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Optimization of microwave sol–gel synthesis of N-Ce-AC/TiO_2 for adsorption/photodegradation of tetracycline

Nur Athirah Awatif Abdul Rahman[a], Azduwin Khasri[a,*], Noor Hasyierah Mohd Salleh[a], Mohd Ridzuan Mohd Jamir[b], Sabah Ansar[c], Raj Boopathy[d], Achmad Syafiuddin[e,f,*]

[a]*Faculty of Chemical Engineering & Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia, emails: azduwin@unimap.edu.my (A. Khasri), nurawatif8@gmail.com (N.A.A.A. Rahman), hasyierah@unimap.edu.my (N.H.M. Salleh)*
[b]*Faculty of Mechanical Engineering & Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia, email: ridzuanjamir@unimap.edu.my*
[c]*Department of Clinical Laboratory Sciences, College of Applied Medical Sciences, King Saud University, P.O. Box: 10219, Riyadh 11433, Saudi Arabia, email: sansar@ksu.edu.sa*
[d]*Department of Biological Sciences, Nicholls State University, Thibodaux LA 70310, USA, email: ramaraj.boopathy@nicholls.edu*
[e]*Environmental Health Division, Department of Public Health, Universitas Nahdlatul Ulama Surabaya, 60237 Surabaya, East Java, Indonesia, email: achmadsyafiuddin@unusa.ac.id*
[f]*Center for Environmental Health of Pesantren, Universitas Nahdlatul Ulama Surabaya, 60237 Surabaya, East Java, Indonesia*

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ABSTRACT

Nitrogen (N) and cerium (Ce) co-doped titanium dioxide (TiO_2) supported activated carbon (AC) (N-Ce-AC/TiO_2) were synthesized to remove antibiotic tetracycline from aqueous solution via adsorption and photodegradation. The sol–gel technique, aided by microwave radiation, was used to synthesize N-Ce-AC/TiO_2. Central composite design under response surface methodology was used to optimize the variables comprising urea (N source) (*A*: 0.02–0.20 g), cerium(III) nitrate hexahydrate (Ce source) (*B*: 0.02–0.20 g), activated carbon (*C*: 0.10–0.50 g), and microwave power (*D*: 600–800 W), where the degradation of tetracycline was the response. Characterization of the produced catalyst was carried out by means of X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and the Brunauer–Emmett–Teller method for determining surface-texture parameters. N-Ce-AC/TiO_2 prepared with 0.50 g activated carbon, doped with 0.02 g urea and 0.20 g cerium, and activated at microwave power 600 W for 15 min exhibited 91.08% tetracycline removal when subjected to 7 W of UV irradiation, according to the results of optimal variable preparation.

Keywords: Activated carbon; Adsorption; Microwave radiation; Photodegradation

1. Introduction

Industrial waste often becomes a hot topic issue when it comes to water pollution discussion [1–7]. Emerging industrial waste in an environment not only poses a threat to the health and safety of humans but also endangers the aquatic ecosystem, and this issue is becoming alarming each day [8–13]. For instance, the source of this pollution could come from agro-industries [14], pharmaceutical waste [15], unplanned urbanization [16], illegal dumping [17], and the textile industry [18]. There is a diverse type of contaminants that can be found in wastewater, such as heavy metals [19], pesticides [20], detergents [21], dyes [22], and emerging pollutants [23]. The antibiotic residue is often associated with

* Corresponding authors.

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emerging pollutants as it can easily be found in standard drainage system such as household sewer since antibiotic is consumable by humankind. When this pharmaceutical product enters the water ecology, it does not only affect the aquatic ecosystem but also increase the spread of antibiotic resistance. Tetracycline is one of the common antibiotics used to treat infection and reduce acne [24,25]. However, prolonged use led to the rapid emergence of antibiotic resistance due to consistent residue released into the water system [26].

