

Novel method for removal of NO_x and SO₂ by sustainable electrochemical process using Ag(I)/Ag(II) redox mediator

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(Received 21 January 2008 • accepted 1 May 2008)

Abstract—The objective of this work was to develop a process for removal of industrial waste gases like NO, NO₂ and SO₂ by electrochemically generated Ag(I)/Ag(II) redox mediator system in aqueous nitric acid medium. 100% removal efficiencies were achieved in these studies for removal of NO_x and SO₂ with Ag(II) ions in room temperature and atmospheric pressure. This Ag(I)/Ag(II) redox mediator system can be regenerated continuously during the scrubbing process.

Key words: NO_x Removal, Scrubber, Electrochemical, Oxidation, Ag(I)/Ag(II) Redox Mediator

INTRODUCTION

Nitrogen oxides (NO_x) which consist of nitric oxide (NO) and nitrogen dioxide (NO₂), are emitted primarily from combustion processes. In the normal conditions of atmospheric pressure and 25 °C, nitric oxide is a colorless and odorless gas, while nitrogen dioxide is a pungent reddish-brown gas. They are both noxious and directly responsible for large contributions to the formation of acid rain and resultant acidifications, photochemical smog and general atmospheric visibility degradation. For these reasons, the emissions of NO, NO₂, NO_x and SO₂ from industrial processes are closely monitored and regulated.

NO₂ can be effectively absorbed in some aqueous solutions [1-3], but NO is not. In industrial emission, the waste gases are mostly NO (more than 95%). Therefore, NO oxidation to NO₂ is a crucial step followed by NO₂ absorption for an effective chemical scrubbing system. Absorbents like chlorine dioxide [4,5] and ozone etc. are injected to improve the slow oxidation rate of NO in air, or an oxidizing agent such as sodium chlorite [6,7], hydrogen peroxide, sodium hypochlorite [8] is added to the scrubbing solution. In recent years, potassium permanganate systems have been used for two-stage chemical scrubbing systems.

Several wet chemical scrubbing processes are available for their efficient removal of NO_x reviewed by Joshi et al. and Jethani et al. [9]. Similarly, the chemical scrubbing wet methods for SO₂ removal have been reviewed by Un et al. [10] and for both pollutants were reviewed by Arousseau et al. [11]. But in most of the conventional chemical processes, the absorbents or oxidizing agents were used in lower pHs and low concentrations at which the oxidation or absorption is higher oxidizing power of the absorbents. But, the absorption or chemical reaction is good at higher pHs and high concentration only for the removal of waste gases.

In particular, NO_x and SO₂ can be removed by chemical absorption using a redox mediator which can be generated or regenerated at an electrode surface in an aqueous medium and it is reviewed by Arousseau et al. [11-13]. Kensal et al. [14] proposed electro gen-

erated reactants by indirect oxidation or mediated electrochemical oxidation (MEO) is often preferred and several metal ions such as Ti^{4+/3+}, V^{3+/2+}, Cr^{3+/2+} are considered for these purposes. Tzedakis et al. [15] have claimed some patents for direct electrochemical gas scrubbing, and some patents and publications have also reviewed using the Ce(III)/Ce(IV) redox mediator system for gas scrubbing [11,16-18]. Bringmann et al. [19] have reported off-gases removal using the electrochemically generated redox mediators like Mn(III)/Mn(II), Co(III)/Co(II) in nitric and sulphuric acid mediums.

The basic principle of electrochemical gas purification is absorption or reaction of the pollutant species from the gas phase into a liquid electrolyte where the electrochemical oxidation or reduction takes place either directly at the electrode of an electrochemical cell or mediated electrochemical oxidation process (MEO) via a redox mediator like Ce(III)/Ce(IV), Ag(I)/Ag(II) etc. A high degree of conversion and high removal efficiency could be achieved by using a redox mediators for the indirect reduction of nitrogen oxide with Ag(II) ions in nitric acid medium and which increases the conversion of NO to NO₂.

