaction is the pH value that should be optimized (Valero 2008).

Due to the high amounts of suspended solids in the wastewater, a successful chemical method needs a preliminary separation process to improve efficiency and therefore cost reduction (Mahmudabadi *et al.* 2018). Coagulation–flocculation followed by clarification is one of the most practical technologies extensively used on an industrial scale for wastewater treatment to remove TSS and turbidity (Liakos & Lazaridis 2014; Gökçek & Özdemir 2020). These processes cause the aggregation of small particles into larger, settleable and more easily removed flocs by adding inorganic coagulants that destabilize the charged colloids and thus neutralize the forces, which keep them apart (Sahu *et al.* 2014). Generally, this process involves three main parts: rapid mixing, flocculation and settling. At first, the addition and rapid dispersion of the proper coagulants throughout the wastewater are performed by rapid mixing (coagulation). Coagulated particles are then combined by mechanically induced velocity gradients via slow mixing (flocculation). Finally, the flocs are separated in the clarification unit by gravity (Housni *et al.* 2020). Based on previous works, it was observed that iron (III) chloride ($FeCl_3$) is the preferred coagulant. Moreover, a pH of 12 is optimum for the coagulation step. However, there is no study or report on the optimization of other main coagulation–flocculation operational parameters, including coagulant dose, rapid and slow mixing conditions and settlement time.

The goal of this article is to find an optimal method for wastewater treatment of the DMAZ production unit. To this end, we evaluated the applicability of a hybrid process involving coagulation–flocculation for removing the TSS and turbidity, followed by chemical reactions with nitrous acid to reduce the organic load (BOD and COD) and sodium azide from the wastewater. In the first step, an experimental design based on the Taguchi method was selected to evaluate the effect of controlling parameters such as coagulant dose, rapid and slow mixing speed and finally settlement time. The optimized process in the first unit was followed by a chemical reaction and pH optimized for the second unit. It hopes that the results of this research will help to reuse the treated wastewater for consumption in the process or safe release to the environment.

2. MATERIALS AND METHODS

2.1. Wastewater characterization

The raw wastewater contains DMAZ, di methyl aminoethyl chloride (DMAEC), sodium azide, sodium chloride, sodium hydroxide and water. The weight percent of the components is given in Table 1.

Table 1 | Chemical contents of the DMAZ wastewater

Chemical content	Weight percentage
DMAEC	4.12
NaN_3	11.80
NaOH	1.14
NaCl	14.54
DMAZ	1.94
Water	66.46
Total	100.00

In the wastewater, the concentration of sodium azide (NaN_3), as a major hazardous pollutant, was measured using the spectrophotometric method (Hajiaghabozorgy *et al.* 2014).

The wastewater quality in terms of parameters such as COD, BOD_5, turbidity and TSS was monitored after its filtration through a 0.45 μm membrane using standard methods (Rice *et al.* 2017). All measurements were conducted before and after 12 h of pre-sedimentation.

2.2. Chemicals

The chemicals used in the experiments were iron (III) chloride ($FeCl_3$), sodium nitrite ($NaNO_2$) and sulfuric acid (H_2SO_4). All materials were commercial grade that purchased from Mobtakeran Shimi Co. (Iran).

Sodium azide (NaN_3), acetic acid ($C_2H_4O_2$), sodium acetate ($C_2H_3NaO_2$) and copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) were consumed for analysis. All the chemical reagents were of analytical grade and purchased from Merck Co. (Germany). Moreover, pH of the solutions was adjusted via sulfuric acid.

2.3. Analysis

After each experiment, the treated wastewater samples were held at 4 °C in dark conditions. All analytical methods were performed based on the standard methods (Rice *et al.* 2017).

The organic matter removal was investigated in terms of COD and BOD, which were performed according to Methods 5220 C and 5210 D of standard methods for examining water and wastewater, respectively (Rice *et al.* 2017).

To measure TSS according to Method 2540D, the wastewater sample was filtered through a pre-weighted filter. The residue on the filter was dried in an oven at 103–105 °C until the weight of the filter became constant. TSS was calculated as in the following equation:

$$TSS(mg \cdot L^{-1}) = \frac{(A - B) \times 1,000}{V} \tag{1}$$

where A, B and V are the final weight of the filter, initial weight of the filter and the volume of wastewater filtered, respectively.

Turbidity values were measured according to Method 2130B using a turbidimeter (model HI 98703). The pH of the samples was measured by a calibrated pH meter (model Proline B210).

