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Removal of NO by Using Fe^{3+}-H_2O_2 Mixed Reagent Solution in Lab-Scale Bubbling Reactor with Addition of EDTA

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The removal of NO by using Fe^{3+}-H_2O_2 mixed reagent solution with the addition of EDTA was investigated in a lab-scale bubbling reactor. The effects of pH value, H_2O_2 concentration, NO inlet concentration and reaction temperature were assessed. The experimental results indicated that addition of EDTA into Fe^{3+}-H_2O_2 mixed reagent solution can improve NO removal efficiency under weakly acidic conditions. When NO concentration exceeded 600 ppm, the gas-liquid reaction between NO and absorption liquid was controlled by liquid-film. The removal efficiency of NO increased with increasing reaction temperature.

Key Words: Nitric oxide, Removal, Fe^{3+}-H_2O_2 mixed reagent, EDTA.

INTRODUCTION

SO_2 and NO emitted from coal-fired power plants cause serious environmental problems such as acid rain and photochemical smog[1]. To control the emission of SO_2, limestone-based wet scrubbing process is one of the most effective methods[2] and studied extensively during the past several decades[3-6]. As for NO control, selective catalytic reduction process is widely used[7]. The separated pollutants control strategy results in high investment and operation cost. If the insoluble NO is oxidized into soluble NO_2, then it can be absorbed in a wet flue gas desulfurization scrubber. In recent years, many oxidants such as $NaClO_2$[1,8], $NaClO_3$[9], $KMnO_4$[10] and Fenton reagent[11] were used for removal of NO by using oxidation- absorption process.

Fe^{3+}-H_2O_2 mixed reagent, as a kind of Fenton-like reagent, its solution can also generate hydroxyl redical ($^{\bullet}OH$) for NO oxidation. When the pH value of Fe^{3+}/H_2O_2 mixed reagent solution is about 3, it has the best oxidation performance[12]. However when the pH value raises beyond 3, due to the low solubility of $Fe(OH)_3$, the generation rate of hydroxyl redical would decrease, as a result, the oxidation ability of Fe^{3+}-H_2O_2 mixed reagent solution decreases too[13]. It is well known that the typical operation pH range for a limestone-based wet flue gas desulfurization scrubber is 5-6. Therefore, if the solubility of Fe^{3+} under weakly acidic conditions is improved, Fe^{3+}-H_2O_2 mixed reagent may be used for NO oxidation and absorption in a limestone-based wet flue gas desulfurization scrubber. EDTA could be added to modify Fenton systems to maintain adequate oxidation ability at circumneutral pH[14,15]. In the present work, we used EDTA as a chelating agent to improve the solubility of Fe^{3+} and the absorption process of NO into Fe^{3+}-H_2O_2 mixed reagent solution was investigated in a lab-scale bubbling reactor and the effects of operating parameters such as pH value, H_2O_2 concentration, NO inlet concentration and reaction temperature on removal efficiency of NO were investigated and discussed.

EXPERIMENTAL

All experiments were performed in a lab-scale bubbling reactor as shown in Fig. 1, which was also used in our previous work[11]. Its dimater and height are 10 cm and 15 cm, respectively. The solution was stirred at a constant speed of 200 rpm. The pH value of the solution was kept at a desired value with an error of 0.02 by titrating with 1 M NaOH. NO was diluted to the desired concentration with pure N_2 in a mixing box before entering the bubbling reactor. The flue gas flow rate and the solution volume were kept at 2 L/min and 700 mL, respectively. $Fe_2(SO_4)_3$ and H_2O_2 were used to prepare the Fe^{3+}-H_2O_2 reagent. A water bath was used to control the reaction temperature with an error of ± 0.2 ºC. The concentration of NOx in the outlet gas stream was measured by using a continuous flue gas analyzer (NDIR 60i, Thermo Scientific Co. Ltd.). And a Peltier gas dryer was used to protect the flue gas analyzer against water mist.The experimental conditions was summarized in Table-1.

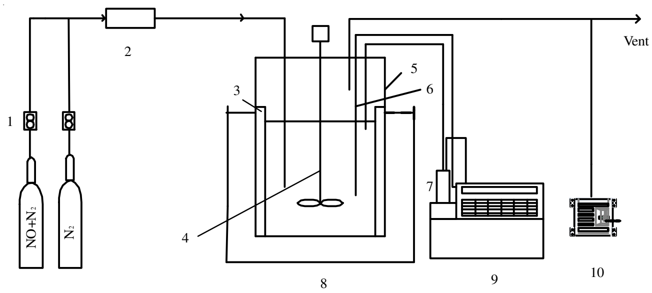

Fig. 1. Schematic of the experimental apparatus; 1. Mass flow controller, 2. Mixing box, 3. Baffle, 4. Stirrer, 5. Bubbling reactor, 6. pH electrode, 7. NaOH bottle, 8. Water bath, 9. Autotitrator, 10. Flue gas analyzer

TABLE-1
EXPERIMENTAL CONDITIONS FOR REMOVAL NO BY USING Fe^{3+}-H_2O_2 –EDTA SOLUTIONS

pH	H_2O_2 concentration (mol/L)	NO inlet concentration (ppm)	Reaction temperature (K)
2-6	0.5-1.5	250-1000	298-333

Each experimental run was 10 min and the outlet NOx concentration value was recorded per mintue. The average concentration value within 10 min was used as the outlet concentration c_{out}. Then the removal efficiency can be given by:

$$\eta = \frac{c_{in} - c_{out}}{c_{in}} \times 100\ \% \tag{1}$$

where η is NO removal efficiency, c_{in} is the concentration of NO in the inlet gas stream and c_{out} is the average concentration of NOx in the outlet gas stream.

