Pol. J. Environ. Stud. Vol. 30, No. 3 (2021), 2013-2025
DOI: *10.15244/pjoes/127891* ONLINE PUBLICATION DATE: 2021-01-29

Original Research

Photocatalytic Process Optimization by Numerical Simulation Based on the Removal Efficiency of Carbamazepine under Different Operating Conditions

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Received: 4 July 2020
Accepted: 26 September 2020

Abstract

Carbamazepine as a typical ingredient in pharmaceuticals and personal care products (PPCPs) cannot be removed by conventional wastewater treatment processes due to its biorefractory property. In this paper, the effects of photocatalytic operating conditions of wastewater treatment such as stirring speed, composite material dosage, light intensity, and irradiation time on the degradation of carbamazepine by ATC were studied. Considering the aspects of technology, economy, and environment, the photocatalytic process scheme was optimized for carbamazepine wastewater treatment using ATC. The results were analyzed and simulated by response surface methodology (RSM). The effects of various factors and their interactions on the treatment efficiency were analyzed using a multiple quadratic regression equation, by which the optimal process parameters and the process conditions with optimal response were achieved. Under low material dosage (less than 2 g/L), the pair-wise interactions among irradiation time, light intensity, and stirring speed contributed more to the treatment efficiency than medium (2 g/L to 4 g/L) or high (more than 4 g/L) material dosage. The operation cost under low material dosage was relatively low, which shows that material cost is one of the most important factors in the actual photocatalytic process.

Keywords: Ag-TiO_2, carbamazepine, photocatalytic operating conditions, response surface methodology, photocatalytical degradation

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Introduction

Pharmaceuticals and personal care products (PPCPs) as a new form of environmental pollutant have become a focus of worldwide attention, like in Germany, Italy, America, Japan and so on [1-6]. Carbamazepine (CBZ), a type of PPCPs used in antiepileptic and mood stabilising clinical treatment, has been frequently detected in aquatic environments due to their extensive use and refractory properties [7-9]. However, the conventional processes of sewage treatment plants cannot effectively remove carbamazepine, mostly below 10% [10-12]. As a result, most of CBZ discharged into surface water environment and may cause potential harm to aquatic ecosystem and human health.

At present, the commonly used treatment methods for carbamazepine mainly include biodegradation, adsorption technology, membrane separation technology, and advanced oxidation processes. Yang et al. [13] studied the treatment of trace organic pollutants by white rot fungus and its lignin-modifying enzyme. The authors found that the degradation efficiencies towards carbamazepine were 31% and 15% respectively. Liu et al. [14] used graphene and carbon nanotubes to absorb ketoprofen, carbamazepine, and bisphenol A. They found that ionic strength had strong influence on the adsorption process, and the adsorption effect of graphene was better than that of carbon nanotubes. Cabrera-Lafaurie et al. [15] used modified clay to adsorb salicylic acid, chlorobeic acid, carbamazepine, and caffeine. Among those, the adsorption effect towards carbamazepine was the best, while that towards chlorobeic acid was the worst. However, the absorbents transform the substance from one phase to another rather than being completely eliminated. The energy consumption of adsorbent regeneration is large with the adsorption capacity reduced after regeneration. These factors lead to problems that hinder the use of the adsorption method. Lin et al. [16-17] have used nanofiltration and reverse osmosis technology to treat ibuprofen, carbamazepine, and triclosan. The results showed that the membrane technology had good treatment efficiency on these substances, but the investment and operation costs of membrane technology were high, and the system was prone to be blocked, necessitating high-level pretreatment and regular chemical cleaning. Problems of concentrate treatment also existed.

Advanced oxidation processes include Fenton oxidation, sonolysis, ozonation and photocatalysis as well as combinations. Photocatalysis is one of the technologies that has attracted great attention in the last years. Furthermore, this technology is particularly suitable for the treatment of relatively low water volumes with contaminants at low concentration. TiO_2 has been the most widely used photocatalyst, due to its high activity, photostability, low cost, chemicalstability and biocompatibility [18]. The photocatalytic oxidation technology represented by TiO_2 not only involves the advantages of oxidation and degradation but also decomposes trace organic intermediates in the water, and thus can be employed as a supplement and enhancement to the conventional treatment. In addition, photocatalytic technology can make full use of the continuously available solar energy which is cost-efficiency and environmentally friendly. The technology provides new methods and ideas for the removal of refractory organics and has good application prospects [19-20]. During the past two decades, researchers focused work on TiO_2 modifications and novel efficient photocatalysts development [9, 18]. Very recently, our group have used Ag-doped TiO_2 and chitosan (CTS) to prepare ATC (Ag-TiO_2-CTS), which has an improved effect on the adsorption and photocatalytic degradation efficiency towards carbamazepine. After treatment using ATC for 1h, the carbamazepine removal rate arrived at around 95%, which is higher than the control test without catalyst (less than 2% removal efficiency). It has also found that the removal rate increases by about 45% compared with the usage of naked-TiO_2. Even after repeated recycling, the degradation efficiency towards carbamazepine was maintained above 80%.

Recent studies have shown that the removal efficiency of PPCPs is influenced by operating conditions [21]. However, at present, most researchers are concerned about how to prepare composite photocatalytic materials with high degradation efficiencies (pollutant removal rate) and stable performance (removal rate after recycling). Furthermore, there is little research on how to effectively apply the photocatalysis materials to sewage plants or water supply plants, and how the operating conditions of photocatalysis process affect the degradation efficiency towards PPCPs. In the present study, the composite photocatalytic material ATC was used to treat carbamazepine in water. The effects of operating conditions including stirring speed, material dosage, light intensity, and irradiation time on the degradation process of carbamazepine were studied. Finally, the optimal operating conditions for pollutant degradation were obtained by numerical simulation. This study can provide support for the practical application of ATC, and it can also provide reference for other high-performance photocatalytic materials under photocatalytic process.

