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Simultaneous absorption of NO and SO_2 into Fe^{II}–EDTA solution coupled with the Fe^{II}–EDTA regeneration catalyzed by activated carbon

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The simultaneous removal of NO and SO_2 from flue gases can be realized with Fe(II)–ethylenediamineteraacetate(EDTA) solution. Activated carbon is used to catalyze the reduction of Fe^{III}–EDTA to Fe^{II}–EDTA to maintain the capability of removing NO of the Fe–EDTA solution. The reductant is the sulfite/bisulfite ions produced by SO_2 dissolving into the aqueous solution. Experiments have been performed to determine the effects of activated carbon of coconut shell, Fe^{II}–EDTA concentration, Fe/EDTA molar ratio, SO_2 partial pressure, NO partial pressure and $SO_4{}^{2-}$ concentration on the combined elimination of NO and SO_2 with Fe^{II}–EDTA solution coupled with the Fe^{II}–EDTA regeneration catalyzed by activated carbon. According to the experimental results, activated carbon not only catalyzes the reduction of Fe^{III}–EDTA by sulfite/bisulfite greatly but also avoids the release of N_2O. The NO removal efficiency increases with the initial Fe^{II}–EDTA concentration and SO_2 partial pressure. The ratio of Fe/EDTA and the $SO_4{}^{2-}$concentration has little effect on the catalytic reduction of Fe^{III}–EDTA. The optimal initial NO concentration range is from 600 ppm to 900 ppm. The experimental results manifest that the Fe^{II}–EDTA solution coupled with catalytic regeneration of Fe^{II}–EDTA can maintain high nitric oxide removal efficiency for a long period of time.

1. Introduction

Combustion of fossil fuels generates NO_x and SO_2 pollutants that have given harmful effects on environment and human health. The removal of these contaminants to comply with the strict environmental emission standard is of imperative necessity. The existing wet flue-gas-desulfurization (FGD) scrubbers have obtained high SO_2 removal efficiency. But they are not excellent for NO_x because 90–95% of the NO_x present in typical flue gas streams is NO which is almost insoluble in aqueous solutions. Meanwhile, among the existing treatment processes for removing NO_x from the flue gases, selective catalytic reduction (SCR) using NH_3 at 300–500 °C is supposed to be the best available NO_x control technology [1–4]. However, application of the SCR is limited because of its high capital and operating costs. There is still an urgent need for a more economical method for controlling NO_x emission.

The approach that adds iron(II)(EDTA) (EDTA, ethylenediaminetetraacetate) into the scrubbing liquor to promote the solubility of NO via formation of iron(II)(EDTA)NO has been researched extensively [5–9]. Although Fe^{II}–EDTA can obtain a high NO removal efficiency, it is easily oxidized to Fe^{III}–EDTA that is not capable of binding NO [10–12]. As a result, the concentration of the active iron(II)(EDTA) in the scrubbing solutions decreases quickly as the absorption proceeds. Thus NO removal efficiency drops immediately. Many methods [13–17] have been put forward to regenerate Fe^{II}–EDTA to sustain the NO removal efficiency. Although iron–(III)(EDTA) can be reduced to iron(II)(EDTA) by sulfite/bisulfite ions, the regeneration rate is slow because of low rate constants and low sulfite/bisulfite concentration in limestone slurries. The regeneration of iron(II)(EDTA) with element iron or electrolysis is too expensive to be put into industrial application. The consumption of the reducing agents such as hydrazine, $Na_2S_2O_4$ is too high to be industrialized.

It is well known that activated carbon has been successfully applied in industry as a catalyst due to its enormous surface area, porous structure and characteristic flexibility. For example, Quintanilla et al. [18] investigated catalytic performance of activated carbon for the wet air oxidation of phenol. Georgi et al. [19] reported their research on the oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. Mackenzie et al. [20] tested the catalytic effects of activated carbon on hydrolysis reactions of chlorinated organic compounds. Santos et al. [21] explored the catalytic characteristics of activated carbon in the decolourisation of dye solutions by oxidation with H_2O_2. Rivera-Utrilla and Sánchez-Polo [22] presented the experimental results of the ozonation of 1,3,6-naphthalenetrisulfonic

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acid under the catalysis of activated carbon in aqueous solutions.

