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Research Article

Simultaneous Removal of NO$_x$ and SO$_2$: A Promising Ag(II)/Ag(I) Based Mediated Electrochemical Oxidation System

The present study is a first attempt towards utilizing a Ag(II)/Ag(I) based mediated electrochemical oxidation (MEO) system for the simultaneous clean-up of NO$_x$ and SO$_2$ gases in simulated flue gas-air mixtures on a laboratory-scale scrubber column integrated with an electrochemical reactor, and to rationalize the efficient application of the MEO process for flue gas abatement and pollution control. Experiments were carried out with individual gas components followed with the mixture, and the effect of input NO and input SO$_2$ concentrations was examined on the NO$_x$ and SO$_2$ removal efficiencies at 20°C. Complete oxidation of NO to NO$_2$ with 100% NO removal efficiency and 80% NO$_x$ removal efficiency was achieved along with 100% SO$_2$ removal efficiency, highlighting the potentially far greater efficiency of the Ag(II)/Ag(I) based MEO system in functionality and selectivity. Significant research work in this direction can be anticipated in the near future.

1 Introduction

The combustion of fossil fuels in power plants, incinerators, and boilers results in the emission of nitrogen oxides (NO$_x$) consisting of nitric oxide and nitrogen dioxide, as well as SO$_2$. They are both noxious and directly responsible for large contributions to the formation of acid rain and resultant air acidification, photochemical smog and general atmospheric visibility degradation. While SO$_2$ is removed very effectively by wet flue gas desulfurization (WFGD) [1], NO is insoluble in water, and thus, its removal is difficult, necessitating special methods, e.g., selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), scrubbing, etc., to be developed for its recovery [2]. Among these technologies, scrubbing methods are the most competitive economically and have the advantage of simultaneously controlling other acidic gases and particulates [3].

It is well known that NO$_2$ can be effectively absorbed into some aqueous solutions, but that NO is not absorbed [4]. In general, in the wet chemical scrubbing methods for NO removal, NO is aerially oxidized to NO$_2$, which can easily react with water forming NO$_3^-$ that can be efficiently removed in downstream wet scrubbers. Since the major component of flue gas emitted NO$_x$ is NO (more than 90%), its

oxidation to NO$_2$ is a crucial step for an effective chemical scrubbing system. Thus, the slow oxidation rate of NO by air has been improved by injecting a strong oxidizing agent, e. g., chlorine dioxide [5], ozone [6], or chlorine [7] into the flue gas or by adding an oxidizing agent, e.g., hydrogen peroxide [8], sodium chlorite [9, 10], potassium permanganate [11], or sodium hypochlorite [12] into the scrubbing solution, leading to the availability of several two-stage wet scrubbing processes for the removal of NO$_x$, as reviewed by Joshi et al. [13]. In recent years, studies have been conducted in some systems with metal chelates [14] for the scrubbing of NO$_x$ gases. It should be noted that the presence of ozone oxidizes NO not only to NO$_2$ but also to higher order nitrogen oxides, i.e., NO$_3$, N$_2$O$_4$, N$_2$O$_5$, etc., which form NO$_3^-$ with water much more easily for ultimate removal. However, the general problem encountered in the wet scrubbing systems utilizing various chemicals is that they are consumed by the stiochiometric amount of gases treated for removal, necessitating usage of large amounts of expensive chemicals, which also further adds to the environmental pollution issues involved.

The above problems can be circumvented by using electrochemical methods [15, 16], since a clean reagent, i. e., the electron, is used in the redox processes. The electrochemical methods are more attractive because they are relatively simple, energy efficient, and their regulation and automation are easy to achieve. This technology uses the absorption 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 indirectly via a redox mediator. Although some work on direct reduction of NO$_x$ [17] and oxidation of SO$_2$ [18] relating to flue gas has been carried out, the indirect mediated electro-

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Abbreviations: MEO, Mediated electrochemical oxidation, **SCR**, Selective catalytic reduction; **SNCR**, Selective non-catalytic reduction; **WFGD**, Wet flue gas desulfurization

