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Chlorine/UV Induced Photochemical Degradation of Total Ammonia Nitrogen (TAN) and Process Optimization

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Abstract:

Total ammonia nitrogen (TAN) is a worldwide spread pollutant in the surface water system, leading to the reduction of the water treatment efficiency and the generation of highly toxic disinfection by products. Although the chlorine/UV process has been demonstrated to be effective for TAN degradation, no information is available to describe the effects of reaction parameters on the TAN control. In this study, experiments were conducted to investigate the effects of chlorine:TAN molar ratio, UV dose and pH on TAN removal efficiency. Experimental results indicated both chlorine:TAN molar ratio and UV dose represented positive effects, while pH showed a complex effect on the TAN removal. The interaction between chlorine:TAN molar ratio and UV dose was also significant, implying a synergistic effect in the chlorine/UV process. Response surface methodology (RSM) was applied to establish the regression model and optimize the chlorine/UV process. Based on the optimization parameter, the combined process was used to treat the TAN-containing raw water. The experimental results matched well with the predicted response, indicating the proposed model was accurate and reliable. The

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main photodecomposition products were nitrate, accompanied with a slight amount of nitrite. The mechanism of TAN decomposition in the chlorine/UV process was proposed as the UV induced photolysis of chloramine and the intermediate radicals oxidation. This study demonstrated the chlorine/UV process was an effective strategy for TAN control in water treatment.

***Keywords**:* Total ammonia nitrogen; Advanced oxidation process; Ultraviolet; Chlorination; Response surface methodology.

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1. Introduction

Total ammonia nitrogen (TAN) is considered as one of the most important pollutants because of its highly toxic nature and ubiquity in water resources.[1] TAN contamination not only leads to the reduction of water treatment efficiency, but also promotes the generation of highly toxic disinfection by-product (DBP).[2, 3] Chinese government has established the limit for total ammonia nitrogen (TAN) in drinking water to be 0.50 mg /L as nitrogen.[4]

Conventional methods for drinking water treatment such as coagulation, filtration and activated carbon adsorption represent very limited efficiency of TAN degradation.[5] Although TAN could be oxidized by breakpoint chlorination, this process would consume 8-10 fold of chlorine than disinfection process.[6, 7] Furthermore, the generation of toxic DBP restrict the application in ammonia control.[8, 9] Therefore, there is a great need to develop a stable, inexpensive and non-toxic method for TAN control.

Recently, advanced oxidation process (AOP) has been demonstrated to be an efficient water treatment method. As a novel AOP technology, UV_{254} induced photolysis

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of chlorine would generate oxidative radicals such as hydroxyl radical (OH·) and chlorine radical (Cl·), which could effectively oxidize and/or mineralize numerous pollutants. [10] Chlorine/UV process has been evidenced to be a more effective AOP than UV/H_2O_2, due to a relative higher absorptivity and quantum yield. [11, 12]

The chlorine/UV process has been evaluated for the decomposition of emerging contaminants [13], natural organic matter (NOM) [14, 15] and disinfection by-product (DBP) [16]. This process also is a potential alternative disinfection process based on its performance in inactivating waterborne pathogenic microorganisms.[17] Our previous study has confirmed that the chlorine/UV process represented more advantages than breakpoint chlorination for TAN decomposition, in terms of chemicals saving and short reaction time. [18] However, more systematic studies are needed to understand the effect of reaction variables on the TAN removal efficiency in this combined process.

The main objectives of this study were to investigate the effects of the three independent factors (chlorine dose, UV_{254} dose, and pH) on the TAN removal and optimize the reaction parameter for the chlorine/UV process. Response surface

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methodology (RSM) was applied to evaluate the interaction of the independent factors. A mathematical model was established to predict and optimize the operating conditions for TAN removal in the chlorine/UV process.[19] [20] The verification experiments were conducted to assess the feasibility of the regression model. The decomposition products of TAN containing raw water formed in the chlorine/UV process were determined. An appearent mechanism was also proposed.

