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Optimization of Reactive Dyes Degradation by Fenton oxidation Using Response Surface Method

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Abstract
The objective of this study is to determine the influence of various parameters on the degradation of dye (with high COD value) by using Fenton process. Design of experiment was applied for the optimization with respect to: initial concentration of Fe^{2+} and H_2O_2 to ascertain their respective effects on the treatment efficiency. The progress of dye degradation was analyzed by monitoring the Chemical Oxygen Demand (COD). The experimental results show that the initial concentration of H_2O_2, and Fe^{2+}, had great influence on degradation of dye by Fenton process. Application of optimum operation conditions of: Fe^{2+}/Dye = 10 and Fe^{2+}/H_2O_2= 25 at constant pH=3, mineralization of 78% was achieved for the dye with initial COD value of 1228 mg/L. Based on the degradation effciency , the optimized initial concentration of Fe^{2+} and H_2O_2 has a proven influence in treatment of wastewater with high COD value by Fenton process.

Keywords:Textile, *Reactive dyes, Response Surface Methodology, COD, chemical oxidation*

1. Introduction
Over 700 000 tons of approximately 100,000 types of dyes and pigments are manufactured annually worldwide [1] . One of the major environmental concerns in the textile industry is that approximately 140 000 tons or 20% of manufactured pigments and dyes are discharged as industrial effluents during the textile dyeing and finishing processes into natural waterways. Dyes used in textile industry are resistant to degradation under aerobic conditions. Large volume of wastewater with high dye content is released by textile industry and discharged into water bodies where it causes health problems and can be toxic to aquatic life [2].

Many different conventional approaches have been used to treat dyes such as physical adsorption, electrochemical oxidation, chemical oxidation, chemical coagulation/flocculation and biological anaerobic/aerobic decomposition [3]. All these methods are costly, inefficient, causing phase transfer of the pollutant, or resulting in the production of secondary waste products which needs additional treatment [4]. Thus, there is a need for inexpensive and more effective waste effluent treatment technology. a study inthis context is deemed mandatory as a result of the devastating effects of the pollutant on the aquatic eco systems.

Based on literature review, several papers about utilizing advanced oxidation process for the treatment of textile wastewater, textile dyes and simulated dyestuff effluents have been published. it has been reported that, Advanced Oxidation Processes (AOPs) is effective for decolourization and appreciable biodegradation of pollutants compared to conventional methods [5, 6]. The AOPs, such as UV/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$, Fe^{2+}/H_2O_2, $UV/Fe^{2+}/H_2O_2$, and UV/TiO_2 are upcoming technologies for treating wastewater as they generate a powerful nonspecific hydroxyl radical [7-9].

Among AOPs, Fenton oxidation may offer many advantages due to its environmental friendliness, high mineralization efficiency, and low operational cost [10, 11]. Besides it also, can be operated at room temperature and pressure. Fenton's reagent, a mixture of ferrous ions and hydrogen peroxide can produce • OH radicals under acidic conditions. These radicals are high oxidant species (E0 = 2.8 V versus NHE),which is characterized by low selectivity of attack, with rate constants usually in the order of 106–109 L/(mol^{-1} s^{-1}).

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

$M + \bullet OH \rightarrow HM_{oxid}$ (2)

The main objective of this work is to determine the influences of various parameters on the degradation of RBB dye by Fenton process in aqueous solution. The effects of initial concentration of H_2O_2, and Fe^{2+} were investigated to determine the optimal operating conditions for better degradation. Chemical Oxygen Demand (COD) of the mixture was determined to rate the performance of the degradation process.

2 Methodology

2.1 Materials and Analysis

The dye used in this study, Remazol Brilliant Blue (RBB) has been obtained from Sigma Aldrich. Chemical used in this study were hydrogen peroxide (30 % w/w), ferrous sulphate ($FeSO_4.7H_2O$), sulphuric acid (H_2SO_4), and sodium hydroxide (NaOH). These chemicals are of analytical grade have been purchased from Merck and used without any purification. The degradation efficiency was assessed by COD analysis using Spectroquant TR320.

2.2 Experimental procedure

The experiments were designed according to RSM using Design of Experiment (statistical software). Central Composite Design (CCD) was used. Batch experiments were conducted in 250mL beaker. The RBB of 1000 mg/L (with high COD value > 1000 mg/L) was used in all experiments. The initial pH ws fixed at 3. Required amount of ($FeSO_4.7H_2O$), was added into the reactor and pH of the solutions was adjusted with Eutech pH meter model. The pH was adjusted using dilute aqueous solution of Sulphuric Acid and Sodium Hydroxide. The experiment started with the addition of appropriate amount of hydrogen peroxide. Samples were collected at 90 minutes and analyzed. The degradation of organic matter in the solution was monitored by determination of COD. Residual H_2O_2 was confirmed by using test strips (Merck Merekoquant Peroxide Test).

3. Results and discussion

Response surface methodology (RSM) was applied in the experiments. RSM is an experimental methodology that identifies optimal conditions of a process. RSM is used to optimize the parameters which help reduce the number of experiment significantly and detect the possible interactions between the parameters.

