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EVALUATION OF BIOFILTRATION MATERIALS FOR H₂S REMOVAL

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Abstract. H_2S concentrations in Biogas are limited by environmental regulations. Hence, there are multiple purification methods as biological filtration are developed to meet the standards. In a typical biofiltration process, a bed of organic or inorganic porous materials is forced through a humid gaseous stream that contains the H_2S pollutant, because it helps microbial growth and serves as the deck for the bioprocess, and is the most important part of a biofilter and the whole process of Biogas purification from H_2S . An ideal packing medium ought to possess a number of characteristics, including a high mechanical resistance, the capacity to provide essential nutrients to a diverse microbial population, a large buffer capacity, a suitable moisture-holding capacity, a high specific area, and high porosity. The physicochemical properties and H_2S removal efficiency of the biochar, compost, expanded schist, and waste of cellular concrete will be discussed and compared in this study.

Keywords: H₂S, biogas, biofiltration, packing medium, physicochemical.

Introduction

Anaerobic digestion is a supportable stage and monetarily accessible innovation that can create crude biogas from squandered natural materials through complex biochemical cycles (Zhang et al., 2022; Das et al., 2022a, 2022b). Many elements influence the interaction effect for producing high-quality Biogas and among them, working circumstances (for example pH, temperature, or maintenance time), and the design of the anaerobic digester (Bahraminia et al., 2020; Das et al., 2022a, 2022b; Morgado et al., 2018; Khan et al., 2021). This innovation shows incredible potential for the administration of natural squanders produced from agriculture, industry, and metropolitan activities (Zhang et al., 2022). It is gotten from domesticated animals' fertilizer, agriculture build-ups, biodegradable pieces of metropolitan waste, wastewater slime, modern parks, normal decay processes, wastewater treatment cycles, and food deposits are modest and plentiful wellsprings of natural matter for biogas creation by means of anaerobic digestion (Khalil et al., 2019; Nhut et al., 2020; Hou et al., 2018). As a green elective fuel to petroleum gas, exhaustive biogas purging is expected preceding its application. Biogas can be utilized to create heat and steam, electric power, vehicle fuel, gas-powered motors (which requires H₂S expulsion) or turbines (which requires a severe siloxane evacuation), or could be utilized for petroleum gas lattice

infusion (Das et al., 2022a, 2022b; Torres et al., 2020; Zhang et al., 2021).

Crude biogas, a final result of Anaerobic Digestion, primarily comprises around 20–45% carbon dioxide, 40– 70% methane, and more modest measures of different gases including water vapor (H_2O), and Oxygen (O_2), nitrogen (N_2) and ammonia (NH_3 for the most part) (Figure 1). CH_4 is the main wanted constituent in crude biogas for its calorific worth (Das et al., 2022a, 2022b). In the best scenario that biogas is expected to be utilized as a transportation fuel or infused into flammable gas networks, it is important to eliminate destructive gasses like H_2S (Torres et al., 2020).

Excessive exposure to H_2S can result in a variety of symptoms, including nausea, eye irritation, mild conjunctivitis, and irritation of the respiratory (Prasertcharoensuk et al., 2022; Das et al., 2022a, 2022b). Depending on the environmental conditions, H_2S is responsible for the deterioration of materials caused by biogenic corrosion, the poisoning of catalysts during steam reforming, and the foul odor caused by sulfur-oxidizing microorganisms (Ghimire et al., 2021; Haosagul et al., 2020; Juntranapaporn et al., 2019). In addition, during combustion, H_2S is oxidized into acidic sulfur dioxide (SO₂), which can be extremely corrosive to metal surfaces (Ghimire et al., 2021; Nhut et al., 2020).

The aim of the study is to determine biofiltration material's physicochemical properties, and sorption

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COMPOSITION OF RAW BIOGAS

Figure 1. Composition of raw Biogas in percentage (approximate data) (Das et al., 2022a, 2022b)

capacity and to evaluate modified biofiltration materials for H_2S removal (by selected and modified models); to experimentally evaluate the most important characteristics of the selected biofiltration materials (such as surface area, porosity, humidity, pH, etc.); to evaluate of H_2S sorption capacity of the selected biofiltration materials under static and dynamic conditions.

