# Novel Process for Simultaneous Removal of $NO_x$ and $SO_2$ from Simulated Flue Gas by Using a Sustainable Ag(I)/Ag(II) Redox Mediator

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The objective of this work is to develop a sustainable process for simultaneous removal of waste gases such as NO, NO<sub>2</sub>, and SO<sub>2</sub> by an electrochemically generated Ag(I)/Ag(II) redox mediator system. High removal efficiency was achieved for NO and SO<sub>2</sub> by the wet scrubbing method at room temperature and atmospheric pressure. This removal is achieved through oxidation and absorption by contacting the gaseous stream with redox mediator ions that offer specific or selective solubility for the solute gases to be recovered in a wet scrubber. The process parameters such as gas velocity, liquid velocity, Ag(I) concentration, and HNO3 concentration were investigated to explore the possibility of complete removal of waste gases. The Ag(I)/Ag(II)-based mediated electrochemical oxidation process proved to be guite effective for simultaneous removal of NO, NOx, and SO2 from the simulated flue gas mixtures containing NO and SO2 over a wide concentration range of 100-400 ppm. Studies were carried out with individual gas components for the mixture, and the effect of input NO and input  $SO_2$  concentrations on the  $NO_x$  and  $SO_2$  removal efficiencies at 20 °C was examined. Complete oxidation of NO to NO<sub>2</sub> with 100% NO removal efficiency and 92% NO<sub>x</sub> removal efficiency was achieved along with 100% SO<sub>2</sub> removal efficiency, highlighting a potentially far greater efficiency of the Aq(I)/Aq(II)-based system in functionality and selectivity. Active research work in this direction is anticipated in the near future.

# Introduction

Combustion of fossil fuels in stationary sources such as power plants, incinerators, and boilers results in emission of  $SO_2$  and nitrogen oxides  $(NO_x)$ . Although the flue gases from these sources mainly contain nitric oxide (NO) and nitrogen dioxide  $(NO_2)$ , the major component of  $NO_x$  is NO.  $NO_x$  consist of NO and  $NO_2$  and are emitted primarily from combustion processes. 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,  $NO_2$ , and  $SO_2$  from industrial processes are closely monitored and regulated.

Wet flue gas desulfurization (WFGD) is the most widely used process that can remove  $SO_2$  efficiently. However,  $NO_x$  cannot be removed as efficiently. Technologies for  $NO_x$  removal include easily removed  $SO_2$  combustion control and postcombustion treatment methods. Postcombustion methods include selective noncatalytic reduction (SNCR), selective catalytic reduction (SCR), and wet scrubbing. Many new technologies are being developed for high-efficiency, lowcost, simultaneous removal of  $SO_2$  and  $NO_x$ , including the nonthermal plasma, electric beam irradiation, and absorption process. Among these technologies, the wet scrubbing method is one of the most cost-effective methods that have an advantage of controlling other acid gases.

In the wet scrubbing process, two kinds of reactions are used for  $NO_x$  conversion. In one reaction,  $NO_x$  is reduced to  $N_2$  directly by N radicals. In the other kind,  $NO_x$  is oxidized into  $NO_2$ ,  $N_2O_3$ ,  $N_2O_4$ ,  $N_2O_5$ , etc. by  $O^{\bullet}$  and  $O_3^{\bullet}$  radicals. About 95% of  $NO_x$  is NO in the coal combustion flue gas, but NO is insoluble in water and difficult to remove. However, highorder nitrogen species such as  $NO_2$ ,  $N_2O_3$ , and  $N_2O_5$  can react with water, forming  $NO_2^-$  and  $NO_3^-$  species which can be efficiently removed in the downstream wet scrubber such as the WFGD system. Therefore, simultaneous removal of  $NO_x$  and  $SO_2$  is possible in the packed column, packed towers, or scrubber by preoxidation of NO.

