Degradation of Congo Red Dye Using Homogeneous Photo Fenton Catalyst Coupled with Oxygen Kinetics and Statistical Analysis

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Both authors managed the analyses of the study and managed the literature searches. Both authors read and approved the final manuscript.

ABSTRACT

Experimental design DoE (box behnken design BBD) and statistical analysis approaches were employed to determine the effect of Congo red dye (C.R) concentration, photo catalyst dose (Fe²⁺) and follow of oxygen gas as an oxidant on the degradation of C.R. The results show that the concentration oppositely affects the degradation yield whereas the remaining two factors show positive effect, throughout all experiments oxygen molecule shows crucial role in their positive effect with p-value about 0.01 which is very significant value. The accepted regression model was linear with significance p-value 0.032 that mean all factors show good agreement in linear relationship and the interactions was not important. Degradation kinetics was also applied to investigate the effect of increasing dye concentration on degradation rate constant with and without photo catalysis dose and oxidant (O₂). It appears that the degradation of peak at 498nm is second order The result was in good agreement with that of statistical analysis that are 0.0435, 0.0545 and 5.4 Mₗ·min⁻¹ with photo catalysis 12, 8 and 4 PPM dye, 4O₂ mL/min,20PPM Fe²⁺ respectively, in case without photocatalyst the results were 0.0025 and 0.0207 Mₗ·min⁻¹ with 12 and 4 PPM in turn.
Keywords: Congo red dye; kinetic of photodegradation; response surface methodology; experimental design.

1. INTRODUCTION

Due to the rapid industrialization and population increase during the later years, the demand to the chemical has been surged quickly [1,2]. Some chemicals are harmful enough to damage internal and external body tissues and cause many other diseases including cough, asthma and respiratory track problems. The most commonly used chemicals which cause the mentioned problems to human and environment are pesticides and dyes which they are widely utilized in domestic purposes, and therefor come in contact with water body through agricultural, industrial and house holding purposes [2-4].

1.1 Advanced Oxidation Process

One of the most powerful methods to overcome organic waste chemicals from environmental pollution is advanced oxidation process (AOPs), in which semiconductors (photocatalyst) are used to break down organic pollutants to its main constituents mainly CO$_2$ and H$_2$O by a process called mineralization [5].

The AOPs works when electromagnetic radiation (photons) strikes the surface of semiconductor, however, the energy of photon has to be higher than that of gap energy of photocatalyst as shown in Fig. 1. As a result the electron jumps from valence band to conduction band and then redox reaction take place; the products of reaction is oxygen free radical and the later attack the molecule of interest and degrade it as in the following diagram [2–5].

In this research ferrous ion as a homogeneous photo catalyst coupled with oxygen was studied according to the following equations:

\[ Fe^{+2} + O_2 + h\nu \rightarrow Fe^{+3} + O_2^- \]
\[ O_2^- + H^+ \rightarrow HO_2 \]
\[ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \]
\[ HO_2 + Fe^{+2} \rightarrow Fe(OH)^{+2} \]

In the photo Fenton process, the Fe(OH)$^{+2}$ is the photo active species which is responsible for photocatalytic degradation [6,7].

1.2 Statistical Analysis

Design of experiment (DOE) is a totally significant piece of chemo measurements. The universally benefits of DOE is to guarantee that the conditions between test conditions (parameters) and the result (yield) of the analyses (the reactions) can be evaluated dependably at low spending plan and exertion, for example with the insignificant number of trials and less amount of chemicals. DOE can be isolated into a few subtopics, for example, confirming factors from an enormous arrangement of factors which is called (screening structures), finding the impact of a blend organization on the reaction factors tended to (blend plans), discovering wellsprings of blunder in an estimations framework, concocting ideal conditions in consistent procedures (evolutionary operation, EVOP) or batch process (response surface methodology, RSM), or planning tests for ideal parameter estimation in numerical models (optimal design or optimization) [8].

Design of experiment models (DoE) has been applied to streamline the effect of different variable in photo catalytic degradation. Thus; to choose the effect of exploratory factors by ordinary strategies, tests were finished with conscious changes of the particular parameters the requests. These examinations ought to be rehashed to each impact parameters bringing about dependable number of runs [8,9].

It is basic to fit a scientific model condition for a reason to portray the reaction conduct in the test field by selected DOE. In general, this model is suitable for illustrating a plane surface, as indicated by the equation:

\[ R = \beta_0 + \sum \beta_i X_i + \varepsilon \]

R is the response, $\beta_0$ is the constant term, $\beta_i$ is represents the coefficients of the linear parameters, $X_i$ represents the parameters and $\varepsilon$ is the irregular blunder or commotion to the response. On specific events, it is called essential impacts model since it incorporates just the principle impacts of the factors [8–11].
If interaction between parameters is contained, then the first-order model can follow up as following equation:

\[ R = \beta_0 + \sum \beta_iX_i + \sum \beta_{ij}X_iX_j + \sum \beta_{ii}X_i^2 + \epsilon \]

Where \( \beta_{ij} \) indicates the quadratic coefficients of the variables and \( i < j \).