Since activated carbon has been proven capable of transferring electrons for reduction reactions, it has been reported that a number of chemical species can be reduced in the presence of granular activated carbon. The authors put forward to utilize activated carbon as a catalyst to speed up the regeneration of iron(II)(EDTA) with sulfite/bisulfite as a reductant to maintain the NO removal efficiency with iron(II)(EDTA) solution to realize the simultaneous removal of SO_2 and NO from flue gas streams. A study on this technology is reported in this paper.

2. Theoretical

It is well known that NO is insoluble in water, Fe^{II}–EDTA may react with dissolved NO according to the following equations:

$$NO(g) \rightarrow NO(aq) \tag{1}$$

$$Fe^{II}\text{–}EDTA^{2-} + NO(aq) \rightarrow Fe^{II}\text{–}EDTA(NO)^{2-} \tag{2}$$

In the meantime, the SO_2 existing in the gas stream also dissolves into the aqueous solution:

$$SO_2 + H_2O \rightarrow {SO_3}^{2-} + 2H^+ \tag{3}$$

$$SO_2 + H_2O + {SO_3}^{2-} \rightarrow 2{HSO_3}^- \tag{4}$$

However, the oxygen existing in the flue gases may oxidize Fe^{II}–EDTA to Fe^{III}–EDTA (Eq. (5)) during the gas scrubbing. NO removal efficiency will decrease quickly as the operation proceeds because the Fe^{II} EDTA concentration declines.

$$4Fe^{II}\text{–}EDTA^{2-} + O_2 + 4H^+ \rightarrow 4Fe^{III}\text{–}EDTA^- + 2H_2O \tag{5}$$

To maintain the NO removal efficiency, Fe^{III}–EDTA must be reduced to Fe^{II}–EDTA once again. Electrochemical half-cell reduction potential of $E^0_{Fe(III)-EDTA/Fe(II)-EDTA}$ is 0.141 V and that of $E_{SO_4^{2-}/SO_3^{2-}}$ is 0.20 V in the acidic solution. Therefore, the reduction of Fe^{III}–EDTA by sulfite/bisulfite cannot proceed successfully under acidic solution. However, most of the FGD processes are operated under pH lower than 7.0. To accelerate the reduction of Fe^{III}–EDTA, activated carbon can be used as a catalyst. The sulfite/bisulfite ions produced by SO_2 absorption into the aqueous solution act as reductants. The mechanism of Fe^{III}–EDTA catalytic reduction can be expressed as follows:

The activated carbon may accelerate Fe^{III}–EDTA ions' disintegration into Fe(III) ions and EDTA ions (Eq. (6)):

$$Fe^{III} - EDTA \xrightarrow{AC} Fe^{III} + EDTA \tag{6}$$

Electrochemical half-cell reduction potential of $E_{Fe^{3+}/Fe^{2+}}$ (0.771 V) depicts that Fe^{III} ions are strong oxidants. Sulfite can be oxidized by Fe^{3+} easily under acidic conditions. Therefore, the following reaction may take place:

$$2Fe^{III} + {SO_3}^{2-} + H_2O \xrightarrow{AC} {SO_4}^{2-} + 2Fe^{II} + 2H^+ \tag{7}$$

Fe^{II}–EDTA is produced once again by Fe(II) binding with EDTA. Thus the NO removal efficiency can be sustained for a long time.

$$Fe^{II} + EDTA \rightarrow Fe^{II}\text{–}EDTA \tag{8}$$

On the other hand, the NO binded with Fe^{II}–EDTA may be reduced to N_2O (Eq. (9)) by sulfite.

$$2Fe^{II}\text{–}EDTA(NO)^{2-} + {SO_3}^{2-} \rightarrow 2Fe^{II}\text{–}EDTA^{2-} + N_2O + {SO_4}^{2-} \tag{9}$$

