



## Optimization of parameters on photocatalytic degradation of chloramphenicol using TiO<sub>2</sub> as photocatalyst by response surface methodology

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### Abstract

The experimental design methodology was applied for modeling and optimizing the operation parameters on photocatalytic degradation of chloramphenicol (CAP) using TiO<sub>2</sub> as photocatalyst in a photoreactor. Three experimental parameters (including pH, TiO<sub>2</sub> concentration and CAP initial concentration) were adopted to obtain the preliminary information. The multivariate experimental design was employed to establish a quadratic model as a functional relationship between the degradation rate of CAP and three experimental parameters. The interaction effects and optimal parameters were obtained by using Design Expert software. The optimal values of the operation parameters under the related constraint conditions were found at pH 6.4, TiO<sub>2</sub> concentration of 0.94 g/L and CAP initial concentration of 19.97 mg/L, respectively. The degradation rate of CAP approached 85.97% under optimal conditions. The regression analysis with  $R^2$  value of 0.9519 had a good agreement between the experimental results and the predictive values. In addition, pH and TiO<sub>2</sub> concentration had a significant influence on the degradation rate of CAP.

**Key words:** chloramphenicol; photocatalysis; TiO<sub>2</sub>; response surface methodology

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### Introduction

In recent years, pharmaceuticals and personal care products (PPCPs) have been continually discharged into the aquatic environment without any restriction, which are emerging as a potential threat to the ecosystem and the public, and PPCPs have been increasingly detected in sewage water, natural water, surface water and ground water (Rabiet et al., 2006; Nakada et al., 2008; Murakami et al., 2009; Loraine and Pettigrove, 2006; Richardson et al., 2005; Sui et al., 2009; Yu and Chu, 2009). The main problem of PPCPs is reported to act as inhibitor of multixenobiotic resistance, especially for medicines which creates adverse effects on aquatic organisms (Jjemba, 2006).

Among the medicines, antibiotics receives extensive concern because of a wide usage in USA, Europe, and Asia, etc. (Kasprzyk-Hordern et al., 2009; Feitosa-Felizzola and Chiron, 2009; Arikan et al., 2008; Leung et al., 2008; Gulkowska et al., 2007; Phillips, 2007). Chloramphenicol (CAP) as a representative antibiotic is applied to inhibiting Gram-positive and Gram-negative bacteria, and its residual parts with metabolites from the excrement of human and animals get into the surface water and ground water after the sewage treatment (Sui et al., 2009; Gulkowska et al., 2007). As a consequence,

researchers have been making efforts to find out the ways of inactivating or eliminating the residual parts of CAP (Peng et al., 2006; Klavarioti et al., 2006; Chatzitakis et al., 2008).

Conventional methods for removing CAP include chemical precipitation, active carbon adsorption, activated sludge process, etc. However, these techniques have certain disadvantages of the high cost or the problem of sludge disposal. Advanced oxidation process (AOP) is considered as the best method which uses the semiconductor as photocatalyst to mineralize toxic organic chemicals, and has been demonstrated that heterogeneous photocatalysis using TiO<sub>2</sub> (anatase) as photocatalyst has the best effect. Moreover, the advantages of AOP are mild operation condition and low costs (Peng et al., 2006; Pérez-Estrada et al., 2007; Bahnemann et al., 2007).

Degradation of CAP using TiO<sub>2</sub> as catalyst has been studied by several researchers (Chatzitakis et al., 2008; Bahnemann et al., 2007; Yang et al., 2008; Tariq et al., 2009; Naeem and Ouyang, 2009; Fang et al., 2007). However, the previous works are based on the conventional method by changing a parameter while the other parameters are the constants, and the method does not consider the effects of the parameters combination. Response surface methodology (RSM) is a method which combines mathematics and statistics to analyze the relative significance of several influence factors even in the complicated system,

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therefore RSM can determine the optimal condition and reduce the study time and the cost by the comprehensive analysis of mathematics and statistics (Fu et al., 2007; Secula et al., 2008; Li et al., 2008; Mei et al., 2009).

To face the serious problems of antibiotics pollution, it is necessary to change the conventional method of the study (single factor study), so as to guide the actual process effectively. To our knowledge, there is no such information available in the literature for the optimization of the operation parameters on photocatalytic antibiotics using  $\text{TiO}_2$  as photocatalyst by RSM. The present work focused on the effects of parameters (pH,  $\text{TiO}_2$  concentration and CAP initial concentration) on the degradation rate of CAP (concentration variation) under various experimental conditions in a batch reactor. Initially, the preliminary information of suitable reaction conditions for optimizing the CAP degradation was obtained, and then a quadratic model was made to optimize the parameters of CAP degradation with RSM on the basis of the preliminary experiments. This research not only provides information for predicting and optimizing the degradation process of CAP under the related constraint conditions, but also can provide a new method to deal with antibiotics pollution.

