Mineralization of quinoline in aqueous solution by microwave-assisted catalytic wet peroxide oxidation system: process optimization, products analysis and degradation route research

Zhipeng Li, Feng Liu, Bo Zhang, Yi Ding, Hong You and Chao Jin

ABSTRACT

The experimental design methodology was used to optimize the experimental parameters of quinoline mineralization by microwave-enhanced catalytic wet peroxide oxidation (CWPO). Initial pH value, temperature, H_2O_2 dosage, and microwave power were selected as independent variables. The mineralization efficiency approached 83.82% under the optimized conditions: initial pH 6.00, temperature 60 °C, H_2O_2 dosage 0.09 mol/L, and microwave power 565.10 W. Regression analysis with an R^2 value of 0.9867 showed a good agreement between the experimental results and the predicted values. Furthermore, based on the detection and identification of products by gas chromatography mass spectrometry, the oxidation degradation pathways of quinoline were proposed. The energy balance and costs analysis indicated that the total cost of the microwave-enhanced CWPO process for wastewater treatment was 40.60 yuan/m^3.

Key words | catalytic wet peroxide oxidation, degradation route, microwave, quinoline, response surface methodology

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INTRODUCTION

In order to satisfy the rapidly growing water demand and resolve a shortage of water sources around the world, wastewater recycling is presently considered as an effective approach to provide the sustainable water resources (Shannon *et al.* 2008). The existence of biorefractory pollutants in effluent is one of the major obstacles for water recycling (Gaya & Abdullah 2008). Quinoline together with its derivatives in industrial wastewater has attracted increasing attention in the recent years because of its very harmful effect on the health of humans and animals (Rameshraja *et al.* 2012). Thus, an effective treatment method is needed to completely remove quinoline to promote the water recycling and eliminate its threat.

Catalytic wet peroxide oxidation (CWPO) is a promising approach totally due to the almost complete removal of organic pollutant without secondary pollutions under a mild temperature (<373 K) and atmosphere pressure range (Zhou *et al.* 2014). The hydroxyl radicals are produced in the wet catalytic oxidation process to mineralize pollutants. Furthermore, H_2O_2 is not only a principal oxidant (Jackson & Hewitt 1999), but is also an environmental-friendly chemical reagent because its decomposition products are H_2O and O_2 (Rokhina & Virkutyte 2010). Some contaminants such as phenol and its derivatives (Ribeiro *et al.* 2014; Pinho *et al.* 2015) and dyes (Ribeiro *et al.* 2012) have been demonstrated to effectively remove CWPO with a catalyst.

Although a previous study reported in the literature led to a significant removal of TOC (total organic carbon), the time required for treatment is usually long (>30 min) (Li *et al.* 2018). Furthermore, some methodologies such as ozonation and semiconductor photocatalysis require large amounts of energy to supply the process (Homem *et al.* 2013). Microwave-enhanced catalytic oxidation has gained been of wide interest to numerous scientific communities

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in the fields of wastewater treatment (Serpone *et al.* 2010; Homem *et al.* 2013; Ahmed *et al.* 2014), because it has higher energy efficiency and promotes the ion flexibility, the transmission of charge supports to the surface (Liu *et al.* 2013). In recent years, several studies have emerged on the application of microwave irradiation to promote the oxidative degradation of refractory compounds, and these suggested that the use of microwave irradiation increases the efficiency of traditional processes (Zhang *et al.* 2016, 2017). Therefore, the utilization of microwave heating could be an alternative for pollutant degradation in a short period of time.

At present, to explore the influencing factors of a process when the factors are independent, the most commonly used method is the traditional one-factor-at-a-time (OFAT) (Sakkas *et al.* 2010). However, this method cannot explain the interactions between the detached variables system. Additionally, the OFAT method is time-wasting and costly owing to chemical costs. So the current research tendency is to use effective statistical techniques instead of the OFAT method, such as response surface methodology (RSM) (Lucas 1994; Khuri & Mukhopadhyay 2011), which is in terms of statistical experimental design (Sakkas *et al.* 2010). It is an effective technique for a multivariable system to seek the optimal conditions (Rashid *et al.* 2009; Babaei *et al.* 2011). The method can establish a continuous variable surface model, and the number of the experimental runs is relatively small, which can save labour and material resource.

Since the main emphasis of previous studies has been quinoline degradation of the solution, reports on the analysis of products are very scanty and little information on degradation routes of quinoline is also available. Hence, the key objectives of the present study are to: (a) seek the optimization reaction conditions in terms of the mineralization efficiency of quinoline in microwave-assisted CWPO systems using Cu/Ni catalyst; (b) identify the intermediates of quinoline; and (c) propose the degradation pathway of quinoline.

MATERIAL AND METHODS

Reagents

H_2O_2 (relative molecular mass = 30%) was acquired from Sinopharm Chemical Reagent Co., Ltd. Quinoline (C_9H_7N, molecular weight = 129.16 g/mol) was acquired from Sinopharm Chemical Reagent Co., Ltd and selected as a target contaminant. All other chemicals were AR and provided by Chengdu Xiya Chemical Factory, P. R. China.

Experimental apparatus

The microwave heating equipment used in the study is a laboratory microwave heating furnace (MKX-H1C1A, MAKEWAVE, China). The maximum microwave power is 1.30 kW, the microwave frequency is 2,450 ± 50 MHz, and the temperature range is 273 to 573 K. Supported Cu/Ni bimetal oxides were used as catalyst in microwave-assisted CWPO of quinoline in a fixed bed. The catalyst was prepared by excessive impregnation method (Wang *et al.* 2014); the impregnation liquid contained 40 mL mixed liquor of $Cu(NO_3)_2$ and $Ni(NO_3)_2$ (C_{total} = 1.50 mol/L, Cu:Ni = 4:1) and 20 g of γ-Al_2O_3/TiO_2 (20–40 mesh). The γ-Al_2O_3/TiO_2 belonged to the microwave dielectric ceramics with ultra-low dielectric constant ($\leq$20).