chemical oxidation (MEO) process has been found to be more suitable for NO_x and SO_2 removal from flue gases [19–23]. In this process, a metal ion of high oxidation capacity, e.g., Ag^{2+} ($E^0 = 1.98$ V (NHE)), Co^{3+} ($E^0 = 1.82$ V (NHE)), Ce^{4+} ($E^0 = 1.62$ V (NHE)), Mn^{2+} ($E^0 = 1.51$ V (NHE)), etc., is utilized as a mediator to oxidize the organic pollutants or waste gases, and the oxidized form of the mediator is electrogenerated in a divided/undivided cell in a closed cycle. The Ce(IV)/Ce(III) redox couple has been used in the current authors' research group for the oxidation of organic compounds [24–29] because of its excellent selectivity, and this redox system has also been used in the treatment of waste biological materials [30], as well as in processes for the removal of NO_x and SO_2 from waste gases [19–21, 23]. Aurousseau et al. [21] studied a wet scrubbing process for SO_2 removal relevant to industrial waste gases using electrogenerated Ce(IV) in sulfuric acid. Hoffmann et al. [23] used electrogenerated Ce(IV) in an acidic medium for simultaneous removal of NO_x and SO_2 from a mixture with a total removal of SO_2 and almost 45% removal efficiency of NO_x gases. In a study relating to NO and NO_2 off-gases emanating from the cathode compartment of an electrochemical cell due to nitric acid reduction, Bringman et al. [22] used electrogenerated Co(III) and Mn(III) in a sulfuric acid medium for NO_x to HNO_3 conversion with conversion efficiencies of 36 and 97%, respectively, at 20°C.

Hence, Ce, Mn and Co have been used as mediators for NO_x and SO_2 removal, but no reference is cited on the use of Ag(II), despite the fact that it is more oxidizing than Co(III), Ce(IV), or Mn(II) in acidic media, and it has been proven to be highly efficient for organic destruction [31–37]. This study presents the first report on some preliminary work performed on the simultaneous removal of NO_x and SO_2 related to an industrial flue gas mixture using the Ag(II)/Ag(I) based MEO redox system. The present studies show that the silver system works with 100% removal efficiency reached in a short time of ca. 60 s not only for SO_2 but also for NO gas, and efficiently sustains a consistent performance over the 120 min duration studied.

2 Experimental

2.1 Materials

Silver(I) nitrate (99.8%) from Junsei Chemical Co. Ltd., Japan, nitric acid (60%) from Sam Chun Chemicals, Korea, and sulfuric acid (95%) from DC Chemicals Co Ltd, Korea were used as received. Mesh-type Pt and Ti electrodes were purchased from Wesco, Korea. Nafion® 324 membrane was purchased from Dupont, USA. All the solutions were made using water purified by reverse osmosis (Human Power III plus, Korea). NO (concentration 99.5%) and SO_2 (concentration 9980 µmol/mol) gas cylinders were obtained from Inter Gas, Korea.

2.2 Apparatus and Process

A schematic diagram of the setup used for the gas removal experiments is shown in Fig. 1. There were three main components: an electrochemical cell reactor, scrubber-I, and scrubber-II. The Ag(II) redox mediator required for the mediated electrochemical oxidation of the gases was generated in the electrochemical cell, and the oxidation of the gases by Ag(II) occurred in scrubber-I. The electrochemical cell was integrated with scrubber I, so that electrochemical generation of Ag(II) ions and the scrubbing of NO_x and SO_2 could
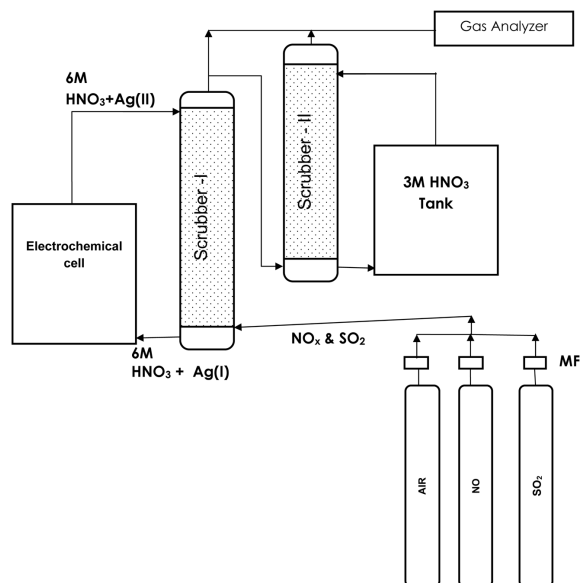

Figure 1. Schematic diagram for continuous removal of NO_x and SO_2 from NO_x-SO_2-Air mixtures by Ag(II)/Ag(I) based mediated electrochemical oxidation process.

be carried out simultaneously in a continuous mode. The second stage scrubber-II was used for absorption of NO_2 emitted from Scrubber-I. All the processes were conducted at room temperature and atmospheric pressure conditions.