Through the years, extensive treatment methods have been presented to treat antibiotic residue present in wastewater, such as ultrasonic radiation [27], membrane filtration [28] advanced oxidation process [29] adsorption [30–33], and photocatalyst [34]. A cost-effective, non-destructive, and green method is preferable for treating tetracycline in wastewater, such as adsorption and photocatalysis. In the adsorption method, the material with a high surface area could increase the adsorptive ability of tetracycline removal in wastewater and activated carbon (AC) fits this role. However, the pores on the AC surface after the activation process influence the adsorption time due to the limited number of active sites available for reaction, thus lowering the reaction rates and degradation efficiency [35]. Meanwhile, titanium dioxide (TiO_2) was often used as a photocatalyst in photocatalysis due to its large surface area as a catalyst [36]. However, TiO_2 causes limitations in catalyst recovery treatment [37]. In order to overcome these drawbacks, combining these two methods increase high photocatalytic activity than using AC or TiO_2 alone [38].

Another issue that arises during the preparation of a catalyst is the synthesis and activation process. In order to get a homogenous and well-controlled porosity in a catalyst structure, the sol–gel method was used in this study. However, the sol–gel method necessitates a lengthy pretreatment period [39]. It also involves the use of a furnace to calcinate the catalyst, but this conventional method is time-consuming since it is a slow process [40]. To address these limitations, the introduction of co-doped elements into TiO_2 is desired to enhance catalyst performance [41]. Thus, in this work, the aim was to find the optimum preparation of N-Ce-AC/TiO_2 for removal of tetracycline with different mixture formulations using response surface methodology (RSM) via an adsorption–photodegradation process where N-Ce-AC/TiO_2 catalyst was synthesized using the sol–gel method assisted by microwave for fast activation, energy efficiency, and improved catalyst characteristics [42].

2. Material and methods

2.1. Materials

Acetic acid (CH_3COOH), isopropanol (C_3H_8O), potassium hydroxide (KOH) and urea ($(NH_2)_2CO$) (N) were purchased from HmbG Chemicals (Malaysia). Cerium(III) nitrate hexahydrate ($CeH_{12}N_3O_{15}$) (Ce) and titanium(IV) isopropoxide (TTIP) were supplied from ACROS Organics. Hydrochloric acid (HCl) was obtained from Fisher Chemical. Tetracycline antibiotics ($C_{22}H_{24}N_2O_8$) were purchased from Santa Cruz, USA. All reagents were analytical grade and used as received. Merbau wood was obtained from Klang, Selangor, Malaysia.

2.2. Preparation of activated carbon

Merbau wood was chopped into smaller pieces, washed to remove impurities, and dried for 24 h at 100°C in a drying oven. Merbau wood was then inserted into a crucible and placed in a muffled furnace for the charring process at 500°C for 1 h. The produced char was then prepared for activation using the microwave irradiation technique under the optimum condition described in the previous study with some modifications [43]. First, char was impregnated with 30% KOH at a ratio of 0.94 g/g and dried for 24 h at 100°C in a drying oven. The impregnated char was then inserted onto a cylinder quartz tube attached to the inlet and outlet of the carbon dioxide (CO_2) gas tube of a 2.4 GHz Microwave Samsung (EMM2001W, Sweden). As CO_2 was purged through the inlet at a 300 L/min flow rate, the irradiation power was set at 460 W (W) for 4 min.

2.3. Preparation of N-Ce-AC/TiO_2 catalyst

The sol–gel method assisted with microwave radiation was used to prepare N-Ce-AC/TiO_2 composite by following a similar method described in the previous study with some modifications [44,45]. In the sol–gel process, two solutions were mixed to produce TiO_2 sol. The first solution was titanium precursor, where 5 mL of TTIP was diluted to 15 mL isopropanol and manually stirred for 10 min. The second solution was 5 mL acetic acid diluted into 10 mL distilled water along with urea (0.02–0.20 g) as a nitrogen source and cerium(III) nitrate hexahydrate (0.02–0.20 g) as a cerium source, and occasionally stirred for 10 min. First, the acetic acid solution was added into titanium precursor solution dropwise, manually, using a 10 mL syringe while stirring vigorously using a magnetic stirrer for 1 h until sol formation was seen. Then, activated carbon (0.10–0.50 g) was added to the mixture solution and stirred for 5 min before drying in a dry oven for 24 h at 100°C, forming a solidified catalyst known as N-Ce-AC/TiO_2. The catalyst was further activated using a domestic microwave oven at different power levels (600–800 W) for 15 min. The range of urea, cerium, and activated carbon dosages, along with microwave power, were pre-determined by central composite design (CCD) in RSM [46].

