Evaluation of Textile Wastewater Treatment Using Combined Methods: Factor Optimization *via* Split Plot RSM

Karimi, Asadollah*+
Department of Chemical Engineering, Faculty of Engineering, University of Maragheh, Maragheh, I.R. IRAN

Mohamadi, Hatam; Fathifar, Esmaeil
Environmental Engineering Research Center, Faculty of Chemical Engineering,
Sahand University of Technology, Tabriz, I.R. IRAN

ABSTRACT: *The increase in the consumption of textile products as well as the use of dye compounds has increased the pollution of the effluent in these industries. Discharge of this wastewater without proper treatment can cause groundwater pollution, poisoning, and serious health effects. Dyed pollutants contain benzene rings and are more resistant to conventional biological treatment such as activated sludge. In this study, two combined processes in series were applied for the treatment of towel dyeing wastewater. An experimental design was used to optimize the process. In a batch reactor, the Anodic Oxidation (AO) process and the Electro-Fenton (EF) were compared using four anodes and cathodes. The performance of AO method in dye removal and COD reduction was better than EF method. A good agreement is attained between the predicted value using experimental design and actual results. The correlation coefficient of dye removal, energy consumption, and COD was achieved 0.966, 0.997, and 0.900, respectively. The results showed that under optimum operating conditions of AO process (voltage=6.5 V, t= 6 min, and pH =9.5) decreased 97% of dye index and 61% of COD amount. This condition was obtained by consuming 6.7 kWh of energy per cubic meter of wastewater (0.07 \$/m^3). The output of the optimal AO entered the Reverse Osmosis (RO) system, in the last step. TDS of effluent was reduced 98% in the membrane and also the COD decreased from 980 to 13 ppm under 6 bar pressure.*

KEYWORDS: *Textile wastewater; Advanced oxidation; Dye removal; Reverse osmosis.*

INTRODUCTION

The textile industry is one of the largest water-consuming industries, and the amount of wastewater produced by the industry is far higher than in other industries. With the developing textile and dyeing industries, the amount of water and other chemicals in this industry has increased. So that the water consumption is between 25 to 250 cubic meters per ton of product. These industries produce large quantities of dyed wastewater which is

* *To whom correspondence should be addressed.*
\+ *E-mail: a.karimi@maragheh.ac.ir*
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usually toxic, resistant to biodegradation, and environmentally sustainable. Due to a complex ring structure, conventional biological methods for the removal of most synthetic dyes are not effective [1]. Most of the textile wastewater pollutants are related to washing and dyeing processes. It contains large amounts of salt and alkalis. Due to the variety of production methods and raw materials in the industry, it produces very different contaminants. According to Environmental Protection Agency (EPA) effluent standards of wastewater must be less than 700 µs/cm, 30 mg/L, 120 mg/L, and 5 mg/L for Electrical Conductivity, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Total Dissolved Solids (TDS) respectively (for agricultural use) [2-3].

