Application of Catalyst/UV/PU Nanocomposite for Removal of Tetracycline: Response Surface Methodology for Optimization and Kinetic Study

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Abstract

Background: Discharging antibiotics into the environment could cause great concern for scientists. In the present study, tetracycline (TC) antibiotic was photodegraded with titanium dioxide (TiO2) and zinc oxide (ZnO) fixed on the polyurethane (PU) in the presence of ultraviolet (UV) irradiation and optimized through response surface methodology (RSM).

Methods: This experimental study was conducted on the most effective variables (pH, contact time, TC concentration, and catalyst doses) for experimental design. The experiments of degradation with the process of PU/UV/nanocatalyst composite were conducted with a reactor glass vessel (1000 mL) as batch mode.

Results: The results showed that the quadratic model can be used for the interpretation of experiments. The results of the model represented that all parameters had a significant effect on the tetracycline removal, and the degradation of antibiotics was obtained at the optimum condition that was 95% for ZnO/UV/PU and 97% for TiO2/UV/PU. The main radical for the degradation of TC was hydroxyl ions based on the scavenger study and the first-order kinetic model was best fitted with data. The highest removal efficiency was obtained at pH of 5.2, catalyst dose of 2.64g/m2, TC concentration of 25.21, reaction time of 82 min using ZnO/UV/PU and pH of 5.8, catalyst dose of 2.9 g/m2, TC concentration of 25.12, and reaction time of 90 min using TiO2/UV/PU.

Conclusion: It could be concluded that the process of nanocatalyst fixed on polyurethane can significantly eliminate the antibiotic in the presence of ultraviolet irradiation from the effluent of the wastewater treatment plant.

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Keywords: Tetracycline, Nanocomposite, Optimization, Kinetic study, Nanocatalyst

Introduction

Utilization of antibiotics for medical purpose are widely increased; they are also used in animal feeds because of disease prevention and stimulation growth. Therefore, a major concern that has recently been raised is associated with antibiotics in water bodies. Generally, common antibiotics are classified as aminoglycosides, macrolides, quinolone, sulfonamides, and tetracycline (TC) according to the chemical structure.[1] Even at low concentrations, antibiotics could lead to an adverse effect on ecosystems and human beings due to bioaccumulation, chronic and acute effects, high water solubility, high persistent, bioactivity, and string effects on the microbial resistance

and community.[2]

Tetracycline (TC) with the chemical formula of $C_{22}H_{24}N_2O_8$ has been extremely applied in human cure and livestock therapy as well as the agricultural industry. This type of antibiotic could be used for bacterial infections like gonorrhea, acne, and infections of the urinary tract.[3] Many technologies have been used to eliminate antibiotics from aqueous solutions such as biological treatment, electrochemical process, adsorption, membrane process, and photocatalysts. It appears that the common biological and physical methods could not sufficiently remove the pharmaceutical compounds.[4] These methods have some disadvantages like complexity, high required energy, low efficiency, and/or incomplete removal. The favorable results obtained from AOPs for degradation of antibiotics and its potential for radical generation and non-selectivity have attracted more attentions for using this process in the pharmaceutical process.[5,6] On the other hand, photocatalysts can play an important role in generating more radicals and mineralizing the organic compounds into water and carbon dioxide.[7] In this method, the semiconductor agent acts as a catalyst and the surface of its particle must be exposed to irradiations to generate the hydroxide radicals, and then organic compound degradations could be carried out through the radicals produced. The photocatalytic activity of nanocatalyst particles (TiO2 and ZnO) powerfully depends on the size of crystallite, surface area, morphological characteristic, and pore and phase structure.[8]

Recently, the photocatalysis process by ZnO and TiO_2 has been widely investigated for degradation of recalcitrant compounds because of low cost, stability, high activity, surface area, great functionality, and environmental friendliness for their synthesis. However, the tendency of these photocatalysts to agglomeration and their difficult recovery cause this process to modify.[9] Polyurethane consists of a soft and hard segment. The soft segment includes polyether or polyester macrogel, and the hard segment is produced from the reaction of a diisocyanate with diamine or diol. Therefore, the separation of the soft and hard phases could be carried out easily.

Production of polyurethane/nanophotocatalyst composite could improve the disadvantage of the nanocatalysis process through developing appropriate dispersion of nanocatalysts and increasing the light absorption, surface area, and the storage of electron capacity.[10]

Besides, response surface methodology (RSM), as a statistical and mathematical method, could effectively assess the relative significance of dependent and independent variables and optimize the conditions to reach the high efficiency of the independent variable.[11] Therefore, the objectives of the present study are not only to synthesize the polyurethane nanocatalyst (PU/NC) composite and determine the characterization of them, but also to propose a novel experimental design through response surface methodology in studying the degradation and optimization of tetracycline removal from aqueous solutions.

