

Removal of N-2RBL Nylosan red dye from aqueous solution by Fenton using response surface methodology

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ABSTRACT

In this study, the optimization of N-2RBL Nylosan red (NR) dye degradation by Fenton process ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) using response surface methodology (RSM) was evaluated. A 2^3 full factorial design was employed to design runs and analyse the effects of three independent factors: stirring speed (150–800 rpm), dye concentration (50–500 μM) and treatment time (30–1,440 min), as well as the interaction factors on the reaction rate (%). According to the results, treatment time had the most significant impact on the removal efficiency of NR. The interactions factors of dye concentration and stirring speed, and stirring speed and treatment time have the strongest effects, expressed by the high values of interactions coefficient. The analysis of variance showed a coefficient of determination (R^2) of 100%. The maximum dye removal efficiency of 96.74% was achieved at optimum conditions with Nylosan red concentration of 50 μM , stirring speed of 800 rpm and treatment time of 1,440 min.

Keywords: Azo dye; Advanced oxidation process; Experimental design; Optimization; Degradation

1. Introduction

The first living things were born in water more than two billion years ago. Given the vital importance of water for life on earth, its quality makes it a valuable resource. Often the quality of water is more important than its quantity. The quality of water affects how we use it, but the reverse is also true. When we use water, we alter its quality.

Dyes are an important part of synthetic organic compounds. In general, these synthetic dyes are more attractive in terms of practicality and economy, but they are also

more polluting. Synthetic dyes, most of which are toxic, are widely used in the textile industry. These substances are classified into two families, water-soluble and water-insoluble dyes. Water-soluble dyes are harmful to the environment, their discharge into aquatic systems causes environmental damage due to their toxicity [1], which requires treatment. However, the complexity of these pollutants and their colour greatly affect the effectiveness of conventional treatments applied.

The various dyes that are used in excess to improve dyeing discharges from the textile industry are a huge nuisance

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to human health and aquatic life, especially azo ones, contain in their structure one azo group ($-N=N-$) linked to at least one aromatic ring [2]. As a result, wastewater is highly concentrated in dyes whose low biodegradability makes biological treatments difficult to apply, which is a source of environmental degradation.

To eliminate or reduce pollution caused by dyes, various processes are currently well mastered on a laboratory scale and applied on a large scale in industry, including several techniques: physical, physicochemical, advanced oxidation, biological, recovery treatment [3,4]. Some of these techniques do not eliminate all the pollution, others are often costly or generate secondary pollution that requires further treatment like adsorption [5,6].

Among the processes that allow the abatement COD of effluents, such as dyes, to be reduced are advanced oxidation processes using the Fenton reagent (Fe^{2+}/H_2O_2), which produce, in situ, highly reactive entities such as HO^\bullet hydroxyl radicals.

The latter have a very high oxidising power. Advanced oxidation processes allow the most recalcitrant molecules to be broken down into biologically degradable molecules or mineral compounds such as H_2O and CO_2 , without by-products [7].

The Fenton process is an efficient process for the synthetic dye's treatment [8–11]. The hydroxyl radicals react very rapidly with the organic compounds to lead to the mineralisation of the organic material [7].

The formation of hydroxyl radicals (OH^\bullet) known to be strong oxidants of organic pollutants and also to the production of ferric ions Fe^{3+} , according to the following mechanism [12].



The experimental design consists of simultaneously varying the levels of one or more factors in each test. This will make it possible, on the one hand, to greatly reduce the number of experiments to be carried out while increasing the number of factors studied and, on the other hand, to detect the interactions between the factors and the determination of the so-called optimal setting of these factors in relation to a response. This technique is used to reduce the time and cost of the treatment [7]. The tricky point in using experimental designs is to minimise the number of experiments to be carried out without sacrificing the precision of the results [13–16].

The main advantages of the Fenton process are mainly the generation of HO^\bullet radicals which lead to the mineralization of dyes. On the other hand, the response surface methodology provides a simple method to predict the results. However, using experimental designs to minimize the number of experiments should be conducted without sacrificing precision of the results.

There are several parameters that influence the Fenton process, for example: reagents concentration – ratio $[Fe^{2+}]/[H_2O_2]$, dye concentration, temperature, treatment time, initial pH and stirring speed.

