Simultaneous removal of NO and SO\textsubscript{2} from simulated flue gas using Fe (II) EDTA coupled with catalytic regeneration

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\textbf{ABSTRACT}

Experiments were performed in a packed column to investigate the absorption of NO and SO\textsubscript{2} into Fe (II) EDTA complex. The effect of various operating variables such as amount of activated carbon, pH, liquid flow rate, temperature, O\textsubscript{2} content, and sulfite/bisulfite on the absorption of NO and SO\textsubscript{2} by Fe (II) EDTA solution was examined. Fe (II) EDTA was regenerated by catalytic reduction of Fe (III) EDTA by sulfite ions in the presence of activated carbon. SO\textsubscript{2} is almost 100\% absorbed in the scrubbing solution during all the experiments. The rate of NO absorption increased with the amount of activated carbon. Absorption of NO increased with pH and reached to the maximum value at a pH of \textasciitilde 7.5 and decreased thereafter. The rate of NO absorption increased with the liquid flow rate and decreased with increasing O\textsubscript{2} content. However, NO absorption decreased with the increasing temperature in the absence of activated carbon and increased in the presence of activated carbon. Further, the rate of NO Absorption improved with the sulfite/bisulfite concentration.

\textbf{Keywords:} Fe (II) EDTA, nitric oxide, sulfur dioxide, absorption, activated carbon

\textbf{INTRODUCTION}

Nitrogen oxides (NO\textsubscript{x}) and sulphur oxides (SO\textsubscript{x}) are the major air pollutants found in the flue gases emitted from chemical industries and power plants. NO\textsubscript{x} and SO\textsubscript{2} are responsible for acid-rain, global warming, smog and destruction of forest ecosystems. The removal of acidic gases has become need of the hour in order to comply with stringent environmental emission standards. Technologies for removal of sulphur oxides has attained an advanced stage of development, however, no efficient method to control NO\textsubscript{x} emission has been reported yet. More than 90\% of NO\textsubscript{x} emitted from power plants consists of nitric oxide (NO) which is relatively inert.

Absorption of NO can be carried out either by using strong oxidative absorbent or by complex forming reagents. Wet scrubbers have been the workhorses of the chemical industry for decades and successfully used for removal of several acidic gases. In general, additives are added into scrubbing system to oxidize relatively inert NO into NO\textsubscript{2} which can be subsequently removed by alkaline absorbents. Aqueous solutions of numerous oxidative absorbents such as hydrogen peroxide [1], per acid [2], organic tertiary hydro peroxides [3], sodium chlorite [4-8], KMnO\textsubscript{4} [9,10] and chlorine dioxide [11,12] have been investigated to determine their efficiency in the removal of NO\textsubscript{x}.

Several other liquid absorbents, namely Urea [13], FeSO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4}[14], Fe (II) EDTA [15], Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} [16], Na\textsubscript{2}SO\textsubscript{3} [17], and Fenton reagent [18] have also been explored in the past to remove NO\textsubscript{x} from the exhaust gases. Numerous studies have been made to improve NO absorption, including the addition of various Fe (II) chelates to bind NO [19-24]. Though Fe (II) EDTA has emerged as potential absorbent to achieve a reasonably high NO removal efficiency yet it is easily oxidized to Fe (III) EDTA that is not capable of binding NO, and thus NO removal efficiency decreases immediately [25-27]. Literature reveals several studies to regenerate Fe (II) EDTA to maintain
high NO removal efficiency [28-30]. Some reducing agents such as hydrazine, Na₂S₂O₄, Na₂SO₃ are used to realize the regeneration of Fe (II) EDTA. However due to low rate constants and high consumption, none of these methods have been put into commercial applications.

Inadequate studies have been reported to investigate the absorption of NO into Fe (II) EDTA solution coupled with activated carbon to regenerate Fe (II) EDTA to maintain high NO absorption. Activated carbon has been applied in industry successfully as a catalyst due to its large surface area, porous structure, characteristic flexibility and low cost. It is an efficient catalyst which may speed up the regeneration of Fe (II) EDTA in the presence of sulfite/bisulfite.

