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Response surface methodology based optimization of photocatalytic degradation of 2,4-dichlorophenoxyacetic acid

Gopalram Keerthiga*, Akash Balakrishnan, Kiruthika Sathiasivan

Department of Chemical Engineering, SRM Institute of Science & Technology, Kattankulathur, Kancheepuram 603203, Tamil Nadu, India, emails: keerthigagopal@gmail.com (G. Keerthiga), akash.chemicalengg@gmail.com (A. Balakrishnan), kiruthis@srmist.edu.in (K. Sathiasivan)

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ABSTRACT

Remediation of pesticides by advanced oxidation process gains enormous interest due to its feasible applications at the polluted site. The 2,4-dichlorophenoxyacetic acid (2,4-D), a common herbicide in water bodies, poses a major environmental threat to humans and aquatic organisms. However, the advanced oxidation process offers a possible solution for its effective recovery. Optimisation of the critical parameter will support the possible recovery process of the 2,4-dichlorophenoxyacetic degradation. In the present study, response surface methodology based analysis of variance optimization was made for a modified TiO_2 catalyst in a glass fabricated photocatalytic reactor for 2,4-dichlorophenoxyacetic acid degradation. The variables investigated were pH (2–10), initial 2,4-D concentration (10–100 mg/L), and catalyst loading (25–150 mg/L). The maximum removal efficiency of 97% has been achieved at the optimized variable of 87.5 mg/L of catalyst dosage at 55 mg/L of 2,4-D concentration at pH 6.

Keywords: Optimization; 2,4-Dichlorophenoxyacetic acid degradation; TiO_2/chitosan beads; Photocatalysis; Analysis of variance

1. Introduction

During the past decade, the whole world faced massive challenges due to the limited availability of clean water. Rapid industrialization, population boom, and natural disasters contributed to water pollution of existing resources [1]. The leaching of pesticides, herbicides, etc., from agricultural land also contributes to water pollution in rural areas [2,3]. So, a quick and pragmatic solution is necessary to overcome the problems associated with water pollution. Different pesticides, including 2,4-dichlorophenoxyacetic acid (2,4-D), are commonly used pesticides in developing countries like India [4,5]. The low-cost, highly effective 2,4-D in low dose with better stability against environmental conditions makes it ideal as a herbicide for commercial crops [6]. The widespread usage of different pesticides resulted in detecting other ecological units such as soil, water, and air. Moreover, the uptake of 2,4-D in small quantities and the potential toxicity will affect the birds, fish, trees, etc. [7]. Other routes like water runoff from agricultural systems, dumping expired pesticides, and industrial releases of pollutants are considered as direct sources of water contamination [8]. It eventually causes both surface water and groundwater contamination [9]. In addition to that, it may also cause severe health problems like neuroendocrine disruption, genetic damage etc. [10]. So, the removal of 2,4-D from wastewater streams is mandatory to ensure the availability of safe water.

Due to the usage of chemical reagents, high treatment cost, incomplete removal, and production of toxic products, most conventional treatment methods fail to address the remediation of 2,4-D [10,11]. Therefore, photocatalysis attained significant research interest due to its ability to completely degrade the organic pollutants into carbon dioxide and water molecules [12]. Among different photocatalysts, TiO_2, a semiconductor-based photocatalyst, was

* Corresponding author.

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chosen as base material due to its high efficiency, low-cost, physical stability, photostability etc. [12,13]. However, the inability of nano-sized TiO_2 for large scale application are due to its limited utilization of natural sunlight, aggregation of nano-sized photocatalyst, problems in recovery and reusability of the photocatalyst [14]. The catalyst immobilization will aid in catalyst reusability and minimization of the catalyst loss and further improve the economic feasibility of the process [15,16].