Several wet scrubbing processes are available for the removal of NO<sub>x</sub> as reviewed by Joshi et al. (1). Similarly, the wet chemical scrubbing methods for SO<sub>2</sub> removal have been reviewed by Srivastava et al. (2), and both pollutants have been reviewed by Jin et al. (3). NO<sub>2</sub> can be effectively absorbed in some aqueous solutions, but NO is not. Therefore, NO oxidation to NO2 is a crucial step followed by NO2 absorption for an effective chemical scrubbing system. Absorbents such as ozone and chlorine dioxide and chlorine are injected to improve the slow oxidation rate of NO in air (4-6), or an oxidizing agent such as sodium chlorite (7), sodium hypochlorite (8), hydrogen peroxide (9), or potassium permanganate (10) is added to the scrubbing solution. In some systems, studies have been conducted with metal chelates (11) for scrubbing of  $NO_x$  gases. A number of chemicals have been employed as absorbents or oxidizing agents for the removal or destruction of NO, NO2, NOx, and SO2 in an aqueous medium in various wet scrubbing systems. These types of chemicals are consumed on the stoichoimetric amount of gases treated for removal and are relatively unstable and quite expensive.

However, while using the electrochemically generated redox mediators as the oxidizing agents for waste gas removal or treatment, the problems stated above do not arise, since the mediators are generated continuously without any disposal or consumption of solutions during the removal and having good oxidation powers. Thus, the removal of  $NO_x$  and  $SO_2$  by means of a wet scrubbing technique using aqueous redox mediators such as the Ag(I)/Ag(II), Ce(III)/Ce(IV), Mn(II)/(III), and Co(II)/Co(III) systems appears to be very attractive.

Electrochemical methods are available for the removal of  $NO_x$  and  $SO_2$  by direct and indirect electrochemical processes (12, 13). In direct electrolysis, the waste gases  $NO_x$  and  $SO_2$  can be removed by oxidation on the electrode surface with a suitable electrolyte medium, and in indirect electrolysis, the removal can be achieved by using a redox mediator such as Ce(III)/Ce(IV) and Mn(II)/Mn(III), which can be regenerated at an electrode surface in an aqueous medium. In mediated electrochemical oxidation or indirect electrochemical processes, the redox mediators are used

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as oxidizing agents for the destruction of liquid or removal of wastes. Using the Ce(III)/Ce(IV) redox mediator system, Balaji and Kokovkin et al. (14-18) performed indirect electrochemical oxidation for liquid organic destruction, and gas scrubbing and purification have been investigated using Ce(III)/Ce(IV) by Aurousseau et al. (19, 20).

Bringmann et al. (21) have reported off-gas removal using electrochemically generated redox mediators such as Mn(III)/Mn(II) and Co(III)/Co(II) in nitric and sulfuric acid media. Nzikou et al. (22), Hoffman et al. (23), and Juttner et al. (24) have reviewed the simultaneous removal of  $SO_2$  and  $NO_x$  using the cerium(IV) ions in sulfuric acid medium and investigated the kinetics and solubility data for  $NO_x$  and  $SO_2$  in the mediated redox solution. Kreysa et al. (25), and Velzen et al. (26) have studied the desulfurization process with a Cu electrode in sulfuric acid medium and HBr systems.

Recently, in our group, Matheswaran et al. (27-29) investigated the use of the Ag(II)-mediated electrochemical oxidation process for the liquid destruction of organic compounds to  $CO_2$  and water in aqueous nitric acid medium.

Redox mediators such as Ce(III)/Ce(IV), Mn(II)/(III), and Co(II)/Co(III) have been used as oxidants for  $NO_x$  and  $SO_2$  removal or treatment, but no reference is cited on the use of Ag(II), in spite of the fact that it is more oxidizing than Co(III), Ce(IV), or Mn(II) in an acidic medium and it has been proved to be highly efficient for organic destruction (30-34).

