Chemical Engineering Journal 157 (2010) 427–433

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Sonochemical degradation of Congo red: Optimization through response surface methodology

Kannappan Panchamoorthy Gopinath, Karuppan Muthukumar*, Manickam Velan

Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai 600 025, India

ARTICLE INFO

Article history:
Received 26 August 2008
Received in revised form 2 December 2009
Accepted 3 December 2009

Keywords:
Congo red
Sonolysis
RSM
Oxidative species

ABSTRACT

The pollution due to textile dye effluents has been a major concern and the investigations involving various efficient techniques are being carried out to overcome this problem. This study presents the degradation of Congo red, an azo dye, using ultrasound and the degradation process was optimized by response surface methodology (RSM). The dye solution was subjected to ultrasound irradiation of 30 kHz at various initial concentrations and pH. The results showed that the initial dye concentration and pH of the dye solution influenced the % decolorization and low initial values resulted in high % decolorization. The toxicological studies were carried out with bioluminescent assay indicated that the resulting products of sonolytic degradation were non-toxic. The production of oxidative species during the degradation was analyzed spectrometrically using iodometry and Fricke dosimetry. The degradation of Congo red was also confirmed by spectrograms obtained at different time intervals. Kinetic studies were carried out to determine the rate of the reaction and the influencing parameters such as pH and initial concentration were optimized using response surface methodology (RSM).

1. Introduction

In recent decades, the pollution of water sources by industrial effluents has been a major concern and the investigations involving various techniques are carried out to successfully face this problem. Effluents discharged by textile dyeing, food additives, cosmetics and printing industries are rich in color and this create aesthetic problem to the public. The color is mainly due to the usage of dyes and they differ in their classification mainly based on their functional groups. Azo dyes, an important class of dyes, contribute about 70% of the total dyes used [1] and are found to be genotoxic and mutagenic to human population and other living beings [2–4]. Government agencies are enforcing stringent rules and regulations, especially in the developed countries, with respect to the treatment of industrial effluents containing dyes [5].

The azo dyes containing azo bonds (–N=N–) have complex structure that resist biodegradation under aerobic conditions [6]. On the other hand, the reduction reaction of azo bond gives colorless aromatic amines which are known to be carcinogenic and toxic [7]. In such cases, the treatment of azo dye containing effluents by aerobic degradation yield aromatic amines and for which the final fate in the environment is almost unknown. Over the past few years, various advanced oxidative processes, and many hybrid technologies, to completely or partially degrade the azo dyes into non-toxic end products, are reported [8,9]. Recently, significant interest has been shown in the application of ultrasound for the degradation of dyes [6,10–12]. Sonochemical reactions are induced by directing high frequency waves into liquids thereby producing cavitation bubbles known as micro-bubbles and the adiabatic collision of such bubbles creates extreme temperature and pressure, which induce pyrolytic fragmentation reactions [13].

Sonochemical degradation of Basic Blue 41 [14], C.I. Direct Red 23 [15], Methyl Orange [16], C.I. Reactive Black 5 [17], C.I. Reactive Yellow 84 [18] and Remazol Black B [19] have been reported in the literature. Furthermore, the influence of various parameters on sonolytic degradation of dyes was also reported to optimize the process. In contrast to the classical optimization processes, which did not account the effect of different combination of parameters, response surface methodology (RSM) provides elaborative vision over various combinations of parameters. RSM is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses [20,21]. RSM is an important tool to develop novel processes, optimizing their performance and improving their design and formulation of new products. RSM shows promising results in industrial research, especially where large number of variables influences the system [22]. Hence, the main aim of the present

* Corresponding author. Tel.: +91 44 22203545x21.
E-mail addresses: muthukumar@annauniv.edu, chemkmk@gmail.com (K. Muthukumar).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.12.002

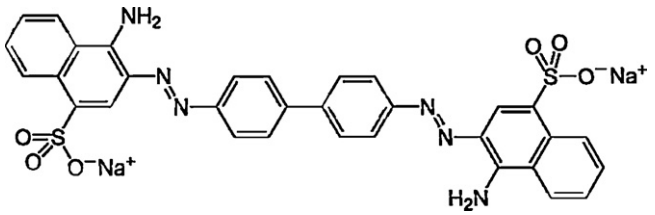

Fig. 1. Structure of Congo red.

study was to investigate the sonochemical degradation of Congo red and to optimize the process using RSM.

2. Materials and methods

2.1. Chemicals and reagents

Congo red was obtained from S.D. Fine-Chemicals Ltd. (Mumbai, India) and was used as supplied and its chemical structure is shown in Fig. 1. Analytical grade NaOH (S.D. Fine-Chemicals) and HCl (Merck) were suitably diluted with deionised water and used for the adjustment of pH.