Among different biopolymers, chitosan, a natural biopolymer extracted from the exoskeletons of shell-fish was chosen as the supporting agent [17,18]. The existence of amino and hydroxyl groups makes them unique and finds prominent application in wastewater reclamation [19,20]. Chitosan is a material found a wide variety of applications ranging from drug delivery to water treatment, food packing, cosmetics, etc. [14,21,22]. Due to the ease of formulation, new materials of composites, sheets, membranes, beads, etc. can be formed [23–25].

The addition of chitosan exhibited a multifunctional performance with TiO_2 by adopting an in-situ adsorption-photocatalytic process, especially for the organic pollutants [26]. The motivation to use chitosan-based beads is not limited to the following (i) to minimize catalyst loss, (ii) to improve stability of the catalyst, (iii) to avoid aggregation of nano-sized particles, (iv) to aid in ease in the recovery of photocatalyst, (v) to enhance the reusability of catalyst, and (vi) to aid continuous photocatalytic degradation at its site [27,28]. Thus, in this study, chitosan/TiO_2 beads were synthesized for the redemption of 2,4-D in wastewater.

Optimization is an essential strategy for enhancing the performance of any system, process, or product to attain benefits [29–31]. The optimization is generally monitored by analysing the impact of different factors on the experimental values [32]. Previously, removal of humic acid has been optimized using response surface methodology (RSM) based techniques [33] and by addition of nanocarbon and nanozeolite [34]. The gradual change of a single parameter is referred as one-variable-at-a-time which can be compared with the effect of multivariable. Analysis of variance (ANOVA) based optimization method considers the influence of all the interacting parameters. However, it is mandatory to enhance the total number of experiments for the performance of the study. This creates additional expenses in terms of time and labour and material consumption [32,35]. So, the utilization of RSM is preferred.

RSM is the most used tool for minimizing the number of experiments to provide sufficient optimized results. So, this approach reduces the cost related to labour and time requirements. In the past decade, predominantly speaking very few works were focussed on the mathematical modelling of the photocatalytic degradation of pesticides using modified TiO_2 photocatalyst. So, in this study, we aimed to study the response surface methodology based on photocatalytic degradation of 2,4-dichlorophenoxyacetic acid using modified TiO_2 based photocatalyst.

2. Materials and methods

Chemicals like TiO_2, glacial acetic acid, sodium hydroxide, 2,4-dichlorophenoxyacetic acid, and hydrochloric acid purchased from Fischer Scientific India Pvt. Ltd. were of analytical grade [35]. Chitosan (85% deacetylated) was purchased from Pelican Biotech (Alapuzha, India). Double distilled water was used throughout the study.

2.1. Preparation of modified TiO_2 catalyst

Chitosan flakes were treated with acetic acid before adding TiO_2 in the ratio of 1:0.5 and kept for stirring until it attained uniformity. The homogenized chitosan-TiO_2 mixture was further dispersed into a basic medium to yield beads. The formed beads were washed with distilled water to attain neutral pH. The neutralized beads were cross-linked with glutaraldehyde to achieve higher stability. Finally, these beads were washed, dried, and stored for further applications [29,35].

2.2. Characterization of modified TiO_2 catalyst

The surface morphology of catalyst was investigated using field emission scanning electron microscopy (FE-SEM, FEI Quanta 200), X-ray diffraction (XRD) by PANalytical X'Pert Pro and differential reflectance spectroscopy (DRS) UV using Shimadzu UV-3600 Plus. The elemental composition of the prepared photocatalyst was studied by energy-dispersive analysis of X-ray (EDAX) spectroscopy.

2.3. Photocatalytic degradation of 2, 4-D

The photocatalytic removal of 2,4-D was conducted in a fabricated glass reactor connected with a UV lamp of 16 W and 254 nm wavelength as discussed by Balakrishnan et al. [16]. The reactor has provision for lamp hosting into a quartz tube, which in turn activates the pollutants. Using an aerator, the pollutant, and catalyst were continuously aerated (2.5 mL/min).

