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A central composite design for the optimization of the removal of the azo dye, methyl orange, from waste water using the Fenton reaction

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Abstract: In this study the degradation of Methyl Orange, using Fenton reaction was studied and optimized using central composite design as a response surface methodology. The effects of various experimental parameters in this reaction were investigated using the central composite design. 28 experiments, with 4 factors and 5 levels for each factor were designed. These factors (or variables) were: the initial concentration of Fe(II), the initial concentration of H₂O₂, the initial concentration of oxalate and the reaction time. A full-quadratic polynomial equation between the percentage of dye degradation (as the response) and the studied parameters was established. After removing the non-significant variables from the model, response surface method was used to obtain the optimum conditions. The optimum ranges of variables were: 0.25–0.35 mM for the initial concentration of Fe(II), 5–17 mM for the initial concentration of H₂O₂, 4–9 mM for the initial concentration of oxalate, and 50–80 min for the reaction time. In addition, the results of extra experiments showed that these optimized values can be used for real samples and lead to a high value for the response.

Keywords: design of experiments; decolourization; Fenton reaction; Methyl Orange.

INTRODUCTION

There are many branches of industry which use various colorants (synthetic dyes).^{1,2} The wastewater from the manufacture of dyes generally contains residual dyestuffs, dye intermediates as well as unreacted raw materials, such as aromatic amines with alkyl-, halogen-, nitro-, hydroxyl-, sulphonic acid-substituents, and inorganic sodium salts.³ Dyes are organic compounds that can be dangerous

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to the environment. The discharge of coloured waste is highly problematic, firstly due to the toxic nature of some dyes or of their biodegradation products and secondly due to their visual impact because dyes are visible even at low concentrations.⁴ For example, the textile industry is one of the top water polluting Industries in terms of spent volume, as well as colour and chemical composition of the residual wastewater. Residual textile dyes usually transform into toxic aromatic amines which are light resistant and, once in the environment, they exhibit recalcitrant properties.^{5,6} Effluents from the textile industry commonly contain high concentration of organic and inorganic chemicals and are characterized by very high chemical oxygen demand (*COD*) and total organic carbon (*TOC*) values as well as strong colour.⁷ The release of such coloured wastewaters into the environment is a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life.⁸

Azo dyes, constituting the largest class among the synthetic colorants, are considered as widespread environmental pollutants associated with many important industries, such as textile, food colorants, printing and cosmetic manufacture.⁹ The release of azo dyes into the environment is of great concern, due to coloration of natural waters and toxicity, mutagenicity, and carcinogenicity of the dyes and their biotransformation products.¹⁰

Methyl Orange is an azo dye that can be used as an indicator in acid–base titrations. This dye is also used in textile industries and is an orange-coloured anionic dye which has an absorbance maximum at 464 nm. Methyl Orange is a harmful compound that exists in textile waste waters and has various harmful effects on human beings. For example, it may cause eye or skin irritation, or inhalation may cause gastrointestinal irritation with nausea, vomiting, and diarrhoea.^{11,12} To avoid the dangerous accumulation of dyes in the environment, there is a need to develop effective methods for the degradation of such organic pollutants, either to less harmful compounds or, more desirable, to their complete mineralization.¹³

There are many different technological processes, such as adsorption,¹ biodegradation, chemical methods (*e.g.*, chlorination and ozonation), electrocoagulation, electrochemical reduction and oxidation, indirect electro-oxidation with strong oxidants and photocatalytic degradation, which can be used for the treatment of waste waters, including those containing synthetic dyes.^{14,15}

In recent years, oxidation processes (OPs) have attracted attentions for the destruction of dyes. Fenton oxidation, in which hydroxyl radicals are generated from Fenton reagents, is one of the OPs methods.¹ The Fenton reaction is already in use for industrial wastewater purification processes. It is well-known that, in theory, the most important characteristic of the Fenton processes is the formation of OH radicals, which are highly oxidative, non-selective, and able to decompose many organic compounds.^{7,16} It is also well-accepted that the advantages of Fen-

ton processes are the complete mineralization of organic compounds at ambient temperature and the easy separation of the heterogeneous catalysts from the treated wastewater. The Fenton reaction has many other advantages in the degradation of pollutants, for example its reagents are environmentally safe, cheap and easy to obtain and use.