Methods

Chemicals

Tetracycline (≥98.1%) was obtained from Sigma-Aldrich, Australia. dioxide titanium, and zinc oxide nanoparticles, Ammonia solutions, tertbutyl alcohol, toluene, Tetrahydrofuran (THF), sulphuric acid, methyl isothiocyanate, pentaerythritol, and ethanol sodium hydroxide (NaOH, 32%) were obtained from Merck, Germany. All chemicals were utilized without further treatment and had analytical grades. Deionized water was employed for the whole steps of the experiments.

Preparation of Polyurethane/Photocatalyst Nanocomposite

Polyurethane was synthesized at room temperature. Firstly, 4.4-diphenylmethane diisocyanate (MDI) (6 g) was added to the 50 mL of toluene and agitated until completely dissolved. Dried nanoparticles in a vacuum oven, completely dry reaction medium, and pre-dried solvent were applied for the synthesis of PU because of the high reactivity of the isocyanate group. The temperature of the reaction spontaneously raised to 60ºC. Subsequently, pentaerythritol (5mL) was increased under rapid stirring. Then, the mixture was reflexed for 1h and dried at 120ºC to provide the desired polyurethane polymer.[10] After that, synthesized PU (5 g) was dissolved in tetrahydrofuran (THF) and mixed for 24 h. Then, various amounts of nanocatalysts (TiO2 and ZnO) were added to the solution in different steps at the ultrasonic bath to obtain a homogeneous solution. Ultrasonic sound wavescan lead to penetration of the nanocatalysts into the swollen polymer. Finally, the obtained nanocomposite was dried on the magnesium tape at 25ºC and then put in an oven at 50ºC to evaporate the solvent.[10]

Analysis and Characterization

The morphology and catalyst surface structure of synthesized nanocomposite was determined through scanning electron microscopy (SEM, TESCAN MIRA3, England) equipped with energy-dispersive X-ray spectroscopy (EDX). The XRD analysis (Philips PW1730, Germany) was employed to identify the mineral and distribution elements. HPLC (Cecil CE49000, England) with UV/Vis CE 4900 was used as a detector for the analysis of TC concentration. MACHEREY-NAGEL column (Germany), C18ec (250mm × 4.6mm) was used in this way. The volume

of injection and wavelength of measurement was 20 µL and 288 nm. The orthophosphoric (65%) and buffer 65% (NaH_2PO_4) was applied as the mobile phase.

Experimental Design

Response surface methodology (RSM) was employed in order to detect the interactions of the selected variables. In addition, this methodology was used to optimize dependent variables based on the maximum response (efficiency removal) in three levels. The range of independent variables was pH: 3-11, reaction time: 0-90 min, TC Concentration: 25-50 mg/L and Photocatalyst Concentration on the polyurethane surface: 1-3 g/m^2. The box-boncken method was used in this study for modeling. Design-Expert software (version 11) was utilized for experimental design and data analysis.

In this study, 29 experimental runs were developed that include 5 replicates using 2k (k was the variable number). The removal efficiency of TC was measured through the following equation:

$$Y = \beta_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_{ii} Xi^2 \sum_{i=1}^{k} \sum_{i=1}^{k} B_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y represents the response variable (TC removal efficiency %); β_0, $B_{i,}$ and B_{ij} refers to the constant coefficient, coefficients of the model, respectively. The coded independent variables are X_i and X_j.[12]

Experimental Set-up and Degradation Study

The exact amount of TC was dissolved in double deionized water for the preparation of TC stock (1000 mg/L). The experiments of degradation with the process of PU/UV/nanocatalyst composite were done with a reactor glass vessel (1000 mL) as the batch mode. The temperature of the reactor was kept at 30±1°C through a water bath. The UV-C lamp with medium-pressure (λ_{max}=247.3 nm, 125 W) was equipped with a quartz cover with an external diameter, internal diameter, and length of 2.5 cm, 2 cm, and 12.5 cm, respectively. The UV lamp was put in the middle of the reactor and 5 cm was considered as a free height to prevent the reactor overflow. Finally, the aluminum foil was used to avoid exposure to UV radiation. The generated nanocomposites were precipitated on the bottom of the reactor and baffles. Returning the effluent of the reactor was carried out using a pump and baffles installed in the reactor in order to agitate the reactor contents. Sodium hydroxide (0.1 N) and hydrochloric acid (0.1 N) were used for pH adjustment.

