



A systematic study of the iron hydroxide-based adsorbent for removal of hydrogen sulphide from biogas

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ARTICLE INFO

Keywords:

Biogas
Hydrogen sulphide
Separation techniques
Adsorption
Mesoporous adsorbents
Iron hydroxide

ABSTRACT

This study was aimed to evaluate the hydrogen sulfide (H₂S) removal efficiency of an economic iron hydroxide-based adsorbent from simulated biogas mixture with an H₂S concentration range of 500–10300 ppm. The properties of these porous materials such as crystal structures, surface patterns, surface area, pore volume and pore size were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET measurements. The H₂S adsorption capacity (Ads^{cap}) is nearly independent of the drying temperature of hydroxide-based adsorbent over the range of temperatures tested (100–200 °C) as well as relative humidity (0–80%) under equal conditions of H₂S concentration. In addition, the experimental results revealed that the Ads^{cap} increased exponentially from 23.3 to 48.7 wt% with the increased retention time from 0.5–52.9 s and decreasing space velocity from 7433 to 68 h⁻¹. At the same time, Ads^{cap} increased linearly from 20.57 to 35.18 wt% with the increasing H₂S concentration from 500 to 10300 ppm.

1. Introduction

Methane (CH₄) is the main component of the biogas generated in a Landfill-Based Anaerobic Digestion (LBAD) process. The second component of the biogas consisted of carbon dioxide (CO₂) and then some other minor components such as Nitrogen (N₂), hydrogen sulphide (H₂S) and sulphur compounds are also present [1,2]. Methane can play a different role in different levels [3]. On the one hand, CH₄ is known as the main reason for aggravation of the greenhouse effect and global warming like CO₂ or H₂S, on the other hand, it is an important renewable energy source alternative to fossil fuels [4,5]. Energy recovery from capture and use biogas from landfills and the anaerobic digestion of wastes is becoming more common, but the processes are still dependent upon the presence of H₂S [6]. This hazardous gas combined with water vapor (H₂O) can form a strong acid (H₂SO₄) and H₂, which cause in turn the corrosion of engines and pipelines [7,8]. As a consequence, the control and prevention of corrosion are of vital interest for a rapid development of biogas production and substrate utilization. Seen from an applicability point of view, it is quite logic that H₂S must be removed from digestion gas generated in an LBAD process before they can be used as fuel for stationary engines and renewable energy source [9,10]. Thus, an economic and high-performance method for the removal of H₂S from digestion gas is necessary.

Different adsorption materials are commonly used for H₂S removal

from digestion gas, biogas, and other types of gas mixtures. However, these microporous and mesoporous materials used in this field of study are often expensive and complicated to treat [10]. Recently, Florent et al. examined a high surface area cobalt oxyhydroxide (CoOOH) and its composites with graphite oxide (GO) as H₂S reactive adsorbents at ambient conditions [11]. Employing a sample of CoOOH, they obtained an adsorption capacity regarding H₂S of 69.1 mg/g under dry gas conditions. The importance of the OH groups of MOOH composites through the role of surface chemistry and morphology in the reactive adsorption of H₂S for different transition metals like M = Cobalt [12], M = Zinc [13] and M = Iron [14] was revealed by different authors under comparable conditions. In another previous research, Cd/GO-based composite adsorbents with various hydroxide to carbonate ratios were studied as H₂S adsorbents at ambient conditions [15]. This study found that the H₂S adsorption capacity was 45.8 mg/g. Zirconium hydroxide/graphite oxide composites were studied as adsorbents of H₂S at room temperature by Seredych et al. [16], and the H₂S adsorption capacity was 41.3 mg/g. In addition, a copper-zinc oxide supported on mesoporous silica showed an absorption capacity for H₂S of 80 mg/g [17].

Iron-based materials have received considerable attention over the last few years for their relatively low cost and because they can be used at room temperature and atmospheric pressure [14,18–25]. Among the heterogeneous experiments investigated by different authors, there is

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still a lack of systematic information about the H₂S removal efficiency of the iron hydroxide-based adsorbent from simulated digester gas mixture under different operating conditions like drying temperature, H₂S concentration, relatively humidity, retention time and the space velocity. In the present study, the effects of variations in drying temperature from 60 °C to 200 °C, H₂S concentration from 500 to 10300 ppm, relative humidity from 0 to 80% at room temperature, retention time from 0.5–52.9 s and the space velocity from 68 to 7433 h⁻¹ were investigated systematically and correlated with the observed H₂S adsorption properties of iron hydroxide-based adsorbent.

2. Experimental

2.1. Preparation of iron hydroxide-based adsorbent

In brief, to a solution of FeCl₃ (35 wt%) under vigorous stirring on a magnetic stirrer was added NaOH solution (25 wt%) until the pH was between 7.5 and 8. This process was described in detail in Ref. [24]. The iron hydroxide-based precipitate was collected by filtration using a vacuum pump, washed with distilled water, and dried at 100 °C for one day. In particular, the washing process with distilled water was repeated until pH = 7. Since iron oxide can be formed through the crystallization process such as aging or calcination, the generated iron hydroxide was confirmed to have a change in absorptivity according to the drying temperature.