The electrochemical cell was a plate-and-frame type narrow gap divided flow cell configuration. Mesh type Pt/Ti and Ti of geometrical area of 140 cm², separated by a Nafion 324 membrane, were used as anode and cathode, respectively. A 1000 mL solution of 0.1 M Ag(I) in 6 M nitric acid and an equivalent volume of 2.5 M sulfuric acid, taken in separate anolyte and catholyte glass reservoirs, were continuously circulated through the anode and cathode compartments of the electrochemical cell at a constant flow rate. The electrolysis for generation of Ag(II) redox mediators was conducted galvanostatically by applying a constant current of 10 A by a locally made constant current source from Korea Switching Instruments.

The NO_x and SO_2 removal system was composed of NO, SO_2 and an air supply, scrubbing liquid tank, the scrubbers-I and II, data logging and gas analysis systems. Simulated flue gas-air mixtures of different composition, obtained by controlled mixing of air, NO and SO_2 using mass flow controllers (MFC), were introduced at the bottom of the scrubber-I at a constant gas flow rate. Simultaneously, the scrubbing solution (6 M HNO_3 with Ag(II)) was introduced in a counter-current flow pattern at a constant liquid flow rate. The outlet gas concentrations of NO, NO_2 and SO_2 were measured continuously with respect to time during the reaction. The outlet scrubbing solution containing the reduced form of silver, i. e., Ag(I), was passed through the electrochemical cell for Ag(II) generation, and was further re-circulated.

The outlet gas from scrubber-I was fed into scrubber-II for NO_2 removal by continuous washings with 3 M HNO_3. The details on the scrubber-I and scrubber-II and the experimental conditions are given in Tab. 1. The gas compositions were measured by a gas analyzer instrument (NO_2-Teledyne Model No.9110, NO &SO_2-Fuji ZSU). The gas removal efficiencies were calculated from the inlet and outlet concentration of NO, NO_2 and SO_2.

Table 1. Experimental conditions for NO_x and SO_2 scrubbing systems.

System No.	Electrochemical Cell System	Gas Scrubbing System
1	Anode: Pt/Ti	Scrubber-I: Glass column-ID = 5 cm, *H* = 120 cm, Glass Raschig rings-diameter = 1 cm
2	Cathode: Ti	Gas flow rate: 10 L/min
3	Anolyte: 0.1 M $AgNO_3$ in 6 M HNO_3	Liquid flow rate: 2 L/min
4	Catholyte: 2.5 M H_2SO_4	Scrubbing liquid: Ag(II) redox mediator containing 6 M HNO_3
5	Diaphragm: Nafion 324 membrane	Scrubber-II: PVC column-ID = 5cm, *H* = 200 cm, PTFE Raschig rings-diameter = 2 cm
6	Current density: 7 A/dm^2	Gas flow rate: 10 L/min
7	Anolyte and catholyte flow rate: 2 L/min	Liquid flow rate: 4 L/min
8	Temperature: 20°C	Scrubbing liquid: 3M HNO_3
9	Anolyte and catholyte volume: 1 L	–
10	Electrode areas: 10 cm × 14 cm	–

3 Results and Discussion

Gas removal experiments were initially conducted for individual gases NO_x or SO_2 from their respective simulated gas-air mixture. Subsequently, the simultaneous removal of NO_x and SO_2 from the NO-SO_2-air mixture was carried out under similar experimental conditions.
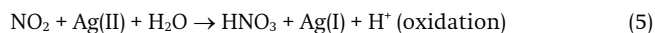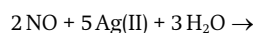
3.1 Removal of NO and NOx

NO-air mixtures with initial NO feed concentrations in the range 100 to 400 ppm were studied. It should be mentioned that the initial gas analysis always showed additional NO_2 of ca. 10 to 15% of the initial NO concentration, possibly due to air oxidation of NO.

Figure 2 shows the NO concentration profile and its removal efficiency with respect to time measured at the outlet of scrubber-I. It is interesting to note that except for the highest 400 ppm concentration, the NO concentration was reduced to almost zero, irrespective of the initial feed concentration range from 300 to 100 ppm, with the removal efficiency reaching 100% in a short span of 60 to 80 s. Thereafter, it was sustained for the extended 120 min time period studied.

