Synergistic Treatment of Low-concentration Organic Waste Gas by Micro-nano Bubble Coordinated with Peroxymonosulfate

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Abstract Continuous dynamic experiment was conducted for the treatment of low-concentration organic waste gas with xylene as a representative, using micro-nano bubble and peroxymonosulfate working in synergy. The degradation rule of xylene under different conditions such as the ORP value of the spray liquid, pH value of the spray liquid, liquid – gas ratio of the spray liquid, residence time of xylene, and initial concentration of xylene was investigated. The results showed that at a low concentration, the pH value of the spray liquid had little effect on the degradation rate of xylene. The degradation rate of xylene rose with the increase of the ORP value of the spray liquid, the liquid – gas ratio of the spray liquid, the residence time of xylene, and the initial concentration of xylene.

Key words Micro-nano bubble; Peroxymonosulfate; Synergy; Low concentration; Organic waste gas

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Volatile organic compounds (VOCs) are a major class of compounds that pollute the atmospheric environment. Most of these organic compounds are toxic, and some have been listed as carcinogens, such as vinyl chloride, benzene, polycyclic aromatic hydrocarbons, *etc*. Typical compounds include benzene series, esters, halogenated hydrocarbons with low molecular weight, and alcohols[1]. Most of the organic waste gases generated in industry are of low concentration, such as furniture, plywood, paint spraying, printing, footwear and other industries. Low-concentration organic waste gases are not suitable for direct incineration treatment. If incineration treatment is required, concentration must be carried out first to increase the concentration of organic matter. At present, biological degradation, chemical degradation, adsorption and other processes are commonly used to treat low-concentration organic waste gas. The biological method has a lower cost and less secondary pollution, but its applicable concentration is narrow and its resistance to fluctuations is poor[2]. In addition, the treatment effect of organic waste gases with high toxicity (such as dichloromethane) or difficult biodegradation (such as those containing benzene ring structure) is not satisfactory. The chemical degradation method has a thorough degradation effect, but the operating cost is high. Although adsorption method has high degradation rate and low operating cost, it requires hazardous waste disposal or desorption and regeneration of saturated adsorbents to achieve recycling. The regeneration of adsorbents usually adopts the thermal desorption method, and the high-concentration organic waste gas desorbed still needs to be treated. This processing has the characteristic of high energy consumption and is prone to secondary pollution. Advanced oxidation technology is a recently emerging organic waste gas treatment technology, which has attracted much attention due to its fast reaction rate, mild reaction conditions, and high treatment efficiency[3]. Advanced oxidation technology can effectively break the chemical bonds of organic compounds by inputting external energy. At the same time, these energy can also affect the reaction medium, and more oxidative free radicals could be produced, such as hydroxyl groups, excited oxygen, sulfate ions, *etc.*, thereby enhancing the degradation ability of organic compounds. New oxidants represented by peroxymonosulfate have received widespread attention in the field of organic wastewater treatment. Peroxymonosulfate is easily activated in a normal temperature and pressure environment, producing oxidative free radicals such as hydroxyl, excited oxygen, sulfate ions, *etc.* Its oxidizing property is higher than those of ozone or hydrogen peroxide.

This experiment investigated the degradation of xylene using micro nano bubbles in collaboration with peroxymonosulfate, and explored the degradation laws of xylene under different conditions such as ORP of spray liquid, pH value of spray liquid, liquid – gas ratio of spray liquid, residence time of xylene, and initial concentration of xylene.

1 Experimental materials and methods

1.1 Experimental materials Xylene: 99.9% of purity (China National Pharmaceutical Group Chemical Reagent Co., Ltd.); concentrated sulfuric acid: 98% of concentration (China National Pharmaceutical Group Chemical Reagent Co., Ltd.); sodium hy-

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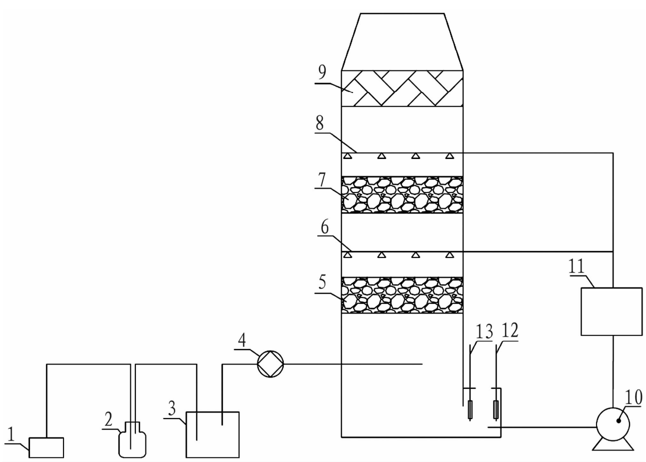
droxide solution: 10% of concentration (Shenzhen Chengyuan Technology Co., Ltd.); peroxymonosulfate: 99.5% of purity (Nantong Runfeng Petrochemical Co., Ltd.).

