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Removal of nitric oxide and sulfur dioxide from flue gases using a Fe^{II}-ethylenediamineteraacetate solution

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Abstract−The combined absorption of NO and SO_2 into the Fe(II)-ethylenediamineteraacetate(EDTA) solution has been realized. Activated carbon is used to catalyze the reduction of Fe^{III}-EDTA to Fe^{II}-EDTA to maintain the ability to remove NO with the Fe-EDTA solution. The reductant is the sulfite/bisulfite ions produced by SO_2 dissolved into the aqueous solution. Experiments have been performed to determine the effects of activated carbon of coconut shell, pH value, temperature of absorption and regeneration, O_2 partial pressure, sulfite/bisulfite and chloride concentration on the combined elimination of NO and SO_2 with Fe^{II}-EDTA solution coupled with the Fe^{II}-EDTA regeneration catalyzed by activated carbon. The experimental results indicate that NO removal efficiency increases with activated carbon mass. There is an optimum pH of 7.5 for this process. The NO removal efficiency increases with the liquid flow rate but it is not necessary to increase the liquid flow rate beyond 25 ml min^{-1}. The NO removal efficiency decreases with the absorption temperature as the temperature is over 35 °C. The Fe^{2+} regeneration rate may be speeded up with temperature. The NO removal efficiency decreases with O_2 partial pressure in the gas streams. The NO removal efficiency is enhanced with the sulfite/bisulfite concentration. Chloride does not affect the NO removal. $Ca(OH)_2$ and MgO slurries have little influence on NO removal. High NO and SO_2 removal efficiencies can be maintained at a high level for a long period of time with this heterogeneous catalytic process.

Key words: Fe^{II}-EDTA, Nitric Oxide, Absorption, Activated Carbon, Sulfur Dioxide

INTRODUCTION

The roles of NO_x and SO_2 pollutants in acid-rain formation and the destruction of forest ecosystems have been established. The removal of these contaminants to comply with environmental emission standard is imperative. The development of efficient processes for simultaneous NO_x and SO_2 control in power-plant flue gas is particularly important because fossil-fuel-fired steam boilers represent a major source of sulfur and nitrogen oxide emissions. Wet processes have certain economic advantages in combined NO_x and SO_2 elimination. Nitric oxide is 90-95% of the NO_x present in typical flue gas streams [1]. The existing wet flue gas desulfurization (FGD) scrubbers have obtained high SO_2 removal efficiency, but they are not excellent for NO because of its low solubility in water. Meanwhile, among the existing treatment processes for removing NO_x from the flue gases, selective catalytic reduction (SCR) using NH_3 at 300-500 °C is supposed to be the best available NO_x control technology [2-5]. However, application of the SCR is limited because of its high capital and operating costs. There is still an urgent need for a more economical method for controlling NO_x emission.

Several methods have been developed to enhance NO absorption, including the addition of various iron(II) chelates to bind and activate NO [6-12]. Although Fe^{II}-EDTA can obtain a high NO removal efficiency, it is easily oxidized to Fe^{III}-EDTA that is not capable of binding NO, and NO removal efficiency decreases immediately [13-15]. Therefore, many methods have been reported to regenerate Fe^{II}-EDTA to sustain the NO removal efficiency [16-20]. Some reducing agents such as hydrazine, $Na_2S_2O_4$, Na_2SO_3 are used to realize the regeneration of Fe^{II}-EDTA. Because of low rate constants and high consumption, none of these methods have been put into commercial application.

Activated carbon has been applied in industry successfully as a catalyst due to its large surface area, porous structure, characteristic flexibility and low cost. For example, Singoredjo et al. [21] explored the selective catalytic reduction of NO with NH_3 under the catalysis of activated carbons. Alvárez et al. [22] presented the catalytic effect of activated carbon on regeneration processes for wastewater treatment. Muñiz et al. [23] investigated the catalytic performance of activated carbon in selective catalytic reduction of NO.

The authors put forward a novel heterogeneous catalytic system to reduce NO and SO_2 simultaneously with the Fe-EDTA solution. The activated carbon is used as a catalyst to speed up the regeneration of Fe^{II}-EDTA with sulfite/bisulfite as a reductant. The mechanism of this process can be illustrated as follows.

It is well known that NO is insoluble in water. Henry's constant for NO in water is very small at about 1.25×10^{-3} mol l^{-1} atm at 50 °C. However, the coordination reaction between nitric oxide and Fe^{II}-EDTA in the liquid phase will enhance the nitric oxide solubility in the aqueous solution.

$$NO(g) \rightarrow NO(aq) \tag{1}$$

$$Fe^{II}-EDTA^{2-}+NO(aq) \rightarrow Fe^{II}\text{-}EDTA(NO)^{2-} \tag{2}$$

Meanwhile, the SO_2 existing in the gas stream also dissolves into the aqueous solution:

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$$SO_2+H_2O\rightarrow SO_3^{2-}+2H^+ \quad (3)$$

$$SO_2+H_2O+SO_3^{2-}\rightarrow 2HSO_3^- \quad (4)$$

However, the oxygen coexisting in the flue gases oxidizes Fe^{II}-EDTA to Fe^{III}-EDTA (Eq. (5)) during the gas scrubbing and Fe^{III}-EDTA lacks the ability to combine NO. As a result, NO removal efficiency will decrease quickly as the operation proceeds.

$$4Fe^{II}-EDTA^{2-}+O_2+4H^+\rightarrow 4Fe^{III}-EDTA^-+2H_2O \quad (5)$$

To maintain the NO removal efficiency, Fe^{III}-EDTA must be reduced to Fe^{II}-EDTA once again. Electrochemical half-cell reduction potential of $E^0_{Fe(III)-EDTA/Fe(II)-EDTA}$ is 0.141 V and that of $E_{SO_4^{2-}/SO_3^{2-}}$ is 0.20 V under acidic conditions. Therefore, the reduction of Fe^{III}-EDTA by sulfite/bisulfite cannot proceed successfully in the acidic solution. However, most of the FGD processes are operated under pH lower than 7.0. To accelerate the reduction of Fe^{III}-EDTA, activated carbon can be used as a catalyst in the regeneration of Fe^{II}-EDTA. The sulfite/bisulfite ions produced by SO_2 absorption into the aqueous solution act as reductants.

The activated carbon may accelerate Fe^{III}-EDTA ions' disintegration into Fe(III) ions and EDTA ions (Eq. (6)):

$$Fe^{III}-EDTA\xrightarrow{AC}Fe^{III}+EDTA \quad (6)$$

Electrochemical half-cell reduction potential of $E_{Fe^{3+}/Fe^{2+}}$ (0.771v) reveals that Fe^{III} ions are strong oxidants. Sulfite can be oxidized by Fe^{III} easily under acidic conditions. Therefore, the following reaction may take place:

$$2Fe^{III}+SO_3^{2-}+H_2O\xrightarrow{AC}SO_4^{2-}+2Fe^{II}+2H^+ \quad (7)$$

Fe^{II}-EDTA is produced once again by Fe(II) binding with EDTA. Thus the NO removal efficiency can be sustained for a long time.

$$Fe^{II}+EDTA\rightarrow Fe^{II}-EDTA \quad (8)$$

According to the discussion above, Fe^{II}-EDTA can be regenerated quickly by sulfite/bisulfite under the catalysis of activated carbon to maintain the NO removal efficiency. This technology not only realizes the absorption and reduction of nitric oxide but also realizes the absorption and oxidation of sulfur dioxide in the same absorber. Combined removal of NO and SO_2 from the flue gases may be easily achieved by retrofitting the existing wet scrubbers for desulfurization. This method can keep high NO and SO_2 removal efficiencies for a long time with a low operation cost. A study on this technology is reported in this paper.

EXPERIMENTAL

1. Reagents and Preparation

$FeSO_4\cdot 7H_2O$ (>99.0%), Na_2EDTA (>99.5%) and Na_2SO_3 (>97.0%) were obtained from China National Medicines Co., Ltd. NO (5,000 ppm in N_2), SO_2 (7,000 ppm in N_2) and N_2 (>99.99%) from Shanghai Standard Gas Co. Ltd. Deionized water was applied to prepare the solutions. Activated carbon was obtained from Shanghai Activated Carbon Co., Ltd.

2. Experimental Set-up

Experiments for the simultaneous removal of NO and SO_2 were performed in a packed column (18 mm i.d., 1,000 mm long) absorber.

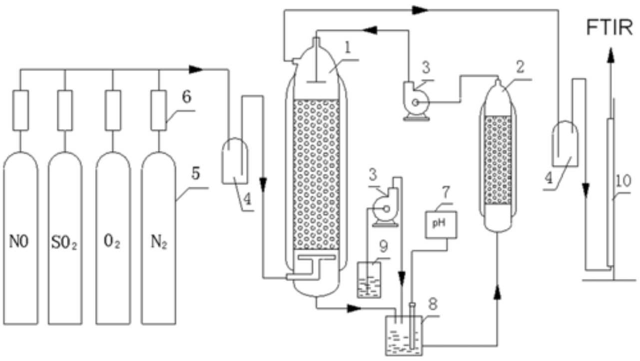

Fig. 1. Schematic of experiments performed in a packed column.

