Practical and Theoretical Study of the Adsorption Performances of Straw-Based Tertiary Amine-Supported Material toward Sulfur Dioxide in Flue Gas

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The primary and secondary amines of tetraethylenepentamine (TEPA) were N-methylated into tertiary amines through the Eschweiler-Clarke reaction. A straw-based tertiary amine-supported material (STA) was developed for SO_2 removal, using a wet impregnation process. The effect of the adsorption conditions, such as the moisture content, flow rate, and adsorption temperature, as well as the regeneration performances were studied. Experimental results showed that STA has high SO_2 adsorption capacity (approximately 100 mg/g) and can be regenerated at 100 °C. Furthermore, the adsorption of SO_2 molecules on tertiary amine was studied using density functional theory (DFT). The most stable geometries of the adsorption structure in five possible positions, the geometric changes after the adsorption, and the corresponding adsorption energies were analyzed. The results showed that modified TEPA (M-TEPA) has four potential adsorbed sites (N(1,3,4,5)) with a small adsorption energy, indicating that the adsorption is weak. Moreover, the energy of the adsorbed SO_2 on the N(1,3,4,5) is less than zero, indicating that the adsorption process is exothermic and spontaneous. The theoretical investigation agreed well with the experimental results.

Keywords: Straw; Density functional theory; Amine-supported material; Sulfur dioxide; Adsorption

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INTRODUCTION

SO_2 is a major source of atmospheric pollution and has significant impacts upon human health (Kan *et al.* 2010; Mathieu *et al.* 2013). SO_2 emissions are a precursor to acid rain (Mathieu *et al.* 2013). Environmental Protection Agency (EPA) statistics show that the largest sources of SO_2 emissions result from fossil fuel combustion at power plants (73%). Therefore, there is great interest in removing SO_2 from flue gas (Arcibar-Orozco *et al.* 2013).

Scrubbing SO_2 using an amine solution is the traditional absorption process for flue gas desulfurization (FGD) (Van *et al.* 1997; Verma and Verma 2009; Rahmani *et al*. 2015). The advantages of this process are the high desulfurization efficiency, lower regeneration temperature, and absence of secondary pollution. However, the absorption technology has some inherent disadvantages, such as equipment corrosion and high consumption of energy and water (Jo *et al.* 2014; Tailor *et al.* 2014a). An alternative adsorption process uses solid sorbents, which are less corrosive on equipment, simple to operate, and consume little or no water (Tailor *et al.* 2014b; Zhao *et al.* 2014), but the activation temperatures of most adsorbents are all above 350 °C, resulting in high regeneration cost (Ma *et al.* 2003). In recent years, amine-supported materials have gained tremendous popularity as adsorbents for acid gases removal, as they combine the advantages of amine solution absorption with the adsorption technology. Several studies have been conducted on the application of amine-supported materials in separating CO_2 from the flue gas (Aaron and Tsouris 2005; Chang *et al*. 2009; Watabe and Yogo 2013; Zhao *et al*. 2014; Lee *et al*. 2015), while there are very few reports on SO_2 adsorption on amine-containing materials (Zhi *et al*. 2011; Tailor *et al*. 2014).

Flue gas consists of SO_2, CO_2, NO, and other acid gases, where the concentration of CO_2 is almost 1000 times higher than the concentration of SO_2 (Rao and Rubin 2002). Thus, adsorbents should show high selectivity for SO_2 adsorption. Tertiary amines do not react with CO_2 under dry conditions. Even in the presence of water vapor, the reaction is slow and limited, yet tertiary amines react readily with SO_2 (Bollini *et al*. 2011; Hong *et al*. 2014; Tailor *et al*. 2014).

There are two methods for preparing amine-supported material: grafting and impregnation (Chang *et al*. 2009; Sanz *et al*. 2013; Watabe and Yogo 2013; Guo *et al*. 2015). In this paper, straw-based tertiary amine-supported materials were developed using wet impregnation. This study determined the effect of adsorption conditions on SO_2 adsorption behavior and regeneration performance. Moreover, the adsorption mechanism of SO_2 on tertiary amine was examined through density functional theory (DFT).

