Empowering a novel O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique to deal with thiourea-containing photovoltaic wastewater†

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Photovoltaic wastewater contains a large amount of thiourea that cannot be directly treated by biological methods because of its biotoxicity. In this study, a novel O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique was used as a pre-treatment process to degrade thiourea. The effects of H$_2$O$_2$ and catalyst loading were investigated, and the transformation pathway of thiourea was predicted based on the intermediates detected by UPLC-Vion-IMS-QToF. The synergy technique degraded 89.14% thiourea within only 30 min, and complete degradation occurred after 150 min. The TOC removal of O$_3$/H$_2$O$_2$ + BiPO$_4$/UV was 1.8, 1.5, and 1.9 times that of O$_3$/H$_2$O$_2$ and BiPO$_4$/UV/H$_2$O$_2$ single processes and O$_3$/H$_2$O$_2$ + UV process, respectively, which was due to the synergy between H$_2$O$_2$ residues and BiPO$_4$. In addition, thiourea was mainly degraded by ·OH into thiourea dioxide and melamine (polymerized by other intermediates) and then further degraded into biuret and methyl carbamate by the holes of BiPO$_4$, followed by complete mineralization into H$_2$O and CO$_2$. These results confirm that the O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique is a promising option for the degradation of thiourea.

1. Introduction

Thiourea is widely used in numerous industries, especially in the photovoltaic industry. It is used in chemical bath deposition to produce CdS polycrystalline films for thin-film solar cells. Hence, wastewater from photovoltaic plants contains a large amount of redundant thiourea. It degrades slowly in the natural environment and has serious effects on human health. Due to the biological toxicity of thiourea, it cannot be directly treated by biological methods. Advanced oxidation processes (AOPs) can be an alternative method for the pre-treatment of photovoltaic wastewater containing high concentration of thiourea, transforming thiourea into other substances without biotoxicity.

Considering that photovoltaic wastewater contains high concentrations of organic matter and salts, the process we use cannot further introduce excess salt as it will be over-discharged. An O$_3$/H$_2$O$_2$ Fenton-like process was selected as it generates extraordinarily reactive hydroxyl radicals (·OH) by the reaction of ozone and hydrogen peroxide without salt introduction. These radicals subsequently attack and decompose contaminants in the water, and the process is usually effective, simple, environment-friendly and economically sustainable. The O$_3$/H$_2$O$_2$ method enables rapid degradation of various recalcitrant organic compounds such as perfluorinated chemicals, dibutylsulfoxide, dimethyl sulfoxide, phenol and linear alkyl benzene. However, using H$_2$O$_2$ alone in the O$_3$/H$_2$O$_2$ process is not sufficient as excess H$_2$O$_2$ residues not only affect the degradation efficiency but also increase COD of the water sample and affect the post-treatment process.

Some studies have improved the utilization efficiency of H$_2$O$_2$ residues by employing photo-irradiation. Nevertheless, ·OH generated by UV or O$_3$/H$_2$O$_2$ is inferior in organic mineralization as ·OH tends to abstract hydrogen from C–H bonds or add hydrogen to unsaturated carbon–sulfur bonds; if these bonds are not present (e.g., oxalic acid, which is one of the intermediates in the degradation of phenol), the oxidation ability of ·OH will be limited. A photocatalyst, namely, bismuth phosphate (BiPO$_4$) is considered an alternative as it can generate holes, which enhance the mineralization efficiency. It has been proven to be an efficient catalyst and has an optical indirect band gap of 3.85 eV. The photocatalytic activity of BiPO$_4$ is twice that of titanium dioxide (TiO$_2$ P25, Degussa).

BiPO$_4$ possesses excellent photocatalytic activity due to the inductive effect of PO$_4$ since it can separate electrons and holes. BiPO$_4$ has been applied for the removal of dyes and phenols. BiPO$_4$ not only improves the mineralization efficiency but also has a synergistic effect with H$_2$O$_2$. In a previous study, BiPO$_4$ coupled with 60 mg L$^{-1}$ H$_2$O$_2$ significantly improved the degradation efficiency of phenol. Adequate H$_2$O$_2$
interacted with BiPO₄, improving the photocatalytic efficiency of BiPO₄ by increasing the separation efficiency of e⁻ and h⁺ through the capture of e⁻ by H₂O₂. Based on these facts, the O₃/H₂O₂ + BiPO₄/UV synergy technique was developed in this study. We hypothesize that H₂O₂ residues after O₃/H₂O₂ treatment will be utilized by BiPO₄/UV, which is a novel approach.

In this study, we report the improvement in thiourea transformation efficiency and TOC removal by using the O₃/H₂O₂ + BiPO₄/UV synergy technique coupled with the investigation of the utilization efficiency of residual H₂O₂. We have also investigated the effects of H₂O₂ concentration and catalyst loading. The possible transformation pathway of thiourea is predicted in the end.