Thus, the removal of nitrogen oxides (NO_x) containing NO, NO₂ and SO₂ by means of a wet technique using aqueous redox mediated systems in nitric acid medium solutions containing an oxidizing agent such as Ag(II) appears to be very engaging, since the Ag(II)/Ag(I) redox system has the higher standard reduction potential ($E^{\circ} = 1.9$ eV (NHE)).

From the literature, it is found that no work has been carried out or examined for the removal of NO_x and SO₂ by MEO process with Ag(I)/Ag(II) redox mediator system in nitric acid medium. Hence, in this work the applicability of mediated electrochemical oxidation of Ag(I)/Ag(II) redox system and employing the same for removal of NO_x and SO₂ in an aqueous medium has been investigated with the objective to obtain removal or destruction data and optimization of process parameters.

EXPERIMENTAL

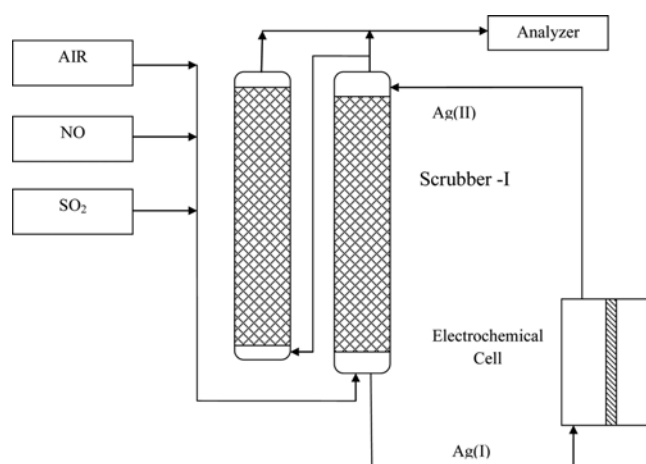
Mediated electrochemical oxidation of Ag(I)/Ag(II) redox system was performed in a divided electrochemical flow cell in nitric acid medium at room temperature. In the electrochemical cell 0.1 M

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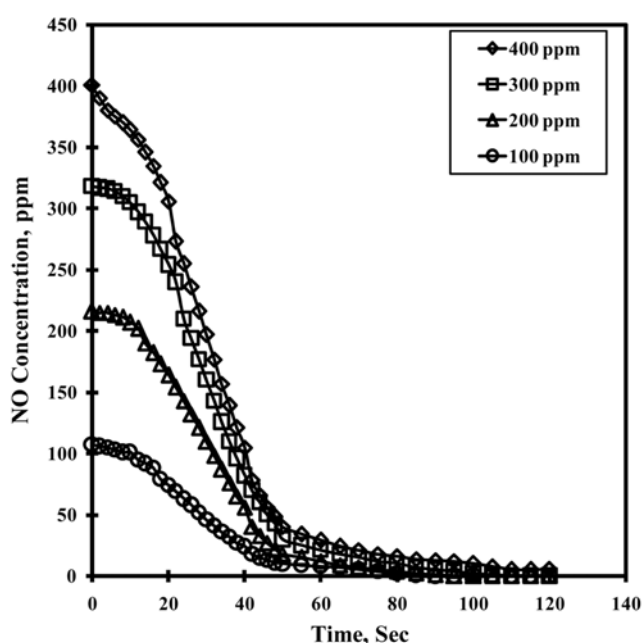
Table 1. Experimental condition for NO_x and SO₂ scrubbing systems

Electrochemical cell system	Gas scrubbing system
1. Anode: Pt/Ti	1. Scrubber-I : Glass column-ID=5 cm, H=120 cm Glass Raschig rings=1 cm
2. Cathode: DSA	2. Gas flow rate: 10 L/min
3. Anolyte: 0.1 M AgNO ₃ in 6 M HNO ₃	3. Liquid flow rate: 2 L/min
4. Catholyte: 2.5 M H ₂ SO ₄	4. Scrubbing liquid: Ag(II) redox mediator containing 6 M HNO ₃
5. Diaphragm: Nafion 324 membrane	5. Scrubber-II: PVC column-ID=5cm, H=200 cm PTFE Raschig rings-dia=2 cm
6. Current density: 7 A/dm ²	6. Gas flow rate: 10 L/min
7. Anolyte and catholyte: 2 L/min flow rate	7. Liquid flow rate: 4 L/min
8. Temperature: 20 °C	8. Scrubbing liquid: 3 M HNO ₃
9. Anolyte and catholyte volume: 1 L	
10. Electrodes area: 10 cm×14 cm	

