Bioprocess Engineering 23 (2000) 167–173 © Springer-Verlag 2000

Photocatalytic decolorization of congo red over ZnO powder using Box–Behnken design of experiments

G. Annadurai, T. Sivakumar, S. Rajesh Babu

Abstract Photocatalytic decolorization of congo red under sunlight illumination has been examined using ZnO catalyst. Batch experiments were conducted and Box–Behnken design has been employed to study the effect of different variables on the photodecolorization. Four variables such as dye concentration (0.05, 0.075, 0.10 g/l), weight of catalyst ZnO (0.025, 0.14, 0.25 g/l), pH (4, 7, 10) and time (1, 2, 3 (h)) were used to identify the significant effects and interactions in the batch studies. A second order polynomial regression model has been developed using the experimental data. It was found that the photodecolorization potential of ZnO was strongly affected by the variations in dye concentration, weight of catalyst ZnO, pH and time. The experimental values were in good agreement with the predicted values and the correlation coefficient was found to be 0.9982. Optimum conditions of the variables for the maximum photodecolorization are dye concentration (0.05 g/l) ZnO (0.16 g/l), pH (7.0) and time (2.0) (h). The maximum percentage of photodecolorization was observed to be 97%.

1 Introduction

The presence of harmful pollutants in the discharge of waste waters is a topic of global concern. Out of the total of 6,40,000 tons of dye production in 1975, 3,60,000 tons were used by textile industries and 10 to 20% of these consumed by the textile industries was let into waste water [1]. Other industries such as pulp and paper, leather, wool, silk, etc. also use dyes in large quantities which result in increased discharge. Discharge of these colored wastes into natural water bodies is undesirable from aesthetic point of view. Textile waste water is notoriously known to contain strong colour, high COD concentration level and suspended solids [2]. Dyes are toxic and may be carcinogenic. Environmental contamination by these toxic chemicals is a serious global problem. Based on the chemical structure of the chromophoric group, dyes are classified as anthroquinone dyes, triacrylomethane dyes, direct dyes, reactive dyes, azodyes and heterocyclic dyes. The decolorization of such dyes have been carried out with different methods by many workers [3–17]. Since colored solution containing dyes may cause skin cancer due to photosensitization and photodynamic damage, techniques like dissolved air-floatation [18], coagulation [19], ion-exchange, reverse osmosis, adsorption [20] and oxidation with peroxide (or) ozone are usually applied for the removal and destruction of dyes in waste water [21]. Currently no single economically feasible method can be relied upon for treating textile effluents. Conventional carbon adsorption and coagulation, flocculation and electrochemical methods resulted in poor colour removal and also disposal problems. But the photocatalytic decolorization process is more effective when compared to other processes. Recently the TiO_2/UV based degradation of various organic pollutants present in waste is recognized to have emerged as an alternative waste water treatment technology [21]. Photo catalytic process using sunlight is much more advantageous than any other because of its low operating cost. Increasing attention has been given recently to photocatalytic reactions occurring on semiconductor particles suspended in aqueous solutions. Researchers have examined photocatalytic reactions using sun light illuminated TiO_2 in a variety of systems as a means to split water in order to produce H_2 [22]. As environmental problems became more series, scientists have begun to use these same ZnO systems to degrade organic contaminants in water. Previous research has proved the ability to degrade organic compounds with TiO_2, including surfactants, phenols, herbicides chloroform, pesticides and carboxylic acids. Many of these compounds can be totally and efficiently mineralized. The TiO_2/ZnO semiconductor oxides photocatalytic reaction is now generating commercial interest because of its low cost, simplicity, and ability to achieve extremely low residual organic contaminant levels. Several improvements must be made before these systems can become economically attractive. Improvement is to be made to increase the contact area between the semiconductor oxides and the solution, which can be done by using porous semiconductor oxide films made by sol gel method [22, 23]. Advantage of the photocatalytic process is its mild operation conditions and the fact that it can be powered by ZnO in sunlight, thus reducing significantly the otherwise required electric power and therefore the operating costs [24–26]. Variety of semiconductor powders (metatoxides, sulphides and others) acting as photocatalysts have been used. Most attention was given to

Received: 17 August 1999

G. Annadurai, T. Sivakumar (✉), S. Rajesh Babu
Department of Chemical Engineering,
Alagappa College of Technology,
Anna University, Chennai – 600 025, India

We wish to express our sincere thanks to Mr. Mark Anderson, DOE Instructor and State Ease Corporation Principal for his suggestion and to use his design experiments (version 5.0.7 1997).

