Feasibility of membrane processes for the recovery and purification of bio-based volatile fatty acids: A comprehensive review

Feasibility of Membrane Processes for the Recovery and Purification of Bio-Based Volatile Fatty Acids: A Comprehensive Review

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Contents

Abstract

Volatile fatty acids (VFAs) can be produced from fermentation/anaerobic digestion of wastes and are a valuable substrate for numerous applications, such as those related to the food, tanning, petrochemicals, pharmaceuticals, cosmetics, and chemicals industry. They are also inexpensive raw materials for developing alternative sources of energy. However, the separation and purification of VFAs produced from fermented wastewaters are not straightforward goals, due to the low concentration of these compounds in the fermentation broths and owing to the complexity of these mixtures. Cost-effective and sustainable technologies must be developed to recover VFAs efficiently and allow their beneficial use. In this paper, a comprehensive review of VFAs recovery/purification methods is provided, with focus on membrane-based processes. First, the VFAs production methods, application, and conventional processes (distillation, precipitation, adsorption, and extraction) for their recovery are briefly reviewed. Then, the ability of various membrane-based techniques to separate and purify VFAs are evaluated and discussed in detail. This discussion includes the processes of microfiltration/ultrafiltration, nanofiltration, reverse osmosis, forward osmosis, membrane distillation, electrodialysis, membrane contractor, and pervaporation. Extensive background and examples of applications are also provided to show the effectiveness of membrane processes . Finally, challenges and future research directions are highlighted.

Keywords: Bio-based Volatile fatty acids, Separation, Purification, Membrane processes

1. Introduction

Volatile fatty acids (VFAs) are saturated or unsaturated carboxylic acids consisting of short chains of carbon (usually six or fewer carbon atoms), e.g., acetic, formic, propionic, butyric acid [1]. VFAs are water-soluble organic acids "capable of being distilled at atmospheric pressure" [2]. These chemicals are inaccurately called short-chain fatty acids (SCFAs) in various reports [3, 4]. VFAs are commonly produced via engineered biochemical degradation of agricultural and food products, e.g., agro-industrial lignocellulosic wastes, and as a by-product of petrochemical processes [1, 5-8]. Moreover, VFAs are naturally produced through microbial fermentation of organic matter in landfill leachate, food and water wastes, and generally in all environmental systems [9]. These compounds are important intermediates and metabolites of biological processes and accordingly, their presence in the environment ascertains the presence of bacterial activity. Numerous materials, including antimicrobials, alcohols, aldehydes, ketones, esters, and olefins, are synthesized using VFAs [10, 11]. Applications of VFAs are thus widespread, including feed for microbial fuel cells [12, 13], cosmetics and textiles [14, 15], fermentation feed for hydrogen [16] and biofuel production [17, 18], carbon resource alternatives for wastewater treatment plants [19] and phosphorous removal processes [20], synthesis of biopolymer and bioplastics [21, 22]. Therefore, the production, purification, and recovery of VFAs are critical for several industrial applications, such as those related to renewable energy, fuel production, and water and wastewater treatment. While organic wastes have great potential to be utilized as feeds in biological process for VFAs production [5], the presence itself of VFAs may inhibit these fermentation- based technologies [23]. Aggregation of produced VFAs may alter the process, transformation pathways, and render some reaction thermodynamically unfavorable [23]. To control the efficient and stable production of VFAs, their continuous harvesting from the fermentation medium is critical [24].

Progress in the development of downstream VFA recovery processes has been remarkable in recent years [25], together with the improvement of detection methods [2, 9] and purification techniques [26, 27]. VFAs recovery from fermented or digested effluents or from the waste streams of these processes is a challenging process because of the low concentration of the acids and the complex physicochemical nature of these solutions [27]. Furthermore, extensive pretreatment of these streams is frequently needed to increase the practicability of the recovery process [28]. Various techniques exist that can be applied to recover organic acids from aqueous solutions, including electrodialysis [29], chemical precipitation [30], ion-exchange [31], solvent extraction [32], distillation [33, 34], adsorption [35] and membrane processes [27, 36]. Specifically, membrane-based separation is potentially efficient, cost-effective, and eco-friendly, thus it is a promising option for VFAs recovery and purification [24]. Membrane technologies, such as electrodialysis, microfiltration, ultrafiltration, nanofiltration/reverse osmosis, forward osmosis, membrane contactor, membrane distillation, pervaporation are commonly applied in the fractionation, clarification, desalination, and concentration of salts and organics [37-41]. This review discusses the production, application and purification of VFAs with special focus on membrane technology as an economical and promising process for their recovery. Also, research challenges, technology restrictions and future research directions are highlighted.

2. Production methods of VFAs

Nowadays, most of the VFAs required for industrial applications are produced via chemical routes [42]. However, due to issues related to the availability and price of global petroleum resources, as well as to increasing awareness of their environmental effects in terms of pollution and climate change, the interest in alternative methods of VFAs production has renewed [43-45]. Biological

VFAs production methods could be classified in anaerobic digestion and dark fermentation. These approaches can be implemented on a number of substrates derived from diverse liquid or solid food or agricultural sources along with other complex effluent streams, such as industrial or municipal wastewaters [1]. The combination of different types of waste has also been applied to produce VFAs [46].