The mechanisms of Fenton reactions are available in the literatures.^{17,18} When using Fenton reactions, several parameters, such as the concentration of iron salt and H_2O_2 have an important effect on the percentage removal of a dye and therefore should be optimized. In addition, in the present study, the salt sodium oxalate was also used to catalyze the removal reaction.

Optimizing refers to improving the performance of a system, a process, or a product in order to obtain the maximum benefit from it. The term optimization has been commonly used in chemistry as a means of discovering conditions at which a procedure produces the best possible response.¹⁹ The response surface methodology (RSM) is a statistical method that is useful for the optimization of chemical reactions and/or industrial processes and is widely used for experimental design. Whenever multiple system variables may influence the outputs; RSM can be utilized to assess the relationship between the dependent (response) and independent variables, as well as to optimize the relevant processes.^{20,21} This methodology was already applied to study and optimize advanced oxidation processes.^{22,23} The response surface methodology was used to assemble a model in order to describe the way in which the variables are related and the way in which they influence the response.

In this research, finding optimal conditions for the effective factors on degradation of Methyl Orange by a Fenton reaction using an experimental design method (Central Composite Design, CCD) was investigated.

EXPERIMENTAL

Instruments

The solutions were stirred on a MTOPO magnetic stirrer model MS3300 and the absorbance of the solutions were measured using a PG-mode T80 UV-Vis double-beam spectrophotometer (Japan) utilizing a 1-cm quartz cell. The adjustment of the pH of the solutions was controlled by a pH-meter BEHINEH (UK).

Reagents

Methyl Orange ($M_w = 269.31 \text{ g mol}^{-1}$), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ($M_w = 278 \text{ g mol}^{-1}$), H_2O_2 ($a = 30 \text{ \% v/v}$, $d = 1.11 \text{ kg m}^{-3}$) and $\text{Na}_2\text{C}_2\text{O}_4$ ($M_w = 134 \text{ g mol}^{-1}$) all of analytical grade (Merck) were used and all the solution were prepared with freshly distilled water.

The solution of Fe^{2+} was prepared several times during a day and was used immediately to prevent the exchange of Fe^{2+} to Fe^{3+} . To adjust the final pH of the solutions, solutions of H_2SO_4 (0.010 M) and NaOH (0.010 M) were prepared and used.

Solutions

Each experiment included a solution of 10 ml Methyl Orange (2.5×10^{-2} mM) plus calculated amounts of H_2O_2 (30 % v/v), Fe(II) and oxalate. These amounts were extracted from the table of DOE. The pH of the solutions were adjusted in 3.5 using H_2SO_4 (0.010 M) and NaOH (0.010 M), because the appropriate pH for the Fenton reaction is in the range of 3–5. These reagents were mixed in a 50 ml flask and the flasks were filled to the mark with distilled water. In addition, blanks were prepared in the same manner as the real samples, but without H_2O_2 and oxalate ions. These blanks were also stirred with a magnetic stirrer during the reaction of the corresponding real samples.

After the predetermined time of reaction, the absorbances of these two solutions were measured on a UV–Vis spectrophotometer.

Statistical software

Essential Regression and Experimental Design for Chemists and Engineers (EREGRESS), as an MS Excel Add-In software, was used to design the experiments and to model and analyze the results.

Design of experiments

By using central composite design (CCD) method, 28 experiments (including 4 repetitions at the central point) were designed.

The factors (variables) were: initial concentration of Fe(II) ($[\text{Fe(II)}]_0$), initial concentration of H_2O_2 ($[\text{H}_2\text{O}_2]_0$), initial concentration of oxalate ($[\text{Oxalate}]_0$) and the reaction time. Although the initial concentration of Methyl Orange might be important, this factor was kept constant at a value of 5×10^{-3} mM. This value for the dye concentration was selected from calibration curve of Methyl Orange (the middle point of the linear range in spectrophotometric determination).