The present manuscript attempts to study the absorption of NO as well as SO₂ into Fe (II) EDTA complex and to examine the effect of various operation variables such as amount of activated carbon, liquid flow rate, pH, temperature, O₂ content, and sulfite/bisulfite concentration on the absorption of NO and SO₂. This technique is believed to absorb NO and SO₂ efficiently and also to sustain high NO and SO₂ removal for a longer period of time with a low operation cost.

THEORETICAL BACKGROUNDS

SO₂ is moderately soluble in aqueous solution and undergoes hydrolysis to form bisulfite (HSO₃⁻), sulfite (SO₃²⁻) and disulfite (S₆O₅²⁻) ions [31]. The equilibrium concentrations of all these species depend upon partial pressure of SO₂ and pH of the solution.

Henry’s constant for NO in water is very small i.e. 1.218×10⁻³ M/atm at 45°C [32]. It suggests that NO has poor solubility in water. Fe (II) EDTA tends to bind nitric oxide by coordinate linkage in the liquid phase and thus enhances the solubility of nitric oxide in the aqueous solution as follows:

\[
\text{Fe(II) – EDTA}^– + \text{NO}_{\text{aq}} \xrightarrow{\text{coordination}} \text{Fe(II) – EDTA(NO)}^–
\]  

(1)

However, oxygen coexisting in the flue gas may oxidize Fe (II) EDTA to Fe (III) EDTA as shown below:

\[
4\text{Fe(II) – EDTA}^– + O_2 + 4H^+ \xrightarrow{\text{autoxidation}} 4\text{Fe(III) – EDTA} + 2H_2O
\]  

(2)

Fe (III) EDTA lacks the ability to bind NO. As a result, NO removal efficiency will decrease quickly. It is, therefore, Fe (III) EDTA must be reduced to Fe (II) EDTA in order to maintain the NO absorption.

Sulfite/bisulfate ions are formed by hydrolysis of SO₂ in the scrubbing solution and facilitate the regeneration of Fe(II)-EDTA as follows [21], [24]:

\[
2\text{Fe(III) – EDTA}^– + 2\text{HSO}_3^- \xrightarrow{\text{catalysis}} 2\text{Fe(II) – EDTA}^– + \text{SO}_3^{2-} + 2H^+
\]  

(3)

\[
2\text{Fe(III) – EDTA}^– + 2\text{SO}_3^{2-} \xrightarrow{\text{catalysis}} 2\text{Fe(II) – EDTA}^{2-} + \text{SO}_4^{2-}
\]  

(4)

To accelerate the reduction of Fe (III)-EDTA, activated carbon can be used as a catalyst. It disintegrates Fe (III)-EDTA into Fe³⁺ ions and EDTA ions as follows:

\[
\text{Fe(III) – EDTA} \xrightarrow{\text{catalysis}} \text{Fe}^{3+} + \text{EDTA}^{4-}
\]  

(5)

Standard reduction potential data suggest that sulphite ions (E^\text{SO}_3^{2-}/\text{SO}_4^{2-} = −0.936V) can easily reduce Fe³⁺ ions (E^\text{Fe}^{3+}/\text{Fe}^{2+} = 0.771V) [32]. The reduction of Fe³⁺ ions by the sulfite ions takes place as follows:

\[
2\text{Fe}^{3+} + \text{SO}_3^{2-} + \text{H}_2\text{O} \xrightarrow{\text{reduction}} \text{SO}_4^{2-} + 2\text{Fe}^{2+} + 2H^+
\]  

(6)

Fe²⁺ ions thus produced undergo coordination linkage with EDTA ions and regenerate Fe (II)-EDTA as follows:

\[
\text{Fe}^{2+} + \text{EDTA}^{4-} \xrightarrow{\text{coordination}} \text{Fe(II) – EDTA}^{2-}
\]  

(7)

It is therefore, the NO removal efficiency can be sustained for a long time.