Material and Methods

Preparation of ATC

For ATC (Ag-TiO_2-CTS) material preparation, it needs three synthesis steps including three kind of solution produced. Synthesis step 1, added 8g TiO_2 into 300 mL distilled water in the beaker, then the mixed suspension solution A obtained after ultrasonication in 30 min. Step 2, mixed silver nitrate (0.5%W) into solution A got before and stirred for 30 min. Then the mixture was treated with an ultraviolet lamp (12 W)

for 180 min. Finally, the mixed suspension solution B was obtained. Step 3, 3 mL hydrochloric acid and 8 g chitosan (CTS) were added into suspension solution B. Mixed the suspension last for 3 h until we obtain the mixed emulsion solution C. Last but not the least, the emulsion solution C was dropped into sodium hydroxide solution (0.2 mol/L) using an automatic syringe. Standing overnight, clean the solution using distilled water until the pH of the cleaning solution was neutral. Put the solution into baker to dry at 60ºC, Ag-TiO_2-CTS (ATC) photocatalytic microspheres obtained.

Reagents

Carbamazepine ($C_{15}H_{12}N_2O$, 99%) used in the experiment was purchased from Sigma-Aldrich. Chitosan (($C_6H_{11}NO_4$)N with a deacetylation degree of 80-95%) was purchased from Sinopharm Chemical Reagents, and titanium dioxide (TiO_2, 80% anatase and 20% rutile) was purchased from Evonik Degussa. Acetonitrile (C_2H_3N, chromatographic purity) and acetic acid (CH_3COOH, chromatographic purity) were purchased from Tedia. Sodium hydroxide (NaOH, analytically pure), silver nitrate ($AgNO_3$, analytically pure), and nitric acid (HNO_3, analytically pure) were purchased from the Chengdu Kelong Chemical Reagent Plant, and hydrochloric acid (HCl, analytically pure) was purchased from Liyang Dongfang Reagent Co., Ltd.

Removal of Carbamazepine

The self-made photocatalytic device used in this experiment is shown in Fig. 1. The outer part is made of glass with a diameter of 13 cm; the inner part is made of a glass container with a diameter of 9 cm, and the UV lamp cover is made of quartz with a diameter of 5 cm. The UV lamp (Philips PL-S) was set up with a main wavelength of 365 nm. During operation, the prepared photocatalytic material was added into the simulated wastewater prepared in the laboratory. Aliquots of the samples were removed at given points in time. After filtering through a filter membrane (0.45 μm), the concentration was determined by high performance liquid chromatography (1260, Agilent). To accurately study the effect of ATC on the photodegradation of carbamazepine, the initial concentration of carbamazepine was set to 5 mg/L, which was selected according to the test concentration in the literature [3, 22-24].

To study the effects of operating conditions such as material dosage, stirring speed, light intensity, and irradiation time on the degradation process of carbamazepine, the variables were controlled when designing the experimental scheme under the above conditions.

Material dosage effect test: Added some ATC material, the dosages of ATC were 1, 2, 3, 4, 6, and 8 g/L, into 500 mL carbamazepine solution we prepared before. Then, put the mixed solution in the photocatalytic reaction device. Irradiated under the UV light with an intensity of 20 W, and the stirring speed was fixed at 150 rpm. After 1 h irradiation, the sample was collected through the filter membrane (0.45μm) for testing.

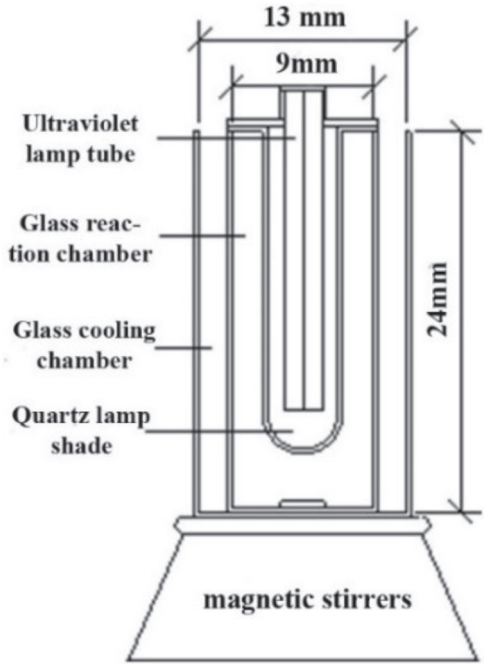

Fig. 1. Schematic diagram of the photocatalytic reaction device.

Stirring speed effect test: Added some ATC material, the dosage of ATC was 7 g/L, into 500 mL carbamazepine solution we prepared before. Then, put the mixed solution in the photocatalytic reaction device. Irradiated under the UV light with an intensity of 12 W, and the stirring speed was adjusted to values of 0, 50, 100, 150, 200, and 250 rpm. After 1 h irradiation, the sample was collected through the filter membrane (0.45 μm) for testing.

Light intensity effect test: Added some ATC material, the dosage of ATC was 7 g/L, into 500 mL carbamazepine solution we prepared before. Then, put the mixed solution in the photocatalytic reaction device. Irradiated under the UV light with intensity set to 4 W, 8 W, 12 W, 16 W, 20 W and 24 W, and the stirring speed was fixed at 150 rpm. After 1 h irradiation, the sample was collected through the filter membrane (0.45 μm) for testing.

Irradiation time effect test: Added some ATC material, the dosage of ATC was 7 g/L, into 500 mL carbamazepine solution we prepared before. Then, put the mixed solution in the photocatalytic reaction device. Irradiated under the UV light with an intensity of 12 W, and the stirring speed was fixed at 150 rpm. After 10 min, 20 min, 30 min, 40 min, 60 min, 80 min, 120 min, 180 min, and 240 min, irradiation, the sample

was collected through the filter membrane (0.45μm) for testing.