In this study, we selected three factors (parameters) for the optimisation of the degradation of N-2RBL Nylosan red (NR) dye by the Fenton process with a full two-level factorial design 2^3 . The experiment matrix is formed by 08 combinations of the three selected factors. The effect of factors and their interactions between factors, comparison of predicted and experimental responses had been studied.

The aim of this work is to study the prediction of Nylosan red dye removal rate using response surface methodology in comparison to the experimental results. Experimentally, we used an anionic dye widely used in the textile industry in contact with a Fenton solution composed of $[Fe^{2+}] = 0.2$ mM and the concentration ratio $[Fe^{2+}]/[H_2O_2] = 1/20$, at pH = 3. To the best of our knowledge, the study of N-2RBL Nylosan red (NR) dye removal from aqueous solution by the Fenton process has not been reported elsewhere, in particular using the response surface methodology.

2. Materials and methods

2.1. Reagents

The chemical structure of N-2RBL Nylosan red (NR) dye ($C_{24}H_{21}ClN_4O_6S_2Na$, MW = 587.97 g/mol, $\lambda_{max} = 500$ nm) is shown in Fig. 1. Ferrous sulphate $FeSO_4 \cdot 7H_2O$, the sulphuric acid H_2SO_4 , sodium hydroxide NaOH and hydrogen peroxide H_2O_2 (30%) were obtained from Sigma-Aldrich (Germany).

2.2. Experimental approach

For each experiment, a 200 μ M solution was prepared by dissolving a proper amount of N-2RBL Nylosan red (NR) dye in distilled water. The pH of the solution was adjusted to 3, by using H_2SO_4 and NaOH, the concentration ratio $[Fe^{2+}]/[H_2O_2]$ was set to 1/20 with $[Fe^{2+}] = 0.2$ mM [17].

The general method followed in all our experiments, according to the literature [7,18], is as follows: in a beaker containing NR stock solution at designed concentration, the pH is adjusted. pH values were measured using a (HI pH-211, HANNA Instruments, Woonsocket, Rhode Island, USA) pH-meter. Then the required mass of $FeSO_4 \cdot 7H_2O$ was added. The Fenton reaction was initiated by adding the required volume of H_2O_2 . The mixture was stirred with a magnetic stirrer (SB 161-3 Stuart, Stone, Staffordshire, UK) at a constant temperature of 303 K using a thermostatic bath. The absorbance of solution should be analysed immediately because the reaction continued after sampling, so the absorbance measurement should be completed within 1 min [19].

Analyses were performed using a UV-Vis spectrophotometer (Jenway 7305 Spectrophotometer, Staffordshire, UK) to determine the extent of colour removal.

The dye removal efficiency was calculated using Eq. (3).

$$\text{Dye removal efficiency (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (3)$$

where A_0 is initial absorbance and A is absorbance after reaction.

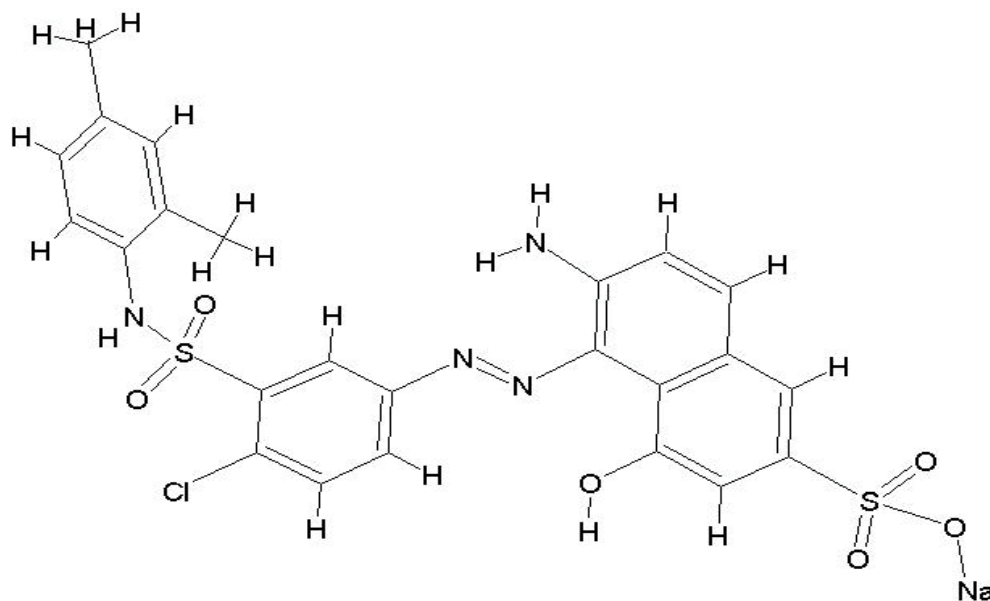


Fig. 1. The molecular structure of Nylosan red dye.