EXPERIMENTAL

Materials

The rice straw was obtained from a county farmland of Sichuan province in China. The tetraethylenepentamine (TEPA), formic acid, formaldehyde, sodium hydroxide, and hydrogen peroxide were purchased from Ke Long Chemical Reagent Company (Chengdu, China). All chemicals were analytical grade and used without further purification. The SO_2 gas was supplied by the Tian Yi Co. Ltd (Chengdu, China). The calculations were conducted using the Accelrys Materials Studio 7.0. (San Diego, CA, USA).

Synthesis of Tertiary Amines

The primary and secondary amines of TEPA were N-methylated into tertiary amines through the Eschweiler-Clarke reaction (Fig. 1) (Clarke *et al*. 1933).

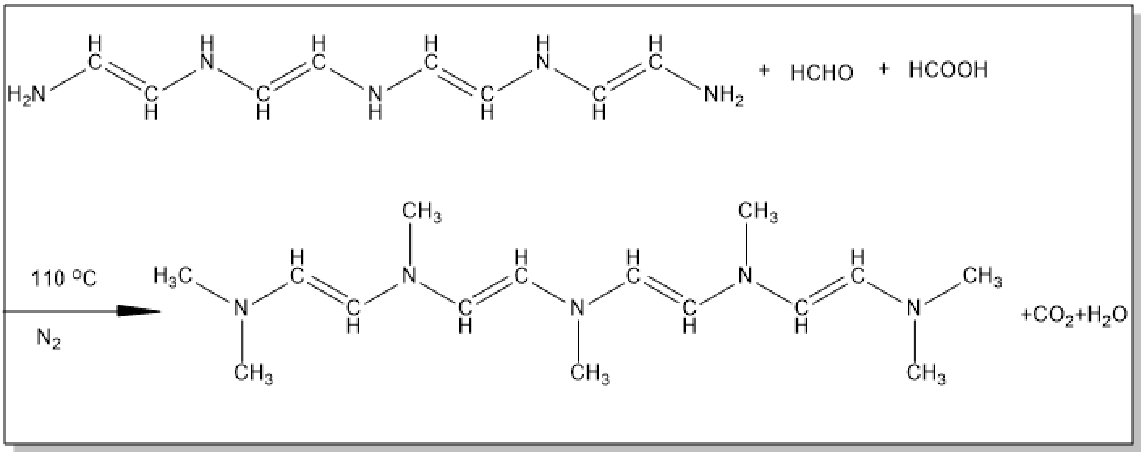

Fig. 1. The Eschweiler-Clarke reaction

A three-necked 150 mL round-bottom glass flask with a magnetic stirrer and a reflux section was initially charged with formic acid (24 g) and formaldehyde (11 g), then 10 g of TEPA was added slowly to the solution. The mixture was heated at 110 °C for 8 h under nitrogen atmosphere. After the reaction, the solution was heated at 110 °C to remove the volatile components. The products were referred to as M-TEPA (modified TEPA).

Synthesis of Straw-Based Tertiary Amine-Supported Material

A wet impregnation process was used to produce the straw-based tertiary amine-supported materials. First, 10 g of M-TEPA was dissolved in methanol (90 g) in a 250 mL glass flask, using sonication for 15 min, and then 10 g of straw was added to the flask. The flask was stirred at 60 °C until the methanol was evaporated. The product was dried at 70 °C for 24 h to obtain the straw-based tertiary amine-supported materials (STA).

SO_2 Absorption and Regeneration

The STA (5 g) was transferred into an adsorption column (Φ 30 mm × 300 mm) and pre-humidified with a certain amount of distilled water. The mixture gas of SO_2 and N_2 (initial SO_2 concentration of ~2000 ppm) went through the reactor at various flow rates. The adsorption temperature varied from 25 to 65 °C. The concentration of SO_2 was measured with the titrimetric method (Yang *et al*. 2012). When the adsorption experiment finished (desulfurization rate less than 10%), the gas mixture was switched to N_2 at a flow rate of 0.4 L/min, and the temperature was raised to 100 °C for 2 h for regeneration. The flow chart of adsorption and regeneration for SO_2 is presented in Fig. 2.

