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Amine-bearing activated rice husk ash for CO_2 and H_2S gas removals from biogas

Nguyen Trung Thanh*

Faculty of Engineering and Environment, An Giang University, Vietnam.

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Abstract

In this study, Triamine–grafted activated rice husk ash (TRI-A-RHA) material was investigated in the CO_2 and H_2S removals from biogas. TRI-A-RHA was synthesized by deposition of Triamine chemical onto the surface of activated rice husk ash support. The TRI-A-RHA exhibited high CO_2 and H_2S adsorption capacities (of ~ 0.34 and 0.14 $mmol.g^{-1}$, respectively) and stabilities at room temperature condition. These could be the TRI-A-RHA adsorbent had high BET surface area and amine functionalization. These findings are suitable for acid separation from natural gas.

Keywords: Amine, Activated rice husk ash, Biogas, CO_2, H_2S

1. Introduction

For transport and using of biogas, the carbon dioxide and hydrogen sulfide gases must be removed typically to below 2% and 1 ppm respectively [1]. The most common method of acid gas removal is liquid-phase chemical scrubbing with amines. However, this technology was showed the drawbacks such as the inefficiency and high regeneration cost for amine solution [2-3].

For gas-phase adsorption technology, the adsorbent has been a key to remove the CO_2 and H_2S gases from natural gas. In recent years, considerable research effort was made to develop novel CO_2 [4-6] and H_2S [7-8] adsorbents with such attributes. However, only a few investigations focused on the development of adsorbents with the ability to remove selectively both CO_2 and H_2S. Recently, Belmabkhout Y et al. [8] reported that CO_2 and, for the first time, H_2S removal over triamine-grafted pore-expanded mesoporous silica (TRI-PE-MCM-41) at room temperature. Using the gas - solid approach, it is expected to combine the high selectivity and reversibility of the acid gas - amine chemistry and the lowenergy requirements for regenerating the solid adsorbent. Adsorption isotherms for dry CO_2, H_2S, and CH_4 were determined for the amine-functionalized material as well as for the PE-MCM-41 silica support. However, synthesis of the expanded mesoporous silica support is complicating. The simple procedure for synthesis of adsorbent has not been found out yet.

Recently, the activated rice husk ash (A-RHA) showed many applications into the environmental engineering in our previous work such as adsorbent for arsenic contaminant in the ground water or/and A-RHA-supported iron and manganese oxides for arsenic removal [9]. In this study, the adsorbent of Triamine – grafted activated rice husk ash (TRI-A-RHA) is investigated in CO_2 and H_2S removal from biogas flow. A-RHA plays the carrier role for Triamine chemical to capture CO_2 and H_2S gases at room temperature. This study shows the TRI-A-RHA adsorbent has high capacities of CO_2 and H_2S gases but this adsorbent is synthesized by a simplier method (than that of TRI-PE-MCM-41).

2. Experimental section

2.1 Generation of support-activating the rice husk ash

The novel support from RHA with high surface area was generated by HF corrosion with a simple generation. In a typical procedure, 20 mg of the dried RHA were added into 80 mL of aqueous HF solution (10 vol.%). After 30 mins for stirring at the ambiance conditions (1 atm and room temperature), the activated RHA (A-RHA) was obtained after the performances such as washing with deionized (DI) water and filtering several times; drying in an oven at 100ºC overnight.

2.2 Generation of adsorbent

Incorporation of the amine functionality was achieved via surface grafting following a procedure described elsewhere. A sample of A-RHA was loaded into a multi-neck glass flask containing 150 mL of toluene. Once a homogeneous mixture was obtained, 0.3 mL per gram A-RHA of distilled deionized water was added and left stirring for 30 min. The glass flask was then submerged in a silicon oil bath set at 85 ºC using a temperature controlled stirring hotplate with an external temperature probe. Triaminesilane (3 mL per gram of A-RHA) was subsequently added to the mixture and left stirring for 16 h. The material was filtered and washed with copious amounts of toluene, then pentane.

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*Corresponding author. Tel.: +084-0907101590
Email address: ntthanh@agu.edu.vn
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Finally, the recovered solid was dried at 100 °C in a natural convection oven for 1 h and was labeled TRI-A-RHA.

2.3 Characterization measurements

Surface of A-RHA support was determined by SEM analysis at National Taiwan University of Science and Technology in Taiwan.

