Study on NO Removal Characteristics of the Fe(II)EDTA and Fe(II)PBTCA Composite System

Liwei Ma, Guoqiang Li, Youqian Wang, Siqi Chai, and Guojie Zhang

ABSTRACT: Fe$^{2+}$ complexation wet denitrification technology has become a research hotspot. It is very important to achieve efficient regeneration of the absorbent and increase NO absorption in the Fe$^{2+}$ complexation system. They are the key to the industrial application of the Fe$^{2+}$ complexation absorption process. In this paper, 2-phosphonate-butane-1,2,4-tricarboxylic acid and ethylenediamine tetraacetic acid were used as ligands to prepare a composite system for the first time. The characteristics of NO removal were investigated under different temperatures, pHs, Fe$^{2+}$ concentrations, O$_2$ contents, NO concentrations, CO$_2$ contents, and SO$_2$ concentrations. Compared with the single ligand, the results show that the denitrification performance of the solution with a complex ligand is significantly improved. In this system, pH 9, 40 °C temperature, and 20 mmol/L Fe$^{2+}$ concentration are the economic ideal conditions for NO removal. The system can realize simultaneous removal of NO and SO$_2$, but SO$_2$ in flue gas has a dual effect on the NO removal reaction.

1. INTRODUCTION

NO$_X$ is one of the major air pollutants produced by burning fossil fuels. It will cause certain harm to the ecological environment, such as acid rain, photochemical smog, global warming, and ozone layer destruction. About 90–95% of NO$_X$ in a typical flue stream is NO, which is almost insoluble in water. Currently, selective catalytic reduction (SCR) denitrification technology, which is relatively mature in the industry, can effectively remove NO in flue gas. However, SCR has some problems, such as high operating cost, catalyst poisoning, high reaction temperature, and ammonia escape.

Fe$^{2+}$ complexation wet denitrification technology is an effective technology for NO removal. Fe$^{2+}$ in solution can quickly capture NO to form a ferrous nitrite complex so as to achieve the purpose of efficient NO removal. With the advantages of low temperature, no pollution, and high capacity, it is one of the most promising processes in the field of NO removal. However, O$_2$ in the flue gas makes Fe$^{2+}$ easily oxidized to Fe$^{3+}$, thus losing the ability of complexing NO, resulting in high operating cost and inability to run steadily. It is very important to achieve efficient regeneration of the absorbent and increase NO absorption in the Fe$^{2+}$ complexation system. They are the key to the industrial application of the Fe$^{2+}$ complexation absorption process. Researchers have developed a variety of advanced technologies to regenerate Fe(II)EDTA, such as bioreduction, catalytic, and reductant reduction methods. However, these techniques have limited regenerative effects. Therefore, Fe$^{2+}$ complexation absorption processes are mostly in the laboratory stage or in the pilot-scale stage. The current research focuses on how to improve the regeneration effect of the Fe$^{2+}$ complexation system. However, there are few reports on how to increase NO uptake in the Fe$^{2+}$ complexation system.

2-Phosphonate-butane-1,2,4-tricarboxylic acid (PBTCA) is a five-component organic acid, belonging to a series of ultra-low phosphorus water quality stabilizers. It has unique corrosion...
and scale inhibition performance, is non-toxic and pollution-free, and is widely used in the treatment of circulating cooling water.38–42 In addition, it is often used as an inhibitor, a scale inhibitor, a dispersant, and a modifier.43–49

PBTCA is a highly effective complexing agent because it contains both phosphonic acid (−PO\(_3\)H\(_2\)) and carboxylic acid (−COOH) groups. In an aqueous solution, PBTCA can also be efficiently complexed with Fe\(^{2+}\) to prevent the formation of the Fe(OH)\(_2\) precipitate and block pipes. In the coking industry, PBTCA as a ligand to make an iron complex catalyst is used for H\(_2\)S removal in gas, with high desulfurization efficiency.49 Therefore, PBTCA, as a ligand in the Fe\(^{2+}\) complexation absorption system, is used in the wet denitrification process of Fe\(^{2+}\) complexation. It is expected to be effective in denitrification and also play a role in corrosion and scale inhibition, but there is no relevant report in the existing literature.

In this paper, PBTCA and ethylenediaminetetraacetic acid (EDTA) were used as ligands to form a complex system. The NO removal characteristics of the system were studied at different temperatures, pHs, Fe\(^{2+}\) concentrations, O\(_2\) contents, NO concentrations, CO\(_2\) contents, and SO\(_2\) concentrations. This study can provide ideas for catalyst optimization of Fe\(^{2+}\) complexation wet denitrification technology and lay a certain foundation for its industrial application.

2. EXPERIMENTAL SECTION

2.1. Materials. FeSO\(_4\)·7H\(_2\)O (≥99.0%), Na\(_2\)EDTA (≥99.0%), Na\(_2\)CO\(_3\) (≥99.8%), and chromic silica gel were purchased from Tianjin KemIou Chemical Reagent Co., LTD. PBTCA (50%), H\(_3\)PO\(_4\) (≥99.0%), and H\(_2\)SO\(_4\) (≥98.0%) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. Anhydrous glucose (99.5%) was purchased from Tianjin Kaitong Chemical Reagent Co., LTD. Nitrogen (N\(_2\), 99.99%), oxygen (O\(_2\), 99.99%), and CO\(_2\) (99.99%) are provided by Taiyuan Anxuhongyun Science and Technology Development Co., LTD. Nitric oxide (1.0% NO, balanced by N\(_2\)) and sulfur dioxide (1.0% SO\(_2\), balanced by N\(_2\)) were provided by Jining Xili Special Gas Co., LTD. The above drugs are analytical grade reagents that can be purchased commercially and can be used without further purification.