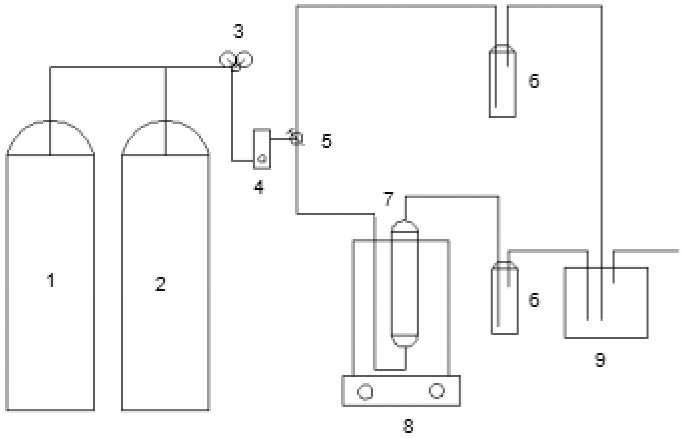

Fig. 2. Flow chart of adsorption of SO_2. Gas supply system (1. SO_2/N_2; 2. N_2; 3. pressure reducing valve; 4. rotameter; 5. three-way valve); heating system (8. Oil bath); adsorption system (7. fixed reactor); detection system (6. H_2O_2 absorption tube); tail gas absorption system (9. NaOH absorption bottle)

Theoretical Investigation

The adsorption mechanism of SO_2 molecules on tertiary amine was studied using the density functional theory (DFT). The DFT calculations were carried out with the DMol^3 code in Materials Studio (Accelrys, San Diego, CA, USA) (Delley 1990; Delley 2000). The geometrical structures were optimized at the GGA/PW91 level (Perdew *et al*. 1992) and double-numerical plus d polarization atomic orbital basis set (DNP) (Kohn and Sham 1965). An orbital cutoff of 4.5 Å was employed in the expansion of the molecular orbitals.

Upon optimizing the adsorption structures, the SO_2 molecule should approach the active atoms in different orientations and behavior to determine the most stable adsorption structures (Yan *et al*. 2014; Zhang *et al*. 2014; Al-Sunaidi and Al-Saadi 2015).

RESULTS AND DISCUSSION

Effect of the Moisture Content

While keeping a single SO_2 concentration (~2000 ppm, balance N_2) and a constant flow rate (0.4 L/min), the effect of moisture content on the adsorption of SO_2 at 25 °C was studied. Figure 3 shows the SO_2 breakthrough curves under the relative humidity (moisture content) of 0%, 20%, 60%, 80%, and 100%. The calculated results of SO_2 adsorption capacity of STA, under these five humidity conditions, were 50.76, 84.73, 103.51, 99.43 and 80.89 mg/g respectively. With the increase of moisture content to 60%, the SO_2 adsorption capacity of STA increased. Further increases in moisture content decreased the SO_2 adsorption capacity of STA. Therefore, the presence of water exerts a positive effect on the SO_2 removal; consequently, the sulfur capacity decreases as the moisture content increases (Yang *et al*. 2012; Ma *et al*. 2013). The results showed that the water can swell the adsorbent, which is conducive to the diffusion of sulfur dioxide, but too much water forms an aqueous film on the surface of the adsorbent and, thus, decelerates the reaction.

