Behaviors of hydrogen sulfide removal using granular activated carbon and modified granular activated carbon

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Abstract. An experimental study on hydrogen sulphide (H₂S) adsorption behaviours using amine-impregnated solid adsorbent (GAC/PEI) was carried out for H₂S concentration in the range of 200 and 400 ppm. The dynamic adsorptions of GAC and modified GAC (2.0 and 1000 g/L PEI) in a fixed-bed column were investigated by determining the breakthrough curves and adsorption capacities of various adsorbents. The adsorbent exhibits an excellent adsorption capacity of 106.87 and 231.45 mgH₂S/g-adsorbent for 200 ppm and 400 ppm H₂S, respectively. The H₂S breakthrough capacity is found to relate to the surface adsorption and chemical adsorption.

1 Introduction

Biogas known as a renewable energy has been produced by anaerobic digestion of animal manure. The biogas can be converted directly into heat energy whereas the by-product can be used for agricultural fertilizer. The main composition of biogas is a mixture composed of approximately 50-70% CH₄, 30-50% CO₂, smaller amounts of NH₃ (80-100ppm), H₂S (500-1,000 ppm) and trace of hydrocarbon (<100 ppm) [1]. The merit of biogas is that it can be used directly to generate electricity and heat energy for engineering applications. However, the disadvantage for use in a gas engine is the reduction in recovery of the energy content in the biogas. Therefore, biogas purification is required by H₂S removal technique to upgrade its property to be similar to natural gas for employing as car fuel. Many technologies have been studied for the H₂S removal such as liquid absorption by amine and solid adsorbent. However, amine aqueous solution adsorption is found to unfit for low concentration of H₂S removal because of expensive cost and corrosion. Activated carbon is a highly microporous material with larger surface area. It is utilized because of their wide availability, low cost and high thermal stability. Schrier et al. [2] investigated the H₂S removal using nanoporous graphene material for gas separation. Mabayoje et al. [3] studied the improvement of H₂S adsorption on the compositions of graphene oxide with copper. Plaza et al. [4] reported CO₂ capture using activated carbon and alumina impregnated with various amine such as DETA, pentaethylenhexamine (PEHA) and polyethyleneimine (PEI). Their result indicated that DETA impregnated on alumina has a high CO₂ adsorption capacity. The carbon-base support derived from sewage sludge impregnated

with PEI can increase the CO₂ adsorption capacity. Gutierrez et al. [5] examined the biogas desulfurization by thermally threaded sewage-sludge. Liu and Wang [6] studied the H₂S removal using 4A molecular sieve zeolite synthesis from attapulgite and showed that the sulphur adsorption capacitor was up to 10 mg/g-sorbent. Wang et al. [7] developed a nanoporous composite sorbent by loading PEI on SBA-15 and MCM-41 and indicated that a high sorption capacity of 87-mg H₂S/g-sorbent is obtained. Chen Q et al. [8] introduced PEI-loaded hierarchical porous silica monolith developed as a high stability, recyclable H₂S sorbent at low temperatures having a large H₂S breakthrough capacity of 1.27-mmol of H₂S/g-sorbent at 22°C. This could easily be regenerated at 75 °C. Boonyawan et al. [9] studied the effect of amine addition on low cost fumed silica (fSi). Their result indicated that the fSi impregnated with PEI at 40 wt.% has the highest H₂S adsorption capacity among amine addition. Wang et al. [10] used the nanoporous composite sorbent PEI/SBA-15 having a high sorption capacity and showed that the moisture had a promoting effect on the removal of H₂S from gas streams. However, few researches have focused on the development of sorbents with the ability to selectively remove H₂S.

The main objective of the present work is to prepare Granular Activated Carbon (GAC) and a PEI-modified GAC on H₂S adsorption performance. The suitable PEI loading concentration (2.0 and 1,000 g/L) on GAC using various concentration of (200 and 400 ppm) H₂S was also prepared.

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2 Materials and Methods

2.1 Preparation and characterize for adsorbents

The commercial Granular Activated Carbon (GAC) was obtained from METRACo., Ltd. It was sieved to sizes ranging from 20–40 mesh and dried at 105°C for 6 hours before impregnation process. Polyethyleneimine (PEI) with average molecular weight 25,000 g/mol obtained from Sima-Aldrich. 15-g of PEI was dissolved in 30-g of 99.9% ethanol solution under stirring for 20 minutes and dilution for various concentrations (2.0%w/w and 1000 g/L). In the wet impregnation process, the 10-g adsorbents (GAC) were placed in a vial containing 20 mL of various PEI concentrations (2.0%w/w and 1000 g/L). The GAC with PEI loading was stirred at 120 rpm speed for 3 hours. Finally, the adsorbent was dried at 80 °C for 10 hours under vacuum conditions. The obtained GAC was impregnated with two PEI concentrations denoted as GAC/PEI-2.0 and GAC/PEI-1000. The characterization analysis of the adsorbent was conducted by scanning electron microscopy analysis for morphological structure based on JSM-6400 (JEOL, Japan) and surface area estimation was performed by N_2 adsorption.

2.2 H₂S adsorption performance testing method

The H₂S adsorption tests were carried out using a stainless-steel tube with 12-mm inner diameter and 200-mm in length at which 1 g of sorbent was packed in the middle of the column support with quartz wool. Before the test, the adsorbent was treated under a N₂ flow of 50 mL/min. Each concentration of H₂S (200 and 400 ppm) was passed through the adsorbent at a flow rate of 5 mL/sec. The H₂S outlet concentration was detected by a biogas 5000-analyser. The adsorption experiment was shown in Fig. 1. In the present work, the breakthrough concentration of H₂S was defined as 25% of the initial concentration. The test was stopped when the outlet H₂S concentration reaches the breakthrough concentration.

