Research Article

Performance and Mechanism of UV/Immobilized Cu-TiO₂ System to Degradation Histidine

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More and more attention is paid to dissolved organic nitrogen (DON) and some specific categories of amino acids are considered to be the direct precursors of nitrogenous disinfection byproducts (N-DBPs). Histidine was chosen to study the efficiency and mechanism of amino acid in UV/Cu-TiO₂ system. Moreover, the influences of pH, organics, and inorganic ion on the photocatalytic efficiency were also investigated. The results show that the degradation rate of DON in the UV/Cu-TiO₂ system was about 50% after 60 min, and it was much lower than that of histidine (72%), which indicated that a part of degraded histidine was oxidized to other N-containing organics. The optimal pH value was 7.0 for the photodegradation of histidine, and the presence of organic compound and inorganic ion would decrease the degradation performance to some extent. After 6 h irradiation, histidine was totally degraded into NH₄⁺, and in the following 2 h, NH₄⁺ was oxidized to NO₃⁻ firstly and then NO₃⁻ was reduced to N₂ and overflowed from water, which should be attributed to the doping of Cu in the TiO₂ and provided a way to totally degrade the DON from the water.

1. Introduction

Total dissolved nitrogen (TDN) is presented as dissolved inorganic nitrogen (DIN) (the sum of NO₃⁻, NO₂⁻, and NH₄⁺ species) and dissolved organic nitrogen (DON) in natural waters. It is a subclass of Natural Organic Matters (NOM) in fresh water, accounting for a portion of 1–5% by weight [1, 2]. In brief, DON is the org-N structure of dissolved organic matters (DOM) [3]. Input of DON to natural waters is largely a result of autochthonous biological process, including extracellular exudate yielded by phytoplankton, N₂ fixation, bacterial respiration, viral cell-lysis, and sloppy feeding by zooplankton and faecal pellet decay. Additionally, external sources of DON arise from sewage and industrial effluents, terrestrial run-off, and atmospheric deposition [4–6]. This nitrogen fraction includes not only a large spectrum of natural compounds like free and hydrolysable amino acids, chlorophyll, and amino sugars but also synthetic compounds like pesticides (e.g., atrazine) [7]. Dissolved organic nitrogen (DON) is currently drawing more and more attention in drinking water treatment for its potential to form nitrogenous

disinfection byproducts (N-DBPs) [7, 8], which are far more carcinogenic or mutagenic than some of the regulated DBPs [9–11]. As to the dissolved organic matters, amino acids are mainly present as combined amino acids and constitute a small proportion (7.2 ± 4.3%) of the total DON [2]. However, some special categories of amino acids were considered as the main precursor of N-DBPs according to former studies [12–15] and some other DON matters may change to amino acids during the water treatment. Therefore, experiments conducted with typical amino acid model compound will be useful to better understand the reactivity of the amine functional group during the process of photocatalytic degradation. In this study, histidine was chosen as the target compound because of its relative higher concentration in raw water and higher potential to form N-DBPs [16, 17]. Currently, studies about DON are mainly focusing on its analytical measurement, structural composition, occurrence, and potential in N-DBPs formation [18–21]. Photocatalytic oxidation using TiO₂ is widely used in water treatment due to its availability, nontoxicity, cheapness, and relatively chemical stability. Additionally, the photocatalytic oxidation

process can be carried out under wide conditions and leads to complete mineralization [12]. Konstantinou and Albanis reported the wide use of heterogeneous photocatalysis with TiO_2 (TiO_2/UV) to effectively degrade NOM from water [13]. However, limited results on its degradation performance for the amino acids by TiO_2 are available. In addition, UV only occupies a small fraction of sunlight, which means an inefficient utilization of solar light by TiO_2 . All of the above limit the wide application of TiO_2 . Cu-doped TiO_2 were selected in this paper, which has been reported to be attributed to increase in visible light adsorption and lengthening of the photogenerated electron-hole pair recombination time [22, 23]. In previous researches [24, 25], Cu- TiO_2 catalyst participated in the reaction in suspended state, which may cause the low recovery rate. Therefore, in this paper, Cu- TiO_2 was immobilized on fiber glass net.

Therefore, the main purpose of this research was to investigate the degradation performance and mechanism of typical amino acids by UV/Cu- TiO_2 system; the proper load of copper ion on the TiO_2 was optimized to enhance the degradation efficiency. Additionally, the effects of pH value, organic compounds, and inorganic ions on photocatalytic efficiency will also be discussed.

