Original Research

Spectrophotometric Determination of Fe(II)EDTA-NO, Fe(II)EDTA/Fe(III)EDTA in Chemical Absorption-Biological Reduction Integrated NO$_x$ Removal System

Yinfeng Xia[1,2], Han Chen[1], Wei Li[2]*

[1]Key Laboratory for Technology in Rural Water Management of Zhejiang Province, Zhejiang University
of Water Resources and Electric Power, Hangzhou, 310018, China
[2]Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Institute of Industrial Ecology
and Environment, Zhejiang University (Yuquan Campus), Hangzhou, 310027, China

Abstract

Fe(II)EDTA-NO, Fe(II)EDTA and Fe(III)EDTA are three key chemical species in the chemical absorption-biological reduction (CABR) integrated NO$_x$ removal system. The original ferrozine method was modified to quickly determine Fe(II)EDTA/Fe(III)EDTA in small volumes of liquid samples. It is shown that the presence of EDTA do create differences in absorbance. The measurement of Fe(II)EDTA and total iron were performed on two separate sample fractions. A spectrophotometric method for direct determination of Fe(II)EDTA-NO was proposed. The results indicated that Fe(II)EDTA-NO could be accurately determined by spectrophotometry under optimized conditions: an absorption wavelength of 438 nm, pH between 5.23~8.07, and operating time under one minute. The final standard curve was given and the mathematic relations among them were also discussed.

Keywords: spectrophotometric method, NO$_x$ removal, Fe(II)EDTA, Fe(II)EDTA-NO, Fe(III)EDTA

Introduction

Nitrogen oxides are hazardous air pollutants, and their emission can cause many environmental problems including acid rain, photochemical smog, doing harm to plants and human health [1, 2]. Environmental and health issues coupled with stringent NO$_x$ emission standards indicate a need for the development of efficient low-cost NO$_x$ reduction technologies. At present, NO$_x$ reduction technologies mainly include selective catalytic reduction, selective non-catalytic reduction, plasma-facilitated catalytic reduction, liquid absorption, adsorption, and biological treatment [3-5].

The traditional biological treatment of nitrogen oxides is limited by the low removal efficiency caused by the mass transfer limitation, since 95% of the nitrogen oxides in the flue gas are insoluble nitric oxide [6]. The chemical absorption-biological reduction

(CABR) integrated NO_x removal system well integrates biological treatment with physicochemical methods, which improves the mass transfer of NO by adding a chelating agent [7]. It obtained a rapid development in recent years attribute to these advantages [8-10]. Much research has been performed on this approach including the choice of chelating agent, microbial strains, kinetics, and the optimal parameters of the bioreactor [11-13]. To break through the limitation of biological reduction rate, electrochemical action was introduced into this system [14]. In this system, NO can be effectively absorbed by the ferrous chelate of Fe(II)EDTA to form Fe(II)EDTA-NO, which can be biologically reduced by denitrifying bacteria. The main reactions involved in this system are as following [14].

$$Fe(II)EDTA + NO(aq) \leftrightarrow Fe(II)EDTA\text{-}NO \quad (1)$$

$$4Fe(II)EDTA + O_2(aq) + 4H^+ \rightarrow 4Fe(III)EDTA$$
$$+ 2H_2O \quad (2)$$

$$24Fe(III)EDTA + C_6H_{12}O_6 \xrightarrow{\text{microorganism}}$$
$$24Fe(II)EDTA + 18H_2O + 6CO_2 \quad (3)$$

$$12Fe(II)EDTA - NO + C_6H_{12}O_6 \xrightarrow{\text{microorganism}}$$
$$12Fe(II)EDTA + 6N_2 + 6H_2O + 6CO_2 \quad (4)$$
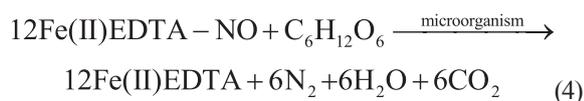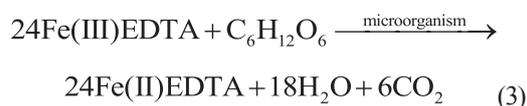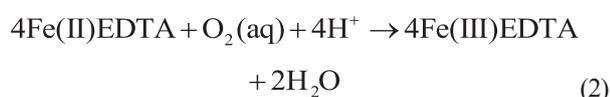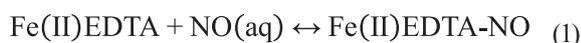
In the course of these processes, part of Fe(II)EDTA is oxidized to Fe(III)EDTA. The reduction of Fe(III)EDTA to Fe(II)EDTA depends on the activity of iron reducing bacteria in the system. That means the effectiveness of the system relies on how to effectively bioreduce Fe(III)EDTA and Fe(II)EDTA-NO in the system [15]. Running state of this system could be detected by monitoring the changes of Fe(II)EDTA, Fe(II)EDTA-NO, and Fe(III)EDTA. Thus, determination of these three chemical species is of great importance in the process of research.

