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Degradation of organic pollutants in groundwater treatment based on catalytic ozonation technology

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ABSTRACT

In this study, a new type of γ-Al_2O_3 supported metal catalyst was prepared by using γ-Al_2O_3 as catalyst and catalyst support, and a new catalytic ozonation system was formed with ozone. Nitrobenzene, a typical toxic organic pollutant which is difficult to be chemically oxidized and biodegraded, and nitrobenzene and aniline, which are common organic pollutants, are used as target materials. The efficiency, catalytic mechanism and influencing factors of the catalytic ozonation system for removing organic pollutants in water are studied in depth. It was found that the preparation process of Mn Fe supported γ-Al_2O_3 catalyst with γ-Al_2O_3 as carrier was simple, high hardness, good wear resistance, stable organic matter removal effect, long-term operation without adding other chemicals, saving operation cost. O_3/Mn Fe supported γ-Al_2O_3 catalytic oxidation is a promising process.

Keywords: γ-Al_2O_3; Catalyst; Ozonation; Organic pollutants; Degradation

1. Introduction

In the process of human industrialization and urbanization, the leakage of crude oil, the discharge of various organic wastewater, the rupture of underground oil pipeline, the leakage of gas pipeline, the use of pesticides, the infiltration of domestic sewage, the sudden accident of underground oil storage tank, the leaching of waste landfill, etc. all lead to the organic pollution of groundwater. Some unexpected accidents may lead to serious organic pollution of groundwater in some areas, especially in the water source area, which will have a serious impact on the life of residents and the surrounding environment. In order to reduce the diffusion of pollutants, for the organic pollution of groundwater caused by some sudden accidents, especially when the concentration of pollutants is high in the initial stage of the accident, the polluted groundwater is usually extracted first, the surface treatment is up to the standard, or the groundwater is reinjected, and the groundwater environment is repaired by the method of air extraction and gas injection. If the extracted high concentration organic polluted wastewater directly enters the sewage treatment plant, it will cause impact or even damage to the original biological treatment system. Therefore, the physical and chemical methods should be used to pretreat the wastewater to reduce the indicators of sewage. There are many methods for surface water treatment. The physical and chemical methods for organic wastewater mainly include coagulation sedimentation method, oxidation-reduction method, electrolysis method, etc. In recent years, some technologies, such as Fenton, have been developed for the removal of organic matter in water. Compared with the traditional treatment methods,

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high efficiency, easy operation and no secondary pollution will become the development trend of environment-friendly chemistry [1,2]. However, the existing technology also has some limitations, such as the high cost of regeneration and replacement of activated carbon, the high cost of equipment and chemical reagents, and the problem of membrane pollution cleaning in membrane filtration.

At present, biological methods are widely used in wastewater treatment, but many highly stable and refractory pollutants are difficult to be removed by biological treatment. Therefore, it is very important to use more effective non biological technology ozone oxidation technology to treat the above pollutants. In recent 10 y, ozone oxidation technology is no longer applied to wastewater treatment alone. There are many limitations of single ozonation technology. One is that ozone cannot oxidize refractory organics such as chloroform; The other is that single ozonation technology cannot completely oxidize refractory macromolecular organics into carbon dioxide and water with small molecules [3]. Therefore, many domestic and foreign scholars have studied the ozone combined process [4,5]. In addition, the catalytic ozonation process has been applied to the treatment of nitrobenzene and leachate.

In recent years, the proliferation of organic pollutants in water has posed a serious threat to water resources. Some organic pollutants are difficult to be degraded by conventional oxidation process, so the efficient removal technology of organic pollutants in wastewater has become a research hotspot in recent years. As a strong oxidant, O_3 has a bright future in the treatment of toxic and harmful pollutants, wastewater decolorization, disinfection and sterilization. There are two ways for O_3 to oxidize organic pollutants in water: direct oxidation of O_3 molecules and indirect oxidation of hydroxyl radicals ($HO^•$) produced by O_3 decomposition [6]. However, there are some problems such as low utilization rate of O_3, low mineralization degree of pollutants and high treatment cost. Therefore, in order to improve the utilization rate of O_3 and improve the removal efficiency and mineralization rate of organic pollutants, the combined oxidation method based on O_3 has been gradually developed as a new advanced oxidation water treatment technology with strong competitiveness and environmental friendliness in recent years, showing great advantages in the treatment of refractory water body [7]. Compared with other traditional water treatment technologies, O_3 combined oxidation method can significantly promote the decomposition of O_3, and generate more active free radicals with strong oxidation ability, such as $HO^•$ and sulfate radical (${}^•SO_4^-$), so as to improve the degradation efficiency of organic pollutants in water. Typical O_3 combination oxidation technologies include O_3/H_2O_2 (O_3/H_2O_2), O_3/UV (O_3/UV), O_3/hydroxylamine (O_3/HA), O_3/persulfate (O_3/PS, O_3/PMS), etc. [8].

