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Research article

High performance regenerative adsorption of hydrogen sulfide from biogas on thermally-treated sewage-sludge

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A B S T R A C T

Biogas desulfurization can be performed by adsorption, although new materials are needed since commercial adsorbents are expensive. In this regard, three types of sewage-sludge were studied as precursors to obtain low-cost adsorbents in a previous paper, attaining the best precursor from a sewage-sludge that was thermally treated up to 700 °C. However, it must be regenerated to make the process feasible. To find an economical and environmentally friendly regeneration process, an experimental design was performed aimed at minimizing the use of resources such as water consumption, time and the temperature required while achieving a high rate of regeneration. The selected in-situ regeneration consists of entering firstly steam at relatively low temperature (<250 °C), against most of published studies, followed by a second step with air. Besides, it can be performed in only 20 min, giving a large feasibility to the overall continuous adsorption process, with very low energy cost and duration for the regeneration. As a relevant result, the thermally treated sewage-sludge was regenerated up to 14 times, and although the adsorption capacity decreased 2.7% on average in each adsorption/regeneration cycle, the cost relative to the adsorbent may be reduced to 20% of the cost of using fresh adsorbent.

1. Introduction

Biogas produced by anaerobic digestion of organic matter from municipal solid waste deposited in a landfill should not be emitted directly to the atmosphere because of its high methane content, which is a greenhouse gas. Instead, biogas can be utilized in internal combustion engines as a renewable source of energy to generate electricity. Nevertheless, biogas also contains H_2S, which has to be removed before using it in engines to prevent the equipment corrosion and the formation of sulfur oxides when combusted [1,2].

Adsorption by activated carbon is one of the most suitable methods for the removal of H_2S from biogas. However, its high operational costs have promoted the search of low-cost alternative adsorbents using natural materials (wood, peat, coal, lignite, etc.) as well as industrial/agricultural/domestic wastes or by-products, such as slag, sludge, fly ash, bagasse fly ash or red mud [3–8]. In this regard, adsorbents from sewage-sludge produced by several thermal treatments have been previously tested, characterized and modeled [9,10]. As a previous result, the adsorbent coded as LG700PA and obtained by pyrolyzing at 500 °C and then by calcinating at 700 °C showed an adsorption capacity twice that of a commercial unimpregnated activated carbon [9]. Furthermore, the scaling-up of the adsorption process concluded that a regeneration of the adsorbent is required to make it feasible [10].

Regeneration methods of activated carbon with solvents, as well as by biological or thermal treatments, are the most commonly used [11,12]. There are other less common regeneration methods such as wet oxidation, electrochemical, supercritical fluid regeneration, microwave irradiation regeneration and regeneration by ultrasounds [13–15]. Chemical regeneration with sodium hydroxide, acids, or an appropriate solvent can be used to remove the solute from the porous structure of the activated carbons. The regeneration is carried out by passing a stream of the solvent through a bed that contains the adsorbent. Usually, these solvents are expensive and harmful, so they need to be recovered for its reuse or management. Biological regeneration uses aerobic or anaerobic micro-organisms to remove biodegradable adsorbates. However, the main problem of this technology is that the temperature, pH and concentration of the solution need to be kept under tight control in order to preserve the colony of micro-organisms at an adequate level. On the other hand, thermal regeneration consists of heating the adsorbent at temperatures between 600 and 1000 °C in different types of furnace such as a rotary kiln, a multiple hearth and a fluidized bed; a purge gas removes the adsorbate as it is being desorbed. As drawbacks, thermal regeneration requires high energy consumption, has to be carried out off-site and causes a loss of material by attrition of about 5% [11,12].

The on-site steam regeneration process is an intermediate treatment between the heat regeneration and solvent extraction. Steam

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Table 1
Parameters used in the study.

Parameter	Value		Unit
Simulated biogas composition	CH_4	60	vol.%
	H_2S	2000	ppmv
	CO_2	(balance)	vol.%
Feed biogas flow-rate	1.1		L/min
Temperature	20 ± 2		°C
Bed length	220		mm
Bed diameter	22		mm
Particle size	1.41–2.83		mm
Bulk density	481.0		kg/m^3
Bed void fraction	0.808		–
Gas density	1.101		kg/m^3

regeneration at high temperature (650–1000 °C) had been proven to be very effective to regenerate different types of adsorbents [14, 16–17]. Adsorbents used for removing volatile organic compounds can be regenerated at low temperature (<200 °C) with high regeneration efficiencies (about 80%) [18], but drying is a necessary and costly step after the steam regeneration. The previous studies found in the literature dealing with regeneration of adsorbents used to remove hydrogen sulfide present in air, not in biogas, utilize cold/hot water washing or thermal treatment where low-to-moderate regeneration efficiencies were reached (about 40%) [19,20]. GBH enterprises has performed a process where they use steam and air at low temperature (<300 °C) to regenerate an activated carbon used at desulfurization of natural gas but the treatment takes at least 9 h [21].