3. Results and discussion

In the present study, three factors at two variation levels (stirring speed (150–800 rpm), dye concentration (50–500 μM) and treatment time (30–1,440 min)) were chosen to optimize the Fenton treatment. The response surface methodology (RSM) was used to determine the relative significance of several affecting factors, even in the presence of complex interactions [20] while reducing number of experiments, time and cost. For a full factorial design, 8 runs ($N = 2^3$) are needed to evaluate the effects.

The experimental factors, their selected levels and the results of the response studied are presented in Table 1 using Ellistat software (version 6.9.2 2021/07 by Pillet Consulting).

According to the polynomial equation based on the first-order model, the three second-order interactions have approximately identical values but different signs. The third order interaction is practically zero. The results obtained make it possible to write the model giving NR removal rate as a function of the three factors levels as follows:

$$Y(\%) = 52.7825 + 6.28x_1 - 7.84x_2 + 31.9x_3 + 2.19x_1x_2 + 2.32x_1x_3 - 1.17x_2x_3 \quad (4)$$

With this model, all responses in the study area can be calculated. It is sufficient to assign values to the x_1 , x_2 and x_3 levels to immediately obtain the elimination rate.

The relationship in legal units, given by the software, is as follows:

$$Y(\%) = 14.01 + 0.03499 \times \text{Speed} - 0.02606 \times \text{Concentration} + 0.04799 \times \text{Time} - 2.991 \times 10^{-5} \times \text{Speed} \times \text{Concentration} - 1.014 \times 10^{-5} \times \text{Speed} \times \text{Time} + 7.392 \times 10^{-6} \times \text{Time} \times \text{Concentration} \quad (5)$$

where x_1 , x_2 and x_3 are codified (± 1) values of stirring speed, dye concentration and treatment time, respectively.

3.1. Effect of studied factors

The effect of stirring speed, dye concentration and treatment time on removal of NR dye at different levels of factors are presented in Fig. 2.

3.1.1. Effect of the stirring speed

The stirring speed of the solution increases contact between HO^\bullet hydroxyl radicals and NR dye particles.

The dye removal rate increases, on average, from 46.505% to 59.06% as stirring speed is increased from 150 to 800 rpm. The dye removal rate in the centre is half of the two averages: 52.7825%.

The dye removal rate increased, on average, from 52.7825% to 59.06% as stirring speed was increased from 475 to 800 rpm. This increase of 6.28% represents the limit effect of the stirring speed factor. The results mean that dye removal efficiency increases when the stirring speed changes from low level to high level [21]. The reason for the "limit" status of the stirring speed according to analysis of variance (ANOVA), may be due to the aspiration of gases such as O_2 and CO_2 into solutions [22,23]. Under the influence high velocity of stirring CO_2 in the solution which produce HCO_3^- and CO_3^{2-} ions [Eqs. (6) and (7)] [23,24]. These ions are capable to complex ferrous iron [Eqs. (8)–(11)], and scavenge the production of hydroxyl radical $\bullet\text{OH}$ which is important for dye degradation, according to the following equations proposed by Tariq and Khan, and Ghiselli et al. [Eqs. (12) and (13)] [23–25].