The degradation studies were conducted for varying concentrations of 2,4-D with an optimal catalyst dosage at room temperature. About 30 min equilibrium adsorption time was fixed prior to the photocatalytic experiments. The degradation rate was calculated at frequent intervals using a UV-Vis spectrophotometer (Cary 60) at 285 nm. The removal efficiency of 2,4-D (%) was estimated using Eq.(1)

$$\text{Percentage 2,4-D removal}\left(\%\right)=\frac{\left(C_o-C\right)}{C_o}\times 100 \tag{1}$$

where C_o and C are initial and final concentration of 2,4-D in mg/L.

2.4. Statistical design of experiment

The central composite design (CCD) model was used to design the experiments and Design-Expert software (Stat-Ease, Inc., Minneapolis, USA). It is used to analyse the experimental responses to figure out the factors that play a crucial role in the removal of 2,4-D using TiO_2 modified photocatalyst. The CCD method was used due to its high accuracy. These models consider the interaction among different factors which may influence the removal

of 2,4-D. According to the experimental design matrix, 20 practical sets randomly were arranged in a predefined range of values, namely, pH (2–10), initial 2,4-D concentration (10–100 mg/L), and catalyst loading (25–150 mg/L). Table 1 shows the predetermined ranges of values for different factors as enlisted.

3. Results and discussion

3.1. Characterisation of the catalyst

The surface morphology of the modified TiO_2 catalyst was studied using scanning electron microscopy (SEM), as shown in Fig. 1a and b. EDAX composition is reflected in Fig. 1c. The microscopic image assures the proper incorporation and impregnation of TiO_2 on the chitosan surface which further indicates homogenized mixing of chitosan with TiO_2. EDAX spectra in Fig. 1c also unveiled different elements like Ti, O, C, and N in the prepared photocatalyst.

Fig. 2a discusses the optical properties of DRS UV spectroscopy for the modified TiO_2 catalyst where the bandgap corresponds to 2.8 eV. The XRD spectra of modified TiO_2 catalyst are depicted in Fig. 2b. The characteristic anatase peak of TiO_2 was detected at 25.7° attributing to (101) plane. The other anatase peaks were reported at 2θ of 38.10°, 47.9°, 54.1°, 62.8°, and 75.2°. An additional peak at 2θ of 19.7° confirms the incorporation of TiO_2 into the structure of chitosan [19].

The surface area of the modified TiO_2 catalyst analyzed using Brunauer–Emmett–Teller was 11.49 $m^2 g^{-1}$, lesser than commercial TiO_2 (Surface area of 33 m^2/g) [20]. The surface area of modified TiO_2 catalyst was lower than that of

Table 1
Central composite design (in actual units) for observed and predicted responses of 2,4-D degradation

Run	Factor 1: pH	Factor 2: Concentration mg/L	Factor 3: Dosage mg/L	Response dosage 1: Experimental percentage degradation	Response dosage 1: Predicted percentage degradation
1	2	100	150	84	86.9
2	10	55	87.5	83	85.4
3	6	55	87.5	73	74.9
4	6	55	87.5	73	74.9
5	2	100	25	63	65.4
6	6	55	25	82	79.12
7	6	55	87.5	73	74.9
8	6	55	87.5	73	74.9
9	10	10	25	70	68.5
10	6	55	87.5	73	74.9
11	10	100	25	46	47.5
12	2	10	150	94	93.9
13	6	100	87.5	71	63.12
14	2	55	87.5	84	78.2
15	2	10	25	94	94.4
16	6	55	87.5	97	94.1
17	10	100	150	77	78
18	6	55	87.5	73	74.9
19	10	10	150	78	77
20	6	10	87.5	75	77.1