1.2 Experimental instruments Spray tower; gas chromatograph (Agilent 7890B); micro nano bubble generation device (Hangzhou Guiguan Environmental Protection Technology Co., Ltd., HGQP-1); pH meter (MEACON meacon); ORP meter (MEACON meacon).

The spray tower is made of PVC material, tower diameter $D = 1.0$ m, height $H = 3.0$ m. Two spray layers are installed vertically inside the tower, with a vertical height of 0.4 m for each layer of filling material. The bottom of the spray tower is a circulating water tank, in which peroxymonosulfate is added. The inlet of the booster pump is connected to the circulating water tank, and the outlet is connected to the micro nano bubble generation device. The generated micro nano bubbles enter the spray layer of the spray tower through pipelines.

1.3 Experimental process The micro nano bubble coordinating with peroxymonosulfate treatment system for low-concentration organic waste gas includes a waste gas generation device, a spray tower, and a micro nano bubble generation device. The experimental device flow is shown in Fig. 1.



Note: 1. Air pump; 2. Bubble bottle; 3. Wind cabinet; 4. Induced draft fan; 5. First filling layer; 6. First spray layer; 7. Second filling layer; 8. Second spray layer; 9. Defogging layer; 10. Booster pump; 11. Micro nano bubble generator; 12. pH meter; 12. ORP meter.

Fig. 1 Schematic diagram of the experimental setup

Xylene solution is added to a 100 ml of bubbling bottle, and an air pump is used to blow air into the bottle to generate high concentration of xylene gas. The high-concentration xylene gas is mixed with air in the wind cabinet to form low-concentration organic waste gas. The organic waste gas in the wind cabinet is sent to the spray tower by an induced draft fan. The organic waste gas is treated by micro nano bubbles coordinating with peroxymonosulfate, and then led out from the top of the spray tower. The concentration of pollutants before the synergistic treatment of micro nano bubbles with peroxymonosulfate enters the gas chromatograph for online analysis through the sampling port in front of the induced draft fan, while the concentration of pollutants after treatment enters the gas chromatograph for online analysis through the sampling port at the top of the spray tower.

1.4 Evaluation method The formula for calculating the degradation rate of xylene is as follows:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

where η is degradation rate of xylene (%); C_{in} is concentration of inlet gas (mg/m^3); C_{out} is concentration of outlet gas (mg/m^3).

2 Results and analysis

2.1 Changes in degradation rate of xylene with ORP of spray liquid Setting the intake concentration of xylene as 200 mg/m^3, the residence time of xylene as 12 s, the pH value of the spray liquid as 7, and the liquid - gas ratio of the spray liquid as 4 L/m^3, the effect of spray liquid ORP on the degradation rate of xylene under the set conditions was studied, and the results were shown in Fig. 2.

As shown in Fig. 2, the degradation rate of xylene rose with the increase of spray liquid ORP. When the ORP of spray liquid increased from 300 to 500 mV, the degradation rate of xylene increased from 20.64% to 81.17%. Under the synergistic effect of micro nano bubbles, peroxymonosulfate generated oxidative free radicals such as hydroxyl, excited oxygen, sulfate ions, *etc.* Their reduction potential E_0 was between +2.6 and +2.8 V, indicating extremely strong oxidizing property. As the ORP of the spray liquid increased, the concentration of oxidizing substances in the spray liquid also increased, so the degradation rate of xylene also rose. The increase of ORP in the spray liquid is directly proportional to the mass of peroxymonosulfate added. In practical engineering, ORP meters can be used to accurately control the redox reaction by using the electrical signal of ORP as a detection and control method, and reduce the amount of oxidant used, thereby reducing operating costs.