The concentration of sodium azide (NaN_3) was measured using the spectrophotometric method based on its complex reaction with copper (II). A UV–vis spectrophotometer equipped with a 1 cm quartz cell (model UV-3101PC, Hitachi Co.) was used for absorbance measurements. According to the recorded UV–vis spectrum of NaN_3 samples in the visible range from 200 to 800 nm, the absorbance was measured at the wavelength of 366 nm as the maximum absorbance wavelength (λ_{max}). To make the measurements by the UV–vis spectrophotometer, all these samples were diluted 1:10 before the analysis (Hajiaghabozorgy *et al.* 2014).

The following equation was used to evaluate the removal efficiency for COD, BOD, TSS, turbidity and NaN_3.

$$E(\%) = \frac{(A_i - A_t)}{A_i} \times 100 \tag{2}$$

where A_i and A_t are the initial and final values of COD (mg·L^{-1}), BOD (mg·L^{-1}), TSS (mg·L^{-1}), turbidity (NTU) and NaN_3 (mg·L^{-1}), respectively.

The most important design parameters for rapid mixing are the agitation intensity and mixing duration. The agitation intensity required for optimum rapid mixing and flocculation is measured by the velocity gradient (G) which determines the probability of the particles coming together. To evaluate the effects of G values and also calculate the impeller speed, the required power was calculated using the Stoke's theorem (Labík *et al.* 2014):

$$P = \mu V G^2 \tag{3}$$

where P, μ, V and G are the power required, the dynamic viscosity, the wastewater volume and the mean velocity gradient during rapid or slow mixing, respectively.

Based on the calculated P, the impeller speed was calculated as in the following equation (Kang *et al.* 2020):

$$N_1 = \sqrt{\frac{P}{N_p \times \rho \times d^5}} \tag{4}$$

where N_1, P, N_p, ρ and d are the impeller speed, the power required, power number of the used impeller, wastewater density (equal to 1,240 kg·m^{-3}) and the impeller diameter (equal to 0.091 m), respectively.

To check the turbulent regime resulting from the correct choice of G value and then impeller speed, the Reynolds number should be calculated. The Reynolds number is calculated in the following equation:

$$Re = \frac{\rho N d^2}{\mu} \tag{5}$$

where ρ, N, d and μ are the wastewater density, the impeller speed, impeller diameter (equal to 0.091 m) and the dynamic viscosity (equal to 0.0013 N·s·m^{-2}).

There is an optimum slow mixing intensity and duration in the flocculation stage. The effect of CAMP number was evaluated as a factor that was reported to be more important than the G and t factors when investigated separately. The CAMP number is calculated according to the following equation (Zhang *et al.* 2013):

$$\text{CAMP number} = G \times t \tag{6}$$

where G is the mean velocity gradient during slow mixing and t is the slow mixing time.

2.4. Experimental setup and procedure

The overall treatment was accomplished in a hybrid process: a coagulation–flocculation process to remove TSS and turbidity as Stage I and a chemical reaction with nitrous acid to remove BOD, COD and NaN_3 as Stage II. The controlling parameters for both sub-processes were optimized in this study. A schematic diagram of the wastewater treatment is shown in Figure 1, which includes four storage tanks for raw wastewater, $FeCl_3$, H_2SO_4 and $NaNO_2$ solutions. According to this diagram, the major operating and processing units are the coagulation and NaN_3 removal reactors.

2.4.1. Coagulation and flocculation

At the beginning of the unit, the coagulation was carried out in a conical bottom tank, which performs the three processes of coagulation, flocculation and settlement. Based on preliminary experiments, iron chloride was used as a proper coagulant and the process was conducted at pH = 12.5 (pH of the raw wastewater).

In this stage, all tests were conducted according to the following procedure:

At first, 12 L of raw wastewater was decanted into the flocculation tank and a certain amount of $FeCl_3$, as a coagulant, was injected. Then, rapid mixing at impeller speed N_1 at time t_1 was performed (t_1 is the rapid mixing time from the mid-point of the short dosing). After that, slow mixing at a speed of 75 rpm for t_2 time was conducted (t_2 is the slow mixing time after the end of rapid mixing time). After t_2 time, to separate coagulated particles, the power supply was switched off and the wastewater was allowed to settle without stirring for t_s time