2. Material and methods

2.1 Solution preparation

Synthetic solutions were prepared using 18.2 MΩ cm Milli-Q deionized water. All the reagents used were of analytical grade. Thiourea was supplied by Aladdin (USA), ammonium chloride by Sinopharm Chemical reagent Co., Ltd. (China) and hydrogen peroxide (30% w/v) by Macklin (USA). For residual H₂O₂ test, potassium titanyl oxalate was purchased from Macklin (USA). Thiourea (1.2 g) and ammonium chloride (0.535 g) (as the source of ammonium nitrogen) were added into 1 L of deionized distilled water to simulate photovoltaic wastewater.

2.2 Preparation of BiPO₄

BiPO₄ nanorods were prepared via the reflux method. In short, 1.956 g of Bi(NO₃)₃·5H₂O (AR, Macklin) and 3.145 g of NaH₂PO₄·2H₂O (AR, Macklin) were added into a flask, followed by mixing with at least 750 mL of deionized water. After the pH was adjusted to 2.2 with concentrated nitric acid (Sinopharm Chemical reagent Co., Ltd.), the flask was placed in an oil bath (120 °C) and mixing was conducted at 800 rpm, followed by heating for 48 hours. The resultant white precipitate was washed three times with deionized water and dried at 120 °C for 12 hours.

2.3 Experimental set-up and procedure

2.3.1 Experimental set-up. A self-designed experimental setup was employed in this study, as shown in Fig. 1. Ozone was generated using a laboratory ozone generator having a maximum generation capability of 32 g h⁻¹. The flow rate was adjusted to 5 L min⁻¹ before inserting into the ozone reaction tower. The volume of the ozone reaction tower was 12 L. To fully mix the gas and liquid phases, a reflux unit was used in the ozone reaction tower with a reflux rate of 2 L min⁻¹. The reflux unit was equipped with a pH meter and a dosing pump to monitor the pH variation and H₂O₂. After O₃/H₂O₂ treatment, samples were transferred into a photo reactor. The photo reactor included two low-pressure mercury lamps (254 nm, 11 W, Philips, China) housed inside a wooden box. The intensity of UV irradiation was 4.73 mW cm⁻², measured by an ultraviolet radiation meter (UV-C, photoelectric instrument factory of Beijing Normal University, China). The Petri factor for the low-pressure UV system was determined to be greater than 0.9.

2.3.2 Experimental procedure

O₃/H₂O₂ + BiPO₄/UV synergy technique. O₃/H₂O₂ + BiPO₄/UV synergy technique was carried out in the self-designed setup (Fig. 1). The optimum conditions for maximizing the TOC residues and specifying the hydrogen peroxide residues of O₃/H₂O₂ treatment were determined by means of a three-factor three-level Box–Behnken experimental design (BBD) combined with the response surface methodology (RSM) to correlate experimentally obtained criteria and experimental conditions given by the Box–Behnken experimental design. The independent variables were the initial concentrations of H₂O₂ (X₁) and

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Fig. 1  Experiment reactor. (1): Photoreactor instrument; (2): agents can for H₂O₂; (3): agents pump; (4): flowmeter; (5): pH-meter; (6): circulating pump; (7): ozone meter; (8): ozone destructor; (9): peristaltic pump; (10): ozonator; (11): wastewater tank; (12): oxygen bottle; (13): reaction tower.
O$_3$ (X$_2$) and the initial pH (X$_3$), which were coded as $-1$, 0 and $+1$, as shown in Table 1.

The total number of experimental trials was 17 based on a three level and a three factor experimental design with three replicates at the centre of the design to estimate a pure error sum of squares. TOC residues, H$_2$O$_2$ residues and the ‘pseudo’-second order rate constant were considered as dependent factors (process responses). Specific experimental conditions of the O$_3$/H$_2$O$_2$ treatment were selected according to the reaction model generated by BBD. The experimental conditions could achieve the desired reaction results of the O$_3$/H$_2$O$_2$ treatment process. After 150 min of the O$_3$/H$_2$O$_2$ treatment, the treated effluent (100 mL) was transferred into a low-pressure (LP) UV collimated beam system with a specific amount of BiPO$_4$ after stirring and ultrasonating for 10 min before irradiation. The UV intensity was 4.73 mW cm$^{-2}$ in average and the BiPO$_4$/UV post-treatment lasted for 180 minutes.

