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

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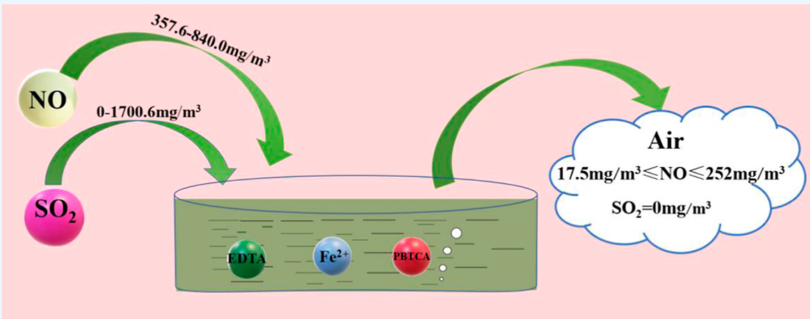

ABSTRACT: Fe^{2+} complexation wet denitrification technology has become a research hotspot. It is very important to achieve efficient regeneration of the absorbent and increase NO absorption in the Fe^{2+} complexation system. They are the key to the industrial application of the Fe^{2+} complexation 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.[1,2] It will cause certain harm to the ecological environment, such as acid rain, photochemical smog, global warming, and ozone layer destruction.[3−7] About 90−95% of NO_X in a typical flue stream is NO, which is almost insoluble in water. Currently, selective catalytic reduction (SCR) denitration technology, which is relatively mature in the industry, can effectively remove NO in flue gas.[8−13] However, SCR has some problems, such as high operating cost,[14−16] catalyst poisoning,[17,18] high reaction temperature,[19,20] and ammonia escape.[21,22]

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.[23] 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.[24−37] 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

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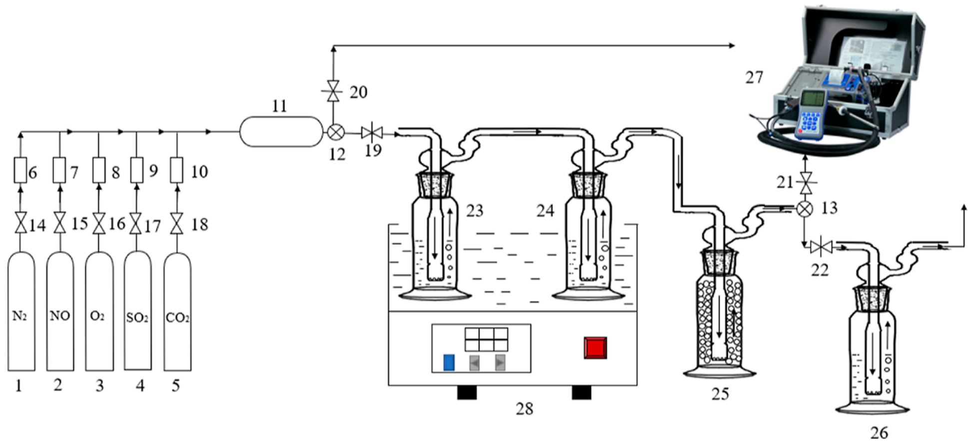

Figure 1. Schematic diagram of the experimental device: 1, N_2 cylinder; 2, NO cylinder; 3, O_2 cylinder; 4, SO_2 cylinder; 5, CO_2 cylinder; 6−10, gas flow meter; 11, mixing cylinder; 12−13, three-way valve; 14−18, pressure reducing valve; 19−22, double-way valve; 23−24, absorption bottle; 25, dry bottle; 26, exhaust gas absorption bottle; 27, flue gas analyzer; and 28, water bath pot.