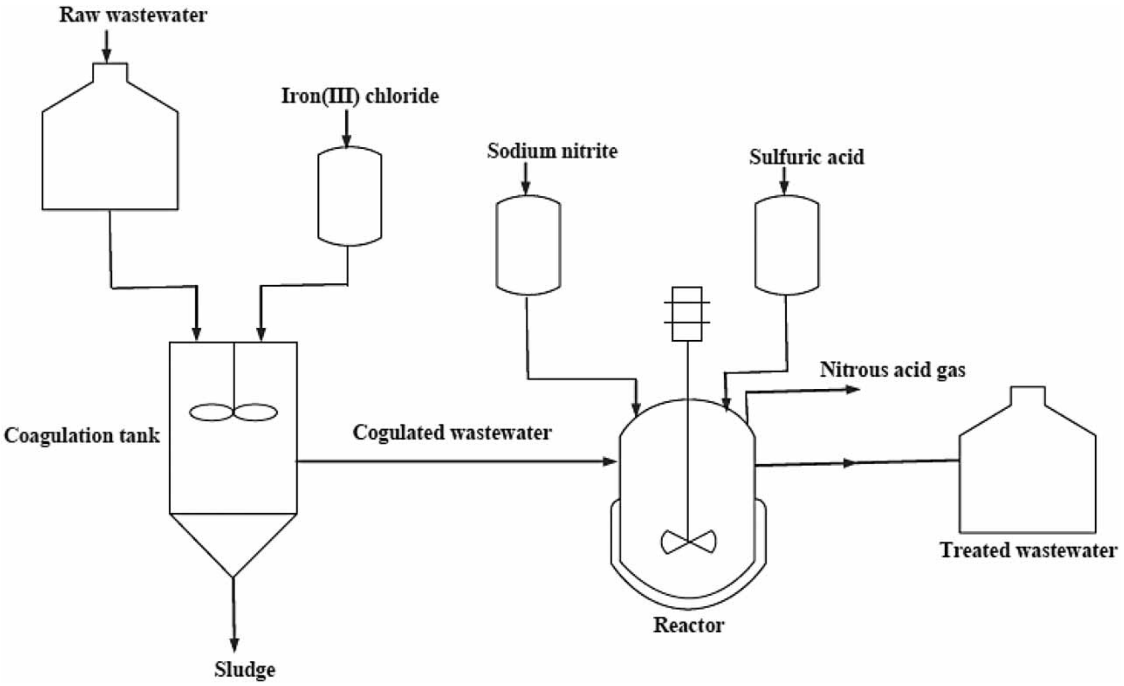


Figure 1 | Schematic diagram of the wastewater treatment.

(t_s is the settlement time). After t_s time, a sample (about 100 mL) was withdrawn from a height of 4 cm below the surface for measuring the residual turbidity and TSS.

The output of the coagulation tank was two-phase: the solid phase (sludge), which is the flocs that formed by the reaction between coagulants and colloidal particles in the effluent, and the liquid phase, which is the output effluent with reduced TSS and turbidity. The settled flocks were removed from the bottom of the tank for environmental disposal and the coagulated effluent was treated in the next step to remove BOD, COD and sodium azide.

2.4.1.1. The Taguchi method for optimization of coagulation process parameters. One of the main objectives of this study is to optimize the coagulation–flocculation process by employing the Taguchi design method to obtain suitable wastewater for reuse. The most important factors for flocculation studies are the appropriate coagulant dose, mixing energy, coagulation time, the CAMP number in flocculation and settling time (Katayon *et al.* 2005). The Taguchi design method was employed to optimize these five factors, while turbidity and suspended solids removal efficiencies were chosen as the main targets (Mohammadi *et al.* 2004). The method involves using an orthogonal array (OA) of L_{18} possessing five factors at three levels. The investigated factors and their levels were based on experimental tests and the recommended range in references (Kumar & Mungray 2020), which are shown in Table 2. The Taguchi method recommends using a signal-to-noise (S/N) ratio to measure the performance characteristics deviating from the desired value. The optimum conditions should also be determined using the S/N ratio. The optimum level of the process parameters is the level with the largest S/N ratio, which is given by the following equation:

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\right)\sum\frac{1}{y_i^2} \tag{7}$$

Table 2 | Controlling factors and levels

Factor	Minimum	Maximum	Level 1	Level 2	Level 3
C_{FeCl_3} (mg·L^{-1})	400	800	400	600	800
$G_{Coagulation}$ (s^{-1})	500	1,000	500	750	1,000
$t_{Coagulation}$ (s)	30	60	30	45	60
CAMP number	2×10^4	2×10^5	36,000	72,000	108,000
t_s (h)	2	8	2	5	8

where n is the number of repetitions under the same experimental conditions and y_i represents the result of each measurement. An analysis of variance (ANOVA) was used to evaluate the experimental results and determine the significance and importance of factors in pollution removal. The Qualitek-4 software was used for this purpose.

The CAMP number is a combination of both time and velocity. Therefore, to generate different values for this number, a constant velocity equal to 75 rpm (according to the average velocity gradient of recommended range 10–75 s^{-1} for flocculation equal to 40 s^{-1} as G_2) was considered and the slow mixing time was evaluated at three levels of 15, 30 and 45 min.