Most dyes components contain one or more benzene rings that can cause irreparable damage to the environment if they enter the environment without treatment [2]. Removing dye components from textile wastewater streams is possible by using physical (including sedimentation and filtration), chemical, biological, or combined methods [4-5]. Due to the high level of COD and benzene rings (such as phenol) in the wastewater, the biological processes cannot be applied directly [6-8]. The biological method is used to remove biodegradable organic components from wastewater. Advanced treatment methods for the removal of compounds such as nitrogen and phosphorus are also proposed [9]. Various advanced treatment methods have advantages and disadvantages and these methods alone cannot be used. So, it is advisable to use combined methods [2]. Advanced oxidation processes (AOP) methods can be considered the most common traditional methods [10]. The hydroxyl radicals (Produced in the AOP process) after fluorine have been identified as the second strongest oxidant [11]. The AOP methods include H_2O_2, Ultra Violet (UV), ozone-based processes, titanium oxide-based processes, and Fenton-based methods [12]. In the last two decades, the interest in advanced electrochemical oxidation (EAOPs) has developed in the AOP process [13-17]. The simplest and most convenient method among EAOP processes is the Anodic Oxidation (AO) process [18-19]. If H_2O_2 is generated electrochemically and also Fe^{2+} is present in the solution, it will be known as the Electro-Fenton (EF) process [13]. In the Fenton method, the $[Fe^{2+}]/[H_2O_2]$ ratio should be optimized to enhance the efficiency of the process [20]. Oxidants in the Fenton reaction may also be catalytically active metals such as chromium, cerium, copper, cobalt, manganese, and ruthenium [21]. Due to the high cost, high consumption of iron, and the acidic medium is not widely used in industry [22]. The efficiency of all EAOP methods depends on different operating conditions such as the initial concentration of contaminants, the electrolyte potential of the electrode, temperature and pH [23] Because of the high operating costs of EAOPs, they recommend using biological processes and chemical and electrical coagulation and membrane for economic optimization [23]. In the research, the wastewater of the textile industry containing azo dye was treated by the electro-Fenton method. The results showed that under optimum conditions after 360 minutes, reduced 95% of COD and consumed 13.1 kW [24]. In a laboratory scale (batch system) four advanced oxidation methods including UV/O_3, UV/H_2O_2, H_2O_2/O_3, and $O_3/H_2O_2/UV$ were accomplished to remove the dyeing of textile wastewater. The results showed that the percentage of dye removal was the highest by O_3/H_2O_2 /UV method and was the lowest in UV/H_2O_2 with 89.2% and 40.7%, respectively [25]. In 2014, a study was carried out on the dyeing of acidic and alkaline dyes. They investigated the dyeing removal individually and in combination *via* coagulation, flocculation, and nano-filtration methods. Through the coagulation and flocculation process, 90% removal at the optimum condition was achieved. The type of nano-filter was Hollow Fiber (HF) and able to remove the dye-based completely. Also, the combination of coagulation and flocculation methods with nano-filtration improved the performance of treatment [26]. EO and EF methods were used for de-colorization of three different dye types. At pH=3 and 0.5 mM Fe (Fe^{2+}) the results presented the superiority of the EF method over the EO method [27]. The reverse osmosis membrane clogging at the semi-industrial scale has been studied and analyzed. The effluent to the membrane has a COD of about 200 mg/L [28]. Using the electro-Fenton method, dye wastewater studies on dye removal of Methylene Blue (MB) were carried out and the effect of different operating conditions was evaluated. Under optimum conditions, the removal of dye and COD were 92% and 70%, respectively [29]. The membrane technology has been considered an alternative to conventional dye removal processes [3]. The most important problem in membrane systems is membrane clogging. There are various methods to solve this problem,

Table 1: Some of the specification of the case study wastewater.

Parameter	Value
EC (µs/cm)	13000
BOD (mg/L)	987
COD (mg/L)	2503
Total suspended solids (TSS) (mg/L)	300
Volatile Suspended Solid (VSS) (mg/L)	200
TDS (mg/L)	7000
pH	9-10
(Total Nitrogen) TN (mg/L)	34

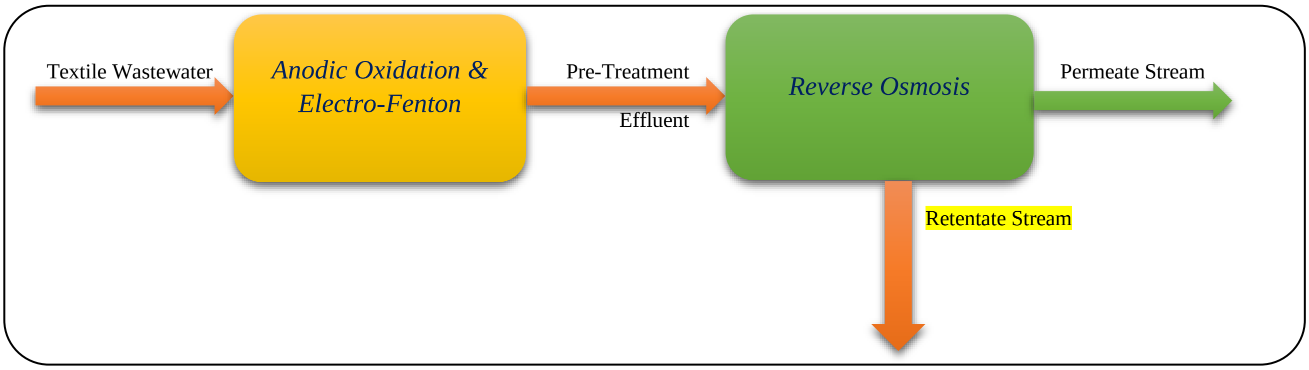


Fig. 1: The general scheme of the treatment steps.