Microwave-enhanced CWPO was conducted with a 1 L reactor, made of polytef, in the microwave oven. The pH was regulated either with 0.20 mol/L NaOH or with 0.20 mol/L HCl. The quinoline aqueous solution was used for the simulation of real wastewater with the concentration of 100 mg/L. The scheme of the reaction is shown in Figure 1. The wastewater was fed into a water tank, and the H_2O_2 solution was added to achieve a specific H_2O_2/quinoline ratio. The heat quantity in the effluent was exchanged with that in the influent in a heat exchanger, and the wastewater was heated to the reaction temperature by the heat exchanger. And then the wastewater was fed into the catalytic reaction zone. Lastly, the wastewater was treated in the catalytic reaction zone. All experiments were executed in a regular reaction time of 18 min.

According to a previous study (Zhang *et al.* 2016), in the experiments, the condensing unit was used to maintain a constant temperature in the solution in the main reactor. To avoid the extreme conditions (high temperature and pressure) produced by microwave irradiation, the buffer pool was linked to a condenser tube which was connected to the atmosphere. Furthermore, the buffer pool was fixed in a constant temperature bath, so that the reaction was carried out at a mild temperature and atmospheric pressure. A sampling point was fixed at the position of the buffered beaker. In order to avoid the loss of catalyst, a filter (pore size less than 20 mesh) was installed in the top of the reactor.

Analytical procedures

Samples were acquired at different time intervals and immediately were filtered through 0.45 μm filter membrane

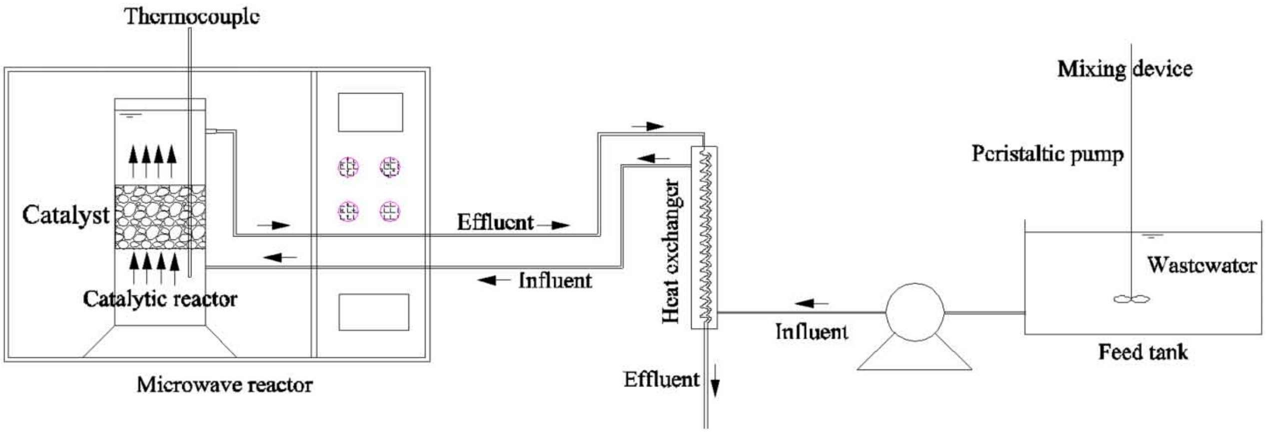


Figure 1 | Experimental device for microwave assisted catalytic wet hydrogen peroxide oxidation.

