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Removal of *p*-chlorophenol in wastewater through catalytic ozonation using MnO_x/Al_2O_3

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In order to study the effect of catalytic ozonation with MnO_x/Al_2O_3 in wastewater purification, the effect of the catalyst MnO_x/Al_2O_3 on the removal of p-chlorophenol from water samples was simulated. The results showed that the addition of catalyst for 10 min of reaction could improve the removal efficiency by 20.15% in comparison with ozone alone. The catalyst was prepared by the impregnation method with a 1.5 $mol\cdot L^{-1}$ precursor solution of manganese nitrate. The removal efficiency was good at a calcination temperature of 500ºC, and the removal rate reached 81.75% after 20 min of reaction. The catalyst was stable, and the removal rate of the catalyst after repeated use was 70.12% after 20 min of reaction. The characterization results show that the surface of the catalyst MnO_x/Al_2O_3 has a more active reaction platform than the carrier Al_2O_3, which is helpful to improve the catalytic activity.

Keywords: Catalytic ozonation; MnO_x/Al_2O_3; *p*-chlorophenol

INTRODUCTION

With the increasingly serious industrial wastewater pollution, the toxicity, bioaccumulation and other characteristics of organic pollutants in wastewater can harm human health [1]. The organic pollutants in the organic wastewater include aromatic compounds, phenols and heterocyclic compounds, and their damage to the water environment gradually increases. The removal of organic pollutants in wastewater generally includes: adsorption, coagulating sedimentation, advanced oxidation, etc. [2,3]. The catalytic ozonation technology has the characteristics of rapid response, low cost and no secondary pollution. It has a wide application prospect for the deep treatment of industrial wastewater.

The mechanism of catalytic ozonation consists in producing ·OH with strong oxidizing property through the decomposition of the ozone attached to the catalyst surface hydroxyl groups. ·OH can promote free radical chain reactions in the solution and on the catalyst surface [4]. The use of catalyst in the reaction can effectively promote the formation and utilization of active substances such as ·OH. Under mild experimental conditions, the organic pollutants in wastewater can be removed quickly [5,6]. The commonly used catalytic materials are activated carbon [7], honeycomb ceramics and porous metal oxides [8,9], which can load active components or directly serve as a catalyst in ozone degradation reaction, enhance ozone oxidation effect, and effectively remove organic pollutants from wastewater [10]. The catalyst with metal oxides as stable active components determines the removal efficiency of ozone oxidation, high efficiency, long life, etc., and is widely used in the catalytic ozonation research [11,12]. In this paper, the catalyst MnO_x/Al_2O_3 was used to remove the target pollutant *p*-chlorophenol in wastewater, and the catalyst was added to the single ozone system to enhance the oxidation efficiency of ozone and increase the production and utilization rate of ·OH.

EXPERIMENTAL

Materials

Main instruments and reagents

Instruments: ozone generator (Taixing Environmental Protection Equipment Co., Ltd., model QHW-15), constant temperature water bath, pH meter, UV-visible spectrophotometer, tube furnace, drying oven, high performance liquid chromatograph (HPLC, LC-10T), fully automatic specific surface area analyzer (V-Sorb 2800P).

Reagents: methyl alcohol, chromatographically pure, *p*-chlorophenol, calcium carbonate, manganese nitrate, indigo disodium sulfonate, sodium thiosulfate and potassium iodide, all analytically pure. In the preparation of aqueous solutions ultrapure deionized water was used, in which *p*-chlorophenol was not detected.

Test apparatus

As shown in Fig.1, the apparatus is made of ordinary glass and polyethylene plastic, the connecting part is rubber tube, the reaction column is placed in a water bath and the bottom part has an aerating apparatus. Prior to the start of the test, the reaction column was washed with ultrapure water three times and treated by pre-ozonation for 5 min

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to remove impurities remaining in the reaction column. All solutions used in the test were prepared using ultrapure water. The apparatus was placed and conducted in a fume hood.

