Separation and Purification Technology 123 (2014) 200–213

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Biogas desulfurization by adsorption on thermally treated sewage-sludge

F.J. Gutiérrez Ortiz *, P.G. Aguilera, P. Ollero

Departamento de Ingeniería Química y Ambiental, Universidad de Sevilla, Camino de los Descubrimientos, s/n, 41092 Sevilla, Spain

ARTICLE INFO

Article history:
Received 25 May 2013
Received in revised form 21 November 2013
Accepted 29 December 2013
Available online 3 January 2014

Keywords:
Biogas
Hydrogen sulfide
Desulfurization
Breakthrough
Adsorption
Sewage sludge

ABSTRACT

Biogas is a renewable source for power production, but the H_2S present must be removed because it is very corrosive and may damage the combustion engines. The adsorption using activated carbon is one of the most used desulfurization methods. The operational life of the activated carbon could be extended if the H_2S concentration was reduced prior entering the activated carbon bed by using other cheaper adsorbent. Sewage sludge is a possible inexpensive precursor to obtain adsorbents, and thus it would be valorized. An experimental study was performed using three types of sludge from three Spanish locations, which were activated to increase their adsorption capacity. Two thermal treatments were tested using nitrogen (pyrolysis) and air (calcination), as well as three heating temperatures. The adsorption dynamics of the prepared adsorbents were investigated in a fixed-bed column, determining the breakthrough curves and adsorption capacity of adsorbents. Besides, both their surface properties and their chemical properties were analyzed to get more insight about the adsorbent behavior. In addition, the effect of the oxygen content, relative humidity and the chemical impregnation, using different procedures, were also studied. As a relevant result, the adsorbent obtained by calcination at 700 °C of one of the three kinds of sludge showed a capacity twice of that of a commercial activated carbon without impregnation, although somewhat lower than that of a commercial activated carbon impregnated with a NaOH solution. The results showed that the use of this kind of precursors is very attractive to achieve adsorbents with a relative high adsorption capacity valuable to apply them in an economically feasible pretreatment.

1. Introduction

The organic matter that is present in a landfill collecting municipal solid waste is degraded in an anaerobic process, which generates a gas mixture called biogas or landfill gas. Biogas is obtainable in a relatively economical way from anaerobic digestion [1]. The main constituents of biogas are methane and carbon dioxide, but it also contains nitrogen and oxygen, due to air incursion into the gas collection system; oxygen concentration is continuously monitored and held low for safety reasons. Due to the high calorific value of methane and its high concentration, biogas is currently considered a renewable energy source.

When biogas is used as a fuel for electricity generation, several trace compounds may damage the combustion engines, requiring expensive repairs and causing service interruptions. Among all of the specific contaminants to biogas utilization, hydrogen sulfide (H_2S) is the most relevant one, because it is highly corrosive during the combustion process. Because hydrogen sulfide concentration is of up to 1000–2000 ppm, H_2S removal is necessary to avoid operational problems, such as corrosion in pipes, turbines or other units [2], as well as environmental problems such as global warming or acid rain [3].

Biogas desulfurization is normally performed by wet scrubbing, biological methods, adsorption, or selective catalytic oxidation [4]. The activated carbon adsorption process is normally penalized with high operational costs related to the price of the adsorbent. Among these methods, adsorption by dry treated sludge, such as that coming from the municipal wastewater treatment, may be beneficial as a pretreatment of the biogas, before entering another system, such as an adsorber using activated carbon. In this way, the activated carbon would deal with biogas with a lower H_2S concentration, and its useful operational life would be extended. Thereby, sewage sludge, which is an inevitable byproduct of wastewater treatment, could be valorized.

Generally, three sludge-stabilization methods are typically used: thermal, chemical and biological [5]. Surplus sludge produced during the biological treatment of wastewater requires costly disposal procedures. The most frequent methods of disposal are landfill, commercial composting and incineration. With increasing environmental and legislative constraints, increasing

* Corresponding author. Tel.: +34 95 448 72 68/60.
E-mail address: frajagutor@etsi.us.es (F.J. Gutiérrez Ortiz).

1383-5866/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.seppur.2013.12.025

Table 1
Immediate and elemental analyses of activated carbons and sewage sludge.

Parameter (dry basis) wt%	Activated carbon CAT	Activated carbon CAA	Sludge LL	Sludge LF	Sludge LG
Carbon	88.12	73.32	38.49	39.12	36.90
Hydrogen	0.76	0.81	5.42	5.48	5.07
Nitrogen	0.79	0.48	6.54	5.86	4.72
Oxygen	1.37	8.10	19.42	19.77	16.38
Sulfur	0.35	0.30	1.32	1.26	1.54
Ash	Balance	Balance	Balance	Balance	Balance
Ash (wet basis)	(8.25)	(14.67)	(27.11)	(26.79)	(32.96)
Volatiles (wet basis)	(2.48)	(11.84)	(57.42)	(58.56)	(54.62)
Fixed carbon (wet basis)	(85.09)	(59.81)	(9.57)	(8.63)	(5.53)
Moisture (wet basis)	(4.18)	(13.69)	(5.90)	(6.02)	(6.89)

sludge production and lessening disposal options, new recycling alternatives have to be found [6].