## 1 Experiments

### 1.1 Materials

Chloramphenicol ( $\text{C}_{11}\text{H}_{12}\text{O}_5\text{N}_2\text{Cl}_2$ , MW 322.96) was provided by Nanjing Baijingyu Pharmaceutical Co., Ltd. (Nanjing, China) and was used without further purification. Its structure is shown in Fig. 1.

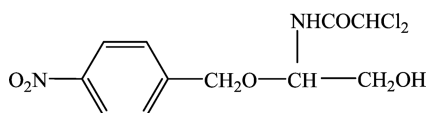


Fig. 1 Structure of chloramphenicol (CAS 56-75-3).

The photocatalyst nano- $\text{TiO}_2$  (particle size 10–20 nm, surface area  $120 \text{ m}^2/\text{g}$ , 100% anatase) was purchased from High Technology Nano Co., Ltd. (Nanjing, China). All other chemicals were analytic reagent grade which were purchased from Country Medicine Reagent Co. (Shanghai, China). The double distilled water was used in the experiments.

### 1.2 Degradation experiments

Irradiation experiments were conducted in a cylindrical reactor with a 300-W medium pressure mercury lamp ( $\lambda \geq 365 \text{ nm}$ ) placed in cooling trap for maintaining constant temperature by water circulation (Fig. 2). The CAP solution containing an appropriate dosage of  $\text{TiO}_2$  powder was prepared in water under the dark during the experiment. The pH value of solutions was adjusted by HCl and NaOH. The solution was stirred for 30 min to reach the adsorption equilibration in the dark before irradiation. At specific time, the samples of solution were withdrawn and filtrated through the filter (pore size  $< 0.22 \mu\text{m}$ ). The filtrate

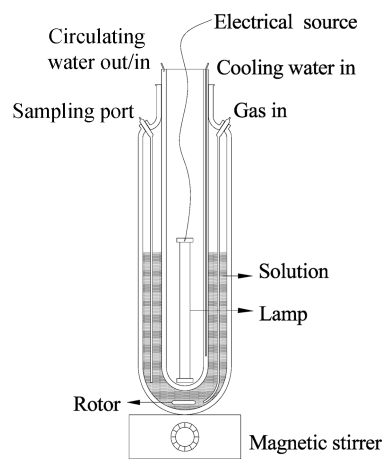


Fig. 2 Schematic diagram of photochemical reaction device.

was determined by UV-Visible spectrophotometer (T6, Pgeneral Co., China). All the optimization experiments were carried out at fixed radiation time of 60 min. All photocatalytic experiments were repeated three times to check the reproducibility of the experimental results.

### 1.3 Analytical procedures

The variation in the CAP concentration was observed from its characteristic absorption band at 278 nm using UV-Visible spectrophotometer. Because a linear dependence between the concentration of CAP and the absorption at 278 nm was observed, the concentration change of CAP was determined at this wavelength during the experimental process.

### 1.4 Experimental design and RSM

The experimental plan has two parts. Initially, the conventional method of study was carried out during the preliminary experiment, namely the single factor study, and three experimental parameters were considered (pH,  $\text{TiO}_2$  concentration and CAP initial concentration). Thereafter, the optimization of three experimental parameters was carried out on the basis of the preliminary information of the single factor study.

In the optimization part, RSM was utilized to optimize the three parameters (pH,  $\text{TiO}_2$  concentration and CAP initial concentration). The three parameters were chosen as independent variables while the degradation rate of CAP as output response variable. Ranges and levels of independent variables are shown in Table 1. The central composite experimental design (CCD) (Mei et al., 2009; Larson and Farber, 2003) was adopted to evaluate the combined effect of the three independent variables by 20 sets of experiments. The fundamental assumption and the experimental implication of RSM have been discussed elsewhere (Utts and Heckard, 2002). An empirical second-order polynomial model for three parameters was expressed as Eq. (1):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (1)$$

where,  $y$  (%) represents response variable (degradation rate of CAP);  $\beta_0$  is interception coefficient,  $\beta_{11}$ ,  $\beta_{22}$  and

**Table 1** Experimental range and level of independent variables for CAP degradation

Independent variable	Range and level				
	$-\alpha$	$-1$	$0$	$+1$	$+\alpha^a$
pH ( $x_1$ )	4.0	5.0	6.5	8.0	9.0
TiO <sub>2</sub> concentration ( $x_2$ , g/L)	0.58	0.75	1.00	1.25	1.42
CAP initial concentration ( $x_3$ , mg/L)	6.6	10.0	15.0	20.0	23.4

$\alpha^a = 1.68$  (star or axial point for orthogonal CCD in the case of three independent variables) and their actual values were rounded.

$\beta_{33}$  are quadratic terms,  $\beta_{12}$ ,  $\beta_{13}$  and  $\beta_{23}$  are interaction coefficients, and  $x_1$ ,  $x_2$  and  $x_3$  are independent variables studied (pH, TiO<sub>2</sub> concentration and CAP initial concentration). Regression analysis and optimization process were performed by Design Expert V.6.0.7 software (Stat-Ease Inc., USA).

### 1.5 Statistical analysis

All analytical tests were carried out in triplicate. Statistical analysis was performed by using Design Expert V.6.0.7 (Stat-Ease Inc., USA). Data were analyzed by the analysis of variance (ANOVA), and the mean values were considered the significant difference when  $p < 0.05$ . The optimal values of the operation parameters were estimated by the three-dimensional response surface analysis of the independent variables and the dependent variable. The actual and the coded values of independent variables are listed in Table 1. The experimental values of CAP degradation rate under various experimental conditions are shown in Table 2.

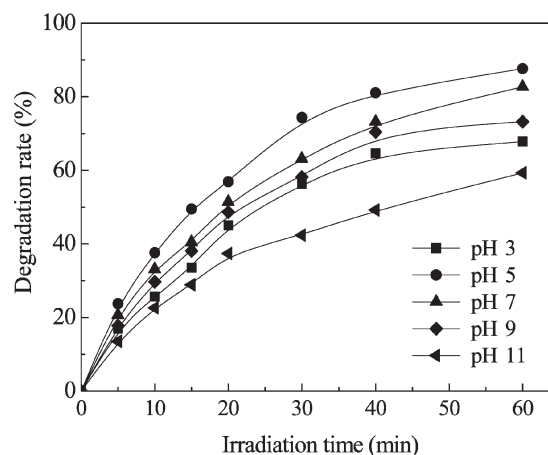
## 2 Results and discussion

### 2.1 Preliminary studies

In order to determine the ranges of pH, TiO<sub>2</sub> concentration and CAP initial concentration for experimental design, the preliminary experiments were conducted. The results of the degradation rate of CAP under different pH values

are shown in Fig. 3. The results imply that the degradation rate of CAP rises slightly when the pH value changes from alkaline (pH 11.0) to weakly acidic (pH 5.0). In addition, it seems that the highest pH (11.0) and the lowest pH (3.0) show a relative low impact on the degradation rate of CAP, and pH 5.0 is the optimum pH for the TiO<sub>2</sub> photocatalytic degradation of CAP in present study.

The role of pH as important parameter in the photocatalytic reactions influences the surface charge properties and the adsorption behavior of TiO<sub>2</sub> (Gaya and Abdullah, 2008). However, it is difficult to interpret the effect of pH value on photocatalytic process. Some researchers



**Fig. 3** Effect of pH on the degradation rate of CAP.  $C_0$  (CAP) = 15 mg/L;  $C_0$  (TiO<sub>2</sub>) = 1.00 g/L.

**Table 2** Experimental designs of the five-level and their experimental results and predictive values

Run	Experimental conditions			CAP degradation rate (%)	
	$x_1$ pH	$x_2$ TiO <sub>2</sub> (g/L)	$x_3$ CAP (mg/L)	Experimental	Predictive
1	6.5(0)	1(0)	15(0)	87.42	87.55
2	8(+1)	1.25(+1)	10(-1)	79.81	80.43
3	6.5(0)	1(0)	15(0)	87.53	87.55
4	6.5(0)	1(0)	15(0)	87.31	87.55
5	6.5(0)	1(0)	23.4(+1.68)	85.17	84.86
6	6.5(0)	1(0)	6.6(-1.68)	85.04	85.33
7	4(-1.68)	1(0)	15(0)	84.56	85.40
8	6.5(0)	1.42(+1.68)	15(0)	81.67	81.83
9	8(+1)	0.75(-1)	20(+1)	79.87	80.89
10	8(+1)	0.75(-1)	10(-1)	83.69	83.55
11	6.5(0)	1(0)	15(0)	87.39	87.55
12	5(-1)	1.25(+1)	20(+1)	85.78	85.93
13	9(+1.68)	1(0)	15(0)	83.55	82.64
14	6.5(0)	1(0)	15(0)	86.86	87.55
15	5(-1)	0.75(-1)	10(-1)	85.11	85.15
16	5(-1)	0.75(-1)	20(+1)	81.37	80.77
17	5(-1)	1.25(+1)	10(-1)	84.84	83.83
18	6.5(0)	1(0)	15(0)	88.81	87.55
19	6.5(0)	0.58(-1.68)	15(0)	80.33	80.12
20	8(+1)	1.25(+1)	20(+1)	84.26	84.25

Values in parenthesis are the coded values.

have been trying to explain the role of pH value among semiconductor surface, solvent molecule and substrate properties (Velegriaki and Mantzavinos, 2008). The method widely accepted is the point of zero charge (PZC) of  $\text{TiO}_2$ , which influences the ionization rate of the surface of  $\text{TiO}_2$ . Bizani et al. (2006) reported that the PZC for the used  $\text{TiO}_2$  P-25 was at pH value of 6 (approximate value), therefore, below this value the surface of the particles was positive charge and above it was negative charge. It can be assumed that the molecule of CAP is the negative charge, thus an electrostatic attraction is developed. However, the strong adsorption leads to a major decrease of the active centers on the catalyst surface, which means the absorption of the light quanta by the catalyst is decreased as well. This could be the reason why the degradation rate of CAP is low in the lowest acidic solution. Moreover, it could be assumed that strong adsorption causes a multilayer of CAP molecules around the catalyst particles, and as a result these molecules are not in direct contact to the catalyst. On the other hand, a decrease of the initial rate is also observed in alkaline solutions, which reflects the difficulty of the CAP molecules to approach the catalyst surface. In this study, it is deduced that higher degradation rate is contributed by the charge interaction between the surface of  $\text{TiO}_2$  and CAP. Due to very large effect at pH 5.0, the following optimal experiment design was carried out in the vicinity of this value.

The following experiments were performed to investigate  $\text{TiO}_2$  dosage as the crucial parameter during degradation process. The results are shown in Fig. 4. It shows that the degradation rate of CAP increases when the concentration of  $\text{TiO}_2$  increases from 0.50 to 1.00 g/L. However, the degradation rate of CAP shows a decreasing tendency after 1.00 g/L. Interestingly, the higher concentration of  $\text{TiO}_2$  (above 1.00 g/L) does not enhance CAP degradation rate, and the degradation rate of CAP also has a similar phenomenon when concentration of  $\text{TiO}_2$  is less than 1.00 g/L. This phenomenon is due to the geometry and the working conditions of the reactor and the definite surface exposed of  $\text{TiO}_2$ . A certain concentration

increase can enhance the hydroxyl radical produced from irradiated  $\text{TiO}_2$  (Klavarioti et al., 2006; Bahnemann et al., 2007; Tariq et al., 2009; Naeem and Ouyang, 2009). However, higher concentration of  $\text{TiO}_2$  particles becomes much easier to aggregate and impedes further penetration of light the reactor (Sohrabi and Ghavami, 2008). In any given application, this optimum  $\text{TiO}_2$  concentration must be determined to avoid superfluous and ensure total absorption of radiation photons for efficient degradation.

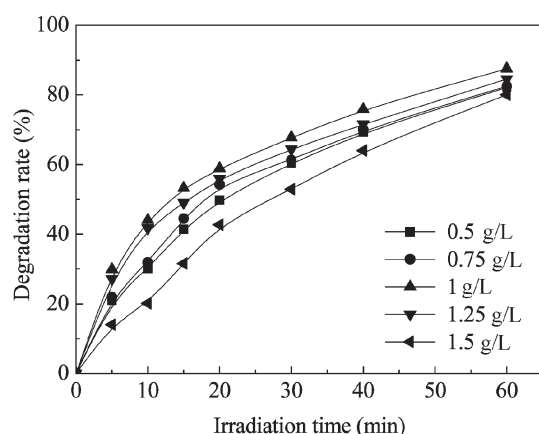
Another important parameter is the initial concentration of CAP in the degradation process, since it influences the initial rate of disappearance of CAP. A set of experiments were conducted to observe relationship between CAP initial concentration and degradation rate of CAP, and corresponding results are shown in Fig. 5. Apparently, in this work, the degradation rate of CAP increases when CAP concentration decreases from 25 to 5 mg/L. After 60 min irradiation, about 90% of CAP was decomposed at 5 mg/L; meanwhile, only about 70% of CAP was degraded at 25 mg/L. Although the higher the initial concentration of CAP, the more the CAP molecules adsorbed on the surface of  $\text{TiO}_2$ ,  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  radicals formed on the surface of  $\text{TiO}_2$  is the constant, therefore, the relative number of  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  radical attacking the CAP molecules is decreased (Aramendía et al., 2005). The trend variation of degradation rate in Fig. 3 just illustrates the above phenomenon, namely, the degradation rate of CAP decreased with the increase of CAP concentration.