2. Materials and methods

2.1 Materials

The chemicals and reagents used in experiments were of the highest purity available purchased from Sigma-Aldrich (St. Louis, MO, U.S.). The solutions were prepared by ultrapure water (Thermo Fisher Scientific Inc, Waltham, MA, U.S.). Chlorine stock solutions (1000 mg/L as Cl_2) were diluted from a sodium hypochlorite solution (10%, by weight). TAN stock solutions (500 mg/L as N) were prepared by dilution of ammonium chloride (CAS No. 12125-02-9, purity more than 99.5%). The stock solutions were stored at 4°C in dark. 0.05 mol/L sulfuric acid and 0.10 mol/L sodium hydroxide were used to

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adjust pH. 0.01 mol/L phosphate buffer was applied to maintain pH in solution.

2.2 The Chlorine/UV Process

The experimental solutions were freshly prepared before experiments. The initial concentration of TAN in experimental sample was 0.07 mmol/L (1 mg/L as N). A series of chlorine solutions were added into TAN samples to achieve a desired chlorine:TAN molar ratio from 0.33 to 1.17 for 180 min chlorination in dark. Then, samples were pumped into a 1.50 L UV reactor (L = 61.00 cm, d = 8.00 cm) equipped with a low pressure Hg lamp (HNG, Germany) with a characteristic wavelength of 254 nm. The schematic of the photochemical reactor were described in our previous published paper.[18] The UV dose imposed to water samples ranged from 40.00 mJ/cm^2 to 140.00 mJ/cm^2, which was adjusted by controlling the flow rate of water samples from 56.00 mL/s to 16.00 mL/s. All experiments were conducted in triplicate and expressed as the average value.

2.3 Detection Method

In the experiments, the concentrations of chlorine, TAN, nitrite and nitrate were

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determined based on the standard methods for the examination of water and wastewater published by American Public Health Association (APHA).[21] Specifically, TAN were monitored according to the ammonia-selective electrode method (4500-NH_3 D) by an ammonia-selective electrode (Orion Co., 95-12, USA). Free chlorine was determined by the DPD colorimetric method (4500-Cl G). Nitrate and nitrite were measured by colorimetric method (4500-NO_2^- B) and ultraviolet spectrophotometric screening method (4500-NO_3^- B), respectively. A pH meter (Thermo Orion Co., 720A, USA) was used to measure pH of solutions. A UV-Visible spectrometer (Cary 300 BIO, Agilent Technologies, CA, U.S.) was applied in absorbance determination. The TAN removal was calculated as Eq. (1), where TAN_0 and TAN_t were initial TAN concentration and final TAN concentration, respectively.

$$TAN\ removal\ (\%) = \left(\frac{TAN_0 - TAN_t}{TAN_0}\right) \times 100\% \qquad (1)$$

2.4 RSM Experimental Design

Response surface methodology (RSM) is an effective and widely applied statistical method for optimizing the processes of water treatment.[22-24] In this study, a three-factor

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and five-level central composite design based on RSM was applied to investigate the effects of three independent factors, in terms of chlorine:TAN molar ratio (X_1), UV dose (X_2) and pH (X_3), on the response value of TAN removal (Y) in the chlorine/UV process. The experimental parameters were selected according to our preliminary experimental results [18] and summarized in Table 1.

[Insert Table 1 here]

2.5 Statistical Analyses

Design Expert 8.0 software (Stat-Ease Inc.) was applied to analyze the variance, establish the mathematical model, and optimize the parameters of the chlorine/UV process. The experimental data were fitted to a second-order polynomial model as defined in Eq. (2), where Y means the predicted response; X_i represents independent variables, β_0, β_i, β_{ij}, β_{ii} represent the intercept, linear coefficients, interaction coefficients and quadratic coefficients, respectively.[25]

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{j-1} \sum_{i=1}^{k} \beta_{ij} \cdot X_i \cdot X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2 \quad (2)$$

3. Results and discussion

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3.1 Model Fitting and Statistical Analysis