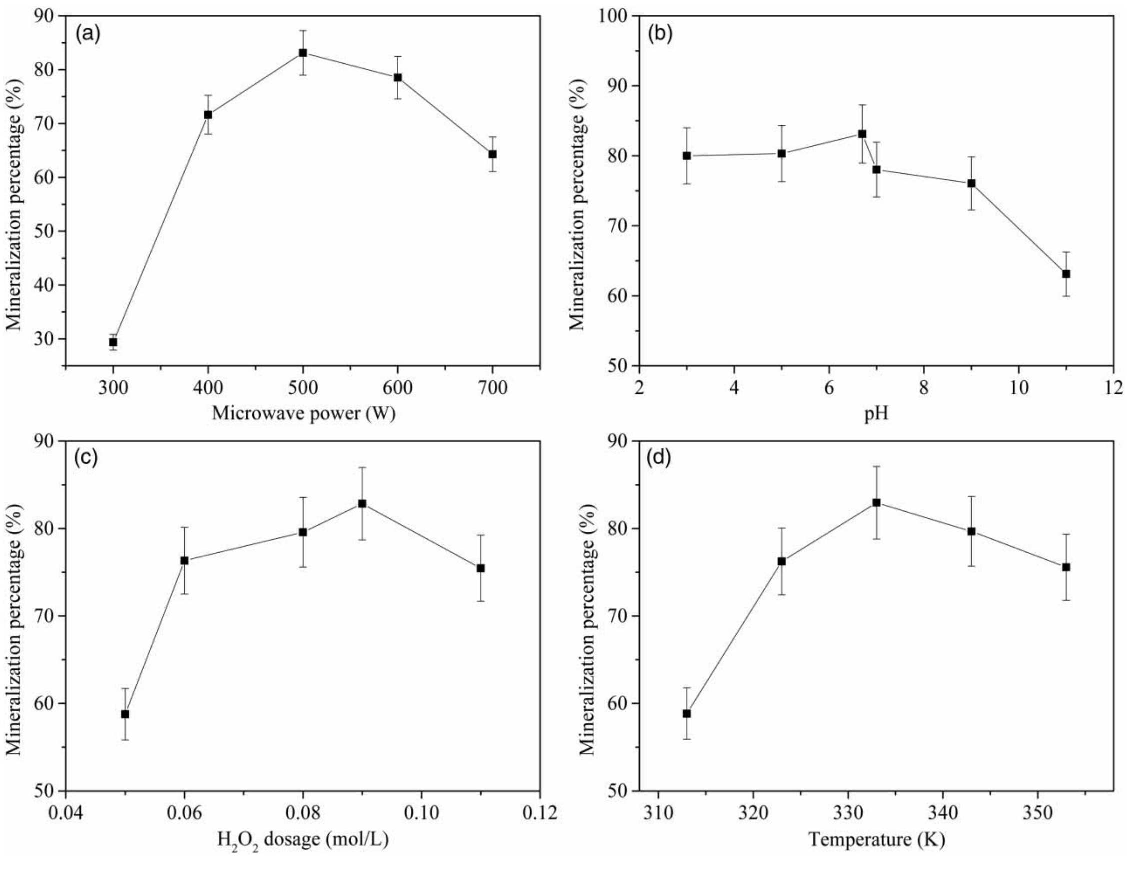


Figure 2 | The independent effect of parameters on quinoline mineralization: (a) microwave power, (b) initial pH value, (c) H_2O_2 dosage, and (d) temperature.

to take out the undissolved substances present in the solution. The quinoline mineralization efficiency was assessed by measuring the TOC, and TOC was analyzed with a TOC-5000A analyzer (Shimadzu Corporation).

Possible intermediate products for the quinoline oxidation degradation by CWPO were detected and identified by gas chromatography and mass spectrometry (GC-MS, Agilent 6890A GC/5975 MSD) analyses. Helium was utilized as the transporter gas. The temperature of the oven was planned at 45 °C for 3 min, followed by a linear increase of 6 °C/min to 325 °C. MS analysis was carried out at 70 eV. The intermediate products' structures were identified from the mass spectra fragmentation patterns by comparison with authentic standards of known compounds.

RESULTS AND DISCUSSION

Effect of the parameters on the microwave-enhanced CWPO of quinoline solutions

According to previous research (Zhang *et al.* 2016), it is essential to select optimal reaction conditions such as the microwave power, the initial pH value, H_2O_2 dosage, and temperature for the microwave-enhanced CWPO reaction. The effects of microwave power, the initial pH value, H_2O_2 dosage, and temperature on quinoline mineralization were investigated and the results are shown in Figure 2.

As revealed in Figure 2(a), the different microwave powers resulted in different quinoline mineralization efficiencies. It can be observed that as the microwave power increased from 300 W to 500 W, the TOC mineralization efficiencies progressively increased and reached the maximum value at microwave power of 500 W. Further increase in microwave power above 500 W caused a decrease in TOC mineralization efficiencies. The reason was that the greater microwave powers (600 and 700 W) could promote the thermal conversion of H_2O_2 into O_2 and H_2O at the surface of the samples.

Figure 2(b) demonstrates the degradation efficiency for quinoline with different pH values. It was observed that the TOC mineralization efficiencies decreased with the increase of pH values.

The TOC mineralization efficiencies as a function of H_2O_2 dosage are depicted in Figure 2(c). When the H_2O_2 dosage was raised from 0.05 to 0.09 mol/L, the TOC mineralization efficiencies increased correspondingly from 58% to 82% (Figure 2(c)). However, when the H_2O_2 dosage was increased from 0.09 to 0.11 mol/L, the TOC mineralization efficiency was reduced.

The changes in TOC mineralization efficiencies with temperature are shown in Figure 2(d). Apparently, the TOC mineralization efficiency was increased from 58% to 81% as the temperature increased from 313 to 333 K. With further increasing of temperature to over 333 K, the TOC mineralization efficiencies decreased.

Optimization of microwave-enhanced CWPO process by RSM

RSM is an effective method for optimization of a multivariable process (Yücel & Göycıncık 2015). In this work, optimum quinoline mineralization efficiency was achieved by RSM (Design Expert 8.0.6). According to the previous experimental results in single-factor experiments (Figure 2), the levels and the ranges of the unrelated factors were determined and are shown in Table 1.

Central composite design (CCD) and Box–Behnken design are common design types used in RSM, although CCD is the most commonly used form of RSM. So in this design, CCD was applied to assess the effect of the four unrelated factors in 30 sets of experiments. A second-order polynomial equation was utilized to accord with the experimental results of CCD like this:

$$Y(\%) = b_0 + b_1A + b_2B + b_3C + b_4D + b_{12}AB + b_{13}AC + b_{14}AD + b_{23}BC + b_{24}BD + b_{34}CD + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 + b_{44}D^2 \quad (1)$$

where Y represents the response value (quinoline mineralization efficiency, R1), b_i, b_{ij}, b_{ii} are the linear regression coefficients and quadratic effects and the coefficients of the interaction conditions, respectively, A, B, C, D are the unrelated factors.

Model fitting and statistical analysis

The experiment responses and the model plan were obtained by CCD for the quinoline mineralization as provided in Table 2.

