Use of Kaolin as Adsorbent for Removal of Hydrogen Sulphide from Biogas

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Biogas desulphurisation needs to be done before being used as the alternative energy sources of fuel. Presently, biogas desulphurisation through the adsorption process is an attractive method due to its simple process and low starting cost. Currently available adsorbent such as activated carbon, metal/metal oxide and zeolite are the key factor for effective biogas desulphurisation by adsorption process. Utilisation of biogas as alternative fuel is not feasible due to presences of hydrogen sulphide. This factor is the main reason to the slow commercialisation of biogas fuel. Introduce of less expensive but high efficiency method for biogas upgrading process will help to overcome this problem. Low cost biogas upgrading process can be established by using low cost adsorbent material which is the main cost associated with biogas purification. Malaysia has large amount deposit of kaolin. Kaolin deposit can be found in states of Perak, Johor, Kelantan, Selangor, Pahang and Sarawak. The present of metal oxides in kaolin makes it possible to be used as H_2S adsorbent. The present work was undertaken to investigate the feasibility of using kaolin for H_2S removal by adsorption. Dynamic tests were carried out at room temperature to evaluate the capacities of the sorbents for H_2S removal using fixed bed reactor. Several reaction parameters such H_2S inlet flowrate, and reaction temperature that affect breakthrough adsorption capacity were studied. Kaolin sample was characterised using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray fluorescence (XRF). The results show that kaolin was able to remove low amount H_2S. Further modification is needed to improve its performance.

1. Introduction

Biogas is a potentially important energy source that can be used for production of heat, electricity and fuel. Typical biogas contains 50 – 65 % methane (CH_4), 30 – 45 % carbon dioxide (CO_2), moisture and traces of hydrogen sulphide (H_2S) as the main component (Gamba and Pellegrini, 2013). One of the barriers that slowdown the application of biogas as the energy source is the existence of hydrogen sulphide (H_2S) gas during the biogas production process. H_2S is not only a threat to human health, it is also poisonous to the mechanical part of the system due to its corrosive properties (Abatzoglou and Steve Boivin, 2009). The composition of H_2S in biogas varies from less than 100 ppm to more than 10,000 ppm. Several countries have regulated specific standard for H_2S level in the biogas before it can be applied as energy source (Sun et al., 2015). H_2S capture and separation can be done through the use of both chemical and physical absorption; membrane separation; or biological method. Uses of these methods are limited to the high cost of operation, production of unwanted by-products, or unwieldy operation (Iovane et al., 2014). For example, plugging and foaming problems are the main disadvantages of chemical absorption process although this technique can achieve 99.99 % of sulphur removal efficiencies or higher (Ying et al., 2014). Iovane et al. (2014) have reported that the membrane separation method is able to upgrade bio-methane for different concentration of inlet conditions. However, their performance can decline due to low membrane selectivity and multiple steps required (modular system) to reach high purity (Huertes et al., 2011). H_2S also can be removed using biological method; additional amount of O_2 during biological process can reduce the purity of the biogas (Zhou

et al., 2015). Direct H_2S oxidation to sulphur at low temperature, is very interesting H_2S removal technique for small scale plant. Adsorption is the most economical and feasible of all the available methods for the capture and separation of H_2S. This is due to the availability of selective low cost adsorbents such as activated carbon, zeolites, naturally occurring materials and synthesised materials (Bkour et al., 2015).

