

Oxidation of Ammonium Sulfite Using Multi-Needle-to-Plate Negative DC Corona Discharge Reactor

Y. Wu, H. Ren, S. Tang, J. Li, N. Lu, and K. Shang

Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), Institute of Electrostatics and Special Power, Dalian University of Technology, PR China

Abstract—For ammonia flue gas desulfurization (FGD) process, the low oxidation rate of ammonium sulfite is a problem that is required to be solved. An experimental study on the oxidation of ammonium sulfite to ammonium sulfate was carried out in the multi-needle-to-plate negative DC corona discharge reactor. Corresponding oxidation rates of ammonium sulfite under the different experimental conditions were investigated and the oxidizing mechanism was also discussed. The results reveal that the oxidation rate of ammonium sulfite increases with the absolute value of discharge voltage and increases first and then decreases as both the flow rate of the ammonium sulfite solution and the initial pH value increase. The oxidation rate of ammonium sulfite can reach the highest under the optimal conditions that the flow rate is 300 mL/min and pH is 7.00. The hydroxyl radicals play a key role in the process of plasma induced ammonium sulfite oxidation. These results would be important for the process optimization of the $(\text{NH}_4)_2\text{SO}_3$ to $(\text{NH}_4)_2\text{SO}_4$ oxidation.

Keywords—Ammonium sulfite oxidation, corona discharge, multi-needle-to-plate electrode, discharge plasma, ammonia flue gas desulfurization

I. INTRODUCTION

Flue gas is sometimes scrubbed with aqueous ammonia to reduce their sulfur oxide content [1]. In China, the ammonia-based wet FGD process has been increasingly used in recent years because of high efficiency, lower investment, less land occupied, rare fouling, etc. Ammonium sulfite which can easily decompose to SO_2 is obtained as a byproduct from the ammonia-based wet FGD process, and ammonium sulfite can be used as fertilizer after being oxidized to high-stability ammonium sulfate. Thus, it is critical to oxidize ammonium sulfite to ammonium sulfate for ammonia flue gas desulfurization (FGD) process.

Non-thermal plasma processes are currently being investigated intensively worldwide for a wide range of air-pollution-control applications, such as SO_2 , NO_x [2-4]. Many researches have demonstrated that the non-thermal plasma process is an attractive end-of-pipe technology to remove SO_2 . At present the dry-type and wet-type plasma reactors were used for removal of SO_2 . In the wet-type processes, water or alkaline solutions such as NaOH, ammonia solution, etc were used as the absorbents and a thin film on the inner wall of de SO_2 reactor was formed to absorb SO_2 in flue gas, and SO_2 can be converted to SO_3^{2-} and SO_4^{2-} in the liquid film. When plasma was applied in wet de SO_2 process, gas-phase discharge plasma could greatly enhance the liquid-phase oxidation of SO_3^{2-} to SO_4^{2-} .

Multi-needle-to-plate discharge reactor has been used for wastewater treatment for many years, demonstrating that it could induce an oxidation process for organic contaminants degradation in aqueous solution

[5-8]. In the multi-needle-to-plate discharge system, the structure is simple and corona discharge can easily occur.

Negative corona discharges are superior for industrial electrostatic precipitation because the spark breakdown voltage is higher than that in the positive corona, which exist in several forms, such as the Trichel pulse corona, pulseless corona, glow corona, spark discharge, etc [9, 10]. Experiments also indicate that the ozone produced in the negative corona is one order of magnitude higher than that in the positive corona. Ozone is one kind of effective oxidants, so a multi-needle-to-plate negative DC corona discharge reactor was developed for oxidation of ammonium sulfite and the oxidation mechanism of ammonium sulfite was also discussed. This study can provide a theoretical basis for further improving the oxidation rate of ammonium sulfite.

II. EXPERIMENTAL

The schematic diagram of the experimental setup for the oxidation of ammonium sulfite is illustrated in Fig. 1. The discharge reactor was made of organic glass with a volume of $321 \times 149 \times 110 \text{ mm}^3$. The HV electrode which was placed in gas phase and was vertical to the surface of ammonium sulfite solution was composed of 84 acupuncture needles, 0.53 mm in diameter. The distance between adjacent needlepoint was 20 mm. The distance from needlepoint to the surface of solution was 30 mm. The ground electrode was the solution of ammonium sulfite. The power supply was negative DC power supply with high voltage from 0 to -40 kV.