Brunauer–Emmett–Teller (BET) surface areas of the A-RHA support and TRI-A-RHA were determined from the N_2 adsorption/desorption isotherms at 77 K (Porous Materials, BET-202A).

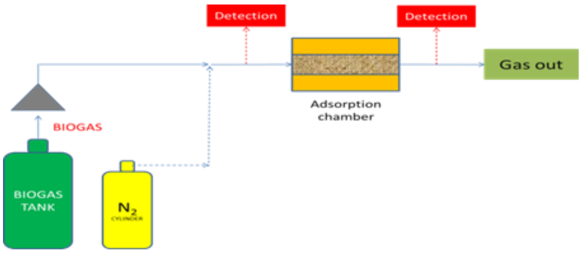

Figure 1 Experimental adsorption system for CO_2 and H_2S removal from biogas

2.4 Degasing and desorption for adsorbent

The degasing and desorption for adsorbent were performed using the homemade system (Figure 1) with the same of experimental conditions. The adsorbent was degased or desorpted (for CO_2 and H_2S gases on the adsorbent surface) under the effects of high temperature (120°C) and nitrogen gas flow (with flowrate of 30 $mL.min^{-1}$) during 2 hrs.

2.5 Experiment for CO_2 and H_2S removal from biogas

In the experiment, the fresh biogas from biogas tank was pumped directly into the adsorption chamber. It was available for adsorbent to adsorb CO_2 and H_2S gases from biogas at room temperature (~30 °C). The gas flow was transferred by the qualitative equipment (Desaga equipment) for gas flowrate. It was noticed that the adsorbent (10 g) was degased by nitrogen gas flow and high temperature before the adsorption was performed; and the adsorption efficiencies were calculated from the determined concentrations (before and after adsorption). In this study, the CO_2 and H_2S concentrations were determined directly with BIOGAS-600 equipment after 5 mins for adsorption.

3. Results and discussion

3.1 A-RHA and TRI-A-RHA materials

The A-RHA support is generated by the corrosion reaction of RHA and HF chemical [4]. The SEM image of A-RHA is showed in the Figure 2. After the activation with HF acid, the surface of the obtained A-RHA is observed with highly porous density. The BET surface area of A-RHA was ~430 $m^2.g^{-1}$. This high surface area of support plays an important role for dispersion of Triamine chemicals onto support surface and enhancing the contacting between adsorbent and biogas. This could improve the CO_2 and H_2S removal of adsorbent. However, the lower BET surface area of the current adsorbent (TRI-A-RHA) (~317 $m^2.g^{-1}$) was observed. This could be the surface of A-RHA support is covered by Triamine chemicals. It is noted that Triaminesilane chemicals were used to functionalize the surface of A-RHA. Thus, Triamine species could be strongly attached onto the surface of A-RHA at the SiO_2 positions.

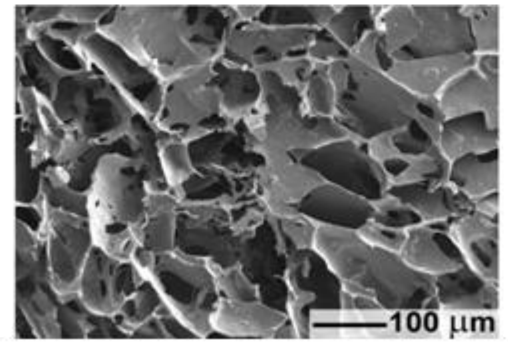

Figure 2 SEM image of A-RHA support

Table 1 Chemical composition of fresh biogas

Gas	Percentage (%)
CO_2	12,6
H_2S	7,8
Others	79.6

3.2 CO_2 and H_2S removal from biogas of TRI-A-RHA material

3.2.1 Chemical composition of biogas

In this study, the biogas was pumped directly from biogas tank and no any treatment for this biogas into the adsorption chamber. The percentages of CO_2 and H_2S gas in biogas are showed in the Table 1 and the percentages of CO_2 and H_2S gases are quite high.

3.2.2 CO_2 and H_2S removal activities of TRI-A-RHA and A-RHA materials

For CO_2 and H_2S removal from biogas, the experiments are performed with the continuous flow system. The results are showed in the Figure 3A and Figure 3B, respectively. For TRI-A-RHA material has the higher capacities for both of CO_2 and H_2S gas than that of A-RHA material. It could be the difference of adsorbent surface decompositon between TRI-A-RHA and A-RHA material. It implies that the functionalization of TRI chemical on A-RHA surface played an important role toward CO_2 and H_2S removal from biogas. Under the effect of flow rate, the efficiency of adsorption should be decreased at the high flow rates. The flow rates are started for decreasing of CO_2 and H_2S adsorptions are 50 and 45 $mL.min^{-1}$, respectively. The decreased efficiences of CO_2 and H_2S adsorptions can be the decreasing of contacting time of biogas and the adsorbent. Additionally, no CO_2 and H_2S detected downstream column until a breakthrough time of ~ 15 and 10 min, respectively.