2.4. Characterization of catalyst

X-ray diffraction powder (XRD) analysis was used to measure the crystalline structure of the synthesized catalyst, N-Ce-AC/TiO_2 using the D2 Phaser X-ray Diffractometer (Bruker Corporation, USA) operated with Cu Kα at 45 kV and 40 mA. The data was collected at 2θ range of 10° to 80° with a step size of 0.20°/s. The structural morphology and surface features were analyzed using the scanning electron microscopy (SEM) instrument model JEOL JSM-6010LV, Japan, at an accelerating voltage of 15 kV with a magnification of 1,000x. In elemental composition analysis, energy-dispersive X-ray spectroscopy (EDX) was used to characterize the elemental composition present in synthesized catalyst and was conducted using the Hitachi TM3000 Tabletop Microscope, Japan.

2.5. Design of experiments

The current work used CCD in RSM for the purpose of optimizing operating factors such as urea (N), cerium (Ce), and AC dose as well as microwave power in the adsorption and photodegradation of tetracycline antibiotic. The experiment and the graphical data were analyzed with Design–Expert software version 7.0 in order to maximize the correlation between each variable and the influence it had on the tetracycline degradation. As can be seen in Table 1, the factorial design consisted of four different variables, each of which had six different center points.

Given that operating variables were an independent factor and tetracycline removal was considered the response, a total of 30 experiments were obtained from CCD- RSM to synthesize the N-Ce-AC/TiO_2 composite via the sol–gel method. The amount of each variable was prepared according to the actual matrix design, as shown in Table 2.

Table 1
Variable factors and levels

Variable factor	Description	Level 1	Level 2	Level 3
		(–1)	(0)	(+1)
A	Urea	0.02	0.11	0.20
B	Cerium	0.02	0.11	0.20
C	Activated carbon	0.10	0.30	0.50
D	Microwave power	600	700	800

2.6. Evaluation of photocatalytic activity

This evaluation was started by adding 0.20 g of the ready composite into an Erlenmeyer flask containing 100 mL of 10 mg/L tetracycline solution, stirred at a constant speed of 300 rpm under a 7 W UV lamp, and installed 8 cm above the flask in a closed and dark photoreactor. The photodegradation was carried out at room temperature under

Table 2
Factors central composite design matrix and experimental data of tetracycline removal

Run	*A*: Urea	*B*: Cerium	*C*: Activated carbon	*D*: Microwave power	Tetracycline removal
	(g)	(g)	(g)	(W)	(%)
1	0.11	0.11	0.30	800	63.52
2	0.11	0.11	0.30	700	69.33
3	0.02	0.02	0.50	600	79.62
4	0.02	0.02	0.50	800	68.35
5	0.20	0.20	0.10	600	56.44
6	0.11	0.11	0.30	600	68.41
7	0.02	0.20	0.10	800	57.14
8	0.20	0.11	0.30	700	86.95
9	0.11	0.02	0.30	700	61.30
10	0.20	0.20	0.50	600	86.67
11	0.02	0.11	0.30	700	73.17
12	0.20	0.02	0.50	600	87.81
13	0.20	0.02	0.10	800	56.98
14	0.11	0.11	0.30	700	72.54
15	0.20	0.02	0.50	800	82.13
16	0.02	0.20	0.10	600	61.05
17	0.02	0.02	0.10	800	38.25
18	0.11	0.11	0.30	700	66.29
19	0.20	0.20	0.10	800	52.67
20	0.11	0.11	0.10	700	54.32
21	0.20	0.20	0.50	800	86.57
22	0.02	0.20	0.50	600	91.08
23	0.11	0.11	0.30	700	69.37
24	0.02	0.20	0.50	800	73.33
25	0.02	0.02	0.10	600	45.33
26	0.11	0.11	0.30	700	71.37
27	0.11	0.11	0.50	700	86.54
28	0.20	0.02	0.10	600	57.75
29	0.11	0.11	0.30	700	66.10
30	0.11	0.20	0.30	700	75.14

atmospheric pressure. First, the suspension was stirred in the dark for 15 min to establish an equilibrium between tetracycline and composite. Then, the UV lamp was turned on for up to 60 min contact time. The percentage removal of tetracycline determined the photocatalytic activity of the catalyst, and it was measured in terms of absorbance using a UV-VIS Spectrophotometer (Shimadzu UV-1800, Japan) at wavelength 360 nm [47]. The equation for tetracycline removal is calculated as follows:

$$\text{Percentage removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where C_0 (mg/L) and C_e are the concentration of tetracycline at initial and final irradiation time.