2.2. Experimental Device. The experimental device is shown in Figure 1, including flue gas supply system, the absorption system, the heating system, the drying system, the gas detection system, and the tail gas treatment system. The flue gas supply system consists of N\(_2\), NO, O\(_2\), SO\(_2\), CO\(_2\), and the corresponding flow controllers. The absorption system is composed of two self-made bubbling reactors with a diameter of 80 mm and a height of 185 mm. The temperature control in the reaction process is mainly achieved by water bath heating. The drying system is composed of a self-made absorption bottle filled with color-changing silica gel. The gas detection system is composed of a flue gas analyzer (Germany ECOM Measurement Technology Company, Isselund Germany). The exhaust gas after the reaction is discharged after being treated by the exhaust gas absorption bottle.

2.3. Experimental Process. The absorbent solution was prepared by FeSO\(_4\)·7H\(_2\)O, PBTCA, Na\(_2\)EDTA, and deionized water, and the pH of the absorbent solution was controlled by H\(_2\)SO\(_4\), H\(_3\)PO\(_4\), and Na\(_2\)CO\(_3\). The pH value was measured by a pH meter (Shanghai Electronic Scientific Instrument Co., LTD., Shanghai, China). Both absorption bottles were filled with 100 mL of absorption solution and placed in a water bath for constant temperature heating. N\(_2\) was used as the protective gas in the whole atmosphere.

Before the experiment, the residual air in the gas path was washed with nitrogen, and then the inlet concentrations of N\(_2\), O\(_2\), NO, SO\(_2\), and CO\(_2\) gases were regulated by the gas flow meter. The gas passes through the absorption bottle and the drying bottle in turn. The flue gas analyzer detects the final content of each gas. When the detection system detects that the denitrification rate is less than 70%, the experiment is stopped and the data is recorded every 1–5 min. When the experiment is over, the residual gas in the gas path is discharged after being treated by the tail gas treatment system.

2.4. Experimental Conditions. In this paper, the optimal coordination ratio of PBTCA and EDTA was determined under the condition of a flue gas flow rate of 0.0738 N m\(^3\)/h and an instantaneous gas–liquid contact time of 0.1025 s\(^{-1}\). On this basis, the characteristics of NO removal were investigated under different temperatures, pHs, Fe\(^{2+}\) concentrations, O\(_2\) contents, NO concentrations, CO\(_2\) contents, and SO\(_2\) concentrations.

The experimental conditions are shown in Table 1.
3. RESULTS AND DISCUSSION

3.1. Effect of Ligand Type on NO Removal. Figure 2 shows the denitrification characteristics of the absorbent solutions with different ligands, where A and B represent EDTA and PBTCA with an equal molar ratio of FeSO₄, respectively. A/B represents the molar ratio of EDTA and PBTCA in the solution. The denitrification conditions are as follows: the concentration of FeSO₄ is 20 mmol/L, the absorption temperature is 40 °C, the pH of the absorption solution is 9, the concentration of the NO inlet is 618.37 mg/m³, and the O₂ content is 12%.

As shown in Figure 2, when only EDTA or PBTCA was in the solution, the highest denitrification rates were 90.87 and 70.00%, respectively. When the molar ratio of EDTA to PBTCA in the solution was 1:1, 2:1, and 3:1, the maximum removal rate could reach 92.64, 94.21, and 93.62%, respectively. When the denitrification rate is above 70%, the absorption solution with EDTA and PBTCA molar ratios of 1:1, 2:1, and 3:1 can run for 22, 24, and 23 min, respectively. Compared with 18 and 1 min in EDTA and PBTCA solutions, it was significantly prolonged. This study was compared with the study using EDTA only, and the comparison results are presented in Table 2.

Table 2 shows that adding PBTCA in the Fe²⁺ + EDTA system improves the denitrification rate of the absorption solution. Under the condition of 12% O₂ and 20 mmol/L Fe²⁺, the highest denitrification rate of the absorption solution can be more than 94%.

In conclusion, adding PBTCA improves the stability of the central ion Fe²⁺ and effectively improves the denitrification capacity of the Fe(II)EDTA solution. In addition, PBTCA changed the REDOX potential of the absorption solution and effectively improved the antioxidant capacity of the solution. The concentration of Fe²⁺ was determined by o-phenanthroline colorimetry at λ = 510 nm. The test results are presented in Figure 2b. When the molar ratio of EDTA to PBTCA is 2:1, C(Fe²⁺) = 277.3939 mg/L. When only the EDTA ligand was used, C(Fe²⁺) = 258.1441 mg/L. At the same time, the initial REDOX potentials of the two absorbents were −462 and −240 mV, respectively. According to the denitrification rate, the Fe²⁺ concentration, and the REDOX potential, it is further proved that PBTCA can effectively improve the antioxidant capacity of the solution. PBTCA can effectively improve the antioxidant capacity of the solution. When the molar ratio of EDTA to PBTCA is 2:1, the denitrification ability of the solution system is the best. It can be seen from the denitrification rate that Fe(II)EDTA has a stronger complexing ability of NO than Fe(II) PBTCA. If the PBTCA concentration is too high, it will compete with EDTA for Fe(II)EDTA and form Fe(II) PBTCA, which is not easy to bind to NO. On the contrary, if the PBTCA concentration is too small, the inhibition effect of Fe²⁺ oxidation is not obvious. In addition, when the molar ratio of EDTA to PBTCA is 2:1, the PBTCA can not only prevent the rapid oxidation of Fe²⁺ but also cannot compete with EDTA for Fe²⁺.