For each factor, 5 levels were defined. These values were designated by the codes: –2, –1, 0, +1 and +2 and are given in Table I.^{21,24}

TABLE I. The variables, their codes and the real experimental values used in the central composite design

Variable	Name	Coded levels				
		–2	–1	0	+1	+2
F_1	$[\text{Fe}^{2+}]_0 / \text{mM}$	0	0.1	0.2	0.3	0.4
F_2	$[\text{H}_2\text{O}_2]_0 / \text{mM}$	0	4.85	9.7	14.55	19.40
F_3	$[\text{Oxalate}]_0 / \text{mM}$	0	5	10	15	20
F_4	Time, min	5	35	65	95	125

RESULTS AND DISCUSSION

A spectrum of a 5×10^{-3} mM solution of Methyl Orange showed a maximum absorbance in the visible region at 464 nm. This wavelength was used to construct a calibration curve of absorbance vs. concentration of Methyl Orange to find the linear range of Methyl Orange absorbance. The obtained calibration curve is shown in Fig. 1. A concentration in middle point of this curve was selected and used for the preparing the dye solution in all experiments.

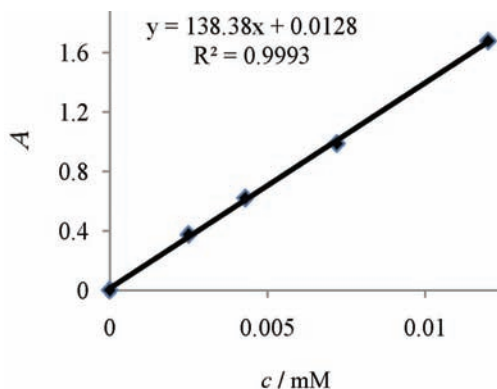


Fig. 1. The calibration curve for Methyl Orange (464 nm).

Analysis of data

After performing the experiments, the percentage of dye degradation for each experiment was calculated from Eq. (1), which was spotted as the response.

$$\text{Degradation} = 100 \left[1 - \left(\frac{\text{sample absorbance}}{\text{blank absorbance}} \right) \right] \tag{1}$$

The values of the blank absorbance, sample absorbance, the difference between the absorbance of blank and the absorbance of sample and the percentage of degradation for each experiment are given in Table II.

TABLE II. The coded values designed by the CCD and the responses

Run No.	[Fe ²⁺] ₀ mM	[H ₂ O ₂] ₀ mM	[Oxalate] ₀ mM	Time min	A _{blank}	A _{sample}	ΔA	Degradation %
1	0	-2	0	0	0.13	0.06	0.07	53.85
2	2	0	0	0	0.193	0.05	0.143	74.09
3	0	0	-2	0	0.162	0.075	0.087	53.7
4	1	-1	1	-1	0.122	0.007	0.115	94.26
5	0	0	0	-2	0.142	0.062	0.08	56.34
6	1	-1	-1	1	0.12	0.045	0.075	62.50
7	1	1	-1	-1	0.194	0.038	0.156	80.41
8	-1	1	1	-1	0.124	0.077	0.047	37.90
9	-1	-1	1	-1	0.092	0.05	0.042	45.65
10	-1	1	1	1	0.133	0.013	0.12	90.23
11	0	0	0	0	0.101	0.007	0.094	93.07
12	0	0	0	0	0.118	0.016	0.102	86.44
13	0	0	0	0	0.128	0.009	0.119	92.97
14	-1	1	-1	1	0.154	0.045	0.109	70.78
15	1	1	-1	1	0.133	0.026	0.107	80.45
16	0	0	0	0	0.115	0.017	0.098	85.22
17	1	1	1	1	0.205	0.002	0.203	99.02
18	-2	0	0	0	0.116	0.105	0.011	9.48
19	0	0	2	0	0.137	0.019	0.118	86.13