In view of the above, if Fe(II)-EDTA can be regenerated quickly by sulfite/bisulfite under the catalysis of activated
carbon, then this technology will be highly efficient and cost effective for the combined removal of NO and SO\textsubscript{2} from the flue gases.

**MATERIALS AND METHODS**

**Materials**

Standard gases included N\textsubscript{2} (99%), SO\textsubscript{2} span gas (99%), and NO span gas (99.9%). N\textsubscript{2} and SO\textsubscript{2} were the products of Anjeon Gas Co., Korea and NO was the product of Mathieson, Co. FeSO\textsubscript{4}·7H\textsubscript{2}O (>99.0%), Na\textsubscript{2}EDTA (>99.5%) and Na\textsubscript{2}SO\textsubscript{3} (>97.0%) were obtained from Samchun Pure Chem. Co. Ltd., Korea. Activated carbon was obtained from Shanghai Activated Carbon Co., Ltd. Aqueous solution of Fe (II)-EDTA is extremely air-sensitive and should be handled under a protective nitrogen atmosphere. The Fe (II)-EDTA solution was prepared by diluting a predetermined amount of Na\textsubscript{2}EDTA solution in degassed water. The pH of the solution was maintained at 9.0 by careful addition of 0.1M H\textsubscript{2}SO\textsubscript{4} solution. When appropriate amount of FeSO\textsubscript{4}·7H\textsubscript{2}O was added to the Na\textsubscript{2}EDTA solution, it gives a slightly green, clear solution with a pH ~5. The pH of the solution can be adjusted to the desired value by the addition of 0.1M NaOH or H\textsubscript{2}SO\textsubscript{4} solution.

**Flue gas treatment unit**

It consists of simulated flue gas supply system, packed column, circulation tank, regeneration reactor, pH control system, data acquisition system, and gas analysis system. The schematic diagram of the experimental apparatus is shown in Fig. 1. Absorption of NO and SO\textsubscript{2} were performed in a packed column (I.D. = 20 mm, height = 1000 mm). The Fe (II)-EDTA regeneration was carried out in a reactor (I. D. = 20 mm, height = 800 mm) packed with activated carbon. The temperature of the packed column and regeneration reactor was controlled by water thermostat (WBC-1506D, JEIO TECH, Korea). The pH of reaction solution was controlled by using an auto-pH control system (KFC-MK-250, Korea) by continuous addition of 0.1M NaOH/H\textsubscript{2}SO\textsubscript{4} solution with the help of peristalsis pump (Cole-Palmer Co., USA). The simulated flue gas was obtained by controlled mixing of SO\textsubscript{2}, NO, and N\textsubscript{2} using mass flow controllers (MFC). Air was introduced into reactor using air pump to maintain the dissolved O\textsubscript{2} concentrations at the desired level. Fe (II)-EDTA solution together with appropriate amount of Na\textsubscript{2}SO\textsubscript{3} was added into circulation tank. The simulated flue gas with a feeding rate of 0.3 L/min is passed from the bottom and scrubbing solution is continuously introduced from the top of the packed column. The initial sulfite concentration was adjusted by adding appropriate amount of Na\textsubscript{2}SO\textsubscript{3} into the Fe (II)-EDTA complex. The absorbent coming out from the packed column was fed into the circulation tank. Fe (II)-EDTA is recycled in the regeneration reactor and then it is directly supplied into the packed column. The experimental conditions and various operating variables are listed in Table 1.

**Gas analysis**

The inlet and outlet gas concentrations were analyzed after removing its moisture in the sample conditioner by the SO\textsubscript{2} analyzer (Model-Ultramat 23, IR type, Siemens, Germany), NO analyzer (Model-42C, Chemiluminescent type, Thermo Environmental Instruments Inc., USA), and DO meter (835A, Thermo Orion, USA).

