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Factorial experimental design for the optimization of catalytic degradation of malachite green dye in aqueous solution by Fenton process

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ABSTRACT

This work focuses on the optimization of the catalytic degradation of malachite green dye (MG) by Fenton process "Fe^{2+}/H_2O_2". A 2^4 full factorial experimental design was used to evaluate the effects of four factors considered in the optimization of the oxidative process: concentration of MG (X_1), concentration of Fe^{2+} (X_2), concentration of H_2O_2 (X_3) and temperature (X_4). Individual and interaction effects of the factors that influenced the percentage of dye degradation were tested. The effect of interactions between the four parameters shows that there is a dependency between concentration of MG and concentration of Fe^{2+}; concentration of Fe^{2+} and concentration of H_2O_2, expressed by the great values of the coefficient of interaction. The analysis of variance proved that, the concentration of MG, the concentration of Fe^{2+} and the concentration of H_2O_2 have an influence on the catalytic degradation while it is not the case for the temperature. In the optimization, the great dependence between observed and predicted degradation efficiency, the correlation coefficient for the model (R^2=0.986) and the important value of F-ratio proved the validity of the model. The optimum degradation efficiency of malachite green was 93.83%, when the operational parameters were malachite green concentration of 10 mg/L, Fe^{2+} concentration of 10 mM, H_2O_2 concentration of 25.6 mM and temperature of 40 °C.

1. Introduction

Dye wastewater is one of the major industrial water pollution sources in developing countries. Industries such as textiles, leather, paper-making, plastics, food, rubber and cosmetics use different types of dyestuffs which also appear in the effluents discharged from some of these industries. Synthetic dyes are toxic as well as noxious, hence they must be removed immediately from aquatic sources, and otherwise they will lead to severe detrimental effect on the individual health and on the sustaining diversified flora as well as aquatic fauna. For example, malachite green (MG) is the most commonly used dye for cotton, silk, paper, leather and also in manufacturing of paints and printing inks. Malachite green has properties that make it difficult to remove from aqueous solutions. It belongs to the same group of triphenylmethane dyes. A lot of studies

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have reported its teratogenic [1], carcinogenic [2] and reproductive abnormalities [3] spanning its effect from various fish to mammals [4].

Dyes in wastewater can be treated by different processes like: adsorption [5–10], membranes processes [11–14], coagulation/flocculation [15–17], combined coagulation/flocculation and adsorption on activated carbon [18], biological processes [19,20], etc. Most of these methods are non-destructive and/or they generate secondary pollution, because the dyes are transferred to another phase and this phase has to be regenerated.

It was necessary to develop novel and cost-effective technologies to treat the dye wastewater. Recently, advanced oxidation technologies have been accepted as efficient ways for the degradation of toxic and refractory organics [21–29]. Advanced oxidation processes, in which oxygen-based radicals ($^{\circ}OH$, HO_2°, and $O_2^{-\circ}$) are generated in situ from water and O_2, have been applied to dye degradation. These species take part in different reactions to degrade dye molecules completely. The processes are cleaner because dyes totally decompose to low-molecular-weight compounds, CO_2 and H_2O, and no significant or solid secondary pollution is generated. Especially, Fenton processes have been proved as one of the best methods for the control of organic pollution, in which cheap and environmentally friendly reagents are employed [30].

Fenton's reaction is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in an acidic medium, which was firstly discovered by Fenton in the 1890s [31]. In the last decades, Fenton's reaction has been introduced into wastewater treatment processes, and it has been well proven that a variety of refractory organics could be effectively degraded through Fenton's reaction without producing any toxic substances in water environment [32,33].

The generation of hydroxyl radicals in Fenton process is described in the following equations [34]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\circ}OH + OH^-$$

$$^{\circ}OH + \text{Pollutants} \rightarrow \text{Degradation by products}$$

Several parameters influence the Fenton process, in particular the pH of solution, the concentration of ferrous ions, the concentration of hydrogen peroxide, the stirring speed, the initial concentration of the element to deteriorate, the volume of the solution, temperature, and contact time. Studying of the effect of each and every factor is quite tedious and time consuming. Thus, a factorial design can minimize the above difficulties by optimizing all the affecting parameters collectively at a time.