mainly based on the pre-treatment of the membrane. The treatment by means of electrical decomposition and advanced oxidation has received much attention in recent years. Considering the above-mentioned and the water crisis it is necessary to make proper use of water resources. In this study, two different treatment methods were accomplished to eliminate the dye and also, reduce the COD and salts components of the textile industry wastewater in a laboratory pilot. In most past studies, a method has been applied to reduce the pollution of textile wastewater. As previous work consequence indicates, a combined method should be used to eliminate or reduce the pollutant of this wastewater. First, use an anodic oxidation pre-treatment and electro-Fenton method to improve the quality of the reverse osmosis system, and then the treated wastewater is introduced into the high-pressure reverse osmosis. Also, the Experiment Design (Split Spot Method) was applied to determine the statistical importance of each parameter. The quadratic polynomial response model for confirming the actual experiments was employed.

EXPERIMENTAL SECTION

Characteristics of the Wastewater

The case study wastewater contains a lot of salt components and on the other hand, the wastewater stream has a high pH (9 to 9.5). Therefore electrochemical-based methods could be a reasonable suggestion. The EO (AO & EF) and RO methods were employed for treating wastewater samples that providing by a towel textile manufacturer in Tabriz. Fig. 1 is indicated the overall scheme of the treatment steps. The specification of primary wastewater was shown in Table 1.

Experimental procedure

The batch reactor was used with a liquid volume of 600 mL. The anodic oxidation reactor is a stirred tank reactor (cylindrical glass column) with a magnetic agitator that is demonstrated in Fig. 2. The reactor was operated at ambient temperature, pressure, and constant stirring. Four carbon electrodes were applied as an anode and cathode.

The pH was measured using a SUNTEXT analyzer. HANON UV-Vis Spectrophotometer was applied for

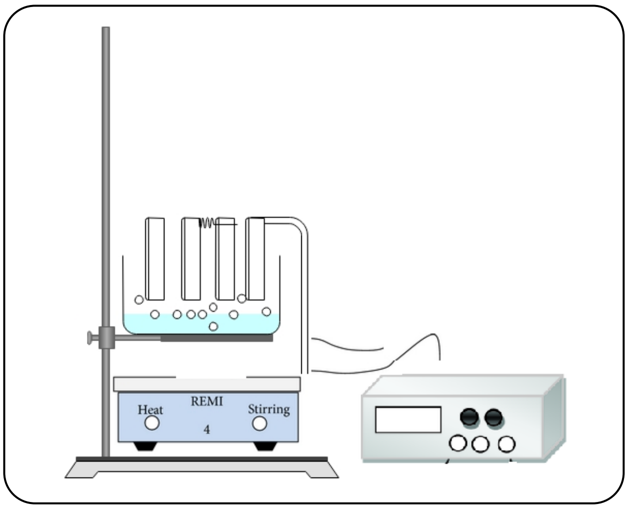


Fig. 2: The Schematic of the batch column reactor systems used.

COD measurement by the dichromate method. For COD analysis $HgSO_4$, Ag_2SO_4, $KHC_6H_4C_2O_4$, and $K_2Cr_2O_7$ were purchased from Merck Chemicals. All solutions were prepared using deionized water. Also, RO membrane (Polyamide) system, model TW30 - 1812- 50 was employed for post-treatment. AUTOLAB and LABTECH were applied as potentiostat devices and power supplies respectively. To determine the range of changes in the operating voltage in the system, a cyclic voltammetry experiment was accomplished by the potentiostat device to distinguish the minimum voltage at which oxidation and reduction reactions occur. During this experiment, the lowest and the highest voltage that can be applied to the system obtained 3.5 and 11.5 V respectively (considering electrode corrosion).