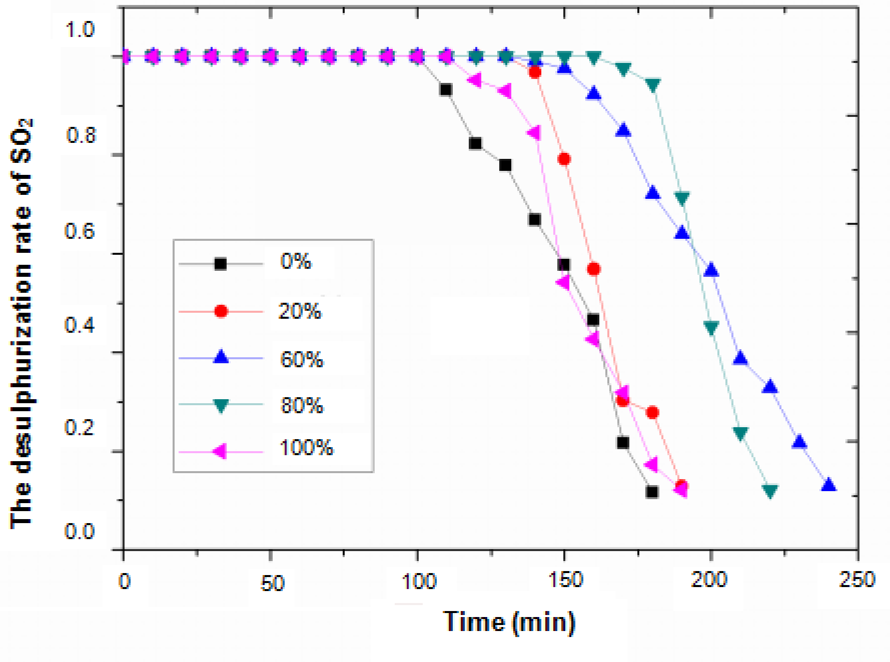

Fig. 3. Variation of the desulfurization rate with moisture content (~2000 ppm SO_2, flow rate 0.4 L/min, adsorption temperature 25 °C)

Effect of the Flow Rate

Keeping a single SO_2 concentration (~2000 ppm, balance N_2) and a constant moisture content (60%), and with variable flow rate from 0.2 L/min to 1.0 L/min, the effect of flow rate on the adsorption of SO_2 at 25 °C was studied. Figure 4 illustrates the saturation time and the adsorption capacities at different flow rates. The resident time in the adsorption column decreased with an increased flow rate, and the saturation time decreased from 400 min to 110 min. However, the low flow rate resulted in a low treatment capacity, which leads to high equipment costs (Ashcraft *et al*. 2013). Therefore, it is important to choose an appropriate flow rate that considers the breakthrough time and treatment capacity.

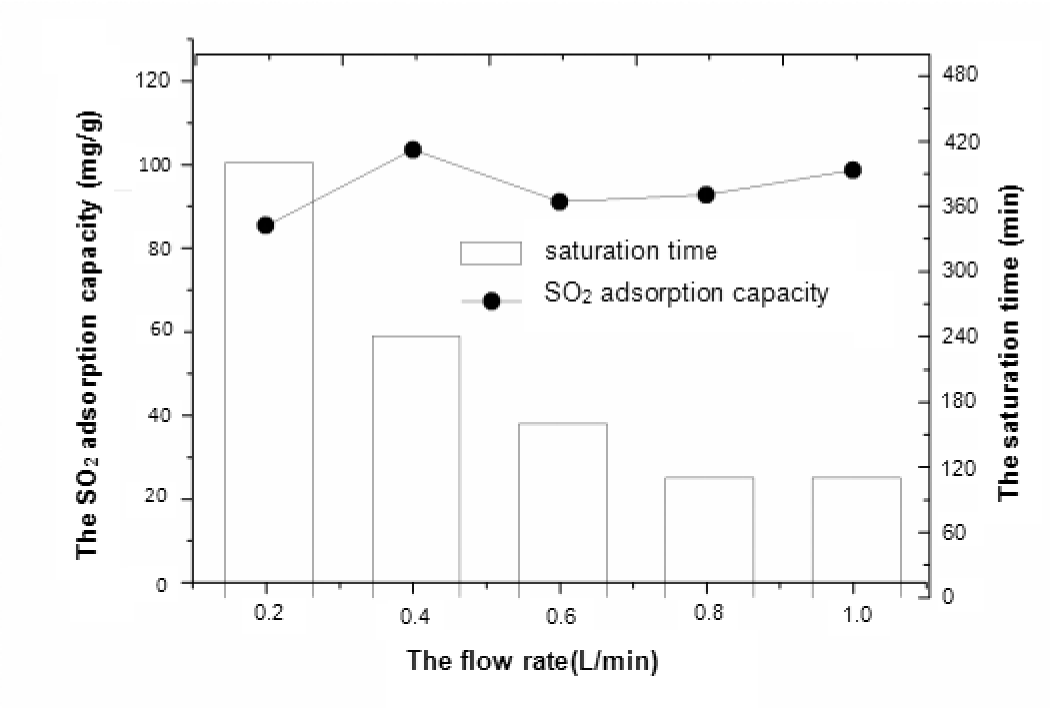

Fig. 4. Adsorption of SO_2 at different flow rate (~2000 ppm SO_2, moisture content 60%, adsorption temperature 25 °C)

