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Influence of operating parameters on performance of SO_2 absorption in fulvic acid solution

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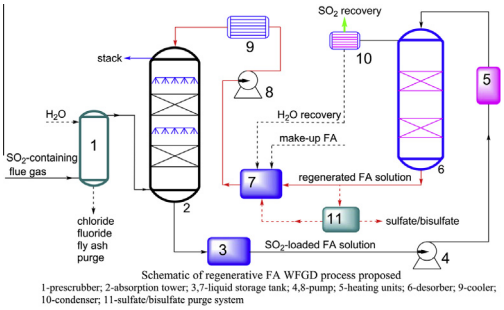
HIGHLIGHTS

- A novel regenerative flue gas desulfurization process by FA solution was developed.
- The optimum concentration of FA solution is 0.08 g mL^{-1}.
- SO_2 absorption efficiency is not affected by pH change in the range from 5.5 to 3.3.
- NO_2 can accelerate the oxidation of bisulfite to sulfate and promote SO_2 absorption.

GRAPHICAL ABSTRACT



Schematic of regenerative FA WFGD process proposed
1-prescrubber; 2-absorption tower; 3,7-liquid storage tank; 4,8-pump; 5-heating units; 6-desorber; 9-cooler; 10-condenser; 11-sulfate/bisulfate purge system

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ABSTRACT

A novel process of flue gas desulfurization by aqueous fulvic acid (FA) solution with acid-base buffering capacity was developed. Experiments were carried out to investigate the influence of operating parameters such as the FA concentration, pH, temperature, gas flow rate, fly ash, O_2, SO_2 inlet concentration, CO_2 and NO_2 on SO_2 absorption efficiency and Duration Time of High Efficiency (DTHE, the time of the SO_2 absorption efficiency above 95%) in a lab-scale bubbling reactor. The results show high FA concentration has more absorption capacity for SO_2, and the optimum concentration of FA solution is 0.08 g mL^{-1}, at which point the absorption efficiency is above 98%. The inlet SO_2 concentration has little influence on absorption efficiency, but DTHE reduces with increasing inlet SO_2 concentration. O_2 has a little effect on absorption efficiency. The SO_2 absorption efficiency is not affected by pH change in the range from 5.5 to 3.3, and maintained above 97.4%. Fly ash can improve SO_2 absorption efficiency and DTHE. NO_2 can accelerate the oxidation of bisulfite to sulfate and promote SO_2 absorption. CO_2 hardly influences on SO_2 absorption efficiency, but the SO_2 absorption capacity decreases with the increasing of CO_2 partial pressure. Furthermore, the thermal stability and regenerability of FA were also evaluated by TG-DTG and XRD, respectively. The results demonstrate that FA with stable performances is a promising regenerative absorbent for the removal of SO_2.

1. Introduction

The emissions of SO_2 are known to cause detrimental impacts on human health and the environment. Therefore, the removal of SO_2 mainly from the burning of fossil fuels in power plants is a goal of many air pollution engineers and researchers. To control SO_2 emissions, great efforts in the development of flue gas desulfurization (FGD) technologies have been made. Among various FGD technologies, the wet lime/limestone scrubbing, takes a leading position owing to high SO_2 removal efficiency and reliability and low utility consumption [1,2].

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Although the once-through non-regenerative wet lime/limestone scrubbing is frequently used in practice, it possesses some drawbacks such as the high capital and operating expenses, the large volume of water required, poor quality of byproduct, and even causing secondary pollution [3]. Therefore, various regenerative wet FGD technologies such as wellman-lord's sodium sulfite process, the citrate process, sodium carbonate eutectic process, magnesium oxide method, amine process and aqueous ammonia process have been developed to try to avoid the drawbacks of once-through wet FGD technologies [4]. Recently, researchers developed an electrochemical membrane reactor for a recycled FGD process, in which NaOH sorbent can be regenerated electrochemically from FGD residuals [5]. However, the processes are usually accompanied by the high operating expenses for the difficulty of absorbents regeneration and the supplement of alkali liquor and the volatility of ammonia. Apart from amine process, several other organic solvents have been used as SO_2 absorbents, due to their high affinity and much milder SO_2 stripping conditions with a simple pressure or temperature swing than conventional scrubbing processes [6]. Nevertheless, organic solvent method is restricted because of the poor SO_2 absorption capacities, the loss of solvents for high volatility, and the contamination of recovered SO_2 [7]. Recently, an innovative SO_2 absorption in ionic liquids (ILs) such as 1, 1, 3, 3-tetramethylguanidinium lactate ([TMG]L) [8], hydroxyl ammonium ILs [9], N-butylpyridinium thiocyanate [10] and non-aqueous acid salt ILs/sulfolane binary mixtures [11], has been investigated. Due to the high production costs of ILs, their industrial applications in FGD could be limited.

