Statistical Optimization of AC/TiO_2-Cu Composite via Response Surface Methodology (RSM)

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ABSTRACT

AC/TiO_2-Cu composite was synthesized via microwave-assisted sol gel method and acts as ternary composite photocatalyst for the removal of antibiotic from an aqueous solution under UV light irradiation through adsorption/photodegradation process. In this study, a statistical optimization experimental design was performed using a face-centered central composite design in response surface methodology for optimizing the synthesize parameters of AC/TiO_2-Cu composite. The influence of experimental factors such as AC/TiO_2 ratio, Cu dosage, and irradiation power with adsorption-photodegradation performance as the response were investigated. The adequacy result of the statistical model between the relationship of the significant factors and responses were successfully specify ($p \leq 0.05$), where all the experimental factors had significant effects for the response. At optimal conditions of x_1 = 0.50, x_2 = 0.31 g, and x_3 = 574 Watts, the findings show a maximum antibiotic removal of 91.10%. Also, the results showed the regression analysis with an R^2 value of 0.9837 indicates satisfactory predictive ability between the experimental results and the predictive values.

Keywords: *AC/TiO_2-Cu; UV Light Irradiation; Response Surface Methodology (RSM); Adsorption-Photodegradation*

ISSN 1823-5514, eISSN 2550-164X

https://doi.org/10.24191/jmeche.v11i1.23598

Received for review: 2022-08-23
Accepted for publication: 2022-10-11
Published: 2022-11-15

Introduction

Environmental water contamination with pharmaceutical effluent is becoming crucial problem with the development of the industrial activity social due to their acute toxicity [1]-[2]. Unfortunately, the discharge of dye effluents into the environment without adequate treatment could easily lead to the water pollution. Ciprofloxacin (CF) is one of the pharmaceuticals which has been extensively used to treat a wide variety of infections for both human and animal diseases. They may also induce transcriptional changes in microbial which contributing to the development of resistant bacteria and genes in ecosystems [3]-[4]. Thus, there is a need for advanced treatment technology to remove the antibiotics prior to being disposed into the water streams to minimize the harmful effects to the environment.

There are various methods that had been employed to overcome the discharge of antibiotics from wastewater, including adsorption, ozonation, precipitation, flocculation, membrane filtration, photocatalysis and biological process [5]-[6]. Among these treatment methods, adsorption and photocatalytic degradation have been extensively used as they are effective technology for the removal of antibiotics from the wastewater due to its simplicity, selectivity, flexibility, low toxicity, and environmentally technology [7].

Titanium dioxide (TiO_2) has been greatest intention as a heterogeneous photocatalyst for the degradation of pollutants because of its non-toxic properties, high chemical stability, and affordability [8]-[9]. The doping of different elements into TiO_2 has gained much attention owing to its synergetic effect, which results in higher photocatalytic activity compared to single element doping [10]. An activated carbon (AC) act as a supporting material for TiO_2 due to their large surface area and developed pore structures [11]. TiO_2 doping with transition metals such as Cu have been widely investigated because they are more earth-abundant, affordable, and less toxic than noble metals [12]. However, there is limited study on the optimization for synthesizing process of AC/TiO_2-Cu.

The preparation condition of the photocatalysts may affect the efficiency of the removal of antibiotic. Therefore, response surface methodology (RSM) design called face-centered central (CCD) model was applied to assess the interaction between the experimental factors and the response variable. RSM-CCD model was applied, which can minimize the experimental runs, time, and cost [13]. Thus, this research aimed to synthesis AC/TiO_2-Cu via the microwave-assisted sol gel method RSM-CCD for the removal of CF through adsorption/photodegradation process.

Materials and Methods

Synthesis of AC/TiO_2-Cu composite

AC was prepared according to the method developed by Khasri et al. [14]. AC/TiO_2 composite was prepared as follows: - 10 mL of Titanium isopropoxide (TTIP) was dissolved into the vigorously stirred of 30 ml isopropanol. The mixture was thoroughly stirred for 15 min and named as solution A. Then, solution B was prepared by mixing 14 mL of glacial acetic acid and 7 mL of deionized water in 15 mL of isopropanol. Next, solution B was added slowly into solution A and stirred thoroughly for 1 h and then aged for 24 h to obtain clear gel form. Then, 1.0 g, 3.0 g, and 5.0 g of AC were added, and the mixture was continuously stirred for 1 h. After solidification, various mass ratio of AC/TiO_2 were prepared under microwave irradiation at 700 W for 15 min. The synthesized composite of AC/TiO_2-Cu was prepared via microwave-assisted sol-gel method by fulfil the requirement of the optimization process. For the preparation of supported AC/TiO_2-Cu, 0.1, 0.3 and 0.5 g of Cu were dissolved in the solution B. Then, was calcined at different irradiation power (400-800 Watts) at 15 min. Finally, the composite obtained was cooling to the ambient temperature for further uses.