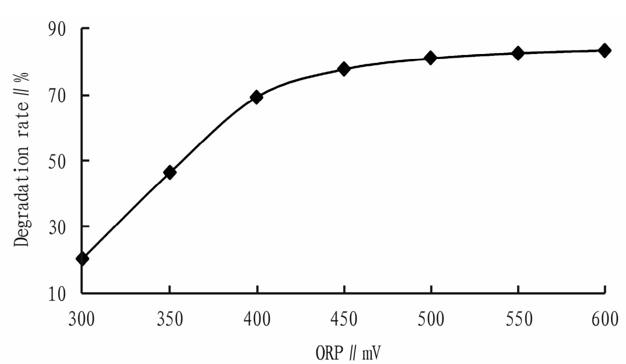


Fig. 2 Changes in degradation rate of xylene with the ORP of spray liquid

2.2 Changes in degradation rate of xylene with the pH value of spray liquid The experiment selected concentrated sulfuric acid and sodium hydroxide solutions to adjust the pH value of the spray liquid. Setting the intake concentration of xylene as 200 mg/m^3, the liquid - gas ratio of spray liquid as 4 L/m^3, the retention time of xylene as 12 s, and the ORP of the spray liquid as 500 mV, the effect of the pH value of spray liquid on the degradation rate of xylene under the set conditions was studied, and the results were shown in Fig. 3.

From Fig. 3, it can be seen that different pH values of spray liquid had little effect on the degradation rate of xylene. The main reason is that persulfate has high activity at pH < 3 and also under alkaline conditions (pH > 10)[4]. Therefore, the activation of persulfate produces oxidative free radicals, such as hydroxyl groups, excited oxygen, sulfate ions, *etc.*, which are not significantly affected by pH values. In practical engineering application, strong alkaline or acidic conditions can cause equipment to corrode, so the use of persulfate under alkaline or acidic conditions has higher requirements for equipment.

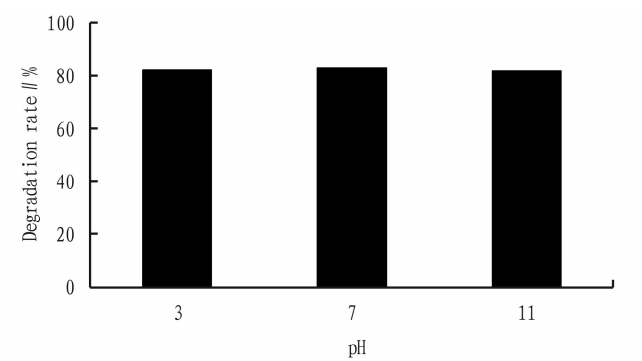


Fig. 3 Changes in degradation rate of xylene with the pH value of spray liquid

2.3 Changes in degradation rate of xylene with the liquid – gas ratio of the spray liquid Setting the intake concentrations of xylene as 200 mg/m^3, the retention time of xylene as 12 s, the pH value of spray liquid as 7, and the ORP of spray liquid as 500 mV, the effect of the liquid – gas ratio of spray liquid on the degradation rate of xylene under the set conditions was studied, and the results were shown in Fig. 4.

As shown in Fig. 4, when the liquid – gas ratio of spray liquid was improved from 1 to 4 L/m^3, the degradation rate of xylene increased from 29.49% to 81.51%. When the liquid – gas ratio of spray liquid reached 4 L/m^3, the degradation rate of xylene tended to stabilize. When the liquid – gas ratio reached 5 L/m^3, the increase in the degradation rate of xylene decreased. The spray liquid contains a large amount of oxidation free radicals generated by the synergistic effect of micro nano bubble and peroxymonosulfate, such as hydroxyl groups, excited oxygen, sulfate ions, *etc.* As the spray liquid continues to increase, the density of the atomized liquid inside the tower gradually increases, allowing for more thorough contact and collision between xylene gas and atomized liquid, and more intense oxidation and decomposition reaction. Therefore, the degradation rate of xylene gradually increases. However, when the liquid – gas ratio of spray liquid reaches a certain value, the probability of gas-liquid contact and collision tends to stabilize. So it has little effect on the degradation effect of xylene even increasing the liquid – gas ratio.

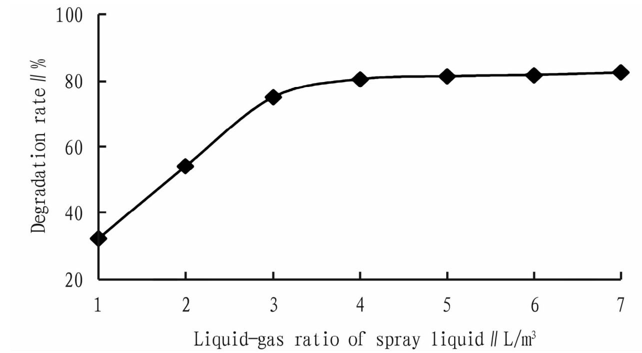


Fig. 4 Changes in degradation rate of xylene with the liquid – gas ratio of spray liquid

2.4 Changes in degradation rate of xylene with residence time Setting the intake concentration of xylene as 200 mg/m^3, the residence time of xylene as 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 s, the liquid – gas ratio of spray liquid as 4 L/m^3, the ORP of spray liquid as 500 mV, and the pH value of spray liquid as 7, the effect of xylene retention time on its degradation rate under set conditions was studied, and the results were shown in Fig. 5.

