Bioresource Technology 268 (2018) 773–786

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

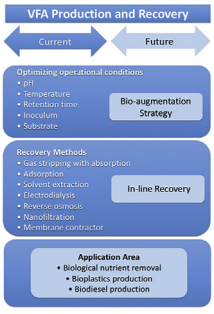
Review

Bio-based volatile fatty acid production and recovery from waste streams: Current status and future challenges

Merve Atasoy[a,1], Isaac Owusu-Agyeman[a,1], Elzbieta Plaza[b], Zeynep Cetecioglu[a,*]

[a] Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[b] Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Bio-based production
Recovery
Volatile fatty acid
Waste streams

ABSTRACT

Bio-based volatile fatty acid (VFA) production from waste-stream is getting attention due to increasing market demand and wide range usage area as well as its cost-effective and environmentally friendly approach. The aim of this paper is to give a comprehensive review of bio-based VFA production and recovery methods and to give an opinion on future research outlook. Effects of operation conditions including pH, temperature, retention time, type of substrate and mixed microbial cultures on VFA production and composition were reviewed. The recovery methods in terms of gas stripping with absorption, adsorption, solvent extraction, electrodialysis, reverse osmosis, nanofiltration, and membrane contractor of VFA were evaluated. Furthermore, strategies to enhance bio-based VFA production and recovery from waste streams, specifically, in-line VFA recovery and bioaugmentation, which are currently not used in common practice, are seen as some of the approaches to enhance bio-based VFA production.

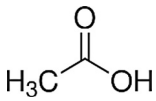
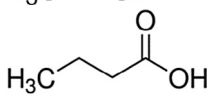
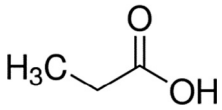
1. Introduction

Environmental sustainability is a goal for the 21st century and to accomplish it, transition into a circular economy which includes resource recovery, reuse and recycling is required. Resource recovery contributes to environmental sustainability by reducing the consumption of raw materials and decreasing amount of waste. Resource recovery from waste streams, which is dealing with United Nations Sustainable Development Goals 6 and 11, is a major research interest, further boosted by the alarming increase in worldwide pollution levels and climate change primarily caused by overuse of fossil fuels. Energy and feedstock demand should be accommodated by

* Corresponding author.
E-mail address: zeynepcg@kth.se (Z. Cetecioglu).
[1] Co-first authors.

https://doi.org/10.1016/j.biortech.2018.07.042
Received 21 May 2018; Received in revised form 6 July 2018; Accepted 8 July 2018
Available online 11 July 2018
0960-8524/ © 2018 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

Table 1
General properties of VFAs.

VFAs	Chemical formula	Market size (kton/year)	Market price (€/ton)	Usage/application	Production methods	References
Acetic acid		14000–17000	400–800	Vinyl acetate monomer (polymers, adhesives, dyes), Food additive, Solvent, Vinegar, Ester production, Chemicals	Chemical synthesis (carboxylation of methanol) and microbial fermentation (oxidative and anaerobic)	Bhatia and Yang (2017))
Butyric acid		90–105	1500–1650	Animal and human food additive, Chemical intermediate, Solvent, Flavouring agent	Chemical synthesis (oxidation of butyraldehyde), Extraction from butter, microbial fermentation	Zigová and Šturdík (2000)
Propionic acid		350–470	2000–2500	Esters used food industry as aroma additive, Food additive, flavoring, Pharmaceuticals, Animal feed supplement, Fishing bait additive	Chemical Synthesis (ethylene hydro formylation, carboxylation of ethylene, direct oxidation of hydrocarbons), by product of acetic acid manufacturing, microbial fermentation	Cheryan (2009)

renewable resources. This puts high demands on the development of next-generation wastewater treatment technologies to produce new chemicals and material from carbon-rich waste streams. This approach could include e.g. microbial consortia to procure energy and valuable products such as volatile fatty acids (VFAs) for downstream industrial applications. Therefore, new approaches are required to achieve the paradigm shift to a bio-based, circular economy.

VFAs are important building block chemicals with a greatly increasing market demand. VFA production is traditionally based on non-renewable petrochemical sources, causing serious negative health and environmental effects. Reported greenhouse gas (GHG) emissions from acetic acid production in the petrochemical industry are 3.3 t $CO_{2eq.}$/t for cradle-to-grave (by incineration without energy recovery). Given that in 2009 in the Energy Savings 2020 Report, the EU committed to reducing its GHG emissions by between 80% and 95% by 2050, this process needs to be replaced with one utilizing renewable sources and bio-based production methods.

Recently, VFA production and recovery are getting more attention due to their high potential as a renewable carbon source, wide range usage area in pharmaceutical, food, chemical industries, and a valuable raw material for products such as biogas (Begum et al., 2018a,b), biodiesel (Fortela et al., 2016), bioplastics (Fradinho et al., 2014; Venkateswar Reddy et al., 2014), biohydrogen (Sydney et al., 2018), electricity via microbial fuel cells (Zheng et al., 2017). Therefore, VFA recovery via anaerobic digestion is gaining traction as a research topic.

As the opposite of the linear economy which is established on "take, make and dispose" model of production, VFA recovery from waste streams is perfectly matched with the one type of circular economy that aimed to circulate at high quality in the production system without entering the biosphere to being restorative and regenerative by design. For example, while potential VFA production capacity of EU countries from dairy industry wastewater is projected as 10 Mt/year (acetic acid eq), an estimated 2 Mt of acetate, 1.28 Mt of butyrate and 1.54 Mt of propionate could be recovered annually. In the global scale, the values are 9.15 Mt acetate, 5.39 Mt butyrate and 6.47 Mt propionate. The calculations were done according to data from European Commission Statistics (http://ec.europa.eu/eurostat/data/database).

The total global market demand for acetic, butyric and propionic acids will be 18,500 kilotons in 2020 which includes; with growing at a compound annual growth rate (CAGR) of 4.27% of 18,296.90 kilotons acetic acids by 2023 (Mordor Intelligence, 2018) with growing at a 15.1% CAGR of 105 kilotons butyric acids in 2020 (Marketsandmarkets, 2018); and with growing at a CAGR of 2.7% of 470.0 kilotons propionic acids by 2020 (Research Grand View, 2018).

The main focus of this review was on VFA production from waste streams by mixed microbial culture and its recovery. There are many current studies from lab scale to pilot scale focusing on VFA production from different waste streams, however, most of them are limited in recovery approach and applications of VFA-rich streams. Most of these studies focused on operational factors which influence acidification. However, there are still barriers to prevent market scale VFA production from waste streams. Two main obstacles should be overcome: 1) Uncontrolled metabolic activities and persistence of methanogens in VFA production via bioprocess and 2) limitations in the recovery of the produced VFAs. Therefore, this review addresses not only recent developments of VFA production but also current challenges on the enhancement of VFA production and their recovery. Moreover, this review presents a critical evaluation of the future application of VFA-rich effluents.

2. VFA production

VFA is a valuable intermediate product produced by anaerobic digestion of substrate including waste streams such as primary sludge, waste activated sludge and food waste. Anaerobic digestion process involves a number of stages in which organic matter is broken down by a consortium of microorganisms in the absence of oxygen and usually lead to the formation of biogas with VFA as an intermediate product. In an anaerobic digestion process, VFA production can be promoted by shortening the reaction time to prevent methanogenesis. Adjusting pH above 8.0 or below 6.0 can also promote VFA production and inhibit the growth of methanogens. In lab scale studies, adding methanogenic inhibitor could also be used to inhibit methanogens and promote VFAs production (Liu et al., 2018; Zhou et al., 2018).

2.1. Properties of VFA

There are different types of VFAs with different properties and applications. A variety of VFAs is on the market including formic, acetic, propionic, butyric, valeric, caproic acid. In this review, the focus was mainly on most common VFAs produced from waste streams. These are acetic, propionic, butyric acids and they are summarized in terms of their chemical structure, market size, applications, properties and production methods in Table 1. In addition to their wide usage area in the chemical, pharmaceutical and food industries, each type of VFA has attractive properties which were given.

Acetic acid is a key building block to manufacture of paint, rubber, plastics, synthetic fibres, textile finishes, pesticides, polymer emulsions, paper coating, in the chemical industries and it is one of the major components of flavours, acidity regulators and preservatives used in the food and beverage industries. In addition to use as a raw material in the various industries, acetic acid producing bacteria are used as producers of certain foods, drinks and cellulose (Bhatia and Yang, 2017; Xu et al., 2011).

Propionic acid is used as a calcium and sodium salts, herbicides, flavours, fragrances, emulsions, environmentally friendly solvents for

coating formulations, artificial fruit flavours, modified synthetic cellulose fibres etc. Also, it can be used as a preservative for food (especially bread and other baked goods as its sodium or calcium salts), animal feed (directly or as its ammonium salt), and grains due to its inhibition of growth of mould and various bacteria. Moreover, propionic acid is not only favourable preservative but also the key element in the manufacturing of vitamin E (Babu, 2014; Moresi and Parente, 2014; Xu et al., 2011).

Butyric acid is the valuable biodiesel source. At the same time, it uses in the animal feeding sector both as a supplement and an antibiotic, due to it has anti-pathogenic properties and the regulations about a usage of antibiotics in the animal feeding. Therefore, it is accepted as a most efficient energy source for animals, especially for poultry and swine. Also, butyric acid is well known for its anticancer effects as it induces morphological and biochemical differentiation in a variety of cells (Xu and Jiang, 2011; Zacharof and Lovitt, 2014). The bio-based butyric acid production is growing due to the fact is it is approved a food flavouring agent (taste and aroma additive) by the U.S. Food and Drug Administration (FDA).

In general, VFAs are produced both synthetically from petrochemical derivatives and biologically through fermentation process. These large amount market demand of VFAs is supplied by about 90% petro-based production methods. Though the production methods for acetic, butyric and propionic acids depend on similar processes, they have some specific production methods. For instance, acetic acid is largely produced from fossil-based feedstocks through carboxylation of methanol (Maitlis et al., 1996; Qian et al., 2016) Even though there are bio-based production methods (oxidative and anaerobic fermentations), they have low productivities due to the inhibition of bacteria at low pH. In the acetic acid production by fermentation, the acetic acid bacteria are classified in ten genera in the family *Acetobacteriaceae*. Although a variety of bacteria can produce acetic acid, mostly members of *Acetobacter*, *Gluconacetobacter*, and *Gluconobacter* are used commercially (Raspor and Goranovič, 2008). Researchers are focused on improving acetic acid productivity by developing bacterial strains with optimised/improved the operation conditions. In butyric acids production, the most used one is chemical synthesis via oxidation of butyraldehyde, which is obtained from propylene derived from crude oil by oxo synthesis. Despite the chemical synthesis of butyric acid is preferred mainly because of its lower production cost and the availability of the starting materials, this way cannot be regarded as a natural product. Therefore, it is not used in the food or beverage industries (Hatti-Kaul et al., 2007). The other semi-chemical production method is extraction from butter which includes 2–4% butyric acid. However, the process is difficult and expensive. A third way is through fermentation which has garnered more attention due to both a growing consumer desire for organic and natural products and a continuous increase in the prices of crude oil (Hatti-Kaul et al., 2007).

Butyric acid is produced as an end product of fermentation of sugar by obligate anaerobic bacteria, first discovered in 1861 by Pasteur; *Clostridium butyricum* being the most prominent and main bacterium, but other organisms such as *C. kluyveri, C. beijerinckii, C. barkeri, C. acetobutylicum, C. thermobutyricum, C. thermopalmarium, C. pasteurianum, Butyribacterium* sp., *Sarcina* sp., *Megasphaera* sp., *Fusobacterium nucleatum, Peptococcus asacelarolyticus, Butyrivibrio fibrisolvens, Pseudobutyrivibrio ruminis,* and *Eubacterium limosum* are also used. For propionic acid production, is mainly carried out via chemical synthesis from petroleum feedstocks by three process routes: ethylene hydro formylation/oxidation, carboxylation of ethylene with carbon monoxide and water, and direct oxidation of hydrocarbons (Xu and Jiang, 2011; Zacharof and Lovitt, 2013).

Propionic acid is also produced, in minor quantities, as a by-product of acetic acid manufacturing. However, fermentation is an attractive alternative method to produce propionic acid from renewable resources. Due to the exhaustion of petroleum resources and the serious environmental pollution caused by the utilization of fossil resources, biological production of propionic acid from renewable resources has increasing attention. In the bio-based production process, *Propionibacterium freudenreichii*, *Propionibacterium acidipropionici*, *Propionibacterium thoenii*, *Propionibacterium shermanii*, and *Propionibacterium jensenii* species have been used mostly (Du et al., 2015).

