J. Indian Chem. Soc.
ISSN: 0019-4522
Vol…./Issue…/pp…

TiO_2/photo-Fenton process for seawater pretreatment: Modeling and optimization using response surface methodology (RSM) and artificial neural networks (ANN) coupled genetic algorithm (GA)

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Manuscript received online: …… (Date), Accepted: … (Date), Published online …… (Date)

Abstract: Fouling due to organic contaminants in reverse osmosis (RO) desalination process leads to recurrent chemical cleaning, elevated operating pressure, and shorter membrane life. The present study evaluates the performance of solar photocatalysis of heterogeneous TiO_2/photo-Fenton process to pre-treat RO feed-seawater under solar irradiation. Modeling and optimization of the process are performed by using both genetic algorithm (GA) coupled with artificial neural network (ANN) method, and response surface methodology (RSM). The performance of organic degradation is evaluated in terms of total organic carbon (TOC) removal. The efficiency of the process is studied as a function of five independent variables: the dosage of TiO_2, airflow rate, pH, reaction time (RT) and dosage of Fe^{2+} (maintaining H_2O_2/Fe^{2+} ratio in the range from 150:1 to 50:1). Both RSM and ANN models were evaluated based on correlation coefficient (R^2), average error (AE) and root means square error (RMSE). GA coupled ANN model was found to be more accurate for determining optimum operating conditions. The obtained optimum values using ANN-GA include a reaction time of 115 min, 0.66 g/L of TiO_2, 0.75 g/L of H_2O_2, 15 mg/L of Fe^{2+}, pH 6.4 and airflow rate of 3.9 L/min. The optimum TOC removal rate was found to be 67.2%. The predicted ANN-GA result (67.2%) corresponds well with the experimental one (TOC removal = 65.4%).

Keywords: Seawater pretreatment, Solar-nano-photocatalysis, Genetic algorithm (GA), Artificial neural network (ANN), Response surface methodology (RSM)

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Introduction

Sustainable water availability is a primary global concern, owing to freshwater scarcity, contamination due to industrial effluents, and use of fertilizers together with wastage and overuse of water. Reverse osmosis (RO) process is increasingly employed to recover freshwater from seawater and effluent wastewater in many parts of the world. However, the technical feasibility and cost-efficacy of this method depend on effective fouling control and contaminant loading[1]. RO feed water that contains humic-substances, high-molecular organic matter, volatile halogenated carbons, microorganisms, and algae cause fouling and reduce the flux and life of the membrane[2,3]. Therefore the abatement of these contaminants from the RO feed seawater is a major concern to improve the performance and cost-efficacy of seawater reverse osmosis (SWRO) systems.

Advanced oxidation processes (AOPs) by UV/Photocatalysts methodology can degrade persistent organic contaminants from the feed water. Remediation of recalcitrant pollutants is directly linked to the development of hydroxyl radicals[4,5]. AOPs may be used in seawater treatment for overall organic degradation and specific contaminant degradation[6]. Several researchers have enhanced the generation of hydroxyl radicals by adding catalysts (TiO_2/ZnO), chemicals (H_2O_2) and using the combination of photocatalytic processes such as (Solar/TiO_2/Fenton), ozonation/photocatalytic TiO_2, and Fenton/UV/TiO_2 photocatalysis. Generation of hydroxyl radical through integrated TiO_2/photo-Fenton process was reported in the previous studies[7]. Due to the dual role of iron as an electron acceptor and as a Fenton reagent, significant improvement in the oxidation of organic contaminants was observed at near-neutral pH. However, little data are available on the synergistic effect of Solar/TiO_2/photo-Fenton/airflow in the seawater pretreatment system for photo-mineralization of organic compounds.

One of the previous research works[8] demonstrated that degradation efficiency of total organic carbon (TOC) was 79% for the photo-Fenton treatment of cleaning waters from seawater desalination reverse osmosis membranes. The highest removal was attained at 1.4 g/L H_2O_2 and 70 mg/L Fe^{2+} under solar irradiation of 60 minutes. It was observed that the addition of TiO_2-P25 accelerated the photo-Fenton process. Another study[9] reported that a 71% removal in the chemical oxygen demand (COD) using Fenton/TiO_2/UV photocatalytic for the mineralization of an oil-water emulsion. When the air was bubbled through the photoreactor, the degradation efficiency was increased to 84%. In an antibiotic degradation using TiO_2 immobilized beads/photo-Fenton process[10], 80% removal efficiency was achieved in 30 minutes irradiation time. The effect of various parameters like H_2O_2 dose, number of TiO_2 immobilized beads, pH, and treatment time on antibiotic removal was modelled and optimized through artificial neural network (ANN) coupled with evolutionary genetic algorithm (GA) techniques.