Table 1 shows the RSM design and experimental results of the decomposition of TAN in the chlorine/UV process. The TAN removals ranged from 20.35% to 73.63% with chlorine: TAN molar ratio ranging from 0.33 to 1.17 and UV dose in the range of 40.00 to 140 mJ/cm^2 at pH from 5.82 to 9.18. All of these parameters were selected at the typical ranges applied in drinking water treatment. It can be seen in Table 1 that the TAN removal highly depended on the experimental parameters of the three factors. These results were used to establish an empirical quadratic polynomial model described in Eq. (3), where Y represents the TAN removal; X_1, X_2, X_3 represent the chlorine:TAN molar ratio, UV dose, and pH, respectively.

$$Y(\%) = -292.83 + 113.08 \cdot X_1 + 0.03 \cdot X_2 + 68.66 \cdot X_3 + 0.27 \cdot X_1 \cdot X_2 + 2.17 \cdot X_1 \cdot X_3 + 0.02 \cdot X_2 \cdot X_3 - 52.55X_1^2 - 9.59X_2^2 - 4.62X_3^2 \quad (3)$$

As shown in Fig. 1, predicted values calculated by Eq. (3) well matched with the actual decomposition results of TAN in the chlorine/UV process. These results suggested that this regression model was adequate to describe the variability of TAN removal as a

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function of chlorine:TAN molar ratio, UV dose and pH value.

[Insert Figure 1 here]

In order to check the significance of the quadratic model [26], significance test (F-test) and analysis of variance (ANOVA) was performed and the results were summarized in Table 2. It can be seen that the probability value (p) of regression model was less than 0.001, suggesting the model was significant for predicted response. The coefficient of determination (R^2) of the model was 0.996, meaning 99.6% variations of the response could be explained by this model. The fact that adjusted R^2 (0.993) was closed to R^2 also confirmed the adequacy of the second-order model. The p value of lack-of-fit was insignificant demonstrated the pure error was insignificant effect on modal fitting.

[Insert Table 2 here]

3.2 Effects of Main and Interaction Variables

The signifcances of main and interaction variables on the response were evaluated by the analysis of p values, as illustrated in Table 3. The p values of all three independent variables were less than 0.001, indicating the linear effects were highly significant for the

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predicted responses. Moreover, the p values of the interaction variables including X_1X_2 and X_1X_3 were less than 0.05, whereas the the p value of X_2X_3 was higher than 0.05. Therefore, the interactions of X_1X_2 and X_1X_3 were significant on the response, but the interaction of X_2X_3 were insignificant terms.

[Insert Table 3 here]

Fig. 2 shows the effects of one independent factor on TAN removal with the other two factors fixed at central level. It can be observed that the chlorine:TAN molar ratio presents a significant positive effect on TAN removal, which was in consistent with our previous study.[18] Chlorination of TAN would form chloramine at the range of molar ratio used in this experiments. It has been reported the chloramine was more sensitive to UV irradiation than parent TAN.[27] UV dose also pressed a positive effect for the TAN removal, due to the photolysis of chloramine dependent on the UV dose. [27] However, pH represented a complicated influence on TAN degradation. The optimal pH of TAN removal was roughly 7.5. This result may be attributed to the fact that pH affected the generation of chloramine by influencing the protonation of both chloramine and TAN. It

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has also been indicated that alkaline conditions could promote the consumption of radicals, thereby reducing the degradation rate of TAN.[17]

[Insert Figure 2 here]

Fig. 3 presents 3D response surfaces for the TAN removal with the interactions of the three independent variables, which also played important roles on TAN removal.[28] Fig. 3 (a) demonstrates the interaction of chlorine:TAN molar ratio and UV dose was obviously significant. The degradation of TAN was more apparent with the increase of both molar ratio and UV dose, indicating a synergistic effect in the chlorine/UV process. There is also an interaction effect between chlorine:TAN molar ratio and pH. As shown in Fig. 3 (b), higher ammonia removal obtained at larger chlorine:TAN molar ratio and pH at around 7.5. These results confirmed the former analysis that pH would affect the extent of chlorination of TAN. At chlorine and TAN molar ratio of 0.77, mono-chloramine was dominant in the system at pH ranging from 6.0 to 9.0. Although the photolysis of mono-chloramine was UV dose dependent, the interaction between UV dose and pH value was not significant resulting in the minor effect of pH on mono-chloramine

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formation, as shown in Fig. 3 (c).

