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Preparation of AC/TiO_2 doped N-Ce Synthesized via Microwave Irradiation for Amoxicillin Photodegradation

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Abstract

Activated carbon (AC) supported with titanium dioxide (TiO_2) doped with nitrogen (N) and cerium (Ce), denoted as AC/TiO_2 doped N-Ce was synthesized for adsorption and photodegradation of amoxicillin (AMX) antibiotic. Photocatalyst was prepared using sol-gel approach assisted by microwave irradiation. 30 experiment runs were generated for photocatalyst production and optimized via Central Composite Design-Response Surface Methodology (CCD-RSM) with observation of four types of variable parameters. The experimental variables consisted of the quantities of urea (N) (x_i: 0.02–0.20 g), amount of cerium (III) nitrate hexahydrate (Ce) (x_j: 0.02–0.20 g), amount of AC (x_k: 0.10 –0.50 g), and microwave power (x_l: 600–800 W). The analysis revealed that AC/TiO_2 doped N-Ce photocatalyst, which was prepared with 0.50 g AC, 0.02 g N, and 0.20 g Ce, and activated with microwave power 600 W in 15 min, achieved a 93.6% AMX removal under UV light irradiation. The photocatalyst was initially subjected to a concentration of 10 mg L^{-1} at 30 °C for a duration of 60 min.

1. Introduction

Widespread of emerging pollutants in water bodies have raised concern globally [1]. Failure to manage EPs properly can harm water ecology, wildlife, human health, and well-being. Common encountered EPs in water environment include pharmaceuticals product such as amoxicillin (AMX) and norfloxacin antibiotics [2], [3], non-steroidal anti-inflammatory drug (NSAID) such as diclofenac and ibuprofen [4], veterinary medicine like tetracycline and triclosan [5], [6], [7], personal care products like perfumes or body washes [8], and industrial additive [9]. These compounds can be found in sediment or water surface [10]. Their widespread usually facilitated by pharmaceutical industry [11], the excretion of incomplete metabolism of antibiotics in animal or human from bodies after consumption [12], hospital waste [13], or industry [14].

According to Hasni et al., [15] and Shamsudin et al., [16], antibiotics, analgesics, or hormonal contraceptives are pollutants that are often reported found in effluents in Malaysia. The common antibiotic found in water bodies is AMX (AMX). The use of AMX increased tremendously over the last decades to treat infections like bronchitis, pneumonia, or skin infections and prevention of animal disease in veterinary field [17]. After consumption, around 50- 70 % of the medicine released into the environment unchanged from original form [18]. AMX enters water ecology and soils, reaching drinking water and groundwater which later consummated by well-being. In worse case, due to prolonged released to environment causing the increased in antibiotic resistance which led to morbidity and mortality in animals and humans [19], [20].

Due to this concerning, many technologies were reported for the elimination of AMX such as supercritical water gasification [21], advanced oxidation process [22], photocatalytic [23] and adsorption [24]. Adsorption and photocatalysis method among preferrable method for treating AMX due to its cost-effectiveness and non-destructive [25]. Activated carbon (AC) often used as adsorbent material due to its ability to provide high surface area but the pores influenced the time taken of absorption process [26]. TiO_2 is a promising photocatalyst due to its superiority in photocatalytic activity but have poor adsorption performance due to recovery treatment limitation [27]. The disadvantages of both methods may be solved by modifying AC-based TiO_2 with dopants, which eliminates the drawbacks of these methods. In the present work, the aim was to optimize the synthesis process of modified photocatalyst (AC/TiO_2) doped with N and Ce via Central Composite Design (CCD) in Response Surface Methodology (RSM), producing AC/TiO_2 doped N-Ce in adsorption-photodegradation of AMX.

2. Material and Methods

2.1 Material

Amoxicillin (AMX) antibiotics ($C_{16}H_{19}N_3O_5S$) were acquired from Santa Cruz, USA. Titanium (IV) isopropoxide (TTIP) and cerium (III) nitrate hexahydrate ($CeH_{12}N_3O_{15}$)(Ce) were obtained via ACROS Organics, Belgium. Isopropanol (C_3H_8O), acetic acid (CH_3COOH), urea ($(NH_2)_2CO$)(N), and potassium hydroxide (KOH) potassium hydroxide (KOH) were purchased from HmbG Chemicals, Germany. Hydrochloric acid (HCl) was procured via Fisher Scientific, Germany. All reagents were analytical grade and used as received.

