Catalytic ozone oxidation treatment of wastewater from a pesticide enterprise

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ABSTRACT

Pesticide production wastewater has complex water quality, many types of pollutants, and large biological toxicity, and can cause a serious impact on the ecological environment when it is ineffectively treated. In this study, catalytic ozone oxidation was used to treat the actual production wastewater from a pesticide company, and the concept of ammonia nitrogen conversion rate was introduced to investigate the actual treatment performance of catalytic ozone oxidation on wastewater. The effects of ozone dosage, hydrogen peroxide dosage, catalyst dosage, reaction time, and reaction pH on chemical oxygen demand (COD) removal rate and ammonia nitrogen conversion rate in wastewater were analyzed. Results showed that the catalytic ozonation significantly reduced the chromaticity of wastewater, and the maximum COD removal and ammonia nitrogen conversion rates were 38.4% and 47.1%, respectively, at reaction pH 8, 3,000 mg/L ozone dosage, 3 mg/L hydrogen peroxide dosage, 50 g/L catalyst dosage, and 120 min reaction time.

Keywords: Catalytic oxidation; Ozone; Pesticide wastewater treatment; COD removal rate; Ammonia nitrogen conversion rate

1. Introduction

Wastewater generated by pesticide enterprises during pesticide production and processing mainly includes the wastewater from the synthesis of pesticides, wastewater purification, and wastewater generated when washing the washing plant and equipment. Pesticide wastewater affected by the type of pesticides and the production and processing processes has the following characteristics: (1) the produced wastewater is large with highly volatile water quality and water volume. As a large agricultural country, incomplete statistics show that the annual discharge of pesticide wastewater by pesticide companies is approximately 150 million tons. The quality and quantity of pesticide wastewater are different because of the stability of pesticide production and the different operating conditions in different enterprises, (2) wastewater has complex water quality and high organic matter concentration. Pesticide production

wastewater contains various organic pollutants, such as sulfides, organic phosphorus, phenolic compounds, and organic nitrogen compounds, because of the wide variety of pesticides, complex raw materials, and complex intermediates produced during production [1]. The concentration of chemical oxygen demand (COD) can reach up to tens of thousands of mg/L, (3) the wastewater is biotoxic and has poor biodegradability. The high concentration of organic substances contained in pesticide wastewater is difficult to be degraded by microorganisms and have a strong inhibitory effect on microorganisms [2], (4) the volatile organic pollutants contained in pesticide wastewater cause it to have a pungent odor, which can damage the respiratory tract and cause poisoning when breathed by humans or other organisms [3]. The harm of pesticide wastewater to the ecological environment is not only manifested in the toxic effect of the irritating odor contained in pesticides [4]. At the same time, most of the organic matter contained in pesticide

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wastewater have neurological and biological toxicity and potential carcinogenic effects on the human body. Random emissions cause serious damage to the ecological environment [5,6]. Therefore, pesticide wastewater treatment has been constantly investigated by environmentalists at home and abroad [7]. However, the condition of pesticide wastewater treatment remains unclear. Relevant data have shown that only 7% of pesticide wastewater discharged from China is treated, and approximately 1% of the treatment standards is met [8]. Therefore, pesticide wastewater treatment technology should be developed.

The methods of pesticide wastewater treatment mainly include physical, chemical, and biological methods. Physical methods mainly include coagulation, sedimentation [9], extraction [10–12], adsorption [13–15], and membrane separation [16]. Chemical methods mainly include Fenton oxidation [17], photocatalytic oxidation [18,19], electrocatalytic oxidation [20], and ozone oxidation [21,22]. Biological methods mainly include biofilm [23] and activated sludge [24]. Pesticide wastewater has poor biodegradability and cannot be directly treated using traditional biological methods [25]. Therefore, this problem can be effectively solved when effective pretreatment measures are used to degrade the chemically stable refractory organic matter in wastewater and improve the biodegradability of wastewater. Conventional physicochemical pretreatment cannot reduce the biological toxicity of wastewater and cannot meet the actual biochemical treatment needs, and certain defects or deficiencies are observed in the actual application. Commonly used physical methods produce waste gas and waste residues in treating pesticide wastewater. For secondary pollution, Fenton oxidation produces iron-containing sludge that is difficult to handle, and photocatalytic and electrocatalytic oxidations are expensive [26]. Ozone oxidation can degrade toxic substances and improve the biodegradability of wastewater, and has been widely investigated at home and abroad [27].

