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Research article

Enhanced drilling waste-water treatment through magnetic nano-composite coagulant application: A central composite design study

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A B S T R A C T

A magnetic nano-composite coagulant has been designed, originally applied in a specific industrial waste-water treatment, and statistically investigated using Central Composite Design (CCD). The generated polynomial models were utilized to achieve a comprehensive understanding of the impact of each ingredient of PolyAluminum Chloride (PAC), PolyAcrylAmide (PAM), and Iron (III) oxide magnetic nano particles (MNP) regarding optimum limits and conditions. The concentration of each of those components has been considered as the main effective factors, which are found to be significantly correlated, affecting the Total Dissolved Solid (TDS) removal (%), the Total Suspended Solid (TSS) removal (%), and the Turbidity Reduction Rate (TRR) NTU/min. The reliable statistical model for each response underscored the pivotal role of MNP in shaping each response variable. The influence of MNP and PAC, emerged as crucial in enhancing TDS removal, by increasing the kinetic energy of charged ions and the chance of the successful displacement reaction, helping to dissolve with a high surface activity, and the adsorption of magnetic heavy ions. The correlated concentration of MNP also exhibited a significant impact on TSS elimination, and TRR, concurrently, which revealed the importance of controlling the bulk density of generated flocs, to prevent premature and immature settling to optimize pollution removal. The highest recorded results are 72.00 %, 77.01 %, and 23.82 NTU per minute for TDS and TSS removal and TRR, respectively. The experimental records, along with the statistical investigation remarked a promising potential of the achieved Magnetic Nano-composite Coagulant (MNC), and generated practical knowledge of its novel application for drilling waste-water management.

1. Introduction

Ever since man discovered the importance of human-environment interaction, the preservation of water resources has been highlighted [1]. It has been reported by the Committee on Climate Change progress report [2] to the UK Parliament that the water demand will outrun its supply by 40 % by 2030, while many nations are struggling with a lack of freshwater already [3]. The significant industrial water consumption, which warns the freshwater resources and environmental safety emphasizes the importance of industrial waste-water management [4]. Although this matter has been spotlighted during the past decade, several problems associated with achieving harmless wastewater management have yet to be solved. In 2018 [5], it was reported that two billion people live in countries that encounter high water stress, worsening as an increase in population and demand for water is experienced. Drilling operations, as one of the critical

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waste-productive industries, has been gaining many concerns in recent years [6]. Hossain et al. [7] reported an investigation of oil-well drilling cost estimation. They reported water consumption, surface casing, and drilling pad supply as the preparation costs, with an average of 18 % of total operation costs, which is logically possible to increase outlay due to the lack of water resources as time passes [2].

It is believed [8,9] that coagulation is the most applied technique, within the industrial waste-water management from the textile industry to paper and mining [10]. Based on several mechanisms, coagulation helps surface neutralization of the suspended solids and boosts the sedimentation process. These mechanisms include charge neutralization, polymer bridging, sweep flocculation, and double-layer compression. Coagulation process, includes a wide range of approaches. In 2022, Ortenero J. et al. [11] investigated the TDS removal using an electrocoagulation approach. They succeeded in-situ generation of Al^{3+}, and Fe^{3+} as electro coagulants using electricity, which helped up to 68.3 % TDS removal. One year later, a more comprehensive study has been done regarding TDS and TSS removal, using electrocoagulation while minimizing energy costs. Utilizing fuzzy optimization, the research develops a model to optimize variable conditions, achieving significant removal efficiencies and cost-effectiveness in the process [12]. According to the report by Owdunni et al. [9] chemical coagulation efficiency is recovered by six main factors: i) High capability of charge neutralization, ii) Optimum molecular weight, iii) Optimum coagulant dosage, iv) Controlled pH, v) Stirring speed, and vi) The time duration of combination. However, it is more practical to consider the optimum coagulant dosage and the initial contaminate concentration ratio as an independent factor, to achieve a more comprehensive attitude of the studies in the near researches.

A large number of researchers [9,13] have applied and studied composites and hybrids regarding waste-water treatment. Iron and aluminum salts, e.g., PAC, as synthetic coagulants, are widely used in industrial waste-water control, which often have a high capability of neutralization [14–16]. In 2010, Cheng et al. [17], conducted a thorough study on monitoring turbidity removal with PAC. PAM is also a dense, and highly surface-charged polymer with a high cross-linking capability, which has been utilized in several applications [18–20]. Since the magnetic phenomenon provides several efficient potentials, magnetic coagulants are propounded with great promising properties [21]. One promising solution to renewable industrial waste management chemicals is the use of MNC, which has shown great potential in effectively removing contaminants from waste-water, as well as in regeneration and cost-effective benefits [22–25]. In 2024, Badawi et al. [26] investigated the application of a novel magnetic composite within the real pulp and paper mill wastewater treatment. In particular, the application of magnetic nanoparticle in waste-water treatment has been studied recently in different methodologies [27], e.g., Magnetic hybrid coagulants (MHC), and Magnetic seeding coagulants (MSC). Regarding the economic considerations, the optimized application of MHC is reported to be more practical [19,23,27,28].

In 2022, Mohamed Noor et al. [24] utilized Moringa Oleifera seed as a natural coagulant and MNP to create an MHC due to palm oil mill effluent treatment. They reached a TSS removal of 80 %, and found the magnetic coagulant regeneratable several times, using an external magnet. Natural coagulants have been successfully advanced by MNP using physical and chemical methodologies; however, there are still limitations such as lack of purity, accessibility issues, negative environmental impacts, and lower efficiency [29]. He et al. [27] also compared the MHC and MSC methods for the same purpose in 2021. He found the turbidity removal capability almost the same, in the case of each methodology. However, they also reported a significant nitrate removal in the case of MHC, and demonstrated that MHC is more suitable for treating waste-water with varying contaminate concentrations. Zhao et al. [28] investigated MHC preparation in three types of synthesis, with varying adherence to composite ingredients. They found that the post-addition of ingredients, during MHC formation can improve the microalgae harvesting efficiency by 91 %. This happened because of the nature of the target contaminate, as it is known that the ion exchange properties of the nano-composite depend on the functional group on the surface of the other layer. The order of mixing and forming the composite has an effect on the functional groups of the last layer. Compared to the functional group of PAC, those of PAM have a much lower ion exchange power. Therefore, it can be concluded that the presence of the PAM between the magnetic core and the PAC causes more efficiency and lower zeta potential [28]. A statistical study was done in 2022 by Sibiya et al. [30] to generate models predicting actual experimental results, within the waste-water treatment. They investigated the impacts of three factors, namely magnetized rice starch dosage as the coagulant, sedimentation time, and mixing rate to study their relation with turbidity and phosphate reduction. Analysis of Variance (ANOVA) has been selected within statistical investigations around related researches so far [30,31]. This showcases the crucial role of this in understanding the governing mechanisms, correlations and optimum conditions.