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 ($-PO_3H_2$) 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_2S 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. $FeSO_4·7H_2O$ (≥99.0%), Na_2EDTA (≥99.0%), Na_2CO_3 (≥99.8%), and chromic silica gel were purchased from Tianjin KemIou Chemical Reagent Co., LTD. PBTCA (50%), H_3PO_4 (≥99.0%), and H_2SO_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 $FeSO_4·7H_2O$, PBTCA, Na_2EDTA, and deionized water, and the pH of the absorbent solution was controlled by H_2SO_4, H_3PO_4, and Na_2CO_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 denitration 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.

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Table 1. Experimental Conditions

items	influence factors	specifications
absorption liquid	temperature (°C)	30, 40, 50, 60
	pH value	5, 7, 9, 11
	Fe^{2+} concentration (mmol/L)	10, 20, 30, 40
smoke	O_2 content (%)	2, 5, 8, 12, 16
	NO concentration (mg/m^3)	357.6, 470.2, 598.8, 716.3, 840.0
	CO_2 content (%)	0, 5, 6, 9, 11
	SO_2 concentration (mg/m^3)	0, 410.1, 843.8, 1243.4, 1300.9, 1700.6

2.5. Analytical Methods. A flue gas analyzer was used to measure NO or SO_2 in flue gas before and after absorption. The absorption efficiency of NO or SO_2 can be defined as

$$\eta_{NO}(\eta_{SO_2}) = \frac{c_{in} - c_{out}}{c_{in}} \times 100\% \quad (1)$$

where η_{NO} stands for NO absorption efficiency, η_{SO_2} stands for SO_2 absorption efficiency, c_{in} stands for the concentration of NO or SO_2 at the inlet, mg/m^3, and c_{out} stands for the concentration of NO or SO_2 at the outlet, mg/m^3.

3. RESULTS AND DISCUSSION

3.1. Effect of Ligand Type on NO Removal. Figure 2 shows the denitrification characteristics of absorbent solutions with different ligands, where *A* and *B* represent EDTA and PBTCA with an equal molar ratio of $FeSO_4$, respectively. *A*/*B* represents the molar ratio of EDTA and PBTCA in the solution. The denitrification conditions are as follows: the concentration of $FeSO_4$ 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/m^3, and the O_2 content is 12%.

As shown in Figure 2, when only EDTA or PBTCA was in the solution, the highest denitration 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 Fe^{2+} + EDTA system improves the denitration rate of the absorption solution. Under the condition of 12% O_2 and 20 mmol/L Fe^{2+}, the highest denitrification rate of the absorption solution can be more than 94%.

In conclusion, adding PBTCA improves the stability of the central ion Fe^{2+} and effectively improves the denitrification capacity of the Fe(II)EDTA solution.[53] In addition, PBTCA changed the REDOX potential of the absorption solution and effectively improved the antioxidant capacity of the solution. The concentration of Fe^{2+} was determined by *o*-phenanthroline colorimetry at λ = 510 nm.[54] The test results are presented in Figure 2b. When the molar ratio of EDTA to PBTCA is 2:1, $C(Fe^{2+})$ = 277.3939 mg/L. When only the EDTA ligand was used, $C(Fe^{2+})$ = 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 denitration rate, the Fe^{2+} 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 denitration 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^{2+} 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 Fe^{2+} 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 Fe^{2+} but also cannot compete with EDTA for Fe^{2+}.

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/): Na_2EDTA ($1671.04/ton) and

