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PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE WASTEWATER USING GREEN SYNTHESIZED Ag/ZnO NANO-COMPOSITE CATALYST UNDER SOLAR RADIATION

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ABSTRACT

A solar active photocatalyst (Ag/ZnO) was synthesized and optimization of the photocatalytic degradation of textile dye bath effluent using the synthesized catalyst was performed by the Taguchi experimental design method. The optimum factor values for maximum percentage COD removal were: initial dye bath effluent concentration - 500 mg L^{-1}, Ag/ZnO concentration - 1000 mg L^{-1} and irradiation time - 90 min. Under optimized conditions percent COD removed from the dye bath effluent was 60.2 ± 8.3%. These results could serve as a basis for the future development of a sustainable and eco-friendly method to treat pollutants in textile dye effluents using a pilot-scale facility.

Key words: Taguchi method, Textile dye wastewater, Silver / Zinc oxide, Photocatalysis.

INTRODUCTION

A wide range of dyes with different chemical structure and properties are used by textile manufacturers to meet ever growing need for quality and quantity. After the textile dyeing operations, wastewaters are collected and treated prior to discharge into receiving water bodies. Treatment is required prior to discharging because dyes and chemicals used during dyeing process are toxic to local ecosystems containing terrestrial and aquatic life[1]. Semiconductor photocatalysis is recognized as one of the effective technologies capable of completely mineralizing pollutants. Among numerous photocatalysts reported in literature, ZnO and TiO_2 are the most dominant catalysts employed for wastewater treatment because of their stability, low cost and easy availability. However, use of TiO_2 and ZnO for large scale application remains challenging because of their low activity in visible light due to a

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wide band gap[2]. Another common issue encountered with the semiconductor photocatalyst is the recombination of electron hole pair. A strategy to overcome these problems and to enhance their photonic efficiency is to use metal-semiconductor composites. Metals, when dispersed on semiconductor, result in (ii) improved absorption of visible light photons through plasmonic surface resonance and (ii) reduced electron-hole pair recombination due to Schottky barrier[3]. A simple bio-inspired synthesis of Ag/ZnO nanocomposite had been reported earlier[3] and the efficiency of the composite for the degradation of a commercial dye, under solar irradiation, had been evaluated[3]. In the present study, the efficiency of the catalysts for degradation of a textile industry effluent was examined and the effects of initial COD of the effluent, catalyst loading and time of reaction on percentage COD removed from the effluent was studied using Taguchi experimental design method. Though several statistical modeling and optimization techniques including the integration of quantitative and qualitative factors[4] were used in photocatalytic degradation experiments, the use of the Taguchi method is very limited. The Taguchi method is advantageous because it is associated with saving time and cost and it also leads to a simple and efficient methodology for the optimization of process variables with less number of experiments when compared to other methods such as Box-Behnken[5,6].

EXPERIMENTAL

Materials and methods

Textile dye waste water

Textile dye bath effluent (COD = 4800 mg L^{-1}, pH = 9) used in this study was collected from a textile industry located in Tiruppur (Tamil Nadu, India). The dye effluent was stored at room temperature before further use in the experiments.

Ag/ZnO Photocatalyst preparation

Synthesis of the Ag/ZnO photocatalyst was reported by Gunasekar and Ponnusami[3]. Reagent grade materials namely zinc oxide (99.9% ZnO, Merck, India), silver nitrate (99.99 % $AgNO_3$, Fischer scientific, India) were purchased and used without further purification. *E. coli* MTCC448 from Microbial Type Culture Collection and Gene Bank (MTCC) were procured and cells were sub-cultured in Luria–Bertani broth (Hi-Media, India) at 200 rpm in an incubated shaker at 35 ± 2ºC. A crude enzyme from *E. coli* was extracted and purified as reported by Gunasekar and Ponnusami[3]. Briefly, 3 mL of 0.5 M plus 9 mL of a crude nitrate peroxide enzyme obtained from *E. coli* were added to 5 g of ZnO in 50 mL double distilled water (DDW) under constant stirring. The mixture was stirred for 60 min and the contents filtered using a Whatman® No. 1 filter paper (110 mm ø) in a Büchner funnel and repeatedly washed with double distilled water. The filtrate was dried at 80ºC for 4 hr, removed from the filter by scrapping and stored in a glass vial for further use.

Photocatalytic reactor setup

Photocatalytic experiments were carried out in a chamber constructed from sheet metal (45 cm long × 28 cm in diameter). Five white florescent light lamps (Philips India Ltd, West Bengal, India) were mounted on the top of the chamber. The lamps were capable of radiating 7700 lux with a total power of 125 W. A 100 mL beaker was used as a reaction vessel and placed on a magnetic stirrer. The chamber was equipped with small Aquarium air pump (Taiyo TI 3800, China) to supply air (oxygen source) into the reaction mixture continuously.