TABLE II. Continued

Run No.	[Fe ²⁺] ₀ mM	[H ₂ O ₂] ₀ mM	[Oxalate] ₀ mM	Time min	A _{blank}	A _{sample}	ΔA	Degradation %
20	0	2	0	0	0.145	0.024	0.121	83.45
21	-1	1	-1	-1	0.119	0.066	0.053	44.54
22	1	-1	1	1	0.134	0.011	0.123	91.79
23	0	0	0	2	0.127	0.003	0.124	97.64
24	1	-1	-1	-1	0.142	0.029	0.113	79.58
25	1	1	1	-1	0.104	0.016	0.088	84.62
26	-1	-1	-1	1	0.147	0.052	0.095	64.63
27	-1	-1	1	1	0.121	0.024	0.097	80.17
28	-1	-1	-1	-1	0.145	0.073	0.072	49.66

Among these 28 experiments, 4 experiments were repetition of the central point (run No. 11, 12, 13 and 16). These are the experiments in which all of the factors are in the centric point of their values. The closeness of the responses of these 4 experiments can be a sign of the accuracy of the experiment process. The relation between the collected response and the variables conforms to the following polynomial equation (full quadratic model as Eq. (2)).

$$Y = b_0 + b_1F_1 + b_2F_2 + b_3F_3 + b_4F_4 + b_{11}F_1F_1 + b_{22}F_2F_2 + b_{33}F_3F_3 + b_{44}F_4F_4 + b_{12}F_1F_2 + b_{13}F_1F_3 + b_{14}F_1F_4 + b_{23}F_2F_3 + b_{24}F_2F_4 + b_{34}F_3F_4 \quad (2)$$

where Y is a response variable of the decolourization efficiency; b_i are regression coefficients for linear effects; b_{ik} are regression coefficients for quadratic effects and F_i are coded experimental levels of the variables.

The analysis of variance (ANOVA) and least squares techniques were used to evaluate the statistical significance of the constructed models. The ANOVA consists of determining which factor(s) significantly affect the response, using the Fisher statistical test (F -test). The significance and the magnitude of the estimated coefficients of each variable and all their possible interactions on the response variable(s) were determined. Such coefficients for each variable represents the improvement in the response, that is, to expect as the variable setting is changed from low to high. Effects with a confidence level less than 95 % (effects with a p -value higher than 0.05) were discarded and pooled into the error term and a new analysis of variance was performed for the reduced model. Note that the p -value represents a decreasing index of the reliability of a result. Four replicates of the central points were performed to estimate the experimental error. In order to show the fitness of the model, regression coefficient (R) maybe be used. However, the adjusted regression coefficient (R_{adj}) and the prediction regression coefficient (R_{pred}) are better criteria than the absolute regression coefficient. Since the regression coefficient (R) always decreases when a regression variable is eliminated from the model, in statistical modelling, the R_{adj} , which takes the number of regression variables into account, is usually selected. In addition, R_{pred} ,

which indicates the predictive power of the model, is chosen for the same reason. This parameter was approximated using prediction error sum of squares, or *PRESS*, that is calculated from the residuals. Hence, R , R_{adj} and R_{pred} together are very convenient to obtain a quick impression of the overall fit and the predictive power of a constructed model.²⁴

In order to find the important factors and build a model to optimize the procedure, initially the full quadratic model including all terms in Eq. (2) was employed. Then by the back elimination process, those terms which were not significant enough were eliminated. These terms included the variables or the interactions which had no effect or very low effect on the response. Each term with a p -value greater than 0.05 was removed from the main equation.