Nitrous oxide is also a harmful pollutant because it has a long duration effect in the depletion of the ozone layer due to its long lifetime (about 150 years). Hence its reduction is a topic of interest [23,24]. It has been reported that N_2O can be adsorbed and reduced by activated carbon to N_2 at temperature over 300 °C [25,26]. Activated carbon has acted as a catalyst in many reduction reactions. In the process discussed in this paper, N_2O may be further reduced to N_2 under the catalysis of activated carbon by sulfite/bisulfite.

$${SO_3}^{2-} + N_2O \xrightarrow{AC} {SO_4}^{2-} + N_2 \tag{10}$$

According to the discussion above, Fe^{II}–EDTA can be regenerated quickly by sulfite/bisulfite under the catalysis of activated carbon to maintain the NO removal efficiency. Such process can also suppress the production of N_2O. This technology not only realizes the absorption and reduction of nitric oxide but also realizes the absorption and oxidation of sulfur dioxide in the same absorber. Combined removal of NO and SO_2 from the flue gases may be easily achieved by re-forming the existing scrubbing scrubbers for desulfurization.

3. Experimental

3.1. Reagents and preparation

$FeSO_4{\cdot}7H_2O$ (>99.0%) and Na_2SO_3 (>97.0%) was obtained from Guoyao and Na_2EDTA (>99.5%) from Dahe; NO (5000 ppm in N_2), SO_2 (7000 ppm in N_2) and N_2 (>99.99%) from Shanghai Standard Gas Co. Ltd. Deionized water was applied to prepare the solutions. Activated carbon of coconut shell was obtained from Shanghai Activated Carbon Co. Ltd.

3.2. Experimental set-up

Experiments for the simultaneous removal of NO and SO_2 were performed in a packed column (18 mm i.d., 1000 mm long) absorber. The Fe^{II} EDTA regeneration was carried out in a fixed-bed (20 mm i.d.) reactor packed with activated carbon of coconut shell. The schematic diagram of the experimental apparatus is shown in Fig. 1. The temperature of the absorber and regeneration reactor was controlled at 50 °C using jackets through which water from thermostatic baths was circulated. The pH value was controlled using NaOH (1.0 mol l^{-1}) by a THORNTON M300 pH/ORP transmitters to keep the pH constant. Two percent of NO in nitrogen was supplied from a cylinder, and was diluted with N_2 to the desired concentration before being fed into the absorber. SO_2 was supplied in a similar manner. Fe^{II}–EDTA solution together with measured amount of Na_2SO_3 was added into the 500 ml glass circulation tank. The initial pH value of Fe^{II}–EDTA solutions was adjusted to the desired value with NaOH (1.0 mol l^{-1}) solution and detected with a pH-electrode. The absorber was operated with a continuous influent gas feeding at 0.3 l min^{-1} from the bottom and a continuous scrubbing solution feeding, at a superficial flow rate of 5 m^3 m^{-2} h^{-1} (25 ml min^{-1}) at the top. The initial ${SO_3}^{2-}$ concentration was adjusted to 0.03 mol l^{-1} by adding appropriate amount of Na_2SO_3 into the Fe–EDTA solution. The absorbent effusing from the packed column was fed into the circulation tank. When the regeneration of Fe^{II}–EDTA started, the absorbent in the circulation tank flew into the regeneration reactor upwardly and directly into the packed column to scrub NO and SO_2. The experimental runs were carried out under atmospheric pressure.

3.3. Analysis methods

Quantitative analysis of gas composition was made by an online Fourier transform infrared spectrometer (FTIR) (Nicolet E.S.P. 460 FT-IR) equipped with a gas cell and the quantitative software package, named Quant Pad. The influent and effluent gas samples were directly introduced into the gas cell of the FTIR, with pipes insulated through the regulated electric coils to obtain the transient N_2O, NO, SO_2, and H_2O concentrations of the gaseous samples.