2.4.2. Chemical reaction with nitrous acid

The second stage of the wastewater treatment unit is the sodium azide removal reaction, as in the following equation:

$$2HNO_2 + 2NaN_3 \rightarrow 2NO + 3N_2 + NaOH \tag{8}$$

This reaction is exothermic, so a reactor equipped with a cooling system was applied. Nitrogen oxide was exited into a chemical scrubber for removal. It should be noted that nitrous acid (HNO_2) is produced from the *in situ* reaction of sulfuric acid and sodium nitrite (Denisaev *et al.* 2013):

$$H_2SO_4 + 2NaNO_2 \rightarrow Na_2SO_4 + 2HNO_2 \tag{9}$$

The reaction process was conducted according to the following procedure:

The wastewater was first decanted into the reactor and an appropriate amount of the 20% aqueous solution of sodium nitrite (based on NaN_3 concentration) was added. The reaction mixture was mixed at 100 rpm for 5 min. Then, a certain amount of the 20% aqueous sulfuric acid solution was added gradually to reach a desired pH level. The sequence of addition is important. In other words, if the acid is added before the nitrite, highly toxic HN_3 vapors will be evolved. The mixing operation was performed at 100 rpm for 1 h. At the end of removal, the treated wastewater sample (500 mL) was withdrawn from the reactor and tested for residual NaN_3, BOD and COD measurements.

Based on the experimental work, the addition of sodium nitrite (Step 2) and sulfuric acid (Step 4) is accompanied by the release of gas and foam formation. From the process safety point of view, the reactants should be slowly added with sufficient mixing time.

2.4.2.1. pH optimization in NaN_3 removal reaction. The most important controlling factor for NaN_3 removal reaction is pH of the solution. Therefore, pH was measured and optimized after determining the amount of NaN_3 present in the effluent at four values of 5, 5.5, 6 and 6.5. For this purpose, the $NaNO_3$ solution was added and then sulfuric acid was used to adjust the solution's pH and simultaneously nitrous acid production. To evaluate the effect of this stage on the wastewater treatment, BOD, COD and sodium azide concentration were measured in the optimum coagulation and flocculation experiments.

3. RESULTS AND DISCUSSION

3.1. Wastewater characteristics

The characteristics of the DMAZ wastewater before and after the pre-sedimentation stage are presented in Table 3. Also, the sodium azide concentration was 112,866 mg·L^{-1}.

Table 3 | Characteristics of DMAZ wastewater

	Turbidity (NTU)	TSS (mg·L^{-1})	BOD_5 (mg·L^{-1} O_2)	COD (mg·L^{-1} O_2)
Raw wastewater	194	1,820	6,150	29,416

It is seen that the wastewater contains high levels of turbidity, TSS, BOD_5 and COD. All parameters exceeded the permissible discharging limits of Iranian standards and must be treated before they can be discharged to any receiving source.

While BOD_5 reflects biodegradable organic matter, COD represents total organic matter. By comparing these two values, the biodegradability of DMAZ wastewater could be estimated. The COD to BOD_5 ratio for DMAZ effluent was around 4.78, indicating its very low biodegradability and the inability of the biological process to improve treatment (the precondition for using this method is COD to BOD_5 ratio < 3) (Lee & Nikraz 2014). Therefore, other specific methods are required to treat this type of wastewater.

3.2. Results of the Taguchi method for TSS and turbidity removal in the coagulation–flocculation unit

According to the Taguchi experiment design, 18 experiments were performed in the coagulation–flocculation unit to determine the optimum experimental conditions for maximum removal of turbidity and TSS. The experimental runs as L_{18} OA and the obtained results for TSS and turbidity removal are presented in Table 4. According to this table, high removal efficiencies (in terms of TSS and turbidity) were achieved. Although the removal efficiencies (in terms of TSS and turbidity) were obtained; however, all TSS and turbidity are not above 99%. Removal efficiency in terms of TSS is less than 99%, for example, in Run 5. Also, in some cases, the removal efficiency in terms of turbidity is less than 99%, such as in Runs 2, 5, 6, 7, 10, 12, 13 and 18. The maximum removal is observed at Run number 15 (99.79% removal of turbidity and 100% TSS removal), while the minimum is obtained from Run number 5 (94.23 and 98.9% for the removal of turbidity and TSS, respectively). Based on the initial turbidity and TSS of the DMAZ wastewater (Table 3), the obtained turbidity and TSS should be as low as possible to use for the next applications. Thus, these limitations should be prevalent. Under the same conditions, each experiment was repeated at least three times and the average of these values was introduced to the Qualitek-4 software.