TiO_2/ZnO because of their high photocatalytic activity, resistance to photocorrosion, and low cost [27, 28]. The present investigation has been undertaken to study the photocatalytic decolorization of congo red by ZnO under sunlight illumination. In recent years, many studies have demonstrated that the semiconductor oxides such as TiO_2, ZnO etc. are able to decolorize a broad spectrum of structurally diverse organo pollutants [21, 26, 29, 30]. Methodology for the degradation of congo red from synthetic solution involves standardization of the various parameters to achieve maximum performance in terms of degradation under optimum conditions. Hence, the author reports application of the response surface methodology using the Box–Behnken design of experiments [7, 31–35].

2 Design of experiments

Design of experiments is a technique for conducting experiments that compromises nothing in thoroughness, but delivers results in a fraction of time. Design of experiments is a methodology for systematic application of statistics to experimentation. Generally, this is less time consuming than classical methods. Design of experiments works in both laboratory research and manufacturing processes. Using statistics, experiments develop mathematical models that predict low changes in input (or) control, variables (e.g. dye concentration, weight of the catalyst, time, pH) interact to produce changes in output variables (or) responses (% decolorization, adsorption, degradation) in a system. Experiments produce a model, which show that low variables and responses are related by performing a planned reference of experiments. The sequence is called a design [36].

The Box–Behnken design experiments uses ZnO as a catalyst. It is an alternative and more efficient approach, which is increasingly used in photodecolorization system. Basically this optimization process involves three major steps viz., performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking response and checking the adequacy of the model. The response surface methodology uses the Box–Behnken design of experiments to develop a mathematical correlation between Dye concentration, weight of catalyst ZnO, pH and time which are chosen as the critical variables and designated as X_1, X_2, X_3 and X_4. Decolorization was subjected to analysis of variance (ANOVA), appropriate to the design of experiments [37, 38]. The decolorization of dye was related to four variables by a multinormal of the following nature:

$$Y = b_0 + \sum b_i X_i + \sum_{i \le j} \sum b_{ij} X_i X_j + \sum \sum_{j \le k} \sum b_{ijk} X_i X_j X_k + \varepsilon \ , \quad (1)$$

where Y is the predicted response, i, j and k take values from the number of variables. b_0 is the constant; b_i represents linear coefficient, b_{ij} and b_{ijk} are quadratic and cubic coefficients where $i = j$ and $i = j = k$, respectively. These refer to interactions of first or second order, respectively, X_i, X_j and X_k are the levels of independent factors and ε is the random error. The low, middle and high level of each variable were designated as -1, 0 and +1 respectively and listed in Table 1. The actual design of experiments is listed in Table 2. The four significant independent variables X_1, X_2, X_3 and X_4 and the mathematical relationship of the response Y on these variables can be approximated by the second order quadratic model equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \ , \quad (2)$$

where Y predicted response; b constant; X_1 dye concentration (g/l), X_2 ZnO (g/l), X_3 pH and X_4 time (h), b_1, b_2, b_3 and b_4 linear coefficients, b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} cross product coefficients, b_{11}, b_{22}, b_{33} and b_{44} quadratic coefficients. The simplest possible model (quadratic second order model) can be used to explain the mathematical relationship between the controllable variables and response. The regression equation obtained after analysis

Table 1. The level of variables chosen for the trials

Dye concentration (g/l) (X_1)	ZnO concentration (g/l) (X_2)	pH (X_3)	Time (h) (X_4)
0.05 (−1)	0.025 (−1)	4 (−1)	1 (−1)
0.075 (0)	0.14 (0)	7 (0)	2 (0)
0.10 (+1)	0.25 (+1)	10 (+1)	3 (+1)

Table 2. The actual design of experiments

Trial no	X_1	X_2	X_3	X_4
1	−1	−1	0	0
2	1	−1	0	0
3	−1	1	0	0
4	1	1	0	0
5	0	0	−1	−1
6	0	0	1	−1
7	0	0	−1	1
8	0	0	1	1
9	−1	0	0	−1
10	1	0	0	−1
11	−1	0	0	1
12	1	−1	0	1
13	0	1	−1	0
14	0	−1	−1	0
15	0	1	1	0
16	0	0	1	0
17	−1	0	−1	0
18	1	0	−1	0
19	−1	0	1	0
20	1	0	1	0
21	0	−1	0	−1
22	0	1	0	−1
23	0	−1	0	1
24	0	1	0	1
25	0	0	0	0
26	0	0	0	0
27	0	0	0	0
28	0	0	0	0
29	0	0	0	0

of variance gives the level of decolorization as a function of different concentration of dye, weight of catalyst (ZnO), pH and time. Regression model containing linear (X_1, X_2, X_3, X_4) quadratic ($X_1^2, X_2^2, X_3^2, X_4^2$) and six interaction ($X_1X_2$, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_3X_4) terms plus 1 block term was employed by using the design expert (Stat-Ease Inc. statistics made Easy, Minneapolis, MN ver. 5.0.7.1997). The design is preferred because relatively few experimental combinations of the variables are adequate to estimate potentially complex response functions. A total of 29 experiments were necessary to estimate 15 coefficients of the model.

