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## Photocatalytic performance of biochar-modified $\text{TiO}_2$ ( $\text{C}/\text{TiO}_2$ ) for ammonia–nitrogen removal†

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Biochar-modified  $\text{TiO}_2$  ( $\text{C}/\text{TiO}_2$ ) was prepared by a sol-gel method in this study to improve the photocatalytic capacity for ammonia–nitrogen ( $\text{NH}_3\text{-N}$ ) removal from aqueous solutions. The results showed that biochar was successfully modified on  $\text{TiO}_2$  and helped improve its photocatalytic performance for pollutant degradation. The removal capacity of ammonia–nitrogen on the synthesized photocatalyst performed well at pH 10 with 1 g  $\text{L}^{-1}$   $\text{C}/\text{TiO}_2$  under both 60 (12.25 mg  $\text{g}^{-1}$ ) and 120 min (16.31 mg  $\text{g}^{-1}$ ) irradiation (xenon lamp, AM1.5, 25 A). Characterization of  $\text{C}/\text{TiO}_2$  through scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectrometry (FT-IR) analyses showed the successful introduction of biochar on  $\text{TiO}_2$ . SEM-EDS and BET analyses displayed that  $\text{C}/\text{TiO}_2$  had a larger surface area and more pores than the raw materials. XRD spectroscopy illustrated that  $\text{C}/\text{TiO}_2$  had typical characteristic peaks of anatase- $\text{TiO}_2$  and presented a good photocatalytic degradation performance. It was confirmed from XPS and FT-IR analyses that  $-\text{COOH}$  groups were present in  $\text{C}/\text{TiO}_2$  and originated from biochar modification, and these enhanced the photocatalytic performance. Through radical quenching experiments, it was found that superoxide radicals ( $\text{O}_2^-$ ) played a dominant role in  $\text{NH}_3\text{-N}$  photocatalytic reactions with hydroxyl radicals ( $\text{OH}$ ) and valence band holes ( $\text{h}^+$ ) playing a synergistic role.  $\text{N}_2$  was the main degradation product after 6 h  $\text{NH}_3\text{-N}$  photocatalytic degradation, which was much larger than  $\text{NO}_3^-/\text{NO}_2^-$  (both almost undetected) and  $\text{NH}_3$  (ca. 2 times lower than  $\text{N}_2$ ). The new composite  $\text{C}/\text{TiO}_2$  has potential for ammonia–nitrogen degradation in wastewater treatment and favorable for treating sewage sludge.

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### 1. Introduction

In recent years, water pollution has become and increasing concern attracting widespread attention. Population growth and industrial development have led to a range of serious environmental problems, including pollution from ever-increasing wastewater discharges. In 2020, 984-thousand tons of  $\text{NH}_3\text{-N}$  was discharged in China, which came from industrial, agricultural, and domestic wastewaters. Among this, more than 70% of  $\text{NH}_3\text{-N}$  originated from domestic wastewater (707-thousand tons).<sup>1</sup> An excess of  $\text{NH}_3\text{-N}$  in water can have detrimental consequences, including causing algal bloom, red tide, and the reproduction of algae, which can indirectly harm peoples' health.<sup>2,3</sup> It is thus essential to treat  $\text{NH}_3\text{-N}$ -contaminated water appropriately.

Blow-off, adsorption, and chemical precipitation are some common treatment methods for treating such waters, especially

for low-concentration  $\text{NH}_3\text{-N}$  polluted wastewaters. However, there are some limitations to these methods. For example, free  $\text{NH}_3$  can lead to air pollution, which is a health risk to people.<sup>4</sup> Adsorption is a reversible process, which can thus limit its application because of both efficiency and cost concerns.<sup>5,6</sup> Taking the deficiencies of traditional methods into consideration, it is crucial to explore new technologies.<sup>7</sup> Effectively changing  $\text{NH}_3\text{-N}$  into innocuous nitrogen is regarded by many as a perfect way to treat  $\text{NH}_3\text{-N}$  polluted wastewater.

Photocatalytic methods involve a newly developed advanced oxidation process, and have been proved to be the most promising technology nowadays due to their high efficiency, low toxicity, and environmental friendliness.<sup>8,9</sup> Semiconductor powders are widely used as photocatalysts.<sup>10</sup> Specifically,  $\text{TiO}_2$  has notable advantages, including stable chemical properties, high photocatalytic activity, nontoxicity, strong oxidizing ability, and low cost.<sup>11,12</sup> It is the most used conventional photocatalyst and has shown good achievements in treating  $\text{NH}_3\text{-N}$  pollutants in water.<sup>7</sup> There are some research reports confirming that  $\text{NH}_3\text{-N}$  can be removed efficiently by  $\text{TiO}_2$  photocatalysts from aqueous solutions.<sup>4,13</sup>  $\text{TiO}_2$  has three main crystalline phases: anatase, rutile, and brookite. Among these, anatase  $\text{TiO}_2$  shows

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the most prominent photocatalytic activity.<sup>14</sup> However, it still has some drawbacks.  $\text{TiO}_2$  is limited by its large bandgap ( $E_g > 3.2$  eV); thus, it can only be excited by about 7% energy of the solar light. Moreover, it is also limited by fast electron–hole recombination.<sup>15,16</sup> Thus, it is essential to overcome these difficulties to facilitate the use of  $\text{TiO}_2$  as per its potential.

Researchers have devoted effort to modifying  $\text{TiO}_2$ , for instance by ion doping, semiconductor composite modification, noble metal deposition, *etc.* to enhance the performance of photocatalysts. Non-metal anion doping has been demonstrated to be an effective way to improve the photoactivity, with C-doping the most common one reported. Compared to traditional  $\text{TiO}_2$ , carbon-doped  $\text{TiO}_2$  has a much narrower bandgap, which extends its photoresponse to visible light for enhancement of its photocatalytic activity and inhibits the generation of electron–hole pairs.<sup>10,17,18</sup>

Recently, various allotropes of carbon materials have been adopted to modify  $\text{TiO}_2$ . Biochar is a carbonaceous material with a high surface area, porous structure, low cost, and good sustainability.<sup>19,20</sup> There is a large amount of municipal sewage sludge generated as a by-product of wastewater treatment plants, which deserves urgent attention. The beneficial utilization of those solid wastes is an important and advanced way to solve environmental issues compared to traditional methods for its disposal, like incineration, landfill, *etc.* Thus, transforming sewage sludge into biochar was attractive and feasible.<sup>21</sup> Biochar provides a versatile and efficient platform for the synthesis of functionalized carbon materials. Compared to conventional activated carbon, biochar performs much better in  $\text{TiO}_2$  modification due to its greater number of inner elements, such as N, S, and more abundant surface functional groups like carbonyl and carboxy groups.

In our study, the feasibility of biochar-modified  $\text{TiO}_2$  for the photocatalytic decomposition of  $\text{NH}_3\text{-N}$  in wastewater was evaluated. Dehydrated sewage sludge-based biochar was used to prepare a  $\text{C}/\text{TiO}_2$  composite photocatalyst through a sol–gel method. The removal capacity of  $\text{NH}_3\text{-N}$  was studied under different operations. SEM-EDS, BET, XRD, XPS, and FT-IR characterizations of the photocatalysts were performed and discussed in detail for better understanding the performance of the biochar-modified  $\text{TiO}_2$  for  $\text{NH}_3\text{-N}$  removal. It was hoped it would achieve a combination of adsorption and photocatalytic activity for  $\text{NH}_3\text{-N}$  treatment, considering that various elements in biochar have integrated effects on photocatalytic reactions compared to a single element material. Moreover, Li Zhang *et al.* proved that with the help of adsorptive biochar, pollutants could easily gather around the photocatalysts and be efficiently removed by the accelerated photocatalytic reactions.<sup>22</sup> It was expected that this would be helpful for the innovative modification of titanium dioxide for use as a photocatalyst to realize resource utilization through  $\text{NH}_3\text{-N}$  degradation.

## 2. Materials and methods

### 2.1 Preparation of $\text{C}/\text{TiO}_2$ photocatalyst

Dehydrated sewage sludge from a local municipal wastewater treatment plant (WWTP) was collected as the raw material to

prepare the biochar, as described in our previous work, for further utilization.<sup>23,24</sup>

First, 20 mL ethanol and 7.2 mL butyl titanate were mixed in a container and shaken for 0.5 h (450 rpm). Hydrochloric acid was then added into the solution and stirred together for 0.5 h in order to maintain an acidic condition. Next, 0.2 g biochar powder was added to the above solution and stirred (450 rpm) for another 0.5 h to ensure a thorough mixing. Finally, 5.6 mL deionized water and 4.4 mL ethanol were added to the solution and kept stirring until gel formation.