Design experiments and regression model equation of AC/TiO_2-Cu

Design-expert® software version 11 (Stat-Ease Inc., Minneapolis, US) for RSM-CCD was applied for regression of statistical analyses of the AC/TiO_2-Cu preparation via microwave-assisted sol-gel method by varying the experimental factors: x_1 = AC/TiO_2 ratio, x_2= Cu dosage, and $x_3 = \text{irradiation power}$. RSM-CCD is a collection of statistical and mathematical techniques which are used to evaluate the influence of the independent parameters on the response [15]. Analysis of variance (ANOVA) was used to validate the adequacy of developed model for response surface quadratic model, which define the interaction between the process variables and the responses. The statistical significance was evaluated by the F-test, while the accuracy of the fitted polynomial model was determined by the coefficient of R^2 [16]. The complete experimental design matrix with response result was shown in Table 1.

Adsorption/photodegradation experiment

The adsorption/photodegradation studies was carried out in a photoreactor equipped with a 250 mL double-walled borosilicate glass, a 7 W UV lamp with a main emission wavelength of 254 nm as the light source, and a magnetic stirrer. Initially, 0.2 g of AC/TiO_2-Cu was added into 200 mL of CF solutions with concentration of 100 mg/L. Then, the mixture was stirred at 200 rpm for 30 min to ensure the adsorption–desorption equilibrium. The UV lamp was then turned on. The distance between the reactor and lamp housing was 8.5 cm. After 120 min, 3 mL of the suspension was obtained and analysed at 254 nm using a Shimadzu UV-Vis spectrophotometer. The percentage (%) of adsorbate removal was calculated by using Equation (1):

$$CF\ removal\ (\%) = \frac{C_{0-}C_t}{C_0} \times 100\% \quad (1)$$

where C_o (mg/L) and C_t(mg/L) are the initial concentrations of adsorbates after the adsorption–desorption process and final concentrations of adsorbates at time, t (min), respectively.

Results and Discussion

Regression of statistical optimization

The complete experimental design matrix given by statistical software for the synthesizing of AC/TiO_2-Cu with experimental range and coded level of variables was given in Table 1. The experimental results for CF removal (Y_{CF}) were 39.3 to 94.2 %.

Table 1: Experimental design matrix of AC/TiO_2-Cu composite

Run	Factors			Response
	AC/TiO_2 ratio	Cu dosage (g)	Irradiation power (W)	CF Removal, Y_{CF} (%)
1	0.1	0.1	800	39.3
10	0.5	0.1	400	68.2
11	0.1	0.5	400	50.4
9	0.5	0.5	400	73.7
18	0.1	0.1	400	46.1
7	0.5	0.1	800	70.3
14	0.1	0.5	800	47.1
4	0.3	0.3	800	81.8
15	0.3	0.1	600	70.2
5	0.5	0.5	800	68.7
8	0.1	0.3	600	64.2
20	0.5	0.3	600	94.2
16	0.3	0.3	400	85.6
3	0.3	0.3	600	82.2
13	0.3	0.3	600	88.3
17	0.3	0.3	600	86.1
6	0.3	0.3	600	85.8
19	0.3	0.3	600	82.6
12	0.3	0.3	600	88.3

The relationship between the variables and responses interpreted in the final empirical models in the form of coded factors after excluding the insignificant terms were represented by Equation (2):

CF removal, Y_{CF}:

$$Y_{CF} = 86.23 + 12.8\,x_1 + 2.12\,x_2 - 1.68x_3 - 1.025x_1x_2 + 0.9\,x_1x_3 - 0.45\,x_2x_3 - 8.65\,x_1^2 - 1505\,x_2^2 - 4.15x_3^2 \quad (2)$$

