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Simultaneous absorption of NO and SO₂ by combined urea and Fe^{II}EDTA reaction systems

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SO₂ and NO emitted from coal-fired power plants have caused serious air pollution in China. In this work, a novel mixed absorbent, Fe^{II}EDTA/urea, was employed for simultaneous removal of SO₂ and NO in a packed tower, with a corresponding optimal ratio of 0.014 mol L⁻¹ : 5%. The effects of various factors, such as mixed absorbent constitutions, reaction temperature, pH, O₂ concentration, as well as concentrations of SO₂ and NO, on simultaneous removal were investigated. The desulfurization efficiency was 95–99% in all tests, whereas denitrification was affected significantly by various conditions. NO removal efficiency decreased increasing oxygen concentration as well as increasing NO concentration. With an increase in temperature, pH, or SO₂ concentration, NO removal efficiency increased first and then decreased. Under optimal conditions, SO₂ removal efficiency was 100% and NO removal efficiency could exceed 91% within 80 min. The reaction mechanism was speculated according to relevant literature.

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1. Introduction

Emission of SO₂ and NO accounts for 90–95% of NO_x in fuel combustion from power plants and results in various environmental problems (e.g., acid rain, photochemical smog, and other pollution) to damage the environment and human health.¹ Usually, wet flue gas desulfurization (WFGD) such as the limestone–lime method² and selective catalytic reduction (SCR)^{3,4} processes can, respectively, realize SO₂ and NO removal for industrial application on a large scale. However, the combination of WFGD and SCR processes for simultaneous desulfurization and denitrification suffer from the need for huge areas of chemical plants, intricate processes, high operating costs, ammonia leakage, and spent catalysts. There is an urgent need for a more economical method for controlling NO and SO₂ emission.

The simultaneous absorption technologies of NO and SO₂ can be split into “dry” and “wet” processes. The former includes plasma degradation, electron beam radiation photocatalysis, sorbent adsorption, and microwave catalytic decomposition, and necessitates high cost and complex processes to obtain high absorption efficiency of SO₂ and NO.^{5–9} Wet processes applied to industrial furnaces are promising ways to conform to an ultra-low emission standard.

Simultaneous desulfurization and denitrification by wet processes mainly adopt oxidation absorption using KMnO₄,¹⁰

NaClO₂,¹¹ NaClO,¹² O₃ (ref. 13–15) Fenton reagents,¹⁶ UV/H₂O₂,¹⁷ thermal/transition metal ions/persulfate,¹⁸ or ultrasound/Fe²⁺/heat-coactivated persulfate.¹⁹ However, oxidation absorption processes are mostly at pilot exploration or laboratory stages due to their significant costs, low oxidation efficiency or secondary pollution. Therefore, trying to exploit new and more promising NO_x and SO₂ simultaneous removal wet technologies has important theoretical and practical importance.

Reducing absorption with urea ((NH₂)₂CO) and complexing absorption (e.g., Fe(II)EDTA, hexamminecobalt(II)) are also employed for simultaneous removal of NO and SO₂.^{20,21} However, NO removal through the reduction of (NH₂)₂CO is not satisfactory. NO removal efficiencies are usually <40% without other additives because of the low solubility of NO in solution. Complex absorption could weaken the impact of the low solubility of NO, but they are easily oxidized, and lose their complexing ability.²² Therefore, simultaneous removal of NO and SO₂ by reducing absorption or complexing absorption is barely satisfactory.

Previously, we combined urea and Fe(II)EDTA for NO removal. We noted a synergistic reaction between urea and Fe^{II}EDTA upon NO absorption in which urea could restrain Fe^{II}EDTA oxidation and, importantly, it could react with Fe^{II}EDTA–NO to generate Fe^{II}EDTA, N₂, and CO₂.²³ A mixed absorbent was shown to improve NO removal efficiency significantly, and could maintain >76% for 80 min at optimal conditions in our previous study. However, simultaneous removal of SO₂ and NO with a mixed urea ((NH₂)₂CO) and Fe^{II}EDTA system has not been shown. It is necessary to study the effect of the interrelationship between SO₂ and NO on their

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removal efficiencies by mixed absorbents containing Fe^{II}EDTA and ((NH₂)₂CO).

We wished to investigate the simultaneous removal of SO₂ and NO from flue gas using a mixed urea ((NH₂)₂CO) and Fe^{II}EDTA system in a “packing tower”. The key influencing factors and mechanism of simultaneous removal of SO₂ and NO were investigated. Our results could provide crucial theoretical guidance for follow-up studies and industrial applications of this technology.

2. Experimental section

2.1 Chemicals

FeSO₄·7H₂O (99.0%), urea (99.0%), C₁₀H₁₄N₂O₈Na₂·7H₂O (99.0%), NH₄Fe(SO₄)₂·12H₂O (99.0%) and CaCl₂ (99.0%) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (China). N₂ (99.999%), SO₂ (99.99%) and NO (99.99%) were provided by Guangzhou Yuejia Gas Co. (China). Other reagents were of analytical grade.