The oxidative species were analyzed using Solution A, Solution B and Fricke solutions. Solutions A and B were prepared by following the procedure described by Klassen et al. [23]. Solution A was prepared by mixing 33 g of KI, 1 g of NaOH and 0.1 g of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ in 500 ml of distilled water. Solution B was prepared by mixing 10 g of potassium hydrogen phthalate in 500 ml of distilled water. The Fricke solution was prepared with 1 mM of $Fe(NH_4)_2(SO_4)_2$, 0.4 M of H_2SO_4 and 1 mM of NaCl contained in 250 ml of dye solution.

2.2. Ultrasound equipment

The schematic diagram of the experimental setup is shown in Fig. 2. A tank type sonochemical reactor was obtained from Saisonics (Chennai, India) with an operating frequency of 30 kHz. The tank was made up of stainless steel and the bottom of the tank was fitted with ultrasonic transducer. The equipment was provided with timer control and temperature indicator.

2.3. Decolorization experiments

The dye solution of known concentration was loaded into the tank of the sonochemical reactor and irradiated for a definite

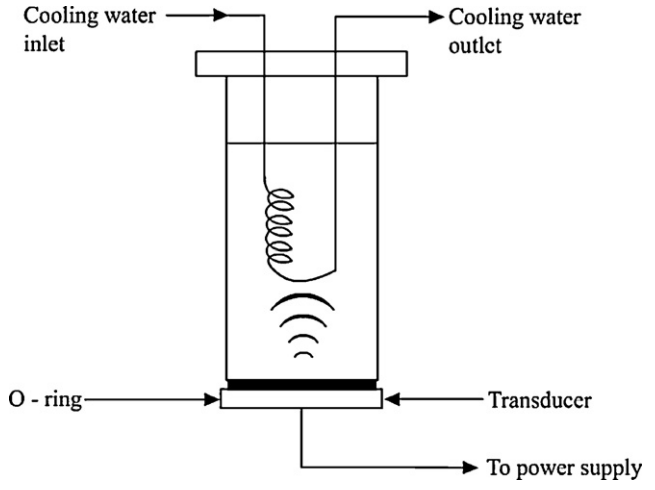

Fig. 2. Experimental setup for sonochemical reactor.

period. At constant time intervals, samples were withdrawn and analyzed for its absorbance at 510 nm. To study the effect of pH, sonication was conducted at various initial pH (i.e., 3–9). The effect of initial dye concentration was investigated by varying the dye concentration from 100 to 500 mg/l. The % decolorization was determined as given below:

$$\%\text{Decolorization} = \frac{[\text{dye}]_i - [\text{dye}]_o}{[\text{dye}]_i} \times 100 \quad (1)$$

where $[\text{dye}]_i$ is the initial dye concentration (mg/l) and $[\text{dye}]_o$ is the observed dye concentration (mg/l) at time t (min).

2.4. Analysis of oxidative species

The oxidative species production during sonication process was analyzed using Fricke dosimetry and iodide dosimetry. Formation of hydroxyl radical ($OH^\bullet$) was confirmed by iodide dosimetry which follows the reaction scheme as given below:

$$OH^\bullet + I^- \rightarrow OH^- + I_3^- \quad (2)$$

Aliquots of the sonicated dye solution were added into quartz cuvette containing an equal amount of solutions A and B. Absorbance was recorded at 351 nm to determine the formed I_3^-.

Formation of the $OH^\bullet$ and H_2O_2 was confirmed by oxidation of Fe^{2+} into Fe^{3+} and the corresponding scheme is given in Eqs. (3) and (4):

$$Fe^{2+} + OH^\bullet + H^+ \rightarrow Fe^{3+} + H_2O \quad (3)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH^\bullet \quad (4)$$

The Fricke solution containing dye sample (1000 ml of 300 mg/l Congo red) was loaded into the sonicator. Samples were withdrawn at regular time intervals and the Fe^{3+} formed during sonication by above mentioned reaction scheme was determined using UV spectrophotometer at 304 nm and to avoid the effect of inferences, Congo red solutions of any time 't' were used as a blank.

2.5. Degradation analysis

Sonicated samples withdrawn from the reactor were suitably diluted with distilled water and then analyzed with UV–vis spectrophotometer to determine changes in its absorption spectrum (300–700 nm).

2.6. Toxicity measurements

The toxicity of the dye solution (sonicated and non sonicated) was determined by Microtox Model 500 analyzer, which utilizes freeze dried *Vibrio fischeri* bacteria as test organisms. The basic principle of this test system is bacterial cellular activity inhibition in the presence of toxic compounds which results in a reduction in the degree of luminescence which in turn is used as a measure of toxicity.

2.7. Kinetic study of sonolysis of Congo red

The rate equation for the sonolytic degradation of Congo red was arrived assuming quasi-steady-state and is given in Eq. (5). The detailed explanation and derivation of this expression is given in Appendix A:

$$r_{CR} = \frac{k_q[\text{dye}]}{1 + K_q[\text{dye}]} \quad (5)$$

where $k_q = k_d k_{CR}/k_1[H_2O_2]$ and $K_q = k_{CR}/k_1[H_2O_2]$.

Table 1
RSM design for ultrasonic decolorization.