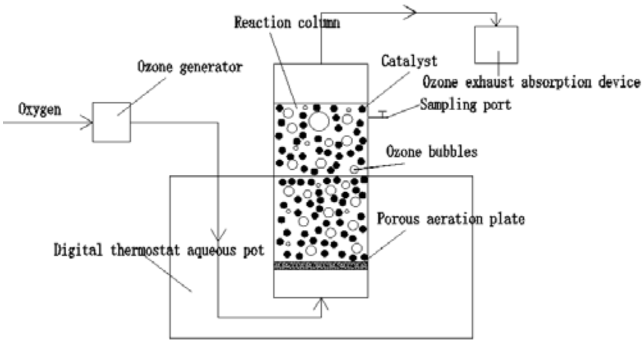

Fig. 1. Test apparatus

In the test, the appropriate amount of sample solution was taken at different time points, sodium thiosulfate solution (0.5 mL, 0.01 mol·L^{-1}) was added to stop the reaction, the sample solution was analyzed by HPLC (High Performance Liquid Chromatography), the test exhaust was introduced into a KI solution (2%) for absorption. Simulated industrial wastewater (50.0 mg·L^{-1} *p*-chlorophenol) was used.

Pretreatment of catalyst

Catalyst carrier is an important factor affecting the catalyst performance. The carrier should have unique structure (specific surface area, pore structure) to ensure the thermal stability and mechanical strength of the catalyst, and is the active center of the reaction. In the catalytic ozonation system, the commonly used carriers are Al_2O_3, TiO_2, honeycomb ceramics, activated carbon, etc. The reaction conditions of catalytic ozonation are mild, the reaction solution contains no strong acid and alkali, and will not cause great damage to the catalyst structure. Al_2O_3, honeycomb ceramics and activated carbon have porous structure and large effective specific surface area, which are suitable to a catalyst carrier. In the catalytic ozonation system, ozone adsorption ability of the catalyst surface and the ability to generate·OH determines the catalytic capacity. Metal oxides MnO_x, TiO_2 and other materials are widely used in catalytic ozonation to improve the production and utilization rate of ·OH. Al_2O_3 has a large specific surface area and high mechanical strength, this test loads MnO_x by taking Al_2O_3 as the carrier to study its effect in ozonation reaction.

Carrier Al_2O_3 (Φ5 mm, YiPu Catalyst Co., Ltd.) was grinded, passed through a 60 mesh nylon sieve, baked for 15 h at 95°C in the drying oven after being washed, and then roasted for 5 h at 500 °C in the tube furnace to remove surface impurities, then, after natural cooling the carrier Al_2O_3 was preserved. The treated Al_2O_3 was impregnated in a 1.5 mol·L^{-1} solution of manganese nitrate, stirred continuously for 24 h, aged at 105 °C for 24 hours, washed with ultrapure water, dried at 105 °C for 10 h, and roasted at 500 °C for 5 h to obtain the catalyst MnO_x/Al_2O_3.

Analysis method

Determination of *p*-chlorophenol in water samples: *p*-chlorophenol was determined by HPLC with the chromatographic column (4.6 mm×250 mm, 5μm, C-18-AR-II). Detection wavelength was 280 nm, mobile phase consisted of methanol and water (volume ratio of 7:3), flow rate =1.0mL·min^{-1}. The samples analyzed by liquid chromatography were compared with standard samples by qualitative and quantitative analysis.

Determination of ozone concentration in water samples using the indigo disodium sulfonate method was used with a UV-visible spectrophotometer at a wavelength of 610 nm. Catalyst characterization: the specific surface area and pore volume of the catalyst samples were determined using a fully automated specific surface area and porosity analyzer.

