

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# 1 Denitrification Utilizing a Vaporized Enhanced-Fenton Reagent:

## 2 Kinetics and Feasibility

3 Yi Zhao<sup>\*</sup>, Runlong Hao

4 (School of Environmental Science and Engineering, North China Electric Power  
5 University, Baoding 071003)

6 **Abstract** This paper proposed a novel integrative process for NO removal, in which,  
7 NO was initially oxidized by a vaporized enhanced-Fenton reagent (EF) composed of  
8 hydrogen peroxide, ferrous and peroxyacetic acid (PAA) then absorbed by Ca(OH)<sub>2</sub>.  
9 The effects of EF constitution, the reaction temperature, the pH of EF solution and the  
10 SO<sub>2</sub> concentration on NO removal were investigated systematically, and the  
11 experimental results indicated that both of FeSO<sub>4</sub> and PAA can significantly promote  
12 the oxidation rate of NO; the decreasing pH and the increasing temperature played a  
13 key role in enhancing NO removal. The NO depletion exhibited a pseudo-first-order  
14 kinetics pattern in 1-2 half-lives based on the macrokinetics of NO oxidation. And the  
15 rate constants determined in the temperature range of 60 to 120 °C were well fitted to  
16 the Arrhenius equation, yielding the apparent activation energy of 14.1 kJ/mol. The  
17 mechanism of NO oxidation was also speculated.

18 **Keywords** Denitrification; Kinetics; Enhanced-Fenton reagent; Feasibility analysis;  
19 Apparent activation energy

### 20 1 Introduction

21 The SO<sub>2</sub> and NO of coal combustion gases emitted from the thermal power  
22 stations have brought great harm to the human health and the ecosystem; therefore,  
23 both of them have been received considerable concern in recent years. As the largest

24 coal-fired country in the world, Chinese government has tried the best effort to control  
25 the air pollution, and a large number of Wet Flue Gas Desulfurization systems  
26 (WFGD) and Selective Catalytic Reduction systems (SCR) have been installed for  
27 flue gas treatment of coal-fired power plants. Whereas, the SCR-WFGD lay-out has  
28 the large and complex systems, and the high capital and operating costs, so the  
29 simultaneous removal technology that has the characters of simplified equipment, the  
30 smaller occupying areas and the lower operating cost has a good development and  
31 application prospect, in which, several advanced flue gas treatment technologies, such  
32 as the electrochemistry [1-2], the gas solid phase adsorption [3-4], the gas solid phase  
33 catalysis [5-6], the liquid phase absorption [7-8] and the liquid phase oxidation [9-17]  
34 were attempted for simultaneous removal of SO<sub>2</sub> and NO. However, because of the  
35 high costs or technical problems, these simultaneous removal technologies can not  
36 still completely replace the combination of WFGD and SCR technologies. Therefore,  
37 to develop new flue gas treatment technologies has become one of the major  
38 development trends in the coal-fired flue gas control field.

39 Compared with other developing methods, the oxidation method seems to be one  
40 of the promising ways for simultaneous removal of SO<sub>2</sub> and NO, the core of which is  
41 to rapidly oxidize the insoluble NO to NO<sub>2</sub>, and then absorbed by the followed flue  
42 gas Circulation Fluid Bed (CFB) or WFGDs. The potential reagents can be used in  
43 the oxidation process include O<sub>3</sub>, KMnO<sub>4</sub>, NaClO<sub>2</sub>, NaClO, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KFeO<sub>4</sub> and  
44 H<sub>2</sub>O<sub>2</sub>, etc [7-10, 18-20]. However, some of the classical oxidants either have the  
45 lower economical efficiencies or may release several hazardous byproducts that can

46 adversely affect the environment. For example, sodium chlorite is considered as one  
47 of the most effective reagents, but it is estimated that about 1.38 pounds of  $\text{NaClO}_2$  is  
48 needed to remove 1 pound of  $\text{NO}_x$ ; therefore, its cost is of prohibitive. In addition,  
49 high removal efficiency of NO can also be obtained by using permanganate; however,  
50 its cost is too high to be applied in the industry. What's worse, a large number of  
51 heavy metals, manganese and chlorine species that can cause secondary pollution  
52 will remain in the removal products. Ozone is an environmentally benign and  
53 effective gas oxidant, but the energy consumption of its generation is too excessive.  
54 Therefore, the development of innovative absorbent for NO removal is urgency, and  
55 the research emphasis should focus on the following three aspects: the relative lower  
56 cost, the high removal efficiency and the less secondary environmental impact.

57 Given the above requirements,  $\text{H}_2\text{O}_2$  is likely to be the most suitable basic  
58 oxidant due to the superiorities of environmental friendly and lower price. However,  
59 its weak oxidizability makes it difficult to effectively and completely oxidize NO.  
60 For this, in the paper, we selected peroxyacetic acetic (PAA) and ferrous as the  
61 additives to enhance the oxidizing ability of  $\text{H}_2\text{O}_2$  and then prepared a  $\text{H}_2\text{O}_2$ -based  
62 complex oxidant (CO). In addition to that, a novel flue gas cleaning process was  
63 proposed, in which, NO was initially oxidized to  $\text{NO}_2$  by vaporized CO and then  
64 absorbed by  $\text{Ca}(\text{OH})_2$ . To our knowledge, there were no reports in the field of NO  
65 removal on the usage of the vaporized CO as well as the novel approach.

66 The main objective of our research is to evaluate the macrokinetics and technical  
67 feasibility of the novel process on removing NO, so the bench scale kinetics tests

68 were conducted to determine reaction order and apparent activation energy with  
69 respect to NO; factors affecting the treatment, including the CO constitution, the pH  
70 of CO solution, the reaction temperature and the SO<sub>2</sub> concentration, were assessed.

## 71 **2 Materials and Experiments**

### 72 **2.1. Reagents and Preparation of CO Solution**

73 The reagents used were analytical grade (Kermel Company, Tianjin). 30% (w/w)  
74 of H<sub>2</sub>O<sub>2</sub>, 16% (w/w) of PAA and 99% (w/w) of FeSO<sub>4</sub> · 7H<sub>2</sub>O were used to prepare CO  
75 solution, in which the fresh solutions of FeSO<sub>4</sub>, PAA and H<sub>2</sub>O<sub>2</sub> were added in a  
76 beaker in turn by using pipettes (10-1000 µl and 1-5 ml) and then shaken mildly. And  
77 its pH was adjusted by 1 mol/L of H<sub>2</sub>SO<sub>4</sub> and 1 mol/L of NaOH. In addition, Ca(OH)<sub>2</sub>  
78 was employed as the absorbent for absorbing the reaction products of NO, and  
79 anhydrous CaCl<sub>2</sub> was used the dryer to avoid the damage of flue gas analyzer.