Bio-based production methods cannot compete economically with the petro-based production methods. In general, there are two most important reasons; one of them is the lower manufacturing cost of petro-based production methods and another one is the lower efficiency of bio-based production methods. However, both adverse effects on the environment (GHG emissions, high amount of chemical requirement, high amount of energy requirement, huge amount of waste and wastewater production during and after production process, and depleting sources of petroleum make to shift the petrol-based production to bio-based methods obligatory (Besselink et al., 2017; Mansouri et al., 2017; Wu et al., 2016). On the other hand, recent researches and developments have suggested shifting the current production methods for VFAs, to cradle to cradle technologies (like bio-based methods) from waste/wastewater. The importance of bio-based VFA production methods was defined by Bhatia and Yang (2017) in terms of renewability, degradability, and sustainability. These terms are key parameters to limit global temperature rise to well below 2 °C and given the grave risks, to strive for 1,5°C which was addressed in The Paris Agreement (2016).

The bio-based VFAs production methods have started to improve in terms of increasing efficiency, optimization the operation conditions, providing renewable and sustainable source as a substrate, defining and evaluating the microbial communities with their interactions, and new separation techniques.

One of the most important subjects about bio-based VFAs production methods is optimizing the operation conditions. Therefore, the operation conditions in terms of pH, temperature, type of substrate, retention time, mixed microbial cultures and reactor type effects on VFAs production are evaluated in detail in Section 2.2.

2.2. Effects of operation conditions on VFA production and composition

There have been many studies that have to investigated the effects of operation conditions such as pH, temperature, organic loading rate, retention time, substrate on VFA production (Khan et al., 2016). A comprehensive evaluation was given below for each variable in terms of pH, temperature, retention time, mixed microbial culture, and substrates, respectively. The literature studies were evaluated regarding their maximum VFA production yields, operational conditions and type of substrate in Table 2.

2.2.1. pH

pH is one of the most critical parameters that affects the VFA concentration and composition since it influences both acidogenic process and hydrolysis rate (Begum et al., 2018a,b; Zhao et al., 2018).

Zhao et al., (2018) stated that the stepwise pH fermentation strategy (from pH 9 to 11) does not only enhance the activity of acid-producing bacteria (pH 9) but also inhibit the activities of methanogens (pH 11), which resulted in higher production of VFA.

Chen et al. (2017) defined microbial interactions with pH change. Their results indicated that pH change (from 7 to 10) does not only affect VFA concentration (423 mg COD/g VSS) and composition, but also the microbial community. Moreover, they found that *Clostridia* was the most dominant population in high pH (8,9) while the relative abundance of *Euryarchaeota* decreased sharply from 58% to 2% with increased pH.

Huang et al. (2018) conducted a study to investigate the effect of pH on VFA production by using different pH (3, 5, 7, 9, 10, and 12). Their results indicated that the optimal VFA production occurred under pH 10 and the microbial community interactions were quite different

Table 2
Literature on kinds of VFAs produced from waste streams.

Waste stream	Operational conditions	VFA production	VFA composition (%)				References
			Acetic acid	Propionic acid	Butyric acid	others	
Microalgae biomass	pH 11, RT 15 days, 35 °C, lab scale anaerobic batch reactors	0.83 gVFA/gsCOD	70	10	7	13	Jankowska et al. (2015)
Municipal solid waste	pH 10, RT 10 days, 35 °C, lab scale anaerobic batch reactors	8.320 mgCOD/L as VFA with 94% VFA/sCOD	70	7	13	10	Garcia-Aguirre et al. (2017)
Food waste	pH 6, RT 20 days, 30 °C, anaerobic batch reactor	0.918 gVFA/gVSS	70	5	17	8	Wang et al. (2014)
Food waste	pH 6, RT 17 days, 30 °C, lab scale anaerobic batch reactors	0.79 gCOD/gVS for VFA	30	2	60	8	Yin et al. (2016)
Poultry litter	pH 5.5, RT 4 days, 35 °C, anaerobic batch reactors	0.67 kg VFA/kgVS					Kuruti et al. (2017)
Tuna waste	pH 8, RT 32 days, 35 °C, continuous anaerobic reactor	30.611 mgCOD/L	60	15	10	15	Bermúdez-Penabad et al. (2017)
Waste activated sludge	pH 9, RT 6 days, 55 °C, semi continuous fermenter	423 mgCOD/gVSS					Chen et al. (2017)

under alkaline and acidic pH conditions. Also, the acetic acid was the most important factor to distinct the bacterial community.

In addition to enhancement of VFA production by extracellular pH regulation, recent studies speculated that intracellular pH affects the metabolic pathways in fermentation and influences the VFA composition (Mohd-Zaki et al., 2016; Zhou et al., 2017). The only explanation which still needs a proof was that lower pH makes the consumption of NADH more favourable to increase the NADH/NAD+ ratio, which causes a shift of main product(s) (Temudo et al., 2007).

In some studies, the effects of pH were explored with temperature on VFAs production. One of them was conducted by Garcia-Aguirre et al., (2017). They explored the VFA production under acidic (pH 5.5) and alkaline (pH 10) conditions at both mesophilic and thermophilic temperature. Their result stated, even so, the high temperature influences the VFA production positively (8.320 mg COD/L), the most effective parameter was pH resulting in high VFA production yield (Garcia-Aguirre et al., 2017).

2.2.2. Temperature

Temperature is an important operational factor to improve VFA production due to the fact that it affects the growth of microorganisms, enzyme activity and hydrolysis rate (Zhou et al., 2018). The effect of thermophilic conditions on the microbial community for VFA production under alkaline conditions is not clear yet. However, Hao and Wang (2015) found that thermophilic fermentation led to 10 times more VFAs production compared to mesophilic conditions without pH adjustment and Zhang et al. (2009) informed that thermophilic conditions increased the hydrolysis rate compared to mesophilic conditions which resulted in higher production of VFA.

Like pH, temperature also affects the type of main VFAs product in fermentation. Jiang et al. (2013) reported that butyrate was the main product at 55 °C whereas acetate and propionate were the main products at 35 °C.

Nevertheless, thermophilic conditions positively affect the microbial growth rate. The mesophilic temperature is the most optimum and economical favourable condition for VFA production as the VFAs yields are quite similar at both thermophilic and mesophilic conditions (Jiang et al., 2013; Gruhn et al., 2016).

2.2.3. Retention time

In literature studies, the best retention time depends on the type of substrate due to its hydrolysis rate. However, the retention time can differ with the same substrate (glucose) in some cases. Therefore, retention time does not only depends on the type of substrate but also other operation conditions (Jankowska et al., 2015). Jankowska et al., (2015), showed that the highest VFAs concentration was achieved after 15 days when 5, 10 and 15 days as a retention time were used.

Bolaji and Dionisi, (2017) used 10, 20, and 30 days as retention times for the anaerobic fermentation of vegetable and salad waste. Their results showed that an increase in retention time resulted in better volatile solids (VS) reduction. Also, they detected caproate after 20 and 30 days as a product, although the main products were butyrate and acetate (Bolaji and Dionisi, 2017). Their results suggest that retention time can influence not only VFA yield but also composition.

2.2.4. Mixed microbial culture

In addition to the operation conditions, the type of mixed microbial culture may affect the VFA concentration and composition. Beside mixed microbial cultures from engineering designed reactors treating waste streams, other mixed microbial cultures from natural sources such as sediments, rumen have been used (Blasig et al., 1992; Fu and Holtzapple, 2010). However, the effects of mixed microbial culture from engineering designed reactors on VFA production and composition are discussed.

Though, there is a limited study to reveal the effects of mixed microbial culture on VFA production, one of the study was conducted by Wang et al., (2014). They evaluated the different mixed microbial cultures (aerobic and anaerobic activated sludge) under various pH (4, 5, 6, and no-control), on VFA production with food waste. Their study indicated that the anaerobic activated sludge achieved almost double of the VFA yield (0.918 g VFA/g VSS) when compared with aerobic activated sludge (0.482 g VFA/g VSS). Moreover, VFA composition was in the order of butyric, acetic and propionic acids from the highest to the lowest concentration (70% butyric, 17% acetic, 5% propionic, and 8% others) (Wang et al., 2014).

2.2.5. Substrate

The production of VFA produced is greatly influenced by the kind of substrate used. The amount of VFA produced from a given feedstock depends on the degree of acidification (Begum et al., 2018a,b). The degree of acidification is a key factor in the fermentation process for the production of VFA and it is defined as the percentage of initial COD converted into organic acids and other fermentation products (Jin et al., 1999). The degree of acidification is determined by the readily fermentable organic fraction of the waste stream. In a study with approximately the same initial organic matter and biomass concentration of 8 g COD /L and 2 g VSS/L respectively, it was observed that the fermentation of the eight organic waste streams resulted in different VFA productions due to significant variance in the degree of acidification as shown in Fig. 1 (Silva et al., 2013). Cheese whey, molasses and organic fraction of municipal solid waste streams achieved the highest degree of acidification (up to 40%) with total VFA production of 2707–3374 mg/L as COD, whereas soapy slurry waste and landfill leachate produced only 634 and 240 mg/L as COD with low degrees of

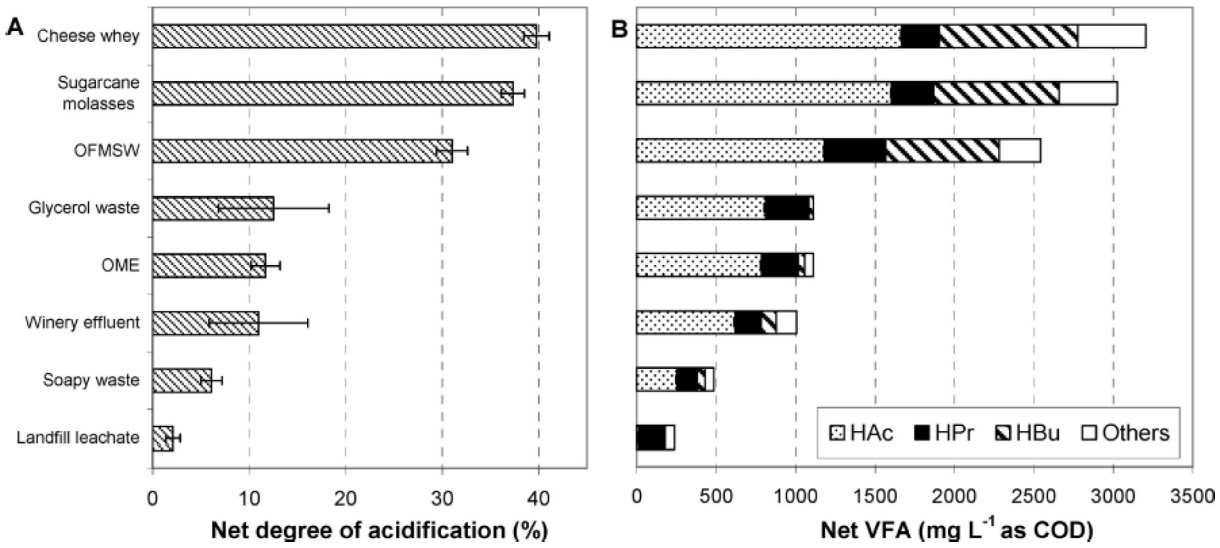


Fig. 1. Impact of waste streams on (A) the degree of acidification and (B) VFA production and composition (Silva et al., 2013).

acidification of 6 and 2% respectively. Glycerol, olive mill effluent and winery effluent achieved medium acidogenic potential with degree of acidification up to 11–13% corresponding to total VFA production of 934–1460 mg/L as COD (see Fig. 1A). Primary sludge is known to produce higher amount (197–256 mg COD/g VSS) of VFA than waste activated sludge (11.3–25 mg COD/g VSS) for a given organic matter to biomass due to a higher readily fermentable organic fraction (Ucisik and Henze, 2008).

In addition to the impact on the quantity of VFA produced, the kind of substrate influences VFA production qualitatively. The composition of VFA reflects the prevailing metabolic pathways of the fermentation process. Several discrete pathways exist simultaneously within the digester of anaerobic fermentation of waste streams. In a mixed culture system, the proportion of pyruvic acid converted to each VFA can be determined by the kind of waste stream used as a substrate and the key enzymes taking part in the VFA production (Chen et al., 2013).

Acetic acid often accounts for 30–80% of VFA produced from waste streams. Valeric acid and other kinds of VFA are usually produced in relatively low quantity. The reason for the difference in VFA composition produced from waste streams can be explained by the characteristics of the organic matter content of the waste stream (Table 2).

It has shown that whereas carbohydrate-rich waste streams support propionic and butyric acid production, valeric and *iso*-valeric acids production are supported by protein-rich waste streams (Garcia-Aguirre et al., 2017; Shen et al., 2014). The fact that protein-rich substrates support valeric acid production, has been confirmed in a study with protein-rich substrates, tofu and egg white, where valeric acid accounted for 18–25% of the total VFA produced, being the second highest after acetic acid (Shen et al., 2017).