Ozone oxidation mainly relies on the direct oxidation of ozone molecules and indirect oxidation of hydroxyl radicals to degrade pollutants [28]. This process has high oxidation efficiency and no secondary pollution. Catalytic ozone oxidation can overcome the low ozone utilization and low oxidation efficiency of traditional ozone oxidation. Most studies on catalytic ozone oxidation treatment of pesticide wastewater have focused on the nature of catalyst and the effect on the removal rate of single pollutant components [29]. Few studies have been conducted on the change of nitrogen form in wastewater [30,31]. The problem of organic nitrogen in pesticide wastewater has been constantly the major problem in pesticide wastewater treatment [32]. High concentration of organic nitrogen in wastewater directly affects the effective residence time of the anaerobic process, thereby affecting the cost of wastewater treatment. Under the premise that the total nitrogen concentration of wastewater is constant, the higher the concentration of ammonia nitrogen is, the lower the concentration of organic nitrogen will be, which is conducive to the actual biochemical treatment of wastewater.

In this study, a self-made metal catalyst with Al_2O_3 as carrier was used to act as catalyst for ozone catalytic oxidation, and the factors affecting the degradation of COD in an actual pesticide wastewater through catalytic oxygen

oxidation were investigated. The effects of ozone dosage, hydrogen peroxide catalyst dosage, reaction time, and pH on COD removal and ammonia nitrogen conversion rates were assessed. The concept of ammonia nitrogen conversion rate was introduced to evaluate the ability of catalytic ozone oxidation from another perspective to convert the organic nitrogen in wastewater into ammonia nitrogen for providing technical reference for better biochemical treatment of actual wastewater.

2. Materials and methods

2.1. Materials

Concentrated sulfuric acid, hydrochloric acid, silver sulfate, mercury sulfate, ammonium ferrous sulfate, ferrous sulfate heptahydrate, potassium hydrogen phthalate, potassium dichromate, absolute ethanol, ammonium chloride, potassium sulfate, sodium thiosulfate, sodium hydroxide, and anhydrous sodium carbonate were of analytical grade and purchased from Sinopharm Shanghai Chemical Reagent Company (China). The ozone catalyst was self-made in the laboratory. Other chemical reagents were purchased and used without purification.

The experimental water sample was taken from wastewater of a pesticide company in Jiangsu Province. The obtained sample was the comprehensive production wastewater of the enterprise. The water quality parameters are shown in Table 1.

2.2. Preparation methodology of ozone catalyst

A certain molar mass ratio of ferric nitrate and manganese nitrate were weighed out for preparing 100 mL of catalyst active factor precursor solution, and the precursor solution was transferred to 250 mL wide-mouth conical flask. A certain amount of pre-treated activated alumina was transferred into an Erlenmeyer flask, and placed in a water bath shaker with shaking for a certain time. The water bath temperature was set to 35°C. The activated alumina after impregnation was put it in an oven to dry for 12 h, and set the temperature to 105°C. The dried catalytic ceramsite was placed in a muffle furnace and calcined at 450°C–750°C for a period of time for the preparation of the final ozone catalyst.