Based on the experimental plan offered in Table 2, a second-order polynomial equation on the basic of the real variables was established that verifies the empirical connections between the response and the unconnected factors:

$$Y = -1725.81171 + 0.36457 \times A + 21.47532 \times B + 9.25471 \times C + 2352.51373 \times D + 1.91695 \times 10^{-3} \times A \times B - 1.35133 \times 10^{-4} \times A \times C + 0.45998 \times A \times D - 0.036520 \times B \times C - 13.19663 \times B \times D - 2.12553 \times C \times D - 3.27623 \times 10^{-4} \times A^2 - 0.78712 \times B^2 - 0.013214 \times C^2 - 10023.58630 \times D^2 \quad (2)$$

Table 1 | Experimental range and levels of the independent test variables

	Ranges and levels		
Variables	**−1**	**0**	**1**
Microwave power (A) (W)	300	500	700
pH (B)	3	6	9
Temperature (C) (K)	313	333	353
H_2O_2 dosage (D) (mol/L)	0.05	0.08	0.11

Table 2 | Experimental designs and experimental results with predicted values

	Experimental conditions				R1	
Run	**A**	**B**	**C**	**D**	**Experimental**	**Predicted**
1	300	9	313	0.05	30.10	33.45
2	500	6	333	0.08	81.87	81.10
3	300	9	353	0.05	34.64	32.86
4	500	9	333	0.08	73.53	73.39
5	700	3	353	0.11	66.99	64.53
6	700	9	353	0.05	44.13	44.10
7	300	6	333	0.08	64.39	60.09
8	500	6	313	0.08	76.79	75.80
9	500	6	333	0.08	80.43	81.10
10	700	9	353	0.11	60.79	58.70
11	500	6	333	0.08	80.37	81.10
12	300	9	313	0.11	44.78	41.81
13	700	3	313	0.11	62.92	63.88
14	500	6	333	0.08	81.98	81.10
15	300	3	313	0.05	28.87	30.13
16	500	6	333	0.08	77.34	81.10
17	500	6	353	0.08	75.13	75.83
18	700	6	333	0.08	71.88	75.91
19	300	9	353	0.11	32.33	35.87
20	500	6	333	0.08	83.79	81.10
21	500	3	333	0.08	74.79	74.65
22	300	3	353	0.05	39.17	38.30
23	300	3	313	0.11	42.55	43.48
24	700	3	313	0.05	41.57	38.93
25	300	3	353	0.11	45.45	46.29
26	700	3	353	0.05	42.81	44.94
27	700	9	313	0.05	48.53	46.86
28	700	9	313	0.11	65.04	66.81
29	500	6	333	0.11	78.66	78.15
30	500	6	333	0.05	63.93	64.17

Table 3 | ANOVA results for the response surface quadratic model

Source	Sum of squares	df	Mean square	F value	*p* value Prob > F
Model	9,524.52	14	680.32	79.36	<0.0001
Residual	128.58	15	8.57		
Lack of fit	105.07	10	10.51	2.23	0.1940
Pure error	23.52	5	4.70		
Cor. total	9,653.11	29			

df: degrees of freedom.

where Y is quinoline mineralization efficiency (%), A is microwave power, B is pH, C is temperature, and D is H_2O_2 dosage.

Analysis of variance (ANOVA) was employed to assess the model feasibility. Based on the results of the response surface quadratic model by ANOVA (Table 3), the model F value is 79.36, indicating that the model is particularly noteworthy.

There is merely a 0.01% possibility that the 'model F-value' this large could happen owing to interference. The model p value is <0.0001, which also demonstrated that the model is noteworthy. The 'lack-of-fit value' of 2.23 suggests that the lack of fit is insignificant compared with pure error. There is a 19.40% possibility that the 'lack-of-fit F value' could take place owing to interference. The insignificant lack of fit verifies the excellent model predictability. The 'predicted R-squared' of 0.9219 is in close agreement with the 'adjusted R-squared' of 0.9742, also verifying the model's good predictability.

The model accuracy is shown in Figure 3, which compares the experiment results with the model-predicted response values for the mineralization of quinoline.

In this study, microwave power and H_2O_2 dosage are extremely significant parameters among the independent variables with $p < 0.0001$. Moreover, all of the second-order effects of microwave power (A), pH (B), temperature (C) and H_2O_2 dosage (D) are noteworthy at p value <0.05.

The quadratic terms' negative coefficients in the polynomial imply their negative effects on catalytic ability (decreased TOC abatement). What is more, the p value >0.05 shows that the model conditions are unimportant. The impact of independent variables and their interactions are shown in Table 4.

The interactions between microwave power and H_2O_2 dosage, pH and temperature are extremely significant. On the basis of the regression model monomial coefficient values, $p(A) < 0.0001$ (microwave power), $p(B) = 0.3785$ (pH), $p(C) = 0.9817$ (temperature), and $p(D) < 0.0001$ (H_2O_2 dosage); so the order of significance among the variables is microwave power > H_2O_2 dosage > pH > temperature. Microwave power and H_2O_2 dosage are highly significant.