## 2.2 Mathematical modeling and optimization of influencing factors

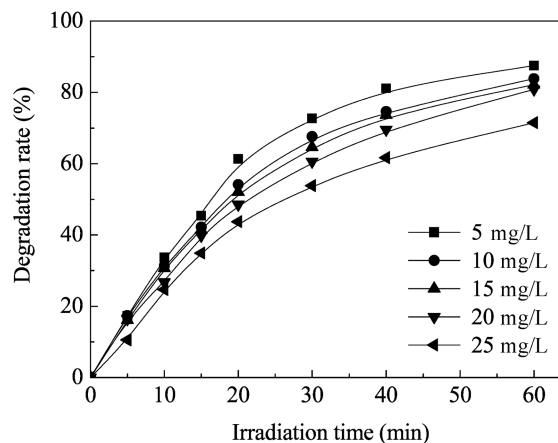
### 2.2.1 Model fitting and statistical analysis

In order to optimize the parameters of CAP degradation process, a central composite design was developed, and a total number of 20 experiments were employed for the response surface modeling (Table 2), the order of experiments was arranged randomly. This approach is used to give a broader insight of the CAP degradation process under UV condition.

According to the experimental design presented in Table



**Fig. 4** Effect of  $\text{TiO}_2$  concentration on the degradation rate of CAP.  $C_0$  (CAP) = 15 mg/L, pH 5.



**Fig. 5** Effect of CAP concentration on the degradation rate of CAP.  $C_0$  ( $\text{TiO}_2$ ) = 1.00 g/L, pH 5.

**Table 3** ANOVA for the response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean squares	F value	p value
Model	134.419	9	14.93	21.97	< 0.0001
Residual	6.80	10	0.68		
Lack of fit	4.63	5	0.93	2.14	0.2117
Pure error	2.16	5	0.43		
Total	141.21	19			
	$R = 0.9756$		$R^2 = 0.9519$		

**Table 4** Coefficient of regression model and their significance

Factor	Coefficient estimate	Degree of freedom	Standard error	F value	95% confidence interval low	95% confidence interval high	p value
Intercept	87.55	1	0.34	—	86.81	88.30	—
$x_1$	-0.82	1	0.22	13.44	-1.31	-0.32	0.0043
$x_2$	0.51	1	0.22	5.13	0.0084	1.00	0.0469
$x_3$	-0.14	1	0.22	0.41	-0.64	0.35	0.5362
$x_1 x_2$	-0.45	1	0.29	2.42	-1.10	0.20	0.1505
$x_1 x_3$	0.43	1	0.29	2.16	-0.22	1.08	0.1720
$x_2 x_3$	1.62	1	0.29	30.84	0.97	2.27	0.0002
$x_1^2$	-1.25	1	0.22	32.91	-1.73	-0.76	0.0002
$x_2^2$	-2.33	1	0.22	114.72	-2.81	-1.84	< 0.0001
$x_3^2$	-0.87	1	0.22	16.22	-1.36	-0.39	0.0024

2, an empirical second-order polynomial equation was established, which was written in terms of actual factors as follows:

$$y = 87.55 - 0.82x_1 + 0.51x_2 - 0.14x_3 - 0.45x_1x_2 + 0.43x_1x_3 + 1.62x_2x_3 - 1.25x_1^2 - 2.33x_2^2 - 0.87x_3^2 \quad (2)$$

where,  $y$  is the CAP degradation rate (%),  $x_1$ ,  $x_2$  and  $x_3$  are the terms of coded value for pH value, TiO<sub>2</sub> concentration and CAP initial concentration, respectively.

The experimental data were statistically analyzed for analysis of variance (ANOVA), and the results are shown in Table 3. The ANOVA of the empirical second-order polynomial model indicates that the model is highly significant, as the  $F$  value for the model is 21.97. There is only a 0.01% chance that the “model  $F$  value” could occur because of noise. The  $p$  value of the model is < 0.0001, which also confirms that the model is highly significant. A lack-of-fit value of 2.14 implies that the lack of fit is not significant relative to the pure error when  $p$  value is 0.2177, > 0.05, this also supports the fitness of the model.