Factorial design is employed to achieve the best overall optimization of a process [35,36]. The design determines the effect of each factor on the response as well as how the effect of each factor varies with the change in level of the other factors [37]. Interaction effects of different factors could be attained using design of experiments only [35,36]. This technique was used to reduce the number of experiments, time, overall process cost and to obtain better response. The advantages of factorial designs over one-factor-at-a time experiments are that they are more efficient and they allow interactions to be detected [38]. The studies using the experimental designs showed the relevance of this methodology [39,40].

In our work, the optimization of the catalytic degradation of malachite green in aqueous solution by fenton process, using a 2^4 factorial experimental design was performed. Four factors were chosen to build the full factorial design with two levels. The effects of factors and their interaction and compatibility of the chosen model with the response have been studied.

2. Materials and methods

2.1. Reagents

In all experiments, we used analytical grade chemicals. The malachite green oxalate form: $C_{23}H_{25}N_2$, C_2HO_4, 0.5[UNI002] CH_2O_4, of molecular weigh 463.5 g/mol, was supplied by Sigma-Aldrich (United Kingdom). Ferrous sulfate $FeSO_4 \cdot 7H_2O$, the sulfuric acid H_2SO_4 (95–97%) and sodium hydroxide NaOH were purchased from Sigma-Aldrich (Germany). The hydrogen peroxide H_2O_2 (30%) was obtained from Soparma (Morocco).

2.2. Experimental procedures

A stock solution of 20 mg/L was prepared by dissolving required mass of MG dye in deionized water and the other solutions were prepared by dilution. The degradation tests were performed in a beaker containing 50 mL of malachite green solution at designed concentration. The pH of the solution was adjusted to 3 by addition of H_2SO_4 (1 M). Thereafter, the required mass of ferrous sulfate was added. The Fenton reaction was initiated by adding the required volume of hydrogen peroxide (H_2O_2). The mixture was kept at a constant stirring of 300 rpm at the temperature of the experiment.

2.3. Analysis

Concentration of MG was determined by measuring absorbance at 618 nm using a TOMOS V-1100 spectrophotometer.

Prior to the measurement, a calibration curve was obtained by using standard MG solution with known concentrations. Because the reaction continued after sampling, the measurement of absorbance of reaction solution was done within 1 min. The pH measurements of the different solutions were performed using an EZODO PL-600 pH meter.

The degradation efficiency (De%) was defined as follows:

$$De(\%) = \frac{C_i - C_f}{C_i} * 100$$

where De is the degradation efficiency (%)after 1 h of reaction, C_f is the concentration of dye after reaction, and C_i is the initial concentration in solution.

2.4. Experimental design and statistical analysis

A statistical methodology was adopted to optimize the Fenton process. A factorial model is composed of a list of coefficients multiplied by associated factor. In a 2^k factorial experimental design k factors are varied over 2 levels. For a given combination of the k factors, more then one test can be performed. These are referred as replicates, r. Therefore, the total number of tests is given as: $\mathbf{N = r \times 2^k + C}$.

where **C** represents the number of center-point measurements used to test for quadratic terms in the low-to-high range. Center points are used to estimate pure error and curvature in the model. In this study N=17 (r=1, k=4, C=1).

The polynomial equation based on the first-order model with four parameters (X_1, X_2, X_3 and X_4) and their interaction terms can be given in the form of the following expression:

$$De = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{12}X_1 x_2 + b_{13}X_1 x_3 + b_{14}X_1 x_4 + b_{23}X_2 x_3 + b_{24}X_2 x_4 + b_{34}X_3 x_4 + b_{123}X_1X_2 x_3 + b_{124}X_1X_2 x_4 + b_{134}X_1X_3 x_4 + b_{234}X_2X_3 x_4 + b_{1234}X_1X_2X_3x_4 \quad (1)$$

where b_0 is the average value of the result; b_1, b_2, b_3 and b_4 are the linear coefficients; and b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, b_{34}, b_{123}, b_{124}, b_{134}, b_{234} and b_{1234} represent the interactions coefficients. The letters X_1, X_2, X_3 and X_4 represent the factors in the model. Combinations of factors (such as $X_1 \times _2$) represent interactions between the individual factors in that term.