2.2. Experimental apparatus

A schematic diagram of the experimental setup is shown in Fig. 1. The system comprised three main parts: gas-simulation system, packed tower, and a gas sampling-analysis system. Absorption of NO and SO₂ was conducted in the packed tower of length 1000 mm and internal diameter 20 mm. The pressure in the packed tower was atmospheric. The concentration of NO and SO₂ was measured by a flue gas analyzer (KM950, KANE International) after drying with anhydrous calcium chloride. The resolution and accuracy of this gas analyzer for NO was 1 ppmv and ±5%, respectively.

2.3. Simultaneous removal of SO₂ and NO by urea and Fe^{II}EDTA

At first, the pressure of the mixed gas cylinder was set to 0.2 M Pa. According to the pressure and volume of the mixed

gas cylinder, the volume of the desired NO and SO₂ concentrations was obtained. NO and SO₂ were poured successively into the mixed gas cylinder by adjusting the corresponding rotameter. The desired O₂ concentration was obtained by mixing air and N₂. The absorbing liquid was prepared by adding urea to Fe^{II}EDTA solution. The pH of the mixed solution was adjusted by NaOH solution and H₂SO₄. The experiment was started after N₂ flowed through the reactor to clean up the remaining air. Absorption was carried out for 80 min, and data were measured every 10 min. The absorbing-liquid volume was ~300 mL, the gas flow rate was 0.8 L min⁻¹, and the flow rate of the absorption liquid was 45 mL min⁻¹. The effect of mixed absorbent constitutions, temperature, pH, O₂ concentration of simulated flue gas, as well as SO₂ and NO concentrations on simultaneous desulfurization and denitrification were noted.

2.4. Analytical methods

The concentrations of NO and SO₂ were analyzed by a flue gas analyzer (KM950). NO and SO₂ removal efficiency were defined as

$$\eta = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \quad (1)$$

where η is NO or SO₂ removal efficiency given as %; C_{in} is the inlet concentration of NO or SO₂ in ppmv; C_{out} is the outlet concentration of NO or SO₂ in ppmv.

$$\bar{\eta} = \frac{1}{T} \int_0^T \eta(t) dt \quad (2)$$

where $\bar{\eta}$ is the average removal efficiency of NO or SO₂, T is the total absorption time (min), and $\eta(t)$ is the removal efficiency of NO or SO₂ as a function of time.

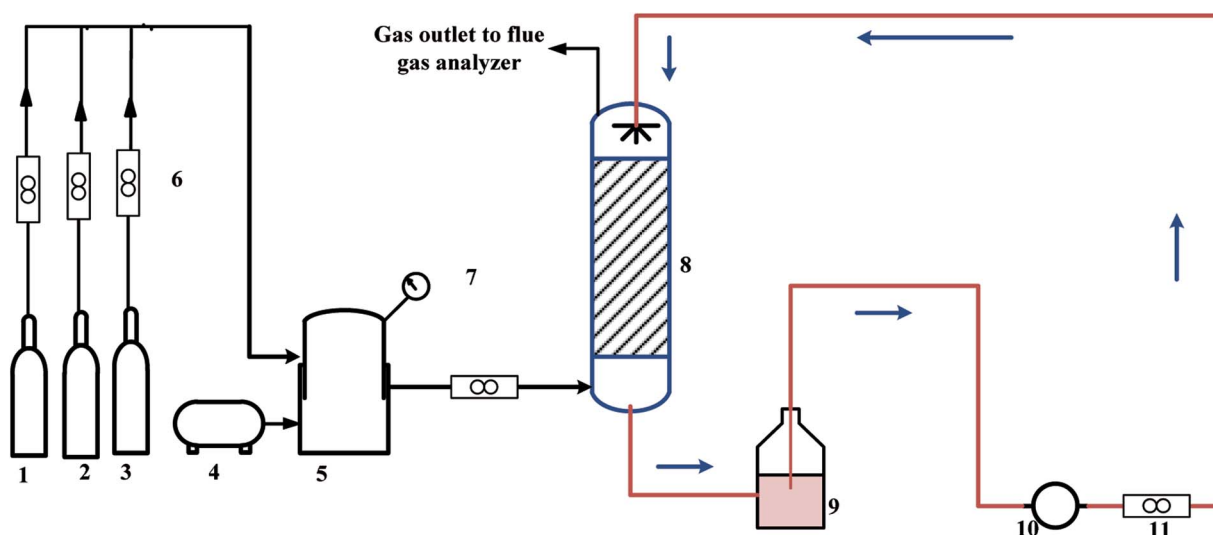


Fig. 1 Experimental apparatus for NO and SO₂ removal (schematic): (1) NO cylinder, (2) N₂ cylinder, (3) SO₂ cylinder, (4) air compressor, (5) mixed cylinder, (6) gas rotameter, (7) piezometer, (8) packed tower, (9) liquid storage tank, (10) pump, (11) liquid rotameter.

