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Simultaneous desulfurization and denitrification through an integrative process utilizing $NaClO_2/Na_2S_2O_8$

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ABSTRACT

SO_2 and NO emitted from coal-fired power plants have caused serious air pollution in China. In this paper, a novel complex oxidant, $NaClO_2/Na_2S_2O_8$, was prepared for simultaneous removal of SO_2 and NO through a pre-oxidation method. The cooperative effect as well as mechanism between $NaClO_2$ and $Na_2S_2O_8$ was elucidated, with the corresponding best ratio of 4 wt%:4 wt%. The effects of various reaction factors on the simultaneous removal were investigated, i.e. the adding rate of the complex oxidant, the pH of the complex oxidant, the reaction temperature, the flue gas residence time and the coexistence gases. The experimental results indicated that the desulfurization process was mainly controlled by the sodium humate (HA-Na) absorption, while the denitrification was significantly affected by various conditions. Under the optimal conditions, the removal efficiencies for SO_2 and NO were 100% and 82.7%, respectively. Compared with our previous works, $NaClO_2/Na_2S_2O_8$ has some superiorities of less dosage of the complex oxidant, rapid reaction rate and more efficient in NO removal. According to the characterizations of removal products by XRD, FT-IR and UV–Vis, and the literature references, the reaction mechanism was speculated.

Research article

1. Introduction

SO_2 and NO_x, mainly is NO which accounts for 90–95% of NO_x [1], from coal-fired power plants have resulted in the regional haze, photochemical smog and acid rain, etc. The mature air pollution control devices (APCD) for SO_2 and NO in coal-fired power plants are the wet flue gas desulfurization (WFGD) and selective catalytic reduction (SCR) systems. Although the combination of WFGD and SCR can meet the emission standards of SO_2 and NO_x, the stage-treatment strategy has a few problems, i.e. large occupying area, complicated system, high running cost, NH_3 escape and the spent catalyst that is difficult to dispose. Hence, simultaneous removal of SO_2 and NO has become one of the leading research directions in the field of air pollution control.

Recently, some advanced technologies have been developed. Guo et al. [2] proposed a method of combination of Na_2SO_3 assisted electrochemical reduction and direct electrochemical reduction to simultaneously remove NO_x and SO_2, the reaction system could convert NO_x and SO_2 into N_2 and SO_4^{2-} with the efficiencies of 99% and 98%, the activated carbon was used as catalyst to accelerate the regeneration of Fe(II)-ethylene diamine tetraacetic acid (EDTA). This method used less chemical reagents, but the electrochemical character restricted its commercial application. As we all know, hydrogen peroxide and its derivant, hydroxyl radicals, are excellent oxidants due to the characters of environmental friendly and strong oxidation capacity, many scholars have utilized these oxidation species to remove SO_2 and NO_x. Ye et al. [3] utilized a vacuum ultraviolet radiation to generate the reactive oxygen species to remove SO_2 and NO_x, the results indicated that ozone, hydrogen peroxide and hydroxyl radical dominated the reactions, and the concentrations of H_2O and O_2 as well as the flow rate significantly affected the radicals production. Yuan et al. [4] synthesized a novel TiO_2-aluminum silicate fiber (TAS) photocatalyst to remove SO_2, NO and Hg^0, the simultaneous removal efficiencies of 33%, 31% and 80% were obtained at the conditions of temperature of 120 °C and UV intensity of 3 mW/cm^2. Zhong et al. [5,6] prepared two catalysts, hematite and Ce-Ti composite, to motivate H_2O_2 producing hydroxyl radicals, and a combined system of catalysis-oxidation and ammonia absorption was used to remove SO_2 and NO simultaneously. The results indicated that the desulfurization efficiency was nearly 100% under all conditions, the NO removal was primarily affected by the amount of ozone and H_2O_2 flow. This method has two advantages of non-secondary pollution and minimal waste production, but the large amount of oxidant used (0.4 mL/min vs 240 mL/min of simulated flue gas flow) and too long flue gas residence time (approximately 15 s) were inadvisable.

In the previous works [7–9], we had carried out the experiments of simultaneous removal of multi-pollutants in flue gas through a two-stage treatment of pre-oxidation and post-absorption by H_2O_2-based complex oxidants. The experimental results were good, but the oxidant

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dosage (4.1 mol/L of complex oxidant, 0.25 mL/min of complex oxidant addition vs 4 L/min of simulated flue gas flow) and the flue gas residence time (3.8–5.0 s) were still a little unsatisfactory from the view of application.

$NaClO_2$ is an alkaline oxidant, which is the most potential reagent can be used in the field of flue gas cleaning. ClO_2^- and its derivant, ClO_2, are the main oxidizing species when $NaClO_2$ participates in reaction. In the previous research [10], we prepared a $NaClO_2$-based complex oxidant to simultaneously remove SO_2, NO and Hg^0, the performance of this complex oxidant on the simultaneous removal was perfect, while the selected concentration of $NaClO_2$ was 1.5 mol/L (14 wt%), which would result in a problem of high operation cost that might be encountered in the future application.

Persulfate (PS) is an acidic and environmental friendly oxidant, which has been used in the fields of total organic carbon (TOC) degradation and in situ chemical oxidation (ISCO) of subsurface contamination for a long time [11–16]. PS can be activated by the alkaline atmosphere, thermal catalysis or H_2O_2, with producing some active radicals such as $SO_4^{\cdot}$ (2.5–3.1 V) and HO• (2.8 V). In the previous work [7], we conducted the experiment of simultaneous removal of SO_2 and NO by a complex oxidant composed of $Na_2S_2O_8$ and H_2O_2, although the secondary pollution problem was inhibited, it had two shortages of a little low denitrification efficiency (79.6%) and a relative long residence time (4.8 s).