In this study, the influence of four main factors has been investigated: Concentration of MG (X_1), Concentration of ferrous ions (X_2), Concentration of hydrogen peroxide (X_3) and temperature (X_4). The degradation efficiency of MG was considered as dependents factors (response). Table 1 illustrates the four parameters and their chosen levels for the experiment. The factors levels were coded as −1 (low), 0 (central point) and +1 (high). A total of sixteen experiments were carried and another in the center of the experimental field. The results were analyzed with 95% confidence intervals using the JMP 12.0.1 Statistical Discovery Software from Statistical Analysis System (SAS).

3. Results and discussions

3.1. Modeling of the degradation efficiency

Table 2 shows the experimental design matrix and the results of the response studied. The table indicates that response varied an important ways in the considered experimental domain. This last could likely contain the required optimal zone. The exploitation of experimental results allowed us to estimate the main effects and interaction effects that are grouped in the Table 3.

By substituting the coefficients b_i in Eq. (1) by their values we get:

$$De = 78.51 - 4.67 x_1 + 5.24 x_2 - 6.85 x_3 + 2.29 x_4 + 2.8X_1 x_2 + 1.1X_1 x_3 - 0.34X_1 x_4 + 2.53X_2 x_3 - 1.05X_2 x_4 + 0.44X_3 x_4 + 0.19X_1X_2 x_3 - 1.29X_1X_2 x_4 + 0.40X_1X_3 x_4 - 0.74X_2X_3 x_4 - 1.16X_1X_2X_3x_4$$

Table 1
Experimental ranges and levels of independent variables used in the optimization.

Coded variable (Xi)	Description	Experimental field		
		Min. value (−1)	Central point (0)	Max. value (+1)
X_1	Concentration of malachite green (mg/L)	10	15	20
X_2	Concentration of ferrous ions (mM)	5	7.5	10
X_3	Concentration of hydrogen peroxide (mM)	25.6	38.4	51.2
X_4	Temperature (°C)	27	33.5	40

Table 2
Design matrix in coded, real units and the experimental responses.

Experiment	Coded variables				Real variables				De (%)
	X_1	X_2	X_3	X_4	[MG]	$[Fe^{2+}]$	$[H_2O_2]$	Temperature	
1	–	–	–	–	10	5	25.6	27	88.26
2	+	–	–	–	20	5	25.6	27	72.72
3	–	+	–	–	10	10	25.6	27	88.81
4	+	+	–	–	20	10	25.6	27	84.25
5	–	–	+	–	10	5	51.2	27	68.44
6	+	–	+	–	20	5	51.2	27	50.29
7	–	+	+	–	10	10	51.2	27	76.67
8	+	+	+	–	20	10	51.2	27	80.30
9	0	0	0	0	15	7.5	38.4	33.5	76.07
10	–	–	–	+	10	5	25.6	40	93.83
11	+	–	–	+	20	5	25.6	40	75.82
12	–	+	–	+	10	10	25.6	40	93.62
13	+	+	–	+	20	10	25.6	40	85.57
14	–	–	+	+	10	5	51.2	40	72.46
15	+	–	+	+	20	5	51.2	40	64.37
16	–	+	+	+	10	10	51.2	40	83.35
17	+	+	+	+	20	10	51.2	40	77.39

Table 3
Main and interaction coefficients of the factors.

