Simultaneous desulfurization and denitrification method using O₃ and NO Micro-nano bubbles systemthe

Dong Jianga, Hongrui Sunb, Hualei Xia, Guanghui Yang, Dengxin Li e, *

College of Environmental Science and Engineering, Donghua University, Shanghai, China

a976313172@qq.com, b2581282194@qq.com, c1393089459@qq.com, d1139393078@qq.com, *elidengxin@dhu.edu.cn

Abstract. This paper adopts O₃ and NO micro-nano bubble systemthe to study the Simultaneous desulfurization and denitrification method. In this paper, the effects of O₃ inflow, NO concentration, transition metals ion concentration of Mn²⁺ and pH on NO and SO₂ absorption rate were studied. The results showed that when the molar concentration of Mn²⁺ were 2 mmol/L in O₃ and NO micro-nano bubble system, [O₃]/[NO] was 1, NO volume fraction was 5000 ppm, SO₂ volume fraction was 6250 ppm, pH was 5, NaCl concentration was 0.5 g/L, the NO and SO₂ absorption rate reached up to 79.29 and 100 % respectively.

Keywords. O₃, Micro-nano bubbles, simultaneous removal of SO₂ and NOₓ.

1. Introduction

At present, the limestone-gypsum method is widely used for the desulphurization, which can achieve a removal rate of 90% [1]. Selective catalytic reduction (SCR) method used for denitrification can which can also achieve a removal rate of 90% [2]. The successive desulfurization and denitification technologies have the disadvantages of large occupied area, complicated system and high operating costs. Therefore, simultaneous removal of SO₂ and NOₓ is the current research hotspot. The solubility of SO₂ is relatively high, so the efficiency of wet desulfurization technology is high. The solubility of SO₂ is relatively high, so the efficiency of wet desulfurization technology is high. Due to the low solubility of NOₓ, it is necessary to add an oxidizing agent to oxidize NO to NO₂ which have higher solubility in the wet denitrification process. Simultaneous desulfurization and denitrification by wet oxidation methods include sodium hypochlorite, ozone and hydrogen peroxide. Most of them are still in the research stage, except that a few have already achieved industrialization [3-6].

Micro-nano bubbles refer to a kind of bubble mixture whose bubble diameter is between several hundred nanometers and tens of micrometers. The micro-nano bubbles have a smaller diameter than those produced with ordinary aeration method, therefore, their characteristics are special [7]. Micro-nano bubbles have the advantages of small particle size, long retention time in water, good mass transfer efficiency and the generation of hydroxyl radicals with strong oxidizing power when the bubbles burst [8]. The application of micro-nano bubbles in various fields has attracted people's attention [9]. In the environmental field, micro-nano bubbles can promote the degradation of pollutants and improve the gas-liquid mass transfer efficiency in the sewage treatment [10].
O₃ is an oxidant with high catalytic efficiency. The oxidation product is O₂ and does not cause secondary pollution. Studies have shown that hydroxyl radicals can increase the oxidation capacity of O₃, providing a theoretical basis for the synergistic oxidation of micro-nano bubbles and O₃[11].

2. Experimental part

2.1. Experimental instruments and materials
The main experimental equipment: Yunnan Xiazhi XZCP-K-0.75 micro/nano-bubbles generator; Dai an DX-120 ion chromatograph; ozone generator; N4 UV-visible spectrophotometer; MODEL 6010 portable pH meter.

The main experimental materials: NaCl (AR), HCl (AR), NaOH (AR), MnCl·4H₂O (AR), 5%NO, 5%SO₂.

2.2. Experimental steps
The micro bubble generator's inlet flow rate was 12 L/min, the air intake volume was 2 L/min, and absorption device volume was 50 L. The inlet pressure was 0.2 MPa and the system ran stable for 3 min. The volumetric concentrations of NO, SO₂, and O₃ were controlled by gas pressure reducing valves and gas buffer tanks. Henceforth, the effect of reaction parameters such as the amount of O₃, transition metal ion catalyst (Mn²⁺), degree of salt medium, pH and SDS concentration on the rate of NO and SO₂ oxidation absorption were studied.

2.3. Analytical methods
The NO absorption rate was calculated as follows:

\[ \eta = \frac{c_1 \cdot q_1 \cdot t}{m_1} \]  (1)

\[ m_1 = \frac{M \cdot A}{22.4} \times \frac{273}{273+T} \times \frac{P_1}{P_0} \times 10^{-6} \times q_2 \times t \]  (2)

In Equation 1: \( \eta \) is the NO absorption rate, %; \( c_1 \) is the mass concentration of NO₃⁻ and NO₂⁻ (in N) in the absorption liquid, mg / L; \( q_1 \) is the inflow, L / min; \( t \) is the system running time, min; \( m_1 \) is the mass of intake NO (in N).