In the current study, statistical relations between independent input factors like TiO_2 dosage, Fe^{2+}dosage, pH of the solution, airflow rate and irradiation time for the treatment of seawater were evaluated and optimized through response surface methodology (RSM) and ANN-GA optimization techniques. The operational conditions to achieve optimum degradation of total organic carbon (TOC) were evaluated, and the optimum solution is suggested for the

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overall process improvement in RO seawater pretreatment. To the best of the knowledge of present research group, the number of studies dealing with the application of RSM and ANN-GA modeling-optimization strategy for RO seawater pretreatment using Solar/TiO_2/photo-Fenton/Aeration process is very terse and here lies the novelty of the present article.

Results and discussion

Overall, 50 experimental runs were conducted as designed by central composite design (CCD). The main effects and interaction between five input factors are considered to assess the validity of treating seawater using TiO_2/photo-Fenton solar photocatalysis. The effectiveness of TiO_2 solar photocatalysis is improved by the addition of Fenton reagent. As given in Table 1, the experimental responses show that the TOC removal efficiency range from 5.28 % to 48.45 %.

In the Fenton process, Fe^{2+} is responsible for the decomposition of H_2O_2 and thereby resulting in the generation of hydroxyl radicals ($^{\bullet}OH$)[11]. The major step involved in the production of hydroxyl radical is shown in equation (1). Hydroxyl radicals play a crucial role in photo Fenton process, degrading most of the organic pollutants into CO_2, H_2O and inorganic ions through hydroxylating or dehydrogenating reactions[12]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$

Several studies have shown the synergistic effect of TiO_2/photo-Fenton process in the treatment of wastewater and industrial effluents. Previous research[13] reported that the highest TOC mineralization of methyl orange was achieved using $Fe_2O_3/TiO_2+H_2O_2$ under UV irradiation. In another study for the treatment of cleaning waters from seawater desalination reverse osmosis membranes, 77% removal of TOC was achieved in 180 minutes by adding 1200 mg L^{-1} of H_2O_2 with 250 mg L^{-1} of TiO_2 [8].

RSM modeling:

In the present study, analysis of variance (ANOVA) technique was used for statistical analysis of the data to determine main and interaction effects between input factors and process response. As per ANOVA results, TOC removal model has been found significant by F-test at 95% confidence level (Prob<0.05). F-ratio of 40.69 with shallow probability values ((Prob>F)<0.05) shows that the model is significant enough to predict the response and optimum values. The final statistical regression model, in terms of their actual and coded factors, is shown in Table 2.

From the coded equation (Table 2), by comparing the coefficients of main effects, it is evident that Fe^{2+} dosage (factor-C), airflow rate (factor-D) and solar irradiation time (factor-E) have a positive impact on TOC removal (+2.26, +4.42 and +1.50 respectively). The factor $A\,(pH)$, whose coefficient is +1.04, is the least influential parameter among the main effects. Among two-factor interactions, CD interaction (Fe^{2+} dosage and airflow rate) is the highest with a positive coefficient of +7.14. The negative coefficient of AD interaction (-3.58) indicates that the interaction between pH and airflow rate affects the TOC removal in an antagonistic way. Several studies have demonstrated the interaction and main effect of airflow in advanced oxidation processes for treating organic pollutants[14,15]. A study

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conducted to remove TOC from petroleum refinery wastewater[15] indicates that the availability of oxygen in the air acts as an oxidizing agent for the organics present in the wastewater. When aeration is employed, the oxygen present in the air can work as a scavenger of photon-induced electrons on the TiO_2 surface. The scavenging process prevents the electron-hole recombination and thereby enhancing the overall reaction rate. Another study[9] reported that Fe^{2+}, H_2O_2 and TiO_2 dosage were the significant factors in the advanced oxidation process using Fenton/TiO_2/UV photocatalytic for the mineralization of an oil-water emulsion. Due to the synergistic interactive effect of process parameters, the organic removal works well over a wide range of pH.