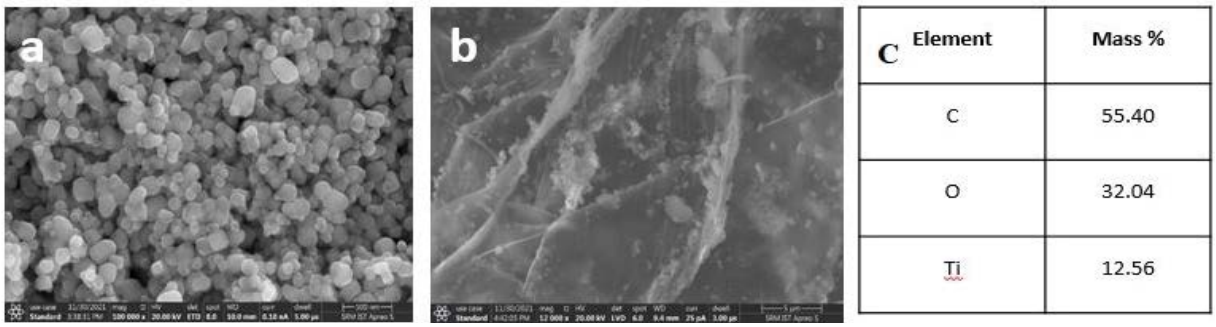

Fig. 1. (a, b) SEM of modified TiO_2 catalyst and (c) EDAX composition of modified TiO_2 catalyst.

commercial TiO_2 as photocatalytic activities of TiO_2 do not significantly depend on the catalyst surface area [36].

3.2. Design of experiment using central composite design

A central composite rotatable design derived from half fractional factorial design was studied for three significant variables. Parameters chosen for photocatalytic degradation of 2,4-D comprises concentration (X_1), pH (X_2), and 2,4-D dosage (X_3) [35]. The interaction of dependent variables was studied using Design-Expert software (version 13). According to the Montgomery method, the total number of experiments to be studied was 20 [32].

Table 1 shows the list of experiments performed and its response for predicted and experimental degradation of 2,4-D. At the optimized pH of 6, the concentration of 55 mg/L, and dosage of 87.5 mg/L, the maximum 2,4-D removal efficiency of 97% was recorded. The overall efficiency for 2,4-D degradation varied between 46%–97%.

The statistical significance of the CCD model by ANOVA is tabulated in Table 2. The R^2 value for the predicted ANOVA model is 0.93, which indicates the good correlation between experimental and predicted values [32]. The statistical model could explain 93% prediction of 2,4-D degradation against the 7% non-responsiveness of the model. Fig. 3 shows the experimental degradation vs. ANOVA-based predicted degradation for 2,4-D and indicates a good correlation between observed and predicted values.

From Table 2, lower pH (2, 6) favors the highest degradation of 2,4-D with an *F*-value of 35.9, whereas the interactive effect of pH with concentration (*AB*) and dosage (*AC*) does not significantly affect the degradation efficiency of 2,4-D. Similarly, the *p*-value less than 0.05 indicates the effect of significant variables chosen in this study.

The coded equation of the ANOVA model helps to make the predictions about each given response for the given levels. The coded equation helps to identify the relative impact of factors by comparing them with its coefficient.

