Oxidation of ammonium sulfite by a multi-needle-to-plate gas phase pulsed corona discharge reactor

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Abstract. The oxidation of ammonium sulfite in the ammonia-based flue gas desulfurization (FGD) process was investigated in a multi-needle-to-plate gas phase pulsed corona discharge reactor in this paper. The effect of several parameters, including capacitance and peak pulse voltage of discharge system, electrode gap and bubbling gas flow rate on the oxidation rate of ammonium sulfite was reviewed. The oxidation rate of ammonium sulfite could reach 47.2% at the capacitance, the peak pulse voltage, electrode gap and bubbling gas flow rate equal to 2 nF, -24.6 kV, 35 mm and 4 L min\(^{-1}\) within treatment time of 40 min. The experimental results indicate that the gas phase pulsed discharge system with a multi-needle-to-plate electrode can oxidize the ammonium sulfite. The oxidation rate increased with the applied capacitance and peak pulse voltage and decreased with the electrode gap. As the bubbling gas flow rate increased, the oxidation rate increased first and then tended to reach a stationary value. 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.

1. Introduction
Ammonia-based flue gas desulfurization (FGD) is a well known technique with high desulfurization efficiency [1], which flue gases are scrubbed with aqueous ammonia to reduce their sulfur oxide content [2]. In China, the ammonia-based wet FGD process has been increasingly used in recent years because of high efficiency, lower cost, less land occupied, rare fouling, etc. Ammonium sulfite as a byproduct of desulfurization is easily decomposed into SO\(_2\) and NH\(_3\) which produce secondary pollution in the environment, while ammonium sulfate whose chemical property is stable can be used as a fertilizer or in fertilizers in agriculture. Thus, it is critical to oxidize ammonium sulfite to ammonium sulfate efficiently for ammonia flue gas desulfurization (FGD) process.

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Over the past few decades, several oxidation technologies, such as air diffusion method, catalytic oxidation technology and advanced oxidation technology (AOT), have been utilized for the purpose of oxidizing ammonium sulfite generated in FGD process [1, 3, 4]. The oxidation of ammonium sulfite by using air diffusion method is usually limited by the gas-liquid mass transfer coefficient of oxygen and thus needs consuming more time. Catalytic oxidation technology could efficiently oxidize the concentrated ammonium sulfite [3] and lots of researches focus on the use of homogeneous catalyst, but the method can cause secondary pollution. Therefore, these methods could not meet the econo-technical norms in the oxidation of ammonium sulfite field.

Advanced oxidation technologies (AOTs) including UV photolysis, photocatalysis, sonochemistry, supercritical water oxidation, electrical discharge plasma technology and electron-beam irradiation, etc, has been widely used in wastewater disposal fields. In the application of electrical discharge plasma technology, glow discharge, dielectric barrier discharge and pulsed corona discharge are the three main discharge types used for the purpose of water disposal [5]. Most previous works have been investigated in pulsed corona discharge plasma systems [6]. The technique has a higher energy efficiency compared to other AOTs because of the very short pulse width (approximately 500–1000 ns) and the fast pulse rise time (nanosecond level) and can produce more various reactive chemical radicals such as ·OH, ·O, ·O₂ and molecular species such as H₂O₂,O₃ [7, 8]. All these active species have high oxidation potentials to oxidize the ammonium sulfite. Therefore, the pulsed corona discharge technology can be used as one promising candidate for the oxidation of ammonium sulfite with low operation costs. The ammonium sulfite oxidation reactions are a series of radical chain reactions. The net reactions can be written as:

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2(NH₄)₂SO₄ + O₂ \rightarrow 2(NH₄)₂SO₄ \]  \hspace{1cm} (1)

\[
2NH₄HSO₃ + O₂ \rightarrow 2NH₄HSO₄ \]  \hspace{1cm} (2)

In the pulsed high voltage discharge system, the structure of the discharge reactor (needle-to-wire, needle-to-plate, wire-to-plate and ring-to-cylinder), which was determined by the configuration of the discharge electrode and ground electrode, could influence the formation of active species and organic degradation [9, 10]. 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 [6, 11]. In liquid discharge reactor, the effect of conductivity is critical to the formation of discharge in water. Compared with this reactor, gas phase reactor is not affected by conductivity.

In this paper, we have investigated the feasibility of using multi-anode pulse discharge reactor to oxide the ammonium sulfite. The experiment was carried out to determine the effect of such factors such as the capacitance, the peak pulse voltage, electrode gap and bubbling gas flow rate on the oxidation rate of ammonium sulfite. This paper could provide some experimental support for further improvement the oxidation of ammonium sulfite caused by the non-thermal plasma technology.
2. Experimental sections

The power supply was realized by making use of rotating spark gap to produce pulsed high voltage (figure 1). It consisted of a 0–50 kV adjustable DC power supply, a storage capacitor ($C_e$), an adjustable pulse-forming capacitance ($C_p$, 2 nF) and a rotating spark-gap switch ($G$). Typical voltage...
and current waveforms of input into the reactor by the pulsed power source are shown in figure 2. The rise time and width of the voltage was less than 100 ns and 500 ns, respectively.

The oxidation of ammonium sulfite was carried out in a multi-needle-to-plate gas phase pulsed corona discharge reactor (figure 3). This reactor used was a Plexigas™ cylinder vessel, 11 cm in internal diameter and 12 cm in height. The ground plate electrode which consisted of a 90 mm diameter stainless-steel plate of 1.5 mm thickness was placed in gas phase. The high voltage needle electrode which produced positive streamer corona discharge at its needle tips was placed in water. The distance from needlepoint to plate was adjustable between 30 mm and 50 mm. The high voltage electrode, comprised of one needle in the center and the other six distributed uniformly around a circle of 15 mm radius, was secured within a resin disc. Each needle consisted of a No. #12 stainless-steel hypodermic pinhead. Silicone insulation encased the needle tips that protruded from the resin disc, with only 1 mm of length exposed in water. The air flowed into the gas chamber, through the seven needles and into the liquid chamber, forming gas bubbles.