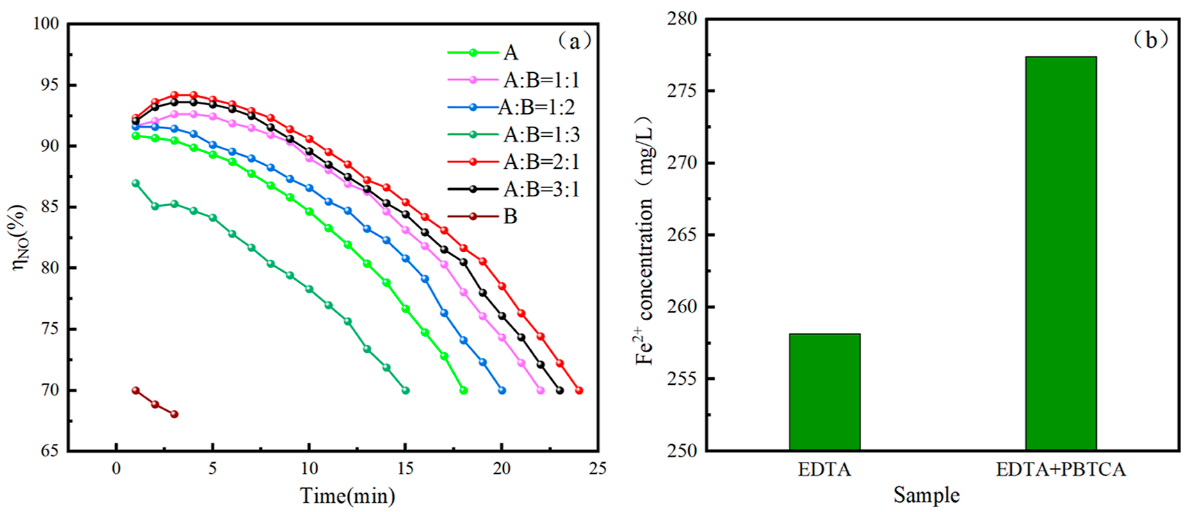

Figure 2. (a) Effect of ligand type on NO removal. (b) Fe^{2+} concentration.

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Table 2. Comparison of Effects from Various Denitration Systems[a]

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

[a] η_{max} represents the highest denitration 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 denitration rate and denitration 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 30−60 °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%.

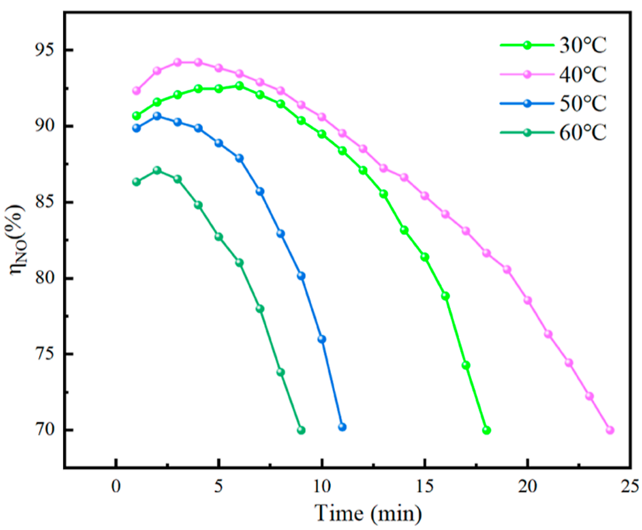

Figure 3. Effect of absorption solution temperature on NO removal.

3.2. Effect of Absorption Solution Temperature on NO Removal. As shown in Figure 3, 40 °C has the best denitration efficiency and the longest denitration time. When the temperature decreases or increases, both the denitration efficiency and the denitration 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 denitration rate is more than 70% and the absorption liquid temperature is 40 °C, its running time can reach 24 min. However, when the absorption liquid temperature increases to 60 °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_L 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 denitration 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 denitration.

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 °C, the NO inlet concentration is 618.37 mg/m^3, and the O_2 content is 12%.

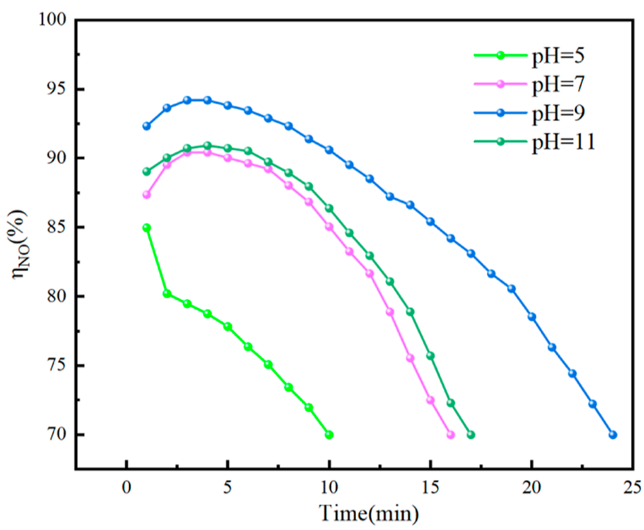

Figure 4. Effect of pH of absorption solution on NO removal.