1. Packed column
2. Regeneration reactor
3. Pump
4. Buffer tank
5. Cylinder
6. Mass flow meter
7. pH online control
8. Tanker
9. NaOH solution
10. Soap-film flow meter

The Fe^{II}-EDTA was regenerated in a fixed-bed (20 mm i.d.) reactor packed with activated carbon of coconut shell. The schematic diagram of the experimental apparatus is shown in Fig. 1. The temperature of the absorber and regeneration reactor was controlled at 50 °C using jackets through which water from a thermostatic bath was circulated. The pH value was controlled using CaO (5%weight) slurry by a THORNTON M300 pH/ORP transmitter to keep the pH constant. Two percent of NO in nitrogen was supplied from a cylinder, and was diluted with N_2 to the desired concentration before being fed into the absorber. SO_2 was supplied in a similar manner. Fe^{II}-EDTA solution together with measured amount of Na_2SO_3 was added into the 500 ml glass circulation tank. The initial pH value of Fe^{II}-EDTA solutions was adjusted to the desired value with NaOH (1.0 mol l^{-1}) solution and detected with a pH-electrode. The absorber was operated with a continuous influent gas feeding at 0.3 l min^{-1} from the bottom and a continuous scrubbing solution feeding, at a superficial flow rate of 5 m^3 m^{-2} h^{-1} (25 ml min^{-1}) at the top. The initial SO_3^{2-} concentration was adjusted to 0.03 mol l^{-1} by adding appropriate amount of Na_2SO_3 into the Fe-EDTA solution. The absorbent effusing from the packed column was fed into the circulation tank. When the regeneration of Fe^{II}-EDTA started, the absorbent in the circulation tank flowed into the regeneration reactor upwardly and directly into the packed column to scrub NO and SO_2. The experimental runs were carried out under atmospheric pressure.

3. Analysis Methods

Quantitative analysis of gas composition was made by an online Fourier transform infrared spectrometer (FTIR) (Nicolet E.S.P. 460 FT-IR) equipped with a gas cell and the quantitative software package, Quant Pad. The influent and effluent gas samples were directly introduced into the gas cell of the FTIR, with pipes insulated through the regulated electric coils to obtain the transient N_2O, NO, SO_2, and H_2O concentrations of the gaseous samples. This setup was conveniently operated to monitor the overall removal of NO and SO_2.

RESULTS AND DISCUSSIONS

1. Effect of the Amount of Activated Carbon

Experiments were performed to test the effect of the amount of

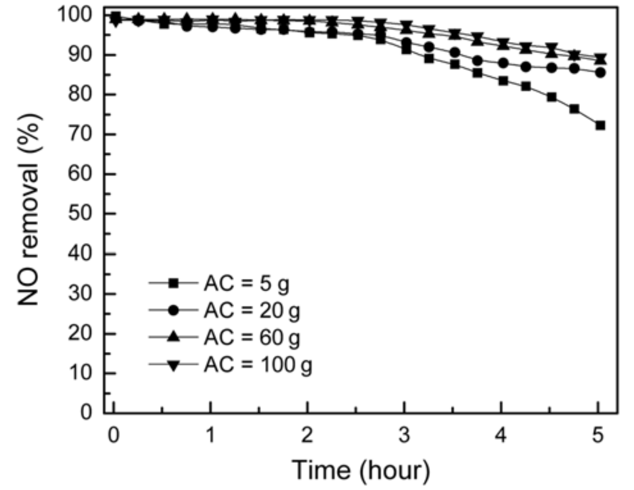

Fig. 2. Effect of the amount of activated carbon on NO removal (Temp=50 °C, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2= 1,500 ppm, O_2=5%, pH=6.5).

activated carbon in the regeneration reactor on NO removal at 50 °C. The experimental results are shown in Fig. 2. It illustrates that NO removal efficiency increases with the amount of activated carbon. For example, after 5 h operation, NO removal efficiency is maintained at 72.2%, 85.5%, 88.5% and 89.4% with the amount of activated carbon in the regeneration reactor of 5 g, 20 g, 60 g and 100 g, respectively. As discussed previously, activated carbon is the catalyst for the regeneration of Fe^{II}-EDTA. More activated carbon can provide more surface area and active sites to catalyze the Fe^{II}-EDTA regeneration. Therefore, more activated carbon added in regeneration reactor is beneficial to NO removal. However, NO absorption efficiency increases little when the amount of activated carbon increases over 60 g. The reason may be that more activated carbon may adsorb more Fe^{2+} ions, which is disadvantageous for NO elimination. The experiments also demonstrate that no SO_2 is detected in the outlet gas streams. In other words, almost all SO_2 is scrubbed with the Fe^{II}-EDTA solution.

