

The Efficiency of Carbon Dioxide and Hydrogen Sulphide Adsorption using Impregnated Granular Activated Carbon and Zeolite

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ABSTRACT: *In this work, adsorbents granular activated carbon (GAC), granular activated carbon with acetylene (CVD/GAC) and zeolite A were applied for carbon dioxide (CO₂) and hydrogen sulphide (H₂S) gas removal. The adsorbents were characterised by scanning electron microscope (SEM) and X-ray diffraction (XRD). Polyethyleneimine (PEI) in ethanol with initial concentration of 0.2 g l⁻¹ and 1 mol dm⁻³ lithium nitrate (LiNO₃) were prepared to improve the adsorption capacity. In the impregnation process, various adsorbents, i.e., GAC, CVD/GAC and zeolite A were placed in a vial containing 0.2 g l⁻¹ of PEI and 1 mol dm⁻³ of LiNO₃ solution, at different ratios of adsorbent and various solutions of 30%W/W. The adsorbents (GAC, PEI/CVD/GAC:PEI/GAC, LiNO₃/CVD/GAC:LiNO₃/GAC, zeolite 5A, PEI/zeolite 5A and LiNO₃/zeolite 5A) were tested by using the synthetic biogas (45% CO₂, 10% N₂, 45% CH₄ and 105 mg dm⁻³ of H₂S). The performance of CO₂ and H₂S adsorption results have shown that PEI/CVD/GAC is the best adsorbent for low concentration of H₂S and LiNO₃/5A is the best adsorbent for CO₂ adsorption. The purity of the outlet methane was 96.6%, 97.3%, 98.1%, 81.53%, 80.6% and 93.6% for zeolite 5A, LiNO₃/5A, PEI/5A, GAC, LiNO₃/CVD/GAC and PEI/CVD/GAC, respectively. The selectivity in the H₂S/CH₄ ratio of GAC is higher than zeolite 5A. The adsorption selectivity of the CO₂/CH₄ ratio of LiNO₃/5A is higher than GAC.*

Keywords: Activated carbon, zeolite A, polyethyleneimine chemical vapour deposition granular activated carbon, carbon dioxide adsorption, hydrogen sulphide adsorption

1. INTRODUCTION

Biogas is produced from anaerobic degradation of organic materials. It is a mixture composed of approximately 50%–70% CH₄, 30%–50% carbon dioxide (CO₂), smaller amounts of NH₃ (80–100 ppm), hydrogen sulphide (H₂S, 500–1,000 ppm) and hydrocarbon (<100 ppm).¹ The advantage of biogas is that it can be used to generate electricity and heat energy. However, biogas purification is required to remove CO₂ and H₂S in order to upgrade it to natural gas grade substitute for car fuel. H₂S corrodes vital mechanical components within the engine generator and vehicle engines if not removed. When burning H₂S, the compound will be converted to SO₂, which is a pollutant. H₂S is the foul smell inherent in wastewater treatment plants, animal processing and food processing plants.² Removal of CO₂ and H₂S using amine aqueous solution absorption has been an industrial method for decades. However, amine absorption is unfit for H₂S removal in low concentration due to loss of solution, corrosion and high cost of removal.^{3,4}

In many research works on CO₂ removal by adsorption, the adsorbents should have attributes such as being low-cost raw materials, exhibiting low heat capacity, fast kinetics, high CO₂ adsorption capacity, high CO₂ selectivity, and thermal and chemical stabilities over several cycling rounds. Activated carbon is the carbonaceous adsorbent which is used for CO₂ adsorption because of low cost and high thermal stability. Carbon molecular sieve (CMS), which is the narrow pore size distribution of activated carbon, is a characteristic that allows high adsorption. Zhang et al. determined the adsorption capacity of activated carbon at 2.27 mmol g⁻¹ at 298 K.⁵ The amine or high oxidising agent impregnated on adsorbent will increase the rate of adsorption. Improvement of CO₂ adsorption such as through polyethyleneimine (PEI) impregnation and chemical vapour deposition process can increase the adsorption capacity of granular activated carbon. Rewadee et al. conducted the preparation of CVD/GAC from coffee bean, which is an effective adsorbent for CO₂ removal, and using synthetic biogas (30% CO₂, 20% N₂ and 50% CH₄).⁶