ANN modeling:

Artificial neural network (ANN) is an intelligent computation methodology used to emulate the learning strategies of the human brain and biological neurons[16,17] ANN is a promising tool to efficiently approximate nonlinear complex correlations exist between input-output parameters in systems involving advanced oxidation processes[18]. In this study, 50 sets of experimental data obtained from RSM-CCD modeling were used to develop the network. Various combinations of training functions, number of neurons in the hidden layer have been tried to improve the accuracy of the network. A Levenberg-Marquardt backpropagation algorithm with tan-sigmoidal transfer function has been utilized because it has least mean square error (MSE). The number of neurons in the hidden layer has been varied to achieve maximum accuracy. The best topology of the ANN architecture was found to be 5-12-1 with five input nodes, 12 neurons in the hidden layer and one output node.

The trained optimum ANN model has given a regression coefficient of 0.99752 with root mean square error $(RMSE)$ of 0.98381. Fig.1 shows the regression plot of experimental versus predicted values for optimum ANN model. The fitted ANN model demonstrates a good correlation among targets and model-output during testing $(R = 0.99163)$, validation $(R = 0.99924)$ and training $(R = 0.99881)$. Both RSM and ANN models have been assessed based on the correlation coefficient (R^2), root means square error $(RMSE)$ and average error (AE). The formulae for computing these statistical parameters are shown in equations (2), (3) and (4) respectively.

The values for R^2, $RMSE$ and AE for RSM model were found to be 0.9458, 3.6 and 3.78 respectively, while for ANN model the same values were obtained as 0.99752, 0.98381 and 2.31 respectively. When compared to actual experimental (Table 1), ANN predicted results were found to be more accurate than RSM prediction of TOC removal at the same input settings.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_p - y_o)^2}{\sum_{i=1}^{n}(y_o - y_m)^2} \quad (2)$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_p - y_o)^2} \quad (3)$$

$$AE = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{|y_o - y_p|}{y_o}\right) \times 100 \quad (4)$$

where y_p is the predicted target value, y_m is the mean of experimental values, y_o is the observed target value, and n is the number of input data points.

Optimization using RSM :

By using the RSM model (Table 2), the optimization process was performed to

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determine the optimum value of TOC degradation. The optimization steps involve identifying the desirability function (DF) in the range of 0.0 (least desirable) to 1.0 (most desirable) for optimum degradation of TOC. For the construction of desirability indices of factors and responses, five possible "goals" need to be defined (maximize, minimize, target, in-range and equal-to). The Design-Expert program scans for the largest overall desirability by combining individual desirability values into a single number. In this study, the desired goals for input operating conditions are selected as "within-the-range", and the response TOC is defined as "maximum" to achieve the highest degradation efficiency. The optimized conditions were attained as follows: the pH of 5.478, TiO_2 dose 0.4 g/L, 15 mg/L of Fe^{2+} dosage, airflow rate 4.0 L/min and 120 minutes of solar irradiation. The response surface plot of TOC removal at optimum conditions is demonstrated in Fig.2. The TOC removal under these optimized conditions was 59.34 %.

The RSM optimum results were compared with other research studies that employed TiO_2-photo-Fenton photocatalysis for organic removal. One of the previous research works[9] reported, 71% removal of chemical oxygen demand (COD) using Fenton/TiO_2/UV photocatalytic for the mineralization of oil-water emulsion. When the air was bubbled through the photoreactor, the degradation efficiency was increased to 84 %. Similar results were obtained in another study[19] for the treatment of oily wastewater, where 80% degradation efficiency was achieved (at optimum pH ranging between 6 and 7) by employing TiO_2/artificial-UV/Fe^{2+}/H_2O_2 photocatalytic-Fenton reagent process. However, the present work shows that TiO_2/photo Fenton photocatalysis is very efficient in organic removal more economically by using free solar energy. The synergistic effect of TiO_2 integrated with photo-Fenton can lead to enhanced production of reactive oxidants, and thereby efficient mineralization is achieved. The same synergism leading to increased removal efficiency was demonstrated in a previous study[7], where 78% of benzoic acid degradation was achieved at circum-neutral pH (6.5-7.5).

Optimization of ANN model using Genetic algorithm (GA):

ANN-GA is one of the most efficient methods for modeling and optimization of nonlinear processes where input-output data are generated empirically in the domain space[20]. GA is an optimization technique developed based on the principle of natural evolution[21]. The GA strategy starts with the initialization of population known as chromosomes, followed by fitness evaluation based on an objective function. The genetic propagation of chromosomes is based on the selection of the fittest and then through operators like crossover and mutation. In the current study, optimization of five process parameters is investigated for TiO_2/photo-Fenton RO pretreatment process. The photocatalytic process factors which represent the input space of the developed ANN have been optimized using GA. This is attained by searching for the optimum solution those results in maximum TOC removal. The objective function used for maximizing TOC removal in the ranges of factors investigated has been applied. The developed ANN model has been used as the fitness function to evaluate the quality of the individual solution from the population.