2.3. Experimental methodology

A self-made ozone catalytic oxidation reactor unit was used in the experiment. O_3 dosage in the reactor was jointly determined in terms of oxygen (purity ≥ 99%) inlet

Table 1
Water quality parameters of pesticide wastewater

Water quality index	Value
pH	6.0–9.0
COD (mg/L)	23,752.0
Ammonia nitrogen (mg/L)	385.0
Total nitrogen (mg/L)	1,182.0
Kjeldahl nitrogen (mg/L)	824.0

pressure using an ozone generator (ozone generator, CF-G-3-010g, Qingdao Guolin Company, China) and its current size using a rotor flowmeter. The model of the ozone generator is CF-G-3-10G, the ozone generation amount is 10 g/h. The gas flow rate is 0.07–0.08 Nm³/h. The ozone concentration is 120–150 g/m³. A porous plate at the bottom of the reactor unit was used to ensure that O_3 enters the reactor uniformly, and the O_3 tail gas was absorbed and eliminated using activated carbon.

The device was continuously operated during the experiment. O_3 was preoxidized for 3 min to remove the organic matter on the surface of the reactor and the catalyst (self-made). After a certain time period, the water sample in the reactor was sampled to detect its COD and ammonia nitrogen. Kjeldahl nitrogen and total nitrogen concentrations were evaluated in terms of COD removal and ammonia nitrogen conversion rates. Single-factor optimization was used to investigate the effects of ozone dosage, hydrogen peroxide dosage, catalyst dosage, reaction time, reaction pH, and catalytic oxidation reaction. The ammonia nitrogen concentration of the wastewater sample was measured through Nessler reagent spectrophotometry. Kjeldahl nitrogen concentration detection was conducted by converting the organic nitrogen in water samples to ammonia nitrogen via Nessler spectrophotometry (UV spectrophotometer, New Century T6, Beijing Pu Analysis General Instrument Co., Ltd., China). Analysis of total nitrogen concentration was conducted to ensure no reduction in ammonia nitrogen caused by spillover effects during the reaction. Potassium dichromate was used to detect the COD concentration in wastewater samples.

- Calculation formula of COD removal rate is shown in Eq. (1):

$$R_{COD} = \frac{COD - COD_0}{COD_0} \times 100\% \qquad (1)$$

where R_{COD} is the COD removal rate in the water sample, COD is the COD concentration in the water sample at the end of the reaction, mg/L, and COD_0 is the initial COD concentration of water sample, mg/L.

- Calculation formula of NH_3–N conversion rate is shown in Eq. (2):

$$R_N = \frac{N - KN_0}{KN_0} \times 100\% \qquad (2)$$

where R_N is the conversion rate of ammonia nitrogen in the water sample, N is the concentration of ammonia nitrogen in the water sample at the end of the reaction, mg/L, and KN_0 is the initial Kjeldahl nitrogen concentration of water sample, mg/L.