This study reports on some preliminary work carried out on the simultaneous removal of NOx and SO2 related to industrial waste flue gas using the Ag(I)/Ag(II)-based MEO redox system. Hence, in this study, an investigation was carried out by using silver(II)-mediated electrochemical oxidation for simultaneous removal of  $NO_x$  and  $SO_x$  from simulated flue gases in an aqueous medium. Since the Ag(I)/ Ag(II) redox system has a higher standard reduction potential, the removal efficiency is high when compared to those of conversional removal processes. We also attempted to investigate the effect of various operating parameters for  $NO_x$  and  $SO_x$  removal efficiency using Ag(I)/Ag(II) redox mediators in a laboratory-scale scrubbing system. Our studies show that the silver system works with 100% removal efficiency, reaching this value in a short time of around 60 s not only for SO<sub>2</sub> but also for NO gas, and the system efficiently sustains the same performance for over 120 min.

# **Experimental Section**

The experimental system for  $NO_x$  and  $SO_2$  removal is divided into two parts; i.e., in the first part the Ag(II) redox mediators are generated by the mediated electrochemical oxidation process in a divided cell, and in the second part the Ag(II) redox mediators are used as a scrubbing liquid for  $NO_x$  and  $SO_x$  gas removal in a scrubber by the wet scrubbing method. Both electrochemical generation of Ag(II) ions and the scrubbing of  $NO_x$  and  $SO_x$  can be carried out simultaneously in a continuous mode. All the processes were conducted at room temperature and atmospheric pressure conditions and are presented in Figure 1.

Electrochemical Generation of the Ag(II) Redox Mediator. The electrochemical system consists of anolyte and catholyte tanks, coupled to an electrochemical cell. The electrochemical cell is in a plate and frame type narrow gap flow cell configuration. The cell consists of an anode and cathode separated by a Nafion 324 membrane. The anode and cathode were Pt/Ti and DSA mesh type electrodes placed in a cell with a very narrow interelectrode distance. The electrolyte used in the anolyte was 0.1 M AgNO<sub>3</sub> in 6 M nitric acid, and in the catholyte 2.5 M sulfuric acid was used. The electrolysis for generation of Ag(II) redox mediators was

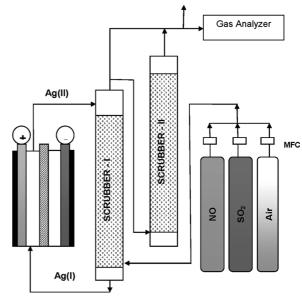


FIGURE 1. Schematic diagram for the removal of  $NO_x$  and  $SO_2$  by using the mediated electrochemical oxidation process.

conducted galvanostatically by applying a constant current of 10 A, and the cell voltage was measured with respect to time.

Wet Scrubbing for Removal of  $NO_x$  and  $SO_2$  Using the Ag(II) Redox Mediator. The removal  $NO_x$  and  $SO_2$  system is composed of a simulated gas supply, a scrubbing liquid tank, scrubbers, and data logging and gas analysis systems. The simulated gas mixture was obtained by controlled mixing of air and NO using the mass flow controllers (MFCs). Simulated gas was introduced at the bottom of the scrubber at constant initial NO and  $SO_2$  concentration, and the scrubbing liquid Ag(II) redox solution was introduced at the top of the scrubber in counter current flow mode. The known initial concentration of NO and  $SO_2$  gas was fed to the scrubber at constant gas and liquid flow rates at room temperature and atmospheric pressure. In wet scrubbing, the scrubber is required to oxidize the NO to  $NO_2$ ,  $NO_2$  to  $HNO_3$ , and  $SO_2$  to  $H_2SO_4$  with Ag(II) redox mediator ions as the scrubbing liquid.

The NO, NO<sub>2</sub>, and SO<sub>2</sub> analyses were carried out using a gas analyzer instrument (NO<sub>2</sub>, Teledyne model no. 9110; NO and SO<sub>2</sub>, Fuji ZSU). The inlet and outlet concentrations of NO, NO<sub>2</sub>, and SO<sub>2</sub> were analyzed with respect to time. From the NO and SO<sub>2</sub> gas analysis, the conversion and removal efficiencies for NO<sub>x</sub> and SO<sub>x</sub> were calculated on the basis of feed the inlet and outlet concentrations.

