



A sustainable mediated electrochemical process for the abatement of NO_x from simulated flue gas by using Ag(I)/Ag(II) redox mediators

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ABSTRACT

Electrochemical removal of NO and NO₂ by using Ag(I)/Ag(II) redox mediator system in nitric acid medium by two-stage scrubbing process was investigated. Experiments were carried out for the complete removal of NO and NO₂ from the stimulated flue gas at room temperature and atmospheric pressure. The process parameters like current density, Ag(I) concentration, HNO₃ concentration, initial concentration of NO, Ag(I) concentration and temperature were studied and optimized. A removal efficiency of >99% was achieved using this sustainable redox process. Ag(II)/Ag(I) can be regenerated and reused for the scrubbing of waste gases continuously and there is no other gases emission during scrubbing.

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1. Introduction

Nitrogen oxides (NO_x), collectively referred to 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 and NO_x from industrial processes are closely monitored and regulated.

A lot of activities developed in the industrialized society generate large amounts of waste (solid, liquid and gas) discharged on a recipient medium [1–6]. Up to now, the role of electrochemistry in the treatment of effluents has been relatively small in favor of other methods used at a greater scale. Nevertheless, when toxic waste is hardly compostable, electrochemistry presents great advantages, being able to complement and even supersede commonly used methods.

The removal of pollutants such as NO, NO₂, SO₂, from industrial gas waste represents a large domain of investigations. Electrochemical processes, which do not require the continuous and large amounts of chemical reagents, can bring a helpful contribution in the proposal or development of de-pollution processes.

An increasing demand for off-gas purification, particularly smaller scale power plants, combustion units and chemical plant and industrials, encouraged the development of new concepts of electrochemical gas purification methods, techniques or processes. Many gaseous pollutants, such as chlorine, hydrogen sulphide, nitrous oxides, nitrogen dioxide and sulphur dioxide permit electrochemical conversion in an aqueous medium at room temperature and atmospheric pressure environment. Different concepts of electrochemical gas purification were cited in the literature [7–15].

In electrochemical reaction, the initial step is absorption of the pollutant species into a liquid-phase or electrolyte. Since the solubility of the gases in aqueous solutions at room temperature condition is too small, the transfer of ions from the gas phase into the liquid-phase or solution phase must be supported by a reaction. During this reaction, the electron converts the primarily dissolved species permanently to more soluble one. The above reaction is either directly via conversion at the electrode of an electrochemical cell or indirectly via chemical reaction with a redox mediator, which can be electrochemically regenerated in a continuous generation after the reaction. Homogeneous or heterogeneous catalysts have been applied as redox mediators. The advantage of heterogeneous mediators is that a separation of the reaction products from the mediator is not necessary. Both the electrochemical conversion of the pollutant and the electrochemical regeneration of the redox mediator can be achieved by an in-cell or ex-cell processes [16–21]. Recently Balaji and co-workers [22–25] demonstrated MEO processes for the destruction of organic liquids using Ag(I)/Ag(II) redox mediators in nitric acid medium.

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The flue gases contain not only SO_2 but also NO and NO_2 , and the development of electrochemical processes for the simultaneous removal of both NO_x and SO_2 is still ideal and has been the subject of recent investigations. In particular NO_x and SO_2 can be removed by chemical absorption using a redox mediator which can be generated or regenerated at an electrode surface in an aqueous medium. Kelsall et al. [26] proposed electro-generated reactants such as Ti^{3+} , V^{2+} , Cr^{2+} ion, but indirect oxidation or mediated electrochemical oxidation (MEO) is often preferred and several redox mediators can be considered for these purposes.

Juttner et al. [7] have claimed some patents for electrochemical gas scrubbing and Arousseau et al. [16] also claimed patents using the Ce(III)/Ce(IV) redox mediator system for gas scrubbing and Bringmann et al. [19] for off-gases removal using Mn(III)/Mn(II) , Co(III)/Co(II) systems.

The solid-state electrochemical cell is a possible alternative for catalytic NO_x decomposition technology and demonstrated the NO reduction over a Pt electrode deposited on a Y-doped ZrO_2 (YSZ) solid electrolyte. Bredikhin et al. [27] showed that by applying direct voltage to the YSZ-based electrochemical cell, NO gas molecules can be decomposed into nitrogen gas and oxygen ions at the cathode.