PBTCA not only improves the properties of the absorption solution but also saves the cost of flue gas denitration. The price of the two ligands is found on the Alibaba website (https://chem.1688.com/): Na₂EDTA ($1671.04/ton) and

---

**Table 1. Experimental Conditions**

| items | influence factors | specifications |
|-------|------------------|---------------|
| absorption liquid | temperature (°C) | 30, 40, 50, 60 |
| smoke | pH value | 5, 7, 9, 11 |
|       | Fe²⁺ concentration (mmol/L) | 10, 20, 30, 40 |
|       | O₂ content (%) | 2, 5, 8, 12, 16 |
|       | NO concentration (mg/m³) | 357.6, 470.2, 598.8, 716.3, 840.0 |
|       | CO₂ content (%) | 0, 5, 6, 9, 11 |
|       | SO₂ concentration (mg/m³) | 0, 410.1, 843.8, 1243.4, 1300.9, 1700.6 |

25. Analytical Methods. A flue gas analyzer was used to measure NO or SO₂ in flue gas before and after absorption. The absorption efficiency of NO or SO₂ can be defined as

\[ \eta = \frac{c_{\text{in}} - c_{\text{out}}}{c_{\text{in}}} \times 100\% \]

where \( \eta_{\text{NO}} \) stands for NO absorption efficiency, \( \eta_{\text{SO₂}} \) stands for SO₂ absorption efficiency, \( c_{\text{in}} \) stands for the concentration of NO or SO₂ at the inlet, mg/m³, and \( c_{\text{out}} \) stands for the concentration of NO or SO₂ at the outlet, mg/m³.

---

![Figure 2. (a) Effect of ligand type on NO removal. (b) Fe²⁺ concentration.](https://chem.1688.com/)
Table 2. Comparison of Effects from Various Denitration Systems

| absorbent                  | experimental condition | denitrification effect | references |
|---------------------------|------------------------|------------------------|------------|
| Fe$^{3+}$ + EDTA          | 3% $O_2$, $Fe^{2+}$; 25 mmol/L | $\eta_{\text{max}} > 97\%$ | 50         |
| Fe$^{3+}$ + EDTA          | a $O_2$, $Fe^{3+}$; 50 mmol/L | $\eta_{\text{max}} > 70\%$ | 36         |
| Fe$^{3+}$ + EDTA          | 6.5% $O_2$, $Fe^{3+}$; 36 mmol/L | $\eta_{\text{max}} > 94\%$ | 24         |
| Fe$^{3+}$ + EDTA          | 5% $O_2$, $Fe^{3+}$; 75 mmol/L | $\eta_{\text{max}} > 97\%$ | 51         |
| Fe$^{3+}$ + EDTA          | 5% $O_2$, $Fe^{3+}$; 20 mmol/L | $\eta_{\text{max}} > 91\%$ | 52         |
| Fe$^{3+}$ + EDTA + PBTCA  | 12% $O_2$, $Fe^{3+}$; 20 mmol/L | $\eta_{\text{max}} > 90\%$ | this work  |
| Fe$^{3+}$ + EDTA + PBTCA  | 12% $O_2$, $Fe^{3+}$; 20 mmol/L | $\eta_{\text{max}} > 94\%$ | this work  |

$\eta_{\text{max}}$ represents the highest denitrification rate and $a$ represents the presence of oxygen, but the specific oxygen content is not given.

PBTCA ($2611$/ton). According to the price of 1000 L absorption solution, $12.42$ is needed for ligand only for EDTA. When ligand $n$ (EDTA)/$n$ (PBTCA) = 2:1, $13.04$ of ligand is required. According to the denitrification rate and denitrification time, the volume of the absorbent solution containing EDTA for the removal of 1 ton of NO is 28% more than the volume of the absorbent solution containing $n$ (EDTA)/$n$ (PBTCA) = 2:1. The cost of the absorption solution containing $n$ (EDTA)/$n$ (PBTCA) = 2:1 for removing 1 ton of NO is 24% lower than that containing only EDTA. In addition, PBTCA also has unique corrosion and scale inhibition properties to prevent pipeline corrosion and blockage.

Figure 3 shows the denitrification characteristics of the PBTCA and EDTA composite system at $30\text{–}60\, ^\circ\text{C}$. The denitrification conditions are as follows: the concentration of $FeSO_4$, EDTA, and PBTCA is 20 mmol/L, 13.33 mmol/L, and 6.67 mmol/L, respectively. The pH of absorption solution is 9, the concentration of the NO inlet is 618.37 mg/m$^3$, and the $O_2$ content is 12%.

3.2 Effect of Absorption Solution Temperature on NO Removal. As shown in Figure 3, $40\, ^\circ\text{C}$ has the best denitrification efficiency and the longest denitrification time. When the temperature decreases or increases, both the denitrification efficiency and the denitrification time decrease. After running for 6 min, the denitrification rates at all temperatures reached the highest point, which were 92.67, 94.21, 90.67, and 87.10%, respectively. When the denitrification rate is more than 70% and the absorption liquid temperature is $40\, ^\circ\text{C}$, its running time can reach 24 min. However, when the absorption liquid temperature increases to $60\, ^\circ\text{C}$, its running time is only 9 min.

The above results show that the temperature has four effects on NO removal by complexation absorption. First, increasing the temperature can increase the energy of the molecules, accelerate the movement of the molecules, and increase the mass-transfer coefficient $K_a$ of NO gas.$^{55}$ Second, high temperature will reduce the solubility of NO, which is not conducive to gas–liquid mass transfer, and the strong influence of molecular acceleration is also weakening.$^{56}$ Third, higher temperature will increase the oxidation degree of Fe$^{2+}$, thus reducing the denitrification capacity. Finally, the stability of Fe(II)EDTA-NO formed by NO complexation with Fe(II)-EDTA tends to weaken at higher temperatures. Keeping an appropriate temperature is the key to ensure continuous and efficient denitrification.