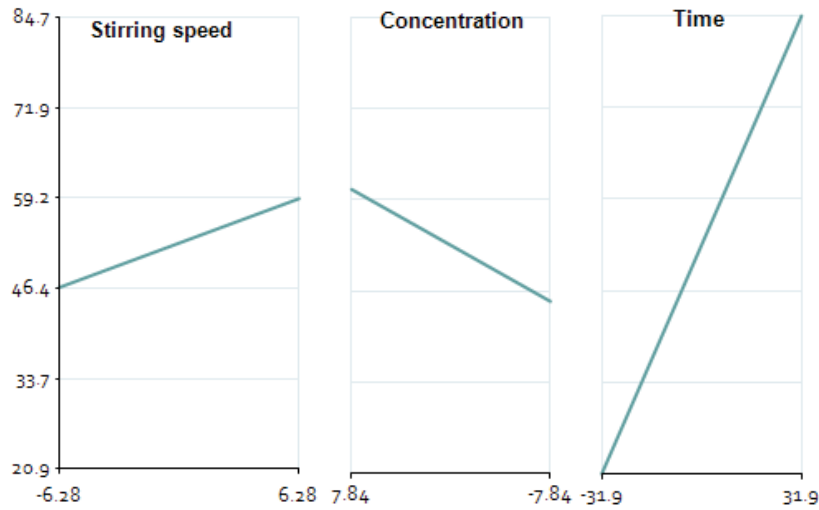
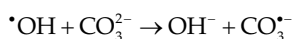
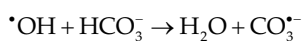
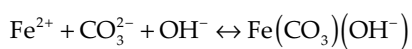
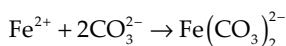
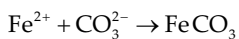
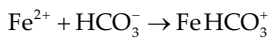
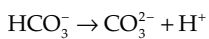


Fig. 2. Effect of stirring speed, dye concentration and time on the removal rate of Nylosan red dye by Fenton process.

Table 1
2³ factorial design matrix

| Run | Stirring speed (rpm) | Concentration (μM) | Time (T) min | Removal rate _{experimental} (%) | Removal rate _{predicted} (%) |
|-----|----------------------|--------------------|--------------|--|---------------------------------------|
| 1 | -1 | -1 | -1 | 18.41 | 19.13 |
| 2 | -1 | -1 | +1 | 85.9 | 85.18 |
| 3 | -1 | +1 | -1 | 6.21 | 5.49 |
| 4 | -1 | +1 | +1 | 75.5 | 76.22 |
| 5 | +1 | -1 | -1 | 41.43 | 40.71 |
| 6 | +1 | -1 | +1 | 96.74 | 97.46 |
| 7 | +1 | +1 | -1 | 17.59 | 18.31 |
| 8 | +1 | +1 | +1 | 80.48 | 79.76 |

| Factor | Level | |
|----------------------|-------|-------|
| | -1 | +1 |
| Stirring speed (rpm) | 150 | 800 |
| Concentration (μM) | 50 | 500 |
| Time (min) | 30 | 1,440 |



3.1.2. Effect of dye concentration

The dye removal rate decreases, on average, from 60.62% to 44.945% as concentration is increased from 50 to 500 μM. The dye removal rate in the centre is half of the two averages: 52.7825%.

The dye removal rate decreases, on average, from 52.7825% to 44.945% as concentration is increased from 275 to 500 μM. This increase of -7.84% represents the effect of the concentration factor.

These results show that the effect of the concentration factor is negative. This is consistent with the results found in the literature, where the authors studied the degradation of malachite green (MG) dye by Fenton process, the concentration of MG had a negative effect [7,23]. However, increasing the dye concentration increases the number of dye molecules in the solution for the same number

of hydroxyl radicals, which leads to the decrease of the degradation rate. This can also be seen in the response surface illustrated in Fig. 5, which is representation of Eq. (5).

3.1.3. Effect of treatment time

The dye removal rate increases, on average, from 20.91% to 84.655% as treatment time is increased from 30 to 1,440 min. The dye removal rate in the centre is half of the two averages: 52.7825%.

The dye removal rate increases, on average, from 52.7825% to 84.655% as treatment time is increased from 735 to 1,440 min. This 31.9% increase represents the significant effect of the time factor. These results mean that dye removal efficiency increases as treatment time changes from low level to high level, which indicates that longer reactions better facilitated dye degradation. Such behaviour has already been reported in the literature [21,26–28].

These results show that the time factor is the most influential in this study.

3.2. Interaction effects between factors

In Fig. 3 the interaction graphs show the effects of one factor at the low level and the high level of another factor.