In conventional gas purification methods, that is in dry as well as wet scrubbing methods, various chemicals were employed for the treatment, destruction or removal of NO , NO_2 and NO_x in aqueous medium in various wet scrubbing systems [1–6]. These types of chemicals are consumed by the equal amount of gases treated for removal. But while using the Ag(II) as the oxidizing agent, the above problems did not arise and also Ag(II) can be generated continuously without any disposal or consumption of solutions during the treatment time. And during the treatment reaction, the earlier chemicals will produce the NO_2 in higher ratio when compared to Ag(II) redox mediator. The major advantage is that the treatment time of NO , NO_2 and NO_x is very less, i.e., in the order of 50–100 s only and while in conventional methods it will be two or three times fold of this treatment time.

Ag(II) is known for being one of the most powerful oxidizing agents in acidic medium. It is more oxidizing than the Co(III) , Mn(II) , or Ce(IV) redox mediator ions and can be used for the destruction of organic compounds or the dissolution of nuclear wastes. The potential of the Ag(II)/Ag(I) redox couple vs. the normal hydrogen electrode (NHE) lies between 1.91 V/NHE and 1.96 V/NHE in nitric acidic medium. Besides, this potential is superior to the thermodynamic potential of water (1.23 V/NHE). Some authors such as Farmer et al. [28], Lehmani et al. [29], Galla et al. [30] and Sequeira et al. [31] have studied the kinetics of the oxidation of Ag(I) into Ag(II) in nitric acid medium. They showed that the Ag(II)/Ag(I) system is fast and reversible using various electrochemical techniques.

Electrochemical removal of nitrogen oxides containing NO , NO_2 by means of a wet technique using aqueous redox mediated system of Ag(I)/Ag(II) in nitric acid medium solution containing an oxidizing agent such as Ag(II) appears to be very encouraging, as it results in the complete destruction or removal of NO_x at ambient temperature and atmospheric pressure [32].

The objectives of this research were to investigate the mediated electrochemical oxidation technique for the removal of NO , NO_2 , NO_x in aqueous medium with Ag(I)/Ag(II) redox system at room temperature and atmospheric pressure. Process parameters studies like effect of current density, Ag(I) concentration, HNO_3 concentration and temperature were also carried out for NO_x removal in order to evaluate the applicability of this technique for the process development and scale-up studies.

2. Experimental

Removal of NO and NO_2 gases was carried with Ag(I)/Ag(II) redox mediator in nitric acid medium by wet scrubbing method.

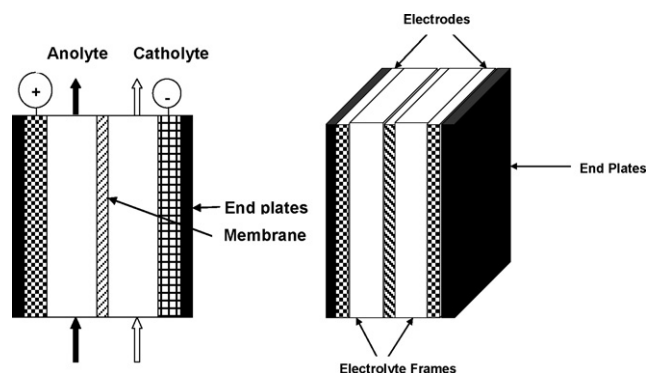


Fig. 1. Schematic diagram of electrochemical flow cell employed for the generation of Ag(II)/Ag(I) redox mediators.

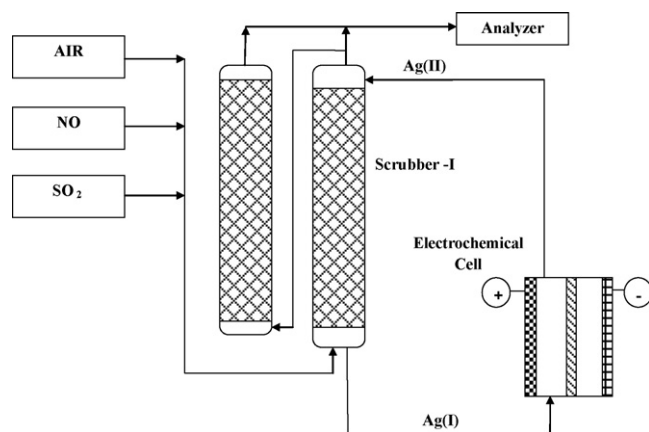


Fig. 2. Schematic flow diagram for the removal of NO_x and SO_2 by using the electrochemically generated Ag(II)/Ag(I) redox mediators.