[Insert Figure 3 here]

3.3 Optimization of Chlorine/UV Process

The optimization of the chlorine/UV process was conducted in order to obtain feasible, economical and maximum parameters for TAN removal. Design Expert 8.0 software was applied to optimize the reaction process based on the ridge analysis.[19] The constraints of the three variables were defined as minimum for both chlorine:TAN molar ratio and UV dose, whereas keeping pH in the range of 6.0 to 9.0. Table 4 concluded the optimum parameters for the different target response. Confirmation experiments were also performed and experimental results well matched with the predicted response. These results confirmed that the model could successfully optimize the chlorine/UV process for TAN removal.

[Insert Table 4 here]

The TAN containing raw water was used to monitor the pH variation and determine the nitrogenous products during the chlorine/UV process. Water samples were collected

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from a drinking water treatment plant with initial TAN concentration of 1 mg/L and background nitrate concentration of 1.42 mg/L. Un-buffered water samples were used to investigate the variation of pH fixed chlorine: TAN molar ratio of 0.88. A decrease in pH from 7.3 to 7.0 was observed with the increase of UV doses from 40.00 mJ/cm^2 to 140.00 mJ/cm^2. The slight decrease of pH was probably due to the formation of a proton during oxidation of TAN. In addition, the evolution of various products may also lead to pH variation. As shown in Fig. 4, the concentration of TAN was gradually decrease with the crease of UV exposure and then kept stable at UV dose of around 80.00 mJ/cm^2. It can be observed that nitrate was the main product in the TAN photodecomposition, accompany with a slight formation of nitrite. The generation of nitrite may result from the photo decay of nitrate at a relative high UV dose. [29]

[Insert Figure 4 here]

3.4 Mechanism of TAN Decomposition in the Chlorine/UV process

The mechanism of degradation of TAN chlorine in the chlorine/UV process could be summarized in two aspects: direct photodecomposition of chloramine and indirect

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oxidation by intermediate radicals. In the first place, at chlorine:TAN molar ratio ranging from 0.3:1 to 1.2:1, chloramine was formed due to the high reaction rate constant of the chlorination of TAN,[30] accompany with the residual TAN in the system. Previous study indicated the absorptivity of TAN at 254 nm was close to 0,[18] while chloramine represented a relative high sensitivity of UV_{254} irradiation.[27] It has been reported that the molar absorptivity of mono-chloramine was 388 $M^{-1}s^{-1}$ and its quantum yield was 0.62.[27] These data indicated that UV_{254} induced photo decay primarily imposed to chloramine in the solution.

In the second place, the oxidative radicals would promote the degradation of TAN. The photo degradation of chloramine induced the cleavage of Cl-N bond, yielding aminyl radicals and chlorine radicals, as shown in Eq. (4).[16] In addition, the photodecomposition of free chlorine would produce hydroxyl radicals and chlorine radicals expressed in Eq. (5).[11] As described in Eq. (6-7), both hydroxyl radicals and chlorine radicals were effective for TAN oxidation and formed aminyl radicals.[31]

Based on the oxidation process shown in Eq. (8-10), the aminyl radicals would be

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further oxidized to nitrite, nitrate, and N_2O by the presence of dissolved oxygen in the system.[27, 32, 33] These photodecay products were conformable with the products determined in our research, as shown in Fig. 4.

$$NH_2Cl \xrightarrow{hv} \cdot NH_2 + \cdot Cl \tag{4}$$

$$HOCl \xrightarrow{hv} \cdot OH + \cdot Cl \tag{5}$$

$$NH_3 + \cdot OH \rightarrow \cdot NH_2 + H_2O \tag{6}$$

$$NH_3 + \cdot Cl \rightarrow \cdot NH_2 + H^+ + Cl^- \tag{7}$$

$$\cdot NH_2 + O_2 \rightarrow \cdot NH_2O_2 \tag{8}$$

$$NH_2O_2 \cdot \rightarrow HNOOH \rightarrow NO + H_2O \xrightarrow{O_2} HNO_2 \xrightarrow{O_2} HNO_3 \tag{9}$$

$$2NH_2O_2 \cdot \rightarrow 2HNOOH \rightarrow 2HNO + H_2O_2 \rightarrow N_2O + 2H_2O + O_2 \tag{10}$$