Kinetic Study

The mechanism and rate of reactions could be determined through kinetic studies. In the present study, the kinetics of TC removal with PU/UV/nanocatalysts was estimated with three zero, first and second-order models at the optimum condition.

Results

Characteristics

XRD images were employed to evaluate the structure of nanocatalysts (TiO2 and ZnO). Figure 1 (a) and (b) represents the variations in the crystallinity of TiO2 and ZnO and phase identification. As can be seen, the main peaks for TiO2 located at 2Θ of 25, 38, 48, 54, 55, 63, and 69º are associated with the TiO2 composition. In addition, the peaks of 2Θ at 32, 35, 37, 47, 57, 63, 67, 68, 69, 73 and 78 are connected to the (100), (002), (101), (102), (110), 103), (200), (112), (201), (004) and, (002) planes which were related to the ZnO composition, respectively.

The EDX results presented in Table 1 showed that the number of elements was equale to 74.88 (50.3% weight), and 25.12% (49.67% weight) of oxygen and titanium for TiO_2 and 51.56 (18.7% weight), 48.44% (81.3% weight) of oxygen and zinc for ZnO.[13]

The images of TEM of nanocatalysts (TiO2 and ZnO) used in this study are shown in Figure 1 (e) and (f). As can be observed, the nanocatalyst particles were monodispersed and closely spherical.

Degradation of TC with TiO2/UV/PU and ZnO/UV/PU

RSM was used to evaluate the efficiency of *TiO2/UV/PU and ZnO/UV/PU* processes on the removal of TC. Also, the effects of variables and interaction between dependent variables (pH, catalyst dose, contact time, and initial TC concentrations) on the response variable (removal efficiency of TC) were investigated. The values of dependent variables and response (removal efficiency of TC) are shown in Table 2. The catalytic effects of nanocatalysts in the process of TiO2/UV/PU and ZnO/UV/PU of the 29 experimental runs fluctuated from 48 to 95% and 49 to 96%, respectively.

The results of statistical analysis including variance analysis (ANOVA) and regression analysis of the selected model) are shown in Table 3. The maximum value of the F-value was calculated for a dose of nanocatalyst (98.67 with TiO_2/UV/PU and 75.93 for ZnO/UV/PU, which showed that this variable had the most impact on the TC degradation. While solution pH with an F-value of 53.23 for TiO_2/UV/PU and contact time of 4.64 for 33.62 for Zn/UV/PU had the lowest impact on the TC degradation. It should be stated that all dependent variables had a significant effect on the response variable, but the effect of interaction of dependent variables on the response was insignificant.