2.2. Material characterization

The crystal structure of all samples was checked by means of X-ray diffractometer (Rigaku D/max 2000 ultima plus) at room temperature. Brunauer-Emmett-Teller (BET) specific surface areas were measured by nitrogen adsorption-desorption at 73.3 K using a KS-A-0094 instrument. The specific surface area, pore volume, and pore size were calculated from the desorption branch of N₂ adsorption/desorption isotherms using the BET formula using the software. To have an idea about the microstructure morphology and textural properties of the iron hydroxide-based adsorbent, Scanning Electron Microscope (SEM) analysis were carried out on a Philips XL 30 SFEG in the high-resolution mode. Elemental chemical composition analysis using an EDAX Apollo XL (EDAX Inc., Mahwah, NJ, USA) X-ray Energy Dispersive Spectrometer (EDS) were performed to complete the material characterization.

2.3. H₂S adsorption capacity (Ads^{cap}) test of iron hydroxide-based adsorbent

To evaluate the performance of iron hydroxide-based adsorbent on H₂S adsorption capacities, an H₂S adsorption system was built in-house. A schematic diagram of the H₂S fixed-bed adsorption system is shown in Fig. 1. The experimental apparatus consisted of a gas mixing chamber, H₂S adsorption system, and measurement system. The gas mixture was carried out in the H₂S adsorption system by feeding a gas mixture of H₂S and balanced N₂. Uniform distribution of the gas mixture inside the H₂S adsorbent column was ensured by a gas mixing chamber. In each test, 4 ml of iron hydroxide-based adsorbent was placed into the reaction tube (inner diameter = 10 mm; height = 80 mm, particle size = 12–20 mesh), which was placed in a temperature-controlled chamber at 25 °C. A gas chromatography (GC) method is developed for rapid analysis of H₂S permeable component in the permeate gas. The method uses a Gas Chromatography-Pulsed Discharge Detector (IGC 7200, DS science), which was connected with a data system.

The H₂S adsorption capacity (Ads^{cap}) was evaluated by the following equations:

$$M_{abs} = QC_{out} \int_0^t \left(1 - \frac{C_{out}}{C_{in}}\right)$$

$$W = \frac{M_{ads}}{M_L} \times 100$$

where M_{abs} is the adsorbed hydrogen sulfide amount (g), Q the volumetric flow rate (L/min), t is the breakthrough time (min) to reach C_{out} which in turn is determined when 5% or more of the total H₂S concentration was detected, C_{in} the H₂S inlet concentration in N₂ (mg/L), C_{out} breakthrough concentration (mg/L), and finally W express the absorptivity in terms of percentage (%).

H₂S adsorption capacity (Ads^{cap}) of the iron hydroxide-based adsorbent was systematically measured as a function of (1) drying temperature conditions between 60 and 200 °C, process variables like (2) space velocity 68–7433 hour⁻¹, (3) retention time 0.5–52.9 s, (4) relative humidity varying from dry conditions (0%) to high wetness conditions (80%) and (5) H₂S concentrations over a range of concentrations from 500 to 10300 ppm.

3. Results and discussion

3.1. Material characterization

Fig. 2 shows the XRD pattern in the region of $2\theta = 5\text{--}100$ of the iron hydroxide-based adsorbent. It can be seen that the iron hydroxide-based adsorbent obtained in this work is amorphous. The figure shows that the XRD pattern of iron hydroxide-based adsorbent shows a broad peak between 30° and 40° and another faint peak centered at above 63°, which is typical of an extremely poorly-crystalline iron oxyhydroxide [25–27]. In detail, the diffraction pattern matches the ferrihydrite phase in which only two peaks are visible at 36 (110) and 63 (300) 2θ [14,27]. This result indicated that iron hydroxide-based adsorbent product is an amorphous phase.

The results for the nitrogen isothermal sorption at 73.3 K of iron hydroxide-based adsorbent is presented in Fig. 3. Looking at the desorption-adsorption, there is a gap between desorption and adsorption curve which means there is a hysteresis loop which in turn indicates that the iron hydroxide-based adsorbent is porous in nature. In addition, it can be seen from the inset of Fig. 3 that the as-prepared iron hydroxide-based adsorbent shows a very large specific surface area and its BET value reaches 269.8 m²/g. The mean pore volume and average pore diameter were estimated to be 0.28 cm³/g and 3.7 nm, respectively. These obtained data are agreed with the characteristic of mesoporous structure [14,20,22,23,27].

Fig. 4 shows a selections of microstructures of amorphous iron hydroxide-based adsorbent observed by SEM and a representative EDS analysis showing the chemical composition of its surface. Quantitative element analysis was conducted to estimate the chemical composition ratio of iron hydroxide-based adsorbent on the surface and in the bulk of some samples. Analysis results of the chemical composition by using EDS are presented in Table 1. Average chemical compositions (wt%, at %) of the amorphous iron hydroxide-based adsorbent was calculated based on EDS spectra. It can be confirmed that the adsorbent composition is composed approximately of about 20 at% Iron, and about 40 at % Oxygen and may be represented by the following approximate formula: Fe(OH)₃. In fact, as seen in Fig. 4 (g), the Fe and O peaks are clearly observed with Fe/O ratio of approximately 1/2 [20]. Another point to be noted here is that there is no big compositional distinction in this regard between bulk and surface regions. Besides Fe and O atoms, as seen in Table 1, the presence of Na atoms is also shown although it is very small (~4 at%). This seems to indicate that some Na ions was still present in the iron hydroxide-based adsorbent and it was not completely washed off with water during the purification of the material.

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