Determination of Carbamazepine

About the chromatography conditions of carbamazepine, an Agilent ZORBAX Exlipse XDB-C18 column (150×4.6 mm, 5 μm) was used. The mobile phase was acetonitrile: water (60:40, V/V); the flow rate was 1 mL/min; the column temperature was 20ºC; the detection wavelength was 285 nm; the injection volume was 20 μL, and the retention time was 4 min.

Results and Discussion

Effect of ATC Dosage on the Removal Efficiency Towards Carbamazepine

The effect of ATC dosage on the removal efficiency towards carbamazepine during the photocatalytic reaction in water is shown in Fig. 2. After 1h irradiation with the light intensity 20 W, the removal efficiency towards carbamazepine increased gradually with the ATC material dosage increasing. However, when the dosage of ATC was higher than 4 g/L, the removal efficiency did not increase in proportion with the increase in the ATC dosage. When the ATC dosages were 1, 2, 4, and 8 g/L, the removal efficiencies towards carbamazepine were 32%, 56%, 80%, and 82%, respectively. The ATC dosage was increased by a factor of 2, 4, and 8, while the removal efficiency towards carbamazepine only increased by a factor of 1.75, 2.5, and 2.6. When the ATC dosage was higher than 4 g/L, the removal efficiency tended to reach a plateau with the increasing dosage.

Clearly, the ATC dosage had a significant impact on the photocatalytic oxidation of carbamazepine. In general, when the ATC dosage was low, the contact probability of target pollutants and catalysts increased with the increase in the catalyst dosage. Also, due to the increasing catalyst amount, more oxidation groups were produced under the same irradiation conditions. All of these factors can promote the photocatalytic oxidation and improve the removal efficiency towards carbamazepine. However, when the dosage of ATC exceeded a certain concentration range (more than 4 g/L), the removal efficiency was restricted. The removal efficiency reduces by the screening effect once the further increment of dosage beyond the optimum amount [25, 26]. At this moment, the light energy can not be available adequately due to the scattering phenomena appeared [27]. It makes active sites on the surface of the ATC do not generate more e-/h+. Therefore, increase in degradation efficiency rate does not occur.

Effect of Stirring Speed on the Removal Efficiency Towards Carbamazepine

The stirring speed directly affected the mixing degree of ATC and carbamazepine in water as well as the degradation effect. Fig. 3 shows the removal efficiency towards carbamazepine during the photocatalytic reaction after 1 h irradiation at different stirring speeds with the light intensity 12 W.

In general, with increasing stirring speed, the removal efficiency towards carbamazepine increased rapidly at first, then rose slightly and maintained at a relatively stable level. The removal efficiency towards carbamazepine in water was 64% with the light intensity 12 W for 1 h without stirring (the stirring speed was 0). When the stirring speed increased to 100 rpm, the removal efficiency towards the pollutants in water increased by 15%, and the removal efficiency towards carbamazepine in water was close to 80%. With the increase in stirring speed, the diffusion rate of carbamazepine to the surface of ATC was increased, and the reaction efficiency was improved. However, when the stirring speed was higher than 100 rpm, although the removal efficiency towards carbamazepine fluctuated slightly, it tended to be stable on the whole,

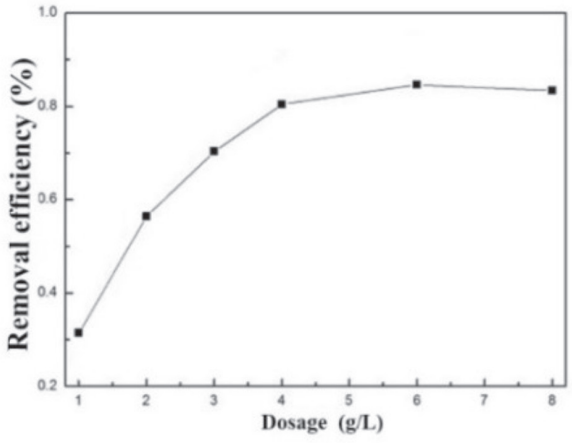

Fig. 2. Effect of dosage on the removal efficiency towards CBZ.

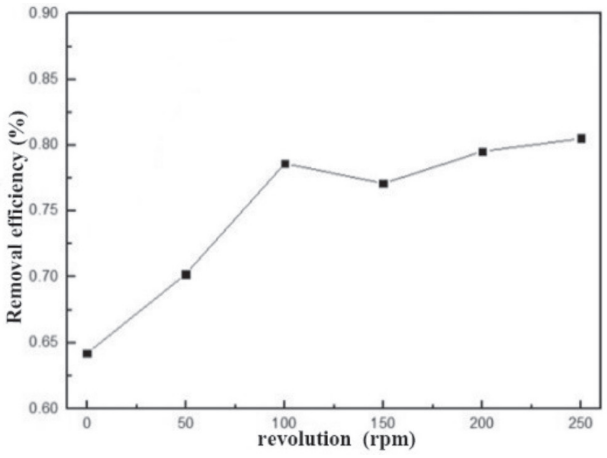

Fig. 3. Effect of stirring speed on the removal efficiency towards CBZ.

and further increases in the stirring speed did not significantly change the photocatalytic effect of ATC towards removal of carbamazepine. With the increasing stirring speed, more and more carbamazepine rely on the ATC surface, but available active sites on the ATC surface are limited. This is should be the main reason why the stirring speed does not influence on the removal of the pollutant at high speed (more than 100 rpm).

Effect of Light Intensity on the Removal Efficiency Towards Carbamazepine

With an increase in light intensity, from 4 W to 24 W, the removal efficiency towards carbamazepine during the 1h photocatalytic reaction in water increased as Fig. 4. Light intensity increasing improved the excitation energy, thus increasing the concentration of oxidation groups in the solution and improving the degradation effect of ATC towards carbamazepine. When the light intensity was 4 W, the removal efficiency towards carbamazepine was 73%; when the light intensity was increased to 24 W, the removal efficiency towards carbamazepine was 83%. The removal efficiency of carbamazepine increased by 10% when the light intensity was increased by a factor of 6 with the ultraviolet intensity range from 8.47e-06 to 5.86e-05, see Table 1.

