



**Adsorption of Hydrogen Sulphide using Zeolite ZSM –
5 for the Enhancement of Fermentative Biohydrogen
Production**

by

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LIST OF ABBREVIATIONS

ADMBR	Anaerobic Dynamic Membrane Bioreactor
Ag ₂ SO ₄	Silver Sulphate
APHA	American Public Health Association
ASBR	Anaerobic Sequencing Batch Reactor
ATR	Attenuated Total Reflectance
BET	Brunauer-Emmer-Teller
BJH	Barret-Joyner-Halenda
CH ₄	Methane Gas
CO ₂	Carbon Dioxide
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
FE-SEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
GC-TCD	Gas Chromatography with Thermal Detector
H ₂	Hydrogen
H ₂ S	Hydrogen Sulphide
H ₂ SO ₄	Sulphuric Acid
HgSO ₄	Mercury Sulphate
HPLC	High-Performance Liquid Chromatography
HPR	Hydrogen Production Rate
HRT	Hydraulic Retention Time
HY	Hydrogen Yield
IPD	Intra-Particle Diffusion
IUPAC	International Union of Pure and Applied Chemistry
IWK	Indah Water Konsortium
K ₂ Cr ₂ O ₇	Potassium Dichromate
MFW	Mixed Fruit Waste
N ₂	Nitrogen
P1O	Pseudo-First Order
P2O	Pseudo-Second Order

pH	Potential Of Hydrogen
SEM	Scanning Electron Microscope
SMP	Soluble Metabolite Product
SO ₂	Sulphur Dioxide
TACB	Thermophilic Anaerobic Closed Bioreactor
TC	Total Carbohydrate
TSS	Total Suspended Solid
UASB	Up-Flow Anaerobic Sludge Blanket Reactor
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solid
WWTP	Wastewater Treatment Plant
ZSM-5	Zeolite Socony Mobile-5

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LIST OF SYMBOLS

A	Pre-exponential factor
C	Thickness of boundary layer (mg/g)
C ₁	Weight of dried residue, filter, and crucible (mg)
C _e	Equilibrium adsorbate concentration
C _f	Concentration of H ₂ S at breakthrough point (ppm)
C _{H,i}	Fraction of H ₂ in the headspace reactor at current (i) time interval (ml)
C _{H,i-1}	Fraction of H ₂ in the headspace reactor at previous (i-1) time interval (ml)
C _i	Inlet concentration of H ₂ S (ppm)
D ₁	Weight of filter and crucible (mg)
D ₂	Weight of dried residue, filter, and crucible after ignition (mg)
e	Euler's number (2.71828)
E _a	Activation energy
H _m	Maximum hydrogen production
H _t	Cumulative hydrogen production (ml)
k ₁	Rate constant pseudo first order (min ⁻¹)
k ₂	Rate constant pseudo second order (g/mg.min)
k _A	Rate constant avrami (min ⁻¹)
K _D	Distribution coefficient (ml/g)
k _{id}	Intra-particle diffusion rate constant (g.min ⁻¹ /mg)
m	Mass of adsorbent (g)
M _w	Molar mass of H ₂ S (g/mol)
n	Avrami exponent
q _e	Adsorption capacity at equilibrium (mg/g)
q _t	Adsorption capacity at time (mg/g)
R	Universal rate constant (8.314 J/mol.K)
R _m	Maximum hydrogen production rate (ml/h)
t	Time (min)
T	Temperature (K)
V _c	Volume of the adsorption column (m ³)
V _{G,i}	Total biogas volumes at current (i) time intervals (ml)

$V_{G,i-1}$	Total biogas volumes at previous (i-1) time intervals (ml)
$V_{H,i}$	Cumulative hydrogen gas volumes at current (i) time interval (ml)
$V_{H,i-1}$	Cumulative hydrogen gas volumes at previous (i-1) time interval (ml)
V_m	Molar volume of gas (L/mol)
ΔG	Gibbs free energy
ΔH	Enthalpy
ΔS	Entropy
λ	Lag phase time (h)

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Penjerapan Hidrogen Sulfida menggunakan ZSM – 5 untuk Peningkatan Pengeluaran Penapaian Biohidrogen