3. Results and discussion

3.1. Characterizations of N-Ce-AC/TiO_2 catalyst

The XRD patterns of N-Ce-AC/TiO_2 were analyzed, and the results are shown in Fig. 1. At 2θ of 25.2°, the unique peak of crystal plane anatase TiO_2 was clearly discernible and corresponded to index (101) [48]. The Scherrer equation was used to compute the average size of the crystallites, and the results showed that the average diameter of N-Ce-AC/TiO_2 was 5.48 nm correspondingly. The morphological characteristics of the N-Ce-AC/TiO_2 catalyst were analyzed with SEM, and the results are depicted in Fig. 2. The SEM micrograph clearly displays a smooth surface region, indicating that TiO_2 particles are loaded uniformly on the AC surface and that the distribution of dopants N and Ce is well dispersed along the AC-TiO_2 lattice. Because of the structure, light may go through the material more easily, which results in greater photocatalytic activity [49]. EDX often known as EDX analysis, would help augment the information that is now accessible in order to verify the successful dopant integrations that have occurred inside the TiO_2 framework. Fig. 3 displays the findings of an additional study that was conducted by employing EDX mapping and microanalysis in order to gain insight into the surface elemental compositions of N-Ce-AC/TiO_2. The percentage (%) weight reveals that dopant is present in the catalyst, as outlined in Table 3. On the catalyst, the following elements were found in the following weight percentages: N (1.39 wt.%), Ce (1.77 wt.%), C (45.53 wt.%), Ti (14.62 wt.%), and O (36.79 wt.%). Peaks reflecting their respective energies were seen. This demonstrates that dopants containing N and Ce are capable of successfully replacing Ti in the TiO_2 lattice [50]. The SEM study, which demonstrated that the N-Ce-AC-TiO_2 photocatalyst possessed a homogeneous surface, is being supplemented by the current investigation.

3.2. Central composite design

A total of 30 experiments were designed to synthesize N-Ce-AC/TiO_2 using CCD, where urea (*A*), cerium (*B*), activated carbon (*C*), and microwave power (*D*) were treated as independent factors that attribute the removal efficiency of tetracycline, denoted as a response. A quadratic model was generated from this CCD design to see the interaction between both factors and response. The regression model on the independent factors was evaluated, and analysis of variance (ANOVA) results are presented in Table 4. The model generates a *p*-value < 0.0001, which is less than the significant level of 0.05, thus proving sufficient evidence that independent variables involved in this synthesis were significant in the given response. The crucial data for tetracycline removal were *A*, *B*, *C*, *D*, *AB*, A^2, and D^2, where these variables highly influenced the response. In RSM, when the *p*-value is higher than 0.05 for lack-of-fit means, the generated model is fit and suitable for photodegradation of tetracycline using N-Ce-AC/TiO_2 as similar finding was also reported by Khasri et al. [51]. The following equation presented the empirical model relationship between independent factors and response:

$$\begin{aligned} Y = {} & +70.51 + 3.70A + 3.48B + 14.56C - 3.07D - 3.34AB \\ & + 0.55AC + 1.86AD - 0.58BC - 0.046BD - 1.20CD \\ & + 8.20A - 3.64B^2 - 1.43C^2 - 5.90D^2 \end{aligned} \quad (2)$$

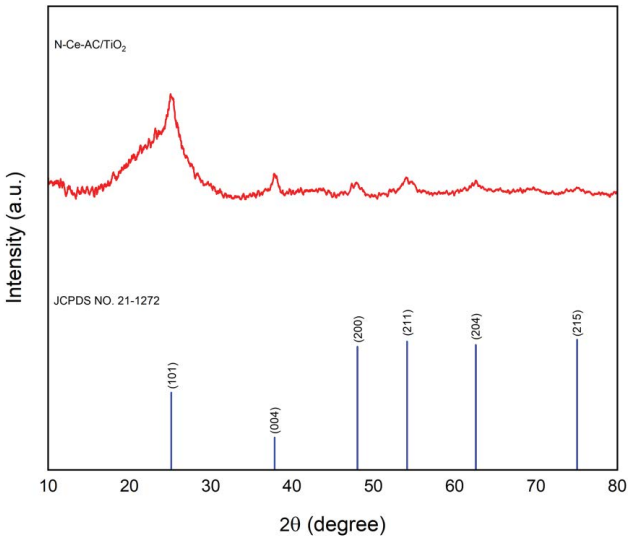

Fig. 1. X-ray diffraction patterns of synthesized catalyst, N-Ce-AC/TiO_2.