Fig. 2 shows the current-voltage characteristic curve of the negative DC corona discharge. It can be observed that the absolute value of discharge current increases with the absolute value of discharge voltage. The discharge inception voltage was -4.2 kV and the sparking voltage was -25 kV.

Corresponding author: Yan Wu
e-mail address: wuyan@dlut.edu.cn

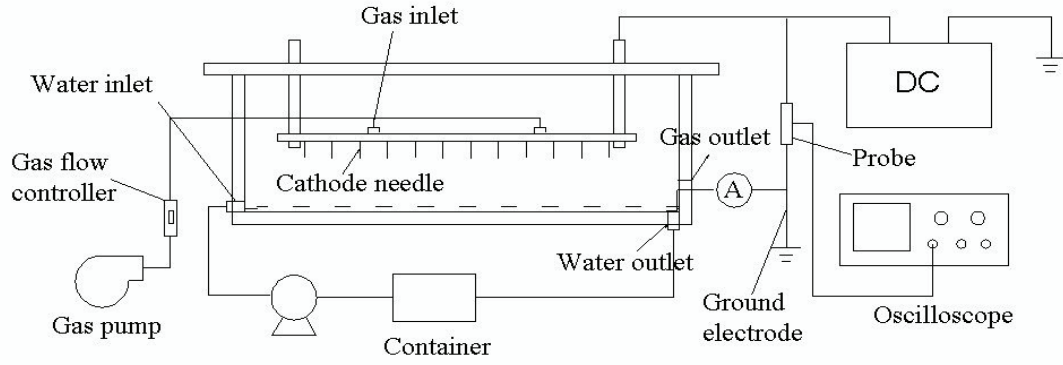


Fig. 1. Schematic diagram of the experimental setup.

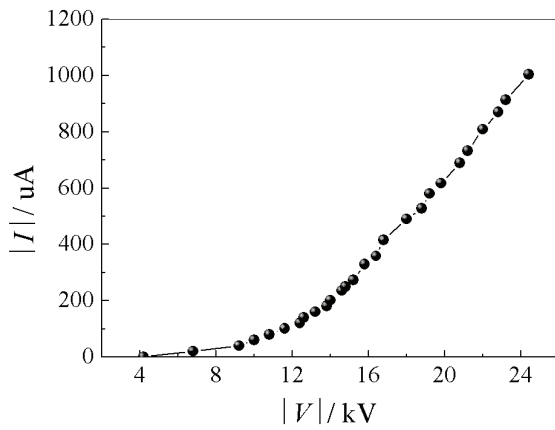


Fig. 2. Current-voltage characteristics of the negative DC corona discharge.

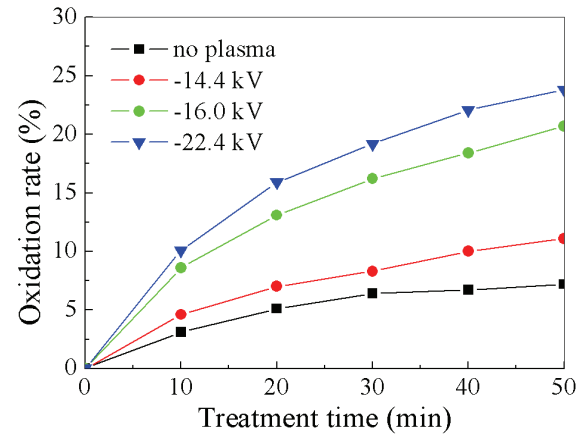


Fig. 3. Effect of discharge voltage on the oxidation rate of ammonium sulfite.

The used ammonium sulfite solution was prepared via ammonium sulfite of analytical grade. In every batch of discharge experiment, ammonium sulfite solution was prepared using distilled water with the volume of 400 mL. The initial pH of ammonium sulfite solution was adjusted by adding hydrochloric acid. In all experiments, the air flow rate was kept at 0.1 L/min. For liquid circulation, ammonium sulfite solution in container was pumped into the discharge reactor, and then was diffused into the discharge region. Subsequently, the solution flowed back into the container. The solution flow rate ranged from 150 to 450 mL/min. The treatment time was 50 min and 2.0 mL of the sample was taken out of the container at an interval of 10 min. The concentration of sulfite ion was determined by means of iodometric titration. Sulfites are firstly oxidized by excessive iodine and then are titrated back with sodium thiosulfate.