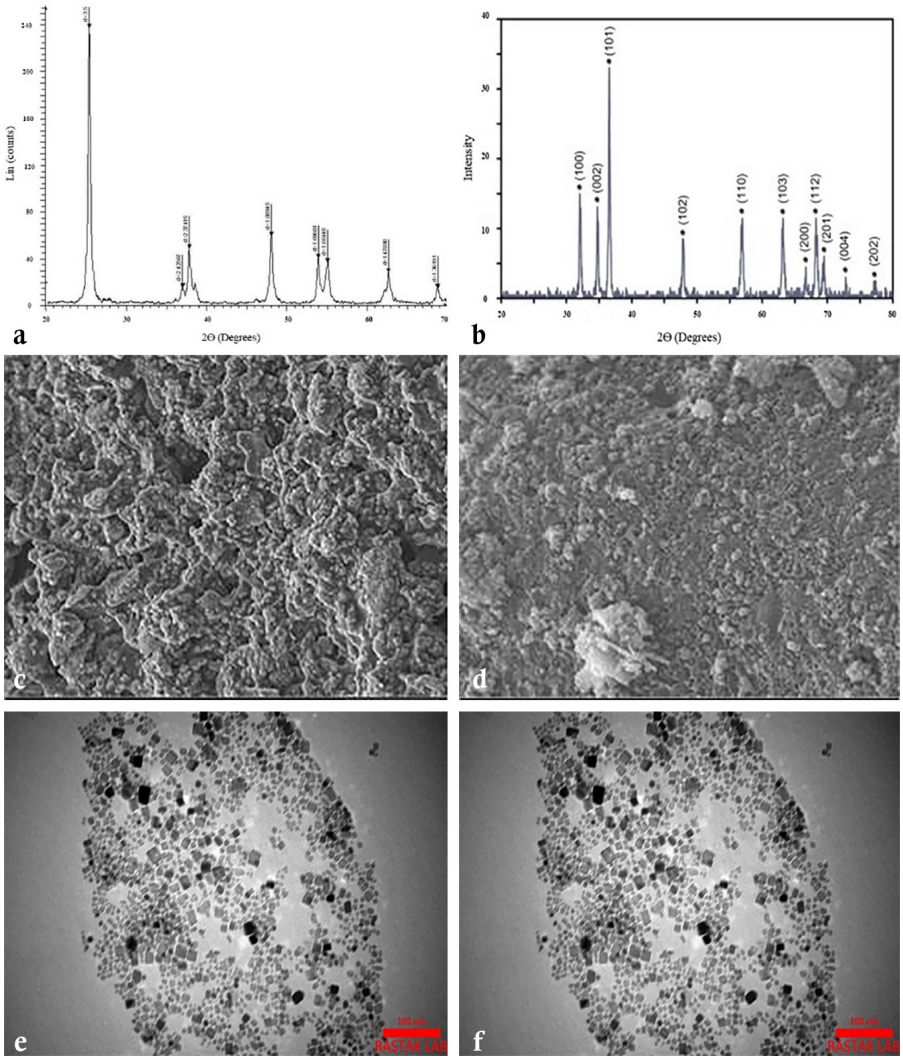

Figure 1: Characteristics of nanocatalysts; XRD Images of nanocatalysts (a) TiO2 and (b) ZnO; SEM images of nanocatalysts of (c) TiO2 and (d) ZnO; TEM images of nanocatalysts of (e) TiO2 (f) ZnO

Table 1: Results of EDX for nanocatalysts of TiO2 and ZnO

ZnO			TiO2		
Element	**Atomic (%)**	**Weight (%)**	**Element**	**Atomic (%)**	**Weight (%)**
ZnK	48.44	81.3	TiK	25.12	49.67
OK	51.56	18.7	OK	74.88	50.33
Total	100	100	Total	100	100

Based on P-value ((less than 0.05 (0.0001) and F-Value (23.16) coefficients, the selected quadratic model had a significant effect on the decomposition of TC in the process of photocatalysts in the presence of ZnO/UV/PU. Based on the conducted model, the efficiency of TiO2/UV/PU and ZnO/UV/PU for the TC degradation can be computed with (1) and (2) Eq., respectively.

$$TiO_2/UV/PU = 75.4 - 6.1A + 8.75D - 12.075A^2 \quad (1)$$

$$ZnO/UV/PU = 72.6 - 5.6A + 10.25B - 9.8C + 8.08D - 10.75A^2 \quad (2)$$

Investigation of Effective Parameters

The 3D images of effective variables on the removal of TC using TiO_2/UV/PU and ZnO/UV/PU are shown in Figures 2 and 3a, showing the effect of catalyst dose (g/cm^2) and initial pH on the TC removal. As can be seen in these Figures, the removal efficiency of TC increased with an increase in catalyst dose. On the other hand, the removal efficiency of TC initially increased with an increase in pH and then decreased. The maximum removal was obtained at the highest amount of catalyst dose (3g/m^2) and relative acidic pH (about 6).

Figure 2 and 3 b show 3-D images of the effect of TC antibiotic concentration and the initial pH of the solution on the removal of TC using TiO2/UV/PU and ZnO/UV/PU. As can be observed, the antibiotic removal efficiency decreased with increasing the

Table 2: The results of experimental runs and values of variables on the TC removal using TiO2/UV/PU and ZnO/UV/PU

Run	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
	A:pH	B:Cata Dose	C:Concentration	D:Reaction time	UV/TiO2/PU	UV/ZnO/PU
unit	-	g/m2	mg/L	min	(%)	%
1	7	2	25	20	87	82
2	3	2	37.5	20	62	63
3	7	2	37.5	55	64	66
4	11	2	37.5	20	48	53
5	11	2	25	55	66	67
6	7	3	37.5	20	82	84
7	11	2	37.5	90	73	74
8	11	3	37.5	55	69	62
9	7	2	37.5	55	72	77
10	11	2	50	55	48	49
11	11	1	37.5	55	49	50
12	7	2	25	90	94	93
13	3	2	25	55	77	77
14	3	2	37.5	90	78	84
15	3	3	37.5	55	86	87
16	7	1	37.5	90	79	83
17	7	2	37.5	55	77	77
18	7	3	50	55	76	79
19	7	2	37.5	55	74	78
20	7	3	37.5	90	95	96
21	7	3	25	55	91	90
22	3	1	37.5	55	59	60
23	7	2	50	20	63	64
24	3	2	50	55	59	58
25	7	1	37.5	20	59	63
26	7	1	50	55	51	59
27	7	2	50	90	79	82
28	7	1	25	55	79	78
29	7	2	37.5	55	76	79

