

# Optimization of Photocatalytic Degradation of Tetracycline Using Titania Based on Natural Zeolite by Response Surface Approach

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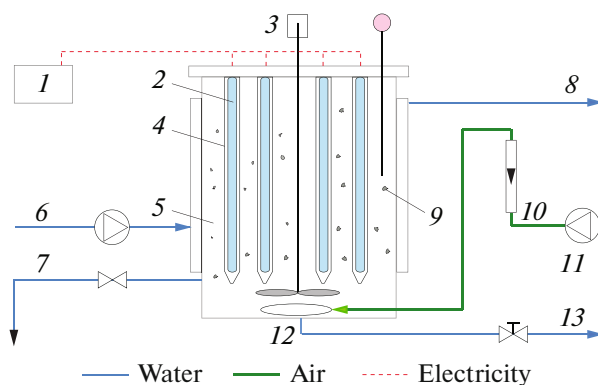
**Abstract**—Tetracycline (TC) is one of the most commonly applied antibiotic and due to the risk posed by antibiotic-resistant pathogens, the need for treating these wastewater is beyond question. Photocatalytic degradation of TC in aqueous solution was studied using TiO<sub>2</sub> based on natural zeolite (clinoptilolite, CP) under UV irradiation in a batch reactor. For the first time, in order to propose an accurate model for the photocatalytic degradation of TC under UV light, central composite design based on response surface methodology was employed to assess the individual and interactive effects of several classic parameters on both TC degradation and TOC removal (mineralization). In order to analyze the process, three significant variables pH, catalyst concentration, and tetracycline concentration and tetracycline degradation as the process response were studied. The results of the experiments were fitted to quadratic polynomial models. A maximum degradation of TC of more than 77% was achieved at the optimum conditions (pH 5.9, catalyst concentration of 0.30 g L<sup>-1</sup> and TC concentration of 8 mg L<sup>-1</sup>) within 60 of irradiation. The mineralization or oxidation profile, represented as the total organic carbon, was decreased significantly during the optimum conditions, achieving value near 54% after 4 h. The experimental values agreed with the predicted ones, indicating suitability of the model employed and the success of model in optimizing the conditions of photocatalysis. The quadratic model had high *R*<sup>2</sup> coefficient (0.980) and high *F*-value, confirming that the model was valid to predict the experimental results. Moreover, the adjusted *R*<sup>2</sup> is very close to the *R*<sup>2</sup> value as another evidence for goodness of the model fit. Initial TC concentration and catalyst dosage are the major factors affecting the photocatalytic degradation of TC using TiO<sub>2</sub>/CP.

**Keywords:** tetracycline, design of experiment, natural zeolite, mineralization

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## INTRODUCTION

Over the past few years, antibiotics and their metabolites have been detected in surface water, ground water, wastewater, and drinking water at levels ranged from ng L<sup>-1</sup> to µg L<sup>-1</sup> [1, 2]. The wide use of antibiotics is beneficial for preserving human health, but results in their undesirable accumulation in different environmental compartments as a secondary effect, which cannot be effectively eliminated by traditional biological methods [3–5]. Tetracycline (TC) is one of the most commonly applied antibiotic and its production and usage rank second worldwide after antimicrobial sulfonamides [6]. Because it is biologically active, stable and non-biodegradable, its release to the environment threatens aquatic life and increases the risk posed by antibiotic-resistant pathogens [7]. Thus the need for treating these wastewaters is beyond question. Recently, heterogeneous photocatalytic degradation of organic pollutants in the presence of nanostructured semiconductors attained the maximum efficiency of mineralization [2, 8–12]. Investigation of photocatalytic degradation of pollutants has usually been made by the single-variable-at-a-time (SVAT, the most common practice holding all other variables constant) method in previous studies [11–13]. Nevertheless, the SVAT approach possesses many drawbacks, such as being time-consuming, inability to account for interactions between different variables and inefficiency in predicting the true optimum conditions. Response surface methodology (RSM) is a useful statistical method which can determine the optimal condition and reduce the study time and the cost by the comprehensive analysis of mathematics [14]. For the first time, in order to propose an accurate model for the photocatalytic degradation of TC under UV light, central composite design (CCD) based on RSM was employed to assess the individual



**Fig. 1.** Schematic diagram of photocatalytic reactor set up: (1) lamps controller; (2) lamp; (3) electric stirrer; (4) quartz tube; (5) aqueous solutions; (6) cooling water; (7) sampling port; (8) water out; (9) suspended catalyst; (10) rotameter; (11) air pump; (12) sparger; (13) drain.

and interactive effects of several classic parameters on both TC degradation and total organic carbon (TOC) removal (mineralization).  $\text{TiO}_2$  based on natural zeolite was used as photocatalyst for the study.

