EXPERIMENTAL INVESTIGATION, MODELING, AND OPTIMIZATION OF COMBINED ELECTRO-(FENTON/COAGULATION/FLOTATION) PROCESS BY MEANS OF DESIGN OF EXPERIMENTS AND ARTIFICIAL INTELLIGENCE SYSTEMS

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ABSTRACT

In the present study, combined Electro-(Fenton/Coagulation/Flotation) (EF/EC/El) process was studied via degradation of Disperse Orange 25 (DO25), an organic dye, as a case study. Influences of seven operational parameters including initial pH of solution (pH_0), applied voltage between anode and cathode (V), initial ferrous ion concentration (C_{Fe}), initial Hydrogen peroxide concentration (C_{H2O2}), initial DO25 concentration (C_0), applied aeration flow rate (F_{Air}), and process time (t_P) were measured on the dye removal efficiency (DR%). Combined design of experiments (DOE) was designed and experiments were conducted in accordance with the design. The experimental data collected in a laboratory scaled, handmade glass cylindrical batch reactor equipped with four graphite bar electrode as cathode, an Aluminum sheet (Al) electrode as an anode, an aeration pump equipped with air filter and air distributer, 150 rpm mixer, and DC power supply. The DR% of 98 was achieved under experimental conditions at pH_0 4, V 10, C_{Fe} 7.5, C_{H2O2} 0, C_0 140, and F_{air} 0. The data was used for model building by employing two more popular models in this kind of studies: normal and reduced multiple regression model (MLR & r-MLR) and artificial neural network (ANN & r-ANN). Further statistical tests were applied to exhibit models goodness and to compare models. Based on statistical comparison, ANN models obviously outperformed SMLR models. Finally, optimization process was carried out using genetic algorithm (GA) over the outperformed ANN model. The optimization procedure causes optimal point which gave an insight of optimal operating conditions of the combined process.

Keywords: Design of Experiments; Artificial neural network; Genetic algorithm, Dye Removal; Electro-(Fenton /Coagulation/Flotation).

1. Introduction

Several methods have been developed for the removal of organic pollutant especially synthetic textile from wastewaters to decrease their impact on the environment including adsorption on inorganic or organic matrices, photocatalysis, oxidation processes, microbiological or enzymatic decomposition. Application of adsorptive bubble separation techniques, electro-flotation, Fenton, electro-Fenton, coagulation, electro-coagulation processes and some combination of these methods has also been assessed in recent years. The previous Reports revealed that the efficiencies drastically are dependent on the method and operational parameters.

The new resistant organic compound degradation difficulties inspires the researches to use the combined procedures because of more efficiency and less process time by using synergetic effects advantages. But, the drawbacks of the idea are complex design of combined reactor and the interference of coupled method in common reactor. Then, finding the proper combination of methods with high compatibility is new research interest.

The electro-coagulation (EC) technique as well as Electro-Fenton (EF) and Electro-flotation (EL) are considered to be potentially effective approaches to treat several types of wastewaters. EC is a process consisting of metallic hydroxides flocs generation within the wastewater by electro-dissolution of soluble anodes, usually made of iron or aluminum. The hydrogen gas produced at the cathode in the electrocoagulation unit could create and float the flocs. In the other word, the electrocoagulation mainly plays the role of destabilizing and aggregating the fine particles, and the electroflotation is responsible for floating the flocs formed in the effluent of the electrocoagulation unit. It make easy to use synergetic effect of couple method of EC/EL. Also, because electrocoagulation happen in anode and floatation in cathode, there are no interferences between the processes. The several publication about EC/EF approve the compatibility of the combined methods.

Oxidation of alcohols in the presence of H_2O_2 and $Fe(H_2O)_6^{2+}$ was reported by Fenton in 1894. Among the AOPs, Fenton's treatment was found to be effective in treating wastewater containing several organic pollutions such as phenols, aniline, herbicides, and dyes. The Fenton's treatment has two different stages, First, Fenton's oxidation based on hydroxyl radicals (·OH) and second, Fenton's coagulation based on ferric coagulation following the oxidation stage. In these days, in situ generation of Fenton reagents induced by electrochemistry has become the focus of increasing research because it can oxidize organic compounds quickly and economically. Many persistent organic pollutants have successfully been degraded by the method. This process consists of either electro-generation of H_2O_2 by the reduction of dissolved oxygen on the electrodes such as graphite, mercury pool, carbon fiber, carbon-felt, carbon-polytetrafluoroethylene and generation of Fe^{2+} by the reduction of externally applied Fe^{3+}. It avoid the high cost of H_2O_2, maintain almost constant H_2O_2 concentration and regenerate Fe^{2+} more effectively.