Table 4 | Taguchi's L_{18} OA design and experimental results for TSS and turbidity removal efficiency

	Controlling factor					**Removal efficiency (%)**	
Run	**C_{FeCl_3} (mg·L^{-1})**	**G_1 (s^{-1})**	**t_1 (s)**	**$G_2 \times t_2$**	**t_s (h)**	**TSS**	**Turbidity**
1	400	500	30	36,000	2	99.89	99.19
2	400	750	45	72,000	5	99.73	98.86
3	400	1,000	60	108,000	8	99.84	99.16
4	600	500	30	72,000	5	99.78	99.31
5	600	750	45	108,000	8	98.9	94.23
6	600	1,000	60	36,000	2	99.56	98.19
7	800	500	45	36,000	8	99.07	95.36
8	800	750	60	72,000	2	99.78	99.22
9	800	1,000	30	108,000	5	99.84	99.42
10	400	500	60	108,000	5	99.78	98.54
11	400	750	30	36,000	8	99.89	99.32
12	400	1,000	45	72,000	2	99.78	98.77
13	600	500	45	108,000	2	99.73	98.99
14	600	750	60	36,000	5	99.78	99.15
15	600	1,000	30	72,000	8	100.00	99.79
16	800	500	60	72,000	8	99.95	99.55
17	800	750	30	108,000	2	99.89	99.46
18	800	1,000	45	36,000	5	99.18	95.52

3.2.1. Analysis of the signal/noise ratio to determine the optimal conditions

In order to analyze the experimental results and evaluate the influence of each factor on the TSS and turbidity removal, the S/N ratio for each factor should be computed. Table 5 lists the average S/N ratios for each level of the variables for both turbidity and TSS removal efficiency. Moreover, Figures 2 and 3 show the effects of five controlling factors on the averaged S/N ratios for turbidity and TSS removal efficiency, respectively. The mean S/N ratio for each controlling parameter at any level was determined by averaging the S/N ratio values of all experiments at that level.

Table 5 | S/N ratio to determine the optimized conditions for turbidity and TSS removal by coagulation method

	Average S/N ratio					
	Level 1		**Level 2**		**Level 3**	
Variables	**Turbidity**	**TSS**	**Turbidity**	**TSS**	**Turbidity**	**TSS**
C_{FeCl_3} (mg·L^{-1})	98.973	99.818	98.276	99.625	98.088	99.618
G_1 (s^{-1})	98.489	99.700	98.373	99.661	98.475	99.700
t_1 (s)	99.415	99.881	96.954	99.398	98.968	99.781
$G_2 \times t_2$	97.788	99.561	99.250	99.836	98.299	99.663
t_s (h)	98.970	99.771	98.466	99.681	97.901	99.608