Since Fe(II)EDTA-NO and Fe(II)EDTA are both unstable, it needs a simple and rapid method to accurately reflect the running state of the system. Absorption spectra of Fe(II)EDTA-NO had previously been obtained by Littlejohn and Chang, which indicated the feasibility of spectrophotometric determination [16]. Nonetheless, it still needs further study to take the coexistent system of Fe(II)EDTA-Fe(III)EDTA-Fe(II)EDTA-NO into consideration. Much research had been performed on spectrophotometric determination of Fe^{2+} and Fe^{3+} dependent on the formation of iron(II)-1,10-phenanthroline complex [17, 18]. However, few report focused on the determination of ferrous chelate, especially Fe(II)EDTA and Fe(III)EDTA in the coexistent system. Therefore, it is necessary to study analytical methods of coexistent system, to evaluate the chelating impact of EDTA on iron and to establish proper conditions.

In this paper, an effective method for the determination of key chemical species in this system was proposed and the relationship among them was pointed out. Based on the spectrophotometric determination of ferrous iron by 1, 10-phenanthroline [19], with consideration of the chelating impact of EDTA on iron, an effective method was developed to detect the valence state of iron through optimizing determining conditions according to the characteristic of this system. The determination of Fe(II)EDTA-NO was also studied. At last, the mathematical relation among these three specifies was discussed. The results of this study will provide a simple, rapid, and reliable method for the determination of key chemical species in CABR integrated system.

Experimental

Reagents and Solutions

All reagents used were provided by Shanghai Chemical Reagent Co., China and were analytical reagent grade unless stated otherwise. Oxygen-free distilled water was used throughout.

Distilled water with resistivity higher than 1 MΩ·cm can meet the requirements of this method. Most importantly, it should be degassed before use to avoid the interference of dissolved oxygen in distilled water.

Solutions (1 mmol/L) of Fe(II)EDTA were prepared by dissolution of the appropriate amount of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and Na_2EDTA in water. Solutions (1 mmol/L) of Fe(III)EDTA were prepared by dissolution of the appropriate amount of $FeCl_3 \cdot 6H_2O$ and Na_2EDTA in water. Solutions of hydroxylamine hydrochloride (1 g/L), phenanthroline (1.5 g/L), NaAc (1 mol/L), and HCl (2 mol/L and 0.1 mol/L) were prepared by dissolving appropriate amount of hydroxylamine hydrochloride, phenanthroline, NaAc and concentrated HCl in water, respectively.

Solutions of Fe(II)EDTA-NO were prepared by introducing NO (5% in N_2, Zhejiang Jingong Gas Co., China.) into the solutions of Fe(II)EDTA after the pH was adjusted to 5 with a 0.1 mol/L solution of NaOH, which was prepared by dissolution of the appropriate amount of NaOH in water.

Standard stock solution (100 μg/mL) of iron was prepared by dissolving 0.7020 grams of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in 50 mL of (1+1) sulfuric acid and diluting to 1 liter.

Apparatus

Spectral scans were made with a Techcomp 8500 UV-VIS spectrophotometer (Shanghai, China). All other absorbance measurements were made on a Unico2000 spectrophotometer (Shanghai, China) using 1.00 cm cells. A SevenGo SG2 pH meter from Mettler Toledo was used for all pH measurements.

The inlet and outlet NO concentrations were measured with a chemiluminescent NOx analyzer (Thermo, model 42i-HL).

Determination of Fe(II)EDTA-NO

As the Fe(II)EDTA-NO solution is dark green and its color increases along with the concentration, the concentration of Fe(II)EDTA-NO was directly determined from a standard curve for correlating absorbance to concentration of Fe(II)EDTA-NO.

Determination of Fe(II)EDTA and Fe(III)EDTA

The order and times of addition of the following recommended procedure are critical.

