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A design approach for evaluating Fenton process using Response surface method

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Abstract—the aim of the purpose study was to identify the optimal parameters of real and synthetic wastewater treated by Fenton process. The effects of temperature, pH, the ratio $[H_2O_2]/[FeSO_4]$ were explored using the analysis of variance (ANOVA). Vinyl sulfonic and azoic dyes were used as model pollutants. Response surface methodology was applied to evaluate the influence of three factors on the color and COD removal. The optimization of Fenton process was studied. The optimum conditions predicted for both wastewaters were temperature 40°C, pH about 3, 50 as [H2O2]/[FeSO4] for real wastewater and 30 for synthetic effluent. The results obtained for the synthetic effluent are similar to the real effluent behaviour. The COD removal of the synthetic wastewater was higher than the real effluent, unlike the color removal.

Index Terms—Effluent, Fenton process, Optimization, RSM, Textile, Wastewater, COD, color removal

1 INTRODUCTION

Fenton process was discovered in 1894 by HJH Fenton [1] [2]. Its usefulness was not recognized until 1930 [3], when Haber and Weiss [4] suggested a radical mechanism for the catalytic decomposition of H_2O_2 by iron salts [5]. Many works, treating the nature of oxidizing species in Fenton reaction, have been carried out and numerous reactions have also been proposed [6], [7], [8], [9].

Initiation

$Fe^{2+} + H_2O_2 \rightarrow OH^- + OH^\bullet + Fe^{3+}$ Equation 1

Propagation

$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+$ Equation 2

$Fe\text{-}OOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet$ Equation 3

$HO_2^\bullet + Fe^{2+} \rightarrow H_2O_2 + Fe^{3+}$ Equation 4

$HO_2^\bullet \rightarrow O_2^- + H^+$ Equation5

$O_2^- + Fe^{2+} \rightarrow H_2O_2 + Fe^{3+}$ Equation 6

$OH^\bullet + O_2^{\bullet -} \rightarrow OH^- + Fe^{3+}$ Equation 7

Termination

$OH^\bullet + H_2O_2 \rightarrow O_2^\bullet + H_2O$ Equation 8

$OH^\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ Equation 9

$OH^\bullet \rightarrow H_2O_2$ Equation 10

$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$ Equation 11

$HO_2^\bullet + O_2^- \rightarrow HO_2^- + O_2$ Equation 12

Fenton oxidation takes place according to complex process involving several types of reactions [10], [11] [12]:

- Initiation reactions (formation of radical OH• species);
- Propagation reactions involving radical species OH• which will react with other organic molecules or with the oxygen dissolved in the solution;
- Termination reaction

The decomposition of H2O2 with a catalytic Fe3+ generates OH• radical [11] [14]. This radical is extremely reactive. Lin and Ping [15] found that Fenton process is very effective in reducing of COD content and decolorizing of wastewater which contain acid, basic, direct or reactive dyes. This process remains an efficiency performance in various industrial effluents.

Fenton reaction depends on several parameters: pH, temperature and the ratio $[H_2O_2]/[FeSO_4]$ [12].

In the past, many studies had developed some methodologies for optimization study of test factors. Response surface methodology has been widely applied for optimization [17], [18], [19], [20]. It has been successfully used by different researchers. According to yuejin [21], the RSM method provides a wide range of in formations with a small number of experiences, the effect of variables on the desirable response and also their interactions [21]. Nevertheless, there is luck of works treating Fenton optimization and studying the influence of reaction parameters on the quality of real wastewater. Solomon et al underlined that the chemical treatment combined with biological process lead the highest quality of effluent with 80% of COD and color removal. Other authors proved that a value of 98,7% of removal efficiency was predicted, but this is under ZnO and PS catalytics. Based on previous research studies, it seems important to treat another type of real effluent with different catalytic.

The present paper focuses on the parameters that affect degradation from azoic and vinylsulfonic wastewater by Fenton process. The principal objectives were to identify an approach that explain the relation between the factors (temperature, pH, [H2O2]/[FeSO4]) and the response (color removal, COD removal, MES) and to develop optimum conditions for Fenton reaction using response surface methodology.