2. Effect of Liquid Flow Rate

Experiments have been performed to investigate the effect of liquid flow rate on NO removal at 50 °C. The experimental results depicted in Fig. 3 show that the NO removal efficiency increases with the increase of the liquid flow rate. For example, after 5 h operation, the NO removal efficiency decreases from 99% at the start of the operation to 62.6% when the liquid flow rate is 17 ml min^{-1}. But the NO removal efficiency is still sustained at 85.5% when the liquid flow rate is 25 ml min^{-1}. On the other hand, the NO removal efficiency increases little when the liquid flow rate increases above 25 ml min^{-1}. The explanation may be as follows. When the liquid flow rate is below 25 ml min^{-1}, the reaction is liquid film controlling. The liquid mass transfer coefficient increases, and the mass transfer resistance in the liquid becomes small with the liquid flow rate. Therefore, the NO removal efficiency increases with the liquid flow rate. However, when the liquid flow rate increases above 25 ml min^{-1}, the mass transfer resistance in the liquid gets very small and the mass transfer resistance in the gas phase may become the main mass transfer resistance. Thus, increasing the liquid flow rate further over 25 ml min^{-1}, the NO absorption rate changes little.

3. Effect of pH

Knowledge of the optimum pH is very important since pH affects not only degree of ionization and speciation of adsorbate during reaction but also the surface charge of the activated carbon. A series of experiments were conducted at 50 °C to examine the effect of pH on NO removal. Fig. 4 demonstrates the effect of pH on NO removal without the catalytic regeneration of Fe^{II}-EDTA. The optimum pH value for NO removal with the Fe^{II}-EDTA solution is 7.5. The NO removal efficiency decreases as the pH is lower or higher. The decrease of NO removal efficiency with the descent of pH value results from the fact that the Fe^{II}-EDTA concentration decreases as the pH lowers than 6. Fe^{II}-EDTA (normal chelate) is almost quantitatively formed from the equimolar amounts of $FeSO_4$ and EDTA at a pH greater than 6. However, the concentrations of Fe^{II}-EDTA and Fe^{II}-HEDTA (protonated chelate) formed decrease as the pH value drops below 6. The lower pH value, the less Fe^{II}-EDTA produced. On the other hand, the drop of NO removal efficiency with a

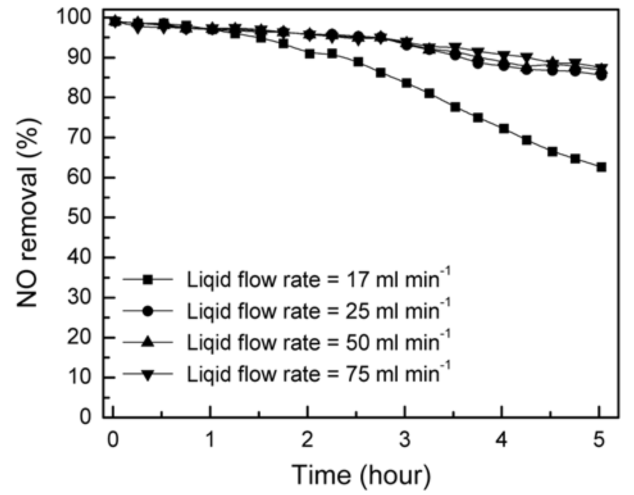

Fig. 3. Effect of liquid flow rate on NO removal (Temp=50 °C, Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,500 ppm, O_2=5%, pH=6.5).

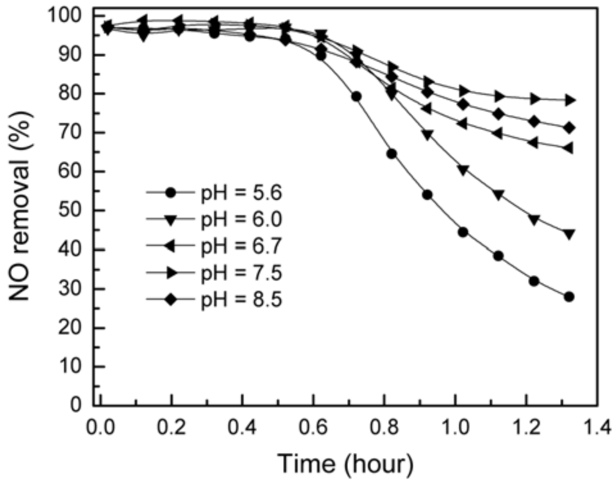

Fig. 4. Effect of pH on NO removal without regeneration (Temp= 50 °C, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,500 ppm, O_2=5%).

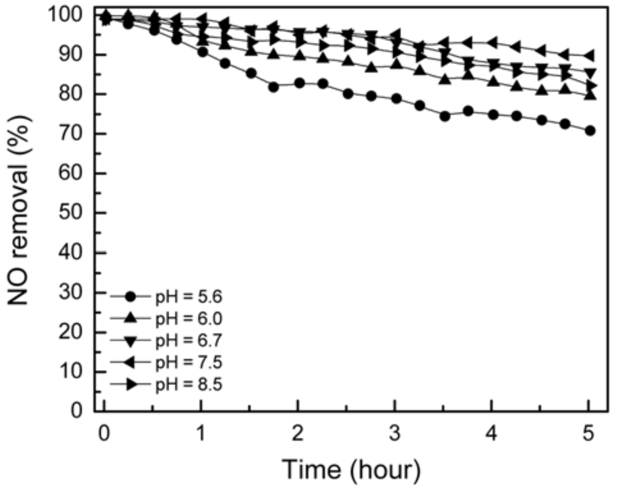

Fig. 5. Effect of pH on NO removal coupled with the catalytic Fe^{II}-EDTA regeneration (Temp=50 °C, Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,500 ppm, O_2= 5%).