In consideration of that PS can be activated by strong alkalinity, it seems that $NaClO_2$ is a proper cooperator for $Na_2S_2O_8$, from which, both of $NaClO_2$ and $Na_2S_2O_8$ can be activated. To our knowledge, there were no reports in the field of simultaneous removal of SO_2 and NO on the usage of $NaClO_2/Na_2S_2O_8$, as well in the field of waste water treatment. In addition, as a result of the good performance of sodium humate (HA-Na) on absorbing the oxidation products of SO_x and NO_x, HA-Na was employed as an absorbent in this study [17,18]. The aim of this paper is to evaluate the feasibility of $NaClO_2/Na_2S_2O_8$ on simultaneous removal of SO_2 and NO, and the effects of various factors were assessed including the complex oxidant constitution, the adding rate of $NaClO_2/Na_2S_2O_8$, the pH of $NaClO_2/Na_2S_2O_8$, the vaporization temperature, the residence time of flue gas and the coexistence gases in the simulated flue gas, and the cooperative effect as well as mechanism between $NaClO_2$ and $Na_2S_2O_8$ and the reaction mechanism of simultaneous removal of SO_2 and NO were proposed.

2. Experimental

2.1. Materials and apparatus

The reagents used in the experiments are analytical reagent (Kermel Company, Tianjin). 99.5 wt% of $Na_2S_2O_8$ and 99 wt% of $NaClO_2$ were used to prepare the complex oxidant. 0.02 mol/L of HA-Na was employed as an absorbent [18]. NaOH and H_2SO_4 were used to adjust the pH of the complex oxidant, whose pH range was 5–12.

It can be seen from Fig. 1 that the experiments are conducted on a fixed-bed system that consists of the generation of simulated flue gas, the combination of complex oxidant vaporization with air pollutants oxidations, the absorptions of oxidation products and the detection of tail gas. Five cylinder gases, SO_2 (Fig. 1, 1), NO (Fig. 1, 2), O_2 (Fig. 1, 3), CO_2 (Fig. 1, 4) and N_2 (Fig. 1, 5), (North special gas company, Baoding) are used to generate the simulated flue gas. The concentrations of the gases are 2000–4000 mg/m^3 for SO_2, 300–700 mg/m^3 for NO, 2–6% for O_2 and 6–12% for CO_2, and balanced by N_2, the inlet flow of simulated flue gas ranges from 2 to 6 L/min. The complex oxidant (Fig. 1, 10) is pumped into a custom-design vaporization device (Fig. 1, 9) by a peristaltic pump (Fig. 1, 11) (BT100-1F, Longerpump, Baoding). The vaporization device is heated by a thermal control electric heater (Fig. 1, 8) (ZDHW, the temperature range is from 80 to 160 °C (±3 °C), Zhongxingweiye company, Beijing). The temperature of the vaporization device is detected by a thermal couple (Fig. 1, 12) (XMTD, Baoding). The spherical reactor (Fig. 1, 9) includes the vaporization of oxidants combining pre-oxidation part, with the volume of 100 cm^3, which is made by borosilicate glass. HA-Na solution (Fig. 1, 15) is used to absorb the oxidation products, whose temperature is 50 °C (±0.1 °C) controlled by a thermostatic water bath (Fig. 1, 9) [18]. An on-line pH (Fig. 1, 14) detector is used to detect the pH of HA-Na solution over time. The reacted flue gas was detected by a multifunctional flue gas

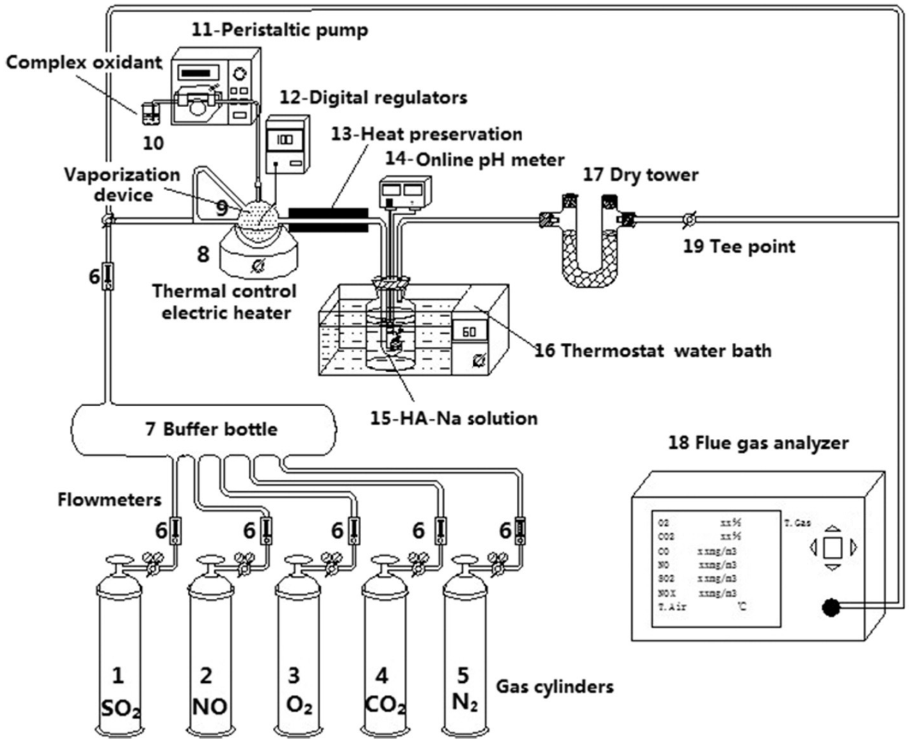

Fig. 1. Schematic diagram of the experimental apparatus.