RESULTS AND DISCUSSION

Reaction mechanism between NO and Fe^{3+}-H_2O_2 mixed reagent solution:

1) Fenton-like reaction[16]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}O_2H + H^+ \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + H^- \tag{3}$$

When EDTA is present in the solution, Fenton-like reaction can be expressed as follows[12]:

$$Fe(III)EDTA + H_2O_2 \rightarrow Fe(II)EDTA + {}^{\bullet}O_2H + H^+ \tag{4}$$

$$Fe(II)EDTA + H_2O_2 \rightarrow Fe(III)EDTA + {}^{\bullet}OH + OH^- \tag{5}$$

Hydroxyl redical is the main intermediate in Fenton-like reaction[17], it can oxdize[18] NO into NO_2^-, NO_2 and NO_3^-:

$$NO + OH^{\bullet} \rightarrow NO_2^- + H^+ \tag{6}$$

$$NO + OH^{\bullet} \rightarrow NO_2 + \cdot H \tag{7}$$

$$NO_2^- + OH^{\bullet} \rightarrow NO_3^- + \cdot H \tag{8}$$

Effect of pH on NO removal efficiency: Effect of pH on NO removal efficiency is shown in Fig. 2. It is clear that NO removal efficiency increases with pH value up to 3 and then keeps relatively stable with the increase of pH value. The ferrous ions generated in reaction (2) react with hydroxide ions to form ferric hydroxo complexes such as $[Fe(H_2O)_5OH]$ and $[Fe(H_2O)_6]^{3+}$ [19]:

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+ \tag{9}$$

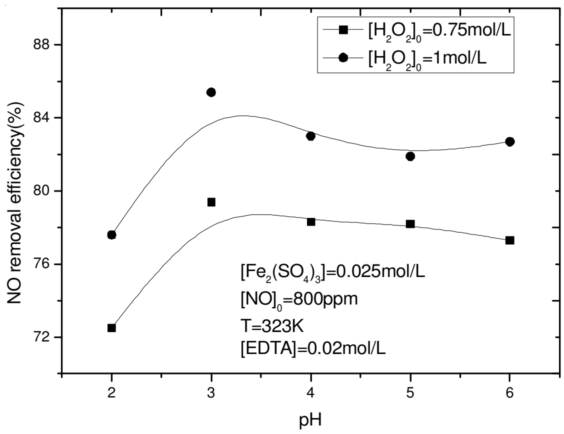

Fig. 2. Effect of pH on removal efficiency of NO

It has been proven that $[Fe(H_2O)_5OH]^{2+}$ has stronger catalysis effect for ${}^{\bullet}OH$ generation than $[Fe(H_2O)_6]^{3+}$ [20]. Therefore, when pH is below 3, $[Fe(H_2O)_5OH]^{2+}$ is easily converted into $[Fe(H_2O)_6]^{3+}$, so the concentration of ${}^{\bullet}OH$ decreases, which is unfavourable to NO removal. When the value of pH > 3, due to the formation of Fe^{3+}(EDTA), the solubility of Fe^{3+} is kept at a relatively high value, as a result, increase of pH only has a slight impact on NO removal efficiency at this time.

Effect of H_2O_2 concentration on NO removal efficiency: Fig. 3 shows the effect of H_2O_2 concentraion on NO removal efficiency. It is obvious that NO removal efficiency increases with H_2O_2 concentration. However, above a concentration of 1.25 mol/L, NO removal efficiency increases slowly. The similar phenomenon was also observed by Liu *et al.*[18], who investigated the process of simultaneous removal of NO and SO_2 by using UV/H_2O_2 advanced oxidation technique. The increase of H_2O_2 concentration accounts for the production of large amount of ${}^{\bullet}OH$ described as reaction (3) and reaction (5), which is helpful to NO removal. But with the increase of H_2O_2 concentration, the side reactions would take place in the solution and cause the decrease of ${}^{\bullet}OH$ concentration[20,21]:

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{10}$$

$$2OH^{\bullet} \rightarrow H_2O_2 \tag{11}$$

Besides that, the oxidation abilities of ${}^{\bullet}O_2H$ and H_2O_2 are lower than that of ${}^{\bullet}OH$. As a result, when the concentration of H_2O_2 is over 1.25 mol/L, NO removal efficiency nearly keeps at a stable value with the increase of H_2O_2 concentration.