Fe^{II}-EDTA solution of pH greater than 7.5 is attributed to the formation of $Fe(OH)_2$ deposit. Under basic condition, Fe^{2+} will combine with OH^- to form precipitate of $Fe(OH)_2$. $Fe(OH)_2$ is oxidized to $Fe(OH)_3$ instantaneously. Therefore, Fe^{II}-EDTA concentration in the basic solution will be reduced and the ability to absorbing NO will be weakened.

Experiments have also been done to investigate the influence of pH on NO removal when the catalytic regeneration of Fe^{II}-EDTA starts. The experimental results are depicted in Fig. 5. A conclusion similar to that drawn from Fig. 4 can be obtained from Fig. 5 that NO removal efficiency increases as the pH value increase from 5.0 to 7.5. After 3.5 hour continuous treatment, the NO removal declines to 74.4% with a Fe^{II}-EDTA solution of pH 5.6, while the NO removal efficiencies are still sustained at 91% and 93% with a pH of 6.7 and 7.5, respectively. It can also be seen from Fig. 5 that the NO removal efficiency decreases as the pH value increases further above 7.5. After 5 hours operation, the NO removal efficiency decline to 82% with a pH of 8.5; but the NO removal efficiency is still sustained at 89.7% with a pH of 7.5. From the experimental results, the optimum pH value may be 7.5.

According to the experimental results shown in Fig. 4 and Fig. 5, it can be concluded that activated carbon displays excellent catalytic characteristics in the simultaneous removal of SO_2 and NO with the Fe-EDTA solution. For example, at pH 5.6, after 1 hour operation, the NO removal efficiency drops to 44.4% without the Fe^{II}-EDTA regeneration while the NO removal efficiency is still maintained at 90.7% with the catalytic regeneration of Fe^{II}-EDTA.

4. Effect of Temperature

Experiments were performed with a liquid flow rate of 25 ml min^{-1} and pH 6.5 to investigate the effect of temperature on NO absorption into Fe-EDTA solution without the regeneration of Fe^{II}-EDTA. From the experimental results shown in Fig. 6 we can conclude that the NO removal efficiency decreases with temperature. For example, after 2 hour run, the NO removal efficiency is 59.3% at 35 °C while 48.8% at 70 °C. The solubility of NO in the aqueous solution decreases with temperature, which gives rise to the decrease of NO removal efficiency when the temperature rises above 35 °C.

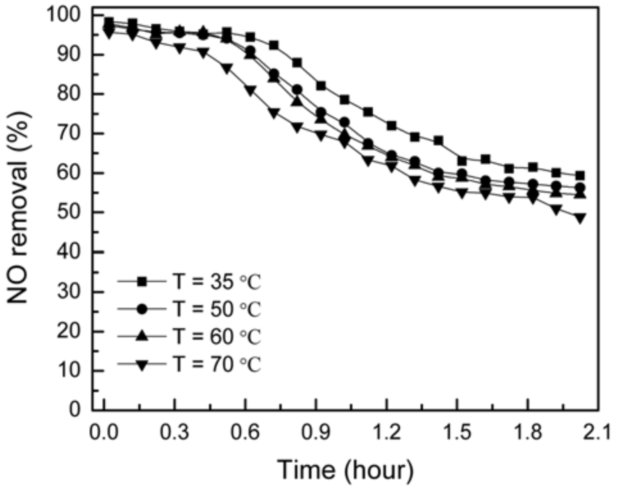

Fig. 6. Effect of temperature on NO removal without regeneration (Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,500 ppm, O_2= 5%, pH=6.5).

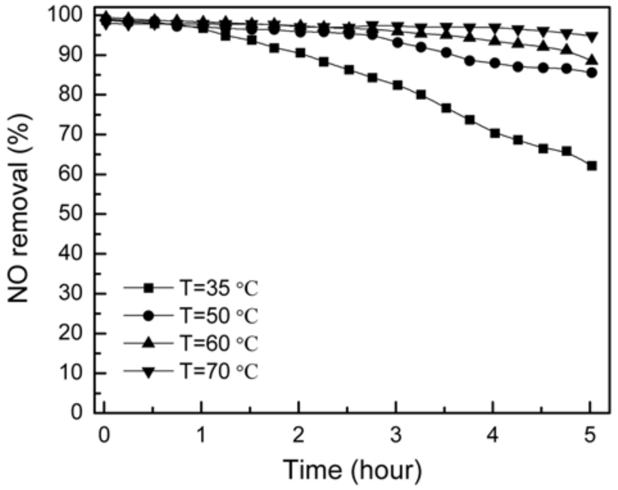

Fig. 7. Effect of temperature on NO removal coupled with the catalytic Fe^{II}-EDTA regeneration (Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,500 ppm, O_2= 5%, pH=6.5).