This study is aimed at reaching a high performance regeneration of sewage-sludge adsorbents previously obtained and used to remove hydrogen sulfide from biogas, optimizing the energy consumption that is one of the main drawbacks of regenerative adsorption. To achieve this objective, a systematic methodology was followed by using different stages involving steam and air at different temperatures and durations, by limiting them to reduce the cost of regeneration and make feasible a continuous biogas desulfurization by regenerative adsorption. To our knowledge, no other similar study has been addressed; this fact along with the final high performance regenerative process achieved for biogas desulfurization, which consumes a relatively low energy, confers a remarkable novelty to this research.

2. Experimental section

2.1. Materials

The LG700PA adsorbent was used to investigate the steam regeneration of thermally treated sewage-sludge adsorbents previously used to remove H_2S from biogas [9]. Briefly, this adsorbent was produced in a tubular furnace by heating 100 g of LG sludge at a rate of 5 °C/min up to 700 °C and holding this temperature for 30 min. The characterization of this sludge can be found elsewhere [9]. The thermal treatment was carried out under inert atmosphere up to 500 °C, using a nitrogen flow-rate of 1 L/min and, beyond this temperature, under oxidant atmosphere at an air flow-rate of 0.125 L/min up to 700 °C. In addition, two commercial activated carbons, labeled as CAT and CAA, were tested to compare the results of the selected adsorbent regeneration. CAT is a fresh activated carbon without impregnation, while CAA is activated carbon impregnated with a NaOH solution. Before the tests, the adsorbents were milled and sieved to obtain a particle size range from 1.41 to 2.83 mm. Experiments were carried out by using a certified mixture of CH_4 (60 vol.%), H_2S (2000 ppmv) and CO_2 (balance) as simulated biogas. The simulated biogas would match a biogas to be dried before entering the adsorber, although some desulfurization experiments were carried out with a humid gas in a previous paper [9], obtaining a small impact on the adsorption process studied. The detailed procedure of adsorbent production is fully described elsewhere [9].

2.2. Methods

2.2.1. Experimental adsorption/regeneration unit

The hydrogen sulfide adsorption test was performed before and after each regeneration process to register the breakthrough curves and evaluate the regeneration efficiency of adsorbents. To perform this test, a determined amount of adsorbent (34 g) was packed in a horizontal reactor (22 mm ID, 220 mm fixed length) made of stainless steel

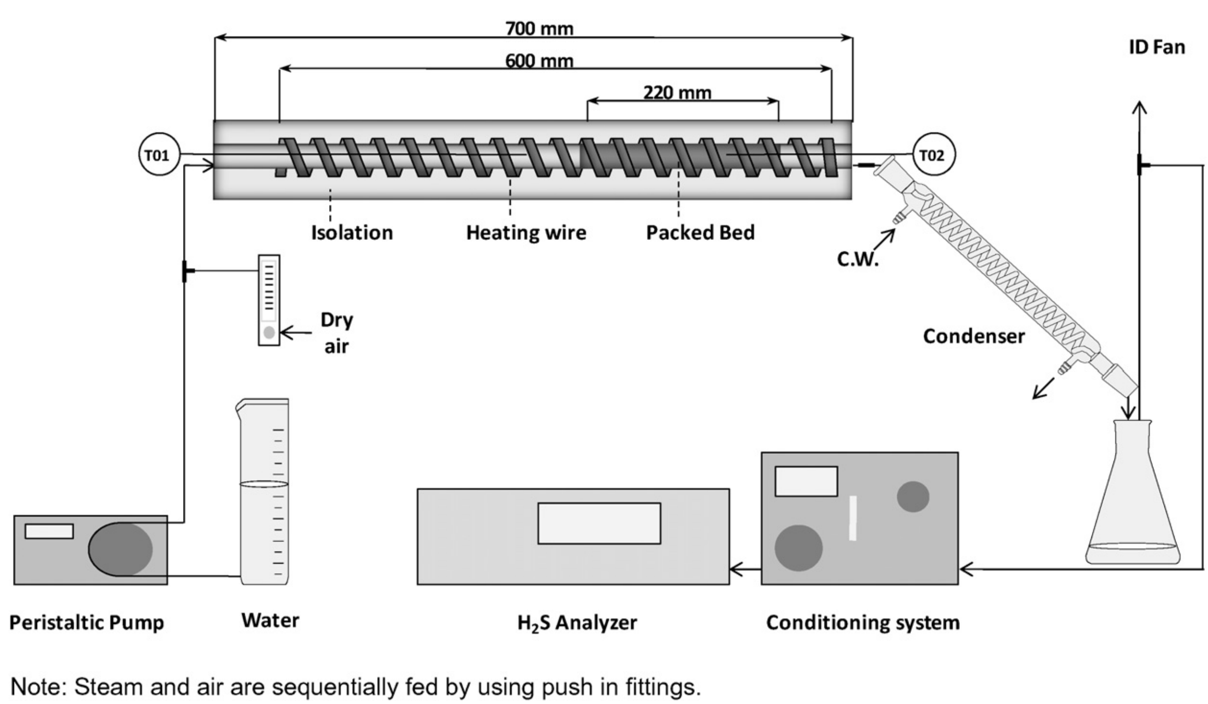

Fig. 1. Scheme of the experimental unit for regeneration.