The reduced model using significant linear, quadratic and interaction parameters is defined in the form of the polynomial equation:

$$Y = b_0 + b_1[\text{Fe(II)}]_0 + b_{11}[\text{Fe(II)}]_0[\text{Fe(II)}]_0 + b_{22}[\text{H}_2\text{O}_2]_0[\text{H}_2\text{O}_2]_0 + b_{33}[\text{oxalate}]_0[\text{oxalate}]_0 + b_{14}[\text{Fe(II)}]_0\text{Time} + b_{24}[\text{H}_2\text{O}_2]_0\text{Time} + b_{34}[\text{oxalate}]_0\text{Time} \quad (3)$$

Obviously, $[\text{Fe(II)}]_0$, $[\text{H}_2\text{O}_2]_0$, $[\text{Oxalate}]_0$ and the interactions between the time and $[\text{Fe(II)}]_0$, the time and $[\text{H}_2\text{O}_2]_0$, and the time and $[\text{Oxalate}]_0$ are significant and have important effects on the percentage decolourization.

There were not large differences between the R values, which revealed that the experimental data showed a good fit to the quadratic equation and therefore an acceptable model had been achieved. The R values, standard error and prediction error sum of squares (*PRESS*) are presented in Table III.

TABLE III. Some characteristics of the constructed model

$ R $	0.952
R^2	0.906
R^2 adjusted	0.873
R^2 for prediction	0.815
Standard error	7.738
Run No.	28
<i>PRESS</i>	2349.81

Response surfaces and selection of optimized values

After analysis of the data, the response surfaces of the full quadratic model between the response and the variables were depicted. *Via* these surfaces, the relations between the percentage of dye degradation and the effective factors are graphically given. These surfaces are shown in Fig. 2. The optimized ranges for each factor that leads to the best response (the highest percentage of dye degradation) were extracted from these surfaces. The optimized ranges are presented in Table IV.