O$_3$/H$_2$O$_2$ + UV process. The experimental procedure of the O$_3$/H$_2$O$_2$ + UV process was similar to that of the O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique. Experimental conditions of the O$_3$/H$_2$O$_2$ treatment were also selected according to the reaction model generated by BBD. The conditions were the same as that of the O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique to compare their mineralization efficiencies. However, BiPO$_4$ was not added in the post-treatment process. Samples were directly transferred into the LP UV collimated beam system.

O$_3$/H$_2$O$_2$ single-process. The initial experimental conditions and the procedures of the O$_3$/H$_2$O$_2$ single-process were the same as those of the O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique; however, there was no post-treatment in this process. The O$_3$/H$_2$O$_2$ treatment was sustained for 330 minutes.

BiPO$_4$/UV/H$_2$O$_2$ process. BiPO$_4$/UV/H$_2$O$_2$ process was carried out in the LP UV collimated beam system in the same manner as before. The initial amounts of H$_2$O$_2$ and BiPO$_4$ loadings were equal to those used in the O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique. A specific amount of BiPO$_4$ was added after agitation and ultrasonication for 10 min before irradiation. The experiment was continued for 330 minutes.

A water sample (3 mL) was taken every 30 minutes from the reactor in each experiment mentioned above to analyse the TOC concentration and H$_2$O$_2$ residues. Moreover, three replicates were made for each analytical measurement.

### 2.4 Analytical methods

The concentration of thiourea was analyzed by a HPLC system (Agilent 6120B, USA) equipped with a multi-wavelength UV detector (ESI, Text S1†). TOC was monitored with a Multi N/C 3100 TOC/TN analyzer. H$_2$O$_2$ was measured by a spectrophotometric method$^{22}$ using a HACH DR6000 UV-vis spectrophotometer. Ammonium nitrogen was determined by salicylic acid spectrophotometry (HJ 536-2009 in China). Nitrate nitrogen, sulfate and chloride were determined by ion chromatography (Metrohm 820 IC). The morphology and the structure of the BiPO$_4$ photocatalyst were examined with a scanning electron microscope (SEM) and powder X-ray diffraction (XRD). The Brunauer Emmett Teller (BET) specific surface area and the pore size distribution of the BiPO$_4$ photocatalyst were characterized by nitrogen adsorption at 77 K with Micromeritics 3020. The degradation by-products of thiourea were analysed via high resolution mass spectrometry analysis carried out on Water I-Class Acquity UPLC (Waters, UK) coupled with Vion IMS QToF (Waters, UK) (ESI, Text S2†).

### 3. Results and discussion

#### 3.1 Experimental design and condition selection

The Box–Behnken statistical experiment design was employed to investigate the effects of three independent variables on the TOC and H$_2$O$_2$ residues as response functions. Table 2 depicts the three-factor three-level Box–Behnken experimental design and the observed and predicted values for the TOC and H$_2$O$_2$ residues by the developed quadratic model.

As mentioned before, RSM was used to estimate the parameters, indicating an empirical relationship between the input variables and the response, as shown in eqn (1) and (2). The quadratic model equation for predicting the response function (TOC, H$_2$O$_2$ residues) could be expressed by the following second-order polynomial equation in terms of the coded factors:

$$
Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j
$$

| Run | H$_2$O$_2$ | O$_3$ | pH | TOC Observed | Predicted | H$_2$O$_2$ Observed | Predicted |
|-----|-----------|------|----|-------------|-----------|-------------------|----------|
| 1   | 1         | 0    | -1 | 173.4       | 173.4     | 1046.9            | 1053     |
| 2   | -1        | -1   | 0  | 179.2       | 177.4     | 2.22              | 0.86     |
| 3   | -1        | 0    | -1 | 175         | 176.9     | 9.93              | 0.86     |
| 4   | 0         | 0    | 0  | 175.6       | 168.2     | 442.27            | 416.51   |
| 5   | 0         | -1   | 1  | 172.8       | 174.4     | 316.08            | 329.84   |
| 6   | 1         | 1    | 0  | 160.2       | 161.8     | 855.02            | 862.77   |
| 7   | 0         | 0    | 0  | 168.8       | 168.2     | 415.98            | 416.51   |
| 8   | 0         | 1    | -1 | 175.6       | 174       | 350.26            | 336.5    |
| 9   | 0         | -1   | -1 | 175         | 174.7     | 389.69            | 410.97   |
| 10  | -1        | 0    | 1  | 182.4       | 182.2     | 0.86              | 0.86     |
| 11  | 0         | 1    | 1  | 167.6       | 167.9     | 242.47            | 221.18   |
| 12  | 0         | 0    | 0  | 166.2       | 168.2     | 405.46            | 416.51   |
| 13  | 0         | 0    | 1  | 164.8       | 168.2     | 392.32            | 416.51   |
| 14  | 1         | 0    | 1  | 163.4       | 161.6     | 844.51            | 858.04   |
| 15  | 1         | -1   | 0  | 157         | 157.3     | 1120.6            | 1093.3   |
| 16  | 0         | 0    | 0  | 165.4       | 168.2     | 426.5             | 416.51   |
| 17  | -1        | 1    | 0  | 166         | 165.8     | 14.53             | 41.82    |
Here, Y and Z are the predicted responses for TOC and H₂O₂ residues, and X₁, X₂ and X₃ are the independent variables.