Coefficient of determination ( $R^2$ ) is defined as the ratio of the explained variable to the total variation and a measure of the degree of fit. When  $R^2$  is close to 1, the model fits the actual experimental data better. The smaller the value of  $R^2$ , the less relevant the model fits the actual data (Larson and Farber, 2003; Utts and Heckard, 2002). Joglekar and May (1987) suggested that, for a good fit of a model,  $R^2$  should be at least 0.80. The  $R^2$  value for these response variables is higher than 0.80, which indicates that the regression model explains well the CAP degradation process by TiO<sub>2</sub> photocatalysis well. The  $R^2$  value is 0.9519 for the CAP degradation rate. From another point of view, the fit degree of the model is high enough to 95.19% of CAP degradation rate. Therefore, this empirical second-order polynomial equation can be applied to predicting CAP degradation rate within the experimental range.

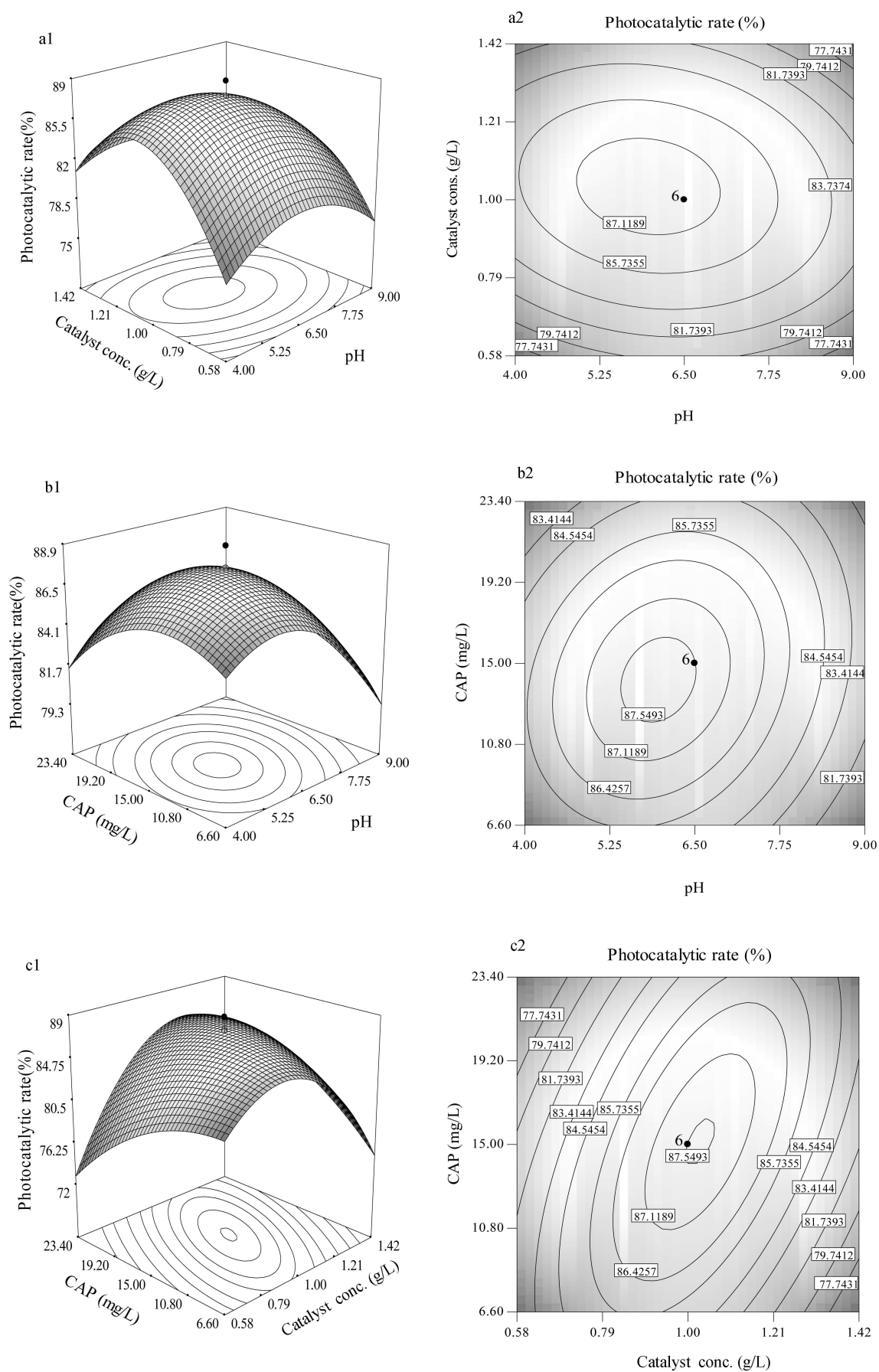
In the present study, the independent variables of the quadratic model, including pH value ( $x_1$ ), the second-order effect of pH value ( $x_1^2$ ), TiO<sub>2</sub> concentration ( $x_2^2$ ), CAP initial concentration ( $x_3^2$ ), and interactions between the TiO<sub>2</sub> concentration ( $x_2$ ) and CAP initial concentration ( $x_3$ ) are highly significant parameters because of  $p < 0.001$ . Moreover, the first-order effect of TiO<sub>2</sub> concentration ( $x_2$ ) is significant at  $p < 0.05$ . Additionally, the value of  $p > 0.05$  means that the model terms are insignificant. Table 4 shows the first-order effect of CAP initial concentration ( $x_3$ ) and interactions between pH value ( $x_1$ ) and TiO<sub>2</sub> concentration ( $x_2$ ), and between pH value ( $x_1$ ) and CAP initial concentration ( $x_3$ ) are insignificant.