### 80 **2.2. Experimental apparatus and procedures**

81 The bench scale experiments were carried out through a self-designed  
82 experimental system, which mainly consisted of the simulated flue gas generation, the  
83 vaporization of CO solution, the integration of preoxidation and absorption and the  
84 tail gas detection, as shown in Fig. 1. The simulated flue gas was generated from N<sub>2</sub>,  
85 SO<sub>2</sub>, NO, O<sub>2</sub> and CO<sub>2</sub> provided in the compressed cylinders (1-5) (North special gas  
86 company, Baoding). A peristaltic pump (12) (BT100-1F, Longerpump, Baoding) was  
87 employed to pump CO solution (11) into the vaporization device of CO solution (9)  
88 that was heated by a thermal control electric heater (10) (ZDHW, Zhongxingweiye  
89 company, Beijing). The reactor was an U-type quartz tube (14) with a length of 30 cm

90 and an inner diameter of 2.5 cm, heated by a thermostat oil bath (16) (DC-RB,  
91 Duchuang technology company, Beijing). The temperatures of vaporization device (9)  
92 and reactor were detected by thermal couples. The inlet and outlet flue gas were  
93 detected by a flue gas analyzer (18) (ECOM-J2KN, RBR Company, Germany), which  
94 can detect various gases such as O<sub>2</sub> in a range of 0-21% ( $\pm 0.01\%$ ), CO in a range of  
95 0-10000 ppm ( $\pm 10$  ppm), NO in a range of 0-5000 ppm ( $\pm 1$  ppm), NO<sub>2</sub> in a range of  
96 0-1000 ppm ( $\pm 1$  ppm) and SO<sub>2</sub> in a range of 0-5000 ppm ( $\pm 1$  ppm), in a working  
97 temperature range of 25-85 °C. The pH of CO solution was detected by a pH meter  
98 ( PHS-3C, Youke company, Shanghai).

99 During the experiments, NO and N<sub>2</sub> were metered through mass flow controller  
100 (6) and mixed in a buffer bottle (7), in which NO and other coexistence gases were  
101 diluted by N<sub>2</sub> to the desired concentrations, from which the simulated flue gas was  
102 formed. Then the CO solution (11) was pumped by peristaltic pump (12) into the  
103 vaporization device (9), where it was vaporized immediately. At the same time, the  
104 vaporized CO carried by the simulated flue gas oxidized NO in the reactor (14).  
105 Finally, the unreacted oxidants, the iron precipitates and NO<sub>x</sub> were absorbed by  
106 Ca(OH)<sub>2</sub> supported on the glass wool. The method for controlling NO oxidation time  
107 was designed as followed. Based on the volumes of the reactor and the vaporization  
108 device and the inlet flue gas flow, the time ( $\Delta t$ ) that NO/N<sub>2</sub> fills fully the reactor and  
109 the vaporization device was calculated and determined as a duration for CO addition.  
110 During the experiments, NO/N<sub>2</sub> was input until the gas flow was constant, at the  
111 moment, the CO was pumped into the vaporization device lasting a duration of  $\Delta t$ .

112 And then the flue gas was switched to bypass in order to control the reaction time of  
113 NO oxidation. Subsequently, turn on the main path to output the reacted flue gas for  
114 detecting the concentrations of NO and NO<sub>2</sub>.

### 115 **2.3 Investigations of Various Influencing Factors**

116 In order to investigate the influences of ferrous and PAA on NO removal, the  
117 experiments with different CO constitutions, such as H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/PAA and  
118 H<sub>2</sub>O<sub>2</sub>/PAA/FeSO<sub>4</sub>, were carried out. Due to the generation of hydroxyl radicals  
119 mainly depends on the ferrous concentration, the effects of the ferrous concentrations  
120 in CO solution,  $3 \times 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $7 \times 10^{-3}$  and  $9 \times 10^{-3}$  mol/L, were studied. Additionally, a  
121 series of experiments on the CO solution pH, 0.53, 1.02, 2.03, 2.98 and 4.04, were  
122 conducted to investigate the effect of pH. Based on the actual temperature conditions  
123 of a typical coal-fired power plant, seven temperature points, 60, 70, 80, 90, 100, 110  
124 and 120°C and four SO<sub>2</sub> contents, 520, 1050, 1560 and 2100 mg/m<sup>3</sup>, were selected to  
125 evaluate the effects of reaction temperature and SO<sub>2</sub> on NO removal. Based on the  
126 data of temperature dependent, the apparent activation energy of NO removal was  
127 calculated using the Arrhenius equation.

## 128 **3 Results and Discussion**

### 129 **3.1 NO oxidation**

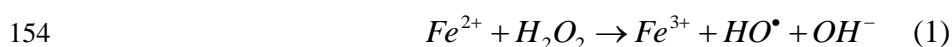
## 130 **3 Results and Discussion**

### 131 **3.1 NO oxidation**

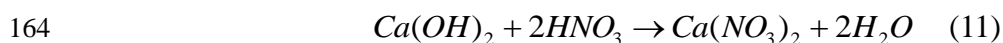
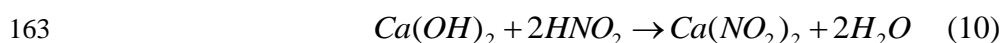
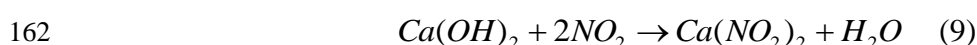
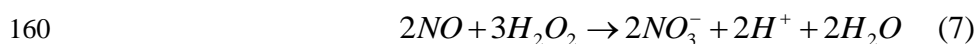
132 First of all, the reaction mechanism of NO oxidation by vaporized CO was  
133 analyzed. The components in CO are H<sub>2</sub>O<sub>2</sub>, PAA and ferrous, in which, the former

134 two are oxidants, the later is catalyst. It has been known that the combination of H<sub>2</sub>O<sub>2</sub>  
 135 and ferrous can generate hydroxyl radicals (HO·) (Eq.1) that is an active oxidant  
 136 produced from ferrous catalyzing H<sub>2</sub>O<sub>2</sub>. Also, a similar catalytic action between PAA  
 137 and ferrous can occur, from which, the oxidation potential of PAA is significantly  
 138 enhanced in the acidic condition [21], of which the product is still hydroxyl radicals  
 139 (Eq.2). As for H<sub>2</sub>O<sub>2</sub> and PAA, their synergy in the acidic condition has been revealed  
 140 previously, in which, the acetic acid resulting from the reduction or the decomposition  
 141 of PAA (Eq.3), can participate in the reaction between H<sub>2</sub>O<sub>2</sub> and PAA (Eq.4), leading  
 142 to an inhibition on H<sub>2</sub>O<sub>2</sub> decomposition and maintaining the concentration of PAA.  
 143 Therefore, all of the three components in CO can improve the performance of  
 144 vaporized CO oxidizing NO.