### **Result and Discussion**

Removal of  $NO_x$  by the Ag(II) Redox Mediator. The experiments were conducted for the continuous removal of NO and  $NO_2$  at room temperature and atmospheric pressure by circulating the electrochemically generated Ag(II) redox mediator solution into scrubber I as the scrubbing solution. Air mixed with NO gas was used to simulate the actual flue gas.

After stabilization of the water oxidation of the Ag(I)/ Ag(II) redox system with nitric acid in the electrochemical cell, the Ag(II) redox mediator concentration is measured, and it is used as a scrubbing solution in the scrubber. The Ag(II) redox mediator solution was circulated at a velocity of 0.025 m/s (2 L/min) continuously in both the scrubber and the electrochemical cell, and the continuous scrubbing of the flue gas was achieved efficiently without any byproducts or any other gases at a gas velocity of 0.13 m/s (10 L/min) in the scrubber.

Figure 2 shows the concentration profile of the removal of NO on the initial concentration of NO from 100 to 400

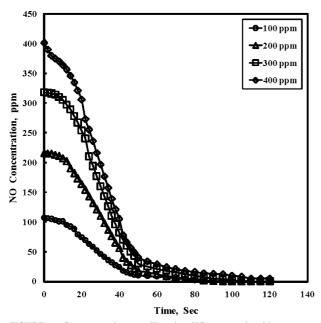


FIGURE 2. Concentration profiles for NO removal with respect to time ([NO] = 400 ppm, [Ag(I)] = 0.1 M in 6 M HNO\_3, gas velocity 0.13 m/s, liquid velocity 0.025 m/s, at 20  $^{\circ}$ C).

ppm in the simulated flue gas. Studies were carried out for different NO feed concentrations ranging from 100 to 400 ppm. The NO concentration was reduced from the initial feed concentration of 100–400 to 0 ppm, and the 100% removal efficiency was attained in a short span of 60–90 s and was sustained thereafter for as long as 120 min (2 h).

Hoffmann et al. (23) and Bringmann et al. (21) have proposed a mechanism for the removal of off-gases by redox mediator ions in the Ce(III)/Ce(IV) system. The following reaction mechanism was predicted for the removal of NO and  $NO_2$  with Ag(II) ions in the scrubber:

$$2NO + 5Ag(II) + 3H_2O \rightarrow NO_2 + HNO_3 + 5Ag(I) + 5H^+ (1)$$

$$NO_2 + Ag(II) + H_2O \rightarrow HNO_3 + Ag(I) + H^+$$
 (2)

$$HNO_2 + Ag(II) + H_2O \leftrightarrow HNO_3 + Ag(I) + 2H^+$$
 (3)

During the scrubbing, the above reaction mechanism took place, and the product of  $HNO_3$  and a small amount of  $NO_2$  were released from scrubber I. The total amount of NO charged into scrubber I was completely oxidized by the Ag(II) ions in scrubber I at fixed gas and liquid velocities. The NO was oxidized to  $HNO_3$  very rapidly by Ag(II) ions, which is shown in eqs  $1{\rm -}3$ .

Bringmann et al. (21) have reviewed the Co(III)/Co(II) system in 3 M  $\rm H_2SO_4$  as a redox mediator, and a removal efficiency of 36% was observed for  $\rm NO_x$  removal. The low efficiency has been attributed to the kinetic interaction. However, in their studies, they found that the Mn(III)/Mn(IV) system in 6 M  $\rm H_2SO_4$  has a good efficiency. The abatement of the  $\rm NO_x$  system has been studied by Aruosseau et al. (25) in an electrochemical redox system with Ce(III)/Ce(IV), and they also studied the kinetics of Ce(III)/Ce(IV) for  $\rm NO_x$  removal. Fe<sup>II</sup>(EDTA) was also examined as a complexing agent in sulfuric acid medium for redox systems, and Nzikou et al. (22) have studied  $\rm NO_x$  removal on direct electrolysis with some complex formations.