Figure 4 shows the denitrification characteristics of the PBTCA and EDTA composite system at pH = 5–11. The denitrification conditions are as follows: the concentrations of FeSO$_4$, EDTA, and PBTCA are 20, 13.33, and 6.67 mmol/L, respectively. The absorption liquid temperature is $40\, ^\circ\text{C}$, the NO inlet concentration is 618.37 mg/m$^3$, and the $O_2$ content is 12%.

3.3 Effect of pH of Absorption Solution on NO Removal. As shown in Figure 4, except for pH = 9, the denitrification time increases and the denitrification rate increases with the increase of pH. When the experimental ran for 4 min, the denitrification rates of pH = 5, 7, 9, and 11 all reached the highest point, which were 84.98, 90.44, 94.21, and 90.93%, respectively. When the denitrification rate is above 70% and
the absorption solution pH is 9, the operation time can reach 24 min. However, when the absorption solution pH increases to 11, the operation time is only 17 min.

The above results show that the pH has dual effects on the removal of NO by the complexation absorption method. First, when the pH of the absorption solution is too low, there will be reaction 2, and Fe(II) will be oxidized to Fe(III) and lose the ability of complexing NO. At the same time, the denitrification rate is reduced and the denitrification time is shortened. Second, when the pH of the absorption solution is too high, reaction 3 will occur, and Fe(III) will generate Fe(OH)_2 precipitation and deactivate.

### (2)

\[ 4\text{Fe(II)EDTA}^{2+} + \text{O}_2 + 4\text{H}^+ = 4\text{Fe(III)EDTA}^- + 2\text{H}_2\text{O} \]

### (3)

\[ \text{Fe}^{3+} + 2\text{OH}^- = \text{Fe(OH)}_2 \]

#### 3.4. Effect of Fe^{2+} Concentration NO Removal

As shown in Figure 5, the denitrification rate increases with the increase of Fe^{2+} concentration in the absorption solution. Both the time required for the highest denitrification rate and the overall denitrification time increased. The concentration of absorption solution was 10, 20, 30, and 40 mmol/L, and the highest denitrification rates were 86.92, 94.21, 95.75, and 97.17%, respectively. When the denitrification rate is above 70% and the concentration of Fe^{2+} in the absorption solution is 10 mmol/L, the running time is only 7 min. On the contrary, when the concentration of Fe^{2+} is increased to 40 mmol/L, the running time can reach 26 min.

Figure 5 shows the denitrification characteristics of the PBTCA and EDTA composite system at a Fe^{2+} concentration of 10–40 mmol/L. The denitrification conditions are as follows: the flue gas temperature is 40 °C, the pH of the absorption solution is 9, the NO concentration is 618.37 mg/m³, and the O_2 content is 12%.

The results showed that the concentration of the absorption liquid Fe^{2+} complex absorption removal NO has a positive impact. With the increase of ferrous complex concentration, more unstable water molecules in the solution bind to the complex site of the central ion Fe^{3+}, resulting in the increase of its kinetic instability. A large amount of NO can be captured quickly, so that the solubility of NO in the absorption solution increases correspondingly, and the denitrification rate of the absorption solution is improved. However, it can also be seen from the figure that the extent of increase in denitrification time does not match the extent of increase in Fe^{2+} concentration. This is mainly because when the concentration of Fe^{3+} increases, the oxidation rate of Fe^{3+} will be accelerated as well as the absorption of NO. Moreover, increased Fe^{3+} concentration will increase the operating cost. The optimum concentration of Fe^{3+} is 20 mmol/L.

Figure 6 shows the denitrification characteristics of the PBTCA and EDTA composite system with an O_2 content of 2–16%. The denitrification conditions are as follows: the flue gas flow range is 0.0666–0.07722 N m⁻³/h, and the instantaneous gas–liquid contact time is 0.0925–0.1073 s⁻¹. The concentration of FeSO₄, EDTA, and PBTCA was 20, 13.33, and 6.67 mmol/L, respectively. The absorption temperature was 40 °C, the pH of the absorption solution was 9, and the concentration of NO inlet was 618.37 mg/m³.

#### 3.5. Effect of O_2 Content on NO Removal

As shown in Figure 6, with the increase of O_2 content, the denitrification rate decreases, and the time required for the highest denitrification rate and the overall denitrification time become shorter. When the O_2 content was 2, 5, 8, 12, and 16%, the highest denitrification rates were 96.13, 95.39, 94.66, 94.21, and 90.56%, respectively. When the denitrification rate is above 70% and the O_2 content in the gas is 2%, the operation time can reach 58 min. In contrast, when the O_2 content increased to 16%, the running time was only 13 min.

The results show that the O_2 content has a negative effect on NO removal by complexation absorption. The greater the O_2 concentration in the gas inlet, the greater the amount of Fe^{3+} oxidized to Fe^{4+}. Therefore, when the concentration of Fe(II)EDTA decreases, the solution will lose the ability to form the complex with NO and the denitrification time will become shorter.  

Figure 7 shows the denitrification characteristics of the PBTCA and EDTA composite system at a NO concentration of 357.55–840.00 mg/m³. The denitrification conditions are as follows: the flue gas flow range is 0.072–0.084 N m⁻³/h, and the instantaneous gas–liquid contact time is 0.1005–0.1056 s⁻¹. The concentrations of FeSO₄, EDTA, and PBTCA were 20, 13.33, and 6.67 mmol/L, respectively. The absorption
The temperature was 40 °C, the pH of the absorption solution was 9, and the O₂ content was 12%.