Zeolite has played a major role in the development of adsorption technology. The framework of zeolite consists of an assemblage of aluminate and silicate tetrahedral, and shared oxygen atoms to form an open crystal lattice. Zeolite molecular sieve is widely used as sorbent for gas separation due to its large surface area. The sorption process based on solid adsorbents are being actively pursued, especially using inorganic porous materials such as zeolite 13X and using different recycling configurations and high performance by pressure swing adsorption. Although low silica materials have high adsorption capacity and selectivity at low pressure, they are sensitive to moisture, which inhibits the CO₂ adsorption. The CO₂

adsorption capacity on zeolite A, X and Y is higher than silicoaluminophosphate (SAPO) zeolite.⁷ Zeolite 5A has been proven effective for CO₂ and H₂S removal. Wang et al. produced the nanoporous composite sorbent called “molecular basket” by loading PEI on molecular sieve such as MCM41 and SBA15.⁸ Yong et al. produced adsorbents with strong oxidising ability, using transition metals of Zn, Cu and Fe, which have been studied for H₂S adsorption and oxidation.^{9–11} The main objective of this work is to prepare the adsorbents impregnated with LiNO₃ and PEI (GAC, LiNO₃/GAC, PEI/GAC, zeolite 5A, LiNO₃/zeolite 5A and PEI/zeolite 5A), and investigate their CO₂ and H₂S removal performance.

2. EXPERIMENTAL

2.1 Preparation and Characterisation of Adsorbents

Commercial granular activated carbon (GAC) was purchased from METRA Co. Ltd. It was dried at 200°C for 2 h. The modified granular activated carbon or carbon molecular sieve (CMS) prepared by chemical vapour deposition on granular activated carbon (CVD/GAC) was deposited with acetylene by a chemical vapour deposition process under 15 ml min⁻¹ of acetylene and followed with 50 ml min⁻¹ of nitrogen flow at 800°C for 30 min. Zeolite 5A was purchased from Thai Silicate Co. Ltd. It was crushed and screened in 325 µm and dried at 200°C for 2 h.

PEI with average molecular weight 100,000 g mol⁻¹ was obtained from Sigma Aldrich. An amount of 15 g of PEI was dissolved in 30 g of ethanol with initial concentration of 0.2 g l⁻¹ under stirring for 20 min. In the impregnation process, 10 g of GAC and CVD/GAC were placed in a vial containing PEI solution in the adsorbent/solution ratio of 30% w/w. The adsorbents (GAC, CVD/GAC and zeolite 5A) with PEI loading were stirred at 120 rpm for 3 h. It was dried at 105°C overnight. The obtained products are PEI/GAC, PEI/CVD/GAC and PEI/zeolite 5A, respectively.

About 2 g of various adsorbents (LiNO₃/GAC, LiNO₃/CVD/GAC and LiNO₃/zeolite 5A) was prepared by impregnation adsorbents (GAC, CVD/GAC and zeolite 5A) with 1 M of LiNO₃ in the adsorbent/solution ratio of 30% w/w under agitation for 60 h at room temperature. It was dried at 105°C overnight. The obtained products were washed to remove the soluble impurities off and calcinations, in order to remove volatile compounds. The final product was dried at 105°C overnight and kept in the desiccators. Scanning electron microscope (SEM) analysis was carried out by using JSM-6400 (JEOL, Japan). X-ray diffraction (XRD) was performed using Cu-Kα radiation (Rigaku Corp., Japan).

2.2 Adsorption Experiments

The sorption tests were carried out using a SS-304 tube with the inner diameter of 3 cm and 100 cm in length in which 70 g of the sorbents (GAC, PEI/CVD/GAC, LiNO₃/CVD/GAD, zeolite 5A, PEI/zeolite 5A and LiNO₃/zeolite 5A) was packed. A synthetic biogas (45% CO₂, 10% N₂, 45% CH₄ and 105 mg dm⁻³ H₂S) was passed through the sorbent at the flow rate of 30.0 ml min⁻¹ at room temperature. The outlet of CO₂ and H₂S concentration was detected by a biogas 5000 Analyser as shown in Figure 1. The breakthrough concentration of CO₂ and H₂S was defined as 50% and 10%, respectively of the initial concentration. The test was stopped when the outlet CO₂ and H₂S concentration reached the breakthrough concentration.

The removal efficiency can be calculated by using the Equation 1:

$$\text{Removal efficiency (H}_2\text{S or CO}_2\text{)} = (C_0 - C_e) \times 100 / C_0 \quad (1)$$

where C_0 is the initial of CO₂ or H₂S concentration, and C_e is the outlet of CO₂ or H₂S concentration.