The experimental system is divided into two parts, i.e., Ag(II) redox mediator generation process and NO_x gas treatment unit. All the processes are carried out in room temperature and atmospheric pressure conditions. Electrochemical cell and a schematic diagram of the experimental system are shown in Figs. 1 and 2, respectively.

2.1. Mediated electrochemical oxidation process for Ag(I)/Ag(II) redox mediator

The electrochemical system consisted of an anolyte, a catholyte tank, each with a capacity of 2.0 L coupled to an electrochemical cell. The electrochemical cell is plate and frame type narrow gap flow cell configurations. The cell consisted of an anode and cathode separated by a Nafion 324 membrane. The anode and cathode were Pt/Ti and DSA mesh type electrodes, respectively. The electrolyte used in the anolyte was 0.1 M AgNO_3 in 6 M nitric acid and in the catholyte 2.5 M sulphuric acid was taken. The catholyte vessel was provided with a gas scrubber to scrub any vapour produced during the electrolysis. The anolyte and catholyte solutions were circulated through the cell using magnetic ceramic FHP pumps at 2 L/min flow rate. The anolyte and catholyte flow rates always will be the same in all the experiments trails. The electrochemical cell was conducted galvanostatically by applying constant current of 10 A and the cell voltage was measured with respect to time of electrolysis.

2.2. Removal of NO_x using electrochemically generated Ag(I)/Ag(II)

The removal of NO_x system is composed of NO gas and air supply system, scrubbing liquid supply system, glass scrubbing unit, data acquisition system and sampling cum analysis system. The scrubber

is (ID 5 cm; height 120 cm) a glass vessel filled with Rasching rings (10 mm) as a packing material having internal volume of 2.4 L. The NO-air-gas mixture was obtained by controlled mixing of air and NO gas by using mass flow controllers (MFC). NO-air-gas mixture was introduced at the bottom of the scrubber at constant initial concentration and the scrubbing liquid Ag(II) solution introduced at the top of the scrubber in counter current flow pattern.

Temperature of the electrochemical cell vessel was controlled within 20 ± 0.1 °C. The pH and concentration of scrubbing solution were controlled by using an auto-pH control system and by continuous generation of Ag(II) redox mediators in the electrochemical cell. The inlet and outlet gas concentrations were analyzed. The known concentration of gas was passed into the scrubber in a particular gas and liquid flow rates at room temperature and atmospheric pressure. The first stage scrubber would be required to oxidize the NO to NO₂ and to remove the NO₂. The second stage scrubber is also used for NO₂ removal. The oxidation of NO takes place in the first stage with scrubbing liquids is Ag(II) in nitric acid solutions as an oxidizing agent.

The NO, NO₂, NO_x and SO₂ analyses were carried out by the Teledyne Gas analyzer instrument Model No. 9560. The feed concentration of NO, NO₂ and SO₂ is analyzed for initial concentration and during the reaction the NO and NO₂ were analyzed with respect to time of reaction. Based on the feed and final concentration of NO, SO₂ and NO₂, the NO_x and SO₂ removal efficiency were calculated.

3. Result and discussions

3.1. Removal of NO_x and SO₂ by Ag(I)/Ag(II) redox mediators

Fig. 3 shows the effect of concentration of the feed NO gas at the scrubber with experimental of time for four initial concentrations of NO (100–400 ppm). It is clear that the concentration of feed NO drops within 40–60 s of time. The following reaction occurs during the removal or treatment of NO with air in this first stage of the scrubber.

3.1.1. Reaction mechanism at scrubber for NO reaction

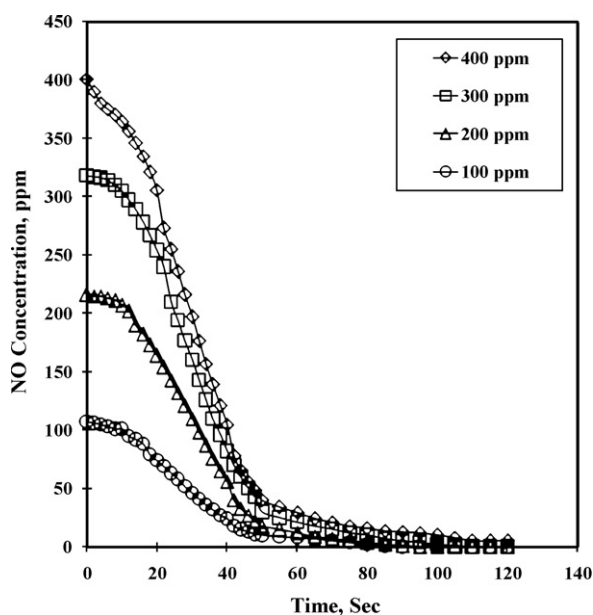
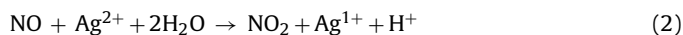