bi	Interactions coefficients
b_0	78.37
b_1	−4.67
b_2	5.24
b_3	−6.85
b_4	2.29
b_{12}	2.80
b_{13}	1.10
b_{14}	−0.34
b_{23}	2.53
b_{24}	−1.05
b_{34}	0.44
b_{123}	0.19
b_{124}	−1.29
b_{134}	0.40
b_{234}	−0.74
b_{1234}	−1.16

3.2. Main effects

From the equation of the model, it was noted that the effects of the concentration of ferrous ions and the temperature are positive, we can affirm that X_2 and X_4 have a positive effect on the response, which is important for the X_2 and lower for X_4. This result means that the degradation efficiency increases when the two factors changes from low level to high level. On the other hand the concentration of MG and the concentration of hydrogen peroxide have a negative effect. We can confirm that X_1 and X_3 have a negative effect on the response. This means that, the degradation efficiency falls when the factors passed from the low levels to the high levels. However an excess of hydrogen peroxides can have a behavior of limiting factor because it can become a trap for the hydroxyl radicals and so cause a decrease of the kinetics of degradation by inhibition of the Fenton reaction. Literature studies confirm that the increase in the concentration of Fe^{2+} ions always leads to an increase in the speed of reaction [40–43].

3.3. Interaction effects between factors

Fig. 1 shows the interaction effects of the factors in the low level and the high level of another factor. The figure indicates that $X_{1\times2}$ and $X_{2\times3}$ interactions are the most important interactions because the lines of its effects are not parallel. Other interactions have straight effects which are practically parallel. Subsequently, Figs. 2 and 3 showed the response surface presented as a function of $[Fe^{2+}]$ concentrations and $[H_2O_2]$ at a temperature of 40 °C and hydrogen peroxide concentrations of 25 mM and 10 mg/L, respectively. Fig. 2 shows that the degradation efficiency increases with the increase in concentration of Fe^{2+} and rating

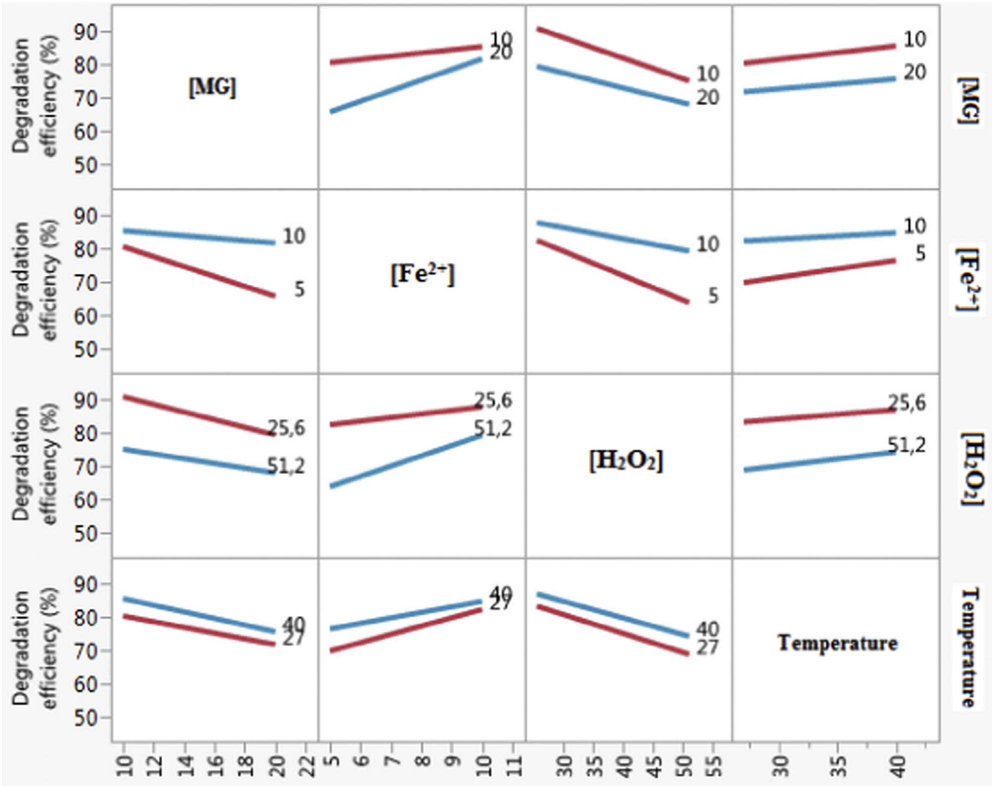

Fig. 1. Effects of interactions between the four factors.