2. Methods

2.1. Materials. Histidine was purchased from J & K Scientific Ltd. (Beijing, China), and other reagents were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). All the chemicals used were at least of analytical grade.

Blank TiO_2 and Cu-doped TiO_2 were prepared by referring to the reported sol-gel method [9]. TiO_2 was prepared by a conventional sol-gel method using butyl titanate (TBT) (80 mL) in ethanol (320 mL) as a precursor. The hydrolysis solution of TBT solution was achieved by adding double distilled water (DDW) of 8 mL. Sol-gel synthesis in acidic solution was performed by substituting DDW of 8 mL by 2.5 mL nitric acid/water (volume ratio = 1:4). In addition, Cu-doped TiO_2 were obtained by dissolving the corresponding amount of copper precursor, $\text{Cu}(\text{NO}_3)_2$, into the initial ethanol or acid/ethanol solution. The resulting sol was obtained after 24 hours under room temperature. Glass fiber nets selected in this study were 15 cm $\times$ 30 cm and were full of holes (15 mm $\times$ 15 mm). The holes are in favor of the attachment of Cu- TiO_2 particles to glass fiber nets. Glass fiber nets were impregnated with the sol for 5 min and dried under room temperature and finally calcined at 500°C for 2 h. After repeating for 3–4 times, Cu- TiO_2 photocatalysts supported on glass fiber nets were obtained, and the weight of Cu- TiO_2 adhering to one piece of glass fiber net is 1.0 g. According to our previous work [10], when copper loading was 1.0%, Cu- TiO_2 showed the best photocatalytic performance for DON degradation. Therefore, the photocatalyst used in the following experiments was Cu- TiO_2 (1.0%).

2.2. Analytical Methods. In this paper, the characteristics of blank TiO_2 and Cu- TiO_2 were examined by X-ray diffraction (XRD), diffuse reflectance ultraviolet-visible spectroscopic

(DR-UV-Vis) analysis, and X-ray photoelectron spectroscopy (XPS). DR-UV-Vis was conducted on a Lambda 950 spectrometer with the wavelength ranges of 175–3300 nm. The X-ray diffraction measurement was performed with a Bruker D8 diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) at 40 kV, 30 mA over the 2θ range 10–70°. The samples were coated with a layer of platinum-palladium prior to scanning at 100 K magnification. XPS spectra were obtained on a VG Scientific ESCA-Lab220i-XL hemispherical electron analyzer, which worked at a pressure $< 3 \times 10^{-9}$ Torr, with a dual X-ray source working with K Br at 300 W.

NO_3^- , NO_2^- , and NH_4^+ were measured by Monitoring and Analysis Methods of Water and Wastewater 4th [26]. Total dissolved nitrogen (TDN) was measured using a TOC analyzer (Multi N/C 2100, Germany). DON was determined from the difference between measured TDN and sum of measured DIN species using the following:

$$\text{DON (mg/L)} = \text{TDN} - (\text{NH}_3\text{-N} + \text{NO}_2\text{-N} + \text{NO}_3\text{-N}). \quad (1)$$

Amino acids were analyzed by HPLC with 6-aminoquinolyl-N-hydroxysuccinimidyl (AQC) derivatization [27]. Briefly, the reaction between AQC and amino acids (and ammonia also) leads to the formation of fluorescent complexes separated on AccQ.Tag Waters (3.9 mm $\times$ 150 mm, C18) HPLC column and detected at excitation and emission wavelengths of 240 and 395 nm, respectively. The HPLC system consisted of a Waters TM 600 gradient pump, a Merck AS-4000 autosampler, a column heater, and a 474 Waters TM fluorescence detector.

The isoionic point of Cu- TiO_2 was measured by the following method. The homogeneous solution was obtained by dissolving Cu- TiO_2 powder into pure water and ultrasonic dispersion for 15 min. The pH value of the solutions was adjusted by 0.1 M HCl and 0.1 M NaOH, and the zeta potential of the solution under different pH value was measured by Nano-Z Zeta Potential analyzer. When the zeta potential of the solution was zero, the pH value was the isoionic point of Cu- TiO_2 .