Effect of the Adsorption Temperature

Keeping a single SO_2 concentration (~2000 ppm, balance N_2), a constant flow rate (0.4 L/min), and a constant moisture content (60%), experiments were performed at 25, 35, 45, 55, and 65 °C to study the effect of temperature on the adsorption of SO_2. Figure 5 shows the adsorption capacities under different temperatures. The SO_2 adsorption capacity decreased from 90.2 to 61.9 mg/g when the adsorption temperature increased from 25 to 65 °C, indicating that high temperature inhibits SO_2 adsorption. This effect is ascribed to the exothermic reaction between the SO_2 and adsorbent, which means that at lower temperatures, the reaction has a higher equilibrium constant.

Effect of the Regeneration Cycles

Figure 6 presents the cyclic analyses of STA over five cycles with adsorption at 25 °C and regeneration at 100 °C. No significant change in SO_2 adsorption capacity was observed over five cycles, and the working capacity remained constant (~100 mg/g) over five cycles. This data reveals that the interaction between the SO_2 and the tertiary amines is weak; therefore SO_2 can desorb at high temperature. These results provide evidence that the adsorbent can be regenerated at 100 °C. In addition, the STA was pre-humidified with water, indicating that the adsorbent is stable under humid conditions. This result agrees with a previous report (Tailor *et al*. 2014).

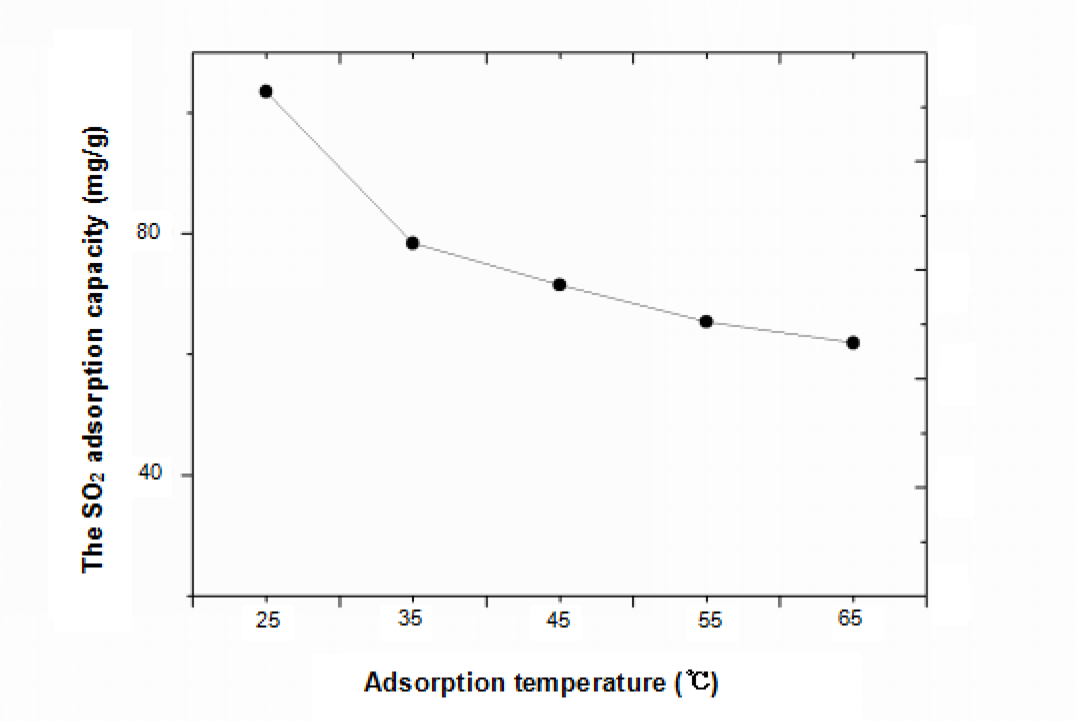

Fig. 5. Influence of adsorption temperature on adsorptive capacity of SO_2 (~2000 ppm SO_2, flow rate 0.4 L/min, moisture content 60%)