Numerous studies have been conducted to investigate the potential of induced magnetic properties in industrial coagulants. However, an economically viable approach for optimizing drilling waste-water treatment has yet to be realized. Given the critical role of operational conditions on drilling rigs, the complex nature of the waste produced during drilling operations, and the limitations of available resources and infrastructure, it is essential to develop an efficient approach that is also economically feasible. The forthcoming investigation focuses on the synthesis of an MNC through a post-addition method for the treatment of waste-water produced during oil well drilling activities in the Mansour Abad oil field. PAC, PAM, and MNP are examined as the primary constituents in the formulation of this nano-composite. The individual efficacy of each component, along with their synergistic effects, is scrutinized concerning the removal of TDS, TSS, and TRR, through statistical modeling.

2. Materials and methods

2.1. Materials

Commercial MNP (99 % purity, Average Particle Size: 20–30 nm, Bulk density 0.84 g/cm^3) were purchased from Nano-Sani Company. Anionic polyacrylamide (PAM) (MW $> 20 \times 10^6$, CAS No.: 9003-05-8), and polyaluminum chloride (PAC) (Aluminum oxide (Al_2O_3) content 30.74 %, Basicity 80 %) supplied from Narbon company. Deionized distilled (DI) water was used as the solvent and dispersion media.

In order to address the uniformity of waste samples and to solve transportation challenges, waste-water was produced synthetically by adding the desired amount of DI to naturally dried waste sludge, generated from one of the southern Iranian oil field drilling operation. The initial amount of TDS and TSS were 6.74 and 9.22 g/l, respectively. The appearance characteristics of the effluent are also evaluated as very low transparency and brick-red color.

2.2. Synthesis of MNC

In order to identify the performance of MNC prepared by the post-addition method, the preparation started by introducing the desired quantity of MNP into 10 ml of DI water and dispersed through the use of ultrasonic waves at a temperature of 50 °C for a duration of 15 min. This procedure was employed to achieve a uniform dispersion of fine particles within the solution. The essential amount of polyacrylamide was then added to the solution and subjected to the same ultrasonic conditions for a period of 50 min, with the aim of stabilizing the MNP in the polymer network. The solution was then added to the prepared waste-water sample, following immediate polyaluminum chloride addition (see Fig. 1).

2.3. Jar test procedure

The efficiency evaluation and identification of behavior mechanisms were done with the help of a jar test. This is carried out using a 50 ml falcon, waste-water and the coagulator agent. The procedure was started by adding 10 ml nano-composite solution into the 50 ml sterilized falcon containing prepared 30 ml waste-water, at room temperature. The selected amount of PAC was then added instantly to the mixture, shaken aggressively for 5 min, and then let settle. After a settling time of 3 and 20 min, a supernatant 5 ml sample was taken from the top of the treated water for TRR determination (NTU/min). TDS and TSS are measured according to the Standard Methods Committee of the American Public Health Association [32]. Their removal efficiency (%) was calculated using the same sample after 20 min of settling. Respectively, TRR and the removal efficiency are determined using equations (1) and (2).

$$TRR\ (NTU/min) = \frac{Turbidity\ after\ 3\ minutes - Turbidity\ after\ 20\ minutes}{17} \quad (1)$$

$$E\ removal\ (\%) = \frac{E_0 - E_{20}}{E_0} \times 100 \quad (2)$$

E removal is the removal efficiency of the parameter E, subtended TDS and TSS. E_0 is the measured concentration of E in the untreated sample, and E_{20} represents the measured E followed by 20 min of settling time.

2.4. Statistical analysis and response surface design of experiments (DOE)

In the case of the parametric study, several parameters always affect the performance. Statistical modeling is a key to reaching a better view of how the mutual effects of selected factors work. Response Surface Methodology (RSM) has been selected as an economic experimental investigation, by reducing the number of required experimental runs for a more efficient investigation, which helps interacting variables understanding [33]. Based on CCD, under the RSM, a total of twenty experiments were designed, each containing varying levels of MNP, PAM, and PAC as the three main building blocks of the nano-composite, as the coagulant dosages are reported as the most determinative factors in pollution removal, at a constant pH [34]. PAC is known as an efficient coagulant with a high surface neutralization capability, while PAM has extreme potential as a cross-linking agent, along with its flocculation property. The levels were determined based on the definition and measurement of Dosage to Contaminate Ratio (DCR) in the other studies conducted on different types of waste-water and concentrations of coagulants. DCR is a dimensionless number defining the ratio of coagulant dosage to the waste-water contaminant, which is specified in equation (3). Consequently, the domains obtained for three components, as the focus factors on behavior studies, were used in the mutual influence of the parameter investigations, which are tabulated in Table 1. PAC and PAM levels are tried to select due to their pre-used concentration domains according to previous studies [19,27,28,35] adjusted by the DCR coefficient. Considering economic aspects and related accomplishments, MNP concentration is also selected from 0.08 to 0.49 g/l, with due attention to the previous studies [19,24].

Meanwhile, TDS and TSS removal efficiency (%) and TRR (NTU/min) were selected as the three responses were selected. Design

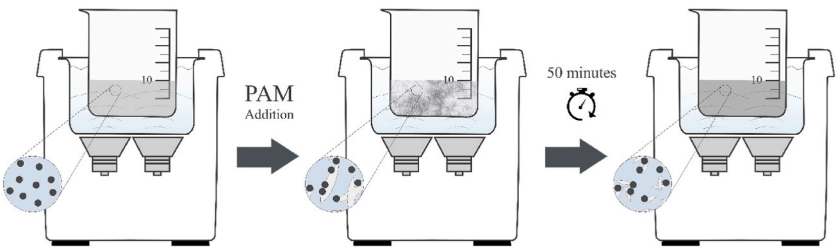

Fig. 1. Schematic of nano-composite preparation, using post-addition method.

Expert 13.0.0 software was used to design and analyze the model generated and further optimization studies. In the process of studying the parameters' effectiveness, after selecting the model used for each answer, the ANOVA analysis results were investigated and evaluated to indicate the statistical significance of the responses. The values of the f-value and p-value corresponding to each other were calculated, and by this means, the effectiveness of each of the parameters on all three results was identified. Also, R^2 and adjusted R^2 were taken into consideration in the statistical analysis [31]. Next, by power transferring the response functions according to the Box-Cox transformation method, this process was repeated so that the obtained response was found more meaningful.

$$\textit{Dosage to Contaminate Ratio} = \frac{\textit{Coagulant dosage}\left(\frac{g}{l}\right)}{\textit{Initial Solid Content}\left(\frac{g}{l}\right)} \times 10^5 \tag{3}$$

The drilling wastewater treatment numerical optimization procedure involved selecting two scenarios. The operational scenario aims to achieve the highest removal rates of TDS, TSS, and TRR to determine the potential of produced MNC under ideal conditions, without considering economic factors. In contrast, the adjusted economic scenario prioritizes satisfactory outcomes while incorporating the minimum feasible additives in the wastewater. The primary objective here is to maximize TSS removal, with minimizing chemical consumption as a secondary goal. This approach seeks to reduce the final cost of MNC application, prevent overdosing and the subsequent formation of gel-like substances when introducing treated water to the mud circulation, and maintain an efficient yield for TSS removal, which is the most critical parameter in drilling wastewater recycling. Additionally, figurative optimization was conducted to enhance practical application and increase flexibility, defining a region characterized by the level domains of each factor. This optimization results in acceptable minimum thresholds of 60.00 % for TDS removal, 75.00 % for TSS removal, and 15 NTU/min for TRR, respectively.

3. Results and discussions

In this study, CCD is used to study the behavior of MNC, prepared by post-addition magnetic seeding method in drilling operation waste-water treatment. Different variations of dosage were applied to three main factors in nano-composite generation. The functional domain for dosages was found in the DCR range of 2320–3090, while Apparent Turbidity and pollutant removal efficiency decreased beyond this zone. This finding has been reported and confirmed in previous similar studies [20,27,36]. The experimental matrix, including design conditions and three recorded responses, is given in Table 2, which is conducted with the CCD design. Each response was also indicated numerically and mentioned along with the experimental data. As anticipated, higher coagulant dosages, particularly with PAC, resulted in diminished removal of solid content and, notably, increased measurement errors. Essentially, the clogging of filter paper pores by dense polymer networks hindered the passage of dissolved solids. This led to an accumulation of suspended solids and a substantial portion of dissolved solids on the filter paper, causing an increase in weight and introducing errors.

Table 3 is dedicated to the ANOVA analysis associated with the models and each parameter of the polynomial obtained. Variance analysis, along with statistical coefficients tabled in Table 4, confirms that the empirical models generated for all three responses were found to be meaningful and reliable. This attends to a fine understanding of the role of each factor in the coagulation process, and their mutual interactions.

With due attention to Table 3, the most effective parameters in each response behavior are comprehensible, according to the P and F values [31]. PAC and MNP concentration, respectively, play the main roles in TDS removal response, which can be interpreted as a dual effective mechanism. Not only PAC and PAM, as two well-known coagulation-flocculation agents, are affecting TSS removal, but MNP also has a highly effective role as the others. The remarkable interaction of MNP with PAM concentrations in TRR response is also understandable. The effecting mechanism can be determined by each model investigation. The polynomial-generated models are stated below, as Equations (4)–(6). Considering X_i, X_{ii}, and X_{iii} are PAC, PAM, and MNP concentration, respectively.

$$\begin{aligned} \textit{TDS removal}^{1.45} = 0.01\ [&57.39 - 29.48\ X_i + 35.22\ X_{ii} - 12.00\ X_{iii} + 39.32\ X_iX_{ii} + 429.68\ X_iX_{iii} + 43.02\ X_{ii}X_{iii} - 34.66X_i^2 \\ &- 19.1.82\ X_{ii}^2 - 336.72X_{iii}^2\ ] \end{aligned} \tag{4}$$

$$\begin{aligned} \textit{TSS removal}^{3} = 0.01\ [&46.24 - 230.86\ X_i + 129.76\ X_{ii} + 206.20\ X_{iii} - 232.65\ X_iX_{ii} - 257.45\ X_iX_{iii} - 535.25\ X_{ii}X_{iii} + 468.82\ X_i^2 \\ &+ 271.11\ X_{ii}^2 + 627.83\ X_iX_{ii}X_{iii} - 227.58\ X_i^3 - 404.20\ X_{iii}^3] \end{aligned} \tag{5}$$

$$\begin{aligned} TRR = [&190.7915\ X_i - 336.1191\ X_{ii} - 405.5519\ X_{iii} + 737.4230\ X_iX_{ii} + 997.9884\ X_iX_{iii} + 359.4864\ X_{ii}X_{iii} + 275.9698\ X_i^2 \\ &- 4.2830\ X_{ii}^2 - 13.8465\ X_{iii}^2 - 364.1729\ X_iX_{ii}X_{iii} - 426.6871\ X_i^2\ X_{ii} - 601.4331\ X_i^2\ X_{iii}\ ] \end{aligned} \tag{6}$$

Table 1
The determined five levels for each factor.

Parameters (g/l)	Levels				
	1	2	3	4	5
MNP	0.08	0.17	0.29	0.41	0.49
PAM	0.01	0.11	0.26	0.40	0.50
PAC	0.36	0.50	0.70	0.90	1.04

Table 2
Summarized designed experimental data, based on CCD.

STD	Run	Factors			Experimental			CCD prediction		
		PAC	PAM	MNP	TDS rem.	TSS rem.	TRR	TDS rem.	TSS rem.	TRR
		g/l	g/l	g/l	%	%	NTU/min	%	%	NTU/min
12	1	0.70	0.50	0.29	46.14	67.46	14.12	47.06	67.43	14.26
15	2	0.70	0.26	0.29	63.80	73.10	14.35	62.39	73.21	14.72
18	3	0.70	0.26	0.29	62.28	75.00	14.18	62.39	73.21	14.72
1	4	0.50	0.11	0.17	56.68	68.76	23.82	57.56	68.98	23.61
7	5	0.50	0.40	0.41	54.75	72.45	11.73	26.50	72.31	11.68
8	6	0.90	0.40	0.41	71.00	68.76	13.35	70.41	68.70	13.34
14	7	0.70	0.26	0.49	49.70	72.67	17.53	73.10	69.88	14.55
16	8	0.70	0.26	0.29	63.35	73.32	15.34	62.39	73.21	14.72
2	9	0.90	0.11	0.17	56.68	75.16	15.23	57.33	75.20	15.22
6	10	0.90	0.11	0.41	72.00	72.02	15.47	72.64	71.90	15.45
9	11	0.36	0.26	0.29	41.84	77.01	14.65	40.68	77.23	14.28
13	12	0.70	0.26	0.08	50.74	72.67	10.60	49.73	73.06	10.44
10	13	1.04	0.26	0.29	43.77	74.73	8.10	74.91	67.17	13.00
17	14	0.70	0.26	0.29	60.24	72.67	14.71	62.39	73.21	14.72
5	15	0.50	0.11	0.41	35.00	77.01	12.82	35.11	76.96	12.70
11	16	0.70	0.01	0.29	58.46	75.60	14.65	57.31	75.62	14.68
3	17	0.50	0.40	0.17	48.52	73.97	1023	48.57	74.03	10.24
20	18	0.70	0.26	0.29	62.20	73.21	14.76	62.39	73.21	14.72
4	19	0.90	0.40	0.17	51.63	70.82	10.88	52.11	70.91	10.92
19	20	0.70	0.26	0.29	63.06	72.99	14.82	62.39	73.21	14.72

Table 3
ANOVA statistics summary for each parameter of the generated model.

Response	TDS removal (%)			TSS removal (%)			TRR (NTU/min)		
	Mean Square	F-Value	P-Value	Mean Square	F-Value	P-Value	Mean Square	F-Value	P-Value
Model	0.022	106.53	<0.0001	2.63E-3	16.04	0.0006	12.99	90.95	<0.0001
A-PAC	0.091	445.45	<0.0001	8.98E-5	0.55	0.48	1.71	11.98	0.01
B-PAM	0.012	59.76	<0.0001	9.37E-6	0.06	0.82	0.14	0.98	0.36
C-MNP	7.73E-5	0.36	0.56	4.90E-5	0.30	0.60	23.98	167.80	<0.0001
AB	7.57E-4	3.71	0.09	1.83E-3	11.17	0.01	8.42	58.95	0.0003
AC	0.06	305.40	<0.0001	4.43E-3	27.06	0.001	18.63	130.40	<0.0001
BC	3.31E-4	1.62	0.24	2.28E-3	13.89	0.007	27.13	189.88	<0.0001
A^2	1.61E-3	7.92	0.22	5.52E-5	0.34	0.58	0.48	3.37	0.12
B^2	0.022	106.98	<0.0001	8.37E-4	5.11	0.06	0.11	0.79	0.41
C^2	0.032	156.35	<0.0001	–	–	–	0.56	3.93	0.09
ABC	–	–	–	3.91E-3	23.88	0.002	13.16	92.12	<0.0001
A^3	–	–	–	1.07E-3	6.51	0.04	–	–	–
B^3	–	–	–	1.73E-3	10.56	0.01	–	–	–
C^3	–	–	–	–	–	–	–	–	–
A^2B	–	–	–	–	–	–	20.49	143.37	<0.0001
A^2C	–	–	–	–	–	–	28.03	196.17	<0.0001
Lack of fit	1.80E-4	0.83	0.53	1.17E-4	0.64	0.56	0.035	0.22	0.66

Table 4
Variance analysis of generated models.

Response	TDS removal (%)			TSS removal (%)			TRR (NTU/min)		
	R^2	Adj. R^2	Std. Dev.	R^2	Adj. R^2	Std. Dev.	R^2	Adj. R^2	Std. Dev.
Value	0.9917	0.9824	0.0143	0.9618	0.9018	0.0128	0.9945	0.9836	0.3780

3.1. TDS removal model

TDS is a challenging parameter to reduce, using coagulation-flocculation methods. However, there are usually restrictive policies in releasing the ion included treated water into the environment. But as it can be illustrated in Fig. 2, PAC and MNP can significantly increase TDS removal, while Fig. 2 – D, confirms the reliability of the modeling, by depicting both actual and predicted values of TDS removal, in the UAOD system [37].

In Fig. 2A–C, the individual impact of each parameter on TDS reduction is illustrated. It is important to note that these parameters represent the primary terms of the model, and the interplay between them must be considered for accurate assessment. The pronounced steep incline in Graph 2-A signifies the direct and substantial effect of PAC concentration on TDS removal. This phenomenon can be elucidated by the nature of this coagulant, which, upon dissolution in the liquid phase, can engage in substitution reactions through light-induced hydrolysis, leading to the precipitation of soluble sulfate ion salts [38]. MNP concentration has also an in-expected impact on TSD removal peradventure by increasing the kinetic energy of charged ions in the environment and increasing the successful displacement reaction chance (see Fig. 2-C). The magnetic adsorption of heavy magnetic metal ions is also one other probable reason for this behavior, confirmed by previous observations [39,40]. On the other hand, PAM concentration has a neglectable effect on this response due to its enduring structure (see Fig. 2-B).

A fine accordance is observed in the PAC-MNP dual attitude in Fig. 3-A. The concentration increase in both ingredients leads toward a more efficient TDS removal, even higher than 70 %. While the increase of MNP in lower amounts of PAC concentrations plays in the opposite role. PAC concentration does not have a considerable effect on TDS removal in MNP absence, as well. This represents a dual mechanism in dissolved solid sedimentation. For instance, it can be apprehended that the magnetic ions concentration is not much significant in the medium, due to the negative effects of MNP on lower dosages of PAC. However, the dual-stage mechanism involving the absorption and sedimentation of soluble salts in the environment can be discerned. Amplifying the magnetic field generated by

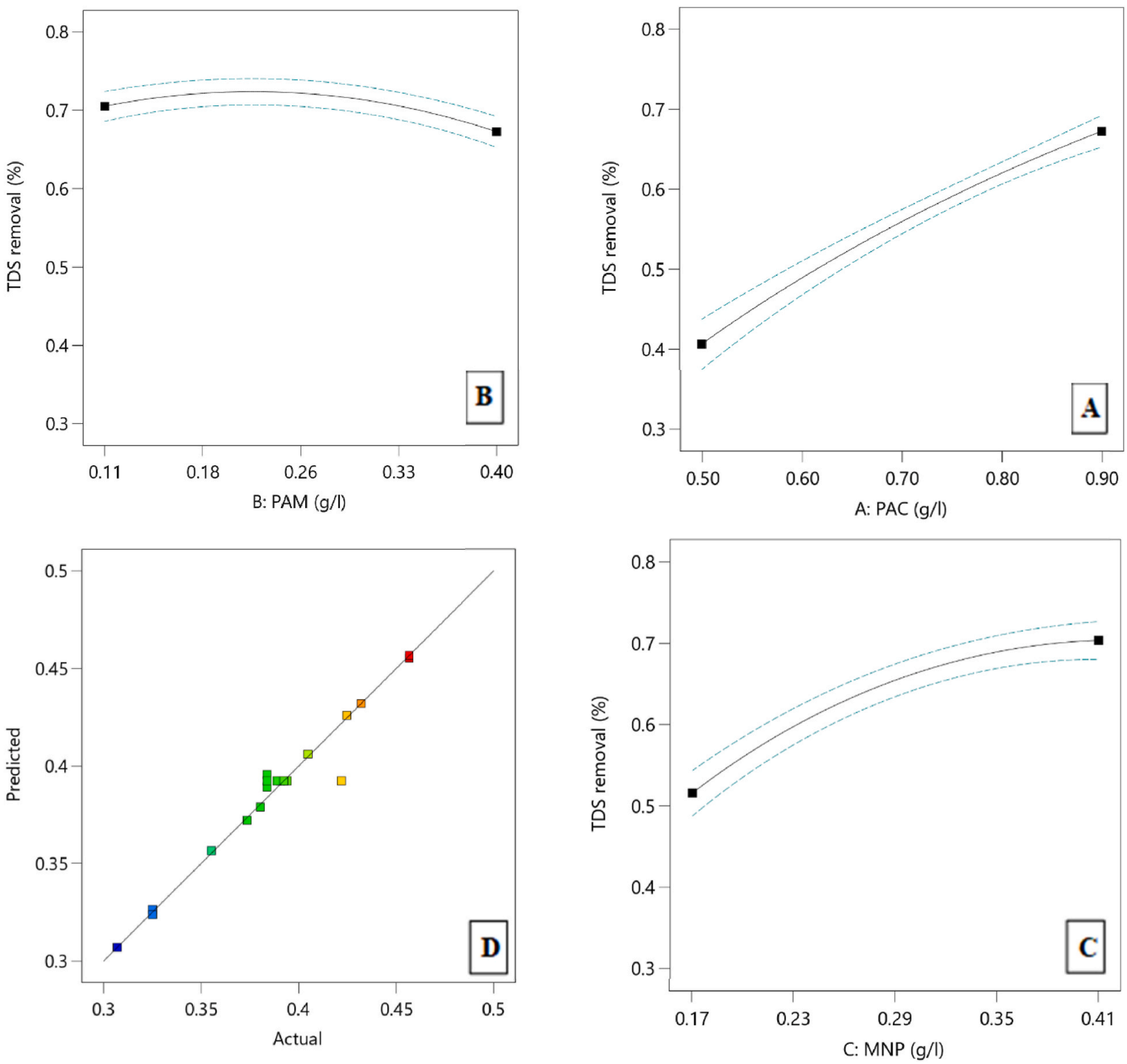

Fig. 2. Single factor trend of TDS removal (%) against A) PAC, B) PAM, and C) MNP, at 0.90, 0.40, and 0.31 g/l respectively. D) The predicted results by the generated model, against actual recorded values.