The statistical significance of the second-order polynomial model to predict the TOC and H₂O₂ residues was tested by the analysis of variance (ANOVA). The results of ANOVA are presented in Table S1 and Table S2 (ESI, Table S1 and S2†). The significance of each coefficient in eqn (1) and (2) was determined by the Fisher’s F-test and the values of probability were greater than F.

A small probability value (p <0.0001) indicated that the model was highly significant. The goodness of fit of the model was validated by the determination coefficient (R²). In this case, R² values were 0.99758 and 0.874188, which showed high significance of the model. Also, the adequate precision greater than 4 (54.69 and 8.84 in this case) showed that the model could be used to navigate the design space defined by BBD. Adequate precision is a measure of the range in the predicted response relative to its associated error. The normality of data can be checked through the high correlation between observed and predicted data shown in Fig. S3 (ESI, Fig. S3†), which indicates their low discrepancies.

To study the interaction effects between the variables (initial concentration of polymer, initial concentration of H₂O₂, pH and recirculation rate), the 3D response surface and 2D contour curves based on the quadratic model were plotted, as shown in Fig. 2(a–f).

As illustrated in Fig. 2(a–f), TOC was significantly affected by the initial H₂O₂ dosage and O₃ concentration. It can be seen that TOC decreased with increasing H₂O₂ dosage and O₃ concentration. The effects of the initial H₂O₂ dosage and the O₃ concentration are mainly due to the generation of ·OH by H₂O₂ and O₃. The more the ·OH, the higher the mineralization efficiency. Also, it can be seen that minimum TOC is achieved at pH of 7. In alkaline solutions, the dissociated form of hydrogen peroxide (HO₂⁻) reacts with ·OH more than 2 orders of magnitude faster than hydrogen peroxide. Therefore, the oxidation efficiency decreases as ·OH species are consumed. However, in acidic solutions, thiourea is stable and relatively hard to be mineralized. As for the amount of H₂O₂ residues, data are illustrated from Fig. 2(d)–(f). The initial H₂O₂ dosage is the main factor that influences the amount of H₂O₂ residues; however, the influence of pH and O₃ concentration is much less pronounced than that of the initial H₂O₂ dosage. This is also confirmed in Table S2,† which shows the significance of the factors and their interaction.

To investigate the mineralization and degradation efficiency of the O₃/H₂O₂ + BiPO₄/UV synergy technique, we chose the initial experimental conditions of O₃/H₂O₂ treatment based on the quadratic model equation calculated by BBD. According to these equations, specific experimental conditions were selected to achieve the maximum mineralization efficiency of thiourea under a targeted amount of H₂O₂ residues. In this experiment, we set the experimental conditions to obtain 70 mg L⁻¹ H₂O₂ residues from the O₃/H₂O₂ treatment with the maximum mineralization efficiency. According to this target, the ozone concentration was set at 55.71 mg L⁻¹, the initial concentration of H₂O₂ was 435 mg L⁻¹, and the initial pH value was 9.20.

### 3.2 Comparison of mineralization efficiencies among different treatment processes

In this study, degradation efficiencies were compared among different treatment processes. As observed in Fig. 3, 89.14% of thiourea was degraded by O₃/H₂O₂ within only 30 minutes. The chemical destruction of thiourea includes a double bond between carbon and sulfur. It can be easily oxidized by an oxidizing agent, especially by strong oxidants such as ozone (E° = 2.07 eV), hydrogen peroxide (E° = 1.28 eV) and hydroxyl radicals (E° = 2.8 eV). The ·OH species generated by O₃/H₂O₂ as well as O₃ and H₂O₂ oxidize thiourea into other products, which may contribute to the degradation of thiourea. The degradation efficiency of thiourea by UV/H₂O₂ and BiPO₄/UV/H₂O₂ processes was also investigated and compared with that of O₃/H₂O₂. In only 30 minutes of reaction time, 69.35% and 71.90% of thiourea were degraded by UV/H₂O₂ and BiPO₄/UV/H₂O₂, respectively, which were much lower than the value obtained for O₃/H₂O₂. The lower degradation efficiency might be due to the absence of O₃ in the process, which reduced their oxidizability.