After achievement of the wet gel, it was sealed for 24 h and then put into an oven (105 °C) for 12 h drying. The xerogel was subsequently ground into powder, and then calcined in a tubular furnace at 500 °C (heating rate: 2 °C min<sup>-1</sup>) for 4 h in a nitrogen atmosphere. After that, the manufactured product was taken out to cool down to room temperature. The product was washed by deionized water several times and dried to obtain the final compound, named as  $\text{C}/\text{TiO}_2$ , with a  $\text{TiO}_2$  and biochar composition.<sup>23</sup>

### 2.2 Experiments

Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) was dissolved in deionized water to prepare  $\text{NH}_3\text{-N}$  bulk solution. As illuminated in Fig. S1 (ESI†), a high-pressure xenon lamp (PL-XQ 500 W) was used as the light source. The details of the xenon lamp are provided in the ESI (Fig. S1†). Here, 100 mL  $\text{NH}_3\text{-N}$  solution (50 mg L<sup>-1</sup>) and a certain amount of the composed photocatalyst were mixed in a 200 mL sealed beaker with magnetic stirring (450 rpm). An outer circulation cooling water system was applied to maintain the reaction system under room temperature. Fig. S2† shows a schematic diagram of the reaction system reaction (see the ESI†). At designed time intervals, samples were taken out and filtered, and the  $\text{NH}_3\text{-N}$  concentration of the supernatant was analyzed *via* a standard method. Excessive doses of dilute sulfuric acid and phenolphthalein solution were provided for tail gas treatment, and the mass of ammonia was determined by the weight deviation after exhaust adsorption.

Quenching agents were added into a series 100 mL  $\text{NH}_3\text{-N}$  (50 mg L<sup>-1</sup>) solutions with 1 g L<sup>-1</sup>  $\text{C}/\text{TiO}_2$  under a high-pressure xenon lamp (AM1.5, 25 A) for 1 h stirring (450 rpm). Samples were taken out and filtered every 20 min, and the concentrations of various nitrogen contents in the supernatant were determined in accordance with standard methods (see the ESI†).

$\text{NH}_3\text{-N}$  removal capacity was calculated by the following equation.

$$X_1 = V \times (C_0 - C_1)/M \quad (1)$$

where  $C_0$  and  $C_1$  (mg L<sup>-1</sup>) are the initial  $\text{NH}_3\text{-N}$  concentration and  $\text{NH}_3\text{-N}$  concentration at reaction time  $t$  (min), respectively,  $V$  is the volume of the solution (L),  $M$  is the weight of the photocatalyst or biochar (g), and  $X_1$  is the  $\text{NH}_3\text{-N}$  removal capacity (mg g<sup>-1</sup>).

Determination of the  $\text{NH}_3\text{-N}$  concentration was done in accordance with the standard method HJ 535-2009 (Nessler's reagent spectrophotometry). The standard method HJ/T346-



2007 (water quality – determination of nitrate–nitrogen – ultraviolet spectrophotometry method) and GB 7493-87 (water quality – determination of nitrogen(nitrite) – spectrophotometric method) were used to determine the concentration of  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , respectively. A PHS-4 pH meter (Shanghai INESA Scientific Instrument Co., Ltd) was used to measure the pH values for the samples.

The commercial titanium dioxide (anatase- $\text{TiO}_2$ ) adopted in this work was analytical grade powder ( $\geq 99.0\%$ ) and was purchased from Kelong Chemical Reagent Co., Ltd. All other chemicals and reagents used to prepare the photocatalysts were analytical grade and provided by Kelong Chemical Reagent Co., Ltd, as well. Propan-2-ol (IPA) and potassium iodide (KI) were applied as quenching agents and both were analytical grade and obtained from Kelong Chemical Reagent Co., Ltd. Nitro blue tetrazolium (NBT) was applied as a quenching agent and was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

All experiments were carried out twice under identical conditions, and the results were collected as the mean values.

### 2.3 Characterization

SEM-EDS was used to determine the surface morphology of the raw materials and the composed photocatalyst. This was completed at the Analytical and Testing Center of Sichuan University using a JSM-7500F field emission scanning electron microscope (JEOL): acceleration voltage of 0.1 kV to 30 kV, resolution of 1.0 nm (15 kV), 1.4 nm (1 kV), and magnification of  $\times 25 \times 800000$ . The BET surface area and pore volume of the samples were measured using a TriStar II 3020 Version 3.02 (Micromeritics Instrument Corporation).

X-Ray diffraction spectroscopy (XRD, EMPYREAN, PANalytical B.V.) was used for phase identification with  $\text{Cu K}\alpha$  radiation at 1.54 Å (X-ray wavelength) from  $10^\circ$  to  $70^\circ$  ( $\theta$ ). The surface element properties were analyzed by X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos) using an  $\text{Al K}\alpha$  source. The functional groups of the materials were detected by Fourier-transform infrared spectroscopy (FT-IR, FNicolet 6700, Thermo Elemental) within the range 4000–400  $\text{cm}^{-1}$ .

## 3. Results and discussion

### 3.1 $\text{NH}_3\text{-N}$ removal

The photocatalytic performance of the biochar, commercial  $\text{TiO}_2$ , and the composed  $\text{C/TiO}_2$  were investigated by adding 1 g  $\text{L}^{-1}$  of biochar,  $\text{TiO}_2$ , or  $\text{C/TiO}_2$  into a series of 100 mL of 50 mg  $\text{L}^{-1}$   $\text{NH}_3\text{-N}$  solutions under the dark and photocatalytic conditions, respectively. The dark groups were carried out under constant stirring (450 rpm) without lighting for 1 and 2 h, while the photocatalysis groups were analyzed with fully mixing under xenon lighting (AM1.5, 25 A) for 1 and 2 h. Also, control group 1 was a blank solution without any adsorbent under dark condition and control group 2 was a blank sample without any photocatalyst under irradiation.

As shown in Fig. 1, the removal capacity of  $\text{NH}_3\text{-N}$  was much different under the varied reaction conditions. Under the dark

condition, there was insignificant  $\text{NH}_3\text{-N}$  removal by all the products (biochar, commercial  $\text{TiO}_2$ , and  $\text{C/TiO}_2$ ), namely lower than 5 mg  $\text{g}^{-1}$  for 1 h and 7 mg  $\text{g}^{-1}$  for 2 h. Compared with the results for control group 1, none of them presented adsorptive capacity for  $\text{NH}_3\text{-N}$  removal. The slight decrease in  $\text{NH}_3\text{-N}$  concentration under the dark conditions was mainly due to the solution stirring and blowing off the ammonia during the experiments for the control groups. Febio Dalanta *et al.* found there was approximately no  $\text{NH}_3\text{-N}$  adsorption on  $\text{TiO}_2$ ,<sup>25</sup> which was the same as our experimental results. While under irradiation, compared to control group 2, both the commercial  $\text{TiO}_2$  and  $\text{C/TiO}_2$  photocatalysts performed well in  $\text{NH}_3\text{-N}$  degradation, with a similar high removal capacity. The  $\text{NH}_3\text{-N}$  removal capacity was *ca.* 12 mg  $\text{g}^{-1}$  for 1 h and 16 mg  $\text{g}^{-1}$  for 2 h on  $\text{C/TiO}_2$ , respectively, which were slightly higher than on commercial  $\text{TiO}_2$ .  $\text{C/TiO}_2$  had a much better  $\text{NH}_3\text{-N}$  removal capacity almost 3 times higher than the one in the dark conditions. It was demonstrated that with external illumination, the degradation ability of  $\text{C/TiO}_2$  on  $\text{NH}_3\text{-N}$  was effectively enhanced by photocatalysis. In terms of the preparation and beneficial utilization of waste, the biochar-modified  $\text{TiO}_2$  has great potential for use in ammonia–nitrogen wastewater treatment.

Taking the application of the composite photocatalysts into consideration, natural waters from Jiang'an River and Mingyuan Lake in our campus were collected and tested (Experiment details are provided in the ESI†). The  $\text{NH}_3\text{-N}$  removal capacity was *ca.* 6.58 mg  $\text{g}^{-1}$  for the Jiang'an River sample and 7.89 mg  $\text{g}^{-1}$  for the Mingyuan Lake sample on  $\text{C/TiO}_2$ , respectively, which were similar to the ones achieved by the commercial  $\text{TiO}_2$  (7.03 mg  $\text{g}^{-1}$  for Jiang'an River water and 7.52 mg  $\text{g}^{-1}$  for Mingyuan Lake water, respectively). Actually, the  $\text{NH}_3\text{-N}$  removal capacities on  $\text{C/TiO}_2$  and  $\text{TiO}_2$  were relatively lower than the one for the synthesized  $\text{NH}_3\text{-N}$  wastewater in the lab due to the complexity of the natural water bodies. The results showed the great potential for practical use of  $\text{C/TiO}_2$  for  $\text{NH}_3\text{-N}$  removal from natural water resources.