2.2 Preparation of AC/TiO_2 doped N-Ce

Modified photocatalyst of AC/TiO_2 doped N-Ce was prepared using sol-gel method like the one described in the previous study [28]. Solution A was prepared by diluting 5 mL TTIP in 15 mL of isopropanol and mixing for 10 min. Next, solution B was prepared by diluting 5 mL acetic acid in 10 mL of distilled water where dopant (N and Ce) was added and stirred for 10 min. Subsequently, solution B was gradually introduced into solution A, one drop at a time, while maintaining continuous stirring for a duration of 60 min. Activated carbon (AC) was added into the mixture and agitated for additional duration of 5 min prior to dry in drying oven at 100 °C for 12 h, producing a solidified photocatalyst (AC/TiO_2 doped N-Ce) followed by activation assisted by domestic microwave oven. The amount of N, Ce, AC and microwave power used was pre-determined by Central Composite Design (CCD) in Response Surface Methodology (RSM) and discussed in Section 2.3.

2.3 Design of Experiment (DOE) in Preparing AC/TiO_2 doped N-Ce

Central Composite Design in response surface methodology (RSM) was chosen in the current work to optimize variable parameters in synthesis of photocatalyst, AC/TiO_2 doped N-Ce for adsorption and photodegradation of AMX antibiotic. The parameters were AC, Ce, N dosage (g) and microwave power (W). Design Expert software version 7.0 was used to analyze the experiment data where variable parameters were varied at three levels. 30 experiments in total were generated from CCD-RSM to optimize the synthesis of AC/TiO_2 doped N-Ce photocatalyst and Table 1 shows the amount of parameter needed and photocatalyst was prepared according to the actual matrix design.

2.4 Photocatalytic Study

The photocatalytic study was evaluated with adsorption method where 0.20 g of synthesized photocatalyst was added into 100 mL of AMX solution (10 mg L^{-1}) and agitated in the dark photoreactor for 15 min to allow interaction between photocatalyst and AMX solution. Later, in photodegradation method, UV light with 7 W was turned on after 15 min up to 60 min. The removal percentage of AMX was determined by measuring the absorbance at wavelength 337 nm [29], using UV-VIS spectrophotometer (Shimadzu UV-1800, Japan). The equation used to calculate AMX removal percentage as follows:

$$\text{Percentage removal } (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where C_o (mg L^{-1}) and C_e (mg L^{-1}) were the concentration of AMX at initial and final irradiation time.

Table 1 *Variable parameters CCD-RSM matrix and experimental data of AMX removal*

Run	x_i: Urea (g)	x_j: Cerium (III) nitrate hexahydrate (g)	x_k: Activated carbon (g)	x_l: Microwave power (W)	AMX Removal (%)
1	0.11	0.11	0.30	700	71.9
2	0.20	0.20	0.50	800	92.3
3	0.20	0.02	0.10	800	45.4
4	0.11	0.02	0.30	700	86.0
5	0.20	0.02	0.50	800	90.8
6	0.20	0.20	0.10	800	47.4
7	0.11	0.11	0.30	800	60.0
8	0.20	0.02	0.10	600	47.2
9	0.02	0.20	0.10	600	55.6
10	0.11	0.20	0.30	700	92.1
11	0.02	0.02	0.50	600	75.9
12	0.11	0.11	0.30	700	73.0
13	0.11	0.11	0.30	700	70.8
14	0.20	0.02	0.50	600	92.6
15	0.11	0.11	0.30	600	70.9
16	0.02	0.20	0.10	800	52.7
17	0.20	0.11	0.30	700	61.7
18	0.02	0.20	0.50	800	82.7
19	0.11	0.11	0.30	700	68.8
20	0.11	0.11	0.50	700	91.3
21	0.11	0.11	0.10	700	58.0
22	0.02	0.02	0.10	600	46.8
23	0.02	0.20	0.50	600	93.6
24	0.02	0.11	0.30	700	63.1
25	0.11	0.11	0.30	700	64.9
26	0.02	0.02	0.10	800	43.4
27	0.11	0.11	0.30	700	71.9
28	0.20	0.20	0.50	800	92.3
29	0.20	0.02	0.10	800	45.4
30	0.11	0.02	0.30	700	86.0