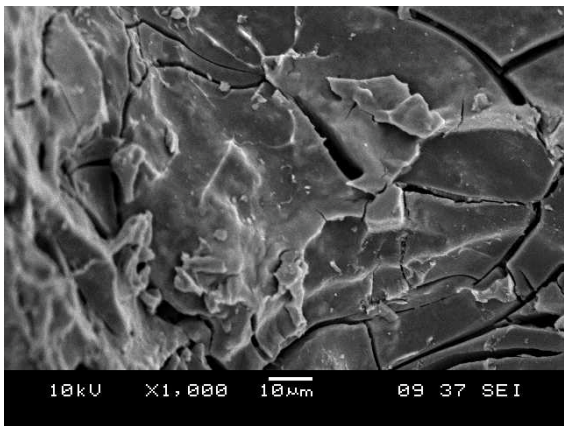

Fig. 2. Scanning electron microscopy image for catalyst N-Ce-AC/TiO_2.

A more significant effect of variables was observed from the lower number of *p*-value recorded in the ANOVA analysis [52]. The analysis shows that urea, cerium, activated carbon, and microwave power were significant factors where the *p*-value for these variables was less than 0.05. The synergistic effect is indicated as a positive sign in the empirical model, while the negative sign refers to an antagonistic effect [53]. The *R*-value squared was 0.9611, and the model's *p*-value was low, implying that the quadratic model for this experiment is highly significant.

Table 3
Elemental compositions of synthesized catalyst from energy-dispersive X-ray spectroscopy mapping analysis

Element compositions	%	N-Ce-AC-TiO_2
Carbon, C	Weight	45.43
Titanium, Ti	Weight	14.62
Oxygen, O	Weight	36.79
Nitrogen, N	Weight	1.39
Cerium, Ce	Weight	1.77

3.3. Validation of model and normality test

Fig. 4 validates the standard probability plot for removing tetracycline using the developed model. The points show close distribution to the straight red line, thus representing the normal probability distribution. Fig. 5 illustrates the predicted vs. actual plot, which expresses a good agreement between actual data and predicted data. Fig. 6 shows the

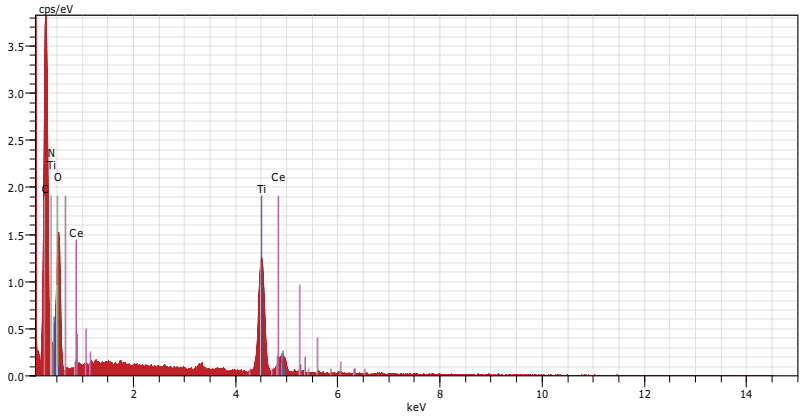

Fig. 3. Elemental spectrum of N-Ce-AC/TiO_2 catalyst in energy-dispersive X-ray spectroscopy analysis.