The adsorption dynamics of the prepared adsorbents was investigated in a fixed-bed column, using a simulated biogas and determining the adsorption capacity of the adsorbents. Three carbon-based adsorbents from dry sewage sludge (low-cost precursors) were tested after suffering a thermal treatment to increase the adsorption capacity. The research work was focused on studying the effects of the thermal treatment, heating temperature, and physicochemical properties of the precursors on the removal of H_2S, in the absence of oxygen and humidity. Additionally, the influences of the relative humidity and the oxygen present in the biogas entering the adsorber were tested, as well as the effect of chemical impregnation.

One of the main novelty aspects of the present study is the use of air as agent to thermally treat the precursors, instead of a pyrolysis (performed under N_2 atmosphere), which has been the usual thermal procedure in the previous studies encountered in the literature. This has a great importance, if the process is to be implanted in a commercial scale, where using air instead of nitrogen would reduce the operating costs. Another significant point of this paper is the use of a simulated biogas, and not a mixture of H_2S and air normally used in most studies found in the literature, because CO_2 may compete against H_2S in adsorption depending on the porous structure of the adsorbent and the alkali constituents, since both of them are acid gases.

2. Experimental section

2.1. Materials

Two commercial activated carbons, labeled as CAT and CAA, were used as references to compare the results using the precursor-sludge. CAT is a fresh activated carbon, without impregnation, while CAA is activated carbon impregnated with a NaOH solution. Both of them were milled and sieved between 1.41 and 2.83 mm, as the rest of the materials tested. Likewise, three types of air-dried sewage-sludge were crushed to pass between 1.41 and 2.83 mm sieve. They are referred to as LG, LL, and LF, respectively, based on their Spanish provenance. Table 1 shows the elemental and immediate analyses of the two activated carbons and the three types of sewage-sludge, as received, i.e., before undergoing any treatment.

Experiments were carried out by a certified mixture of CH_4 (60 vol.%), H_2S (2000 ppmv) and CO_2 (balance).

2.2. Methods

Precursors were treated in order to improve their adsorption capacity by thermal and chemical procedures. Then, they were tested by an experimental unit to obtain their H_2S breakthrough capacity and characterized by different analytical techniques.

2.2.1. Thermal treatment of sludge

Physical activation involves calcination or pyrolysis of a precursor. The thermal treatment was performed in a tubular furnace, illustrated in Fig. 1. The pyrolysis (heat treatment carried out in an inert atmosphere) was performed with 100 g of precursor using a nitrogen flow-rate of 1 L/min from room temperature up to 500 °C. Beyond this temperature, no more nitrogen was used and an air flow-rate of 0.125 L/min passed through the tubular furnace until reaching the final temperature (500 °C, 700 °C or 900 °C). During this latter step, calcination takes place and the metals present in the sample are oxidized. The code of this method was 'PA'. As a second method, the calcination was performed entering air from room temperature up to the final temperature. It was coded using the letter 'A'.

The heating rate was always 5 °C/min and the holding time was always 30 min, which was selected by a prior screening test. After that time, samples were withdrawn from the furnace.

The samples were coded as follows: first, the acronym of the precursor (LL, LF and LG), then the maximum temperature reached, and finally the treatment (PA or A).

2.2.2. Experimental adsorption unit

A lab-scale facility was designed and assembled to carry out the adsorption tests. It consists of three main parts: gas feeding, adsorption system and H_2S analyzer. Fig. 2 depicts a scheme of the experimental unit.

Experiments were carried out at controlled room temperature (20 ± 2 °C), using a simulated biogas flow-rate of 1.1 L/min. The fixed bed tower was a glass tube (30-mm ID and 430 mm height), with a perforated plate acting as gas distributor and adsorbent support. The adsorbent bed was 100 mm height. H_2S was measured by a continuous gas analyzer, based on ultraviolet radiation, with three possible ranges (0–200 ppm, 0–1200 ppm and 0–2500 ppm). A humidification system based on three bubblers serially assembled was used for tests with humidification.

To investigate the effect of humidity on H_2S removal efficiency, specific H_2S removal tests were performed by two ways (at room temperature): (1) by pre-humidifying the adsorbent using a saturated air flow-rate of 1.1 L/min for one hour (in this case, the 'PH' symbol is added at the end of the label), or (2) directly, by using a saturated biogas (100% relative humidity at 20 °C), adding 'H' at the end of the code.

Additionally, the effect of the oxygen on the H_2S removal was studied by adding oxygen (5 vol.%) to the dry biogas stream before entering the fixed bed.

Adsorption/removal capacities, x/M (mg H_2S/g material), were calculated by integrating the corresponding breakthrough curves and by applying Eq. (1) [7]: