Statistical Design of Experiments for Optimizing the Batch Conditions for the Degradation of Congo Red Dye Using Ruthenium Based Catalyst

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Abstract: *To reduce the total number of experiments so as to achieve highest degradation or removal of Congo red dye using Ruthenium and Nickel Oxide impregnated over Activated Carbon as a Catalyst, 4 factors (Sonication time, concentration of dye. Amount of catalyst and Hydrogen Peroxide quantity) and 2 variables were selected (16 Experiments) using factorial design. Using the Statistic tools, we obtained various plots including ANOVA, Fit model, Interaction between the factors, individual effect of the factors and finally the validation of the Design of experiment using the Regression equation obtained.*

Keywords: Congo Red, Factorial Design, Ruthenium, Nickel oxide, impregnation, ANOVA, Regression, Sonication, Bimetallic Catalyst (Ru- NiO, AOP), Waste Water Treatment, Pareto, Residual plot

1. Introduction

Water pollution is a major growing problem in the world. Water is referred to as polluted when it is gets mixed with certain impurities which make it unfit for drinking purposes or any human use. The sources of water pollution are categorized into two groups, Point sources & Nonpoint sources. Dye pollution is one of the major sources which diffuse from dye and textile industries into water hindering the basic characteristics of water i.e. Odorless, tasteless and colorless. Advance oxidation process is considered as the best and economic method to degrade these toxic dyes or chemicals present in water. It generates a highly reactive hydroxyl radical and a strong oxidant which helps to degrade the complex toxic compounds into simpler compounds. For the statistical study of Batch operations, we need to see the interaction between 4 factors which are dye concentration, catalyst quantity, sonication time and hydrogen peroxide dosage.

2. Experiment

0.5 gm of Nickel Chloride is mixed in 70ml distilled water and 0.5 gm of Ruthenium Chloride is mixed in 30 ml of ethanol. Then both the solutions are mixed together and 1gm PVP is added to the solution mixture and 9 gram of Activated Carbon is added to the mixture. The solution mixture was kept on sonication for 1 hour maintaining sonication parameter as;

1. Pulse = 05 second on / 02 second off
2. Probe temperature = 49 degree Celsius
3. Set point temperature = 70 degree Celsius
4. Amplitude = 30%
5. Timer = 1 hour.

After 1 hour of sonication the solution obtained is dried at 100 degree Celsius in hot air oven to achieve dry powder.

2.1 Degradation of Congo Red Dye

A certain volume of Congo Red dye is taken in beaker with a certain amount of catalyst. Few drops of hydrogen peroxide were added and kept on sonication for few hours. Definite volumes of resulting solution at fixed intervals of time were taken out and the samples were analysed for absorbance using UV-spectrophotometer. Percentage Degradation is then calculated according to the following formula;

$$\% \ deg = (A_i - A_f) \times 100 / A_i$$

Where,
% deg = Percentage Degradation
A_i = Initial Absorbance
A_f = Final Absorbance

3. Statistical Design of Experiments

3.1 Full Factorial Design
Table 1 and table 2 given below explain about the various factor and their levels. There are 16 number of experiment with different factor and different level which is obtained using the Minitab software 17.

Factors: 4 Base Designs: 4, 16
Runs: 16 Replicates 1
Blocks: 1 Center pts (total): 0

Table 1: Full 2^4 factorial designs

Factor	Levels	
	+1	-1
Sonication Time (hour)	2	1
Dye Concentration (PPM)	100	50
Catalyst Quantity (Gram)	1	0.5
H_2O_2 Dosage (ml)	30	10

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Table 2: Optimization of Congo Red Dye using Ru-NiO on AC