It is important to see that H_2O_2 and Fe^{2+} production and regeneration accrue in cathode. It make easy to merge the process with electrocoagulation that happen in anode electrode. Also, in the proper current intensity and voltage, production of H_2 from reduction of water continue in the cathode. Then, combined method of EC/EF/EL have synergetic effect with no interferences of processes. Although both EC/EF and EC/EL combination have been used and studied in water and wastewater treatment, EC/EF/EL combination efficiency and effective empirical parameters has not been studied in the previous researches. Then, it is important to examine the feasibility of the EC/EF/EL combination and to investigate the effects of operational variables on it's performance.

Therefore, the objectives of this study is first, to report the degradation of Disperse Orange 25 (DO25) as an organic case study through the synthetic aqueous solution by using simple undivided electrochemical cell equipped with Al anode for Al^{3+} electrochemically generation and graphite cathode for electrochemically Fe^{2+} and H_2O_2 regeneration and H_2 production. Second objective of the study is to investigate the effects of seven operational parameters including initial pH of solution (pH_0), applied voltage between anode and cathode (V), initial ferrous ion concentration (C_{Fe}), initial Hydrogen peroxide concentration (C_{H2O2}), initial DO25 concentration (C_0), applied aeration flow rate (F_{Air}), and process time (t_P) were measured on the dye removal efficiency (DR%) using the combined process by means of design of experiments (DOE). The last but not the least is application and assessment of artificial neural network (ANN) and genetic algorithm (GA) for process modeling and optimization.

2. Materials and methods

Ferrous ammonium sulfate was used to prepare the ferrous standard solution. Hydrogen peroxide 30% solution (Merck, Germany) was used to stock solutions preparation by dilution. The Hydrogen peroxide stock solutions were standardized using titration method with permanganate (Merck, Germany) solution reagent that was standardized itself by using standard oxalic acid (Merck, Germany) solution reagent and titration method. The DO25 ($C_{17}H_{17}N_5O_2$) was purchased from Alvan Sabet Co., Iran. Stock solutions of synthetic wastewater were prepared by dissolving desired amount of DO25 powder in distilled water. The desired concentrations of DO25 were prepared by the stock solution diluting. Graphite electrodes with following characterization were purchased from KIG-Co., Iran. The characterization of graphite electrodes is presented in Table 1. Aluminum sheet electrodes were purchased from local seller and preparing by cutting in desired size. The pH_0 of the solutions was adjusted using NaOH (1M) and H_2SO_4 (1 M) (Merck, Germany).

Table 1: The characterization of graphite electrodes.

Character		Character	
Impregnation	Non	Density (g/cm^3)	1.70
Flexural strength (mpa)	55	Compressive strength (mpa)	155
Modulus	22.000	Rockwell ball size/load	5/100
Hardness	105	Thermal conductivity (w/mk)	12
Thermal expantion (10^{-6}/k)	3		

The presented characterization were certified by the KIG. Co.

Statistical design of experiments is a useful technique to investigate a phenomenon by performing a minimum number of experiments. In this study, 32 runs Taguchi design of experiments was applied for investigation of pH_0, V, C_{Fe}, C_{H2O2}, C_0, F_{Air}, and t_P using Minitab 14. The details of 32 designed runs were presented in table 1. |Furthermore, t_P was investigated in eight levels for each run. The levels of each parameters and its interval were determined by pre-tests.