Generally, anaerobic digestion includes the following four steps [47]: (i) Hydrolysis, which yields small and bioavailable monomers and oligomers by degradation of larger and more complex molecules . (ii) Fermentation, which mainly consists of VFAs production, together with carbon dioxide, and hydrogen. (iii) Acetogenesis, which turns hydrogen and carbon dioxide into acetate. (iv) Methanogenesis, the step during which methane and water are produced from acetate, formaldehyde, carbon dioxide, and hydrogen. Dark fermentation is an altered form of anaerobic digestion in which the fourth step is eliminated. This process involves only the breaking down of complex polysaccharides, proteins, and similar molecules into simpler monomers using hydrolytic reactions and the subsequent fermentation of the resulting molecules through acidogenesis, which leads to VFA production. The anaerobic processes of hydrolysis and acidogenesis may be performed in the same reactor, simultaneously. Acetic acid, propionic acid, butyric acid, isobutyric acid, and isovaleric acid can be effectively synthesized through such microbiological routes.

Consuming various raw materials as the feed, numerous microbes have been investigated and proven capable of producing VFAs, i.e., *Acetobacter, Clostridium, Kluyveromyces Propionobacterium and Moorela.* Conventionally, VFA production has been initiated using pure sugars as feedstock, e.g., glucose or xylose, due to the high yield and suitable pathway control associated with these substrates [15, 48]. However, pure sugars are expensive raw materials, whose extensive use may increase the production costs. Lignocellulosic resources of much lower

purity and economic value are highly available, and their use has been proposed as an alternative to sugars for VFA production. In this case, feedstock pretreatments (physical, chemical and enzymatic) are needed to improve the subsequent microbial conversion of these resources. As pre-treatment may be extensive and cumbersome for some lignocellulosic sources, techno-economic assessments are useful to assess the feasibility of each substrate and to identify the best and most economical transformation route [49, 50]. A recent approach falling within the framework of circular economy, consists of the use of organic-rich wastes as feedstock for VFA production, including wastewater sludge [5, 51] and food waste [16, 52], potentially resulting in a lower production cost. A number of comprehensive reviews have been presented around the microbiological conversion of these waste sources into VFAs, covering the properties of different feed raw materials, pretreatment methods, metabolic pathways, enhancement of biochemical reactions, and the activity of various microbial communities [47, 53].

3. Applications of VFAs

VFAs are extremely valuable substrates for a plethora of applications in the tanning, food, pharmaceuticals, cosmetics, chemicals, petrochemicals, bioenergy, and biomaterials industry [54]. VFAs are also inexpensive raw materials with the potential to be used for developing alternative routes of generating energy. Among the options to substitute fossil fuels, biodiesel is a fuel that can be produced starting from lipids [55-57]. Some bacteria, fungi, and yeast are able to consume VFAs to produce free fatty acids or triglycerides from which biodiesel is obtained through transesterification or esterification with alcohols (e.g., ethanol or methanol) [58-60]. This route would allow the production of biodiesel from a non-edible source, different from oil-rich agricultural commodities (e.g., palm and soybeans), whose employment as starting materials for

energy production has raised ethical and environmental issues [61-63]. Indeed, the microbial lipid synthesized from VFAs has been found highly suitable for biodiesel production [17, 64]. VFAs have also been utilized as precursors in microbial fuel cells (MFC), bio-electrochemical systems using microorganisms to exploit the chemical energy of the organic substrate as a potential cost-effective technology to produce electricity [65-67]. Single-compartment MFC, two-compartment MFC, stacked MFC, and upflow mode MFC, are different types of MFC that have been successfully applied with VFAs as feed [68].

VFAs can also be utilized as substrates under anaerobic conditions in order to produce biogas, which is suitable for power and heat generation due to its high content of methane (65–70 v/v %) [69]. Additionally, VFAs can be converted to hydrogen by electrohydrolysis [70], photo fermentation [71] or in microbial electrolysis cells [72]. There, the protons produced from the electrohydrolysis of VFAs can combine with electrons released from the metal electrode (e.g., copper electrode) by application of direct current voltage to produce hydrogen [70]. In photo fermentation, hydrogen is instead produced by the activity of non-sulfur bacteria consuming VFAs in the presence of light [73]. As dark fermentation produces VFAs in addition to hydrogen, the photo fermentation is commonly combined with dark fermentation as a process of two-stage hydrogen production [74], whereby the VFA-rich effluent deriving from dark fermentation is consumed in downstream photo fermentation to improve the overall hydrogen production [1]. Finally, microbial electrolysis cells are systems in which the protons coming from the microbial oxidation of VFAs at the anode, are reduced at the cathode through the application of an external power supply to yield hydrogen [75, 76]. Since the anodic microorganisms favor simpler VFAs, acetate is consumed at higher rates compared to other VFAs in the fermentation liquid;

accordingly, hydrogen production can be increased by increasing the portion of acetate in the feed liquor [72].