RESULTS AND DISCUSSION

Effect of load mode

Impregnation method takes manganese nitrate as the precursor, adding the treated Al_2O_3; precipitation method adds the solution of calcium carbonate to the manganese nitrate solution by drops; formed precipitate loads to the surface of Al_2O_3, the concentration of each solution was 1.5 mol·L^{-1}. MnO_x was loaded onto Al_2O_3 to remove *p*-chlorophenol in wastewater by impregnation method and precipitation method, the results are shown in Fig. 2. Test conditions: C_{O3}=2.0 mg·L^{-1}, $C_{p\text{-chlorophenol}}$=50.0 mg·L^{-1}, $C_{MnOx/Al2O3}$=2.0 g·L^{-1}, pH=6.5, *t*=20 °C, the follow-up test will adopt the same reaction conditions if not specified.

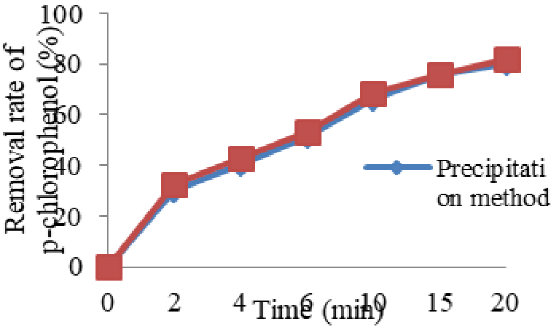

Fig. 2. Effect of load mode

As can be seen from Fig. 2, the removal rate of *p*-chlorophenol reached 80.27% and 82.09%, respectively, after 20 min of reaction using the catalyst. This indicates that the dispersion effect of MnO_x on the carrier surface is good, the precipitation method does not significantly improve the load effect, and there is no obvious removal performance difference of *p*-chlorophenol after calcination of the catalyst.

Effect of impregnation liquid concentration

Fig. 3 shows the comparison of the removal efficiency of *p*-chlorophenol by the catalyst prepared with different concentrations of manganese nitrate precursor solution.

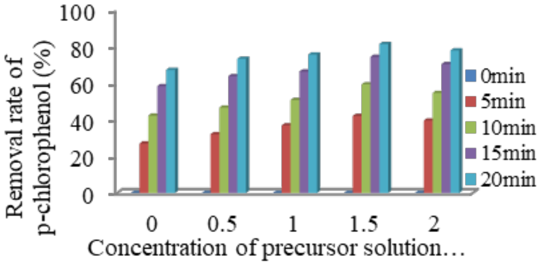

Fig. 3. Effect of precursor solution on MnO_x/Al_2O_3

It is observed that the removal efficiency of *p*-chlorophenol in the solution is enhanced with the increase in precursor solution concentration. When the concentration of precursor solution reached 1.5 $mol \cdot L^{-1}$, the removal efficiency of *p*-chlorophenol was significant, reaching 74.28% in 15 min and 81.31% in 20 min. When the concentration of manganese nitrate precursor solution was increased, the removal rate of p-chlorophenol decreased, and when manganese nitrate solution was 2.0 $mol \cdot L^{-1}$, the removal rate of p-chlorophenol was 70.31% after 15 min of reaction and 77.81% after 20 min. This was so because at a low concentration of precursor solution the loading of MnO_x on the carrier surface was low. After high-temperature calcination, some active sites of the carrier Al_2O_3 were inactivated, so the removal rate of *p*-chlorophenol decreased. When the concentration of the precursor solution was increased, the MnO_x loading on Al_2O_3 surface increases. After high-temperature calcination, a large amount of MnO_x adhered to the surface of the carrier, which blocked the pore structure of Al_2O_3, resulting in reduction of the effective surface area of the carrier, leading to a decrease in the number of active sites on the catalyst surface and in removal efficiency.