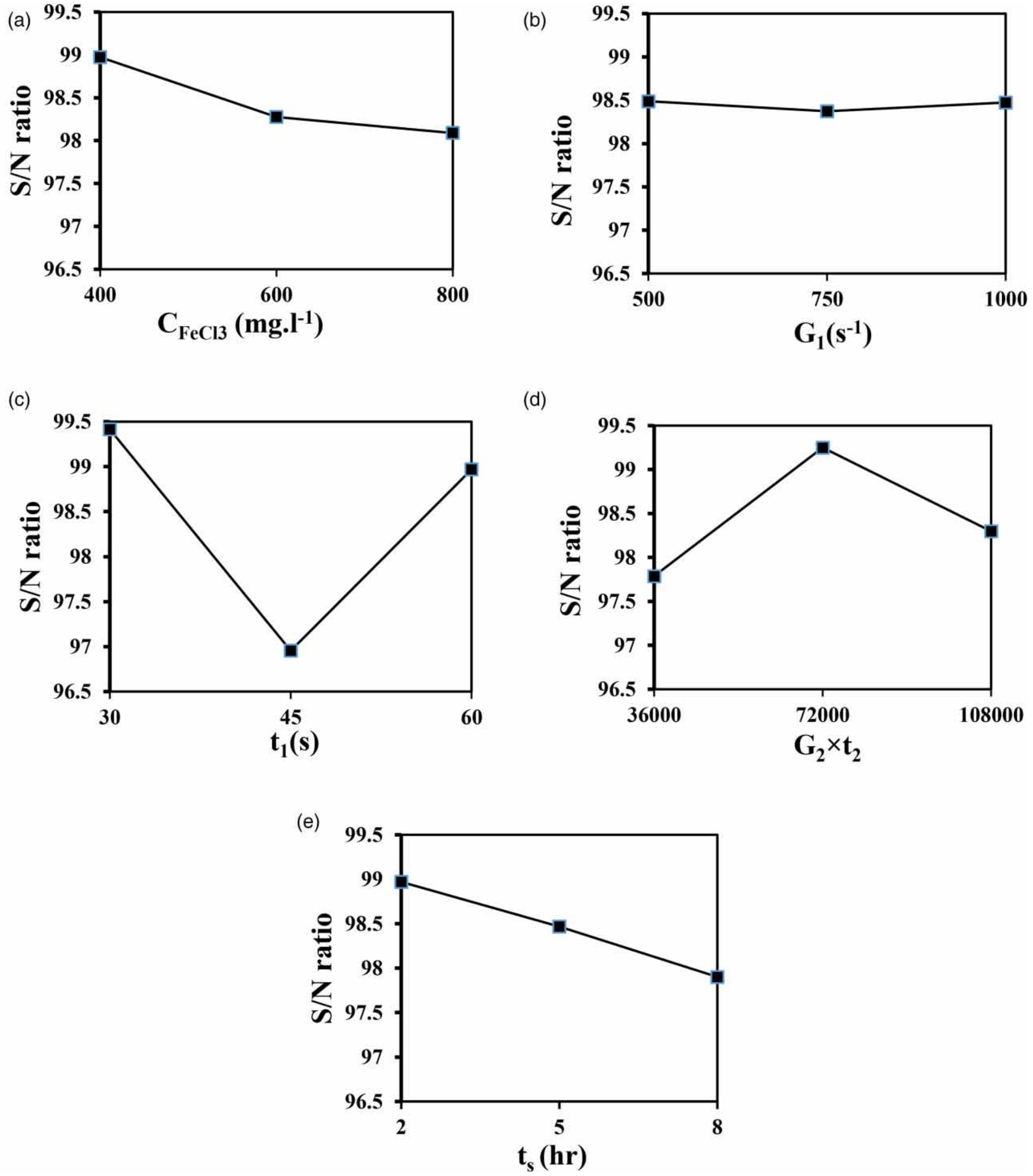


Figure 2 | The effect of experimental parameters on the S/N ratio in turbidity removal.