3.6. Effect of NO Concentration on NO Removal. As shown in Figure 7, with the increase of NO concentration, the denitrification rate increases and the denitrification time becomes longer. When the NO concentration was 357.55, 470.20, 589.78, 716.33, and 840.00 mg/m³, the highest denitrification rates were 92.19, 92.88, 93.55, 93.98, and 95.24%, respectively. When the denitrification rate is above 70% and the concentration of NO is 357.55 mg/m³, the running time is only 15 min. However, when the concentration of NO is increased to 840.00 mg/m³, the running time can reach 28 min. The results show that the concentration of NO has a positive effect on the removal of NO by the complexation absorption method. According to the double membrane theory, the partial pressure of NO in the gas phase increases with the increase of NO concentration. In this way, the gas–liquid mass-transfer driving force of NO is enhanced, more NO will combine with Fe(II)EDTA, and the denitrification time increases.

Figure 8 shows the denitrification characteristics of the PBTCA and EDTA composite system at a CO₂ content of 0–11%. The denitrification conditions are as follows: the flue gas flow range is 0.0738–0.0779 N m⁻³/h, and the instantaneous gas–liquid contact time is 0.1025–0.1152 s⁻¹. The concentrations of FeSO₄, EDTA, and PBTCA were 20, 13.33, and 6.67 mmol/L, respectively. The absorption solution temperature was 40 °C, the absorption solution pH was 9, the NO inlet concentration was 618.37 mg/m³, and the O₂ content was 12%.

3.7. Effect of CO₂ Content on NO Removal. As shown in Figure 8, with the increase of CO₂ content, the denitrification rate decreases and the denitrification time becomes shorter. When the CO₂ content was 0, 5, 6, 9, and 11%, the highest denitrification rates were 94.21, 92.48, 90.39, 88.09, and 84.06%, respectively. When the denitrification rate is above 70% and the CO₂ content is 0%, the operation time can reach 24 min, while when the CO₂ content is increased to 11%, the operation time is only 12 min.

The results showed that when the CO₂ content increased, the maximum NO removal rate and the denitrification time decreased significantly. This indicates that the presence of CO₂ is not conducive to the removal of NO, and CO₂ has a significant inhibitory effect on the denitrification process. Because CO₂ dissolved in water will reduce the pH of the absorption solution, and the greater the concentration, the greater the pH reduction. As shown in eq 2, the active component Fe²⁺ is easily oxidized to Fe³⁺ under acidic conditions, losing the complexing ability of NO and shortening the denitrification time.

Figure 9 shows the denitrification characteristics of the PBTCA and EDTA composite system at a SO₃ concentration of 0–1700.57 mg/m³. The denitrification conditions are as follows: the flue gas flow range is 0.0738–0.0779 N m⁻³/h, and the instantaneous gas–liquid contact time is 0.1025–0.1083 s⁻¹. The concentrations of FeSO₄, EDTA, and PBTCA were 20, 13.33, and 6.67 mmol/L, respectively. The absorption solution temperature was 40 °C, the absorption solution pH was 9, the NO inlet concentration was 618.37 mg/m³, and the O₂ content was 12%.

3.8. Effect of SO₃ Concentration on NO Removal. Figure 9a shows the denitrification rate, denitrification time, and desulfurization rate of absorption solution under different SO₃ concentrations. The removal rate of SO₂ was 100% during the whole process. When the SO₂ concentration was 0 mg/m³, 410.12% mg/m³, 843.76 mg/m³, 1243.43 mg/m³, and 1700.57 mg/m³, the highest denitrification rates were 94.21, 88.04, 88.59, 87.81, and 88.83%, respectively. When the denitrification rate is above 70% and the SO₂ concentration is 0 mg/m³, the running time is only 24 min. However, when the SO₂ concentration is increased to 1700.57 mg/m³, the running time can reach 32 min. The above results show that the presence of SO₂ in flue gas has two effects on the denitrification process. On the one hand, the solubility of SO₂ in Fe(II)EDTA solution is much higher than that of NO. Compared with NO, SO₂ has a competitive advantage in the gas–liquid mass-transfer process and can enter the liquid-phase reaction zone more quickly for reaction. Therefore, the complexation of NO and Fe²⁺ is affected to a certain extent. On the other hand, SO₂²⁻ generated by SO₂ dissolved in water will reduce Fe³⁺ and achieve the effect of regenerating a small amount of absorption liquid, thus making the removal time of NO longer. Figure 9b shows the difference in denitrification rate and denitrification time between the presence and absence of SO₂ in
the solution multiple cycles after the regeneration of absorption solution by Na₂S. The denitrification rate in the first four cycles without SO₂ was higher than that in the presence of 1300.90 mg/m³ SO₂. After the fourth cycle, the denitrification rate without SO₂ was lower than that in the presence of 1300.90 mg/m³ SO₂. The removal rate of SO₂ was 100% during the cycle. When the denitrification rate was kept above 70%, the running time of the experiment with a SO₂ concentration of 0 mg/m³ was only 26 min in the third cycle. On the contrary, when the SO₂ concentration was increased to 1300.90 mg/m³, the running time was up to 30 min. The effective denitrification time in the presence of SO₂ is longer than that in the absence of SO₂ with the increase of cycles. These results indicate that SO₂ has a dual effect on NO removal with the increase of cycles. The main reaction of the first four cycles is the competition of SO₂ and NO with the Fe(II)EDTA reaction, which affects the binding rate of NO and Fe(II)EDTA and reduces the denitrification rate. After the fourth time, the amount of SO₂ dissolved in water to form SO₂⁻ increases, which may combine with Fe(II)EDTA to form Fe(II)EDTA(SO₂⁻). Among them, Fe(II)EDTA-(SO₂⁻) has a stronger complexing ability of NO than that of Fe(II)EDTA, thus increasing the denitrification rate. At the same time, SO₂⁻ formed after SO₂ dissolved in water also enhanced the regeneration of the nitrite complex to a certain extent. Combined with Na₂S reduction, the effective denitrification time is prolonged.