**Fig. 1. Schematic diagram for electrochemical removal of NO_x and SO₂ using Ag(II)/Ag(I) redox mediator.**

AgNO₃ in 6 M HNO₃ was used as an anolyte and 2.5 M H₂SO₄ solution as a catholyte. Ag(II) was electrochemically generated at 7.5 A/dm² current density and room temperature conditions (20 °C). Oxidation and Removal of NO, NO₂ and SO₂ gases from simulated gas were done with electrochemically generated Ag(II) redox mediator ions by wet scrubbing method, and the experimental conditions are given in Table 1. Air was mixed with NO and SO₂ and prepared the simulated NO, SO₂ gas mixture for the experiments. A known concentration (100–400 ppm) of gas feed was fed into the scrubbers at constant gas and liquid flow rates [10 L/min and 2 L/min] at room temperature and atmospheric pressure. In first stage scrubber, NO was oxidized to NO₂ and HNO₃ and it was accomplished by electrochemically generated Ag(II) redox mediator ion in nitric acid medium as scrubbing solution. The unconverted NO₂ gas from the first stage scrubber was fed to the Scrubber-II and the removal of NO₂ was achieved by using 3 M HNO₃ as a scrubbing liquid.

In the same manner, SO₂ was completely converted to H₂SO₄ by the Ag(II) redox mediator ions in the first stage scrubber. The Teledyne Gas analyzer instrument Model No. 9560 was used for NO, NO₂, NO_x and SO₂ analysis. The concentration of NO, NO₂ and SO₂ was measured with respect to time during the reaction course. Based on the feed and final concentration removal efficiencies were

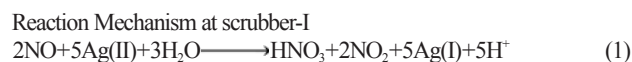
**Fig. 2. NO outlet concentration profiles with respect to time.**
[Ag(I)=0.1 M in 6 M HNO₃, Gas flow rate=10 L/min, Liquid flow rate=2 L/min, 20 °C]

calculated.

RESULT AND DISCUSSIONS

1. Removal of NO

Fig. 2 shows the concentration of the NO gas at the scrubber-I outlet with experimental time for four initial concentrations of NO (100–400 ppm). It is clear that the concentration of NO drops within 60 to 90 seconds of time. The following reaction occurs during the removal or treatment of NO with air in this first stage of scrubber-I.



During the experiment it was found that the above reaction mechanism happened and the product of HNO₃ and some amounts of NO₂ were released from the scrubber-I. The amount of NO charged into the scrubber was almost consumed by the Ag(II) in the scrubber-I. The 400 ppm NO was oxidized completely to NO₂ by Ag(II) ions and the NO₂ was converted to HNO₃ which is shown in reaction steps in Eqs. (1) to (3). Fig. 2 also shows the removal efficiency of NO calculated based on the NO measured at the inlet and outlet of the scrubber-I. It is clear that the efficiency for NO removal attained 100% [400 ppm to 0 ppm] in a short span of 60 to 90 seconds, and thereafter it was sustained for as long as 120 minutes. The NO_x removal efficiency was 82% in the scrubber-I.

After the NO, the byproducts NO₂ [70 ppm] were measured at the outlet of the scrubber-I. It was found to be independent of initial NO concentration; NO₂ was always 5-8% of the initial concentration of NO feed. This unconverted 70 ppm of NO₂ was treated in scrubber-II with 3 M HNO₃ where 35 ppm NO₂ was removed by absorption in HNO₃ medium. It was revealed that, in scrubber-II, the removal efficiency for NO₂ by the HNO₃ medium was 50% only, whereas in scrubber-I the removal efficiency for NO₂ by the Ag(II) redox mediator was 82%. Hence, the overall NO_x removal efficiency was 92% based on the initial 425 ppm of NO_x concentration (400 ppm NO+25 ppm NO₂) and final NO_x concentration (35 ppm).