Fig. 1. Experiment for H₂S adsorption.

3 Results and Discussion

3.1 Characterization of Adsorbent

The scanning electron microscope (SEM) image of GAC and modified granular activated are shown in Fig. 2 and 3, respectively.

Fig. 2. Scanning electron microscope (SEM) images of GAC at magnification scale (x1500 magnification).

Fig. 3. Scanning electron microscope (SEM) images of GAC/PEI-2.0 at magnification scale (x1500 magnification).

Figs. 2 and 3 show the surface morphology of the amine modified adsorbents, as determined by SEM analysis. The adsorbent showed the agglomeration of the primary particles GAC to form larger particles, comparing the SEM image of the GAC/PEI-2.0 with granular activated carbon (GAC) adsorbent.

Table 1. Structure properties of granular activated carbon (GAC) before and after wet impregnation with PEI.

Sample	S_{BET} (m ² /g)	V_t (cm ³ /g)	Pore size (Å)
GAC	981.6	0.5413	22.06
GAC/PEI-2.0	925.8	0.5194	22.44
GAC/PEI-1000	14.6	0.0168	45.94

Table 1 displays the surface area and the pore volume of the adsorbent. The GAC displays a specific surface area of 981.6 m²/g and a pore volume of 0.5413 cm³/g. The modified GAC with PEI is also displayed by the surface area and pore volume obtained. The GAC/PEI-2.0 displays a specific surface area of 925.8 m²/g and a pore volume of 0.5194 cm³/g and GAC/PEI-1000 displays a specific surface area of 14.6 m²/g and a pore volume of 0.0168 cm³/g. This result indicates that the amount of PEI on the GAC has an effect on the GAC properties. The high loading PEI impregnated on GAC will decrease the surface area and pore volume as shown in Table 1. The surface area of GAC/PEI is decreased because of the filled PEI impregnation on granular activated carbon (GAC).

3.2 H₂S Adsorption performance

The result indicates that the lower amount of PEI impregnated on GAC (GAC/PEI-2.0) provides good H₂S adsorption capacity at low initial concentration of H₂S (200 ppm). The increasing amount of PEI impregnated on GAC (1000 ppm) gives poor performance for H₂S adsorption. For high initial concentration of H₂S (400 ppm), GAC shows the best adsorbent. The results can be concluded in Table 2.

Table 2. H₂S adsorption capacity using GAC, GAC/PEI-2.0 and GAC/PEI-1000.

Sample	H ₂ S Adsorption Capacity (mgH ₂ S/g adsorbent)	
	200 ppm	400 ppm
GAC	18.36	231.45
GAC/PEI-2.0	106.87	62.22
GAC/PEI-1000	6.50	11.93

Figs. 4 and 5 show H₂S adsorption performance on various adsorbent (GAC, GAC/PEI-2.0 and GAC/PEI-1000) to find the breakthrough time at low and high H₂S concentration, the breakthrough concentration of H₂S is as 25% of the initial concentration. The breakthrough time at low H₂S concentration, GAC/PEI-2.0, yields higher performance for H₂S adsorption. The result indicates that the GAC/PEI-2.0 give a high H₂S adsorption capacity for low H₂S concentration as shown in Fig. 4 while the GAC shows high H₂S adsorption capacity for high H₂S concentration as shown in Fig. 5.

Figs. 4 and 5 also indicated that the adsorption capacity of adsorbents that strongly depends on the amount of micropores of a specific diameter presented in GAC as well as their volume as given in Table 3.

Table 3. Adsorption time of GAC, GAC/PEI-2.0, and GAC/PEI-1000)

Sample	Adsorption time (Breakthrough 25%)	
	200 ppm	400 ppm
GAC	60.25	375
GAC/PEI-2.0	354.37	102.11
GAC/PEI-1000	18.90	18.99

Fig. 4. H₂S adsorption isotherm of GAC and modified GAC (GAC/PEI-2.0 and GAC/PEI-1000) using low concentration of H₂S (200 ppm)

Fig. 5. H₂S adsorption isotherm of GAC and modified GAC (GAC/PEI-2.0 and GAC/PEI-1000) using high concentration of H₂S (400 ppm)

However, the H₂S adsorption capacity decreases when the amount of PEI is increased. Accordingly, the adsorption process takes place only at the surface of the adsorbent.

It is shown as Figs. 4 and 5 that the merit of PEI-impregnated on modified GAC is due to their larger pore

diameter and the interconnected porous channel networks that prevent clogging of the pores and maintain the porosity of the adsorbents after PEI impregnation. The amine composition from PEI interacts strongly with low concentration of H₂S. However, it may inhibit the adsorption with high concentration of H₂S because of the lower surface area.

The reaction of H₂S on PEI impregnated activated carbon at the normal temperature could be chemical adsorption as the main reaction and physical adsorption. For chemical, H₂S reacts with amine group in PEI structure at carbon surface. The reaction of H₂S amine is shown as:

For H₂S adsorption, the two H atoms in the H₂S molecule interact with a N atom in the amine group in the first type of sorption site, whereas each of the two H atoms in the H₂S molecule interact with a N atom from one of two amine groups in the second type as shown in equation (1) and (2). [11].

4. Conclusion

PEI impregnated on GAC sorbents was developed and tested for H₂S removal. For the breakthrough concentration of H₂S defined as 25% of initial concentration, Granular Activated Carbon (GAC) is the best adsorbent for high concentration of H₂S (400 ppm) while GAC/PEI-2.0 is the best adsorbent for low concentration of H₂S (200 ppm). The chemical adsorption as the main reaction via the amine composition from PEI interacts strongly with low concentration of H₂S. However, it may inhibit the adsorption with high concentration of H₂S because of the lower surface area.

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