3
Materials and methods

3.1
Materials

The congo red dye used in the photodecolorization experiments was obtained from the Department of Textile Technology, Anna University, Chennai, India. ZnO [Chencol Industries India] was used in this study. BET surface area measurements were carried out for ZnO using micromeritics pulse chemisorb 2700 system. Nitrogen was used as the adsorbate in the 30:70 ratio of He:N_2 and the particle size was formed out by Shimadzu particle size analyser (SALD).

3.2
Design of experiments

Experiments were carried out in an open pyrex glass vessel of 300 ml capacity (9.5 cm height, 6.5 cm diameter). Four variables like dye concentration (0.05, 0.075, 0.10 g/l). Weight of catalyst ZnO (0.025, 0.14, 0.25 g/l) pH (4, 7, 10) and time (1, 2, 3 h) served as the critical variables X_1, X_2, X_3 and X_4 as shown in Table 1. Design of experiments (Table 2) was carried out in the pyrex glass vessels of 300 ml capacity with different variables from the Table 2. The mixture was continuously stirred with the help of magnetic stirrer, then irradiated with sunlight and the light intensity was measured by using Digital Lux meter LX-101. At specific time intervals, samples of 2 ml were withdrawn, added 4 ml of water and centrifuged. The supernatant liquid was analysed by Hitachi – U-2000 – spectrophotometer and decolorization was followed by constructing calibration graph for the dye.

4
Results and discussion

The BET surface area for the catalyst (ZnO), was found to be 7.49 m^2/g and the particle size 0.45 microns. The present investigation was undertaken to study the maximum photodecolorization of the congo red with varying weight of ZnO. The more efficient approach which is increasingly being used in photodecolorization is statistically designed experiments. Box–Behnken design of experiments is used in the present study. All the terms regardless of their significance are included in the following equation:

$$Y = 82.0 - 8.83\ X_1 + 1.17\,X_2 + 1.08\ X_3 + 2.25\ X_4 + 3.25\ X_1^2 - 8.0\ X_2^2 - 5.62\ X_3^2 - 7.12\ X_4^2 - 5.0\ X_1X_2 - 1.50\ X_1X_3 - 8.0\ X_1X_4 + 0.75\ X_2X_3 + 1.25\ X_2X_4 + 3.0\ X_3X_4\ . \quad (3)$$

Quadratic regression was significant at the level of 99%. Square regression was significant at the level of 99%. The photodecolorization form the model at each experimental point are summarized and listed in Table 3 along with experimental and theoretical observed values. The coefficients of above equation are calculated using Design expert and their values are listed in Table 4. The summary of the analysis of variance (ANOVA) is given in Table 5.

4.1
Optimization of dye concentration

Contour plot was made representing maximum amount of photodecolorization against dye (0.05 to 0.55 g/l) and weight of catalyst ZnO (0.25 to 0.14 g/l) at maximum photodecolorization of 97%. The optimum values were obtained by the derivatization of Eq. (3) and by solving the inverse matrix. The maximum percentage of decolorization (97%) was achieved at the optimum level of dye concentration (0.05 g/l) and with the optimum weight of the catalyst ZnO (0.16 g/l) as shown in Fig. 1. An increase in dye concentration results in decreased photodecolorization. This indicates the lack of available active sites on

Table 3. Experimental and theoretically predicted values for photodecolorization

Trial no	Experimental value (%)	Predicted value (%)
1	80.00	79.92
2	72.00	72.25
3	92.00	92.25
4	64.00	64.58
5	68.00	68.92
6	67.00	65.08
7	66.41	67.42
8	76.00	75.58
9	77.00	76.71
10	75.00	75.04
11	97.00	97.21
12	63.00	63.54
13	67.00	66.88
14	68.00	67.71
15	67.00	67.54
16	71.00	71.38
17	86.00	85.88
18	72.00	71.21
19	91.00	91.04
20	71.00	70.38
21	65.00	64.71
22	65.00	64.54
23	67.00	66.71
24	72.00	71.54
25	82.00	82.00
26	82.00	82.00
27	82.00	82.00
28	82.00	82.00
29	82.00	82.00