145 According to the above analysis, the main oxidation species in CO are concluded  
 146 as H<sub>2</sub>O<sub>2</sub>, PAA and HO·; especially HO· due to the reaction rates between HO· and NO  
 147 are  $5.5 \times 10^{14} \text{ M}^{-1}\text{s}^{-1}$  or  $10^8\text{-}10^{12} \text{ M}^{-1}\text{s}^{-1}$  [22]. Furthermore, from the perspective of  
 148 electrochemical, the standard electrode potentials of H<sub>2</sub>O<sub>2</sub> (1.770 V), HO· (2.800 V)  
 149 and PAA (1.960 V) are far higher than those of NO<sub>2</sub>/NO (1.049 V), NO<sub>3</sub><sup>-</sup>/NO (0.957  
 150 V), NO<sub>2</sub><sup>-</sup>/NO (0.460 V) and NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> (0.835 V), which also shows the feasibility of  
 151 NO oxidation by vaporized CO (Eqs.5-8) [23-29]. After oxidation, the just generated  
 152 oxidation products are rapidly absorbed by Ca(OH)<sub>2</sub> with producing Ca(NO<sub>3</sub>)<sub>2</sub> and  
 153 Ca(NO<sub>2</sub>)<sub>2</sub> (Eqs.9-11).







### 165 3.2 Reaction Order

166 The NO removal by vaporized CO as a function of reaction time is shown in Fig.  
 167 2. It can be found that the typical NO depletion appears to be exponential to the  
 168 reaction time, indicating that the depletion conforms to the pseudo-first-order kinetics  
 169 pattern in a rapid depletion zone (1-2 half-lives) with respect to NO. Obviously, the  
 170 oxidation rate of NO dominated the NO depletion rate. Therefore, the overall rate of  
 171 NO depletion can be expressed as followed (Eqs.12-13).

172 
$$-\frac{d[NO]}{dt} = k_{obs}[NO] \quad (12)$$

173 
$$k_{obs} = k_1[OH] + k_2[H_2O_2] + k_3[PAA] \quad (13)$$

174 Where  $k_{obs}$  is the pseudo-first-order rate constant that represents an overall rate of  
 175 the NO removal by a variety of oxidizing agents (e.g.,  $H_2O_2$ , PAA, and HO )  
 176 produced in the system;  $[H_2O_2]$ ,  $[PAA]$  and  $[HO]$  are the concentrations of  $H_2O_2$ ,  
 177 PAA, and HO ;  $mmol/m^3$ ;  $[NO]$  is the concentration of NO at any time,  $mg/m^3$ .

178 The reaction order of NO oxidation could be calculated by using the initial rate  
 179 method. A series of curves of the NO depletion versus reaction time under various  
 180 initial NO concentrations were obtained, from which, the initial rates ( $r_0$ ) were  
 181 obtained via the reaction 15. And then the reaction order could be calculated by  
 182 integrating the differential form of the reaction 16. Reaction 17 expresses the relation  
 183 of  $\lg(-d_c/d_t)$  and  $\lg c$ , in which,  $n$  is the reaction order with respect to NO. As shown in  
 184 Fig. 2, the determined reaction order of NO is 1.119,  $R^2$  is 0.998, indicating that the  
 185 reaction order can be considered as pseudo-first-order kinetics.

$$186 \quad c = f(t) \quad (14)$$

$$187 \quad r_0 = \frac{dC_0}{dt} = \frac{df(t)_{t=0}}{dt} \quad (15)$$

$$188 \quad r_0 = -\frac{dC_0}{dt} = k' c_0^n \quad (16)$$

$$189 \quad \lg\left(-\frac{dC_0}{dt}\right) = \lg k' + n \lg c_0 \quad (17)$$

190 Where  $c$  and  $c_0$  are the NO concentrations at each time and at  $t=0$ , respectively,  
 191  $\text{mg}/\text{m}^3$ ;  $r_0$  is the rate of NO depletion at  $t=0$ ,  $\text{ppm}^{-1} \text{ s}^{-1}$ ;  $k'$  is the rate that represents an  
 192 overall rate of the NO removal by a variety of oxidizing agents (e.g.,  $\text{H}_2\text{O}_2$ , PAA, and  
 193  $\text{HO} \cdot$ ) produced in the system,  $\text{ppm}^{1-n} \text{ s}^{-1}$ ;  $n$  is the NO reaction order.

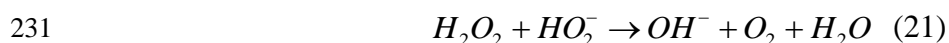
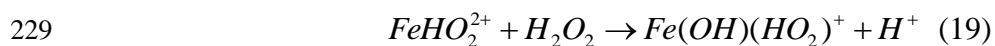
### 194 3.3 Effect of the CO constitution

195 The effect of CO constitution on NO removal was investigated. The experimental  
 196 conditions are shown in Table. 1. It can be seen from Fig. 3 that, for any particular  
 197 constitution, the NO depletion exhibits a pseudo-first-order pattern ( $R^2=0.99$ ). When  
 198  $\text{H}_2\text{O}_2$  is used as the oxidant, the pseudo-first-order rate constant is  $0.01093 \text{ s}^{-1}$ , which  
 199 is the minimum among the three tests. When the CO is made up of PAA and  $\text{H}_2\text{O}_2$ , the

200 rate constant increases to  $0.01486 \text{ s}^{-1}$ . However, the highest rate constant of  $0.02234$   
201  $\text{ s}^{-1}$  is obtained when the CO consists of PAA,  $\text{H}_2\text{O}_2$  and ferrous. Therefore, the  
202 additions of ferrous and PAA can significantly accelerate NO oxidation rate. As for  
203 the efficiency, a similar trend is also observed in Fig. 3, the efficiencies are 59.3%,  
204 79.7% and 87.2% with regarding the CO constitutions of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2/\text{PAA}$  and  
205  $\text{H}_2\text{O}_2/\text{PAA}/\text{ferrous}$ . Therefore, the promotion of ferrous and PAA on the rate and the  
206 efficiency of NO oxidation was demonstrated, the functional mechanism owing to  
207 ferrous and PAA was shown in section 3.1.