Fig. 3. NO feed gas concentration profile as a function of time for different NO feed concentrations [feed NO = 100–400 ppm, air flow rate = 10 L/min, Ag(I) concentration = 0.1 M, at 20 °C].



During the experiment it is found out, the above reaction mechanism has happened and the product of HNO₃ and some amounts of NO₂ are released from the scrubber-I. The amount of NO charged into the scrubber is almost consumed by the Ag(II) in the scrubber-I. In the scrubber-I, the NO is oxidized to NO₂ by Ag(II) ions in HNO₃ acid medium shown as reaction steps in Eqs. (1)–(5). Fig. 3 shows the removal efficiency of NO calculated based on the NO measured at the inlet and outlet of the scrubber. It is clear that the efficiency for NO removal attained 100% in a short span of 40–60 s and thereafter it sustained for a large time as long as 120 min.

After the treatment of NO, NO₂ was measured at the outlet of the scrubber-I. It is found to be independent of initial NO concentration, and NO₂ is always 10–15% of the initial concentration of NO gas feed. This produced NO₂ is treated in the scrubber-II with 3 M HNO₃ where NO₂ is removed by absorption into HNO₃. The removal efficiency for NO and NO_x is 100% and 85% for the scrubber-I and it is 100% and 92% in scrubber-II respectively.

From the literature, it is found that some studies were carried out for the abatement of NO_x using some redox mediators like Ce(III)/Ce(IV), Co(III)/Co(II) and Fe(II)/Fe(III). Nzikou et al. [18] investigated Ce(III)/Ce(IV) couple for NO_x abatement process by voltammetric studies in a platinum rotating disc electrode for the conditions corresponding to the gas scrubbing processes in 5 M sulphuric acid medium. In these studies, it is observed that the charge transfer coefficients were weakly affected by increasing the concentration of sulphuric acid. Conversely, the diffusion coefficients and the rate constants were decreasing functions of the concentration of sulphuric acid.

Aurousseau et al. [16] studied the oxidation of nitrogen oxides in cerium(IV) solution by the liquid-phase oxidation of nitrous acid. In their studies, both sulphuric and nitric acid concentrations have strong influence on the chemical state of nitrous acid. The absorption of NO_x containing gases was treated into the cerium(IV) solutions and concerns of the mass transfer rates and solubility of the various gases in this systems. Moreover, the scrubbing efficiency of NO_x in sulphuric acid medium is reduced by the acid concentration. Kleifges et al. [21] investigated an electrochemical process for the absorption of NO_x from industrial waste gases using Fe(II) EDTA as the complexing agent by an indirect outer cell process using dithionite as the redox mediator. They have also studied the system in the absence and presence of dithionite by using a packed bubble column. In all these electrochemical processes they have either employed as high concentration electrolyte or added some complexing agents in the electrolyte solutions. The removal efficiency is 90% only in all these developed processes. In comparison with above processes, this Ag(I)/Ag(II) redox mediated electrochemical process has high removal efficiency having good oxidizing power of Ag(II) ions. This Ag(II) ions can be regenerated continuously in an electrochemical cell.