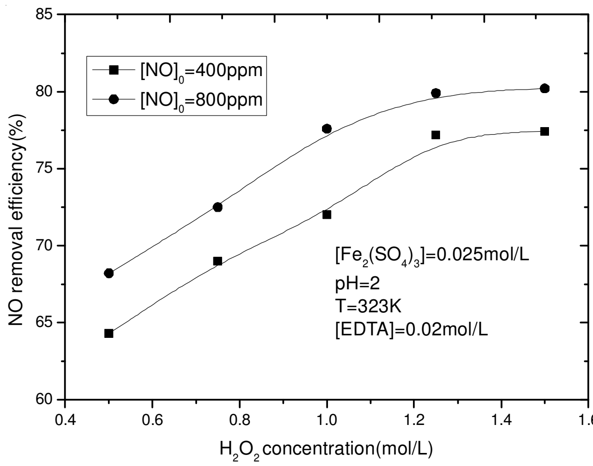

Fig. 3. Effect of H_2O_2 concentration on removal efficiency of NO

Effect of NO inlet concentration on its removal efficiency: Fig. 4 shows the effect of NO inlet concentration on its removal efficiency. When NO inlet concentration is below 600 ppm, removal efficiency of NO increases with increasing NO inlet concentration. However, when NO inlet concentration rises above 600 ppm, its removal efficiency nearly keeps stable. That is to say, the gas-liquid reaction between NO and absorption liquid is controlled by liquid-film when NO inlet concentration is over 600 ppm.

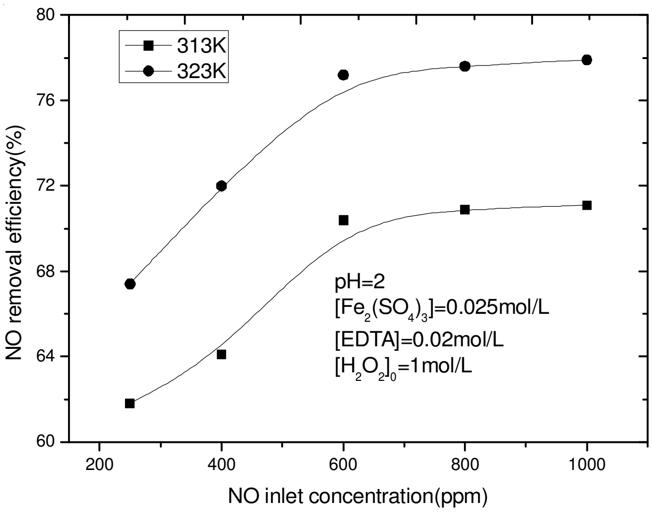

Fig. 4. Effect of NO inlet concentration on removal efficiency of NO

Effect of reaction temperature on removal efficiency of NO: The experimental results detecting the effect of reaction temperature on removal efficiency of NO are shown in Fig. 5. As shown in Fig. 5, removal efficiency of NO increases with reaction temperature. Increasing reaction temperature can promote $^{\bullet}OH$ generation through reaction (2), reaction (4) and the following reaction[22]:

$$H_2O_2 \rightarrow 2OH^{\bullet} \quad (12)$$

In addition, the decomposition of H_2O_2 into H_2O and O_2 is inhibited by EDTA[23], which would increase the utilization ratio of H_2O_2. Thus increasing reaction temperature is favourable to removal of NO.

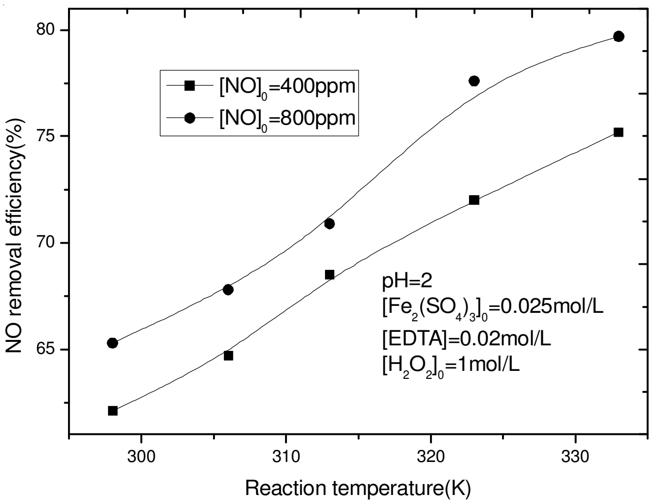

Fig. 5. Effect of reaction temerature on removal efficiency of NO

Conclusion

Experiments on removal of NO by using Fe^{3+}-H_2O_2 mixed reagent solution with the addition of EDTA were carried in a lab-scale bubbling reactor. The results indicated that addition of EDTA into Fe^{3+}-H_2O_2 mixed reagent solution can improve removal efficiency of NO under weakly acidic conditions. When NO concentration exceeded 600 ppm, the gas-liquid reaction between NO and absorption liquid was controlled by liquid-film. The removal efficiency of NO increased with reaction temperature. Therefore, with the addition of EDTA, Fe^{3+}-H_2O_2 mixed reagent can be used in a typical limestone-based wet flue gas desulfurization scrubber for removal of NO.

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