The selectivity of H₂S/CH₄ and CO₂/CH₄ can be carried out by calculating the outlet gas of H₂S/CH₄ and CO₂/CH₄ by using Equations 2 and 3:

$$\text{Selectivity of H}_2\text{S/CH}_4 = \text{mol outlet of H}_2\text{S} / \text{mol outlet of CH}_4 \quad (2)$$

$$\text{Selectivity of CO}_2\text{/CH}_4 = \text{mol outlet of CO}_2 / \text{mol outlet of CH}_4 \quad (3)$$

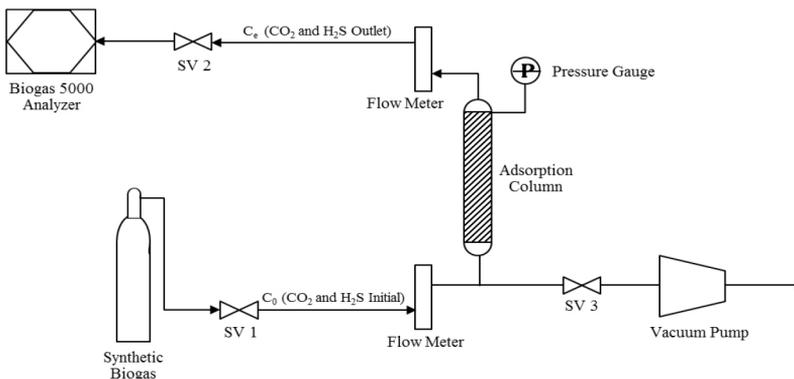


Figure 1: Schematic diagram of adsorption experiments.

3. RESULTS AND DISCUSSION

3.1 Preparation and Characterisation of Adsorbent

SEM images of the GAC, PEI/CVD/GAC, zeolite 5A and $\text{LiNO}_3/\text{zeolite 5A}$ are shown in Figure 2. GAC and PEI/CVD/GAC have a rough shape, as shown in Figures 2(a) and 2(b). Zeolite 5A and $\text{LiNO}_3/\text{zeolite 5A}$ have a cubic shape and size of 2–3 μm as shown in Figures 2(c) and 2(d). SEM technique was applied in order to study surface morphology of adsorbents.

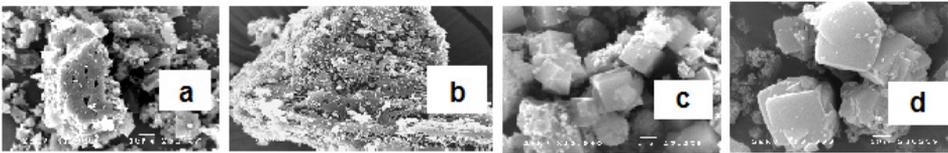


Figure 2: SEM images of (a) GAC, (b) PEI/CVD/GAC, (c) zeolite 5A and (d) $\text{LiNO}_3/\text{zeolite 5A}$.

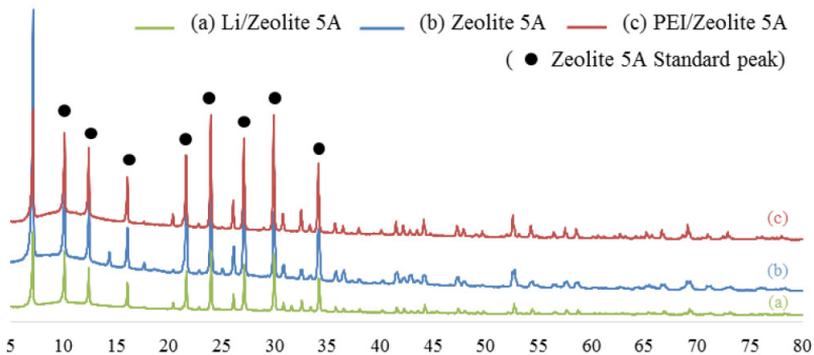


Figure 3: XRD of zeolite 5A, PEI/zeolite 5A and $\text{LiNO}_3/\text{zeolite 5A}$.

The XRD pattern of zeolite 5A, PEI/zeolite 5A and $\text{LiNO}_3/\text{zeolite 5A}$ are shown in Figure 3. The peaks of zeolite 5A, PEI/zeolite 5A and $\text{LiNO}_3/\text{zeolite 5A}$ are in agreement with the standard peaks.