Propionic acid is supported by glycerol-rich wastewater. It was observed that waste stream with 84.7% of the total organic carbon as glycerol produced VFA which was predominantly made of propionic acid of 90.5% (Shen et al., 2014). However, another study by Silva et al. shown contrast results for glycerol waste stream, where 80% of VFA produced was acetic acid with propionic acid accounting for less than 20% (Silva et al., 2013). It has been shown that the operating conditions could have accounted for the difference. It has been observed that the primary fermentation product was propionic acid (74%) at pH 5.5 and 35 °C whereas at pH 10 and 55 °C, with acetic acid was the predominant VFA component (Garcia-Aguirre et al., 2017). It is therefore not very clear how substrate really affects the composition of VFA. To understand in detail the effect of feedstock on VFA composition, the intricate interplay between feedstock characteristics and operating condition and their coupling effect on VFA composition during fermentation of waste streams with mixed culture needs to be systematically investigated.

2.2.6. Combined effects of factors

Besides evaluating the effects of operation conditions on VFA production and composition separately, some studies assessed the coupling effects of the operation conditions. Lee et al., (2014) examined the production and application of VFAs from waste. They reviewed the effects of operation conditions in terms of pH, temperature, retention time, organic loading rate and additives on VFA production. As a conclusion, they suggested further research about not only regulating the operation conditions but also examining the microbial community to feasible VFA production.

Jankowska et al. (2015) conducted a study to determine the effect of pH and retention time on VFA production. They selected a wide pH range from 4 to 12 and different retention times of 5, 10 and 15 days. Following the study, Jankowska et al. (2017) used four different substrates (maize silage, cheese whey, microalgae biomass and glucose) with acidic (5), neutral (7) and alkaline (11) pH conditions for same retention time range to understand the effect of substrate on VFA production and concluded alkaline environment favoured hydrolysis of complex organics while neutral pH was beneficial for VFA production. However, the distribution of VFA depended on the kind of substrate. Fang et al. (2017) investigated the effect of pH (pH from 4 to 12) to enhance the VFA production by using spent mushroom compost (SMC) as a substrate. Hao and Wang (2015) determined the effect of temperature on VFA production by using thermophilic and mesophilic conditions. Also, Yin et al. (2016) used three different substrates (glucose, peptone and glycerol) to determine the effect of substrate on VFA production. Moreover, Slezak et al. (2017) researched the effect of initial organic loading rate (from 4.1 to 48.2 g VS/L) on the process performance in terms of VFA and H_2 production. Yin et al. (2016) conducted a study to understand the effects of redox potential (ORP) and mixed microbial culture on VFA production. These studies demonstrate the importance of synergistic effects of operational parameters on VFA production.

In addition to the effects of pH and temperature on VFA concentration and composition, Zhang et al., (2015) investigated the effects of hydrogen partial pressure. According to their results, the composition of the products was changed from acetate, butyrate and hydrogen at pH 4, to acetate, ethanol, propionate and formate at pH 7 (Zhang et al., 2015).

Kuruti et al., (2017), evaluated the effects of different F/M ratios (0,4 – 0,6 – 0,8 – and 1), with cattle manure and poultry litter under pH

Table 3
VFA recovery methods and their performances.

Methods	Materials used	Conditions and scale	Kind of VFA recovered	Recovery efficiency	References
Gas stripping with absorption	N_2 gas and $CaCO_3$ slurry	5 L fed-batch bioreactor at pH 5 and 35 °C. After digestion, concentrations of VFAs to be recovered were 3.3–184 mmol	Acetic, butyric, propionic, valeric acids	0.92–29.5 mmol of VFA recovered	Li et al. (2015a,b)
	Air and acid for ammonia absorption	4 L anaerobic reactor at pH 10–11 and 35–55 °C. VFA concentration after digestion were up to from 94.4 mg-COD/g-VS	Acetic, propionic, *iso*-butyric, n-butyric, *iso*-valeric and n-valeric acids.	Separated 20.0 mg/g-VS of ammonia-N from 94.4 mg-COD/g-VS of VFAs	Huang et al. (2016)
Adsorption	Polystyrene-divinylbenzene-based resins	21 g and ~400 mL of model solutions for fermented wastewater were used for static (batch) and dynamic (column) absorption respectively. Initial conc of each of VFAs were 0.25–1.25 wt%	Acetic, butyric, propionic and lactic acids	Butyric acid was obtained in mole fractions of up to 0.8	Reyhanitash et al. (2017)
	Ion exchange amino resin	Batch mode adsorption of volume 1 or 50 mL of VFA-rich liquid phase. Grape pomace acidogenic digestate and synthetic mixture of VFA concentrations 19.8 and 19.1 g/L were used	Acetic acid and total VFAs	Up to 88% absorption yield	Rebecchi et al. (2016)
Electrodialysis	ED 64,002 membrane stack with 20 cell pairs	250 mL model VFA solutions with 1000 mg/L each of VFAs and hydrogen fermentation broths from fed batch reactors with volume 500 mL	Acetic, propionic, *iso*-butyric, n-butyric, iso valeric, and n-valeric acids.	Up to 99% of VFAs from model solutions,	Jones et al. (2015)
	ED stack with Neosepta AMX-CMX membranes	Model solution and olive mill wastewaters digestate of VFA concentrations of 3900–5820 and 14500 mg/L	Acetic, propionic and butyric acids	VFAs removals ranged from 30% to 35%	Scoma et al. (2016)
	Bipolar (fumasep FBM), anion exchange (AMI 7001) and cation exchange (CMI 7000) membranes	Synthetic fermentation broth or digestate was fed into a working chamber of volume 40 mL Initial VFA concentration of 30–150 mM	Acetic, propionic acid, butyric	VFA recovery of 98.3%	Zhang and Angelidaki (2015)
Solvent extraction	Trioctylamine (TOA) in n-octanol and ionic liquid	Single-stage and multi-stage cross-current liquid–liquid extraction with 3 mL of a solvent and 5 mL VFA model solution. Initial conc of each of VFAs were 2.5–10 g/L	Acetic, propionic, butyric and lactic acids	VFAs loading of up to 10 wt%.	Reyhanitash et al. (2016)
	Trioctylphosphine oxide (TOPO) in kerosene	Simultaneous acidification of sugar industry wastewater and beet-pulp with effective volume of 500 mL. Digestate VFA concentration was 2910 mg/L. 10 mL of each fermentation broth and solvent was used for extraction	Acetic, propionic, butyric, *iso*-butyric, valeric, *iso*-valeric, caproic, *iso*-caproic and heptanoic acids.	Up to 98% VFA recoveries from AD reactor	Alkaya et al. (2009)
	Medium-chain fatty acids (hexanoic, octanoic and decanoic acids) diluted in organic solvents (Toluene, n-Hexane)	3 mL of the aqueous VFA solution and 3 mL of the extractant solution were used. VFA concentration was1 wt %	Acetic, propionic, butyric acids	Up to 80% extraction efficiency	Rocha et al. (2017)
Nanofiltration (NF)	NF270, HL, DL, DK and LF10 NF membranes	100 mL of VFA rich water was filtered to give 10 mL retentate and 90 mL permeate. Synthetic solutions and digested agricultural wastewater with concentrations 50–100 and 15.81–21.08 mM	Acetic, butyric acid	Retention ratios up to 75% with retentate of concentration 53.94 mM acetate for digested agricultural waste.	Zacharof et al. (2016), Zacharof and Lovitt (2014)
	GE Desal-5 DK and Alfa Laval-NF	10 L model solution with acetic acid concentration of 2–10 g/L	Acetic acid	For GE Desal-5 DK, acetic acid separation factors were 8.87 and 56.5 over xylose and glucose	Zhou et al. (2013a)
Reverse osmosis (RO)	RO98pHt and RO99 RO membranes	10 L model solution with acetic acid concentration of 2–10 g/L	Acetic acid	For RO98pHt, maximum acetic acid separation factors were 223.2 and 348.7 over xylose and glucose	Zhou et al. (2013a)
	RO98pHt	10 L model solution with acetic acid concentration of 2–10 g/L	Acetic acid	maximum separation factors of acetic acid over xylose and glucose were 211.5 and 228.4.	Zhou et al. (2013b)
Membrane contractors	Air-filled and tertiary amine extractant-filled PTFE membranes	Synthetic VFA mixture (1250 mg/L each VFA) and three different anaerobically digested organic-rich wastes. Membrane was placed plastic container filled with 430 mL pure extractant solution	Acetic, propionic, butyric, valeric, and caproic acids	Up to 95% VFA recovery	Aydin et al. (2018)
	PTFE membrane	Synthetic model solution of VFA concentration 0.01–0.1 M and effluent from fermented organic solid waste. 150 mL reservoir for feed and stripping solutions	Acetic, propionic, isobutyric, butyric, isovaleric, valeric, caproic acids	Up to 1.599 membrane selectivity of VFAs over water	Tugtas (2014)

4,5 and 5,5 by using thermal and acidic pretreatments on rapid generation of VFA. Their results indicated that the best VFA yield (0.67 kg VFA/kg VS) achieved at F/M ratio was 1 under pH 5,5 during 4 days retention time (Kuruti et al., 2017).

2.3. Bio-augmentation: A promising strategy

Bio-augmentation is a strategy to improve the removal of specific compounds (e.g., refractory organics or overall chemical oxygen demand) by enhancing the yield of specific microorganisms who are working for particular aims (Peng et al., 2014). Bio-augmentation has been carried out worldwide with four main methods. These include (1) a pre-adapted pure culture addition; (2) a pre-adapted consortium addition; (3) genetically engineered bacteria addition and (4) biodegradation- relevant genes in a vector addition (Herrero and Stuckey, 2015; Peng et al., 2014).

The bio-augmentation methods have been used in anaerobic systems to enhance biogas production or to prevent inhibition caused by acid accumulation in the system. Strang et al., (2017) used mixed cellulolytic consortium to enrich the microbial community for biogas production. The methane yield was increased 22–24% more than non-bioaugmented reactors (Strang et al., 2017). In one of the study, hydrolytic microbes were used to improve methane production during agricultural waste fermentation. The result indicated that the methane yield was increased by 34% (Tsapekos et al., 2017). Likewise, Peng et al., (2014) conducted a study by using cellulolytic bacteria to improve methane production from lignocellulosic substrate fermentation. They increased the methane yield 13% when compared to non-bioaugmented tests (Peng et al., 2014).

There is only one known study on the application of bio-augmentation for VFA production (Reddy et al., 2018). In the study, it was shown that bio-augmented culture gave higher butyric acid (8.9 g/l) and caproic acid (8.1 g/l) production in comparison with non-augmented conditions (6.5 g/l butyric acid and 2.68 g/l caproic acid). This study, together with other studies on the application of bio-augmentation in anaerobic digestion systems, depicts the potential of employing the bio-augmentation strategy for enhancing VFA production from waste streams.

However, the possibility of failure of inoculum for bio-augmentation needs to be addressed in order to ensure successful application (Dianne Stephenson, 1992). Researches focusing on inoculation efficiency should test behaviour under conditions as closely as possible in mimicking the intended microbial conditions (Herrero and Stuckey, 2015). The interaction of the inoculated microorganisms with their new biological and non-biological environments in terms of activity, survival, and migration can be critical in the success of any bio-augmentation strategy (Saïd El Fantroussi and Agathos, 2005). Also, bio-augmentation can change the composition of the indigenous microbial community in either positive or negative ways (competition or inhibition).

An envisaged problem of bio-augmentation method that needs to be overcome is the possibility of the wash-out of new strains. Bio-augmentation can potentially take advantage of compartmentalisation, or the use of membranes in advanced bioreactors, as a way of preventing the wash-out of introduced microorganisms within the bio-system. To support successful bio-augmentation strategies, along with enhancing biodegradation kinetics of the target pollutant, the use of molecular techniques is needed to monitor both the survival and/or activity of the added microorganisms.

3. Recovery of VFA

Recovery of VFAs produced from waste streams is as important as the fermentation process and optimisation of VFA production. It does not make sense to produce VFAs if they cannot be recovered for the intended purpose. However, in a complex waste stream, recovery is the most challenging part of the VFA production chain (Zacharof and Lovitt, 2013). It is even more difficult if individual VFAs, instead of the mixed VFAs, are to be recovered. Recovery of both mixed VFA and individual VFA have been discussed. In this section, various methods for recovery of VFA and current development has been discussed. Table 3 lists the key VFA recovery methods and their performance.

3.1. Gas stripping with absorption

Air/gas stripping is a method that is normally applied in the removal of volatile organic contaminants from water by contacting clean air with contaminated water across a high surface area (Kavanaugh and Trussell, 1980; Singh et al., 1992). Gas stripping process is governed by Henry's law which relates aqueous-phase concentration of a compound to its gas-phase concentration. Recently, the gas stripping phenomenon has been applied for recovery of VFAs from anaerobic digestion reactors. In this method, the bioreactor contents, containing VFAs, are stripped with headspace gas entering via an open tube. The gas containing the VFAs stripped from the bioreactor is then passed through a recovery system containing the absorbent. Salts of VFA are formed which can be recovered after evaporation.

