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A Conceptual Model for the Recovery of Volatile Fatty Acids from Anaerobically Digested Sludge Liquors

[1] Matluck Afolabi, [2] Ogechi Amanda Onukogu, [3] Thompson Odion Igunma, [4] Adeniyi K Adeleke, [5] Zamathula Q Sikhakhane Nwokediegwu

[1] Independent Researcher, Louisiana, USA
[2] Metaspec Consult Ltd, Port Harcourt, Nigeria
[3] Independent Researcher, Florida, USA
[4] Independent Researcher, USA
[5] Independent Researcher, Durban, South Africa

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Corresponding Author: **Matluck Afolabi**

Abstract

Volatile fatty acids (VFAs) are valuable intermediates with wide-ranging applications in the production of bioplastics, bioenergy, and chemicals, offering a promising route for resource recovery from wastewater treatment processes. This study proposes a conceptual model for the selective recovery of VFAs from anaerobically digested sludge liquors, aiming to transform wastewater treatment plants into biorefineries. Anaerobic digestion (AD) of sludge generates a complex mixture of organic acids, primarily acetic, propionic, and butyric acids, along with residual nutrients and solids. The proposed model integrates key components such as phase separation, in-line monitoring, and selective extraction techniques to maximize VFA yield while maintaining system stability. The Sconceptual framework is designed around four main stages: (1) acidogenic fermentation optimization, (2) solid-liquid separation to concentrate VFAs, (3) selective extraction using membrane contactors or ion exchange resins, and (4) downstream valorization through microbial conversion or chemical upgrading. Emphasis is placed on manipulating operational parameters such as pH, retention time, temperature, and carbon-to-nitrogen (C/N) ratio to favor acidogenesis over methanogenesis. Additionally, the model explores the role of microbial community engineering and inhibitors to suppress methane formation and redirect metabolic pathways toward VFA accumulation. Energy and material balances are evaluated to ensure economic feasibility and sustainability. Advanced separation technologies such as forward osmosis, electrodialysis, and solvent extraction are incorporated into the model based on their selectivity and compatibility with sludge matrices. The potential integration with existing treatment infrastructure is also considered to reduce capital expenditure and operational complexity. This conceptual model not only enhances the circular economy potential of wastewater treatment plants but also aligns with climate action goals by minimizing greenhouse gas emissions and recovering valuable carbon streams. Future research directions include pilot-scale validation, techno-economic assessments, and lifecycle analysis to refine and implement the model in diverse treatment scenarios.

Keywords: Volatile Fatty Acids, Anaerobic Digestion, Sludge Liquor, Resource Recovery, Acidogenic Fermentation, Membrane Contactor, VFA Extraction, Wastewater Biorefinery

1. Introduction

Volatile fatty acids (VFAs) are a class of short-chain fatty acids that play a crucial role in various biological processes, including anaerobic digestion (AD), where they are intermediate products of organic matter degradation. VFAs have garnered significant attention due to their potential as valuable chemical feedstocks in a variety of industrial applications. These acids are used in the production of bioplastics, solvents, and biofuels, and they have potential in sectors such as pharmaceuticals, agriculture, and food processing. Given the growing interest in sustainable and circular economy approaches, the recovery of VFAs from waste streams, particularly from anaerobically digested sludge liquors, presents an attractive opportunity to

enhance the economic viability and environmental sustainability of waste treatment processes (Ajayi, *et al*., 2020, Ikeh & Ndiwe, 2019, Orieno, *et al*., 2021).

Traditional anaerobic digestion, a widely used method for treating organic waste, has primarily focused on methane recovery for energy production. While methane is a valuable energy source, the process also generates a significant amount of digestate, which contains VFAs that are typically left behind or lost as waste. The conventional focus on methane production often overlooks the potential of these VFAs, which remain underutilized despite their significant industrial value (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Ogunwole, *et al*., 2022). Furthermore, the accumulation of VFAs in digestate can pose challenges for waste treatment plants, as excessive concentrations of these compounds can lead to operational difficulties and inhibit the efficiency of the anaerobic digestion process.

The recovery of VFAs from anaerobically digested sludge liquors presents an exciting opportunity to promote resource valorization and contribute to the development of a more sustainable, circular economy. By recovering and converting these VFAs into high-value chemicals or energy carriers, industries can not only reduce the environmental impact of waste disposal but also generate additional revenue streams from what would otherwise be considered waste. Furthermore, the recovery of VFAs helps address the challenges of waste treatment plants by reducing the burden on downstream processes, such as nutrient removal and sludge disposal, while simultaneously providing a sustainable source of carbon for industrial applications (Ayo, *et al*., 2023, Elete, *et al*., 2023, Kokogho, *et al*., 2023).

The development of a conceptual model for the recovery of VFAs from anaerobically digested sludge liquors aims to optimize this process by integrating the latest advancements in technology, process design, and resource recovery strategies. The model focuses on improving the efficiency of VFA extraction and conversion processes, identifying key factors that influence VFA yield and quality, and proposing system configurations that can be adapted to various scales and types of industrial operations. This approach aligns with the growing demand for sustainable and efficient resource recovery solutions and supports the broader goals of reducing waste and fostering resource recovery in industrial wastewater treatment.

2.1 Methodology

The methodology employed for developing a conceptual model for the recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors followed a systematic and integrative approach. The research commenced with the identification of central questions aimed at exploring viable tools, techniques, and processes for efficient VFA recovery. A comprehensive literature search was conducted using databases such as ScienceDirect, Scopus, Web of Science, and Google Scholar, focusing on keywords including "anaerobic digestion," "volatile fatty acid recovery," "wastewater treatment," "conceptual model," "optimization tools," and "process simulation." This search incorporated insights from recent frameworks in sustainability, waste-to-resource transitions, and risk-based environmental compliance as identified in references such as Adeoba *et al*. (2018, 2019), Adewoyin (2021, 2022), Adikwu *et al*. (2023), and Castilla-Archilla *et al*. (2023).

The retrieved studies were screened for relevance based on inclusion criteria that prioritized applicability to full-scale wastewater treatment plant scenarios, technical innovation in process design, and alignment with sustainable development goals. Studies that focused exclusively on genetic modeling (e.g., Adeoba's DNA barcoding work) were used metaphorically to inspire the structural mapping of VFA metabolic pathways. Subsequently, key data were extracted from selected studies, focusing on methodologies used, reactor configurations, separation technologies (such as membrane distillation and electrochemical systems), feedstock variability, pH manipulation strategies, and recovery efficiency rates.

The extracted information was synthesized using a qualitative conceptual integration technique, drawing parallels across disciplines such as environmental biotechnology, chemical engineering, and process systems optimization. A conceptual framework was constructed to simulate the key components of VFA recovery: Sludge pre-treatment, anaerobic digestion kinetics, VFA separation and purification, and final integration into downstream value chains. The model incorporates AI-assisted simulation recommendations (Agbede *et al*., 2023), green transition constraints (Afeku-Amenyo *et al*., 2023), and lifecycle environmental assessments.

To ensure the model's applicability to real-world settings, it was validated against established operational datasets and benchmarked using performance indicators such as energy efficiency, economic viability, carbon footprint, and potential for resource recovery. This cross-validation aligns the model with sustainability frameworks and green economy transitions in wastewater infrastructure. The final model offers a scalable and adaptable template for municipal and industrial wastewater facilities, paving the way for enhanced circular economy outcomes and reduced environmental burdens. Would you like help drafting the abstract or results section next?

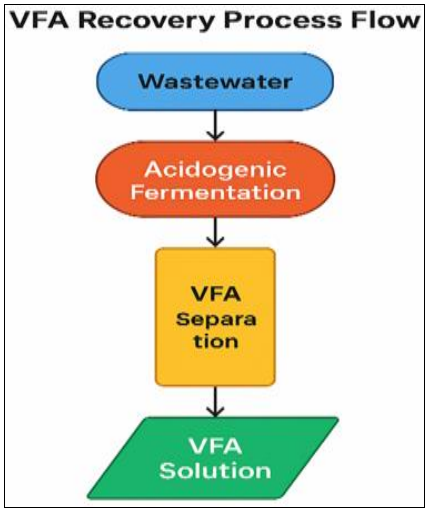

Fig 1: Flow chart of the study methodology

2.2 Characteristics of Anaerobically Digested Sludge Liquors

Anaerobically digested sludge liquors are the liquid by-products of the anaerobic digestion (AD) process, which is commonly used for the treatment of organic waste and sewage sludge. This liquorous effluent contains a complex mixture of dissolved organic compounds, inorganic elements, and microbial communities that have undergone

biochemical transformations during the anaerobic digestion process. The characteristics of these liquors are essential to understanding their potential for volatile fatty acid (VFA) recovery, as the composition of the liquors influences the efficiency of VFA extraction and subsequent utilization.