2 MATERIALS AND METHODS

2.1 Chemical and reagents

All chemical and solvents used for these experiments were purchased from the laboratory CHIMITEX Plus located in Tunisia.

The oxidation phase was performed with Fenton's reagent in a cylindrical reactor. The volume of effluent was placed into this reactor in constant temperature. The pH of the solution was adjusted by H_2SO_4 (95-97%) or NaOH. Fenton's reagent hydrogen peroxide H_2O_2 and iron sulphate $FeSO_4$ were used to generate the production of hydroxyl radicals OH•.

2.2 Textile effluent

The real wastewater used in this study was supplied by a textile manufacturer which deals with finishing and dyeing of cotton fabrics. Samples were collected from the wastewater station. The characteristics of textile effluent are shown in Table1.

Table 1
Characteristics of real wastewater

PARAMETER	VALUE
pH	6.73
CONDUCTIVITY (MS/CM)	13.9
MES (MG/L)	896
ABSORBANCE (=657NM)	2.34
COD (MG/L)	1290

2.3 Experimental design

Response surface methodology collects statistical and technical tools for constructing a function which relates a response and a set of variables. For industrial fields, it is difficult to define a compromise between a set of input variables that influence some output performance measure by a mathematical formulation. In this case, the RSM method can found a function for the response measure based on the values obtained from experiments at some combination of the variables input.

The experimental design was 3^3 full factorial central composite plan with three factors pH, Temperature and the ratio $[H_2O_2]/[FeSO_4]$ requiring 21 experiments. The variables selected of Fenton process were: Temperature (40°-90°C), pH (2-4), $[H_2O_2]/[FeSO_4]$ (20-100). The second order polynomial coefficients were calculated using the "Minitab" software (version 14.1). Statistical analysis was performed using the analysis of variance (ANOVA). The statistical analysis and plots of the response's optimisation were performed using the software 14.1.

3 RESULTS AND DISCUSSIONS

Concentration of H_2O_2, concentration of $FeSO_4$ and pH were found as most influential parameters for the Fenton process. A RSM methodology was employed to study the effect of these parameters and to reach the optimum. Selected variables and their levels are shown in table 2.

Table 2
Summary of variables, their values and coded

Variables	Units	Symbol	Coded levels		
			-1	0	+1
pH	-	X1	2	3	4
[FeSO4]	mM	X2	0.4	0.8	1.2
[H2O2]	mM	X3	36	38	40

The results of the response surface model acting in the form of ANOVA. The analysis of variance was employed for the determination of significant parameters. The regression equation and the coefficient R2 were evaluated to test the fitting model.

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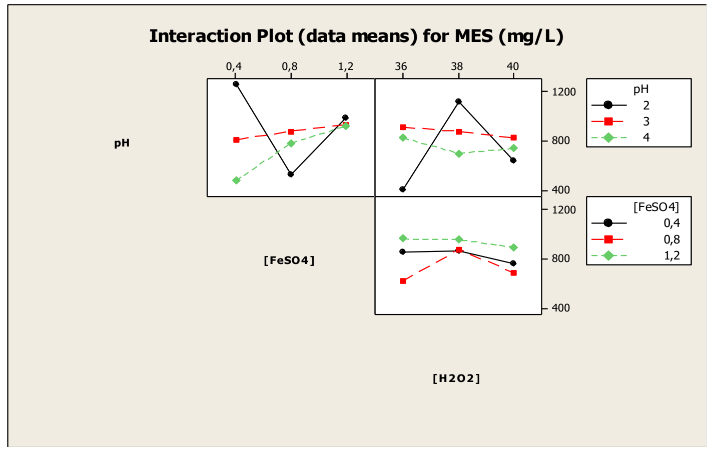
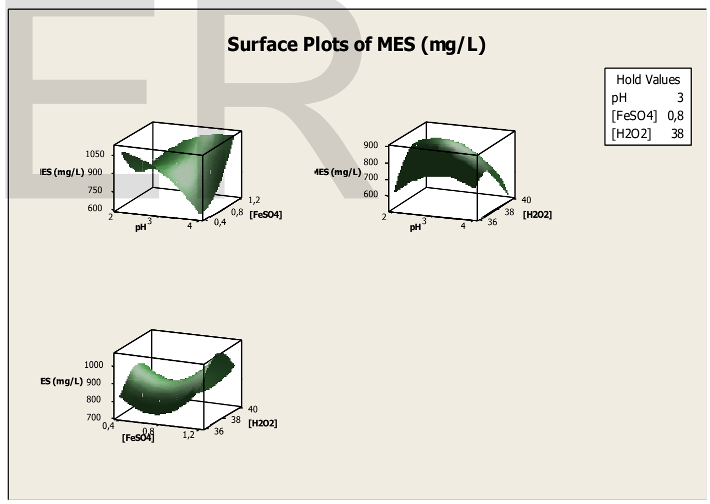
The analysis of quadratic regression demonstrates that the model is very significant. This result is evident from the Fisher's F-test which has a very low probability value [(Pmodel >F). the low value of coefficient of variation (CV = 15.03%) indicates a reliability of the experiments carried out and a better precision