The GA tool in MATLAB software is a minimization tool. Therefore, for estimating fitness values, the negative of optimum output from TOC-ANN model has been used. The values of GA-specific factors, employed in the optimization were Population size=50, number of generation=120, Crossover probability=0.9 and mutation probability=0.05. The fitness curve obtained after convergence to the optimum solution is shown in Fig.3. The acquired optimum conditions using ANN-GA include a reaction time of 115 min, 0.66 g/L of TiO_2, 0.75 g/L of H_2O_2, 15 mg/L of Fe^{2+}, pH 6.4 and airflow rate of 3.9 L/min. Optimum TOC removal has been found to be 67.2 %. The predicted ANN-GA result (67.2 %) corresponds well with the experimental one (TOC removal = 65.4%).

Experimental

Seawater characterization:

The seawater samples for this research study was collected from Muscat, Gulf of Oman,1.68 km away from the shore, at the location 23º 41.921' N, 058º 11.115' E . Seawater sample was collected in sterile bags and kept in the refrigerator (5˚C) until it was taken for photocatalytic treatment. The average values of COD, pH, salinity, dissolved oxygen (DO) and total organic carbon (TOC) of the seawater samples were determined as 5.0 mg/L, 7.96, 34200 mg/L, 5.25 mg/L, and 3.42 mg/L respectively.

Materials:

The catalysts used was Titanium dioxide (TiO_2) Aeroxide P-25 manufactured by Evonik Industries, Germany and 0.1 N of NaOH and HCl of 0.1 N were used for adjusting pH. Hydrogen peroxide (H_2O_2) (35% (v/v)) was supplied by EMPROVE.exp. Ferric Sulfate ($Fe_2O_{12}S_3$) was obtained from Fisher Scientific Company, USA and its molecular weight is 489.96, (CAS: 15244-10-7). The materials as per the design of experiments (DOE) proportions (Table 1) were used in solar photocatalysis of TiO_2/photo-Fenton for TOC degradation.

TOC of each sample was determined using TOC Analyzer (LCSH/CSN) (Make: SHIMADZU Japan). Before analyzing TOC, each sample was filtered using 0.22 μm Millipore Durapore membrane (150 mm-diameter & Ashless-40). The average solar radiant flux was measured using KIPP & ZONEN-CMP 21 Pyranometer and was found to be 720±4 Watts/m^2. All experimental runs were carried out from 11 AM to 2 PM so that maximum UV radiation was received for the photocatalytic treatment. The UVS-E-T Radiometer (Make: KIPP & ZONEN) was used to measure UV irradiance as per ISO 17166:1999, CIE S 007/E-1998 procedure.

Experimental procedure:

The experimental set-up includes a photo-reactor consists of glass tubes connected in parallel, a peristaltic pump for recirculation of seawater through glass tubes, a recirculation tank with magnetic stirrers and an aeration pump. In the photo-reactor, five borosilicate glass tubes (650 mm length × 22 mm inner diameter and 2 mm thickness) were used for seawater recirculation exposed to solar irradiation. The recirculation tank (2.5 litres capacity) is subjected to stirring with magnetic stirrers. Seawater solution runs through the photocatalytic reactor by means of peristaltic pumps at a flow rate of 1.8 L/minute. Parabolic reflectors were installed beneath the reactor tubes to make the solar irradiation to be reflected and diffused to the tubes at optimum intensity. The magnetic stirring, aeration, and recirculation through borosilicate glass tubes ensure good mixing and enough supply of oxygen required for photocatalytic reaction.

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All the experiments were conducted as per the central composite design (CCD) settings (Table1) to estimate the TOC degradation efficiency under solar irradiation.