Table 4. Coefficient of the method

Variables	Coefficient	Standard error	*t*-for Ho Effect = 0	Prob > (*t*)	VIF
b_0	82.0	0.25	–	–	–
b_1	−8.83	0.16	−55.54	<0.0001	1.0
b_2	1.17	0.16	7.34	<0.0001	1.0
b_3	1.08	0.16	6.81	<0.0001	1.0
b_4	2.25	0.16	14.15	<0.0001	1.0
b_{11}	3.25	0.22	15.02	<0.0001	1.08
b_{22}	−8.0	0.22	−36.98	<0.0001	1.08
b_{33}	−5.62	0.22	−26.0	<0.0001	1.08
b_{44}	−7.12	0.22	−32.94	<0.0001	1.08
b_{12}	−5.00	0.28	−18.15	<0.0001	1.0
b_{13}	−1.50	0.28	−5.44	<0.0001	1.0
b_{14}	−8.00	0.28	−29.04	<0.0001	1.0
b_{23}	0.75	0.28	2.72	0.0165	1.0
b_{24}	1.25	0.28	4.54	0.0005	1.0
b_{34}	3.00	0.28	10.89	<0.0001	1.0

Table 5. Regression analysis for the photodecolorization of congo-red quadratic response surface model fitting (ANOVA)

Source	Sum of squares	Degree of freedom	Mean square	*F* value	*P* value
Model	2397.06	14	171.22	564.01	<0.0001
Residual	4.25	14	0.30	–	
Lack of fit	4.25	10	0.42	6.366 E+07	<0.0001
Pure error	0.000	4	0.000		
Correlation Effect	2401.31	28	–		
			R-squared = 0.9982		
			Adj *R*-squared = 0.9965		

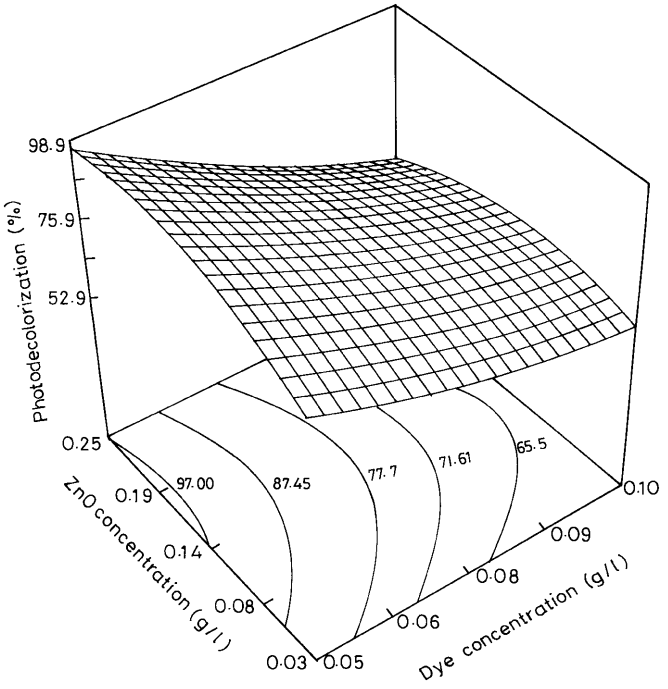

Fig. 1.

the semiconductor oxide surface required for large amount of dye concentration. The significant decrease in the photodecolorization at higher dye concentration levels may also be attributed to strongly inhibited direct excitation of ZnO semiconductor due to diminished penetration depth of sunlight in these highly coloured solutions [21, 39, 40].

4.2 Optimization of weight of the catalyst (ZnO)

Figure 2 shows that the percentage of photodecolorization was found to increase with increase in wt of catalyst ZnO (0.14 to 0.28 g/l) and increase in pH (7 to 10) at the maximum percentage photodecolorization of 97%. Optimum values were found to be weight of catalyst ZnO (0.16 g/l) and pH (7.0). Almost 100% colour removal was observed in about an hour with ZnO under sunlight illumination. Therefore, the probability of the reaction of holes with dye is considered to be roughly proportional to the surface coverage of photodecolorization.