Experimental design and statistical analysis

Optimization of the degradation process was conducted using white florescent light. The optimization study experimental design was conducted using the Taguchi method. The Taguchi method based on three levels and three factors (L_9 orthogonal array) was used to optimize the photocatalytic degradation process. The optimization study was performed using the dye bath effluent (DBE), Ag/ZnO and white florescent light irradiation.

The three factors selected included the dye bath effluent concentration (X_1), the Ag/ZnO concentration (X_2) and irradiation time (X_3) (Table 1). The dye bath effluent (4,800 mg/L COD) was diluted with double distilled water (DDW) to attain the required initial COD and mixed with the Ag/ZnO catalyst. Reaction mixtures containing effluent plus catalyst were prepared based on the Taguchi experimental design. The beakers containing reaction mixture were wrapped and covered with aluminum foil and sonicated for 5 min at 30^{o}C using a sonicator (PCI analytics, Chennai, India) at 30^{o}C temperature to ensure proper dispersion of the catalyst and homogeneous mixing prior to initiating the degradation.

The sample mixture was irradiated with white florescent light (125 W) and liquid samples were removed from the mixture at specified time intervals. The collected samples were centrifuged (REMI elektrotechnic limited, Vasai, India) at 8000 rpm for 10 min. The clear centrate was removed and used for COD analysis and/or color determination. A total of nine experiments were conducted based on the Taguchi design. The experimental factors and levels are shown in Table 1. All experimental conditions were examined in triplicate.

Table 1: Experimental design parameters

Factor	Model Term	Low (1)	Middle (2)	High (3)	Step change values (ΔXi)
Initial COD concentration (mg L^{-1})	X_1	500	750	1000	250
Catalyst concentration (mg L^{-1})	X_2	500	1000	1500	500
Time (min)	X_3	30	60	90	30
Note: Reaction conditions (Initial pH = 9; Initial temperature = 30^{o}C)					

The response variable used to monitor the efficiency of the photocatalytic degradation process is COD removal efficiency. The COD removal efficiency was calculated using Eq. 1.

$$\text{COD Removal Efficiency (\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \qquad \ldots(1)$$

Where COD_0 is the COD of the initial solution taken before the addition of catalyst, COD_t is the COD of the solution from the photoreactor at selected reaction time intervals.

The optimum conditions of the factors were determined using the Taguchi approach and the data analysis and graphical representation of the data was performed using Minitab 16 (Minitab Inc., State College, PA, USA). The goal of this optimization study was to optimize the response (COD removal efficiency) and therefore, a large signal-to- noise ratio (S/N) was selected (Eq. 2). The S/N measures how the response varies relative to the nominal or target value under different noise conditions.

$$\frac{S}{N} = \frac{-10 \times \log\left(\sum Y_i^2\right)}{n} \qquad \ldots(2)$$

where Y_i is the mean COD removal efficiency for the i^{th} experiment and n is the total number of the experiments in the orthogonal array. An analysis of variance (ANOVA) was performed to evaluate the significance of the factors under consideration. Further photocatalytic degradation experiment was performed based on the optimum factor levels predicted by the Taguchi method to validate the model.

Analytical methods

The UV-Visible absorption spectroscopy of liquid samples was conducted using a Thermo Fisher Scientific spectrophotometer (Model: Evolution 201, Shanghai, China) with DDW as a reference. The chemical oxygen demand (COD) of liquid samples was determined in accordance with Standard Methods[7]. pH measurements were performed using a digital pH meter (Systronics, Model – 335, India).

RESULTS AND DISCUSSION

Taguchi optimization study

The experimental and model predicted COD removal efficiency values (Table 2) were plotted to determine the adequacy of the Taguchi method. The correlation coefficient R^2 value of 0.9676 (Fig. 1) indicates that the experimental values is in good agreement with the model predicted values.

Table 2: Experimental and predicted values for percent COD removed and S/N ratio (Taguchi orthogonal array table of L_9)

Run No.	Factors			Response[1]				
				COD Removal (%)			S/N ratio	
	X_1	X_2	X_3	Actual	Predicted	Residuals	Actual	Predicted
1	1	1	1	14.42	13.42	1.01	23.16	22.35
2	1	2	2	18.24	18.40	-0.15	25.22	25.17
3	1	3	3	20.94	21.79	-0.85	26.40	27.25
4	2	1	2	7.61	8.46	-0.85	17.62	18.47
5	2	2	3	20.04	19.03	1.01	25.93	25.12
6	2	3	1	15.55	15.70	-0.15	23.83	23.78
7	3	1	3	9.48	9.64	-0.15	19.51	19.47
8	3	2	1	12.63	13.48	-0.85	21.85	22.70
9	3	3	2	12.29	11.28	1.01	21.76	20.96

Notes: 1. Values indicated are averages of triplicates, 2. Reaction conditions (Initial pH = 9; Initial temperature = 30°C)