However, in the above studies using Ce(III)/Ce(IV) redox mediators, the  $NO_x$  conversion and removal efficiency are low when compared to those of our Ag(I)/Ag(II) redox mediators, and the reactions are more complicated because of the use of complex reactants or reactions in both gas- and liquid-phase scrubbing. In our studies, we found that NO is

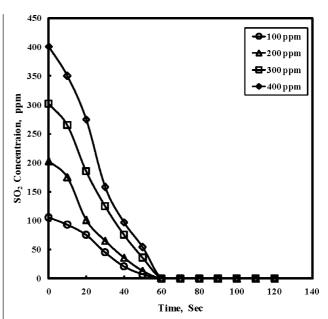


FIGURE 3. Concentration profiles for SO $_2$  removal with respect to time ([SO $_2$ ] = 400 ppm, [Ag(I)] = 0.1 M in 6 M HNO $_3$ , gas velocity 0.13 m/s, liquid velocity 0.025 m/s, at 20  $^{\circ}$ C).

oxidized to  $NO_2$  and  $HNO_3$  with Ag(II) redox mediator ions without any other byproducts.

Removal of  $SO_2$  by the Ag(II) Redox Mediator. In this study, the effects of Ag(II) redox mediators on the removal of  $SO_2$  were studied by applying a wet scrubbing method using the Ag(II) redox mediator solution as a scrubbing liquid at a velocity of 0.025 m/s with air containing  $SO_2$  as a simulated flue gas at a velocity of 0.13 m/s in room temperature conditions. The predicted reaction mechanism in the scrubber may involve the oxidation of  $SO_2$  by Ag(II) ions to form  $H_2SO_4$ . The following reaction occurred during the removal of  $SO_2$  using the Ag(I)/(II) redox mediators in nitric acid medium:

$$SO_2 + 2Ag(II) + 2H_2O \rightarrow H_2SO_4 + 2Ag(I) + 2H^+$$
 (4)

 $SO_2$  is oxidized by Ag(II) ions, and  $SO_4^{2-}$  is formed, which is converted to  $H_2SO_4$  in the scrubbing solutions.

Figure 3 shows the rate of  $SO_2$  removal with the initial concentration of  $SO_2$  with respect to time. The  $SO_2$  removal is very rapid from a 400 ppm initial concentration of  $SO_2$  to 0 ppm with 100% removal efficiency, and the removal or treatment time is within 40–60 s for a 400 ppm initial concentration.

In direct electrolysis,  $SO_2$  is absorbed in aqueous sulfuric acid solution and oxidized at the anode, and the mechanism of  $SO_2$  oxidation in aqueous sulfate solution and the selection of anodes are complex (12). Aurousseau et al. (19) have reviewed the scrubbing of  $SO_2$  with Ce(IV) redox mediators in sulfuric acid medium. During the scrubbing, dithionate and sulfuric acid were formed. The formation of dithionate was significant at a low concentration of 0.5 M sulfuric acid, whereas  $SO_2$  was oxidized at a high concentration of 5 M sulfuric acid. Hence, using the Ag(II) redox mediators for scrubbing of  $SO_2$ , the formation of sulfate and elemental sulfur can be avoided.

**Removal of the NO and SO<sub>2</sub> Mixture.** Experiments were carried out for the simultaneous removal of  $NO_x$  and  $SO_2$  from the simulated flue gas containing  $NO_x$  and  $SO_2$  by the wet scrubbing method using the Ag(I)/Ag(II) redox mediator solution in nitric acid medium as a scrubbing solution.