NO_x gases are well known to establish several complex equilibria in the presence of air [22, 38], see reactions (1–3):

$$2\,NO + O_2 \rightleftarrows 2\,NO_2 \tag{1}$$

$$2\,NO_2 \rightleftarrows N_2O_4 \tag{2}$$

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2 \tag{3}$$

In the scrubber-I section, Ag(II) may oxidize NO and NO_2 to HNO_3 similar to the mechanism proposed for Co(III) and Mn(III) [22], see reactions (4) and (5) as follows:

$$2\,NO + 5\,Ag(II) + 3\,H_2O \rightarrow$$

$$HNO_3 + NO_2 + 5\,Ag(I) + 5\,H^+ \text{ (oxidation)} \tag{4}$$

$$NO_2 + Ag(II) + H_2O \rightarrow HNO_3 + Ag(I) + H^+ \text{ (oxidation)} \tag{5}$$

Ag(II) is also capably of oxidizing HNO_2 similar to Ce(IV) [38] with the overall oxidation represented as reaction (6):

$$HNO_2 + 2\,Ag(II) + H_2O \rightleftarrows HNO_3 + 2\,Ag(I) + 2\,H^+ \text{ (oxidation)} \tag{6}$$
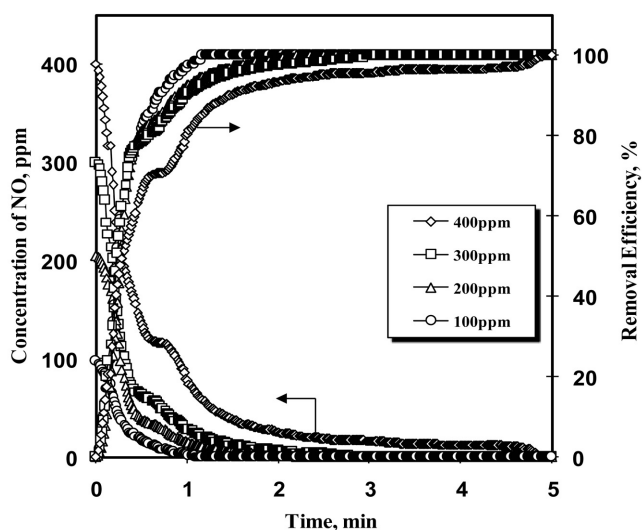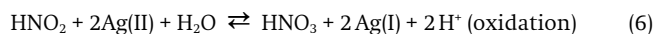

Figure 2. NO concentration at scrubber-I outlet and its removal efficiency as a function of time for various NO feed concentrations (indicated in the figure) treated with electrochemically regenerated Ag(II) in 6 M HNO_3 (gas velocity = 0.13 m/s, liquid velocity = 0.025 m/s, Ag(I) concentration in the cell = 0.1 M, 20°C).

The absorption of NO_2 in scrubber-I may occur as given by reaction (7):

$$NO_{2\,(gas)} \xrightarrow{H_2O,\ HNO_3} NO_{2\,(dissolved)} \text{ (absorption)} \tag{7}$$
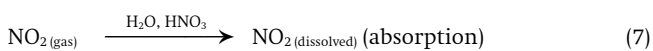
It should be noted that the scrubber-I outlet gas always contained NO_2 gas signifying that all of the NO_2 molecules produced from NO were not absorbed in scrubber-I, and the removal efficiency of NO_x calculated with respect to the initial total concentration of NO and NO_2 was ca. 80% for all initial NO feed concentrations studied.

The subsequent washing of the scrubber-I outlet residual gas with 3 M HNO_3 in scrubber-II efficiently cleaned the NO_2 content resulting in 92% NO_x removal efficiency.

3.2 Removal of SO2

The removal of SO_2 from the simulated SO_2-air mixture by a wet scrubbing method in scrubber-I using the Ag(II) redox mediator in 6
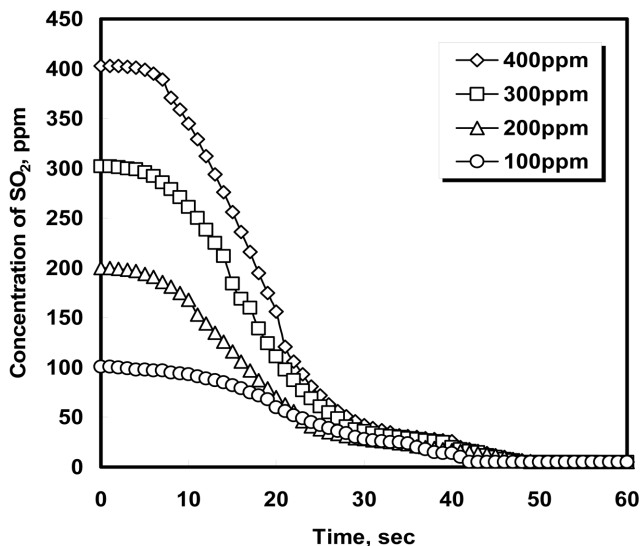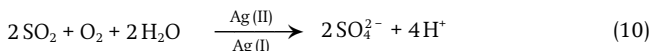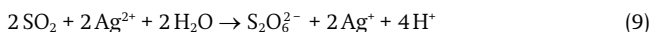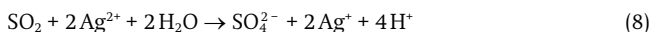
Figure 3. SO$_2$ concentration at scrubber-I outlet and its removal efficiency as a function of time for various SO$_2$ feed concentrations (indicated in the figure) treated with electrochemically regenerated Ag(II) in 6 M HNO$_3$ (gas velocity = 0.13 m/s, liquid velocity = 0.025 m/s, Ag(I) concentration in the cell = 0.1 M, 20°C).