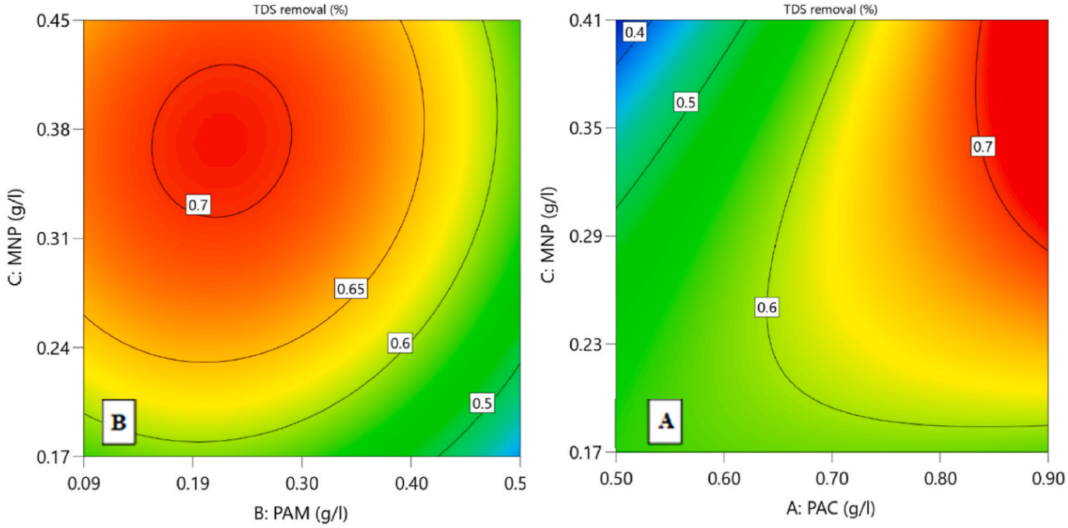

Fig. 3. TDS removal (%) prediction, generated by RSM-CCD. A) PAM Vs. MNP at constant PAC = 0.84 g/l; B) PAC Vs. MNP at constant PAM = 0.26 g/l.

magnetic iron nanoparticles amplifies the turbulence and kinetic energy of dissolved ions in the environment. By exerting a force on charged particles moving within the field, the magnetic field augments their kinetic energy, enhancing the likelihood of successful encounters between ions capable of undergoing substitution reactions with the dissolved ions in the effluent. This catalytic effect accelerates the reaction rate, culminating in TDS reduction.

Conversely, due to the longer and denser structure of PAM strings, their solubility in water is diminished. Consequently, elevating the concentration of this polymer not only prevents TDS removal but also, by intertwining with PAC strands and reducing its solubility, yields toward diminishing the TDS reduction process (Fig. 3).

3.2. TSS removal model

TSS removal is spotlighted the most in waste-water treatment. Fig. 4 elucidates the individual effects of each parameter on TSS reduction, revealing the substantial coagulation potential of both PAM and PAC. PAC and PAM are both high potential surface load neutralizers, with extreme solubility in water. This helps through an efficient coagulation-flocculation process. Both PAC and PAM demonstrate high performance by increasing their concentrations, with diminishing extrapolations. However, it is noteworthy that the performance of these coagulants diminishes at higher concentrations, highlighting the issue of solution over-saturation, which escalates water density and consequently the buoyancy of flocs within the system. Fig. 4-C also, represents a coagulation capability of MNP, provided by the high surface activity of nano-scale particles and its ability to adsorb magnetic sediments. Fig. 4-D, which illustrates the predicted vs. actual diagram related to the applied model, shows fine accuracy trends of both actual and forecasted results in the applied model [37].

In Fig. 5-A, the influence of magnetic nanoparticles on TSS reduction is observed to be negative at higher concentrations of PAM. Conversely, lower concentrations of PAM exhibit an upward trend, aiding in TSS removal. This trend is repeated in the behavior of PAC; the coagulation efficacy of magnetic nanoparticles increases in lower concentrations of other coagulants due to their high surface activity and volumetric mass, which are not hindered by the occupation of hydroxyl functional groups. The same behavior is observable in Fig. 5-B. But in further studies a high relatively of TRR and TSS removal is observed, which explains these findings, more.

MNP in low concentrations also showed coagulator properties. But this property decreased with the increase in the concentration of this material, which apparently can indicate the formation of magnetic agglomerates, reducing the surface activity properties of the particles.