0.5 mL of 2 mol/L HCl is pipetted into a 50 mL volumetric flask. 0.5 mL of sample solution, 2.5 mL of 0.15% phenanthroline and 5 mL of 1 mol/L NaAc are then added successively and immediately. 30 minutes are allowed to complete color development in the thermostatic water bath after the sample is diluted to volume with oxygen-free distilled water. Measurement is made at a wavelength of 510 nm.

A similar procedure is used for the determination of total iron. 0.5 mL of 2 mol/L HCl is pipetted into a 50 mL volumetric flask. 0.2 mL of sample solution, 1 mL 10% hydroxylamine is then added. 5 minutes are allowed to reduce ferric iron to ferrous iron. It shares the same procedure with that of ferrous iron in the subsequent operations. The concentration of iron(III) can be obtained according to the following relation:

$$[Fe(III)EDTA] = [total\ iron] - [Fe(II)EDTA]$$

All the data shown in this study were the mean values of triplicate experiments.

Results and Discussion

Spectral Characteristics

As the Fe(II)EDTA-NO solution is dark green within a certain pH range and its color increases along with the concentration [20], while Fe(II)EDTA or Fe(III)EDTA solution is almost colorless at low concentrations, Fe(II)EDTA-NO may be directly determined by spectrophotometry. According to the absorption spectra of Fe(II)EDTA-NO reported by Littlejohn and Chang, the recommended wavelength was between 420 nm and 460 nm [16]. It is a preliminary result that needs further study to adapt to this coexistent system. Based on their results, a spectral scan of these three chemical species was conducted to verify and perfect it. Fig. 1a) shows that the Fe(II)EDTA-NO solution obtained an obvious absorbance peak at a range of wavelength from 420 to 450 nm, meanwhile, the Fe(II)EDTA solution got very small absorbance value that could hardly interfere with

the results. And the difference of absorbance between Fe(II)EDTA-NO and Fe(III)EDTA or Fe(II)EDTA reached the maximum at the wavelength of 438 nm. So, 438 nm was selected as the optimal wavelength in the determination of Fe(II)EDTA-NO.

The determination of Fe(II)EDTA and Fe(III)EDTA, which needs the help of color reaction, is different from that of Fe(II)EDTA-NO due to their spectral characteristics. In a previous publication, it was shown that tris-1, 10-phenanthroline iron(II) is produced in stoichiometric amounts and spectrophotometrically determined at 510 nm [19]. To confirm its suitability in our case, the percent transmittance of the prepared solution was measured and recorded every 10 nm (every 2 nm around the maximum absorbance) in a wavelength range of 440-550 nm. As Fig. 1b) shows, the colored solution obtained a maximum absorbance at a wavelength of 510 nm, which is highly consistent with the reference data [19]. Therefore 510 nm was selected as the optimal wavelength in the determination of ferrous iron.
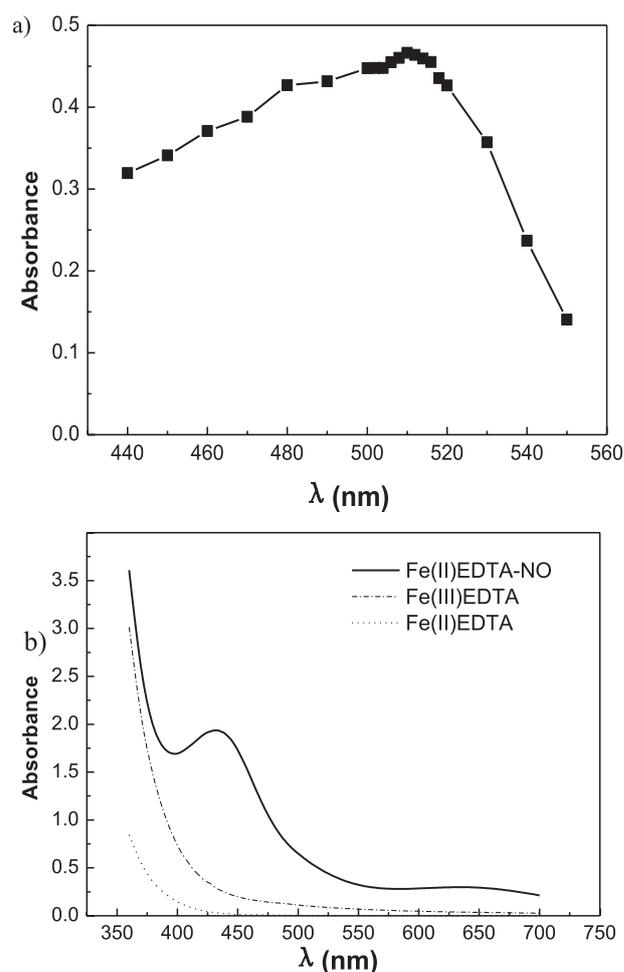
Fig. 1. a) Absorption spectra of Fe(II)EDTA-NO (2.4 mmol/L), Fe(II)EDTA (2.4 mmol/L) and Fe(III)EDTA (2.4 mmol/L). b) Absorption spectra of tris-1, 10-phenanthroline iron(II).