Response surface methodology (RSM) was applied to identify the positive and negative effect of each factor, experimental design (Box behnken design) was also utilized to select the number of required experiments for this research [1,12,13].

2. EXPERIMENTAL PART

2.1 Methods

The photocatalytic degradation were performed using ultraviolet light type (ultraviolet (UV) water sterilization lamp 220v-240v 50/6 Hz (UVC-D215 TS 6W)) as a source of radiation, temperature was kept constant at 23-24°C (ambient temperature). Effect of dye concentration, photo catalyst dose and flow rate of oxygen were studied, all on the basis of experimental design that is derived from minitab16 program (version 2018) as in Table 2.

The solution was taken for each experiment according to run order in Table 2. The mixture was irradiated under ultraviolet light for 35 minutes with continuous stirring. To follow the degradation process, small portion of sample analyze were taken out at regular time intervals; UV-Visible absorbance spectrum was recorded using (UV.-vis. Spectrophotometer type JENWAY 6335). In this research the sample was irradiated within 35 minutes and then put in dark medium for 15 minutes settle down the measurement was performed.

The percentage of dye removal with referring to the absorption spectra at \( \lambda_{\text{max}} \) was calculated using the equation:

\[ \%R = \left[ \frac{A_0 - A_t}{A_0} \right] \times 100 \]

Where \( \%R \) is the removal percent, \( A_0 \) and \( A_t \) are the absorbance at maximum absorbance, at time 0 and \( t \) minutes of photo catalytic processes, respectively [1,14].

2.2 Materials

Congo red C.R dye was supplied from ROTH, Germany and used as received, Table 1 show physical and chemical properties of CR. A stock solution of C.R 50mL/L was prepared in distilled water then diluted to other solutions according to Table 2. The prepared solution was covered by aluminum foil and kept in dark. FeSO\(_4\) was purchased from (ROTH, German) and used as received; different dose was prepared according to needs of experiment as in Table 2. Oxygen bottle was filled with oxygen gas in Kwashe area Semel, flow rate was determined according to Table 2 as well. Calibration curve was drawn and extinction coefficient was measured as in Fig. 2 and Table 4. And all experiment were done according to Table 3.
Table 1. Congo red physical and chemical properties

| IUPAC name | disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate |
|------------|---------------------------------------------------------------------------------------------------------------|
| Formula    | $C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}$                                                                         |
| Molecular weight | 696.66 g/mol                                                                                   |
| Solubility in water | soluble in water, yielding a red colloidal solution                                             |
| Absorption spectra | 497, 347 nm                                                                                   |

Table 2. Levels of the parameters studied in central composite design (ccd) statistical experiment

| Independent variable | Unit | -1(low) | 0(middle) | +1(high) |
|----------------------|------|---------|-----------|----------|
| Initial concentration of dye | ppm  | 4       | 8         | 12       |
| Amount of Fe$^{2+}$ added | mg/L | 0       | 10        | 20       |
| Amount of O$_2$ added | mL/min | 0      | 2         | 4        |

Table 3. Central composite design matrix

| Run order | Initial conc. of dye | Amount of Fe$^{2+}$ added (mg/L) | Amount of O$_2$ added (mL/min) |
|-----------|----------------------|----------------------------------|--------------------------------|
| 1         | 8                    | 20                               | 4                              |
| 2         | 4                    | 10                               | 4                              |
| 3         | 12                   | 10                               | 0                              |
| 4         | 8                    | 10                               | 2                              |
| 5         | 8                    | 0                                | 0                              |
| 6         | 8                    | 20                               | 0                              |
| 7         | 4                    | 20                               | 2                              |
| 8         | 4                    | 10                               | 2                              |
| 9         | 12                   | 0                                | 2                              |
| 10        | 8                    | 0                                | 4                              |
| 11        | 12                   | 20                               | 2                              |
| 12        | 8                    | 0                                | 2                              |
| 13        | 12                   | 10                               | 4                              |

Fig. 2. UV-Visible spectra calibration curve of congo-red dye in water as a solvent 498 nm

Table 4. Optical density and molar extinction coefficient

| Wave length (nm) | O.D. (Optical density or absorbance) | $\varepsilon$ (mol/L.cm) |
|------------------|--------------------------------------|--------------------------|
| 498              | 0.476                                | 10639                    |

$y = 0.0433x$
$R^2 = 0.9866$
Congo red is a secondary di-azo dye. It is soluble in water, yielding a red colloidal solution [15,16]. It has a solid, clearly non-covalent, liking to cellulose fibres. By the by, the utilization of Congo red in the cellulose industries (cotton material, wood mash and paper) has been relinquished, essentially in view of its poisonous quality and inclination to run and change shading when contacted by sweat-soaked fingers [11,17,18].

3. RESULTS AND DISCUSSION

3.1 Experimental Design

Statistical analysis was employed to determine the effect of each factor and their interactions, to select the best model, all models was investigated and for this work linear model showed the best agreement among other models, the following regression equation was obtained:

\[ y = 4.48 - 0.049 X_1 + 0.144 X_2 + 1.35 X_3 \]

Where \( y, X_1, X_2 \) and \( X_3 \) are percentage of C.R. degradation, initial dye concentration, amount of FeSO\(_4\) as catalyst and the follow rate of oxygen gas through the solution respectively.