After anaerobic digestion, the composition of sludge liquors changes significantly. The AD process primarily breaks down complex organic matter into simpler molecules, such as methane (CH4), carbon dioxide (CO2), and VFAs. However, not all of the organic material is converted into methane, and a portion remains in the liquid phase as VFAs, dissolved organic matter, and inorganic nutrients (Bakare, *et al*., 2023, Eyeghre, *et al*., 2023, Lottu, *et al*., 2023). These sludge liquors are typically rich in water, with a significant concentration of dissolved organic compounds and soluble inorganic elements. The presence of these components makes the liquor a promising source for resource recovery, especially in the context of VFA extraction.

One of the most significant components of anaerobically digested sludge liquors is the presence of VFAs. These short-chain fatty acids, including acetic acid, propionic acid, butyric acid, and others, are produced during the hydrolysis and acidogenesis stages of the anaerobic digestion process. VFAs are intermediate products that are formed from the breakdown of complex organic materials such as carbohydrates, proteins, and fats by microorganisms under anaerobic conditions. Among the various VFAs, acetic acid is the most abundant, followed by propionic and butyric acids (Daraojimba, *et al*., 2021, Egbumokei, *et al*., 2021, Sobowale, *et al*., 2021). These compounds are of great interest for recovery because they serve as important carbon sources for microbial growth in industrial applications, such as the production of bioplastics, solvents, and biofuels. Figure 2 shows the schematic set up of the volatile fatty acid production and recovery system presented by Castilla-Archilla, *et al*. 2023.

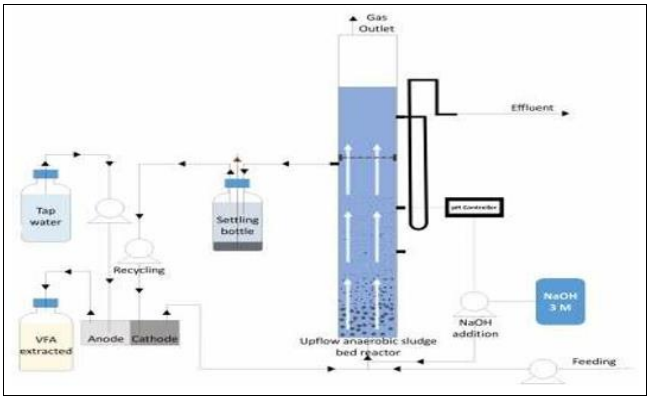

Fig 2: Schematic set up of the volatile fatty acid production and recovery system (Castilla-Archilla, *et al*. 2023)

Acetic acid, as the primary VFA produced during anaerobic digestion, constitutes a significant fraction of the VFA pool in sludge liquors. It is often used as a precursor in the production of chemicals like acetic acid esters, which are valuable in various industrial sectors, including food, pharmaceuticals, and agriculture. Propionic acid, while typically present in lower concentrations than acetic acid, is also highly valuable, especially in the production of propanol, which is widely used as a solvent, as well as in the food industry for use as a preservative. Butyric acid, another significant VFA in the liquor, can be utilized in the production of butanol, a compound with applications in biofuels and chemical manufacturing (Onyeke, *et al*., 2022, Orieno, *et al*., 2022, Ozobu, *et al*., 2022). The presence of these VFAs in the post-AD sludge liquor presents a valuable resource for industries seeking sustainable feedstocks for chemical production.

However, the recovery of VFAs from anaerobically digested sludge liquors is not without challenges. The presence of inhibitory substances in the sludge liquors can negatively affect the efficiency of VFA extraction processes. Methane production, which is the primary objective of anaerobic digestion, competes with the production of VFAs in the anaerobic digestion system. Methanogenesis, the microbial process that produces methane from acetate and other VFAs, can limit the accumulation of VFAs in the liquid phase, thereby reducing the yield of recoverable acids (Chukwuma, *et al*. 2022, Johnson, *et al*., 2022, Ogunwole, *et al*., 2022). The competition between methanogens and acidogenic bacteria is particularly relevant in systems where methane production is the primary focus, as it can result in lower concentrations of VFAs that are available for recovery. Schematic representation of the anaerobic degradation of organic matter AD divided in four steps presented by Fermoso, *et al*., 2019 is shown in figure 3.

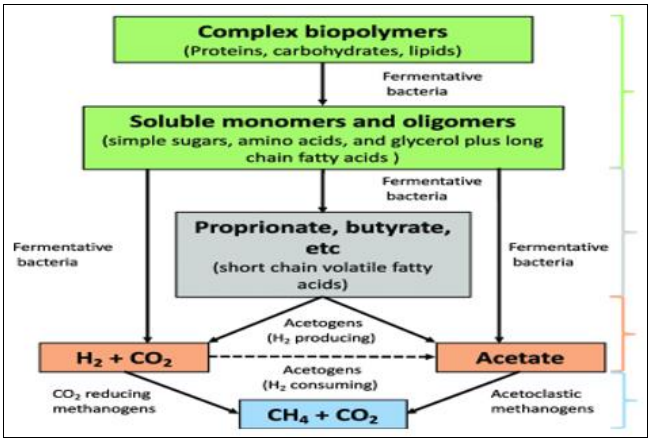

Fig 3: Schematic representation of the anaerobic degradation of organic matter AD divided in four steps: (1) hydrolysis, (2) acidogenesis, (3) acetogenesis, and (4) methanogenesis (Fermoso, *et al*., 2019)

In addition to methanogenesis, other competing microbial processes, such as denitrification and sulfate reduction, may also influence the composition of anaerobically digested sludge liquors. These processes are often driven by the presence of nitrogen and sulfur compounds in the feedstock, which can further complicate the recovery of VFAs. Denitrification, for instance, involves the reduction of nitrates to nitrogen gas by bacteria under anaerobic conditions, potentially consuming organic substrates that could otherwise be used for VFA production (Akintobi, Okeke & Ajani, 2022, Ezeanochie, Afolabi & Akinsooto, 2022). Similarly, sulfate-reducing bacteria can use organic matter to reduce sulfate to hydrogen sulfide, another unwanted by-product in sludge liquors that can interfere with VFA recovery.

Inhibitory substances, such as hydrogen sulfide (H2S) and ammonia (NH3), can also affect the recovery process. These compounds can be toxic to microorganisms involved in VFA production and recovery, reducing the overall yield of VFAs. Hydrogen sulfide, in particular, can accumulate

during sulfate reduction processes, and its presence in sludge liquors can inhibit the activity of acidogenic bacteria that produce VFAs. Ammonia, which is often present in anaerobic digestate due to the breakdown of proteins, can also pose inhibitory effects, especially when present at high concentrations (Adeoba, 2018, Imran, *et al*., 2019, Orieno, *et al*., 2021). The toxicity of ammonia depends on factors such as pH and temperature, and its accumulation in the liquors can slow down or even halt the microbial processes responsible for VFA production.

Moreover, the concentration of organic matter in anaerobically digested sludge liquors is often variable, influenced by factors such as the type of feedstock used in the AD process, the operational conditions (e.g., temperature, retention time), and the characteristics of the microbial community involved. This variability presents a challenge for the efficient recovery of VFAs, as the composition of the liquors can change over time, affecting the efficiency of extraction technologies (Onukwulu, *et al*., 2023, Orieno, *et al*., 2023, Ozobu, *et al*., 2023). The organic matter concentration may vary based on the efficiency of the digestion process, and inconsistent VFA production may result in fluctuating concentrations of these acids, making the recovery process less predictable and harder to scale. Fermoso, *et al*., 2019 presented Processes affecting pH value of anaerobic digesters shown in figure 4.

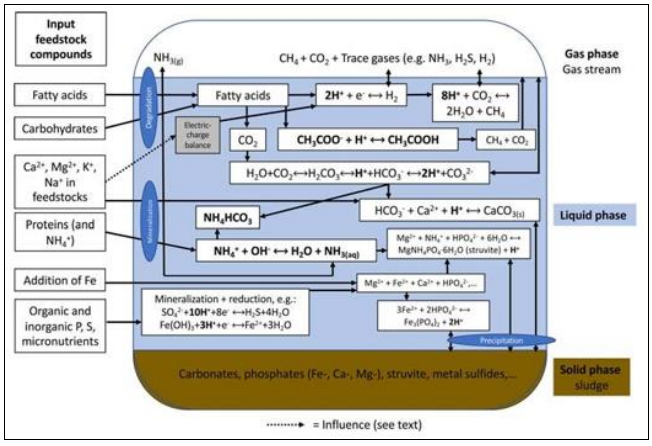

Fig 4: Processes affecting pH value of anaerobic digesters (Fermoso, *et al*., 2019)

The variability of these factors highlights the need for an integrated approach to recovering VFAs from anaerobically digested sludge liquors, one that accounts for both the chemical composition and the biological processes at play. Addressing the challenges posed by inhibitory substances, microbial competition, and organic matter variability requires the development of effective strategies for optimizing the conditions under which VFAs are produced and extracted. This can include modifications to the AD process itself, such as the optimization of retention times, temperature conditions, and microbial community management, to encourage the accumulation of VFAs while minimizing the competing processes that limit their production.