3. Results and discussion

3.1. Effect of ozone dosage on ozone catalytic oxidation efficiency

Fig. 1 shows the COD removal and ammonia nitrogen conversion rates at ozone dosages of 0; 500; 1,000; 1,500;
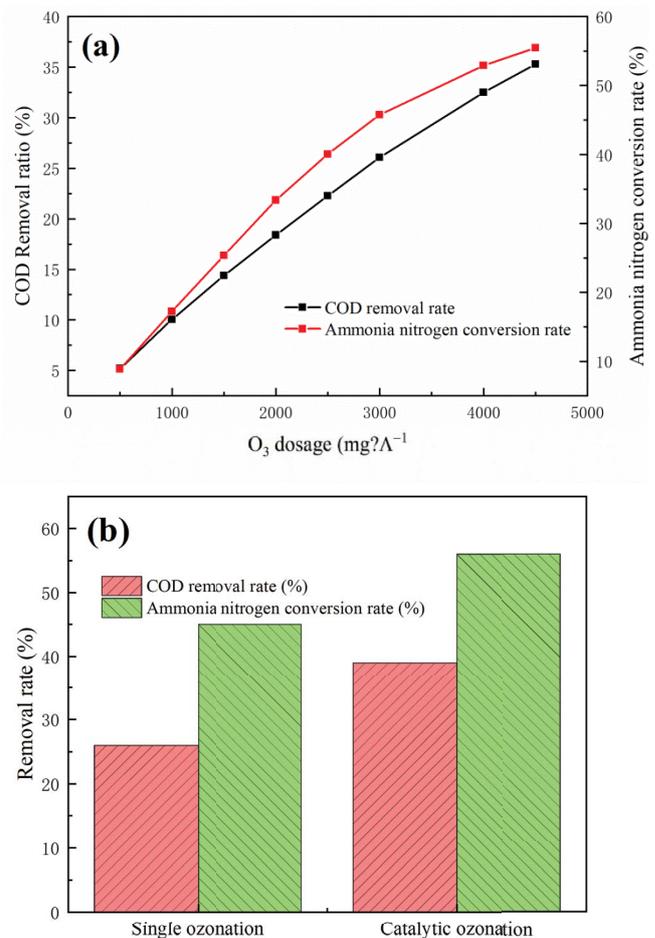

Fig. 1. Effect of ozone dosage on ozone catalytic oxidation efficiency.

2,000; 2,500; 3,000; 4,000; and 4,500 mg/L and reaction time of 60 min. The COD and ammonia nitrogen concentrations in the wastewater continuously increased with the increase in ozone dosage from 0 to 4,500 mg/L during the reaction. The COD removal rate increased from 5.1% to 35.3%, and the ammonia nitrogen conversion rate increased from 8.9% to 55.5%. Ozone was used as an oxidizing agent for ozone oxidation. The amount of ozone added determined the amount of ozone molecules that can be oxidized in the reaction system and the amount of OH formed. The increase in the amount of ozone in the reaction system increased the total mass transfer and concentration of ozone in the solution, thereby increasing the probability of ozone molecules attacking organic pollutants [33]. The increase in ozone concentration in wastewater indicated the increase in •OH concentration in the solution, thereby enhancing the ability of ozone oxidation to remove organic matter from the wastewater and increasing the removal rate of COD and organic nitrogen in the wastewater [34].

3.2. Effect of H_2O_2 dosage on ozone catalytic oxidation efficiency

Fig. 2 shows the COD removal rate and ammonia nitrogen conversion rate of wastewater at 3,000 mg/L ozone
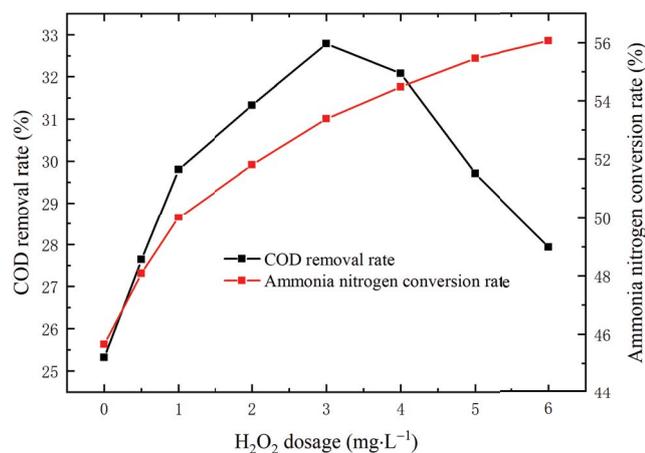
Fig. 2. Effect of H_2O_2 dosage on ozone catalytic oxidation efficiency.