A range of adsorbent materials have been evaluated for the isolation of H_2S. Choo et al. (2013) carried out H_2S adsorption by using virgin activated carbon and impregnated activated carbon. They have found that the adsorbent capacities were affected by the influent concentration, inlet flow rate, adsorbent loading and reaction temperature. Transition-metal oxides and mixed oxides has been used the catalytic oxidation of H_2S. Palma and Barba (2015) using V_2O_5-CeO_2 catalysts for H_2S abatement from biogas by direct selective oxidation to sulphur at low temperature. They reported about 90 % conversion of H_2S to Sulphur. H_2S removal by using natural zeolite was investigated by Paolini et al. (2015) and they have found that natural zeolite from tuff waste were highly selective for H_2S and CO_2 adsorption. Kwasny and Balcerzak (2016) have compared the performance of different adsorbent for biogas desulphurisation. They have found that, zeolite has shown the lowest desulphurisation efficiency. The available literature shows that factors such as active site, surface area, mechanical and thermal stability, pores volume, selectivity are the influenced factors in determination of the adsorbent performances.

Low cost adsorbents collected from naturally occurring materials with high capacity and selectivity is much sought after. Kaolinite is a naturally occurring material that has been used as an adsorbent material for several organic compounds. However, no works has been published on the use of kaolinite as H_2S adsorption. In work, the ability of kaolinite adsorbent as a cost-effective adsorbent for H_2S adsorption is studied. A complete characterisation of the synthesised adsorbent was performed to understand its effectiveness on the chemical and physical adsorption of H_2S. The adsorbent was also tested to determine its capacity and the rate of removal of H_2S from a gas stream. Several reaction parameters such H_2S inlet flow rate, and temperature that affect breakthrough adsorption capacity were studied. For comparison study, the H_2S adsorption capacity of the kaolinite adsorbent was compared to the commercial activated carbon and zinc oxide.

2. Materials and methods

2.1 Materials

Kaolinite was obtained from Kaolin (M) Sdn. Bhd. Hydrogen Sulfide gas (200 ppm) and nitrogen (99.999 %) gases were obtained from Kuantan Gas. Zink oxide was obtained from Merck, and activated carbon from ACS Chemical.

2.2 Method

Prior to desulphurisation experiment, natural kaolin was sieved to obtain a powder that passed through a 100-mesh. The kaolinite adsorbent was then calcined in a muffle furnace at 550 °C for 12 h to remove any volatile organic compound.

2.3 Characterisation and analysis of adsorbents

X-ray diffractometry (XRD) was used for phase identification and the determination of the crystallinity of the adsorbent powders. The chemical composition of the adsorbents was determined using energy dispersive X-ray spectrometry (XRF). The Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups on the surface of particles. The FTIR spectra of the samples were recorded using an FTIR Perkin Elmer spectrometer. 1.5 mg of the sample was mixed with 1 g of KBr powder and pressed using a hydraulic press to obtain a transparent disk. The disk was then dried in an oven for 2 h at 110 °C to remove any water vapor. FTIR spectra were recorded in the transmission mode.

2.4 Adsorption experiment

Adsorption experiments were performed in a fixed bed column (10 mm ID and 100 mm bed thickness) that is placed into a heating block. Analysis of reactor outlet gas stream was carried out by using a gas chromatography with TCD detector. Nitrogen was used as carrier gas in all adsorption experiments. Adsorption experiments were performed by using 5 g kaolin and a gas mixture containing 200 ppm H_2S in nitrogen.