The interaction between the stirring speed and concentration factors is 2.19%. This means that the effect of stirring speed is higher at low concentrations. When the concentration is 500 μM , the effect of stirring speed is 4.09%. When the concentration is 50 μM , the effect of the stirring speed is 8.465%.

This also means that the effect of concentration is greater when the stirring speed is fast. When the stirring speed is 800 rpm, the concentration effect is -10.025% . When the stirring speed is 150 rpm, the concentration effect is -5.65% .

The interaction between the stirring speed and time factors is 2.32%. This means that the effect of stirring speed is higher at low time. When the time is 1,440 min, the effect of stirring speed is 3.955%. When the time is 30 min, the effect of the stirring speed is 8.6%.

This also means that the time effect is greater when the stirring speed is slow. When the stirring speed is 800 rpm, the time effect is 29.55%. When the stirring speed is 150 rpm, the time effect is 34.195%.

The interaction between the concentration and time factors is -1.17% . This means that the effect of concentration is higher when the time is low. When the time is 1,440 min, the

concentration effect is -6.665% . When the time is 30 min, the concentration effect is -9.01% . This also means that the time effect is greater when the concentration is high. When the concentration is 500 μM , the time effect is 33.045%. When the concentration is 50 μM , the time effect is 30.7%.

These results show that interactions between concentration and stirring speed, and stirring speed and time are the most important interactions, because the two lines in each interaction graph do not have the same slope [29,30]. Subsequently, Figs. 4 and 5 show the response surface presented as a function of stirring speed and time at a dye concentration of 100 μM and dye concentration and stirring speed at treatment time of 900 min, respectively. Fig. 4 shows that the dye removal efficiency increases with the increase in stirring speed and the increase in time. In Fig. 5, it can be observed that the dye removal efficiency increases with the increase in stirring speed and the diminution in dye concentration.

3.3. Analysis of variance (ANOVA)

Table 2 shows the ANOVA analysis for dye removal efficiency using Fenton process. Parameters with P -values less than 0.05 (for 95% of statistical meaning) were considered to be significant, also as F -value increases, the effect of the parameters on the response increases [31]. When the hypothesis F -value is greater than F -critical, this shows that the model is significant [32] ($F_{\text{crit}} = 233.99$). It can be seen that the interactions between stirring speed and concentration, stirring speed and time and concentration and time are statistically not significant, because these parameters present P -values greater than 0.05 (for 95% of statistical meaning). The ANOVA results show that the most important factor contributing to the dye removal efficiency is treatment time and the regression model is statically significant.

3.4. Validity of the model

A high R^2 -values, close to 1, is necessary to ensure a satisfactory adjustment of the model and the experimental data [32]. Fig. 6 clearly shows that the removal rates calculated from the developed model Y (%) are nearly identical to the removal rates found experimentally. In this study, the value of the determination coefficient (R^2) is 100%, also, the adjusted R^2 is a standard for how well the model is improved if an extra variable is added, whereas predicted R^2 is an expression of the model's ability to predict

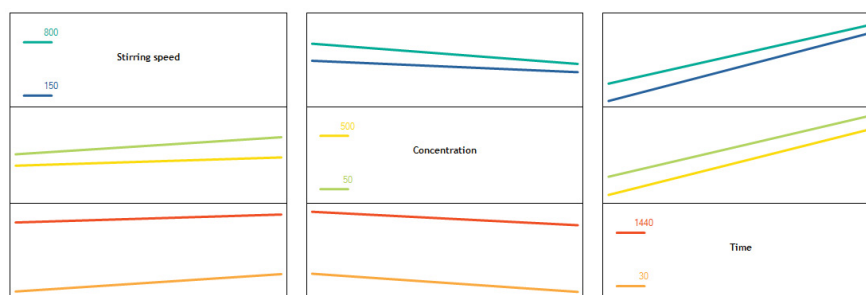


Fig. 3. Diagram of the interactions between stirring speed, concentration and time.