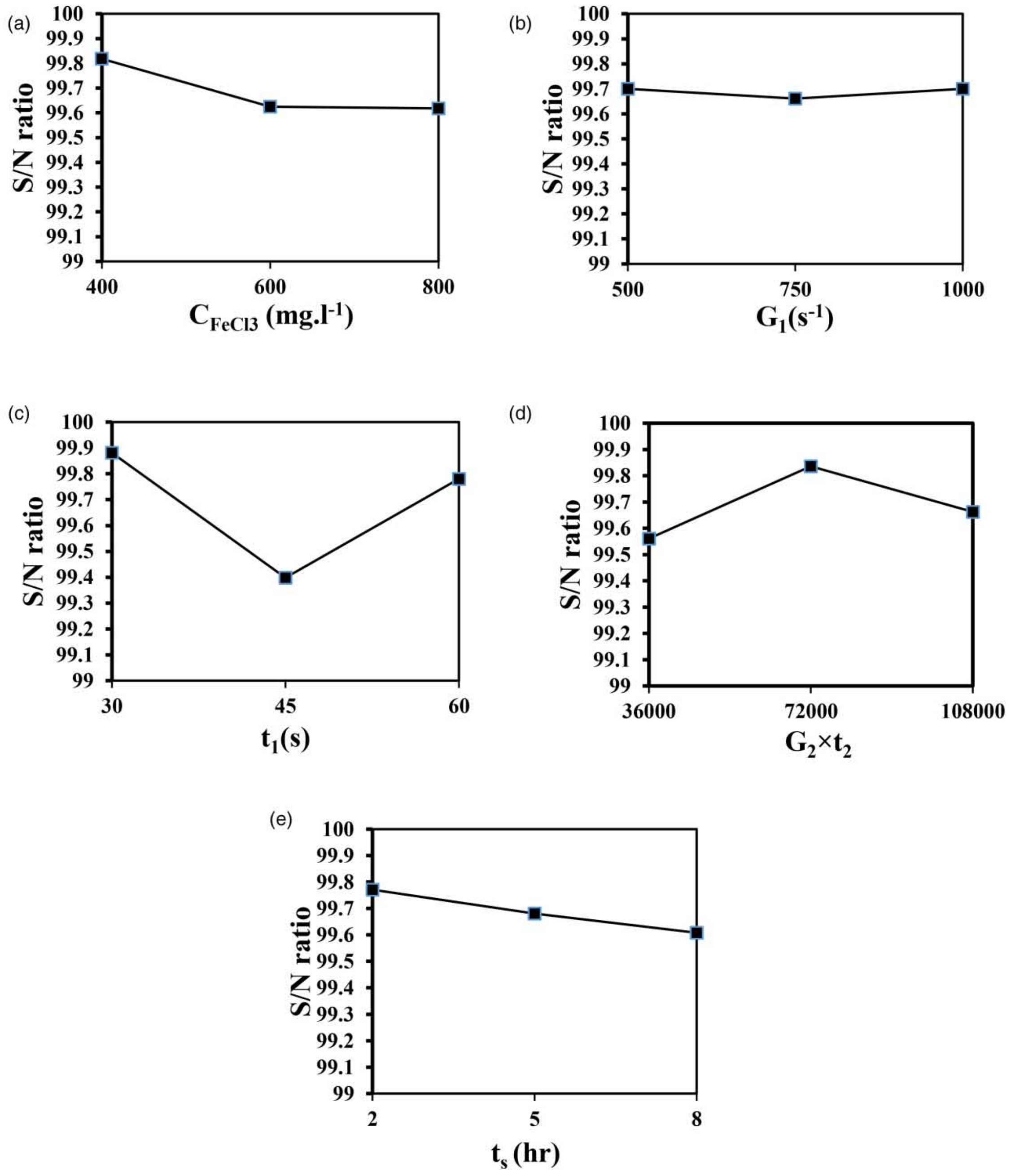


Figure 3 | The effect of experimental parameters on the S/N ratio in TSS removal.

Since in the case of pollution removal efficiency, ‘larger is better’ is the desired case, the optimum level of the controlling factors was the level that corresponds to the highest S/N ratio. The results shown in Figures 2 and 3 reveal the same optimum conditions for turbidity and TSS removal, which are at Level 1 for coagulant concentration, time and speed of mixing and settlement time. Level 2 is for the CAMP number (or $G_2 \times t_2$). The real values for the optimum conditions of the factors are listed in Table 6.

The predicted optimum conditions were the same as the experiment No.1 except for the CAMP number, which is bigger than that of the value in experiment No.1. TSS and turbidity removal of 99.89 and 99.19% were obtained from experiment No.1, respectively. By performing the experiment under optimal conditions, the removal of 100% will be achievable. To evaluate the predicted results, three confirmation experiments were performed under the optimum conditions predicted from the S/N ratio results (Gökkuş *et al.* 2012). According to the predicted result of the Taguchi method, removal efficiency for both TSS and turbidity was 100% in all three experiments.

Table 6 | The optimum conditions for the maximum removal of turbidity and TSS

Controlling factor	Optimum level	Value of optimum level
$C_{\mathrm{FeCl_3}}$	1	400 $\mathrm{mg{\cdot}L^{-1}}$
Gradient velocity (rapid mixing speed)	1	500 $\mathrm{s^{-1}}$ (405 rpm)
Mixing duration	1	30 s
CAMP number or $G \times t$ (slow mixing speed, mixing duration)	2	72,000 (75 rpm, 30 min)
Settlement time	1	2 h

3.2.2. ANOVA results

The ANOVA was carried out to evaluate the contribution of each controlling parameter on the process response and its significance. The ANOVA results are listed in Table 7. As it is shown, the degree of freedom (DOF) for each parameter is 1.

Table 7 | ANOVA results

		S		V		F		S′		P	
	DOF	**Turbidity**	**TSS**	**Turbidity**	**TSS**	**Turbidity**	**TSS**	**Turbidity**	**TSS**	**Turbidity**	**TSS**
C	2	2.597	0.168	1.298	0.084	0.763	1.713	0.000	0.070	0.000	4.233
G	2	0.046	0.010	0.023	0.005	0.013	0.106	0.000	0.000	0.000	0.000
t	2	20.598	0.803	10.299	0.401	6.054	8.173	17.196	0.705	38.065	42.562
$G \times t$	2	6.591	0.236	3.295	0.118	1.937	2.405	3.189	0.138	7.059	8.337
t_s	2	3.435	0.093	1.717	0.046	1.009	0.955	0.033	0.000	0.073	0.000

The percentage contribution (P %) in Table 7 is used for the quantitative evaluation of the controlling parameters. A higher P value means more factor contribution to the response (Abbasi *et al.* 2014). Hence, the most effective factor in the TSS and turbidity removal was the time of rapid mixing speed for coagulation. Rapid mixing speed (or gradient velocity) and settlement time are almost ineffective in pollution removal. The importance order of factors is $t_1 > G_2 \times t_2 > C_{\mathrm{FeCl_3}}$.

3.3. pH optimization results

The nitrous acid removal should be performed in an acidic environment. On the other hand, this condition leads to the production of highly toxic hydrazoic acid. Therefore, the most convenient range for optimum pH is chosen to minimize the production of toxic and hazardous hydrazoic acid in addition to achieve minimum concentration values of NaN_3, BOD and COD. The pH optimization results are presented in Table 8.