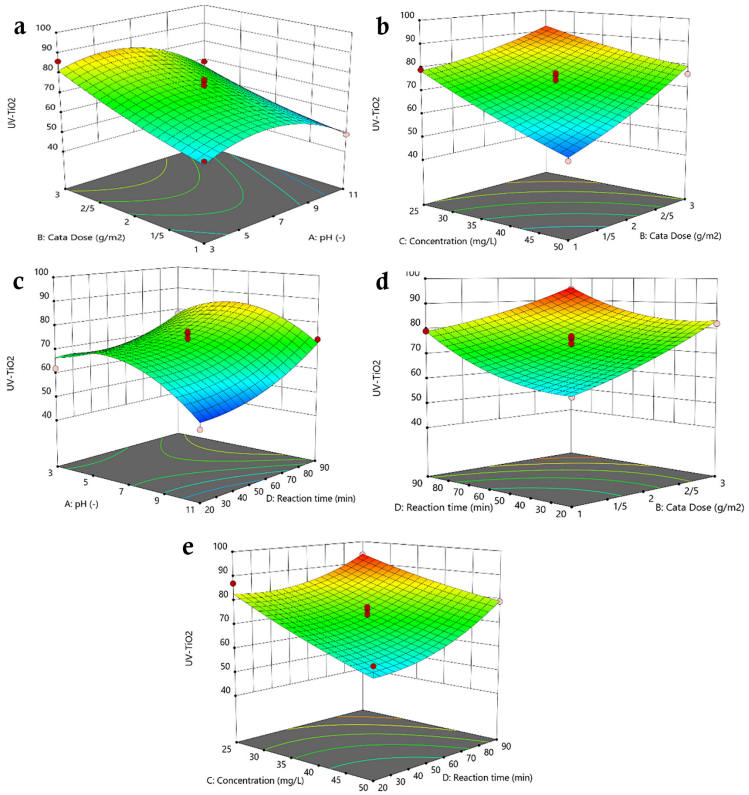

Figure 2: TC removal using TiO2/UV/PU, the effect of (a) pH-catalyst dose (b) pH-TC concentration (c) pH-reaction time (d)reaction time-catalyst dose and (e) reaction time-TC concentration

Table 3: Analysis of variance (ANOVA) and regression analysis for TC removal

TiO_2/UV/PU Process						
Variance Analysis (ANOVA)						
Source	**Sequential p-value**	**Lack of Fit p-value**	Adjusted R^2		Predicted R^2	
Linear	< 0.0001	0.1861	0.6587		0.5527	
2FI	0.9599	0.1239	0.5778		0.1494	
Quadratic	< 0.0001	0.8572	0.9096		0.8284	Suggested
Cubic	0.9288	0.4473	0.8526		-0.5392	Aliased
Regression analysis for the quadratic model						
Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	**P value**	
Model	4845.89	14	346.13	21.13	< 0.0001	significant
A-pH	385.33	1	385.33	23.53	0.0003	
B-Cata Dose	1260.75	1	1260.75	76.98	< 0.0001	
C-Concentration	1160.33	1	1160.33	70.85	< 0.0001	
D-Reaction time	784.08	1	784.08	47.88	< 0.0001	
AB	12.25	1	12.25	0.7480	0/4017	
AC	0	1	0	0	1	
AD	20.25	1	20.25	1.24	0.2849	
BC	42.25	1	42.25	2.58	0.1305	
BD	12.25	1	12.25	0.7480	0.4017	
CD	20.25	1	20.25	1.24	0.2849	
A^2	750.76	1	750.76	45.84	< 0.0001	
B^2	22.60	1	22.60	1.38	0.2597	
C^2	10	1	10	0.6106	0.4476	
D^2	153.63	1	153.63	9.38	0.0084	
Residual	229.28	14	16.38			
Lack of Fit	122.08	10	12.21	0.4555	0.8572	not significant
Pure Error	107.20	4	26.80			
Cor Total	5075.17	28				
ZnO/UV/PU Process						
Variance Analysis (ANOVA)						
Source	**Sequential P value**	**Lack of Fit P value**	**Adjusted R^2**		**Predicted R^2**	
Linear	< 0.0001	0.1727	0.5895		0.4639	
2FI	0.9738	0.1121	0.4862		-0.0270	
Quadratic	< 0.0001	0.9520	0.9172		0.8634	Suggested
Cubic	0.8060	0.9869	0.8861		0.9390	Aliased
Regression analysis for the quadratic model						
Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	**P value**	
Model	4477.41	14	319.81	23.16	< 0.0001	significant
A-pH	456.33	1	456.33	33.05	< 0.0001	
B-Cata Dose	918.75	1	918.75	66.55	< 0.0001	
C-Concentration	768.00	1	768.00	55.63	< 0.0001	
D-Reaction time	884.08	1	884.08	64.04	< 0.0001	
AB	56.25	1	56.25	4.07	0.0631	
AC	0.2500	1	0.2500	0.0181	0.8949	
AD	0	1	0	0	1	
BC	16	1	16	1.16	0.2999	
BD	16	1	16	1.16	0.2999	
CD	12.25	1	12.25	0.8873	0.3622	
A^2	945.77	1	945.77	68.50	< 0.0001	
B^2	10.96	1	10.96	0.7940	0.3879	
C^2	0.6851	1	0.6851	0.0496	0.8269	
D^2	165.42	1	165.42	11.98	0.0038	
Residual	193.28	14	13.81			
Lack of Fit	80.08	10	8.01	0.2830	0.9520	not significant
Pure Error	113.20	4	28.30			
Cor Total	4670.69	28				