208 It is important to investigate the effect of ferrous concentration on NO removal  
209 because the amount of  $\text{HO}\cdot$  generation is directly affected by the ferrous addition.  
210 Therefore, a series of experiments with four ferrous concentrations were conducted at  
211 a fixed NO concentration of  $550 \text{ mg/m}^3$ . It can be seen from Table. 1 and Fig. 4 that  
212 the rate constants are  $0.01107$ ,  $0.02234$ ,  $0.02348$  and  $0.02706 \text{ s}^{-1}$  with respect to the  
213 ferrous concentrations of 3, 5, 7 and 9 mmol/L, indicating that the oxidation rate is  
214 increased evidently as the ferrous concentration rise. Fig. 4 also shows the dependent  
215 of removal efficiency on ferrous concentration. It can be found that the removal  
216 efficiency increases in the ferrous concentration range of 3 to 5 mmol/L, but declines  
217 in the concentration range of 5 to 9 mmol/L. The experimental phenomenon revealed  
218 that more ferrous was beneficial for promoting the oxidation rate rather than the  
219 removal efficiency, which was due to that more ferrous could generate more hydroxyl  
220 radicals in a short time, resulting in an increase of oxidation rate; however, the  
221 ferrous-induced side reactions [25] resulting from excessive ferrous, such as the

222 quenching of hydroxyl radicals (Eq.18) and the decomposition of  $H_2O_2$  (Eq.19),  
 223 would consume lots of effective oxidants and decrease the oxidizability of CO, which  
 224 led to a decline of NO removal efficiency. Not only to that, the generated  $OH^-$  via  
 225 the reaction 18 may destroy the catalytic function of ferrous because of the ferrous  
 226 precipitation, meanwhile, the  $H_2O_2$  decomposition also would be further aggravated  
 227 (Eqs.18, 20-21).



### 232 **3.4 Effect of Reaction Temperature**

233 The effect of reaction temperature on NO removal was investigated. The  
 234 pseudo-first-order kinetics rate constants under various reaction temperatures were  
 235 shown in Table. 2. It can be seen from Fig. 5 that as the temperature increases from  
 236 333 to 393 K, the rate constant increases from 0.00946 to 0.01980  $s^{-1}$  step by step. Fig.  
 237 5 also shows the dependent of removal efficiency on the reaction temperature, it can  
 238 be found that the lower temperature in the range of 333-363 K has an obvious  
 239 promotion on the NO removal efficiency, while the higher temperature in the range of  
 240 363-393 K plays an inhibition role. Thereby the optimal temperature was 363 K,  
 241 which was consistent with the actual temperature conditions of ESP outlet, indicating  
 242 that the vaporized CO had a potential to couple with the ESP system to realize the  
 243 simultaneous removal of  $SO_2$  and NO. During the experiments, some phenomenon of

244 temperature dependent occurred as the temperature variation, i.e. the elevated  
245 temperature in the low temperature range could promote the vaporization rate of CO,  
246 the reactants diffusion and the chemical reaction rate; nevertheless, the excessive  
247 temperature was unfavorable for the chemical reaction because of the intense  
248 decompositions of the reactants and the increase of mass transfer resistance between  
249 the oxidation products and  $\text{Ca}(\text{OH})_2$ .

250 As shown in Fig. 6, obviously,  $\ln k_{\text{obs}}$  decreases linearly with  $1/T$ , therefore,  
251 which is fitted to an Arrhenius model (Eq.22). After fitting, the apparent activation  
252 energy was 14.1 kJ/mol and the  $\ln A$  was 0.58. Compared with some other apparent  
253 activation energies of NO oxidation obtained in previous researches, such as the 42.5  
254 kJ/mol for  $\text{NaClO}_2$  [30], the 27.8 kJ/mol for  $\text{H}_2\text{O}_2/\text{NaOH}$  [31], the apparent activation  
255 energy of vaporized CO oxidizing NO was lower. And the following reasons may  
256 account for the phenomena: compared with the wet bubble reaction system, the  
257 proposed novel method had an advantage of larger contact area between the oxidants  
258 and NO resulting from the vaporization process. In addition to that, the oxidation  
259 potential and reactivity of  $\cdot\text{OH}$  are far higher than  $\text{ClO}_2$ ,  $\text{ClO}_2^-$  and  $\text{HO}_2^-$  employed by  
260 predecessors. Therefore, the reaction barrier of NO oxidation in our reaction system  
261 was much lower.

$$262 \quad k = A \times \exp\left(-\frac{Ea}{RT}\right) \quad (22)$$

263 Then the log-type was deduced as followed (Eq.23):

$$264 \quad \ln k = \ln A - Ea / RT \quad (23)$$

265 Where  $A$  is the pre-exponential factor,  $Ea$  is the apparent activation energy,  $R$  is

266 the universal gas constant, and  $T$  is the absolute temperature.

### 267 **3.5 Effect of pH**

268 The pH has a significant influence on the oxidation potentials of  $H_2O_2$  and PAA  
269 and the stability of ferrous. Therefore, the effect of CO pH on NO removal was  
270 investigated, as shown in Fig. 7 and Table. 2. It can be seen that the rate constants are  
271 0.01423, 0.00909, 0.00698, 0.00496 and 0.00343  $s^{-1}$ , responding to the pH of 0.5, 1.0,  
272 2.0, 3.0 and 4.0. Apparently, the lower pH is favorable for increasing the oxidation  
273 rate. Similarly, as shown in Fig. 7, the removal efficiency is also sharply decreased  
274 from 90.3% to 42.1% as a same variation of pH, which may be due to the following  
275 reasons: 1) at a higher solution pH,  $H_2O_2$  was rapidly decomposed as  $HO_2^-$  (Eq.20)  
276 [32-33], which could adversely accelerate the  $H_2O_2$  decomposition via the reaction 21  
277 [34] and consume  $OH$  (Eq.24), from which, the oxidizability of the reaction system  
278 was decreased with the solution pH increasing. 2) similarly, the elevated pH also had  
279 a great inhibition on PAA and ferrous, as discussed in the section 3.1 and the section  
280 3.3.



### 282 **3.6 Effect of $SO_2$ Concentration**

283  $SO_2$  is a coexistence gas in coal-fired flue gas and has a potential to affect NO  
284 removal. Therefore, the experiments with four  $SO_2$  concentrations, 520, 1050, 1560  
285 and 2100  $mg/m^3$ , were conducted to investigate the effect of  $SO_2$  on NO removal. It  
286 can be seen from Fig. 8 and Table. 2 that  $SO_2$  has no significant influence on the  
287 oxidation rate, but the higher  $SO_2$  concentration in the range of 1050 to 2100  $mg/m^3$

288 has a slight inhibition on the NO removal efficiency, which may be a consequence of  
289 the competition reaction between SO<sub>2</sub> and NO for the limited oxidants. Generally, the  
290 vaporized CO exhibited a good performance on the adaption of SO<sub>2</sub> variation. Hence,  
291 the proposed method can be adaptive to the various coal-types and working conditions  
292 of boiler.