Based on the application research and development status of various combined oxidation technologies of O_3 in wastewater treatment, this paper summarizes the operation parameters, pollutant degradation effect, degradation process and mechanism of each process. It is found that there is no technology that can be widely applied. It is urgent to develop a new water treatment technology with economic, convenient operation and rapid removal of high concentration organic wastewater to solve the increasingly serious problem of water pollution in China. Therefore, this paper uses γ-Al_2O_3 as catalyst carrier to develop an economical, practical, safe and effective ozone catalytic oxidation technology, which can effectively remove refractory organic pollutants in water, explore the reaction mechanism and water treatment efficiency of this kind of ozone catalytic oxidation technology, and provide basic data for the popularization and application of this technology.

2. Mechanism of ozonation

The standard redox potential of ozone is 2.07 V, which is only lower than F_2 (2.87 V) [9]. Ozone mainly (2) hydroxyl radical (${}^•OH$) produced by ozone decomposition indirectly interacts with organic matter in water. There are two ways to interact with organic matter: The direct oxidation between ozone molecules and organic pollutants; The mass transfer efficiency of ozone single oxidation technology is low and extremely unstable in water, resulting in low utilization rate of ozone. Moreover, ozone has selective degradation of organic matters, and the degradation effect of some organic substances is poor [10]. In view of the problems existing in ozone oxidation alone, researchers at home and abroad have proposed ozone catalytic oxidation technology [11].

The mechanism of ozone oxidation dissolved in water is as follows: (1) direct ozonation mechanism, pollutants in wastewater react with ozone directly, the reaction speed is slow and obvious selectivity; (2) indirect ozonation mechanism, ozone decomposes into strong oxidizing-OH (E = 2.8 V) in water, indirectly oxidizes pollutants in water, the reaction speed is very fast, and there is no selectivity It can increase the polarity of organic chain and increase the polarity.

Direct reaction: pollutant + O_3 → product or intermediate

Indirect reaction: pollutant + ${}^•OH$ → product or intermediate

Catalytic ozonation mainly includes photocatalytic ozonation, homogeneous catalytic ozonation and heterogeneous catalytic ozonation. For the research of photocatalytic ozonation, researchers at home and abroad mainly focus on catalytic materials, creating various catalysts with excellent effect [12,13]. It has been reported in many literatures that photocatalytic ozonation has a good degradation efficiency for chloroform, nitrobenzene and aromatic hydrocarbons which are extremely difficult to degrades [14,15]. Homogeneous catalytic ozonation and heterogeneous catalytic ozonation are mainly used to study the carrier of catalytic addition.

Ozone catalytic oxidation is to increase the rate and quantity of ${}^•OH$ generated in the reaction process by adding catalyst, so as to improve the ozone oxidation effect. It can be divided into homogeneous catalytic oxidation and heterogeneous catalytic oxidation [16,17].

Homogeneous catalytic oxidation is the process of homogeneous catalytic ozonation by adding liquid catalysts (metal ions such as Fe^{2+}, Mn^{2+}, CO^{2+}, H_2O_2, etc.) into the ozonation system. Among them, O_3/H_2O_2 catalytic oxidation technology has been widely used in recent years. The reaction formula of O_3 and H_2O_2 is shown in formula (1):

$$2O_3 + H_2O_2 = 2{}^{\bullet}OH + 3O_2 \tag{1}$$

The results show that both ${}^{\bullet}OH$ and O_3 are important oxidants in O_3/H_2O_2 catalytic oxidation system, and the oxidation effect is different with the initial pH of solution and the dosage of H_2O_2. The final design parameters should be obtained according to different water quality.

Heterogeneous catalytic ozonation is to add solid catalyst to the ozonation system to improve the ozonation ability. Because of its strong oxidation ability, it can significantly reduce the ozone dosage, no secondary pollution, and improve the mineralization rate of organic matter, there are many reports. The catalysts involved are mainly divided into three types: supported catalysts (ceramsite support, Al_2O_3 support, etc.), metal oxides (MnO_2, ZnO, TiO_2, etc.), and porous materials (activated carbon, zeolite, etc.) [18]. In recent years, there are many reports on supported catalysts and activated carbon catalysts. At present, there are many hypotheses about the mechanism of heterogeneous ozone catalytic oxidation, and there is no unified theoretical support system, which is the key research direction in the future.

3. Experiment

3.1. Experimental drugs and instruments

3.1.1. Drugs

Potassium bisulfate, analytically pure, Sinopharm Group Chemical Reagent Co., Ltd.; sodium nitrite, analytical pure, Tianjin Yongda Chemical Reagent Development Center; ammonium sulfamate, analytical pure, Sinopharm Chemical Reagent Co., Ltd.; sulfuric acid, 98%, Beijing Chemical Plant; zinc powder, 99%, Tianjin North Tianyi Chemical Reagent Factory; copper nitrate, analytical pure, Tianjin Guangfu Fine Chemical Research Institute; N-(1-naphthyl) ethylenediamine, analytical pure, Guoyao Group Chemical Reagent Co., Ltd.

3.1.2. Instrument

722E spectrophotometer, Shanghai spectral instrument factory.