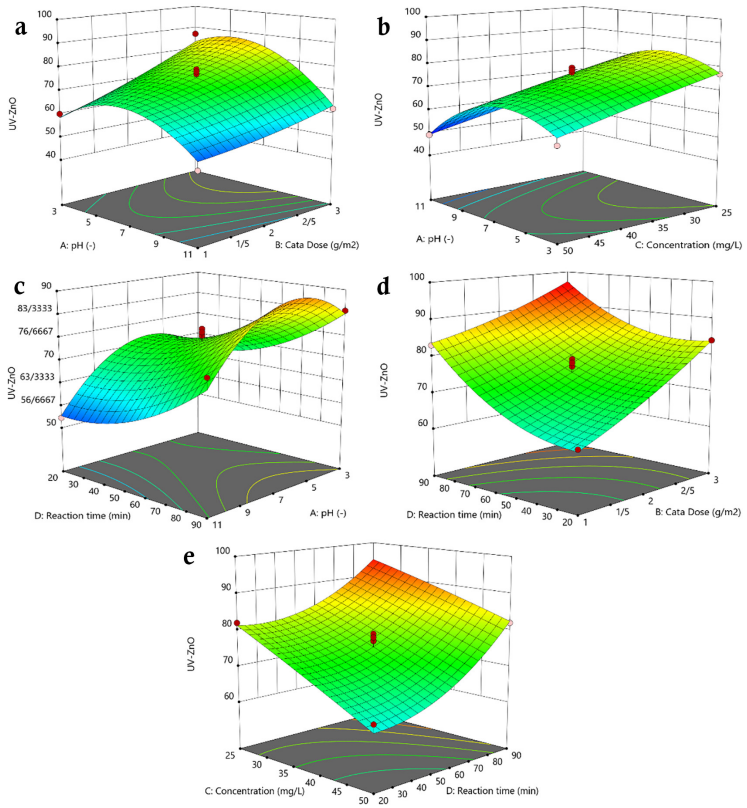

Figure 3: TC removal using ZnO/UV/PU, the effect of (a) pH-catalyst dose (b) pH-TC concentration (c) pH-reaction time (d)reaction time-catalyst dose and (e) reaction time-TC concentration

Table 4: Optimization process of TiO_2/UV/PU and ZnO/UV/PU for TC removal and results of the real wastewater at optimum conditions

Process	pH	Catalyst dose (g/m^2)	TC concentration (mg/L)	Reaction time (min)	Removal efficiency (%) (model)	Removal Efficiency (%) (Laboratory)	Real wastewater
TiO2/UV/PU	5.8	2.9	25.12	90	95	93.6	55
ZnO/UV/PU	5.2	2.64	25.21	82	97	94.9	62

initial concentration of the TC. Besides, as the pH of the solution increased, the efficiency of the TC degradation first increased and then decreased. Therefore, the highest process efficiency was obtained at low concentrations of TC (25 mg / L) and relatively acidic pH (about 6).

Figures 2 and 3 c illustrate the 3-D plot of the TC removal and interaction of reaction time (min) and the initial pH of the solution. As can be seen, the antibiotic removal efficiency increased with increasing reaction time.

The interaction effects of reaction time and catalyst dose on the removal of TC antibiotics are shown in Figures 2 and 3 d. The degradation rates increased with an increase in reaction time and catalyst doses. The highest amount of TC removal was obtained at 3g/L of catalyst dose and reaction time of 90 min.