Using the gas stripping and absorption method, Li et al. (2015b) recovered VFAs from an anaerobic digester of meat work sludge fed repeatedly with glucose doses. In that study, a combination of nitrogen gas stripping and absorption with calcium carbonate slurry was used to recover VFA as calcium salts which consisted of 80% butyrate and 20% acetate with minor quantities of propionate and valerate. It is of interest to know that gas stripping which led to a reduction of pH promoted lactic acid conversion to other valuable VFAs as stripping was done intermittently during the fermentation process.

In a recent study, the gas stripping technique was used in a different way to purify VFA by rather stripping ammonia directly from VFA-rich digestate obtained from dry anaerobic digestion of swine manure or from resultant VFA-rich filtrate from the solid-liquid separation of the mixture of digestate and added water (Huang et al., 2016). The results showed ammonia removal efficiencies up to 99.7% from total VFAs concentration of 94.4 mg-COD/g-VS. It was remarked in the study that the separated liquid containing mixed VFA was a marketable product.

3.2. Adsorption

Adsorption is a surface-based process which involves the adhesion of compounds, ions or molecules from a gas or liquid to a surface. The method of adsorption for recovery of VFA is done by passing VFA-rich digestate through a column of absorbent (usually ion exchange resin). In the process, the carboxylate anion of the VFA is absorbed on the resin by often exchanging with the resin's functional anion and other means. The exhausted resin column is afterward regenerated with an appropriate solvent. Usually, the resin can be used for a number of cycles. Previous studies have shown that mixed VFAs, particularly acetic and butyric acid are well retained by anionic resins with the mechanism of adsorption explained by ion pairing between the carboxylic acids and the resin amine groups as well as non-ionic sorption (Edmiston et al., 2018; Fargues et al., 2010). Those studies did not aim at recovery but rather to remove VFAs which were acting as inhibitory compounds to fermentation processes and there was no focus on recovery of individual VFA.

There are current studies where the use of adsorption as a VFA recovery tool has been investigated (Bertin et al., 2016; Cabrera-Rodríguez et al., 2017; Rebecchi et al., 2016; Reyhanitash et al., 2017). Rebecchi et al. (2016) investigated the VFA recovery efficiency of four different amino resins (including primary amine, tertiary amine and quaternary amine) and concluded that the tertiary amino resin was the best due to its high ion exchange performances in the presence of acetic acid and low price. VFAs adsorption yields of up to 76 and 85% were achieved from grape pomace acidogenic digestate and synthetic VFA

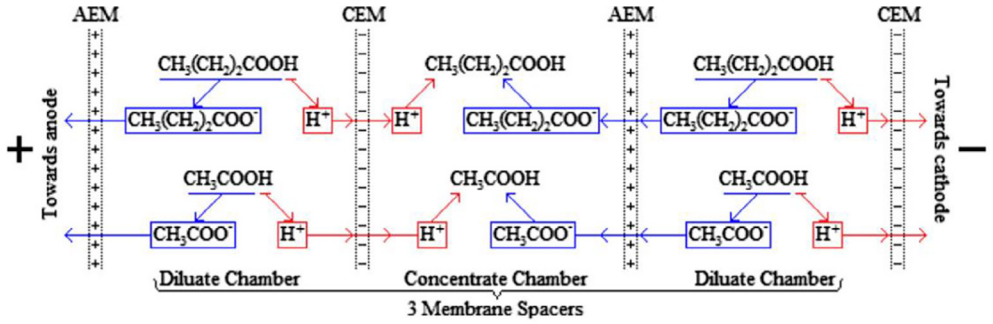


Fig. 2. Schematic of a conventional electrodialysis stack showing the principle for recovery of VFA (Jones et al., 2015).

mixture, respectively. Close to 100% total VFA desorption yields were obtained with ethanol plus 1 M NaOH and water plus 1 M NaOH solutions. There was the recovery of mixed VFA, however, separation of individual VFA was not studied. Adsorption is seen as a promising and cost-effective choice for recovery of VFAs from waste streams as Reyhanitash et al. (2017) did not observe any decrease in adsorption capacity of polystyrene-divinylbenzene-based resins during four successive adsorption–regeneration cycles. However, the presence of chloride, sulphate, and phosphate salts severally reduced VFA adsorption efficiency which calls for further investigation before adsorption can be concluded as the ultimate VFA recovery technique.

3.3. Solvent extraction

Solvent extraction is a purification method that is used to separate compounds or metal complexes, based on their relative solubilities in two different immiscible liquids. Solvent extraction is popular for the recovery of VFAs from dilute aqueous solutions because it provides an effective separation. The mechanism of solvent extraction for recovery of VFA is based on the fact that the extraction equilibrium of the VFAs with extractant (e.g. trioctylamine) can be obtained when a VFA is dissociated in water and extracted into the extractant phase through the solubility of the solute in the extractant phase (Li et al., 2002).

The efficiency of VFA recovery with solvent extraction depends on operational parameters such as pH, kind of VFA, extractant type and composition of the VFA rich digestate. Recovery of VFAs from anaerobic acidification broth obtained by digestion of sugar beet processing wastes using trioctylphosphine oxide (TOPO) in kerosene as an extractant was investigated (Alkaya et al., 2009). It was observed that the maximum VFA recoveries of 61–98% following the trend, acetic < propionic < butyric < valeric acids, were achieved at pH 2.5 and extractant concentration of 20 wt%. Reyhanitash et al. (2016) investigated the VFA extraction efficiency of a number of solvents and found 20 wt% trioctylamine (TOA) in n-octanol, a conventional solvent and trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate [P666,14][Phos], an ionic liquid to be the most promising VFA-extracting solvents due to the relatively high acetic acid distribution coefficients (8.8 and 17 wt%/wt% respectively) obtained for an idealized aqueous solution containing 1 wt% acetic acids.

It is noteworthy to know that dissolved salts could negatively influence VFA recovery efficiency due to co-extraction of salt anions and an increase in of the pH of the aqueous solutions (Reyhanitash et al., 2016). As co-existing anions are inevitable in wastewater, there is a need to devise strategies to overcome such influence or use a more robust system such as electrodialysis for recovery of waste derived VFA with little or no negative effect by co-existing anionic species (Zhang and Angelidaki, 2015). Another downside of solvent extraction is that some extraction solvents may be toxic or inhibitory to microorganisms used for in-line recovery of VFA (Playne and Smith, 1983). In view of this, pertraction (membrane-based solvent extraction) is getting attention as an alternative recovery method for VFA to avoid contact of the toxic extractors with the microbes (de Araújo Cavalcante et al., 2017).

3.4. Electrodialysis

Conventionally, electrodialysis is a membrane separation process used to transport ionic solutes from one solution to another through anion- and cation exchange membranes separated by a spacer gasket in an alternating pattern forming individual cells between two electrodes. If a feed solution is pumped through the cells under the influence of electrical potential difference, the cations migrate towards the cathode and pass through the cation exchange membrane but are retained by the anion-exchange membrane. A reverse happens to anions moving towards the anode, passing through the anion-exchange membrane but being retained by the cation exchange membrane (Strathmann, 2010). This results in concentrating of an electrolyte (salt, acid or base) in alternate compartments (concentrate chambers) while solutions in other compartments (diluent chambers) are depleted of ionic components as illustrated in Fig. 2 for the recovery of acetic (CH_3COOH) and butyric acids ($CH_3(CH_2)_2OOH$).

Jones et al. (2015) used conventional electrodialysis to remove inhibitory VFAs from fermentation broths. Within 60 min of operation, the conventional electrodialysis removed up to 99% of VFAs from model solutions and real fermentation broths, containing up to 1200 mg/1 each of different VFAs. It was remarked that the removed VFAs were recoverable for marketable use. In an attempt to produce biodegradable polyhydroxyalkanoates (PHAs) from waste activated sludge, an integrated system of microfiltration and conventional electrodialysis achieved a VFA concentration of 19.8 g/L (Tao et al., 2016).

Besides the conventional electrodialysis, bipolar membrane electrodialysis system has been assessed for recovery of mixed VFAs from both synthetic and real waste streams where VFAs recovery efficiency of up to 87% was achieved (Shi et al., 2018; Tang et al., 2014; Zhang and Angelidaki, 2015).

3.5. Reverse osmosis and nanofiltration

Reverse osmosis and nanofiltration are membrane processes which use semi-permeable membranes to separate solutes such as salt, organic molecules from solvent (typically water) by allowing the water to pass through the membranes while rejecting the solutes under an elevated working pressure in excess of the osmotic pressure of the solution. In wastewater treatment application, reverse osmosis is used for water reclamation or reuse, nutrient concentration and recovery (Masse et al., 2010; Owusu-Agyeman et al., 2015; Rajabzadeh et al., 2012; Shang et al., 2011).

Recently, reverse osmosis and nanofiltration are getting attention for recovery of VFAs from waste streams. Zhou et al., 2013a employed commercial reverse osmosis membranes to separate acetic acid from monosaccharides in model hydrolyzate solutions and achieved acetic acid separation factors of 223.2 and 348.7 over xylose and glucose respectively (Zhou et al., 2013a). However, the recovery technique was

not used to separate individual VFA from VFA mixture.

In terms of the application of nanofiltration for recovery of VFAs, the suitability of commercial nanofiltration for recovery of VFAs has been investigated (Weng et al., 2010; Zacharof et al., 2016; Zacharof and Lovitt, 2014; Zhou et al., 2013a). It has been shown that nanofiltration membranes are capable of achieving VFA retention of up to 75%, giving VFA-rich concentrates of up to 53.94 mM acetate and 28.38 mM butyrate from the agricultural wastewater (Zacharof et al., 2016; Zacharof and Lovitt, 2014). Moreover, Xiong et al. (2015) acidogenic digestion with VFA separation by nanofiltration membranes and recovered 86% of the VFAs during a 21-day digestion run reducing VFA concentration in the digestate by nearly 90% relative to a control without acid removal.

Performances of reverse osmosis and nanofiltration are influenced by a number factors including solution pH, temperature, solute concentration and pressure. These factors specifically affect the mechanisms governing the retention of solutes by reverse osmosis and nanofiltration (Roy et al., 2017). The retention mechanisms include charge interaction, size exclusion, dielectric effect, Donnan effect (Epsztein et al., 2018; Wadekar and Vidic, 2017; Yaroshchuk and Bruening, 2017).

The effects of pH, temperature, pressure and feed concentration on the VFA retention from a fermentation broth by reverse osmosis were investigated with a synthetic xylose–glucose–acetic acid model solution (Zhou et al., 2013b). The results showed that acetic acid retention increased with the increase in pH and pressure while it decreased with temperature increase. The increase in acetic acid with pH was explained by an increase in charge repulsion between the membrane and acetic acid molecules due to the fact that acetic acid gets deprotonated to negatively charged molecules and the same time the polyamine membrane which was used become more negative with pH increase. Pressure and temperature effect was explained by solution diffusion and transport of solute (Zhou et al., 2013a).

Considering the fact that reverse osmosis/nanofiltration membranes have a range of pore sizes and molecular weight cut-offs, it may be possible to separate individual VFA from mixed VFA produced from waste streams based on the molecular weights of the VFA composition.

3.6. Membrane contractor

A membrane contactor is a membrane separation system that allows a gas phase and a liquid phase to contact with each other in order to promote mass transfer between the two phases through a membrane, without dispersion of one phase within another. Membrane contractors use common hydrophobic microfiltration membranes, but the system differs from pressure-driven filtration systems such as microfiltration and ultrafiltration because an externally applied pressure is not the driving force and there is no convection flow.

Dissolved gases and volatile species such as VFAs be transferred through the hydrophobic membrane from the liquid to gas phase depending on the partial pressure difference or concentration gradient between the two sides of the membrane (Aydin et al., 2018).

Recent attention to VFA production from waste streams has seen some research works towards the recovery of VFA from waste using membrane contractors.

Tugtas, (2014) investigated the use of membrane contractor for recovery of VFA from leachate of fermented organic solid waste and achieved 1.599 selectivity of VFA over water. Moreover, Yesil et al. (2014) observed acetic acid permeate flux of 13.12 $g/m^2 h$ for synthetic water. However, using effluent from anaerobic fermentation of organic municipal solid waste the flux was reduced to 0.240 $g/m^2 h$. The low selectivity for the real wastewater was explained by an increase in pH which left the VFA, particularly acetic acid in their ionic form which was not volatile.