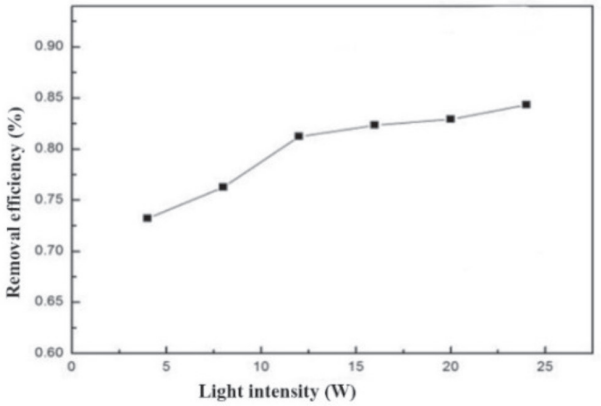

Fig. 4. Effect of light intensity on the removal efficiency towards CBZ.

Table 1. Ultraviolet intensity and removal efficiency under different light intensity.

Light intensity (w)	Ultraviolet intenstiy (einsteins/s)	Removal efficiency (%)
4	8.47E-06	73.22
8	1.77E-05	76.30
12	2.82E-05	81.24
16	3.81E-05	82.33
20	4.8E-05	82.95
24	5.86E-05	84.36

Under dark conditions, the removal efficiency towards carbamazepine by ATC was about 8%. No oxidation groups could be produced in the reaction system, and the degradation and removal of carbamazepine by ATC were mainly realized by adsorption. Clearly, for the removal of carbamazepine from water, the oxidation groups produced from photocatalytic excitation play an important role in the degradation of carbamazepine, and the effect of photocatalytic oxidative degradation is stronger than that of adsorption. However, excessive light intensity would affect the photocatalytic activity due to recombination of the electron-hole pair with the increment of temperature from the light [28].

Effect of Irradiation Time on the Removal Efficiency Towards Carbamazepine

The effect of irradiation time on degradation of carbamazepine by ATC under light intensity 12 and stirring speed 150 rpm is shown in Fig. 5. In the initial 60 min, the removal efficiency towards carbamazepine increased rapidly, and the removal efficiency towards carbamazepine reached 79%. Then, in the 3 h after the initial 60 min, the removal rate towards carbamazepine gradually decreased. Although the removal efficiency towards carbamazepine increased to nearly 99%, it only increased by 20% compared with the initial 60 min. Generally, the degradation of carbamazepine by ATC mainly occurred during the initial 60 min of the photocatalytic reaction, and then although the degradation slowed, the reaction continued, and the removal efficiency was close to 99% after 240 min of continuous irradiation.

In addition, carbamazepine degradation kinetics can be described by the first-order kinetic. The first-order kinetic constant is $0.046s^{-1}$(R^2 = 0.932). This value is higher than the kinetic constant for degradation without catalyst ($0.0002s^{-1}$, R^2 = 0.852).

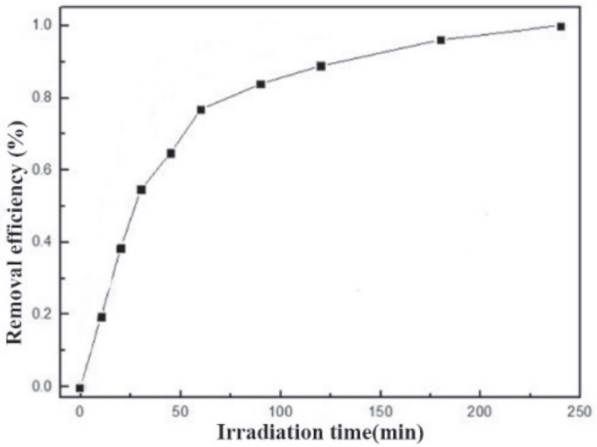

Fig. 5. Effect of irradiation time on the removal efficiency towards CBZ.

Optimization of Process Parameters

In summary, the stirring speed, material dosage, light intensity, and irradiation time all affected the degradation and removal of carbamazepine by ATC. Different reaction conditions not only changed the degradation effect towards target pollutant but also affected the cost of wastewater treatment. Therefore, considering the technical feasibility, economic feasibility, and environmental friendliness of the treatment process, the removal scheme for target pollutants in wastewater by ATC was optimized to further improve the practical application and promotion of the treatment process.

In this study, RSM [29, 30], which is commonly used in the chemical industry, in biosynthesis, and in environmental engineering, was used to analyze and simulate the experimental results. A multiple quadratic regression equation was used to analyze the influence of various factors and their interactions on the response variable. Through the analysis of the model equation, the optimal process parameters were obtained to achieve the optimal conditions.

The test design and data processing software Design-Expert 7.0 was used. The multiple regression equation (model) fitted by the least squares method was

$$Y \times 100\,\% = B_0 + \sum_{i=1}^{n} B_i X_i + \sum_{i=1}^{n} B_{ii} X_i^{\,2} + \sum_{i=1,\, j=1}^{n} B_{ij} X_i X_j + e$$

...where Y is the amount of pollutant removed; B_0 is the intercept, which is a constant; B_i is the linear coefficient; B_{ij} is the coefficient of the interaction; Bii is the quadratic term coefficient; and e is the error.

The experimental results were analyzed by analysis of variance (ANOVA), and by the correlation coefficient (R^2), homogeneity test of variance (F-value and Prob>F) between global variables and corresponding parameters, and signal-to-noise ratio (Adeq Precision). ANOVA was used to determine the goodness of fit of the fitting equation. If the fit was good, the interactions were analyzed according to the fitting equation, and the optimal conditions of the target expectation were obtained, or at least the optimal conditions within the expected range were obtained.