Run	pH_0	V (v)	C_{Fe} (ppm)	C_{H2O2} (ppm)	C_0 (ppm)	F_{Air} (l/min)	Run	pH_0	V (v)	C_{Fe} (ppm)	C_{H2O2} (ppm)	C_0 (ppm)	F_{Air} (l/min)
1	2	0	0	0	20	0	17	2	15	0	6.1	20	2
2	4	5	2.5	1.5	20	0	18	4	10	2.5	4.1	20	2
3	6	10	5	2.7	20	0	19	6	5	5	2	20	2
4	8	15	7.5	4.3	20	0	20	8	0	7.5	0	20	2
5	2	5	2.5	0	80	0	21	2	10	2.5	6.2	80	2
6	4	0	0	1.5	80	0	22	4	15	0	4.5	80	2
7	6	15	7.5	4.2	80	0	23	6	0	7.5	2.3	80	2
8	8	10	5	1.6	80	0	24	8	5	5	0	80	2
9	2	15	5	5	140	0	25	2	0	5	4.2	140	2
10	4	10	7.5	0	140	0	26	4	5	7.5	7	140	2
11	6	5	0	6.1	140	0	27	6	10	0	0	140	2
12	8	0	2.5	4.5	140	0	28	8	15	2.5	2.3	140	2
13	2	10	7.5	2	200	0	29	2	5	7.5	4.1	200	2
14	4	15	5	0	200	0	30	4	0	5	6.7	200	2
15	6	0	2.5	6.1	200	0	31	6	15	2.5	0	200	2
16	8	5	0	4.1	200	0	32	8	10	0	2	200	2

The handmade reactor consisted of a 850 ml (9.5 Diameter-12 Height (cm)) cylindrical glass reactor, 120 rpm magnetic stirrer, DC power supply (RXN-303D-II, Zhaoxin Electronic Tech. Co.), an aluminum electrode as anode, and four connected graphite electrode as cathode was constructed. The anode made of aluminum sheets (40×100×1(mm)) with 40 cm^2 effective immersed surface area. Each cathode electrode made of graphite bar (10 (diameter)×120 (hight)(mm)) with 3 cm^2 effective immersed surface area. The cubic arrangement of four electrodes were used to increase effective current intensity. The electrodes were placed vertically and dipped in 500 ml synthetic waste solutions. The distance between electrodes fixed at 1cm (Figure 1).

In each run, 500 ml DO25 solution was decanted into the reactor. The empirical parameters were adjusted to the desired value based on design of experiments. In each eight desired $t_{P,}$ 10 ml sample was extracted at the specific position of reactor using sampling pipet. Samples were centrifuged for 3 minute in 2000 rpm and then the DR% was calculated for the decanted solution. The concentration of samples was evaluated by standard spectrophotometric method using calibration curve by using DR5000 spectrophotometer. Because of matrix effects, λ_{max} was extracted experimentally from the zero time sample spectra in each run. Finally, the DR% was calculated for samples using equation 1:

$$DR\% = (1-C/C_0) \times 100 \quad (1)$$

Where C_0 and C are concentration of solution before and after process, respectively.

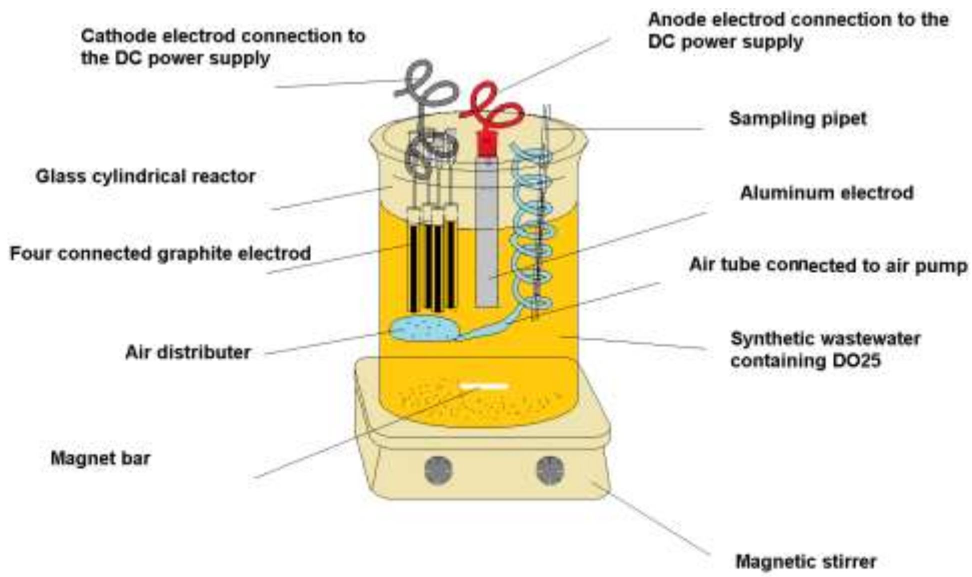

Figure 1: The lab-scale batch experimental setup of proces unit

3. Results and discussions

In whole 32 runs, the DR%'s of samples in different t_P were determined. The obtained DR%'s are presented in the four diagram of figure 2. As can be seen from the diagrams, different operational parameters cause to DR% from less than 1 to up to 98 under experimental conditions at pH_0 4, V 10, C_{Fe} 7.5, C_{H2O2} 0, C_0 140, and F_{air} 0. Then, the combined method can be very effective to degrade DO71 when the operational parameters is fixed in optimum conditions. Based on run 7 results presented in figure 2, the DR% of 90 is achievable in less than 20 minute. It shows that the combined method can degrade the sample dye more rapid than previous presented methods. Also, it is a clear evidence to satisfy the compatibility of methods that were combined.