1. Biological desulfurization of H₂S

The biological methods are based on the implementation of oxidizing bacteria that live in places where there are sufficient sources of sulfur compounds like H_2S (Pudi et al., 2022; Vikrant et al., 2018). Sulfur-oxidizing bacteria (SOB) are essential to the biological process's success (Pudi et al., 2022) (Figure 2).



Figure 2. Schematic of the biofiltration process (Khanongnuch et al., 2019)

Depending on the species, genus, and functional genes of the SOB, as well as the amount of oxygen present in the system, SOBs can convert sulfur compounds like hydrogen sulfide, sulfur, and thiosulfate to elemental sulfur or sulfate.

There are mainly three types of Biofilteration technologies defined and manufactured by other scientists, which are named Biofilter, Biotrickling filter, and Bioscrubber and differ from each other in terms of structure and can be implemented in scientific investigations based on the project budget and the outcome usage and importance.

2. Packing materials

Packing material helps microbial growth and serves as the deck for the bioprocess, it is the most important part of a biofilter (Pudi et al., 2022; Das et al., 2022a, 2022b). In a typical biofiltration process, a bed of organic or inorganic porous materials is forced through a humid gaseous stream that contains the desired pollutant (Vikrant et al., 2018). Pollutant molecules are absorbed from the gas phase and biodegrade in the thin biofilm, which is made up of microorganisms and water (Vikrant et al., 2018). Because they primarily regulate complex phenomena like microbial growth and activities, mass transfer, absorption, and adsorption, the biofilm and packing media are the backbone of biofiltration (Vikrant et al., 2018). In addition, introducing microbes into the media can significantly shorten the time it takes for biofilm to form at the beginning of biofiltration.

For instance, inorganic media like pall rings and lava rocks might require an inoculation period of seven to fourteen days (Vikrant et al., 2018). An ideal packing medium ought to possess a number of characteristics, including a brilliant buffer capacity, good mechanical durability, a vast useful area full of porosity, provide essential factors for various microbial species with necessary nutrients, and an outstanding moist surface and moisture-holding capacity. The two main categories of packing material are inorganic and organic (Pudi et al., 2022; Das et al., 2022a, 2022b; Nhut et al., 2020; Das et al., 2019; Vikrant et al., 2018).

Most well-known environment-friendly organic packing materials are biochar and compost, while, inorganic materials are cellular concrete waste and expanded schist (Pudi et al., 2022; Das et al., 2022a, 2022b; Nhut et al., 2020; Das et al., 2019; Vikrant et al., 2018). For gas desulfurization, inert packing materials like porous ceramics or plastic supports are typically utilized in biotrickling filters, whereas natural filter bed materials are typically utilized in Biofilters (Das et al., 2022a, 2022b). This is due to the fact that organic materials have low mechanical strength and a high capacity for holding moisture (Nhut et al., 2020). As a result, the bed becomes submerged and compacted because of the existing trickling liquid (Pudi et al., 2022). To improve mechanical properties, implementing them with a combination of organic materials like woodchips are under investigation.

Main differences between organic and inorganic packing materials:

- Expanded schist inorganic or synthetic materials must obtain nutrients from outside sources to ensure SOB's growth, organic materials may not require additional nutrients during the start-up phase (Nhut et al., 2020). Also, they are really efficient at storing water inside the biofilter and maintaining the required humid conditions for sulfur-oxidizing bacteria (Nhut et al., 2020).

- Natural organic packing materials have the advan-

tages of low cost, easy availability, good surface properties, and high porosity (Das et al., 2022a, 2022b; Bu et al., 2022).

- Inorganic packing media beats organic packing media in terms of compaction, which results in channelling and a significant pressure drop, as well as a shorter lifespan (typically less than five years) and a simple structure (Zhang et al., 2021; Pudi et al., 2022; Das et al., 2022a, 2022b; Vikrant et al., 2018; Bu et al., 2022) and reduce filter performance.
- Organic beds do not meet some of the requirements for effective biofilter performance in long-term operation systems, such as high nutrient composition, high microbial density, air permeability, buffering capacity, and high porosity (Wu et al., 2020).
- Mechanistic advantages are one of the notable properties of inorganic packing materials such as lava rock and expanded schist (Vikrant et al., 2018).