With the stirring speed, material dosage, light intensity, and irradiation time as variable factors, the removal amount was adopted as the objective function, and a multiple regression equation between removal amount and stirring speed, material dosage, light intensity, and irradiation time could be obtained by fitting the response surface. However, the selection of the values of these four factors often affects the use of materials and operating costs. Therefore, a cost function was obtained by synthetically analyzing the cost reflected by the four factors: stirring speed, material dosage, light intensity, and irradiation time.

$$R = Y/W$$

Here, R is the amount of pollutant removed per unit cost (mg/dollar); Y is the amount of pollutant removed (mg), Y>4 (to ensure a removal efficiency of 80%); W is cost of pollutant removal (dollar).

Taking R as the objective function, an optimization program was written using VB 6.0 software. The program optimized R within a given range of stirring speed, material dosage, light intensity, and irradiation time. The corresponding operating conditions of each factor under the optimal conditions were obtained, and these conditions could be used to guide follow-up research and practical operations.

Selection of Test Factor Level and Establishment of Response Equation

According to the above discussion, the test factors were determined as material dosage, irradiation time, light intensity, and stirring speed. The level of each factor was determined according to the single-factor tests. The center points, high levels, and low levels of the parameters were determined near the optimal conditions obtained from each single-factor test. Values were assigned, and −1, 0, +1 represented low, medium, and high levels, respectively. The value of α was set to 2 to determine the two extreme levels (−α and +α). Table 2 shows the determination of test factors and levels. Here, for description in convenient, use A, B, C, D to stand for material dosage, irradiation time, light intensity and stirring speed respectively.

The test design scheme and results for carbamazepine are shown in Table 3.

According to the test data, the regression equation of the response surface of carbamazepine in coded form is:

$$Y = -1.36846 + 0.33894A + 0.0602B + 0.08118C + 2.4231\times10^{-3}D - 4.2665\times10^{-3}AB + 0.01528AC + 4.282\times10^{-4}AD - 7.58691\times10^{-4}BC + 1.6343\times10^{-4}BD - 4.0064\times10^{-4}CD - 0.01179A^2 - 2.35513\times10^{-4}B^2 - 1.12645\times10^{-3}C^2 - 2.69666\times10^{-5}D^2$$

...where, A, B, C, D stands for the values of material dosage, irradiation time, light intensity and stirring speed respectively.

Table 2. Test factors for the response surface of carbamazepine.

Factor	Variable	Level				
		−2	−1	0	1	2
Dosage (g/L)	A	1	3	5	7	9
Irradiation time (min)	B	15	30	45	60	75
Light intensity (W)	C	4	8	12	16	20
Stirring speed (rpm)	D	0	50	100	150	200

Table 3. Test design and test results of the response surface for carbamazepine.

Standard number	Operation number	Dosage (g/L)	Irradiation time (min)	Light intensity (W)	Stirring speed (rpm)	Removal amount	
						Actual value	Predicted value
9	1	3	30	8	150	1.491075	1.718358
6	2	7	30	16	50	3.661183	3.610422
23	3	5	45	12	0	2.518597	2.622672
1	4	3	30	8	50	1.785344	1.717142
4	5	7	60	8	50	2.570879	3.001131
30	6	5	45	12	100	3.111384	3.064083
8	7	7	60	16	50	4.102205	3.765545
18	8	9	45	12	100	3.775691	3.896353
27	9	5	45	12	100	3.133077	3.064083
11	10	3	60	8	150	2.866643	3.057837
7	11	3	60	16	50	2.799788	2.841785
19	12	5	15	12	100	1.891845	2.10482
10	13	7	30	8	150	2.737885	2.836418
26	14	5	45	12	100	2.780488	3.064083
12	15	7	60	8	150	3.843192	3.663917
25	16	5	45	12	100	3.254867	3.064083
17	17	1	45	12	100	2.007818	1.854533
24	18	5	45	12	200	3.102905	2.966162
20	19	5	75	12	100	3.845065	3.599422
28	20	5	45	12	100	3.040752	3.064083
13	21	3	30	16	150	2.145116	1.855386
16	22	7	60	16	150	3.899195	4.107819
21	23	5	45	4	100	2.743535	2.541269
3	24	3	60	8	50	2.562128	2.566331
14	25	7	30	16	150	3.575983	3.462406
15	26	3	60	16	150	2.852848	3.012779
22	27	5	45	20	100	3.273114	3.442711
2	28	7	30	8	50	2.933147	2.663922
5	29	3	30	16	50	2.104705	2.174682
29	30	5	45	12	100	3.065476	3.064083

The test design scheme and results for carbamazepine are shown in Table 3.

Significance Analysis of the Fitting Equation

The goodness of fit test of the model is an indispensable step in data analysis. If a model function with a poor fit is adopted, it will produce deviations or even yield wrong results. The results of the ANOVA for the model are shown in Table 4.

The variance and residuals of the model were divided by the corresponding degrees of freedom to obtain the respective mean squared errors. The ratio of the two mean squared errors is the F-value. The F value of the carbamazepine model was $12.38 > F(0.05) = 2.42$, which indicates that the model had a high level of significance and the confidence was greater than 95%. The Prob>F was less than 0.0001, further indicating that the model had a high significance level. The model would deviate due to noise [31, 32] with a probability of only 0.01%. The correlation coefficient

Table 4. ANOVA of the response model for carbamazepine.