Additionally, novel recovery methods such as membrane filtration, adsorption, and distillation are being explored to improve the efficiency and selectivity of VFA extraction. These methods can be designed to specifically target the recovery of VFAs, reducing the impact of inhibitory substances and enhancing the overall efficiency of the recovery process. Membrane filtration, for instance, can separate VFAs from other dissolved compounds based on molecular size, while adsorption technologies can selectively capture VFAs onto solid materials (Ojika, *et al*., 2021, Okolo, *et al*., 2021, Onukwulu, *et al*., 2021). These innovations in recovery techniques, coupled with process optimization, hold the potential to improve the economic feasibility and environmental sustainability of VFA recovery from anaerobically digested sludge liquors.

In conclusion, the characteristics of anaerobically digested sludge liquors, particularly the presence of volatile fatty acids and competing microbial processes, play a critical role in determining the feasibility and efficiency of VFA recovery. While VFAs are valuable resources for various industrial applications, their recovery is influenced by the competition between methanogenesis, the presence of inhibitory substances, and the variability of organic matter in the liquors. Addressing these challenges through process optimization, advanced recovery technologies, and a better understanding of microbial dynamics will be key to realizing the full potential of VFA recovery from anaerobically digested sludge liquors. As these technologies continue to develop, the recovery of VFAs will become an increasingly important aspect of sustainable resource management in wastewater treatment and industrial processes.

2.3 Conceptual Framework Overview

A conceptual model for the recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors aims to establish a comprehensive and efficient process for capturing valuable VFAs while enhancing resource recovery and promoting a circular economy. This model incorporates a multi-stage process, each designed to optimize the recovery of VFAs, minimize waste, and maximize the reuse of resources within industrial water treatment systems. The proposed model consists of four main stages: Acidogenic fermentation optimization, solid-liquid separation, selective VFA extraction, and downstream valorization and integration. Each stage builds on the preceding one to ensure that VFAs are extracted in the most efficient manner, with consideration for both the environmental and economic impacts.

The first stage of the model focuses on acidogenic fermentation optimization, a critical step for increasing the concentration of VFAs in anaerobically digested sludge liquors. In this stage, organic material in the sludge is further fermented by acidogenic bacteria to produce a higher yield of VFAs. Optimizing this fermentation process involves controlling several key parameters, including the pH, temperature, retention time, and the type of organic matter being treated (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2023, Mgbecheta, *et al*., 2023). By fine-tuning these variables, the acidogenic fermentation process can be made more efficient, producing a higher concentration of VFAs such as acetic acid, propionic acid, and butyric acid. This optimization step is crucial because it sets the stage for the rest of the process, ensuring that sufficient VFAs are present in the liquid phase to make the recovery process economically viable.

In addition to optimizing the fermentation conditions, this stage also involves managing microbial populations to ensure the dominance of acidogenic bacteria over competing

microbial processes like methanogenesis. Methanogenesis, the production of methane from VFAs by methanogenic archaea, can reduce the availability of VFAs for recovery. Therefore, controlling factors that favor acidogenic bacteria and inhibit methanogenesis, such as adjusting substrate concentrations or introducing inhibitory agents, is necessary to maximize VFA yields (Agho, *et al*., 2021, Ezeanochie, Afolabi & Akinsooto, 2021). Moreover, pretreatment methods such as the addition of external carbon sources or the use of co-substrates can enhance the fermentation process, further increasing VFA concentrations and improving the overall efficiency of the model.

The second stage, solid-liquid separation, involves the separation of the liquid phase containing VFAs from the solid digestate produced during anaerobic digestion. This stage is necessary because anaerobic digestion results in a mixture of solids and liquids, and the VFAs are typically dissolved in the liquid phase. Efficient separation of these phases is crucial for ensuring that the liquid containing the highest concentration of VFAs is isolated and can be further processed. Several methods can be used for this separation, including centrifugation, filtration, and membrane processes like ultrafiltration or microfiltration (Adikwu, *et al*., 2023, Elete, *et al*., 2023, Ndiwe, *et al*., 2023). Each of these methods has its advantages and can be selected based on factors such as the characteristics of the sludge, the desired separation efficiency, and the scale of the operation.

Centrifugation is a common technique for separating solids from liquids, as it uses centrifugal force to drive the denser solid particles to the outer walls of a spinning container, allowing the lighter liquid phase to be collected. Filtration, particularly using membrane-based technologies, can offer higher resolution in separating different fractions of the liquid, which is important when recovering specific VFAs from complex mixtures (Egbuhuzor, *et al*., 2021, Isi, *et al*., 2021, Onukwulu, *et al*., 2021). Membrane filtration is often preferred for its ability to selectively separate VFAs based on their molecular size, while also minimizing the loss of valuable organic compounds. The effectiveness of solid-liquid separation impacts the efficiency of the entire recovery process, as it ensures that the VFA-rich liquid is obtained in a pure and concentrated form for further processing.

The third stage of the process is selective VFA extraction, where the VFAs in the liquid are separated and concentrated for further use or valorization. Given that different VFAs have different chemical properties, selective extraction methods are required to separate individual acids or groups of acids with high precision. Several techniques, including solvent extraction, adsorption, and membrane-based separation, can be employed to selectively extract VFAs from the liquid phase (Daraojimba, *et al*., 2022, Elete, *et al*., 2022, Okolo, *et al*., 2022). Solvent extraction involves using organic solvents to dissolve and separate specific VFAs from the aqueous phase, while adsorption techniques utilize solid adsorbents that have a high affinity for VFAs, selectively capturing them from the liquid. Membrane-based technologies such as reverse osmosis or nanofiltration can also be employed to separate VFAs based on their molecular size and polarity.

In addition to these conventional methods, newer techniques such as electrodialysis and liquid-liquid extraction have shown promise for improving the efficiency of VFA recovery. Electrodialysis, for instance, uses an electric field to drive the transport of ions across selective membranes, allowing for the recovery of VFAs in their ionized form. This method offers several advantages, including high selectivity and low energy consumption, making it an attractive option for industrial-scale VFA recovery (Adewoyin, 2021, Isi, *et al*., 2021, Ogunnowo, *et al*., 2021). Regardless of the method chosen, the goal of selective VFA extraction is to concentrate the VFAs to levels that are suitable for downstream valorization, which is the next stage in the process.

The final stage in the conceptual model is downstream valorization and integration, where the recovered VFAs are converted into valuable products or integrated into other industrial processes. VFAs can be used as feedstocks for the production of bioplastics, solvents, and biofuels, or they can be integrated into anaerobic digestion processes as a supplementary carbon source to enhance methane production. The valorization of VFAs represents a key opportunity for promoting a circular economy, as it allows waste products to be transformed into high-value commodities, reducing the need for virgin resources and lowering environmental impacts (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Onukwulu, *et al*., 2022).

The use of VFAs in bioprocesses is a promising approach to achieving sustainable chemical production. For instance, acetic acid can be used as a precursor in the synthesis of bio-based polymers, while butyric acid can be converted into butanol, a valuable biofuel. By using VFAs as raw materials in these processes, industries can reduce their reliance on fossil fuels and contribute to the transition toward more sustainable, resource-efficient manufacturing. Additionally, the integration of VFA recovery into existing industrial water treatment systems allows for a more efficient use of resources, as the recovery process supports both waste treatment and the generation of valuable products (Attah, *et al*., 2022, Elete, *et al*., 2022, Nwulu, *et al*., 2022).

Furthermore, the integration of VFA recovery into wastewater treatment processes can improve the overall efficiency and sustainability of water reclamation. By combining VFA recovery with other resource recovery techniques, such as nutrient recovery or water recycling, industries can create closed-loop systems that minimize waste, reduce energy consumption, and lower environmental impact. The holistic approach provided by the conceptual model supports the overarching goals of sustainability and resource conservation, aligning with global efforts to reduce the environmental footprint of industrial processes (Afolabi & Akinsooto, 2021, Ogundipe, *et al*., 2021).

