Oxidation of ammonium sulfite in aqueous solutions using ozone technology

Yue Li1, Kefeng Shang1,2, Na Lu1,2, Jie Li1,2*, Yan Wu1,2
1 Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian, China
2 Institute of Electrostatics and Special Power, Dalian University of Technology, Dalian, China
E-mail: lijie@dlut.edu.cn

Abstract. How to deal with unstable ammonium sulfite, the byproduct of flue gas desulfuration by ammonia absorption methods, has been a difficult problem in recent years. Oxidation of ammonium sulfite in aqueous solutions using ozone produced by a surface discharge system was investigated in the paper. The oxidation efficiency of ammonium sulfite by ozone and traditional air aeration were compared, and the factors including ozone concentration, gas flow rate, initial concentration of ammonium sulfite solution and reaction temperature were discussed. The results show that the oxidation efficiency of ammonium sulfite by ozone technology reached nearly 100% under the optimum conditions, which had a significant increase compared with that by air aeration.

1. Introduction

Along with economic development and social progress as well as people’s raised awareness of the environment protection, the researches for industrial flue gas desulphurization technology are increasingly emphasized [1]. In recent years, the technology of ammonia process of desulfurization, which uses ammonia liquid to remove SO2 in flue gas, has been researched and applied. The byproduct produced in this process mainly is ammonium sulfite [2], which can be converted to ammonium sulphate after oxidation treatment. Since ammonium sulphate can be used as fertilizer, recycle of its by-products has high economic value [3]. However, how to convert ammonium sulfite into ammonium sulphate economically and efficiently is one of the keys to achieve industrialization of the ammonia process of desulphurization technology [4].

Ozone is a kind of strong oxidizer inferior to fluorine, which can oxidize a variety of compounds with fast reaction rate and low energy consumption. Meanwhile, it does not produce sludge. In developed countries, the ozone, as a kind of strong oxidizer and disinfectant, is widely applied in food, water treatment, chemical industry, medical service, catering storage, cultivation and other fields [5].

In this paper, the oxidation efficiency of ammonium sulfite by ozone technology and traditional air aeration were compared. In addition, the factors such as ozone concentration, gas flow rate, initial concentration of ammonium sulfite solution and reaction temperature were investigated and the corresponding reasons were analysed as well as the optimized experimental conditions were obtained.

* To whom any correspondence should be addressed.
2. Material and method

2.1 Systematic setup
A schematic diagram of the experimental setup is shown in figure 1. The setup mainly consists of an air pump, an ozone generator, a flow meter and a reactor. The ozone gas, which is produced by an ozone generator, flows into the ammonium sulfite solution placed in the reactor through an aerator and turns sulfite into sulphate. The reactor is an organic glass tube, with the size of 44 mm in height, 2.9 mm in thickness and the inner diameter of 50 mm. It has a capacity of 400 mL ammonium sulfite solution.

![Schematic diagram of the experimental system.](image)

**Figure 1.** Schematic diagram of the experimental system.

2.2. Analysis of ozone
In this paper, the concentration of ozone was analysed by the iodometric method titrated by Na$_2$S$_2$O$_3$ standard solution [6].

O$_3$ reacted with KI as follows:

\[ \text{O}_3 + 2\text{KI} + \text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{I}_2 + \text{O}_2 \] (1)

2.3. Analysis of ammonium sulfite
In this work, ammonium sulfite was also analysed by the iodometric method [7].

(NH$_4$)$_2$SO$_3$ reacted with I$_2$ as follows:

\[ (\text{NH}_4)_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2\text{HI} \] (2)

3. Results and discussion

3.1. Comparison between ozone treatment and traditional air aeration
The ozone treatment was compared with the traditional air aeration in terms of oxidation efficiency, and the result was shown in figure 2. The gas flow rate was 3 L min$^{-1}$, and the initial concentration of ammonium sulfite was 0.2 mol L$^{-1}$.

It was obvious that the oxidation efficiency of ammonium sulfite, which was treated by ozone technology, was nearly 100% after 25 minutes, which was far higher than that (about 50%) by traditional air aeration. This can be explained by the stronger oxidbility of O$_3$ than O$_2$, so O$_3$ can react with ammonium sulfite in a very short time.
3.2. Influencing factors in oxidation

3.2.1. Ozone concentration

The effect of ozone concentration on the oxidation efficiency of ammonium sulfite was illustrated in figure 3, in which the ozone concentration was adjusted by changing the applied voltage connected with the ozone generator. The treatment time was 25 minutes, the gas flow rate was 3 L min⁻¹, and the initial concentration of ammonium sulfite was 0.2 mol L⁻¹.