Run order	Concentration	pH	%Decolorization (experimental)	%Decolorization (predicted)
1	200	4	83.5	83.42
2	100	5	83.4	85.33
3	300	3	84.1	83.59
4	100	3	96.7	97.99
5	200	4	83.2	83.42
6	200	4	83.4	83.42
7	341.421	4	71.01	71.56
8	58.579	4	95.9	93.91
9	200	2.58	95	94.73
10	300	5	68	68.13
11	200	5.41	76	74.83
12	200	4	83.5	83.42
13	200	4	83.5	83.42

Sonolytic degradation of Congo red was carried out at various initial dye concentrations and from that initial rates were obtained, which were in turn used for the determination of rate constants.

2.8. Experimental design and optimization by central composite design (CCD)

Optimum condition for the sonochemical decolorization of Congo red was determined by response surface methodology (RSM) and the important class of second-order design called central composite design (CCD) was used for the analysis. Optimization studies were carried out by considering the effect of two variables such as, initial dye concentration and pH of the dye solution. To describe the effect of initial dye concentration and pH of the dye solution, a 2^2 full factorial CCD leading to 13 sets of experiments were performed. The independent variables chosen in this study were coded according to the equation given below:

$$x_i = \frac{X_i - X_o}{\Delta X} \quad (6)$$

where x_i is the dimensionless coded value of the ith independent variable, X_o is the value of X_i at the center point and ΔX is the step change value. The experimental design and results of the CCD were shown in Table 1. The behaviour of the system is explained by the following second-order polynomial model:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2 \quad (7)$$

where Y is the predicted response (% decolorization); x_1 and x_2 are the code forms of the input variables such as initial dye concentration and pH, respectively; b_0 is a constant; b_1 and b_2 are the linear coefficients; b_{11} and b_{22} are the quadratic coefficients; b_{12} is a cross-product coefficient. A statistical program package was used for regression analysis of the data obtained and to estimate the coefficients of the regression equations. Analysis of variance (ANOVA) was used for graphical analysis of the data in order to obtain interaction of process variables with the response. The quality of fit of polynomial model equations was expressed by the coefficient of determination R^2.

3. Results and discussion

3.1. Decolorization studies

The results of decolorization experiments at various conditions showed that Congo red can be effectively decolorized by the sonication process. The process was found to be efficient and generating less toxic secondary pollutants, which can easily be eliminated from the system by subjecting further to biological treatment.

3.1.1. Effect of initial concentration

The variation of % decolorization at various initial dye concentrations (100–500 mg/l) with respect to time is shown in Fig. 3. The results clearly showed that the %decolorization was decreased with an increase in initial concentration of the dye. The %decolorization was found to be a function of concentration, though the oxidative species play a very important role in it. The formation of oxidative species at different dye concentrations plays a critical role in decolorization. The oxidative species produced may not be sufficient to oxidize the dye molecules as the concentration of dye was increased. So it is evident that the initial dye concentration has significant influence on the decolorization process, considering other parameters are stable.

3.1.2. Effect of pH

The effect of initial pH on sonolytic degradation of dye was studied and the results are shown in Fig. 4. The decolorization was facilitated by low pH levels, due to the protonation of negatively charged $-SO_3^-$ groups and the resulting molecules are highly hydrophobic in nature, which enhanced the reactivity. The hydrogen loss from the protonated sites was occurred in alkaline medium and this resulted in the hydrophilic characteristic of the molecules, which inhibited the decolorization [6,26].

3.2. Analysis of oxidative species

The formation of hydrogen peroxide, during sonolysis, was observed through iodimetry. The formation of oxidative species was initiated by the homolytic cleavage of water molecules by pyrolytic reactions. Both $OH^\bullet$ and H_2O_2 molecules are strong oxidants and their production rates depend on the final temper-

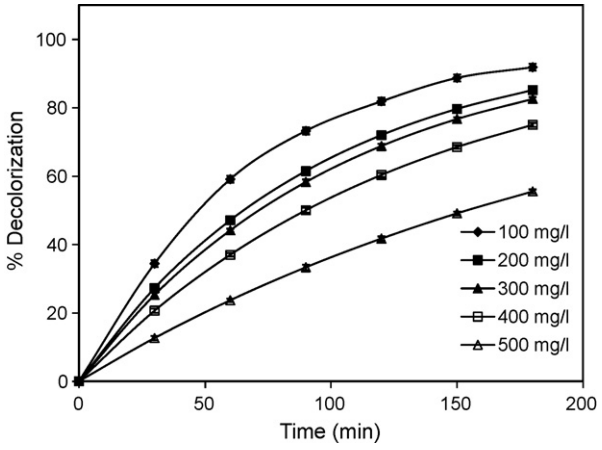

Fig. 3. Effect of initial dye concentration on decolorization.