3.1 MES response

Several experiments were carried out to find the effect of iron sulfate, hydrogen peroxide doses, and pH needed to obtain



good results on MES removal.
Figures 1 and 2 include data about experiments that carried out



for during 60min at 40°C and for pH= 3.

Figure 1. Interaction plot for MES (mg/L)

Figure 2. Surface plots of MES (mg/L)

As mentioned in the first part of this paper, Fenton process is considered as good when the MES removal is high. In the case of this real wastewater, the concentration of H_2O_2 and $FeSO_4$ leads to larger MES removal, with detrimental effects noticed for the highest ratio. In other part, it was found that the increase of pH value can increase the MES loss rate.
At the entrance of the station, we noticed that the MES content is high because the textile water is much polluted. The variation of the MES content is related to the daily flow rates. Indeed, the rejects come from the dyeing, stoning and bleaching.
According to Figure 2 we note an overshoot of the MES value compared to the value required by the standard. Indeed, very

acidic pH(<2) favors the complexation of Fe^{2+} by H_2O_2 and cause a decrease in the concentration of these ions in the reaction medium. This explains a lower level of MES removal compared to pH = 3. For pHs above 4, the ferric ions precipitate in the form of iron hydroxide Fe $(OH)_3$. This precipitate is very stable, the reduction of Fe^{3+} to Fe^{2+} becomes very slow and the generation of Fe2+ as an initiator for the production of OH • radicals, becomes the kinetically limiting step of the process. This justifies the lower MES removal levels at pH = 5.
The small amounts of the catalyst can be consumed by other non-catalytic reagents which require working with a quantity greater than that introduced. These low doses of $FeSO_4$ can also cause the appearance of parasitic reactions between H_2O_2 and OH • because there is not enough iron to react with H_2O_2 thus the concentration of OH • which reacts with organic matter and weak. However, doses of $FeSO_4$ which exceed 0.8 mM are not advantageous. We note that the excess of FeSO4 decreases the efficiency of Fenton because under these conditions iron can play the role of a coagulant. It competes with the OH• hydroxyl radicals.
Figure 2 shows also an inclinaison of the contours from the horizontal screening a significant interaction

3.2 Color removal

The effectiveness of Fenton's reagent depends on several factors: pH, concentration of $FeSO_4$ and concentration of H_2O_2. These are the parameters that most influence the catalytic process. We have studied the effect of all these parameters on color removal; we have carried out tests for durations ranging from 0 to 60 minutes (with a step of 5 minutes).

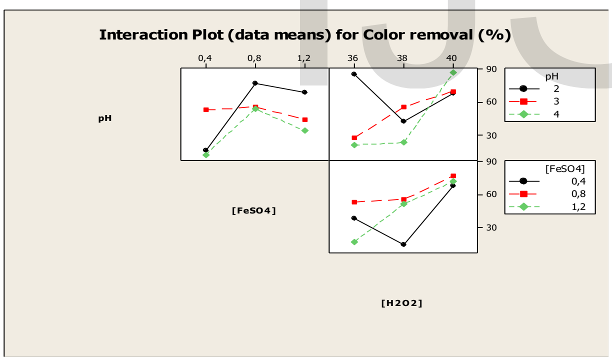


Figure 3. Interaction plot for color removal (%)