As shown in Fig. 5, the degradation rate of xylene rose with its residence time increased. As the residence time of xylene in the system increased from 2 to 12 s, the degradation rate of xylene increased from 12.20% to 81.12%. This is mainly because as the residence time of xylene increases, the probability of contact and collision between xylene and spray liquid increases, and the reaction time of xylene and oxidation free radicals generated by the synergistic effect of a large number of micro nano bubbles and spray liquid increased, so the degradation rate of xylene also rises.

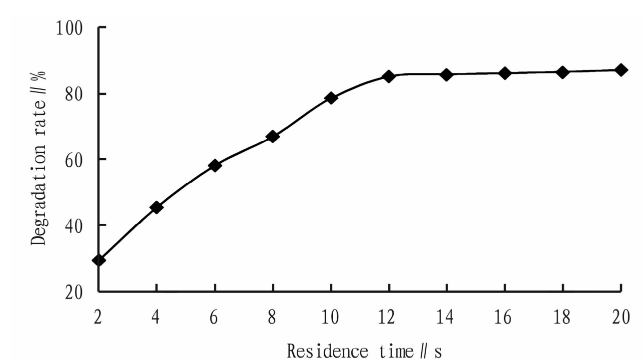


Fig. 5 Changes in degradation rate of xylene with the gas retention time

2.5 Effect of xylene intake concentration on its degradation rate Setting 10 different concentrations of xylene intake, with a xylene residence time of 12 s, a liquid – gas ratio of spray liquid of 4 L/m^3, the ORP of spray liquid of 500 mV, and the pH value of spray liquid of 7, the effect of xylene intake concentration on its degradation rate under set conditions was studied, and the results were shown in Fig. 6.

As shown in Fig. 6, with the increase of intake concentration, the degradation rate of xylene showed an increasing trend, and its removal rate increased from 39.04% to 85.16%. From the perspective of the dual film theory, there are diffusion resistance and chemical resistance in the gas film. At the same time, there is also resistance to the diffusion of gas in the liquid film. As the gas concentration gradually increases, gas – liquid reactions are mainly controlled by gas film control[5]. In this case, the increase in gas concentration will promote the mass transfer of gas in the gas film, resulting in an increase in the amount of gas reaching the gas – liquid interface at the same time, and a higher degradation rate. However, when the gas concentration reaches a certain value, the gas – liquid reaction will shift towards liquid film control. At this point, although it can increase the amount of degradation by improving gas concentration, the amount of degradation is much smaller than the increase in gas concentration, which leads to a small increase in overall degradation rate.

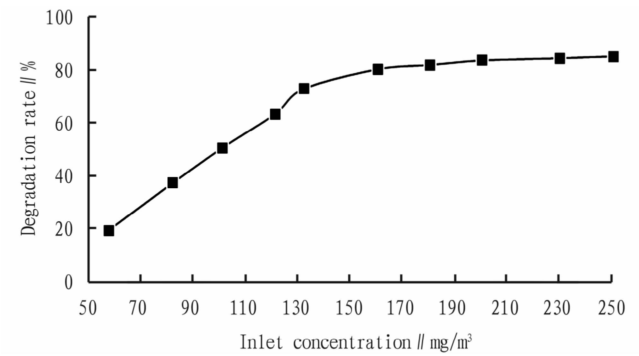


Fig. 6 Degradation rule of xylene with the change in its inlet concentration

3 Conclusions

(1) The use of micro nano bubble in conjunction with peroxymonosulfate can effectively degrade xylene. Under the conditions of ORP of spray liquid of 500 mV, pH value of 7, the liquid – gas ratio of 4 L/m^3, the residence time of xylene of 12 s, and the initial concentration of xylene greater than 160.56 mg/m^3, the degradation rate of xylene was greater than 80%.

(2) While maintaining the initial concentration of xylene unchanged, the degradation rate of xylene increased with the increase of ORP of spray liquid, liquid – gas ratio of spray liquid, residence time of xylene, and initial concentration of xylene.

(3) The change in pH value of spray liquid had little effect on the degradation rate of xylene.

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