Their result is an indication that the form of VFA is extremely important if a membrane contactor is used as a recovery technique. A current study used vapor permeation membrane contractor and achieved VFA recovery of greater than 86% and 95% from landfill leachate and fermentation broth of anaerobically digested organic waste, respectively (Aydin et al., 2018). It is important to state that the recovery depended very much on the kind of VFA with a trend of acetic < propionic < butyric < valeric < caproic acid in order of increasing recovery efficiency.

3.7. In-line VFA recovery

The approach to VFA recovery can have a significant effect on the recovery efficiency regardless of the method used. In-line or in situ recovery of VFA has been shown to increase the recovery efficiency compared to the conventional way where VFA is produced and then later recovered (Ataei and Vasheghani-Farahani, 2008; Roume et al., 2016). Moreover, in situ recovery is beneficial to the VFA production process due to the fact that there is the prevention of inhibitory effects of the VFAs or their consumption in internal conversion reactions especially in the mixed culture environment (Arslan et al., 2017; Trad et al., 2015). In-line recovery of n-caproic acid from fermentation reactor with pertraction system was used to prevent inhibition resulting in a higher production rate of ~3.4 g/(L·d) (Ge et al., 2015).

In a recent study, an acidogenesis-electrodialysis integrated system that coupled a continuous acidogenesis with a batch process of VFA concentration was developed for recovery of high-concentration VFAs from wastewater and gross current efficiency of 75% for acetate, propionate, and butyrate recovery was achieved (Pan et al., 2018). This corresponded to up-concentration of acetate by 4-fold and propionate and butyrate by over 3-fold in the integrated system after 528-h operation. However, there was a decline in VFAs recovery ratios at the later stage which was attributed to reverse diffusion, suggesting the need for optimization before scaling up.

Continuous removal of VFA from the fermentation reactor, while they are being formed, may create a driving force for higher production rates. Ataei and Vasheghani-Farahani (2008) investigated and compared in situ separation of lactic acid from fermentation broth using ion exchange resins with a conventional fermentation system. It was observed that the conventional fermentation system (Batch) without in-line recovery system yielded a maximum lactic concentration of 22 g/L after 5 days. But in extractive fermentation with in situ separation, a maximum value of 37.4 g/L was obtained within 38 h, corresponding to an increase in VFA yield of 60%. It was shown in another study that VFA productivity increased by 1.4 times when fermentation was coupled in line with VFA recovery system of bipolar membrane electrodialysis (Arslan et al., 2017).

It has been suggested that in addition to increased production, an in-situ combination of fermentation and electrodialysis with bipolar membranes for production of lactic acid from fermentation has the potential to reduce VFA production cost by saving a part of the initial investment on membrane materials (Wang et al., 2013, 2012).

4. Application of VFA produced from waste streams

VFAs derived from waste streams have been used in different applications including bioplastics, hydrogen, biodiesel, bioelectricity, biogas productions, and biological nutrient removal from wastewater (Lee et al., 2014). Three of the applications, namely biological nutrient removal, bioplastics and biodiesel, are reviewed in detail below.

4.1. Biological nutrient removal

A practical application of VFA produced from wastewater treatment plants is the use as a carbon source in a denitrification process. Biological nitrogen removal from wastewater involves aerobic nitrification process and anoxic denitrification. The denitrification stage requires a carbon source. Conventionally, commercial chemical carbon

sources such as methanol, glucose and acetate are used. VFAs produced from waste streams presents an economical alternative as the carbon source for the denitrification process.

It is interesting to know that several studies have shown that when used as carbon source, waste derived VFAs perform better than commercial chemicals in terms of removal efficiency and denitrification rate (Kim et al., 2016; Liu et al., 2016a,b; Zhang et al., 2016a,b). It was observed in a study that the removal efficiency of nitrogen and phosphorus improved from 44% and 37% to 92% and 73%, respectively when VFA was used as a carbon source (Lim et al., 2000). Another study has shown that acidogenic liquid with high VFA content (39.26% acetate, 32.14% propionate, 24.52 isobutyrate and 4.04% isovalerate) from the fermentation of food waste outperformed commercial sodium acetate considering the higher denitrification efficiency and the faster denitrification rate (Yan et al., 2018).

The composition of the waste-derived VFA can influence denitrification efficiency and rate. In a study with different kinds of VFAs as carbon sources to feed denitrifying processes, it was observed that acetic and propionic acid-fed processes attained the highest nitrate removal rates. In addition, it was concluded that nitrite accumulation occurs in short-chain VFAs with $\leq$3C (formic, acetic and propionic acid) which exhibited two denitrifying stages (fast and slow) by reaction kinetic analysis (Li et al., 2015a,b).

Full-scale production of waste derived VFAs for biological nitrogen removal is proven to be economically feasible. In a recent study, a full-scale reactor has been used to produce VFA which was then used as an external carbon source for improving biological nitrogen and phosphorus removal in wastewater treatment plant (Liu et al., 2018). It was found that the use of VFA-rich fermented liquid with VFA gave similar efficiency as a commercial acetic acid, obtaining removal efficiencies of nitrogen and phosphorus up to 72.39% and 89.65%, respectively.

4.2. Bioplastics (Polyhydroxyalkanoates)

Polyhydroxyalkanoates are thermoplastic biodegradable polyesters that can be produced from renewable sources. Production of PHA from mixed microbial cultures (MMC) will significantly reduce the cost of PHA. PHA production from waste streams using MMC typically involves the following steps: (1) acidogenic fermentation to obtain VFAs; (2) Enrichment of PHA accumulating MMC i.e. production of biomass yielding MMC with PHA accumulation potential (3) accumulation of PHA in the biomass (4) recovery of biopolymer (Valentino et al., 2017). In a pilot-scale demonstration, it was observed that biomass was able to accumulate up to 49% PHA of volatile suspended solids with VFAs from fermented organic residues as substrates (Bengtsson et al., 2017).

VFA composition determines the PHA composition. A study has shown that PHA produced from fermented cheese whey with VFA composing of lactic (58%), acetic (16%) and butyric (26%) acids was made up of only 3-hydroxybutyrate (3HB), while those obtained from fermented cheese whey composed of acetic (58%), propionic (19%), butyric (13%), lactic (6%) and valeric (4%) acids, were composed of 40% of 3-hydroxyvalerate (3HV) and 60% of 3HB (Colombo et al., 2016). In another study, a fermented substrate contained a mixture of VFAs including acetic, propionic, butyric, valeric and caproic acids and as a result produced PHA containing monomers of 3HB and 3HV (Bengtsson et al., 2017).

A major challenge of PHA production from waste streams with MMC is the diversion of carbon for microbial growth instead of PHA accumulation. This occurs normally due to co-existence of substrates such as methanol, ethanol and 1,3-propanediol (1,3-PDO) with VFAs (Burniol-Figols et al., 2018a; Marang et al., 2014; Tamis et al., 2014). To overcome this challenge, Korkakaki et al. (2016) introduced a sedimentation step after PHA enrichment phase and the supernatant containing methanol was discharged. This increased maximum PHA storage capacity of the culture from 48 to 70 wt%. Recently, Burniol-Figols et al. (2018b) achieved selective consumption of VFA over 1,3-PDO in the accumulation phase in MMC by using microbial biomass enriched in the absence of 1,3-PDO. This led to PHA accumulation of 76 wt%.

4.3. Biodiesel

The emergence of biodiesel as a possible alternative to fossil fuel is largely welcomed due to environmental consideration and the fear of running out of petroleum deposit. However, the issue of using food crop for fuel production as well as growing fuel crops on arable lands has raised concerns. The use of waste-derived feedstock for biofuel production is therefore given the needed attention. Studies have shown that waste-derived VFA can be converted to microbial lipids for biodiesel production (Chi et al., 2011; Fei et al., 2011; Ryu et al., 2013).

As an alternative to edible lipids such as rapeseed oil, palm oil and soybean oil, oleaginous microorganisms carrying microbial high lipid content can be used for biodiesel production. Oleaginous cells convert some organic acids into acetyl-CoA which is then used for the biosynthesis of polyunsaturated fatty acids and lipid accumulation. In an oleaginous cell, lipids can account for more than 70% of the cell biomass (Ratledge, 2004; Ratledge and Wynn, 2002). Oleaginous yeast species such as *Cryptococcus albidus*, *Yarrowia lipolytica*, *Cryptococcus curvatus* have been investigated for economical biodiesel production using VFA produced from waste stream or acetic acid as the only carbon source (Fei et al., 2011; Fontanille et al., 2012; Huang et al., 2018; Liu et al., 2017; Park et al., 2017).

Fei et al., 2011 investigated the use of VFAs for microbial lipid accumulation in cultures of *C. albidus* and achieved lipid content up to 27.8% with lipid yield coefficient on VFAs of 0.167 g/g of *C. albidus* at acetic, propionic, butyric acids ratio of 8:1:1. In another study, VFAs produced via anaerobic digestion of rice straw hydrolysates were used as a carbon source by oleaginous yeast *C. curvattus* (Park et al., 2017). The lipid content in the cells increased up to 28% in batch cultures. Interestingly the waste-derived VFAs from the rice straw resulted in a yield of 0.43 g VFAs/g substrate and 40% higher specific growth rate ($0.305\ h^{-1}$) than synthetic VFAs. VFAs as the carbon source resulted in a cetane number of 56–59, which is suitable for biodiesel production.

Factors such as VFA composition, pH, temperature, strains, concentration can influence the lipid production (Fei et al., 2011; Liu et al., 2017). VFA rich effluent from dark fermentation (bioconversion of organic substrate into biohydrogen. VFA was a by-product) were further used to cultivate oleaginous microalgae for lipid production and the results showed that the maximum algal biomass and lipid content reached 1.01 g /L and 38.5%, respectively, for butyrate-type fermentation effluent (Ren et al., 2018). Propionate-type fermentation effluent gave moderate biomass concentration of 0.9 g/L and total lipid content of 30.2%. The results emphasize the importance of VFA composition in lipid production.

It has been observed that the use of mixed VFAs as carbon source resulted in high lipid production and lipid yield (Liu et al., 2017). This makes the use of VFA from a waste stream a qualified source for lipid production. In studying the effect of temperature and pH on the use of VFAs for microbial lipid accumulation, it was concluded that the optimum culture temperature and pH were 25 °C and pH 6.0 (Fei et al., 2011). However, another study showed that an alkaline pH is more suitable for the synthesis of lipids when using a high concentration of acetic acid as the carbon source (Liu et al., 2017). It is important to know that different oleaginous yeast species were used. Poontawee et al. (2017) screened 418 yeast strains to find efficient oleaginous yeasts and found varying lipid accumulation abilities under the same conditions.

Moreover, inoculation concentration and nitrogen to carbon ratio are important factors for lipid production (Béligon et al., 2015; Liu et al., 2017). Whereas Béligon et al., (2015) highlighted that changes in nitrogen to carbon ratios do not induce drastic changes of lipid content, Liu et al. (2017) concluded that nitrogen to carbon ratio was crucial for the utilization of high-content VFAs. It has been shown in a study that

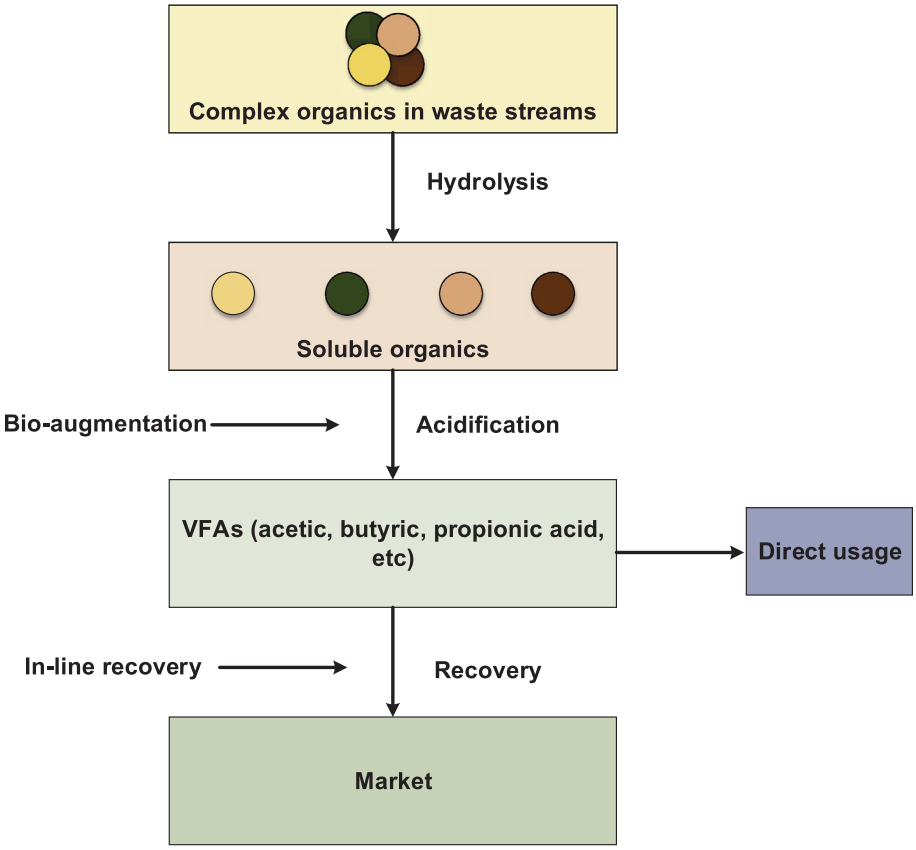


Fig. 3. Schematic diagram showing VFA production and recovery process from waste streams. Bioaugmentation and in-line recovery will enhance production and recovery of VFA respectively.

lipid contents in a batch cultivation of *C. curvattus* increased from 10.2% to 16.8% when carbon to nitrogen ratio increased from about 3.5 to 165 (Liu et al., 2016a,b).