The R^2 value obtained for the model is 0.9837, which considered as relatively high with low standard deviations. This indicated that there is a good agreement between the experimental and predicted values for the responses. ANOVA analyses were justified the model factors based on the proposed pf quadratic model. The adequacy of the developed model was further justified to assist the effect of the significance of the factors and the differences in the model obtained from statistics. In this study, the influence of three various parameters on the removal of CF was investigated, and the results of the analysis ANOVA are depicted in Table 2. The Model F-value of 66.91 indicated that the model was proven to be significant, while there is only a 0.01% chance that a Model F-value could occur due to noise disturbance. The Prob>F value of less than 0.05 indicated that the model terms are significant [17]. In this case, x_1, x_2, x_3, x_1x_2, x_1x_3 , , x_2x_3, x_1^2, x_2^2, and x_3^2 factors were significant model terms. In addition, the lack of fit value of 0.2518 showed the lack of fit was 'not significant' relative to the pure error (P-value > 0.05), suggesting the regression model is well-fitted [18].

3-D Response Surface of MAC

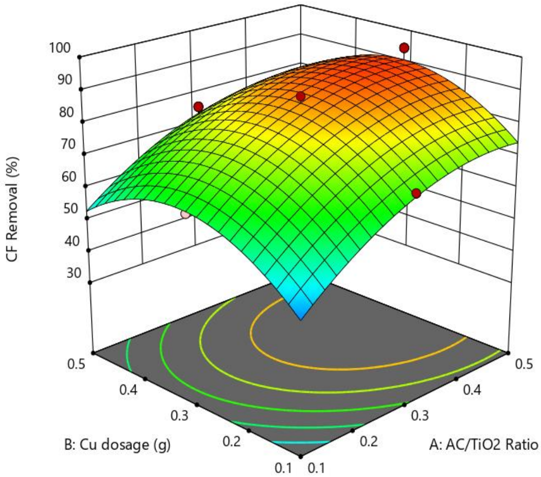
The outcomes of the interaction effects on the factors of the response values can be visually indicated by the 3-D response surface plots based on the model functions. Figure 1a depicts the 3-D response surface plot based on the interaction effect of two significant factors, AC/TiO_2 ratio and Cu dosage on CF removal by AC/TiO_2-Cu with the irradiation power (600 W) fixed at zero level. The removal of CF increased together with the increased AC/TiO_2 ratio to the optimum point. This indicated the increasing of carbon-TiO_2 ratio enhanced the removal efficiency due to increased production of electron-holes pairs [19]. The interaction effects of two significant factors, AC/TiO_2 ratio and irradiation power with Cu dosage (0.3 g) fixed at zero level are shown on the 3D surface response plot as presented in Figure 1b. The CF removal initially increased before decreasing slightly as irradiation power increased. This is due to the enhance of the crystal size and crystal structure at higher irradiation power at the optimum point [20]. Next, Figure 1c displays the 3D surface response of the interaction effect of two significant factors, Cu dosage and irradiation power with AC/TiO_2 ratio (0.5) fixed at zero level. The prolonged irradiation power might destruct the pore structure formed, which would reduce the surface area of the photocatalysts [21].

Table 2: ANOVA for CF removal (Y_{CF})

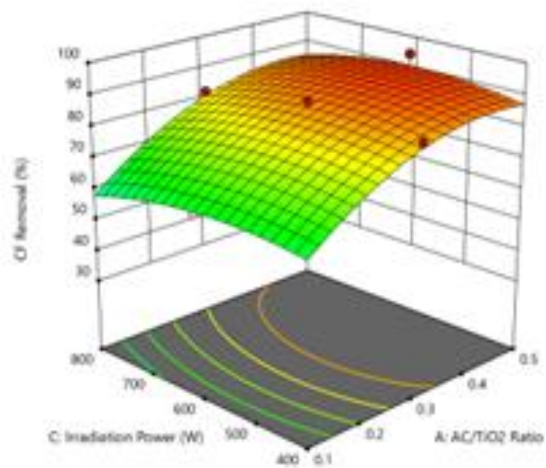
Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	4692.04	9	521.34	66.91	< 0.0001
x_1-AC/TiO_2 Ratio	1638.40	1	1638.40	210.28	< 0.0001
x_2-Cu dosage	44.94	1	44.94	5.77	0.0372
x_3- Irradiation Power	28.22	1	28.22	3.62	0.0862
x_1x_2	8.41	1	8.41	1.08	0.3234
x_1x_3	6.48	1	6.48	0.8317	0.3832
x_2x_3	1.62	1	1.62	0.2079	0.6581
x_1^2	205.76	1	205.76	26.41	0.0004
x_2^2	622.88	1	622.88	79.94	< 0.0001
x_3^2	47.36	1	47.36	6.08	0.0334
Residual	77.91	10	7.79		
Lack of Fit	50.90	5	10.18	1.88	0.2518
Pure Error	27.01	5	5.40		
Cor Total	4769.95	19			