Experimental design and analysis:

Design-Expert software (version 11, Stat-Ease, USA) was used to perform the optimization of TOC removal using RSM and to evaluate the interactive relationship between the input factors. RSM is an experimental statistical modeling technique employed for multivariate analysis using quantitative data to solve multiple regression equations simultaneously[22]. In the current study, Fe^{2+} dosage, TiO_2 dosage, reaction time, airflow rate and pH were chosen as input parameters for seawater organic degradation and their +1 and -1 level was set at 5 and 15mg/L, 0.4 and 0.8 g/L, 60 and 120 minutes, 2 and 4 L/min, and 4 and 8, respectively. The efficiency of the photocatalytic treatment was analyzed in terms of percentage degradation of TOC. In all the experiments, H_2O_2 concentration was fixed at 0.75g/L while H_2O_2/Fe2+ ratio was maintained from 150:1 to 50:1 by varying Fe^{2+} concentration in the range 5 to 15 mg/L. In the photo-Fenton process, Fe^{2+} and H_2O_2 dosages are two significant parameters deciding the overall operational cost as well as efficiency. Hence the selected range of H_2O_2/Fe^{2+} ratio provides useful insight into its influence on TOC removal from RO feed seawater[23]

Since RSM is only appropriate for second-order approximations, interpretation of the effect of input factors is difficult in advanced oxidation processes (AOPs) due to the complexity of the photocatalytic reactions[24]. In this scenario, ANN can be considered as a promising modeling methodology[25]. The capability of ANN to model and simulate complex photocatalytic/advanced oxidation processes was reported in several research studies[23]. Hence in this work, TOC degradation was modelled using both RSM and ANN, and their prediction accuracies were compared. All ANN computation was performed using Matlab R2017a software with ANN toolbox.

Conclusions

In the current work, ANN-GA and RSM methodologies are compared for their generalization and optimization efficiencies in the heterogeneous TiO_2/photo-Fenton process to pre-treat RO feed-seawater under solar irradiation. A central composite design coupled RSM was utilized for model building, and ANN-GA facilitated in identifying optimum operating conditions for maximum TOC removal. Using ANN-GA, optimum conditions were set to 6.4, 0.66 g/L, 15 mg/L, 3.9 L/min and 115 min for pH, TiO_2 dosage, Fe^{2+} dosage, airflow rate and solar irradiation time, respectively. Under the optimum settings, the maximum TOC removal was 67.2%. The predicted ANN-GA result (67.2%) corresponds well with the experimental one (TOC removal = 65.4%). It is evident from this study that, even though RSM is most generally used technique for photocatalytic process optimization, ANN-GA methodology may present a superior alternative. Seawater pretreatment at the optimum operating conditions derived from this work provides enhanced organics degradation by using minimum nano-photocatalysts and resources. The TiO_2/photo-Fenton process by utilizing renewable solar energy is an efficient and economical method for mitigating membrane fouling in seawater reverse osmosis desalination systems.

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Conflict of interest

The authors declare that they have no conflict of interest.

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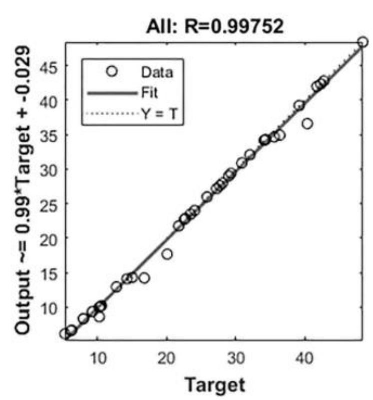

Fig.1. Regression plot of experimental versus predicted values for the optimum ANN model.

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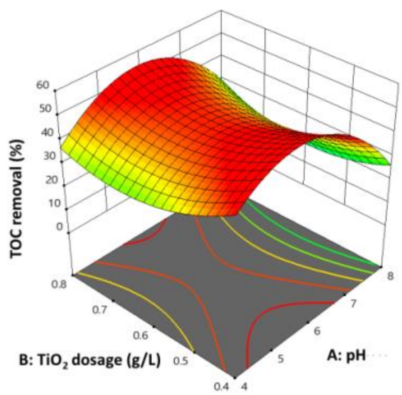

Fig.2. The response surface plot of TOC removal at optimum settings of other input variables.

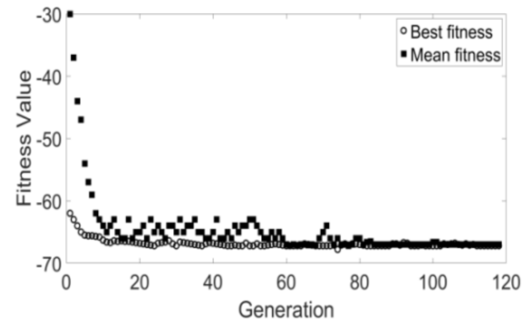

Fig.3. Genetic algorithm fitness curve converged at the optimum value of TOC removal (67.2 %).