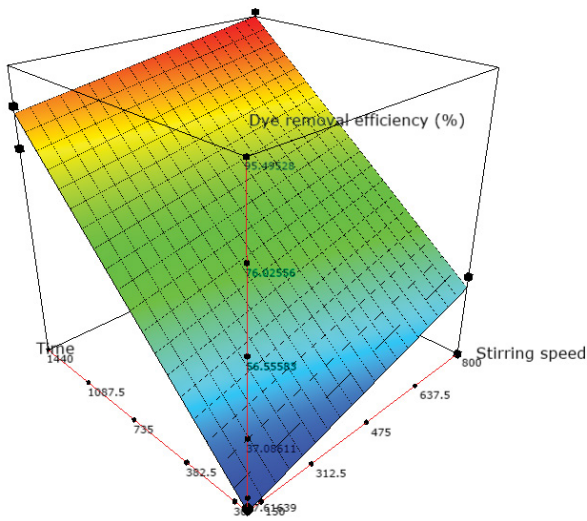


Fig. 4. Response surface as a function of stirring speed and time, at a dye concentration of 100 μM .

a new point [33]. The adjusted determination coefficients R^2 Adj. = 99.7% which indicate to the model is significant, The R^2 Pred. was in reasonable agreement with the R^2 Adj., where R^2 Pred. is 97.0%. In Table 1, as an example, for a stirring speed of 150 rpm, dye concentration of 50 μM and treatment time of 30 min, the experimental dye removal rate obtained was 18.41% and the dye removal rate predicted by the software was 19.13%, while for a stirring speed of 150 rpm, dye concentration of 500 μM and treatment time of 30 min, the respective results were 6.21% and 5.49%. This result shows very good agreements between the experimental and predicted values, so we can confirm that our model is valid.

3.5. Model verification

From the model equation, the software can calculate the dye removal rate for a stirring speed, dye concentration and treatment time that belong to the chosen range.

Fig. 7 shows the result of an experiment done in the laboratory, with a stirring speed of 800 rpm, a dye concentration of 50 μM and a treatment time of 180 min. The dye removal

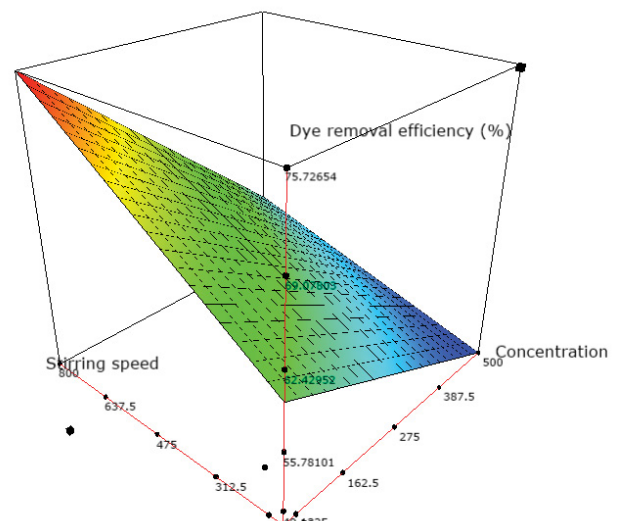


Fig. 5. Response surface as a function of stirring speed and dye concentration, at a time duration of 900 min.

rate obtained experimentally is: $y = 44.27\%$ and the dye removal rate predicted by the software is: $y = 46.75\%$. In conclusion, the result obtained by the model and that obtained experimentally are very close, with a loss of 2.7%. This confirms the validity of the model in the chosen field of study.

3.6. UV-Visible spectrum of the NR dye

The UV-Visible absorption spectra of the NR dye were studied at different times of the Fenton process. The spectrum of the NR solution (Fig. 8) has a large band in the visible range, located around 500 nm related to the azo bond and absorption band in the UV region attributed to the presence of aromatic rings [34]. The peak at 300 nm can be attributed to the cycles of naphthalene. After treatment by the Fenton process, the band at 500 nm, characteristic of the chromophore group tends to decrease with treatment time. This peak disappeared almost completely after 24 h of Fenton treatment time indicating the decolorization of NR dye. In the UV region, a decrease of peaks intensity was observed, indicating the degradation of the aromatic structure of the NR molecules [35,36].