4. Conclusions

This study investigates the removal efficiency the influence factors for TAN decomposition in the chlorine/UV induced photochemical process. The experimental results demonstrated the chlorine/UV process was effective for TAN degradation. Three independent factors (chlorine:TAN molar ratio, UV dose and pH) represented significant

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effects on the TAN removal. Specifically, the effects of both chlorine:TAN molar ratio and UV dose were positive for TAN removal, while the effects of initial pH value was complex. The interaction between chlorine:TAN molar ratio and UV dose is significant, implying a synergistic effect in the chlorine/UV process. A mathematical fitting model was established according to response surface methodology (RSM). ANOVA analysis and confirmation experiments demonstrated that the proposed regression model matched well with the actual chlorine/UV process. The optimum parameter for TAN removal of 70% was chlorine:TAN molar ratio of 0.95, UV dose of 130 mJ/cm^2 and pH at 8.77, respectively. The main products in this process were nitrate, accompanied with a slight amount of nitrite. The decomposition pathways were proposed to be the photodecay of chloramine, as well as the oxidation of intermediate radicals. These conclusions suggest that the UV/chlorine process may represent an effective option for TAN control in water treatment.

Acknowledgements

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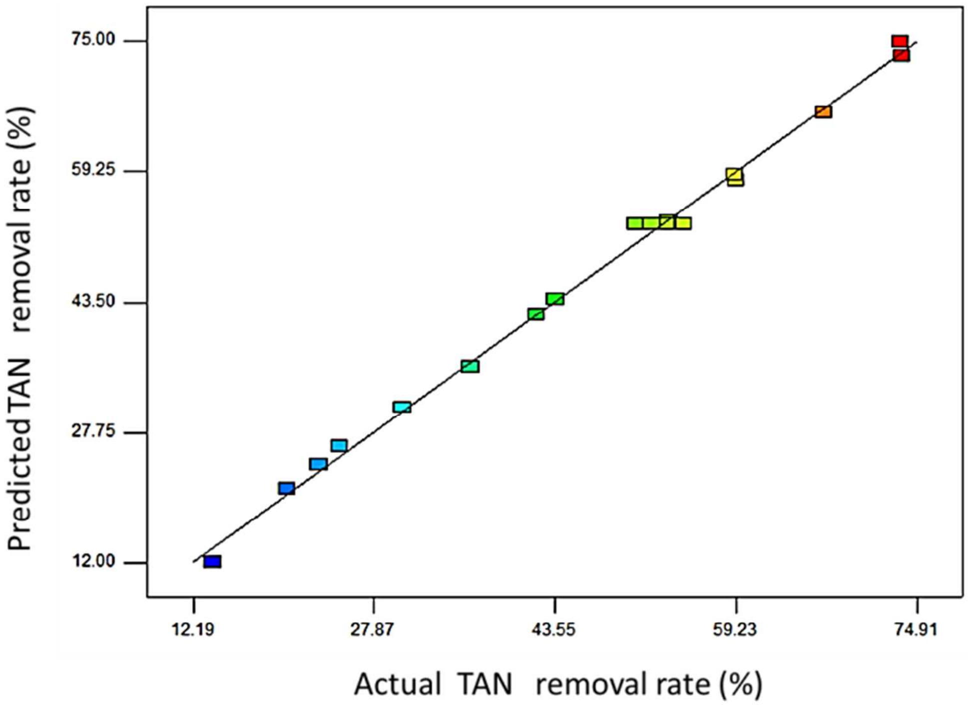

Figure 1 Comparison of predicted value and actual value for TAN removal in the chlorine/UV process. Experimental condition: $[TAN]_0$= 0.07 mmol/L; 0.01 mol/L phosphate buffer