2.3. Experiments. Standard jar-tests were used to study the photodegradation efficiency and mechanism of amino acids. A high pressure Hg lamp (30 W) supplied by Applied Photophysics was used, which showed the main emission line at 365 nm, and UV_{365} intensity was 1970 $\mu\text{W}/\text{cm}^2$. For the UV/Cu- TiO_2 oxidation experiments, raw water was obtained by dissolving certain histidine in pure water, and the concentration of histidine was 30 mg/L. One piece of glass fiber net loading Cu- TiO_2 was fixed on the inner wall of beakers and immersed in 1000 mL water sample. In the meantime, a contrast test was performed with blank TiO_2 . The pH value of the solutions was adjusted by 0.1 M HCl and 0.1 M NaOH. The solutions were put outside simultaneously under UV irradiation for 1 h and continuously stirred during the reaction. Water samples were taken every 10 minutes, and the samples were filtered through 0.45 μm cellulose

FIGURE 1: Schematic of the photocatalytic reactor.

FIGURE 2: XRD diffractograms for blank TiO_2 and Cu-TiO_2 photocatalysts.

acetate membrane filters and placed in sample vials. The photocatalytic reactor was shown in Figure 1.

All experiments were performed in three replicates. Statistical analysis was performed using SPSS 19.0 software (IBM Corporation, USA). The values are expressed as mean $\pm$ standard deviation (SD) and all data were checked for normality. Comparisons between control and treated groups were made by statistical analysis of variance. The value of $p < 0.05$ represents significant difference.

3. Results and Discussion

3.1. Characterization of Cu-Doped TiO_2

3.1.1. XRD Analysis. Figure 2 shows the XRD patterns of blank and Cu-doped TiO_2 photocatalysts. Peaks at 25° , 38° ,

FIGURE 3: Diffuse reflectance spectra for blank TiO_2 and Cu-doped TiO_2 (1.0%).

48° , and 54° were corresponding to TiO_2 anatase phase, which was the most reactive form of TiO_2 [28]. Characteristic peaks indicated that the doped copper ions were not detected. This phenomenon may be due to the fact that ionic radius of Cu^{2+} is $0.72 \text{ \AA}$, which is close to the ionic radius of Ti^{4+} ($0.68 \text{ \AA}$). Therefore, Cu^{2+} was incorporated in the crystalline of TiO_2 and replaced Ti^{4+} to form the lattice imperfection [29].

3.1.2. DR-UV-Vis Analysis. The DR-UV-Vis spectra of Cu-doped TiO_2 and blank TiO_2 are shown in Figure 3. The spectra of TiO_2 show an absorption peak at 350 nm in the UV region. When doped with 1.0% copper onto TiO_2 , considerable shift of the peak towards the visible range at around $400\text{--}800 \text{ nm}$ occurred (red shift). It has been reported that the band at $210\text{--}270 \text{ nm}$ would indicate the $\text{O}^{2-}(2p) \rightarrow \text{Cu}^{2+}(3d)$ ligand to metal charge transfer transition, where the copper ions occupy isolated sites over the support. A band at 350 nm would indicate the formation of $(\text{Cu-O-Cu})^{2+}$ clusters in a highly dispersed state. The broad band between 400 nm and 600 nm is attributed to the presence of Cu^{1+} clusters in partially reduced CuO matrix as well as $(\text{Cu-O-Cu})^{2+}$ clusters. The absorption band at $600\text{--}800 \text{ nm}$ indicates the crystalline and bulk CuO in octahedral symmetry [25]. The incorporation of copper ion caused a red shift and increased the absorption band to the visible or even near-infrared range and this promoted the photocatalytic activity. The optimal doping of copper ion is 1.0%.

3.1.3. XPS Analysis. Figure 4 shows the XPS spectra corresponding to elements on the surface of thin film. There are five kinds of elements (Ti, O, C, Si, and Cu) on the surface of thin film. The presence of Si was due to the fact that the ingredient of the film is SiO_2 . The binding energy of $\text{Ti}_{2p_{3/2}}$ peak at around 457 eV and $\text{Ti}_{2p_{1/2}}$ peak at around 464 eV indicated that Ti was tetravalent. The binding energy of $\text{Cu } 2p_{3/2}$ peak at around 933 eV together with the characteristic shake-up feature at a binding energy of 942 eV is indicative

FIGURE 4: XPS spectra of Cu-TiO₂ photocatalysts (1%).

of Cu²⁺ species, while slightly lower binding energy (932 eV) and the absence of shake-up are characteristic of Cu¹⁺ [27, 28]. Our results point out that the copper species are mainly present as Cu¹⁺ and Cu²⁺.