3.3. Effect of pH of Absorption Solution on NO Removal. As shown in Figure 4, except for pH = 9, the denitration time increases and the denitration rate increases with the increase of pH. When the experiment 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

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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^{2+} will be oxidized to Fe^{3+} 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^{2+} will generate $Fe(OH)_2$ precipitation and deactivate.

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

$$Fe^{2+} + 2OH^- = Fe(OH)_2 \quad (3)$$

3.4. Effect of Fe^{2+} Concentration NO Removal. As shown in Figure 5, the denitration 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 denitration 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.

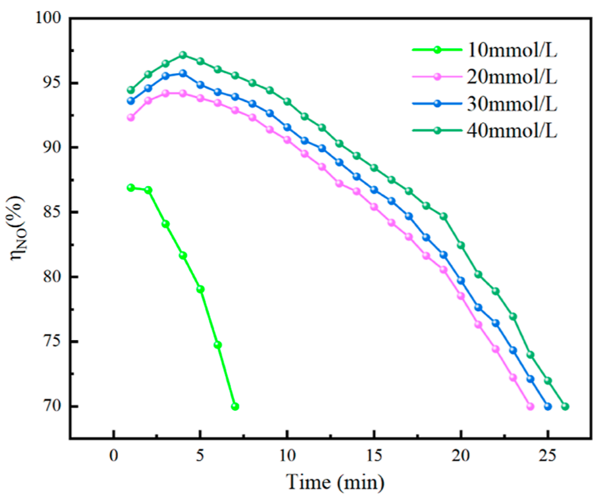

Figure 5. Effect of Fe^{2+} concentration on NO removal.

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 absorption liquid temperature is 40 °C, the pH of the absorption solution is 9, the NO concentration is 618.37 mg/m^3, 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^{2+}, 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 denitration rate of the absorption solution is improved. However, it can also be seen from the figure that the extent of increase in denitration time does not match the extent of increase in Fe^{2+} concentration. This is mainly because when the concentration of Fe^{2+} increases, the oxidation rate of Fe^{2+} will be accelerated as well as the absorption of NO. Moreover, increased Fe^{2+} concentration will increase the operating cost. The optimum concentration of Fe^{2+} 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 $FeSO_4$, 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/m^3.

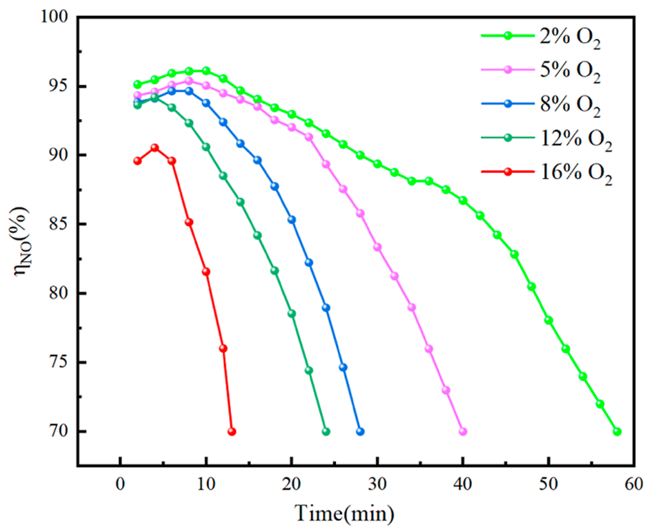

Figure 6. Effect of O_2 content on NO removal.

