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NO_x removal in chemical absorption–biological reduction integrated system: Process rate and rate-limiting step

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HIGHLIGHTS

- We compared the process rates and confirmed the rate-limiting step.
- Rate constants of NO absorption and oxidation were obtained.
- Michaelis–Menten kinetic constants of regeneration part were obtained.
- We proposed some suggestions to enhance the bioreduction process.

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ABSTRACT

Biological reduction of Fe(III)EDTA is considered as the key step that limits the removal efficiency of the chemical absorption–biological reduction integrated system. In this study, the process rates of each reaction step under typical conditions (T = 50 °C, $C_{FeII(EDTA)}$ = 1–5 mmol/L, C_{NO} = 0–500 ppm, C_{O_2} = 1–10%, pH = 7) were determined. Relevant kinetic constants including rate constants of absorption part and Michaelis–Menten kinetic constants of regeneration part were also obtained. On this basis, the theoretical process rates of each reaction step were predicted and compared in a steady state. The results confirmed that the removal rate of NO in this system is limited by the biological reduction of Fe(III)EDTA. Moreover, it indicated that increasing the concentration of total iron appropriately could enhance the bioreduction of Fe(III)EDTA.

1. Introduction

Acid rain is one of the most important global environmental problems, which is very harmful and mostly caused by the large amount of SO_2 and NO_x emissions (Chien et al., 2009). Several sulfur dioxide emission control technologies have been employed in industry, such as wet limestone process, seawater process, etc. (Pandey et al., 2005). On the other hand, only SCR (selective catalytic reduction) and SNCR (selective non-catalytic reduction) have been widely used in the NO_x emission control of coal-fired flue gas (Radojevic, 1998). However, high cost and the risk of ammonia leakage restrain their applications in small and medium sized boilers. One promising approach of removing nitrogen oxides from flue gas is chemical absorption integrated with biological reduction (Li et al., 2006; Zhang et al., 2008; Niu and Leung, 2010; Wang et al., 2013). In this system, absorption and regeneration are two main parts. Each part includes two processes: metal chelate absorption of NO and oxidation of Fe(II)EDTA in absorption part, biological reduction of Fe(II)EDTA–NO and Fe(III)EDTA in regeneration part (Winkelman et al., 2007; van der Maas et al., 2008; Dong et al., 2012; Chen et al., 2012). The main reactions involved in this system can be expressed as following (Li et al., 2007; Zhang et al., 2007):

$$Fe(II)EDTA + NO(aq) \leftrightarrows Fe(II)EDTA - NO \quad (1)$$

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

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

$$12Fe(II)EDTA - NO + C_6H_{12}O_6 \xrightarrow{microorganism} 12Fe(II)EDTA + 6N_2 + 6H_2O + 6CO_2 \quad (4)$$

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Nomenclature

A	nitric oxide NO
O	oxygen
F	Fe(II)EDTA
P	Fe(II)EDTA–NO
Q	Fe(III)EDTA
E	enzyme
EQ	intermediate product
C	concentration (mol m^{-3})
D	diffusion coefficient (m^2 s^{-1})
N	flux of absorption (mol m^{-2} min^{-1})
K	equilibrium constant (mol m^{-3})
R	the ratio of diffusion coefficient
S	the ratio of stoichiometric concentration
γ_L	the transfer coefficient
r_1, r_2	reaction rate, see Eqs. (1), (2) (mol m^{-3} s^{-1})
k_1	reaction rate constant for first order reaction (s^{-1})
k_2	reaction rate constant for second order reaction (M^{-1} s^{-1})
$k_{1,1}$	reaction rate constant for bimolecular reaction (M^{-1} s^{-1})
k_S	half saturation constant (mol m^{-3})
v_{max}	maximum specific reaction rate (mol m^{-3} h^{-1})
t	time (h)

Subscripts

0	initial state
i	interface
m	reaction order
L	liquid phase
t	total
I	first step
−I	first step of reverse reaction
II	second step

It is considered that biological reduction of Fe(III)EDTA is the key step that limits the removal rate of the whole system from previous study (Zhang et al., 2008). However, it was concluded from experimental phenomena, further experiments still need to be done to quantify and compare the process rates of each reaction step for further confirmation.