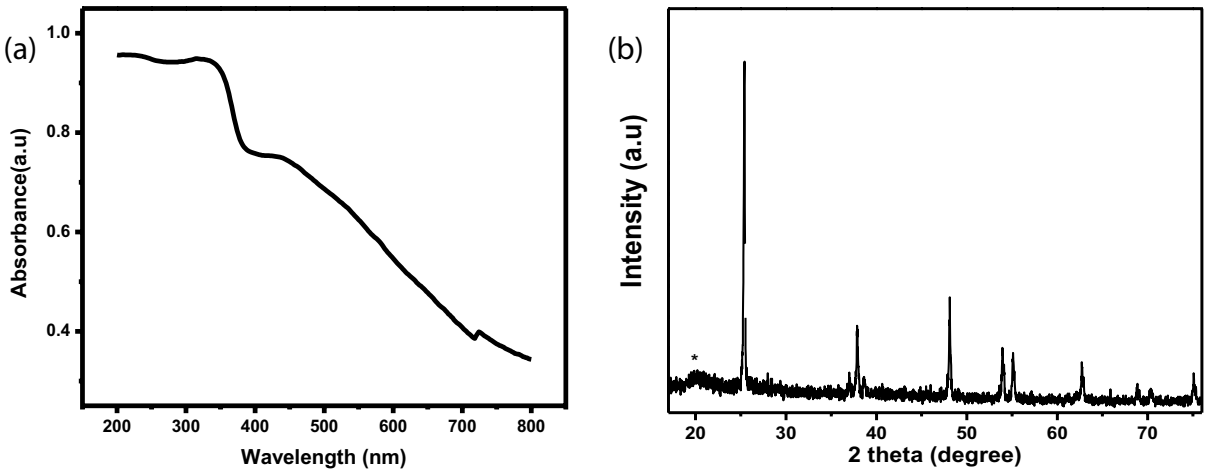

Fig. 2. (a) DRS UV spectroscopy of modified TiO_2 catalyst and (b) XRD spectra of modified TiO_2 catalyst.

Table 2
Analysis of variance (ANOVA) for the effect of variables on 2,4-D degradation (R^2: 0.93)

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
A	635.23	1	635.23	35.91	0.0002
B	490	1	490	27.70	0.0005
C	562.50	1	562.50	31.80	0.0003
AB	32	1	32	1.81	0.2115
AC	40.50	1	40.50	2.29	0.1645
BC	242	1	242	13.68	0.0049
A^2	51.36	1	51.36	2.90	0.1226
B^2	53.44	1	53.44	3.02	0.1162
C^2	320.19	1	320.19	18.10	0.0021
Residual	15919	9	17.69		
Lack of fit	159.19	4	39.80		
Pure error	0.0000	5	0.0000		
Cor. total	2,438.74	18			

A: pH; *B*: Concentration; *C*: Dosage

Eq. (2) lists the parameters obtained after the regression, and Fig. 3 shows the validation of experimental (actual) degradation with predicted degradation.

$$\text{Percentage degradation}(\%) = 74.91 - 8.72A - 7B + 7.5C + 2AB + 2.25AC + 5.50BC - 5.38A^2 - 4.79B^2 + 11.71C^2 \quad (2)$$

The three-dimensional plot with two-dimensional contours were plotted by keeping one variable constant at the midrange and helps to study the interaction of among the variables. Fig. 4 illustrates the degradation of 2,4-D with varying dosage (25 to 125 mg/L) and varying concentration (10 to 100 mg/L). The maximum 2,4-D degradation efficiency was 93% observed for the dosage of 150 mg/L at the lower 2,4-D concentration of 10 mg/L [37]. With an increase in the concentration from 2 to 10 mg/L, the 2,4-D degradation efficiency eventually decreases to 58%. With an increase in catalyst dosage, the 2,4-D degradation increases to 93%, irrespective of the increase in catalyst concentration.

The surface response plot for pH and 2,4-D concentration is illustrated in Fig. 5. The highest 2,4-D degradation efficiency (84%) was observed at lower pH of 2 for a 2,4-D concentration of 15 mg/L [35]. Similarly, with an increase in concentration, the 2,4-D degradation efficiency increases and then decreases to 50% for the concentration of 100 mg/L [38].

The surface response plot for pH and 2,4-D concentration is illustrated in Fig. 6. Lower pH of 2 favours higher degradation of 2,4-D with 150 mg/L. At lower pH, the electrostatic charges ensures the ionic form of the complex molecule to initiate 2,4-D degradation. Photocatalytic degradation of 2,4-D were performed for the optimized ANOVA condition of pH 6, 2,4-D concentration of 55 mg/L and dosage of 87.5 mg/L, and the experimentally observed 2,4-D degradation was reported to be 95%.