Source	Sum of squares	df	Mean square	F-value	p-value of Prob > F	
Model	12.12	14	0.87	12.38	<0.0001	Significant
Residual	1.05	15	0.070			
Pure Error	0.12	5	0.025			
Cor Total	13.16	29				
Std. Dev		0.26	R-squared		0.9204	
Mean		2.92	Adj R-squared		0.8461	
Adeq Precision		12.791				

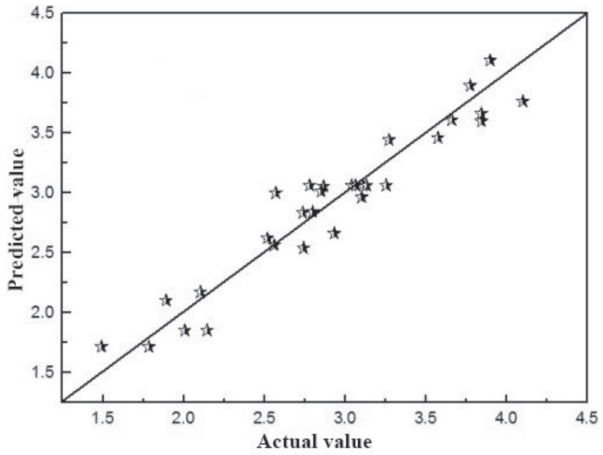

Fig. 6. The predicted value and actual value of the CBZ model.

of carbamazepine was R^2 = 0.9204, and the correlation was greater than 90%. The Adeq Precision of the carbamazepine model was 12.791, which was much higher than 4. This shows that the model was suitable and could be applied.

It can be seen from the figure of predicted and actual values that the actual values of removal efficiency towards carbamazepine were almost all within the range of predicted values±α = 0.05, and the correlation between predicted values and actual values was very good. In the residual graphs shown from Fig. 7 to Fig. 9, except for the large errors of the extreme values added at the endpoints of each factor in the experimental design, the residuals of other points were all within 0.050, and they were nearly normally distributed. The error of the model was mainly system error that was within the controllable range. The above ANOVA indicated that the model can be used to effectively simulate and predict the removal amount of carbamazepine by ATC.

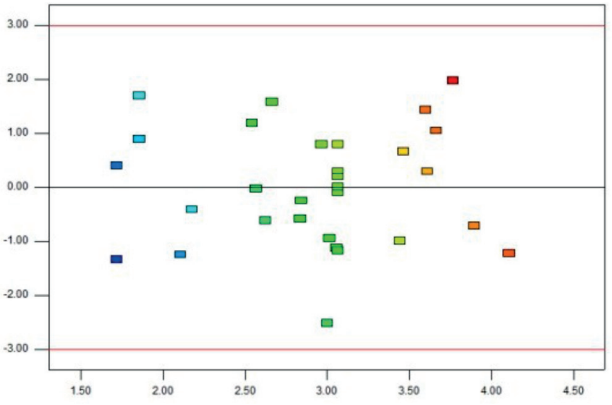

Fig. 8. Residuals plot for the CBZ model.

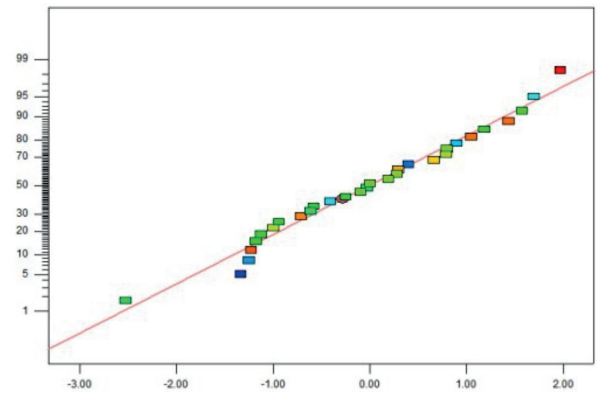

Fig. 7. Normal distribution of probability in the CBZ model.

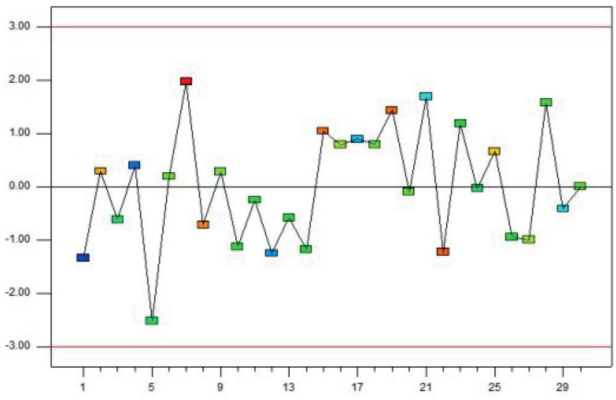

Fig. 9. Residuals plot for the CBZ model in sequential order.

Table 5. Cost analysis.

	Content	Amount	Unit cost	Cost
Material cost	Chitosan	1 kg	13.44 $/kg	0.05$/g
	Titanium oxide	1 kg	63.65$/kg	
	Silver nitrate	40 g	33.95$/100 g	
	Nitric acid	375 ml	2.12$/500 ml	
	Water	1250 L	0.40 $/m3	
	Sodium hydroxide	1250 g	0.42$/kg	
	Ultrasonication	62.5 h*150 W = 9.375 kw h	0.07 $/kw h	
	Ultraviolet cost	370 h*12 W = 4.44 kw h		
	Injection pump	750 h*30 W = 22.5 kw h		
	Drying	73 h*150 W = 10.95 kw h		
	Stirring	12 h*1100 W = 13.2 kw h		
Operating cost	Dosage	A		
	Irradiation time	B		
	Light intensity	C		
	Stirring speed	D		

Establishment of Model on Treatment Cost and Unit Cost

The cost of sewage treatment mainly consists of electricity consumption, chemical reagent costs, maintenance costs, material costs, and control management. Among these, electricity consumption and chemical reagent costs are the most-needed expenses in the production process, and they account for a large proportion. They must be strictly controlled in the production process to effectively reduce the cost. In actual operation, it is necessary to integrate all factors to find the optimal operation mode that not only meets the appropriate requirements but also reduces the operation cost.

Table 5 shows a comprehensive analysis of the cost under the operating conditions in the laboratory, and the following cost model (W) was obtained.

$$W = 0.01A + 1.9\times10^{-6}BC + 1.1\times10^{-6}BD$$

...where, A, B, C, D stands for the values of material dosage, irradiation time, light intensity and stirring speed respectively. The values for different factor is $1\leq A\leq 9$, $15\leq B\leq 75$, $4\leq C\leq 20$ and $0\leq D\leq 200$.