Table 1. Stability of Fe(II)EDTA-NO.

Time (min)	Absorbance	Attenuation (%)	Time (min)	Absorbance	Attenuation (%)
0	0.461±0.00168	0	0	0.363±0.000577	0
5	0.384±0.0110	16.7	1	0.336±0.00351	7.44
10	0.365±0.00166	20.8	2	0.317±0.00551	12.7
20	0.335±0.00103	27.3	3	0.298±0.0102	17.9
30	0.319±0.000100	30.8	4	0.282±0.0150	22.3
60	0.301±0.00193	34.7	5	0.278±0.0205	23.4

Stability of Fe(II)EDTA-NO and Colored Solution

As shown in Table 1, the absorbance of the solution of Fe(II)EDTA-NO decreased sharply (27.3%) as the storage time extended during the first 20 minutes, and relatively gently (7.36%) in the next 40 minutes. Since the attenuation of absorbance with time was obvious, the change in the first five minutes was further studied. As Table 1 shows, even in the first minute, the absorbance still decreased obviously (7.44%). This may be explained by the instability of Fe(II)EDTA-NO according to the formula [21]:

$$Fe(II)EDTA\text{-}NO^{2-} \rightarrow Fe(III)EDTA\text{-}NO^{-}(unstable) \rightarrow Fe(III)EDTA^{-} + NO^{-}(unstable).$$
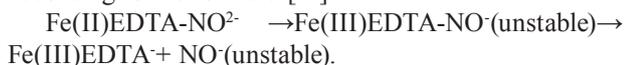
Thus, Fe(II)EDTA-NO should be determined promptly, even one minute can cause considerable error.

Similarly, the stability of the colored solution has great impact on the determination of Fe(II)EDTA, since the stability itself is mostly determined by the temperature. The entire experiment was conducted in a thermostatic water bath at 30ºC to eliminate the effect of temperature. As Fig. 2 shows, the chromogenic reaction in the solution of Fe(II)EDTA was complete 20 minutes after placing the flask into the thermostatic water bath, and the absorbance of the solution could keep stable for a long time. To facilitate the operation, 30 minutes was chosen as the static placing time.

Effect of pH Value

The effect of pH value was tested with different pH in the range of 5-13 for the determination of Fe(II)EDTA. Fig. 3 indicates that the obtained absorbance of the solution of Fe(II)EDTA was higher when the pH value of the medium was held within the range of 5.4-5.7. In the classic determination of Fe(II)EDTA, EDTA binds Fe(II) ions strongly within this range of pH, so that very few free ferrous ions are present in solution [16]. Since the optimal pH for the microorganisms in this system is about 7, the sample solution should be acidized to 5 before determination. Consequently, 0.5 mL of 2 mol/L HCl is pipetted into a 50 mL volumetric flask to adjust the pH to the ideal range.

On the other hand, it can be concluded that pH value also has a great impact on the absorbance of the solution of Fe(II)EDTA-NO. As the pH increased, the absorbance rose at first and then kept stable and finally dropped with a change of color of the solution. The solution appeared as light yellow when the pH

