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Hydrogen sulfide removal using CeO_2/NaOH/PSAC: Effect of process conditions and regeneration study

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ABSTRACT

Present investigations reported in the literature on the preparation of activated carbon that can be used effectively to remove H_2S from biogas. However, apart from the synthesis of a reactive sorbent, the process conditions can also significantly influence the performance of the sorbent. Therefore, the aim of this study is to investigate the effect of process conditions; sorption temperature, H_2S concentration, sorbent loading, flow rate and the presence of other gas components on the performance of activated carbon based sorbent for H_2S removal. In this study, palm shell activated carbon was impregnated with CeO_2 and NaOH. H_2S sorption capacity of the optimized sorbent was found to be increasing with decreasing sorption temperature, minimum at 2000 ppm H_2S, increasing with increasing sorbent loading, maximum at 500 mL/min and maximum at 25% relative humidity. CO_2 and CH_4 were found to affect sorption capacity in a different extent. Regeneration efficiency as high as 78% was achieved using heat treatment at 500 °C regeneration temperature and four hours regeneration time. Selected sorbents were characterized in order to further understand the sorbent properties and characteristics of the reaction.

1. Introduction

Palm oil industry is very important for Malaysian's economy. Unfortunately, enormous amount of palm oil mill effluent (POME) have been produced in the palm oil factories. Recently, anaerobic digestion method has been applied in treating POME. One of the benefits from this technology is the production of biogas during the treatment process. Biogas is combustible, contains high caloric value, and therefore can be utilized in the boiler or gas engine to generate heat and electricity. Regrettably, during the formation of biogas, hydrogen sulfide (H_2S) is also formed and the composition is up to 3000 ppm. H_2S is highly toxic, corrosive and produces offensive rotten egg odor. Therefore, in order to protect the mechanical parts during the utilization of biogas, H_2S must be firstly removed from the biogas stream. Lately, there have been many studies reported in the literature on the preparation of activated carbon that can be used effectively to remove H_2S from biogas. However, apart from the synthesis of a reactive sorbent, the process conditions can also significantly influence the performance of the sorbent.

In this study, palm shell activated carbon was impregnated with CeO_2 and NaOH. The process conditions can affect the H_2S sorption capacity, subsequently affect the overall performance of an sorption column. Among these, sorption temperature appears as the most crucial parameter that affects the performance. The temperature of biogas produced from the anaerobic digestion of POME is generally around 50 °C due to the sunlight heating. The temperature of biogas is very low if compare to the temperature of flue gas from the industrial processes that normally reaches 300–600 °C [1–3]. However, there were also studies using low sorption temperature close to ambient temperature [4–6]. Large difference in sorption temperature would definitely affect the sorption reaction.

Apart from that, other gas components such as CO_2, CH_4 and H_2O in biogas could also affect the sorption capacity of the sorbent. Among these, moisture has the most significant effect towards the sorption reaction. From several studies [6,7], promotional effect of moisture towards H_2S sorption capacity were reported. Higher relative humidity would promote the dissociation of H_2S into HS^-. The dissociation is the first step for the sorption process and is considered as the rate–limiting step in most cases. However,

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controversial finding of the effect of moisture was also reported [8]. Competition between H_2S and water molecules towards the active sites of the sorbent had detrimental effect for H_2S removal. In addition, moisture was found to deactivate the metal species impregnated on the sorbent and restrain the reaction rate. Therefore, effect of moisture was studied in our work because metal oxide (cerium oxide) was also impregnated on the sorbent.

Regeneration is an important process in the sorption process. Without regeneration, the spent sorbent that has lost its original sorption capacity would be disposed and inevitably increase the operating cost of the plant. In general, regeneration of sorbent used for H_2S removal can be performed using water or heat treatment [9–13]. However, the regeneration efficiency was generally lower than 60%. This phenomenon was explained that the sulfur species deposited in the pore structure in the form of elemental sulfur and sulfuric acid that strongly sorbed and could not be removed using simple washing method.

In our previous work, the sorbent CeO_2/NaOH/PSAC was successfully synthesized and utilized in the H_2S removal. In order to achieve the usability of this sorbent in the industrial process, the effect of process conditions towards the sorption capacity must be studied. Therefore, the aim of this study is to investigate the effect of process conditions; sorption temperature, H_2S concentration, sorbent loading, flow rate and the presence of other gas components on the performance of activated carbon based sorbent for H_2S removal.