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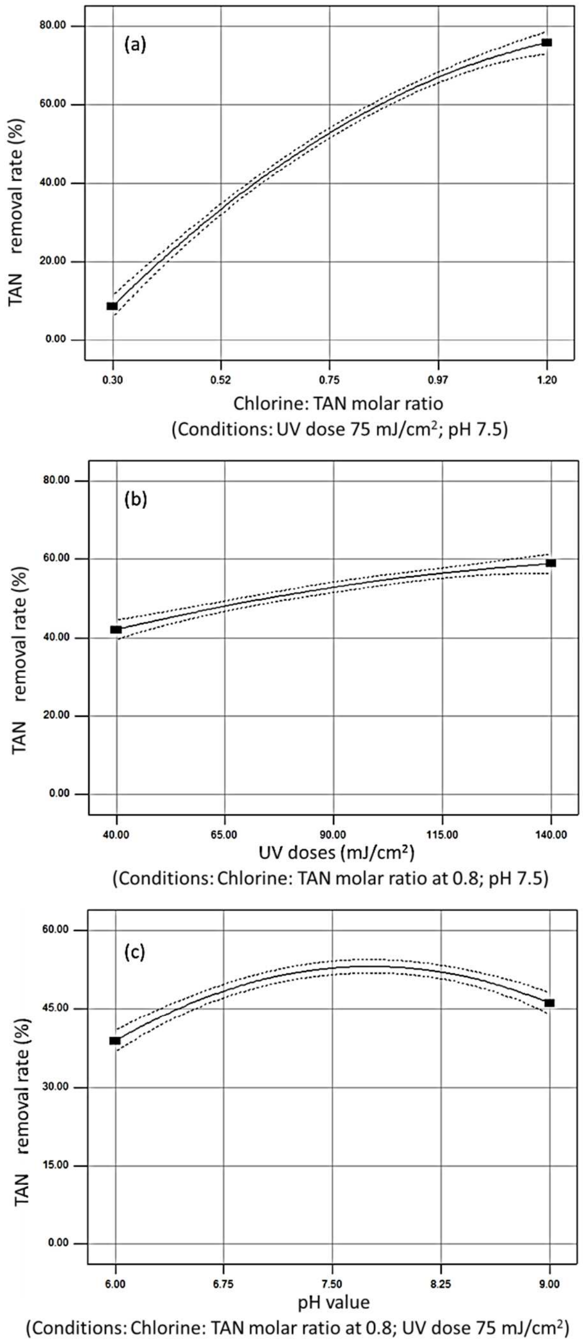

Figure 2 The effects of independent variable on the TAN removal in the chlorine/UV process. (a) Chlorine: TAN molar ratio; (b) UV doses; (c) pH value. Experimental condition: $[TAN]_0$= 0.07 mmol/L; 0.01 mol/L phosphate buffer

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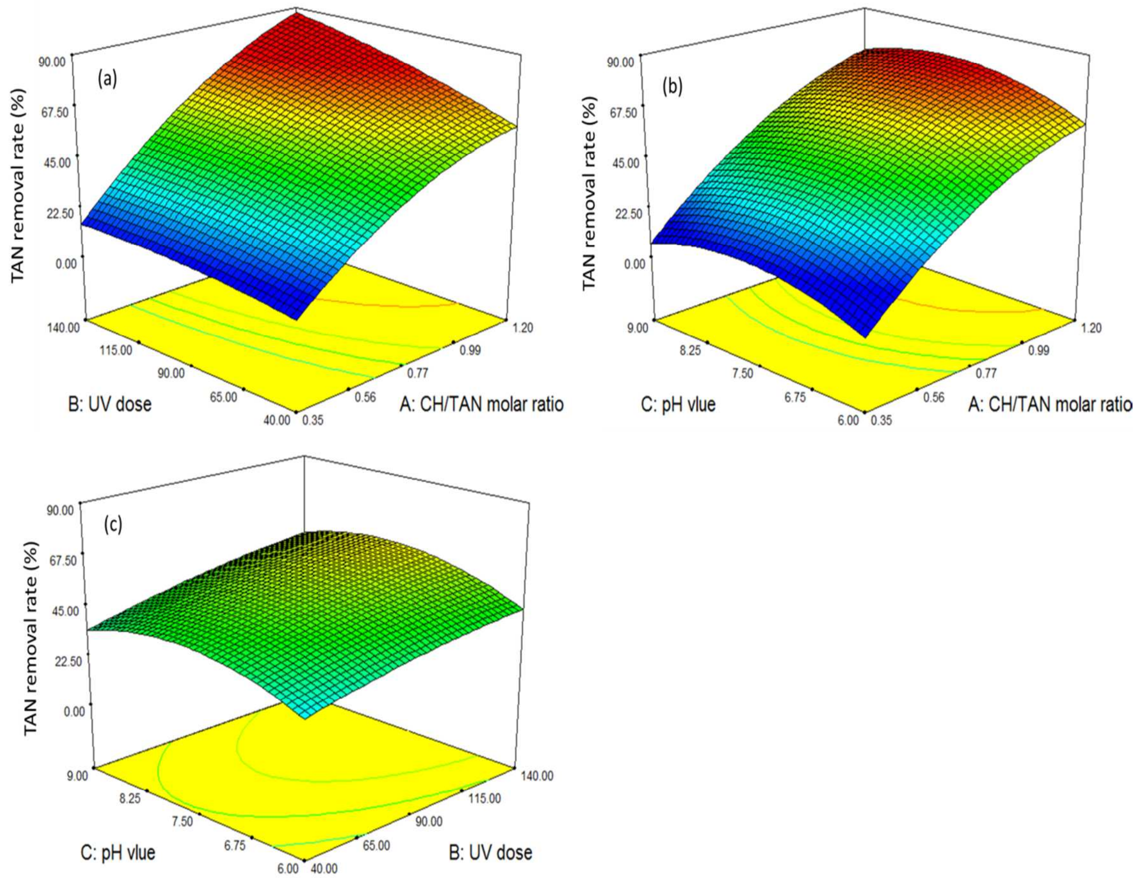