Fig. 2. Stability of colored solution
T = 303 K, [Fe(II)EDTA]$_0$ = 0.04 mmol/L, ■ Fe(II)EDTA.
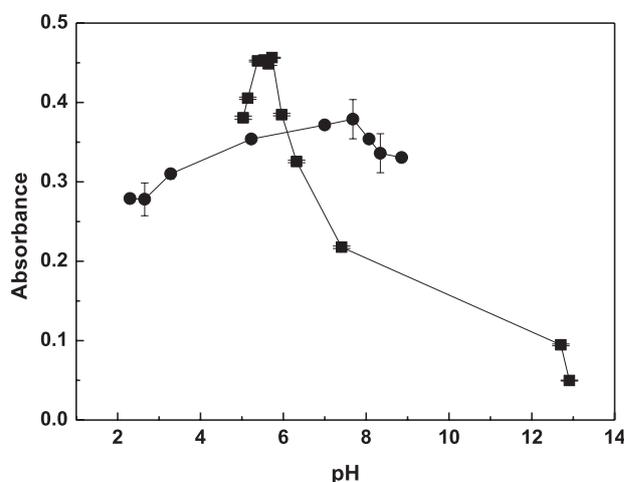
Fig. 3. Effect of pH value on absorbance.
T = 303 K, [Fe(II)EDTA]$_0$ = 0.04 mmol/L, ■ Fe(II)EDTA, ● Fe(II)EDTA-NO.
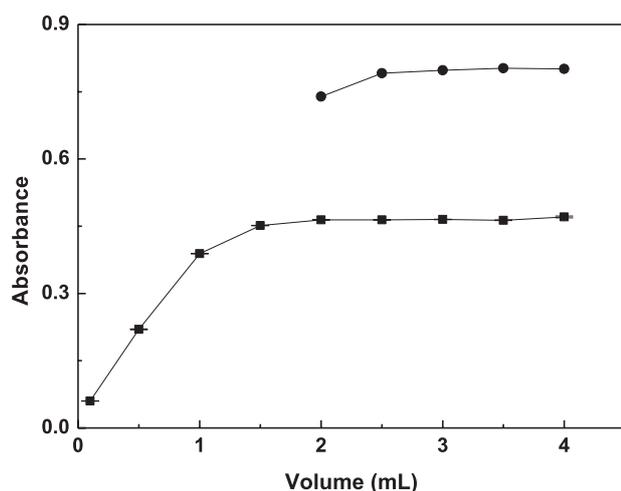
Fig. 4. Effect of dosage of chromogenic reagent on absorbance T = 303 K, ■ $[Fe(II)EDTA]_0$ = 0.04 mmol/L, ● $[Fe(II)EDTA]_0$ = 0.07 mmol/L.

value was about 2, dark green when the pH value was between 5.23-8.07, and red-brown when the pH value reached 12. The reason may be that this complex is prone to transforming to Fe(III)EDTA under strong acidic condition and forming red-brown precipitate under strong alkaline condition. Thus, the ideal pH for the determination of Fe(II)EDTA-NO is within the range of 5.23-8.07. Since the pH of this system is about 7, Fe(II)EDTA-NO could be determined directly. It can greatly reduce the operating time and improve the accuracy of determination.

Effect of Dosage of Chromogenic Reagent and Reductant

The effect of dosage of chromogenic reagent is investigated by adding different amount of chromogenic reagent based on the determination of ferrous iron. From Fig. 4, it is obvious that when the solution contained about 0.04 mmol/L iron, 2 mL 0.15% phenanthroline was enough to complete the reaction and more phenanthroline made no difference. When the concentration of the iron reached to 0.07 mmol/L, the proper dosage of chromogenic reagent increased to 2.5 mL. In the determination of ferrous iron, 2.5 mL 0.15% phenanthroline is enough since the concentration of ferrous iron in this system is between 0.01~0.06 mmol/L.

In the determination of total iron, there was a significant step that completely reducing Fe(III)EDTA to Fe(II)EDTA. During the research of determination of Fe(II)EDTA, hydroxylamine hydrochloride was also added to avoid the oxidation of Fe(II)EDTA. According to the theoretical calculation, 1 mL 10% hydroxylamine hydrochloride is sufficient to provide a reductive environment.

Effect of Coexisting System

Since Fe(II)EDTA-NO, Fe(II)EDTA and Fe(III) EDTA all exist in the scrubbing solution, the effect of coexisting system should also be considered. In determination of Fe(II)EDTA-NO, the effect of Fe(II) EDTA and Fe(III)EDTA was eliminated by choosing an optimal wavelength as mentioned before. Nevertheless, the effect of Fe(II)EDTA-NO and Fe(III)EDTA on the determination of Fe(II)EDTA and total iron should be investigated. As shown in Table 2, the existence of Fe(II)EDTA-NO and Fe(III)EDTA have little impact on the determination of Fe(II)EDTA and total iron. In the case of determining Fe(II)EDTA, Fe(II) was unable to chelate with phenanthroline after forming Fe(II) EDTA-NO. This is because the adducts became more stable after the active center (Fe(II)) binding with NO. On the other hand, Fe(III) was difficult to chelate with phenanthroline because the complexation constant of EDTA and Fe(III) is higher than that of phenanthroline and Fe(III). In the case of determining total iron, Fe(III) EDTA and Fe(II)EDTA-NO are both reduced to Fe(II) EDTA by hydroxylamine. Thus, the effect of Fe(III) EDTA and Fe(II)EDTA-NO are then eliminated.