In conclusion, the proposed conceptual model for the recovery of volatile fatty acids from anaerobically digested sludge liquors offers a comprehensive and integrated approach to maximizing the value of waste products in industrial water treatment. By focusing on optimizing acidogenic fermentation, efficient solid-liquid separation, selective VFA extraction, and downstream valorization, this model presents a promising pathway for resource recovery and contributes to the development of more sustainable, circular industrial processes. As technological advancements continue to improve the efficiency and scalability of each stage, the recovery of VFAs will play an increasingly important role in reducing waste, enhancing resource efficiency, and promoting a more sustainable future.

2.4 Acidogenic Fermentation Optimization

Acidogenic fermentation optimization is a critical step in the recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors. The goal of optimizing acidogenic fermentation is to enhance the production of VFAs, which are valuable intermediates used in various industrial processes, including bioplastics, solvents, and biofuels. In the context of anaerobic digestion, acidogenesis is the phase where complex organic materials are broken down into simpler compounds, primarily VFAs, by specialized microorganisms. The conditions under which acidogenesis occurs directly influence the yield and composition of the VFAs produced. Therefore, careful optimization of the fermentation conditions is essential to ensure maximum VFA production, setting the foundation for efficient recovery in subsequent stages of the process.

One of the most important operational parameters in acidogenic fermentation optimization is the control of pH, temperature, and hydraulic retention time (HRT). pH plays a crucial role in the growth and activity of acidogenic microorganisms, as most of these bacteria thrive in a slightly acidic to neutral environment. The pH range typically favored for acidogenesis is between 5.5 and 7.5, although slight variations in pH can impact the production of different VFAs. For instance, at a lower pH, there is a tendency to promote the production of acetic acid, whereas a higher pH may lead to an increase in propionic and butyric acid production (Onukwulu, *et al*., 2023, Onyeke, *et al*., 2023, Orieno, *et al*., 2023). Controlling the pH within the optimal range is essential for balancing the types of VFAs produced and maximizing the overall yield.

Temperature is another critical factor that influences the rate and efficiency of acidogenic fermentation. Most acidogenic bacteria operate optimally in a mesophilic temperature range of 30–40°C, although thermophilic conditions (50–60°C) can be used to accelerate the process. The temperature affects microbial activity, enzymatic reactions, and the breakdown of organic material (Agho, *et al*., 2022, Ezeafulukwe, Okatta & Ayanponle, 2022). By carefully regulating temperature, it is possible to optimize the fermentation rate and increase the yield of VFAs, ensuring that the microbial communities are working at their peak performance. Furthermore, temperature management can influence the selectivity of VFA production, as different temperature ranges favor the growth of distinct microbial species capable of producing specific types of VFAs.

Hydraulic retention time (HRT) is another key parameter in acidogenic fermentation. HRT is the amount of time the sludge liquor remains in the fermentation reactor, which determines the extent to which organic matter is broken down by the microorganisms. A longer HRT allows for a more complete fermentation process, leading to higher VFA yields. However, excessively long HRTs may also lead to the overproduction of certain VFAs at the expense of others, reducing the efficiency of the overall process (Daraojimba, *et al*., 2022, Kanu, *et al*., 2022, Okolo, *et al*., 2022). On the other hand, a shorter HRT may limit the fermentation process, leading to lower VFA concentrations and incomplete organic matter breakdown. Therefore, the optimization of HRT is crucial for balancing the efficiency and effectiveness of the fermentation process, ensuring that the maximum amount of VFAs is produced in the shortest amount of time.

The adjustment of the carbon-to-nitrogen (C/N) ratio in the fermentation system is another important consideration in optimizing acidogenesis. The C/N ratio influences the balance between carbon and nitrogen availability, which directly affects the microbial activity and the composition of the VFAs produced. A higher C/N ratio generally promotes the growth of acidogenic bacteria, which preferentially utilize carbon for VFA production. However, if the nitrogen content is too low, it can limit microbial growth and reduce the efficiency of acidogenesis (Ojika, *et al*., 2021, Onaghinor, *et al*., 2021, Sobowale, *et al*., 2021). Conversely, if the nitrogen content is too high, it may encourage the growth of methanogenic microorganisms, which produce methane instead of VFAs. The presence of methanogens in the fermentation process is undesirable when the goal is to maximize VFA production, as methane production competes with acidogenesis and reduces the overall yield of VFAs. Therefore, the careful adjustment of the C/N ratio is essential for ensuring that the microbial community remains dominated by acidogens rather than methanogens, optimizing the fermentation conditions for VFA production.

Methanogens are microorganisms that produce methane as a byproduct of organic matter breakdown. In the context of VFA recovery, methanogenesis competes with acidogenesis and reduces the availability of VFAs in the liquid phase, making it an undesirable process. To suppress methanogens and promote acidogenesis, chemical or environmental inhibitors can be introduced into the fermentation system. Several chemical inhibitors, such as sodium 2-bromoethanesulfonate (BES), have been found to specifically target and inhibit methanogenic activity without negatively impacting acidogenic bacteria (Akintobi, Okeke & Ajani, 2023, Eyeghre, *et al*., 2023, Ogunwole, *et al*., 2023). The use of such inhibitors allows for the selective promotion of acidogenesis, ensuring that the maximum amount of VFAs is produced without interference from methanogens. Alternatively, environmental conditions can be adjusted to suppress methanogenesis. For example, adjusting the pH, temperature, or nutrient concentrations can create conditions that are more favorable for acidogenic bacteria and less favorable for methanogens, thereby enhancing VFA production.

Microbial community engineering is another promising approach to optimizing acidogenic fermentation. By manipulating the microbial populations in the fermentation system, it is possible to select for microorganisms that are particularly efficient at producing VFAs. This can be achieved through the addition of specific strains of acidogenic bacteria or by creating conditions that favor the growth of certain microbial species. In some cases, microbial consortia are used to optimize the breakdown of organic matter into VFAs. These consortia may include bacteria capable of hydrolyzing complex substrates, such as lignocellulose, as well as those involved in acidogenesis (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2023, Nwakile, *et al*., 2023). Through microbial community engineering, it is possible to enhance the overall efficiency of the fermentation process, improve the yield of specific VFAs, and reduce the competition between different microbial groups.

In addition to optimizing fermentation conditions, process control strategies such as continuous monitoring and feedback loops are becoming increasingly important in acidogenic fermentation. The use of real-time sensors to monitor key parameters, such as pH, temperature, and VFA

concentration, allows for the dynamic adjustment of operating conditions to maintain optimal fermentation performance. Advanced control systems, such as automated dosing of nutrients or pH adjusters, can help maintain the ideal conditions for acidogenesis, preventing the process from shifting toward methanogenesis or other undesirable microbial activities (Ajayi, *et al*., 2021, Odio, *et al*., 2021, Onukwulu, *et al*., 2021). By continuously optimizing the fermentation conditions, it is possible to achieve higher yields of VFAs and ensure a more stable and predictable fermentation process.

The optimization of acidogenic fermentation for VFA recovery is an area of ongoing research, with a focus on developing more efficient and cost-effective strategies. New technologies, such as high-throughput screening of microbial strains, advanced metabolic pathway analysis, and the use of genetic engineering to enhance the performance of acidogenic bacteria, hold great promise for improving the efficiency of acidogenesis. Additionally, improvements in reactor design and operational control systems will further enhance the scalability and stability of VFA recovery processes (Edwards & Smallwood, 2023, Elete, *et al*., 2023, Nwulu, *et al*., 2023). By optimizing acidogenic fermentation, it will be possible to unlock the full potential of anaerobically digested sludge liquors as a valuable source of VFAs, contributing to the development of more sustainable and resource-efficient waste treatment systems.

In conclusion, optimizing acidogenic fermentation is a crucial step in the recovery of volatile fatty acids from anaerobically digested sludge liquors. By carefully controlling operational parameters such as pH, temperature, HRT, and C/N ratio, it is possible to maximize VFA production while minimizing competition from methanogenic organisms. The use of inhibitors, microbial community engineering, and advanced process control strategies further enhances the efficiency of the fermentation process. As research in this area continues to advance, the potential for recovering valuable VFAs from waste sludge will play an increasingly important role in promoting resource recovery, circular economy principles, and sustainable industrial practices.

2.5 Solid-Liquid Separation Techniques

Solid-liquid separation is a critical step in the recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors. The objective of this process is to separate the liquid phase containing VFAs from the solid residue produced during anaerobic digestion. Efficient separation ensures that the VFA-rich liquid, which holds valuable organic compounds, can be further processed and utilized, while the solid waste can be appropriately treated or disposed of. Various solid-liquid separation techniques can be employed in this stage, each with specific advantages and challenges, depending on the characteristics of the sludge, the desired VFA concentration, and the overall efficiency of the separation process.