**RESULTS AND DISCUSSION**

**Effect of the amount of activated carbon on NO removal**

The effect of the amount of activated carbon on the absorption of NO was examined by performing several experiments with different amounts of activated carbon. It is pertinent to mention here that SO\textsubscript{2} is almost 100% absorbed in the scrubbing solution during all the experiments. Fig. 2 illustrates that NO absorption increased with the amount of activated carbon. On completion of 2 hour operation, absorption of NO was merely 56.2% in absence of activated carbon; however, it was observed 89.2%, 91.9%, 96.9% and 97.1% with 5, 10, 20, 40 and 80 g of activated carbon in the regeneration reactor respectively. Activated carbon catalyzed the regeneration of Fe (II) EDTA. Activated carbon is surface catalyst. More is the amount of activated carbon; more will be its surface area and more number of active sites, thus Fe (II) EDTA regeneration becomes faster with the amount of activated carbon. The rate of NO absorption did not increase significantly when the amount of activated carbon exceeded 20g. It may be due to the fact that Fe\textsuperscript{2+} ions may also be adsorbed over the surface of activated carbon; thereby reducing the rate of absorption of NO.

It can be concluded from the above experimental results that activated carbon has excellent catalytic activity to regenerate Fe (II) EDTA. It not only improved absorption of NO by Fe (II) EDTA scrubbing solution but also helped to maintain a persistently high SO\textsubscript{2} and NO removal efficiency.

**Effect of pH on NO removal**

pH is a crucial factor in the absorption of NO in the scrubbing solution. Numerous experiments were carried out to examine the effect of pH on NO absorption. Fig. 3 demonstrates that effect of pH on absorption of NO in absence of
activated carbon. Absorption of NO decreased after one hour of experimental operation because Fe (II) EDTA is not being regenerated in absence of activated carbon. A weakly alkaline solution absorbed the NO efficiently and the optimum pH for high NO removal efficiency was found to be ~7.5. After an experimental run of 2 hour, maximum absorption of NO was observed at a pH of 7.5. The decrease in rate of NO absorption at lower pH is due to the fact that the reaction as mentioned in Eq. (3) shifted to backward direction. Moreover, reduction of Fe$^{3+}$ to Fe$^{2+}$ by sulfite ion is also not favored at low pH as can be visualized from Eq. (6). In addition, O$_2$ gas will readily oxidize Fe (II) EDTA into Fe (III) EDTA, thereby leading to poor NO absorption. On the other hand, decrease in rate of NO absorption at a pH higher than 7.5 is attributed to the formation of Fe(OH)$_3$ precipitates. Under alkaline conditions, Fe$^{2+}$ ions readily combine with OH$^-$ ions and produce Fe(OH)$_2$ which further undergoes oxidation to Fe(OH)$_3$ instantaneously. Therefore, Fe (II) EDTA concentration will also reduce in the strongly alkaline solution and so the ability to absorb NO.

The experiments have also been carried out to investigate the influence of pH on NO removal in presence of 20g activated carbon. Fig. 4 demonstrates that the rate of NO absorption increased as the pH increased from 5.0 to 7.5. After 4 hour continuous run, the NO removal efficiency of 71.1, 79.8, 86.8, 89.1, 91.2 and 85.8% was observed at a steady state at the pH of 5.5, 6.0, 6.5, 7.0, 7.5, and 8.5 respectively. The optimum pH for NO absorption was again found to be ~7.5.

**Effect of liquid flow rate on NO removal**

The experimental results to investigate the effect of liquid flow rate on the absorption of NO are depicted in Fig. 5. The rate of NO absorption increased with the increasing liquid flow rate. NO absorption was observed almost 99% in the beginning of the operation; however, it decreased to 62.2 % when the liquid flow rate is 10 mL/min. NO absorption is sustained at 87.8% when the liquid flow rate is 20 mL/min. NO absorption increased slightly at a liquid flow rate above 20 mL/min. It is due to fact that NO absorption is liquid film controlling at slow liquid flow rates. The liquid mass transfer coefficient increases and the mass transfer resistance in the liquid become small with the increasing liquid flow rate. Therefore, rate of NO absorption increased with the liquid flow rate. However, at a liquid flow rate above 20 mL/min, the mass transfer in the liquid become very small and the mass transfer resistance in the gas phase may become the main mass transfer resistance thus, NO absorption rate increased marginally.