Table 1 shows the removal capacity of  $\text{NH}_3\text{-N}$  on different photocatalysts in similar studies. As listed in Table 1, the photocatalytic effect  $\text{C/TiO}_2$  for  $\text{NH}_3\text{-N}$  removal was superior to most products. Specifically, the  $\text{NH}_3\text{-N}$  removal capacity on  $\text{C/TiO}_2$  was 16.31 mg  $\text{g}^{-1}$  in our study and was obviously higher than the other photocatalysts under the same irradiation time (2 h). Compared to  $\text{B-SiO}_2@\text{TiO}_2$  (100 : 5) at 150 min and  $\text{Cu/TiO}_2$  at 180 min,  $\text{C/TiO}_2$  had an approximate efficiency for  $\text{NH}_3\text{-N}$  removal in a relatively short reaction time (120 min). In comparison with other photocatalysts,  $\text{C/TiO}_2$  has prominent advantages due to its simple operation, waste sustainable utilization, easy availability, as well as high efficiency for  $\text{NH}_3\text{-N}$  degradation.

### 3.2 Photocatalysis

**3.2.1 Effect of the lighting.** The wavelength and luminous energy are different for UV light, visible light, and sunlight. Thus, the effects of the light source and irradiation intensity on  $\text{NH}_3\text{-N}$  removal were discussed in the study. Three light filters



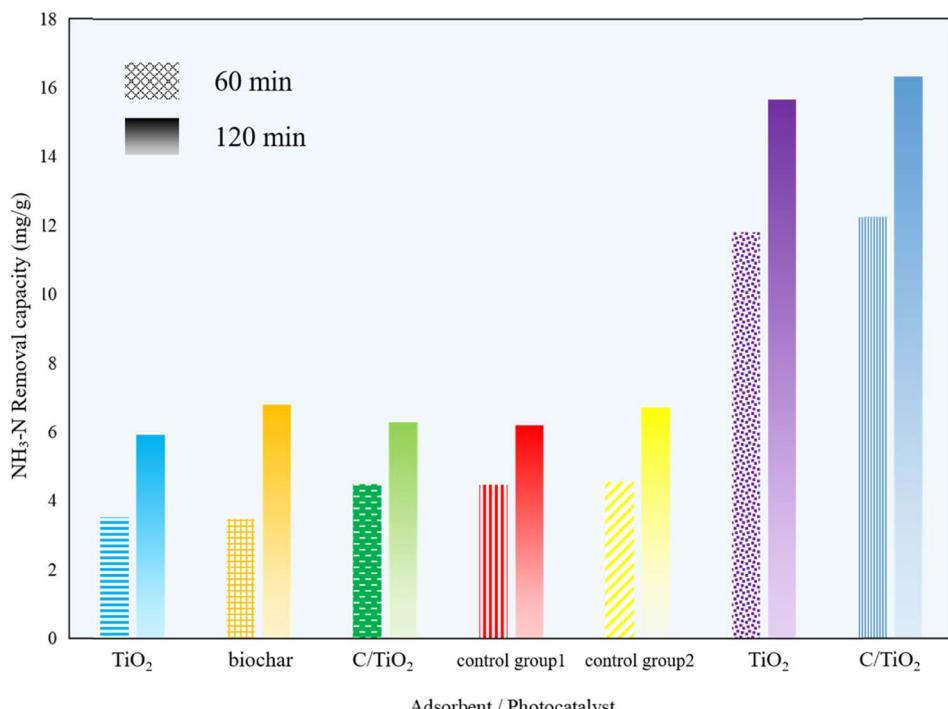


Fig. 1 NH<sub>3</sub>-N removal capacity under different reaction condition times (AM1.5, 25 A, 1 g L<sup>-1</sup> of photocatalyst, pH 10.0, C<sub>0</sub> = 50 mg L<sup>-1</sup>).

Table 1 Degradation of NH<sub>3</sub>-N on different photocatalysts

Photocatalyst	Light source	Light power (W)	pH	Irradiation time (min)	Removal capacity (mg g <sup>-1</sup> )	Reference
C/TiO <sub>2</sub>	Simulated sunlight	500	10.0	120	16.31	This study
TiO <sub>2</sub> /MPVA-Alg	UV	250	10.5	120	1.575	Zendezaban <i>et al.</i> <sup>26</sup>
TiO <sub>2</sub> /perlite	UV	125	11.0	120	14.01	Shavisi <i>et al.</i> <sup>27</sup>
B-SSiO <sub>2</sub> @TiO <sub>2</sub> (100 : 5)	Visible light	100	8.0	150	18.36	Zhou <i>et al.</i> <sup>28</sup>
Cu/TiO <sub>2</sub>	Sunlight	—	—	180	17.50	Wang <i>et al.</i> <sup>29</sup>

(AM1.5, UV cut-off at 400 nm, UV) were installed on a xenon lamp to get different wavelength conditions, which were simulated sunlight (0–2500 nm), visible light (400–760 nm), and ultraviolet light (250–400 nm), respectively. The light intensity was set between 50 mW cm<sup>-2</sup> (low) to 100 mW cm<sup>-2</sup> (high) *via* adjusting the current intensity from 15–25 A. Light source experiments were carried out with a current intensity at 25 A, while different luminous energy experiments were adjusted between 15–25 amp under simulated sunlight (AM1.5) operation.

As shown in Fig. 2a, there was a remarkable light-utilization ability of C/TiO<sub>2</sub> for NH<sub>3</sub>-N degradation. The removal ability through NH<sub>3</sub>-N degradation by C/TiO<sub>2</sub> under the three kinds of light sources increased with prolonging the lighting time, and presented different performances. The photocatalytic reaction excited under simulated sunlight displayed the most prominent capacity compared with the other two light sources. After 60 min, the NH<sub>3</sub>-N removal capacity under simulated sunlight was up to 12.25 mg g<sup>-1</sup>, which was higher than both that under UV and visible light.

As is widely known, TiO<sub>2</sub> can be efficiently excited by the ultraviolet part of sunlight, while an absorption band change can be subsequently found in the composed material.<sup>30–33</sup> Here, C/TiO<sub>2</sub> could effectively absorb ultraviolet light, and also efficiently utilize the relatively long wavelength of visible light. Sunlight represents the sum energy of visible light and ultraviolet light, which made the total light energy absorbed by C/TiO<sub>2</sub> greater than that for ultraviolet light, and led to the improved light-utilization efficiency and removal capacity of NH<sub>3</sub>-N. Thus, C/TiO<sub>2</sub> has advantages in light utilization and photocatalysis compared to the common TiO<sub>2</sub>.

As illuminated in Fig. 2b, the reaction was conducted under a xenon lamp (AM1.5), while the luminous power was adjusted within 15–25 A (300–500 W, over a light intensity range of 50–100 mW cm<sup>-2</sup>). With the increment in light power, the NH<sub>3</sub>-N treatment efficiency by C/TiO<sub>2</sub> also increased. After 60 min, the NH<sub>3</sub>-N removal capacities under the low, medium and high light intensity power were 9.34, 10.87, and 12.25 mg g<sup>-1</sup>, respectively. With the enhancement of the light intensity, more effective photons were generated and the light penetration



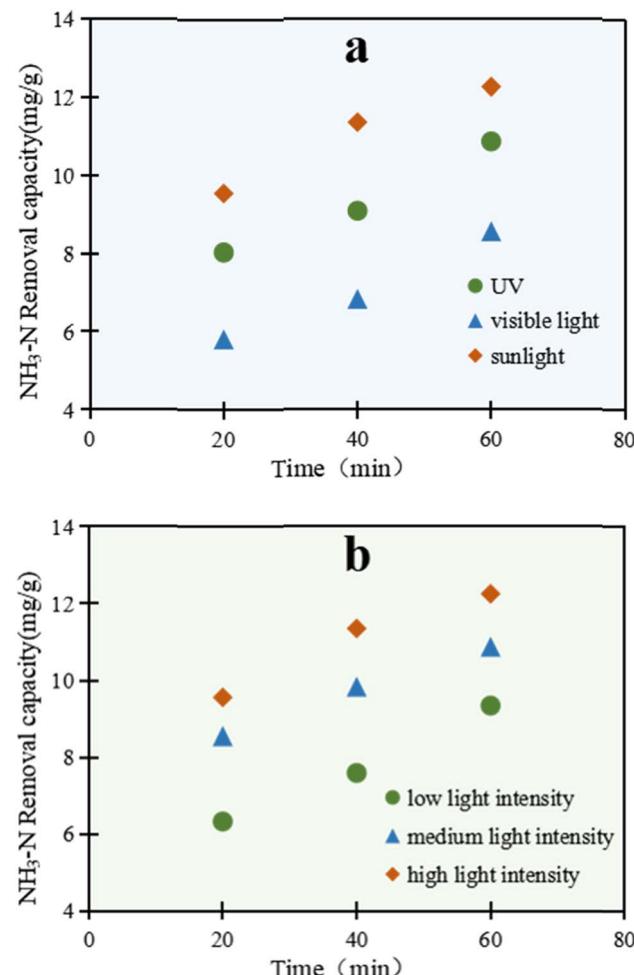


Fig. 2  $\text{NH}_3\text{-N}$  removal capacity under different irradiation intensities by the  $\text{C}/\text{TiO}_2$  photocatalysts, with varying the (a) light source ( $25 \text{ A}, 1 \text{ g L}^{-1} \text{ C}/\text{TiO}_2, \text{pH } 10.0, \text{C}_0 = 50 \text{ mg L}^{-1}$ ); and (b) light intensity, from a low to high intensity of  $50\text{--}100 \text{ mW cm}^{-2}$  ( $\text{AM1.5}, 1 \text{ g L}^{-1} \text{ C}/\text{TiO}_2, \text{pH } 10.0, \text{C}_0 = 50 \text{ mg L}^{-1}$ ).