4.3 Optimization of pH

The three-dimensional plot shows that the maximum percentage of photodecolorization occurs between pH (7 to 10) and between time 2 to 3 h then it reaches maximum of 97% as shown in Fig. 3. Therefore, the optimum values of pH (7.0) and time (2 h) respectively. The primary factor affecting the substrate decomposition in natural system was pH. Photodecolorization at various pH (4 to 10) plays a vital role in the source, as shown in Fig. 3. The optimum pH was found to be pH 7.0. Lower pH values

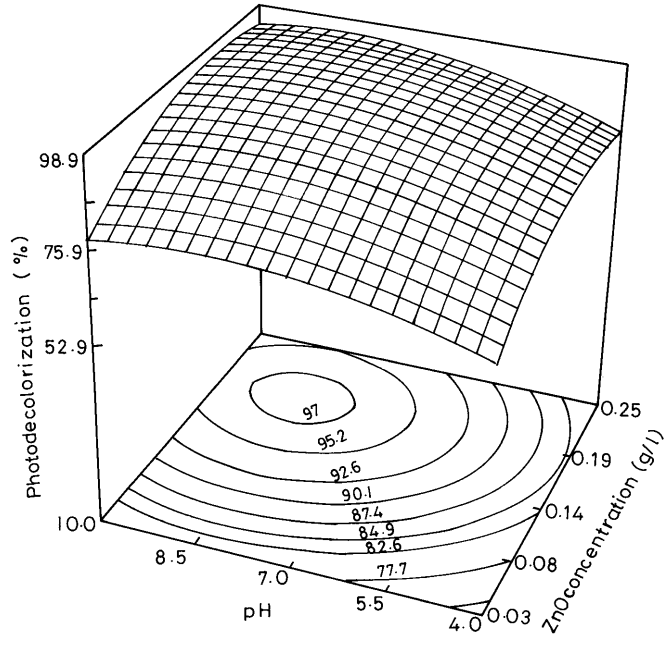

Fig. 2.

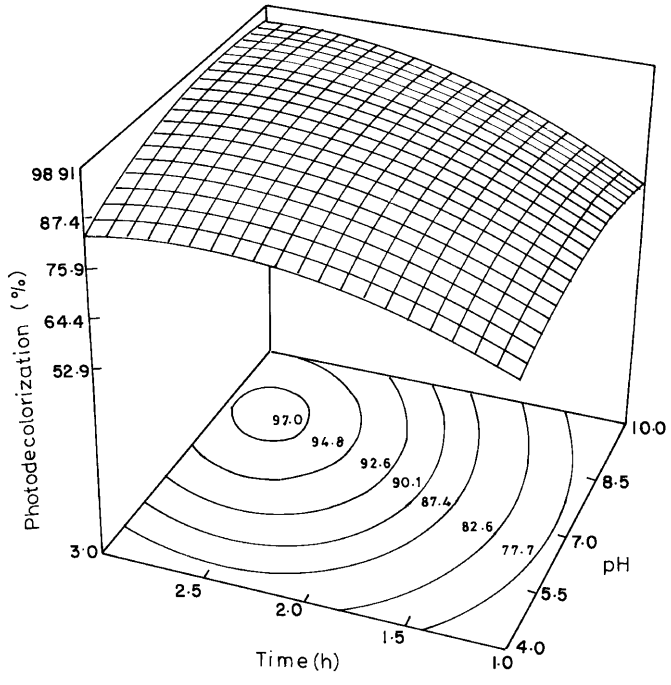

Fig. 3.

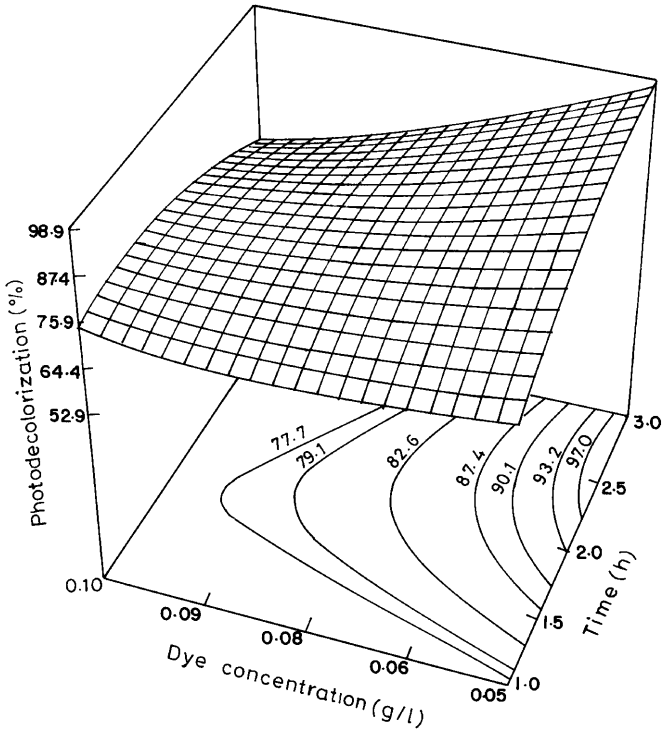

Fig. 4.