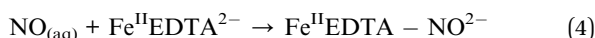


3. Results and discussion

3.1. Effect of mixed absorbent constitutions on simultaneous removal

Fig. 2 shows the effect of urea concentration on simultaneous removal. As the urea concentration increased from 0 wt% to 10 wt%, the SO₂ removal efficiency increased from 94.5% to 99.6%. These experimental results were similar to those in the literature,²⁴ and SO₂ removal efficiency using urea solution was almost the same as that of other technologies, all being up to almost 100%. Hence, urea was a good absorbent for SO₂. Nevertheless, NO removal efficiency was <40% in all tests, suggesting that NO removal could not proceed well without the help of a complexing agent. This is because the solubility of SO₂ in water is 700-times more than that of NO (one volume of water dissolves about 39 volumes of SO₂ or ~0.05 volume of NO at 20 °C).

NO could be captured readily by Fe^{II}EDTA in solution to form stable ferrous-nitrosyl complexes Fe^{II}EDTA-NO (eqn (3) and (4)).²⁵



Previously,²³ we noted the synergistic effect of (NH₂)₂CO and Fe^{II}EDTA on NO removal. Urea can react with Fe^{II}EDTA-NO to produce Fe^{II}EDTA for continued complexing of NO, but can also restrain oxidation of Fe^{II}EDTA to Fe^{III}EDTA. Hence, a combination of Fe^{II}EDTA and urea is suitable and helpful for the removal of NO and SO₂.

Before seeking an optimal concentration ratio of Fe^{II}EDTA to urea, reagent prices were considered to ensure that industrial scale up is prohibitively expensive. According to the data from the Alibaba Internet website, the prices of industrial Fe^{II}EDTA was ~\$1891/ton (\$658.5/kmol), which is approximately five-times higher than that of industrial urea (\$366/ton). Then,

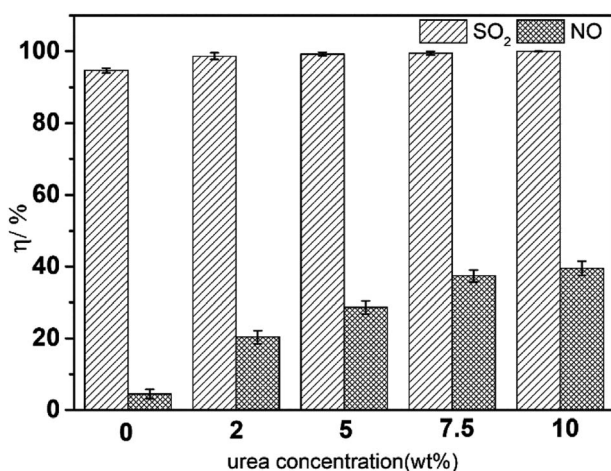


Fig. 2 Effect of the urea concentration on simultaneous removal. *T*, 25 °C; pH = 7.0; Fe^{II}EDTA, 0 mol L⁻¹; O₂ concentration, 7% (v/v); SO₂ concentration, 3000 ppm; NO concentration, 500 ppm.

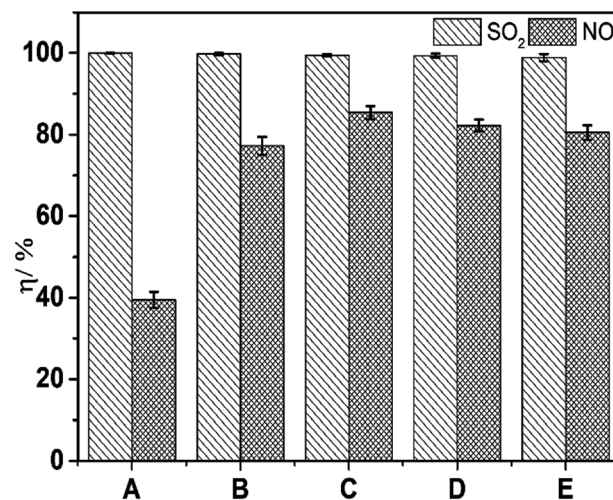


Fig. 3 Effect of the constitutions of complex absorbents on simultaneous removal. *T*, 25 °C; pH = 7.0; O₂ concentration, 7% (v/v); SO₂ concentration, 3000 ppm; NO concentration, 500 ppm; (A), 10 wt% urea; (B), 0.007 mol L⁻¹ Fe^{II}EDTA + 7.5 wt% urea; (C), 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea; (D), 0.022 mol L⁻¹ Fe^{II}EDTA + 2 wt% urea; (E), 0.028 mol L⁻¹ Fe^{II}EDTA.

experiments to determine the optimal concentrations of Fe^{II}EDTA to urea were carried out (Fig. 3).

The prime costs of the five groups from Fig. 3 were identical, and the optimal concentration ratio of Fe^{II}EDTA to urea could be reflected clearly from simultaneous removal efficiencies. As shown in Fig. 3, with the change in the mass ratio, desulfurization efficiency was almost constant at 100%, whereas denitrification efficiency increased significantly. When the concentration ratio of Fe^{II}EDTA to urea increased from 0 mol L⁻¹ : 10 wt% to 0.014 mol L⁻¹ : 5 wt%, the average denitrification efficiency increased from 39.4% to 85.5%, because the Fe^{II}EDTA concentration increased. In addition, the viscosity of the absorption liquid increased because the urea concentration was too high, so the liquid diffusivity of NO decreased.²⁶ As the ratio increased further, NO removal efficiency decreased because a too-low urea concentration can result in with high concentrations of Fe^{II}EDTA-NO and Fe^{III}EDTA accumulating in the complex absorbent. Thus, the optimal ratio of Fe^{II}EDTA to urea was 0.014 mol L⁻¹ : 5 wt%.