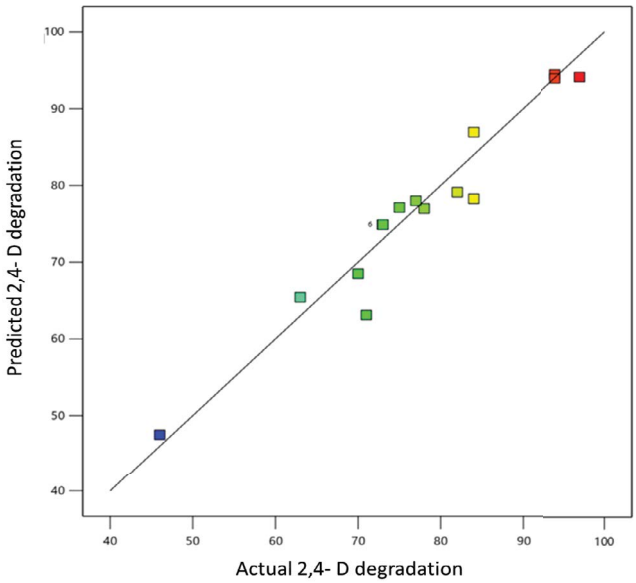

Fig. 3. Degradation of 2,4-D predicted vs. actual degradation.

3.3. Chemical oxygen demand and reusability studies

Chemical oxygen demand (COD) analysis was carried out for testing the viability of 2,4-D degradation. COD of 2,4-D solution (50 ppm) before and after degradation were reported in Table 3. 72% of COD reduction was observed after demineralization of 2,4-D using modified TiO_2 catalyst than compared to 45% of COD reduction for TiO_2.

The success of catalyst immobilization lies in the catalyst recovery and its reusability for further studies. The durability and photostability of modified TiO_2 catalyst needs to be checked for its commercial application [39]. Fig. 7 depicts

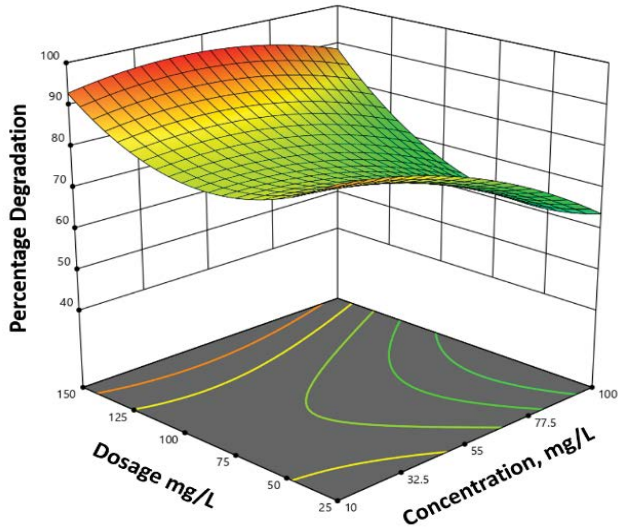

Fig. 4. Response surface and contour plots for varying dosage and concentration of 2,4-D degradation.

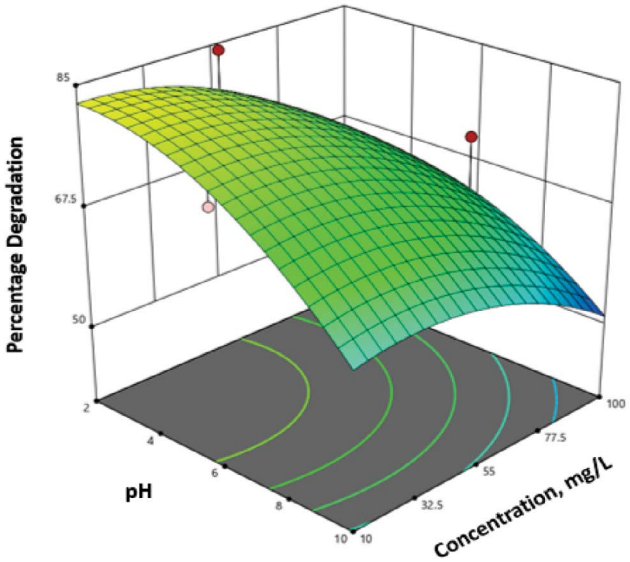

Fig. 5. Response surface and contour plots for varying dosage and concentration for 2,4-D degradation.