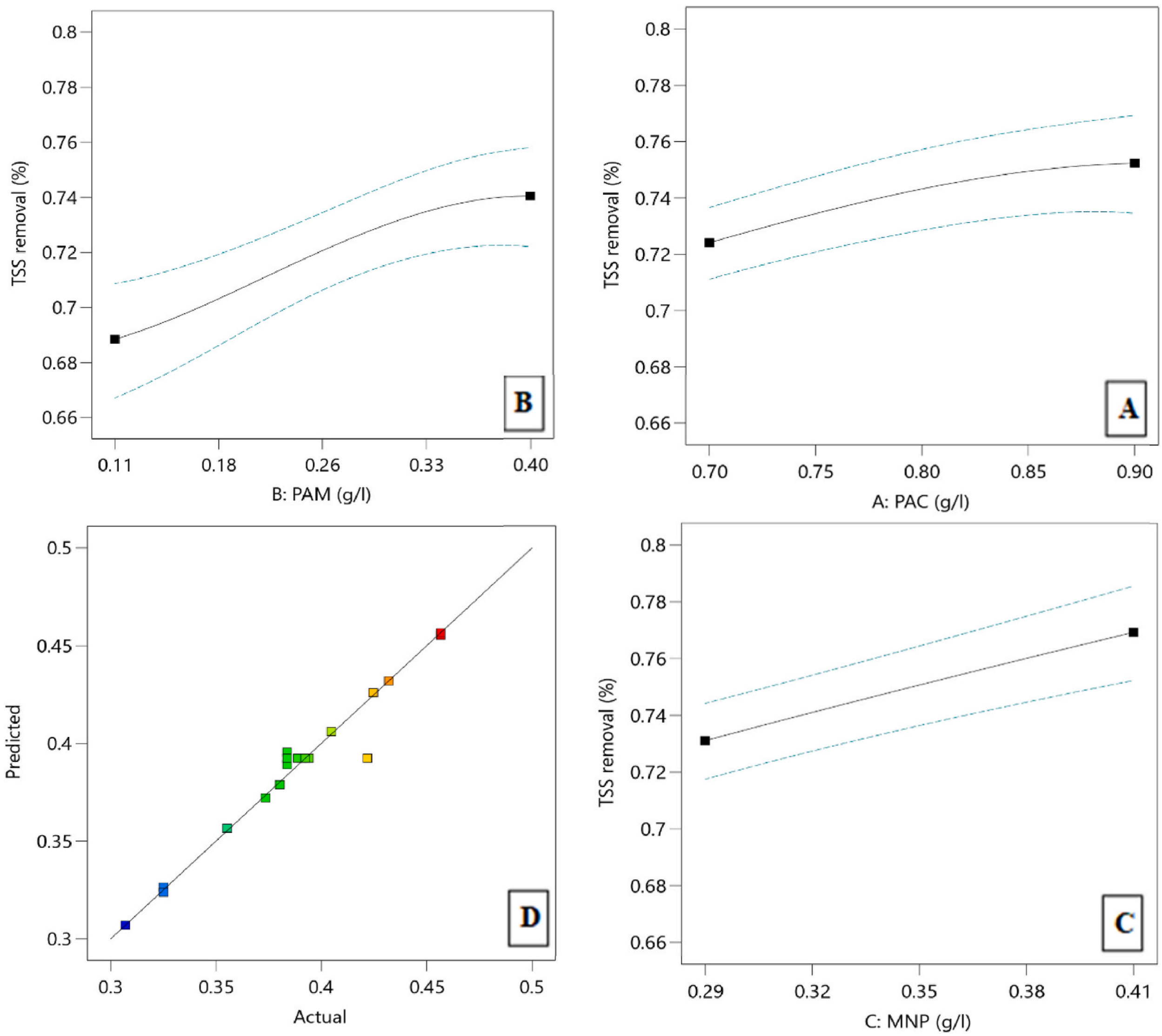

Fig. 4. Single factor investigation of TSS removal generated model, in 0.5, 0.11, 0.17 g/l of A) PAC, B) PAM, and C) MNP concentrations, respectively. D) The predicted vs. actual results congruence.

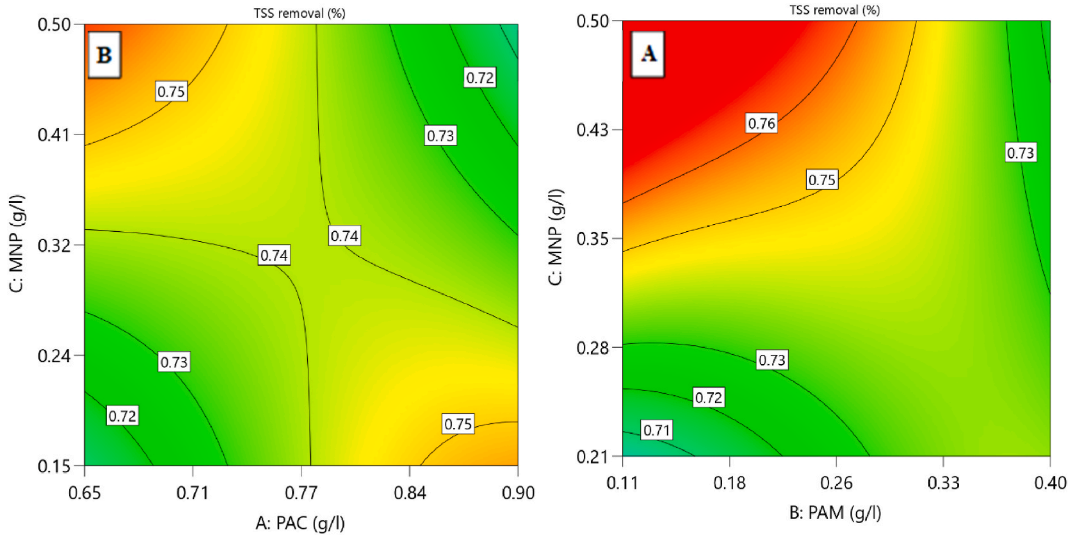

Fig. 5. Contour of mutual interaction of effecting parameters, in TSS removal, at a constant concentration of A) 0.5 g/l PAC, and B) 0.11 g/l PAM.

3.3. Average TRR model

The analysis of the impact of individual composite concentrations on turbidity reduction rates has underscored the significant influence of magnetic nanoparticles. Fig. 6 illustrates the trajectory of these effects for each of the experimental variables. Notably, the alteration in the quantities of polymers does not exert as substantial an impact on the average sedimentation rate as the presence of magnetic nanoparticles. While the volume and weight of the resultant flocs may be influenced by the concentration of coagulants, their effects are comparatively minor in comparison to the molecular mass of magnetic nanoparticles.

It is worth noting that this study did not explore the influence of an external magnet on the average settling velocity. However, it is evident that the magnetic properties of these particles hold the potential to enhance the turbidity reduction rate. The diagnostic predicted response versus the actual ones in terms of TRR model is illustrated in Fig. 6-D [37].

In Fig. 7-B, a notable observation is the significant increase in TRR when minimal foreign polymer is introduced into the environment, highlighting a potential drawback of coagulant addition. The augmentation of coagulants may at times fail to impart sufficient density to the flocs formed, resulting in delayed settling. The TRR may not exhibit uniform behavior compared to TSS removal and can occasionally demonstrate contrasting patterns. For instance, in scenarios characterized by low coagulant concentrations or elevated levels of PAM alongside diminished PAC, TSS levels may remain high despite a lower average turbidity reduction rate. This suggests that coagulated networks featuring low PAC and high PAM content exhibit reduced density. Despite the substantial molecular mass of PAM, this polymer may not possess a pronounced capacity to enhance clot density due to its inherent characteristics.

Conversely, PAM can significantly contribute to network densification owing to its exceptionally high surface charge. A comparative analysis of Fig. 7-A, and 7-B, underscores the pivotal role of MNP concentration. As previously discussed, MNP proves highly effective in augmenting the TRR. However, the interaction between MNP and PAM accelerates the average settling velocity. This correlation serves as further evidence that the structure of PAM clots in isolation lacks significant density. Yet, with the incorporation of MNP within the PAM network, there is a substantial enhancement in clot density, facilitating sedimentation. Fig. 7-A shows a high TRR dependency on PAM concentration in higher MNP dosages. This phenomenon extends to PAC, albeit to a lesser extent. The relatively weak and unstable nature of PAM strings hinders their ability to retain magnetic nanoparticles within their network effectively.

TDS and TSS removal, along with TRR, are illustrated for six selected samples in Fig. 8. High rates of turbidity reduction and lower TSS removal happen at the same time, accordingly. TRR analysis investigations showed the High dependency of TRR on MNP concentration (Fig. 8), which is reasoned by the high molecular weight of Fe_3O_4 magnetic particles entering the floc structure and leading through faster gravity settlement. The highest TRR had happened in the case of STD 1, along with the lowest TSS removal concurrently. In contrast, STD 13 and 9 showed a high TSS removal record contrary to the TRR response.