Table 2
Analysis of variance for NR dye removal

| Source | F | P | Contribution | Status |
|---------------------------------------|----------|--------|--------------|-----------------|
| Regression | 360.2267 | 0.0403 | | Significant |
| Stirring speed | 69.1924 | 0.0762 | 11.9% | Limit |
| Concentration | 15.5923 | 0.1579 | 2.68% | Not significant |
| Time | 473.6461 | 0.0292 | 81.4% | Significant |
| Stirring speed \times Concentration | 9.1669 | 0.2031 | 1.58% | Not significant |
| Stirring speed \times Time | 10.3332 | 0.1920 | 1.78% | Not significant |
| Concentration \times Time | 2.6336 | 0.3516 | 0.453% | Not significant |
| Residuals | | | 0.172% | |

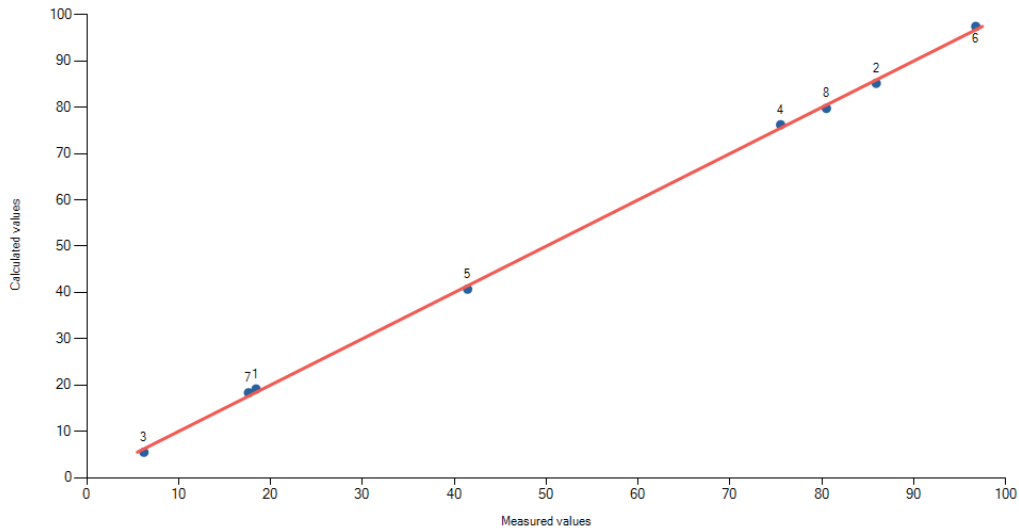


Fig. 6. Variation of the calculated values depending to the measured values.

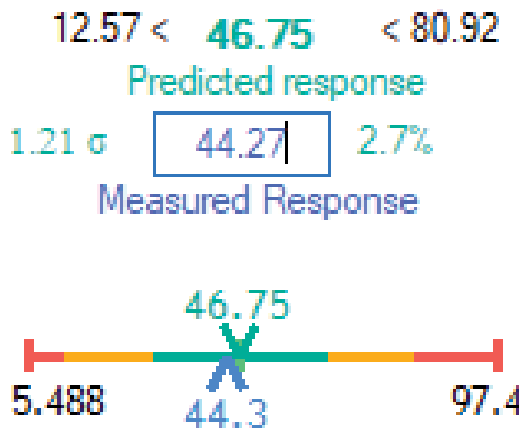


Fig. 7. Predicted response vs. measured response.

3.7. Effect of reaction time

Measurements of absorbance at λ_{max} of NR dye as a function of time gave the results shown in Fig. 9. This figure shows that for the Fenton system, the oxidation kinetics is divided into two steps: The first is fast characterized by the formation of hydroxyl radicals HO^{\bullet} , which are very reactive towards compounds existing in the dye. The second-stage, its kinetics is slow, which corresponds to the degradation of radical intermediates more refractory to oxidation.

This result is confirmed by other works found in the literature [27,37,38].