Bringmann et al. [19] reviewed that for the Co(III)/Co(II) system in 3 M H₂SO₄ used as a redox mediator for NO gas treatment, a removal efficiency of 36% was observed for NO removal and the low efficiency was attributed to the kinetic interaction. As against the Co(III)/Co(II) system, they studied the Mn(III)/Mn(IV) system in 6 M H₂SO₄ which was found to give an efficiency of 97% for NO removal. Hence, the 100% removal efficiency obtained in this present study by Ag(I)/Ag(II) redox mediator system in 6 M HNO₃ may be associated with the high oxidizing power of the Ag(II) ions in 6 M HNO₃ acid medium.

2. Removal of SO₂ Using Ag(II)/Ag(I) Redox Mediator

In this study, experiments were conducted for the removal of SO₂ by wet scrubbing method using the Ag(I)/Ag(II) redox mediator solution in nitric acid medium at room temperature and atmospheric pressure. During the reaction, SO₂ reacted with Ag(II) ions and formed SO₄²⁻ which was converted to H₂SO₄ acid in the scrubbing solutions.

The main purpose of this study was to explore the removal of SO₂ in aqueous medium with the use of Ag(I)/Ag(II) redox mediator solution in nitric acid medium. It was observed that the SO₂ removal was very rapid when compared to the NO_x removal in this Ag(I)/Ag(II) redox mediator medium in 20 to 40 seconds only for 400 ppm of concentration in 10L/min gas flow rate at room temperature. Interestingly, a removal efficiency of 100% within low treatment time in this MEO based Ag(I)/Ag(II) redox mediator system was achieved, when compared to the conventional removal methods. Hence, this type of rapid removal or destruction process will increase the removal efficiency in high order and also improve the economics of the processes for industrial sectors.

The rate of SO₂ removal with the initial concentration of feed with respect to time is given in Fig. 3. The SO₂ concentration decreases rapidly with respect to time and it is in the order of 20 to 40 seconds. Fig. 3 shows the initial concentration of SO₂ from 100-400 ppm and the removal efficiency attains 100% with this time duration. It is interesting to note that as for the case of NO removal,

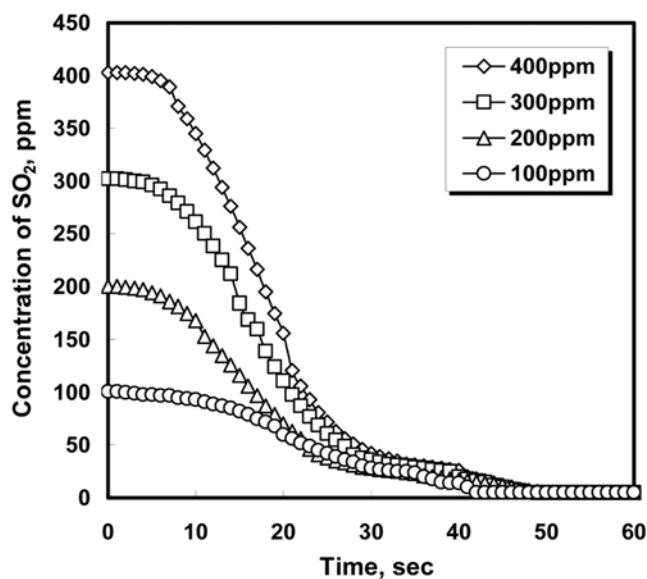
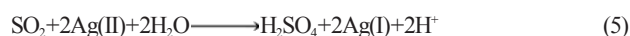


Fig. 3. SO₂ outlet concentration profiles with respect to time.

[Ag(I)=0.1 M in 6 M HNO₃, Gas flow rate=10 L/min, Liquid flow rate=2 L/min, 20 °C]

for SO₂ also, the redox system shows a continuous uninterrupted performance as long as 120 minutes. The same property of Ag(II) redox mediator is observed for all the concentrations of SO₂ from 100-400 ppm.