It may be noted that Bringmann et al. [19] the Co(III)/Co(II) system in 3 M H₂SO₄ as a redox mediator, the removal efficiency of 36% was observed for NO removal and the low efficiency has been attributed by the kinetic interaction. As against Co(III)/Co(II) system, the Mn(III)/Mn(IV) system in 6 M H₂SO₄ has been found to give an efficiency of >90%. However, no correlation between initial NO concentration and conversion efficiency was given due to the accuracy of actual gas flow rates. Bredikhin et al. [27] showed that by applying direct voltage to the YSZ-based electrochemical cell,

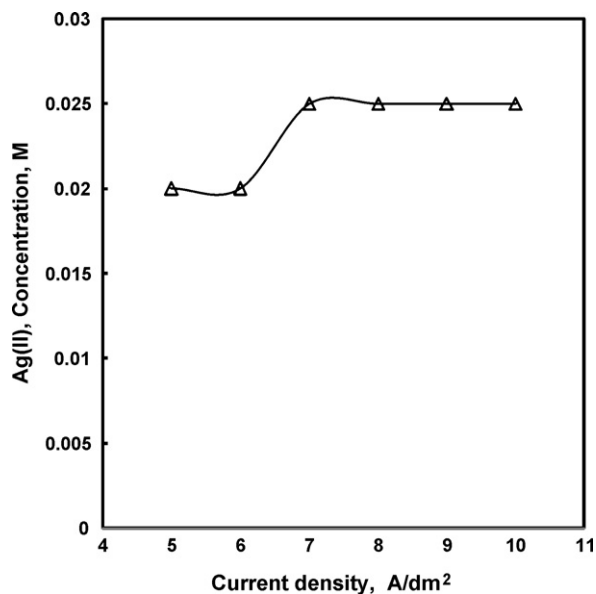


Fig. 4. Ag(II) concentration profile as a function of current density [Ag(I)=0.1 M, HNO₃ = 6M, current density = 5–10 A/dm² at 20 °C].

NO gas molecules can be decomposed into nitrogen gas and oxygen ions at the cathode. These types of processes are viable for the industrial waste gases treatment or purifications.

Hence, we have demonstrated a process for the removal efficiency of NO and NO_x in 100% and 92%. The present studies by Ag(I)/Ag(II) redox mediator system in 6 M HNO₃ may be associated with high oxidizing power of the Ag(II) ions in 6 M HNO₃ acid medium.

3.2. Effect of current density

Studies were carried out to find out the effect of current density on the generation of Ag(II) redox ions in 6 M nitric acid medium. 0.1 M silver nitrate in 6 M nitric acid was taken as an electrolyte in divided narrow gap flow cell at 20 °C experimental conditions. Current densities ranging 1–10 A/dm² were chosen in this study and the results are presented in Fig. 4. From the studies it was concluded that the maximum oxidation efficiency of 25% was achieved for Ag(II)/Ag(I) redox system with the above experimental conditions. From the figure, it is observed that the Ag(II) generation concentration is increased with increased current density and also found that after 7 A/dm² current density the concentration is not affected constant up to 10 A/dm². Hence, 10 A/dm² was the optimum current density for the electrochemical generation of Ag(II) redox mediators in nitric acid medium.

3.3. Effect on Ag(I) concentration

Experiments were conducted for the generation of Ag(II) ions by MEO of Ag(I) at different concentrations to explore the economics process. In electrochemical process electrolyte cost is the vital role for calculating the production cost. Hence, in this section, the effect of Ag(I) has been studied. Fig. 5 shows the removal efficiency of NO and NO_x based on the Ag(II) concentration in the scrubber-I. The removal efficiencies were increased with the increase of Ag(I) concentration from 0.01 to 0.05 M. At 0.05 and 0.1 M Ag (I) concentration, the removal efficiency is almost the same. Hence, from this study it is revealed that 0.05 M concentration is an optimum concentration for the removal of NO and NO_x in 100% and 85%, respectively.

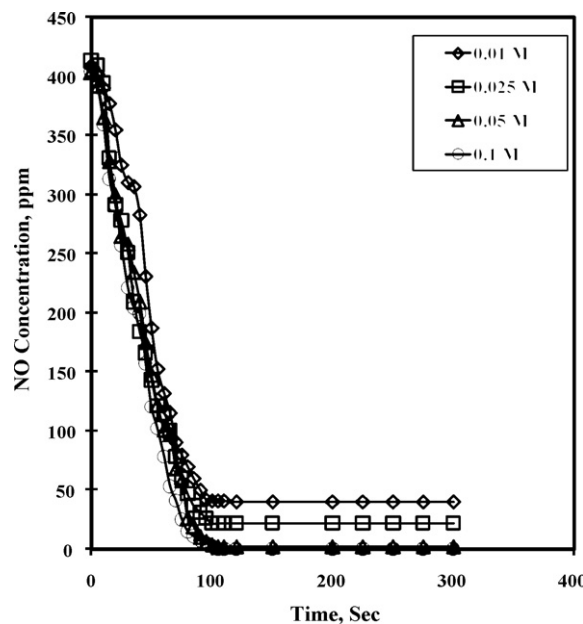


Fig. 5. NO feed concentration with respect to time as a function of Ag(I) concentration [feed NO = 400 ppm, air flow rate = 10 L/min, at 20 °C].