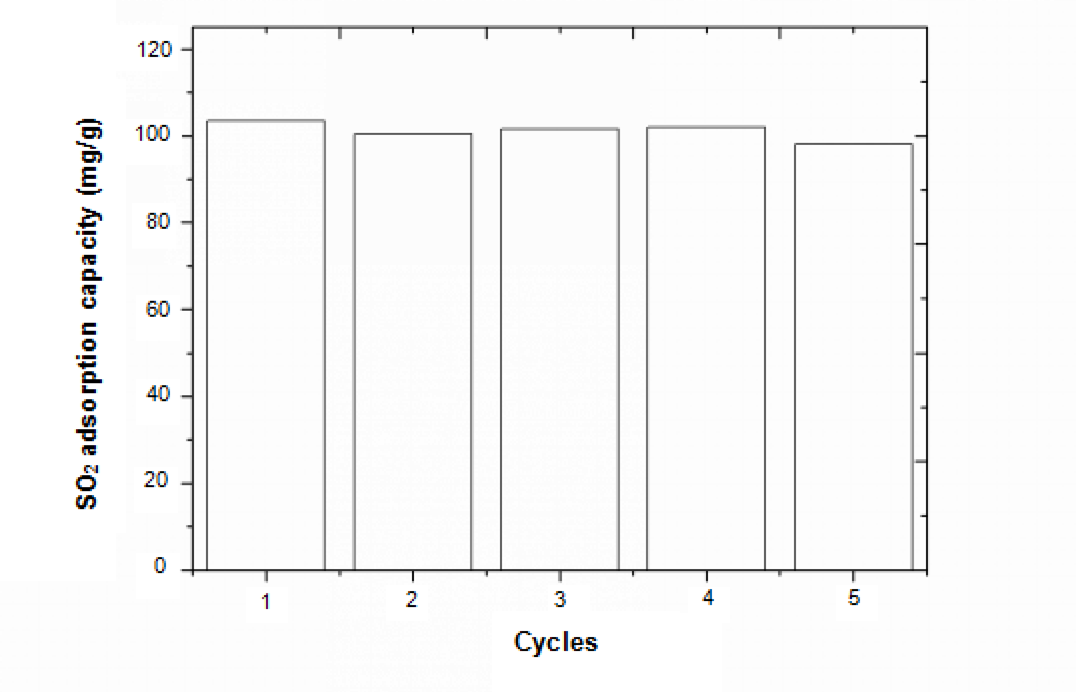

Fig. 6. Influence of regeneration cycles on adsorption capacity (adsorption at 25 °C and regeneration at 100 °C)