Experiments were performed with different regeneration temperatures while the NO and SO_2 absorption temperature was kept at 50 °C. It can be concluded from in Fig. 7 that the nitric oxide absorption efficiency increases with the regeneration temperature. For example, after the reaction has proceeded for five hours, the NO removal efficiency is maintained at 62.2% with a regeneration temperature of 35 °C, while that is sustained at 94.8% with a regeneration temperature of 70 °C. Dynamically, the redox reaction rate increases as temperature rises. More Fe^{II}-EDTA ions will be regenerated at a higher temperature. This factor contributes to the improvement of NO removal.

5. Effect of Oxygen

There exists residual oxygen in the flue gases. Therefore, it is necessary to determine the effect of oxygen partial pressure in the

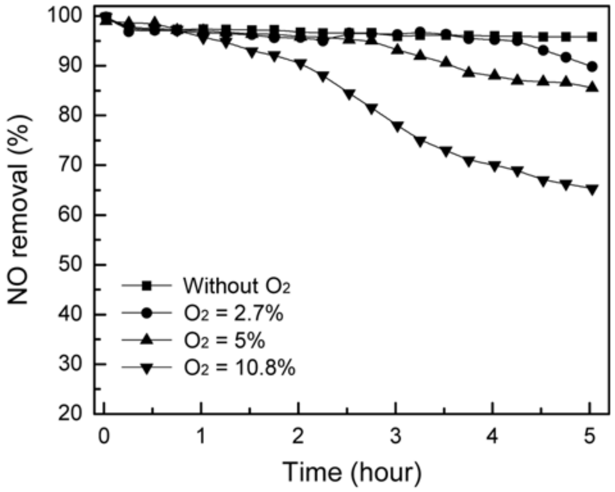

Fig. 8. Effect of oxygen on NO removal (Temp=50 °C, Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2= 1,500 ppm, pH=6.5).

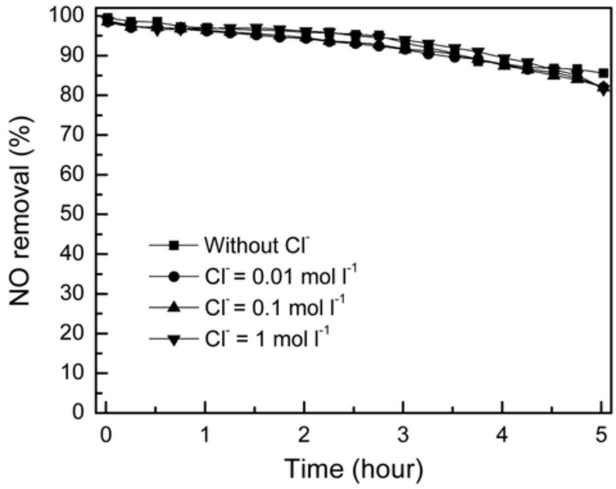

Fig. 10. Effect of chloride concentration on NO removal (Temp= 50 °C, Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO= 600 ppm, SO_2=1,500 ppm, O_2=5%, pH=6.5).

feed gas on NO removal with the Fe-EDTA solution. The experimental results depicted in Fig. 8 demonstrate that oxygen existing in the gas phase harms the nitric oxide absorption into the Fe^{II}-EDTA solution. After 5 h run, the removal efficiency of NO drops from 99% at the start of run to 87% when 5% oxygen exists in the gas phase, while that of NO is still maintained at 97% under the anaerobic condition. The reason may be that oxygen may oxidize Fe^{II}-EDTA to Fe^{III}-EDTA that cannot chelate nitric oxide. Furthermore, oxygen may oxidize sulfite/bisulfite to SO_4^{2-}, which may decrease the concentration of reductant for Fe^{III}-EDTA reduction. These two effects are attributed to the decrease of NO removal efficiency.

6. Effect of Sulfite/Bisulfite Concentration

Sulfite/bisulfite may be produced by sulfur dioxide dissolving into the aqueous solution. Sulfite/bisulfite is the reductant for the reduction of Fe^{III}-EDTA. Therefore, it is of great importance to study the effect of sulfite/bisulfite concentration on NO removal. A series of experiments were performed with different initial sulfite/bisulfite concentration in the scrubbing solution while other conditions remained constant. The experimental results depicted in Fig. 9 indicate that the presence of sulfite/bisulfite in the solution improves the NO removal. After 2 hours operation, the NO removal efficiency decreases from 99% at the start of the operation to 30.1% without sulfite/bisulfite in the solution. However, the NO removal efficiencies are still maintained at 85.5% and 91.9% after 5 hours operation with the initial sulfite/bisulfite concentration of 0.03 mol l^{-1} and 0.05 mol l^{-1}, respectively. The reason is that a high sulfite/bisulfite concentration is beneficial to the regeneration of Fe^{II}-EDTA, which is favorable to NO absorption into the Fe-EDTA solution. From Fig. 9 we can conclude that NO removal efficiency may be maintained at a high level if the sulfite/bisulfite concentration is about 0.01 mol l^{-1}. Such sulfite/bisulfite concentration can be obtained in the lime or limestone desulfurization process.