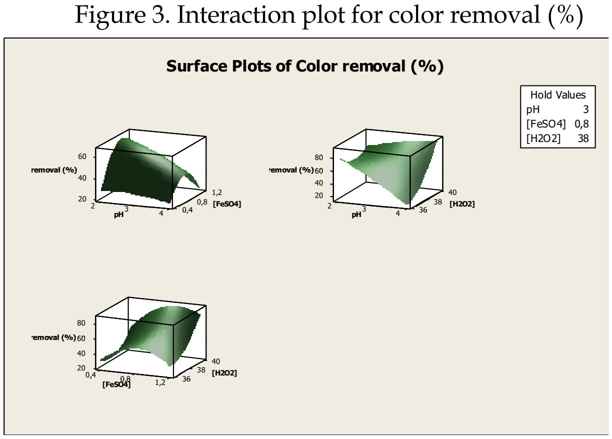


Figure 4. Surface plots of color removal (%)

The real wastewater has a large range of pH values. The pH solution is an important parameter affecting the removal efficiency. It affects the mechanism of oxidation dye. In fact, a change in pH value involves a variation of Fe^{2+} concentration and the rate of production of OH• radicals.
The reagent H_2O_2 plays also a main role as an oxidizing agent in the Fenton reaction. Increasing the concentration of H_2O_2 could promote the efficiency of degradation as shown in Figure 3. This increase promotes a significant production of the hydroxyl radicals OH•.
Using iron sulfate FeSO4 as a catalyst accelerates the Fenton reaction by lowering the activation energy of this chemical reaction. The quantity of iron introduced must then be well chosen. In fact, if the catalyst is dosed in a smaller quantity, the yield will be insufficient. If on the other hand this quantity is dosed in excess, we will witness an unpleasant phenomenon which will be detailed later.
We observe in Figure 4, that the more the iron concentration increases, the more the discoloration rate increases. We also note that the shape of the curves obtained in the presence of 0.8 mM; 1.2 mM and 2.2 mM is similar. The longer the duration of treatment, the more these curves tend to become confused. Similarly, for these curves, the higher the concentration, the better the discoloration even at the start of the Fenton process. This is not the case for discoloration in the presence of 0.4 mM $FeSO_4$. In this case, the best level of discoloration did not exceed 10% for a period of 5 minutes.

3.4 Multi-objective optimization

The optimization of the various parameters of Fenton process was targeted to maximize the color removal and to minimize the MES (Table 3).

Table 3
Response and their target

	Goal	Lower	Target	Upper	Weight	Import
Color removal	Maximum	0	100	100	1	1
COD (mg O_2/L)	Minimum	1000	1000	2000	1	1
MES (mg/L)	Minimum	30	30	2000	1	1

The DOE tool was employed to determine the optimum Fenton process condition to get desirable responses. Each response was transformed in to individual desirability function, which varies from 0 to 1 (lower to higher desirability). An overall desirability was obtained by combining the three individual desirability values of different individual values of variables.
Results of the calculated optimal conditions are shown in the table 4:

Table 4
Predicted responses at optimal conditions: pH=4; [FeSO4]=0.97 mM;[H2O2]=40 mM

	Value	Individul desirability	Overall desirability
Color removal	91,33	0,91	0,85431
COD (mg O_2/L)	307,83	1	
MES (mg/L)	655,12	0,68	

The prediction was validated by maintaining real experiment. The obtained results were found close to the predicted values, suggesting that full factorial design could be effectively used to optimize the present wastewater treatment to ameliorate the efficiency of Fenton method.

3.4 Discoloration kinetics

We followed the discoloration as a function of time under the optimal conditions. We then plotted the evolution curve of the normalized absorbance A / A0 as a function of time (with A0: Initial absorbance). The results are reported in Figure 5.