The O₃/H₂O₂ process only reduced 23.125 mg L⁻¹ TOC, whereas O₃/H₂O₂ + UV achieved TOC reduction of 22.5 mg L⁻¹; also, the performance of the BiPO₄/UV/H₂O₂ single-process was much lower than that of the O₃/H₂O₂ + BiPO₄/UV synergy technique. Nevertheless, Fig. 3 shows that the O₃/H₂O₂ single-process achieved more TOC removal in the first half of the treatment process than the BiPO₄/UV/H₂O₂ single-process; however, in the second half, the TOC removal rate of the O₃/H₂O₂ single-process was exceeded by that of the BiPO₄/UV/H₂O₂ single-process. Based on this phenomenon, the O₃/H₂O₂ + BiPO₄/UV synergy technique was applied to exert higher TOC removal and generate synergy effect. The amount of TOC removal by the O₃/H₂O₂ + BiPO₄/UV synergy technique was 1.8 and 1.5 times higher than that of the O₃/H₂O₂ single-process and the BiPO₄/UV/H₂O₂ single-process, respectively. Also, the TOC removal was much higher than that without BiPO₄ addition, which was 1.9 times that of the O₃/H₂O₂ + UV process. This is mainly due to two factors. The first factor is the synergy between BiPO₄ and H₂O₂ residues from O₃/H₂O₂. The H₂O₂ residues from O₃/H₂O₂ are not wasted, and they further generate ·OH through UV irradiation; H₂O₂ residues can also capture e⁻ generated in BiPO₄, which can increase the separation efficiency of e⁻ and h⁺. Also, a part of H₂O₂ is utilized in O₃/H₂O₂; thus, we can avoid the negative effect on the synergy between BiPO₄ and H₂O₂ due to excess H₂O₂. In BiPO₄/UV/H₂O₂ single-process, excess H₂O₂ shows inhibition of the synergy between BiPO₄ and H₂O₂; it can occupy the holes in BiPO₄ but cannot improve the separation efficiency of e⁻ and h⁺. Thus, the TOC removal of the BiPO₄/UV/H₂O₂ single-process is limited.
The second factor is the electron transfer oxidation of holes. \( \cdot \)OH tends to abstract hydrogen from C–H bonds or add hydrogen to unsaturated carbon–sulfur bonds; thus, it is superior in thiourea degradation but inferior in further mineralization. As for O3/H2O2, it can only generate \( \cdot \)OH that is inferior in mineralization; thus, the amount of TOC removal is much lower than that of the processes containing BiPO4. In contrast, BiPO4 in BiPO4/UV can generate holes that can directly mineralize the by-products of O3/H2O2.

3.3 Comparison of H2O2 utilization among different treatment processes

The O3/H2O2 + BiPO4/UV synergy technique could greatly improve the utilization efficiency of hydrogen peroxide, especially in the BiPO4/UV process, as shown in Fig. 1. After the treatment of O3/H2O2, about 70 mg L\(^{-1}\) hydrogen peroxide was retained, which could be utilized by BiPO4 photocatalysis in less than 1 h. The O3/H2O2 single-process and O3/H2O2 + UV needed
more than 2 and 3 hours to consume hydrogen peroxide residues. Even though the consumption rate of hydrogen peroxide was higher in the BiPO4/UV/H2O2 single-process, the TOC removal rate of thiourea was 15%, as mentioned before, which was much lower than that of the O3/H2O2 + BiPO4/UV synergy technique. It has been proven that hydroxide radicals are quenched by additional hydrogen peroxide species;24,25 thus, the hydroxide radicals generated in BiPO4/UV/H2O2 single-process were not attached to thiourea but were consumed by extra H2O2 according to equation:26

\[
H_2O_2 + \cdot OH \rightarrow H_2O + HO_2. \tag{3}
\]

Therefore, excess H2O2 could lead to the consumption of active oxidizing hydroxyl radicals by a reaction other than the thiourea mineralization reaction, consequently reducing the rate of the latter reaction and wasting considerable H2O2 reagent.

In the O3/H2O2 + BiPO4/UV synergy technique, it is believed that H2O2 generates more \( \cdot OH \) in BiPO4/UV because of the synergy between BiPO4 and H2O2. Electron spin resonance (ESR) was carried out to investigate the hydroxyl radicals generated by H2O2, BiPO4 or both BiPO4 and H2O2 under UV irradiation. We measured hydroxyl radicals by ESR using DMPO as the spin-trap reagent. As shown in Fig. 5, the characteristic four peaks of DMPO-\( \cdot OH \) with the intensities of 1 : 2 : 2 : 1 appeared in all spectra. The intensity of \( \cdot OH \) generated in BiPO4 after the addition of 70 mg L\(^{-1}\) hydrogen peroxide was much higher than that in the H2O2 system and BiPO4 system. The result was in accordance with that of Elmolla’s research.27 As an electron scavenger, H2O2 can react with \( e^- \), as shown in the following equation:

\[
H_2O_2 + 2e^- \rightarrow \cdot OH + OH^- \tag{4}
\]