**Effect of temperature on NO removal**

The experiments were carried out for a period of 2 hour with a liquid flow rate of 25 mL/min, and pH of 7.5 at 35, 45, 55, 65°C to investigate the effect of temperature on NO absorption into Fe (II) EDTA solution in absence of activated carbon. The rate of NO absorption decreased with temperature as can be seen in Fig. 6. After experimental run of 2 hour, absorption of NO was found 58.4, 52.6, 47.2 and 44.6% at 35, 45, 55, 65°C. The rate of NO absorption decreased with temperature because solubility of NO in the aqueous solution decreases with temperature.

Experiments were also performed at 35, 45, 55, 65°C for a period of 2 hour with a liquid flow rate of 25 mL/min, and pH of 7.5 to investigate the effect of temperature on NO absorption into Fe (II) EDTA solution in presence of 20g activated carbon. It is evident from Fig. 6 that absorption of NO increases with the rise in temperature. It is due to the fact that higher temperature favors the regeneration of Fe (II)-EDTA and thus enhances the absorption of NO.

**Effect of oxygen on NO removal**

Since flue gases always contain oxygen, therefore, it is necessary to determine the effect of oxygen content in the flue gas on the absorption of NO. Fig. 7 demonstrated that oxygen present in the flue gas hampers the absorption of NO into Fe (II) EDTA solution. After experimental run of 4 hour, the absorption of NO dropped slightly from 99 to 96.8% in absence of oxygen gas. However, NO removal reduced to 94.6, 86.8 and 70.2% in presence of 2, 4, 8 % oxygen content in the simulated flue gas. It is due to the fact that oxygen present in the flue gas oxidizes Fe (II) EDTA into Fe (III) EDTA. The later lacks the ability to bind NO. In addition, oxygen may oxidize sulfite/bisulfite to sulphate ion and thus concentration of reductant in the scrubbing solution also decreases that is why regeneration of Fe (II) EDTA does not take place efficiently.

**Effect of sulfite/ bisulfite concentration on NO removal**

Sulfite/bisulfite ions are the major reducing agents present in the scrubbing solutions which are formed by dissolution of sulfur dioxide into the aqueous solution. Sulfite/bisulfite ions not only reduce Fe (III) EDTA into Fe (II) EDTA but also reduce Fe$^{3+}$ ions into Fe$^{2+}$ ions as suggested in Eq. (4) and Eq. (6). Therefore, it is highly desirable to investigate the effect of concentration of sulfite/bisulfite on the absorption of NO. A series of experiments were performed for a period of 2 hour at 45°C, pH of 7.5 with different initial sulfite/bisulfite concentrations in the scrubbing solution. The experimental results in Fig. 8 indicate that the presence of sulfite/bisulfite in the scrubbing solution improved the absorption of NO. After an experimental run of 2 hour, NO absorption decreased from initial 99% to 28.6% in absence of initial sulfite/bisulfite ions however, NO removal is
still maintained at 74.8, 84.6 95.4 and 98.2% with the initial sulfite/bisulfite concentration of 0.01, 0.02, 0.04 and 0.06 mol/L respectively. It is due to the fact that sulfite/bisulfite ions facilitate the regeneration of Fe (II) EDTA. It is therefore essential to optimize sulfite/bisulfite concentration in the scrubbing solution in order to achieve high NO absorption efficiency. Further, higher NO removal in alkaline medium is also due to the fact that SO₂ being acidic gas easily combine with alkali and yield sulfite/bisulfite ions which enhance the NO absorption by regenerating Fe (II) EDTA.