3.2. Analysis method

3.2.1. Determination of aniline

In this paper, N-(1-naphthyl) ethylenediamine azo spectrophotometry was used. 5 mL water sample diluted 30 times was put into a 25 mL colorimetric tube, added water to 10 mL, and shaken up. Add 10% potassium bisulfate solution 0.6 mL, adjust pH to 1.5–2.0 (test with precision pH test paper), add 1 drop of 5% sodium nitrite solution, shake well, and place for 3 min. Add 0.5 mL of 2.5% ammonium sulfamate solution, shake well, and place for 3 min. After the bubbles are removed, add 1.0 mL of 2% Neda solution, dilute with water to the scale, shake well, and place for 30 min. At the wavelength of 545 nm, the absorbance was determined with 10 mm cuvette and water as reference. The standard curve is shown in Fig. 1.

3.2.2. Determination of nitrobenzene

The reduction azo photometry method was used. 5 mL of two water samples diluted 30 times were respectively put into a conical flask, and water was added to 20 mL. The water sample (1) was added with 2.0 mL concentrated hydrochloric acid, 0.5 g zinc powder and 2 drops of 10% copper sulfate solution. After being placed for 15 min, the mixture was filtered and transferred to a 50 mL volumetric flask for washing and constant volume. Add 2.0 mL concentrated hydrochloric acid and 2 drops of 10% copper sulfate solution to water sample (2), add water to the mark line, and mix well. Take 10 mL of each solution (1) and 10 mL of two solutions, respectively, into a 25 mL colorimetric tube, add 10% sodium hydroxide solution until white flocculent precipitation (pH5) appears, add water to the mark line, and shake well. Add 1 mL of 20% potassium bisulfate solution and mix well until the white precipitate disappears. Add 1 drop of 5% sodium nitrite solution and shake the hook. Place for 3 min, add 0.5 m1 of 2.5% ammonium sulfamate solution, shake well, place for 3 min, add 1.0 mL of 2% N-(1-naphthyl) ethylenediamine solution, and shake well. After being placed for 30 min, the absorbance was measured with a 10 mm cuvette at the wavelength of 545 nm with water as the reference. Another 20 m1 of water was put into a conical flask, 2.0 mL of concentrated hydrochloric acid and 0.5 g of zinc powder were added. The blank absorbance was measured by the same operation procedure as that of water sample. The difference between the absorbance measured by (1) and (2) after removing the blank absorbance is the absorbance of nitrobenzene and aniline in water sample respectively. The standard curve is shown in Fig. 2.

3.3. Preparation of metal/Al_2O_3 catalyst

Metal/γ-Al_2O_3 catalyst was prepared by impregnation method. The impregnation method has the following advantages: firstly, the ready-made carrier materials with certain shape and size can be used to avoid the molding process; secondly, the suitable support can be selected to

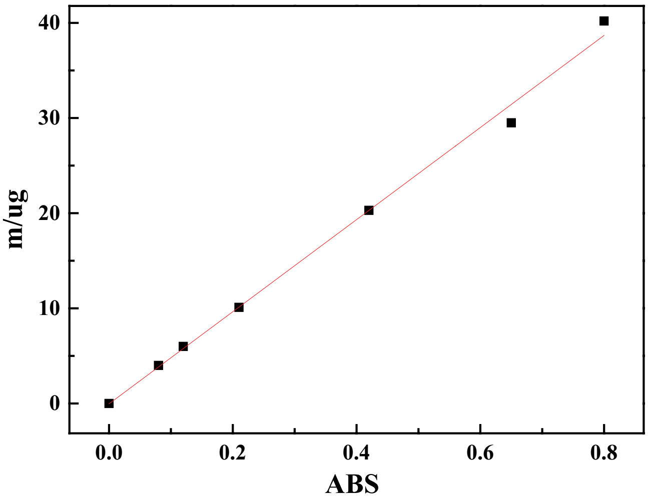

Fig. 1. Standard curve of aniline solution, obtained aniline standard curve: $M = 48.4 \times \text{abs}-0.036$, $R^2 = 0.9945$.

provide the physical structure characteristics required by the catalyst, such as specific surface area and strength; thirdly, because all the impregnated components are distributed on the surface of the support, the amount of the impregnated materials can be reduced and the utilization rate is high. γ-Al_2O_3 was immersed in 10% (by weight of metal elements) salt solution (Fe(III), Ce(III), Cu(II), Mn(II) as nitrate, Ni(II) as sulfate and Co(II) as chloride) for 24 h. After being taken out, it is dried in the air at room temperature, dried in an oven at 85°C for 12 h, roasted at a certain temperature for several hours, and cooled naturally to room temperature. The prepared catalyst was soaked in distilled water, drained, repeated several times until no metal ions were detected, and then dried for standby.

Various single component metal oxides were supported on γ-Al_2O_3 and calcined at 450°C for 4 h. The performance of various supported single component metal catalysts for ozonation was compared. The semi continuous flow operation mode was adopted in the experiment. 30 g catalyst and reaction solution (initial concentration of nitrobenzene was 558.82 mg/L, pH value was 6–7) were added into the reactor, the temperature of water bath pot was adjusted to 25°C, and then the ozone generator was turned on for 5 min, then ozone was continuously injected into the reactor, the O_3 dosage was 116.7 mg/min, and the catalytic time was 30 min.