ability was improved too. Meanwhile, the probability of electron transition was strengthened, with a higher generation of active free radicals on the  $\text{C}/\text{TiO}_2$  surface. Consequently, the photocatalytic degradation capacity for  $\text{NH}_3\text{-N}$  increased. Moreover, the increased photons made more  $\text{NH}_3\text{-N}$  molecules absorb light energy and become activated, which was conducive to the photocatalytic reactions. However, with further increasing the light intensity, the  $\text{NH}_3\text{-N}$  photodegradation by  $\text{C}/\text{TiO}_2$  became stable and showed insignificant further change due to the limitation of the light quantum efficiency. Here, the probabilities of collision between activated electrons and holes were greatly enhanced and consequently led to annihilation under strong light irradiation; however, when the amount of  $\text{C}/\text{TiO}_2$  was constant, the number of electron-hole pairs did not increase with the increment in the number of photons.<sup>34</sup>

**3.2.2 Effect of the irradiation time.** First,  $1 \text{ g L}^{-1} \text{ C}/\text{TiO}_2$  was added into  $100 \text{ mL} \text{NH}_3\text{-N}$  solution ( $50 \text{ mg L}^{-1}$ , pH 10.0), and the photocatalytic reaction was carried out under a xenon lamp (AM1.5, 25 A) for 6 h. Samples were taken out and filtered at set

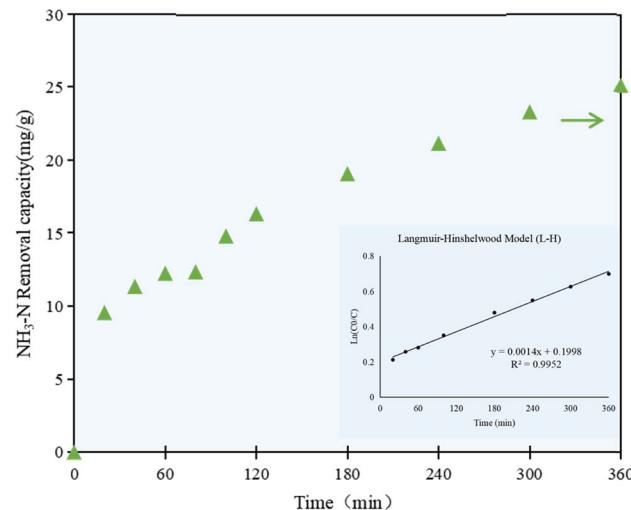


Fig. 3  $\text{NH}_3\text{-N}$  removal capacity at different irradiation times by the  $\text{C}/\text{TiO}_2$  photocatalysts ( $\text{AM1.5}, 25 \text{ A}, 1 \text{ g L}^{-1} \text{ C}/\text{TiO}_2, \text{pH } 10.0, \text{C}_0 = 50 \text{ mg L}^{-1}$ ).

time intervals, and the  $\text{NH}_3\text{-N}$  concentration of the supernatant was analyzed.

As shown in Fig. 3, the  $\text{NH}_3\text{-N}$  removal capacity by the  $\text{C}/\text{TiO}_2$  photocatalyst increased with prolonging the irradiation time, while the  $\text{NH}_3\text{-N}$  concentration in the solution decreased simultaneously. The  $\text{NH}_3\text{-N}$  removal capacity increased rapidly to  $12.25 \text{ mg g}^{-1}$  in the first 60 min, and then had a continuing and stable increment of  $11.05 \text{ mg g}^{-1}$  after 5 h reaction, while it was still slightly raised by *ca.*  $2.0 \text{ mg g}^{-1}$  at 6 h of reaction. A high  $\text{NH}_3\text{-N}$  removal capacity was achieved at the end of the experiment, which was more than 2 times higher than that at 1 h reaction.

The  $\text{NH}_3\text{-N}$  removal capacity on  $\text{C}/\text{TiO}_2$  showed a rapid growth phase in the first 60 min, then increased steadily in the following 300 min, which proved that the change in the removal capacity was continuous and stable with prolonging the irradiation time. While the photocatalytic activity on  $\text{C}/\text{TiO}_2$  gradually increased with the progression of the reaction, the  $\text{NH}_3\text{-N}$  concentration decreased steadily and reached a plateau due to the limited pollutant available. Taking energy-saving and efficiency into consideration, further experiments were performed under light for 60 min.

According to the concentration of ammonia-nitrogen in the solution at the set irradiation time intervals, the kinetic model for the photocatalytic reaction was studied. As shown in Fig. 3, the correlation coefficient  $R^2$  was calculated to be 0.9952, which proved that the photocatalytic reaction of  $\text{C}/\text{TiO}_2$  well fitted the Langmuir-Hinshelwood model (L-H). The L-H theory is based on the principles of adsorption and desorption, and it represents a multiphase catalytic mechanism where surface reactions are the controlling steps for the adsorbed molecules. According to the experimental data and the kinetic model, the photocatalytic reaction occurred on the surface of the catalyst, while the rate of the catalytic reaction depended on the reaction between the surface-adsorbed molecules, and the adsorption and desorption processes were in a dynamic equilibrium state.<sup>35</sup>

**3.2.3 Effect of the catalyst dosage.** The dosage of a photocatalyst plays a vital role in the photocatalytic reaction. Here,  $0.5\text{--}2.0\text{ g L}^{-1}$   $\text{C/TiO}_2$  was added into  $100\text{ mL}$  of  $50\text{ mg L}^{-1}$   $\text{NH}_3\text{-N}$  solution ( $\text{pH } 10.0$ ), and the photocatalytic reaction was carried out under a xenon lamp (AM1.5, 25 A) for 1 h. During the reaction, samples were taken out and filtered at set time intervals, and the  $\text{NH}_3\text{-N}$  concentration of the supernatant was analyzed via the standard method.

The  $\text{NH}_3\text{-N}$  photocatalysis removal capacity results with varying the  $\text{C/TiO}_2$  dosage ( $0.5\text{--}2.0\text{ g L}^{-1}$ ) are shown in Fig. 4. It was confirmed that the  $\text{NH}_3\text{-N}$  removal capacity was enhanced with the  $\text{C/TiO}_2$  dosage increasing, and obviously increased from  $9.59\text{ mg g}^{-1}$  to  $12.25\text{ mg g}^{-1}$  as the  $\text{C/TiO}_2$  dosage increased from  $0.5$  to  $1.0\text{ g L}^{-1}$ , while it showed an insignificant increment when the  $\text{C/TiO}_2$  dose was increased further to  $1.5$  and  $2.0\text{ g L}^{-1}$ .

The highest  $\text{NH}_3\text{-N}$  degradation was obtained with  $2\text{ g L}^{-1}$  photocatalyst due to the larger contact surface area, more photocatalytic activity points, and more active free radicals produced. Otherwise, the  $\text{NH}_3\text{-N}$  removal capacity would be affected by the continuous dosage increment. Though a large number of photocatalytic activity sites would be provided by a high photocatalyst concentration, excessive  $\text{C/TiO}_2$  will lead to much higher turbidity in the solution and provide a shielding effect for the lighting, thus weakening the degradation capacity.<sup>36</sup> Meicen Guo *et al.* also demonstrated that the scattering of light to the photocatalyst would be raised by an overdose of CNTS- $\text{TiO}_2$ .<sup>37</sup> In view of the energy and efficiency, a favorable  $1\text{ g L}^{-1}$   $\text{C/TiO}_2$  was adopted in our tests.

**3.2.4 Effect of the pH.** The pH of a solution has a crucial impact on the photocatalytic performance. To test this,  $1\text{ g L}^{-1}$   $\text{C/TiO}_2$  was added into  $100\text{ mL}$   $\text{NH}_3\text{-N}$  solution ( $50\text{ mg L}^{-1}$ ), and the photocatalytic reaction was carried out under a xenon lamp (AM1.5, 25 A) for 1 h. The solution pH was adjusted in the range of pH 3–11 by adding 1 M HCl or NaOH. During the reaction, samples were taken out and filtered at set time

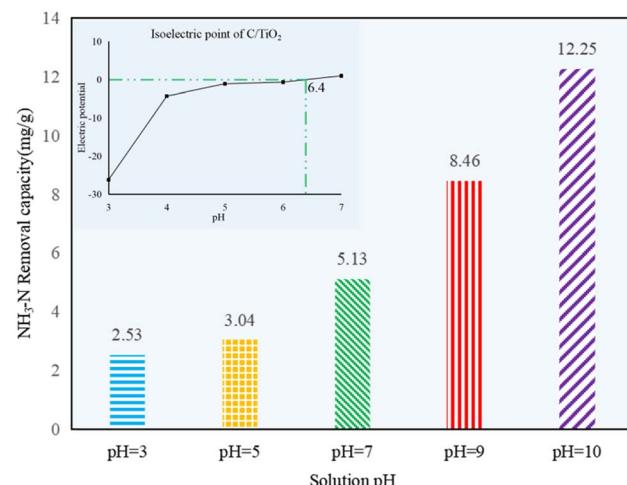


Fig. 5  $\text{NH}_3\text{-N}$  removal capacity at different initial solution pH values (AM1.5, 25 A,  $1\text{ g L}^{-1}$   $\text{C/TiO}_2$ ,  $C_0 = 50\text{ mg L}^{-1}$ ).

intervals, and the  $\text{NH}_3\text{-N}$  concentration of the supernatant was then analyzed.