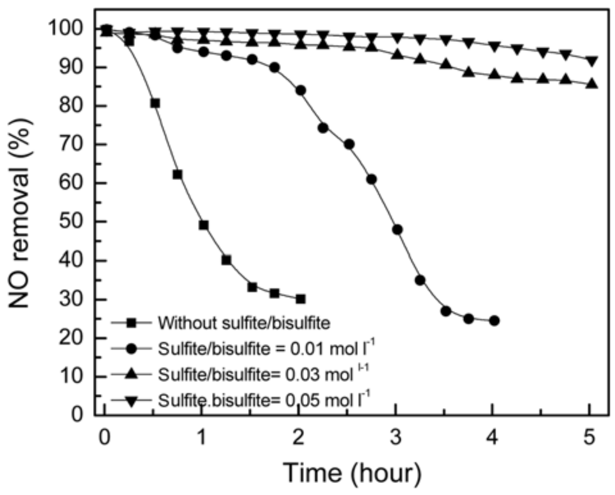

Fig. 9. Effect of sulfite/bisufite concentration on NO removal (Temp =50 °C, Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO =600 ppm, SO_2=1,500 ppm, O_2=5%, pH=6.5).

7. Effect of Chloride Concentration

The chloride concentration in the scrubbing solution will increase as the desulfurization process proceeds. It is necessary to explore the effect of chloride concentration on NO absorption into the Fe-EDTA solution. Fig. 10 demonstrates that the chloride concentration has little influence on NO removal with the Fe-EDTA solution. For example, after 4.5 h run, the NO removal efficiencies obtained are 86.8%, 85.8%, 84.9% and 86.3% with the Fe-EDTA solutions containing chloride ions of 0 mol l^{-1}, 0.01 mol l^{-1}, 0.1 mol l^{-1} and 1 mol l^{-1}, respectively. The reason may be that chloride does not combine with Fe-EDTA or adsorb on the activated carbon. Therefore, the adverse effect of chloride on NO removal with the Fe-EDTA solution is negligible.

8. Effect of Different Solutions for pH Control

Lime and MgO are usually applied in the FGD process. It is necessary to test the possibility of retrofitting the existing lime and MgO desulfurization processes for simultaneous elimination of SO_2 and NO with the Fe-EDTA technology studied in this paper. Experiments were made at pH 6.5 with 5% $Ca(OH)_2$ or 5% MgO slurries keeping pH constant. The experimental results are shown in Fig. 11. Fig. 11 illustrates that $Ca(OH)_2$ and MgO slurries have little influence on NO removal. The NO removal efficiency is sustained at 91.9% with

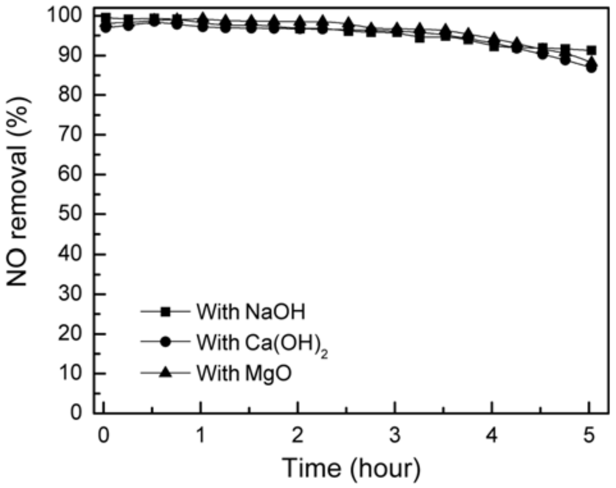

Fig. 11. Effect of different solutions for pH control on NO removal (Temp=50 °C, Activated carbon=20 g, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,500 ppm, O_2=5%, pH=6.5).

NaOH after 4.5 hours run, and it is also maintained at 90.3% and 91.4% with $Ca(OH)_2$ and MgO, respectively. Thus such Fe-EDTA technology can be used to reform the existing lime FGD process and MgO FGD process to realize the combined scrubbing of SO_2 and NO.