2.1. Biochar

The application of biochar in the AD digester is regarded as a lucrative strategy for the management of agricultural waste and the recovery of sulfur for the remediation of soil fertility (Cano et al., 2019; Choudhury & Lansing, 2021). Biochar is produced through the thermal degradation of biomass/organic waste under an oxygen-starved environment (pyrolysis) or in a low-oxygen environment (gasification) at temperatures less than 700 °C. Biochar is made from rice hull, camphor, and bamboo (Zhang et al., 2022) because of its large surface area, high pore size distribution, and good ion exchange capacity, it is utilized as a sorbent to remove a wide range of contaminants (Cano et al., 2019). Biochar can be thought of as a kind of precursor for activated carbon, which needs to be activated again with steam or chemicals (Cano et al., 2019; Choudhury & Lansing, 2021). The sorption and oxidation of H₂S on biochar were probably caused by the presence of oxygen functional groups like carboxylic and hydroxide 28 radical groups (Zhang et al., 2022). Studies on biochar substrates prepared from sewage sludge, anaerobically digested fibers, and agricultural waste highlighted the importance of the alkaline surface in H₂S removal because the alkaline nature was suspected to aid in the H₂S dissociation for further oxidation reactions (Choudhury & Lansing, 2021). Biochar could be a cheaper scrubbing solution because it can be made from a variety of raw waste materials (Choudhury & Lansing, 2021). Due to its abundance of alkali metals (Na and K) and alkaline earth metals (Ca and Mg), biochar has a high pH buffering capacity (Zhang et al., 2022; Choudhury & Lansing, 2021). It was also reported that biochar's leaching of Na⁺, K⁺, and Mg²⁺ might help methanogens grow and digest food more efficiently (Zhang et al., 2022) The residence time of biochar, which can range from 10 minutes to a few hours, one of its beneficial properties (Cano et al., 2019). The findings demonstrated that, in comparison

to activated carbon, biochar modified with magnetite completely eliminated H₂S, outperforming pristine biochar by more than 90% (Zhu et al., 2020). A different study demonstrated that adding 3 grams of poplar wood biochar to 500 grams of manure resulted in the removal of up to 78% H₂S without affecting the yield of methane (Zhu et al., 2020). The addition of biochar to a mesophilic AD reactor resulted in the removal of over 95% H₂S from the chicken manure treatment reactor (Zhang et al., 2022). Choudhury and Lansing (2021), compared the H₂S adsorption performance of biochar to AC and found that biochar's adsorption capacity was 3.7 times greater than AC's (Activated Carbon) (19 g m⁻³ h⁻¹ AC).



Figure 3. Scanning electron microscopy picture of the Biochar before the adsorption of H_2S (Lin et al., 2021)

As can be clearly seen in the Figure 3, the holes that existed before the adsorption of H_2S inside the Biochar have been filled and consequently can impact the purification efficiency of the biofilter (as stated before, clogging is one of the major obstacles to organic packing materials).

2.2. Compost

Expanded schist provides advantages such as the presence of nutrients within the media, easy availability, high nutrient retention capability, and appropriate release of nutrients during cell growth a vibrant microbial population with extremely active bio-layers compost has been utilized conventionally in biofilters as a natural packing material (Das et al., 2019). In composting, bark, wood residue, yard waste, and agricultural waste serve as the primary substrates (Cano et al., 2019; Das et al., 2019). On the other hand, when subjected to higher pressure drops than inorganic carriers, these communities rapidly degrade at low pH (Vikrant et al., 2018). utilized a compost biofilter to investigate long-term H₂S removal and achieved removal efficiencies exceeding 85 percent. Mature compost can provide conditions favourable to the proliferation of microorganisms due to its large surface area and permeable pore space. Mature compost can absorb gases when used as a filter, and the diverse bacteria in the compost can also help reduce gas emissions.

As it is demonstrated in Figure 4, fluctuation in compost packing media's temperature according to the H₂S



Figure 4. Fluctuation of ambient and compost temperatures based on H₂S concentration (Yuan et al., 2018)

concentration existing in the biofilter demonstrates its accurate reflection and identification of such a hazardous gas while the ambient temperature didn't significantly change.

In an experiment conducted by (Figure 5) (Das et al., 2019), a fair comparison between the H₂S removal efficiency of the Compost and Biochar + Compost. In the end, different experimental conditions of the experiments with compost alone defined as Phases I-III and Phases IV-V with EBRTs in a row 119s, and 80s are related to the experiments with Compost alone. While Phases VII, VIII and X with EBRTs in a row 119s, the 80s, and 80s, were in relation to the experiments conducted with a combination of Compost + Biochar. As it is obvious, those with the addition of Biochar illustrated a better performance in every condition in comparison to those with compost alone, in terms of H₂S removal from Biogas. Hence, the importance of using Biochar as an organic packing material is proven.