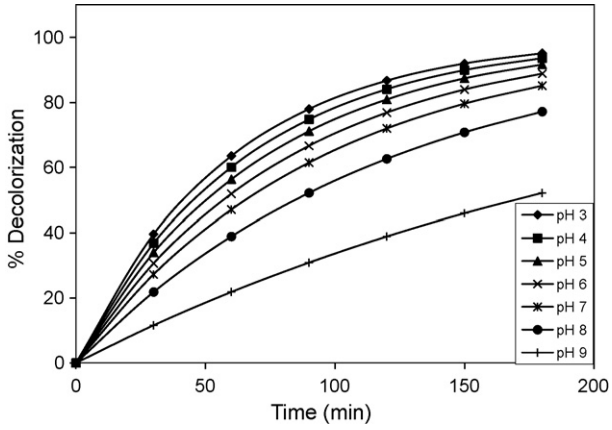

Fig. 4. Effect of pH on decolorization.

ature and pressure at the time of bubble collapse. The Fricke and iodine dosimeters confirmed the formation of oxidative species in the present investigation. The hydrogen peroxide formation with respect to time is shown in Fig. 5 and the rate of hydrogen peroxide production was found to be 1.02 mM/min. The formation of Fe^{3+} with respect to time is shown in Fig. 6 and the rate of formation of ferric ions was found to be 0.01 mM/min. From Eqs. (3) and (4), it can be seen that the formation of Fe^{3+} ions mainly depend upon the concentration of oxidative species.

3.3. Degradation analysis

The continuous UV–vis spectrograms of the treated Congo red solution were obtained at different time intervals and the results are shown in Fig. 7. The absorption spectra of Congo red show two distinct peaks, the first at near UV region (300–350 nm) and the second at near visible region (500–600 nm). A peak near UV region is responsible for molecules having benzene like structures and the latter is responsible for the dark red color of aromatic rings pertaining to azo groups [24]. The decay of both peaks can be clearly observed from Fig. 7. The decay of peak at visible region is due to the fragmentation of the azo links by immediate $OH^{\bullet}$ attack (hydroxylation) [13], which is proposed as the first step in the degradation of the azo dyes [25].

The disappearance of peak near UV region is considered as the evidence of aromatic fragment degradation in the dye molecule and its intermediates. The decay of these peaks may be compared with the degradation rate of Congo red shown in Fig. 3. As treatment time increased the decolorization, in turn amplitude of peak, decreased. The % decolorization increased with respect to the treatment time and correspondingly the amplitude of the peak decreased with respect to time.

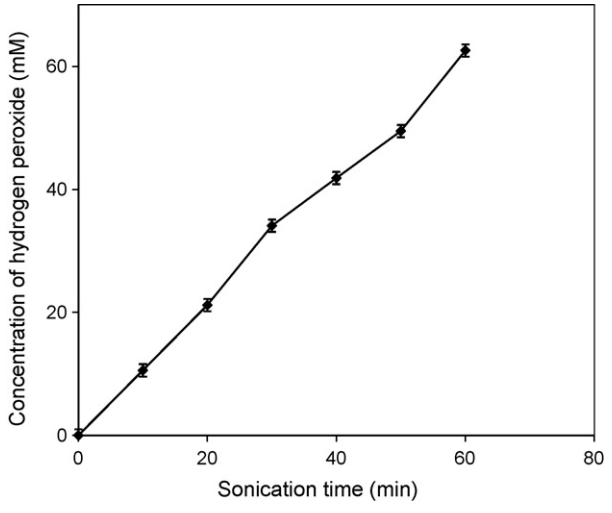

Fig. 5. Effect of sonication time on concentration of hydrogen peroxide (300 mg/l Congo red, pH 7).

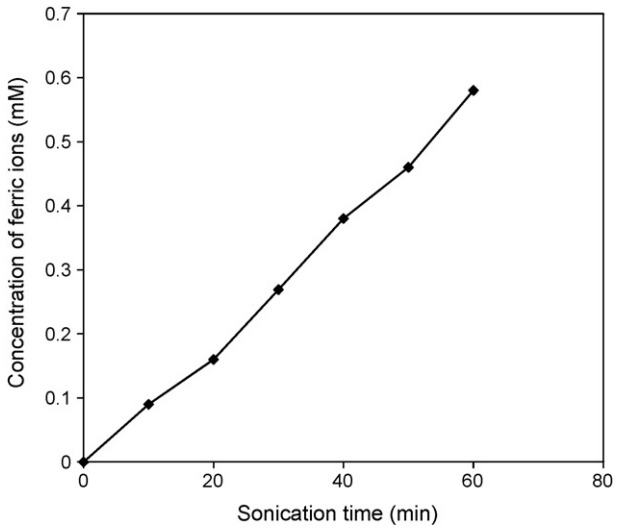

Fig. 6. Effect of sonication time on concentration of Fe^{3+} (300 mg/l Congo red, pH 7).

3.4. Toxicity analysis

Oxidative degradation processes may produce organic intermediates which are more toxic sometime than the dye. So to analyze the toxicity of the intermediate samples, bioluminescence assay was carried out with marine bacteria *V. fischeri*. The inhibition was measured for every 1 h and the assay showed no toxic intermediates. Therefore, it can be concluded that under the experimental conditions followed in this study, the compounds obtained after the degradation showed no harmful effects.