3. Results and discussion

3.1 Characterisation of the adsorbents

XRD was used to determine the phases and crystallinity of kaolin adsorbent used in this study. Figure 1 shows the XRD patterns for the kaolin adsorbent. The peaks at 2θ = 21°, 26.6°, 36.5°, etc are showing the quartz are the main component in raw kaolin. The kaolinite peaks are detected at 2θ = 12.5°, 25° and 46°.
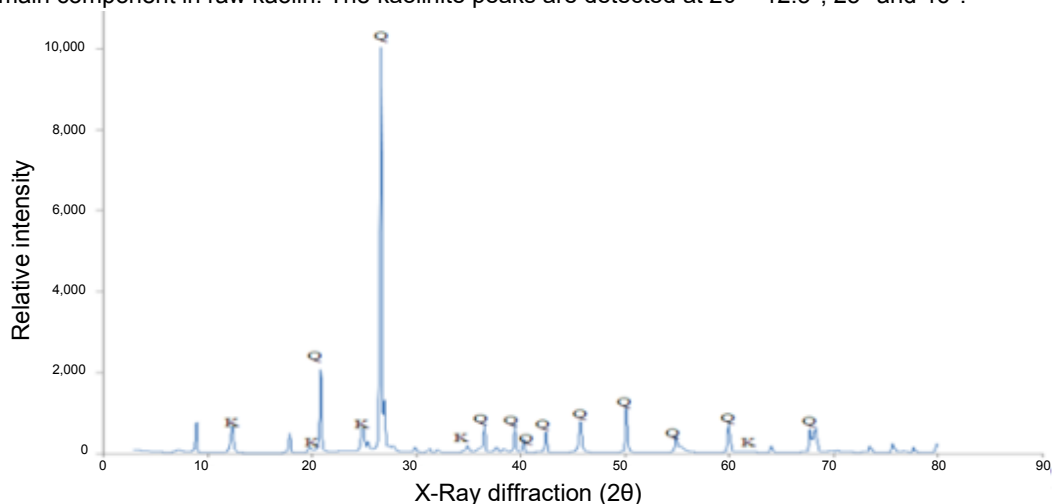

Figure 1: XRD pattern for the kaolin adsorbent

X-ray Fluorescence (XRF) spectrometry was used to determine the percentage of all chemical elements that present in the kaolin sample. Table 1 shows the results of the XRF elemental characterisation and physical properties of the kaolin sample. Major components of kaolin are Al and Si, and with trace quantities of metals such as Ni, Cu, Zn, Rb, Zr, Mo, etc. The total amount of Al and Si in the product is 21.41 % and 70.08 %.

Table 1: The chemical composition of kaolin adsorbent from XRF analysis

Chemical Properties		Physical Properties	
Aluminium (Al_2O_3)	21.41 %	Moisture content	< 1.5 %
Silica (SiO_2)	70.08 %	pH (30 % solid)	3.5 - 6.0
Iron (Fe_2O_3)	0.55 %	100 Mesh Residue	< 10.0 %
Potassium (K_2O)	2.72 %	60 Mesh Residue	< 0.5 %
Magnesium (MgO)	4.74 %		
TiO	0.29 %		
Trace Metals	0.19 %		
Loss on Ignition @ 1,025 °C	2.0 - 6.0 %		

Figure 2 shows the FTIR spectra for kaolin. In the kaolin spectrum, there are three major peaks at 3,694, 3,620, and 536 cm^{-1} attributed to OH stretching of inner-surface hydroxyl groups, OH stretching with inner bulk hydroxyl groups, and Si-O perpendicular stretching. Kaolin peaks at 1,114 cm^{-1} due to Si-O stretching (longitudinal mode) and 1,031 cm^{-1} due to in-plane Si-O stretching. The intensity of the peak at 912 cm^{-1} corresponding to the deformation of inner surface OH groups. The FTIR bands at 789 and 694 cm^{-1} assigned to Si-O-Al stretching of raw kaolin.
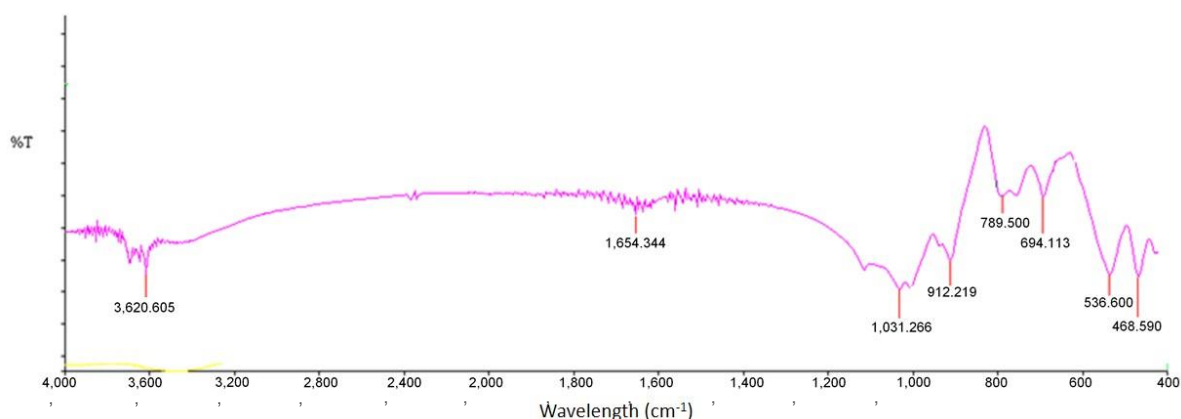
Figure 2: FTIR spectra of kaolin adsorbent