The used ammonium sulfite solution was prepared via ammonium sulfite of analytical grade. The total volume of the treated ammonium sulfite solution was 400 mL, and its concentration $C_0$ was equal to 0.3 mol L$^{-1}$. 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 was kept at 225 mL min$^{-1}$. Sulfite ion was titrated in iodine solution by using dextrin solution as an indicator. Details of the method are reported in the national standard [12].

The input power $W$ of a pulsed discharge system can be calculated from the following formula:

$$W = \frac{1}{2} CFV^2$$

Here $C$ is the storage capacitance, $f$ the pulse frequency and $V$ the DC source voltage. If the energy in this reaction system is neglected, the input energy can be calculated by the above formula.

3. Results and discussion

3.1 Effect of capacitance

The influence of the capacitance on the oxidation rate of ammonium sulfite was displayed in figure 4 (a). It was obvious that increasing the capacitance benefited the oxidation of ammonium sulfite, due to a higher energy input introduced in the discharge. When the capacitance was improved from 1 to 2 nF, the oxidation rate of ammonium sulfite enhanced rapidly from 7.9% to 29.7%, while from 2 to 3 nF, the oxidation rate improved a few, only from 29.7% to 32.3%.

The energy efficiency was used as an indicator to evaluate the energy consumption of the system, which was shown in figure 4 (b). As the capacitance increased, the oxidation rate went up at first and then decreased. Thus, 2 nF was chosen for our experiments.
3.2 Effect of peak pulse voltage

Figure 5 showed typical results of the effect of peak voltage on the oxidation rate of ammonium sulfite. It could be seen that the oxidation rate increased with treatment time and the peak voltage within treatment time of 40 min, the oxidation rate increased from 29.7% to 48.3% as the peak voltage increased from 22.6 to 26.6 kV. Since, the electrical field strength becomes larger and the density of plasma active species and oxidant agents increases with the voltage [13, 14]. In consideration of the oxidation rate, the maximum discharge voltage reviewed in this paper was chosen as 24.6 kV.

Figure 5. Effect of peak voltage on the oxidation rate of ammonium sulfite. (C=2 nF, f=50 Hz, d=10 mm, C₀= 0.3 mol L⁻¹, Qₐ𝑖𝑟=3 L min⁻¹)
3.3 Effect of the electrode gap

The effect of the electrode gap on the oxidation rate of ammonium sulfite was studied by varying gas layer heights (GH, i.e. the height from the gas–liquid interface to the surface of the top stainless-steel plate). At fixed LH (LH, i.e. the height from the tip of the needle to the gas–liquid interface, 25 mm), as shown in figure 6, the oxidation rate of ammonium sulfite decreased with the increase of GH at a treatment time of 40 min. In experiment, fewer streamers were observed at a wider GH. In fact, the increase of GH increased the electrode gap, and the resistance between two electrodes therefore increased. As a result, more energy was consumed to conquer the increased resistance and less energy was supplied to the plasma channels in the solution [15], resulting in the decrease of the oxidation rate.

Figure 6. Effect of the electrode gap on the oxidation rate of ammonium sulfite.
(U=24.6 kV, C=2 nF, f=50 Hz , C₀= 0.3 mol L⁻¹, Qair=3 L min⁻¹)

3.4 Effect of bubbling gas

Figure 7 showed the oxidation rate of ammonium sulfite at different flows of bubbling gas. The oxidation rate increased with the treatment time (figure 7 (a)). Figure 7 (b) showed the results at a treatment time of 50 min. It was concluded that the oxidation rate increased first and then tended to reach stationary values. Only 36.3% ammonium sulfite was oxidized at 40 min at the bubbling gas flow rate of 2 L min⁻¹, while more than 46% ammonium sulfite was oxidized at the rate equal to and higher than 4 L min⁻¹ at the same discharge time. The reason for the increase of oxidation rate was that more bubbling gas could make much more ozone and •OH generated in the reactor during discharge, which could speed up the oxidation of ammonium sulfite. It was also seen from figure 7 that the oxidation rate at 4 L min⁻¹ was very close to that at 5 and 6 L min⁻¹. Higher bubbling flux means more wastage energy. Therefore, bubbling flux was kept at 4 L min⁻¹ in the experiment.
Figure 7. Effect of the bubbling gas on the oxidation rate of ammonium sulfite.
(U=24.6 kV, C=2 nF, f=50 Hz, d=10 mm, \(C_0\) = 0.3 mol L\(^{-1}\))

4. Conclusions
An experimental study on the oxidation of ammonium sulfite (initial concentration of 0.3 mol L\(^{-1}\)) in aqueous solutions was carried out in a multi-needle-to-plate gas phase pulsed corona discharge reactor. The main findings are as follows.

1) A multi-anode gas phase pulse discharge reactor could realize the oxidation of ammonium sulfate. The oxidation rate of ammonium sulfite after 40 min treatment processing could reach 47.2% at the capacitance, the peak pulse voltage, electrode gap and bubbling gas flow rate equal to 2 nF, -24.6 kV, 35 mm and 4 L min\(^{-1}\).

2) The increase of the capacitance and peak pulse voltage improved the oxidation of ammonium sulfite, while the increase of electrode gap inhibited the oxidation of ammonium sulfite. The oxidation rate of ammonium sulfite increased first and then tended to reach stationary values with the solution flow rate.

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