3.2 Effect of temperature on simultaneous removal

The temperature of the absorption liquid plays a significant part in the transfer of NO or SO₂ from the gas phase to the liquid phase, and is governed by the diffusion, dissolution and reaction characteristics of the species in solution. The dependence of simultaneous removal on temperature was evaluated. As shown in Fig. 4a, the absorption temperature had a slight effect on desulfurization but a significant effect on NO removal. The denitrification efficiency increased slightly when the reaction temperature was 25–30 °C but, when the reaction temperature increased from 30 °C to 50 °C, there was a decrease in average NO removal efficiency from 86.2% to 58.1%. The effect of temperature on NO removal is highly complicated. On the one



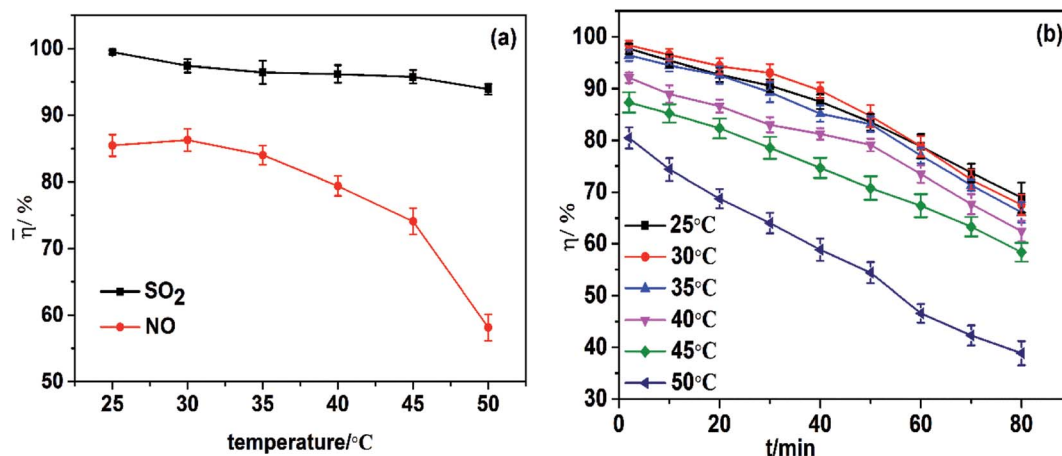
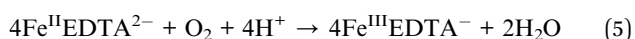


Fig. 4 (a) Effect of temperature on simultaneous removal. (b) Effect of temperature on NO removal efficiency. pH = 7.0; Fe^{II}EDTA and urea concentration composition, 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea; O₂ concentration, 7% (v/v); SO₂ concentration, 3000 ppm; NO concentration, 500 ppm.

hand, a high temperature can accelerate the movement of molecules and increase the chemical rate. As the temperature increases, these factors result in an increase in NO removal efficiency. On the other hand, a lower temperatures is favorable for the formation of iron(II) nitroxyl species.²⁷ Simultaneously, as the temperature increases, the solubility of NO and O₂ in the aqueous solution decreased and the consequent decomposition of Fe^{II}EDTA begins to dominate the process. In addition, a higher temperature accelerates the change of Fe^{II}EDTA to Fe^{III}EDTA. As the temperature increases, these factors can cause a decrease in NO removal efficiency. Hence, the slight decrease and then rapid decrease in NO removal efficiency with an increase in temperature was a result of the interaction of many positive and negative aspects. In summary, 30 °C was the best absorption temperature. However, the temperature of flue gases emitted from industrial boilers is typically ~100 °C. Hence, before simultaneous desulfurization and denitrification by mixed absorbent Fe^{II}EDTA/urea in industrial applications, flue gases at high temperatures can be treated by different cooling technologies such as water cooling, vaporization cooling, and spray cooling.

3.3 Effect of the pH on simultaneous removal

pH is a vital parameter on SO₂ and NO removal using a Fe^{II}EDTA and urea mixed solution. To investigate the effect of the initial pH of the mixed solution on simultaneous absorption, experiments were carried out by changing the pH of the absorption liquid from 5.0 to 11.0. Hence, the effect of the pH of mixed absorbents on simultaneous removal was investigated. As shown in Fig. 5a, an alkaline atmosphere was favorable for desulfurization and the average SO₂ removal efficiency increased from 95.5% to 100%. Similarly, NO removal efficiency increased from 66.3% to 88.0% with increasing pH from 5.0 to 9.0, which could be because a low pH can promote further oxidation of Fe^{II}EDTA:²⁸



A sharp decrease in average NO removal efficiency from 87.4% to 60.0% was observed when the pH was between 10.0 and 11.0 because Fe²⁺ hydrolyzes readily and forms a precipitate in strong alkaline solution,²⁹ which greatly affects NO absorption. Thus, the optimal pH of the mixed absorbent was determined to be 9.0–10.0.