4. Catalytic oxidation of organic pollutants by O3/Mn Fe supported alumina

4.1. Effect of catalyst dosage on ozonation of nitrobenzene and aniline

Semi continuous flow operation mode was adopted in the test. Firstly, the catalyst and reaction solution (pH = 6–7) were added into the reactor, and the temperature of the water bath was adjusted to 25°C. After the ozone generator was turned on and stabilized for 5 min, it was cut into the reactor to continuously inject ozone with the dosage of 116.7 mg/min, and samples were taken at different times for analysis.

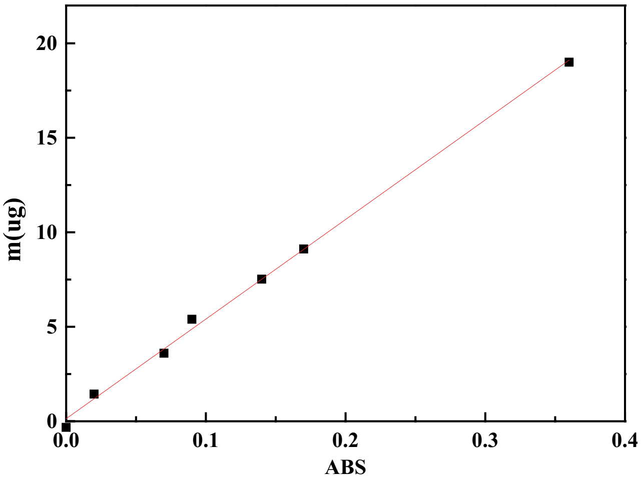

Fig. 2. Standard curve of nitrobenzene solution, the obtained standard curve of nitrobenzene: $M = 52.71 \times ABS + 0.136$, $R^2 = 0.9971$.

The removal effect of aniline is shown in Fig. 3. The removal rate of aniline increased with the increase of reaction time, and the removal rate of aniline in the first 2 min was significantly faster than that in the subsequent time. After 5 min of reaction, the removal rate of aniline was 85.5%, while for Mn Fe/γ-Al_2O_3 catalytic ozonation system, the removal rate of aniline reached 86.4% within 2 min. This may be due to the introduction of Mn Fe/γ-Al_2O_3, which promotes the degradation of aniline. Aniline is easy to be oxidized by ozone. The intermediate products produced in the catalytic process may inhibit the role of hydroxyl radicals, and finally promote the addition of catalyst has no obvious effect on the total removal rate of aniline.

The removal effect of nitrobenzene under different Mn Fe/γ-Al_2O_3 catalyst dosage is shown in Fig. 4. With the increase of catalyst dosage, the removal rate of nitrobenzene by ozone increased. After 30 min reaction, the removal rates of nitrobenzene were 32.6% and 39.9% at low catalyst amount (10 and 20 g/L), which were 14% and 21% higher

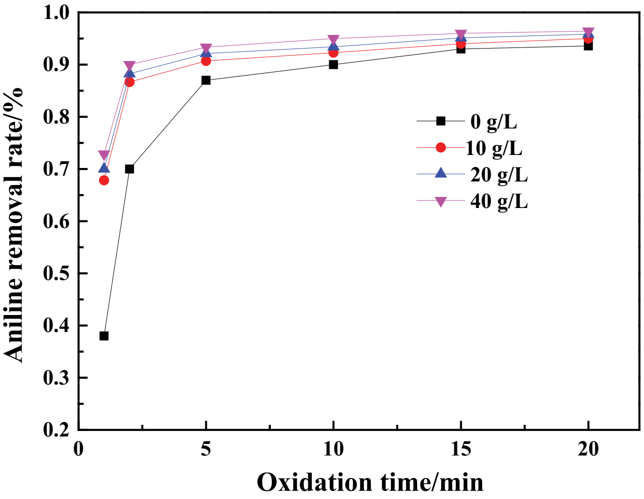

Fig. 3. Effect of catalyst dosage on aniline degradation efficiency.

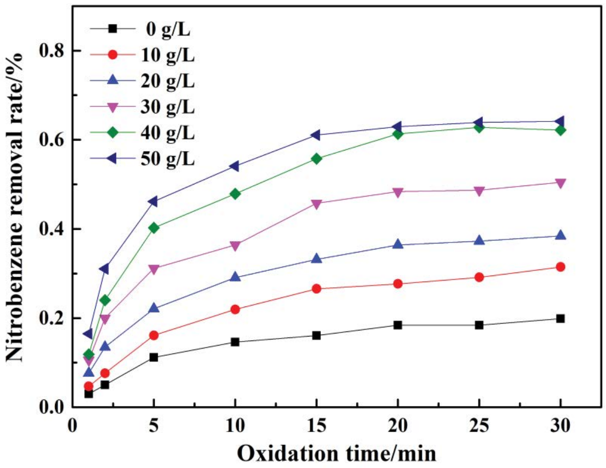

Fig. 4. Effect of catalyst dosage on nitrobenzene degradation efficiency.