Experimental design

Via experiment design could express the effectiveness of each input factor (X_1, X_2, X_3, ...) for output factor (Y_1, Y_2, Y_3, ...) in the form of an equation $Y_i = F(X_i)$, and also one of the most reliable statistical methods is to improve the objective function. The design of the experiment calculates the influence of each of the chosen factors on the responses and predicts a mathematical model. The reduction of the experiment time, the reduction of experiment costs, determining important variables, and determining optimal conditions are some of the purposes of experiment design. The experiment design methods can be factorial, Taguchi, Response Surface Methodology (RSM), etc., which each have their specific advantages, disadvantages, and also their own applications. RSM is a collection of beneficial statistical and mathematical methods for modeling and analyzing problems in which the desired response is affected by different variables and the ultimate purpose is to optimize the response. RSM has significant applications in process design, optimization, and improvement of experiment designs and also, anticipates the achieved response, in points within the experimental domain. Response surface methodology approximates the experimental variability (pure error). This method is more practical than other experiment design methods because it involves the interactions of variables. Therefore, the first step in RSM is to distinguish a fundamental relationship with the appropriate approximation between dependent and independent variables. Indeed, RSM method includes much more than model fitting and a survey of actual experiments. This method is classified as a two-section Design of Experiments for First-Order Models and Design of Experiments for Second-Order Models. Also, the Design of Experiments for Second-Order Models is divided into Central composite designs, Uniform shell (Doehlert) designs, Box–Behnken designs, and Hybrid and related designs [30]. In recent years, the use of the RSM method has expanded and also has been applied to analyze, optimize, and evaluate the interaction of independent factors in chemical, biochemical, and environmental processes.

As mentioned above, one of the specifications of RSM is to predict the obtained response. Although the first-order models can anticipate the response, the quadratic polynomial models are the more reliable procedures to predict responses than other models. A split-plot design was applied to obtain a suitable mathematical model for the prediction of the behavior of the oxidation process and optimal treatment conditions. When some factors (independent variables) are difficult or impossible to change, random experiment design becomes impossible completely. As a result, Split-Plot makes it possible to study a combination of easy-to-change and difficult (or impossible) factors. The pH, voltage, air flow, and the presence or absence of iron were selected as the independent variables. Since the electro - Fenton process in an acidic medium has better results, the pH range varies from 2 to 9.5. To determine the range of voltage changes in the system, the potentiostat device was used for measuring the lowest voltage. For determining the range of the independent variables, preliminary experiments were conducted. Table 2 exhibited the independent variables of the experimental design.

Table 2: Experimental ranges and levels of the independent test variables.

Independent Variables	Value		
pH	X_1	2-9.5	
Voltage (V)	X_2	3.5-11.5	
Air flow (Q)	X_3	Low-High	1→Low 2→ High
Iron	X_4	0-1	0 Related to AO 1 Related to EF

Table 3: The results of Pre-treatment via anodic oxidation and electro-Fenton process.

RUNNING	VALUE						
	Level value of each variable in the experimental run						
	pH	Voltage	Air Flow	Iron	Dye Removal (%)	Energy Consumption (KWh)	COD (mg/L)
1	5.4	6.9	1	1	98.4	9.2	672
2	5.4	11.5	0	1	87	32.9	948
3	5.4	3.5	0	0	43	0.86	2013
4	5.4	11.5	2	0	97.9	30.6	687
5	7.8	11.5	1	0	97.8	32.9	840
6	7.8	7.1	2	1	89	10.8	902
7	7.8	3.5	0	1	35	1.2	2201
8	7.8	6.7	1	0	97.3	8.2	695
9	9.5	9.3	0	0	97.5	19.9	693
10	9.5	11.5	2	1	99	32.9	632
11	9.5	3.5	2	0	53	1.0	1880
12	9.5	3.5	1	1	21	0.9	2310
13	5.04	3.5	2	1	35	1.2	2198
14	5.04	7.21	1	0	97	9.8	704
15	5.04	11.5	1	1	92.5	29.9	813
16	5.04	7.7	0	1	97.1	11.8	701
17	2	11.5	0	0	96.4	37.5	724
18	2	3.5	0	1	81	1.4	1090
19	2	7.4	1	0	98.7	11.3	666
20	2	10.9	2	1	79	31.3	890
21	2	3.9	2	0	74	1.0	1258

RESULT AND DISCUSSION

Comparison of actual values with experimental design values

The twenty-one experiments with different operating conditions were performed on the textile wastewater stream. Table 4 demonstrated the results of Pre-treatment *via* anodic oxidation and electro-Fenton methods. As shown in Table 3, the removal amount of dye was observed 98.7% by the anodic oxidation method and 99 % *via* the electro-Fenton method. Also, the percent of COD removal varies from 2310 to 623 in the anodic oxidation method. To be obvious, the maximum point of treatment is the tenth run.