The primary goal of solid-liquid separation is to isolate the liquid phase that contains VFAs and other soluble components, such as organic matter, dissolved nutrients, and small particles, from the solid fraction, which is typically composed of larger particles, fibers, and undigested organic material. The liquors produced during anaerobic digestion contain a range of volatile fatty acids, including acetic acid, propionic acid, and butyric acid, which are produced during the acidogenesis stage (Afeku-Amenyo, *et al*., 2023, Fiemotongha, *et al*., 2023, Sobowale, *et al*., 2023). These acids represent a valuable source of carbon for various industrial applications, such as the production of bioplastics, solvents, and biofuels. Therefore, the separation of VFAs from the solid sludge is essential for optimizing the recovery and subsequent valorization of these valuable compounds.

Several solid-liquid separation methods are commonly used in the treatment of anaerobically digested sludge, including sludge thickening, dewatering, centrifugation, filtration, and gravity settling. Each of these techniques has its specific advantages depending on the characteristics of the sludge and the desired outcomes. The first step in the solid-liquid separation process typically involves sludge thickening. Sludge thickening is a process that concentrates the solids in the sludge by reducing the volume of water (Ayo-Farai, *et al*., 2023, Ezeanochie, Afolabi & Akinsooto, 2023). This is typically achieved through gravity-based settling or the addition of chemicals, such as polyelectrolytes, that promote flocculation. The goal of thickening is to increase the solid content of the sludge, making it easier to handle and process further. However, thickened sludge still contains a significant amount of water, which means that additional separation steps are required to remove the remaining liquid phase and recover the VFAs.

Dewatering is a subsequent process that reduces the water content of the thickened sludge. Dewatering techniques typically include mechanical processes such as filter pressing, centrifugation, and screw presses. These methods work by applying mechanical forces to force water out of the sludge, resulting in a more solid, manageable residue. Dewatering is particularly useful for reducing the volume of the sludge, making it easier to transport or dispose of, but it does not typically result in a high concentration of VFAs in the liquid phase (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Ogunnowo, *et al*., 2022). While dewatering removes a substantial portion of the water, some of the VFAs will still be trapped within the solid fraction, requiring further separation to recover the liquid that contains the highest concentration of valuable acids.

Centrifugation is one of the most effective methods for solid-liquid separation in the context of VFA recovery. This technique relies on centrifugal force to separate particles from the liquid phase based on their density. When a mixture of solid and liquid is placed in a centrifuge, the solid particles are pushed outward toward the perimeter of the centrifuge bowl, while the liquid remains closer to the center. Centrifugation can achieve very fine separation, allowing for the isolation of a liquid phase that contains a high concentration of VFAs. Additionally, centrifugation can be used to separate various fractions of the sludge based on particle size, enabling the targeted recovery of the VFA-rich liquid (Adeoba & Yessoufou, 2018, Oyedokun, 2019, Uzozie, *et al*., 2023). One of the advantages of centrifugation is its ability to process large volumes of sludge rapidly, making it a scalable and efficient technique for VFA recovery in industrial settings. However, centrifugation systems can be expensive to operate and maintain, as they require significant energy input and specialized equipment.

Filtration is another technique commonly used for solid-liquid separation in wastewater treatment and VFA recovery. Filtration works by passing the sludge through a filter medium, such as a membrane or fabric, which

physically separates the solid particles from the liquid phase. The choice of filtration method depends on the particle size of the solids and the desired level of separation. For example, microfiltration and ultrafiltration are commonly used to separate finer particles, while coarse filtration methods can be used for larger solids (Ojika, *et al*., 2023, Okolo, *et al*., 2023, Okuh, *et al*., 2023). Filtration can be particularly effective for separating VFAs from the sludge liquor because it can selectively retain particles while allowing the liquid containing dissolved VFAs to pass through. One of the advantages of filtration is its relatively low energy consumption compared to centrifugation, but it may have lower capacity and efficiency in handling large volumes of sludge. Additionally, the choice of filtration membrane or medium is crucial, as membrane fouling can reduce efficiency and increase operational costs over time.

Gravity settling is a simpler and more passive method for separating solid and liquid phases in wastewater treatment. In this process, sludge is allowed to settle under the influence of gravity, and the supernatant liquid is then decanted off. While gravity settling is energy-efficient and easy to implement, it is less effective in separating smaller particles or extracting VFAs from the liquid phase (Adewoyin, 2022, Elete, *et al*., 2022, Nwulu, *et al*., 2022). The settling process is often used in conjunction with other separation techniques, such as centrifugation or filtration, to enhance the overall recovery of VFAs. Gravity settling is more commonly employed for the initial thickening of sludge, after which more efficient methods, such as centrifugation or filtration, are used to further separate the liquid and solid phases.

After the solid-liquid separation, the liquid phase that remains contains dissolved organic compounds, including the VFAs of interest. However, the concentration of VFAs in this liquid may still be relatively low, and additional steps may be required to concentrate the VFAs before they are extracted. Membrane-based technologies, such as reverse osmosis or nanofiltration, can be employed to concentrate the VFAs by selectively removing water and other dissolved compounds from the liquid (Afolabi & Akinsooto, 2023, Hanson, *et al*., 2023, Ogunwole, *et al*., 2023). These technologies work by applying pressure to force water through a semi-permeable membrane, leaving behind the more concentrated VFA solution. Membrane filtration can significantly increase the concentration of VFAs in the liquid phase, making it easier to recover and extract these valuable compounds in subsequent stages of the process.

The concentration of VFAs in the liquid phase is a key factor that influences the efficiency of VFA recovery processes. By optimizing the solid-liquid separation techniques, industries can increase the concentration of VFAs, which improves the overall yield of the recovery process and makes it more economically viable. For instance, by combining centrifugation, filtration, and membrane filtration, industries can obtain a VFA-rich liquid that is suitable for selective extraction, leading to a higher recovery rate and improved product quality (Daraojimba, *et al*., 2023, Gidiagba, et al., 2023, Onukwulu, et al., 2023). The ability to concentrate VFAs in the liquid phase is particularly important when dealing with large volumes of wastewater or digestate, as it enables the efficient recovery of these valuable compounds.

In conclusion, solid-liquid separation is a critical stage in the recovery of volatile fatty acids from anaerobically digested sludge liquors. Techniques such as sludge thickening, dewatering, centrifugation, filtration, and gravity settling play essential roles in isolating the VFA-rich liquid from the solid fraction. The optimization of these separation methods is crucial for enhancing the efficiency of the VFA recovery process, as it ensures that the liquid phase containing the highest concentration of VFAs is separated and can be further processed. As technologies such as membrane filtration and advanced centrifugation continue to improve, the overall effectiveness and economic feasibility of VFA recovery from anaerobically digested sludge liquors will continue to evolve, providing significant benefits in terms of resource recovery and sustainability in industrial wastewater treatment.

2.6 Selective VFA Recovery Technologies

Selective recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors plays a crucial role in maximizing the value of organic waste materials while also contributing to the sustainability of waste treatment processes. As VFAs are valuable intermediates in the production of biofuels, bioplastics, and other chemicals, efficiently recovering these acids from complex waste streams is essential for resource recovery and waste valorization. Various selective VFA recovery technologies have been developed to isolate and concentrate VFAs from sludge liquors, each with unique mechanisms and advantages. These technologies are critical for optimizing the recovery process, ensuring high purity and yield of VFAs, and enhancing the economic feasibility of their recovery.

One of the key technologies employed for selective VFA recovery is the use of membrane contactors. Membrane contactors are a class of separation devices that enable the selective transfer of VFAs from the aqueous phase to a non-aqueous phase, typically an organic solvent, without the need for traditional dispersion or phase mixing. This technology relies on the use of a hydrophobic membrane that separates the aqueous phase containing VFAs from the organic solvent. The VFAs are transferred through the membrane based on their affinity for the solvent, which selectively extracts them from the aqueous phase (Banso, *et al*., 2023, Ezeanochie, Afolabi & Akinsooto, 2023). This method allows for high selectivity and efficiency, as the membrane provides a stable interface between the phases, facilitating mass transfer without requiring mechanical mixing or large amounts of energy. Additionally, membrane contactors are relatively simple to operate and offer the advantage of being scalable for industrial applications.

The non-dispersive phase separation of membrane contactors reduces the risk of fouling, which is a common challenge in other separation methods, such as filtration or adsorption. Fouling occurs when particles, organic matter, or biofilms accumulate on the surface of the separation medium, reducing its efficiency. The use of membrane contactors mitigates this issue because the membrane's structure prevents the accumulation of solids and allows for continuous recovery of VFAs over extended periods (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2023, Ogunnowo, *et al*., 2023). Moreover, membrane contactors can be integrated into larger, multi-stage recovery systems, allowing for the selective extraction of different VFAs in sequence, based on their chemical properties. This capability makes membrane contactors an attractive option for

applications that require high purity or specific VFA recovery from complex mixtures.