than that of ozonation alone. When the dosage of catalyst is more than 30 g/L, the oxidation ability of organic compounds in the process of catalytic ozonation is lower than that of catalyst dosage. After 30 min, the removal rates of nitrobenzene were increased by 38% and 48% respectively at 30 and 40 g/L catalyst dosage. The reason may be due to the increase of Mn Fe/γ-Al_2O_3 dosage, which makes the active sites on the surface of Mn Fe/Al_2O_3 increase, which is more conducive to the production of hydroxyl radicals. Meanwhile, the increase of Mn Fe/γ-Al_2O_3 dosage also increases the collision probability between nitrobenzene, ozone and Mn Fe/γ-Al_2O_3, thus speeding up the reaction rate. However, it can be seen from the figure that the oxidation of nitrobenzene by Mn Fe/γ-Al_2O_3 catalyst in ozone process increases slightly with the increase of catalyst dosage. It can be seen that there is an optimal dosage of catalyst in the process of Mn Fe/γ-Al_2O_3 catalytic ozonation, and the optimum dosage is 40 g/L.

4.2. *Effect of adsorption of catalyst on ozonation of nitrobenzene and aniline*

The heterogeneous catalytic process with solid catalyst can be divided into five stages [19]:

1) Diffusion process: reaction components transfer from the main body of the fluid to the surface of the solid catalyst (including internal diffusion and external diffusion);
2) Adsorption process: the reaction components are adsorbed on the active center of the catalyst surface, and the reactant molecules are in the activated adsorption state;
3) Surface reaction process: chemical reaction on the surface of catalyst;
4) Desorption process: the reaction products are desorbed on the catalyst surface;
5) Product diffusion process: the reaction products are transferred to the main body of the fluid (including internal diffusion and external diffusion).

In the steps (1)–(5), the first and fifth steps are the material transfer of the reaction body on the surface of the catalyst, which is called diffusion process; the second and fourth steps are the process of chemical adsorption and chemical desorption on the particle surface; the third step is the surface reaction kinetic process on the particle surface. The above five steps are in series. The adsorption of nitrobenzene and aniline on the catalyst was investigated in the experiment. Mn Fe/γ-Al_2O_3 catalyst is a polar adsorbent, so it has a certain adsorption capacity for polar molecules aniline and nitrobenzene. Semi continuous flow operation mode was adopted in the test. Add the reaction solution (0.5 L, pH = 6–7) into the reactor, adjust the temperature of the water bath pot to 25°C, and then turn on the ozone generator to stabilize for 5 min. Cut the ozone into the reactor and inject ozone continuously with the dosage of 116.7 mg/min; Add 20 g catalyst into the reactor, cut the ozone into the reactor and continuously inject ozone with the ozone dosage of 116.7 mg/min; Add 40 g catalyst The samples were collected at different time for analysis. Fig. 5 shows the comparison of aniline removal efficiency by ozonation alone, catalyst adsorption and Mn Fe/γ-Al_2O_3 catalytic ozonation. It can be seen from the figure that the adsorption rate of aniline by Mn Fe/γ-Al_2O_3 is about 10%, while the removal rate of aniline after 15 min of ozonation alone and 5 min of catalytic ozonation can reach more than 95%. Therefore, the adsorption of aniline on catalyst plays a small role in the process of catalytic ozonation, mainly the oxidation reaction.

Fig. 6 shows the comparison of the removal efficiency of nitrobenzene by ozonation alone, catalyst adsorption and Mn Fe/γ-Al_2O_3 catalytic ozonation. It can be seen from the figure that the adsorption rate of nitrobenzene by Mn Fe/γ-Al_2O_3 is about 10%. The removal rate of nitrobenzene is about 18.3% after 30 min of ozonation alone, and 65.7% after 30 min of catalytic ozonation. For the oxidation process of nitrobenzene catalyzed by Mn Fe/γ-Al_2O_3, it can be inferred that the adsorption has a certain contribution to the removal of organic matter. However, the removal of organic matter by catalytic ozonation is not a simple superposition

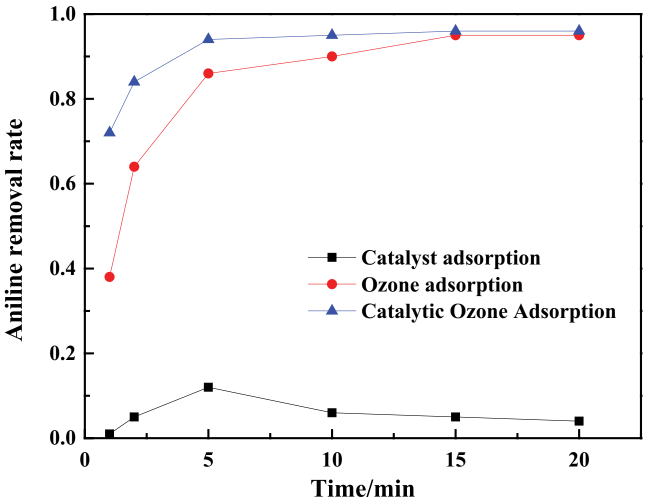

Fig. 5. Effect of adsorption of different catalysts on aniline degradation efficiency.