#### 293 **4 Conclusions**

294 This study made an effort to explore the macrokinetics of NO oxidation by a  
295 vaporized H<sub>2</sub>O<sub>2</sub>-based complex oxidant (CO). The reaction order was 1.119 with  
296 respect to NO, which could be considered as the pseudo-first-order kinetics in a rapid  
297 depletion zone (1-2 half-lives). The effects of the CO constitution, the ferrous  
298 concentration, the reaction temperature, the pH of CO and the SO<sub>2</sub> concentration on  
299 NO removal were investigated experimentally. The rate constants of temperature  
300 dependent were well fitted to an Arrhenius model, from which, the apparent activation  
301 energy of NO oxidation was calculated as 14.1 kJ/mol. The experimental results  
302 demonstrated that the novel process can rapidly and effectively remove NO, which  
303 provided a viable alternative option to reduce the NO<sub>x</sub> emission from coal-fired power  
304 plants.

#### 305 **Acknowledgments**

306 The authors appreciate the financial support by a grant from the National High  
307 Technology Research and Development Program of China (863 Program, No.  
308 2013AA065403), Hebei provincial Natural Science Foundation, P. R. China  
309 (B2011502027), Program for Changjiang Scholars and Innovative Research Team in

310 University (IRT1127) and Zhejiang Provincial Engineering Research Center of  
311 Industrial Boiler & Furnace Flue Gas Pollution Control, Hangzhou, P. R. China  
312 (311202).

### 313 **References**

- 314 [1] S.J. Chung, K.C. Pillai, I.S. Moon, A sustainable environmentally friendly NO<sub>x</sub>  
315 removal process using Ag(II)/Ag(I)-mediated electrochemical oxidation, Sep.  
316 Purif. Technol. 65 (2009) 156–163.
- 317 [2] M. Govindan, S.J. Chung, Il.S. Moon, Simple Technical Approach for Perpetual  
318 Use of Electro generated Ag(II) at Semi pilot Scale: Removal of NO and SO<sub>2</sub> as  
319 a Model System, Ind. Eng. Chem. Res. 51 (2012) 2697–2703.
- 320 [3] P. Davini, SO<sub>2</sub> and NO<sub>x</sub> adsorption properties of activated carbons obtained from a  
321 pitch containing iron derivatives, Carbon. 39 (2001) 2173–2179.
- 322 [4] Q. Tang, Z.G. Zhang, W.P. Zhu, Z.D. Cao, SO<sub>2</sub> and NO selective adsorption  
323 properties of coal-based activated carbons, Fuel. 84 (2005) 461–465.
- 324 [5] K. Krishna, M. Makkee, Coke formation over zeolite and CeO<sub>2</sub>-zeolite and its  
325 influence on selective catalytic reduction of NO<sub>x</sub>, Appl. Catal. B 62 (2005)  
326 35-44.
- 327 [6] M.J. Sang, D.K. Sang, Removal of NO<sub>x</sub> and SO<sub>2</sub> by CuO/γ-Al<sub>2</sub>O<sub>3</sub> sorbent/catalyst  
328 in a fluidized-bed reactor, Ind. Eng. Chem. Res. 39 (2000) 1911–1916.
- 329 [7] L. Wang, W.R. Zhao, Z.B. Wu, Simultaneous absorption of NO and SO<sub>2</sub> by FeII  
330 EDTA combined with Na<sub>2</sub>SO<sub>3</sub> solution, J. Chem. Eng. 132 (2007) 227–232.
- 331 [8] X.L. Long, W.D. Xiao, W.K. Yuan, Kinetics of gas–liquid reaction between NO



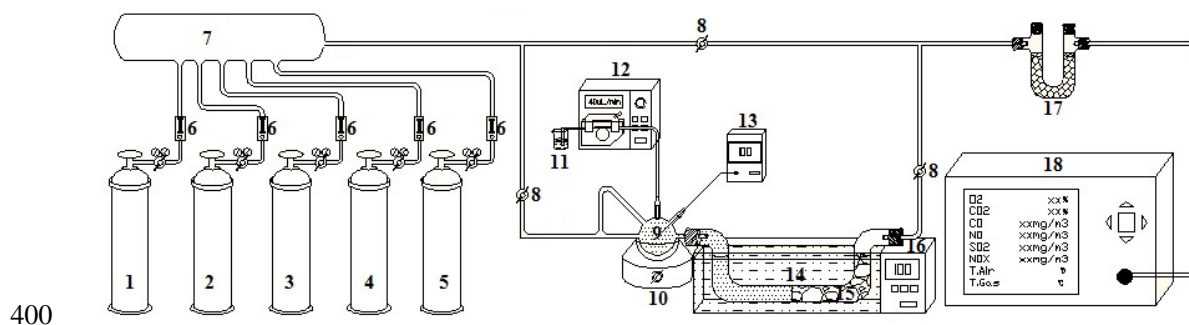
- 332 and  $\text{Co}(\text{NH}_3)_6^{2+}$ , *J. Hazard. Mater. B* 123 (2005) 210–216.
- 333 [9] H. Chu, T.W. Chien, B.W. Twu, The absorption kinetics of NO in  $\text{NaClO}_2/\text{NaOH}$   
334 solutions, *J. Hazard. Mater. B* 84 (2001) 241–252.
- 335 [10] J.C. Wei, Y.B. Luo, B. Yu, Removal of NO from flue gas by wet scrubbing with  
336  $\text{NaClO}_2/(\text{NH}_2)_2\text{CO}$  solutions, *J. Ind. Eng. Chem.* 15 (2009) 16–22.
- 337 [11] Y. Zhao, T.X. Guo, Z.Y. Chen, Y.R. Du, Simultaneous removal of  $\text{SO}_2$  and NO  
338 using  $\text{M}/\text{NaClO}_2$  complex absorbent, *Chem. Eng. J.* 160 (2010) 42–47.
- 339 [12] Y. Zhao, Y.H. Han, T.Z. Ma, T.X. Guo, Simultaneous Desulfurization and  
340 Denitrification from Flue Gas by Ferrate (VI), *Environ. Sci. Technol.* 45 (2011)  
341 4060–4065.
- 342 [13] C. Brogren, H.T. Karlsson, I. Bjerle, Absorption of NO in an alkaline solution of  
343  $\text{KMnO}_4$ , *Chem. Eng. Technol.* 20 (1997) 396–402.
- 344 [14] P. Fang, C.P. Cen, Z.X. Tang, P.Y. Zhong, D.S. Chen, Z.H. Chen, Simultaneous  
345 removal of  $\text{SO}_2$  and  $\text{NO}_x$  by wet scrubbing using urea solution, *Chem. Eng. J.*  
346 168 (2011) 52–59.
- 347 [15] Y.X. Liu, J. Zhang, C.D. Sheng, Y.C. Zhang, L. Zhao, Simultaneous removal of  
348 NO and  $\text{SO}_2$  from coal-fired flue gas by UV/ $\text{H}_2\text{O}_2$  advanced oxidation process,  
349 *Chem. Eng. J.* 162 (2010) 1006–1011.
- 350 [16] Y.X. Liu, J. Zhang, Photochemical Oxidation Removal of NO and  $\text{SO}_2$  from  
351 Simulated Flue Gas of Coal-Fired Power Plants by Wet Scrubbing Using  
352 UV/ $\text{H}_2\text{O}_2$  Advanced Oxidation Process, *Ind. Eng. Chem. Res.* 50 (2011)  
353 3836–3841.