Effect of calcination temperature

The calcination temperature in preparing the catalyst MnO_x/Al_2O_3 by the impregnation method affects the catalytic activity. The mechanical strength of MnO_x/Al_2O_3 can be increased by calcination, and the active component can be retained. At the same time, the surface impurities of MnO_x/Al_2O_3 can be removed, so that the catalyst MnO_x/Al_2O_3 has a more effective surface area and a richer pore structure. This requires a suitable calcination temperature. The high calcination temperature not only damages the surface pore structure of the catalyst, but also affects the formation of MnO_x/Al_2O_3 surface active components and crystal structure, leading to the reduction of MnO_x/Al_2O_3 specific surface area.

Fig. 4 shows the comparison of the removal efficiency of *p*-chlorophenol by the catalyst (concentration of precursor solution 1.5 $mol \cdot L^{-1}$) after 5 h of calcination at temperatures of 300 °C, 400 °C, 500 °C, 600 °C.

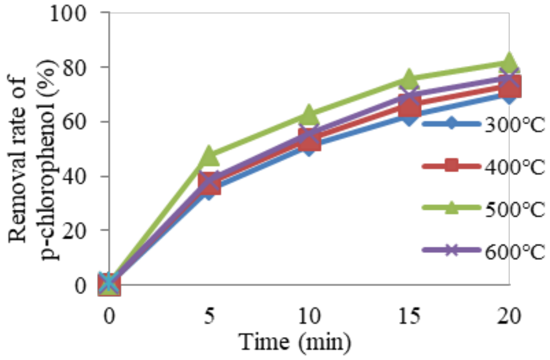

Fig. 4. Effect of calcination temperature on MnO_x/Al_2O_3

The results show that the calcination temperature has a significant effect on the removal of *p*-chlorophenol by the catalyst MnO_x/Al_2O_3 When the calcination temperature gradually increased, the removal rate of p-chlorophenol first increased and then decreased, and catalytic ozonation was better at a calcination temperature of 500 °C. When the temperature was raised from 300 °C to 500 °C, the removal rate of *p*-chlorophenol increased from 70.20% to 81.75% after 20 min of reaction, and the removal rate of p-chlorophenol was reduced to 76.36% at 600 °C. Because the temperature gradually increased in the catalyst crystal formation process, the catalyst surface generated more active sites and increased catalytic activity. When the catalyst MnO_x/Al_2O_3 calcination temperature reached 500 °C, the active sites were evenly distributed on the surface of MnO_x/Al_2O_3 after calcination, achieving a balance. The temperature increase will change the surface crystal structure of MnO_x/Al_2O_3, decrease the active sites and reduce the catalytic activity, and the removal rate will decrease. The preparation conditions of MnO_x/Al_2O_3 in the follow-up test are as follows: concentration of precursor solution: 1.5 $mol \cdot L^{-1}$, calcination temperature: 500 °C.

Effect of reaction temperature

In the case of ozone, the reaction temperature has two effects: as the temperature increases, the reaction rate increases, and the number of activated molecules increases; while the solubility of ozone in water is negatively correlated with temperature, the temperature increases, the ozone in solution decreases, and the utilization rate decreases. Fig. 5 shows the removal rate of *p*-chlorophenol and the volatilization of *p*-chlorophenol at temperatures *t* of 10, 20, 30, 40, 50, 60 ºC under the conditions of O_3+MnO_x/Al_2O_3 and O_3 alone. The reaction conditions only changed the reaction temperature, other conditions remained unchanged.