Fig. 3. Effect of catalyst dosage on ozone catalytic oxidation efficiency.

dosage, 60 min reaction time, and 0, 0.5, 1, 2, 3, 4, 5, and 6 mg/L hydrogen peroxide dosages. The COD removal rate first increased and decreased, whereas the ammonia nitrogen conversion rate gradually increased when the dosage of hydrogen peroxide was 0–6 mg/L. The COD removal rate in the wastewater reached the highest, which was 32.79%, and the ammonia nitrogen conversion rate was 53.4% when the dosage of hydrogen peroxide was 3 mg. The addition of a certain amount of hydrogen peroxide to the ozone oxidation system triggered ozonolysis to produce ${}^{\bullet}OH$, whereas the high hydrogen peroxide concentration inhibited the ozone decomposition [35]. The excess hydrogen peroxide in the reaction system consumed ozone, thereby affecting the removal of COD. The data of ammonia nitrogen conversion rate indicated that the introduction of hydrogen peroxide into the system was beneficial to the conversion of organic nitrogen to ammonia nitrogen because of the degradation of partial organic nitrogen into ammonia nitrogen caused by the degradation of COD [36].

3.3. Effect of catalyst dosage on ozone catalytic oxidation efficiency

Fig. 3 shows the effect of catalyst dosage on ozone catalytic oxidation efficiency. The COD removal and ammonia nitrogen conversion rates in the wastewater first increased and gradually changed with the increase in catalyst dosage. The catalyst dosage increased from 0 to 500 g/L, and the corresponding COD removal rate increased from 33.3% to 40.2%. The ammonia nitrogen conversion rate increased from 52.1% to 61.3%. Compared with the unadded catalyst, The addition of catalyst significantly increased the COD removal and ammonia nitrogen conversion rates of wastewater compared without the addition of catalyst, indicating that the self-made catalyst triggered ozonolysis to produce ${}^{\bullet}OH$. The COD removal and ammonia nitrogen conversion rates were basically balanced, which were 41.2% and 59.8%, respectively, when 66.6 g/L of catalyst was added to the system. The surface area of the catalyst in the reaction system accordingly increased, and the effective contact area between the catalyst and O_3 molecule increased with the increase in amount of catalyst. On the one hand, the dissolution of O_3
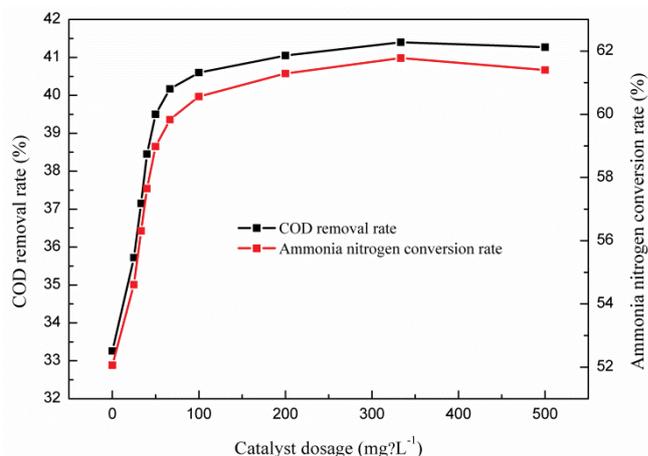
molecules in the wastewater was promoted, thereby increasing the effectiveness of O_3 in the wastewater. The concentration ultimately affected the amount of ozone molecules and the amount of ${}^{\bullet}OH$ formed. On the other hand, the adsorption and decomposition of O_3 on the catalyst surface were promoted [37].