Some data were missing data that were removed and 230 data remained that were presented in figure 2. The glance of the diagrams can illustrate the influences of operational parameter on DR%. Opposite to the t_P that have obvious positive influences on DR% that is reported frequently, the influences of other six parameters are unclear (figure 1). Then, it make essential to use the statistical tools to clarify the parameters influences and to distinct the effective parameters for modeling and optimization.

Then, multiple linear regression (MLR) and stepwise multiple linear regression (SMLR) were applied to investigate parameters influences. The MLR model was developed for DR% and the statistical details of the model are shown in table 2.

Table 3: The MLR and r-MLR models along with parameters influences statistics

Parameters	MLR				r-MLR			
	coeff.	St. coeff.	t-value	p-value	coeff.	St. coeff.	t-value	p-value
constant	1.36	-	0.29	0.77	-2.40	-	-0.68	0.50
pH_0	-0.90	-0.07	1.74	0.08		-		
V	2.04	0.32	-1.85	0.06	2.04	0.39	9.77	0.00
C_{Fe}	2.79	0.23	8.94	0.00	2.81	0.27	6.70	0.00
C_{H2O2}	0.39	0.01	6.45	0.00		-		
C_0	-0.06	-0.15	-0.31	0.75	-0.06	-0.14	-3.54	0.00
F_{Air}	-8.84	-0.28	-4.12	0.00	-8.47	-0.29	-7.26	0.00
t_P	0.39	0.55	-7.64	0.00	0.39	0.51	12.76	0.00

model goodness parameters	MLR				r-MLR			
	F value	R^2	p-value	RMSE	F value	R^2	p-value	RMSE
	62.8	57.1	0.00	18	73.7	0.59	0.00	19

Based on coefficients presented in table 2, among the parameters, t_P, V, C_{H2O2}, and C_{Fe} have positive influences that reported frequently and it is logical, too. The F_{Air}, C_0, and pH have negative influences on DR%. The negative influences of pH and C_0 frequently reported in this kind of studies, when the negative effect of air should be interpret. It is important to see that based on unbiased standardized coefficient presented in table 2, C_{H2O2} and almost pH have negligible effect. However the negligible influences for H_2O_2 and especially for pH is questionable, but it may accrued due to conflict of combined methods and compensation the negative and positive influences. Based on the unbiased parameters, t_p, V, and F_{Air} have more important influences on DR%.

The statistical parameters obtained from analysis of variances (ANOVA) shows that influences of some parameters is meaningless and should be omitted from the model. Then, stepwise multiple linear regressions was used to remove the meaningless variables as an appropriate common statistical tools. The obtained reduced MLR model (r-MLR) using the stepwise algorithm is presented in table 2 along with its statistical details. As presented in table 2, two parameters, pH and C_0 were removed by SMLR algorithm in significant alpha level of 0.05.

Furthermore, table 2 and model goodness parameters indicate that the MLR and r-MLR models do not have a good predictability for DR%. It can rise from the complex mechanism of process. Simple linear method of MLR and SMLR can't model the process and can't distinct the nonlinear influences or interaction of the important parameters such as pH and C_0. The artificial neural network (ANN) is parallel computational procedure consisting of highly interconnected processing elements groups named neurons. Owing to their inherent nature to model and learn 'complexities', ANNs have found wide applications in various areas of wastewater treatment. The facts inspires us to use ANN as more powerful nonlinear modeling approach to get the good predictable model. Also, the ANN was applied to determine the importance of pH and C_0 in nonlinear ANN model. The reduced ANN (r-ANN) model and ANN model based on r-MLR and MLR model parameters was constructed.