ABSTRAK

Penghasilan biohidrogen daripada sisa buah campuran (MFW) adalah sumber tenaga yang boleh diperbaharui. Walau bagaimanapun, kehadiran hidrogen sulfida (H_2S) yang sangat toksik dan menghakis, mungkin mengurangkan prestasi dan mengehadkan penggunaan peralatan penukaran tenaga. Penjerap termasuk zeolit, bio-arang, dan karbon teraktif sangat terkenal untuk merawat gas yang memudaratkan seperti H_2S . Oleh hal yang demikian, penyelidikan ini memeriksa kebolehlaksanaan penggunaan zeolit ZSM-5 untuk menjerap H_2S sebagai agen pengaktifan untuk meningkatkan kualiti biohidrogen dibawah keadaan termofilik. Larutan campuran yang kaya dengan karbohidrat daripada MFW telah digunakan pada kepekatan awal 5 g/L semasa proses penapaian yang dijalankan dalam bio-reaktor tertutup anaerobik termofilik (TACB) pada pH awal 6 dan suhu 60 °C. Bakteria pengeluar hidrogen melalui laluan panapaian asid butarik adalah mikrob yang paling lazim dalam pengeluaran biohidrogen. Isipadu penghasilan biohidrogen dan kecekapan degradasi substrat masing-masing adalah 22511.60 mL dan 85% per jumlah karbohidrat telah diperolehi dalam eksperimen yang telah dijalankan. Biogas yang terhasil menjalani proses penjerapan pada zeolit ZSM-5. Kesan dos penjerap dan tindak balas suhu pada hasil hidrogen dan penyingkiran H_2S telah disiasat. Hasil hidrogen selepas proses penjerapan meningkat daripada 89% kepada 92.78%. Optimum dos penjerap dan suhu tindak balas untuk penjerapan H_2S adalah masing-masing 0.8 g (0.00889 mg/g) dan 25 °C (0.00890 mg/g). Zeolit telah melalui kitaran penjerapan dan penjanaan semula secara berterusan, yang mana kapasiti penjerapan 0.00890 mg/g untuk 3 kitaran menunjukkan kestabilan dan kebolehgunaan semula penjerap. Akan tetapi, kapasiti penjerapan mula berkurangan pada kitaran ke-4. Penyingkiran H_2S pada zeolit ZSM-5 dipadankan dengan baik dengan model kinetik Avrami yang menunjukkan H_2S dijerap melalui beberapa laluan penjerapan dengan penjerapan berbilang lapis di atas permukaan heterogen. Sebahagian besar penjerapan berlaku secara fizikal, eksotermik, semakin rawak, dan tak spontan. Resapan intrazarah telah dikenal pasti mengawal kadar penjerapan. Kapasiti penjerapan H_2S yang lebih tinggi dan penjanaan semula ditunjukkan oleh zeolit dalam kajian ini mengesahkan kesesuaiannya sebagai penjerap alternatif dalam meningkatkan kualiti biohidrogen dibawah kondisi termofilik.

Adsorption of Hydrogen Sulphide using ZSM – 5 for the Enhancement of Fermentative Biohydrogen Production

ABSTRACT

Biohydrogen production from mixed fruit waste (MFW) is a renewable energy source. However, the presence of highly toxic and corrosive hydrogen sulphide (H_2S) might reduce performance and limit energy conversion equipment use. Adsorbents including zeolites, biochar, and activated carbons have become popular for treating harmful gases like H_2S . Thus, the research examined the feasibility of employing ZSM-5 zeolite for H_2S adsorption as an activating agent to improve biohydrogen quality from thermophilic condition. A suspension rich in carbohydrate from MFW was used at initial concentration 5 g/L during the fermentation process was conducted in a thermophilic anaerobic closed bioreactor (TACB) at an initial pH 6 and temperature 60 °C. Hydrogen-producing bacteria via the butyric acid fermentation route were the most prevalent microbes in biohydrogen generation. Volumetric biohydrogen yield and substrate degradation efficiency was 22511.60 mL and 85% per total carbohydrate, respectively obtained in the experiments performed. The biogas that was produced had undergone adsorption process on zeolite ZSM-5. The effect of dosage of adsorbents and reaction temperature on the hydrogen yield and H_2S removal investigated. The hydrogen yield after adsorption process increased from 89% to 92.78%. The optimum dosage and reaction temperature for H_2S adsorption were 0.8 g (0.00889 mg/g) and 25 °C (0.00890 mg/g), respectively. The zeolite was subjected to consecutive regeneration and adsorption cycle where H_2S adsorption capacities of 0.00890 mg/g were maintained for 3 cycles demonstrating reusability and stability of the sorbents. However, the adsorption capacity starts reducing at the fourth cycle. The H_2S removal on zeolite ZSM-5 was the best represented by Avrami kinetics model showing that H_2S were adsorbed via multiple adsorption pathways with multilayer adsorption on heterogenous surface. The adsorption is physical adsorption, exothermic, increasingly random, and non-spontaneous. Intra-particle diffusions were found to critically control the rate of adsorption. Higher H_2S adsorption capacity and regenerability shown by fibrous zeolite in this this study confirmed its applicability as an alternative sorbent in enhance biohydrogen quality under thermophilic conditions.