3.2. Photocatalytic Activity

3.2.1. Degradation Effects of DON and Histidine. As seen from Figure 5(a), both doped and undoped systems could degrade histidine effectively, while the degradation through the Cu-TiO₂ adsorption or photodegradation by UV separately was negligible. Moreover, according to the reported research by Castaño et al. [30], lixiviation was neglectful compared to the removal effect of histidine. Thus, the reaction product between UV and TiO₂ may be responsible for the degradation performance. It is well known that TiO₂ under the ultraviolet radiation could produce electron-hole pairs on its surface; then the electron-hole pairs react with the water,

including org-N rich matters. However, Cu-TiO₂ achieved better performance than blank TiO₂, and it may be due to the fact that the recombination of excited electrons and holes in undoped system was relatively high, but in doped system the recombination of photogenerated carriers was suppressed effectively [10, 31]. Besides, the incorporation of copper ion caused a red shift and increased the absorption band to the visible or even near-infrared range and this promoted the photocatalytic activity (Figure 3). Figure 5(b) shows similar results for the degradation of DON. As seen from Figures 5(a) and 5(b), in the same reaction condition, the degradation rate of DON was significantly lower than that of histidine (50% versus 72%). This could be explained by the fact that amino acids can not be mineralized completely and be transformed to other org-N matters, which also can be detected by DON. Seen from the degradation rate of DON, only a small part of DON was directly oxidized to inorganic ion.

FIGURE 5: Degradation of DON and amino acids by doped and undoped system (Cu-TiO₂: 1%; pH = 7.0; UV₃₆₅ intensity: 1970 $\mu\text{W}/\text{cm}^2$).

FIGURE 6: Effect of pH value on the photocatalytic system (Cu-TiO₂: 1%; UV₃₆₅ intensity: 1970 $\mu\text{W}/\text{cm}^2$).

3.3. Influence of Water Parameters on the Photocatalysis

3.3.1. Effect of pH. In raw water, pH value changes with the climate and the growth of plankton (especially algae and aquatic plants), while pH value affects not only the electriferous state of the surface of TiO₂, but also the ionization degree of target compound in reaction system. Therefore, it is necessary to figure out the influence of pH value on the photocatalytic efficiency and the corresponding experimental results were shown in Figure 8.

It can be seen from Figure 6 that DON degradation rate increased first and then decreased with the increase of pH value. The degradation rate of DON was up to 50% when pH value is 7. In this study, the point of zero charge of TiO₂ is 6.5, and the isoionic point of histidine is 7.59 [32]. We may

discover that both the catalysts and histidine are negatively charged when pH value of solution is higher than 7.59. On the contrary, both catalysts are positively charged when pH value of solution is lower than 6.5. When pH value is in the range of 6.5 and 7.59, the catalysts are negatively charged and histidine is positively charged, which enhances the chance of the collision between TiO₂ and histidine.

3.3.2. Effect of Organic Compound and Inorganic Ions. There are large quantity of natural organic materials (NOM) and inorganic ion in raw water, and their presence will affect the degradation efficiency of target compound. So it is essential to investigate the effect of organics and inorganic ion on the photocatalytic system. Due to the measurement method of DON, the organic compound chosen as the representative should not contain N element, so isopropanol was selected. Cl⁻ was chosen as the typical inorganic ion. The results are shown in Figure 9.

It can be seen from Figure 7 that the degradation efficiency of DON decreased with the increases of isopropanol and Cl⁻ concentration. It may be due to the fact that organics and Cl⁻ consume OH⁻ radicals in the water [33]. Besides, there is competitive adsorption between Cl⁻ and target compound.

3.4. Proposed Mechanism. To confirm the oxidation extent of DON in water, the concentrations of total dissolved nitrogen (TDN), ammonium nitrogen (NH₄⁺), nitrate nitrogen (NO₃⁻), and nitrite nitrogen (NO₂⁻) were determined in the different reaction time. The results are shown in Figure 10.

Seen from Figure 8, the main categories of nitrogen showed different variation tendency. The concentrations of TDN, NO₃⁻, and DON decreased, while the concentration of NH₄⁺ kept increasing. No NO₂⁻ was detected during the whole oxidation process. The decrease of TDN means

FIGURE 7: (a) Effect of isopropanol on the degradation efficiency (Cu-TiO₂: 1%; pH = 7.0; UV₃₆₅ intensity: 1970 $\mu\text{W}/\text{cm}^2$). (b) Effect of Cl^- on the degradation efficiency (Cu-TiO₂: 1%; pH = 7.0; UV₃₆₅ intensity: 1970 $\mu\text{W}/\text{cm}^2$).