To evaluate the accuracy of the experiments, six experiments (2, 6, 11, 16, 18, and 21) were repeated randomly. The results show very little difference with the experiments which can be due to device or human error. A comparison of the obtained results through the experiment with the predicted values by the software are shown in Fig. 3 to 5. Fig. 3 to 5 demonstrates the distribution of model errors. If the model error follows the normal distribution, points

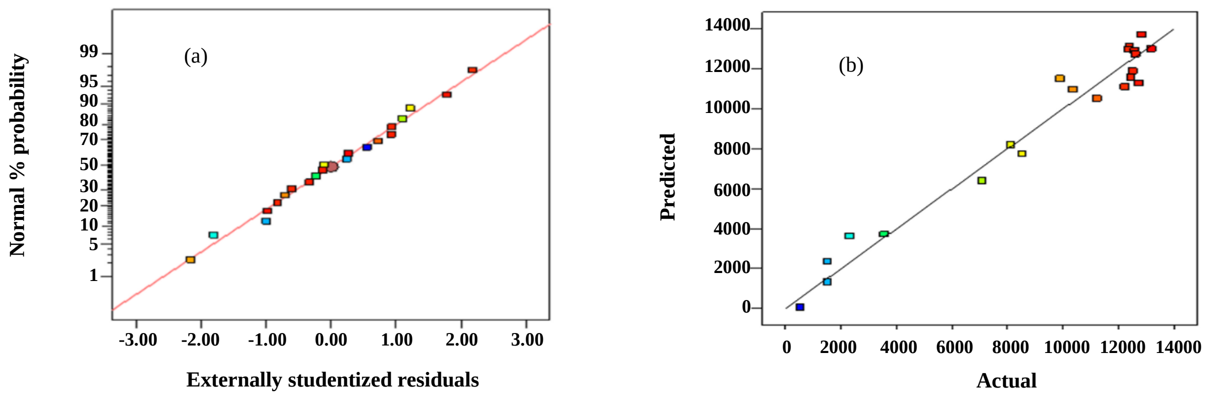


Fig. 3: (a) comparison of actual values from the experiment (b) experimental design prediction for dye removal.

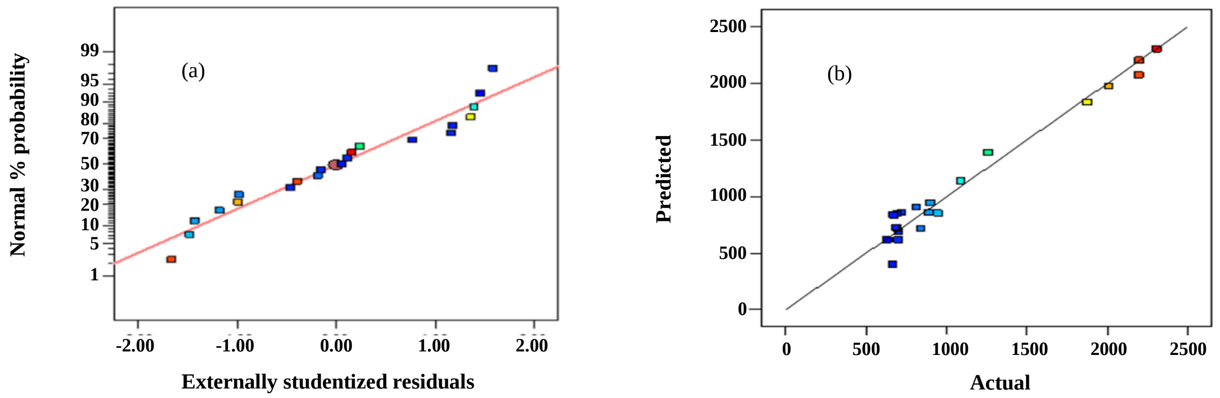


Fig. 4: (a) Comparison of actual values from the experiment (b) and experimental design prediction for the amount of COD.

are distributed around the reference line. Otherwise, the distribution of errors is not regular, which can be assumed as an inefficiency indicator. The results show a good agreement between predicted values and actual results. The correlation coefficient between the actual and predicted values for dye removal is appropriate (R^2=0.966). Therefore, the model can predict the process efficiency effectively [31].