Figure 4 shows the effect of the Ag(II) redox mediator on the simultaneous removal of  $NO_x$  and  $SO_2$ with respect to time. It is clear that the initial NO and  $SO_2$  concentrations

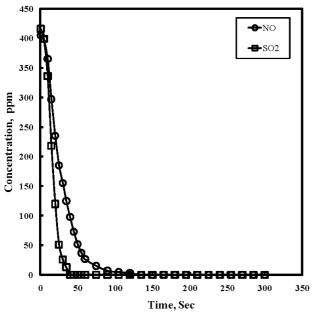


FIGURE 4. NO and  $SO_2$  concentration profiles with respect to time ([NO] and  $[SO_2]=400$  ppm, [Ag(I)]=0.1 M in 6 M HNO<sub>3</sub>, gas velocity 0.13 m/s, liquid velocity 0.025 m/s, at 20 °C).

decrease with time from 400 to 0 ppm at a gas velocity of 0.13 m/s (10 L/min). The scrubbing liquid Ag(II) redox mediator is circulated at a velocity of 0.025 m/s (2 L/min) at room temperature and atmospheric pressure. Ag(II) is regenerated in the electrochemical cell, and the solution is circulated into the scrubber for effective scrubbing of waste gases continuously with a 100% removal efficiency for NO and SO<sub>2</sub> for as long as 120 min. As shown in the figure, the maximum removal efficiency is attained in a short span of 40–90 s. This clearly indicates that the Ag(I)/Ag(II) redox mediator has a high removal efficiency for not only the individual gases of NO and SO<sub>2</sub> but also the mixture of NO and SO<sub>2</sub> for a long treatment.

The effects of the NO concentration on the removal of the NO–SO $_2$  gas mixture was investigated at constant initial SO $_2$  concentration. The results are shown in Figure 5. The removal efficiency is constant for NO, NO $_{x}$ , and SO $_2$  with a mixture feed concentration of 100-400 ppm, but in the case of NO removal, the removal efficiency decreased with an increased NO concentration at 400 ppm, and there was only a minor decrement in the NO removal efficiency at a 400 ppm NO concentration. It is clear that the removal efficiency of the mixture of NO and SO $_2$  is not affected by the NO concentration.

Effect of the Gas Velocity on the Removal of NO<sub>x</sub> and SO<sub>2</sub>. A series of experiments was performed in the scrubber at different gas velocities from 0.07 to 0.39 m/s (from 5 to 30 L/min), provided the liquid velocity was held constant at 0.026 m/s (2 L/min), the NO and SO<sub>2</sub> concentration was set at 400 ppm, the Ag(I) concentration was 0.1 M in 6 M HNO<sub>3</sub>, and the temperature was 20 °C. The gas and scrubbing liquid were passed through the scrubber with counter current flow.

Figure 6 shows the effect of the gas velocity on the removal efficiency of NO, NO $_x$ , and SO $_2$  from the simulated flue gas. The removal efficiency remained constant for NO and SO $_2$ , and it decreased with increased gas velocities for NO $_x$ . The gas flow rate related to the volume of the reactor is a very important economic viability parameter for scrubbing of gas processes

We found that the abatement of NO,  $NO_{\infty}$  and  $SO_2$  is enhanced at lower gas velocity because of the higher residence time in the scrubber. The outlet concentration of NO and  $SO_2$  is decreased from 400 to 0 ppm at 0.07 m/s and to 0 ppm at 0.39 m/s with 100% removal efficiency, but for

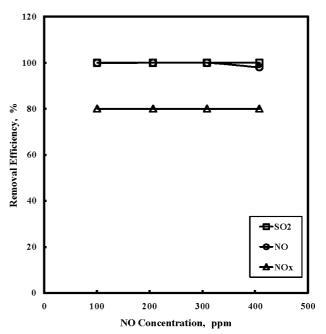


FIGURE 5. NO and  $SO_2$  removal efficiency with respect to NO concentration (100–400 ppm) ([ $SO_2$ ] = 400 ppm, [Ag(I)] = 0.1 M in 6 M HNO<sub>3</sub>, gas velocity 0.13 m/s, liquid velocity 0.025 m/s, at 20 °C).