The oxidation rate of ammonium sulfite at anytime (X_t) can be calculated from the following formula:

$$X_t(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

Here X_t is the oxidation rate of ammonium sulfite (%), C_0 is the initial concentration of ammonium sulfite (mol/L), C_t is the concentration of ammonium sulfite (mol/L).

III. RESULTS AND DISCUSSIONS

A. Effect of discharge voltage

Fig. 3 shows typical results of the effect of applied voltage on the oxidation rate of ammonium sulfite, when the flow rate and pH value of solution are 150 mL/min and 7.7, respectively. The ammonium sulfite is unstable and can be oxidized to ammonium sulfate by the oxygen in air, which is the natural oxidation. It could be seen that the oxidation rate increased with treatment time and the increasing of the absolute value of discharge voltage was benefit to the increasing of the oxidation rate. At a treatment time of 50 min, the oxidation rate of ammonium sulfite increased from 11.1% to 23.8% as the absolute value of discharge voltage increased from 14.4 to 22.4 kV. Since, the electrical field strength becomes larger and the density of plasma active species and oxidant agents increases with the voltage [11, 12]. In consideration of the oxidation rate, the maximum

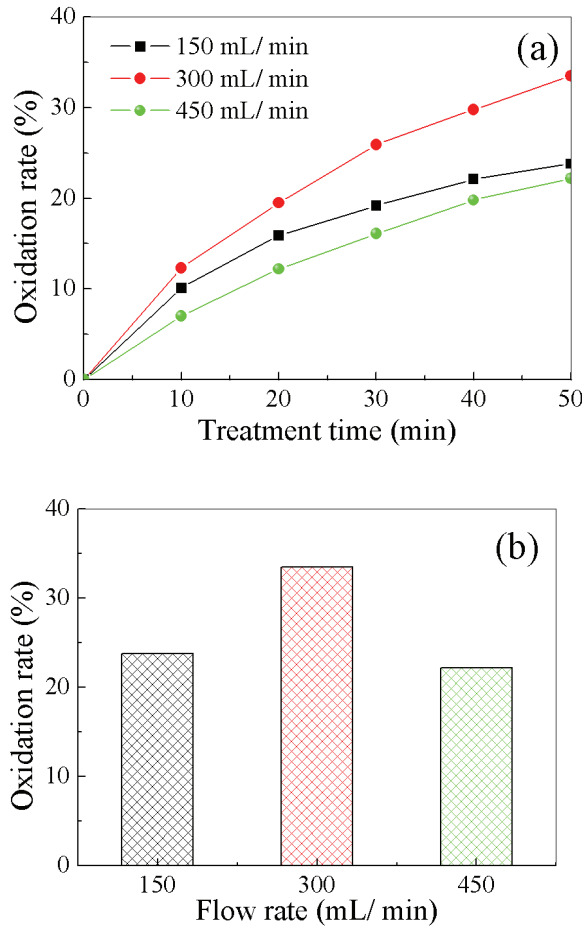


Fig. 4. Effect of flow rate of the solution on the oxidation rate of ammonium sulfite.

discharge voltage examined in this paper was chosen as -22.4 kV.

B. Effect of solution flow rate

In this experiment, 150 mL/min was chosen as the minimum flow rate because this flow rate was necessary to cover the entire surface of the bottom of reactor. Fig. 4 shows the oxidation rate of ammonium sulfite at different time and solution flow rate, while Fig. 4(b) only shows the oxidation rate of ammonium sulfite after treatment for 50 min. In this experiment, the discharge voltage and pH are -22.4 kV and 7.7, respectively. As seen in Fig. 4(b), the oxidation rate increased first and then decreased with the solution flow rate. At the solution flow rate of 300 mL/min, the oxidation rate could reach the highest value of 33.5%. At the lowest solution flow rate, the residence time of solution in the reactor is long enough for efficient oxidation. However, temperature of the solution also increased to greater extent. An increase in temperature of solution resulted from higher water evaporation and greater water vapor concentration in air, so the corona discharge state maybe changed and the ozone production was inhibited. This negative effect can be suppressed when solution flow rate is higher. Thus the