Fig. 4 presented a comparison of the obtained results with the prediction of values. As can be seen from Fig. 4, the model error follows the suitable distribution, the results have been distributed around the reference line. The COD of the correlation coefficient is acceptable (R^2=0.900).

The correlation coefficient of energy consumption based on Fig. 5 is close to one (R^2=0.997). This model has the highest efficiency in the prediction of values.

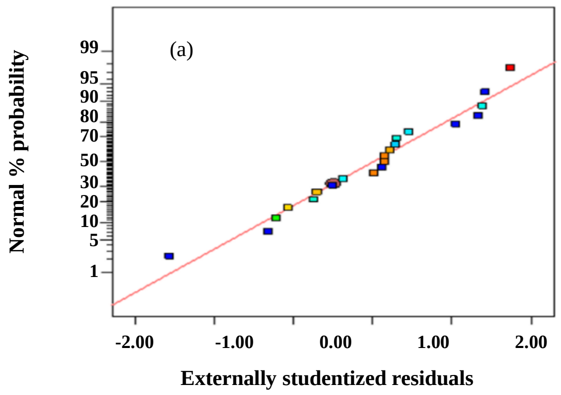
The quadratic polynomial models

The use of the experimental design is effective when the relationship between the system variables and the response is not specified. The relationship between voltage, airflow, pH, and type of oxidation process on the amount of dye removal, COD level, and energy consumption is unclear. Therefore, due to the lack of developed equations, the experimental design should be applied. The quadratic polynomial models were obtained to predict each response via implementing multivariate regression analysis. The quadratic polynomial models are widely used in RSM due to their numerous advantages. In order to achieve the most suitable polynomial model for the data, several features must be present simultaneously. Therefore, a suitable mathematical model should have the following characteristics:

1) The correlation coefficient (R) of the model is close to 100%.

2) The p-value is related to the main significant factors (less than 0.005).

3) Explain the answer well with the model (the residual must be less).



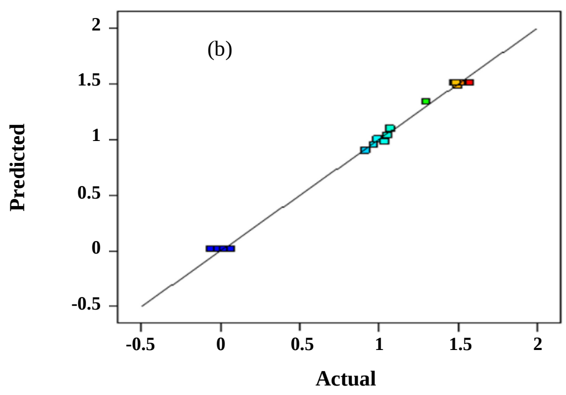


Fig. 5: (a) Comparison of actual values from the experiment (b) and experimental design prediction for energy consumption.

4) There are no discarded data.

5) The distribution of residuals is normal.

The general form of the quadratic polynomial response equation that includes the interaction terms (Eq. (1)) for each of the anodic or electro-Fenton oxidation processes is as follows:

$$Y^{\lambda} = a + b*pH + c*V + d*Q + e*pH*V + f*pH*Q + g*Q*V + h*pH^2 + i*V^2 + j*Q^2 \quad (1)$$

Where Y and λ indicate the response variable and model correction factor (power factor) respectively. Based on the Box-Cox diagram, these coefficients are calculated for each model. The predicted values of dye removal have been estimated *via* the quadratic polynomial model. Eq. (2) and (3) illustrated the response variable for AO and EF processes respectively.

$$Y^{2.06} = -3635.72 - 1618.58pH + 4891.58V - 1269.45Q + 142.20pH*V + 382.43pH*Q - 314.09\ V^2 \quad (2)$$

$$Y^{2.06} = -3282.74 - 1618.58pH + 4891.03V - 2923.45Q + 142.21pH*V + 382.43pH*Q\ 314.09V^2 \quad (3)$$