CHAPTER 1 : INTRODUCTION

1.1 Background of Study

The detrimental impact on the natural environment is expected to occur due to factors such as population growth, urbanisation, and rapid industrialization. Additionally, growing nations face pressing challenges in the form of wastewater generation and energy scarcity, which are considered to be of utmost importance (Kollmann et al., 2023; Kookana et al., 2020). These factors are closely linked to the phenomenon of economic expansion and its corresponding impact on energy use. Currently, over 85% of the global energy demand is satisfied by non-renewable resources, namely petroleum (34%), coal (27%), and natural gas (24%), resulting in significant emissions of detrimental gases and the generation of a substantial volume of wastewater (Trade Organization & Renewable Energy Agency, 2023). The situation has been found to have a detrimental effect on the global climate, human health, and the ecology (Ye et al., 2020). The necessity to tackle these difficulties has led to an increasing interest in hydrogen as an energy carrier and other forms of renewable energy sources (Amin et al., 2022).

The utilisation of wastewater as a renewable energy resource, namely in the form of hydrogen gas, is considered a viable and economically efficient alternative (Chaurasia & Mondal, 2022). Moreover, hydrogen is recognised as the most lightweight petrol on the planet and is widely regarded as a promising fuel source for the future. According to De Bhowmick et al. (2019), the energy density of this substance is more than that of petrol, being three times higher than that of petrol or diesel. Consequently, it has the potential to serve as a substitute for fossil fuels in order to address global energy demands. Hydrogen serves as a crucial raw material for various industrial sectors and refineries,

while also functioning as a significant provider of thermal energy and power. Furthermore, the production of biohydrogen technology can be derived from a range of environmental pollutants, including sewage sludge, industrial and agricultural waste, and municipal solid waste (Šabić Runjavec et al., 2023). Nevertheless, the generation of biohydrogen gas through anaerobic digestion poses challenges to energy conversion systems due to the presence of noxious, malodorous, and corrosive trace compounds, including hydrogen sulphide (H_2S). These molecules have the potential to diminish the quality of biohydrogen gas (Wang et al., 2019a). In order to address these concerns, it is imperative that the initial phase of purification adheres to stringent quality criteria when intended for utilisation as a substitute for natural gas, particularly in terms of energy production. This approach serves to mitigate the adverse environmental effects associated with gaseous emissions (Zulkefli et al., 2019).

Various techniques have been employed for the removal of hydrogen sulphide (H_2S), including thermal treatment, incineration, catalytic oxidation, membrane separation, biological processes, and adsorption (Georgiadis et al., 2021). The aforementioned methods have demonstrated notable efficiency and effectiveness. However, it is important to acknowledge that they are characterised by a high energy consumption, which may result in the emission of secondary pollutants. Additionally, the implementation of these methods entails substantial capital and overhead expenses (Berhe et al., 2019). Nevertheless, the utilisation of the adsorption technology is well recognised as a highly efficient and economically viable approach for the remediation of hazardous gases (Rathi & Kumar, 2021). The conventional methods employed for hydrogen sulphide (H_2S) removal in biogas production encompass adsorption into liquid media, such as water or caustic soda, adsorption onto solid materials like iron oxide, activated

carbon, or zeolite, and the utilisation of oxidising sulphide bacteria in the presence of air or oxygen to convert evolved sulphur compounds into elemental sulphur through biological processes (Pudi et al., 2022).

Hence, several adsorption methods employed for the elimination of low-concentration hydrogen sulphide (H_2S) from biogases at reduced temperatures, the dry solid adsorption technique is widely acknowledged as the most efficient, environmentally friendly, and economically viable approach. The materials employed in the dry adsorption process are typically categorised into four types in various studies: metal-based materials, carbon-based materials, porous materials, and polymeric materials. The removal of sulphurous compounds at low temperatures was investigated by Mu et al., (2023) using molecular sieves and porous adsorbents. Zeolites exhibit molecular sieving properties owing to their exceptional mechanical ability to adsorb polar molecules. According to Boer et al. (2023), it has emerged as a promising material for the separation and purification of gases at low temperatures.