- 354 [17] C.D. Cooper, C.A. Clausen, L. Pettey, Investigation of UV enhanced H<sub>2</sub>O<sub>2</sub>  
355 oxidation of NO<sub>x</sub> emissions, *Environ. Eng.* 128 (2002) 68–72.
- 356 [18] Y.S. Mok, Absorption–reduction technique assisted by ozone injection and  
357 sodium sulfide for NO<sub>x</sub> removal from exhaust gas, *Chem. Eng. J.* 118 (2006)  
358 63-67.
- 359 [19] P. Fang, C.P. Cen, X.M. Wang, Z.J. Tang, Z.X. Tang, D.S. Chen, Z.H. Chen,  
360 Simultaneous removal of SO<sub>2</sub>, NO and Hg<sup>0</sup> by wet scrubbing using urea+KMnO<sub>4</sub>  
361 solution, *Fuel. Process. Technol.* 106 (2013) 645–653.
- 362 [20] X.H. Xua, Q.F. Ye, T.M. Tang, D.H. Wang, Hg<sup>0</sup> oxidative absorption by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>  
363 solution catalyzed by Ag<sup>+</sup> and Cu<sup>2+</sup>, *J. Hazard. Mater.* 158 (2008) 410–416.
- 364 [21] E.S. Huyser, G.W. Hawkins, Ferrous Ion Catalyzed Oxidations of 2-Propanol  
365 with Peroxyacetic Acid, *J. Org. Chem.* 48 (1983) 1705-1708.
- 366 [22] Y.X. Liu, J. Zhang, C.D. Sheng, Study on the Kinetics of NO Removal from  
367 Simulated Flue Gas by a Wet Ultraviolet/H<sub>2</sub>O<sub>2</sub> Advanced Oxidation Process,  
368 *Energy. Fuel.* 25 (2011) 1547–1552.
- 369 [23] E.S. Hwang, J.N. Cash, M.J. Zabik, Ozone and Hydrogen Peroxyacetic Acid  
370 Treatment To Reduce or Remove EBDCs and ETU Residues in a Solution, *J.*  
371 *Agric. Food Chem.* 49 (2001) 5689-5694.
- 372 [24] E.S. Huyser, G.W. Hawkins, Ferrous ion catalyzed oxidations of 2-propanol with  
373 peroxyacetic acid, *J. Org. Chem.* 48 (1983) 1705-1708.
- 374 [25] B. Ensing, F. Buda, E.J. Baerends, Fenton-like Chemistry in Water: Oxidation  
375 Catalysis by Fe(III) and H<sub>2</sub>O<sub>2</sub>, *J. Phys. Chem. A* 107 (2003) 5722-5731.

- 376 [26] M. Kitis, Disinfection of wastewater with peracetic acid: a review, *Environ. Int.*  
377 30 (2004) 47-55.
- 378 [27] J.C. Farrand, D. Johnson, Peroxyacetic acid oxidation of 4-methylphenols and  
379 their methyl ethers, *J. Org. Chem.* 36 (1971) 3606-3612.
- 380 [28] G.B. Payne, P.H. Williams, Notes-reaction of mesityl oxide with peroxyacetic  
381 acid, *J. Org. Chem.* 24 (1959) 284-286.
- 382 [29] J.D. Laat, T.G. Le, Kinetics and Modeling of the Fe(III)/H<sub>2</sub>O<sub>2</sub> System in the  
383 Presence of Sulfate in Acidic Aqueous Solutions, *Environ. Sci. Technol.* 39  
384 (2005) 1811-1818.
- 385 [30] F. Liu, Experimental and Mechanism Study on Simultaneous Removal of SO<sub>2</sub>  
386 and NO<sub>x</sub> using jet bubble reactor. North China Electric Power University, 2009.
- 387 [31] T.X. Guo, Experimental Investigation on Simultaneous Removal SO<sub>2</sub> and NO<sub>x</sub> in  
388 Liquid Phase by New-type Complex Absorbent. North China Electric Power  
389 University, 2011.
- 390 [32] Q.H. Hu, C.L. Zhang, Z.R. Wang, Y. Chen, K.H. Mao, X.Q. Zhang, Y.L. Xiong,  
391 M.J. Zhu, Photodegradation of methyl tertbutyl ether (MTBE) by UV/ H<sub>2</sub>O<sub>2</sub> and  
392 UV/TiO<sub>2</sub>. *J. Hazard. Mater.* 154 (2008) 795–803.
- 393 [33] F. Yuan, C. Hu, X.X. Hu, ; J.H. Qu, M. Yang, Degradation of selected  
394 pharmaceuticals in aqueous solution with UV and UV/H<sub>2</sub>O<sub>2</sub>. *Water. Res.* 43  
395 (2009) 1766–1774.
- 396 [34] W.M. Wang, J.Song, X. Han, Schwertmannite as a new Fenton-like catalyst in the  
397 oxidation of phenol by H<sub>2</sub>O<sub>2</sub>. *J. Hazard. Mater.* 262 (2013) 412–419.