As explained before, an appropriate amount of H2O2 will capture the electrons in BiPO4, increasing the separation efficiency of \( e^- \) and \( h^+ \). This reaction also motivates H2O2 to generate \( \cdot OH \). As a result, the electron capture process combined with the UV irradiation process increases \( \cdot OH \) generation; thus, it accelerates the consumption rate of residual H2O2 from O3/H2O2 treatment. Also, more \( \cdot OH \) generation indicates less residual H2O2, and it will change the ratio of \( \cdot OH \) and H2O2; thus, \( \cdot OH \) scavenger reaction will be limited and H2O2 will be used efficiently. Nonetheless, the residual H2O2 from O3/H2O2 not only increases the separation of \( e^- \) and \( h^+ \) in BiPO4, but also results in \( \cdot OH \) generation. Thus, high degradation of thiourea by O3/H2O2 and residual H2O2 is efficiently utilized by the synergy between H2O2 and BiPO4, attaining faster H2O2 consumption and higher TOC removal.

### 3.4 Effect of hydrogen peroxide

To investigate the effect of H2O2, different concentrations of H2O2 were employed in the O3/H2O2 + BiPO4/UV synergy technique. Based on the BBD model introduced before, we could predict the amount of residual H2O2 of O3/H2O2 under different H2O2 concentrations. We set 70 mg L\(^{-1}\), 140 mg L\(^{-1}\) and 280 mg L\(^{-1}\) as target H2O2 residues; 17.34 mL, 22.09 mL and 47.63 mL H2O2 were selected as initial concentrations.

Table 3 shows various experimental parameters. Under these treatment conditions, we compared the TOC removal rates between BiPO4/UV and UV after the treatment of O3/H2O2. Fig. 6(a) shows that BiPO4 can significantly improve TOC removal under about 70 mg L\(^{-1}\) residual H2O2. The TOC removal was 2.8 times that of the treatment without BiPO4 addition. However, along with the increase in residual H2O2, the mineralization ability of BiPO4/UV was inhibited. We can see from Fig. 6(b) and (c) that the mineralization efficiency of BiPO4/UV was lower than that of the treatment without the BiPO4 addition in the initial 60 and 90 minutes. This phenomenon can be explained by the following equation:28

![Fig. 4 Comparison of H2O2 utilization in different processes. The concentration of thiourea was 1.2 g L\(^{-1}\), the concentration of ammonia nitrogen was 140 mg L\(^{-1}\), the initial concentration of H2O2 was 435 mg L\(^{-1}\), O3 concentration was 55.71 mg L\(^{-1}\), UV intensity was 4.73 mW cm\(^{-2}\), and the BiPO4 loading was 0.5 g L\(^{-1}\).](image)

![Fig. 5 DMPO spin-trapping ESR spectra under UV irradiation for 2 min at room temperature water in the presence of BiPO4, H2O2 or both BiPO4 and H2O2.](image)

![Fig. 6(a) Comparison of H2O2 utilization in different processes. The concentration of thiourea was 1.2 g L\(^{-1}\), the concentration of ammonia nitrogen was 140 mg L\(^{-1}\), the initial concentration of H2O2 was 435 mg L\(^{-1}\), O3 concentration was 55.71 mg L\(^{-1}\), UV intensity was 4.73 mW cm\(^{-2}\), and the BiPO4 loading was 0.5 g L\(^{-1}\).](image)
H₂O₂ + 2h⁺ → O₂ + 2 H⁺  \hspace{1cm} (5)

Excess H₂O₂ might be absorbed on the surface of the BiPO₄ photocatalyst and can react with the holes on the surface of the catalyst. Since holes govern the mineralization efficiency of thiourea, consumption of holes by the absorbed H₂O₂ can result in retarded photocatalytic mineralization efficiency of thiourea. Also, excessive H₂O₂ can counteract the synergy between H₂O₂ residues and BiPO₄ photocatalyst. Excessive H₂O₂ may scavenge the holes as well as ·OH generated by e⁻ and H₂O₂. Thus, adequate H₂O₂ can improve the synergy between residual H₂O₂ and BiPO₄, but superfluous H₂O₂ may cause negative effects and lead to the decline in the mineralization efficiency of the O₃/H₂O₂ + BiPO₄/UV synergy technique.