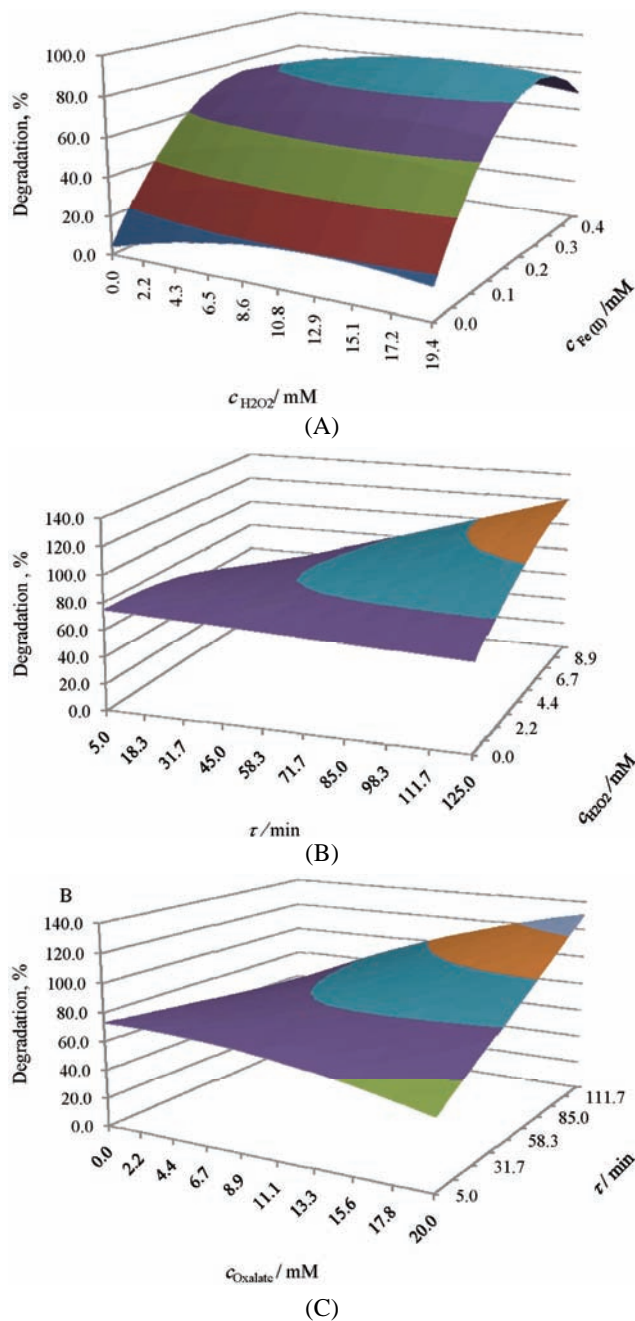


Fig. 2. Response surfaces of the full quadratic model between the percentage dye degradation and the three variables and the interaction between the variables. A – $[\text{H}_2\text{O}_2]$ and $[\text{Fe(II)}]$, B – time and $[\text{H}_2\text{O}_2]$ and C – $[\text{oxalate}]$ and time.

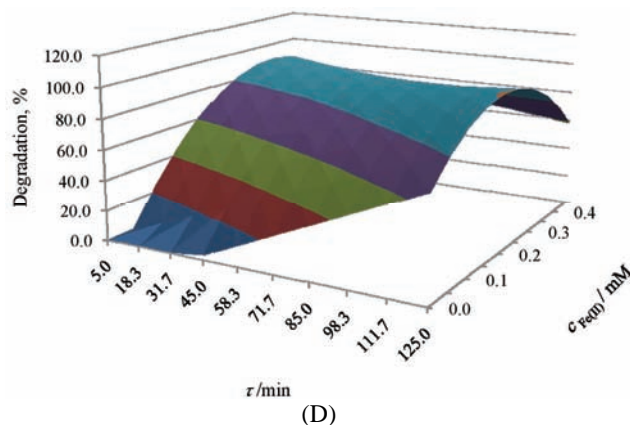


Fig. 2. (Continued) Response surfaces of the full quadratic model between the percentage dye degradation and the variable. D – time and [Fe(II)].

TABLE IV. The optimized ranges for the 4 relevant variables

Variable	Optimized range
[Fe(II)] ₀ / mM	0.25–0.35
[H ₂ O ₂] ₀ / mM	5–17
[Oxalate] ₀ / mM	4–9
Time, min	50–80

In order to test the accuracy of the obtained optimized ranges of the variables, it was necessary to select the middle point of each optimum range and repeat the experiments using these values. Five repetitive experiments were performed under these conditions. As can be seen, all the responses were similar to each other and yielded 92–100 % dye degradation. These results confirmed that the obtained optimized ranges for this reaction could lead to high percentages of dye degradation (Table V).

TABLE V. The results of 5 repetitions of the optimum conditions

Run No.	[Fe ²⁺] ₀ / mM	[H ₂ O ₂] ₀ / mM	[Oxalate] ₀ / mM	Time, min	A _{blank}	A _{sample}	ΔA
1	0.3	11	6.5	65	0.165	0.002	97
2	0.3	11	6.5	65	0.169	0.013	92
3	0.3	11	6.5	65	0.17	0.009	94
4	0.3	11	6.5	65	0.164	0	100
5	0.3	11	6.5	65	0.165	0.003	98

The relative standard deviation (*RSD*) of these repeated experiments was estimated for the responses to study the precision of the experiments and closeness of the responses. The value of the *RSD* was 3.31 %.

Effect of variables

Effect of $[Fe(II)]_0$. With increasing $[Fe(II)]_0$, an increasing trend was observed in the percentage of dye degradation; but increasing of the $[Fe(II)]_0$ more than a specific limit can lead to a plateau or a decrease in the percentage of dye degradation. This is because with increasing $[Fe(II)]_0$, the $\cdot OH$ generation increases; but the generation of high concentrations $\cdot OH$ could cause the undesirable reactions between OH and the H_2O_2 present in the solution.

Effect of $[H_2O_2]_0$. With increasing $[H_2O_2]_0$, the degradation increases because of the more intensive generation of $\cdot OH$. Increasing the $[H_2O_2]_0$ to higher than the optimized value has no significant effect on the dye removal. The reason could be further reaction between $\cdot OH$.

Effect of $[oxalate]_0$. According to Eq. (3) and Fig. 2, there is an interaction between the concentration of oxalate and the reaction time. Increasing the concentration of sodium oxalate (as a catalyst) increased the dye removal after long durations of the reaction.