3. Results and Discussion

3.1 CCD-RSM Model Analysis

The synthesis of AC/TiO_2 doped N-Ce using CCD-RSM was subjected to a total of 30 experiments. A quadratic model was generated to examine the interaction between both components and the resulting response. Table 2 represents the ANOVA results of the regression model. The yielded p-value < 0.0001, which is lower than the significance level of 0.05. This indicates that the variable parameter utilized to develop the photocatalyst had a substantial impact on the observed response. The significant parameters established from ANOVA table after excluding the insignificant terms (p value < 0.05) for AMX removal were x_i, x_j, x_k, x_l, x_ix_j, x_ix_k, x_i^2, x_j^2, and x_l^2. In the empirical model, a negative sign indicates an antagonistic impact while a positive sign indicates a synergistic effect [30], [31]. The quadratic model employed in this experiment has a high level of significance, as confirmed by the low p-value and high R-value squared (R^2 = 0.9767). The relationship between parameters and AMX removal response was presented as the following equation:

$$\text{AMX Removal, \%} = +71.89 + 1.97x_i + 3.35x_j + 18.55x_k - 2.20x_l - 2.61x_ix_j + 3.25x_ix_k - 11.49x_i^2 + 15.11x_j^2 - 8.50x_l^2 \quad (2)$$

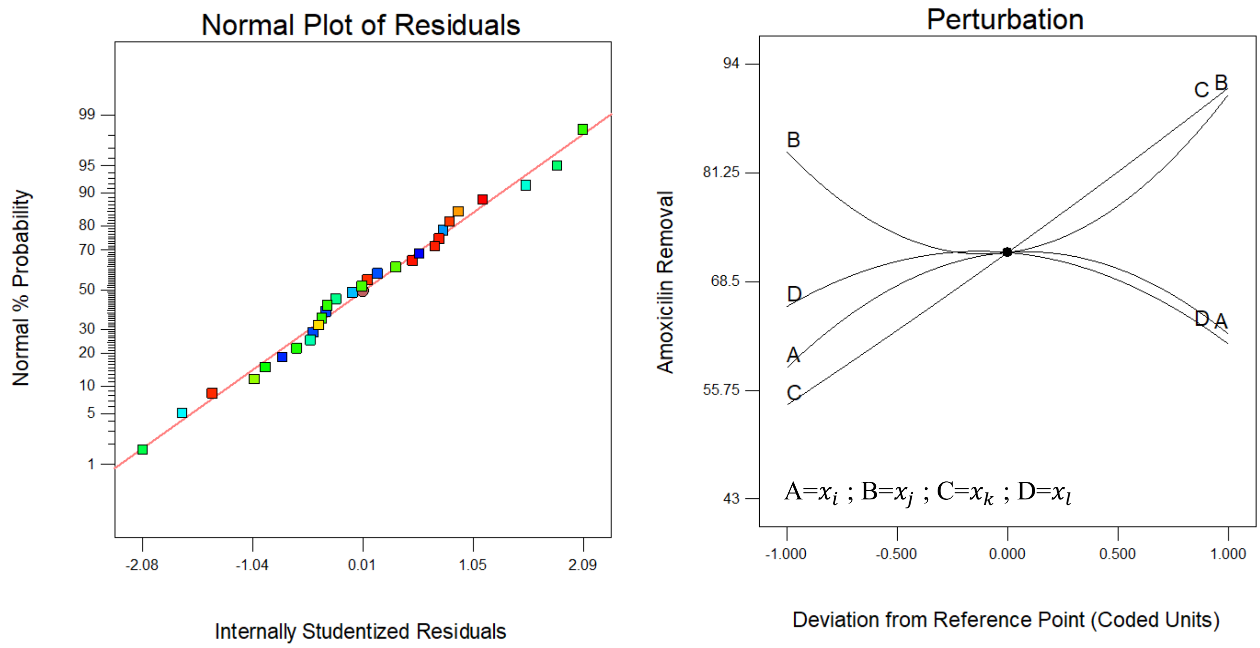
Table 2 *Analysis of variance (ANOVA) of quadratic model for AMX removal*

