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Reversible absorption of SO_2 by amino acid aqueous solutions

Renpan Deng, Lishan Jia*, Qianqian Song, Shuai Su, Zhongbiao Tian

Department of Chemical Engineering and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

HIGHLIGHTS

- β-Alanine solution is found to be excellent absorbent for SO_2 removal.
- 20–30 °C is optimal for SO_2 absorption, and 150 °C is optimal for desorption.
- The neutral environment (pH = 6.8) was found to be optimal for SO_2 removal.
- SO_2 interacts with β-alanine by some weak interactions, such as hydrogen bonds.
- The absorbent has an excellent regeneration performance.

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ABSTRACT

Six water-soluble amino acids (glycine, L-α-alanine, DL-alanine, β-alanine, proline and arginine) aqueous solutions were applied to remove SO_2 from SO_2–N_2 system in this report. All the tested amino acids solutions were found to be excellent absorbents for SO_2 removal, and SO_2 saturation uptake of β-alanine solution was the highest under the same experimental conditions. The effects of amino acid concentration, SO_2 concentration, absorption temperature, desorption temperature and initial pH value of the absorbent on the removal of SO_2 were investigated with β-Ala solution. The experimental results showed that SO_2 saturation uptake increased with the increase in β-alanine solution and SO_2 concentration. Room temperature (20–30 °C) was found to be optimal for SO_2 absorption. Additionally the SO_2 desorption capacity increased with increasing desorption temperature. The neutral environment pH value of 6.8 was found to be optimal for SO_2 removal. Ten continuous absorption–desorption cycles showed that the absorbent had an excellent regeneration performance. ^{13}C NMR and ultraviolet analyses offer ample evidence to speculate that the bonding between SO_2 and β-alanine was not covalent but some weak interactive forces, such as dispersion force, induction force, dipole–dipole force and hydrogen bond.

1. Introduction

Sulfur in coal and oil is converted to sulfur dioxide (SO_2) during combustion. SO_2 is a conspicuous atmospheric pollutant that poses major threats to the environment and human life [1–4]. Currently, flue gas desulfurization (FGD) is one of the most widely used techniques to control SO_2 emission [5]. However, the main flaw of the technique is the difficult regeneration of absorbents [6,7]. In addition, although SO_2 is a very important and useful source for many intermediates in chemical productions [8], it is difficult to recycle SO_2 during the FGD process as it forms stable sulfite or sulfate. Consequently, it is particularly important to develop renewable absorbents for SO_2 removal.

Several absorbents have been developed over the years; these can be categorized as inorganic salts, organic solvents and ionic liquids (ILs). Among the inorganic salts, the use of Na_2CO_3 and $NaHCO_3$ solutions for desulfurization has been widely explored [9–11]. The desulfurization principle of such absorbents is similar to that of limestone and lime in that it leads to the formation of stable sulfites or sulfates resulting in difficult regeneration of the absorbents. Organic solvents have been used for SO_2 removal since the forties of last century [12]. Many organic solvents, such as dimethylacetamide [13], methyldiethanolamine [14] and ethylenediamine [15] have been found to be good solvents for SO_2. However, these solvents are highly toxic, volatile, degradable and as such not environmentally friendly [16,17]. Ionic liquids (ILs) have attracted much attention from the industrial and academic communities as 'green solvents' due to their remarkable properties: extremely low vapor pressure, high thermal and chemical stability, and excellent solvating power for both organic and inorganic compounds [18–20]. Wu and co-workers earlier on reported that 1,1,3,3-tetramethylguanidine (TMG) lactate ILs could effectively absorb SO_2 from simulated flue gas [21]. The use of other ILs such as those based on 1,1,3,3-tetramethylguanidinium

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* Corresponding author. Tel.: +86 592 2188283; fax: +86 592 2184822.
E-mail address: Jials@xmu.edu.cn (L. Jia).

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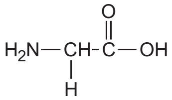
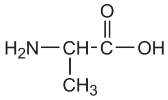
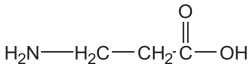
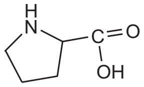
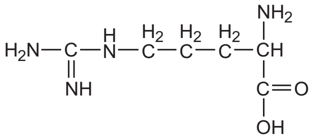
Table 1
Some basic information of the six tested amino acids.