4. CONCLUSIONS

(1) The introduction of PBTCA on the basis of ligand EDTA can effectively improve the denitrification capacity of Fe(II)EDTA solution. When the molar ratio of EDTA to PBTCA is 2:1, the denitrification capacity of the solution is the strongest, and the highest denitrification rate can reach 94.21%.

(2) Temperature and pH have a dual effect on NO removal. When the temperature increased from 30 to 40 °C, the maximum denitrification rate increased from 92.67 to 94.21%, while when the temperature continued to increase to 60 °C, the maximum denitrification rate decreased to 87.10%. In the range of pH 5–11, with the increase of pH from 5 to 9, the NO removal rate increased from 84.98 to 94.21%, while with the increase of pH from 9 to 11, the highest denitrification rate decreased to 90.93%.

(3) When the concentration of Fe²⁺ in the absorption solution increased from 10 to 40 mmol/L, the highest denitrification rate increased from 86.92 to 97.17%.

(4) Both O₂ and CO₂ are not conducive to the removal of NO. When the O₂ content increased from 0 to 16%, the maximum denitrification rate decreased from 96.13 to 90.56%.

(5) With the increase of CO₂ content from 0 to 11%, the maximum denitrification rate decreased from 94.21 to 84.06%. With the continuous increase of O₂ or CO₂ content, the more obvious the inhibition of NO absorption by absorption solution, the lower the denitrification rate of absorption solution.

(6) With the increase of NO concentration from 357.55 to 840.00 mg/m³, the NO removal efficiency increased slightly.

(7) SO₂ has a dual effect on NO removal. On the one hand, at the beginning of the cyclic reaction, SO₂ will compete with NO to react with Fe(II)EDTA and the denitrification rate is reduced. On the other hand, SO₂⁻ formed after SO₂ dissolved in water also enhanced the regeneration of nitrite complex to a certain extent. Meanwhile, with the progress of the reaction, SO₂⁻ and Fe(II)EDTA will form Fe(II)EDTA(SO₂⁻) with a stronger NO complexing ability.

AUTHOR INFORMATION

Corresponding Author
Guoqiang Li — State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, People’s Republic of China; orcid.org/0000-0003-1841-4693; Email: liguoqiang01@tyut.edu.cn

Authors
Liwei Ma — State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, People’s Republic of China
Youqian Wang — State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, People’s Republic of China
Siqi Chai — State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China
Guojie Zhang — State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China; orcid.org/0000-0001-5830-3539