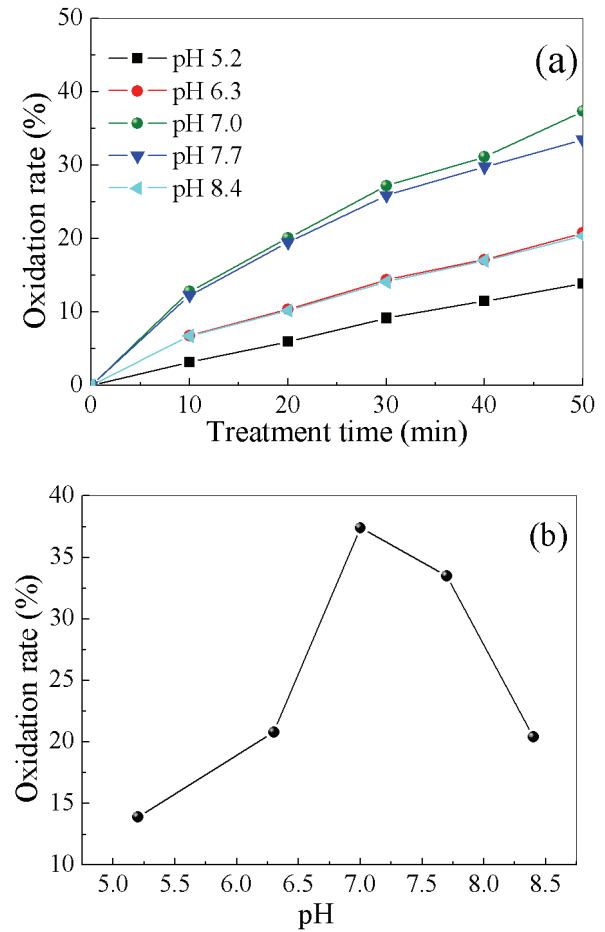


Fig. 5. Effect of initial pH on the oxidation rate of ammonium sulfite.

oxidation rate increased with the solution flow rate when solution flow rate was lower than 300 mL/min. But at the highest flow rate of 450 mL/min, the residence time of the solution in the reactor is too short for efficient oxidation, so the oxidation rate is lowest at a solution flow rate of 450 mL/min.

C. Effect of initial pH

The oxidation rate of ammonium sulfite at different time and pH values are plotted in Fig. 5, when discharge voltage and solution flow rate are -22.4 kV and 300 mL/min, respectively. Fig. 5(b) is only shown the oxidation rate after treatment for 50 min. The pH value is controlled between 5.2-8.4 to keep no SO_2 slip. From Fig. 5(b) it can be observed that at pH value lower than 7.0, the oxidation rate of ammonium sulfite increased with pH value, while at pH value higher than 7.0, the oxidation rate decreased with pH value. The curves indicate that the oxidation rate was highest under neutral conditions and more effective under alkaline solution conditions than under acidic conditions. For explaining the phenomenon, further experiment is needed.

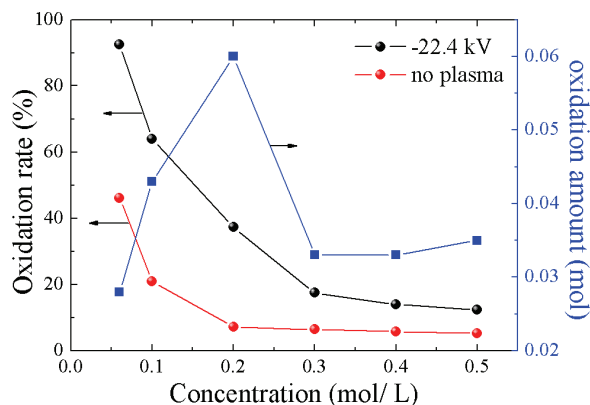


Fig. 6. Effect of initial concentration on the oxidation rate and oxidation amount of ammonium sulfite.