StdOrder	RunOrder	CenterPt	Blocks	time	ppm	catalyst	h2o2	%degrad
C1	C2	C3	C4	C5	C6	C7	C8	C9
6	1	1	1	2	50	1.0	10	97
14	2	1	1	2	50	1.0	30	100
11	3	1	1	1	100	0.5	30	80
7	4	1	1	1	100	1.0	10	83
4	5	1	1	2	100	0.5	10	85
12	6	1	1	2	100	0.5	30	90
16	7	1	1	2	100	1.0	30	96
15	8	1	1	1	100	1.0	30	82
1	9	1	1	1	50	0.5	10	83
10	10	1	1	2	50	0.5	30	96
3	11	1	1	1	100	0.5	10	78
2	12	1	1	2	50	0.5	10	92
8	13	1	1	2	100	1.0	10	91
9	14	1	1	1	50	0.5	30	93
13	15	1	1	1	50	1.0	30	89
5	16	1	1	1	50	1.0	10	89

4. Results & Discussion

4.1 Screening of factors for the degradation of Congo Red

The degradation of dye using the Catalyst depends on various parameters which include sonication time, dye concentration, Catalyst quantity and Hydrogen peroxide dosage. Optimization of these factors is a very hectic process, so in order to overcome this situation; we are using Statistical Design of Experiment (DOE) to optimize the whole process. For this, we are using MiniTab 17 Software to get DOE, Regression equations and ANOVA tables.

Table 3: Factorial Fit: %Degratation versus Time, PPM, pH, H2O2 Dosage

Term	Effect	Coef
Constant		89.00
time	8.75	4.3750
ppm	-6.75	-3.375
catalyst	3.75	1.875
h2o2	3.5000	1.750
time*ppm	1.0000	0.5000
time*catalyst	1.5000	0.7500
time*h2o2	0.7500	0.3750
ppm*catalyst	1.000	0.5000
ppm*h2o2	-0.7500	-0.3750
catalyst*h2o2	-1.7500	-0.8750
time*ppm*catalyst	-0.2500	-0.1250
time*ppm*h2o2	1.5000	0.7500
time*catalyst*h2o2	1.5000	0.7500
ppm*catalyst*h2o2	1.000	0.5000
time*ppm*catalyst*h2o2	-0.7500	-0.3750

4.2 Factorial Regression: RESI1 versus time, ppm, catalyst, h2o2

Analysis of Variance
Table 4: Analysis of Variance

Source		Adj SS	Adj MS
Model	15	58.2500	3.8833
Linear	4	0.0000	0.0000
time	1	0.0000	0.0000
ppm	1	0.0000	0.0000
catalyst	1	0.0000	0.0000
h2o2	1	0.0000	0.0000
2-Way Interactions	6	33.7500	5.6250
time*ppm	1	4.0000	4.0000
time*catalyst	1	9.0000	9.0000
time*h2o2	1	2.2500	2.2500
ppm*catalyst	1	4.0000	4.0000
ppm*h2o2	1	2.2500	2.2500
catalyst*h2o2	1	12.2500	12.2500
3-Way Interactions	4	22.2500	5.5625
time*ppm*catalyst	1	0.2500	0.2500
time*ppm*h2o2	1	9.0000	9.0000
time*catalyst*h2o2	1	9.0000	9.0000
ppm*catalyst*h2o2	1	4.0000	4.0000
4-Way Interactions	1	2.2500	2.2500
time*ppm*catalyst*h2o2	1	2.2500	2.2500
Error	0		
Total	15	58.2500	

Estimated effects and coefficient for %degradation in coded units.

Table 5: Regression Analysis: %DEGRATATION versus TIME, PPM, pH, H2O2 Dosage

Coefficients

Term	Coef	SE Coef	T-Value	P-Value
Constant	76.88	3.25	23.62	0
time	8.75	1.15	7.6	0
ppm	-0.135	0.023	-5.87	0
catalyst	7.5	2.3	3.26	0.008
h2o2	0.175	0.0575	3.04	0.011

S	R-sq	R-sq (adj)	R-sq(pred)
2.30119	91.07%	87.82%	81.10%

Analysis of Variance
Table 6: Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	4	593.75	148.437	28.03	0
time	1	306.25	306.25	57.83	0
ppm	1	182.25	182.25	34.42	0
catalyst	1	56.25	56.25	10.62	0.008
h2o2	1	49	49	9.25	0.011
Error	11	58.25	5.295		
Total	15	652			