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c01641

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Susianto; Pettrissans, M.; Zoulalian, A. Influence of the pH on the interactions between nitrite and sulfite ions. Kinetic of the reaction at pH 4 and S. Ind. Eng. Chem. Res. 2001, 40, 6068–6072.
(2) Sun, C.; Zhang, Y. Complexing absorption of NO by Cobalt(II)–Histidine. Energy Fuels 2017, 32, 688–695.
(3) He, F.; Deng, X.; Ding, J. Simultaneous absorption of NO and SO₂ by combined use and FeII-EDTA reaction systems. RSC Adv. 2018, 8, 32338–32145.
(4) Zhu, X.; He, F.; Xia, M.; Liu, H.; Ding, J. Evaluation of Fe(III)/EDTA reduction with ascorbic acid in a wet denitration system. RSC Adv. 2019, 9, 24386–24393.
(5) Ye, J.; Shang, J.; Li, Q.; Xu, W.; Liu, J.; Feng, X.; Zhu, T. The use of vacuum ultraviolet irradiation to oxidize SO₂ and NO for simultaneous desulfurization and denitrification. J. Hazard. Mater. 2014, 271, 89–97.
(6) Hao, R.; Mao, X.; Wang, Z.; Zhao, Y.; Wang, T.; Sun, Z.; Yuan, B.; Li, Y. A novel method of ultraviolet/NaClO reaction system for NO removal: Mechanism and kinetics. J. Hazard. Mater. 2019, 368, 234–242.
(7) Hao, R.; Zhao, Y.; Yuan, B.; Zhou, S.; Yang, S. Establishment of a novel advanced oxidation process for economical and effective removal of SO₂ and NO. J. Hazard. Mater. 2016, 318, 224–232.
(8) Jiang, W.; Xu, Q.; Wei, X. Use of cobalt(II) chelates of monothiol-containing ligands for the removal of nitric oxide. J. Hazard. Mater. 2019, 374, 50–57.
(9) Lee, I. Y.; Kim, D. W.; Lee, J. B.; Yoo, K. O. A practical scale evaluation of sulfated V₄O₅/TiO₂ catalyst from metatitanic acid for selective catalytic reduction of NO by NH₃. Chem. Eng. J. 2002, 90, 267–272.
(10) Long, X.-L.; Xiao, W.-D.; Yuan, W.-K. Simultaneous absorption of NO and SO₂ into hexaminecobalt(II)/iodide solution. Chemosphere 2005, 59, 811–817.
(11) Amin, N. A. S.; Chong, C. M. SCR of NO with C,H₈ in the presence of excess O₂ over Cu/Ag/CeO₂-ZrO₂ catalyst. Chem. Eng. J. 2005, 113, 13–25.
(12) Wu, Z.; Wang, L.; Zhao, W. Kinetic study on regeneration of FeII-EDTA in the wet process of NO removal. Chem. Eng. J. 2008, 140, 130–135.
(13) Wang, Y.; Li, H.; Wang, S.; Wang, X.; He, Z.; Hu, J. Investigation of sulfated CaCl₂/TiO₂ catalyst for simultaneous removal of HgO and NO in SCR process. Fuel Process. Technol. 2019, 188, 179–189.
(14) Du, Q.; Zhao, H.; Ming, L.; Gao, J.; Zhao, G.; Wu, S. Experimental investigation on the kinetics of NO complex absorption through FeII-EDTA solvent in a double-stirred reactor. Ind. Eng. Chem. Res. 2011, 50, 4425–4431.
(15) He, F.; Deng, X.; Chen, M. Kinetics of FeII-EDTA complex reduction with iron powder under aerobic conditions. RSC Adv. 2016, 6, 38416–38423.
(16) Adewuyi, Y. G.; Khan, M. A. Nitric oxide removal by combined persulfate and ferrous–EDTA reaction systems. Chem. Eng. J. 2015, 281, 575–587.
(17) Wang, J.; Wu, C.; Chen, J.; Zhang, H. Denitrification removal of nitric oxide in a rotating drum biofilter. Chem. Eng. J. 2006, 121, 45–49.
(18) He, F.; Zhu, X.; Zhong, L.; Li, Z.; Qian, Y. Nitric oxide removal from flue gas by ferrate(VI)/urea solutions. Chin. Chem. Lett. 2021, 32, 3175–3179.
(19) Adewuyi, Y. G.; Owsu, S. O. Aqueous absorption and oxidation of nitric oxide with oxone for the treatment of tail gases: Process Feasibility, Stoichiometry, Reaction Pathways, and Absorption Rate. Ind. Eng. Chem. Res. 2003, 42, 4084–4100.
(20) Tsai, C.-H.; Yang, H.-H.; Jou, C. G.; Lee, H. M. Reducing nitric oxide into nitrogen via a radio-frequency discharge. J. Hazard. Mater. 2007, 143, 409–414.
(21) Sakai, M.; Su, C.; Sasaoka, E. Simultaneous removal of SO₂ and NOₓ using slaked lime at low temperature. Ind. Eng. Chem. Res. 2002, 41, 5029–5033.
(22) Xu, Z.-H.; Xiao, X.; Jia, Y.; Fang, P.; Huang, J.-H.; Wu, H.-W.; Tang, Z.-J.; Chen, D.-Y. Simultaneous removal of SO₂ and NO by O₃ oxidation combined with wet absorption. ACS Omega 2020, 5, 5844–5853.
(23) He, F.; Zhu, X.; Chen, X.; Ding, J. Performance, mechanism, and kinetics of NO removal by combined ascorbic acid and FeII-EDTA reaction systems. Fuel 2021, 282, 119070.
(24) Xu, C.; Chang, G.-G.; Liu, H.-X.; Xu, W.-J.; Zhang, G.-X. Highly efficient heterogeneous catalytic reduction of Fe(II)/EDTA-NO in industrial denitrification solution over Pd/AC catalyst. Ind. Eng. Chem. Res. 2019, 58, 22875–22883.
(25) Suchecki, T. T.; Mathews, B.; Augustyniak, A. W.; Kumazawa, H. Applied kinetics aspects of Ferric EDTA complex reduction with metal powder. Ind. Eng. Chem. Res. 2014, 53, 14234–14240.
(26) Kumaraswamy, R.; van Dongen, U.; Kuenen, J. G.; Abma, W.; van Loosdrecht, M. C.; Muyzer, G. Characterization of microbial communities removing nitrogen oxides from flue gas: the BioDeNOₓ process. Appl. Environ. Microbiol. 2005, 71, 6345–6352.
(27) Dong, X.; Zhang, Y.; Zhou, J.; Li, N.; Chen, M. Reduction of Fe(III)/EDTA in a NOₓ scrubber liquor by a denitrifying bacterium and the effects of inorganic sulfur compounds on this process. Bioresour. Technol. 2012, 120, 127–132.
(28) Yang, X.-J.; Yang, L.; Long, L.; Xiong, J.; Wang, K. Kinetics of the Fe(III)-EDTA reduction by sulfite under the catalysis of activated carbon. Energy Fuels 2011, 25, 4248–4255.
(29) Long, X.-L.; Yang, L.; Chou, X.-W.; Li, C.; Yuan, W.-K. Reduction of Fe(III)/EDTA− catalyzed by activated carbon modified with ammonia solution. Environ. Prog. Sustainable Energy 2014, 33, 99–106.
(30) He, F.; Deng, X.; Chen, M. Mechanism and kinetics of FeII/EDTA-NO reduction by iron powder under anaerobic condition. Fuel 2016, 186, 605–612.
(31) Adewuyi, Y. G.; Khan, M. A. Nitric oxide removal from flue gas by combined persulfate and ferrous–EDTA solutions: Effects of persulfate and EDTA concentrations, temperature, pH and SO₂. Chem. Eng. J. 2016, 304, 793–807.
(32) Yan, B.; Yang, J.; Guo, M.; Chen, G.; Li, Z.; Ma, S. Study on NO enhanced absorption using FeII-EDTA in (NH₄)₂SO₄ solution. J. Ind. Eng. Chem. 2014, 20, 2528–2534.
(33) Jiang, W.; Wang, X.; Xu, Q.; Xiao, J.; Wei, X. The regeneration of Fe-EDTA denitration solutions by nanoscale zero-valent iron. RSC Adv. 2019, 9, 132–138.
(34) He, F.; Qian, Y.; Xu, J. Performance, Mechanism, and Kinetics of Fe(III)EDTA reduction by thiourea dioxide. Energy Fuels 2019, 33, 3331–3338.
(35) Wang, X.; Zhang, Y.; Dong, X.; Chen, M.; Shi, Z.; Zhou, J. Fe(II)EDTA–NO reduction by sulfide in the anaerobic aqueous phase: Stoichiometry and Kinetics. Energy Fuels 2013, 27, 6024–6030.
(36) Zhu, H.; Nie, Z.; Hu, Y.; Wang, J.; Bai, H.; Li, Y.; Guo, Q.; Wang, C. Experimental study on denitration performance of iron Complex-Based absorption solutions and their regeneration by Zn. Energy Fuels 2019, 33, 8998–9003.
(37) He, F.; Deng, X.; Chen, M. Evaluation of Fe(II)EDTA-NO reduction by zinc powder in wet flue gas denitrification technology with Fe(II)EDTA. *Fuel* 2017, 199, 523–531.