Table 1: Experimental conditions and operating variables

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbent</td>
<td>Fe (II) EDTA Complex</td>
</tr>
<tr>
<td>Inlet NO concentration</td>
<td>500 ppmv</td>
</tr>
<tr>
<td>Inlet SO₂ concentration</td>
<td>1500 ppmv</td>
</tr>
<tr>
<td>Sulfite/bisulfate Concentration</td>
<td>Zero to 0.06 mol/L</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>5 - 80 g</td>
</tr>
<tr>
<td>Gas feeding rate</td>
<td>0.3 L/min</td>
</tr>
<tr>
<td>Liquid flow rate</td>
<td>10- 50 mL/min</td>
</tr>
<tr>
<td>pH</td>
<td>5.5 to 8.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>35 – 65°C</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Zero – 8 %</td>
</tr>
</tbody>
</table>

Figure 1: A schematic diagram of experimental system

1 – Packed column, 2 – Regeneration reactor, 3 – pump, 4 – Sample conditioner, 5 – Gas cylinder, 6 – Mass flow controller, 7 – pH control system, 8 – Circulation tank, 9 – NaOH/H₂SO₄ solution, 10 – Gas analyzing system
Figure 2: Effect of amount of activated carbon on NO removal
(Fe (II) EDTA = 0.01M, NO = 500 ppm, SO$_2$ = 1500 ppm, O$_2$ = 4%, pH = 7.5, 45°C, Run = 2hr)

Figure 3: Effect of pH on NO removal in absence of activated carbon
(Fe (II) EDTA = 0.01M, NO = 500 ppm, SO$_2$ = 1500 ppm, O$_2$ = 4%, 45°C, Run = 2hr)
Figure 4: Effect of pH on NO removal in presence of activated carbon
(Fe(II) EDTA = 0.01M, AC = 20g, NO = 500 ppm, SO$_2$ = 1500 ppm, O$_2$ = 4%, 45°C, Run = 4hr)

Figure 5: Effect of liquid flow rate on NO removal
(Fe(II) EDTA = 0.01M, AC = 20g, NO = 500 ppm, SO$_2$ = 1500 ppm, O$_2$ = 4%, pH = 7.5, 45°C, Run = 4hr)
Figure 6: Effect of temperature on NO removal in presence as well as absence of activated carbon
(Fe (II) EDTA = 0.01M, NO = 500 ppm, SO$_2$ = 1500 ppm, O$_2$ = 4%, pH = 7.5, Run = 2hr)

Figure 7: Effect of oxygen on NO removal
(Fe (II) EDTA = 0.01M, AC = 20g, NO = 500 ppm, SO$_2$ = 1500 ppm, pH = 7.5, 45°C, Run = 4hr)
CONCLUSION

The simultaneous absorption of NO and SO$_2$ into aqueous Fe (II) EDTA scrubbing solution was studied in a packed column. The operating variables included 500 ppm NO, 0.01 mol/L Fe (II) EDTA solution, pH of 5-8.5, and temperature of 35-65°C respectively. SO$_2$ is almost 100% absorbed in the scrubbing solution. NO absorption reached to maximum value in slightly alkaline solution of pH ~7.5. Activated carbon emerged as a potential catalyst for regeneration of Fe (II) EDTA. This technology can be efficiently used for combined removal of NO and SO$_2$. Absorption of NO increased with the liquid flow rate. Higher temperature is favorable for efficient NO removal in presence of activated carbon as it accelerates the regeneration of Fe (II) EDTA. Higher content of oxygen in the flue gas hampers the absorption of NO by oxidizing Fe$^{2+}$ into Fe$^{3+}$ and simultaneously converted sulfite/bisulfite into sulfate ions. Sulfite/bisulfite ions produced by dissolution of SO$_2$ into the aqueous solution are the major reducing agents which help in regeneration of Fe (II) EDTA. The NO removal efficiency can be enhanced by addition of sulfite/bisulfite in the scrubbing solution. It is pertinent to say that High NO and SO$_2$ removal efficiencies can be maintained for a longer time using Fe (II) EDTA complex when it is coupled with catalytic regeneration.

REFERENCES