Oxidation of Fe(II)EDTA is an undesirable process in this system though it is inevitable due to the presence of oxygen in flue gas. Understanding the oxidation mechanism and behavior is essential for minimizing its negative effects on the whole system. Enhancing the biological reduction of Fe(II)EDTA–NO and Fe(III)EDTA is the main challenge to improve the NO removal efficiency.

In this work, a series of experiments were done to determine the process rates of each reaction step. Relevant kinetic constants were obtained and utilized to predict the theoretical process rates. The rate-limiting step was found through the comparison of the theoretic process rates of each reaction step.

2. Experimental section

2.1. Chemicals

All reagents used were provided by Shanghai Chemical Reagent Co., China and were analytical reagent grade. All gases employed in this study were purchased from Zhejiang Jingong Gas Co., China. Oxygen-free distilled water was used all through the experiments.

2.2. Microorganism cultivation and media composition

Two kinds of microorganisms, *Pseudomonas* sp. strain DN-2 (Zhang et al., 2007) and *Escherichia coli* strain FR-2 (Li et al., 2007), were mixed cultivated to form biofilm. The basal medium was made up of the following compositions (per liter): Glucose (1000 mg), KH_2PO_4 (300 mg), Na_2SO_3 (70 mg), $MgCl_2$ (100 mg), $CaCl_2$ (20 mg), $NaHCO_3$ (5400 mg), trace element (2 mL). The trace elements required for the bacteria growth consisted of the following compounds (per liter of the solution): $CoCl_2$ (240 mg), $MnCl_2{\cdot}4H_2O$ (990 mg), $CuSO_4{\cdot}5H_2O$ (250 mg), $Na_2MoO_4{\cdot}2H_2O$ (220 mg), $NiCl_2{\cdot}6H_2O$ (190 mg), H_3BO_4 (14 mg), $ZnCl_2$ (100 mg) (Zhang et al., 2008).

2.3. Experimental setup

All the kinetic experiments were carried out in a thermostatic organic glass reactor as shown in Fig. 1. A sieve-plate column with an inner diameter of 0.04 m and an effective volume of 0.57 L was used to absorb the simulated flue gas. A packed column with an inner diameter of 0.12 m, an effective volume of 3 L and a filler volume of 2 L was used to reduce the absorption products. The biological packing is a PVC cylinder with a diameter of 8 mm, a height of 10 mm and a specific surface area of 1200 m^2/m^3.

The simulated flue gas consisted of N_2, O_2, CO_2 and NO were mixed in a mixing chamber after metering by the mass flow meters (Beijing Sevenstar Qualiflow Electronic Equipment Manufacturing Co., Ltd. Model D07-12A). The gas flow rate was set at 1000 mL min^{-1}. A vacuum pump was used to circulate the solution in the reactor at a flow rate of 10 L h^{-1}. Two holding tanks with different volumes were used alternatively with the change of the reaction liquid volume. The reactor was placed in the thermostatic water bath at 50 °C and water was pumped into the heating jacket by a submersible pump to maintain the typical flue gas temperature between 45 and 55 °C after FGD process.

During the NO absorption and oxidation of Fe(II)EDTA step, the biological packing tower was excluded from the system to eliminate the influence of microbial action. Before the regeneration step, the bioreactor was restarted under intermittent operation mode with an average running time of 8 h every day.

2.4. Absorption part

During the absorption of NO, 3.5 L of fresh Fe(II)EDTA medium with different concentrations (1, 2, 3, 4, 5 mM) were added into the holding tank before the start-up of each experiment. The pH was adjusted to 6.8–7.0 by adding NaOH or HCl solution. Initial concentration of Fe(II)EDTA was measured before absorption. The reactor was loaded with simulated gas containing NO (500 ppm), CO_2 (15%, v/v) and N_2. The pH and concentrations of NO (every 10 min), Fe(II)EDTA (every 40 min), Fe(II)EDTA–NO (every 40 min) and total iron (every 80 min) were measured and recorded at regular intervals.

During oxidation, the recycled liquid was replaced by 3.5 L of fresh Fe(II)EDTA (3 mM) medium. The pH was adjusted and the initial concentration of Fe(II)EDTA was measured before the oxidation experiment. The simulated gas contained O_2 (1–10%, v/v), CO_2 (15%, v/v), and N_2. The pH and concentration of Fe(II)EDTA were measured every 10 min.

2.5. Regeneration part

During the biological reduction of Fe(III)EDTA, the recycled liquid was replaced by 4 L of Fe(III)EDTA with a concentration of