The objective function is obtained based on the above analysis:

$$R = Y/W$$

Here, R is the amount of pollutant removed per unit cost (mg/dollar); Y is the amount of pollutant removed (mg), Y>4 (to ensure a removal efficiency of 80%); W is cost of pollutant removal (dollar).

Using VB6.0 program software to optimize the objective function R, the results for carbamazepine were A(material dosage) = 5, B(irradiation time) = 75, C(light intensity) = 8, and(D stirring speed) = 200; the removal efficiency was 80%, and R = 1.105. Combinations near the optimal condition were selected as shown in Table 6. In the actual operation process, it is necessary to select an appropriate combination as a reference for operating conditions according to the actual situation.

Surface Analysis of Photocatalysis of Carbamazepine by ATC

According to the response surface and its corresponding contour map based on the model of pollutant removal amount per unit cost, the effects of the interactions between any two experimental factors on the pollutant removal amount per unit cost can be evaluated, and the best range of each factor can be determined. The shape of the contour can reflect the strengths of the effects of the interactions between various factors.

Fig. 10 shows the surface and contour map of the effects of the interactions among stirring speed, material dosage, light intensity, and irradiation time on the removal amount of carbamazepine per unit cost. It can be seen that the removal amount of carbamazepine per unit cost decreased with an increase in dosage when other parameters were kept constant. When the dosage increased from 1 g/L to 2 g/L, the R value decreased sharply. When the dosage increased from 2 g/L to

Table 6. Combination of operating conditions.

No.	Dosage (g/L)	Irradiation time (min)	Light intensity (W)	Stirring speed (rpm)	Removal efficiency (%)	R
1	5	75	8	200	80	1.105
2	6	65	20	100	80	0.939
3	6	65	20	150	81	0.944
4	6	70	12	200	80.6	0.934
5	6	70	16	150	80.6	0.940
6	6	70	16	200	81.2	0.941
7	6	70	20	100	80.6	0.943
8	6	70	20	150	82	0.957
9	6	70	20	200	81.2	0.939
10	6	75	4	200	80.2	0.928
11	6	75	8	200	82	0.948
12	6	75	12	150	80	0.931
13	6	75	12	200	83	0.931
14	6	75	16	150	82	0.953
15	6	75	16	200	83.4	0.963
16	9	75	20	100	80.8	0.944
16	6	75	20	150	83.2	0.966
18	6	75	20	200	83	0.958

4 g/L, the R value decreased gradually. When the dosage was greater than 4 g/L, the decrease in R value gradually slowed. According to the analysis in Fig. 2, the main reason is that when the dosage was between 1 g/L and 2 g/L, the removal amount increased the fastest, and then the rate gradually became slow; when the dosage was greater than 4 g/L, the removal amount barely increased. Clearly, with the increase in dosage, the cost increased linearly, but the increase in removal amount was less than the increase in cost, resulting in the decrease in the R value with the increased dosage. It can be seen from Section 3.3 and Section 3.4 that increases in irradiation time and light intensity led to the increase in the removal amount of carbamazepine and also increased the cost. However, from Fig. 10, it can be seen that the removal amount of carbamazepine per unit cost increased steadily with the increase in irradiation time and light intensity, which shows that the irradiation time and light intensity had a greater effect than cost on the removal of target pollutants by ATC. As can be seen from the surface and contour map in Fig. 10, with the increase in the stirring speed, the removal amount of carbamazepine per unit cost increased at first and then decreased. Although the operation cost was relatively low under a low stirring speed, the low stirring speed resulted in the ATC not fully contacting the target pollutant, and the reaction was not as efficient, so the removal amount of the target pollutant was lower, and the R value was less. Similarly, excessive stirring speed did not have a great impact on the increase in the removal amount of the target pollutant, while it brought a large amount of operation cost. The R value was thus also reduced.

Comparing the effects of pair-wise interactions among stirring speed, ATC dosage, irradiation time, and light intensity, it can be seen that when the dosage was increased from 1 g/L to 4 g/L, this had the greatest impact on the R value, followed by irradiation time, light intensity, and stirring speed. Under the influence of dosage, the maximum value of the removal amount of carbamazepine per unit cost reached more than 2.5. However, the maximum value of removal amount of carbamazepine per unit cost could only reach 1 under the effects of pair-wise interactions among irradiation time, light intensity, and stirring speed. Under low material dosage (less than 2 g/L), the pair-wise interactions among irradiation time, light intensity, and stirring speed can contribute much more to the treatment efficiency than medium (2 g/L to 4 g/L) or high (more than 4 g/L) material dosage. When the dosage was low, the operation cost was relatively low, which to some extent shows that the material cost is the most important factor in the actual utilization process. Clearly, it can be seen from Section 3.1 that low dosage would also reduce the removal efficiency towards target pollutants, so it is necessary to optimize the dosage selection in the actual application process.