2. Experimental

2.1. Chemicals

The PSAC used in this study was steam activated and purchased from Victory Element Sdn Bhd, Malaysia. Upon receiving, the PSAC was sieved to 1–2 mm and dried at 80 °C in an oven. In the PSAC impregnation, extra pure cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and analytical reagent grade sodium hydroxide (NaOH) in pellet form supplied by Merck Sdn Bhd were used. Purified nitrogen (99.99% N_2) was used in the calcination of the impregnated activated carbon and regeneration of the spent sorbent. In H_2S sorption test, three types of gases (99.99% CH_4, 99.99% CO_2 and 1% H_2S, balance CH_4) in cylinders supplied by Wellgas Sdn Bhd, Malaysia were used to simulate the industrial biogas.

2.2. PSAC impregnation

In our previous work, the sorbent CeO_2/NaOH/PSAC was successfully synthesized and optimized for H_2S removal. The optimized sorbent was prepared using the following procedures in order to study effect of process conditions and regeneration. Cerium nitrate solution at 5 wt% cerium corresponding to PSAC amount was first added to 2.50 g PSAC in a conical flask. PSAC was used as a support due to its high surface area and capability to accommodate gas-solid reaction effectively. Then, sodium hydroxide at 1.0 M was added to the flask slowly. Sodium hydroxide was added to cerium nitrate to produce cerium oxide. Cerium oxide was used to catalyze the oxidation of hydrogen sulfide. In addition, sodium hydroxide would increase the surface pH of PSAC to enhance hydrogen sulfide sorption. Subsequently, the mixture was shook in a water bath shaker at room temperature for 1.5 h impregnation time. After that, the impregnated activated carbon will be filtered and dried in an oven at 80 °C. The dried impregnated activated carbon was then subjected to 400 °C calcination temperature and three hours calcination time under the flow of N_2 at 50 mL/min.

2.3. Sorption test

H_2S sorption test was carried out using a packed bed reactor test rig. The composition of simulated biogas was adjusted by controlling the flow rate of gases using Aalborg AFC26 mass flow controllers. CO_2 and CH_4 were passed through a humidification system at specific temperature (30–45 °C) to provide moisture to the biogas inlet stream. H_2S/CH_4 was not passed through the humidification system because H_2S is soluble in water. The path of the biogas after the humidification system to the reactor is insulated to avoid condensation of moisture. The diameter of the stainless steel tubular reactor used is half inch. The flow rate of the biogas was 250–1000 mL/min with CO_2, H_2S and CH_4 in specific concentration. The PSAC loading was 1.0–2.5 g and placed in the middle of the tubular reactor and supported with approximately 0.05 g glass wool. Sorption temperature (30–70 °C) was controlled using a Linberg/Blue M tube furnace. Concentration of H_2S at the outlet stream was analyzed using an IMR 6000 gas analyzer via electrochemical sensor calibrated for 0–5000 ppm H_2S. The workspace of the test rig was ventilated as a safety procedure just in case there was a leakage of hazardous H_2S.

2.4. Regeneration study

Regeneration of the spent sorbent was performed using water and heat treatment. Water washing of spent sorbent was performed using cold (30 °C) and hot water (70 °C). 1.30 g of spent sorbent in a conical flask was added with 50 mL of deionized water at either 30 °C (cold) or 70 °C (hot). The conical flask was placed in a water bath shaker at corresponding temperature and shook for five hours. The deionized water in the conical flask was changed every interval hour. After that, the water regenerated sorbent was dried in an oven at 80 °C. For heat regeneration, 1.35 g of the spent sorbent was placed in the middle of a tubular reactor and supported with approximately 0.05 g glass wool. Regeneration temperature (400–600 °C) was controlled using a Linberg/Blue M tube furnace. The regeneration process was performed using a flow of 50 mL/min of N_2 for regeneration time between three to five hours.

2.5. Characterization

Several characterizations were performed on selected sorbents to analyze their surface properties, functional groups and morphologies/composition. N_2 adsorption-desorption was carried out with a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Prior to analysis, the samples were degassed for 5 h. SEM–EDX analysis was carried out by a Quanta FEG 450 at accelerating voltage of 3 kV. TGA was performed using a Perkin Elmer TGA7 with a heating rate of 10 °C/min under a 100 mL/min flow of purified air. Elemental analysis was performed using a Perkin Elmer 2400 CHNS Analyzer. XRF was performed using Rikagu RIX 3000. XPS was performed using a High Resolution Multi Technique X–Ray Spectrometer (Axis Ultra DLD XPS, Kratos). The pass energy used was 25 eV and the charging effect was corrected using the C 1s peak at 284.5 eV.

3. Result and discussions

3.1. Sorption temperature study

Sorption is a process that is highly affected by temperature. In the removal of H_2S using CeO_2/NaOH/PSAC, increasing temperature from 30 to 60 °C will result a decrease in the sorption capacity, as shown in Fig. 1. Then, further increase of temperature from 60 to 70 °C had no significant effect on the sorption capacity. At higher