3.4 Effect of O₂ concentration on simultaneous removal

Industrial flue gases in China, in general, contain 3–11% (v/v) oxygen, which has a considerable effect on the oxidation of Fe^{II}EDTA.³⁰ The O₂ concentration in flue gas was varied from 3% to 11% (v/v) and its effect on simultaneous absorption illustrated in Fig. 6a. SO₂ removal efficiency was almost unchanged at ~99%, and the average NO removal efficiency decreased from 91.9% to 75.6% with an increase in O₂ concentration from 3% to 11% (v/v). Low NO removal efficiency under high O₂ concentration was due to the oxidation of Fe^{II}EDTA to Fe^{III}EDTA.

3.5 Effect of SO₂ and NO concentrations on simultaneous removal

In practice, the components as well as the concentrations of flue gas are varied with boiler loads and operational conditions. Thus, simultaneous-removal experiments with various concentrations of SO₂ and NO were carried out. As shown in Fig. 7a, the effect of SO₂ on desulfurization was dependent on its concentration. When the SO₂ concentration increased from 500 ppm to 3000 ppm, the average desulfurization efficiency increased from 94.3% to 99.5% and, then, as the SO₂ concentration increased further to 4000 ppm, desulfurization efficiency began to decrease. The reason for the increase in SO₂ removal efficiency was that the increase in SO₂ concentration enhanced mass transfer and then promoted the gas–liquid mass transfer rate, so efficiency was increased. When the SO₂ concentration was excessive, despite mass transfer being promoted further, the



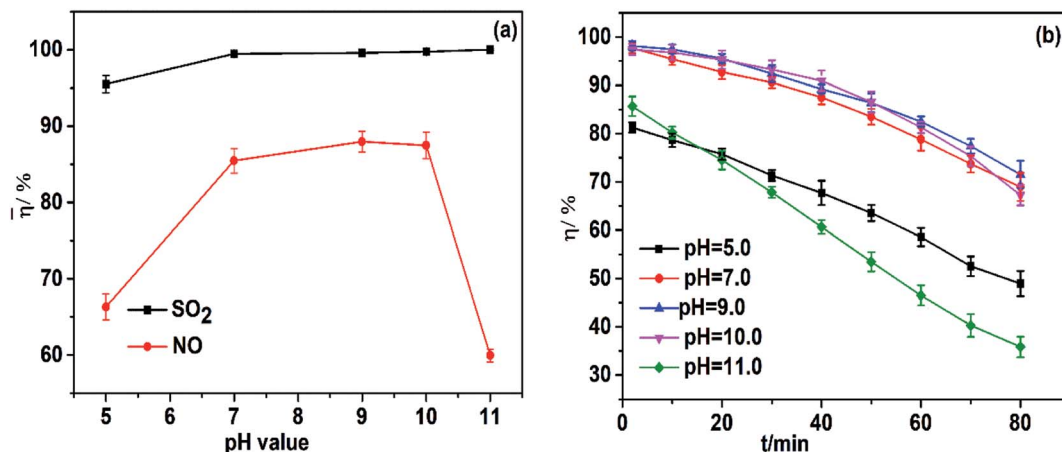


Fig. 5 (a) Effect of pH on simultaneous removal; (b) effect of pH on NO removal efficiency. T , 25 °C; Fe^{II}EDTA and urea concentration composition, 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea; O₂ concentration, 7% (v/v); SO₂ concentration, 3000 ppm; NO concentration, 500 ppm.

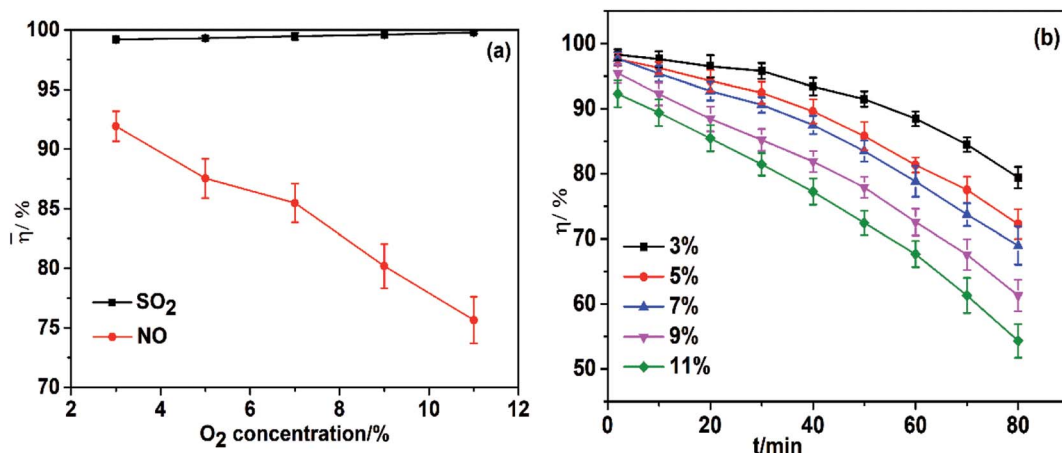
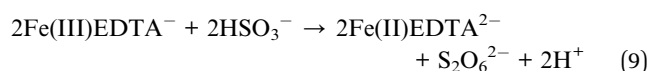
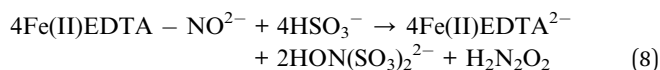
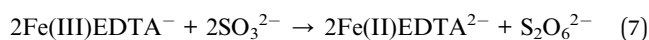
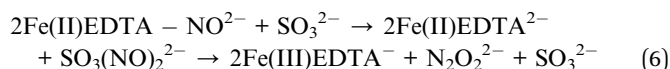