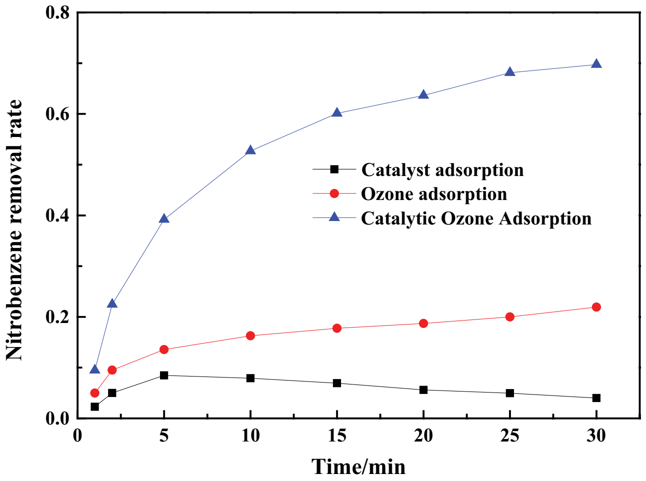

Fig. 6. Effect of catalyst adsorption on nitrobenzene degradation efficiency.

of the oxidation of organic matter by ozone and the adsorption of organic matter by catalyst. Surface hydroxylation is an important surface characteristic of metal oxides in water. The adsorbed organic compounds continue to carry out catalytic decomposition reaction on the surface of the catalyst. The surface hydroxyl groups of metal oxides are the adsorption points of anionic, cationic and ionic organic compounds on the surface of metal oxides in aqueous solution. The reactants are chemically adsorbed on the catalyst surface to form an activated adsorption state, thus reducing the reaction activation energy, accelerating the reaction speed and controlling the reaction direction [20,21].

4.3. Effect of ozone addition on ozonation of nitrobenzene and aniline

Semi continuous flow operation mode was adopted in the test. Firstly, 20 g catalyst and reaction solution (0.5 L, pH = 6–7) were added into the reactor, and the temperature of water bath was adjusted to 25°C. Then, the ozone generator was turned on and stabilized for 5 min. Then, the reactor was cut into to continuously inject ozone, adjust the dosage of O_3, and sample at different times for analysis.

The effect of ozone dosage on catalytic ozonation of aniline is shown in Fig. 7. With the increase of ozone dosage, the removal rate of aniline also increased. When the ozone dosage was 33.3 mg/min, the removal rate of aniline could reach 64.4% after oxidation for 1 min, and 74% when the dosage of ozone was 116.7 mg/min. The removal rate of aniline was more than 92% after 5 min of ozone oxidation. However, the removal rate of aniline was only 11% when air was used instead of ozone. It can be seen that the oxidation effect of ozone on aniline is much stronger than that of air, and the larger the ozone dosage, the better the oxidation effect.

Fig. 8 shows the effects of O_3/Mn Fe/γ-Al_2O_3 on the removal efficiency of nitrobenzene under five ozone dosages (O_3 dosage: 0 mg/min; O_3 dosage: 33.3 mg/min; O_3 dosage: 66.7 mg/min; O_3 dosage: 100 mg/min; O_3 dosage: 116.7 mg/min). It can be seen from Fig. 8 that with the increase of ozone dosage, the removal rate of nitrobenzene by O_3/Mn Fe/γ-Al_2O_3 also increases gradually. Under the same other conditions, the removal rates of nitrobenzene were 8%, 30.8%, 55.3%, 66.0% and 66.7% respectively after 30 min of reaction under the five ozone dosages; the oxidation rate slowed down after 10 min oxidation at low ozone dosage (less than 33.3 mg/min), and the oxidation rate slowed down after 15 min oxidation at high ozone dosage (more than 66.7 mg/min).

4.4. Effect of initial reaction concentration on ozonation of nitrobenzene and aniline

The reaction solutions with different concentrations were prepared and operated in semi continuous flow mode. Firstly, 20 g catalyst and reaction solution (0.5 L, pH = 6–7) were added into the reactor, and the temperature of water bath was adjusted to 25°C. Then, the ozone generator was turned on and stabilized for 5 min. Then, the reactor was cut into and continuously filled with ozone with the dosage of 116.7 mg/min. Samples were taken at different times for analysis. It can be seen from Fig. 9 that when the initial aniline concentration is 51.2 and 105.7 mg/L, the aniline concentration decreases rapidly in the first 1–2 min, and the aniline removal rate reaches about 93%. However, when the initial concentration of aniline was 210.6 mg/L, the same removal rate was achieved after 5 min. When the concentration of aniline in aqueous solution is high, intermediate products are formed and a certain amount of ozone is consumed, which indirectly affects the removal of aniline. When the initial concentration of 210.6 mg/L aqueous solution is 10 min, the removal rate of aniline is more than 95%. The results show that the amount of ozone is the main factor to determine the removal rate of aniline. It also shows that ozone is very effective in the removal of aniline.