3.4. Effect of HNO₃ concentration

In MEO process, the acid concentration is important parameter for the generation of redox mediator. The acid concentration may enhance the yield of generation of mediators. Hence, studies were carried out for the Ag(I)/Ag(II) redox mediator system with various HNO₃ concentrations. Fig. 6 shows the concentration effect on the NO and NO_x removal efficiency at 400 ppm of NO feed gas in the scrubber-I. Further, the removal efficiencies of NO and NO_x were increased with increase of acid concentration. It is clear that the concentration of HNO₃ plays a role with Ag(I) ions during the MEO process.

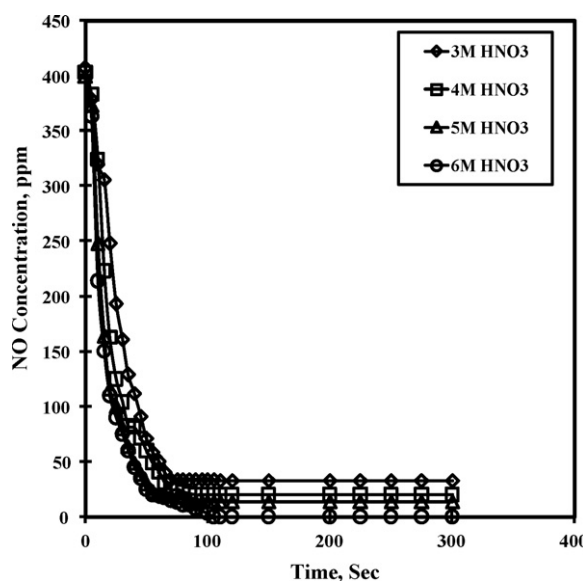


Fig. 6. NO feed concentration with respect to time as a function of HNO₃ concentration [feed NO = 400 ppm, air flow rate = 10 L/min, Ag(I) concentration = 0.1 M, at 20 °C].

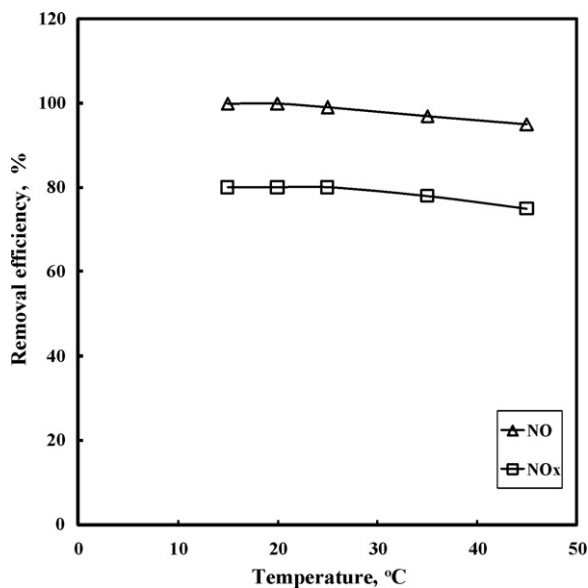


Fig. 7. NO_x removal efficiency profile as a function of temperature [feed NO = 400 ppm, air flow rate = 10 L/min, Ag(I) concentration = 0.1 M].

3.5. Effect of temperature

Studies were carried out to examine the effect of temperature on scrubbing liquids [Ag(II) solution]. The liquid temperature is increased from 15 to 45 °C and the efficiencies for the removal of NO and NO_x are examined. As seen from Fig. 7, it is clear that the increase of the liquid has given marginal decrease in removal efficiency when compared to the room temperature experimental conditions. And also found that there is a small impact on the removal efficiency when the temperature increases.

3.6. Scrubbing of NO_x and SO₂ with and without regeneration of Ag(I)/Ag(II) redox mediators

Studies were carried out to compare the scrubbing the NO_x flue gas with and without regeneration of Ag(II)/Ag(I) redox mediators. First, electrolysis was carried out for the generation of Ag(II) mediator ion into known concentration and then the known concentration of Ag(II) ion was used for the scrubbing of NO_x gases in the wet scrubber. The experiments were carried out for with and without regeneration of Ag(II) ion in the electrochemical cell.