Standard Curve

The standard curve of Fe(II)EDTA was obtained by adding different amount of 1 M Fe(II)EDTA based on the recommended procedure of determination of Fe(II)EDTA. As Fig. 5 shows, the equation of standard curve was y = 0.0900A with R = 0.9999, SD = 2.53E-4, P<0.0001 and the ratio of concentration and diluted times less than or equal to 0.8.

The standard curve of Fe^{2+} was obtained by adding different amount of 1 M $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ based on the recommended procedure of determination of Fe(II)EDTA. The equation is y = 0.110A with R = 1, SD = 3.00E-11, P<0.0001. This result demonstrates that the existing form of iron matters, which may be

Table 2. Effect of coexistence system.

The known concentrations (mmol/L)			The measured concentrations (mmol/L)	
Fe(II)EDTA-NO	Fe(II)EDTA	Total iron	Fe(II)EDTA	Total iron
4.96	1.50	28.0	1.49	27.4
1.38	5.65	12.0	5.48	11.6
0	3.00	9.00	2.96	8.95
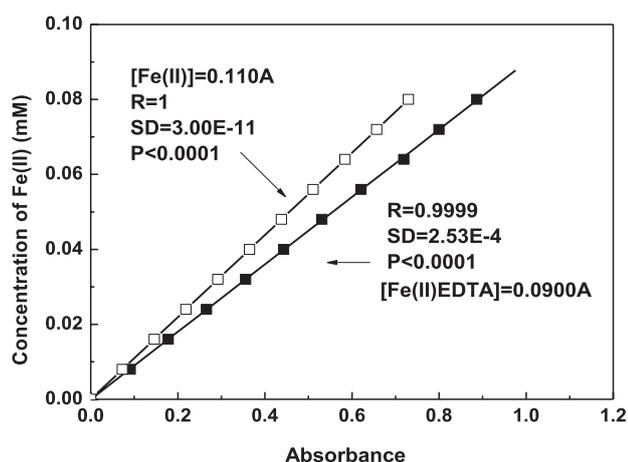
Fig. 5. Standard curve for determination of Fe(II)EDTA and Fe^{2+} T = 303 K, pH = 5.5.
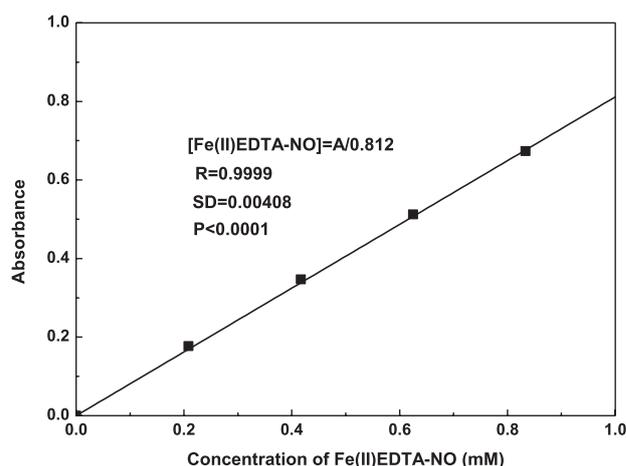
Fig. 7. Standard curve for determination of Fe(II)EDTA-NO.
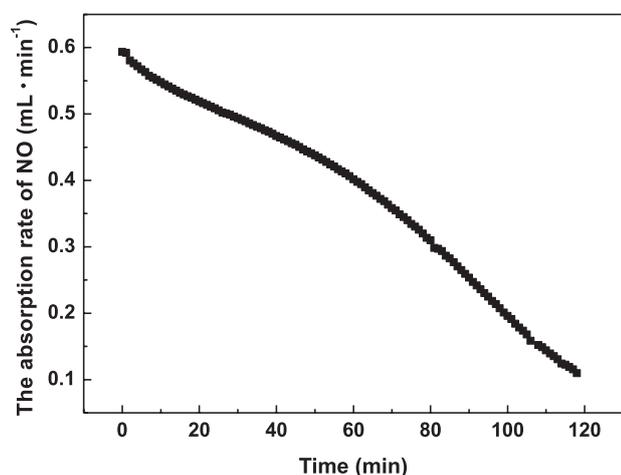
Fig. 6. Absorption rate-time curve of NO
T = 293K, $[Fe(II)EDTA]_0$ = 15 mmol/L, gas flow rate of N_2 = 0.8 L/min, gas flow rate of NO = 7.7 mL/min.