Regression equation shows that the initial concentration has negative effect that means when dye concentration is increased the degradation is lead to decreas, while the other two factors shows positive effect [1].

The two Tables 5 and 6 show analysis of variance (ANOVA) and the measured percentage of degradation respectively with the fitting or predicted one on the bases of regression equation. Figs. 3 and 4 show contour plot, and residual plot for the current work [11].

The absorbance of Congo red in water has been recorded at \( \lambda_{\text{max}} \) of 497 nm was estimated by an UV-noticeable spectrophotometer Perkin-Elmer Lambda 25 utilizing a matched 1.0 cm quartz cell. The abatement of absorbance estimation of tests at \( \lambda_{\text{max}} \) of color after illumination by light in a specific time interims demonstrated the pace of debasement and thusly, photograph corruption productivity of the color. The debasement rate was determined as:

\[
\% \text{ of degradation} = 100 \times \left( \frac{C_o - C_t}{C_o} \right) = 100 \times \left( \frac{A_o - A_t}{A_o} \right)
\]

Where, \( C_o \) and \( C_t \) are the initial concentration and the concentration of dye in time of \( t \), respectively, \( A_o \) and \( A_t \) are the absorbance before degradation and the absorbance of sample in time \( t \), respectively and \( t \) is irradiation time.

3.2 Kinetic Study

The rate of Congo-red degradation has been estimated by examining degradation of peak at (498nm). Different methods were applied including, plotting log-log graphical method, the theoretical approach and correlation coefficient have been used in order to determine the order of CR degradation. It appears that the degradation of peak 498nm is second order as in the following two Figs. 5 and 6 [15–17,19,20]. Table 7 shows rate constant with and without catalyst, it shows that concentration inversely affects the degradation yield in both cases this may be due to the fact that high concentration quenches photo degradation process through two ways, formation of excimer and explex and formation of new molecule as an intermediate product which absorb the light and decrease the quantum efficiency [2,4,5,21,22].

![Contour plot of Congo red photo catalytic degradation: FeSO\(_4\) vs O\(_2\); dye conc. vs O\(_2\); FeSO\(_4\) vs dye conc](image-url)
Table 5. ANOVA results for the degradation of congo red dye

| Source                        | DF | F-value | P-Value |
|-------------------------------|----|---------|---------|
| Model                         | 3  | 4.61    | 0.032   |
| Linear                        | 3  | 4.61    | 0.032   |
| Initial concentration of dye  | 1  | 0.05    | 0.832   |
| Amount of Fe²⁺ added          | 1  | 2.96    | 0.119   |
| Amount of O₂ added            | 1  | 10.66   | 0.010   |

Table 6. Calculated percentage of degradation with predicted (fitted) percentage of Congo red degradation

| Obs. | % of deg. observed | %Fitted |
|------|--------------------|---------|
| 1    | 11.027             | 12.374  |
| 2    | 10.820             | 11.132  |
| 3    | 3.103              | 5.328   |
| 4    | 7.027              | 8.230   |
| 5    | 3.090              | 4.086   |
| 6    | 4.082              | 6.964   |
| 7    | 10.526             | 9.866   |
| 8    | 8.725              | 5.722   |
| 9    | 8.436              | 6.594   |
| 10   | 8.459              | 9.496   |
| 11   | 13.613             | 9.473   |
| 12   | 7.553              | 6.791   |
| 13   | 10.334             | 10.739  |

Table 7. The rate constant k of congo-red degradation at different condition

| No. | Experiment                          | Rate constant (M⁻¹.min⁻¹) |
|-----|-------------------------------------|---------------------------|
| 1   | 12 ppm dye, 4O₂ mL/min, 20PPM Fe²⁺  | 0.0435                    |
| 2   | 8 ppm dye, 4O₂ mL/min, 20PPM Fe²⁺  | 0.0549                    |
| 3   | 4 ppm dye, 4O₂ mL/min, 20PPM Fe²⁺  | 5.408                     |
| 4   | 12 ppm Dye, without catalysis      | 0.0025                    |
| 5   | 4 ppm Dye, without catalysis      | 0.0207                    |

Fig. 4. Residual plot
CONCLUSION

All things considered, on the basis of statistical analysis combination effects of the three factors (dye concentration, photo catalyst dose and amount of oxygen as the oxidant)) were studied and it was found that the proportion is linear with the p-value 0.032 with regards to linear model, and according to the current work the amount of oxygen has a positive significant effect with p-value 0.01. On the other hand dye concentration affects negatively that has been shown in regression equation, further experiment was carried out to estimate this negatively effect of dye concentration and kinetics were also studied as well, the results were in agreement with that of design of experiment data the reason behind this is quenching of formed new product with radiations. The degradation was much higher in case of catalyst than that without catalysis as shown in Tables 6 and 7.

SUGGESTION FOR FUTURE WORK

Further researches are going to be done so that to find out a super active photo catalyst that can be used in domestic and industrial purposes.
COMPETING INTERESTS

Authors have declared that no competing interests exist.

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