The results are shown in Fig. 8. From the figure it is revealed that, without regeneration of Ag(II)/Ag(I) redox mediators, the scrubbing of NO_x gas with 100% removal efficiencies was achieved only up to 5 min duration only and after the removal efficiency is decreased due to the decreased Ag(II) mediator ions concentration. Hence, from the studies it is concluded that without regeneration of redox mediators, 400 ppm of NO_x flue gas was treated for 5 min with 1 L solution of Ag(II)/Ag(I) redox mediators with 10 L/min of gas flow rates and 2 L/min of scrubbing liquid flow rates at room temperature conditions. And with regeneration of Ag(II)/Ag(I) redox mediators, 100% removal efficiency was for the NO_x removal as long as for 120 min with the above experimental conditions.

3.7. Effect of cell voltage during scrubbing

Fig. 9 shows the effect of cell voltage during the scrubbing of flue gas by using the electrochemically generated Ag(II)/Ag(I) redox mediator. The main aim of this study is to find the effect of cell voltage during the regeneration of Ag(II)/Ag(I) ions for long time scrubbing time. During the generation of Ag(II) ions, the cell volt-

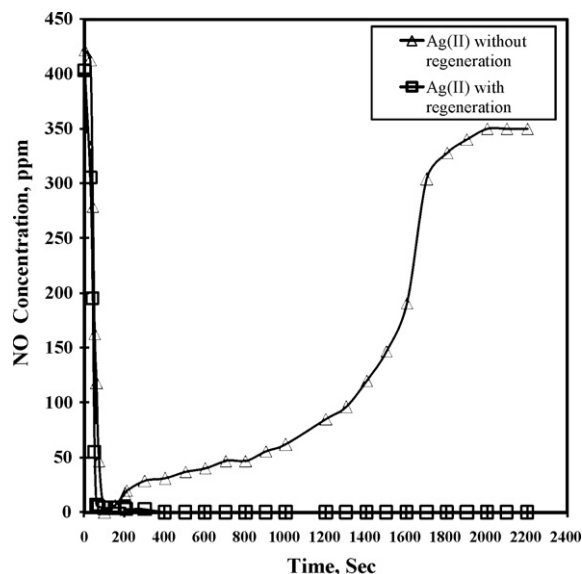


Fig. 8. NO feed concentration profile with respect to time for with and without regeneration of Ag(II) mediator ions [feed NO = 400 ppm, air flow rate = 10 L/min, Ag(I) concentration = 0.1 M, at 20 °C].

age was 2.8 V and it is observed with respect to every 10 min up to 60 min duration of electrolysis. From the figure it can be found that the cell voltage increased slowly that is with minor increment with increasing time. It is observed clearly that the cell voltage is not increased with time during the scrubbing.

3.8. Continuous regeneration of Ag(I)/Ag(II) redox mediators

Studies were carried out for the continuous regeneration of Ag(II) redox ion mediators for 120 min duration with scrubbing of NO_x flue gas. It is performed during the scrubbing of NO_x gas. Fig. 10 shows the trend of the Ag(II) concentration maintained during the scrubbing of flue gas. The removal efficiency remains constant 100% for the above duration and it was observed that the electrochemical regeneration of Ag(II) ions favored on the scrubbing of NO_x for continuous run.

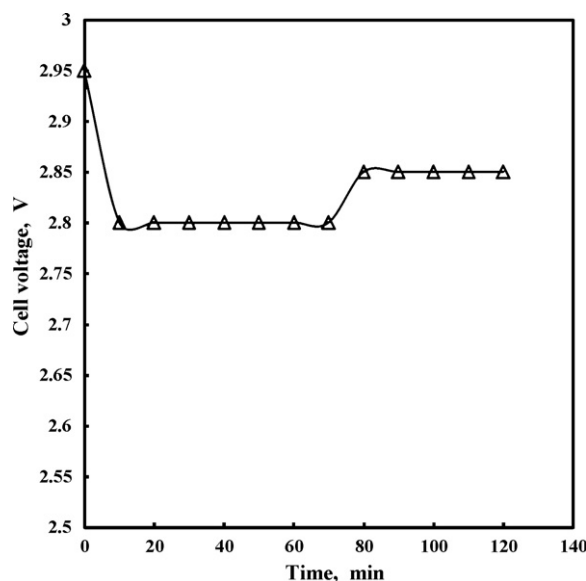


Fig. 9. Cell voltage profile as a function of time for the generation of Ag(II) redox mediator ions [Ag(I) = 0.1 M, HNO₃ = 6 M, current density = 10 A/dm² at 20 °C].