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	7806.15	14	557.58	44.82	< 0.0001
x_i-Urea (N)	69.76	1	69.76	5.61	0.0317
x_j-Cerium (III) nitrate hexahydrate (Ce)	201.66	1	201.66	16.21	0.0011
x_k-Activated Carbon (AC)	6191.57	1	6191.57	497.68	< 0.0001
x_l-Microwave Power (W)	87.13	1	87.13	7.00	0.0183
$x_i x_j$	108.64	1	108.64	8.73	0.0098
$x_i x_k$	169.43	1	169.43	13.62	0.0022
$x_i x_l$	16.10	1	16.10	1.29	0.2731
$x_j x_k$	2.51	1	2.51	0.20	0.6599
$x_j\ x_l$	1.15	1	1.15	0.093	0.7651
$x_k x_l$	1.83	1	1.83	0.15	0.7066
x_i^2	341.97	1	341.97	27.49	< 0.0001
x_j^2	591.41	1	591.41	47.54	< 0.0001
x_k^2	1.30	1	1.30	0.10	0.7505
x_l^2	187.13	1	187.13	15.04	0.0015
Residual	186.61	15	12.44		
Lack of Fit	146.47	10	14.65	1.82	0.2630
Pure Error	40.14	5	8.03		
Cor Total	7992.76	29			

3.2 Validation of Model and Normality Test

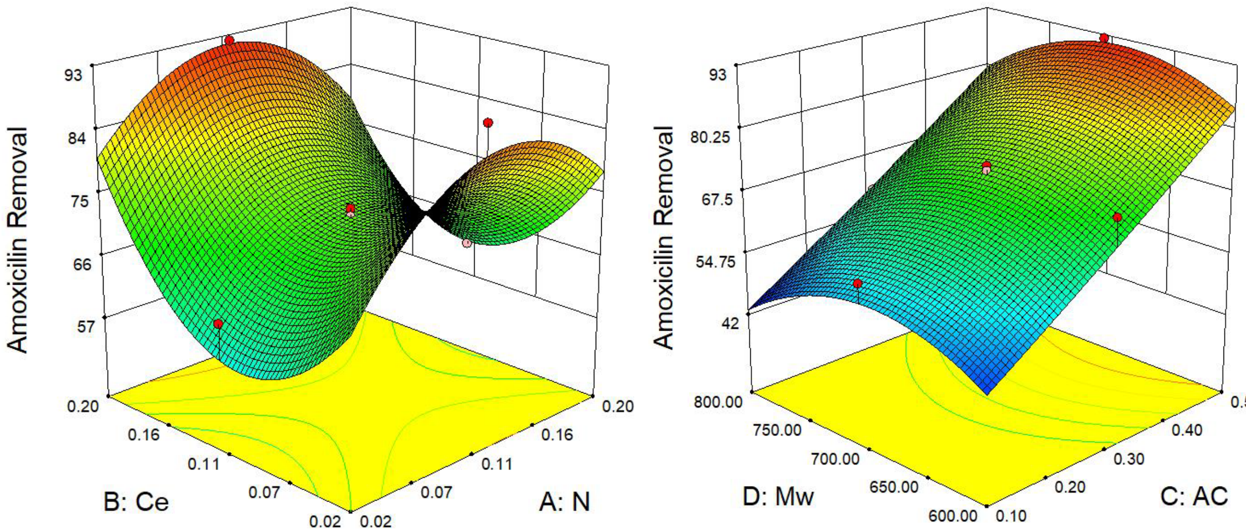
Analysis on the residuals was performed to validate the normality in data set distribution for developed model of AMX removal and presented in Fig. 1(a). A linear pattern of residuals was observed between the straight red line which indicate the normal distribution for this model. Perturbation plot which illustrated in Fig. 1(b), help to explain the effect of x_i (N), x_j (Ce), x_k (AC), and x_l (W) as variables involve in AMX removal. The curvature of factor A shows a decrease in AMX removal when the dosage was increased. Similar pattern was observed in variable D where at lower microwave power, high AMX removal was reported. A sharp step was depicted by variable C in perturbation plot which shows a heavy influence of activated carbon in removal of AMX. An increase in C dosage also led to a high degradation percentage. When there is an increase of B dosage, the AMX removal also increases. The influence of each variable in antibiotic removal seen in perturbation plot is also like the ANOVA analysis denoted in Table 2 where variable C (p-value < 0.0001) has the highest influence followed by variable B (p-value = 0.0047), A (p-value = 0.0342) and D (p-value = 0.0360).