3.5. Kinetics

The rate equation given by Eq. (5) was found to fit the experimental data well and the results are shown in Fig. 8. Kinetic parameters k_q and K_q values were obtained with Matlab7.0 and values are 6.85×10^{-3} min^{-1} and 2.1×10^{-3} l/mg, respectively. The

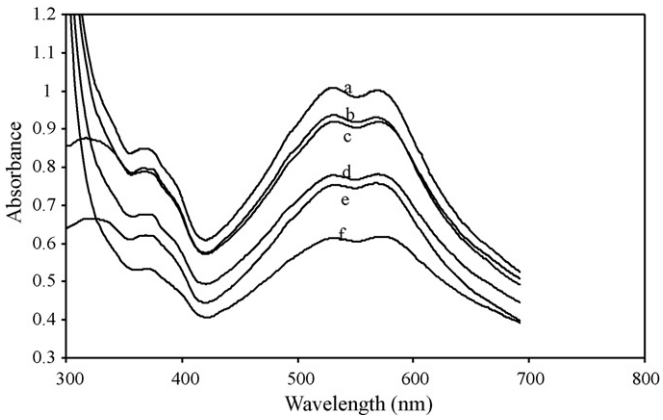

Fig. 7. Changes in absorption spectra during sonochemical degradation of 300 mg/l of Congo red at various time intervals (a: 0 min; b: 30 min; c: 60 min; d: 90 min; e: 120 min; f: 150 min).

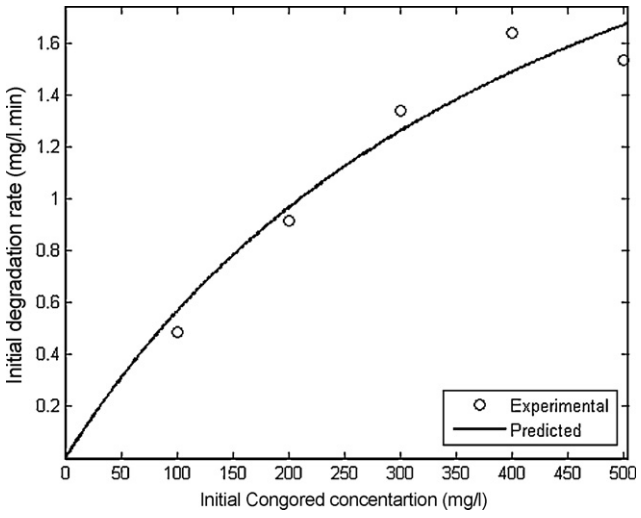

Fig. 8. Kinetic model for sonolytic degradation of Congo red.

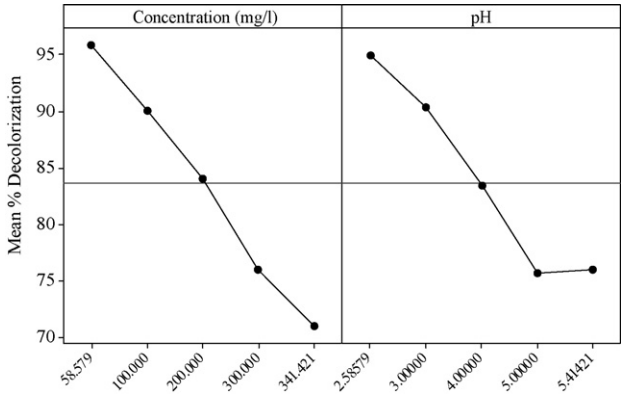

Fig. 9. Main effect plots for concentration and pH.

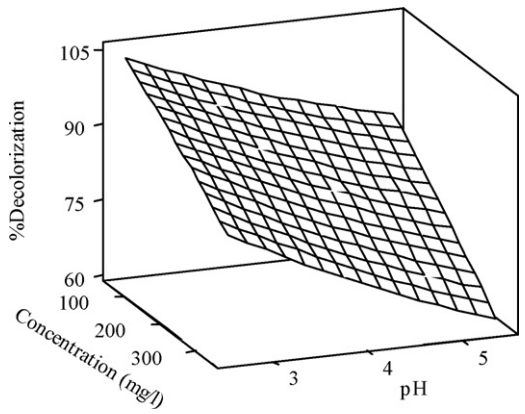

Fig. 10. Response surface area plot.