(38) Wang, Z.; Cai, L. Study of organic phosphonocarboxylic acids as water stabilizing agent. I. Corrosion and scale inhibition of 2-phosphonobutane-1, 2, 4-tricarboxylic acid. *J. East China Inst. Chem. Technol.* 1989, 15, 605–614.

(39) Liao, H. Synthesis process, properties and application of PBTCA. *Sichuan Chem.* 2000, 4, 12–13.

(40) Yin, D.; Wang, J.; Zhang, X. Synthesis and structure of PBTCA. *J. Dalian Univ. Technol.* 2001, 41, 42–45.

(41) Zhang, B.; Zhang, L.; Li, F.; Hu, W.; Hannam, P. M. Testing the formation of Ca-phosphate precipitates and evaluating the anionic polymers as Ca-phosphate precipitates and CaCO3 scale inhibitor in simulated cooling water. *Corros. Sci.* 2010, 52, 3883–3890.

(42) Liang, X.; Liu, Y. Preparation of PBTCA by low pressure hydrolysis. *Guangdong Chem. Ind.* 2021, 48, 1–4.

(43) Shen, Z.; Ren, H.; Xu, K.; Geng, J.; Ding, L. Inhibition effect of phosphorus-based chemicals on corrosion of carbon steel in secondary-treated municipal wastewater. *Water Sci. Technol.* 2013, 67, 2412–2417.

(44) Liu, C.; Zhang, W.; Song, S.; Li, H.; Liu, Y. Flotation separation of smithsonite from calcite using 2-phosphonobutane-1,2,4-tricarboxylic acid as a depressant. *Powder Technol.* 2019, 352, 11–15.

(45) Yang, B.; Zhu, Z.; Yin, W.; Sun, Q.; Sun, X.; Han, H.; Sheng, Q.; Yao, J. Selective adsorption of an eco-friendly and efficient depressant PBTCA onto dolomite for effective flotation of fluorapatite from dolomite. *Chem. Eng. J.* 2020, 400, 125780.

(46) Zhang, G.; Ge, J.; Sun, M.; Pan, B.; Mao, T.; Song, Z. Investigation of scale inhibition mechanisms based on the effect of scale inhibitor on calcium carbonate crystal forms. *Sci. China, Ser. B: Chem.* 2007, 50, 114–120.

(47) Desroches, M. J.; Castillo, I. A.; Munz, R. J. Determination of particle size distribution by laser diffraction of Doped-CeO2 powder suspensions: Effect of Suspension Stability and Sonication. *Part. Part. Syst. Charact.* 2005, 22, 310–319.

(48) Huang, Y.; Zheng, H.; Li, H.; Zhao, C.; Zhao, R.; Li, S. Highly selective uranium adsorption on 2-phosphonobutane-1,2,4-tricarboxylic acid-decorated chitosan-coated magnetic silica nanoparticles. *Chem. Eng. J.* 2020, 388, 124349.

(49) He, Y.; Yu, Y.; Guan, J.; Chen, Y.; Zhang, S.; Lu, S. Research and application of PBTCA in coking enterprises. *Henan Metallurgy* 2020, 8, 21–24.

(50) Li, W.; Wu, C.-Z.; Shi, Y. Metal chelate absorption coupled with microbial reduction for the removal of NOx from flue gas. *J. Chem. Technol. Biotechnol.* 2006, 81, 306–311.

(51) Yu, H.; Zhu, Q.; Tan, Z. Absorption of nitric oxide from simulated flue gas using different absorbents at room temperature and atmospheric pressure. *Appl. Energy* 2012, 93, 53–58.

(52) Zhang, Y. Performance and mechanism of FeIIEDTA denitrification solution regeneration by iron-active carbon micro-electrolysis. Master’s Thesis, Xiangtan University, Hunan, China, 2017.

(53) Luo, Q. *Coordination Chemistry*; Beijing Science Press, 2012.

(54) Suchecki, T. T.; Mathews, B.; Kumazawa, H. Kinetic study of ambient-temperature reduction of FeIIEDTA by Na2S2O3. *Ind. Eng. Chem. Res.* 2005, 44, 4249–4253.

(55) Adewuyi, Y. G.; Khan, M. A.; Sakyi, N. Y. Kinetics and modeling of the removal of nitric oxide by aqueous sodium persulfate simultaneously activated by temperature and Fe2+. *Ind. Eng. Chem. Res.* 2014, 53, 828–839.

(56) Adewuyi, Y. G.; Khan, M. A. Simultaneous NO and SO2 removal by aqueous persulfate activated by combined heat and Fe2+: experimental and kinetic mass transfer model studies. *Environ. Sci. Pollut. Res.* 2020, 27, 1186–1201.

(57) Yan, B.; Yang, J.; Guo, M.; Zhu, S.; Yu, W.; Ma, S. Experimental study on FeIIICit enhanced absorption of NO in (NH4)2SO3 solution. *J. Ind. Eng. Chem.* 2015, 21, 476–482.

(58) Adewuyi, Y. G.; Sakhi, N. Y.; Arif Khan, M. A. Simultaneous removal of NO and SO2 from flue gas by combined heat and Fe2+ activated aqueous persulfate solutions. *Chemosphere* 2018, 193, 1216–1225.

(59) Zhang, Y. Removal of Nitrogen Oxides from Flue Gas by EDTA Complexation Absorption Method. Master’s Thesis, China University of Petroleum (East China), Shandong, China, 2012.