It was found that the oxidation efficiency of ammonium sulfite had an apparent promotion with the increase of ozone concentration, which was close to 100% when the ozone concentration reached 702 ppm. It could be explained that the more effective collision probability between ozone and sulfite happened with the higher ozone concentration, which could enhance the oxidation of ammonium sulfite.

Figure 2. Efficiency of air aeration and ozone induced ammonium sulfite oxidation.

Figure 3. Oxidation efficiency of ammonium sulfite as functions of ozone concentration.
3.2.2. Gas flow rate

The influence of ozone flow rate on the oxidation efficiency of ammonium sulfite was shown in figure 4, in which the gas flow rate was adjusted by a flow meter in range of 1 to 3 L min\(^{-1}\). The treatment time was 25 minutes, the ozone concentration was 702 ppm, and the initial concentration of ammonium sulfite was 0.2 mol L\(^{-1}\).

It was obvious that the oxidation efficiency of ammonium sulfite had a significant increase as gas flow rate increased. Meanwhile, ammonium sulfite was totally oxidized when the flow rate reached 3 L mol\(^{-1}\). The reason was that on condition of the same ozone concentration, a bigger flow rate could lead to a larger total quantity of ozone exposed to the solution.

![Figure 4. Oxidation efficiency of ammonium sulfite as functions of gas flow rate.](image)

3.2.3. Initial concentration of ammonium sulfite

![Figure 5. Oxidation efficiency of ammonium sulfite as functions of initial concentration.](image)

Figure 5 showed the comparison of the reaction efficiency in different initial concentration solutions. The treatment time was 25 minutes, the ozone concentration was 702 ppm, and the gas flow rate was 3 L min\(^{-1}\), the reaction temperature was 30 ℃. It could be seen from figure 5 that the oxidation efficiency of ammonium sulfite decreased with the increase of the initial concentration. This was because the density of ozone approximately remained constant at the given ozone flow rate. The higher initial concentration of pollutants would need more ozone, which might become insufficient for the decomposition of ammonium sulfite.
3.2.4. Reaction temperature

The effect of reaction temperature on the oxidation of ammonium sulfite was investigated, in which the temperature was controlled at certain value by a waterbath, and the result was shown in figure 6. The treatment time was 25 minutes, the ozone concentration was 702 ppm, and the gas flow rate was 3 L min$^{-1}$, the initial concentration of ammonium sulfite was 0.2 mol L$^{-1}$.

The figure illustrated that the increase of the reaction temperature facilitated the oxidation of ammonium sulfite. The reasons could be stated as the following three points. Firstly, high temperature of the solution could reduce the stability of ozone, which would benefit the oxidation reactions of ammonium sulfite. Secondly, the increase of temperature could enhance the transfer of particles, which improved the reaction rates between ammonium sulfite and oxidative species. Thirdly, the increasing chaos of the particles enlarged the equivalent resistance of solution and enhanced the effective voltage [8].

![Figure 6. Oxidation efficiency of ammonium sulfite as functions of reaction temperature.](image)

4. Conclusion

An ozone oxidation system was employed to oxidize ammonium sulfite in aqueous. The oxidation efficiency of ammonium sulfite by ozone and traditional air aeration was compared and the effect of experimental conditions including ozone concentration, reaction temperature etc on the oxidation of ammonium sulfite was examined. The results show that ozone oxidation presented a better performance; an increase in the ozone concentration, gas flow rate and reaction temperature advanced improved the oxidation efficiency of ammonium sulfite; Meanwhile, reduction of the initial concentration of ammonium sulfite would bring lower oxidation efficiency.

Acknowledgments

This work is partially supported by the Fundamental Research Funds for the Central Universities [Grant NO. DUT12RC (3)12].

References

[1] Wang Y J and Wang W Y 2011 Boiler Manufactures (in Chinese). 3 45
[2] Hikita H, Asai S and Tsuji T 1978 J. Chem. Eng. Jpn. 11 236
[3] Kang H W, Zhou Y B and Li J P 2009 Guangzhou Chemical Industry (in Chinese ). 37 132
[4] Wang C Y, Li H Y and Xue S K 2009 Guangzhou Chemical Industry (in Chinese ). 36 139
[5] Li H and Yu Y Q 2009 Guangzhou Chemical Industry (in Chinese ). 37 12
[6] Birdsall C M, Jenkins A C and Spandinger E 1952 Anal. Chem. 24 662
[7] Nair S A, Yan K P, Safitri A, Pemen A J M, van Heesch E J M and Ptasinski K J 2004 *J. Electrostat.* **178** 261

[8] Yu Z M, Lu F, Ye Q Z, Liang F H and Li J 2009 *High Voltage Engineering (in Chinese).* **35** 36