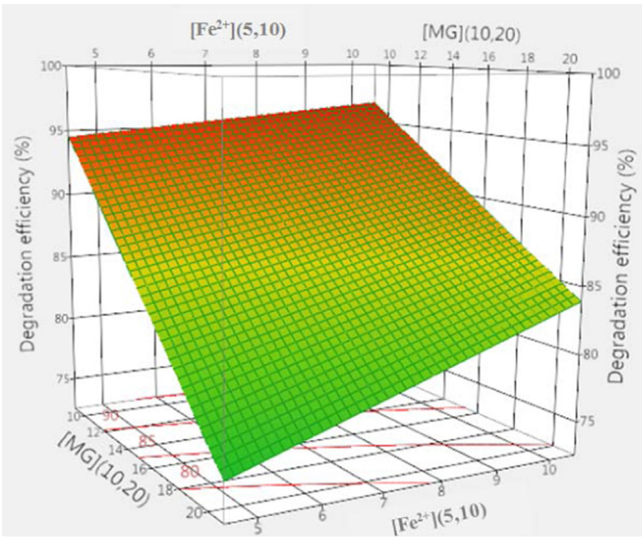

Fig. 2. Response surface as a function of [MG] and $[Fe^{2+}]$ ($[H_2O_2]$=25 mM; T=40 °C).

decrease concentration of MG. In Fig. 3, it can also be observed that the degradation efficiency increases with the increase in concentration of Fe^{2+} and the diminution in concentration of hydrogen peroxide H_2O_2.

3.4. Analysis of variance (ANOVA)

In this study the analysis of variance was performed by the Student test (Table 4). The main and interaction effects of each factor having Prob < 0.05 are considered as potentially significant. In other words, the Prob. whose values estimated

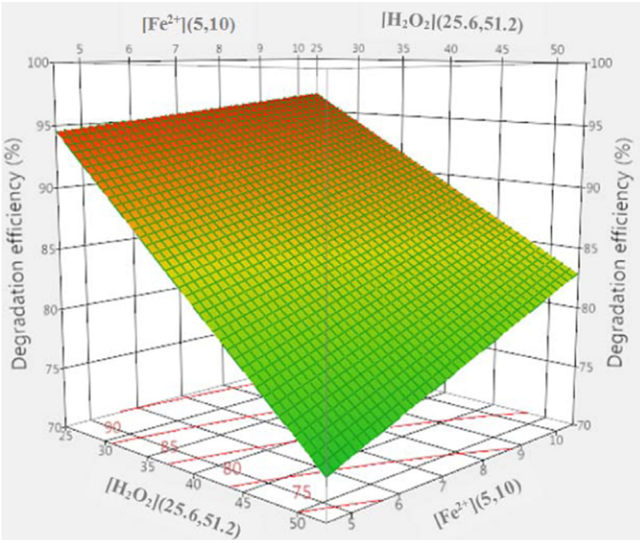

Fig. 3. Response surface as a function of $[Fe^{2+}]$ and $[H_2O_2]$ ([MG]=10 mg/L; T=40 °C).

Table 4
ANOVA test.

