Extraction and Purification of Volatile Fatty Acids

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Volatile fatty acids (VFA) are intermediary degradation products during anaerobic digestion (AD) that are subsequently converted to methanogenic substrates, such as hydrogen (H_2), carbon dioxide (CO_2), and acetic acid (CH_3COOH). VFA recovered from the AAD fermentation can be further converted to sustainable biofuels and bioproducts. This text describes the latest developments in the extraction techniques of VFA from complex organic materials.

arrested anaerobic digestion (AAD) waste valorization volatile fatty acids (VFA)
high-value bio-products VFA extraction

1. Introduction

Volatile fatty acids (VFA) are intermediates produced during anaerobic digestion (AD) and have a high market value due to their wide range of applications from food to chemicals, textiles, pharmaceuticals, energy, and materials, including bioplastics [1][2]. VFA are short-chained organic fatty acids comprising C2-C6 carbon atoms, such as acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid [2][3][4] traditionally produced from fossil fuels. Due to their versatility, they are in high demand, with an estimated global market of 18.5 million tons in the year 2020 and is projected to rise annually by 3% [5]. Meeting the rising demand with fossil fuel-based pathways has deleterious effects on the climate due to the simultaneous production of greenhouse gases (GHGs). On the contrary, organic wastes rich in lignocelluloses such as green and food waste, and agricultural residues such as straw and manure have an untapped potential of being ideal substrates to produce VFA due to their high carbon content. Bio-based approaches such as anaerobic fermentations offer a sustainable alternative to produce VFA than the petrochemical pathways whose carbon footprint is higher and uses fossil fuel-based resources as raw material, depleting and over exploiting the planet's non-renewable energy reserves [2]. VFA can further serve as platform molecules to produce biofuels, biochemicals, and biomaterials through various upgrading and conversion pathways based on catalytic reactions. Currently, the sugar platform [6][7][8][9][10][11] is one of the main routes investigated and commercialized for liquid biofuel production through fermentation. Sugar platform involves fermenting pure sugars to ethanol and subsequently to liquid biofuel. Though this pathway has high yield (0.46 g ethanol/g sugar), it is hindered by high costs involved with enzymes, pretreatment, and need for high sugar content biomass [4][12][13]. While the VFA platform is still an emerging technology, it needs further development for higher process yield (g VFA/g substrate), productivity (g VFA/L-day), and cost-effective energy-efficient separation methods to recover VFA from the fermentation broth with residual materials from the raw material input [4][14].

2. Extraction and Purification of VFA

VFA in the fermenter require safe extraction that does not disturb the microbial process for practical applications. In addition, continuous extraction of VFA will prevent product inhibition and acid-induced stress on microbes, thus avoiding microbial toxicity and maintaining consistent microbial performance for improved productivity [15][16]. Separation of VFA usually involves more than one stage: (1) Primary extraction stage that removes VFA from the fermentation broth and (2) Secondary purification stage to purify the VFA and concentrate them for potential sale in the market or for upgrading. The current default techniques for VFA purification are traditional distillation, evaporation, and crystallization [17]. However, due to the low dilute acid concentrations in the fermentation broth, evaporating large volume of water is required, making these techniques energy-intensive and expensive [17][18]. Liquid–liquid extraction (LLE) [19] is a separation method based on the affinity of target species (VFA) and requires using a solvent and sometimes a cosolvent [20]. Though LLE has demonstrated high efficiencies in extracting VFA, the process is not environmentally friendly and needs an additional stage to recover the spent solvent, where solvent losses can significantly increase the operational costs of the separation process [21][22]. Other factors such as solvent toxicity, cost, ease of regeneration and selectivity are some of the limitations of this process. In a recent study, hydrophobic deep eutectic solvents (HDES), a new generation of water-immiscible designer solvents, were evaluated for their efficiency in extracting VFA from fermented wastewater. An efficiency of 88% was reported with a four-staged extraction operation with successful regeneration using vacuum evaporation. Hence, these HDES solvents present a greener way of extracting VFA due to their low cost, sustainable manufacturing, and non-toxic nature [16]. Several operations such as electrocoagulation [23], electrodialysis [24][25], adsorption [26][27][28], extractive distillation [29] and many other membrane-based operations [30] have been explored to extract VFA. While every tested method was feasible for separating the VFA, the process needs to be efficient and economical, including regenerating chemicals and materials used in multiple cycles. Membrane-based separation and adsorption using ion exchange resins are emerging technologies for recovering VFA directly from the fermentation broth [31][32]. The following sections will review VFA recovery using ion-exchange systems (**Table 1**) and membrane-based technologies (**Table 2**).

Table 1. Summary of recent works on VFA recovery using adsorption (ion-exchange).