The effect of the initial concentration of nitrobenzene on the degradation efficiency of nitrobenzene was investigated. The results are shown in Fig. 10. When the initial concentration of nitrobenzene was 57.3, 113.1, 227.9 and 551.2 mg/L, the effect on the removal rate of nitrobenzene

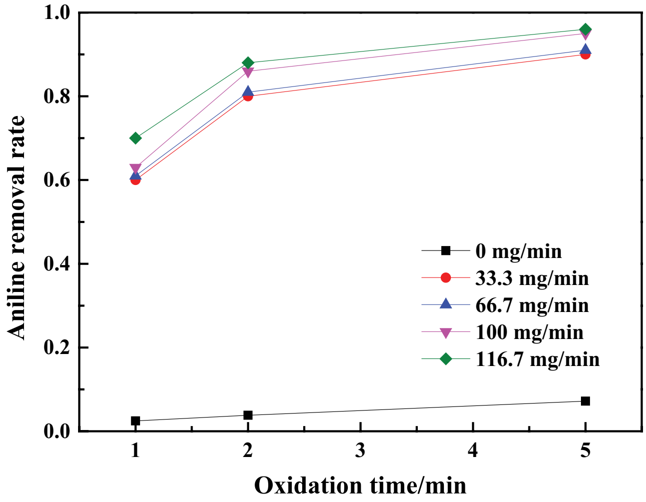

Fig. 7. Effect of ozone dosage on aniline degradation efficiency.

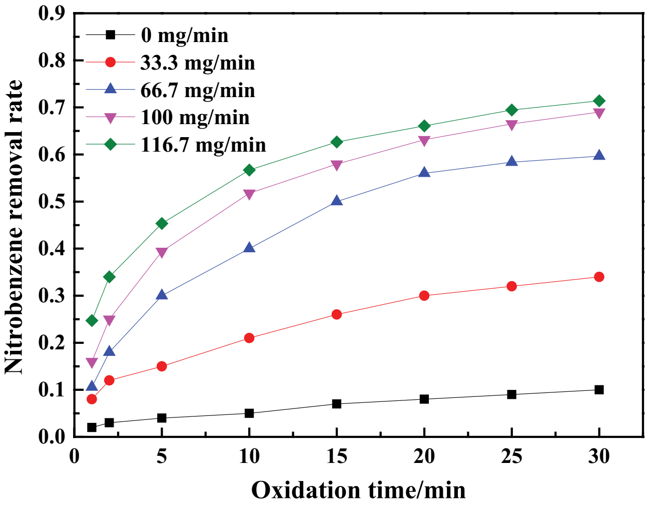

Fig. 8. Effect of ozone dosage on nitrobenzene degradation efficiency.

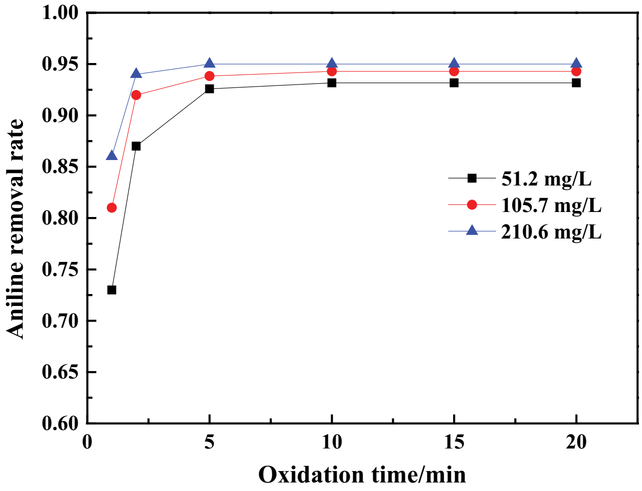

Fig. 9. Effect of initial aniline concentration on aniline removal rate.

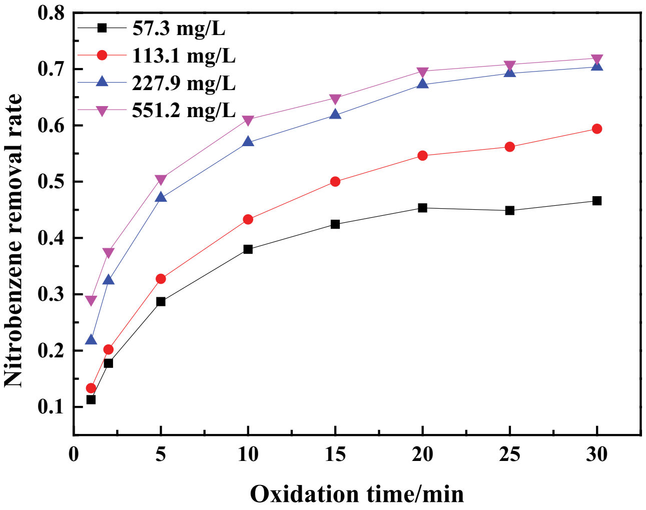

Fig. 10. Effect of initial concentration of nitrobenzene on the removal rate of nitrobenzene.

was positive. The higher the initial concentration of nitrobenzene, the faster the removal rate of nitrobenzene. Further increasing the initial concentration of nitrobenzene has little effect on the removal rate.