FIGURE 8: Changes of TN, NO_3^- , and NH_4^+ in the DON degradation in the UV/Cu-TiO₂ system (Cu-TiO₂: 1%; pH = 7.0; UV₃₆₅ intensity: 1970 $\mu\text{W}/\text{cm}^2$).

FIGURE 9: Variation of the main categories of nitrogen in the pure histidine in the UV/Cu-TiO₂ system (Cu-TiO₂: 1%; pH = 7.0; UV₃₆₅ intensity: 1970 $\mu\text{W}/\text{cm}^2$).

the production and overflow of N_2 during the oxidation process, which may be caused by the photocatalyzed reduction of NO_3^- . For the lowered concentration values of the TDN and NO_3^- were nearly the same. In addition, the increase of NH_4^+ may be due to the oxidation of DON. However, the transformation mechanism for the pure histidine by the photocatalyzed oxidation was not clear for the presence of nitrate in the histidine used in the experiment. Granular activated carbon (GAC) adsorption method was used to degrade the nitrate in the water sample before the oxidation

process until nitrate was not detected. After adsorption, the DON concentration was still about 1.45 mg/L after the adsorption for its poor degradation by the GAC's adsorption approach. Besides, reaction time was extended to about 8 h until DON was totally degraded into inorganic nitrogen and the transformation occurred between the inorganic nitrogen ions; the results are shown in Figure 9.

Seen from Figure 9, the histidine was totally degraded into NH_4^+ and the concentration of TDN kept consistent in the first 6 h reaction time, which indicated that the main

FIGURE 10: The photocatalytic degradation mechanism of DON.

reaction in this phase was to oxidize the histidine into NH_4^+ . In the following 2 h, concentration of NH_4^+ decreased, while the concentration of NO_3^- increased. In addition, the concentration of TDN decreased. The above results demonstrated that NH_4^+ was oxidized to NO_3^- firstly and then NO_3^- was reduced to N_2 and overflowed from water. Compared with results shown in Figure 9, we may conclude that the reaction between the categories of nitrogen in the water may have some sequence in the oxidation process of histidine. The oxidation of histidine had the priority to other reactions; then the further oxidation of NH_4^+ to NO_3^- and the following reduction of NO_3^- to N_2 happened. What needs to be noted in the reaction process was the formation of N_2 and the decrease of TDN's concentration, which was not found in the oxidation of UV/immobilized TiO_2 system [6]. The reason may lie in the doping of copper ion. According to former studies, the doping of copper ion could not only improve the oxidation ability to certain compounds in water [34] but also enhance the reduction efficiency of nitrate to N_2 and the degradation performance of TN through the way of photocatalyzed reaction [35]. The formation of N_2 may lead to the total degradation of nitrogen from water and had special important significance for the water sources which had been in serious eutrophication. The enhanced conversion rate from the nitrate to N_2 may be explained as follows: the bandgap energies of the Cu- TiO_2 and blank TiO_2 were calculated based on DR-UV-Vis spectra (Figure 3) analysis according to our former study [9], and bandgap energy of blank TiO_2 was 3.15 eV, while Cu- TiO_2 was 2.95 eV. We may find that the copper doping causes the decrease of bandgap energy because of the dispersion of metal and metal nanoparticles diffusion in the TiO_2 matrix. Electron

can be easily excited from the defect state to the conduction band of TiO_2 by photon. Based on the results above and reported mechanism [36–38], a possible photocatalytic oxidation approach was proposed in Figure 10.

4. Conclusions

Surface properties and photocatalytic activity of blank and Cu-doped TiO_2 were investigated. The XRD patterns show that Cu- TiO_2 is in anatase phase, which is the most reactive form of TiO_2 . SEM images imply that the size of Cu- TiO_2 particles is small and homogeneous. DR-UV-Vis analysis shows that the incorporation of copper ion caused a red shift and increased the absorption band to the visible or even near-infrared range and this promoted the photocatalytic activity.

UV/Cu- TiO_2 system has a good performance in degrading histidine, and the concentration of DON and histidine was examined. The results show that the degradation rate of histidine is 72% after 60 min, which is much higher than that of DON (50%). Besides, histidine is totally degraded into NH_4^+ in the first 6 h; in the following 2 h, NH_4^+ was oxidized to NO_3^- firstly and then NO_3^- was reduced to N_2 and overflowed from water. Thus, the photocatalytic system (UV/Cu- TiO_2) has a tremendous potential in solving the environmental problem caused by DON. The optimal pH value is 7.0, and the presence of isopropanol and Cl^- decreases the degradation efficiency.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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