Therefore, the seven and five operational parameters applied as inputs of ANN and r-ANN models, respectively, whilst the DR% was considered as dependent variable. Data set was randomly divided into three parts; 60% (157 data) as training set, 20% (53 data) as a validation set, and 20% (52 data) as testing set. The training set was used to adjust the parameters of the models, testing set to calculate its estimation power, and validation set to prevent over-train. Back propagation algorithm has been used as it is very fast and can be employed quite easily.

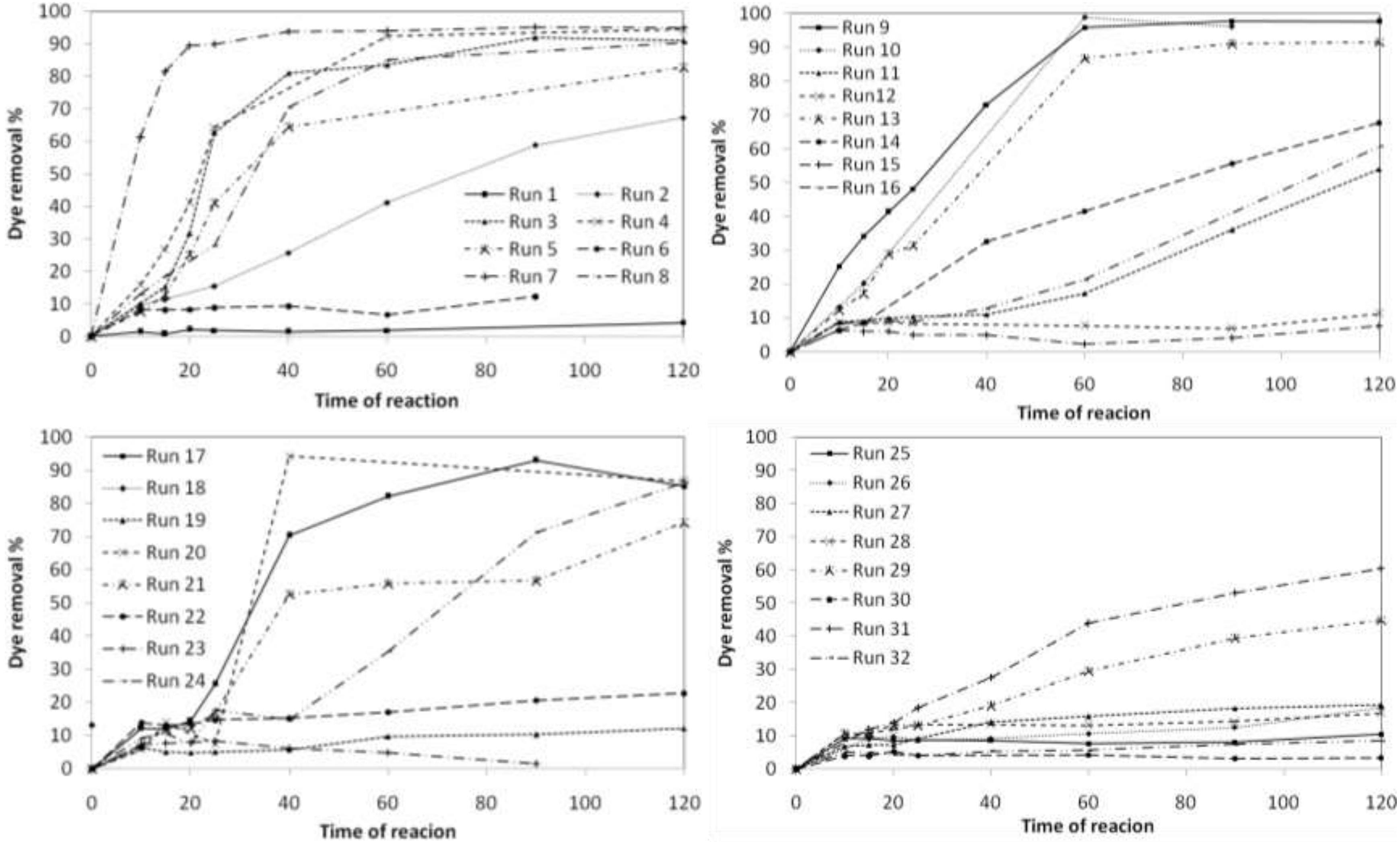

Figure 2: The experimental DR% results of whole 32 runs

The number of hidden layers, neurons of each hidden layer, and learning rate were determined via a trial and error. The best selected net has one hidden layer with 11 neurons and 0.21 learning rate (7:11:1 net) for ANN model. The best selected net has one hidden layer with 8 neurons and 0.17 learning rate (5:8:1 net) for r-ANN model. The 'tansig' transfer function was selected for input and hidden layers and 'purelin' for output in both models. Once the networks trained, the weights and bias of each neuron and layer were saved in the ANN model. Then, they were used to estimate the test set. Finally, the consistency of the ANN models was revealed by tests quantified with predictive Q^2 and R^2 when the reliability or accuracy of the models was revealed by Root-Mean-Square Error (RMSE). The test results of ANN and r-ANN model goodness presented in table 3.