Fig. 6 (a) Effect of O₂ concentration on simultaneous removal; (b) Effect of O₂ concentration on NO removal efficiency. T , 25 °C; Fe^{II}EDTA and urea concentration composition, 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea; pH = 7.0; SO₂ concentration, 3000 ppm; NO concentration, 500 ppm.

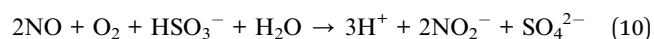
reaction rate became the controlling step, so SO₂ removal resulting from SO₂ accumulation decreased.

Fig. 7b reveals that NO removal efficiencies decreased with operation time, and when the SO₂ concentration increased from 500 ppm to 3000 ppm, the average efficiency of NO removal increased from 80.3% to 85.5%. Then, as the SO₂ concentration increased further to 4000 ppm, the average denitrification efficiency decreased to 82.6%. The reasons for the increase in NO removal were as follows:



Sulfite and hydrosulfite ions can restore the active component Fe^{II}EDTA from Fe^{II}EDTA–NO, and Fe^{III}EDTA accumulates in the mixed absorption liquid.³¹ Thus, denitrification efficiency was increased with an appropriate increase in SO₂ concentration. However, if the SO₂ concentration was >4000 ppm, a small amount of SO₂ would compete with NO for the limited complexant (Fe^{II}EDTA) in the gas phase. Moreover, absorption competition between SO₂ and NO also occurred in urea solution, resulting in an increase in mass transfer resistance between NO and aqueous phases, from which the denitrification efficiency began to decrease.

The effect of the NO concentration on simultaneous removal is shown in Fig. 8a. An increase in the NO concentration from 300 ppm to 500 ppm could increase SO₂ removal efficiencies because NO₂ (the oxidation product of NO) could accelerate the oxidation of sulfite to sulfate (eqn (10) and (11)).³²



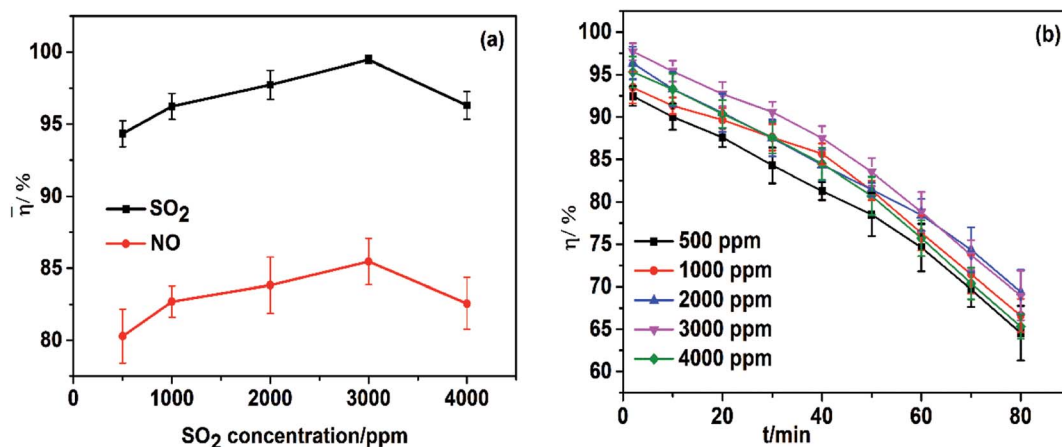
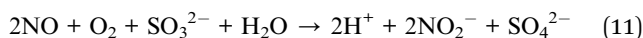


Fig. 7 (a) Effect of SO₂ concentration on simultaneous removal; (b) effect of SO₂ concentration on NO removal efficiency. *T*, 25 °C; Fe^{II}EDTA and urea concentration composition, 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea; pH = 7.0; O₂ concentration, 7% (v/v); NO concentration, 500 ppm.



A further increase in the NO concentration causes severe competition between SO₂ and NO for the absorbent, resulting in a decrease in SO₂ removal. The increase of the NO concentration would cause a linear decrease in denitrification efficiency, which could be interpreted as a decrease in the molar ratio of oxidant to NO.