RSM analysis

Three-dimensional surfaces, which were produced by mapping the response value on the Z-axis against two unrelated factors while maintaining other independent factors at the constant levels, can be used to select the

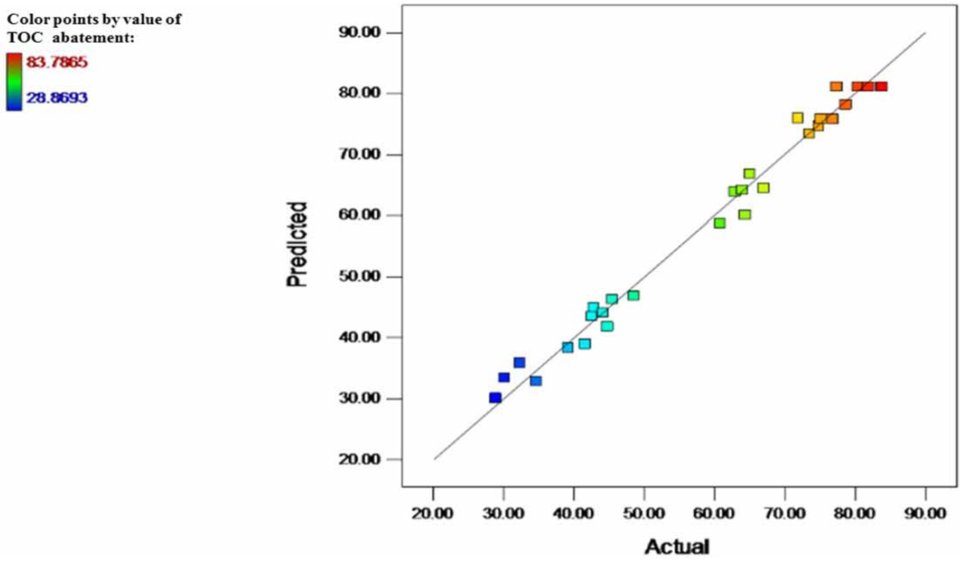


Figure 3 | Experimental values plotted against predicted values derived from the model.

Table 4 | Coefficients of regression and their significances

Factor	Coefficient estimate	df	F value	Standard error	95% CI low	95% CI high	*p* value
Intercept	81.1	1	–	0.91	79.17	83.04	–
A	7.91	1	131.42	0.69	6.44	9.38	<0.0001
B	− 0.63	1	0.82	0.69	− 2.1	0.84	0.3785
C	0.016	1	$5.43*10^{-4}$	0.69	− 1.45	1.49	0.9817
D	6.99	1	102.52	0.69	5.52	8.46	<0.0001
AB	1.15	1	2.47	0.73	− 0.41	2.71	0.1370
AC	− 0.54	1	0.55	0.73	− 2.1	1.02	0.4716
AD	2.9	1	15.67	0.73	1.34	4.46	0.0013
BC	− 2.19	1	8.96	0.73	− 3.75	− 0.63	0.0091
BD	− 1.25	1	2.90	0.73	− 2.81	0.31	0.1090
CD	− 1.34	1	3.35	0.73	− 2.9	0.22	0.0873
A^2	− 13.1	1	51.91	1.82	− 16.98	− 9.23	<0.0001
B^2	− 7.08	1	15.17	1.82	− 10.96	− 3.21	0.0014
C^2	− 5.29	1	8.44	1.82	− 9.16	− 1.41	0.0109
D^2	− 9.95	1	29.90	1.82	− 13.82	− 6.07	<0.0001

df: degrees of freedom; CI: confidence interval.

optimal conditions of the variables in the form of graphical representations and are extensively applied to get better comprehension of the interactions between factors within the considered range. The interaction effects between the four unrelated factors and the response are presented in Figure 4.

Figure 4(a) illustrates that the mineralization efficiency of quinoline increases with increasing microwave power from 300 W to 600 W in weak-acid environment. When microwave power reached 600 W, the quinoline mineralization no longer increases as the microwave power increases, which implies the microwave power has an optimum value. In low microwave power, the mineralization efficiency is low no matter in low or high pH. The positive effect of microwave power is that microwave heating is a heating of the molecular level which can generate strong interaction between microwave and the metal point on the catalyst surface, accelerating the oxidation reaction (Wójtowicz et al. 2000).