5. Current challenges and future perspectives

Bio-based VFAs production from waste stream would be a promising way for resource recovery. However, further developments are still required to enable sustainable and economically feasible production and recovery methods. In this paper, the effects of different operational parameters, substrates, and mixed microbial cultures have been reviewed for bio-based VFA production as well as recovery methods have been examined as summarised in Fig. 3. Moreover, new technologies and methods such as in-line recovery methods for proper VFA recovery have been reviewed. However, there are many challenges that need to be resolved to make VFA production and recovery from waste streams a profitable option for carbon recovery. It is seen from this study, the most important challenges are optimizing the operational parameters for VFA production and selecting feasible recovery method.

5.1. VFA production

In bio-based VFA production from the waste streams, besides a number of studies about optimizing operation conditions, it is momentous to consider the following suggestions which are needed to be filled through more studies to analyse microbial community structure and to evaluate their interactions with VFAs production metabolic pathways. Moreover, using new waste-streams as a substrate such as different industries waste/wastewater will ensure sustainable, economically feasible and environmentally friendly approach.

Application of bio-augmentation strategy would be proper for enhancing the VFAs production as well as ensure one-type acid production. Nevertheless, there are some challenges for application of bio-augmentation which are discussed in Section 2.3. These challenges need to be addressed through research studies before bio-augmentation can be used to enhance VFA production from waste streams.

5.2. VFA recovery

Recovery will inevitably add to the total cost for VFA production from waste streams. In as much as VFA produced from waste streams needs to be recovered for usage, care needs to be taken in order not to incur too much cost which will not be economically feasible. The challenge now will be to select cost-effective recovery methods that will lead to maximum VFA recovery at a minimal cost. There is, therefore, the need for an extensive cost-benefit analysis for all VFA recovery methods.

It needs to be emphasized that decision on the choice of recovery methods will need to take into consideration the intended application of the recovered VFA. Some of the recovery methods such as pressure driven reverse osmosis and high voltage electrodialysis can be costly due to high energy cost, even though they may recover VFA with high purity. Knowledge of how different recovery methods will affect the suitability of applications of VFA will help in the selection of methods. In that case, if VFA recovered from a low-cost method with relatively low purity will be suitable for a particular application, there will be no need to use a high-cost method even if it can produce VFA with better purity. This suggests that that studies on the suitability of different VFA recovery methods for various application are essential.

It has been seen from section 3 that the recovery methods can recover total VFAs from VFA-rich effluents, however, separation of the various VFA composition is a major challenge. Strategies to separate the various components of VFA recovered will make the VFA from waste streams more valuable. The application of new methods, modification

of existing methods and/or combination of methods to recover and separate the individual VFAs present opportunity for new research.

6. Conclusions

Production of VFA from waste streams is getting the needed attention due to its benefits. Effects of operation conditions, substrate and mixed microbial cultures on VFA production and composition were reviewed. To understand in detail the effect of operating conditions and their combined effects on VFA production and composition, systematic studies are required. In addition, recovery methods have been evaluated and it is opined that the choice of recovery methods is based on the application of VFA. In-line VFA recovery and bioaugmentation, which are not used in common practice, are discussed as the approaches to enhance bio-based VFA production and recovery.

Acknowledgment

The authors would like to acknowledge the financial support provided by Vinnmer Marie Curie Incoming Grant (2016-04070).

References

Alkaya, E., Kaptan, S., Ozkan, L., Uludag-Demirer, S., Demirer, G.N., 2009. Recovery of acids from anaerobic acidification broth by liquid–liquid extraction. Chemosphere 77, 1137–1142.
Arslan, D., Zhang, Y., Steinbusch, K.J.J., Diels, L., Hamelers, H.V.M., Buisman, C.J.N., De Wever, H., 2017. In-situ carboxylate recovery and simultaneous pH control with tailor-configured bipolar membrane electrodialysis during continuous mixed culture fermentation. Sep. Purif. Technol. 175, 27–35.
Ataei, S.A., Vasheghani-Farahani, E., 2008. In situ separation of lactic acid from fermentation broth using ion exchange resins. J. Ind. Microbiol. Biotechnol. 35, 1229.
Aydin, S., Yesil, H., Tugtas, A.E., 2018. Recovery of mixed volatile fatty acids from anaerobically fermented organic wastes by vapor permeation membrane contactors. Bioresour. Technol. 250, 548–555.
Babu, S.K. and B.V., 2014. Propionic Acid Production via Fermentation Route using Renewable Sources 2–11.
Begum, S., Anupoju, G.R., Sridhar, S., Bhargava, S.K., Jegatheesan, V., Eshtiaghi, N., 2018a. Evaluation of single and two stage anaerobic digestion of landfill leachate: effect of pH and initial organic loading rate on volatile fatty acid (VFA) and biogas production. Bioresour. Technol. 251, 364–373.
Begum, S., Rao, G., Sridhar, S., Bhargava, S.K., Jegatheesan, V., Eshtiaghi, N., 2018b. Bioresource Technology Evaluation of single and two stage anaerobic digestion of land fi ll leachate : E ff ect of pH and initial organic loading rate on volatile fatty acid (VFA) and biogas production 251, 364–373.
Béligon, V., Poughon, L., Christophe, G., Lebert, A., Larroche, C., Fontanille, P., 2015. Improvement and modeling of culture parameters to enhance biomass and lipid production by the oleaginous yeast Cryptococcus curvatus grown on acetate. Bioresour. Technol. 192, 582–591.
Bengtsson, S., Karlsson, A., Alexandersson, T., Quadri, L., Hjort, M., Johansson, P., Morgan-Sagastume, F., Anterrieu, S., Arcos-Hernandez, M., Karabegovic, L., Magnusson, P., Werker, A., 2017. A process for polyhydroxyalkanoate (PHA) production from municipal wastewater treatment with biological carbon and nitrogen removal demonstrated at pilot-scale. N. Biotechnol. 35, 42–53.
Bermúdez-Penabad, N., Kennes, C., Veiga, M.C., 2017. Anaerobic digestion of tuna waste for the production of volatile fatty acids. Waste Manage. 68, 96–102.
Bertin, L., Martinez, G., Domingos, J.M.B., Rebecchi, S., Fava, F., 2016. Recovery of volatile fatty acids by solid phase extraction and their employment in concentrated feeding solution for polyhydroxyalkanoates production. N. Biotechnol. 33, S18.
Besselink, H., Brouwer, B., van der Burg, B., 2017. Validation and regulatory acceptance of bio-based approaches to assure feedstock, water & product quality in a bio-based economy. Ind. Crops Prod. 106, 138–145.
Bhatia, S.K., Yang, Y.-H., 2017. Microbial production of volatile fatty acids: current status and future perspectives. Rev. Environ. Sci. Bio/Technol. 16, 327–345.
Blasig, J.D., Holtzapple, M.T., Dale, B.E., Engler, C.R., Byers, F.M., 1992. Volatile fatty acid fermentation of AFEX-treated bagasse and newspaper by rumen microorganisms. Resour. Conserv. Recycl. 7, 95–114.
Bolaji, I.O., Dionisi, D., 2017. Acidogenic fermentation of vegetable and salad waste for chemicals production: effect of pH buffer and retention time. J. Environ. Chem. Eng. 5, 5933–5943.
Burniol-Figols, A., Varrone, C., Le, S.B., Daugaard, A.E., Skiadas, I.V., Gavala, H.N., 2018b. Combined polyhydroxyalkanoates (PHA) and 1,3-propanediol production from crude glycerol: selective conversion of volatile fatty acids into PHA by mixed microbial consortia. Water Res. 136, 180–191.
Burniol-Figols, A., Varrone, C., Daugaard, A.E., Le, S.B., Skiadas, I.V., Gavala, H.N., 2018a. Polyhydroxyalkanoates (PHA) production from fermented crude glycerol: study on the conversion of 1,3-propanediol to PHA in mixed microbial consortia. Water Res. 128, 255–266.
Cabrera-Rodríguez, C.I., Moreno-González, M., de Weerd, F.A., Viswanathan, V., van der Wielen, L.A.M., Straathof, A.J.J., 2017. Esters production via carboxylates from anaerobic paper mill wastewater treatment. Bioresour. Technol. 237, 186–192.
Chen, Y., Luo, J., Yan, Y., Feng, L., 2013. Enhanced production of short-chain fatty acid by co-fermentation of waste activated sludge and kitchen waste under alkaline conditions and its application to microbial fuel cells. Appl. Energy 102, 1197–1204.
Chen, Y., Jiang, X., Xiao, K., Shen, N., Zeng, R.J., Zhou, Y., 2017. Enhanced volatile fatty acids (VFAs) production in a thermophilic fermenter with stepwise pH increase – Investigation on dissolved organic matter transformation and microbial community shift. Water Res. 112, 261–268.
Cheryan, M., 2009. Acetic Acid Production. Appl. Microbiol. Ind. |, 144–149.
Chi, Z., Zheng, Y., Ma, J., Chen, S., 2011. Oleaginous yeast Cryptococcus curvatus culture with dark fermentation hydrogen production effluent as feedstock for microbial lipid production. Int. J. Hydrogen Energy 36, 9542–9550.
Colombo, B., Sciarria, T.P., Reis, M., Scaglia, B., Adani, F., 2016. Polyhydroxyalkanoates (PHAs) production from fermented cheese whey by using a mixed microbial culture. Bioresour. Technol. 218, 692–699.
de Araújo Cavalcante, W., Leitão, R.C., Gehring, T.A., Angenent, L.T., Santaella, S.T., 2017. Anaerobic fermentation for n-caproic acid production: a review. Process Biochem. 54, 106–119.
Dianne Stephenson, T.S., 1992. Bioaugmentation for enhancing biological wastewater treatment. Biotechnol. Adv. 10, 549–559.
Du, G., Liu, L., Chen, J., 2015. White Biotechnology for Organic Acids, Industrial Biorefineries & White Biotechnology. Elsevier B.V.
Edmiston, P.L., Gilbert, A.R., Harvey, Z., Mellor, N., 2018. Adsorption of short chain carboxylic acids from aqueous solution by swellable organically modified silica materials. Adsorption 24, 53–63.
Epsztein, R., Shaulsky, E., Dizge, N., Warsinger, D.M., Elimelech, M., 2018. Role of ionic charge density in donnan exclusion of monovalent anions by nanofiltration. Environ. Sci. Technol. 52, 4108–4116.
Fang, W., Ye, J., Zhang, P., Zhu, X., Zhou, S., 2017. Solid-state anaerobic fermentation of spent mushroom compost for volatile fatty acids production by pH regulation. Int. J. Hydrogen Energy 42, 18295–18300.
Fargues, C., Lewandowski, R., Lameloise, M.L., 2010. Evaluation of ion-exchange and adsorbent resins for the detoxification of beet distillery effluents. Ind. Eng. Chem. Res. 49, 9248–9257.
Fei, Q., Chang, H.N., Shang, L., Choi, J., Kim, N., Kang, J., 2011. The effect of volatile fatty acids as a sole carbon source on lipid accumulation by Cryptococcus albidus for biodiesel production. Bioresour. Technol. 102, 2695–2701.
Fontanille, P., Kumar, V., Christophe, G., Nouaille, R., Larroche, C., 2012. Bioconversion of volatile fatty acids into lipids by the oleaginous yeast Yarrowia lipolytica. Bioresour. Technol. 114, 443–449.
Fortela, D.L., Hernandez, R., French, W.T., Zappi, M., Revellame, E., Holmes, W., Mondala, A., 2016. Extent of inhibition and utilization of volatile fatty acids as carbon sources for activated sludge microbial consortia dedicated for biodiesel production. Renew. Energy 96, 11–19.
Fradinho, J.C., Oehmen, A., Reis, M.A.M., 2014. Photosynthetic mixed culture polyhydroxyalkanoate (PHA) production from individual and mixed volatile fatty acids (VFAs): substrate preferences and co-substrate uptake. J. Biotechnol. 185, 19–27.
Fu, Z., Holtzapple, M.T., 2010. Consolidated bioprocessing of sugarcane bagasse and chicken manure to ammonium carboxylates by a mixed culture of marine microorganisms. Bioresour. Technol. 101, 2825–2836.
Garcia-Aguirre, J., Aymerich, E., González-Mtnez. de Goñi, J., Esteban-Gutiérrez, M., 2017. Selective VFA production potential from organic waste streams: assessing temperature and pH influence. Bioresour. Technol. 244, 1081–1088.
Ge, S., Usack, J.G., Spirito, C.M., Angenent, L.T., 2015. Long-term n-caproic acid production from yeast-fermentation beer in an anaerobic bioreactor with continuous product extraction. Environ. Sci. Technol. 49, 8012–8021.
Gruhn, M., Frigon, J.C., Guiot, S.R., 2016. Acidogenic fermentation of Scenedesmus sp.-AMDD: comparison of volatile fatty acids yields between mesophilic and thermophilic conditions. Bioresour. Technol. 200, 624–630.
Hao, J., Wang, H., 2015. Volatile fatty acids productions by mesophilic and thermophilic sludge fermentation: biological responses to fermentation temperature. Bioresour. Technol. 175, 367–373.
Hatti-Kaul, R., Törnvall, U., Gustafsson, L., Börjesson, P., 2007. Industrial biotechnology for the production of bio-based chemicals – a cradle-to-grave perspective. Trends Biotechnol.
Herrero, M., Stuckey, D.C., 2015. Bioaugmentation and its application in wastewater treatment: A review. Chemosphere 140, 119–128.
Huang, W.W., Huang, W.W., Yuan, T., Zhao, Z., Cai, W., Zhang, Z., Lei, Z., Feng, C., 2016. Volatile fatty acids (VFAs) production from swine manure through short-term dry anaerobic digestion and its separation from nitrogen and phosphorus resources in the digestate. Water Res. 90, 344–353.
Huang, X., Shen, Y., Luo, H., Liu, J., Liu, J., 2018. Enhancement of extracellular lipid production by oleaginous yeast through preculture and sequencing batch culture strategy with acetic acid. Bioresour. Technol. 247, 395–401.
Jankowska, E., Chwialkowska, J., Stodolny, M., Oleskowicz-Popiel, P., 2015. Effect of pH and retention time on volatile fatty acids production during mixed culture fermentation. Bioresour. Technol. 190, 274–280.
Jankowska, E., Chwialkowska, J., Stodolny, M., Oleskowicz-Popiel, P., 2017. Volatile fatty acids production during mixed culture fermentation – The impact of substrate complexity and pH. Chem. Eng. J. 326, 901–910.
Jiang, J., Zhang, Y., Li, K., Wang, Q., Gong, C., Li, M., 2013. Volatile fatty acids production from food waste: Effects of pH, temperature, and organic loading rate. Bioresour. Technol. 143, 525–530.
Jin, D., Chen, J., Lun, S., 1999. Production of poly(hydroxyalkanoate) by a composite anaerobic acidification–fermentation system. Process Biochem. 34, 829–833.