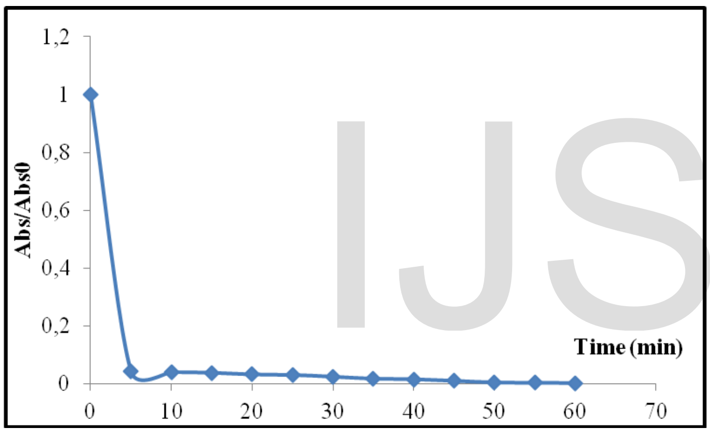


Figure 5. Evolution of the normalized absorbance under optimal conditions

Discoloration by this process begins upon the introduction of the catalyst and the oxidant. From Figure 5, we see that the absorbance follows an exponential decay as a function of time, which suggests that the rate of decomposition of the dye molecule is rapid.

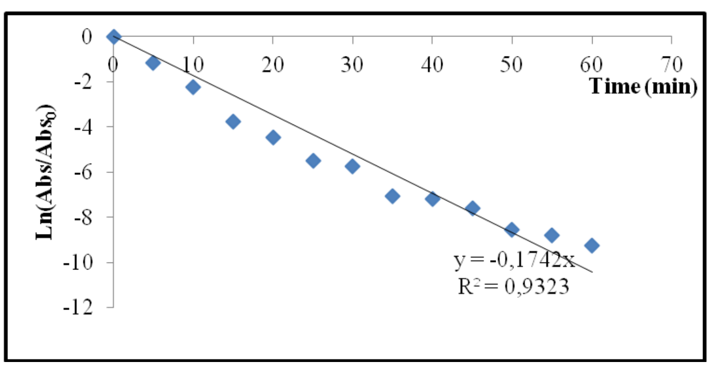


Figure 6. Ln(A/A_0) at the optimal conditions

The apparent kinetic constant calculated for the conditions: pH = 3, [FeSO4] = 0.8 mM and [H2O2] = 41 mM is equal to 0.1742 min-1.

If we compare this constant with work done on a synthetic textile reject, treated by the Fenton process, we found that this process is competitive and very interesting since the application is simple, the reagents are available and the result is satisfactory.

Following the same approach, we calculated the kinetic constants under all the conditions mentioned above at different pH values, concentration of [H2O2] and that of [FeSO4]. The result is summarized in the following table:

Table 5. Apparent kinetics of discoloration under different operating conditions

Paramètre	Valeur	k (min^{-1})
pH	2	0,11
	3	0,14
	4	0,078
	5	0,076
[$FeSO_4$]	0,4 mM	0,021
	0,8 mM	0,054
	1,2 mM	0,067
	2,2 mM	**0,07**
[H_2O_2]	36 mM	0,031
	41 mM	0,04
	44 mM	**0,044**

4 Conclusion

In the present study different types of wastewater (synthetic and real) have been tested from Fenton process. The main hypothesis is based on the difference between the two effluents in terms of oxidation efficiency. Indeed, the synthetic effluent is composed from one type of pollutant which is very easy to break it down to small molecules. While for the real wastewater, secondary reactions can be appears between molecules which prevented the decomposition process. Mathematical models were used to define a relationship between input parameters (pH, Temperature, [H2O2]/[FeSO4]) and output variables using response surface methodology. Analysis of variance was selected to identify the adequacy between the model and its variables.

The main results can be drawn as follows:

1. The analysis of Fenton parameters using RSM approach, allows the investigation of influence of each factor on the response outputs: color removal, COD and MES;
2. Based on the RSM optimization process, the optimum parameters for the Fenton oxidation were temperature of 40°C, pH equal to 3 and a ratio[H2O2]/[FeSO4] about 50 for real effluent and 30 for synthetic wastewater;
3. Statistical analysis shown that the COD removal was about 78% for the synthetic wastewater. Moreover, the real wastewater had only 65%;
4. For both wastewaters, color removal increased with a rate of 95% which related to the breakage of the chromospheres' group;
5. The following results indicate that Fenton reaction can be combined with flocculation/coagulation to

guarantee a better quality of treated effluent according to the Tunisian standard for discharge wastewater.

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