As shown in Fig. 5, the  $\text{NH}_3\text{-N}$  removal capacity was strongly affected by the solution pH, and it increased obviously with the pH changing from acid to alkaline. Compared to the control group 1 in Fig. 1, there was no efficient  $\text{NH}_3\text{-N}$  removal by photocatalysis in acid conditions, as noted by the very limited reduction in the  $\text{NH}_3\text{-N}$  amount (less than  $3.04\text{ mg g}^{-1}$ , which was lower than the  $4.46\text{ mg g}^{-1}$  of the control group). However, the  $\text{NH}_3\text{-N}$  removal capacity was *ca.* 4 or 5 times higher at pH 10.0 than the ones in acidic solution, indicating the photocatalysis performed better under alkaline conditions.

The surface charge of the photocatalyst and the existing form of  $\text{NH}_3\text{-N}$  in water can seriously be affected by the solution pH. Negative charges appeared on the photocatalyst under alkaline conditions. Here, the  $\text{OH}^-$  concentration was increased while  $\text{H}^+$  concentration was decreased with pH increasing, and more  $\cdot\text{OH}$  would be excited by  $\text{C/TiO}_2$  under light irradiation, so the removal capacity of  $\text{NH}_3\text{-N}$  on  $\text{C/TiO}_2$  was improved.<sup>10</sup> Besides,  $\text{NH}_4^+$  and  $\text{NH}_3$  are two forms of N in  $\text{NH}_3\text{-N}$  solution. More  $\text{NH}_3$  appeared as the pH increased. Satoshi Shibuya *et al.* found that it was much more efficient for photocatalysis when ammonia existed in the molecular form, and  $\text{NH}_3\text{-N}$  removal capacity would be more prominent when mainly molecular ammonia existed.<sup>38</sup> The  $\text{pH}_{\text{pzc}}$  of  $\text{C/TiO}_2$  was around 6.4 (Fig. 5). Thus, the photocatalyst had positive charges on its surface when the solution pH was lower than its  $\text{pH}_{\text{pzc}}$  and displayed negative charges when the solution pH was higher than 6.4. Ammonia can be much easier gathered onto the  $\text{C/TiO}_2$  surface by electrostatic attraction in alkaline solution, while it could hardly be attracted to  $\text{C/TiO}_2$  under acidic condition. However, Marco Altomare *et al.* confirmed that the  $\text{NH}_3\text{-N}$  removal rate would decrease at pH higher than 10.5 due to the competitive adsorption of hydroxide anions on the surface of the photocatalyst.<sup>39</sup> Thus, the  $\text{NH}_3\text{-N}$  removal capacity was much better in an appropriate alkaline environment (pH 10.0).<sup>4</sup>

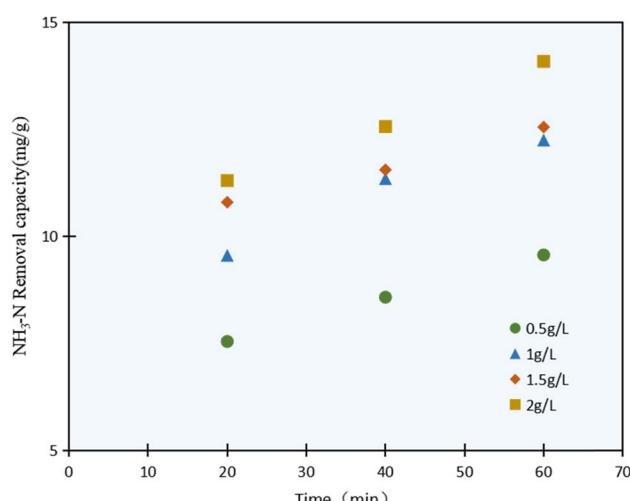


Fig. 4  $\text{NH}_3\text{-N}$  removal capacity with various  $\text{C/TiO}_2$  dosages (AM1.5, 25 A, pH 10.0,  $C_0 = 50\text{ mg L}^{-1}$ ).



### 3.3 Characterization

**3.3.1 SEM-EDS and BET.** As shown in Fig. 6, C/TiO<sub>2</sub> displayed an irregular granular and obvious porous structure compared to commercial TiO<sub>2</sub>. The porous biochar in C/TiO<sub>2</sub> enhanced its ability to attract NH<sub>3</sub>-N around the C/TiO<sub>2</sub> for better photocatalytic reaction.<sup>22</sup> Besides, C/TiO<sub>2</sub> had more pores and a bigger specific surface area than raw biochar according to our previous research, which are favorable for enhancing the NH<sub>3</sub>-N photocatalytic degradation.<sup>40</sup> According to the analysis of the EDS data, the C wt% in C/TiO<sub>2</sub> was *ca.* 17.6% higher than that of pure TiO<sub>2</sub>, while the Ti wt% in C/TiO<sub>2</sub> was 61.0% lower than that of the commercial TiO<sub>2</sub>. These indicate that the introduction of biochar on TiO<sub>2</sub> was successful and stable. Table 2 lists the EDS results for TiO<sub>2</sub>, biochar, and C/TiO<sub>2</sub>, confirming Si, Fe, and other elements were successfully introduced in C/TiO<sub>2</sub> after biochar modification, which enhanced its photocatalytic ability.<sup>41-43</sup>

The N<sub>2</sub> adsorption/desorption isotherms of C/TiO<sub>2</sub> are shown in Fig. 7, where it can be seen there was a hysteresis loop at a relative pressure ( $P/P_0$ ) ranging from 0.6 to 0.85, which illustrated that the biochar-modified TiO<sub>2</sub> exhibited a typical type-IV isotherm with the existence of a mesoporous

Table 2 EDS results for TiO<sub>2</sub>, biochar, and C/TiO<sub>2</sub><sup>a</sup>

Element	TiO <sub>2</sub> (wt%)	Biochar (wt%)	C/TiO <sub>2</sub> (wt%)
C	2.86	11.67	20.46
O	18.53	7.44	17.47
Ti	78.62	—	17.62
Si	—	1.89	3.80
Fe	—	0.65	0.41
Zn	—	16.93	1.40
Other	—	61.42	38.84

<sup>a</sup> C in commercial TiO<sub>2</sub> might arise from the impurities during measurement, while the Au in C/TiO<sub>2</sub> was from the gold-spraying treatment.

structure. From the calculated BET data, the proportion of mesopores was over 90% and the specific surface area of the C/TiO<sub>2</sub> photocatalyst increased from 11.88 (pure TiO<sub>2</sub>) to 119.47 m<sup>2</sup> g<sup>-1</sup> after modification, which was about 9 times higher than that of the pure TiO<sub>2</sub>. The inset in Fig. 7 shows the pore-size distribution for C/TiO<sub>2</sub> and pure TiO<sub>2</sub>, showing that the pure TiO<sub>2</sub> had little mesoporous structure, while the proportion of the mesoporous structure in C/TiO<sub>2</sub> was significantly enhanced, and the total pore volume of C/TiO<sub>2</sub> also showed