3.4. Effect of reaction time on ozone catalytic oxidation efficiency

Fig. 4 shows the effect of reaction time on ozone catalytic oxidation efficiency. The COD removal and ammonia nitrogen conversion rates in the wastewater were basically consistent with the change of reaction time. In the early stage of reaction, the COD removal and nitrogen conversion rates increased with the extension of reaction time and remained basically unchanged after the reaction period. After 90 min of COD reaction, the concentration reached equilibrium, and the corresponding COD removal rate was 38.4%. The ammonia nitrogen concentration reached equilibrium after 120 min of reaction, and the corresponding ammonia nitrogen conversion rate was 44.9%. With the gradual extension of reaction time, the dissolved O_3 concentration in the wastewater and the amount of ${}^{\bullet}OH$ produced by the decomposition continuously increased. On the one hand, the increase in reaction time increased the effective contact time of the pollutants and the oxidizing O_3 and OH [38]. On the other hand, the increasing concentration of O_3 and ${}^{\bullet}OH$ in wastewater increased the oxidative degradation of pollutants. The reaction time continued to increase, and the degraded pollutants in the wastewater gradually reached equilibrium [39]. The difference between COD removal and ammonia nitrogen conversion rates may be because of the continuous conversion of small molecular organic nitrogen compounds that contributed to COD less than that of ammonia nitrogen after 90 min.

3.5. Effect of water pH value on ozone catalytic oxidation efficiency

Fig. 5 shows the effect of water pH value on ozone catalytic oxidation efficiency. The COD removal and ammonia
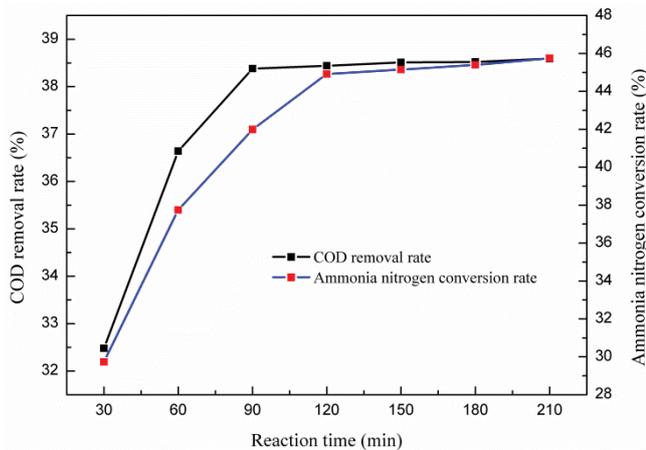
Fig. 4. Effect of reaction time on ozone catalytic oxidation efficiency.

Fig. 6. Ultraviolet-visible (UV-vis) spectrum of wastewater before and after catalytic ozone oxidation treatment.

3.6. Discussion on degradation process

Fig. 6 shows the UV-vis spectra and the color change of wastewater before and after catalytic ozone oxidation. The catalytic ozone oxidation reaction conditions are described as follows: reaction pH of 8, 3,000 mg/L ozone dosage, 3 mg/L hydrogen peroxide dosage, 50 g/L catalyst dosage, and 120 min reaction time. As shown in Fig. 7, the absorption peaks of raw water and wastewater after catalytic ozonation were mainly concentrated at 190–500 nm because of the absorption peak interval of the aromatic compound and the raw water of pesticide wastewater contained a certain amount of aromatic compound. The absorption peak at the range of 190–500 containing a certain amount of hetero peak was caused by the chromophore of other heterocyclic organic compounds [43]. At the same time, the UV absorption peak of wastewater after catalytic ozonation significantly reduced, indicating that catalytic ozonation reduced the concentration of organic matter in pesticide wastewater [44]. The biodegradability of wastewater was immensely reduced by the oxidative degradation of organic substances, such as benzene ring, in the wastewater [45]. The color change of the water sample before and after catalytic oxidation of ozone was observed in Fig. 7. After catalytic ozonation, the color of wastewater significantly reduced, which was beneficial to the discharge of tail water in actual wastewater treatment [46]. In addition, the catalytic oxidation experiments were conducted over 150 h with 5.0% reduction of COD removal efficiency.