Table 4
ANOVA of quadratic model for removal of tetracycline

Source	Sum of squares	df	Mean square	*F*-value	*p*-value Prob. > *F*
Model	4,993.24	14	356.66	26.47	<0.0001
A-Urea (N)	246.79	1	246.79	18.31	0.0007
B-Cerium (Ce)	217.50	1	217.50	16.14	0.0011
C-Activated carbon (AC)	3,818.51	1	3,818.51	283.35	<0.0001
D-Microwave power (P)	169.40	1	169.40	12.57	0.0029
AB	178.02	1	178.02	13.21	0.0024
AC	4.76	1	4.76	0.35	0.5610
AD	55.09	1	55.09	4.09	0.0614
BC	5.35	1	5.35	0.40	0.5382
BD	0.03	1	0.03	0.00	0.9610
CD	23.21	1	23.21	1.72	0.2091
A^2	174.13	1	174.13	12.92	0.0027
B^2	34.36	1	34.36	2.55	0.1311
C^2	5.31	1	5.31	0.39	0.5395
D^2	90.10	1	90.10	6.69	0.0207
Residual	202.14	15	13.48		
Lack of fit	168.16	10	16.82	2.47	0.1646
Pure error	33.98	5	6.80		
Cor. total	5,195.38	29			

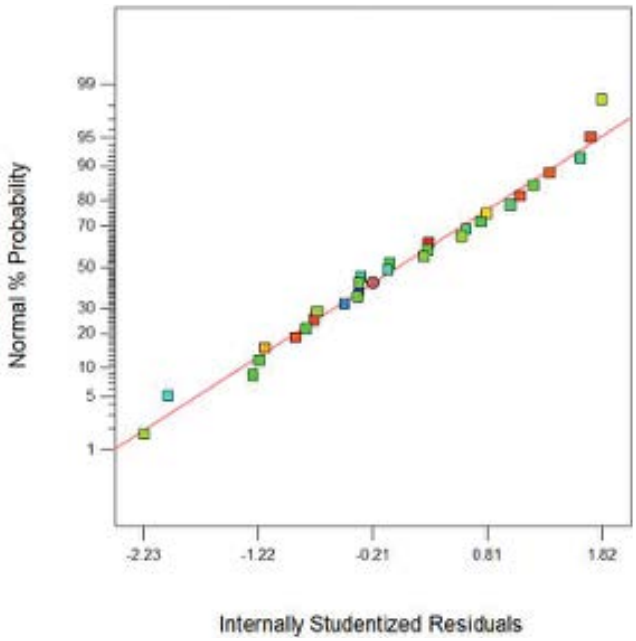

Fig. 4. Standard probability plot for the developed quadratic model of tetracycline removal.

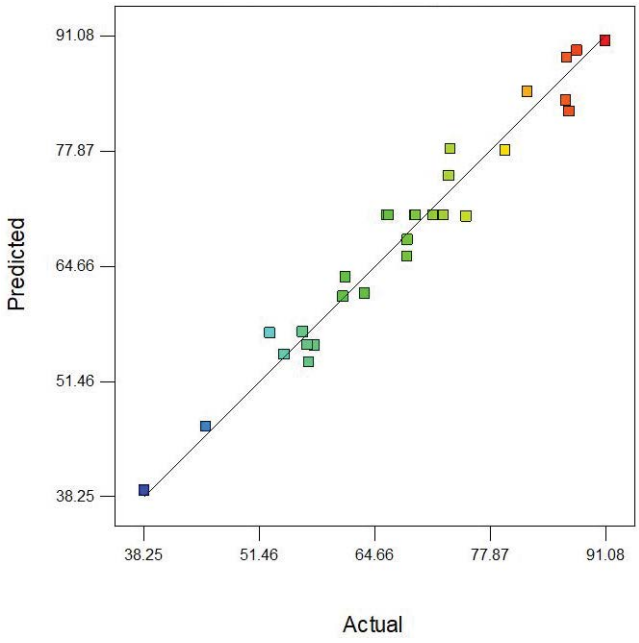

Fig. 5. Predicted vs. actual plot for the developed quadratic model of tetracycline removal.

perturbation of urea (*A*), cerium (*B*), activated carbon (*C*), and microwave power (*D*), identifying variables that were affecting the removal of tetracycline. The plot shows curvature of factors such as urea, cerium and microwave power and depicts tetracycline removal as sensitive to these variables. A sharp steepness can be seen for activation carbon, meaning the removal of tetracycline was heavily influenced by this factor. Fig. 7 illustrates the 3-dimensional surface plot