Fulvic acid (FA) is one fraction of humic substances that is soluble under all pH conditions, which formed by the breakdown of plant and animal tissue through chemical and biological processes. It is worth noting that one of the most important properties of FA is high buffering capacity at wide pH value range, resulting from the dissociation of acidic functional groups such as carboxylic and phenolic groups [12]. FA can be extracted from a variety of sources such as peat [13], soil and biomass residues [14]. To our knowledge, FA extracted from biomass residues has been industrialized on account of accessible raw materials and low cost [15,16]. In China, a lot of biomass residues such as crop stalks are abandoned or burnt without any utilization, which causes environmental pollution. However, theses biomass residues can be produced into FA. In view of good buffering capacity of FA and biomass residues utilization, we developed a novel wet regenerable FGD process in which SO_2 from flue gas was first absorbed by aqueous FA solution in a bubbling reactor, and then desorbed from loaded solution by heating, the regenerated FA solution was recovered and reused for absorbing SO_2. Meanwhile, the desorbed SO_2 could be recovered and used to produce sulfuric acid or liquid sulfur dioxide. This FA solution process would neither require a large quantity of water nor cause the problem of disposal of large amounts of waste such as wastewater, $CaSO_4$ and waste carbon dioxide. In the conventional wet limestone FGD, absorbing one ton of SO_2 gas will consume 1.823 ton of limestone (the purity of 90%, Ca/S = 1.05). In the process of FA solution, one ton of SO_2 gas will consume 7.327 ton of FA, and the circulation of FA is about 4 times that of limestone. However, FA can be thermally regenerated for the reabsorption of SO_2 many times. Therefore, as a regenerative FGD absorbent, FA is promising to be used in a large scale. Previously, we have examined the feasibility and durability of FA as a regenerative FGD absorbent by the performances of absorption/desorption cycles and obtained the absorption mechanisms of SO_2 in FA solution [16].

In the present paper, we aim to investigate the influence of various operating parameters such as the FA concentration, pH, temperature, gas flow rate, fly ash, O_2 concentration, SO_2 inlet concentration, CO_2 and NO_2 on the SO_2 absorption efficiency and desulfurization time in a lab-scale bubbling reactor, and to obtain the optimal operating parameters for an efficient SO_2-removal. Furthermore, the thermal stability and regenerability of FA are also evaluated. This study is an essential preliminary to the large-scale application of FA solution process.

2. SO_2 absorption mechanism

From our previous study, the major mechanism of SO_2 absorption into FA solution is the acid-base buffer reaction [16], which can be represented in Fig. 1. Trace fulvates in FA play a decisive role in the process of SO_2 absorption. The following processes should be taken into consideration:

Diffusion of SO_2 through the gas film near the gas – liquid interface (1)

$$SO_2(g) \rightleftarrows SO_2(aq) \quad (2)$$

$$SO_2(aq) + H_2O(aq) \rightleftarrows H_2SO_3(aq) \quad (3)$$

$$H_2SO_3(aq) \rightleftarrows HSO_3^-(aq) + H^+(aq) \quad (4)$$

$$HSO_3^-(aq) \rightleftarrows SO_3^{2-}(aq) + H^+(aq) \quad (5)$$

$$FA^-(aq) + H^+(aq) \rightleftarrows FA(aq) \quad (6)$$

Diffusion of dissolved chemical species in liquid film (7)

The dissolution of SO_2 in the liquid phase (8)

For the SO_2–FA–H_2O systems, Fig. S1 shows the composition curves of sulfite species corresponding to pH value. It can be seen that reactions (3) and (4) are dominating in FA absorbing SO_2 gas, reaction (5) is of only minor importance. When oxygen is present in simulated flue gas, sulfate can form (Eqs. (9) and (10)), but the SO_4^{2-} formation rate is very slow in contrast with the hydrolysis of SO_2 itself (Eqs. (3) and (4)). Therefore, the absorption of SO_2 into FA solution does not depend on sulfate formation as a significant step.

$$2SO_3^{2-}(aq) + O_2(aq) \rightarrow 2SO_4^{2-}(aq) \quad (9)$$

$$2HSO_3^-(aq) + O_2(aq) \rightarrow 2SO_4^{2-}(aq) + 2H^+(aq) \quad (10)$$

As is well known, it is inevitable that trace amounts of metal ions such as Na^+, Ca^{2+} and Mg^{2+} are introduced into industrialized production of FA. Hence, our FA sample contains trace metal ions (3.49 wt.% Na^+, 3.66 wt.% Ca^{2+}). These cations are able to bind to FA and occupy proton-binding sites of FA, thus trace metal fulvates (FA–Na, FA–Ca) are present in FA sample. In liquid phase, these occupied proton-binding sites can be discharged. The most abundant cation-binding groups in FA are carboxylate, next come phenolate groups. Our FA samples (pH 5.5) possess carboxylate groups ($-COO^-$) and no phenolate groups ($-O^-$), because phenolate groups in FA can be completely protonated at pH below 7.5. Because of the lower acidity of FA compared to that of SO_2 [16], carboxylate groups (–COONa, $-(COO)_2Ca$) in FA can indirectly interact with SO_2 in aqueous solution (reaction (11)).

$$R-(COO)_nM + nSO_2 + nH_2O \rightarrow R-(COOH)_n + M(HSO_3)_n \quad (11)$$

where $R-(COO)_nM$, $R-(COOH)_n$ and M are the structural formulas of metal fulvates, FA and metal cations (Na^+ and Ca^{2+}), respectively. On the basis of two film theory, the SO_2 absorption is jointly controlled by the gas film resistance and liquid film resistance, instantaneous equilibrium is assumed for reactions (3)–(6) throughout