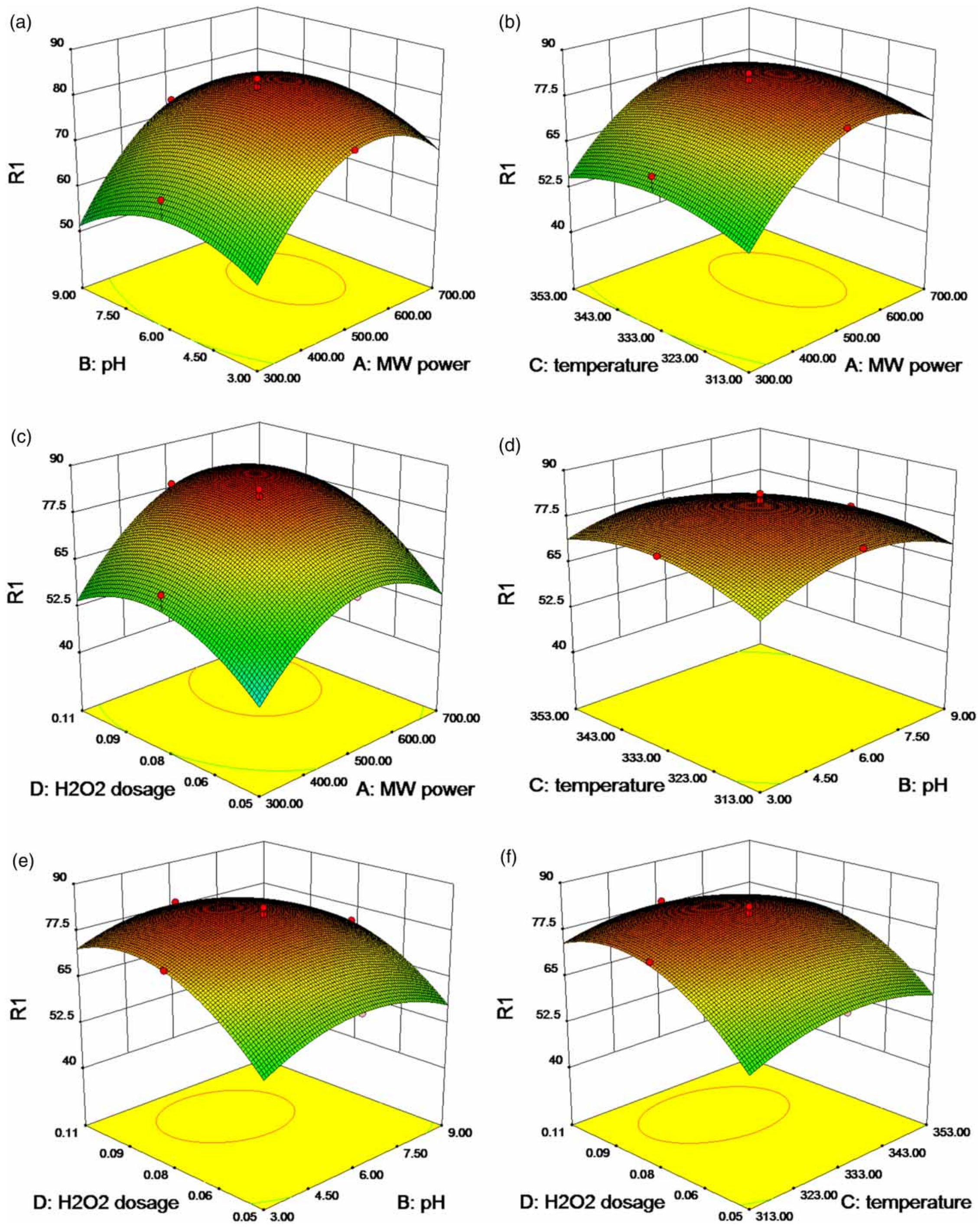


Figure 4 | Response surface showing effect of interaction of (a) microwave power and pH, (b) microwave power and temperature, (c) microwave power and H_2O_2 dosage, (d) temperature and pH, (e) pH and H_2O_2 dosage, and (f) temperature and H_2O_2 dosage on mineralization efficiency of quinoline.

Figure 4(b) demonstrates the effects of microwave power and temperature on quinoline mineralization. It is noteworthy that in comparison with microwave power, the effect of temperature on the mineralization efficiency of quinoline is not obvious, which is consistent with the variance analysis above. In this system, microwave power acts as the main inducer and fortifier to accelerate the reaction (Zhang *et al.* 2012).

The effects of microwave power and H_2O_2 dosage on quinoline mineralization efficiency are displayed in

Figure 4(c). It is obvious that at the beginning as microwave power and H_2O_2 dosage increase, the mineralization efficiency increases significantly. When the microwave power was higher than 550 W and H_2O_2 dosage higher than 0.09 mol/L, the mineralization efficiency of quinoline decreases with the increase of the two factors. This trend shows that the interaction effects of microwave power and H_2O_2 dosage at high levels do not enhance the mineralization efficiency of quinoline. This behavior can be explained by the high microwave power promoting the decomposition of H_2O_2 to produce HO•, but at higher H_2O_2 concentration, H_2O_2 can also act as a scavenger of HO• (Tizaoui *et al.* 2010; Zhou *et al.* 2014), which will decrease the content of hydroxyl radicals, so the quinoline mineralization efficiency decreases.

Figure 4(d) shows the effects of temperature and pH on mineralization of quinoline. Mineralization efficiency varies smoothly with the temperature and pH changing. It is concluded that the interaction effects of pH and temperature make the mineralization efficiency remain steady at a certain level.

Figure 4(e) shows that at higher H_2O_2 dosage, the mineralization efficiency of quinoline is higher, but the H_2O_2 dosage has an upper limit. pH in lower range has a better mineralization efficiency. The interaction effects of pH and H_2O_2 dosage have an optimal range with the H_2O_2 dosage ranging from 0.08 mol/L to 0.09 mol/L and pH ranging from 4.00 to 6.00. It can be explained that in acidic conditions, H_2O_2 has low decomposition efficiency due to its stability, but the hydrogen ion in the solution can prevent the loss of HO• produced by the decomposition of H_2O_2; so, in acid condition, mineralization efficiency increases with the increase of pH, while under alkaline conditions, hydroxyl radicals can be captured by hydroxide ions, which will reduce the mineralization efficiency (Tatibouët *et al.* 2005; Herney-Ramirez *et al.* 2010).

The effect of interaction of temperature and H_2O_2 dosage on the mineralization efficiency of quinoline is shown in Figure 4(f). It has a similar trend to the effect of pH and H_2O_2 dosage on quinoline mineralization. Even so, H_2O_2 dosage has a more remarkable effect on the mineralization efficiency of quinoline as it corresponds to the generation of hydroxyl radicals directly, the core factor of microwave-enhanced CWPO system.

Model validation and confirmation

In order to find and confirm the optimum conditions of the mineralization of quinoline, the desirability function was used. This system utilizes five possibilities as an aim to acquire satisfactory parameters, which are maximum, none, minimum, in range, and targets. In this study, the supreme goal is to optimize independent variables to achieve the maximum mineralization efficiency of quinoline. Therefore, the goal of response is 'maximize'. So the standards for all factors in agreement with response are displayed in Table 5.

The weight gives additional attention to upper or lower bounds, and the importance represents the significance of the goal values in Table 5. As a higher mineralization efficiency is the key target, an 'importance' of 5 was regarded as the maximum aim. According to the settings and boundaries mentioned above, the optimal parameters for optimal quinoline mineralization efficiency (83.82%) were established (Figure 5): pH value 6.00, microwave power 565.10 W, H_2O_2 dosage 0.09 mol/L and temperature 332.04 K.