A Central Composite Design (CCD) is used in RSM. The experimental factors and levels of the process variables studied for RBB degradation efficiency of the Fenton process are depicted in Table 1. The data were evaluated by analysis of variance [12] using Design Expert Version 8.0.1.

Table 1: Experimental range and levels of the process variables studied

Factor name	Low actual value	High actual value
Fe^{2+}: Dye	10	50
Fe^{2+}: H_2O_2	5	25

Concentration of Fe^{2+} and H_2O_2 are the primal factors in improving the efficiency of the Fenton process. However, both H_2O_2 and Fe^{2+} are capable of inhibiting the oxidation reactions if either of them is not at their optimum. On the other hand, the optimal parameters of H_2O_2 and Fe^{2+} are affected by properties of the pollutants analyses and expected degree of wastewater degradation.

The influence of the initial mass ratio of the ferrous salt and Hydrogen Peroxide, Fe^{2+}/H_2O_2, on the mineralization extent was investigated. The experiments were conducted at pH 3 due to that hydrogen peroxide and ferrous ions are more stable when pH is lower than 3.5.
In this study, a quadratic model has established the correlation between the degradation of RBB and the factors that investigated. The ANOVA results of this developed model, indicate that the model is significant for RBB degradation efficiency with a R2 value of 0.9986. For this model, P > F is less than 0.05, indicating that the term is significant in this model. A: Fe2+: Dye, B: Fe^{2+}: H_2O_2 were significant factors, and A, B, AB, B2 are significant model interactions.

The maximum degradation efficiency was reached with a mass ratio of Fe^{2+}: Dye of 1:10. RBB degradation efficiency of 78% was achieved after 90 minutes of reaction. The result obtained, connote that changes in the process variable ratio of Fe^{2+} and dye concentration within the specified range have a significant impact on COD removal. It obviously implies that the interactive effects of Fenton reagents depend on the amount of organic matter to be oxidized. According to the model, Fe^{2+} : Dye should be elevated to 1:10 to maintain the same COD removal efficiency for initial effluent COD of 1228 mg/L.

Based on the study, the response surface of the degradation efficiency increased with the increasing mass ratio of Fe^{2+} : H_2O_2 from 5 to 25. The result showed that, the maximum value of the degradation efficiency of RBB was 78 % at 10 mg of Fe^{2+} and 250 mg of H_2O_2 (Figure 1).

Table 2: Characterization of dye solutions used in the experiment

Dye	***C* (mg/L)**	**pH**	**COD (mg/L) l**	**λ_{max} (nm)**
RBB	1000	6.48	1228	510

Table 3**:** Optimum reagent doses to maximize the COD removals

Responses	Dye (mg/L)	Fe^{2+} (mg)	H_2O_2 (mg)
COD Removal	1000	10	250

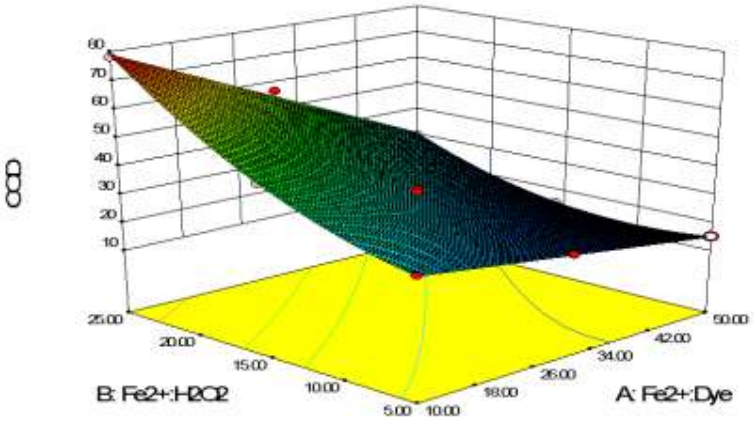

Figure 1: Plots for percent COD removal from synthetic RBB as a function of mass ratio A: Fe^{2+}: Dye, B: Fe^{2+}: H_2O_2 (t_r = 90 min; initial pH = 3).

4. Conclusion

Treatment of RBB by Fenton oxidation process was investigated in this study. The experimental results show that the initial concentration of H_2O_2, and Fe^{2+}had great influence on degradation of dye by Fenton's process. The optimal operation conditions dye oxidation by Fenton process were found to be Fe^{2+}/Dye = 10 and Fe^{2+}/H_2O_2= 25 at constant pH=3. 0. Degradation of RBB in terms of COD removal was investigated. COD values decreased from 1228 mg/L to 270 mg/L after treatment when the optimum values of the studied paarameters were applied. High level of mineralization of 78 % were achieved by using Fenton process. The study revealed that the response surface methodology and the CCD statistically experimental design could provide statically significant results for Fenton process can determine the optimal conditions to enhance the overall RBB degradation efficiency. Studied independent variables and their interactions were found to be effective for degradation

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6. References

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