4.5. Effect of reaction temperature on ozonation of nitrobenzene and aniline

O_3/Mn Fe/γ-Al_2O_3 oxidation system belongs to gas, liquid and solid three-phase system. The effect of temperature on the reaction system is that, on the one hand, increasing the temperature can reduce the activation energy of the reaction, thus increasing the apparent rate constant of the oxidation reaction; on the other hand, increasing the temperature reduces the driving force of ozone transfer from gas phase to liquid phase. Moreover, too high temperature will accelerate the decomposition rate of ozone. Semi continuous flow operation mode was adopted in the test. Firstly, 20 g catalyst and reaction solution (0.5 L, pH = 6–7) were added into the reactor, and the water bath was adjusted to different temperatures. Then, the ozone generator was turned on and stabilized for 5 min. Then, the reactor was cut in and ozone was continuously injected. The O_3 dosage was 116.7 mg/min. Samples were taken at different times for analysis.

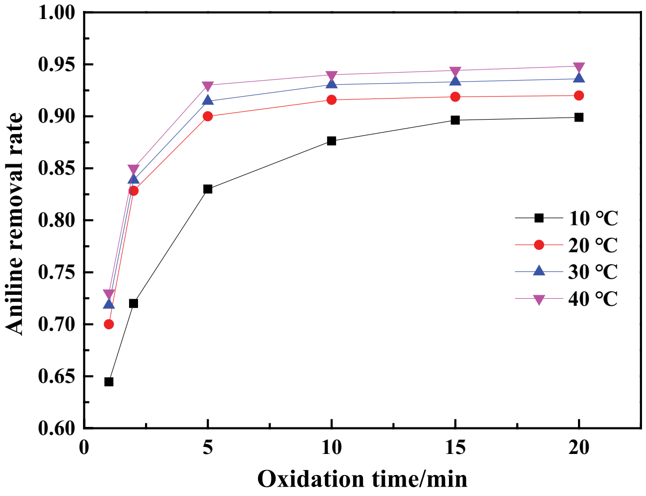

Fig. 11. Effect of different temperature on aniline degradation efficiency.

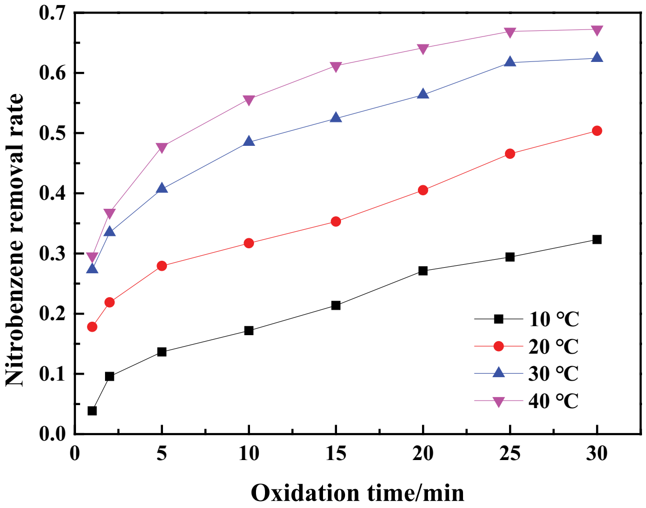

Fig. 12. Effect of different temperature on nitrobenzene degradation efficiency.

Fig. 11 shows the effect of O_3/Mn Fe/γ-Al_2O_3 system on Aniline Removal at different temperatures. It can be seen from the figure that the reaction rate of aniline and ozone increases with the increase of reaction temperature, and the aniline removal rate increases from 90.3% to 95.5%, but the reaction temperature between 30°C and 40°C has little effect on the removal of aniline. Therefore, the reaction temperature of aniline and ozone is 30°C.

The effect of temperature on the degradation rate of nitrobenzene is shown. When the reaction temperature of nitrobenzene and ozone increased, the reaction rate increased, and the removal rate of nitrobenzene increased from 33% to 66.8% by O_3/Mn Fe/γ-Al_2O_3. It can be seen that the effect of temperature on the catalytic ozonation of nitrobenzene is significant, especially when the temperature changes from 10°C to 20°C, the removal rate increases slowly from 20°C to 30°C. When the temperature exceeds 30°C, the concentration of ozone in water decreases due to high temperature, which affects the removal of organic matter.

5. Conclusion

The effect of O_3/Mn Fe/γ-Al_2O_3 catalyst system on the removal of aniline and nitrobenzene was studied by semi continuous flow method:

- The O_3/Mn Fe/γ-Al_2O_3 catalytic oxidation system has good removal rate of nitrobenzene and aniline. (1) Under the same experimental conditions, the removal rates of aniline and nitrobenzene by ozonation were 86.4% (5 min) and 25.56% (30 min), respectively, while the removal rates of aniline and nitrobenzene in O_3/Mn Fe/γ-Al_2O_3 system were 93.9% (5 min) and 67.7%, respectively; (2) The removal rates of aniline and nitrobenzene were 10.4% and 9.3% respectively, and there was desorption of catalyst; (3) The removal rates of aniline and nitrobenzene were affected by ozone dosage, initial concentration and reaction system temperature.

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