## Figures

398

399 **Fig. 1**

400

401 Schematic diagram of the experimental apparatus of the fix-bed.

402 1-5 CO<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, NO, O<sub>2</sub> gas cylinders; 6-flowmeters; 7-buffer bottle; 8-tee joint;

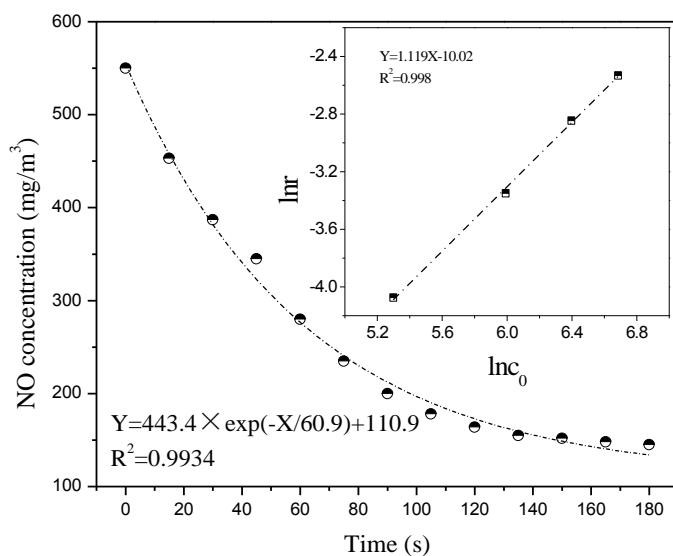
403 9-vaporization device; 10-thermal control electric heater; 11-CO solution;

404 12-peristaltic pump; 13-thermal couple; 14-reactor; 15-Ca(OH)<sub>2</sub>; 16-thermostat oil

405 bath; 17-dryer; 18-flue gas analyzer.

406

407

408 **Fig. 2**

409

410 Determination of reaction order with respect to NO.

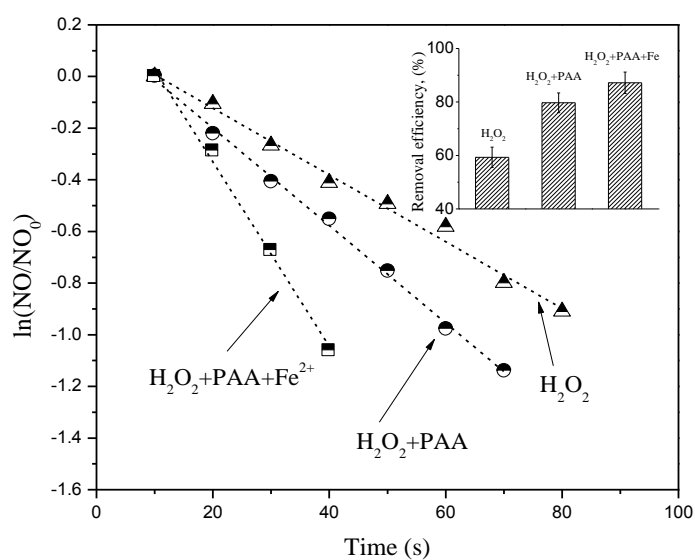
411 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200 $\mu$ l/min; CO

412 solution pH is 0.7, reaction temperature is 363 K, NO concentration is 550 mg/m<sup>3</sup>.

413

414

415 **Fig. 3**



416

417 Pseudo-first-order depletion of NO at various CO constitutions.

418 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200 $\mu$ l/min; CO

419 solution pH is 0.7, reaction temperature is 363 K, NO concentration is 550 mg/m<sup>3</sup>.

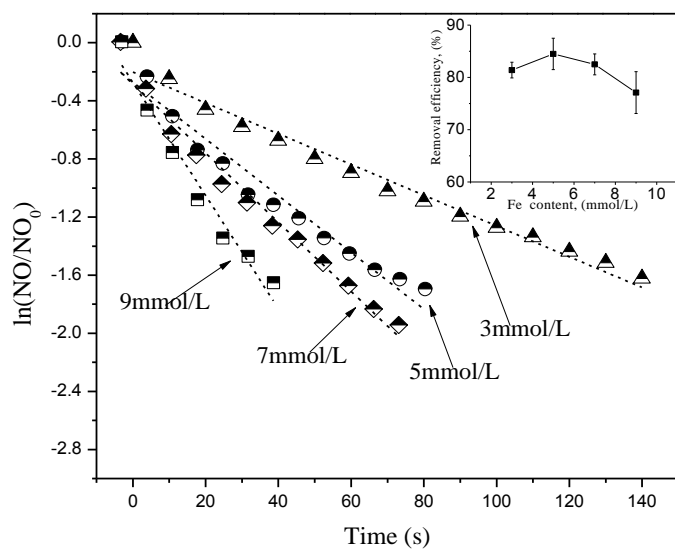
420

421

422

423

424

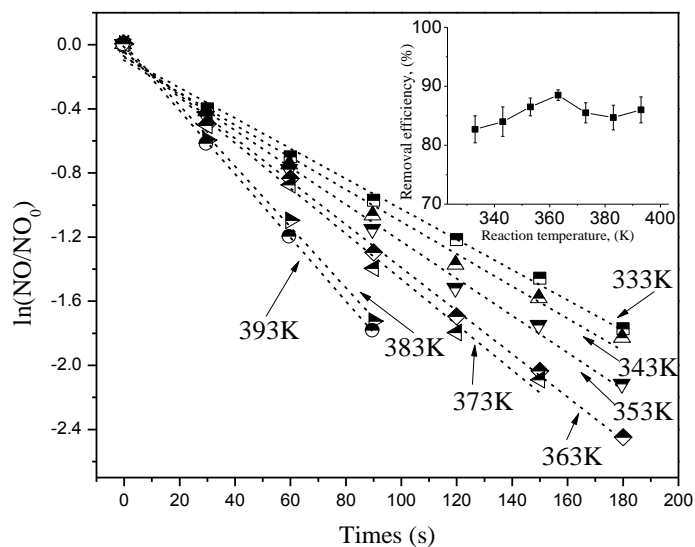
425 **Fig. 4**

426

427 Pseudo-first-order depletion of NO at various ferrous concentrations.

428 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200  $\mu\text{l}/\text{min}$ ; CO429 solution pH is 0.7, reaction temperature is 363 K, NO concentration is 550  $\text{mg}/\text{m}^3$ .

430

431 **Fig. 5**

432

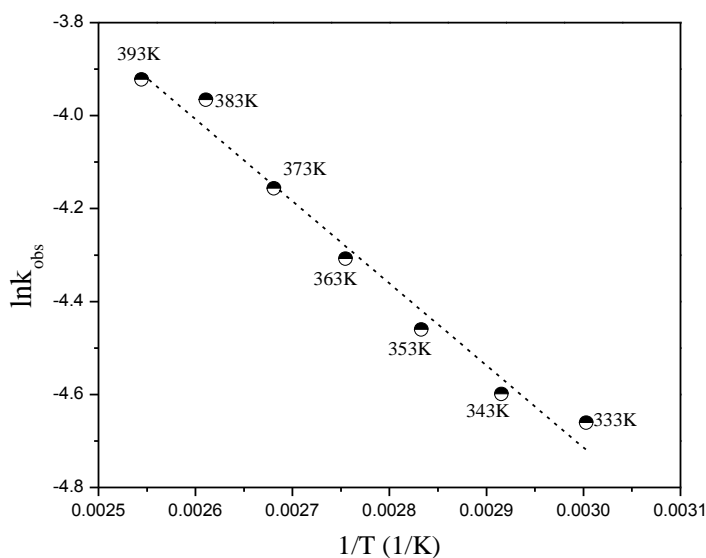
433 Pseudo-first-order depletion of NO under various reaction temperatures.