Effect of time. Although during the passing the time, the reaction will go to completion, (increasing the time has a positive effect on the percentage of dye removal), it is advantageous (especially economically) to optimize the time simultaneously with the other parameters to have the best responses.

Interaction parameters. Eq. (3) and the response surfaces (Fig. 2) show that the time interacted with all three of the effective variables, more or less. Other interactions were non-significant or low-significant.

Real samples

After acquiring the optimized values for the effective variables and testing them with extra experiments, these experimental qualifications were applied on a real sample which was a derivative from the waste water of a local textile factory (Urmia, Iran).

The results showed that the optimum values that could lead to acceptable responses, had been achieved by CCD and the response surface method. The spectra of a real sample before and after treatment by the proposed method are presented in Fig. 3. Using Eq. (3), a percentage degradation of 79.87 % was achieved for the removal of Methyl Orange from the real sample.

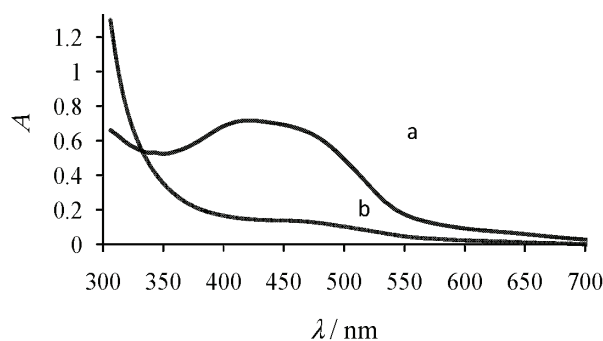


Fig. 3. a) The spectrum of a real sample before application of the Fenton reaction (blank solution) and b) the spectrum of the real sample after application of the Fenton reaction (sample solution).

CONCLUSION

The response surface methodology was shown to be a valuable approach to optimize a process based on the Fenton reaction. In order to obtain the optimized conditions for the removal of Methyl Orange from a textile wastewater, 28 experiments (including 4 repetitions of central points) were designed using CCD method. The optimized ranges were 0.25–0.35 mM for $[\text{Fe(II)}]_0$, 5–17 mM for $[\text{H}_2\text{O}_2]_0$, 4–9 mM for $[\text{Oxalate}]_0$, and 50–80 min for the reaction time. These conditions were applied on a real sample and an acceptable response was achieved.

ИЗВОД

ДИЗАЈН ЦЕНТРАЛНОГ КОМПОЗИТА У ОПТИМИЗАЦИЈИ УКЛАЊАЊА АЗО БОЈЕ, МЕТИЛ-ОРАНЖА, ИЗ ОТПАДНИХ ВОДА ФЕНТОНОВОМ РЕАКЦИЈОМ

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У овој студији је проучавана деградација метил-оранжа, коришћењем Фентонове реакције, и оптимизована помоћу дизајна централног композита и методологије површине одговора. Ефекти разних експерименталних параметара у овој реакцији испитивани су дизајнирањем централног композита. Дизајнирано је укупно 28 експеримената, са 4 фактора и 5 нивоа за сваки фактор. Ови фактори (или променљиве) били су: почетна концентрација Fe(II) , почетна концентрација H_2O_2 , почетна концентрација оксалата и време реакције. Утврђен је квадратни полином који повезује проценат деградације боје (као одговор) и проучаваних параметара. Након уклањања променљивих из модела које нису значајне, за одређивање оптималних услова употребљен је метод површине одговора. Оптимални опсези променљивих били су: 0,25 до 0,35 mM за почетну концентрацију Fe(II) , 5 до 17 mM за почетну концентрацију H_2O_2 , 4 до 9 mM за почетну концентрацију оксалата, и 50 до 80 min за време реакције. Такође, резултати додатних експеримената су показали да се ове оптимизоване вредности могу употребити за стварне узорке и добијање одговора значајне висине.

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