Figure 4. NO, NO$_2$ and SO$_2$ concentrations at scrubber-I outlet during their simultaneous removal from a 400 ppm NO-400 ppm SO$_2$-Air mixture treated with electrochemically regenerated Ag(II) in 6 M HNO$_3$ (gas velocity = 0.13 m/s, liquid velocity = 0.025 m/s, Ag(I) concentration = 0.1 M in 6 M HNO$_3$, 20°C). NO$_2$ concentration at scrubber-II outlet treated with 3 M HNO$_3$ is also included (gas velocity = 0.13 m/s, liquid velocity = 0.05 m/s, 20°C).

M HNO$_3$ acid is demonstarted in Fig. 3 for different SO$_2$ feed concentrations. It can be clearly seen that the SO$_2$ concentration in the outlet gas stream fell sharply, and within 40 s the entire amount of SO$_2$ was removed completely.

The direct oxidation of SO$_2$ by transition metals, and oxidation of SO$_2$ by the oxygen contained in air catalyzed by transition metals have been studied by several authors, and depending on sulfuric acid concentration, the formation of sulfate and dithionate ions have been proposed as reaction products [21]. Similar reactions for SO$_2$ oxidation in the present case of the Ag(II)/Ag(I) redox system forming highly water-soluble forms may be expected, see reactions (8 – 10):

$$SO_2 + 2\,Ag^{2+} + 2\,H_2O \rightarrow SO_4^{2-} + 2\,Ag^+ + 4\,H^+ \tag{8}$$

$$2\,SO_2 + 2\,Ag^{2+} + 2\,H_2O \rightarrow S_2O_6^{2-} + 2\,Ag^+ + 4\,H^+ \tag{9}$$

$$2\,SO_2 + O_2 + 2\,H_2O \xrightarrow[\text{Ag(I)}]{\text{Ag(II)}} 2\,SO_4^{2-} + 4\,H^+ \tag{10}$$

A comparison of Fig. 2 for the NO system and Fig. 3 for the SO$_2$ system clearly illustrates that although the Ag(II) redox mediator effectively removed SO$_2$ and NO with 100% efficiency, the SO$_2$ gas was removed more quickly and easily compared to the NO.

3.3 Simultaneous Removal of NO$_x$ and SO$_2$

In a set of experiments, simultaneous removal of NO$_x$ and SO$_2$ from simulated flue gas containing a 400 ppm NO/400 ppm SO$_2$ air mixture was studied. The NO$_x$ and SO$_2$ concentration profiles measured at the outlets of both scrubber-I and scrubber-II over time are presented in Fig. 4. The Ag(II) in scrubber-I removed both NO and SO$_2$ quite effectively, approaching 100% cleaning efficiency, as was the case for individual gases. At the same time an 80% NO$_x$ removal effi-
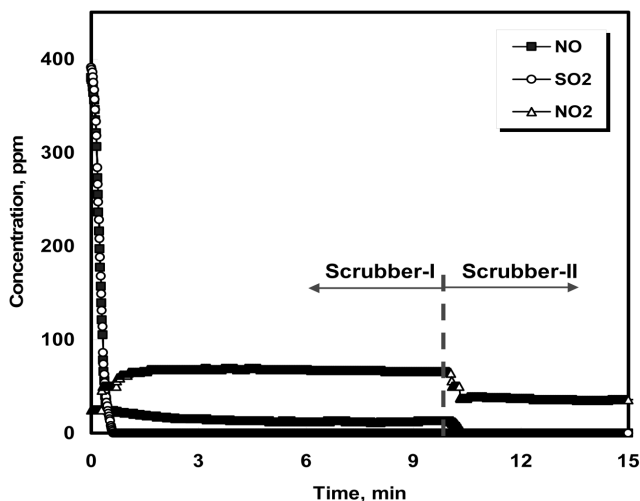
ciency was observed. At the end of scrubber-II, the measurement of the NO$_2$ concentration showed a 92% NO$_x$ removal efficiency.