3.2 Adsorption experiments

Adsorption experiments were carried out by using kaolin samples with an average particle diameter of 250 mm and with a gas mixture containing 200 ppm H_2S in nitrogen. Table 2 shows the comparison of H_2S adsorption capacity of the kaolin adsorbent with activated carbon and pure zinc oxide. From the result, it shows that the adsorption performance of kaolin adsorbent is only 0.087 mg H_2S/g adsorbent which is very low compared to commercial zeolite A 2.1 mg H_2S/g adsorbent, activated carbon 51.68 mg H_2S/g adsorbent and 58.30 mg H_2S/g adsorbent for ZnO sorbent.

Table 2: Kaolin adsorbent H_2S adsorption capacity compare to activated carbon and zinc oxide adsorbents

Adsorbent	Adsorption capacity (mg H_2S/g sorbent)
Kaolin	0.087
Commercial Zeolite A	2.1
Activated Carbon	51.68
Zinc Oxide	58.30

3.3 Effect of gas flow rate

Adsorption breakthrough curves obtained at different gas flow rate 10, 20 and 30 mL/min are given in Figure 3. In all these experiments 5 g of sorbent was used. From the experiments (as summarised in Table 3), the adsorbent adsorption capacity has reduced as the gas flow rate was increase from 10, 20, and 30 mL/min at 9.9, 8.7 and 3.0 mg H_2S/100 g adsorbent. The contact time between the gas and adsorbent are the key factor determine the adsorption capacity. Increase the gas flow rate will reduce the contact time and thus reduce the adsorption capacity (Dhage et al., 2008).
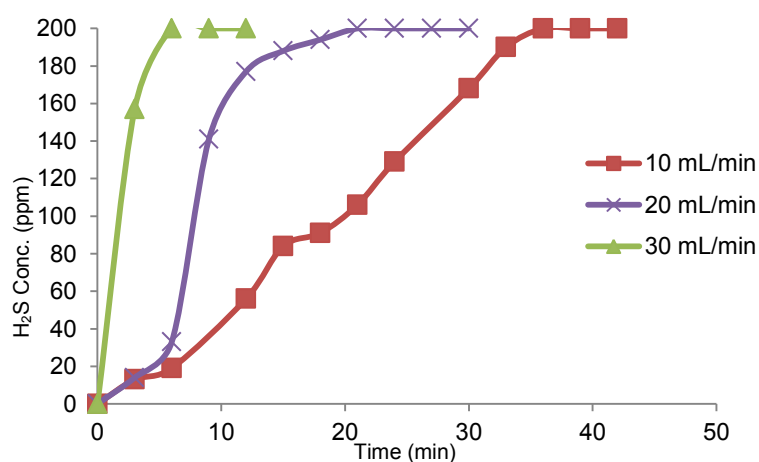

Figure 3: Breakthrough curves of kaolin at different flow rates

Table 3: The breakthrough time and capacity at breakthrough time and saturation for inlet flow rate