Ion exchange and adsorption resins are also commonly used for selective VFA recovery due to their high specificity and ability to concentrate target compounds from aqueous solutions. Ion exchange resins are materials that can exchange ions from the aqueous phase with those on the resin surface. In the case of VFA recovery, resins with functional groups that have a high affinity for specific VFAs are employed (Agho, *et al*., 2023, Ezeamii, *et al*., 2023, Ogu, *et al*., 2023). These resins selectively adsorb the VFAs based on their ionic properties, allowing for the concentration and separation of VFAs from the rest of the liquid phase. One of the major advantages of ion exchange resins is their high selectivity, which enables the recovery of specific VFAs, such as acetic or propionic acid, with minimal loss of other compounds.

The regeneration potential of ion exchange resins is another important feature that enhances their economic viability. After the resin becomes saturated with VFAs, it can be regenerated by washing it with a suitable elution solution, such as a high-concentration acid or base, which displaces the adsorbed VFAs and restores the resin for reuse (Akintobi, Okeke & Ajani, 2022, Kanu, *et al*., 2022, Onukwulu, *et al*., 2022). This regeneration process makes ion exchange resins an environmentally and economically sustainable solution, as they can be recycled multiple times, reducing the need for frequent replacement and minimizing waste.

However, the use of ion exchange resins for VFA recovery is not without challenges. For example, the capacity of the resins can be influenced by the presence of competing ions in the solution, such as sodium, calcium, or magnesium, which can reduce the resin's efficiency. Additionally, the recovery of VFAs using ion exchange resins requires careful management of flow rates, resin contact time, and the concentration of elution solutions to ensure optimal recovery and regeneration (Ajayi, *et al*., 2023, Isong, *et al*., 2023, Nwulu, *et al*., 2023). Despite these challenges, ion exchange and adsorption resins remain a popular and effective technology for selective VFA recovery, particularly when high specificity is required.

Electrodialysis and forward osmosis are other promising technologies for selective VFA recovery, particularly for charged VFAs. Electrodialysis is a membrane-based process that uses an electric field to drive the movement of ions across selective ion-exchange membranes, allowing for the separation of positively and negatively charged ions. In the context of VFA recovery, electrodialysis can be used to selectively separate charged VFAs, such as acetate, propionate, and butyrate, from the liquid phase (Edwards, Mallhi & Zhang, 2018, Tula, *et al*., 2004, Vindrola-Padros & Johnson, 2022). The electric field facilitates the movement of the VFAs towards the respective electrodes, where they can be concentrated in a separate compartment. Electrodialysis has the advantage of being highly efficient and can achieve very high purity in the recovered VFAs. It also offers the benefit of low energy consumption when compared to traditional distillation or evaporation processes.

Forward osmosis, on the other hand, is a membrane filtration process that uses osmotic pressure differences between two solutions to drive water through a semi-permeable membrane. In this process, a draw solution with a high osmotic pressure is used to extract water from the VFA-rich liquor, leaving behind concentrated VFAs in the feed solution. This method is particularly advantageous for recovering VFAs from dilute solutions, as it does not require high-pressure pumps or complex filtration systems. Forward osmosis is also energy-efficient because it relies on natural osmotic pressure differences rather than mechanical forces, making it an attractive option for large-scale VFA recovery from waste streams (Ojika, *et al*., 2023, Okolo, *et al*., 2023, Olurin, *et al*., 2023). However, forward osmosis is still under development in the context of VFA recovery, and more research is needed to optimize its performance and scalability for industrial applications.

Solvent extraction is one of the most widely used methods for VFA recovery, especially when dealing with complex mixtures of VFAs and other organic compounds. In this process, an organic solvent is selected based on its ability to selectively dissolve VFAs, while leaving other compounds in the aqueous phase. The solvent is then mixed with the VFA-containing liquor, and the VFAs are transferred into the organic phase, where they can be separated and concentrated. After the extraction process, the VFAs can be recovered by separating the organic solvent from the VFA solution, typically through distillation or evaporation (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Onukwulu, *et al*., 2022). One of the key challenges in solvent extraction is selecting the appropriate organic solvent that has a high affinity for VFAs and does not interfere with other components in the liquor. The solvent should also be easy to recover and recycle, minimizing environmental impact and operational costs.

The dynamics of phase separation in solvent extraction are influenced by various factors, such as temperature, pH, and the concentration of VFAs in the solution. For instance, temperature can significantly affect the solubility of VFAs in the organic solvent, with higher temperatures often promoting more efficient extraction. Similarly, the pH of the aqueous solution can influence the ionization state of the VFAs, affecting their solubility and the efficiency of the extraction process (Adeoba, etal., 2018, Omisola, *et al*., 2020, Uzozie, *et al*., 2023). By carefully controlling these parameters, it is possible to optimize the solvent extraction process for maximum VFA recovery. Despite its effectiveness, solvent extraction requires careful management to minimize the use of hazardous solvents and ensure that the recovered VFAs meet quality standards for industrial applications.

In conclusion, selective VFA recovery technologies, such as membrane contactors, ion exchange resins, electrodialysis, forward osmosis, and solvent extraction, offer promising solutions for isolating and concentrating VFAs from anaerobically digested sludge liquors. Each technology has unique advantages, such as high selectivity, efficiency, and low energy consumption, which make them suitable for different VFA recovery applications. By selecting the appropriate technology based on the characteristics of the sludge, the desired VFA profile, and the scalability of the process, industries can maximize the recovery of these valuable compounds and contribute to the development of more sustainable and circular waste treatment systems. As these technologies continue to evolve, they will play an increasingly important role in the resource recovery landscape, helping to meet the growing demand for sustainable chemicals and biofuels.

2.7 Valorization Pathways for Recovered VFAs

Valorization of recovered volatile fatty acids (VFAs) represents a critical step in the sustainable use of waste products and the development of a circular economy. VFAs are intermediates in the anaerobic digestion process and hold significant potential for creating valuable products when extracted and transformed efficiently. Once recovered from anaerobically digested sludge liquors, these acids can be converted into a wide range of valuable products, including bioplastics, solvents, biofuels, and specialty chemicals. Valorization not only helps offset the costs associated with waste treatment but also contributes to reducing dependence on fossil-derived resources, fostering sustainability in industrial processes. This process involves several pathways, including biological, chemical, and integrated approaches within existing biorefinery or wastewater treatment infrastructure.

One of the primary valorization pathways for recovered VFAs is their biological conversion into bioplastics, specifically polyhydroxyalkanoates (PHAs). PHAs are a class of biodegradable plastics that are produced by microorganisms as intracellular carbon and energy storage compounds. They have gained significant attention as a sustainable alternative to conventional petroleum-based plastics due to their biodegradability and environmental benefits. VFAs, particularly short-chain VFAs such as acetic acid, propionic acid, and butyric acid, are excellent substrates for the microbial production of PHAs (Daraojimba, *et al*., 2023, Ezeh, *et al*., 2023, Olurin, *et al*., 2023). By feeding these VFAs to specific bacteria, such as *Cupriavidus necator* or *Pseudomonas putida*, microorganisms can convert VFAs into PHAs through a fermentation process. This biotechnological pathway offers several advantages, including the use of renewable resources and the ability to produce biodegradable plastics that can help address the growing issue of plastic pollution.

The process of PHA production from VFAs involves the accumulation of VFAs within the microbial cells, which are subsequently converted into polymers by enzymes that polymerize the monomers into long chains. The type of VFA used can influence the properties of the resulting PHA, such as its crystallinity, thermal properties, and mechanical strength. For example, the use of mixed VFAs from anaerobic digestate allows for the production of a diverse range of PHA polymers with tailored characteristics, providing opportunities for customization based on the application requirements (Adeoba, Tesfamichael & Yessoufou, 2019, Ubamadu, *et al*., 2023). The biological conversion of VFAs into PHAs thus offers a promising route to valorizing waste while providing a sustainable alternative to petrochemical-derived plastics. By integrating this process with existing wastewater treatment plants or biorefineries, industries can reduce costs, generate value-added products, and contribute to environmental sustainability.

In addition to bioplastics, another valuable pathway for VFA valorization is their chemical upgrading to esters, alcohols, and other specialty chemicals. VFAs are highly reactive compounds due to their carboxylic acid functional group, making them ideal feedstocks for chemical conversion processes. For instance, the esterification of VFAs with alcohols can yield various esters, which are used in a wide range of applications, including as solvents, flavorings, fragrances, and plasticizers (Onukwulu, *et al*., 2023, Onyeke, *et al*., 2023, Oyeyipo, *et al*., 2023). Acetic acid, one of the most common VFAs, can be converted into esters such as ethyl acetate, a solvent used in paints, coatings, and adhesives. Similarly, propionic acid can be transformed into esters like propyl acetate, which is used as a solvent in the formulation of coatings and inks.