As shown in Fig. 7, we also investigated the residual H₂O₂ consumption rate by BiPO₄/UV under conditions described in Table 3. The consumption rate of residual H₂O₂ by UV was calculated under 70 mg L⁻¹, 140 mg L⁻¹ and 280 mg L⁻¹ H₂O₂ concentrations, which conformed to pseudo first order reaction kinetics (eqn (6)):

\[
\frac{-\ln \left( \frac{c[H₂O₂]_t}{c[H₂O₂]₀/average} \right)}{c[H₂O₂]₀} = k₀t + c \quad (6)
\]

Here, \(k₀\) is the reaction kinetic constant, \(c\) is the intercept, \(c[H₂O₂]_t\) is the H₂O₂ concentration after reaction for different periods, and \(c[H₂O₂]₀\) is the initial H₂O₂ concentration. The residual H₂O₂ consumption rates by the BiPO₄/UV system with different H₂O₂ concentrations were fit to eqn (7):

\[
\frac{-\ln \left( \frac{c[H₂O₂]_t}{c[H₂O₂]₀/average} \right)}{c[H₂O₂]₀} = k₀t^2 + k₄t + c \quad (7)
\]

Here, \(k₀\) and \(k₄\) are the coefficients of the BiPO₄/UV system with different H₂O₂ residues, \(c\) is the intercept, \(c[H₂O₂]_t\) is the H₂O₂ concentration after reaction for different periods, and \(c[H₂O₂]₀\) is the initial H₂O₂ concentration.

As shown in Fig. 7, BiPO₄ can accelerate H₂O₂ consumption under 70 mg L⁻¹ of residual H₂O₂. Nevertheless, along with the increase in residual H₂O₂ to 140 mg L⁻¹ and 280 mg L⁻¹, BiPO₄ inhibited H₂O₂ consumption at the beginning; however, after

### Table 3: Different experimental parameters for the O₃/H₂O₂ treatment

| Run | H₂O₂ (mL) | O₃ (mg L⁻¹) | pH | TOC Observed | TOC Predicted | H₂O₂ Observed | H₂O₂ Predicted |
|-----|-----------|-------------|----|--------------|---------------|---------------|---------------|
| 1   | 17.3      | 57.71       | 9.2| 175.63       | 178           | 74.47         | 70            |
| 2   | 22.1      | 62.88       | 7.5| 174.75       | 172           | 138.10        | 140           |
| 3   | 47.6      | 77.10       | 9.7| 167.75       | 169           | 239.53        | 280           |

Fig. 6 Effect of different H₂O₂ residues of the H₂O₂/O₃ pre-treatment on the TOC removal: parameters carried out according to Run 2 with 74.47 mg L⁻¹ H₂O₂ residues, Run 3 with 138.10 mg L⁻¹ H₂O₂ residues and Run 3 with 239.53 mg L⁻¹ H₂O₂ residues.
the residual H₂O₂ was partially consumed, the consumption rate was expedited and exceeded the rate of the UV system. This phenomenon shows inactivation of H₂O₂ in the BiPO₄/UV system under high concentrations of H₂O₂ residues because UV irradiation is first absorbed by the BiPO₄ photocatalyst. Under this circumstance, less H₂O₂ can be driven to generate ·OH, and the consumption amount of H₂O₂ decreases. Although, e⁻ and h⁺ on the surface of BiPO₄ can consume H₂O₂ as explained before, considering that the amount of the BiPO₄ photocatalyst is constant under these three conditions, the consumption amount of H₂O₂ does not change. Thus, the consumption rate of H₂O₂ in BiPO₄/UV post-treatment decreases along with the increase in H₂O₂ concentration. This influences the TOC removal rate of the O₃/H₂O₂ + BiPO₄/UV synergy technique and also the utilization efficiency of the H₂O₂ reagent.

3.5 Effect of photocatalyst loading

The amount of BiPO₄ is another important parameter in the O₃/H₂O₂ + BiPO₄/UV synergy technique. To investigate the effect of BiPO₄ loading on the TOC removal of thiourea by the O₃/H₂O₂ + BiPO₄/UV synergy technique, 0.2 g L⁻¹, 0.5 g L⁻¹, 1.0 g L⁻¹ and 1.5 g L⁻¹ of BiPO₄ were loaded in the post-treatment process. We used TOC removal to show the treatment effect and used the ratio between the TOC removal and the BiPO₄ loading to show the catalyst efficiency. As shown in Fig. 8, when the amount of BiPO₄ was increased from 0.2 g L⁻¹ to 0.5 g L⁻¹, the TOC removal improved from 6.125 mg L⁻¹ to 30.875 mg L⁻¹ and the catalyst efficiency was greatly enhanced. However, upon further increasing the BiPO₄ loading to 1.0 g L⁻¹ and 1.5 g L⁻¹, neither the TOC removal nor the catalyst efficiency decreased significantly, revealing negative effect on thiourea mineralization. This phenomenon showed a similar tendency to that reported in other researches: the mineralization efficiency cannot always increase with the increase in catalyst loading. Many studies have shown that the mineralization efficiency of a photocatalyst is strongly affected by the number of active sites and the photoabsorption ability of the catalyst used. Adequate catalyst loading increases the generation rate of e⁻/h⁺ pairs; hence, we observe the formation of ·OH for enhancing photodegradation and the formation of holes for enhancing mineralization. However, an excess dosage of the catalyst decreases light penetration via the shielding effect of suspended particles and thereby reduces the degradation and mineralization rates. Although the O₃/H₂O₂ + BiPO₄/UV synergy technique exhibits a synergistic effect between H₂O₂ and BiPO₄, it still cannot avoid the shielding effect. Excess BiPO₄ reduces the incident light intensity by reflection despite the large number of active sites present.