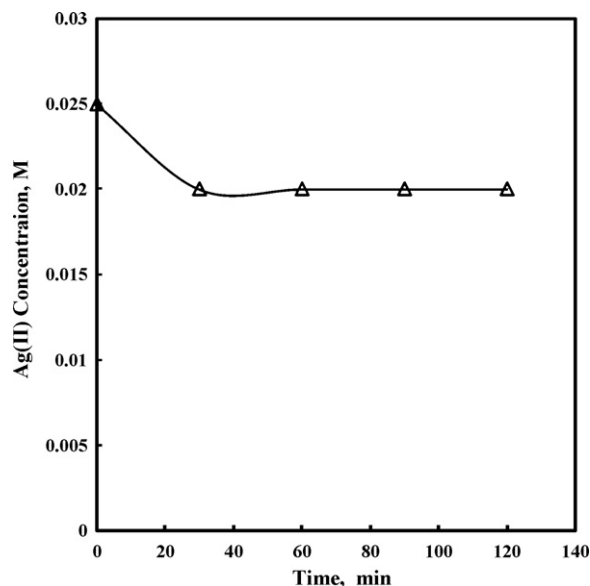


Fig. 10. Ag(II) concentration profile as a function of time on the removal of NO_x [$\text{Ag(I)} = 0.1 \text{ M}$, $\text{HNO}_3 = 6 \text{ M}$, current density = 10 A/dm^2 at 20°C].

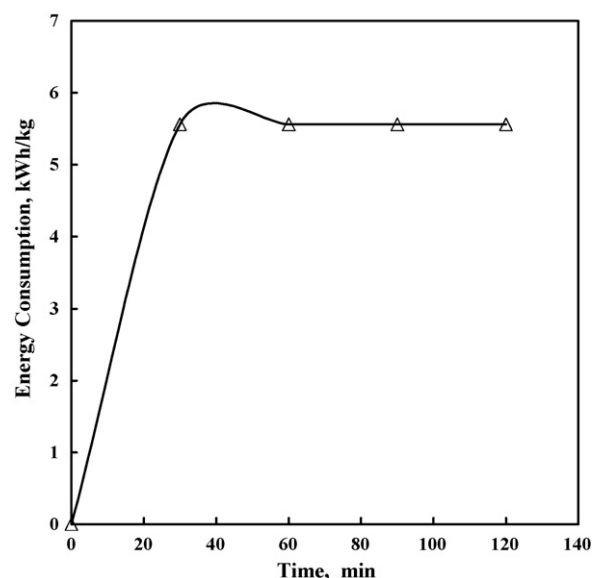


Fig. 11. Energy consumption profile as a function of time for the generation of Ag(II) redox mediator ions [$\text{Ag(I)} = 0.1 \text{ M}$, $\text{HNO}_3 = 6 \text{ M}$, current density = 10 A/dm^2 at 20°C].

3.9. Energy consumption for the generation of Ag(I)/Ag(II) redox mediators

Fig. 11 shows the results of the energy consumption for the electrochemical generation of Ag(II)/Ag(I) redox mediator in nitric acid medium at 20°C experimental conditions. During the electrolysis the cell voltage was 2.8 V at the temperature of 20°C . And also found the constant cell voltage trend was observed for the long

time regeneration of Ag(II) and scrubbing processing as well. From the studies it was revealed that the energy consumption is constant on the treatment or removal of waste gases of NO and NO_2 per hour of scrubbing. This is also one of the advantages of this process.

4. Conclusions

The removal efficiency data for NO and NO_2 were obtained by treating the NO_x waste gases with Ag(II) ions by silver mediated electrochemical oxidation technique. NO was completely removed (100%) with relatively high destruction rates and NO_x was also removed with 92% removal efficiency. The removal rate of NO_x was slightly lower than NO removal efficiency. The redox mediator Ag(II)/Ag(I) can be regenerated and reused for the wet scrubbing. The effects of gas feed concentration, current density, temperature, Ag(I) concentration, HNO_3 concentration were also studied and optimized.

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