The superior performance of the Ag(II)/Ag(I) based MEO process in the NO$_x$/SO$_2$ removal with 100, 80 and 100% removal efficiencies for NO, NO$_x$, and SO$_2$, respectively, can be realized from a simple comparison with other systems studied earlier for simultaneous NO$_x$ and SO$_2$ removal [23, 39]. The Ce(IV)/Ce(III) based MEO system was studied by Hoffmann et al. [23], and Jin et al. [39] involved the use of ClO$_2$ for chemical oxidation. Both Ce(IV)/Ce(III) and ClO$_2$ showed 100% SO$_2$ removal, as observed with the Ag(II) ions in the present work. However, their performance towards NO and NO$_x$ removal was poorer. The Ce(IV)/Ce(III) showed only 20 and 45% removal yields for NO and NO$_x$, respectively, whereas 66 to 72% NO$_x$ removal efficiency was found with the ClO$_2$ system. The high removal efficiency by Ag(II)/Ag(I) system for NO and NO$_x$ (100 and 80%) can be attributed to its higher oxidizing capability as a result of its more favorable redox potential, i. e., E^0 = 1.98 V (NHE), compared to 1.62 V for the Ce(IV)/Ce(III) system and 0.95 V and 1.27 V for ClO$_2$ in the gas and solution phases, respectively [39].

3.4 Effect of Input Concentrations of NO and SO$_2$ on Simultaneous Removal of NO$_x$ and SO$_2$

The effect of input NO and SO$_2$ concentrations on the simultaneous removal of SO$_2$ and NO$_x$ was investigated by feeding different gas-air mixtures containing equal concentrations of NO and SO$_2$ into scrubber-I. The gas removal efficiencies calculated from the Scrubber-I outlet gas analyses are displayed in Fig. 5 for NO, SO$_2$ and NO$_x$. It was found that the NO or SO$_2$ removal efficiency remained almost constant at ca. 100% when the input gas-air mixture containing equal NO and SO$_2$ concentrations was increased from 100 to 400 ppm. Similarly, the input NO and SO$_2$ concentrations did not affect the NO$_x$ removal efficiency, which was found to be ca. 80%.
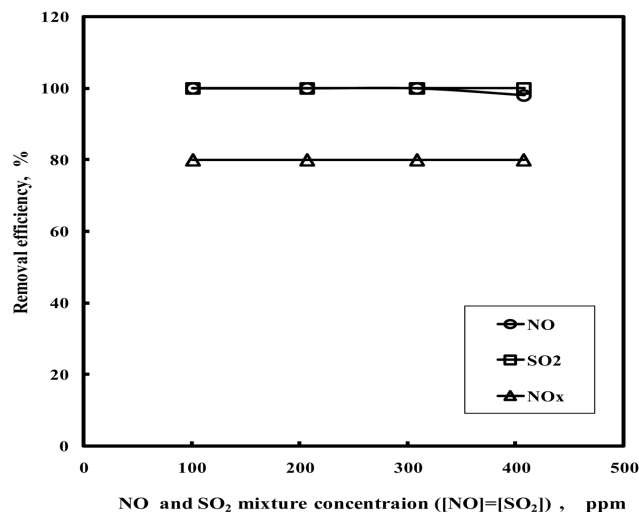
Figure 5. Effect of input NO and SO_2 concentrations in the feed mixture on NO, NO_x and SO_2 removal treated with electrochemically regenerated Ag(II) in 6 M HNO_3 in scrubber-I. Feed mixture contained equal concentrations of NO and SO_2 (gas velocity = 0.13 m/s, liquid velocity = 0.025 m/s, Ag(I) concentration in the cell = 0.1M, 20°C).