Table 8 | Optimization results for NaN_3 removal

pH	$C_{\mathrm{NaN_3}}$ ($\mathrm{mg{\cdot}L^{-1}}$)	COD ($\mathrm{mg{\cdot}L^{-1}}$)	BOD ($\mathrm{mg{\cdot}L^{-1}}$)
6.5	76,830	15,939	1,900
6.0	28,131	11,638	1,600
5.5	3,678	543	90
5.0	15,546	11,132	1,300

According to Table 8, this process has made significant changes in the values of BOD, COD and NaN_3 concentration. Moreover, it is observed that the highest removal efficiency has been achieved at pH of 5.5 as the optimum condition.

3.4. Overall performance of the wastewater treatment process

Raw wastewater with 197 NTU of turbidity, 1,820 $\mathrm{mg{\cdot}L^{-1}}$ of TSS, 112,866 $\mathrm{mg{\cdot}L^{-1}}$ of NaN_3, 29,416 $\mathrm{mg{\cdot}L^{-1}}$ of COD and 6,150 $\mathrm{mg{\cdot}L^{-1}}$ BOD was treated in a hybrid process of coagulation and chemical reaction with nitrous acid. The overall performance of the process is shown in Table 9.

Table 9 | Effects of the overall combined process on the wastewater quality

	Turbidity (NTU) [Removal %]	**TSS (mg·L^{-1}) [Removal %]**	**BOD (mg·L^{-1}) [Removal %]**	**COD (mg·L^{-1}) [Removal %]**	**NaN$_3$ (mg·l^{-1}) [Removal %]**
Raw wastewater	(194)	(1,820)	(6,150)	(29,416)	(112,866)
Coagulation process	(0) [100]	(0) [100]	(8,500) Increased BOD	(30,458) Increased COD	(99,087) [12.2]
Removal reaction	(15.8) Increased turbidity	(28) Increased TSS	(90) [98.9]	(543) [98.2]	(3,678) [96.3%]
Removal efficiency of the total process	[91.9]	[98.5]	[98.5]	[98.1]	[96.7]

As seen from the results, the coagulation–flocculation unit completely removed the turbidity and TSS, but BOD and COD values increased, which appears due to the addition of a chemical coagulant to the wastewater. A small percentage of sodium azide was also settled during this process. Of course, this is a good outcome for the unit because in case of removing large amounts of sodium azide, the output sludge will be rich of sodium azide with a high degree of sensitivity and explosive properties. Since the factories producing DMAZ are usually located in desert regions and near the launch station of satellites, sodium azide in the sludge is dried via ambient heat and sunlight. On the other hand, sodium azide appears to be susceptible to photodecomposition by solar radiation. Photodecomposition occurs relatively slowly (Chang & Lamm 2003). However, due to the hazards of sodium azide, it is not recommended to deposit in the large volumes.

In the second unit of the hybrid process, the output BOD, COD and NaN$_3$ concentration of the coagulation unit decreased by a significant removal efficiency of 98.9, 98.2 and 96.3%, respectively. In this unit, TSS and turbidity values were increased due to the addition of the chemicals to the wastewater for chemical treatment and producing Na$_2$SO$_4$ byproduct (a non-toxic chemical in soil). Also, it has been reported that nitric oxide or NO gas (from Equation (8)) is effectively removed by adding ammonia and a contact catalyst for the NO-ammonia reaction (Si *et al.* 2021). However, the performance of the overall wastewater treatment is positive and able to significantly improve the quality of the effluent and remove a high percentage of the available organic matter. Turbidity, TSS, BOD, COD and NaN$_3$ concentration decreased by 91.9, 98.5, 98.5, 98.1 and 96.7%, respectively. Conclusively, sodium azide as the most hazardous pollutant was destroyed to a great extent.

4. CONCLUSIONS

A hybrid process of coagulation–flocculation and chemical reaction with nitrous acid was applied for DMAZ wastewater treatment. The conditions for optimization for both units were investigated. From the results of designed experiments by the Taguchi method, the optimal removal of TSS and turbidity was found with the parameters iron (III) chloride dosage of 400 ppm, the rapid mixing time of 30 s and gradient velocity of 500 s^{-1}, CAMP number of 72,000 and sedimentation rate of 2 h. This optimization resulted in the complete removal of TSS and turbidity in the first unit. In latter unit, the optimum pH for the wastewater in the removal reactor was obtained as 5.5 and the removal efficiencies of 98.9, 98.2 and 96.3% were achieved for BOD, COD and NaN$_3$, respectively. It was founded that under the optimal conditions, the overall hybrid process has the removal efficiencies of 91.9, 98.5, 98.5, 98.1 and 96.7% for TSS, turbidity, BOD, COD and NaN$_3$, respectively.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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