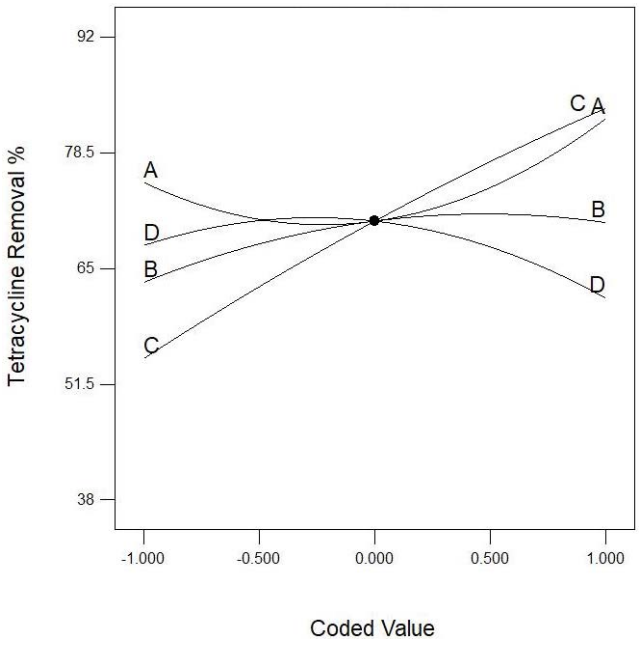

Fig. 6. Perturbation curves for tetracycline removal model.

of A × B, A × C, B × C, and C × D, where the red region represents a high relationship between the factors while the blue area represents the least. As shown in Fig. 7a, where interaction between two variables, urea and cerium (A × B), was observed, a high cerium dosage with a low urea dosage in the catalyst gave high removal of tetracycline. For variables urea and activated carbon (A × C) (Fig. 7b) and cerium and activated carbon (B × C) (Fig. 7c), an increase in activated carbon dosage also increased the removal rate of tetracycline. Meanwhile, for interaction between activated carbon and microwave power (C × D) (Fig. 7d), the slope decreased when the catalyst was prepared at high microwave power, but the removal rate was high at lower watts. Thus, high percentage removal can be observed when the cerium and activated carbon dosage in the catalyst is higher than the urea dosage and activated at the lowest microwave power. Higher activated carbon in the synthesized catalyst can increase the adsorption rate since a larger surface area provides a more active site for photocatalytic activity [31,32]. A high dosage of cerium with a trace amount of urea shows a high charge transport process allowing a high degradation rate, which is consistent with the report in the literature [54].

3.4. Response optimization

Table 5 depicts the desired optimum variables from the quadratic model and validation from the synthesized catalyst. The highest tetracycline removal was reported when the minimum variable for A and D co-existed with a maximum variable for B and C in the synthesized composite. Thus, the validation experiment for the optimum condition in preparing N-Ce-AC/TiO_2 for tetracycline removal followed the same. The estimated removal of tetracycline under these optimal conditions was 90.45%, indicating proper conformity, including suitability between the experimental and estimated percentage of tetracycline removal.