## EXPERIMENTAL

$\text{TiO}_2$  based on natural zeolite ( $\text{TiO}_2/\text{clinoptilolite}$ :  $\text{TiO}_2/\text{CP}$ ) was prepared via simple method by mixing 1 g  $\text{TiO}_2$  P25 with 5 g of natural zeolite in powder form with subsequent treatment according to our previous investigation [15]. Common TC ( $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_8$ ) pharmaceutical 250 mg capsule was purchased from Daru Company, Iran. All the water used was deionized.

### *Photocatalytic Experiments*

Photocatalysis experiments were carried out in the homemade cylindrical photocatalytic reactor. It was made of Pyrex with an effective volume of 300 mL and equipped with four UV-C lamps (4W from Philips Co., Japan) as irradiation source (Fig. 1). Prior to photocatalytic experiments, adsorption study was carried out. Samples of the reaction solution were obtained at regular intervals, filtered by centrifuge and analyzed by UV-Vis spectrophotometer. The degradation efficiency of TC was calculated by  $(C_0 - C)/C_0 \times 100$ .

### *Experimental Design and Statistical Analysis*

Based on the literature [9], three operational factors: pH (4–10), catalyst ( $0.3\text{--}0.8\text{ g L}^{-1}$ ) and initial TC concentration ( $8\text{--}14\text{ mg L}^{-1}$ ) were introduced as those with the most significant impact, which were considered as the system variables, and TC degradation efficiency was calculated as the process response. CCD has been extensively used along with RSM to optimize various physical, chemical and biological processes using Design Expert software version 8.0.4.1 [16]. Total organic carbon measurements were performed by TOC analyzer (Anatoc, Australia). UV-Vis spectra for determination of TC concentration were obtained on a Shimadzu UV-1650PC spectrophotometer.

## RESULTS AND DISCUSSION

### *Statistical Analysis*

Experimental and predicted values obtained for degradation of TC at the design points are presented in Table 1. Degradation efficiency of TC (%) is correlated to independent variables with a second-order polynomial by the following equation:

$$\text{TC} = 127.5 - 9.3A - 38.1B + 4.7C + 1.7AB - 0.4AC + 10.3BC + 0.3A^2 - 26.6B^2 - 0.4C^2. \quad (1)$$

**Table 1.** Experimental design matrix

Independent variables			Degradation efficiency (%) after 60 min	
TC concentration, mg L <sup>-1</sup>	TiO <sub>2</sub> /CP concentration, g L <sup>-1</sup>	initial pH	experimental	predicted
8	0.3	10	70	69
11	0.55	1.95	58	53
5.95	0.55	7	98	96
14	0.8	10	68	61
11	0.55	7	70	65
11	0.55	7	70	65
11	0.97	7	72	70
16.05	0.55	7	59	50
14	0.3	10	36	31
14	0.3	4	57	52
8	0.3	4	75	75
11	0.55	7	70	65
8	0.8	4	71	68
11	0.55	7	63	65
14	0.8	4	58	51
8	0.8	10	97	93
11	0.55	7	70	65
11	0.55	12.05	63	57
11	0.13	7	58	50
11	0.55	7	70	65

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA), indicating  $F$ -value of 49.79 and  $R^2 = 0.98$ , implying that the model was statistically significant (Table 2) [17, 18]. Moreover, the adjusted  $R^2$  is very close to the  $R^2$  value, which is another evidence for goodness of the model fit [19, 20]. The lack of fit  $F$ -value of 0.82 is not significant as the  $P$ -value is 0.5814. From these results, it can be concluded that the obtained model is adequate to describe the relationship between the degradation efficiency and three factors for degradation of TC. Initial TC concentration and catalyst dosage are the major factors affecting the photocatalytic degradation of TC using TiO<sub>2</sub>/CP. The three-dimensional response surface plots represent an infinite number of combinations of the two selected variables with the other maintained at its respective zero coded level. The results of Fig. 2, a revealed that the rate of degradation of TC decreased with increase in concentration irrespective of the dose of catalyst. By increasing the initial concentration of TC, higher amounts of reactant and reaction intermediates are adsorbed at the surface of the photocatalyst. Therefore, the demand of reactive species ( $\cdot\text{OH}$  and  $\cdot\text{O}^{2-}$ ) needed for the degradation of TC also increases. However, the formation of  $\cdot\text{OH}$  and  $\cdot\text{O}^{2-}$  on the catalyst surface remains constant for a given light intensity, catalyst amount, and duration of irradiation. Hence, the available  $\cdot\text{OH}$  radicals are inadequate for the TC degradation at higher concentrations. Similar results were reported by others and usually attributed to the limited amount of active sites available for the adsorption of reactant at higher concentration [21, 22]. According to Fig. 2b, at constant pH, efficiency increased by increasing the amount of catalyst dosage. The saddle nature of the plots confirms that a significant interaction exists between these two factors (BC). It is found that when TiO<sub>2</sub>/CP loading were increased, the photodegradation was enhanced. Increased loading of the catalyst increases the generation rate of electron/hole pairs and, thus, the formation of  $\cdot\text{OH}$  radicals leading to the enhancement of photodegradation. Maximum degradation of tetracycline more than 94% was achieved at tetracycline con-

**Table 2.** ANOVA for the response surface quadratic model

Source of variations	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	3338.06	9	370.90	49.79	<0.0001
Residual	74.49	10	7.45	0.82	0.5814
Lack of fit	33.66	5	6.73		
Pure error	40.83	5	6.17	—	—
Total	3412.55	19	—	—	—

$R^2 = 0.98$ ; Adj  $R^2 = 0.96$ .