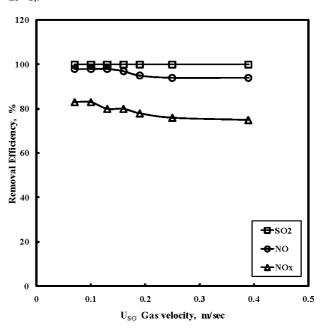


FIGURE 6. NO, NO $_{x}$ , and SO $_{2}$  removal efficiency with respect to the gas velocity ([NO] and [SO $_{2}$ ] = 400 ppm, [Ag(I)] = 0.1 M in 6 M HNO $_{3}$ , liquid velocity 0.025 m/s, at 20  $^{\circ}$ C).

 $NO_x$  it is decreased from 425 to 70 ppm at 0.07 m/s and to 88 ppm at 0.39 m/s. For  $NO_x$ , the removal efficiency is 83% and 77% at 0.07 and 0.39 m/s gas velocities, respectively. These findings led us to conclude that the  $NO_x$  removal efficiency is dependent on the gas velocities in the scrubber. That is, the conversion of  $NO_2$  is decreased with higher gas velocities with the Ag(II) redox system. For the NO and  $SO_2$  removal efficiency, the scrubber behaves implicitly for low to high gas velocities and gives a 100% removal efficiency.

Effect of the Ag(I) Concentration on Removal of  $NO_x$  and  $SO_2$ . In wet scrubbing, the scrubbing liquid plays a crucial role in improving the removal efficiency and conversion of waste gases. A number of experiments were conducted to

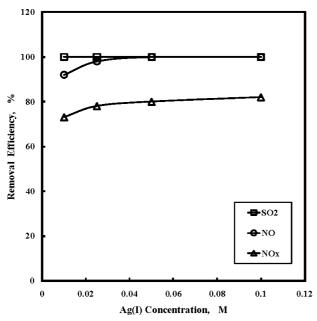


FIGURE 7. NO, NO<sub>x</sub>, and SO<sub>2</sub> removal efficiency with respect to the Ag(I) concentration ([NO] and [SO<sub>2</sub>] = 400 ppm, [Ag(I)] = 0.01–0.1 M in 6 M HNO<sub>3</sub>, gas velocity 0.13 m/s, liquid velocity 0.025 m/s, at 20  $^{\circ}$ C).

observe the effects of the Ag(I) solution concentration from 0.01 to 0.1 M for the removal of NO,  $NO_{xy}$ , and  $SO_2$ .

The variation of the outlet concentration of NO, NO<sub>2</sub>, and  $SO_2$  for different Ag(I) concentrations is shown in Figure 7 for an initial NO and  $SO_2$  concentration of 400 ppm, a gas velocity of 0.13 m/s, a liquid velocity of 0.025 m/s, and a temperature of 20 °C. Figure 7 shows the effects of the Ag(I) concentration. The removal efficiency is increased with increased Ag(I) concentration up to 0.05 M. Note that, after the concentration is increased, the efficiency remains constant for high concentrations.

The 400 ppm initial concentration of NO is reduced to 32 ppm at 0.01 M Ag(I) with 92% removal efficiency and to 0 ppm at 0.1 M Ag(I) concentration with 100% removal efficiency. The same pattern is observed for the  $NO_x$  removal. The 425 ppm concentration of  $NO_x$  is reduced to 110 ppm at 0.01 M Ag(I) with 74% removal efficiency and to 80 ppm at 0.1 M Ag(I) concentration with 81% removal efficiency. For the  $SO_2$  removal, the initial concentration of 400 ppm is reduced to 0 ppm from 0.01 to 0.1 M Ag(I) concentration with 100% removal efficiency. It seems that this concentration does not affect the  $SO_2$  removal.