4. Conclusion

The experimental results of catalytic ozone oxidation treatment of actual wastewater from pesticide enterprises showed that the use of self-made catalyst and the addition of hydrogen peroxide in the ozone reaction system transformed the nitrogen in the wastewater into ammonia nitrogen and improved the COD removal rate in wastewater. The destruction of organic nitrogen during pesticide wastewater treatment ensured the biochemical treatment and discharge of wastewater. The single-factor experiment results showed
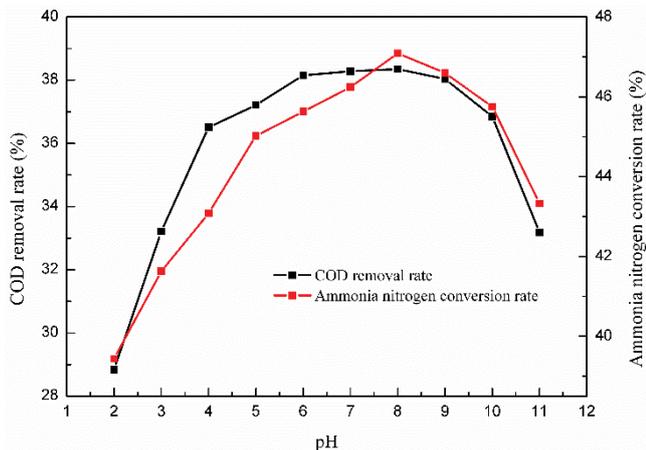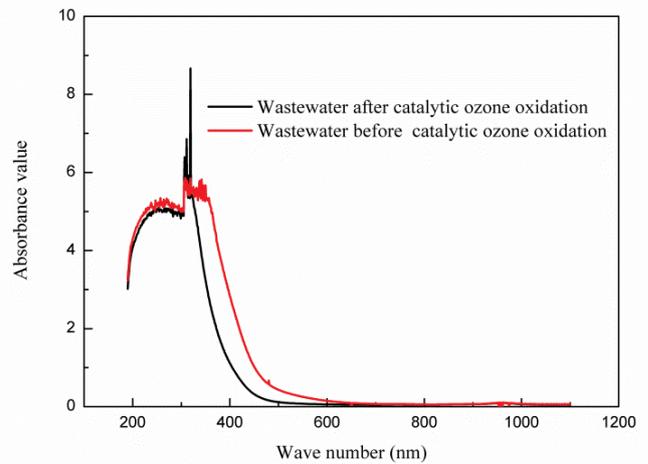

Fig. 5. Effect of water pH value on ozone catalytic oxidation efficiency.

nitrogen conversion rates in the wastewater first increased and decreased with the increase in reaction pH from 2.0 to 11.0. The COD removal and ammonia nitrogen conversion rates increased when the reaction increased from 2.0 to 8.0. At pH 8, the COD removal and ammonia nitrogen conversion rates were the highest, which were 38.4% and 47.1%, respectively. But the rate of COD and TOC removal efficiencies in the optimum nano-MgO/CNT/Graphite/O_3 process were 12.73 (13.24/1.04 mg COD/L min) and 7.11 (1.44/0.2 mg TOC/L min) times as high as those in the single ozonation (SOP), respectively [40]. The COD removal and ammonia nitrogen conversion rates decrease when the reaction pH was >8.0. Studies have shown that OH– in wastewater is beneficial to initiate the organic chain reaction of $^\bullet$OH, thereby promoting the formation of $^\bullet$OH in wastewater and strengthens the degradation of pollutants in wastewater [41]. The high concentration of OH generated in a short time period will interact and be quenched when the decomposition rate of ozone in the wastewater is fast [42]. The COD removal and ammonia nitrogen conversion rates decrease when the pH of the wastewater is high.

Fig. 7. Color change of wastewater (a) before and (b) after catalytic ozone oxidation treatment.

that catalytic ozonation significantly reduced the color of wastewater. The wastewater COD removal and ammonia nitrogen conversion rates were the best, which were 38.4% and 47.1%, respectively, at reaction pH of 8, 3,000 mg/L ozone dosage, 3 mg/L hydrogen peroxide dosage, 50 g/L catalyst dosage, and 120 min reaction time.

Acknowledgments

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