3.6 Mineralization mechanism of thiourea

To elucidate the degradation pathways of thiourea by the O₃/H₂O₂ + BiPO₄/UV synergy technique, the reaction intermediates were detected by UPLC-IM-QTOF-MS (ESI, Fig. S4†); four compounds were identified with peaks of m/z 107 and m/z 126 after O₃/H₂O₂ treatment as well as m/z 102 and m/z 74 after BiPO₄/UV treatment. Product 1 was identified as thiourea dioxide with m/z 107, whereas product 2 was identified as melamine with m/z 126. Besides, after the treatment of BiPO₄/UV, product 3 was identified as biuret with m/z 102.

Based on the analytical intermediates mentioned above, the transformation pathway of thiourea by the O₃/H₂O₂ + BiPO₄/UV synergy technique is illustrated in Fig. 9. The first step of the O₃/H₂O₂ treatment mainly contributed to thiourea degradation by hydroxyl radicals together with direct oxidation by hydrogen peroxide and ozone. Thiourea was converted to thiourea dioxide and melamine. We predicted that with further oxidation of hydroxyl radicals, an unstable intermediate was generated and polymerized into melamine immediately.

The mechanism of hydroxyl radicals’ oxidation mainly occurred via the following two steps: first, the addition to unsaturated carbon; second, hydrogen abstraction from saturated carbon. According to this, hydroxyl radicals were weak in melamine mineralization. However, the treatment of BiPO₄/UV after O₃/H₂O₂ not only increased the amount of hydroxyl...
radicals, but also introduced the process of hole mineralization. Thus, after the first step of O$_3$/H$_2$O$_2$, BiPO$_4$/UV served as the second step to generate holes that carried out the electron transfer oxidation so that melamine and thiourea dioxide can be further transformed into biuret and then mineralized into H$_2$O and CO$_2$. In addition, the H$_2$O$_2$ residues from O$_3$/H$_2$O$_2$ not only increased the separation of e$^-$/h$^+$ but also induced ·OH generation through the reaction between e$^-$ and H$_2$O$_2$; thus, more ·OH species could be generated, which contributed to acceleration of thiourea degradation and mineralization. No thiourea was detected after treatment with the O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique, and it was transformed into substances introduced before without biotoxicity, which can be further treated by biological methods in a municipal wastewater treatment plant.

4. Conclusions

TOC removal, H$_2$O$_2$ utilization and the transformation pathway of thiourea by the newly invented O$_3$/H$_2$O$_2$ + BiPO$_4$/UV synergy technique was investigated in this study. Higher mineralization and degradation efficiency of thiourea was attained compared with that of O$_3$/H$_2$O$_2$ and BiPO$_4$/UV/H$_2$O$_2$ single-processes and O$_3$/H$_2$O$_2$ + UV process. Thiourea could be completely transformed into substances without biotoxicity. The synergy between H$_2$O$_2$ and BiPO$_4$ improved the TOC removal and also the utilization of residual H$_2$O$_2$ left from the O$_3$/H$_2$O$_2$ treatment. H$_2$O$_2$ captured e$^-$ on BiPO$_4$, which increased the separation of e$^-$ and h$^+$ and generated more ·OH in a shorter period. The amount of added H$_2$O$_2$ influenced both O$_3$/H$_2$O$_2$ and BiPO$_4$/UV steps, especially BiPO$_4$/UV, because the addition of excess H$_2$O$_2$ tended to generate more residual H$_2$O$_2$, which influenced the synergy between H$_2$O$_2$ and BiPO$_4$ and decreased the amount of TOC removal. Excessive catalyst loading showed a negative effect on the mineralization efficiency. O$_3$/H$_2$O$_2$ mainly degraded thiourea into thiourea dioxide and melamine by ·OH, and BiPO$_4$/UV degraded them into biuret and methyl carbamate, followed by their further mineralization into CO$_2$ and H$_2$O.

Conflicts of interest

The authors have no conflicts of interest to declare.

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