Terme	Estimation	Standard error	t ratio	Prob. > |t|
[H₂O₂](25.6,51.2)	-6,850625	0,923526	-7,4179*	0,0177*
[Fe²⁺](5,10)	5,235625	0,923526	5,6692	0,0297*
[MG](10,20)	-4,670625	0,923526	-5,0574*	0,0369*
[MG]*[Fe²⁺]	2,803125	0,923526	3,0352	0,0936
[Fe²⁺]*[H₂O₂]	2,533125	0,923526	2,7429	0,1112
Temperature(27,40)	2,291875	0,923526	2,4817	0,1312
[MG]*[Fe²⁺]*Temperature	-1,291875	0,923526	-1,3989*	0,2968
[MG]*[H₂O₂]	1,099375	0,923526	1,1904	0,3560
[Fe²⁺]*Temperature	-1,054375	0,923526	-1,1417*	0,3719
[Fe²⁺]*[H₂O₂]*Temperature	-0,736875	0,923526	-0,7979*	0,5086
[H₂O₂]*Temperature	0,441875	0,923526	0,4785	0,6795
[MG]*[H₂O₂]*Temperature	0,401875	0,923526	0,4352	0,7059
[MG]*Temperature	-0,343125	0,923526	-0,3715*	0,7459
[MG]*[Fe²⁺]*[H₂0₂]	0,185625	0,923526	0,2010	0,8593

are located outside the limits (blue line) correspond for active effects coming with significant factors, such as $[H_2O_2]$, $[Fe^{2+}]$ and [MG]. As against that the temperature did not greatly influence the other factors (X_1, X_2, and X_3). This can be explained by the fact that the initiation step of radical mechanism requires low activation energy [44].

3.5. Validity of the model

The fit of the model was further checked by the coefficient of determination R^2. The R^2 value is always between 0 and 1. The closer the R^2 value is to 1, the better the model predicts the response [45]. Fig. 4 presents the variation of the observed efficiency depending to the predicted efficiency. It is found that there is a correlation between the two performances with a coefficient of about 0.986. That is to say that 98% of results are explained by the model. In addition according to Table 5, the F-ratio is significant, so the model adopted in this study (full factorial design) is acceptable and validated.

In summary, the optimal reaction conditions to degrade the malachite green were: pH =3; [MG]=10 mg/L; $[Fe^{2+}]$= 10 mM; $[H_2O_2]$=25.6 mM and T =40 °C. Under these conditions and with a 60 min treatment, it was possible to reduce 93.83% of the dye by Fenton treatment.

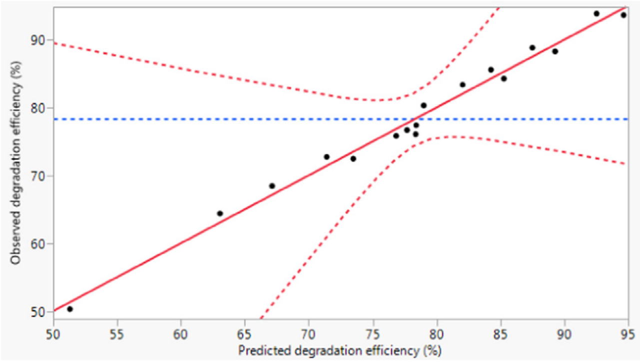

Fig. 4. Variation of the observed efficiency depending to the predicted efficiency.

Table 5
Analysis of variance.

Source	df	SS	MS	F-ratio
Model	14	1931.611	137.972	10.110
Residual	2	27.293	13.646	
Total	16	1958.904		
R^2 = 0.986	R^2_{adj} = 0.889			

4. Conclusion

Optimization of the degradation of malachite green by the Fenton process using full factorial design allowed us to determine the optimal conditions to have a better degradation of malachite green. According to this study, we find that the main parameters influencing the Fenton process are: concentration of MG, concentration of ferrous ions and concentration of hydrogen peroxide. The interaction between concentration of malachite green and concentration of ferrous ions, and the interaction between concentration of ferrous ions and concentration of hydrogen peroxide were the most important interactions. The experimental results obtained during this study show that the Fenton process is effective for the degradation of textile dyes. The excellent correlation between predicted and observed degradation efficiency, high and significant R^2=0.986 and R^2_{adj}=0.889 values, giving good accordance between the model and experimental data which confirmed the validity and practicability of the adopted model.

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