The chemical conversion of VFAs into alcohols is another valuable pathway. For example, the reduction of acetic acid can yield ethanol, which is a renewable biofuel used in the transportation sector. Butyric acid, another common VFA, can be converted into butanol, a high-value alcohol with applications in the production of biofuels, plastics, and solvents. Butanol can be produced through chemical methods, such as hydrogenation or via fermentation processes. The chemical upgrading of VFAs into alcohols and esters not only creates valuable products but also provides an opportunity to integrate renewable feedstocks into the chemical industry, reducing reliance on petroleum-based raw materials (Agbede, *et al*., 2023, Iwe, *et al*., 2023, Obianyo & Eremeeva, 2023).

In addition to esters and alcohols, VFAs can also be converted into other specialty chemicals, such as biopolymers, surfactants, and industrial acids. The versatility of VFAs in chemical synthesis makes them an attractive feedstock for a variety of high-value applications, allowing industries to diversify their product portfolios and generate additional revenue streams from waste materials. The chemical conversion of VFAs can be achieved through a range of processes, including esterification, hydrogenation, and fermentation, depending on the desired product (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2023, Nwulu, *et al*., 2023). These conversion processes are relatively well-established in the chemical industry, providing a solid foundation for the large-scale implementation of VFA valorization strategies.

A third important valorization pathway for VFAs involves integrating their recovery and conversion into existing biorefinery or wastewater treatment infrastructure. Biorefineries are facilities that process renewable feedstocks, such as agricultural waste, biomass, or waste products, into biofuels, chemicals, and other value-added products. By incorporating VFA recovery and valorization into biorefinery systems, industries can create a more sustainable and efficient process that reduces waste, lowers energy consumption, and generates additional revenue streams (Ajiga, Ayanponle & Okatta, 2022, Noah, 2022, Ogundipe, Sangoleye & Udokanma, 2022). The integration of VFA recovery into wastewater treatment plants, in particular, offers significant potential for improving the overall sustainability of water treatment processes.

Anaerobic digestion, a key component of many wastewater treatment systems, produces VFAs as intermediate products during the breakdown of organic matter. Currently, most anaerobic digestion processes focus on methane production as the primary value product. However, by incorporating a VFA recovery stage into the treatment process, these systems can be optimized to produce not only biogas but also valuable VFAs, which can be used for further conversion into bioplastics, chemicals, or biofuels (Akintobi, Okeke & Ajani, 2023, Izuka, *et al*., 2023, Onukwulu, *et al*., 2023). Integrating VFA recovery into existing infrastructure minimizes the need for additional equipment or infrastructure, reducing the overall investment required for valorization. Furthermore, wastewater treatment

plants typically have access to a continuous supply of organic waste, making them an ideal setting for large-scale VFA production.

In addition to biorefineries and wastewater treatment plants, other industrial processes, such as food processing, agriculture, and pulp and paper mills, can also serve as potential sites for VFA recovery and valorization. These industries generate large amounts of organic waste, which can be converted into VFAs through anaerobic digestion. By integrating VFA recovery into these processes, industries can not only reduce waste and improve resource efficiency but also produce valuable products that contribute to the circular economy (Onaghinor, *et al*., 2021, Orieno, *et al*., 2022, Sobowale, *et al*., 2022). This integrated approach aligns with global sustainability goals and offers a pathway for industries to reduce their environmental footprint while generating economic value.

The valorization of VFAs also supports the broader goal of achieving a circular economy, where waste is treated as a resource rather than a liability. By recovering and transforming VFAs into valuable products, industries can close the loop on waste treatment processes, ensuring that the by-products of industrial activities are reused rather than disposed of. This approach not only reduces waste but also helps to reduce the reliance on non-renewable resources, such as petroleum, and mitigates the environmental impact of industrial operations (Onyeke, *et al*., 2022, Orieno, *et al*., 2021, Ubamadu, *et al*., 2023). In this way, VFA recovery and valorization can play a key role in advancing sustainable industrial practices and contributing to the development of a more sustainable and resource-efficient economy.

In conclusion, the valorization of recovered VFAs from anaerobically digested sludge liquors offers a promising pathway to sustainable resource recovery. Biological conversion to bioplastics, chemical upgrading to esters and alcohols, and integration into biorefinery and wastewater treatment infrastructure provide valuable opportunities for the efficient use of waste materials. These valorization pathways not only create valuable products but also contribute to reducing waste, minimizing environmental impact, and promoting the development of a circular economy. As technology continues to advance and the demand for sustainable products increases, VFA recovery and valorization will play an increasingly important role in shaping the future of waste treatment and resource management.

2.8 Sustainability, Techno-Economic, and Lifecycle Considerations

The recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors holds significant promise for enhancing the sustainability and economic viability of wastewater treatment processes. As industries and municipalities strive to meet environmental targets and reduce their carbon footprints, the recovery and valorization of waste by-products like VFAs become increasingly important. These acids, produced during the anaerobic digestion of organic matter, represent a valuable resource that can be transformed into bioplastics, solvents, biofuels, and other high-value chemicals. A conceptual model for the recovery of VFAs from anaerobically digested sludge liquors must be assessed not only on its technical feasibility but also on its sustainability, techno-economic viability, and lifecycle impacts.

The sustainability of any technology or process is intrinsically linked to its energy and material balance. In the context of VFA recovery, energy consumption is a critical consideration, as the recovery process should not exceed the energy savings or revenue generated from the VFAs. A holistic analysis of the energy balance includes not only the energy required for the extraction and concentration of VFAs but also the energy savings that may arise from the diversion of organic waste to a useful product rather than disposal (Ojika, *et al*., 2023, Ojo, *et al*., 2023, Okolo, *et al*., 2023). This analysis is essential to determine whether the recovery process itself is energy-positive, contributing to the overall reduction of energy consumption in wastewater treatment or related processes.

For example, the process of anaerobic digestion itself produces biogas, primarily methane, which can be utilized for power generation or as a renewable fuel source. The integration of VFA recovery into this process could potentially lead to a more efficient use of organic carbon. The VFAs recovered could serve as valuable chemical feedstocks for bioplastics, solvents, or biofuels, which in turn could replace fossil-derived chemicals. Additionally, certain technologies used in VFA recovery, such as membrane filtration or electrodialysis, can be energy-intensive, requiring a careful evaluation of their overall energy consumption (Egbuhuzor, *et al*., 2023, Fiemotongha, *et al*., 2023, Nwulu, *et al*., 2023). A well-designed system will need to minimize energy losses and ensure that the energy required for VFA recovery is balanced by the energy produced through biogas generation or the subsequent use of recovered VFAs. Optimizing the material flow, ensuring efficient recovery, and minimizing waste throughout the process are essential components of achieving a sustainable and energy-efficient system.

Cost-effectiveness and return on investment (ROI) are fundamental to the adoption and scaling of VFA recovery technologies. While the technical potential of VFA recovery is well-established, its economic viability is a significant barrier for widespread implementation. The initial capital investment required for implementing VFA recovery systems, including the installation of specialized equipment such as membrane contactors, filtration units, or electrodialysis systems, can be substantial (Agho, *et al*., 2023, Ezeamii, *et al*., 2023, Nwankwo & Etukudoh, 2023). Furthermore, operational costs associated with energy consumption, maintenance, and labor must be considered. However, the costs associated with these investments can be offset by the revenue generated from the sale of recovered VFAs, which can be used as feedstocks for high-value products like biofuels, bioplastics, and industrial chemicals.

Moreover, VFA recovery can improve the efficiency of wastewater treatment plants by reducing the volume of sludge that needs to be disposed of, leading to potential savings in disposal costs. Additionally, the integration of VFA recovery into existing wastewater treatment plants offers the potential for improved overall plant performance and reduced environmental impacts, which can further enhance the return on investment. The economic viability of VFA recovery depends on several factors, including the local market value of recovered VFAs, government incentives, and regulatory frameworks that support the adoption of sustainable technologies (Ajayi, *et al*., 2020, Ofori-Asenso, *et al*., 2020). A thorough techno-economic analysis, considering both direct and indirect costs and

benefits, is essential to assess the long-term profitability of VFA recovery.