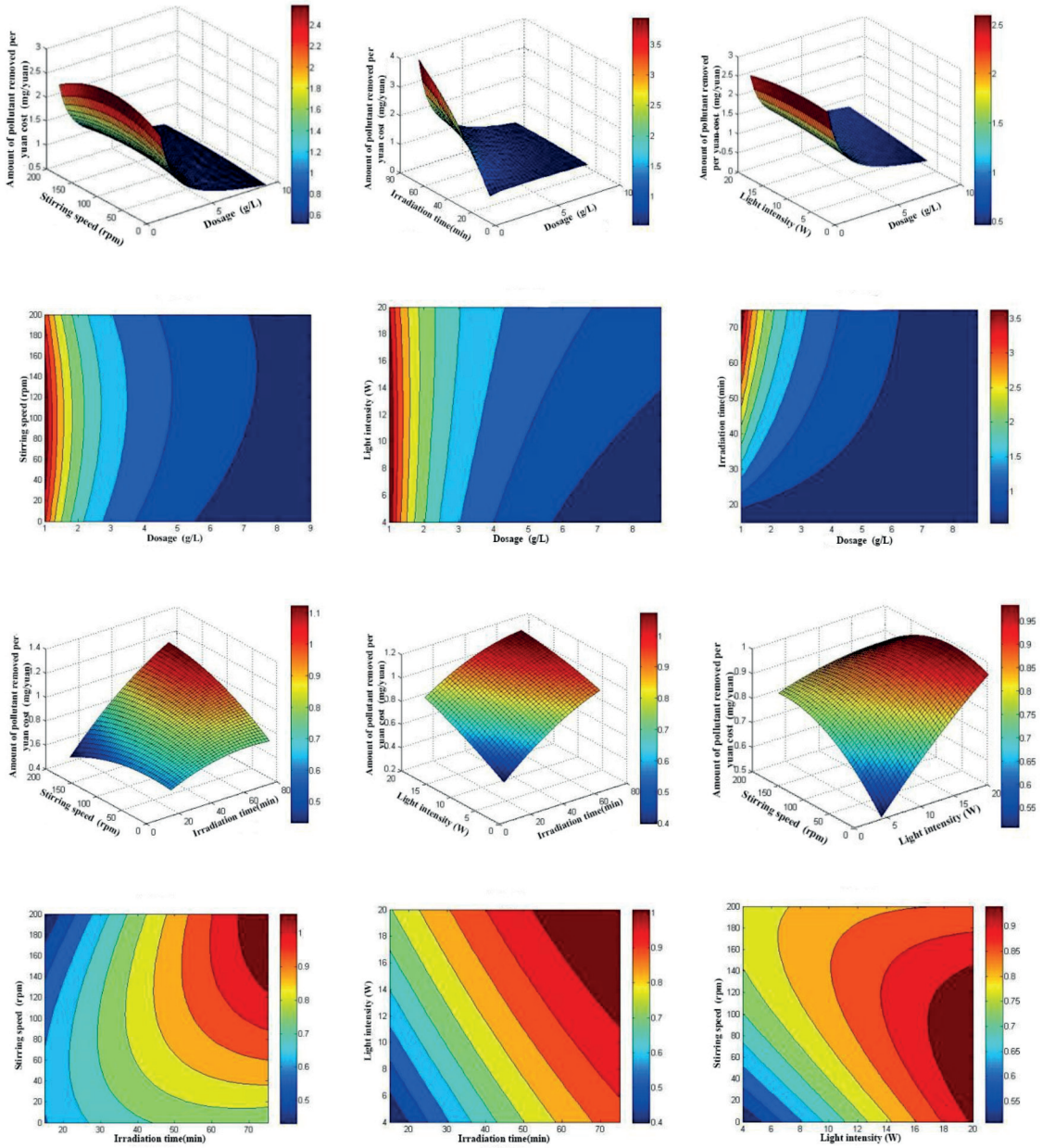

Fig. 10. Effects of interactions among stirring speed, material dosage, light intensity, and irradiation time on the removal amount of CBZ per unit cost.

According to the surface map of the effects of the interactions between irradiation time and light intensity, the surface increased uniformly and presented as a diamond shape, and the contour was evenly distributed from the lower left corner to the upper right corner, indicating that the effect of irradiation time and light intensity on the removal efficiency towards carbamazepine was relatively uniform. The number of contours on the irradiation time axis is more than that on the light intensity axis, which means that the influence of irradiation time was greater than that of light intensity. In addition, a longer irradiation time (more than 70 min) and higher stirring speed (more than 160 rpm) or a longer irradiation time (more than 65 min) and higher intensity (more than 16 W) could result in a higher R value. By analyzing the effects the interaction between light intensity and stirring speed on the R value of carbamazepine, it can be seen that the number of contours on the light intensity axis was more than that on the stirring speed axis, so the influence of light intensity change was greater than that of the stirring speed. Higher light intensity (more than 18 W) and moderate stirring speed (around 100rpm) could lead to higher R values.

Conclusions

The photocatalytic operating conditions, including stirring speed, composite material dosage, light

intensity, and irradiation time, all had influence on the removal of carbamazepine from wastewater, in similar patterns. With an increase in each factor, the removal efficiency towards carbamazepine increased correspondingly, finally tending to be stable. After 240 min of continuous irradiation, the removal efficiency towards carbamazepine reached about 99%.

Compared with the irradiation time, light intensity, and stirring speed, the ATC material dosage could affect the treatment efficiency significantly, which shows that material cost is an important factor in the actual process operation followed by irradiation time, light intensity, and stirring speed. Comparing the effects of pair-wise interactions, it showed that under low material dosage (less than 2 g/L), the pair-wise interactions among irradiation time, light intensity, and stirring speed can contribute treatment efficiency. In addition, Longer irradiation time (more than 70 min) and higher stirring speed (more than 160 rpm) or a longer irradiation time (more than 65 min) and higher intensity (more than 16 W) could also lead to higher per cost treatment efficiency.

To further optimize the process, studies that investigate the effect of organic community and chemical agents added into the wastewater treatment plants in site other than the scale used in this study are recommended. In addition, the modified photocatalysis materials introduced in powder, which is inconvenient for recycling. Further investigations on friendly material recycling methods, like fixed material filling or painting, are needed to conduct. However, this study does significantly showed that removal efficiency of PPCPs is influenced by operating conditions, which can guide the photocatalysis materials effective application in the sewage plants or water supply plants. The optimal operating conditions for pollutant degradation obtained by numerical simulation can also provide support for the practical application of ATC. Finally, the cost of wastewater treatment for particular pollutants disposal can be obtained easily.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No.: 51579072; 51679102) and the Fundamental Research Funds for the Central Universities (No.: B19020074).

Conflict of Interest

The authors declare no conflict of interest.

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