4. Conclusion

The degradation of NR dye by the Fenton process was studied using 2^3 factorial designs. Effect of three factors: stirring speed, dye concentration and treatment time was

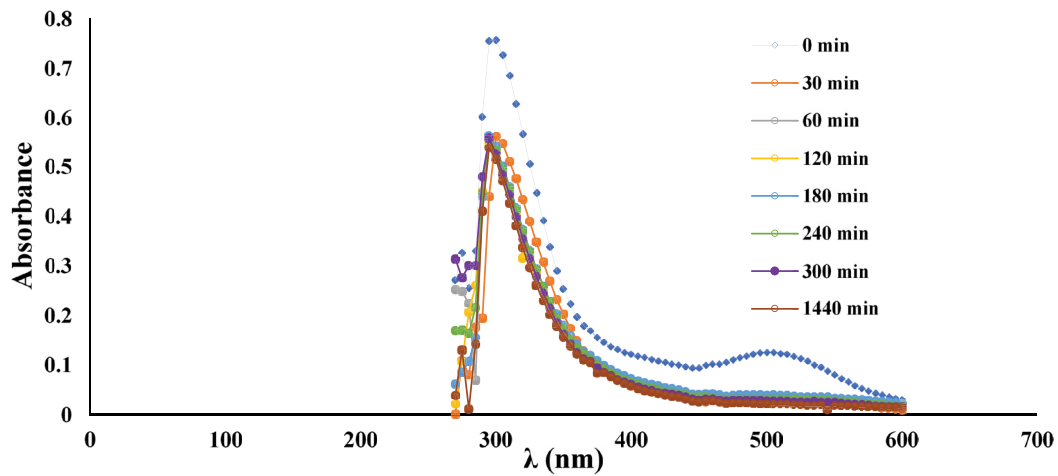


Fig. 8. UV-Vis spectrum of NR dye at different treatment times of the Fenton: pH = 3, $[Fe^{2+}] = 0.2 \text{ mM}$, $[Fe^{2+}]/[H_2O_2] = 1/20$, $[RN] = 500 \mu\text{M}$, $T = 303 \text{ K}$.

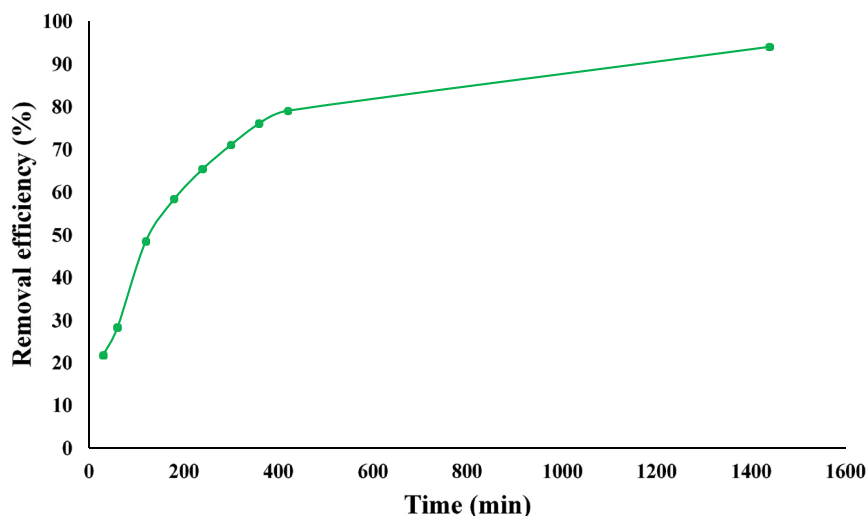


Fig. 9. Evolution of removal efficiency as a function of time. $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/20$, $[\text{Fe}^{2+}] = 0.2 \text{ mM}$, $T = 303 \text{ K}$, $\text{pH} = 3$, $[\text{RN}] = 200 \text{ }\mu\text{M}$.

investigated. The optimal reaction conditions to degrade the NR dye were: stirring speed = 800 rpm, $[\text{NR}] = 50 \text{ }\mu\text{M}$ and $t = 1,440 \text{ min}$. The corresponding experimental and predicted results of NR removal rate by Fenton treatment at the same conditions were: 96.74% and 97.46% respectively. According to the regression model and ANOVA results, the treatment time had the most significant effect on NR of 31.9%. Moreover, the interaction between dye concentration and stirring speed, and stirring speed and treatment time were the most important interactions. This finding was evaluated and confirmed using ANOVA. The high values of the determination coefficient ($R^2 = 100\%$) and the adjusted determination coefficients ($R^2 \text{ Adj.} = 99.7\%$), giving good agreement between the model and experimental data which confirmed the validity of the adopted first-order model. The experimental results obtained during this study show that the Fenton process is effective for the degradation of NR dye and the design of experiments using (RSM) can be considered as a good method for the experimental design and statistical analysis.

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