Another important consideration when evaluating the sustainability of VFA recovery technologies is their environmental impact, particularly in terms of greenhouse gas (GHG) emissions. Anaerobic digestion is already recognized as a sustainable waste treatment process due to its ability to convert organic waste into biogas, a renewable energy source. By adding VFA recovery to the process, the environmental impact could be further reduced by enhancing the recovery of valuable compounds from waste rather than allowing them to remain in the digestate or be lost in the effluent (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Nwulu, *et al*., 2022). VFAs, when used as raw materials for bioplastics or biofuels, can significantly reduce the reliance on fossil fuels, contributing to a reduction in GHG emissions across the supply chain.

The recovery of VFAs also mitigates the environmental burden of waste disposal. In many regions, large quantities of sludge generated during wastewater treatment must be landfilled or incinerated, both of which contribute to GHG emissions. By recovering valuable products such as VFAs, the need for waste disposal is minimized, thereby reducing the carbon footprint associated with waste management (Ojika, *et al*., 2023, Okolo, *et al*., 2023, Okuh, *et al*., 2023). Additionally, using VFAs in the production of bioplastics and biofuels can displace the use of petrochemicals, which are responsible for significant environmental impacts, including carbon emissions, resource depletion, and pollution. Therefore, the integration of VFA recovery not only reduces GHG emissions directly associated with wastewater treatment but also contributes to broader environmental sustainability goals.

The compatibility of VFA recovery systems with existing wastewater treatment plants is a key factor in determining their widespread adoption. Many wastewater treatment facilities are already under significant operational constraints and may face challenges in integrating new technologies without disrupting existing processes. Therefore, the conceptual model for VFA recovery must consider how it can be integrated into existing infrastructure with minimal disruption, while improving the overall performance of the plant (Onukwulu, *et al*., 2023, Onyeke, *et al*., 2023, Ozobu, *et al*., 2023). This can be achieved by adopting modular, scalable solutions that can be added to existing treatment systems incrementally, reducing the need for large upfront capital investments and ensuring that the plant can continue to function efficiently during the integration process.

The integration of VFA recovery into existing wastewater treatment plants can also improve the sustainability of these facilities by providing an additional revenue stream from recovered VFAs. This could offset the cost of the technology itself, making it more attractive to plant operators and municipalities. Moreover, as regulations around resource recovery and sustainability continue to tighten, the adoption of VFA recovery can help facilities meet stricter environmental standards and contribute to achieving sustainability goals (Adeoba & Yessoufou, 2018, Oyedokun, 2019, Uzozie, *et al*., 2023). For example, in many regions, regulatory frameworks are evolving to support the recovery and reuse of waste products, such as VFAs, rather than allowing them to be discarded as waste. The ability to comply with these regulations can provide economic and environmental benefits to plant operators, enhancing the overall feasibility of VFA recovery technologies.

Lifecycle assessment (LCA) is an essential tool for evaluating the overall sustainability of VFA recovery technologies. LCA considers the environmental impacts associated with every stage of a product's life, from raw material extraction to production, use, and disposal. For VFA recovery, this means assessing the environmental footprint of the entire recovery process, including energy consumption, emissions, and waste generation (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Ogunnowo, *et al*., 2022). By conducting a thorough LCA, it is possible to identify potential areas for improvement, such as optimizing energy use, reducing emissions, or minimizing waste. LCA can also help determine the net environmental benefits of recovering VFAs, such as the reduction in GHG emissions or the displacement of fossil fuels, providing a comprehensive picture of the sustainability of the technology.

In conclusion, the recovery of volatile fatty acids from anaerobically digested sludge liquors offers a promising pathway for enhancing the sustainability, techno-economic viability, and environmental performance of wastewater treatment processes. By optimizing energy and material balances, ensuring cost-effectiveness, and minimizing environmental impacts, VFA recovery technologies can contribute significantly to the circular economy and resource recovery (Ayo-Farai, *et al*., 2023, Ezeanochie, Afolabi & Akinsooto, 2023). The integration of VFA recovery into existing wastewater treatment plants can provide multiple benefits, including reduced waste, increased revenue, and improved sustainability. As research and development in this area continue to progress, VFA recovery will play an increasingly important role in achieving sustainable water treatment and contributing to broader environmental and economic goals.

2.9 Conclusion, Challenges and Research Gaps

The recovery of volatile fatty acids (VFAs) from anaerobically digested sludge liquors offers significant potential for advancing the sustainability of wastewater treatment processes while enabling the recovery of valuable products from waste. The conceptual model outlined for the VFA recovery process integrates a series of technologies and methodologies aimed at optimizing acidogenic fermentation, enhancing VFA extraction, and ensuring that the recovery process is both economically viable and environmentally beneficial. By focusing on key stages such as acidogenic fermentation optimization, solid-liquid separation, selective VFA extraction, and downstream valorization, this model demonstrates a promising pathway for achieving resource recovery in the context of wastewater treatment.

Despite its potential, there are several challenges and research gaps that must be addressed to fully realize the benefits of VFA recovery from anaerobic digestion. One of the primary challenges is the recovery efficiency and selectivity of VFAs. Given the complex composition of the anaerobically digested sludge liquors, which contain a mixture of VFAs, organic matter, nutrients, and other compounds, the separation and concentration of specific VFAs in an efficient manner remains a significant hurdle. Techniques such as membrane filtration, electrodialysis, and

solvent extraction are commonly used, but each has limitations in terms of recovery efficiency, selectivity, and energy consumption. Achieving high purity and recovery of individual VFAs, while minimizing losses, is essential for making the recovery process economically viable. Further optimization of these separation technologies is needed to improve selectivity and minimize operational costs.

Another key challenge is the issue of biofouling and membrane degradation, particularly in membrane-based technologies such as membrane contactors and electrodialysis. Biofouling occurs when microorganisms, organic matter, or particulates accumulate on the membrane surface, reducing the efficiency of the process and increasing maintenance requirements. Membrane degradation, which occurs over time due to exposure to chemicals, high pressures, or temperature variations, can also compromise system performance. Developing more robust, self-cleaning, and durable membrane materials will be crucial to minimizing these challenges and ensuring the long-term stability of VFA recovery processes.

Scalability and process stability represent additional challenges for VFA recovery. While laboratory-scale studies have demonstrated the technical feasibility of VFA recovery, scaling these processes to industrial and municipal levels poses challenges related to system complexity, operational consistency, and cost management. The integration of VFA recovery into existing wastewater treatment plants requires careful consideration of the capacity, flow rates, and treatment processes already in place. Systems that can adapt to varying waste characteristics and operational conditions without compromising recovery efficiency or plant performance are essential for large-scale implementation. Developing modular, flexible, and scalable recovery systems that can be easily integrated into existing infrastructure will be a key factor in the widespread adoption of VFA recovery technologies.

The need for pilot-scale demonstrations is also critical for validating the conceptual model and identifying real-world limitations and potential solutions. While theoretical models and small-scale studies provide valuable insights, they often fail to capture the complexities of large-scale operations, including variations in influent quality, seasonal fluctuations, and operational challenges. Pilot-scale demonstrations provide an opportunity to test the proposed recovery technologies in real-world settings, assess their economic viability, and refine the model based on practical data. These trials are essential for generating the data needed to support full-scale implementation and to determine the long-term sustainability of the process.

Despite these challenges, the potential benefits of VFA recovery are substantial. The ability to recover and valorize VFAs from wastewater treatment not only contributes to reducing waste and lowering operational costs but also provides a pathway to generating valuable by-products that can be used in various industrial applications. VFAs can be converted into bioplastics, solvents, biofuels, and other chemicals, promoting a circular economy where waste is viewed as a resource rather than a liability. Moreover, integrating VFA recovery into existing wastewater treatment plants can improve the overall sustainability of these facilities by reducing waste disposal costs, lowering energy consumption, and contributing to the production of renewable products.

Addressing the challenges associated with VFA recovery will require interdisciplinary research and collaboration among experts in wastewater treatment, microbiology, chemical engineering, and materials science. Research should focus on optimizing fermentation processes to increase VFA yields, developing new membrane materials and separation techniques to enhance recovery efficiency, and exploring novel methods for valorizing recovered VFAs into high-value products. Additionally, greater focus should be placed on the environmental and economic assessments of VFA recovery technologies, including lifecycle analyses and cost-benefit evaluations, to ensure that the recovery process is not only technically feasible but also economically viable in the long term.

In conclusion, the recovery of volatile fatty acids from anaerobically digested sludge liquors represents a promising avenue for advancing sustainable wastewater management and resource recovery. The conceptual model outlined for this process provides a comprehensive framework that integrates fermentation optimization, selective extraction, and downstream valorization, creating opportunities for the circular economy. However, several challenges remain, including improving recovery efficiency, reducing biofouling, ensuring scalability, and validating the model through pilot-scale demonstrations. Overcoming these challenges through continued research and technological development will enable the full potential of VFA recovery to be realized, making a significant contribution to sustainable resource management and the transition to a circular economy.

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