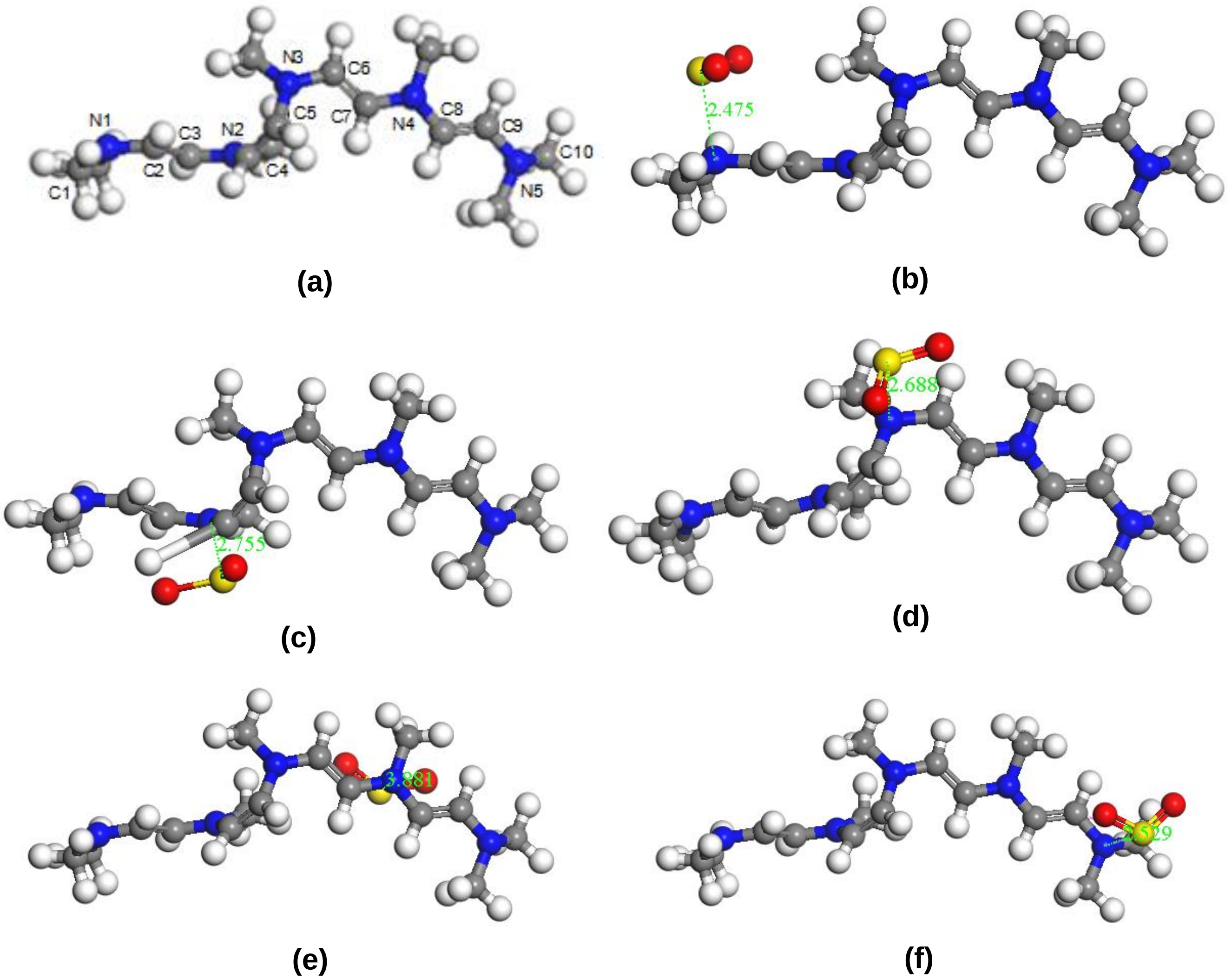

Fig. 7. (a) The most stable geometries of M-TEPA; adsorption structures of **(b)** SO_2-N_1-STA; **(c)** SO_2-N_2-STA; **(d)** SO_2-N_3-STA; **(e)** SO_2-N_4-STA; and **(f)** SO_2-N_5-STA

Theoretical Investigation

Figure 7 depicts the most stable geometries of one tertiary amine molecule (M-TEPA) and one SO_2 molecule. The adsorption structure of the adsorbed SO_2 molecule by tertiary amine in five possible positions are shown (N_1 through N_5).

The adsorption energy (E_{ads}) can be described by the following formula,

$$E_{ads} = E(A) - E(B) - E(C) \tag{1}$$

where $E(A)$ is the total energy of the adsorption structure energy, $E(B)$ is the total energy of one isolated gas molecule in its optimized structure, and $E(C)$ is the total energy of one tertiary molecule in its optimized structure (Carrasco *et al*. 2014). The distance between the S and N atoms (Å), the bond lengths of C-N and SO_2 (Å), the angles of $\angle O_1SO_2$ in optimized structure, as well as the corresponding E_{ads}, are listed in Table 1.