434 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200 $\mu$ l/min; CO

435 solution pH is 0.7, NO concentration is 550 mg/m<sup>3</sup>.

436

437 **Fig. 6**



438

439 Arrhenius plots for the removal of NO.

440 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200  $\mu$ l/min; CO

441 solution pH is 0.7, NO concentration is 550 mg/m<sup>3</sup>.

442

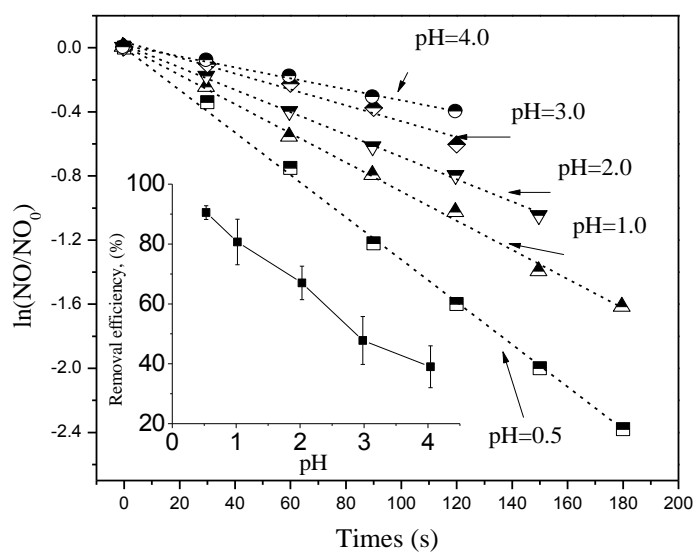
443

444

445

446

447

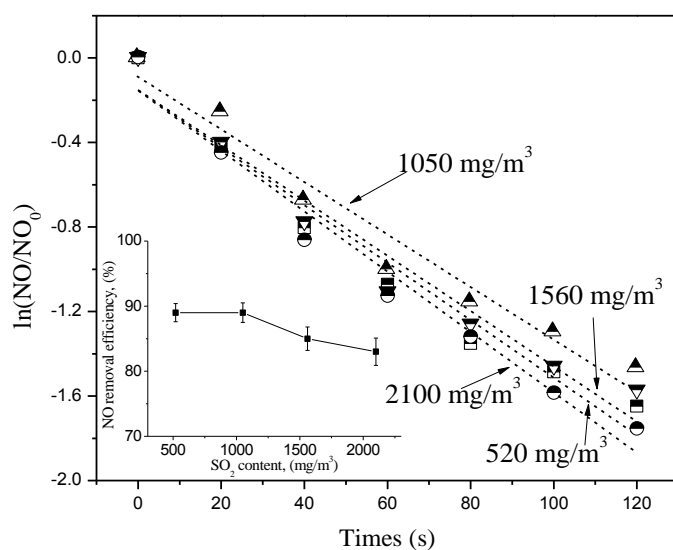
448 **Fig. 7**

449

450 Pseudo-first-order depletion of NO under various pH.

451 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200  $\mu\text{l}/\text{min}$ ;452 reaction temperature is 363 K, NO concentration is 550  $\text{mg}/\text{m}^3$ .

453

454 **Fig. 8**

455



456 Pseudo-first-order depletion of NO under various SO<sub>2</sub> contents.  
 457 Simulated flue gas inlet velocity is 4.0 L/min, adding rate of CO is 200 µl/min;  
 458 reaction temperature is 363 K, NO concentration is 550 mg/m<sup>3</sup>.

459

460

461

462

463

## Tables

464

465 **Table 1**

466 Pseudo-first-order kinetics parameters of NO removal at various CO constitutions.

Test	CO constitution			t <sub>1/2</sub> , s	Rate constant (k, s <sup>-1</sup> )	Denitrification efficiency	Correlation coefficient, R <sup>2</sup>
	H <sub>2</sub> O <sub>2</sub> , mol/L	PAA, mol/L	Fe <sup>2+</sup> , mmol/L				
1	4	0	0	63.4	0.01093	59.3%	0.98993
2	4	1	0	46.6	0.01486	79.7%	0.99725
3	4	1	5	31	0.02234	87.2%	0.99301
4	4	1	3	62.6	0.01107	81.4%	0.98083
5	4	1	7	51.4	0.02348	82.5%	0.98227
6	4	1	9	25.6	0.02706	77.1%	0.95897

467

468

469

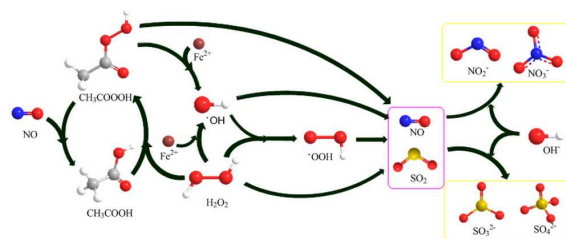
470

471 **Table 2**

472 Pseudo-first-order kinetics parameters of NO removal under various reaction  
 473 conditions

	Reaction conditions			$t_{1/2}$ , s	Rate constant ( $k, s^{-1}$ )	Removal efficiency	Correlation coefficient, $R^2$
	Temperature (K)	pH	NO/ SO <sub>2</sub> (mg/m <sup>3</sup> )				
1	333	0.7	550	73.3	0.00946	83.2	0.99264
2	343	0.7	550	68.9	0.01006	84.3	0.98695
3	353	0.7	550	60	0.01156	86.7	0.99432
4	363	0.7	550	51.5	0.01346	88.9	0.99765
5	373	0.7	550	45.7	0.01517	85.3	0.99266
6	383	0.7	550	36.6	0.01895	84.9	0.99738
7	393	0.7	550	35	0.01980	85.4	0.99967
8	363	0.5	550	48.7	0.01423	90.3	0.98734
9	363	1.0	550	76.2	0.00909	81.1	0.99673
10	363	2.0	550	99	0.00698	68.7	0.99785
11	363	3.0	550	140	0.00496	48.7	0.96773
12	363	4.0	550	202	0.00343	42.1	0.99213
13	363	0.7	550/520	45.9	0.01511	88.6	0.95714
14	363	0.7	550/1050	51.6	0.01344	88.3	0.95388
15	363	0.7	550/1560	53	0.01308	84.7	0.94676
16	363	0.7	550/2100	48.5	0.01429	85.5	0.96450

474



Macrokinetics and feasibility of denitrification using a vaporized enhanced-Fenton reagent were determined.