4.3 Optimization for degradation of Congo Red Dye %degradation

After doing the screening of various factor for the percentage degradation of Congo Red Dye, it has been found that there are certain factor which play crucial role in degradation as shown in the fig 1 shows the factors which are significant and some are not significant and fig 2 show how different factors are interacting among themselves. And fig 3 and 4 shows how the different factors are working

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under the given level. The %degradation of Congo Red using Ru-NiO over AC catalyst follows Regression equation which is given below:

Regression Equation
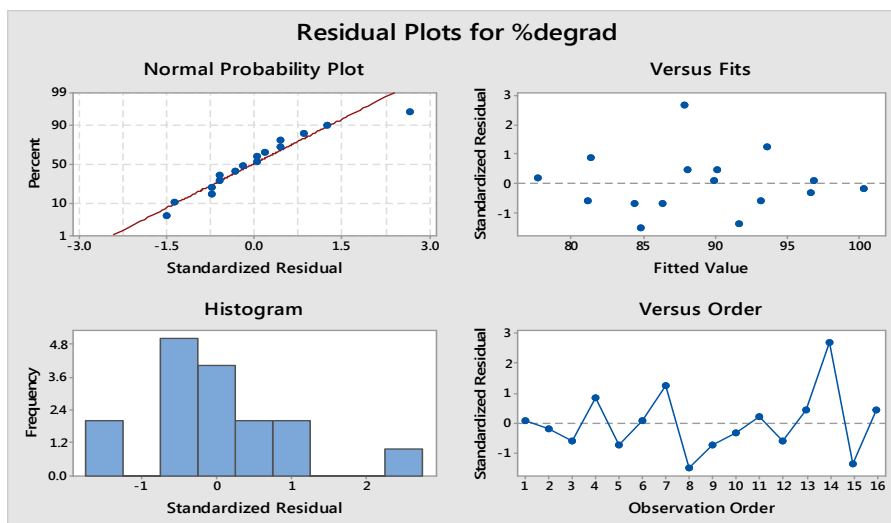%degrad = 76.88 + 8.75 time - 0.1350 ppm + 7.50 catalyst + 0.1750 h2o2

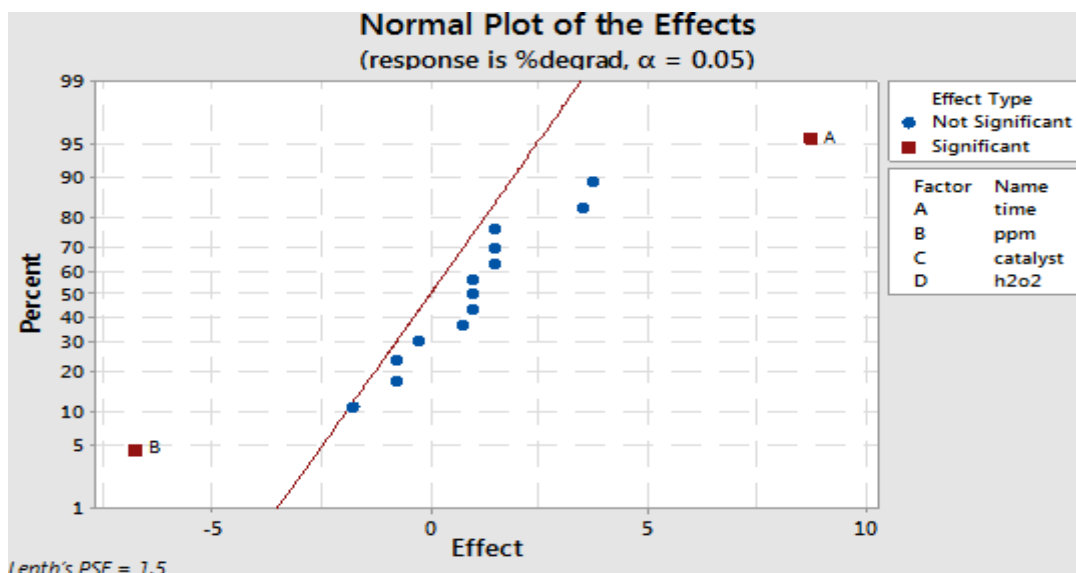**Figure 1:** Residual plot on the effect on %degradation.
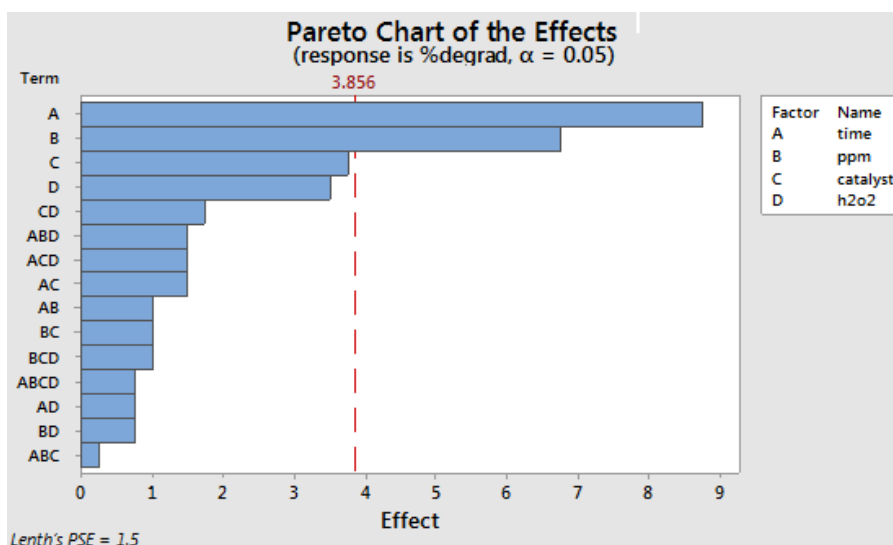