In Equation 2: The molar volume of gas at 22.4 L/mol standard conditions, M is the molar mass of N, g / mol; A is NO gas volume fraction, ppm; T is the room temperature, °C; \( P_1 \) is the pressure after gas depressurization, Pa; \( P_0 \) is the atmospheric pressure, Pa; \( q_2 \) is the gas flow rate, mL/min; \( t \) is the system running time, min.

The concentration of NO₂⁻ and NO₃⁻ in the absorbent was determined by UV spectrophotometry; the sulfate was determined by ion chromatography; the pH of the solution was measured by the MODEL 6010 portable pH meter.

3. Results and discussions

3.1. Effect of [O₃] / [NO] on NO and SO₂ absorption rate
The influent pH was set at 7, the influent flow rate was 10 L / min and the NO and SO₂ inlet flow rate was 200 mL/min and 250 mL/min respectively, the volume concentration of O₃ was 50 ml/min, 100 ml/min, 150ml/min, 200 ml/min and 250 ml/min respectively. The inlet pressure was 0.2 MPa, the
system ran stable for 3 min. After this, we waited for a certain time period, so that the solution becomes clear. Henceforth, the impact of $[\text{O}_3]/[\text{NO}]$ on the NO absorption rate is shown in Figure 1.

![Figure 1](image)

**Fig.1.** Effect of $[\text{O}_3]/[\text{NO}]$ on removal of NO and SO$_2$

Figure 1 shows that when $[\text{O}_3]/[\text{NO}]$ was 1.25, the removal rate of SO$_2$ reached 100%. Studies have shown that O$_3$ has good oxidation of SO$_2$ dissolved in water and the oxidation product is sulfate. Compared with common aeration, SO$_2$ dissolves more easily in water in micro-nano bubble systems. When $[\text{O}_3]/[\text{NO}]$ was 0.25, the oxidation efficiency of NO is not high due to the lack of O during the reaction, with resulted in a large amount of NO$_2^-$ in the solution. With $[\text{O}_3]/[\text{NO}]$ increased, NO absorption rate was 52.18% ($[\text{O}_3]/[\text{NO}]=1$) and 52.42% ($[\text{O}_3]/[\text{NO}]=1.25$). and changes have stabilized. Therefore, $[\text{O}_3]/[\text{NO}]$ was selected as 1.

3.2. Effect of Mn$^{2+}$ on NO and SO$_2$ absorption rate

A 40L solution was prepared using MnCl$_2$·4H$_2$O. The concentrations of the metal were 1 mmol / L, 2 mmol / L, 3 mmol / L and 4 mmol / L and 5 mmol/L respectively. The influent water pH was 7 and the water inflow was 10 L / min. The NO, SO$_2$ and O$_3$ inlet flow rate was 200 mL/min, 250 mL/min and 200ml/min respectively. Other conditions were the same, variable ion concentrations were investigated for the absorption of NO and SO$_2$ under Micro-nano bubble gas-liquid system, the results are shown in Figure 2.

As can be seen from FIG. 2, the SO$_2$ removal rate reached 100% when Mn$^{2+}$ was added to the micro-nano gas-liquid system. When the concentration of Mn$^{2+}$ was less than 4 mmol/L, the denitrification rate was greatly improved, and reached a maximum of 71.6% when the concentration of Mn$^{2+}$ was 4 mmol/L, and the NO absorption efficiency decreases afterwards. This is because Mn$^{2+}$ binds to hydroxyl radicals generated when bubbles collapse, and then reacts with NO and SO$_2$ to form a complex reaction, which is eventually oxidized by ozone. In addition, a large amount of NO and SO$_2$ complex with ions, resulting in a decrease in the mass transfer rate of NO in the gas-liquid two phases and in the NO absorption efficiency.
3.3. Effect of pH on NO and SO\textsubscript{2} absorption rate
A 40L solution was prepared with MnSO\textsubscript{4} \cdot 4H\textsubscript{2}O having a concentration of 4 mmol / L. The pH of the water was controlled at 3, 5, 7, 9, and 11 respectively, the water inflow was 10 L / min and other conditions were the same. The impact of pH on the absorption of NO and SO\textsubscript{2} under Micro-nano bubble gas-liquid system is shown in Figure 3.