Jones, R.J., Massanet-Nicolau, J., Guwy, A., Premier, G.C., Dinsdale, R.M., Reilly, M., 2015. Removal and recovery of inhibitory volatile fatty acids from mixed acid fermentations by conventional electrodialysis. Bioresour. Technol. 189, 279–284.
Kavanaugh, M.C., Trussell, R.R., 1980. Design of aeration towers to strip volatile contaminants from drinking water. J. Am. Water Works Assn. 72, 684–692.
Khan, M.A., Ngo, H.H., Guo, W.S., Liu, Y., Nghiem, L.D., Hai, F.I., Deng, L.J., Wang, J., Wu, Y., 2016. Optimization of process parameters for production of volatile fatty acid, biohydrogen and methane from anaerobic digestion. Bioresour. Technol. 219, 738–748.
Kim, H., Kim, J., Shin, S.G., Hwang, S., Lee, C., 2016. Continuous fermentation of food waste leachate for the production of volatile fatty acids and potential as a denitrification carbon source. Bioresour. Technol. 207, 440–445.
Korkakaki, E., van Loosdrecht, M.C.M., Kleerebezem, R., 2016. Survival of the fastest: selective removal of the side population for enhanced PHA production in a mixed substrate enrichment. Bioresour. Technol. 216, 1022–1029.
Kuruti, K., Nakkasunchi, S., Begum, S., Juntupally, S., Arelli, V., Anupoju, G.R., 2017. Rapid generation of volatile fatty acids (VFA) through anaerobic acidification of livestock organic waste at low hydraulic residence time (HRT). Bioresour. Technol. 238, 188–193.
Lee, W.S., Chua, A.S.M., Yeoh, H.K., Ngoh, G.C., 2014. A review of the production and applications of waste-derived volatile fatty acids. Chem. Eng. J. 235, 83–99.
Li, C., Cao, J., Ren, H., Li, Y., Tang, S., 2015a. Comparison on kinetics and microbial community among denitrification process fed by different kinds of volatile fatty acids. Process Biochem. 50, 447–455.
Li, Z., Qin, W., Dai, Y., 2002. Liquid−liquid equilibria of acetic, propionic, butyric, and valeric acids with trioctylamine as extractant. J. Chem. Eng. Data 47, 843–848.
Li, X., Swan, J.E., Nair, G.R., Langdon, A.G., 2015b. Preparation of volatile fatty acid (VFA) calcium salts by anaerobic digestion of glucose. Biotechnol. Appl. Biochem. 62, 476–482.
Lim, S.-J., Choi, D.W., Lee, W.G., Kwon, S., Chang, H.N., 2000. Volatile fatty acids production from food wastes and its application to biological nutrient removal. Bioprocess. Eng. 22, 543–545.
Liu, H., Han, P., Liu, H., Zhou, G., Fu, B., Zheng, Z., 2018. Full-scale production of VFAs from sewage sludge by anaerobic alkaline fermentation to improve biological nutrients removal in domestic wastewater. Bioresour. Technol. 260, 105–114.
Liu, J., Liu, J.-N., Yuan, M., Shen, Z.-H., Peng, K.-M., Lu, L.-J., Huang, X.-F., 2016b. Bioconversion of volatile fatty acids derived from waste activated sludge into lipids by Cryptococcus curvatus. Bioresour. Technol. 211, 548–555.
Liu, J., Huang, X., Chen, R., Yuan, M., Liu, J., 2017. Efficient bioconversion of high-content volatile fatty acids into microbial lipids by Cryptococcus curvatus ATCC 20509. Bioresour. Technol. 239, 394–401.
Liu, F., Tian, Y., Ding, Y., Li, Z., 2016a. The use of fermentation liquid of wastewater primary sedimentation sludge as supplemental carbon source for denitrification based on enhanced anaerobic fermentation. Bioresour. Technol. 219, 6–13.
Maitlis, P.M., Haynes, A., Sunley, G.J., Howard, M.J., 1996. Methanol carbonylation revisited: thirty years on. J. Chem. Soc. - Dalt. Trans. 2187–2196.
Mansouri, S.S., Udugama, I.A., Cignitti, S., Mitic, A., Flores-Alsina, X., Gernaey, K.V., 2017. Resource recovery from bio-based production processes: a future necessity? Curr. Opin. Chem Eng.
Marang, L., Jiang, Y., van Loosdrecht, M.C.M., Kleerebezem, R., 2014. Impact of non-storing biomass on PHA production: an enrichment culture on acetate and methanol. Int. J. Biol. Macromol. 71, 74–80.
Marketsandmarkets, 2018. Butyric Acid Market by Application (Animal Feed, Chemicals Intermediate, Food & Flavors, Pharmaceuticals, Perfumes, Others), by Type (Synthetic Butyric Acid, Renewable Butyric Acid) by Geography (APAC, North America, Europe, Row) - Global Analysis and For. Pune, Maharashtra.
Masse, L., Massé, D.I., Pellerin, Y., Dubreuil, J., 2010. Osmotic pressure and substrate resistance during the concentration of manure nutrients by reverse osmosis membranes. J. Membr. Sci. 348, 28–33.
Mohd-Zaki, Z., Bastidas-Oyanedel, J., Lu, Y., Hoelzle, R., Pratt, S., Slater, F., Batstone, D., 2016. Influence of pH regulation mode in glucose fermentation on product selection and process stability. Microorganisms 4, 2.
Moresi, M., Parente, E., 2014. FERMENTATION (INDUSTRIAL) | production of some organic acids (citric, gluconic, lactic, and propionic). Encycl. Food Microbiol. 1, 804–815.
Mordor Intelligence, 2018. Acetic Acid Market - Segmented by End-user Industry, Application, and Geography – Growth, Trends, and Forecast (2018–2023). Hyderabad (India).
Owusu-Agyeman, I., Malovanyy, A., Plaza, E., 2015. Pre-concentration of ammonium to enhance treatment of wastewater using the partial nitritation/anammox process. Environ. Technol. 36, 1256–1264.
Pan, X.-R., Li, W.-W., Huang, L., Liu, H.-Q., Wang, Y.-K., Geng, Y.-K., Lam, P.K.-S., Yu, H.-Q., 2018. Recovery of high-concentration volatile fatty acids from wastewater using an acidogenesis-electrodialysis integrated system. Bioresour. Technol. 260, 61–67.
Park, G.W., Chang, H.N., Jung, K., Seo, C., Kim, Y.-C., Choi, J.H., Woo, H.C., Hwang, I., 2017. Production of microbial lipid by Cryptococcus curvatus on rice straw hydrolysates. Process Biochem. 56, 147–153.
Peng, X., Aragão, R., Achu, I., Liu, J., 2014. Impact of bioaugmentation on biochemical methane potential for wheat straw with addition of Clostridium cellulolyticum. Bioresour. Technol. 152, 567–571.
Playne, M.J., Smith, B.R., 1983. Toxicity of organic extraction reagents to anaerobic bacteria. Biotechnol. Bioeng. 25, 1251–1265.
Poontawee, R., Yongmanitchai, W., Limtong, S., 2017. Efficient oleaginous yeasts for lipid production from lignocellulosic sugars and effects of lignocellulose degradation compounds on growth and lipid production. Process Biochem. 53, 44–60.
Qian, Q., Zhang, J., Cui, M., Han, B., 2016. Synthesis of acetic acid via methanol hydrocarboxylation with CO2 and H2. Nat. Commun. 7, 11481.
Rajabzadeh, A.R., Ruzich, N., Zendehboudi, S., Rahbari, M., 2012. Biomass leachate treatment and nutrient recovery using reverse osmosis: experimental study and hybrid artificial neural network modeling. Energy Fuels 26, 7155–7163.
Raspor, P., Goranovič, D., 2008. Biotechnological applications of acetic acid bacteria. Crit. Rev. Biotechnol. 28, 101–124.
Ratledge, C., 2004. Fatty acid biosynthesis in microorganisms being used for Single Cell Oil production. Biochimie 86, 807–815.
Ratledge, C., Wynn, J.P., 2002. The biochemistry and molecular biology of lipid accumulation in oleaginous microorganisms. Adv. Appl. Microbiol. 51, 1–52.
Rebecchi, S., Pinelli, D., Bertin, L., Zama, F., Fava, F., Frascari, D., 2016. Volatile fatty acids recovery from the effluent of an acidogenic digestion process fed with grape pomace by adsorption on ion exchange resins. Chem. Eng. J. 306, 629–639.
Reddy, M.V., Hayashi, S., Choi, D., Cho, H., Chang, Y.C., 2018. Short chain and medium chain fatty acids production using food waste under non-augmented and bio-augmented conditions. J. Clean. Prod. 176, 645–653.
Ren, H.-Y., Kong, F., Ma, J., Zhao, L., Xie, G.-J., Xing, D., Guo, W.-Q., Liu, B.-F., Ren, N.-Q., 2018. Continuous energy recovery and nutrients removal from molasses wastewater by synergistic system of dark fermentation and algal culture under various fermentation types. Bioresour. Technol. 252, 110–117.
Research Grand View, 2018. Global Propionic Acid Market By Application (Animal Feed, Calcium & Sodium Propionate, Cellulose Acetate Propionate). San Francisco.
Reyhanitash, E., Zaalberg, B., Kersten, S.R.A., Schuur, B., 2016. Extraction of volatile fatty acids from fermented wastewater. Sep. Purif. Technol. 161, 61–68.
Reyhanitash, E., Kersten, S.R.A., Schuur, B., 2017. Recovery of volatile fatty acids from fermented wastewater by adsorption. ACS Sustainable Chem. Eng. 5, 9176–9184.
Rocha, M.A.A., Raeissi, S., Hage, P., Weggemans, W.M.A., van Spronsen, J., Peters, C.J., Kroon, M.C., 2017. Recovery of volatile fatty acids from water using medium-chain fatty acids and a cosolvent. Chem. Eng. Sci. 165, 74–80.
Roume, H., Arends, J.B.A., Ameril, C.P., Patil, S.A., Rabaey, K., 2016. Enhanced product recovery from glycerol fermentation into 3-carbon compounds in a bioelectrochemical system combined with in situ extraction. Front. Bioeng. Biotechnol. 4.
Roy, Y., Warsinger, D.M., Lienhard, J.H., 2017. Effect of temperature on ion transport in nanofiltration membranes: diffusion, convection and electromigration. Desalination 420, 241–257.
Ryu, B.-G., Kim, J., Kim, K., Choi, Y.-E., Han, J.-I., Yang, J.-W., 2013. High-cell-density cultivation of oleaginous yeast Cryptococcus curvatus for biodiesel production using organic waste from the brewery industry. Bioresour. Technol. 135, 357–364.
Saïd El Fantroussi, S., Agathos, N., 2005. Is bioaugmentation a feasible strategy for pollutant removal and site remediation? Curr. Opin. Microbiol. 8, 268–275.
Scoma, A., Varela-Corredor, F., Bertin, L., Gostoli, C., Bandini, S., 2016. Recovery of VFAs from anaerobic digestion of dephenolized Olive Mill Wastewaters by Electrodialysis. Sep. Purif. Technol. 159, 81–91.
Shang, R., van den Broek, W.B.P., Heijman, S.G.J., van Agtmaal, S., Rietveld, L.C., 2011. Wastewater reuse through RO: a case study of four RO plants producing industrial water. Desalin. Water Treat. 34, 408–415.
Shen, L., Hu, H., Ji, H., Cai, J., He, N., Li, Q., Wang, Y., 2014. Production of poly(hydroxybutyrate–hydroxyvalerate) from waste organics by the two-stage process: Focus on the intermediate volatile fatty acids. Bioresour. Technol. 166, 194–200.
Shen, D., Yin, J., Yu, X., Wang, M., Long, Y., Shentu, J., Chen, T., 2017. Acidogenic fermentation characteristics of different types of protein-rich substrates in food waste to produce volatile fatty acids. Bioresour. Technol. 227, 125–132.
Shi, L., Hu, Y., Xie, S., Wu, G., Hu, Z., Zhan, X., 2018. Recovery of nutrients and volatile fatty acids from pig manure hydrolysate using two-stage bipolar membrane electrodialysis. Chem. Eng. J. 334, 134–142.
Silva, F.C., Serafim, L.S., Nadais, H., Arroja, L., Capela, I., 2013. Acidogenic fermentation towards valorisation of organic waste streams into volatile fatty acids. Chem. Biochem. Eng. Q. 27, 467–476.
Singh, S.P., Wilson, J.H., Counce, R.M., Lucero, A.J., Reed, G.D., Ashworth, R.A., Elliott, M.G., 1992. Removal of volatile organic compounds from groundwater using a rotary air stripper. Ind. Eng. Chem. Res. 31, 574–580.
Slezak, R., Grzelak, J., Krzystek, L., Ledakowicz, S., 2017. The effect of initial organic load of the kitchen waste on the production of VFA and H2 in dark fermentation. Waste Manage. 68, 610–617.
Strang, O., Ács, N., Wirth, R., Maróti, G., Bagi, Z., Rákhely, G., Kovács, K.L., 2017. Bioaugmentation of the thermophilic anaerobic biodegradation of cellulose and corn stover. Anaerobe 46, 104–113.
Strathmann, H., 2010. Electrodialysis, a mature technology with a multitude of new applications. Desalination 264, 268–288.
Sydney, E.B., Novak, A.C., Rosa, D., Pedroni Medeiros, A.B., Brar, S.K., Larroche, C., Soccol, C.R., 2018. Screening and bioprospecting of anaerobic consortia for biohydrogen and volatile fatty acid production in a vinasse based medium through dark fermentation. Process Biochem.
Tamis, J., Lužkov, K., Jiang, Y., van Loosdrecht, M.C.M., Kleerebezem, R., 2014. Enrichment of Plasticicumulans acidivorans at pilot-scale for PHA production on industrial wastewater. J. Biotechnol. 192, 161–169.
Tang, J., Jia, S., Qu, S., Xiao, Y., Yuan, Y., Ren, N.-Q., 2014. An integrated biological hydrogen production process based on ethanol-type fermentation and bipolar membrane electrodialysis. Int. J. Hydrogen Energy 39, 13375–13380.
Tao, B., Passanha, P., Kumi, P., Wilson, V., Jones, D., Esteves, S., 2016. Recovery and concentration of thermally hydrolysed waste activated sludge derived volatile fatty acids and nutrients by microfiltration, electrodialysis and struvite precipitation for polyhydroxyalkanoates production. Chem. Eng. J. 295, 11–19.
Temudo, M.F., Kleerebezem, R., Van Loosdrecht, M., 2007. Influence of the pH on (Open) mixed culture fermentation of glucose: a chemostat study. Biotechnol. Bioeng. 98, 69–79.