4 Conclusions

An Ag(II)/Ag(I) based MEO process proved quite promising for the simultaneous removal of NO, NO_x, and SO_2 from simulated flue gas mixtures containing NO and SO_2 over a wide concentration range of 100 to 400 ppm. It exhibited almost 100% efficiency towards NO and SO_2 removal, and 80% towards NO_x removal. Input NO and SO_2 concentrations had a negligible effect on the removal efficiency of the three components. The removal efficiencies by electrogenerated Ag(II), especially towards NO and NO_x gases, were much larger compared to the Ce(IV) based MEO system and ClO_2 based chemical system, studied previously for the simultaneous removal of NO_x and SO_2, thereby confirming the higher oxidation potentialities of the Ag(II)/Ag(I) based MEO system. With the additionally integrated second-stage scrubber-II, 92% NO_x removal was achieved, thereby signifying a new sustainable flue gas removal process with almost zero emission of waste gases for industrial application. The effect of various experimental parameters, e. g., gas flow rate, liquid flow rate, scrubber dimensions, packing material, etc., on the NO_x and SO_2 removal efficiencies and the removal rate by the Ag(II)/Ag(I) system are under investigation, and the results will be communicated separately.

References

[1] J. Cheng et al., Sulfur removal at high temperature during coal combustion in furnaces: a review, *Prog. Energy Combust. Sci.* **2003**, *29*, 381.

[2] J. O. L. Wendt, W. P. Linak, P. W. Groff, R. K. Srivastava, Hybrid SNCR-SCR Technologies for NOx Control Modeling and Experiment, *AIChE J.* **2001**, *47*, 2603.

[3] C. L. Yang, H. Shaw, H. D. Perlmutter, Absorption of NO promoted by strong oxidizing agents: 1. Inorganic oxy-chlorites in nitric acid, *Chem. Eng. Commun.* **1996**, *143*, 23.

[4] G. A. Chappell, Development of aqueous processes for removing NOx from flue gases, *EPA-R2-72-051*, **1972**.

[5] T. Senjo, M. Kobayashi, Removal of nitrogen oxides from waste gases, *Japanese Patent 49130362*, **1973**.

[6] H. Shaw, Aqueous solution scrubbing for NO control in munitions incineration, *Proc. of the ASME Winter Annual Meeting*, Paper no.76-WA/FU-9, New York **1976**.

[7] E. M. Hixon, Removal of nitric oxide from gas streams via direct chlorine injection, *Proc. of the AFRC Int. Symp., Paper no.36*, **1990**.

[8] S. Robenson, Hydrogen peroxide: first aid for air pollution, *Natl. Environ. J.* **1993**, 13.

[9] C. L. Yang, H. Shaw, H. D. Perlmutter, Absorption of NO promoted by strong oxidizing agents – inorganic oxy chlorides in nitric acid, *Chem. Eng. Commun.* **1996**, *143*, 23.

[10] C. Brogren, H. T. Karlsson, I. Bjerle, Absorption of NO in an Aqueous Solution of $NaClO_2$, *Chem. Eng. Technol.* **1998**, *21*, 61.

[11] C. Brogen, H. T. Karlsson, I. Bjerle, Absorption of NO in an alkaline solution of $KMnO_4$, *Chem. Eng. Technol.* **1997**, *20*, 396.

[12] R. J. Chironna, B. Altshuler, Chemical aspects of NO_x scrubbing, *Pollut. Eng.* **1999**, *31(4)*, 32–36.

[13] J. B. Joshi, V. V. Mahajani, V. A. Juvekar, Absorption of NO dissolved in gases, *Chem. Eng. Commun.* **1985**, *33*, 1.

[14] J. G. M. Winkelman, F. Gambardella, H. J. Heeres, A rate based reactor model for BiodeNO$_x$ absorber units, *Chem. Eng. J.* **2007**, *133*, 165.

[15] S. Trasatti, Electrochemistry and environment: The role of electro catalysis, *Int. J. Hydrogen Energy* **1995**, *20*, 835.

[16] K. Juttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, *Electrochim. Acta* **2000**, *45*, 2575.

[17] K. H. Kleifges, E. Juzeliunas, K. Juttner, Electrochemical study of direct and indirect NO reduction with complexing agents and redox mediator, *Electrochim. Acta* **1997**, *42*, 2947 (and references therein).

[18] U. T. Un, A. S. Koparal, U. B. Ogutveren, Sulfur dioxide removal from flue gases by electrochemical absorption, *Sep. Purif. Technol.* **2007**, *53*, 57 (and references therein).

[19] N. L. Weinberg, Method for purification of air. Electro-incinerator Technologies, Inc., *European Patent EP-A-0328 782 (88 121 693.1)*, **1992**.

[20] P. J. Dyens et al., Electrochemical Ce(IV)-assisted process of SO_2/NO_2 containing gas treatment, *French Patent 92 08 214*, **1992**.