Hence, the Ag(I) concentration affects the  $NO_x$  and  $SO_2$  removal efficiency. Increasing the Ag(I) concentration offers a significant advantage in improving the removal efficiency and conversion.

Effect of the HNO<sub>3</sub> Concentration on the Removal of  $NO_x$  and  $SO_2$ . The effect of the HNO<sub>3</sub> concentration on the removal of NO, NO<sub>x</sub>, and SO<sub>2</sub> was studied at 20 °C, 0.1 M Ag(I) concentration, a gas velocity of 0.13 m/s, and a liquid velocity of 0.025 m/s. As shown in Figure 8, the 400 ppm initial concentration of NO is reduced to 40 ppm with 3 M and to 0 ppm with 6 M acid concentrations. The same pattern was observed for the  $NO_x$  removal. Thus, 425 ppm  $NO_x$  is reduced to 107 ppm with 3 M and to 75 ppm with 6 M acid concentrations. For the SO<sub>2</sub> removal, the initial concentration of 400 ppm is reduced to 0 ppm from 3 to 6 M acid concentrations, and it seems that this concentration range does not affect the SO<sub>2</sub> removal. From the studies, it is clear that the NO and NO<sub>x</sub> removal efficiency is increased from 90% and 72% at 3 M acid concentration to 100% and 82%, respectively, with an increase to 6 M acid concentration.

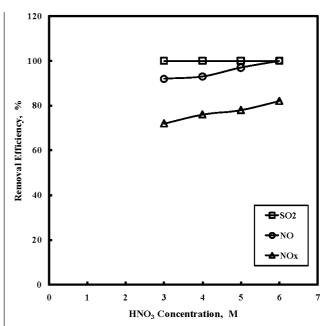


FIGURE 8. NO, NO<sub>x</sub>, and SO<sub>2</sub> removal efficiency with respect to the HNO<sub>3</sub> concentration ([NO] and [SO<sub>2</sub>] = 400 ppm, [Ag(I)] = 0.1 M, [HNO<sub>3</sub>] = 3–8 M, gas velocity 0.13 m/s, liquid velocity 0.025 m/s, at 20 °C).

Finally, these findings led us to conclude that the NO and  $\mathrm{NO}_x$  removal efficiency is dependent on the Ag(I) concentration, gas velocity, and  $\mathrm{HNO}_3$  concentration and the  $\mathrm{SO}_2$  removal efficiency is independent of the Ag(I) concentration, gas velocity, and  $\mathrm{HNO}_3$  concentration by using the Ag(I)/Ag(II) redox mediators.

Investigations were carried out for the development of a process for simultaneous removal of industrial waste gases such as NO, NO<sub>2</sub>, and SO<sub>2</sub> by using an electrochemically generated Ag(I)/Ag(II) redox mediator system in aqueous nitric acid medium. The results show that the Ag(I)/Ag(II) redox mediator system has a good oxidizing power for the removal of NO<sub>x</sub> and SO<sub>2</sub> at room temperature and atmospheric pressure.

The NO and  $SO_2$  removal efficiency was investigated as a function of process parameters including the NO and  $SO_2$  concentration, gas velocity, Ag(I) concentration, and  $HNO_3$  concentration. The merits of the Ag(I)/Ag(II) redox system can be summarized as follows.

- (1) NO is oxidized to NO<sub>2</sub> in 100% conversion.
- (2) There is no feed out at higher concentration of the NO feed (400 ppm).
- (3)  $NO_2$  is absorbed and converted to  $HNO_3$  in a high percentage.
- (4) No other byproduct is produced during the treatment process.
- (5) There is continuous removal of NO, NO<sub>2</sub>, and SO<sub>2</sub> for a long period (as long as 120 min).
- (6) There is no consumption of Ag(I) during the removal of waste gases (29, 30).
- (7) Concentration of Ag(II) is maintained by continuous regeneration (29, 30).
- (8) The Ag(I)/Ag(II) system can be reused: the process is cost-effective.
  - (9) The operation of the system is comparatively easier.

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