The possible oxidation reaction in the scrubber may involve the oxidation of SO₂ by Ag(II) ions to form SO₄²⁻ which converted to H₂SO₄ acid. The following reaction is occurring during the removal of SO₂ using the Ag(I)/Ag(II) redox mediator ions in nitric acid medium at room temperature.



CONCLUSIONS

Studies were carried out on developing a process or method for the efficient removal of industrial waste gases like NO, NO₂ and SO₂ from simulated gas by an electrochemically generated Ag(I)/Ag(II) redox mediator system in aqueous nitric acid medium. Experiments were performed with 0.1 M Ag(I) in 6 M HNO₃ medium at a gas flow rate of 10 L/min at 20 °C. From the studies it is found that Ag(I)/Ag(II) redox mediator system has good oxidizing power for the removal of NO_x and SO₂ at room temperature and atmospheric conditions.

This is a sustainable process for removal of NO_x, SO₂ that can be used for the removal of flue gases like the mixture of NO_x and SO₂ and other odor gases in high removal efficiency. In order to develop new sustainable processes or methods for the complete removal of NO_x and SO₂, for the green atmosphere of the global scenario, this type of MEO process will help for zero emission of waste gases from industries.

ACKNOWLEDGMENTS

Research performed as part of the Core Environmental Technology

Development Project for Next Generation (Eco-Technopia-21) of Korea Institute of Environmental Science and Technology (KIEST). This work performed in the framework of the project by the Ministry of Commerce, Industry and Energy (MOCIE) through Regional Innovation Centre (RIC).

REFERENCES

1. C. L. Clifton, N. Altstein and R. E. Hule, *Environ. Sci. Technol.*, **22**, 586 (1988).
2. D. Littlejohn, Y. Wang and S. G. Chang, *Environ. Sci. Technol.*, **27**, 2162 (1993).
3. C. H. Shen and G. T. Rochelle, *Environ. Sci. Technol.*, **32**, 1994 (1998).
4. T. Senjo and M. Kobayashi, Japanese Patent 49130362 (1973).
5. H. F. Hartmann, G. M. Brown and B. Kean, *J. Inst. Fuel*, **39**, 325 (1996).
6. C. Brogren, H. T. Karlsson and I. Bjerle, *Chem. Eng. Technol.*, **21**, 61 (1998).
7. C. L. Yang, H. Shaw and H. D. Perlmutter, *Chem. Eng. Commun.*, **143**, 23 (1996).
8. S. Robenson, *Natl. Environ. J.* (1993).
9. J. B. Joshi, V. V. Mahajani and V. A. Juvekar, *Chem. Eng. Commun.*, **33**, 192 (1985).
10. U. T. Un, A. Savas Koparal and U. B. Ogutveren, *Sep. Purif. Technol.*, **53**, 57 (2007).
11. M. Arousseau, F. Lapique and A. Storck, *Ind. Eng. Chem. Res.*, **33**, 191 (1994).
12. P. Hoffmann, C. Roizard, L. Lapique, S. Venot and A. Maire, *Institution of Chemical Engineers. Trans IChemE*, **75(B)**, 43 (1997).
13. K. Jutter, U. Galla and H. Schmieder, *Electrochim. Acta*, **45**, 2575 (2000).
14. T. Tzedakis and A. Savall, *Chem. Eng. Sci.*, **46**, 2269 (1991).
15. S. Balaji, S. J. Chung, M. Matheswaran and I. S. Moon, *Korean J. Chem. Eng.*, **24**, 1009 (2007).
16. M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, *Bull. Korean Chem. Soc.*, **28**, 1387 (2007).
17. M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, *Electrochim. Acta*, **53**, 1897 (2007).
18. M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, *J. Ind. Eng. Chem.*, **13**, 231 (2007).
19. J. Bringmann, K. Ebert, U. Galla and H. Schmieder, *J. Appl. Electro. Chem.*, **27**, 870 (1997).
20. V. V. Kokovkin, S. J. Chung, S. Balaji, M. Matheswaran and I. S. Moon, *Korean J. Chem. Eng.*, **24**, 749 (2007).