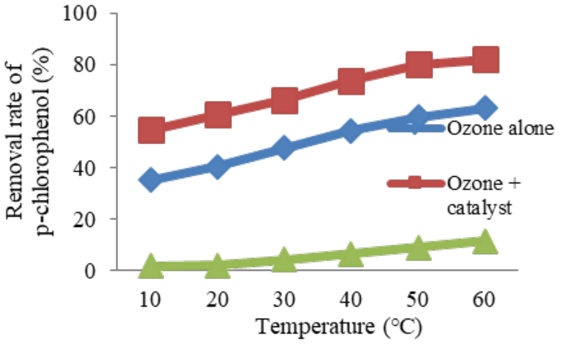

Fig. 5. Effect of reaction temperature on the removal of *p*-chlorophenol

It can be seen from Fig. 5 that the volatilization of *p*-chlorophenol increases with the increase in reaction temperature, the volatilization rate is 1.65% at 10 ºC and 11.37% at 60 ºC. The removal rate of p-chlorophenol by O_3+MnO_x/Al_2O_3 and O_3 system alone gradually increased with the increase of reaction temperature. When the temperature rose from 10ºC to 60ºC, the removal rate of p-chlorophenol by O_3+ MnO_x/Al_2O_3 increased from 54.67% to 82.13% after 10 min of reaction, and the removal rate of ozone alone increased from 35.26% to 63.17%. The removal rate was by 20.15% higher than that of ozone alone after 10 min of reaction at a normal temperature of 20 ºC, and the removal efficiency by using O_3+MnO_x/Al_2O_3 was significantly increased. The catalyst promoted the formation of ·OH by ozone decomposition over the experimental temperature range, the removal of organic pollutants from wastewater by catalytic ozonation is significant.

Stability of MnO_x/Al_2O_3

The catalyst (MnO_x/Al_2O_3) was used repeatedly (1, 2, 5, 8 and 10 times), each time during 10 h. Fig. 6 shows the results of the repeated removal of *p*-chlorophenol by MnO_x/Al_2O_3. It can be seen that repeated use of MnO_x/Al_2O_3 has a certain effect on the removal efficiency. The increase in the time of use and the decrease in removal efficiency are due to the presence of certain substances in the removal process that are attached to the surface and pore structure of the catalyst and cover some active centers, leading to inactivation of some active sites on the MnO_x/Al_2O_3 surface, even causing some MnO_x/Al_2O_3 to completely lose activity.

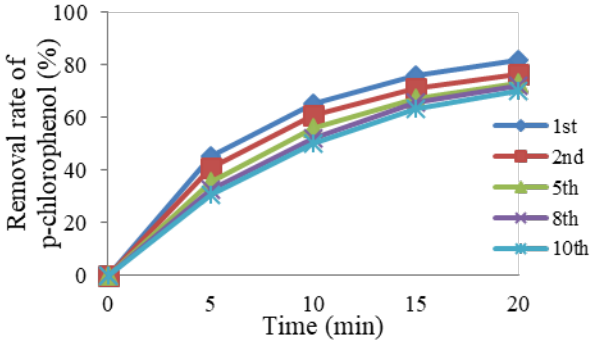

Fig. 6. Effect of repeated use of the catalyst on the removal of *p*-chlorophenol

The repeated use of the catalyst can decrease the activity of the catalyst, but the decrease degree is small. After 100 h of use, the removal rate of p-chlorophenol was still above 70.12% after 20 min of reaction.

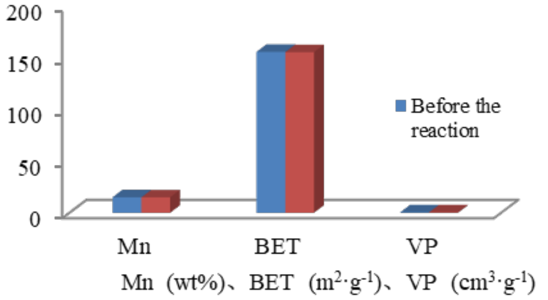

Fig. 7. Measurement results of MnO_x/Al_2O_3specific surface area

Fig. 7 shows the results of specific surface area measurement of the catalyst MnO_x/Al_2O_3, Mn content, specific surface area and pore volume of MnO_x/Al_2O_3 before and after the reaction (not used and used 10 times). It was found that MnO_x/Al_2O_3 had a slight decrease in specific surface area and a 0.1 wt% decrease in Mn content, MnO_x/Al_2O_3 pore volume slightly increased, but the change was very small, so after the catalyst MnO_x/Al_2O_3 has been used 10 times and for a total of 100 h, the specific surface area and surface morphology only had minor changes.