It can be observed that these equations have fewer than terms of general form. According to variance analysis (ANOVA), pH value was not significant in this model (P-value = 0.08). But the interaction of pH is significant, it is better not to omit the equation. Voltage, kind of oxidation, and air flow variables were also significant. The prediction of COD equation has been provided in Eq. (4). According to the Box-cox diagram, the best value for λ is -0.5.

$$Y^{-0.5} = 0.008523 - 0.001558pH + 0.007725V + 0.00017pH*V - 0.000483V^2 \quad (4)$$

Due to variance analysis (ANOVA), the pH parameter and type of oxidation (AO & EF) are not significant. The voltage terms and the second voltage power were also significant (P-value < 0.05). According to a study on energy consumption, this answer follows a simpler model than the previous two responses (Eq. (5)). In the final model, only the voltage dependence is observed. It is obvious that the amount of voltage is a prominent factor in calculating energy consumption.

$$Y^{0.2} = -1.38844 + 0.467559V - 0.018716V^2 \quad (5)$$

Impact of independent variables

To better evaluate the results, the effect of the independent variables should be surveyed. The energy consumption based on voltage is ascending. Also, the energy consumption relative to voltage is observed identical to both AO and EF processes. Therefore, choosing the optimal point of energy consumption requires the choice of the lowest voltage possible so that the highest percentage of dye removal and COD decreasing is achieved. Voltage has a positive effect on dye removal and the amount of COD [32]. If the voltage increases, the effluent COD rate will reduce due to the formation of OCl^- in the wastewater media possibly. In high treatment times, the difference between high voltage conversion is low (7%), so choosing the highest voltage is not suitable for treatment [33]. The many uncertainties exist about the effect of pH on the anodic oxidation process [22].

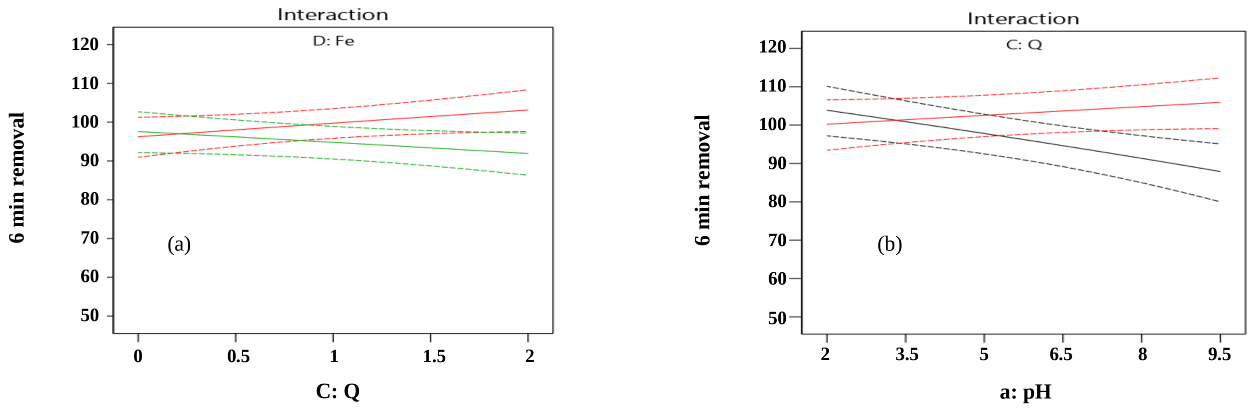


Fig. 6: Interaction of parameters a) airflow and Iron, b) airflow and pH on in dye removal.

The Study of pH effect on AO and AO-H_2O_2 shows some inconsistencies. Some consequence indicates that pH = 3 (approximately) is better than higher pH. In this study, based on the prediction model, the percentage of dye removal decreases with an increase in pH amount. The enhancement in the aeration rate increases the percentage of dye removal because leads to an increase in the generation of hydroxyl radicals at the electrode surface in the AO process [34]. The effect of aeration on the EF process is almost neutralized under medium pH and mild voltage conditions. This phenomenon may be related to the release of iron (some color) into the environment during this reaction. The interaction effects show that there are interfering effects between airflow and iron existence, as well as airflow and pH. The interaction effects are illustrated in Fig. 6.