Figure 2: The normal plot of effect on %degradation.

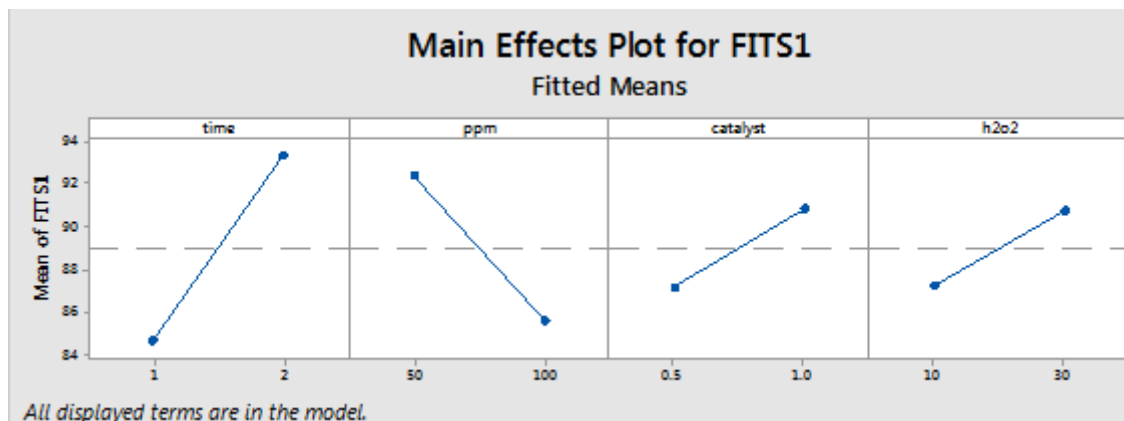**Figure 3:** The pareto chart of the effect on %degradation

Figure 4: Effect of different factor on %degradation

5. Conclusion

Full 2^4 factorial designs were applied for the screening of the factor which would influence the overall optimization of Congo red dye degradation with the Bimetallic Ru-NiO impregnated over AC catalyst. The optimum conditions for the different factors are obtained by the regression equation:
%degrad = 76.88 + 8.75 time - 0.1350 ppm + 7.50 catalyst + 0.1750 h2o2
We can validate this equation by putting up the values of any Design of experiments value, the final % degradation thus obtained should be approximately equal to the experimental values which concludes the validity of the Regression equation.

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