Reactor Temperature (mL/min)	Time (min)		Sulphur capacity (mg S/100 g adsorbent)	
	t_b (H$_2$S = 50 ppm)	t_s (H$_2$S = 200 ppm)	Breakthrough Capacity	Saturated Capacity
10	11	36	5.6	9.9
20	5.5	21	5.4	8.7
30	-	6	-	3.0

3.4 Effect of reaction temperatures

The temperature selection is important during adsorption process. The type of adsorption either physical adsorption or chemical adsorption depends on the temperature. Physical adsorption of H$_2$S is more favourable at ambient temperature meanwhile, chemical adsorption depends on the temperature for chemical adsorption to occur (Cal et al., 2000). Figure 4 show the breakthrough curve gathered at different adsorption temperature 30, 55 and 80 °C. From the adsorbent breakthrough curve, it can be observed that the performance of kaolin sorbents for H$_2$S adsorption has increased as reaction temperature was increased. From this work, it can be observed that both chemical and physical adsorption were taking place during H$_2$S removal by kaolin adsorbent (Table 4). At low temperature (30 °C) the physical adsorption was dominant, meanwhile at higher temperature the mechanism of H$_2$S removal was governed by chemical adsorption. At higher temperature of 80 °C, a significant increase in capacity (26.0 mg H$_2$S/100 g sorbent) can be observed. This result shows that, the kaolin sorbent favour chemical adsorption. The trace metals that present in the kaolin have acting as active site during H$_2$S adsorption process. This result shows the agreement with the others work that reported that the trace metal in sorbent play important role during H$_2$S adsorption (Dou et al., 2015).
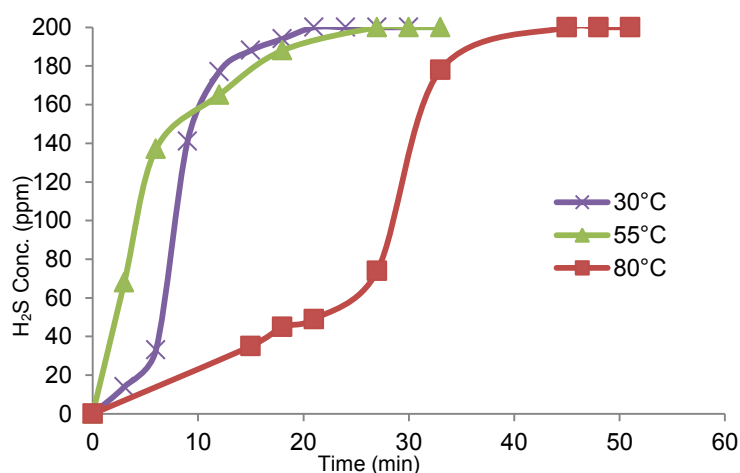

Figure 4: Breakthrough curves of kaolin at different temperatures

Table 4: The breakthrough time and capacity at breakthrough time and saturation for each reactor temperature

Reactor Temperature (°C)	Time (min)		Sulphur capacity (mg S /100 g adsorbent)	
	t_b (H$_2$S = 50 ppm)	t_s (H$_2$S = 200 ppm)	Breakthrough Capacity	Saturated Capacity
30	5.5	21	5.4	8.7
55	2.5	27	2.3	6.3
80	22	45	20.2	26.0

4. Conclusions

The sulphur adsorption capacity of kaolin was found to decrease from about 9.9 mg H$_2$S/100 g sorbent to 3.0 mg H$_2$S/100 g sorbent as flow rate was increased from 10 to 30 mL/min. The kaolin adsorbent show chemical adsorption favourable due to adsorption capacity was higher at high temperature. The H$_2$S adsorption capacity of kaolin adsorbent is 0.087 mg H$_2$S/g sorbent and it is less than one percent of the adsorption capacity of activated carbon and zinc oxide sorbent at the same condition. It was concluded that kaolin cannot

be an effective sorbent for H_2S removal. With some modification on kaolin properties might be able to increase the H_2S adsorption.

Acknowledgments

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