9. Long-term Operation

The experiment of simultaneous absorption of NO and SO_2 into the Fe-EDTA solution coupled with the regeneration of Fe^{II}-EDTA catalyzed by activated carbon for a long period of time was carried out in the packed tower shown in Fig. 1. The absorption was carried out at 50 °C with 5% O_2 in the gas phase and an initial Fe^{II}-EDTA concentration of 0.01 mol l^{-1}. The inlet NO and SO_2 concentrations were 600 ppm and 1,700 ppm, respectively. The inlet gas flow rate was 300 ml min^{-1} and the liquid flow rate of scrubbing solution feeding into the regeneration reactor and the absorber was 25 ml min^{-1}. The regeneration reactor packed with 100 g activated carbon of coconut shell was operated at 50 °C throughout the experiment. The pH of solution was controlled by adding 5% CaO slurry through online pH controller for a steady value at pH 6.5. The NO removal efficiency is shown in Fig. 12. The changes of pH value and sulfite/bisulfite concentration bring about the fluctuation of the nitric oxide removal efficiency. The experimental results shown in Fig. 12 indicate that the nitric oxide removal efficiency can be maintained at a high level for a long time by Fe-EDTA solution coupled with the regeneration of Fe^{II}-EDTA catalyzed by activated carbon of coconut shell. During the whole operation, no SO_2 is detected in the outlet gas stream by FTIR. In the process studied in this paper, the catalytic regeneration of Fe^{II}-EDTA can be realized successfully at a sulfite/bisulfite concentration of 0.01 mol l^{-1}. It is possible to maintain the sulfite/bisulfite concentration above 0.01 mol l^{-1} in the CaO FGD process. Therefore, such process can be used to retrofit the existing CaO FGD process to realize the combined removal of NO and SO_2.

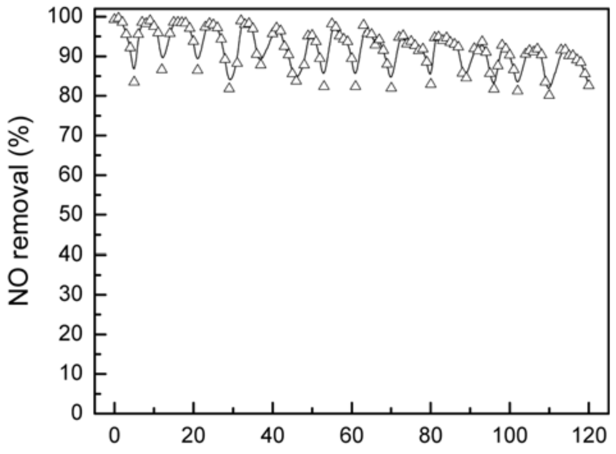

Fig. 12. NO removal efficiency vs. time, showing the effect of regeneration on removal efficiency (Activated carbon=100 g, Fe-EDTA=0.01 mol l^{-1}, NO=600 ppm, SO_2=1,700 ppm, O_2=5%, Temp=50 °C, pH=6.5).

CONCLUSIONS

A heterogeneous catalytic system has been invented to realize the combined removal of NO and SO_2 from the exhaust gases with the Fe-EDTA solution. The following specific conclusions for such catalytic system can be drawn from the experimental results:

1. Activated carbon can speed up the reduction of Fe^{III}-EDTA to Fe^{II}-EDTA greatly to maintain the capability of absorbing NO with Fe^{II}-EDTA solutions. The Fe^{III}-EDTA conversion increases with activated carbon mass.

2. pH value is an important factor affecting the NO removal efficiency. There exists an optimum pH for this process. From the experimental results in this study, the best pH is 7.5.

3. The NO removal efficiency increases with the liquid flow rate when the process is liquid mass transfer controlling. It is not necessary to increase the liquid flow rate beyond 25 ml min^{-1}.

4. Temperature plays an important part in this process. The NO removal efficiency decreases with the absorption temperature as it is over 35 °C. The Fe^{2+} regeneration rate may be speeded up with the temperature, which is beneficial to NO removal.

5. O_2 coexisting with NO in the gas streams is harmful to NO removal with the Fe-EDTA solution. The NO removal efficiency decreases with the O_2 concentration in the gas streams.

6. Sulfite/bisulfite produced by SO_2 dissolving into the aqueous solution is the reductant for the reduction of Fe^{III}-EDTA. The NO removal efficiency is enhanced with the sulfite/bisulfite concentration in the Fe-EDTA solution. Fe^{III}-EDTA can be reduced quickly by sulfite/bisulfite with a concentration lower than 0.03 mol l^{-1} under the catalysis of activated carbon.

7. Chloride ions do not affect the NO removal efficiency in such simultaneous NO and SO_2 scrubbing process.

8. $Ca(OH)_2$ and MgO slurries have little influence on NO removal. Such Fe-EDTA technology can be used to reform the existing lime FGD process and MgO FGD process to realize the combined scrubbing of SO_2 and NO.

9. High NO and SO_2 removal efficiencies can be maintained at a high level for a long period of time with this heterogeneous catalytic process. The experimental results demonstrate that this technology has a bright promise in the treatment of NO and SO_2 pollutants. It is imperative to carry out further studies into such process.

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