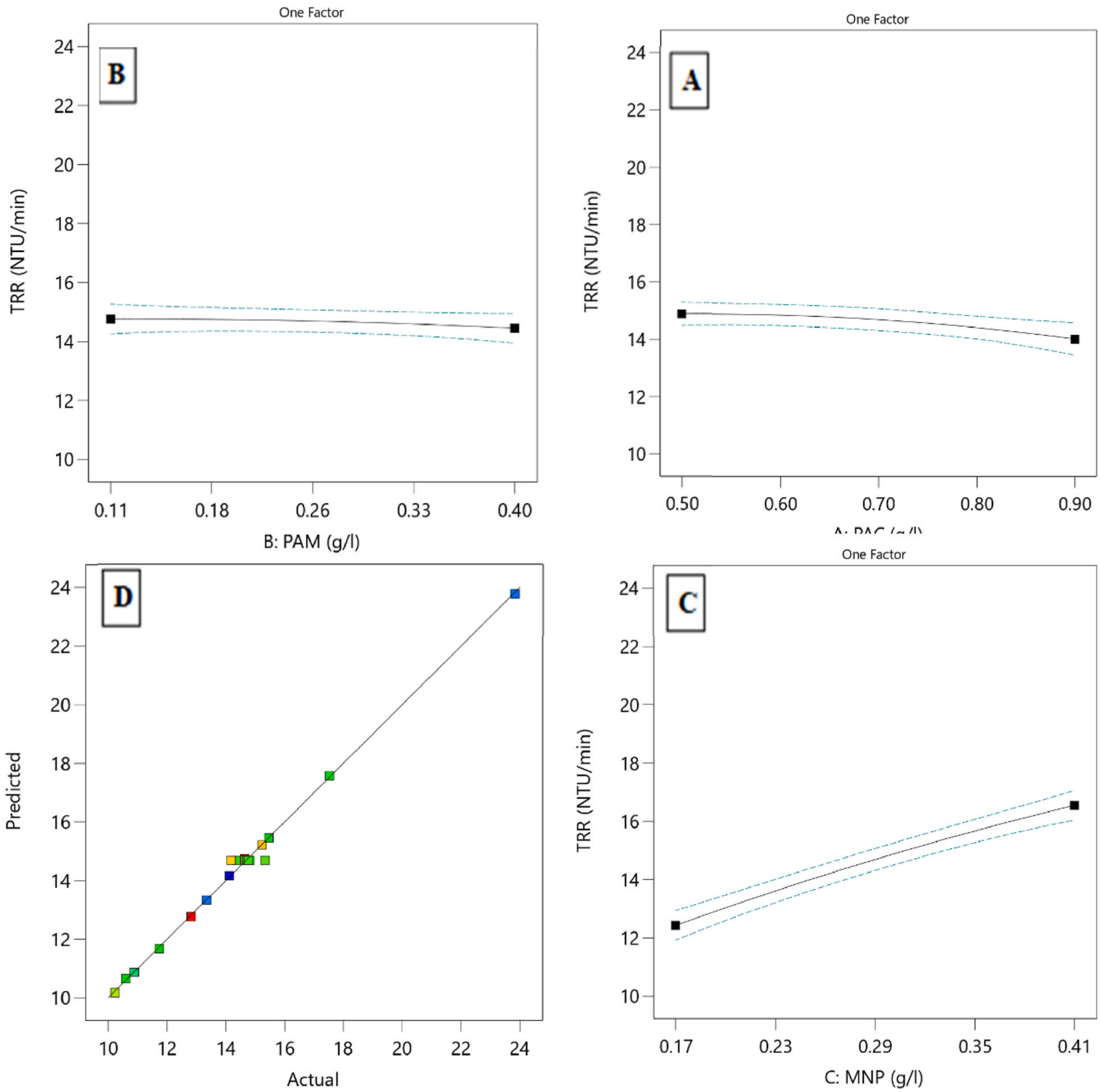

Fig. 6. Single factor investigation of TRR generated model, in 0.7, 0.26, 0.29 g/l of A) PAC, B) PAM, and C) MNP concentrations, respectively. D) The predicted vs. actual results congruence.

3.4. Numerical and figurative optimization

Using Design Expert 13.0.0, two numerical optimizations were obtained, focusing on two scenarios: operational and adjusted economic. The optimum concentrations of MNC application are presented in Table 5. The operational scenario achieved the highest removal rates of 66.90 % for TDS, 73.69 % for TSS, and 19.12 NTU/min for TRR, corresponding to optimal concentrations of 0.99 g/L PAC, 0.05 g/L PAM, and 0.27 g/L MNP. In contrast, the adjusted economic scenario resulted in a higher TSS removal rate of 76.51 %, but with lower TRR and TDS removal rates at 15.62 NTU/min and 54.56 %, respectively. The optimal concentrations for the adjusted economic scenario were 0.89 g/l PAC, 0.50 g/l PAM, and 0.17 g/l MNP.

Overall, the sedimentation process is slowed by the lower PAC and MNP concentrations, which not only significantly reduces the cost of chemicals consumed but also increases the TSS removal rate. However, an additional 22.41 % more time is required for the

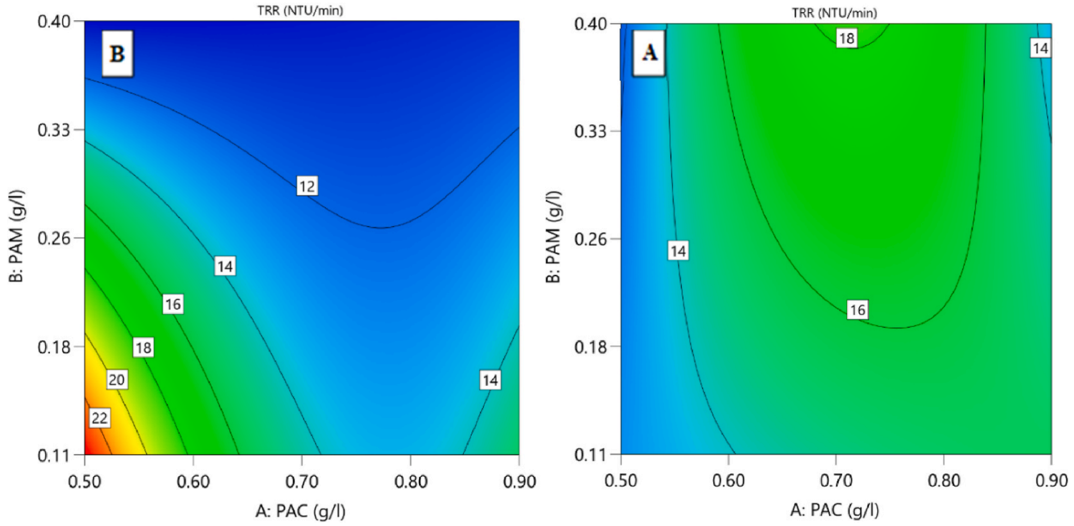

Fig. 7. Contour of mutual interaction of effecting parameters, in TRR, at constant MNP concentration of A) 0.41, and B) 0.17 g/l.