Since Fe(II)EDTA in the solution could not bind NO with 100% efficiency, the amount of NO absorbed by a Fe(II)EDTA solution of certain concentration should be measured. Via continuous measurement of import and export concentration of NO and gas flow, the absorption rate-time curve was obtained as Fig. 6 shows, from which the amount of NO captured in solution could be calculated by graphical integration. The concentration of Fe(II)EDTA-NO could be known for Fe(II)EDTA-NO is produced in stoichiometric amounts.

As Fig. 7 shows, the equation of standard curve was A = 0.812[Fe(II)EDTA-NO] with the R = 0.9999, SD = 0.00408, P<0.0001 and the ratio of concentration and diluted times being less than or equal to 0.9. It demonstrated that Fe(II)EDTA-NO could be directly determined from a standard curve for correlating absorbance to concentration of Fe(II)EDTA-NO.

Application

To detect the running state of the CABR integrated NOx removal system, the proposed method was applied to determine the three key chemical species. The samples were obtained from a biological packing tower. The sample solutions were firstly filtered by a 0.45 μm filter membrane (provided by Shanghai Xinya Purification Device Co., China) to eliminate the effect of microorganism or other particles. The subsequent

due to the chelating impact of EDTA on iron. Despite the complexation constant of phenanthroline and Fe(II) is 21.3, the complexation constant of EDTA and Fe(II) is also as high as 14.8, which may interfere with the complexation between phenanthroline and Fe(II). Therefore, the first standard curve was chosen to determine the ferrous and ferric iron in this system considering the existing form of iron.

Table 3. Determination of Fe(II)EDTA-NO, Fe(II)EDTA and total iron in samples.

Time (h)	Fe(II)EDTA-NO (mmol/L)	Fe(II)EDTA (mmol/L)	Total iron (mmol/L)	Recovery (%)
0	0	/	6.00	/
2	0.459	3.59	5.92	98.7
4	0.639	3.21	5.87	97.8
6	0.812	2.89	5.85	97.5
8	1.03	2.75	5.85	97.5

procedure is the same with that proposed in this paper. The initial concentration of total iron is 6.00 mmol/L, the inlet gas containing 500 ppm NO is at a flow rate of 1 L/min, and liquid flow rate is 10 L/h. Fe(II)EDTA-NO, Fe(II)EDTA and total iron were determined every two hours. The results are listed in Table 3. Comparing the predicted results with target values of total iron, the proposed methods are reliable.

Conclusions

The proposed method for determination of Fe(II)EDTA-NO, which took the advantage of its spectral characteristic and took the effect of coexistent system into consideration, is simple, rapid and sensitive. The optimized conditions are an absorption wavelength of 438 nm, pH between 5.23~8.07, and operating time under one minute. Despite that much research had been performed on the determination of Fe^{2+} and Fe^{3+}, few focused on the determination of Fe(II)EDTA and Fe(III)EDTA. The presence of EDTA do create differences in absorbance, which may be due to the chelating impact of EDTA on iron. In addition, the coexistent system is another key point that needs further study. For the determination of Fe(II)EDTA and total iron, the recommended wavelength is 510 nm, pH is about 5, and chromogenic reaction time is 20 minutes. The results indicated that spectrophotometric determination of Fe(II)EDTA based on the formation of iron(II)-1,10-phenanthroline complex is simple and accurate under optimal conditions.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