Figure 5. Impact of the inlet loading rate on the biofilter's ability to remove waste and kinetic expression (Das et al., 2019)

2.3. Waste of cellular concrete

Waste of cellular concrete may have an H_2S elimination capacity of up to 32 (g m⁻³ h⁻¹) (Wu et al., 2020) (Figure 6). Complex Physico-chemical interactions between H_2S and the various components of cellular



Figure 6. Cellular concrete waste after the desulfurization project (Wu et al., 2020)

concrete (primarily calcium oxide CaO from the calcium silicate hydrate CaO $SiO_2 nH_2O$ and ferric oxide Fe₂O₃) are to blame for these results (Zhang et al., 2021). These interactions change the material's mechanical structure to calcium sulfate (gypsum CaSO₄ 2H₂O) and result in the production of elemental sulfur (Zhang et al., 2021).

A Biofilter with cellular concrete waste as a packing material was tested for its ability to treat H_2S in the air (Xia et al., 2019). It was demonstrated that H_2S removal can only be achieved under wet conditions (Xia et al., 2019). At an H_2S concentration of 50 ppm and an EBRT of 56 s, removal efficiency ranged from 40 to 45 percent (Xia et al., 2019). The formation of gypsum was primarily attributable to reactions between H_2S and calcium carbonate (Xia et al., 2019).

2.4. Expanded schist

Expanded schist, according to a recent study, is a good material for treating high H₂S loading rates (up to $30 \text{ g m}^{-3} \text{ h}^{-1}$) at low empty bed residence times (EBRTs) and for its mechanical stability, removal efficiency, and efficacy (Wu et al., 2020). Expanded schist, in addition to having a large surface area and high structural porosity, was shown to be a material that provides the ideal environment for microorganisms by itself over a brief period of time (Wu et al., 2020). Biofilms that are thicker and porous are thought to increase microbial activity, which in turn increases pollutant conversion and results in an efficient H₂S treatment (Wu et al., 2020). At low EBRT (EC ranged from 10 to 22 g m⁻³ h⁻¹ for EBRTs from 16 to 35 s), the biological treatment of H₂S with expanded schist as a packing material produced promising results in terms of elimination capacities and removal efficiencies (RE > 90%) (Zeng et al., 2019).

In the Figure 7, expanded schist represents the elimination capacity of the biofilter which illustrated different values according to the implemented specific packing materials. C_{In} represents the concentration of H_2S in the inlet-pumped biogas in the system. It can be concluded, that based on the current experiment condition and variables, Biofilter packed with the concrete waste showed better performance than the results obtained from a mixture of cellular concrete waste and mathematical modelling, in terms of H_2S purification from biogas.



Figure 7. Capacity to eliminate versus concentration of H_2S . Points for experiments (blue line: waste from cellular concrete; green line: a mixture of expanded schist and cellular concrete waste; red circle: expanded schist) and the results obtained from mathematical modelling (Lebrun et al., 2019)

Conclusions

The removal of corrosive contaminants, such as H_2S , is necessary for the production of syngas, direct combustion, and electricity. Among all, biological technologies are appealing because they are economical, friendly to the environment, and provide the opportunity to recover products with added value.

One of them main components of a biofilter is the physicochemical properties of the implemented packing material. Relying on research analysis accomplished by other authors, in terms of inorganic packing materials cellular concrete waste demonstrated outstanding performance to H_2S removal from Biogas in comparison to expanded schist.

In terms of organic packing material, a combination of Compost and Biochar illustrated an outstanding performance on Biogas purification from H_2S , hence they could be a further case study to analyse their function even when separately or together combined with the cellular concrete waste.

However, by analysing the advantage of combing best-performed packing materials (whether organic or inorganic) and suitable sulfur-oxidizing microorganisms, the obstacles that biological H_2S removal from the Biogas method is facing right now, can be reduced while environmentally friendly factors affecting the whole.

Analysing the advantages of using the best quality packaging materials (organic or inorganic) and appropriate sulfur-oxidizing microorganisms can reduce the problems currently encountered in H_2S neutralization in biogas.

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