The Figure 4 was showed that the adsorbent bed was completely saturated with CO_2 (after 15 min), and H_2S (after 10 min), corresponding to the final CO_2 and H_2S dynamic adsorption capacities of ~ 0.34 and 0.14 $mmol.g^{-1}$, respectively. The result of stability of adsorbent is showed in the Figure 5. It shows that TRI-A-RHA material is very high stability for CO_2 and H_2S adsorptions at the room temperature. It is noticed that one point in Figure 5 was

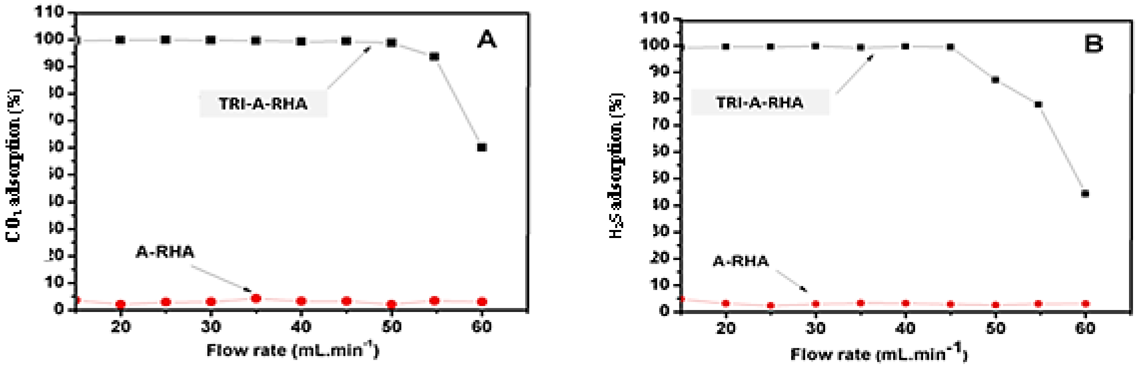

Figure 3 Percentage of CO_2 (A) H_2S (B) removal of TRI-A-RHA and A-RHA materials

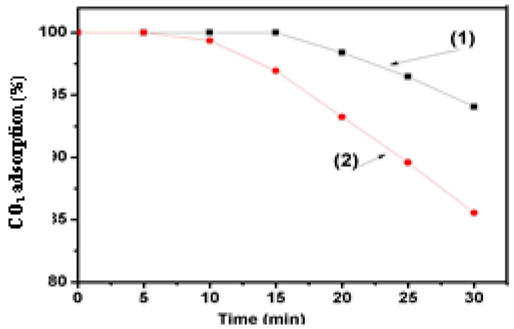

Figure 4 Effect of adsorption time to CO_2 (1) and H_2S (2) removal of TRI-A-RHA material

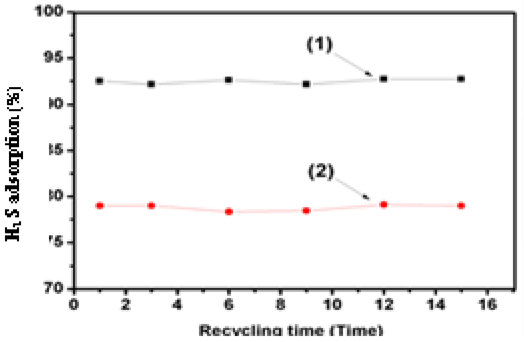

Figure 5 Stability of TRI-A-RHA material in CO_2 (1) and H_2S (2) removal

identifed as after reactivation for material (it means the saturated adsorbent was renewed after 10 min for biogas adsorption).

4. Conclusions

The TRI-A-RHA material is synthesized by the simple procedure. On the basis of CO_2 and H_2S adsorption measurements, it has been demonstrated that TRI-A-RHA shows very high CO_2 and H_2S adsorption capacities and stabilities at room temperature. These could be the TRI-A-RHA adsorbent had high BET surface area and amine functionalization. This material can removal acid gas from the natural gas stream.

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