3.5. Effect of O_2 Content on NO Removal. As shown in Figure 6, with the increase of O_2 content, the denitration rate decreases, and the time required for the highest denitration rate and the overall denitration 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 denitration 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^{2+} oxidized to Fe^{3+}. Therefore, when the concentration of Fe(II)EDTA decreases, the solution will lose the ability to form the complex with NO and the denitration 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/m^3. The denitration conditions are as follows: the flue gas flow range is 0.072−0.076 N m^3/h, and the instantaneous gas−liquid contact time is 0.1000−0.1056 s^{-1}. The concentrations of $FeSO_4$, EDTA, and PBTCA were 20, 13.33, and 6.67 mmol/L, respectively. The absorption

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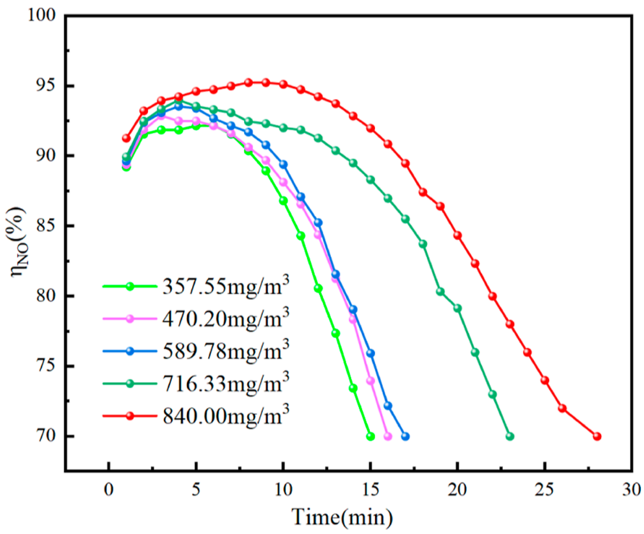

Figure 7. Effect of NO concentration on NO removal.

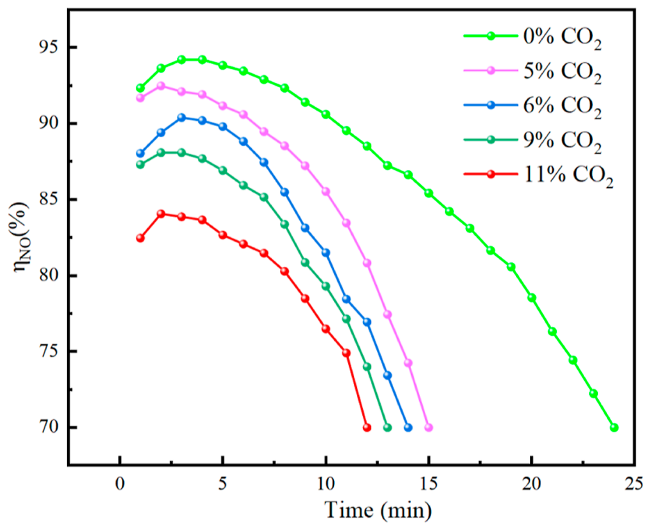

Figure 8. Effect of CO_2 content on NO removal.

temperature was 40 °C, the pH of the absorption solution was 9, and the O_2 content was 12%.

3.6. Effect of NO Concentration on NO Removal. As shown in Figure 7, with the increase of NO concentration, the denitration rate increases and the denitration time becomes longer. When the NO concentration was 357.55, 470.20, 589.78, 716.33, and 840.00 mg/m^3, 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/m^3, the running time is only 15 min. However, when the concentration of NO is increased to 840.00 mg/m^3, 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,[57] 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 denitration time increases.