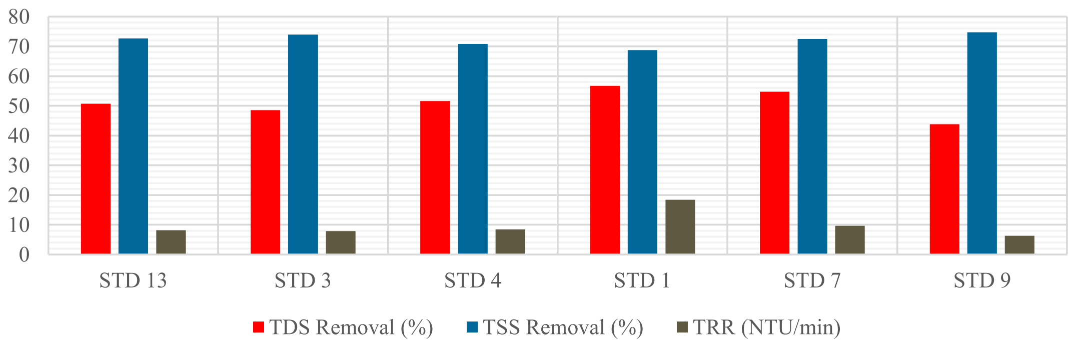

Fig. 8. TDS removal (%), TSS removal (%), and TRR (NTU/min) results for samples with STD of 1, 3, 4, 7.

Table 5
Numerical optimization of TDS, and TSS removal along with TRR in two operational and adjusted economical scenarios.

Row	Scenario	Concentrations (g/l)			Responses		
		PAC	PAM	MNP	TDS rem. (%)	TSS rem. (%)	TRR (NTU/min)
1	Operational	0.99	0.05	0.27	66.90	73.69	19.12
2	Adjusted Economical	0.89	0.05	0.17	54.56	76.51	15.62

sludge to settle. Although the improvement in TSS removal of 2.05 % may not seem substantial, the reduced project cost and decreased chemical usage represent a significant advancement.

Considering the complex situations encountered at drilling sites and the often limited accessibility of facilities, along with the necessity for structural flexibility, a figurative optimization was performed. This optimization approach, while less precise than numerical methods, is focused on practical application in real-world settings.

In this figurative optimization, constraints were established to achieve specific performance targets: a minimum of 60.00 % TDS removal, 75.00 % TSS removal, and maintaining a TRR of 15 NTU/min. Additionally, an MNP concentration of 0.2 g/L was selected, as it is considered an acceptable optimum level based on previous numerical optimization results. These criteria effectively defined a small operational domain for each component involved in the treatment process. As illustrated in Fig. 9, the permitted range for PAC concentrations is set between 0.83 and 0.99 g/L. Meanwhile, the concentration of PAM remains at a lower limit, ranging from 0 to 0.05 g/L. This optimization framework not only addresses the performance requirements but also takes into consideration the practical

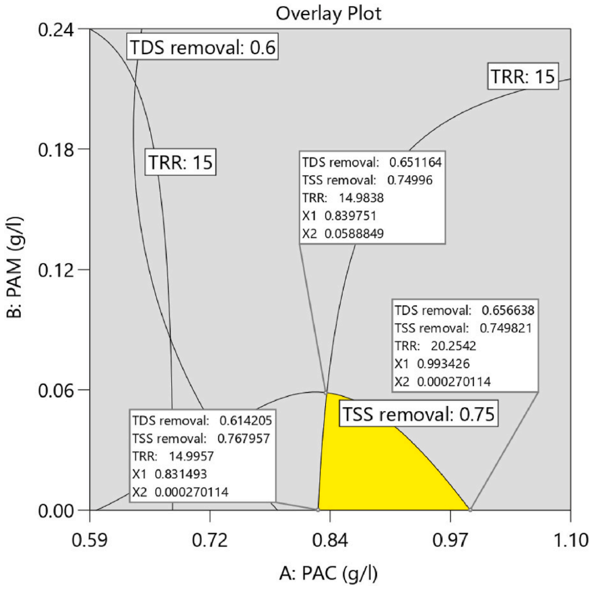

Fig. 9. Graphical optimization of magnetic nano-composite applied in drilling operation waste-water treatment, at a constant MNP concentration of 0.2 g/l.

limitations and operational flexibility needed in the challenging environments of drilling operations.

4. Conclusions

This study explored the application of a magnetic nano-composite coagulant (MNC) synthesized via the post-addition method to treat wastewater from a well drilling operation in the Mansoor Abad oil field, Behbahan, Iran. PAC, PAM, and MNP were the primary factors evaluated using a CCD method to study their effects on three responses of TDS removal (%), TSS removal (%), and average Turbidity Reduction Rate (NTU/min). Key findings include.

- The use of polymer-based magnetic coagulants for drilling wastewater treatment proved effective in removing pollutants and suspended solids.
- High concentrations of coagulants can lead to negative effects, such as increased water turbidity.
- The maximum removal rates achieved were 72.00 % for TSS, 77.01 % for TDS, and 23.82 NTU/min for TRR.
- A significant inverse relationship between the rates of turbidity removal and TSS was observed. Samples that settled rapidly post-coagulation displayed lower TSS removal rates subsequently. This finding can be attributed to the pivotal role of time in facilitating interactions between coagulants and contaminants, allowing for enhanced absorption of contaminants through prolonged interaction periods.
- MNP, in combination with PAC, played a key role in TDS removal, while higher concentrations of PAC and PAM together reduced coagulation efficiency. MNP helped to balance the polymer behavior by forming cohesive coagulation clusters.
- The analysis of TSS response models revealed that high concentrations of PAC and PAM together reduce coagulation efficiency. However, MNP played a crucial role in stabilizing the polymers by forming cohesive coagulation clusters.
- A significant relationship was observed between TRR and TSS removal, where higher TRR coincided with lower TSS removal. This indicated that higher MNP concentrations accelerated sedimentation, limiting the interaction time between polymers and pollutants.
- Additionally, Numerical optimization scenarios indicated that economic and operational conditions could yield efficient removal rates with optimal coagulant concentrations.

CRediT authorship contribution statement

Behrad Shadan: Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Arezou Jafari:** Supervision. **Reza Gharibshahi:** Validation, Project administration, Conceptualization.

Data availability statement

Data used to support the findings of this study are available from the corresponding author upon request.

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Declaration of competing interest

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.

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Abbreviations

MNC	Magnetic Nano-composite Coagulant
MNP	magnetic Nano Particles
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
TRR	Turbidity Reduction Rate
PAC	PolyAluminum Chloride
PAM	PolyAcrylAmide
NTU	Nephelometric Turbidity Unit
DCR	Dosage to Contaminate Ratio
CCD	Central Composite Design
RSM	Response Surface Method
DI	Deionized distilled
DOE	Design of Experiment
ANOVA	Analysis of Variance

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