According to the monomial coefficient value of regression model,  $x_1 = 0.0043$  (pH),  $x_2 = 0.0496$  (TiO<sub>2</sub> concentration) and  $x_3 = 0.5362$  (CAP initial concentration), the order of priority among the main effect of impact factors is CAP initial concentration ( $x_3$ ) > TiO<sub>2</sub> concentration ( $x_2$ ) > pH value ( $x_1$ ).

## 2.2.2 Response surface analysis

Three-dimensional surfaces and contour plots are graphical representation of regression equation for the optimization of reaction conditions and are the most useful approach in revealing the conditions of the reaction system. The results of the interactions between three independent variables and dependent variable are shown in Fig. 6.

Figure 6a shows the interaction effect of pH value and TiO<sub>2</sub> concentration on CAP degradation rate. As can be seen in the plots, the interactions effects of pH value and TiO<sub>2</sub> concentration on the degradation rate of CAP depict a spherical response surface; there is a local maximum region under the certain ranges of pH value and TiO<sub>2</sub> concentration. In addition, there is an increase in the degradation rate of CAP with an increase of pH value whether TiO<sub>2</sub> concentration at the low level or at the high



**Fig. 6** Effects of pH, catalyst concentration ( $\text{TiO}_2$  concentration) and CAP initial concentration on the degradation rate of CAP. (a) CAP initial concentration was kept constant at 15 mg/L; (b) the catalyst concentration ( $\text{TiO}_2$ ) was kept constant at 1 g/L; (c) the value of pH was kept constant at 5.

level. However, pH value beyond the optimum level results in a decrease of CAP degradation rate when TiO<sub>2</sub> change in experimental range. At the same time, the effect of TiO<sub>2</sub> concentration change on the CAP degradation rate has similar trends no matter pH value is at the low level or at the high level. The results are in accordance with the preliminary experimental results. More information of the interaction between pH value and TiO<sub>2</sub> concentration can be obtained from the contour plots. An increase in the degradation rate of CAP can be observed with pH value from 4 to 6 while TiO<sub>2</sub> concentration from 0.58 to 1 g/L. However, both pH value and TiO<sub>2</sub> concentration beyond 6 and 1 g/L result in a decrease in degradation rate of CAP. This trend can lead to the conclusion that the interaction effect with pH value and TiO<sub>2</sub> concentration beyond the optimum value cannot enhance the degradation rate of CAP.

The effects of pH value and CAP concentration on the degradation rate of CAP are shown in Fig. 6b. From the figure it can be seen the interaction effects of pH value and CAP initial concentration on the degradation rate of CAP depict a bell-shaped response surface. With the pH value and CAP initial concentration up to the optimum points, the degradation rate of CAP approaches the maximum level. However, the trend of CAP degradation rate goes downward after the optimum points of pH value and CAP initial concentration. The contour plots show the optimum region of CAP degradation rate is pH value in the range of 5.25–6.50 and CAP initial concentration in the range of 12–16 mg/L, respectively.