The 3-D plot of TC removal with the effects of reaction time and antibiotic concentration is shown in Figures 2 and 3 d. The results revealed that antibiotic removal efficiency decreased with raising the TC concentrations. The maximum removal efficiency was given at reaction time of 90 min and Tc concentrations of 25 mg/L.

Considering the experimental design carried out using Design-Expert software, the optimal conditions of the process were obtained by the maximum possible option of the response (removal of TC). The results of the process optimization are presented in Table 4. The accuracy of the predicted values was proven in the laboratory. the results of the model were close to the predicted model that confirmed the model accuracy. Besides, the TC removal efficiency was investigated on the real wastewater effluent from the hospital at optimum conditions. The removal efficiency of TC was decreased from 95 to 55% and 97 to 62% for TiO_2/UV/PU and ZnO/UV/PU, respectively.

Kinetic Study

Figure 4 shows the kinetic study (zero, first, and second-order model) for TC removal from aqueous solution at optimum conditions and different contact times. According to the results, the kinetic constant for degradation of the TC antibiotic with TiO2/UV/PU and ZnO/UV/PU was 0.036 and 0.033 min^{-1}, respectively.

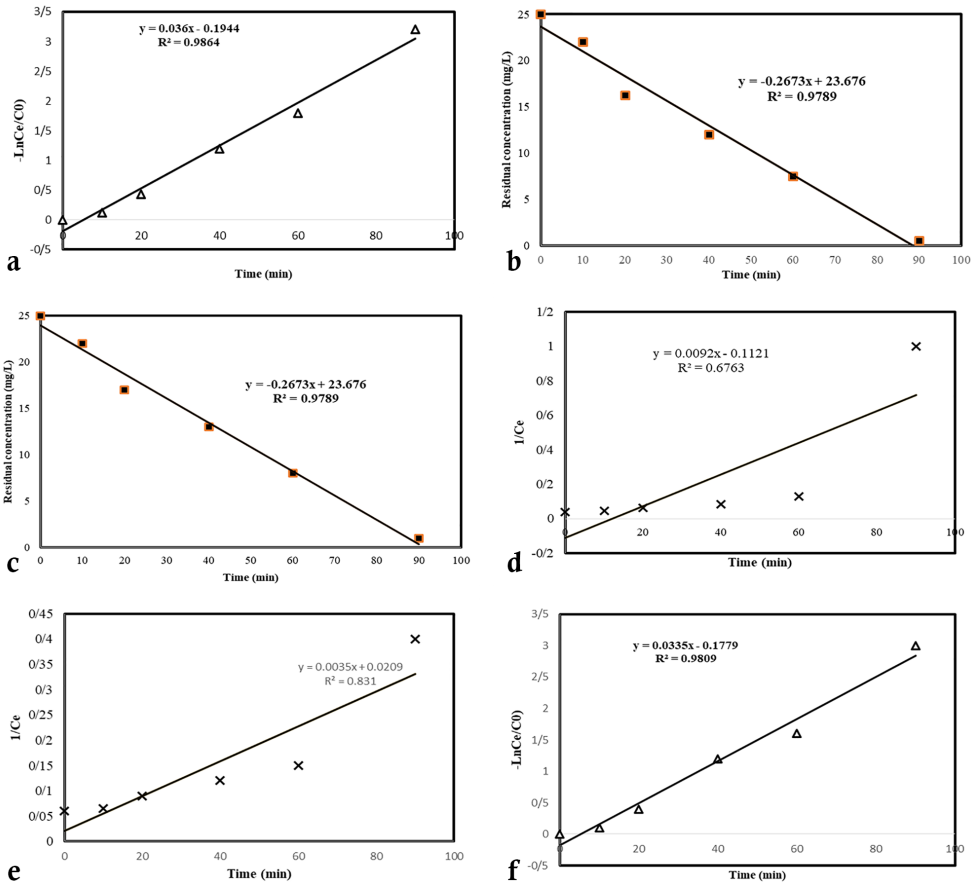

Figure 4: Kinetic study of TC removal using TiO_2/UV/PU (a) zero-order (b) first-order and (c) second- order and ZnO/UV/PU (d) zero-order (e) first order and (f) second-order kinetic model (initial TC concentration: 25mg/L, catalyst dose: 2.9 g/m^2, pH:5.8, and reaction time: 90 min)