Materials Used	VFA Recovered	Acid Recovery Efficiency (%)	Regeneration Method	References
Purolite A103S Plus	Ac, Bu	66.16	Not reported	[33]
Amberlyst A21	Total VFA	Up to 80	Not reported	[34]
Amberlite IRA-67	Ac, Bu, La	75	Thermal	[35]
Amberlite IRA-67, Dowex optipore L-493	Ac, Pr	Up to 85	Alkali wash	[26]
Amberlite FPA53	Ac	42.36	Strong alkali wash	[15]

Materials Used	VFA Recovered	Acid Recovery Efficiency (%)	Regeneration Method	References
Non-functionalized polystyrene-divinylbenzene-based resin	Total VFA	75.5	N_2 stripping	[27]
Activated Carbon	Ac, Bu	Up to 80	Not reported	[28]
Amberlite IRA-67	La	Not reported	Alkali wash	[36]

Operation Technique	VFA Recovered	Recovery Efficiency	Fouling/ Regeneration	Membrane Details	References
Vapor permeation	Total VFA	Up to 95%	Not reported	Trioctylamine-filled PTFE membrane; area—19.25 cm^2	[32]
Membrane extraction	Total VFA	Not reported	Water rinsing	Silicone membrane; area—24.3 m^2/L_{ferm}	[37]
Membrane extraction coupled with electrodialysis	Total VFA	Up to 98%	Alkali wash	PTFE membrane; membrane configuration—1,3 and 5 membranes stacked. Total active area of 64 cm^2, 192 cm^2 and 320 cm^2 respectively.	[38]
Membrane extraction	Total VFA	Up to 21.5%	Not reported	Silicone membrane; area—125 cm^2	[39]

2.1. Adsorption

Adsorption is a physicochemical method where the solute compound adheres to an added surface. Several studies have shown promising results for mixed VFA extraction using adsorption. Extraction of VFA is typically achieved using ion-exchange resins. VFA in the fermentation broth can be separated using anion exchange resin, where the unprotonated carboxyl group (negative charge) allows ionic bonding with the positively charged functional group [33]. Anion exchange resins are further classified into weak and strong base resins. Weak base anion resins are functionalized with a base group such as pyridine, imidazole and primary, secondary, or tertiary amine.

In contrast, strong base anion resins are predominantly functionalized with quaternary ammonium compounds [17]. A resin screening study studied 11 different anion resins and activated carbon for selective recovery of acetic acid and adsorption kinetics were developed [26] using model VFA solution in water. Resins functionalized by the tertiary amine group can adsorb the VFA as charge-neutral units to maintain neutrality and are usually preferred [27]. Amberlite^{TM} IRA-67, a weak base ion exchange resin, was successfully used to extract lactic acid successively, with no loss in adsorption capacity after resin regeneration. However, a loss in capacity for acetic acid extraction of 4.9% per reuse is observed [36]. Another important aspect of using ion-exchange resin is the opportunity to reduce end-product inhibition of VFA on its formation by continuously keeping the VFA concentration under the inhibitory levels for VFA. A 1.6-fold increase in acetic acid production using continuous in-situ extractive fermentation with the ion exchange resin Amberlite FPA 53 was found during homoacetogenic fermentation of H2 and CO2 with *Acetobacterium woodii* [15]. When studying resin re-generation and re-usability, several studies used VFA dissolved in pure water as model solutions to test the resins, and often no reduction in the adsorption capacity of the resin was noticed in these studies over extended periods [27]. Since fermentation of wet organic waste is very different from these model studies, it might be beneficial to identify the anions in the fermentation broth, which are responsible for resin exhaustion and eliminate these compounds wherever possible to prolong the operational time of the resin and decrease the need for regeneration. Deposition of salts inside the resin pores could further reduce the adsorption capacity of the resin and could be difficult to prevent for complex wastes, but this needs further study [36].

2.2. Membrane-Based Technologies

Several membrane-based technologies exist, such as vapor permeation membrane contactors [32] and membrane contactors for liquid–liquid extraction [19], which can be used to extract VFA. One of the drawbacks of using solvent extraction is the solvent toxicity to the organisms [3]. It is, therefore, important to avoid direct contact with the fermentation broth to the solvent [40]. However, it is proposed that energy demand can be lowered up to 70% using liquid–liquid extraction with a product recovery of 99% using solvents such as hexyl acetate and nonyl acetate [41]. Using synthetic VFA mixtures, Aydin, Yesil and Tugtas [32] tested air-filled and solvent-filled PTFE membranes for their effectiveness in removing VFA and found the highest efficiency of over 95% with PTFE-trioctylamine during VFA recovery. However, membranes are susceptible to severe fouling by suspended solids in the fermentation broth, which remains a challenge. A solvent-free membrane extraction, using water as an extractant and silicone membrane, has been proposed to solve the problems with fouling, which could solve the problems with existing membrane-based technologies [37]. Several other membrane operations such as nanofiltration, microfiltration, pervaporation, membrane contactors [30] and electrodialysis are still being explored but are hindered by high operational costs and the need for particle removal. VFA extraction from different model anaerobic effluents using various membrane technologies such as reverse osmosis (RO), nanofiltration (NF), forward osmosis and supported liquid membrane technology was evaluated where RO achieved the highest retention while permeance was highest in NF [42]. Green extraction of VFA is now trending research. In one recent study, membrane extraction was coupled with electrodialysis to avoid loss of nutrients in bioreactors while increasing the extraction efficiency of VFA. This study showed a recovery efficiency of up to 98% [38]. Several other studies employing energy-efficient extraction of VFA, such as solar-assisted membrane distillation (MD), pressure-driven operations [43], and electroactive membranes, show a promising result by overcoming the current challenges such as fouling, high energy use, and permeability selectivity [44].

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