The effects of TiO<sub>2</sub> concentration and CAP initial concentration on CAP degradation rate are shown in Fig. 6c. From the response surface figure, it is clear that the degradation rate of CAP gradually increases with both TiO<sub>2</sub> concentration and CAP initial concentration increasing, however, the trend of CAP degradation rate is decreased under the higher level of TiO<sub>2</sub> concentration and CAP initial concentration. The contour plots show the optimum region of CAP degradation rate is TiO<sub>2</sub> concentration in the range of 0.9–1.1 g/L and CAP initial concentration in the range of 12–16 mg/L, respectively. This may lead to conclusion that the CAP degradation rate significantly decreases when TiO<sub>2</sub> concentration and CAP initial concentrations are too high or too low, both of TiO<sub>2</sub> concentration and CAP initial concentration have the respective optimal levels.

### 2.2.3 Optimization of influencing factors

The objective of the optimization is to determine the optimum value of variables from the model obtained via experimental design and analysis. The previous works tend to concentrate on how to maximize the target product, and ignore some aspects of consideration with respect to reaction conditions, such as economic cost, ecological factor, subsequent treatment, etc. Therefore, in present work, the higher degradation rate of CAP not only is obtained from optimization, but also some special conditions of pH value, TiO<sub>2</sub> concentration and CAP initial concentration also are considered at the same time. While, there are four aspects

of considerations. First, the maximum degradation of CAP which is the main objective of optimization just like other previous paper published. Second, the optimal level of pH value is close to the neutral as far as possible because of no readjustment after degradation process, the solution could be discharged directly to aquatic environment after removal of catalyst. Third, the relative small amount of catalyst has an advantage of subsequent treatment. Last, CAP is degraded as much as possible under above three constraint conditions.

Thus, the optimization of CAP degradation rate under constraint conditions was as follows: (1) maximize CAP degradation rate ( $y$ ); (2) pH was close to the neutral as much as possible ( $x_1$ ), the range of level:  $-0.5 < x_1 < +1$ ; (3) minimize TiO<sub>2</sub> concentration ( $x_2$ ), the range of level:  $-1.68 < x_2 < +1.68$ ; (4) maximize CAP initial concentration ( $x_3$ ), the range of level:  $-1.68 < x_3 < +1.68$ .

Based on the models and the related constraint conditions, numerical optimization was carried out with the help of Design Expert v.6.0.7 considering each value of response. The optimum conditions for the maximum CAP degradation rate under related constraint conditions were found to be pH value of 6.4 (rounded data), TiO<sub>2</sub> concentration of 0.94 g/L, and CAP initial concentration 19.97 mg/L. Under optimal conditions, the model predicted a maximum CAP degradation rate of 85.97%. These results imply that there exist optimal reaction conditions for degradation rate of CAP by TiO<sub>2</sub> photocatalysis.

### 2.2.4 Verification of the results

To confirm the model adequacy for predicting maximum degradation rate of CAP, the model was validated by carrying out experiments in 500 mL reactor using the optimum conditions. Three replicative experiments were carried out in reactor, which yielded an average maximum CAP degradation rate 85.87% (Table 5). The good agreement between the predictive results and experimental results verified the validity of an optimal point. It is feasible to optimize the degradation rate of CAP with response surface methodology.

**Table 5** Optimum value of the process parameter for constraint conditions and their experimental value

Parameter	Optimum value	CAP degradation rate $y$ (%)	
		Predictive	Experimental
$x_1$ (pH)	6.4	85.97	85.87
$x_2$ (TiO <sub>2</sub> , g/L)	0.94		
$x_3$ (CA, mg/L)	19.97		

## 3 Conclusions

The photocatalytic degradation of CAP in the presence of TiO<sub>2</sub> (P-25) was investigated in the present study, focusing on the influence of some parameters such as pH, TiO<sub>2</sub> concentration and CAP initial concentration. The multivariate experimental design was employed to establish a quadratic model as the functional relationship between the degradation rate of CAP and the three in-

dependent variables. In the present study, the response surface methodology was successfully employed to find out the significance of factors at different levels during CA degradation process.

The optimal values of process parameters under the related constraint conditions were following: pH 6.4,  $\text{TiO}_2$  0.94 g/L and CAP 19.97 mg/L. Under the optimal conditions, the degradation rate of CAP approached 85.97%. Also it was noted that the three parameters tested had significant effect on the degradation rate of CAP, which was verified by our statistical analysis  $R^2$  value of 0.9519. In addition, a satisfactory goodness-of-fit was observed between the predictive results and the experimental results. The results of this study have clearly indicated that response surface methodology is a useful tool for optimizing process conditions of CAP by  $\text{TiO}_2$  photocatalysis.

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