Table 4: Statistical characteristics of ANN model

model	ANN			r-ANN		
Data set	Train set	validation set	Test set	Train set	validation set	Test set
R^2	0.99	0.97	0.96	0.98	0.92	0.91
Q^2	0.99	0.97	0.96	0.98	0.92	0.91
RMSE	2.1	6.2	5.1	3.5	9.8	7.9

The comparison of table 1 and table 2 clearly confirm that ANN models outperformed MLR ones. It confirms the complex non linear nature of the process. Also the meaningful of goodness decline in r-ANN rather than ANN not only confirm the importance of pH and Cdye but also approve the non linear complex nature of the process, too. As a golden goal of each modeling study, the optimization of process was considered in this study too. The optimized parameters can be used to identify the parameters influences quality as well as quality.

Then, genetic algorithm (GA) was used to optimize the experimental parameters using the best obtained models. GA is adaptive heuristic search algorithms based on the evolutionary ideas of natural selection and genetic. GA toolbox in MATLAB was used for generating the optimal solution for DR% using 'ga' function. Four MATLAB functions using four MLR, r-MLR, ANN and r-ANN models were written for creating fitness functions for the optimization problem. The DR% component to be maximized was negated in the vector valued fitness function since 'GA minimizes all the objectives. The result of GA solution is tabulated in table 4.

Table 5: GA optimization result.

model	Parameters							
	pH_0	V (volt)	D_{Fe} (ppm)	D_H(ppm)	C_0 (ppm)	A	t	DR%
ANN	6.1	0.3	3.1	7.2	22	0.5	8	98.9
r-ANN	-	11	6.7	-	130	2.0	20	96.5
MLR	2.1	15	7.5	7.4	21	0.0	10	56.0
r-MLR	-	15	7.4	-	20	0.0	16	53.3

As can be seen from table 5, the optimization process approved that ANN and r-ANN models are more compatible with experimental results when they can predict almost 99% as an optimum value of DR%. Also, the obtained optimum values of experimental parameters are different for these four models that should be discussed. ANN and r-ANN model as a more powerful accurate model should have more logical values.

In this study, the effect of initial pH was investigated from 2 to 8. The optimum values for pH was 6.1 in ANN model and 2.1 in MLR. Both 2.1 and 6.1 are acidic condition that is frequently reported as a more desirable condition for these kind of process but there are meaningful differences between 2.1 and 6.1 that can be judged by the ANN and MLR model quality. However the low pH (pH=2.1) cause to more hydrogen electro-generation or Fenton reagent efficiency, but pH equal to 6 is in the efficient range of pH for electrocoagulation using Aluminum. Then, it may be logical that combination of several methods have several optimum values for one parameter like pH. The optimum values for voltage are different from 0.3 to 15. However the more voltage make the electrodic process easy, but it can cause to inversion of efficiency in electrocoagulation process by production of coagulant more than efficient amount.

About the Fenton reagents, Fe^{2+} and H_2O_2, maximum available concentration in their investigated ranges (7.5 ppm) were selected as the optimum values by whole four optimization process. It rise from the importance and strength of Fenton and electro Fenton rather than other methods. Also, it may be raised from bad range selection for these parameters.

Table 5 shows that more C_0 and less A make essential to apply more t. It is frequently reported that more C_0 need more time of process. Also, the less aeration make weak the flotation and electro-Fenton.

4. Conclusion

The present study clearly show the power of compatible combined method of EF/EC/EI as a fast applicable method for degradation of DO25. The study also confirm the deep influences of several operational parameters on the efficiency of method. The applied design of experiment, modeling and optimization process was successful to get the determined statistical goals. The artificial intelligent systems such as ANN and GA that were applied in the study, present an acceptable performance in modeling and optimization of the complex combined method. The statistical tools were applied to distinct the effective operational parameters and also to determine the quantity of the influences.

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