Characterization analysis of MnO_x/Al_2O_3

The active sites and the adsorption sites on the catalyst surface are determined by their specific surface area, pore volume, pore size, etc. The catalyst plays an important role in catalytic ozonation. Catalytic ozone reaction occurs on the surface of the catalyst. The unsaturated oxygen atoms and metal ions on the catalyst surface correspond to Lewis bases and acids, while Brønsted acid, Lewis base and acid sites are the active centres of the catalyst. The test measured the specific surface area of the catalyst MnO_x/Al_2O_3 and the carrier Al_2O_3, the results are shown in Table 1.

Table 1. Specific surface area measurement results of Al_2O_3 and MnO_x/Al_2O_3

	Mn, (wt%)	BET, ($m^2 \cdot g^{-1}$)	VP, ($cm^3 \cdot g^{-1}$)
Al_2O_3	0	182.6281	0.58595
MnO_x/Al_2O_3	15.02	155.7832	0.57987

As shown in Table 1, the specific surface area and pore volume of the carrier Al_2O_3 are larger than that of the catalyst surface because MnO_x is loaded on the carrier surface at high temperature. The Mn content in the catalyst is 15.02 wt%. According to preliminary test results, the removal efficiency of *p*-chlorophenol by the ozonation using the catalyst MnO_x/Al_2O_3 can improve the catalytic activity of the reaction system.

Although the effective specific surface area and pore volume of MnO_x/Al_2O_3 decreased, the catalytic activity of MnO_x/Al_2O_3 was still good, indicating that the number of active sites on the catalyst surface did not decrease. It can be seen that the catalyst MnO_x/Al_2O_3 surface can provide a more favorable reaction platform, promote the adsorption of organic compounds in the solution and the decomposition of ozone, effectively removing the organic pollutants in the wastewater.

CONCLUSIONS

(1) The preparation conditions of the catalyst MnO_x/Al_2O_3 were screened out by using *p*-chlorophenol (50 $mg \cdot L^{-1}$) as the target pollutant, comparing with the removal efficiency using different loading methods, concentrations of precursor and calcination temperatures. The effects of different preparation methods (impregnation method and precipitation method) on the catalytic activity were not obvious. The catalytic activity of the catalyst MnO_x/Al_2O_3 was influenced by the calcination temperature – as the calcination temperature increased, both MnO_x/Al_2O_3 surface activity and the catalytic activity of the catalyst increased. However, the catalytic activity of MnO_x/Al_2O_3 will be weakened when the calcination temperature is too high. The favorable calcination temperature is 500ºC. MnO_x/Al_2O_3 was prepared at the calcination temperature of 500 ºC and with a 1.5 $mol \cdot L^{-1}$ manganese nitrate precursor solution the removal rate of *p*-chlorophenol was 81.75% after 20 min of reaction.

(2) After the catalyst MnO_x/Al_2O_3 has been used 10 times for a total of 100 h, the catalytic effect was still good, and the removal rate of *p*-chlorophenol was above 70.12% after 20 min of reaction and repeated use. When the temperature rose from 10 ºC to 60 ºC, the volatilization rate of *p*-chlorophenol increased, the removal efficiency by O_3+ MnO_x/Al_2O_3 and O_3 system alone gradually increased with the increase in temperature. O_3+MnO_x/Al_2O_3 catalyst system can effectively remove p-chlorophenol in wastewater in the mentioned temperature range.

(3) The analysis of carrier Al_2O_3 and catalyst MnO_x/Al_2O_3 showed that the Mn content in the catalyst was 15.02 wt%. Compared with carrier $A1_2O_3$, the specific surface area and pore volume of the catalyst MnO_x/Al_2O_3 were reduced, but MnO_x/Al_2O_3 surface can provide more active reaction platforms, thus creating a place for the generation and reaction of ·OH and helping to improve the catalytic performance.

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