3.6 Validation experiments

Comprehensive consideration of the process parameters and experimental data led to optimal experimental conditions for simultaneous removal using a mixed absorbent were determined: 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea, SO₂ and NO initial concentration of ~3000 and ~300 ppm, respectively, a temperature of 30 °C, pH of 9.0, and O₂ concentration of 3%. In this case, SO₂ removal efficiency was 100% and NO removal efficiency could exceed 91% within 80 min under

optimal conditions with 300 mL of absorbing liquid volume, gas flow rate of 0.8 L min⁻¹, and flow rate of the absorption liquid of 45 mL min⁻¹.

3.7 Reaction mechanism

The mechanism involved in simultaneous desulfurization and denitrification using Fe^{II}EDTA and urea was speculated according to our previous work and related literature.^{23,24,31} The desulfurization mechanism was relatively simple because SO₂ is highly soluble in water. If the reactions take place in the liquid phase, SO₂ can react with the ammonium carbamate generated by urea hydrolysis. The possible forms of sulfur species are SO₃, SO₂·H₂O, HSO₃⁻, SO₃²⁻, and SO₄²⁻, of which HSO₃⁻ and SO₄²⁻ are the main forms of S⁴⁺ species and S⁶⁺ species, respectively. In the present study, the reaction between SO₃²⁻ and urea-hydrolysis products could promote SO₂ absorption. Hence, the gas-liquid reaction between SO₂ and (NH₂)₂CO solution was completely gas-film controlled. The related reactions were:

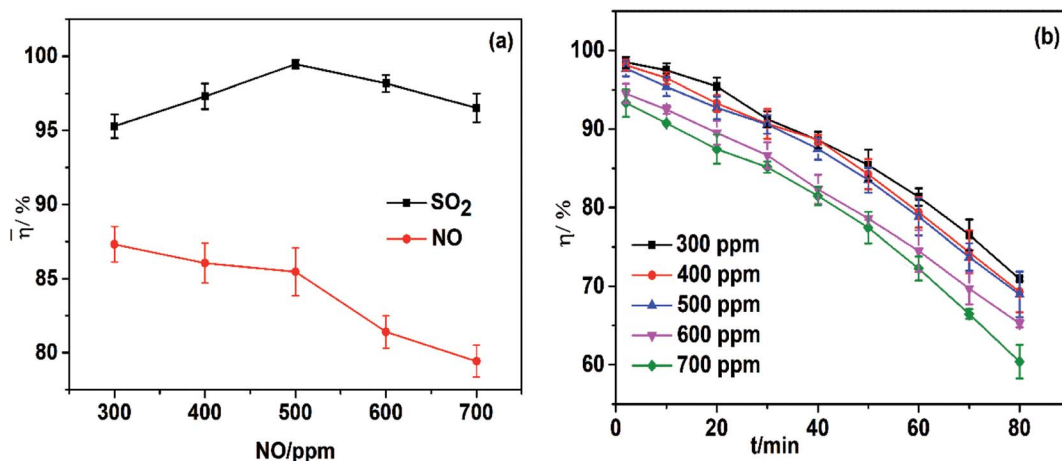


Fig. 8 (a) Effect of NO concentration on simultaneous removal; (b) effect of NO concentration on NO removal efficiency. *T*, 25 °C; Fe^{II}EDTA and urea concentration composition, 0.014 mol L⁻¹ Fe^{II}EDTA + 5 wt% urea; pH = 7.0; O₂ concentration, 7% (v/v); SO₂ concentration, 500 ppm.