References

1. AMOATEY P., OMIDVARBORNA H., BAAWAIN M.S., AL-MAMUN A. Emissions and exposure assessments of SOX, NOX, PM10/2.5 and trace metals from oil industries: A review study (2000-2018). Process Saf. Environ., **123**, 215, **2019**.
2. QIE F., ZHU J., RONG J., ZONG B. Biological removal of nitrogen oxides by microalgae, a promising strategy from nitrogen oxides to protein production. Bioresour. Technol., **292**, 122037, **2019**.
3. SHARIF H.M.A., MAHMOOD N., WANG S., HUSSAIN I., HOU Y., YANG L., ZHAO X., YANG B. Recent advances in hybrid wet scrubbing techniques for NO$_x$
4. and SO$_2$ removal: State of the art and future research. Chemosphere, **273**, 129695, **2021**.
5. SCHROEDER C., SCHROEDER W., YANG S., NYSTROM A., CAI Z., SUBRAMANIAN S., LI S., GUNDERSEN M.A., CRONIN S. Plasma-enhanced NOx remediation using nanosecond pulsed discharges in a water aerosol matrix. Fuel Process. Technol., **208**, 106521, **2020**.
5. XU G., GUO X., CHENG X., YU J., FANG B. A review of Mn-based catalysts for low-temperature NH$_3$-SCR: NO$_x$ removal and H$_2$O/SO$_2$ resistance. Nanoscale, **13** (15), 7052, **2021**.
6. HE F., ZHU X., CHEN X., QIAN Y., DING J. Simultaneous removal of NO and SO$_2$ from flue gas by FeIIEDTA/sodium dithionite solutions. J. Chem. Technol. Biotechnol., **95** (5), 1392, **2020**.
7. 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., **81**, 306, **2006**.
8. LI W., LI M., ZHANG L., ZHAO J., XIA Y., LIU N., LI S., ZHANG S. Enhanced NO$_x$ removal performance and microbial community shifts in an oxygen-resistance chemical absorption–biological reduction integrated system. Chem. Eng. J., **290**, 185, **2016**.
9. LIN T., ZHOU, Z., LIU Y., WANG X., JING G. Evaluation of Fe(III)EDTA and Fe(II)EDTA-NO reduction in a NOx scrubber solution by magnetic Fe$_3$O$_4$-chitosan microspheres immobilized microorganisms. Biotechnol. Bioproc. E., **19**, 175, **2014**.
10. ZHANG Y., SUN L., ZHOU J. Simultaneous Biological and Chemical Removal of Sulfate and Fe(II)EDTA-NO in Anaerobic Conditions and Regulation of Sulfate Reduction Products. Minerals, **9**, 330, **2019**.
11. LIU N., JIANG J.L., CAI L.L., LI W. Characterization and optimization of Fe(II)Cit-NO reduction by Pseudomonas sp. Environ. Technol., **32** (16), 1947, **2011**.
12. JING G.H., ZHOU J., ZHOU Z.M., LIN T.M. Reduction of Fe(III)EDTA(-) in a NOx scrubbing solution by magnetic Fe$_3$O$_4$-chitosan microspheres immobilized mixed culture of iron-reducing bacteria. Bioresour. Technol., **108**, 169, **2012**.
13. WANG X.Y., ZHOU Z.M., JING G.H. Synthesis of Fe$_3$O$_4$ poly(styrene–glycidyl methacrylate) magnetic porous microspheres and application in the immobilization of Klebsiella sp. FD-3 to reduce Fe(III)EDTA in a NOx scrubbing solution. Bioresour. Technol., **130**, 750, **2013**.
14. XIA Y., SHI Y., ZHOU Y., LIU N., LI W., LI S. A New Approach for NOx Removal from Flue Gas Using a Biofilm Electrode Reactor Coupled with Chemical Absorption. Energ. Fuel., **28** (5), 3332, **2014**.
15. LI W., WU C.Z., ZHANG S.H., SHAO K., SHI Y. Evaluation of microbial reduction of Fe(III)EDTA in a chemical absorption-biological reduction integrated NOx removal system. Environ. Sci. Technol., **41**, 639, **2007**.
16. LITTLEJOHN D., CHANG S.G. Kinetic study of ferrous nitrosyl complexes. J. Phys. Chem., **86**, 537, **1982**.
17. TESFALDET Z.O., VAN STADEN J.F., STEFAN R.I. Sequential injection spectrophotometric determination of iron as Fe(II) in multi-vitamin preparations using 1,10-phenanthroline as complexing agent. Talanta, **64** (5), 1189, **2004**.
18. YOKOYAMA T., TSUJI H., KAMADA T., ZENKI M. Capillary electrophoretic separation between Fe(II) and Ni(II) precomplexed with 1,10-phenanthroline in a high concentration buffer of n-butyric acid/n-butyrate and its application. Anal. Bioanal. Chem., **372**, 832, **2002**.

19. BYDALEK T.J., POLDOSKI J.E., JOHN D.B. Spectrophotometric determinations based on the formation of tris-1, 10-phenanthroline iron(II). Anal. Chem., **42**: 929, **1970**.

20. HISHINUMA Y., KAJI R., AKIMOTO H., NAKAJMA F. Reversible binding of NO to Fe(II)EDTA. B. Chem. Soc. JPN, **52** (10), 2863, **1979**.

21. MAIGUT J., MEIER R., ZAHL A. Elucidation of the solution structure and water-exchange mechanism of paramagnetic $[Fe^{II}(edta)(H_2O)]^{2-}$. Inorg. Chem. **46**, 5361, **2007**.