D. Effect of ammonium sulfite concentration

Fig. 6 shows typical results of the effects of initial ammonium sulfite concentration on discharge oxidation rate, natural oxidation rate and oxidation amount. When discharge voltage, solution flow rate and initial pH were -22.4 kV, 300 mL/min and 7.0 respectively. All results were obtained after 50 min of treatment. Within the present tests with a concentration of 0.06-0.5 mol/L, discharge oxidation rate and natural oxidation rate dropped with the concentration of ammonium sulfite. As an example, under the concentration of 0.06 mol/L, the discharge oxidation rate and natural oxidation rate were about 92.5% and 46.2%, respectively, while, they were about 12.3% and 5.3% under the concentration of 0.5 mol/L. The reasons for the decrease in oxidation rate are that its oxidation amount increases with the initial concentration of ammonium sulfite.

In addition, with regard to the oxidation amount equal to discharge oxidation amount minus natural oxidation amount presented in Fig.6, it seems that the oxidation process can be divided into two reaction regions by the initial concentration of around 0.2 mol/L. For a concentration of lower than 0.2 mol/L, the oxidation amount increased with the concentration. At a concentration of higher than 0.2 mol/L, the oxidation amount dropped and then tended to reach stationary values. One possible explanation for the increased oxidation amount is an increasing in the collision probabilities between discharge active species and sulfite ions. The dropped oxidation amount may be due to a decrease of O_2 solubility with solution concentration [13] and the diffusion coefficient also changes. Further investigation is needed to clarify the mechanism.

E. Oxidizing mechanism of ammonium sulfite

Corona discharge creates hydroxyl radical (OH), ozone (O_3), oxygen atom (O), and hydrogen peroxide (H_2O_2) [8, 14] which play a key role in the degradation of contaminants [13, 14]. Among the produced oxidants in corona discharge, the hydroxyl radical has the highest oxidability [8]. Methanol is good scavenger of OH

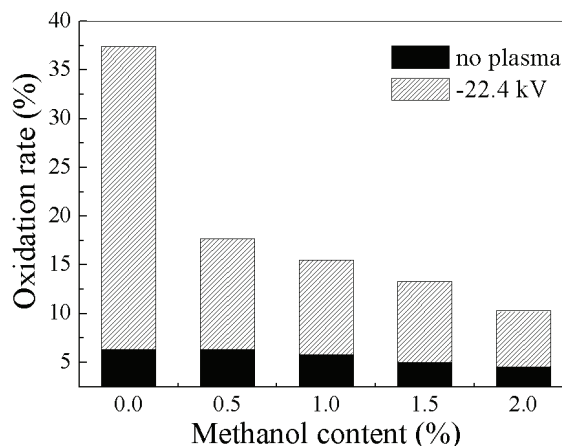


Fig. 7. Effect of methanol content on the oxidation rate of ammonium sulfite.

radical in the liquid solution due to the large reaction rate constant ($k=0.9 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$ [17]) while it reacts poorly with ozone due to the small reaction rate constant ($k=0.02 \text{ M}^{-1} \text{ S}^{-1}$). Fig. 7 shows the effect of methanol content on the oxidation rate of ammonium sulfite, when discharge voltage, solution flow rate and initial pH are -22.4 kV, 300 mL/min and 7.0, respectively. The oxidation rate decreased from 37.4% to 10.3% as the methanol content increased from nonexistence to 2.0%. The oxidation of ammonium sulfite was restrained obviously, so the hydroxyl radical play a main role in the oxidation of ammonium sulfite. Kim [2] also concludes that OH radical is the main species in the liquid-phase conversion of HSO_3^- to SO_4^{2-} .

IV. CONCLUSIONS

An experimental study on the oxidation of ammonium sulfite (initial concentration of 0.2 mol/L) in aqueous solutions was carried out in a multi-needle-to-plate negative DC corona discharge reactor. The main findings are as follows.

1) A multi-needle-to-plate negative DC corona discharge reactor could realize the oxidation of ammonium sulfate. The oxidation rate of ammonium sulfite after 50 min treatment processing could reach 37.4% at discharge voltage, solution flow rate and pH equal to -22.4 kV, 300 mL/min and 7.0.

2) The oxidation rate of ammonium sulfite increased with the discharge voltage and the oxidation rate of ammonium sulfite increased first and then decreased when the flow rate of the ammonium sulfite solution and the initial pH increased. The oxidation rate was the highest under neutral conditions, followed by alkaline solution conditions and acidic conditions.

3) The hydroxyl radicals created by corona discharge played a key role in the plasma-induced ammonium sulfite oxidation.

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