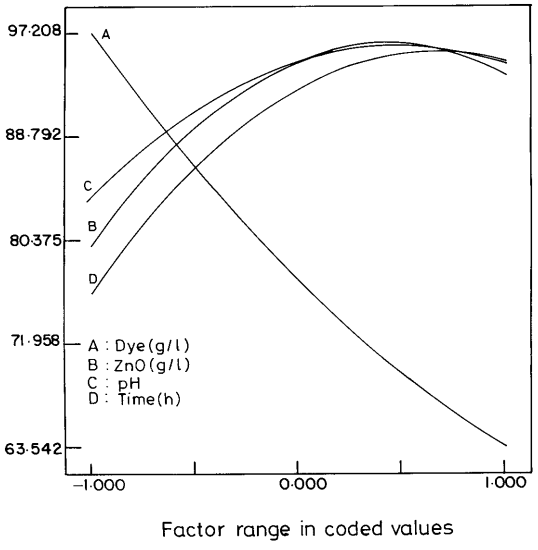

Fig. 5.

were found to be unfavourable because of the dissolution of semiconductor oxide (ZnO). Similarly at higher pH values, the adsorbent surface becomes more negatively charged which repels the dye anions and hence resulting in lengthening of degradation time.

4.4
Optimization of time (h)

From Fig. 4, the maximum percentage of photodecolorization (97%) was observed for time 2 to 3 (h) and dye concentration (0.05 to 0.07 g/l). Optimum level of photodecolorization (97%) was obtained at time (2 h) and dye concentration (0.05 g/l). The experiments for 2 to 3 h and as shown in Fig. 4 with an initial concentration of 0.07 g/l and below, a photodecolorization efficiency of 97% (or) greater was achieved within a period of one or two (h). The percentage of photodecolorization can be increased from 97% only when the time and weight of catalyst increased.

4.5
Factor plot

From the factor plot (Fig. 5) it can be observed that factors such as concentration of dye, weight of catalyst (ZnO),

pH and time used in the present study have their individual effect on the photodecolorization [41–43]. The gradual increase in the rate of photodecolorization was seen with decreasing dye concentration from (0.05 g/l) coded value (−1); (0.075 g/l) coded value (0) to 0.10 g/l coded value (+1). Increasing pH from 4 (coded value −1), 7.0 coded value (0) to 10.0 coded value (+1); catalyst (ZnO) from (0.025 g/l) coded value (−1) through 0.14 g/l coded value (0) to 0.25 g/l coded value (+1) and time from 1 (h) coded value (−1); 2 through coded value (0) to 3 (h) coded value (+1). But the optimum level are found to be dye (0.05 g/l) coded value (+1); ZnO (0.16 g/l) coded value (0); pH (7.0) coded value (0) and time (2 h) coded value (0).

5
Conclusion

Optimization of the process of photocatalytic degradation of dyes of the sunlight, with addition of varying levels of dye, ZnO concentration and pH and time (h) was analysed by Box–Behnken design experiment which works on regression analysis of the experimental data collected. The catalyst (ZnO) has been found to be the most efficient photocatalyst for the decolorization of dyes with sunlight. The predicted model has been tested with the support of ANOVA. Almost 100% decolorization was achieved in this photocatalytic method. Sunlight illumination seems to be more advantageous requiring a smaller amount of catalyst for complete decolorization. The empirical modelization technique used for the evaluation of the relationship between a set of controlled experimental parameters was made. It requires a-prior-knowledge of the process to achieve a statistical model graphical presentation facilitated with results from designed experiments. The model predicted decolorization upto 97% within a confidence level of 99% using ZnO.