Figure 3 Response surfaces plotted on the effects of two independent variables on the TAN removal in the chlorine/UV process. (a) Chlorine: TAN molar ratio and UV dose; (b) Chlorine: TAN molar ratio and pH; (c) UV dose and pH. Experimental condition: $[TAN]_0$= 0.07 mmol/L; 0.01 mol/L phosphate buffer

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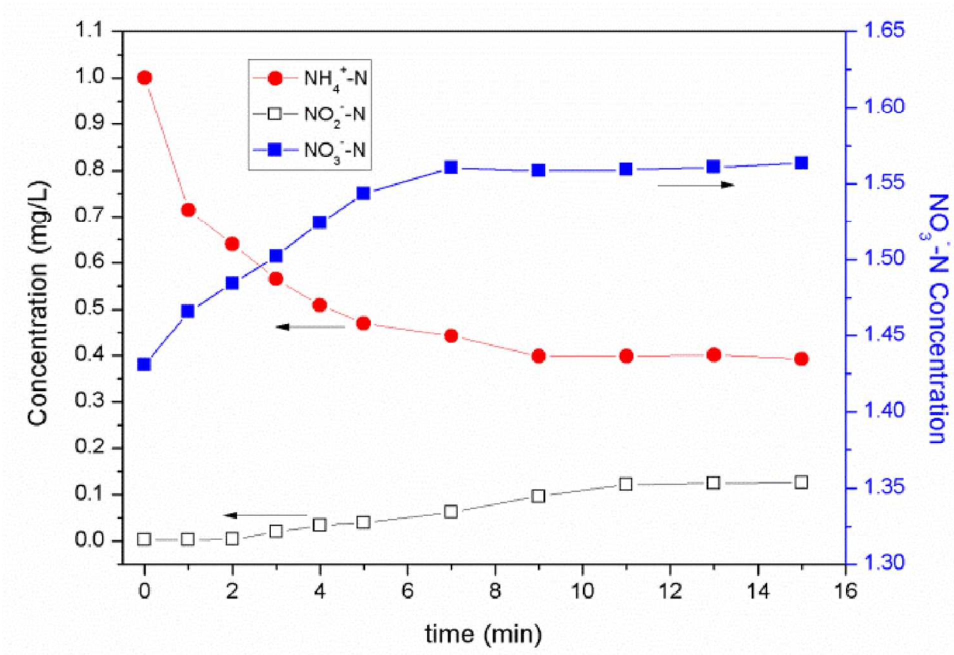