In order to verify the model's feasibility to forecast the optimal quinoline mineralization efficiency, a compliance test was conducted in a 1 L reactor utilizing the optimal parameters. An average maximum TOC abatement of 83.02% was attained from three experiments repeatedly. The satisfactory consistency between the predicted results and the experimental data verify the model's feasibility to simulate the microwave-enhanced CWPO of quinoline system.

Identity of quinoline decomposition intermediates over supported Cu/Ni catalyst

In order to better comprehend the quinoline catalytic oxidation degradation pathway, GC-MS analysis was

Table 5 | Optimization of the independent responses to find the overall desirability response

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Microwave power	in range	300	700	1	1	3
pH	in range	3	9	1	1	3
Temperature	in range	313	353	1	1	3
H_2O_2 dosage	in range	0.05	0.11	1	1	3
R1	maximize	28.8693	83.7865	1	1	5

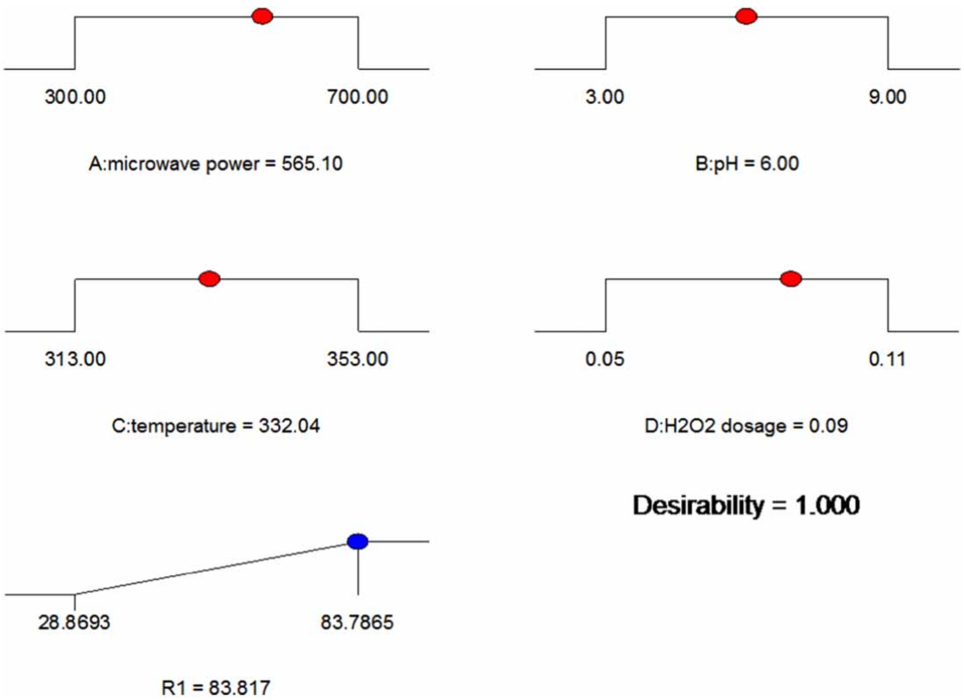


Figure 5 | Optimized process condition for quinoline mineralization efficiency.

employed to identify intermediate compounds produced during the catalytic oxidation degradation process of quinoline over Cu/Ni catalyst under microwave irradiation, and Table 6 shows the detection and identification of the key intermediate products by GC-MS.

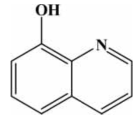
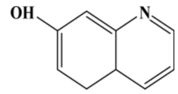
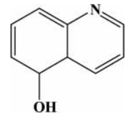
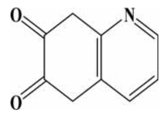
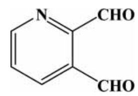
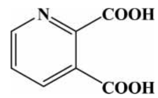
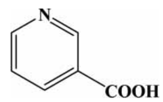
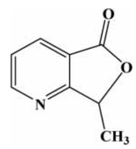
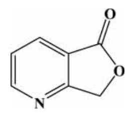
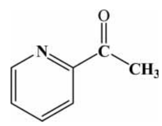
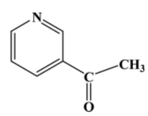
Based on the products detected and identified by GC-MS, we deduce the microwave-enhanced CWPO degradation pathway of quinoline over the as-synthesized Cu/Ni catalyst as shown in Figure 6. It is well accepted that microwave-enhanced CWPO is founded on •OH, which can degrade organic contaminants efficiently.

As presented in Figure 6, first, under microwave irradiation, an electrophilic addition of •OH is excited to attack the benzene ring, leading to formation of hydroxylated derivatives, which are further converted on the catalyst's surface (Zhong *et al.* 2011). Second, with the reaction going on, the formation of these hydroxylated derivatives, such as 8-hydroxyquinoline, 7-quinolinol, and 5-quinolinol, can be further transformed to quinolone derivative. Third, such quinolone derivative can be further converted by •OH, leading to cleavage of the benzene ring, thereby yielding nitrogen-containing intermediate compounds, such as 2,3-pyridinedicarboxaldehyde, 2-acetyl pyridine, furo(3,4-b)pyridine-2(2H)on, 3,4-pyridinedicarboxylicacid, nicotinic acid, and 3-acetyl pyridine. Finally, these nitrogen-containing intermediate compounds are mineralized to form CO_2 and H_2O.