Table 1. Optimized Structure Characteristics

Structure	$d_{(C\text{-}N)}$ (Å)		$\angle O_1SO_2$ (°)	$d_{(O1\text{-}S)}$ (Å)	$d_{(S\text{-}O2)}$ (Å)	$d_{(S\text{-}N)}$ (Å)	$E_{(ads)}$ (eV)
SO_2-N_1-STA	1.458 (1.470)	1.399 (1.401)	116.531	1.484	1.484	2.475	-0.367
SO_2-N_2- STA	1.395 (1.391)	1.406 (1.394)	111.499	1.491	1.690	2.755	0.447
SO_2-N_3- STA	1.410 (1.395)	1.399 (1.395)	117.673	1.482	1.485	2.688	-0.184
SO_2-N_4- STA	1.381 (1.388)	1.391 (1.393)	117.751	1.490	1.490	3.881	-0.030
SO_2-N_5- STA	1.398 (1.405)	1.458 (1.453)	116.980	1.483	1.485	2.529	-0.283

$d_{(C\text{-}N)}$, bond lengths of C-N and SO_2; $\angle O_1SO_2$ the angles of SO_2; $d_{(O1\text{-}S)}$ and $d_{(S\text{-}O2)}$, distance between the O and S atoms; $d_{(S\text{-}N)}$, distance between the S and N atoms; and E_{ads}, adsorption energy. The data inside parentheses are the corresponding bond lengths of C-N in M-TEPA

After the adsorption of SO_2, the configuration of tertiary amine and SO_2 in its optimized structure is changed in some cases compared with the initial structures. For instance, in SO_2-N_3-STA, the bond lengths of C_5-N_3 and N_3-C_6 are elongated to 1.410 and 1.399 Å, respectively; the bond angle of $\angle O_1SO_2$ is changed to 117.673° from 119.611°. The bond lengths of O_1-S, S-O_2 are changed to 1.482 and 1.485 Å, respectively, from 1.463 Å. Moreover, Table 1 illustrates the binding distances between S-N, $d_{(S\text{-}N)}$, and the adsorption energy in five possible positions. The $d_{(S\text{-}N)}$ and $E_{(ads)}$ differ from each other in five possible positions. When SO_2 molecule approaches the $N_{1,5}$ atoms (Fig. 7 (b) and (f)), the $d_{(S\text{-}N)}$ in the final adsorption structure is shorter than others, and the absolute value of $E_{(ads)}$ is greater than the $E_{(ads)}$ of other positions. This can be explained by the occupied space due to the steric effect which means that the SO_2 is more likely to be adsorbed on the nitrogen atom ($N_{(1,5)}$) at both ends. Additionally, the energy of the adsorbed SO_2 on the $N_{(1,3,4,5)}$ is less than zero, implies that the adsorption process is exothermic and spontaneous (Zhang *et al*. 2014). In contrast, the energy of the adsorbed SO_2 on the N_2 is higher than zero, implies that SO_2 is hard adsorbed at this site. Therefore, in theory one molar M-TEPA can adsorb four molar SO_2 under room temperature. These calculation results were similar to the experiment under room temperature. Furthermore, the small adsorption energy suggests that SO_2 is only weakly adsorbed on the M-TEPA, which means that SO_2 can be regenerated at low temperature (100 °C). These findings also agree well with the regeneration experiment.

CONCLUSIONS

1. The SO_2 can be adsorbed on straw-based tertiary amine-supported material with SO_2 adsorption capacity of approximately 100 mg/g at 25 °C.
2. The appropriate amount of water can swell the adsorbent, which is conducive to the diffusion of sulfur dioxide, while water content higher than 60% forms an aqueous film on the surface of adsorbent, resulting in deceleration of the reaction.
3. The flow rate has a great influence on adsorption capacity by changing the resident time. The results of regeneration experiment provided evidence that the adsorbent can be regenerated at 100 °C.
4. The theoretical investigation implies that the M-TEPA has four potential adsorbed sites ($N_{(1,3,4,5)}$) with a small adsorption energy, indicating that the adsorption is weak.
5. The energy of the adsorbed SO_2 on the $N_{(1,3,4,5)}$ is less than zero, suggesting that the adsorption process is exothermic and spontaneous. The theoretical investigation agrees well with the experimental results.

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