Figure 4 Nitrogenous products for TAN decomposition in the UV/chlorine process with background nitrate 1.42 mg/L. Experimental condition: $[TAN]_0$= 1mg/L as N (0.07 mmol/L); Chlorine:TAN molar ratio = 0.88; UV254 irradiance was 8.0×10-5 W/cm^2; pH= 7.5; 0.01 mol/L phosphate buffer

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Table 1 Experimental design matrix and response

Std	Chlorine:TAN molar ratio		UV dose (mJ/cm^2)		pH		Actual Value (%)	Predicted Value (%)
	Coded value	Actual value	Coded value	Actual value	Coded value	Actual value		
1	-1	0.50	-1	60.00	-1	6.50	20.35	20.97
2	1	1.00	-1	60.00	-1	6.50	53.44	53.17
3	-1	0.50	1	120.00	-1	6.50	24.90	26.12
4	1	1.00	1	120.00	-1	6.50	66.87	66.34
5	-1	0.50	-1	60.00	1	8.50	23.11	23.83
6	1	1.00	-1	60.00	1	8.50	59.23	58.20
7	-1	0.50	1	120.00	1	8.50	30.35	30.80
8	1	1.00	1	120.00	1	8.50	73.63	73.20
9	-1.68	0.33	0	90.00	0	7.50	13.89	12.19
10	1.68	1.17	0	90.00	0	7.50	73.48	74.91
11	0	0.75	-1.68	40.00	0	7.50	41.99	42.05
12	0	0.75	1.68	140.00	0	7.50	59.17	58.84
13	0	0.75	0	90.00	-1.68	5.82	36.23	35.70
14	0	0.75	0	90.00	1.68	9.18	43.61	43.87
15	0	0.75	0	90.00	0	7.50	53.92	52.84
16	0	0.75	0	90.00	0	7.50	52.68	52.84
17	0	0.75	0	90.00	0	7.50	53.18	52.84
18	0	0.75	0	90.00	0	7.50	51.94	52.84
19	0	0.75	0	90.00	0	7.50	54.71	52.84
20	0	0.75	0	90.00	0	7.50	50.57	52.84

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Table 2 Analysis of variance for the response surface model

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value
Model	5633.95	9	625.99	307.28	< 0.001
Residual	20.37	10	2.04		
Lack of Fit	9.60	5	1.92	0.89	0.548
Pure Error	10.77	5	2.15		
Cor Total	5654.32	19			
R-Squared	0.996				
Adj R-Squared	0.993				

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Table 3 Analysis of variance for the effects of the three variables

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value
X_1- Chlorine/TAN molar ratio	4749.33	1	4749.33	2331.32	< 0.001
X_2- UV dose	343.66	1	343.66	168.69	< 0.001
X_3- pH vlue	80.57	1	80.57	39.55	< 0.001
$X_1 X_2$	32.16	1	32.16	15.79	0.003
$X_1 X_3$	2.35	1	2.35	1.16	0.048
$X_2 X_3$	1.67	1	1.67	0.82	0.386
X_1^2	155.57	1	155.57	76.37	< 0.001
X_2^2	10.43	1	10.43	5.12	0.047
X_3^2	307.23	1	307.23	150.81	< 0.001

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Table 4 Optimum conditions at different target TAN removal

No.	Experimental parameters			TAN removal (%)			
	Chlorine: TAN molar ratio	UV dose (mJ/cm^2)	pH value	Target value	Actual value	Error	STDEV
Test 1	0.68	112.76	7.39	50	50.32	0.32	±0.49
Test 2	0.88	81.13	7.72	60	59.58	0.42	±0.56
Test 3	0.95	130.34	8.77	70	70.72	0.72	±0.67

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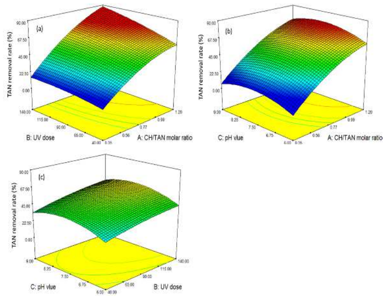

Three independent factors have significant interaction effects on TAN photodecomposition.

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