3.2 Adsorption Performance

The analytical result of the purity of methane (CH_4) in synthetic mixed biogas for GAC, PEI/CVD/GAC, $\text{LiNO}_3/\text{CVD/GAC}$, zeolite 5A, PEI/5A and $\text{LiNO}_3/\text{zeolite 5A}$ were 81.53%, 93.6%, 90.8%, 96.6%, 96.8% and 97.26%, respectively for the first cycle under 1 atm. The maximum cycle of purification for synthetic biogas is seven cycles.

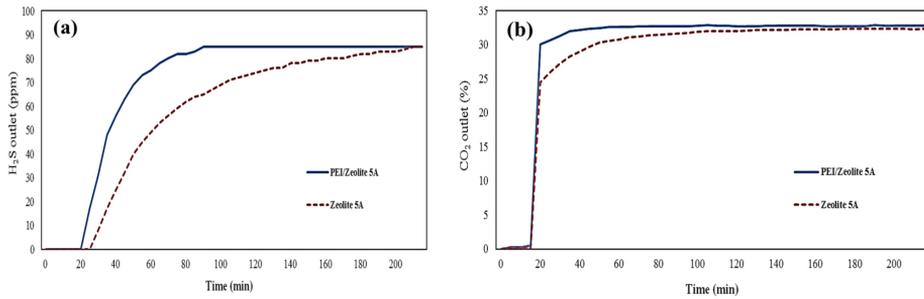


Figure 4: The concentration of (a) H₂S outlet, and (b) CO₂ outlet, using various adsorbent (zeolite 5A and PEI/zeolite 5A).

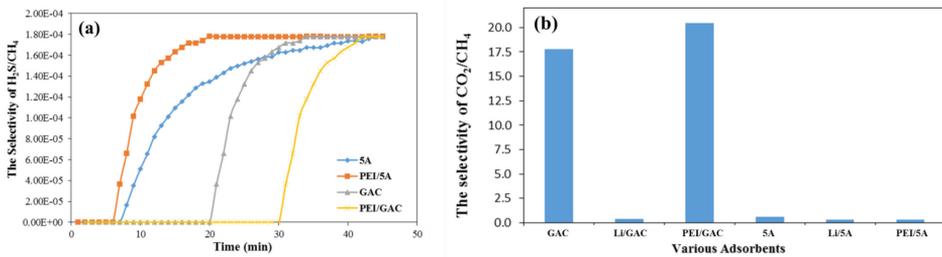


Figure 5: Images of (a) selectivity of H₂S/CH₄ by using various adsorbent (GAC, PEI/GAC, zeolite 5A and PEI/zeolite 5A), and (b) selectivity of CO₂/CH₄ by using various adsorbent (GAC, LiNO₃/GAC, PEI/GAC, zeolite 5A, LiNO₃/zeolite 5A and PEI/zeolite 5A).

The result of the H₂S and CO₂ outlet concentration by using various adsorbent (zeolite 5A and PEI/zeolite 5A) are shown in Figures 4(a) and 5(a). From the results, PEI impregnated on zeolite 5A which is the amine on solid adsorbent can remove the low concentration of outlet H₂S. The data indicate that the impregnation process on zeolite 5A can improve the adsorption efficiency. A higher PEI loading on zeolite 5A (30 wt%) should enhance pore H₂S adsorption capacity, together with the decrease of surface area, pore size and pore volume of the PEI-impregnated support. The selectivity in the H₂S/CH₄ ratio of PEI/GAC is higher than PEI/zeolite 5A. H₂S may have a higher affinity for PEI/GAC because of its polarity. The selectivity of the CO₂/CH₄ ratio of LiNO₃/5A is higher than GAC as shown in Figure 5(b). The adsorbents, such as carbonaceous impregnated with PEI, will increase CO₂ and CH₄ adsorption capacity. While the Li-based zeolite 5A is the chemical adsorbent, the strong ionic will increase the CO₂ adsorption capacity. Finally, the maximum adsorption capacity of the PEI/GAC samples was 3.86 mmol CO₂/g adsorbent. The adsorption capacity decreases when the amount of PEI is increased. The pores of adsorbent prevent CO₂ from diffusing into the pores.

4. CONCLUSION

The carbon molecular sieve by using PEI/impregnated on granular activated carbon by chemical vapour deposition process on granular activated carbon could improve the CO₂ and H₂S adsorption efficiency. The lithium nitrate impregnated on zeolite 5A is a good adsorbent for CO₂ removal.

5. ACKNOWLEDGEMENTS

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