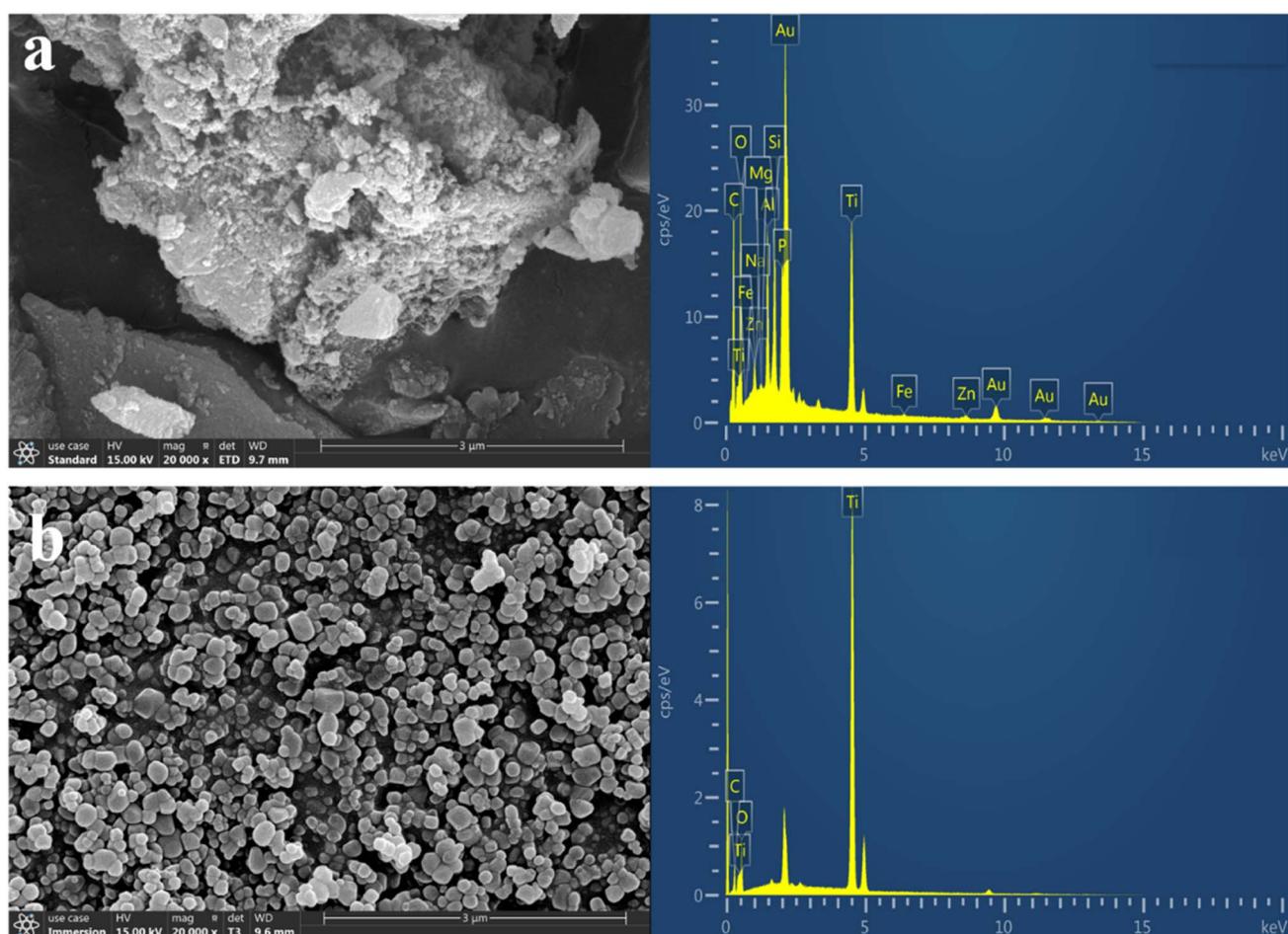


Fig. 6 SEM-EDS analysis for C/TiO<sub>2</sub> and TiO<sub>2</sub> (a) C/TiO<sub>2</sub>; (b) TiO<sub>2</sub>.



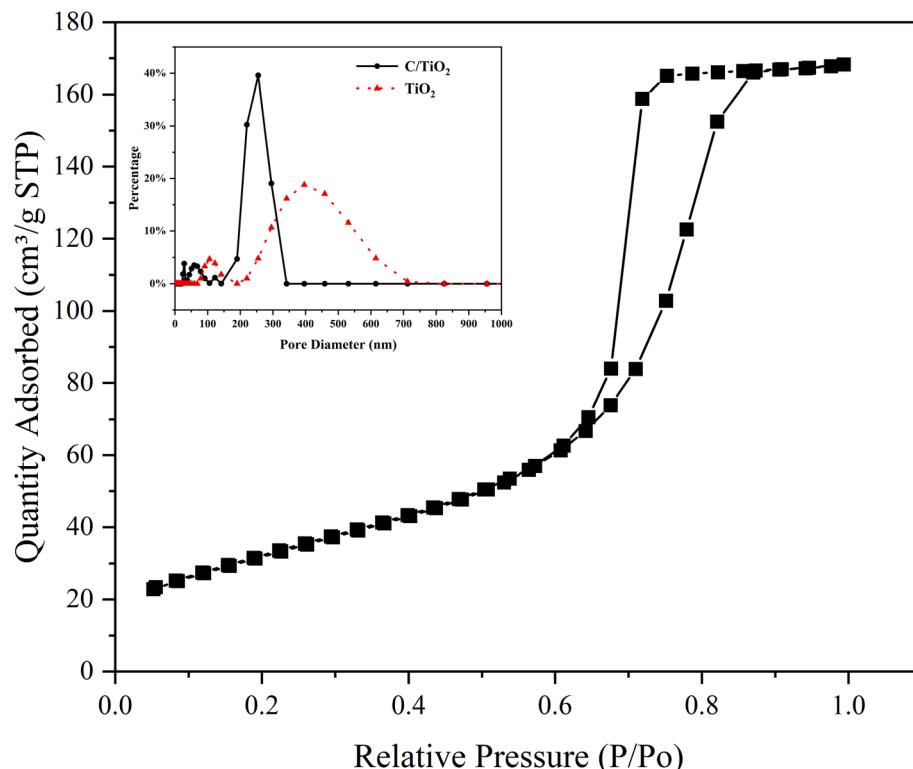


Fig. 7 N<sub>2</sub> adsorption/desorption isotherms of C/TiO<sub>2</sub> and the pore-size distribution curves of TiO<sub>2</sub> and C/TiO<sub>2</sub>.

a remarkable increase. This indicated that the porous structure and pore volume of TiO<sub>2</sub> could be effectively enhanced after biochar modification. Thus, C/TiO<sub>2</sub> had a more developed pore structure, which made the composite material have

a larger specific surface area and more contact area and active points with pollutants.

**3.3.2 XRD.** XRD spectroscopy of the typical anatase-TiO<sub>2</sub>, rutile-TiO<sub>2</sub>, and the composed C/TiO<sub>2</sub> was performed and the

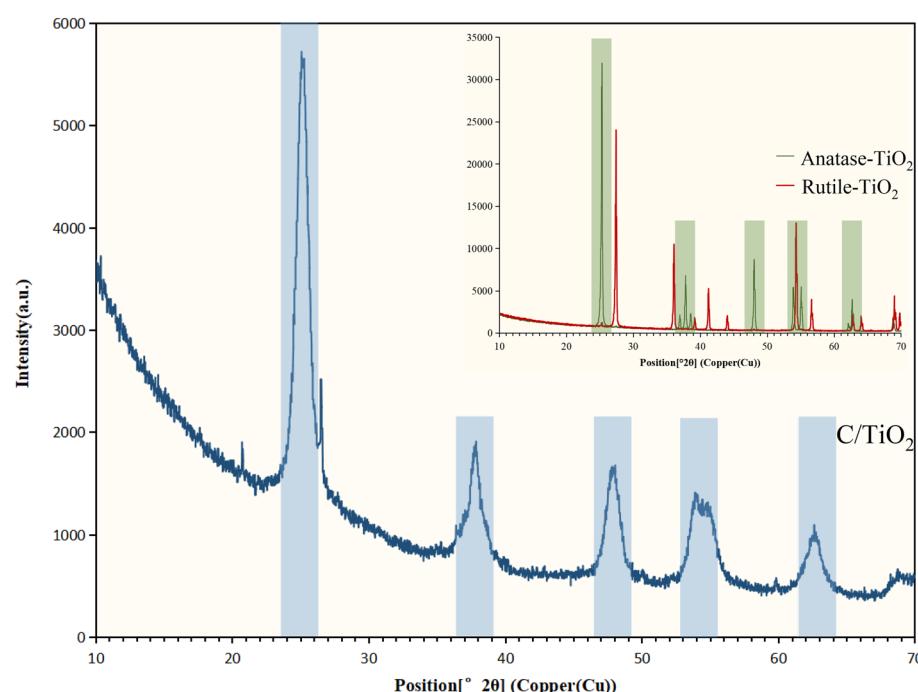


Fig. 8 XRD spectra for C/TiO<sub>2</sub>, anatase-TiO<sub>2</sub>, and rutile-TiO<sub>2</sub>.



spectra are shown in Fig. 8. The standard rutile-TiO<sub>2</sub> has characteristic peaks at  $2\theta = 27.4^\circ, 36.1^\circ, 41.2^\circ, 44.0^\circ, 54.3^\circ, 56.6^\circ$ , and  $64.0^\circ$  (PDF#21-1276), respectively, while a typical anatase-TiO<sub>2</sub> has characteristic peaks at  $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ, 53.9^\circ$ , and  $62.7^\circ$  (PDF#21-1272), respectively. As shown in Fig. 8, the produced C/TiO<sub>2</sub> had characteristic peaks at  $2\theta = 25.1^\circ, 37.8^\circ, 47.8^\circ, 53.9^\circ$ , and  $62.7^\circ$ , respectively, which were roughly consistent with those of a typical anatase-TiO<sub>2</sub>. Due to the lab synthesis, there were slight differences in terms of a superior quality and uniformity between the produced TiO<sub>2</sub> and commercial TiO<sub>2</sub>, and a minor blue-shift was noted on the composed C/TiO<sub>2</sub> as compared to the pure TiO<sub>2</sub>. Moreover, some small peaks appeared in C/TiO<sub>2</sub> that were possibly generated from impurities in the biochar. Though the size growth of TiO<sub>2</sub> nanocrystals was slightly inhibited due to the introduction of the biochar, TiO<sub>2</sub>'s phase structure was unaffected. C/TiO<sub>2</sub> still presented a remarkable anatase structure and good photocatalysis performance. Moreover, the results