3D surface plot and contour plot were used to further demonstrate the influence of variable in AMX removal where the blue area indicates the weakest relationship between the factors, whereas the red region indicates the strongest. Fig. 2(a) represents the 3D response that shows interaction between variable urea (A) and cerium (B). When both dopants impregnated into the AC-TiO_2, higher AMX removal was observed when B dosage present more on the photocatalyst than A. The increasing trend can also be seen in Fig. 2(b) where the removal percentage increased when the activated carbon (AC) dosage increased. Moreover, it also appeared that the microwave power used to activate the photocatalyst shows great influence in the degradation of AMX. When preparing the photocatalyst at 800 W, the removal percentage was lower compared to the removal when photocatalyst was prepared at lower microwave power. This can be explained from higher power used in synthesis system can lead to photocatalyst overheating and reduce the grain size that reduce the photocatalyst efficiency [32], [33]. The removal rate revealed a pattern of increases as the AC dose increased, owing to the substantial availability of active sites over a broad surface area, facilitating photocatalytic activity [34]. AC based TiO_2 prepared with low N and high Ce dosage allows high removal rate, aligning with the findings reported in the literature [35].



(a) **(b)**

Fig. 1 *(a) Normal probability plot for the developed quadratic model in CCD-RSM for AMX removal; (b) Perturbation curve on the influence of each variable in AMX removal*



(a) **(b)**

Fig. 2 *3D response surface plot the influence of (a) N versus Ce ($\boldsymbol{x_i}$ x $\boldsymbol{x_j}$); (b) AC versus microwave power ($\boldsymbol{x_k}$ x $\boldsymbol{x_l}$), in AMX removal*

3.3 Response Optimization

To determine the optimum variables to synthesize AC/TiO_2 doped N-Ce fitting in AMX removal, a suggested conditions of independent variables were chosen from the quadratic model generated in CCD-RSM as tabulated in Table 3. Since the degradation of AMX reported in Table 1 shows the highest removal when photocatalyst was synthesized with minimum variable urea dosage (N)(x_i) and microwave power (W)(x_l), maximum variable of cerium (III) nitrate hexahydrate (Ce)(x_j) and AC (x_k), thus the validation to find optimum condition in preparing the photocatalyst followed the same conditions. The prediction for photocatalyst prepared under same condition was 91.37%. The results from degradation of AMX from photocatalyst using new variable condition shows degradation up to 93.55%, giving 2.33% error percentage. A smaller percentage error in validation process means closer to the actual value and in good agreement. Thus, photocatalyst prepared using same condition is preferrable as optimum variables in preparing AC/TiO_2 doped N-Ce as photocatalyst.

Table 3 *Validation of optimization for AMX adsorption and photodegradation activity*

Independent variables	Conditions
Urea (g) (x_i)	0.02
Cerium (III) nitrate hexahydrate (g) (x_j)	0.20
Activated carbon (g) (x_k)	0.50
Microwave power (W) (x_l)	600
Prediction	91.37%
Experimental	93.55%
Error percentage	2.33%

4. Conclusion

To achieve optimal results in the synthesis of a photocatalyst AC/TiO_2-doped N-Ce, the current study utilized Central Composite Design (CCD) through Response Surface Methodology (RSM). The results of the analysis indicate that a TiO_2-based photocatalyst, which was prepared using 0.02 g N, 0.20 g Ce, 0.50 g AC and activated using microwave irradiation (600 W) in 15 min, exhibited the highest removal rate of AMX (93.55%) within 60 min when exposed to UV light. Therefore, the photocatalyst that was recently developed in this research study provides an effective alternative for the elimination of AMX from water bodies.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

Nur Athirah Awatif Abdul Rahman*: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft.* ***Azduwin Khasri****: Conceptualization, Project administration, Resources, Supervision, Validation, Writing – review and editing.* ***Noor Hasyierah Mohd Salleh****: Resources, Supervision.* ***Mohd Ridzuan Mohd Jamir****: Funding acquisition, Resources, Supervision.*

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