1.2 Problem Statement

The commercial generation of biohydrogen as a biofuel has become a reality. In addition, it presents itself as a compelling substitute for the growing need for fossil-derived natural gas, as a variety of diverse microbial communities have the capacity to generate hydrogen gas through the process of fermentation using a wide array of organic feedstock (Oliveira et al., 2020). Biohydrogen is composed predominantly of hydrogen (H_2) and carbon dioxide (CO_2). However, it is worth noting that it may also include substantial amounts of desirable contaminant molecules, such as hydrogen sulphide

(H₂S), which can vary in concentration depending on the nature of the reactor's input material (Cristiano et al., 2020).

Hydrogen sulphide (H₂S) is a gas that possesses significant toxicity, emits an unpleasant odour, and exhibits corrosive properties. Its presence can have detrimental effects on the production of biohydrogen, as well as induce corrosion on the mechanical components of the reactor (Pudi et al., 2022). The deleterious consequences of hydrogen sulphide (H₂S) in human exposure can result in ocular impairment when the concentration reaches 50 parts per million (ppm). Furthermore, a mere concentration of 300 ppm for a duration of 30 minutes is sufficient to induce unconsciousness in an individual (De Crisci et al., 2019). In order to mitigate the environmental consequences of gaseous emissions and adhere to stringent quality standards for its application as a natural gas alternative, it is imperative to significantly decrease this fraction to the lower threshold of toxicity (Zhai et al., 2022).

Presently, there exists a gap on research pertaining to the removal of hydrogen sulphide (H₂S). However, it is worth noting that the majority of these studies primarily concentrate on the utilisation of simulated H₂S gas, rather than an authentic biogas stream that is sourced directly from an anaerobic reactor (Chen et al., 2022; Jeong et al., 2022). In addition, numerous scholarly investigations have been dedicated to examining the utilisation of natural gas derived from fossil fuels, and synthetic gas adsorbate for the purpose of H₂S removal (Ahmad et al., 2021; Ghimire et al., 2021; Kailasa et al., 2020). Hence, the novelty for this study is investigation pertaining to the elimination of hydrogen sulphide (H₂S) during the process of fermentative biohydrogen synthesis. Consequently,

the primary objective of this research was to investigate the process of H₂S removal through adsorption using adsorbents, specifically zeolite, from a biohydrogen stream.

1.3 Research Objectives

The objective of this study is to mitigate the presence of hydrogen sulphide (H₂S) in the fermentative thermophilic biohydrogen process in order to improve the overall quality of biohydrogen production. Furthermore, the principal objective of this study is to assess the efficacy of zeolite as an adsorbent for hydrogen sulphide removal from a natural biogas stream, while maintaining its original properties intact. The research delineates the precise aims as follows:

- i To determine hydrogen yield (HY) and hydrogen production rate (HPR) in a thermophilic anaerobic closed bioreactor (TACB).
- ii To evaluate the zeolite's adsorption capacity for hydrogen sulphide removal and the effect of biohydrogen concentration at various parameters such as zeolite dose loading and reaction temperature using the breakthrough technique.
- iii To investigate the adsorption process's kinetics, mass transfer and thermodynamics.

1.4 Research Scopes

The primary objective of this study was to investigate the mitigation of hydrogen sulphide generated during thermophilic fermentation biohydrogen production. The present investigation encompasses laboratory-based experimentation focused on the production of biohydrogen yield (mol H₂/mol hexose consumed) and hydrogen production rate (mmol/L/hr) through the fermentation of sewage sludge using wastewater derived from a mixture of fruit waste (5 g/L of suspension MFW) via batch method in thermophilic anaerobic closed bioreactor (TACB) at temperature 60 °C and initial pH of 6.00±0.2. In addition, the study involves the examination of hydrogen sulphide adsorption via fixed bed dry adsorption process at different dosage loading (0.2 g – 1.0 g) and reaction temperatures (25 °C – 125 °C). There are two analyses were conducted act as supporting data for adsorption process such as the characterisation of zeolite ZSM-5 included analysis of the specific surface area and volume, morphology, and chemical functional groups and regeneration of adsorbent. Finally, the adsorption kinetics (pseudo-first order, pseudo-second order, and Avrami), adsorption mass transfer and thermodynamics were investigated by using the results obtained after adsorption process.