Table 1. The five-factor Central composite design (CCD) matrix; input factors at actual levels and the experimental, RSM predicted and ANN predicted results for solar- TiO_2/photo-Fenton treatment of seawater

Run	A: pH	B: TiO_2 dosage g/L	C:Fe^{2+} dosage mg/L	D:Air flow rate L/min	E: Time min	TOC removal (%)		
						Experimental	RSM predicted	ANN predicted
1	6	0.6	10	4	90	41.81	35.68	40.45
2	8	0.8	5	2	60	30.92	30.4	30.25
3	4	0.6	10	3	90	7.95	9.84	9.15
4	8	0.4	5	2	120	34.19	29.65	35.36
5	6	0.6	10	3	90	36.25	31.26	34.68
6	6	0.6	10	3	90	27.85	31.26	34.68
7	8	0.8	15	4	120	34.14	30.24	33.26
8	4	0.4	5	2	60	10.25	15.62	11.06
9	8	0.4	5	2	60	25.88	26.65	24.45
10	8	0.4	15	2	60	8.26	7.54	9.56
11	6	0.6	10	3	120	36.43	32.76	36.24
12	6	0.6	10	3	60	28.12	29.76	29.39
13	8	0.4	15	2	120	7.94	10.54	7.26
14	4	0.4	15	2	60	14.28	15.23	15.38
15	8	0.8	5	4	120	20.11	20.82	19.96
16	4	0.8	5	2	60	9.23	4.23	9.85
17	6	0.6	10	3	90	29.35	31.26	34.68
18	6	0.6	15	3	90	38.04	33.52	37.84
19	6	0.8	10	3	90	34.39	38.74	35.46

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20	8	0.8	15	2	120	10.47	14.29	11.25
21	6	0.4	10	3	90	42.36	42.56	42.57
22	4	0.8	15	2	60	10.35	3.84	11.06
23	8	0.4	5	4	60	12.76	14.07	12.55
24	6	0.6	5	3	90	27.26	29.38	27.85
25	4	0.4	15	4	60	48.45	45.49	48.69
26	8	0.4	15	4	60	22.75	23.49	22.93
27	8	0.8	15	2	60	10.58	11.29	11.68
28	4	0.4	5	4	120	24.09	20.34	22.69
29	6	0.6	10	3	90	30.37	31.26	34.68
30	4	0.8	5	2	120	6.15	7.23	6.95
31	4	0.4	15	2	120	22.59	18.23	23.45
32	4	0.8	5	4	120	6.26	8.95	6.89
33	4	0.8	15	4	60	29.35	34.1	30.25
34	4	0.8	5	4	60	7.98	5.95	8.25
35	6	0.6	10	3	90	34.27	31.26	34.68
36	4	0.4	5	4	60	21.78	17.34	22.55
37	8	0.8	5	2	120	39.23	33.4	37.47
38	6	0.6	10	3	90	28.97	31.26	34.68
39	4	0.8	15	4	120	35.61	37.1	33.47
40	6	0.6	10	3	90	31.25	31.26	34.68
41	8	0.4	15	4	120	29.01	26.49	26.98
42	8	0.8	5	4	60	14.67	17.82	16.37
43	4	0.4	5	2	120	15.03	18.62	16.46
44	6	0.6	10	3	90	28.78	31.26	34.68
45	8	0.4	5	4	120	15.01	17.07	15.86
46	8	0.6	10	3	90	9.28	11.93	10.45
47	4	0.4	15	4	120	42.81	48.49	41.69
48	8	0.8	15	4	60	27.74	27.24	28.83
49	4	0.8	15	2	120	5.28	6.84	6.25
50	6	0.6	10	2	90	23.49	26.85	24.95

Table 2. Final ANOVA regression model equations for TOC removal (%).

TOC removal in coded factors	$= +31.26 + 1.04 \times A - 1.91 \times B + 2.26 \times C + 4.42 \times D + 1.50 \times E + 3.79 \times A \times B - 4.68 \times A \times C - 3.58 \times A \times D + 7.14 \times C \times D - 20.38 \times A\text{^}2 + 9.38 \times B\text{^}2$
TOC removal in actual factors	$= -70.76 + 66.03 \times pH - 347.8 \times TiO_2\ dosage - 1.02 \times Fe^{2+} dosage + 0.877 \times Air\ flow\ rate + 0.055 \times Time + 9.46 \times pH \times TiO_2\ dosage - 0.46 \times pH \times Fe^{2+} dosage - 1.78 \times pH \times Air\ flow\ rate + 1.42 \times Fe^{2+} dosage \times Air\ flow\ rate - 5.09 \times pH^2 + 234.67 \times TiO_2\ dosage^2$