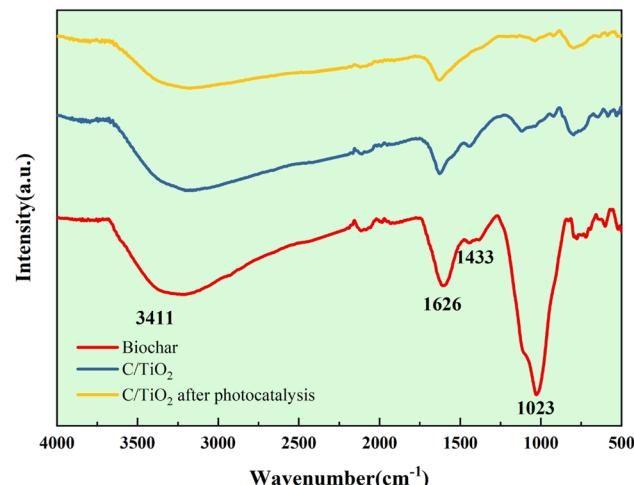
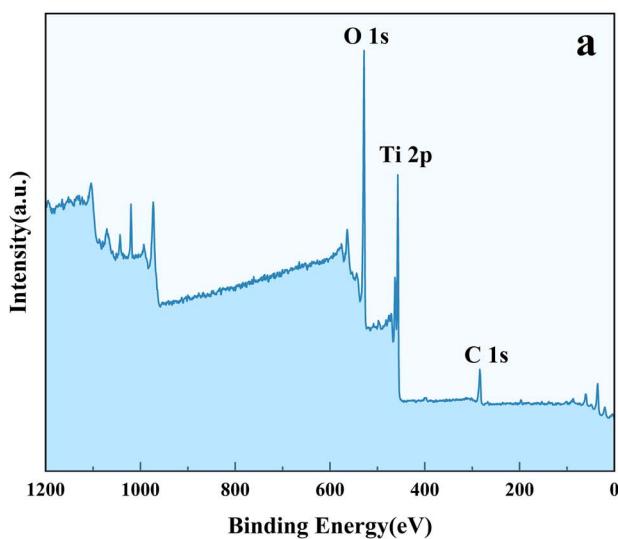


Fig. 10 FT-IR spectra of C/TiO<sub>2</sub> and biochar.

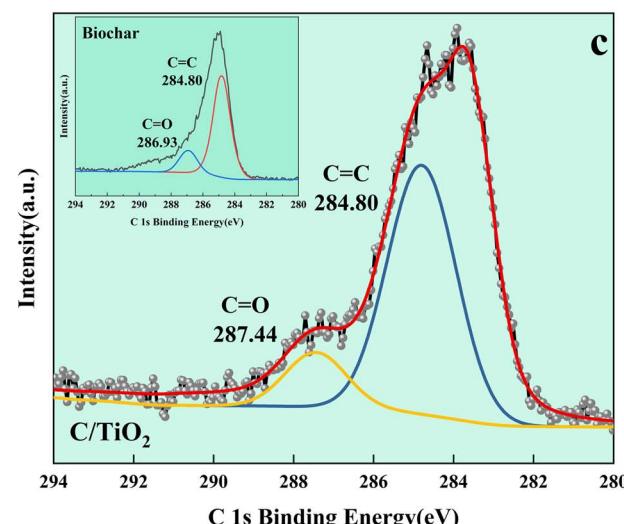
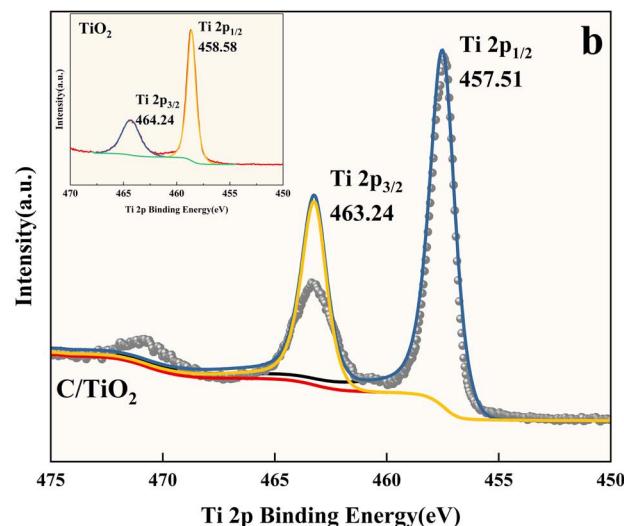


Fig. 9 XPS spectra of C/TiO<sub>2</sub> (a), Ti 2p in C/TiO<sub>2</sub> and biochar (b), and C 1s in C/TiO<sub>2</sub> and biochar (c).

demonstrated that biochar and  $\text{TiO}_2$  were combined successfully.<sup>28</sup>

**3.3.3 XPS.** Fig. 9 shows the XPS spectrum of C/TiO<sub>2</sub>. The full survey spectrum of C/TiO<sub>2</sub> is shown in Fig. 9a, and the high-resolution Ti, C spectra are shown in Fig. 9b and c. All the binding energy values were calibrated against the C 1s at 284.8 eV.<sup>8</sup>

As shown in Fig. 9b, the Ti 2p peaks at 457.51 and 463.24 eV were related to Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> of Ti<sup>4+</sup>, respectively. Compared to the typical TiO<sub>2</sub>, the binding energy was reduced slightly on C/TiO<sub>2</sub> because of the introduction of biochar, which might cause low-load electrons to transfer from the TiO<sub>2</sub> surface to the biochar surface. Thus, the outer layer electron-distribution density of TiO<sub>2</sub> was changed, leading to a reduction of the binding energy. As shown in Fig. 9c, C 1s peaks

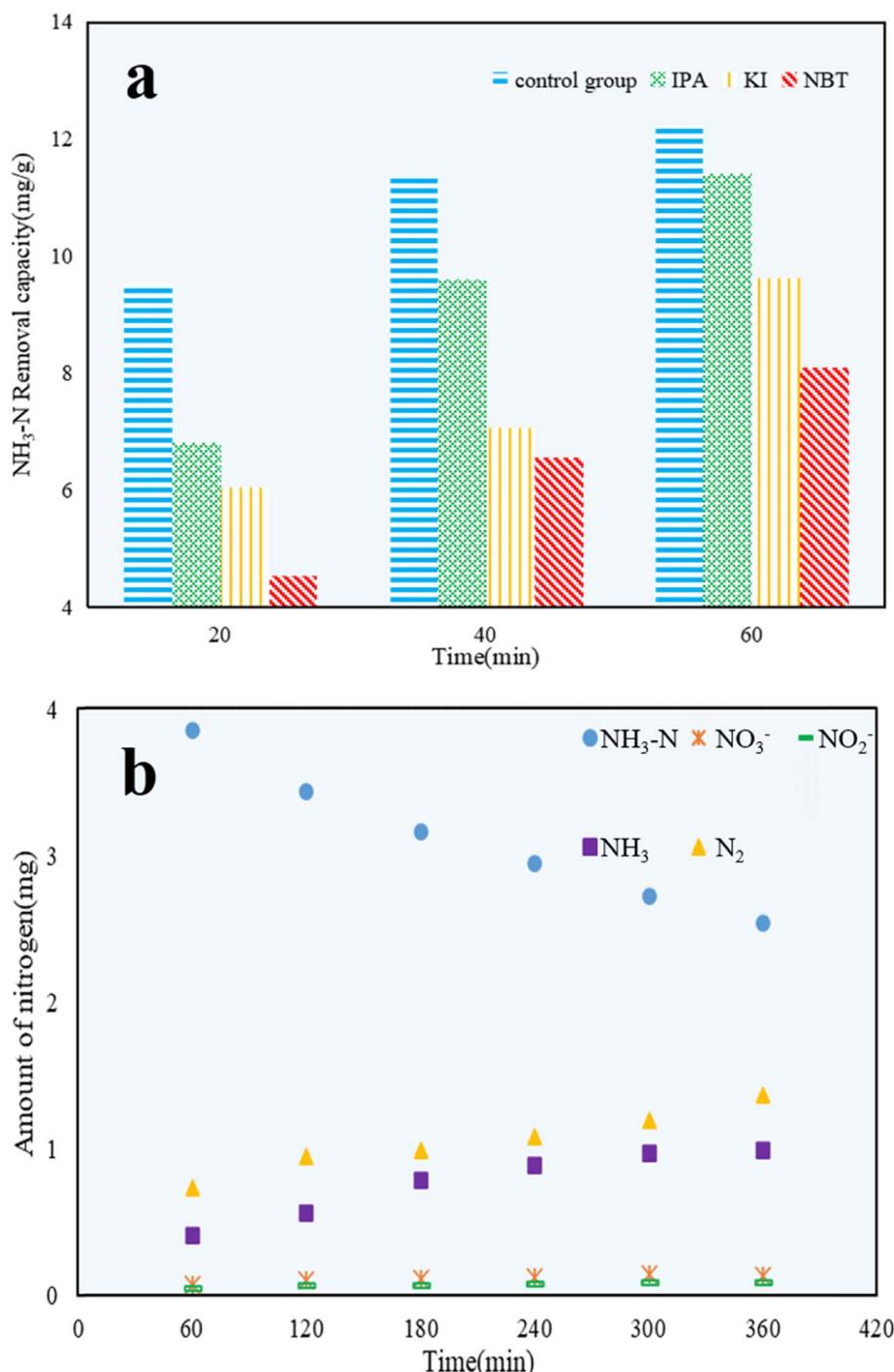


Fig. 11 NH<sub>3</sub>-N removal capacity under different quenching agents (a), and plot of the amounts of NH<sub>3</sub>-N, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub>, and N<sub>2</sub> in the reaction system (b) (AM1.5, 25 A, 1 g L<sup>-1</sup> C/TiO<sub>2</sub>, pH 10.0,  $C_0 = 50 \text{ mg L}^{-1}$ ).