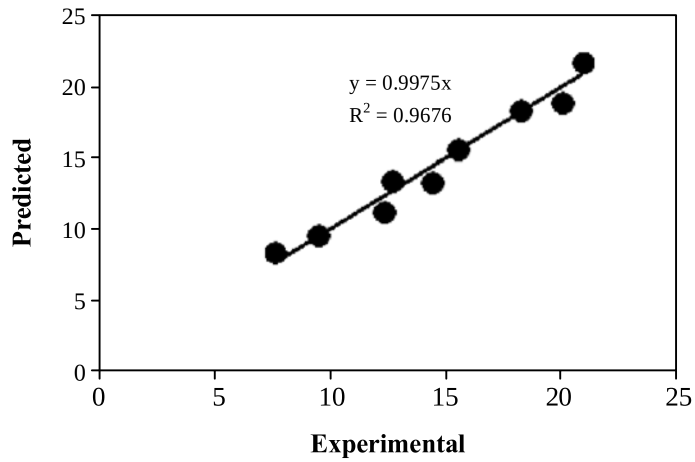

Fig. 1: Predicted versus experimental COD percent removed for Ag/ZnO photocatalysis

The S/N response (Table 2) shows the average of each response characteristic (mean S/N ratios) for each level of each factor. The table includes ranks based on the delta statistic. The delta statistic is the highest minus the lowest average for each factor. Ranks are assigned based on delta values. Rank 1 is the largest delta value, rank 2 is the second largest and so forth. Therefore, the response tables (Table 3) indicate that among the factors under consideration, the Ag/ZnO concentration had the largest influence on the percent COD removed.

Based on the data in Table 3, the statistical significance and the importance of the factors were ranked as Ag/ZnO concentration, the initial dye bath effluent concentration and the time.

Table 3: Response table for signal to noise ratios

Level	DBE (mg COD L^{-1})	Ag/ZnO (mg L^{-1})	Time (min)
2	22.46	24.33	21.53
3	21.04	24.00	23.95
Delta	3.88	4.23	2.41
Rank	2	1	3

Notes: 1. DBE = Dye bath effluent, 2. Reaction conditions
(Initial pH = 9; Initial temperature = 30^{o}C)

Based on the S/N ratio (Fig. 2), the optimum conditions for the quantity of COD removed in the dye bath effluent with white florescent light (125 W) were: an initial concentration of 500 mg COD L^{-1}, Ag/ZnO concentration of 1000 mg L^{-1} and a 90 min irradiation/reaction time. The percent COD removed using a solar radiation photoactivated Ag/ZnO catalyst at the optimum operating conditions reached 60.2 ± 8.3%.

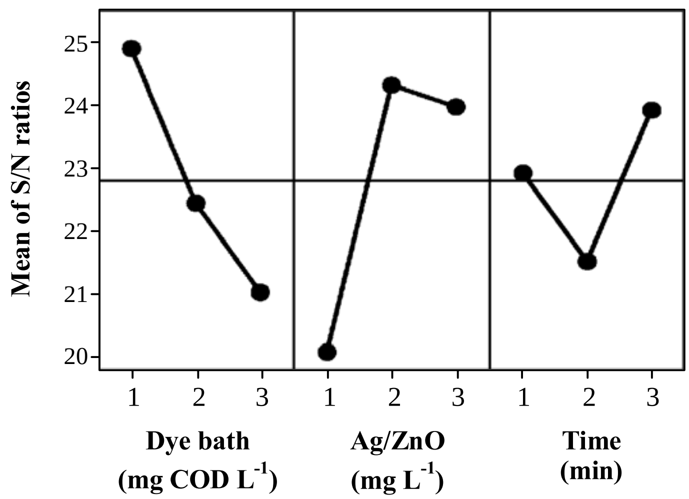

Fig. 2: Signal to noise ratio at levels (1-3) for each factor.

CONCLUSION

The possible application of an eco-friendly photocatalytic degradation process to treat textile dye wastewater effluents was demonstrated in this study. Factors affecting the photocatalytic degradation of the dye bath effluent were optimized using the Taguchi method. The method indicated that the optimum factor values for maximum quantity of COD and color removed were: an initial dye bath effluent concentration of 500 mg L^{-1}, an Ag/ZnO concentration of 1000 mg L^{-1} and irradiation time of 90 minutes. The Taguchi method employed in this study was adequate for the photocatalytic degradation of effluents containing dye as the experimental values were in agreement with the predicted values. A COD removal of 60.2 ± 8.3% was achieved for the sun-light photocatalytic degradation of the dye bath effluent under optimum conditions. Hence, the enzymatically synthesized Ag/ZnO catalyst is a promising material, which can be used to treat textile dye wastewaters using solar energy. Additional work is required to maximize the COD and color removals, which are comparable to the removals for the UV-ZnO reaction.

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