the degradation efficiency of 2,4-D for 8 consecutive cycles performed at optimized conditions. After each run, modified TiO_2 catalyst beads were washed thoroughly to ensure the complete absence of adsorbed molecules followed by drying before being used for further studies. The loss in catalyst loading in each experiment was observed to be less than 2%. The degradation efficiency decreases from 85% to 74% for 8 consecutive cycles (Fig. 7). The reason for the loss in degradation efficiency could be due to adsorption of surface impurities and 2,4-D on the surface of the catalyst.

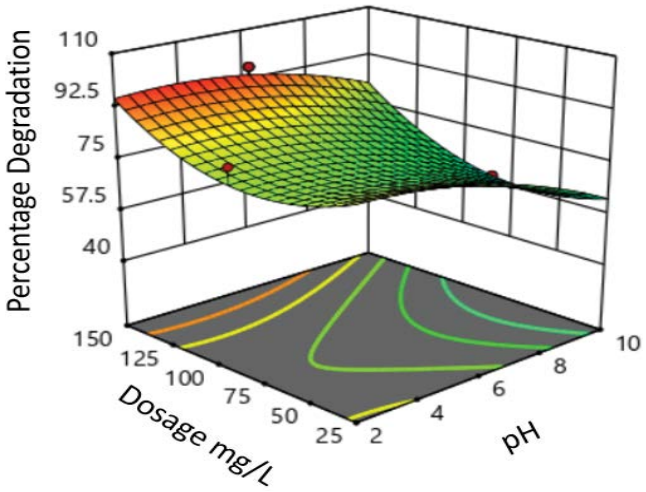

Fig. 6. Response surface and contour plots for varying dosage and pH for 2,4-D degradation.

Table 3
Comparison of COD for modified TiO_2 catalyst and TiO_2

Catalyst	Initial COD (mg/L)	Final COD (mg/L)	COD Reduction %
Modified TiO_2 catalyst	472	125	72
TiO_2	472	256	45

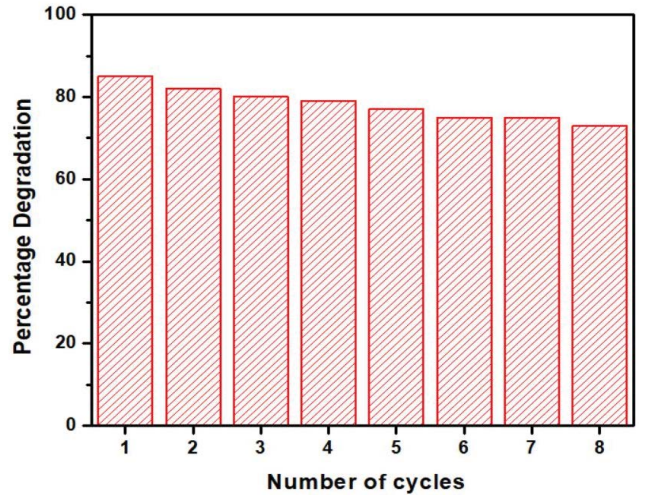

Fig. 7. Reusability study of modified TiO_2 catalyst.

4. Conclusion

In the central composites design, a second-order quadratic polynomial model was fitted to the experimental observation of 2,4-D degradation. The highest *F*-value obtained from the ANOVA design was 36 for the single parameter interaction of pH for photocatalytic degradation of 2,4-D. The quadratic model also brings out the interaction of concentration and dosage (*BC*) and Dosage (C^2) to obtain better degradation of 2,4-D. Adjusted Residual of 0.93 suggested that the developed model is significant with 0.01% noise. The characterization of the catalyst (XRD, UV-Vis, SEM) and its reusability studies of catalyst ensure the feasibility for pesticide degradation.

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