References

1. **Anliker, R.:** Ecotoxicology of dystuff a joint effort by industry. Ecotoxicology and Environmental safe 3 (1979) 59–74
2. **Gurnham, C.F.:** Industrial waste control. Academic press, New York (1965)
3. **Maynard, G.W.:** Dye application manufacture dye intermediates and dyes. In: Kentled Riegels J.A., Hand book of Industrial Chemistry Van Nostrand Reinhold, pp. 809–861. New York (1983)
4. **Annadurai, G.:** Color removal from aqueous environs by waste derived biopolymer, Ph.D. thesis. Department of Chemical Engineering, Anna University, Chennai, India (1997)
5. **Annadurai, G.; Krishnan, M.R.V.:** Batch kinetic studies on adsorption of reactive dye using chitosan. Indian J. Environ. Protection 17 (1997a) 328–333
6. **Annadurai, G.; Krishnan, M.R.V.:** Batch equilibrium adsorption of reactive dye on to natural biopolymer. Iranian Polymer 6 (1997b) 169–175
7. **Annadurai, G.; Krishnan, M.R.V.:** Adsorption of acid dye from aqueous solution by Chitin: Batch kinetic studies. Indian J. Chem. technol. 4 (1997c) 217–222
8. **Annadurai, G.; Sheeja R.Y.:** Use of Box–Behnken design of experiments for the adsorption of verofix red using biopolymer. Bioprocess. Eng. 18 (1998) 463–466
9. **Annadurai, G.; Partha, N.; Srinivasamoorthy, V.R.; Krishnan, M.R.V.:** Factorial design experiment for adsorption of dye on chelating polymers. Indian J. Environ. Protection 17 (1998a) 721–723
10. **Annadurai, G.; Chellapandian, M.; Krishnan, M.R.V.:** Adsorption of basic dye form aqueous solution by Chitosan – Equilibrium studies. Indian J. Environ. Protection 17 (1998b) 721–723
11. **Annadurai, G.; Krisnnan M.R.V.:** Adsorption of basic dye using chitin. Indian J. Environ. Protection 16 (1996) 44–49
12. **Satyahari, D.; Tapas, K.M.; Bimal, C.B.:** Production of some extracellular enzymes by lignin peroxide producing brown – rot fungus, *Polyporus osteriformis* and its comparative abilities for lignin degradation and dye decolorization. Appl. Environ. Microbiol. 60 (1994) 4216–4218
13. **Vyas, B.R.M.; Molitoris, H.P.:** Involvement of an extracellular H_2O_2 dependent ligninolytic activity of the white rot fungus *Pleurotus ostreatus* in the decolorization of Remazol Brilliant Blue-R. Appl. Environ. Microbiol. 61 (1995) 3919–3927
14. **Pasti-Grigsby, M.B.; Paszcznski, A.; Goszcz-Ynski, S.; Crewford, D.L.; Crawford, R.L.:** Influence of aromatic substitution patterns on azo dyes degradability by *Streptomyces*. sp. and *Phanerochaete chrysosporium*. Appl. Environ. Microbiol. 58 (1992) 3605–3613
15. **Frederick, C.; Michel, J.R.; Balachandradass, S.; Eric, A.G.; Adinarayana Reddy, C.:** Role of manganese peroxidase and lignin peroxidase of *Phanerochaete chrysosporium* in the decolorization of kraft-bleaches plant effluent. Appl. Environ. Microbiol. 57 (1996) 2368–2375
16. **Prasad, G.K.; Gupta, R.K.:** Decolorization of pulp and paper mill effluent by white rot fungi. Indian J. Environ. Health 39 (1997) 89–96
17. **Cripps, C.; Bumpus, J.A.; Aust, S.D:** Biodegradation of Azo and Heterocyclic dyes by *Phanerochaete chrysosporium*. Applied Environ. Microbiol. 56 (1990) 1114–1118
18. **Cochen, H.:** The use of ultrafiltration members in treatment of textile dye house waste. 2nd National Conference on bomplete water reuse. Chicago pp. 992–995. Amer. Inst. Chem. Eng. and US Environmental Protection Agency, Washington DC (1978)
19. **Ponswed, J.B.; Wongehansowan, S.:** Mechanism of dye waste water colour removal by magnesium carbonate – hydrate basic water. Sci. Technol. 18 (1986) 139–144
20. **Yoshida, H.; Fukuda, S.; Osamoto, A.; Kataoka, T.:** Recovery of direct dye and acid dye adsorption on Chitosan fiber equilibria. Wat. Sci. Technol. 23 (1991) 1667–1676
21. **Rao, N.N.; Dube, S.:** Photocatalytic degradation of Reactive Orange (R.84) in dye-house effluent using single pass reactor. Advances in Basic and Applied aspects of Industrial catalysis in surface science and catalysis. 113 (1996) 1045–1050
22. **Dony, H.K.; Marc. A.A.:** Photoelectrocatalytic degradation of formic acid using a porous ZnO Thin-film Electrode. Environs. Sci. Technol. 28 (1994) 479–483
23. **Zeltner, W.; Anderson, M.A.:** U.S. Patent 15, 137, 607, for reactor vessel using oxide ceramic membranes (1987)
24. **Gupta, B.P.; Anderson, J.V.:** Solar detoxification of hazardous waste – An overview of the United – State department of Energy program. Solar energy materials 24 (1991) 40–44
25. **Goswami, D.Y.:** Engineering of the Solar Photocatalytic Detoxification and Disinfection Processes. In: Boer, K.W. (ed.) Advances in Solar Energy, Colorads American Solar Energy Society Inc. Bowlder (1995)
26. **Kyriacou, G.K.; Tzoanas, K.; Poulios, I.:** Photocatalytic decomposition of 2,3-dichloropyridine over aqueous suspensions of ZnO. J. Environ. Sci. Health Part-A 32(4) (1997) 963–977
27. **Avranas, A.; Poulios, I.; Cypri, C.; Jannakovadakis, D.:** Heterogeneous photocatalytic decomposition of the cationic surfactant dodecylpyridinum chloride. Appl. Catalysis B Environ. 2 (1993) 289–292
28. **Low, G.; McEvoy, S.; Mathews, K.:** Formation of nitrate and ammonium ions in titanium dioxide mediated photocatalytic degradation of organic compounds containing nitrogen atoms. Environ. Sci. Technol. 25 (1991) 460–463