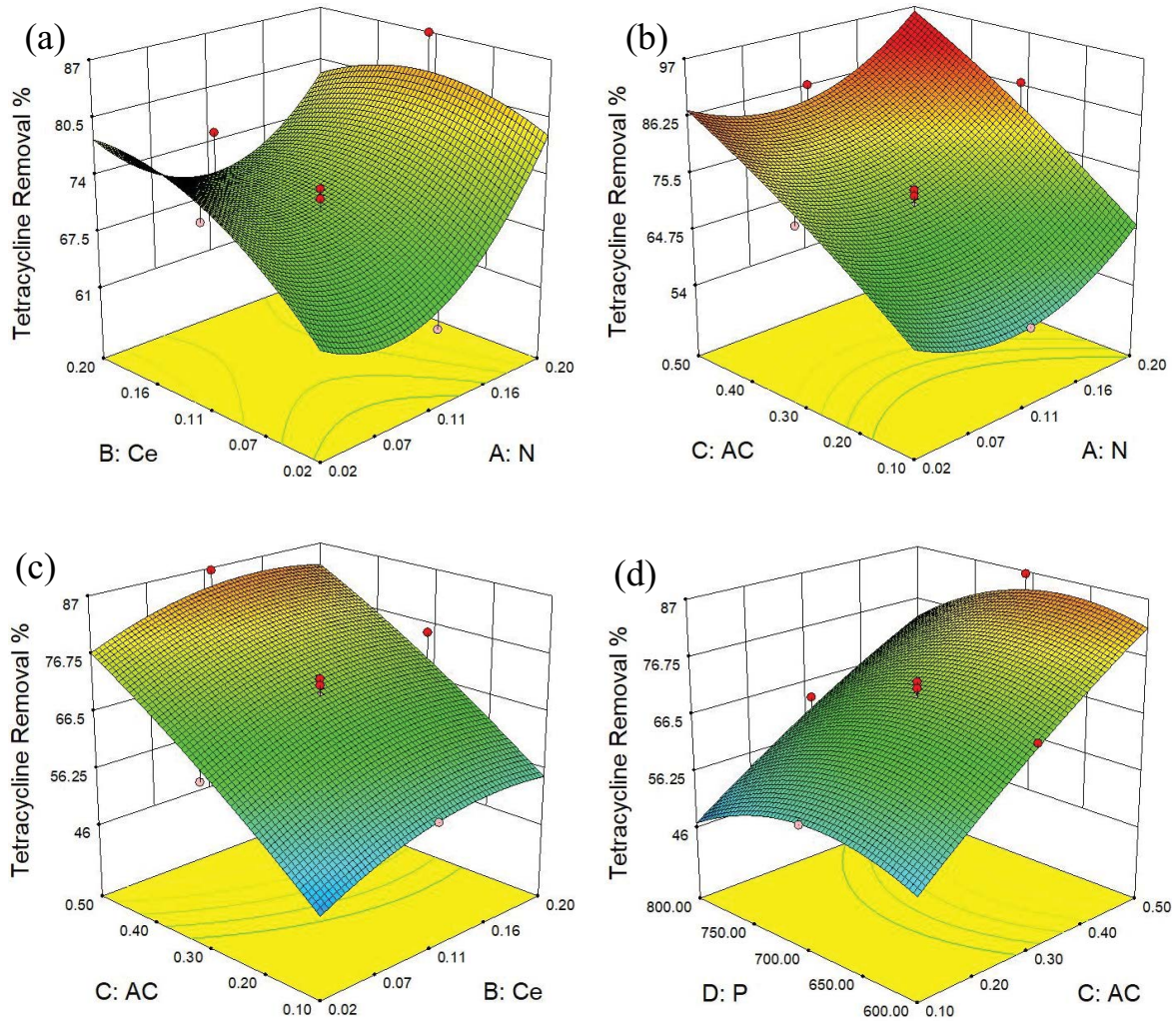

Fig. 7. 3-Dimensional response surface plots of (a) A × B, (b) A × C, (c) B × C and (d) C × D.

Table 5
Optimization validation for adsorption and photodegradation of tetracycline

Independent variables	Goal	Prediction	Experimental	Error percentage
Urea (g)	0.02	90.45	91.08	0.70%
Cerium (g)	0.20			
Activated carbon (g)	0.50			
Microwave power (W)	600			

4. Conclusion

In this paper, a successful application of CCD in RSM to set up the optimized parameters in preparing N-Ce-AC/TiO_2 as a potential catalyst for removing tetracycline from an aqueous solution has been tested, and the results are properly presented. It was discovered that the N, Ce, and AC dosage, along with activation power of microwave radiation, greatly influence tetracycline removal. The predicted percentage of removal based on RSM response was in good accord with experimental results (R^2 = 0.9613). Based on the optimized variable factors, it can be concluded that N-Ce-AC/TiO_2 prepared with 0.02 g N, 0.2 g Ce, and 0.5 g AC under 600 W power, assisted by microwave activation for 15 min was effective enough to be used as a catalyst for the removal of tetracycline from aqueous solution. Additionally, it provides the uniform distribution of doped elements on AC-TiO_2. In addition, the CCD-RSM demonstrates that the modelling presented here offers a suitable and dependable approach to the design and preparation of a new hybrid catalyst for tetracycline degradation in pollution treatment. The strength of this study is the development of a new catalyst material for degradation of tetracycline which can probably be significant for future water remediation. The limitation of this study is that it does not test the material for real wastewater. It is interesting for future study to evaluate capability of the proposed material for real and complex wastewaters.

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Conflicts of interest

The authors declare no conflict of interest.

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