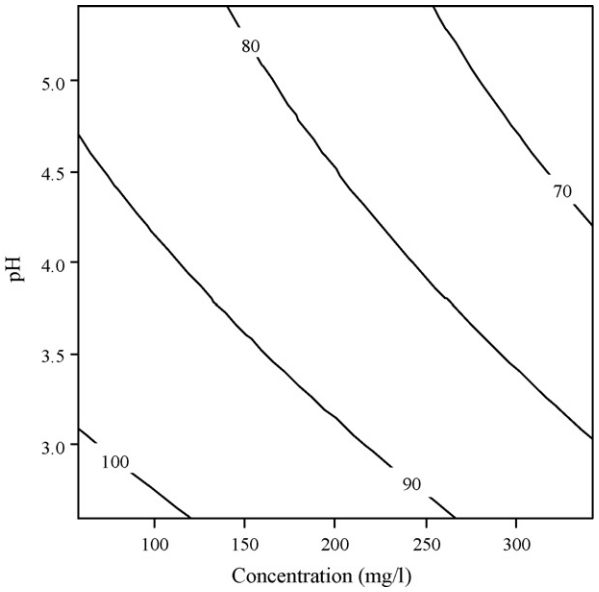

Fig. 11. Contour plot (–70–, –80–, –90–, –100– are %decolorization values).

kinetic equation for sonolytic degradation of Congo red is given as

$$r_{dye} = \frac{0.00685 \cdot [\text{dye}]}{1 + 0.0021 \cdot [\text{dye}]} \quad (8)$$

Similar studies have been reported for sonolytic degradation of Rhodomine blue and Rhodomine B by Priya and Giridhar [27].

3.6. Optimization studies

3.6.1. Experimental design analysis

The batch runs were conducted with experiments designed through CCD to visualize the effects of independent factors on responses and the results were evaluated. Approximating function obtained for decolorization is given as

$$\begin{aligned}\%\text{Decolorization} = {} & 131.33 - 0.037 \cdot \text{Concentration} - 11.1 \cdot \text{pH} \\ & - 3.4 \times 10^{-5} \cdot \text{Concentration}^2 + 0.6831 \cdot \text{pH}^2 \\ & - 0.007 \cdot \text{Concentration} \cdot \text{pH} \end{aligned} \quad (9)$$

ANOVA results of these quadratic models are presented in Table 2, indicating that these quadratic models can be used to navigate the design space. Based on Eq. (9), the global optimum solution for the system is 58 mg/l of initial Congo red concentration and initial pH 3. These values render 100% decolorization when testified for regression model Eq. (9).

3.6.2. Effect plot

The effect of variables on the response (%decolorization) could be analyzed from the effect plots. The main effect plot for the

Table 2
ANOVA table for design analysis.

Source	Degrees of freedom	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	5	901.572	901.572	180.314	110.49	0.000
Linear	2	895.066	895.066	447.533	274.24	0.000
Square	2	4.546	4.546	2.273	1.39	0.310
Interaction	1	1.960	1.960	1.960	1.20	0.309
Residual error	7	11.423	11.423	1.632		
Lack-of-fit	3	11.355	11.355	3.785	222.65	0.000
Pure error	4	0.068	0.068	0.017		
Total	12	912.995				

Table 3
Comparison of decolorization percentages and time requirements of Congo red using different methods (as available in literature).

S. No.	Method	Congo red concentration (mg/l)	Percent removal/time	Refs.
1.	Fungal degradation (*Aspergillus sojae* B – 10)	10	93%/5 days	[28]
2.	Bacterial degradation	100	100%/14 h	[29]
	(*Pseudomonas luteola*)	210	100%/20 h	
3.	Bacterial degradation (*Bacillus* sp.)	100–300	100%/24–27 h	[30]
4.	Sono + Bacterial degradation (*Bacillus* sp.)	100	100%/8 h	[30]
5.	Bacterial (mutant) degradation (*Bacillus* sp. ACT1)	100–1000	100%/18–36 h	[31]
6.	Sonochemical degradation	100	93.4%/3 h	Present study

concentration and pH is shown in Fig. 9. The individual significance of these variables can be predicted from this plot. The concentration was already established as an important parameter controlling the %decolorization of the process and this also has been confirmed from this analysis. The decrease in %decolorization was occurred with an increase in initial concentration.

The combined effect of pH and initial concentration was also analyzed. In classical optimization, one variable is changed at a time keeping remaining parameters as constant. Whereas RSM examines the simultaneous influence of all the involved variables and hence, the main effect plot obtained in this study describes not only the effect of change of one variable but a combined effect of change in both the variables, which is exclusively expressed by considering one variable into account. The plot implies that the change in concentration and pH of the dye solution influences the %decolorization significantly. There was a decrease in the %decolorization with an increase in pH, though the rate of decrease of response is relatively slowed down when the pH was above 5.

3.6.3. Response surface plots

The response surface area and the response surface contour plots are shown in Figs. 10 and 11, respectively. From these plots, it can be interpreted that the %decolorization may reach the level of 100% at pH below 3.2 and initial concentration of dye below 120 mg/l. A significant %decolorization (more than 90%) could be achieved below the initial dye concentration level of 250 mg/l and the pH level of 4.7.

3.7. Comparison with other methods

Sonolytic decolorization process is considered as an efficient process due to its less time consumption compared to other methods reported. Table 3 compares the percentage degradation values and time required to achieve that by various methods reported in the literature with present study. It can be observed from the table that among the methods reported in the literature, sonolytic degradation could provide efficient degradation at lower time.