Discussion

The sharp peaks of X-ray diffraction for nanocatalysts show good crystallinity of the nanocatalysts.[9] The sizes of crystallite particles of TiO2 and ZnO which were computed based on the Debye-Scherrer equation according to the diffraction peaks were 38 nm and 69 nm, respectively. As can be observed in SEM Images, the nanocatalyst particles represent the coral-like loops. It could be evidence to create more surface to absorb the UV irradiation and raise the active sites and finally increase the efficiency of the process.[3] The particle size and shape in TEM Images showed that the nanocatalysts could have a high surface area and distribution of them on the PU support could enhance the efficiency of the catalytic phenomenon in the way it can improve the radical production. An increase in radical production could also increase the degradation rate of TC.[8]

The reason for the difference in antibiotic removal between TiO2 and ZnO results could be the reaction between UV irradiations and these nanocatalysts and the production of an electron and free radicals, while both nanocatalysts (TiO2 and ZnO) have the same electron position and activity and energy bandgap (3.2 eV).[14]

Desired results of P-value, adjusted R^2, and predicted R^2 which were employed as selection criteria of mathematic and statistical model represented the quadratic model that can be applied to prepare the design environment of the experiments for the investigation of the interaction and effect of dependent variables on the degradation of the TC. Then, the experimental data were analyzed through the regression test of the CCD.[15] Favorable results of adequate precision, a sum of squares, P-value, and lack of fit could be concluded based on the fact that variables and quadratic models could be utilized to predict the data and develop the model properly. The low difference between predicted and adjusted regression coefficient, insignificant lack of fit, the significance of p-value, and high F-value indicated the accuracy of the model.[16]

The maximum removal was obtained at the highest amount of catalyst dose (3g/m^2) and relative acidic pH (about 6). Photocatalytic decomposition of organic compounds could be effective by the solution pH due to the effect of pH on the properties of photocatalyst surface, the charge of photocatalyst, and degradation of the contaminant as well as TC state in the solution. High pH could influence the free radical generation and ionic speciation of the surface (negative charge of

nanocatalysts) and decrease the TC degradation. On the other hand, low and high pH is not appropriate for hydroxyl free radical generation. These results were in line with the degradation of tetracycline using MWCNT/TiO_2 nano-composite.[14]

The highest process efficiency was obtained at low concentrations of TC (25 mg / L) and relatively acidic pH (about 6). It should be considered that the number of free radicals is constant at a certain catalyst dosage. Therefore, as the TC antibiotic concentration is raised, the free radical of hydroxide attacks the pollutant rapidly. Such obstacles may interfere with the generation of hydroxyl radicals. On the other hand, some intermediates can also contort and utilize free radicals in water solutions. This leads to a decrease in the degradation of TC molecules and the contact between TC and free radical species.[17]

In high contact time, more free radicals could be generated and there is more opportunity for hydroxyl radical production. However, this circumstance can be continued until a specific time, and then the increasing rate moves more smoothly because of the achieved equilibrium phase between free radical generation and TC degradation.[15]

Increasing the photocatalyst dosage to a specific value could accelerate the TC removal efficiency which instantly leads to the improvement of active sites on the nanocatalyst surfaces. However, the scattering effect phenomenon might decline the TC removal efficiency at a high nanocatalyst amount. High concentrations of nanocatalysts can prevent the penetration of UV irradiations and consequently decrease the free radical hydroxyl.[8, 9]

The kinetic study determines the rate of the reactions for TC removal and final product production (intermediates, water, and carbon dioxide). In this study, the experimental data were best fitted with the first-order kinetic model.[18] According to the results, the kinetic constant for degradation of the TC antibiotic with TiO2/UV/PU and ZnO/UV/PU was 0.036 and 0.033 min^{-1}, respectively. It showed that TC degradation was directly affected by the antibiotic concentration and TC was efficiently removed during the processes. These results were found in a previous study for TC removal from aqueous solutions with catalytic processes.

Conclusion

In this work, the nanocatalysts composite was synthesized using the titanium dioxide/zinc oxide and polyurethane. RSM was used for experimental design and process optimization. The results of the experimental design represented that all dependent variables had a significant effect on the response variables, but the interaction effect of variables was insignificant. The maximum removal efficiency was obtained at a pH of 5.8, catalyst dose of 2.9 g/m2, TC concentration of 25.12, and reaction time of 90 min using TiO2/UV/PU which was 95%. In addition, the highest removal efficiency was 97% at a pH of 5.2 catalyst dose of 2.64g/m2, TC concentration of 25.21, and reaction time of 82 min using ZnO/UV/PU. The main radical for the degradation of TC was hydroxyl ions based on the scavenger study. Kinetic study showed that the first-order model was best fitted with data obtained from TC degradation using nanocatalysts/UV/PU process.

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