appeared at 284.80 and 287.44 eV corresponding to C 1s<sub>3/2</sub> and C 1s<sub>1/2</sub>, respectively. The peak was slightly shifted from 286.93 eV on biochar to 287.44 eV on C/TiO<sub>2</sub> due to the combination between TiO<sub>2</sub> and biochar. The high C content in C/TiO<sub>2</sub> changed its hydrophilicity and resulted in an increment in C=O groups. Then, the introduction of biochar was beneficial to ·OH formation, which could form oxygen vacancies on the composed photocatalyst.<sup>44</sup> Thus, more oxygen was attracted to C/TiO<sub>2</sub>, consequently improving its photocatalytic performance. In conclusion, the introduction of biochar was effective for enhancing the NH<sub>3</sub>-N removal efficiency of the composite.

**3.3.4 FT-IR.** Fig. 10 shows the infrared spectra of the photocatalysts and biochar, which were used to analyze the surface functional group characteristics of the composite. As shown in Fig. 10, the spectra of the three materials were similar. Obviously, the peaks at 1023, 1433, and 1626 cm<sup>-1</sup> were weaker in C/TiO<sub>2</sub> before and after the photocatalysis in comparison with biochar. The peaks around 1023 cm<sup>-1</sup> were assigned to C-O and C-O-C stretching.<sup>45</sup> Moreover, hydroxyl groups (-OH) were also confirmed by the peaks around 1023 cm<sup>-1</sup>, which are usual in hybrid materials prepared from municipal sewage sludges.<sup>46</sup> Compared to the original biochar, the strength of the peak at 1023 cm<sup>-1</sup> on C/TiO<sub>2</sub> was lowered probably due to the very small amount of biochar in the final composite product. The peaks at 1433 cm<sup>-1</sup> were attributed to -COO-Ti vibration.<sup>31</sup> The peaks at 1626 cm<sup>-1</sup> indicated the antisymmetric stretching vibration of ·OH groups and peaks formed by surface moisture through stretching and bending.<sup>47</sup> The peaks at 3411 cm<sup>-1</sup> were generated from the stretching vibrations of the active -OH or -COOH groups. Owing to the successful C-modification from biochar, a large amount of carboxyl groups (-COOH) was present on the surface of the C/TiO<sub>2</sub> composite, which further intensified the interactions between biochar and TiO<sub>2</sub>.<sup>48</sup>

### 3.4 Mechanism

Propan-2-ol (IPA),<sup>49</sup> potassium iodide (KI),<sup>50</sup> and nitro blue tetrazolium (NBT)<sup>51</sup> were added to NH<sub>3</sub>-N solutions to explore the effect of hydroxyl radicals (·OH), valence band holes (h<sup>+</sup>), and superoxide radicals (·O<sub>2</sub><sup>-</sup>) on the photocatalytic reactions, respectively. As shown in Fig. 11a, the photocatalytic efficiency of C/TiO<sub>2</sub> was restrained compared with the control group, which confirmed that h<sup>+</sup>, ·OH, and ·O<sub>2</sub><sup>-</sup> all had certain impacts on the NH<sub>3</sub>-N removal capacity. After 60 min, the NH<sub>3</sub>-N removal capacity of C/TiO<sub>2</sub> under NBT addition was 8.10 mg g<sup>-1</sup>, which was clearly lower than for both cases with IPA and KI addition. It was demonstrated that ·O<sub>2</sub><sup>-</sup> played a major role in NH<sub>3</sub>-N degradation, while both ·OH and h<sup>+</sup> had effects on NH<sub>3</sub>-N removal to some extent too.<sup>52</sup>

Next, 1 g L<sup>-1</sup> C/TiO<sub>2</sub> was added into 100 mL of 50 mg L<sup>-1</sup> NH<sub>3</sub>-N solution (pH 10.0), and the photocatalytic reaction was carried out under a xenon lamp (AM1.5, 25 A) with stirring (450 rpm) for 6 h. The amount of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NH<sub>3</sub> were measured every 1 h, and the amount of N<sub>2</sub> generated was calculated *via* the conservation of mass.

As shown in Fig. 11b, the amounts of NH<sub>3</sub>-N, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub>, and N<sub>2</sub> during the NH<sub>3</sub>-N photocatalytic reaction were calculated and compared. The stable decrease in the amount of NH<sub>3</sub>-N illustrated the continuous photocatalytic degradation of NH<sub>3</sub>-N. Because of the high pH, NH<sub>3</sub> became the main form of NH<sub>3</sub>-N in water. Thus, the increased content of NH<sub>3</sub> was attributed to ammonia blowing off from the solution during the experiments. After 6 h, the amount of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> detected was tiny and could be ignored. The amount of N<sub>2</sub> was much larger than NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>, and was almost 2 times higher than that of NH<sub>3</sub>. This proved that NH<sub>3</sub>-N was mainly converted to the non-noxious N<sub>2</sub>. C/TiO<sub>2</sub> was effective in the photocatalytic reaction and was shown to be a significant method to treat low-concentration NH<sub>3</sub>-N solutions.<sup>53</sup>

## 4. Conclusions

An advanced C/TiO<sub>2</sub> composite photocatalyst using solid waste was prepared by the sol-gel method for the effective and environmentally friendly degradation of NH<sub>3</sub>-N in aqueous solutions. The removal capacity of NH<sub>3</sub>-N on the composite was higher than that on commercial TiO<sub>2</sub> at pH 10 with 1 g L<sup>-1</sup> C/TiO<sub>2</sub> under both 60 and 120 min irradiation (xenon lamp, AM1.5, 25 A). The photocatalytic efficiency of C/TiO<sub>2</sub> under simulated sunlight irradiation displayed good performance and its NH<sub>3</sub>-N removal capacity increased with the light power increasing, while NH<sub>3</sub>-N removal by C/TiO<sub>2</sub> was favorable in a proper alkaline environment (pH 10.0).

The characterization of C/TiO<sub>2</sub> through SEM-EDS, BET, XRD, XPS, and FT-IR showed the successful introduction of biochar onto TiO<sub>2</sub>. As shown in the SEM-EDS and BET analysis, C/TiO<sub>2</sub> had a larger surface area and more pores compared to the raw materials. XRD spectroscopy showed that C/TiO<sub>2</sub> had similar characteristic peaks with anatase-TiO<sub>2</sub>, which indicated that the biochar addition did not change TiO<sub>2</sub>'s effective phase structure. Compared to TiO<sub>2</sub>, some carbon- and oxygen-containing functional groups were presented in C/TiO<sub>2</sub> that originated from the biochar modification, and effectively proved its photocatalytic performance by the XPS and FT-IR results. According to the radical quenching experiment and NH<sub>3</sub>-N photocatalytic degradation analysis, superoxide radicals (·O<sub>2</sub><sup>-</sup>) were proved to be the main oxidant influencing the removal capacity, and N<sub>2</sub> was the main product of the photocatalytic reaction. Compared to commercial anatase-TiO<sub>2</sub>, C/TiO<sub>2</sub> displayed a relatively higher efficiency for NH<sub>3</sub>-N removal, but also had more significance for beneficial solid-waste utilization. This work could provide an economic and meaningful photocatalyst to treat NH<sub>3</sub>-N wastewater. In future research, studies should focus on further improvement of the photocatalytic efficiency, and sustainable utilization and practical application tests should be carried out.

## Author contributions

Jiawei Wang: experiment, data curation, formal analysis, writing – original draft, visualization. Guoqiao Wang: conceptualization, methodology, experiment. Tian Yu: data curation,



writing – original draft, experiment. Nengjie Ding: experiment. Meicheng Wang: experiment. Yao Chen: supervision, methodology, writing – reviewing and editing, visualization.

## Conflicts of interest

There are no conflicts to declare.

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