4. Conclusions

The present study demonstrated that sonolysis is a promising technique for the degradation of Congo red and the following conclusions were arrived from the investigation:

(i) Complete decolorization of Congo red can be achieved using sonochemical degradation.
(ii) The analysis of oxidative species confirmed the production of hydrogen peroxide and hydroxyl radical species under sonolysis and which are responsible for the degradation of Congo red.
(iii) The toxicological studies with bioluminescent assay showed that the products of sonochemical degradation of Congo red were non-toxic.
(iv) The optimum decolorization was achieved at lower pH values (below 4) due to protonation of sulphate ions in acidic medium.
(v) The kinetic mechanism pertaining to the degradation of Congo red was analyzed and the rate equation proposed was found to fit the experimental data well.
(vi) Response surface methodology was used to optimize the initial Congo red concentration and pH values and the optimum values of initial concentration and pH were found to be 58 mg/l and 3, respectively.

Appendix A.

During the sonolysis of Congo red (CR), dye molecules decompose as per the following mechanism

$$\text{Congo red} + \text{OH}^\bullet \xrightarrow{K_{CR}} \text{End products} \tag{A1}$$

Being a batch process, the system can be considered as a closed system. Therefore quasi-steady-state assumption can be used to illustrate the kinetics of sonolysis of Congo red.

Hence,

$$r_{CR} = -\frac{d[\text{dye}]}{dt} \tag{A2}$$

$$r_{CR} = k_{CR} \cdot [\text{dye}] \cdot [\text{OH}^\bullet] \tag{A3}$$

where [dye], $\text{OH}^\bullet$ and K_{CR} are Congo red concentration, hydroxyl radical concentration and rate constant, respectively. Concentration of hydroxyl radicals present mainly depends upon the following three reactions:

(1) Thermolytic dissociation of water:

$$\text{H}_2\text{O} \xrightarrow{k_d} \text{OH}^\bullet + \text{H}^\bullet \tag{A4}$$

(2) Formation of hydrogen peroxide:

$$\text{OH}^\bullet + \text{OH}^\bullet \underset{k_r}{\overset{k_f}{\Leftrightarrow}} \text{H}_2\text{O}_2 \tag{A5}$$

(3) Possible side reaction:

$$\text{H}_2\text{O}_2 + \text{OH}^\bullet \xrightarrow{k_1} \text{HO}_2^\bullet + \text{H}_2\text{O} \tag{A6}$$

where k_d, k_f, k_r and k_1 are rate constants.

Mass balance equations for $[\text{H}_2\text{O}_2]$ and $[\text{OH}^\bullet]$ are given as

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_f[\text{OH}^\bullet]^2 - k_r[\text{H}_2\text{O}_2] - k_1[\text{H}_2\text{O}_2][\text{OH}^\bullet] \tag{A7}$$

$$\frac{d[\text{OH}^\bullet]}{dt} = k_d - k_f[\text{OH}^\bullet]^2 + k_r[\text{H}_2\text{O}_2] - k_1[\text{H}_2\text{O}_2][\text{OH}^\bullet] - k_{CR}[\text{dye}][\text{OH}^\bullet] \tag{A8}$$

Under quasi-steady-state assumption, Eq. (A8) becomes

$$k_d - k_f[OH^\bullet]^2 + k_r[H_2O_2] - k_1[H_2O_2][OH^\bullet] - k_{CR}[dye][OH^\bullet] = 0 \quad (A9)$$

$$[OH^\bullet] = \frac{k_d}{k_1[H_2O_2] + k_{CR}[dye]} \quad (A10)$$

Substituting Eq. (A10) into Eq. (A3) gives

$$r_{CR} = \frac{k_d \cdot k_{CR} \cdot [dye]}{k_1[H_2O_2] + k_{CR}[dye]} \quad (A11)$$

$$r_{CR} = \frac{k_q[dye]}{1 + K_q[dye]} \quad (A12)$$

where $k_q = k_d k_{CR}/k_1[H_2O_2]$ and $K_q = k_{CR}/k_1[H_2O_2]$.

References

[1] J. García-Montaño, X. Domenech, J.A. Garcia-Hortal, F. Torrades, J. Peral, The testing of several biological and chemical coupled treatments for Cibacron Red FN-R azo dye removal, J. Hazard. Mater. 154 (2008) 484–490.

[2] M.S. Tsuboy, J.P.F. Angeli, M.S. Mantovani, S. Knasmüller, G.A. Umbuzeiro, L.R. Ribeiro, Genotoxic, mutagenic and cytotoxic effects of the commercial dye CI Disperse Blue 291 in the human hepatic cell line HepG2, Toxicol. in Vitro 21 (2007) 1650–1655.

[3] G.A Umbuzeiro, H.S. Freeman, S.H. Warren, D.P. Oliveira, Y. Terao, T. Watanabe, L.D. Claxton, The contribution of azo dyes to the mutagenic activity of the Cristais River, Chemosphere 60 (2005) 55–64.