Trad, Z., Akimbomi, J., Vial, C., Larroche, C., Taherzadeh, M.J., Fontaine, J.-P., 2015. Development of a submerged anaerobic membrane bioreactor for concurrent extraction of volatile fatty acids and biohydrogen production. Bioresour. Technol. 196, 290–300.

Tsapekos, P., Kougias, P.G., Vasileiou, S.A., Treu, L., Campanaro, S., Lyberatos, G., Angelidaki, I., 2017. Bioaugmentation with hydrolytic microbes to improve the anaerobic biodegradability of lignocellulosic agricultural residues. Bioresour. Technol. 234, 350–359.

Tugtas, A.E., 2014. Recovery of volatile fatty acids via membrane contactor using flat membranes: experimental and theoretical analysis. Waste Manage. 34, 1171–1178.

Ucisik, A.S., Henze, M., 2008. Biological hydrolysis and acidification of sludge under anaerobic conditions: the effect of sludge type and origin on the production and composition of volatile fatty acids. Water Res. 42, 3729–3738.

Valentino, F., Morgan-Sagastume, F., Campanari, S., Villano, M., Werker, A., Majone, M., 2017. Carbon recovery from wastewater through bioconversion into biodegradable polymers. N. Biotechnol. 37, 9–23.

Venkateswar Reddy, M., Amulya, K., Rohit, M.V., Sarma, P.N., Venkata Mohan, S., 2014. Valorization of fatty acid waste for bioplastics production using Bacillus tequilensis: integration with dark-fermentative hydrogen production process. Int. J. Hydrogen Energy 39, 7616–7626.

Wadekar, S.S., Vidic, R.D., 2017. Influence of active layer on separation potentials of nanofiltration membranes for inorganic ions. Environ. Sci. Technol. 51, 5658–5665.

Wang, X., Wang, Y., Zhang, X., Xu, T., 2012. In situ combination of fermentation and electrodialysis with bipolar membranes for the production of lactic acid: operational compatibility and uniformity. Bioresour. Technol. 125, 165–171.

Wang, X., Wang, Y., Zhang, X., Feng, H., Xu, T., 2013. In-situ combination of fermentation and electrodialysis with bipolar membranes for the production of lactic acid: continuous operation. Bioresour. Technol. 147, 442–448.

Wang, K., Yin, J., Shen, D., Li, N., 2014. Anaerobic digestion of food waste for volatile fatty acids (VFAs) production with different types of inoculum: effect of pH. Bioresour. Technol. 161, 395–401.

Weng, Y.-H., Wei, H.-J., Tsai, T.-Y., Lin, T.-H., Wei, T.-Y., Guo, G.-L., Huang, C.-P., 2010. Separation of furans and carboxylic acids from sugars in dilute acid rice straw hydrolyzates by nanofiltration. Bioresour. Technol. 101, 4889–4894.

Wu, Q.-L., Guo, W.-Q., Zheng, H.-S., Luo, H.-C., Feng, X.-C., Yin, R.-L., Ren, N.-Q., 2016. Enhancement of volatile fatty acid production by co-fermentation of food waste and excess sludge without pH control: the mechanism and microbial community analyses. Bioresour. Technol. 216, 653–660.

Xiong, B., Richard, T.L., Kumar, M., 2015. Integrated acidogenic digestion and carboxylic acid separation by nanofiltration membranes for the lignocellulosic carboxylate platform. J. Membr. Sci. 489, 275–283.

Xu, Z., Jiang, L., 2011. Butyric acid. Compr. Biotechnol. 207–215.

Xu, Z., Shi, Z., Jiang, L., 2011. Acetic and propionic. In: Acids Compr. Biotechnol., second ed. pp. 189–199. https://doi.org/10.1016/B978-0-08-088504-9.00162-8.

Yan, F., Jiang, J., Zhang, H., Liu, N., Zou, Q., 2018. Biological denitrification from mature landfill leachate using a food-waste-derived carbon source. J. Environ. Manage. 214, 184–191.

Yaroshchuk, A., Bruening, M.L., 2017. An analytical solution of the solution-diffusion-electromigration equations reproduces trends in ion rejections during nanofiltration of mixed electrolytes. J. Membr. Sci. 523, 361–372.

Yesil, H., Tugtas, A.E., Bayrakdar, A., Calli, B., 2014. Anaerobic fermentation of organic solid wastes: volatile fatty acid production and separation. Water Sci. Technol. 69, 2132–2138.

Yin, J., Yu, X., Zhang, Y., Shen, D., Wang, M., Long, Y., Chen, T., 2016. Enhancement of acidogenic fermentation for volatile fatty acid production from food waste: effect of redox potential and inoculum. Bioresour. Technol. 216, 996–1003.

Zacharof, M.-P., Lovitt, R.W., 2013. Complex effluent streams as a potential source of volatile fatty acids. Waste Biomass Valorization 4, 557–581.

Zacharof, M.-P., Lovitt, R.W., 2014. Recovery of volatile fatty acids (VFA) from complex waste effluents using membranes. Water Sci. Technol. 69, 495–503.

Zacharof, M.-P., Mandale, S.J., Williams, P.M., Lovitt, R.W., 2016. Nanofiltration of treated digested agricultural wastewater for recovery of carboxylic acids. J. Clean. Prod. 112, 4749–4761.

Zhang, Y., Angelidaki, I., 2015. Bioelectrochemical recovery of waste-derived volatile fatty acids and production of hydrogen and alkali. Water Res. 81, 188–195.

Zhang, P., Chen, Y., Zhou, Q., 2009. Waste activated sludge hydrolysis and short-chain fatty acids accumulation under mesophilic and thermophilic conditions: Effect of pH. Water Res. 43, 3735–3742.

Zhang, F., Chen, Y., Dai, K., Shen, N., Zeng, R.J., 2015. The glucose metabolic distribution in thermophilic (55 °c) mixed culture fermentation: a chemostat study. Int. J. Hydrogen Energy 40, 919–926.

Zhang, H., Jiang, J., Li, M., Yan, F., Gong, C., Wang, Q., 2016a. Biological nitrate removal using a food waste-derived carbon source in synthetic wastewater and real sewage. J. Environ. Manage. 166, 407–413.

Zhang, Y., Wang, X.C., Cheng, Z., Li, Y., Tang, J., 2016b. Effect of fermentation liquid from food waste as a carbon source for enhancing denitrification in wastewater treatment. Chemosphere 144, 689–696.

Zhao, J., Wang, D., Liu, Y., Ngo, H.H., Guo, W., Yang, Q., Li, X., 2018. Novel stepwise pH control strategy to improve short chain fatty acid production from sludge anaerobic fermentation. Bioresour. Technol. 249, 431–438.

Zheng, X., Chen, Y., Wang, X., Wu, J., 2017. Using mixed sludge-derived short-chain fatty acids enhances power generation of microbial fuel cells. Energy Procedia 105, 1282–1288.

Zhou, F., Wang, C., Wei, J., 2013b. Simultaneous acetic acid separation and monosaccharide concentration by reverse osmosis. Bioresour. Technol. 131, 349–356.

Zhou, F., Wang, C., Wei, J., 2013a. Separation of acetic acid from monosaccharides by NF and RO membranes: performance comparison. J. Membr. Sci. 429, 243–251.

Zhou, M., Zhou, J., Tan, M., Du, J., Yan, B., Wong, J.W.C., Zhang, Y., 2017. Enhanced carboxylic acids production by decreasing hydrogen partial pressure during acidogenic fermentation of glucose. Bioresour. Technol. 245, 44–51.

Zhou, M., Yan, B., Wong, J.W.C., Zhang, Y., 2018. Enhanced volatile fatty acids production from anaerobic fermentation of food waste: a mini-review focusing on acidogenic metabolic pathways. Bioresour. Technol. 248, 68–78.

Zigová, J., Šturdík, E., 2000. Advances in biotechnological production of butyric acid. J. Ind. Microbiol.Biotechnol. 24, 153–160.