[21] M. Aurousseau, C. Roizard, A. Storck, F. Lapicque, Scrubbing of sulphur dioxide using a cerium(IV)-containing acidic solution: A kinetic investigation, *Ind. Eng. Chem. Res.* **1996**, *35*, 1243.

[22] J. Bringmann, K. Ebert, U. Galla, H. Schmieder, Oxidative separation of nitrogen oxides from off-gases by electrochemical mediators, *J. Appl. Electrochem.* **1997**, *27*, 870.

[23] P. Hoffmann et al., A process for the simultaneous removal of SO_2 and NO_x using Ce(IV) redox catalysis, *Trans. Inst. Chem. Eng., B* **1997**, *75*, 43.

[24] S. Balaji, S. J. Chung, T. Ramesh, I. S. Moon, Mediated electrochemical oxidation process: Electro-oxidation of cerium(III) to cerium(IV) in nitric acid medium and a study on phenol degradation by cerium(IV) oxidant, *Chem. Eng. J.* **2007**, *126*, 51.

[25] S. Balaji, V. V. Kokovkin, S. J. Chung, I. S. Moon, Destruction of EDTA by mediated electrochemical oxidation process: monitoring by continuous CO_2 measurements, *Water Res.* **2007**, *41*, 1423.

[26] M. Matheswaran, S. Balaji, S. J. Chung, I. S. Moon, Mineralization of phenol Ce(IV)-mediated electrochemical oxidation in methanesulphonic acid medium: A preliminary study, *Chemosphere* **2007**, *69*, 325.

[27] S. Balaji et al., Destruction of organic pollutants by cerium(IV) MEO process: A study on the influence of process conditions for EDTA mineralization, *J. Hazard. Mater.* **2007**, *150*, 596.

[28] V. V. Kokovkin et al., Electrochemical cell current requirements for toxic organic waste destruction in Ce(IV)-mediated electrochemical oxidation process, *Korean J. Chem. Eng.* **2007**, *24*, 749.

[29] S. Balaji et al., Cerium(IV)-mediated electrochemical oxidation process for destruction of organic pollutants in a batch and a continuous flow reactor, *Korean J. Chem. Eng.* **2007**, *24*, 1009.

[30] L. Kaba, G. D. Hitchens, J. O. M. Bockris, Electrochemical incineration of wastes, *J. Electrochem. Soc.* **1990**, *137*, 1341.

[31] J. C. Farmer et al., Electrochemical treatment of mixed and hazardous wastes: Oxidation of ethylene glycol and benzene by silver (II), *J. Electrochem. Soc.* **1992**, *139*, 654.

[32] J. Bringmann, K. Ebert, U. Galla, H. J. Schimider, Electrochemical mediators for total oxidation of chlorinated hydrocarbons: Formation kinetics of Ag(II), Co(III) and Ce(IV), *J. Appl. Electrochem.* **1995**, *25*, 846.

[33] A. Lehmani, P. Turq, J. P. Simonin, Oxidation kinetics of water and organic compounds by Silver(II) using a potentiometric method, *J. Electrochem. Soc.* **1996**, *143*, 1860.

[34] U. Galla, P. Kritzer, J. Bringmann, H. Schmieder, Process for total degradation of organic wastes by mediated electrooxidation, *Chem. Eng. Technol.* **2000**, *23*, 230.

[35] C. A. C. Sequeira, D. M. F. Santos, P. S. D. Brito, Mediated and non-mediated electrochemical oxidation of isopropanol, *Appl. Surf. Sci.* **2006**, *252*, 6093.

[36] M. Matheswaran, S. Balaji, S. J. Chung, I. S. Moon, Silver mediated electrochemical oxidation: production of silver (II) in nitric acid medium and in situ destruction of phenol in semi batch process, *J. Ind. Eng. Chem.* **2007**, *13*, 231.

[37] M. Matheswaran, S. Balaji, S. J. Chung, I. S. Moon, Silver ion catalyzed cerium (IV) mediated electrochemical oxidation of phenol in nitric acid medium, *Electrochim. Acta* **2007**, *53*, 1897.

[38] M. Aurousseau, F. Lapicque, A. Storck, Simulation of NO_x scrubbing by ceric solutions: Oxidation of nitrous acid by Ce(IV) species in acidic solutions, *Ind. Eng. Chem. Res.* **1994**, *33*, 191.

[39] D. Jin, B. Deshwal, Y. Park, H. Lee, Simultaneous removal of SO_2 and NO by wet scrubbing using aqueous chlorine dioxide solution, *J. Hazard. Mater.* **2006**, *135*, 412.