Energy balance and costs analysis

Under the optimized conditions of pH value 6.00, microwave power 565.10 W, H_2O_2 dosage 0.09 mol/L and temperature 332.04 K, the quinoline mineralization efficiency approached 83.82%. Microwave-enhanced CWPO of 100 mg/L quinoline was conducted with a 1 L reactor, made of polytef, in the microwave oven. All experiments were executed in regular reaction time of 18 min. The quinoline removal amount per unit energy consumption was 494.42 mg/kW·h, and the energy consumption per unit quinoline removal amount was 2.02 kW·h/g. The waste heat could be recovered and utilized, and the energy consumption could be reduced. Suppose the thermal efficiency of the heat exchanger was 70%, the quinoline removal amount per unit energy consumption could reach 1,648.07 mg/kW·h, and the energy consumption per unit quinoline removal amount should be 0.61 kW·h/g. If the electricity price was 0.75 yuan/kW·h, the energy cost for wastewater treatment was 38.15 yuan/m^3. The H_2O_2 dosage was 0.09 mol/L, and the consumption of H_2O_2 was 3.06 kg for a ton of

Table 6 | Intermediate products detected and identified by GC-MS under microwave irradiation

Product	Molecular weight	Chemical name	Chemical structure
1	145.16	8-Hydroxyquinoline	
2	145.16	7-Quinolinol	
3	145.16	5-Quinolinol	
4	159.14	5,8-Quinolinedione	
5	135.12	2,3-Pyridinedicarboxaldehyde	
6	165.10	3,4-Pyridinedicarboxylicacid	
7	123.11	Nicotinic acid	
8	140.10	7-Methyl-furo(3,4-b)-pyridine-5(2H)on	
9	135.10	Furo(3,4-b)Pyridine-2(2H)on	
10	121.14	2-Acetyl pyridine	
11	121.14	3-Acetyl pyridine	

wastewater treated. With the H_2O_2 price of 800 yuan/ton, the total cost of microwave-enhanced CWPO process for wastewater treatment was 40.60 yuan/m^3. The data obtained in this study revealed that microwave-assisted CWPO was a promising treatment for degradation of quinoline and its derivatives.

CONCLUSION

In this study, RSM was employed to optimize reaction conditions in the microwave-assisted CWPO of quinoline using Cu-Ni/γ-Al_2O_3/TiO_2 as catalyst. A quadratic model was applied to show the connection between the

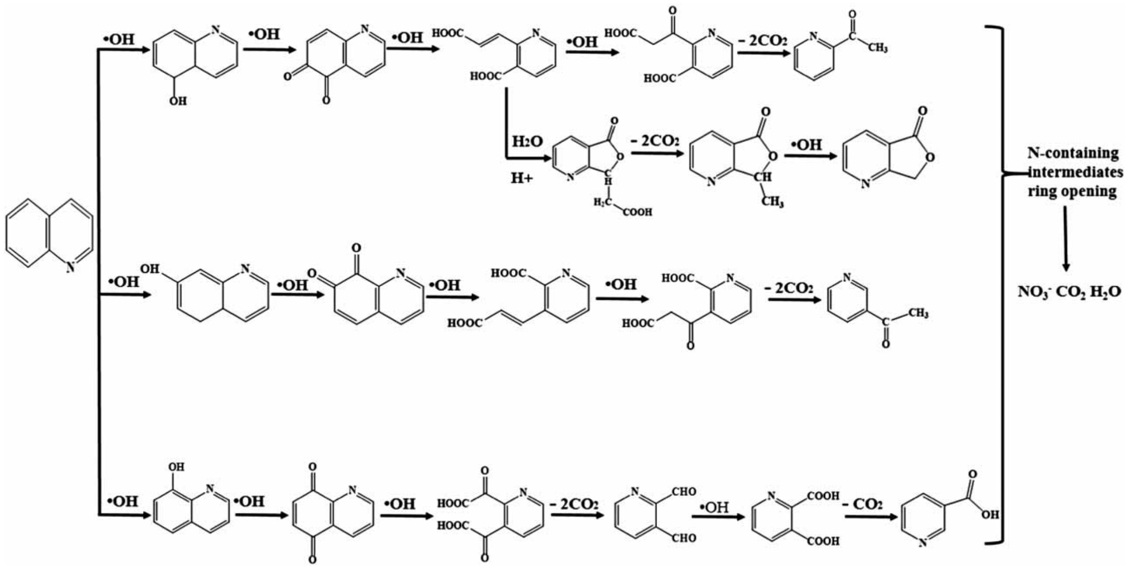


Figure 6 | Possible oxidation pathway of quinoline over supported Cu/Ni catalyst, assuming non-charged intermediates.

quinoline mineralization efficiency and four unrelated factors: initial pH value, temperature, H_2O_2 dosage, and microwave power. Under the optimized conditions of pH value 6.00, microwave power 565.10 W, H_2O_2 dosage 0.09 mol/L and temperature 332.04 K, the quinoline mineralization efficiency approached 83.82%. Regression analysis with an R^2 value of 0.9867 displayed a satisfactory correlation between the experimental value and the predicted results. Based on the detection and identification of products by GC-MS, the oxidation degradation pathways of quinoline were proposed, which mainly involved the cleavage of the benzene ring to form 2,3-pyridinedicarboxaldehyde, 3,4-pyridinedicarboxylicacid, nicotinic acid and so on. Microwave-assisted CWPO system with supported Cu/Ni bimetal oxides catalyst may be an innovative and promising technology to deal with quinoline and its derivatives in wastewater. Considering the energy consumption and H_2O_2 dosage, the total cost of the microwave-enhanced CWPO process for wastewater treatment was 40.60 yuan/m^3.

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