Appellation	Abbreviation	Molecular weight (g/mol)	Molecular structure
Glycine	Gly	75	 $H_2N-\underset{H}{\underset{\vert}{CH}}-\overset{O}{\overset{\Vert}{C}}-OH$
L-α-Alanine	L-α-Ala	89	 $H_2N-\underset{CH_3}{\underset{\vert}{CH}}-\overset{O}{\overset{\Vert}{C}}-OH$
DL-Alanine	DL-Ala	89	 $H_3C-\overset{H}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-COOH \quad HOOC-\overset{H}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-CH_3$
β-Alanine	β-Ala	89	 $H_2N-H_2C-CH_2-\overset{O}{\overset{\Vert}{C}}-OH$
Proline	Pro	115	
Arginine	Arg	174	 $H_2N-\underset{NH}{\underset{\Vert}{C}}-\overset{H}{N}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{NH_2}{\overset{\vert}{\underset{\underset{OH}{\underset{\vert}{C=O}}}{\underset{\vert}{CH}}}}$

[22] and imidazolium [23] for the removal of SO_2 have also been explored. However, commercial ILs are expensive and their preparation processes are complicated resulting in much higher costs and limiting their industrial applications. Recently, we demonstrated that L-α-alanine supported on Al_2O_3 could remove SO_2 efficiently and effectively [24]. In this present paper, we have further expanded our work, and found that several water-soluble amino acid (Gly, L-α-Ala, DL-Ala, β-Ala, Pro and Arg) aqueous solutions showed excellent absorption performances on SO_2, such as high absorption capacity and good regeneration performance. So these amino acids could be alternative desulfurization absorbents. In fact, amino acids as biomolecules are the building blocks for peptides and proteins [25], and are usually used in biochemical and biological syntheses. To our knowledge, amino acids are seldom directly used for environment-related issues. As an extension herein, we have studied the desulfurization performance of six water-soluble amino acids (Gly, L-α-Ala, DL-Ala, β-Ala, Pro and Arg) aqueous solutions. Some basic information of these amino acids is presented in Table 1. The effects of the various factors on the desulfurization performance such as amino acid concentration, SO_2 concentration, absorption and desorption temperature, and the initial pH value of absorbent are investigated by using β-Ala solution. It is hoped that this work could enlighten researchers on the development of such desulfurization absorbents.

2. Materials and methods

2.1. SO_2 absorption experiments

All the amino acids (biochemical reagent (BR)) used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Experiments were performed in a vertically placed glass-made tube reactor (with 8 mm inside diameter and 39.5 cm long) under isothermal conditions. The tube reactor was made relatively long, for two specific advantages: (1) it prevents entrainment caused by the relatively high gas flow rate and (2) it facilitates refluxing and condensing during the desorption process (it requires as high as 150 °C). Approximately 5.0 mL amino acid solution of appropriate concentration was placed in the tube reactor to remove SO_2 from simulated flue gas. The simulated flue gas was a mixture of SO_2 and N_2 with appropriate concentration. The flow rate of the mixture gas was adjusted by a mass flow meter to 60 mL/min. The SO_2 concentration changes at the outlet of the reactor were determined by iodine titration method (HJ/T 56-2000, a standard method of State Environmental Protection Administration of China). The amount of SO_2 absorption capacity was expressed as milligram SO_2 per milliliter amino acid solution (mg/mL).

2.2. SO_2 desorption experiments

After the saturation absorption (SO_2 concentration at the outlet of the reactor was kept constant), the gas mixture was switched to N_2 and the temperature increased to the required desorption temperature at a rate of 10 °C/min; and the N_2 flow was maintained until SO_2 was no longer detected in the vent. Again, the concentration of SO_2 at outlet of the reactor was determined by iodine titration method and the amount of desorbed SO_2 expressed as before (mg/mL). Meanwhile, the absorbent was regenerated during the SO_2 desorption process.

2.3. ^{13}C NMR spectra

The original β-Ala solution, β-Ala solution saturated with SO_2, β-Ala solution after SO_2 desorption at 150 °C and β-Ala solution after ten continuous absorption–desorption cycles were mixed with heavy water (D_2O) in a volume ratio of 9:1 respectively. ^{13}C spectra were then recorded on a Varian Unity INOVA 100 MHz instrument.