[4] R.O.A. Lima, A.P. Bazo, D.M.F. Salvadori, C.M. Rech, D.P. Oliveira, G.A. Umbuzeiro, Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source, Mutat. Res./Genet. Toxicol. Environ. Mutagen. 626 (2007) 53–60.

[5] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.

[6] S. Vajnhandl, A.M. Le Marechal, Case study of the sonochemical decolouration of textile azo dye Reactive Black 5, J. Hazard. Mater. 141 (2007) 329–335.

[7] H.M. Pinheiro, E. Touraud, O. Thomas, Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, Dyes Pigments 61 (2004) 121–139.

[8] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[9] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. II. Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 553–597.

[10] S. Vajnhandl, A.M. Le Marechal, Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes, Dyes Pigments 65 (2005) 89–101.

[11] A. Rehorek, M. Tauber, G. Gubitz, Application of power ultrasound for azo dye degradation, Ultrason. Sonochem. 11 (2004) 177–182.

[12] Y.G. Adewuyi, Sonochemistry: environmental science and engineering applications, Ind. Eng. Chem. Res. 40 (2001) 4681–4715.

[13] N.H. Ince, G. Texcanli, Reactive dyestuff degradation by combined sonolysis and ozonation, Dyes Pigments 49 (2001) 145–153.

[14] M. Abbasi, N.R. Asl, Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO_2 and H_2O_2, J. Hazard. Mater. 153 (2008) 942–947.

[15] S. Song, H. Ying, Z. He, J. Chen, Mechanism of decolorization and degradation of CI Direct Red 23 by ozonation combined with sonolysis, Chemosphere 66 (2007) 1782–1788.

[16] K. Okitsu, K. Kawasaki, B. Nanzai, N. Takenaka, H. Bandow, Effect of carbon tetrachloride on sonochemical decomposition of methyl orange in water, Chemosphere 71 (2008) 36–42.

[17] Z. He, S. Song, H. Zhou, H. Ying, J. Chen, C.I. Reactive Black 5 decolorization by combined sonolysis and ozonation Ultrason, Sonochemistry 14 (2007) 298–304.

[18] Z. He, S. Song, M. Xia, J. Qiu, H. Ying, B. Lü, Y. Jiang, J. Chen, Mineralization of C.I. Reactive Yellow 84 in aqueous solution by sonolytic ozonation, Chemosphere 69 (2007) 191–199.

[19] K. Vinodgopal, J. Peller, O. Makogon, P.V. Kamat, Ultrasonic mineralization of a reactive textile azo dye, Remazol Black B, Wat. Res. 32 (1998) 3646–3650.

[20] R.H. Myers, D.C. Montgomery, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, 2nd ed., John Wiley and Sons, USA, 2002.

[21] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building, 1st ed., Wiley, 1978.

[22] B.K. Korbahti, M.A. Rauf, Application of response surface analysis to the photolytic degradation of Basic Red 2 dye, Chem. Eng. J. 138 (2008) 166–171.

[23] N.V. Klassen, D. Marchington, H.C.E. McGowan, H_2O_2 determination by the I_3^- method and by $KMnO_4$ titration, Anal. Chem. 66 (1994) 2921–2925.

[24] N.H. Ince, M.I. Stefan, J.R. Bolton, UV/H_2O_2 degradation and toxicity reduction of textile azo dyes: Remazol Black – B, a case study, J. Adv. Oxid. Technol. 2 (1997) 442.

[25] J.M. Joseph, H. Destaillats, H.M. Hung, M.R. Hoffmann, The Sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions, J. Phys. Chem. A 104 (2000) 301.

[26] M.A. Behnajady, N. Modirshahla, S. Bavili Tabrizi, S. Molanee, Ultrasonic degradation of Rhodamine B in aqueous solution: influence of operational parameters, J. Hazard. Mater. 152 (2008) 381–386.

[27] M.H. Priya, Giridhar Madras, Kinetics of TiO-catalyzed ultrasonic degradation of Rhodamine dyes, Ind. Eng. Chem. Res. 45 (2006) 913–921.

[28] B.H. Ryu, Y.D. Weon, Decolorization of azo dyes by *Aspergillus sojae* B-10, J. Microbiol. Biotechnol. 2 (1992) 215–219.

[29] C.C. Hsueh, B.Y. Chen, Comparative study on reaction selectivity of azo dye decolorization by *Pseudomonas luteola*, J. Hazard. Mater. 141 (2007) 842–849.

[30] K.P. Gopinath, H.A.M. Sahib, K. Muthukumar, M. Velan, Improved biodegradation of Congo red by using *Bacillus* sp., Bioresour. Technol. 100 (2009) 670–675.

[31] K.P. Gopinath, M. Shreela, A. Joanna, K. Muthukumar, *Bacillus* sp. mutant for improved biodegradation of Congo red: random mutagenesis approach, Bioresour. Technol. 100 (2009) 6295–6300.