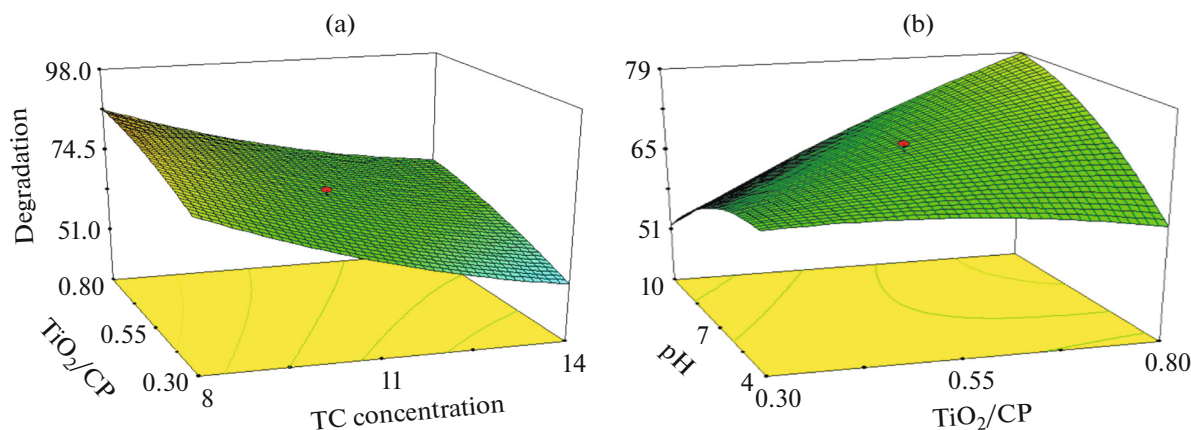
centration of  $8 \text{ mg L}^{-1}$ , catalyst concentration of  $0.8 \text{ g L}^{-1}$  and pH 10 within 60 min of irradiation (see Table 1).

### Optimization of Independent Variables and Validation

In the present study, efforts have been made to minimize the use of the catalyst and to maximize the degradation of TC, during optimization. The optimum conditions for the maximum possible degradation of TC under the described constraints were found out to be: dose of  $\text{TiO}_2/\text{CP}$   $0.3 \text{ g L}^{-1}$ , concentration of TC  $8 \text{ mg L}^{-1}$  and pH of reaction mixture 5.9. Under these conditions the model predicted the degradation of TC to be 77.9%. The result showed the efficient use of RSM to find out the optimum conditions for the photocatalytic degradation of TC using  $\text{TiO}_2/\text{CP}$ . The degradation efficiency was found out from the validation experiment to be about 75%. It was in good agreement with the predicted result, which confirms the adequacy and validity of the model.

### Mineralization Assessment

TOC analysis provided valuable information about the efficiency of the photocatalytic process. The destruction of organic pollutants should be regarded as an overall degradation process that ultimately involves mineralization of both the parent substance and its intermediates. The mineralization or oxidation profile, represented as the TOC, was decreased significantly during the optimum conditions, achieving value near 54% after 4 h. It is remarkable that the TOC removal reached good value, indicating that the oxidation of intermediates promoted a continuous cleavage of the initial organic structures.



**Fig. 2.** The response surface plots of degradation efficiency of TC by  $\text{TiO}_2/\text{CP}$ : (a) TC concentration vs.  $\text{TiO}_2/\text{CP}$  concentration, (b)  $\text{TiO}_2/\text{CP}$  concentration vs. pH.

## CONCLUSIONS

The photocatalytic degradation of TC in an aqueous solution under UV light using an experimental design methodology by titania based on natural zeolite was firstly studied. From the quadratic models developed for degradation and subsequent ANOVA test using Design Expert software, the initial concentration of TC and catalyst dosage were found to be the most influential factors. The quadratic model had high Required coefficient (0.98) and high *F*-value, confirming that the model was valid to predict the experimental results.

The process was optimized under two applied constraints of minimum use of catalyst and maximum degradation of TC under the constraints. The optimum values of the three independent variables were found out as dose of TiO<sub>2</sub>/CP 0.3 g L<sup>-1</sup>, initial concentration of TC 8 mg L<sup>-1</sup> and pH of reaction mixture 5.9 under the applied constraints. Under the optimum condition the degradation of TC was predicted to be 77.9%. Furthermore, the TOC result (54% removal after 4 h) revealed that modified semiconductor could effectively mineralize TC.

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