In Fig. 3, the SO\textsubscript{2} absorption efficiency was 95.02% at pH was 3. At low pH, Mn\textsuperscript{2+} complexes with NO and SO\textsubscript{2} after associating with the hydroxyl radicals generated by bubble collapse, which results in a decrease in the SO\textsubscript{2} absorption efficiency. Based on this the efficiency of NO was also decreased. At pH was 5, the NO absorption efficiency was the highest, reaching 74.18%. When the pH of the solution became larger, the NO absorption efficiency decreased because of the hydrolysis of Mn\textsuperscript{2+}.

3.4. Effect of NaCl concentration on NO and SO\textsubscript{2} absorption rate
A 40L solution was prepared with MnSO\textsubscript{4} \cdot 4H\textsubscript{2}O having concentration of 4 mmol / L. The NaCl was added to the solution with the following concentrations: 0.1 g / L, 0.3 g / L, 0.5 g / L, 0.7 g / L and 0.9 g / L respectively, the influent pH was set at 5. Other conditions remain unchanged, in this the effects of NaCl concentrations on the NO and SO\textsubscript{2} absorption rate were investigated and the results are shown in Figure 4.
As shown in Fig. 4, SO$_2$ absorption efficiency reached 100%. When the NaCl concentration was 0.1g/L~0.5g/L, the NO absorption efficiency gradually increased and then decreased. This is because as the salinity increased, the surface tension of the solution and the stability of the bubble increased, thus the residence time of bubble in the water increased. In addition, with the increase of salinity, the rate of oxygenation of gas and liquid increased, and the concentration of ozone also increased, thereby increasing the absorption efficiency of NO [12]. Due to the low Cl-hydration energy, it was easily adsorbed at the interface of the bubbles. Excessive accumulation of Cl$^-$ on the bubble surface affects the gas's dissolution efficiency, with the increase of salinity.

4. Conclusion

(1) The ozone micro-nano bubble gas-liquid system can significantly increase the efficiency of desulfurization and denitrification. When [O$_3$]/[NO]=1.25, that is, the volume fractions of NO and SO$_2$ are 5000 ppm and 6250 ppm respectively, 52.42% (NO) and 100% (SO$_2$) removal efficiency can be achieved.

(2) In the ozone micro-nano bubble gas-liquid system, Mn$^{2+}$ played a significant role in promoting oxidation.

(3) The results showed that when the molar concentration of Mn$^{2+}$ were 4 mmol/L in O$_3$ micro-nano bubble system, [O$_3$]/[NO] was 1, that is, NO volume fraction was 5000 ppm, SO$_2$ volume fraction was 6250 ppm, pH was 5, NaCl concentration was 0.5 g / L, the NO and SO$_2$ absorption rate reached up to 79.29 and 100% respectively.

References

[1] Sun Xin. Flue gas desulfurization and denitrification technology. Design and Calculation, 2017.88, p. 57–62.
[2] Ma Xiaochun, Duan Yuefei, Zhu Yabo. Study on Control Strategy of Boiler Denitrification SCR Method. Power System Engineering,2013. 1, p. 65–66.
[3] Xinhua Xu,Shih Ger Chang. Removing nitric oxide from flue gas using iron(II) citrate chelate absorption with microbial regeneration. ChemospHere, p. 1628–1636.
[4] Zhou Chunqiong, Deng Xianhe. Simultaneous desulfurization and denitrification of cobalt complex system. Journal of Guangxi Normal University, Natural Science Edition, 2007, 25, p. 79–82.
[5] Wang Xuehai, direction morning. Research progress on simultaneous desulfurization and denitrification of flue gas. Contemporary Chemical Industry, 2008, 37, p. 197–200.
[6] Jiang Yuze. Development and discussion of pulse discharge flue gas desulfurization and denitrification technology. Electrical Equipment, 2005, 6, p. 10–12.
[7] TAKAHASHI M. Base and technological application of micro-bubble and nano-bubble. Materials Integration, 2009, 22, p. 2–19.

[8] Li P, Tsuge H. Ozone transfer in a new gas-induced contactor with microbubbles. J Chem Eng Japan, 2006, 39, p. 1213–1220.

[9] TSUGE H. The latest technology on microbubbles and nanobubbles II. Tokyo: CMC Publishing Co, Ltd, 2010.

[10] Wang Shuai, Li Pan, Yu Shui. Micro-Nano cheongsam characteristics and its application in environmental field. China Water & Drainage, 2013, 20, p. 22–25.

[11] R.G. Rice. Ozone Reference Guide. Electric Power Research Institute, 1996.

[12] Liu Chun, Zhang Lei, Yang Jingliang, Guo Jianbo, Li Zaixing. Oxygen mass transfer characteristics in microbubble aeration. 2010, 4, p. 585–589.