29. **Ken-Ichi, O.; Yasumori, Y.; Hiroki, T.; Masashi, T; Akira, I.:** Heterogeneous photocatalytic decomposition of phenol over ZnO powder. Bull. Chem. Soc. Jpn. 58 (1989) 2015–2022
30. **Ajay, S.; Pratibha Rao, R.P.; Mathur, S.C.; Ameta.:** Photocatalytic reaction of xylidine ponceau on semiconducting zinc oxide powder. J. Photochem. Photobiol. A: Chemistry 86 (1995) 197–200
31. **Box, G.E.P.; Draper, M.R.:** A basis for the selection of a response surface design. J. Amer. Statist. Assoc. 54 (1959) 622–654
32. **Box, G.E.P.; Wilson, K.B.:** On the experimental attainment of optimum conditions. J. Roy. Statist. Soc. B (13) (1957) 1–45
33. **Box, G.E.P.; Hunter, J.S.:** Multifactor experimental design for exploring the response surfaces. Ann. Math. Statist. 28 (1957) 195–214
34. **Box, G.E.P.; Behnken, D.W:** Some new three level design for study of quantative variables. Technomet. 2 (1960) 455–475
35. **Kapat, A.; Rashit, S.K.; Panda, T.:** Optimization of carbon and nitrogen sources in the medium and environmental factors of enhanced production of chitinase by *Trichoderma harzimum*. Bioprocess Eng. 5 (1996) 13–20
36. **Kymberly, K.H.; David, B.:** Design of Experimentals. Chem. Eng. 30 (1997) 142–147
37. **Cochran, W.G.; Cox, G.M.:** Experimental designs. John Wiley and Sons, New York (1957)
38. **Lekha, P.L.; Nagin Chand, B.; Lonsame, L.:** Computerised study of interactions among factors and their optimization thought response surface methodology for the production of tannin acylhydrolase by *Aspergillus niger* PKL 104 under solid state fermentation. Bioprocess Engg. 11 (1994) 7–15
39. **Mathews, R.:** Photooxidation of organic impurities in water using thin films of ZnO. J. Phys. Chem. 91 (1997) 3328–3330
40. **Bahnemann, D.W.; Bockelmann, D.; Goslich R.:** Mechanistic studies of water detoxicifcation in huminated ZnO suspensions. Solar Energy Materials 24 (1991) 564–566
41. **Sajong, O.H.; Sungsue, R.; Jaehun, S.; Sangkyo, K.; Yougjim, B.:** Optimizing conditions for the growth of *lactobacillus casei* YIT 908 in Tryptone – Yeast Extract – Glucose Medium by using response surface methodology. Appl. Env. Microbiol. 61 (1995) 3809–3814
42. **Annadurai, G.; Mathalaibalan, M.; Murugesan, T.:** Box-Behnken design in the development of optimized complex medium for phenol degradation using *Pseudomonas putida* (NICM 2174). Bioprocess Eng. In Print (1999a)
43. **Annadurai, G.; Mathalaibalan, M.; Murugesan, T.:** Design of experiments in the biodegradation of phenol using immobilized *Pseudomonas pictorum* (NICM-2077) on activated carbon. Bioprocess Eng. In Print (1999b)