Process Optimization and Validation

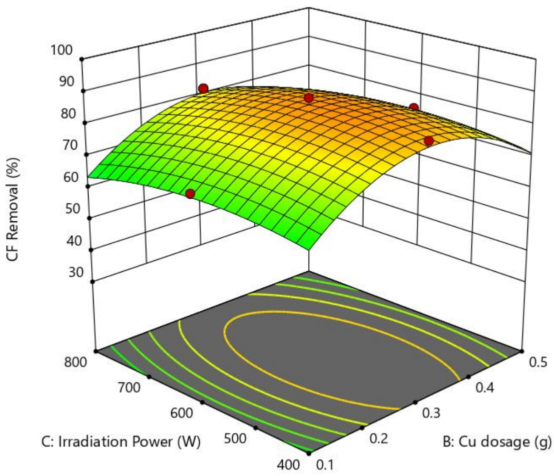
Design Expert software based on RSM-CCD model was used to obtain the optimal conditions of different experimental factors such as AC/TiO_2 ratio, Cu dosage, irradiation power, and irradiation time for the adsorption/ photodegradation removal of CF. The desirable purpose in the RSM-CCD model was fixed on the maximum value for the response of CF removal, while the value of the experimental factors (AC/TiO_2 ratio, Cu dosage, and irradiation power) were set as in range. The model validation for CF removal (Y_{CF}) was shown in Table 3. The optimum conditions can be achieved at the optimum conditions: x_1= 0.50, x_2 = 0.31 min, and x_3 = 574 Watts. The CF removal was 91.10 % was achieved with the optimum preparation conditions. It was found that the small deviation errors between the predicted and the experimental values were 1.25 % for the response. This indicated that the statistical analysis was evaluated the adequacy and the validity of the model.


100
90
80
70
60
50
40
30
CF Removal (%)
0.5
0.4
0.3
0.2
0.1
B: Cu dosage (g)
0.1
0.2
0.3
0.4
0.5
A: AC/TiO2 Ratio

(a)


100
90
80
70
60
50
40
30
CF Removal (%)
800
700
600
500
400
C: Irradiation Power (W)
0.1
0.2
0.3
0.4
0.5
A: AC/TiO2 Ratio

(b)



(c)

Figure 1: 3-D surface plot for the interaction of; (a) AC/TiO_2 ratio and Cu dosage at fixed zero level (irradiation power = 600 W), (b) AC/TiO_2 ratio and irradiation power at fixed zero level (Cu dosage = 0.3 g), and (c) Cu dosage and irradiation power at fixed zero level (AC/TiO_2 ratio = 0.5)

Table 3: Model validation for AC/TiO_2-Cu

AC/TiO_2 Ratio, x_1	Cu dosage, x_2 (g)	Irradiation Power, x_3 (Watts)	Irradiation Time, x_4 (min)	CF removal, Y_{CF} (%)		
				Exp.	Pred.	Err.
0.50	0.31	574	14	91.10	92.25	1.25

Conclusions

In summary, AC/TiO_2-Cu composite prepared through microwaved-assisted sol gel method was successfully prepared via RSM design called face-centred CCD for the removal of CF through adsorption/photodegradation process under UV light. According to the ANOVA analysis, the maximum adsorption/photodegradation efficiency of CF removal was 91.10% by applying AC/TiO_2 ratio (0.50), Cu dosage (0.31 g), and irradiation power (574 W) under the optimum preparation variables. The optimization of the statistical analysis clearly showed that the AC/TiO_2 ratio, Cu dosage, and irradiation power had significant effects on CF removal. The high R^2 value of 0.9837 was justified the reliability of the regression models between the process variables and the responses. The results from this study confirmed the promising ability of the prepared AC/TiO_2-Cu composite as a promising agent in the pharmaceutical wastewater treatment.

Acknowledgment

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number FRGS/1/2019/STG07/UNIMAP/02/2 from the Ministry of Higher Education Malaysia.

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