Optimization of the pre-treatment process

Process economics is one of the most important engineering issues and also current costs are one of the prominent costs in environmental systems. The optimization of the whole process in wastewater treatment can help engineers to improve Process economics [35-36]. So, an optimal process must achieve the highest dye removal and the minimum COD value with the lowest energy consumption. Due to the obtained consequences and the prediction model, the AO process is better than the EF process. According to the above mentioned, optimization of dye removal responses, COD value, and energy consumption were performed. The optimum point was obtained at pH = 9.5, the voltage of 6.2 v, airflow at level 2 (maximum aeration level) with 97% dye removal, 6.7 KWh energy consumption, and 61% COD removal. The experiment was repeated 3 times for optimal conditions. If it considers the industrial electricity tariff this year, the cost of electricity consumed by wastewater will be 0.07 $\$/m^3$ in Iran [37].

Post-treatment via RO

By implementing the optimal point of the anodic oxidation process, it was found that the anodic oxidation process provides the desired quality effluent for dye removal. Due to the COD amount and salt content (such as sodium sulfate and sodium chloride), the effluent didn't meet the environmental standard, and could not be discharged into the environment. One of the best systems for the treatment of this effluent could be the reverse osmosis system. Since the salt content of the effluent is very high (TDS = 7000 mg/L), and the fiber filter is not able to separate the salt content from the effluent properly also, the reverse osmosis system (as the post-treatment) is clogged instantly. Two different samples of effluent were passed through the fiber filter, with pre-treatment (AO effluent) and without pre-treatment. In the first case, the inlet stream had 980 mg/L of COD passing through the membrane under 6 bar pressure. The treated effluent was 70 % permeate and 30 % retentate. The COD value was 13 mg/L in the permeate stream. Tables 4 & 5 indicated the specification of the discharge stream from the RO system.

The second sample with dyed wastewater had good consequences for bleaching in the RO system, but the permeate discharge rate relative to the retentate rate was much lower than the previous sample (with pre-treatment), *able 4: The specification of effluent with pre-treatment.*

Parameter	Input	Permeate Stream	Retentate Stream
Volume Ratio	100%	70%	30%
COD (ppm)	980	13	620
TDS (ppm)	7000	63	14000

Table 5: The specification of effluent without pre-treatment.

Parameter	Input	Permeate Stream	Retentate Stream
Volume Ratio	100%	55%	45%
COD (ppm)	2500	34	1150
TDS (ppm)	7000	71	13600

and the fiber filter became more clogged. The causes of the difference in clogging are the existence of various components as well as the presence of larger pigments in the wastewater. As the reverse osmosis membrane is rapidly clogged by the rich salt stream, so the implementation of pre-treatment is necessary. The EF process causes a delay in reverse osmosis fouling. If the membrane was employed alone for textile wastewater treatment, it was clogged for 2 h due to the high salt concentration. By accomplishing pre-treatment, the RO membrane clogging time was delayed. Chemical cleaning was applied to clean the membrane. The clogging in this membrane was generally based on the chemical attachment that was destroyed by the chemical agent.

CONCLUSIONS

In order to the treatment of the industrial textile wastewater via an AO and EF process as pre-treatment and also, the RO system as post-treatment was implemented in a batch reactor, also modeled and optimized with split plot approaches. The pH, Voltage, airflow, and the presence or absence of iron were selected as the main factors. The actual experiments show 43-98.7% by anodic oxidation and 21-99 percent in electro-Fenton for dye removal in the pre-treatment step, and the amount of COD decreases 7.7 to 75 percent by the AO method. A high correlation coefficient reported based on ANOVA table (R^2adj = 0.996) for energy consumption, (R^2adj = 0.932) for dye removal and (R^2adj = 0.860) for COD. Therefore, the quadratic polynomial response model with the actual experiments confirmed an admitted adjustment. The AO process indicates the best value for the pre-treatment of textile wastewater. The pH=9.5, the voltage of 6.2 V, and airflow at level 2 (maximum aeration level) was specified as the optimum point. The COD of effluent was reduced by 61% in the AO process. The RO was applied to decrease the amount of COD and TDS. The high removal efficiency of 98% and 97% were obtained for TDS and COD in the permeate stream respectively. Performing pre-treatment, caused to delay in the clogging of the RO membrane. According to achieved consequences combined method include of AO method and then RO process has been chosen optimal process for treating textile wastewater.

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