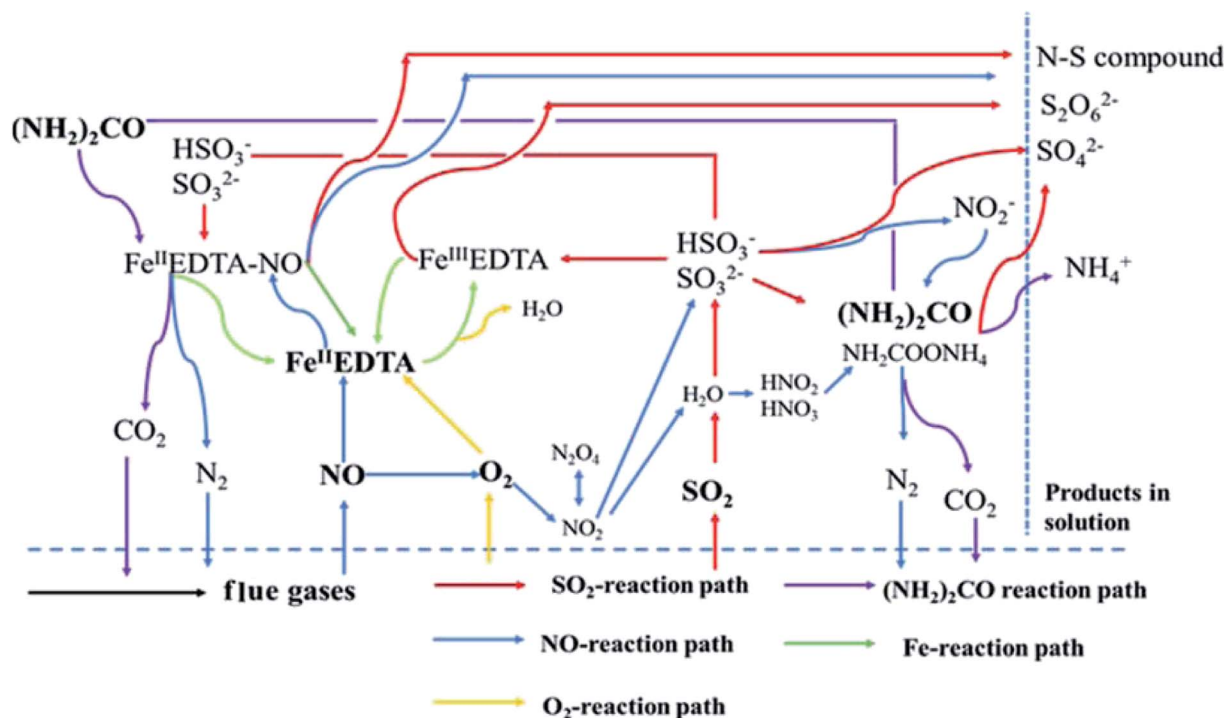
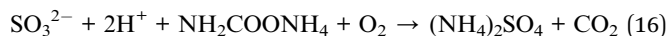
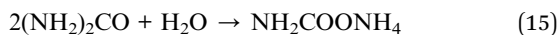
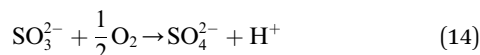
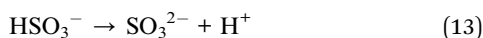
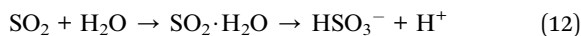
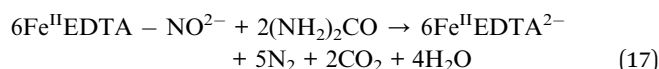


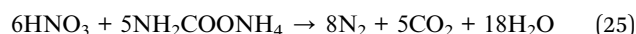
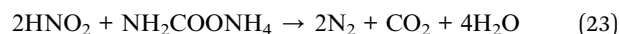
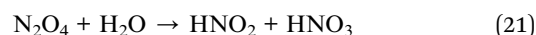
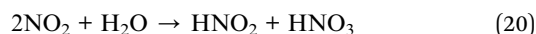
Fig. 9 Simultaneous desulfurization and denitrification using a Fe^{II}/EDTA and urea mixed solution.



The denitrification mechanism was much more complicated. NO having empty anti-bonding π orbitals can form π bonds by overlapping the d orbit of the central ion Fe^{2+} .³³ Thus, NO could be combined readily with $\text{Fe}^{\text{II}}\text{EDTA}$ (eqn (3) and (4)). Meanwhile, in industrial applications, because of O_2 in the flue gas, $\text{Fe}^{\text{II}}\text{EDTA}$ is oxidized readily to $\text{Fe}^{\text{III}}\text{EDTA}$, and activity is lost (eqn (5)). Hence, during absorption, $\text{Fe}^{\text{II}}\text{EDTA-NO}$ and $\text{Fe}^{\text{III}}\text{EDTA}$ are the major byproducts. Urea can solve these problems to some degree (eqn (17)). HSO_3^- and SO_3^{2-} from the absorption liquid after SO_2 removal can also restore $\text{Fe}^{\text{II}}\text{EDTA}$ from $\text{Fe}^{\text{II}}\text{EDTA-NO}$ and $\text{Fe}^{\text{III}}\text{EDTA}$ (eqn (6)–(9)).



Besides being absorbed by $\text{Fe}^{\text{II}}\text{EDTA}$, some NO is oxidized to NO_2 and N_2O_4 , which are dissolved readily in solution, producing nitrous acid and nitric acid, respectively. Subsequently, HNO_2 and HNO_3 can react with urea to form N_2 , which can also react with ammonium carbamate to form N_2 .



The mechanism of simultaneous desulfurization and denitrification using a $\text{Fe}^{\text{II}}\text{EDTA}$ and urea mixed solution is represented in Fig. 9.

4. Conclusion

A mixed absorbent of $\text{Fe}^{\text{II}}\text{EDTA}$ /urea was first employed for simultaneous removal of SO_2 and NO, and the best mass concentration ratio was $0.014 \text{ mol L}^{-1} : 5 \text{ wt\%}$. Desulfurization was affected slightly by different factors, and the SO_2 efficiency was 95–99% in all tests, whereas denitrification was affected significantly by various conditions. NO removal efficiency declined with increasing oxygen concentration as well as the increase in NO concentration. However, with increasing



temperature, pH, or SO₂ concentration, NO removal efficiency initially increased up to the maximum value and then decreased. Under optimal conditions, SO₂ removal efficiency was 100% and NO removal efficiency could exceed 91% within 80 min. These research findings suggest that the Fe^{II}EDTA and (NH₂)₂CO solution could be used as an efficient and low-cost absorbent for simultaneous desulfurization and denitrification.

Conflicts of interest

There are no conflicts to declare.

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