Figure 8 shows the denitrification characteristics of the PBTCA and EDTA composite system at a CO_2 content of 0−11%. The denitration conditions are as follows: the flue gas flow range is 0.0777−0.0829 N m^3/h, and the instantaneous gas−liquid contact time is 0.1025−0.1152 s^{-1}. The concentrations of $FeSO_4$, 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/m^3, and the O_2 content was 12%.

3.7. Effect of CO_2 Content on NO Removal. As shown in Figure 8, with the increase of CO_2 content, the denitration rate decreases and the denitration time becomes shorter. When the CO_2 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 CO_2 content is 0%, the operation time can reach 24 min, while when the CO_2 content is increased to 11%, the operation time is only 12 min.

The results showed that when the CO_2 content increased, the maximum NO removal rate and the denitrification time decreased significantly. This indicates that the presence of CO_2 is not conducive to the removal of NO, and CO_2 has a significant inhibitory effect on the denitrification process. Because CO_2 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 Fe^{2+} is easily oxidized to Fe^{3+} under acidic conditions, losing the complexing ability of NO and shortening the denitration time.

Figure 9 shows the denitrification characteristics of the PBTCA and EDTA composite system at a SO_2 concentration of 0−1700.57 mg/m^3. The denitration conditions are as follows: the flue gas flow range is 0.0738−0.07794 N m^3/h, and the instantaneous gas−liquid contact time is 0.1025−0.1083 s^{-1}. The concentrations of $FeSO_4$, 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/m^3, and the O_2 content was 12%.

3.8. Effect of SO_2 Concentration on NO Removal. Figure 9a shows the denitration rate, denitration time, and desulfurization rate of absorption solution under different SO_2 concentrations. The removal rate of SO_2 was 100% during the whole process. When the SO_2 concentration was 0 mg/m^3, 410.12% mg/m^3, 843.76 mg/m^3, 1243.43 mg/m^3, and 1700.57 mg/m^3, 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 SO_2 concentration is 0 mg/m^3, the running time is only 24 min. However, when the SO_2 concentration is increased to 1700.57 mg/m^3, the running time can reach 32 min. The above results show that the presence of SO_2 in flue gas has two effects on the denitration process. On the one hand, the solubility of SO_2 in Fe(II)EDTA solution is much higher than that of NO. Compared with NO, SO_2 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 Fe^{2+} is affected to a certain extent. On the other hand, SO_3^{2-}/HSO_3^- generated by SO_2 dissolved in water will reduce Fe^{3+} and achieve the effect of regenerating a small amount of absorption liquid, thus making the removal time of NO longer.[58]

Figure 9b shows the difference in denitration rate and denitration time between the presence and absence of SO_2 in

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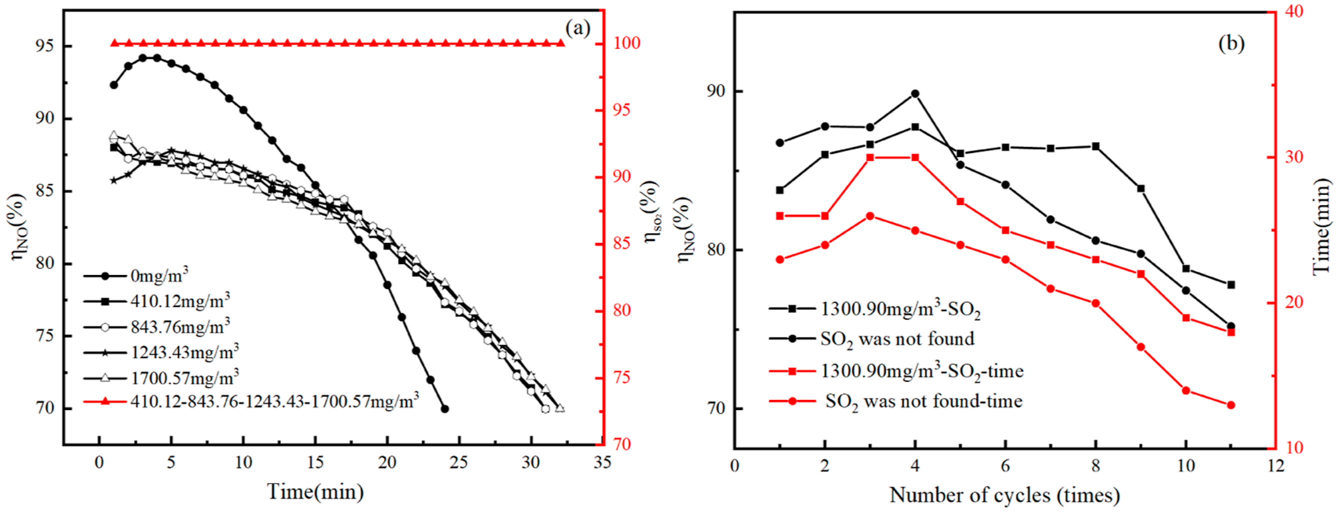

Figure 9. (a) Effect of SO_2 concentration on NO and SO_2 removal. (b) NO removal rate and time under multiple cycles of absorption solution.

the solution multiple cycles after the regeneration of absorption solution by Na_2S. The denitrification rate in the first four cycles without SO_2 was higher than that in the presence of 1300.90 mg/m^3 SO_2. After the fourth cycle, the denitrification rate without SO_2 was lower than that in the presence of 1300.90 mg/m^3 SO_2. The removal rate of SO_2 was 100% during the cycle. When the denitrification rate was kept above 70%, the running time of the experiment with a SO_2 concentration of 0 mg/m^3 was only 26 min in the third cycle. On the contrary, when the SO_2 concentration was increased to 1300.90 mg/m^3, the running time was up to 30 min. The effective denitrification time in the presence of SO_2 is longer than that in the absence of SO_2 with the increase of cycles. These results indicate that SO_2 has a dual effect on NO removal with the increase of cycles. The main reaction of the first four cycles is the competition of SO_2 and NO with the Fe(II)EDTA reaction, which affects the binding rate of NO and Fe(II)EDTA and reduces the denitration rate. After the fourth time, the amount of SO_2 dissolved in water to form SO_3^{2-} increases, which may combine with Fe(II)EDTA to form Fe(II)EDTA(SO_3^{2-}). Among them, Fe(II)EDTA-(SO_3^{2-}) has a stronger complexing ability of NO than that of Fe(II)EDTA, thus increasing the denitration rate.[59] At the same time, SO_3^{2-} formed after SO_2 dissolved in water also enhanced the regeneration of the nitrite complex to a certain extent. Combined with Na_2S reduction, the effective denitration 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 Fe^{2+} in the absorption solution increased from 10 to 40 mmol/L, the highest denitrification rate increased from 86.92 to 97.17%.

(4) Both O_2 and CO_2 are not conducive to the removal of NO. When the O_2 content increased from 0 to 16%, the maximum denitrification rate decreased from 96.13 to 90.56%.

(5) With the increase of CO_2 content from 0 to 11%, the maximum denitrification rate decreased from 94.21 to 84.06%. With the continuous increase of O_2 or CO_2 content, the more obvious the inhibition of NO absorption by absorption solution, the lower the denitration rate of absorption solution.

(6) With the increase of NO concentration from 357.55 to 840.00 mg/m^3, the NO removal efficiency increased slightly.

(7) SO_2 has a dual effect on NO removal. On the one hand, at the beginning of the cyclic reaction, SO_2 will compete with NO to react with Fe(II)EDTA and the denitrification rate is reduced. On the other hand, SO_3^{2-} formed after SO_2 dissolved in water also enhanced the regeneration of nitrite complex to a certain extent. Meanwhile, with the progress of the reaction, SO_3^{2-} and Fe(II)EDTA will form Fe(II)EDTA (SO_3^{2-}) with a stronger NO complexing ability.

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Notes

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