Moving away from processes utilizing VFAs as an indirect source of energy, these valuable acids are also applied in the production of many chemicals. For example, heterotrophic microbial cells can consume acids to produce various copolymers with diverse properties [77, 78]. In particular, VFAs can be used as a carbon source and precursor for polyhydroxyalkanoates (PHA) , biodegradable polymers with a wide range of applications , for instance, as additives of polyvinylchloride and packaging materials [17, 79]. Traditional carbon substrates are costly, representing roughly 30% of the total operating costs in PHA production and thus restricting the implementation of these polymers as replacements for conventional petrochemical-based plastics [80]. The PHA polymer production by microbial fermentation of VFAs may improve the economics of this process [81]. To this purpose, the composition of VFAs should be tweaked through acidogenic fermentation, since the chain length of the VFAs has a great effect on the composition and properties of the final PHA [82, 83]. For instance, acetic and butyric acids promote the production of 3-hydroxybutyrate (3HB), while propionic and valeric acids are usually consumed to yield 3-hydroxyvalerate (3HV) [84, 85]. Ethyl 3-ethoxybutyrate is a new fuel oxygenate with high cetane number and associated with lower emission of pollutants; this compound can be obtained by conversion of PHAs [86]. As another example, the incorporation of 3HV into poly(3HB) leads to the formation of copolymer P(3HB-co-3HV) [87], utilized as food packaging material due to its flexibility and toughness [88]. Valuable chemicals, such as esters, ketones, 1-alcohols, and 2-alcohols can also be produced by converting VFAs [89]. Usually, VFAs are produced through biomass fermentation, which is already pretreated with suitable chemicals to improve digestibility [90]. Then, $CaCO_3$, $NaHCO_2$, or NH_4HCO_3 is added as neutralizing agent

to the fermentation broth to prevent a decrease of the pH as the acids are formed [91]. Consequently, after separation and purification of the produced VFA salts, thermal conversion transforms them into ketones and ultimately hydrogenate them to 2-alcohols [92]. Moreover, 1-alcohols can be produced through hydrogenolysis reaction after esterification of VFAs with alcohol [93].

Another valuable application of VFAs is in the biological removal of nutrients in wastewater treatment units, a necessary step to avoid nutrient enrichment or eutrophication of aquatic ecosystems [94, 95] and a preferred route to physicochemical methods of nutrient removal [96, 97]. Ammonia/ammonium is transformed into nitrates and then into nitrogen through aerobic nitrification followed by anoxic denitrification, while phosphorus removal can be accomplished through enhanced biological phosphorus removal (EBPR) processes [98-101]. The practical range of carbon to nitrogen ratio for combined nitrification/denitrification is 5–10 mg COD/mg N; instead, to remove 1 mg of phosphorus, COD is needed in the range 7.5–10.7 mg [102, 103]. The carbon substrate necessary to perform these transformations is frequently inadequate in typical wastewaters and external carbon substrate is added to achieve an effective biological nutrient removal (BNR) [104]. VFAs are highly appropriate sources of carbon to assist the biological removal of phosphorus and nitrogen from wastewater [19, 105]. VFAs produced directly on site through the anaerobic acidogenesis of organic wastes can be directly applied for BNR [105]. Zheng et al. found that using VFAs produced from waste activated sludge fermentation led to phosphorus and nitrogen removal efficiencies of 82% and 95%, respectively [106]. In nitrogen removal processes, denitrifying bacteria favor VFAs with lower molecular weight and easier metabolic pathways, thus promoting the consumption of acetate as the first VFA, followed by propionate, butyrate, and lastly valerate [51].

Fig. 1 presents the main commercial and industrial applications of various pure VFAs [107]. What follows is thus a brief discussion of the main uses of each of the VFAs. One of the most commercially significant VFAs is acetic acid, which is consumed worldwide with almost one-third of its consumption occurring in the United States [108]. Other than in the applications described just above, acetic acid has important applications in the food industry as a solvent [109], as well as in the preparations of some food products [110]. Additionally, it is applied in the production of acetic anhydride, which is used in the manufacturing of dyes, explosives, perfumes, and antibiotics, as well as in the production of vinyl acetate for further polymerization into polyvinyl acetate, which is in turn applied in paper coatings, latex paint, textile finishing, and adhesives [109, 111]. Acetic acid is also utilized in the production of purified terephthalic acid (PTA), an alternative raw material for manufacturing polyester fibers; in the production of monochloro acetic acid used in bacteriostats, herbicides, preservatives, and finally to obtain carboxy methyl cellulose, glycine, and other laboratory chemicals, such as EDTA [111].

Fig. 1. Commercial and industrial applications of various pure VFAs.

Propionic acid has several applications in the preservation of animal fodder and food grains, the production of herbicides, esters, and flavors [112, 113], in the chemical industry manufacturing plastics and petrochemicals, and finally in the pharmaceutical industry [114, 115]. According to market research estimations, the value of the propionic acid market was $935.7 million in 2012, and this number was anticipated to increase by 7.8% as of 2018 [111].

Butyric acid has several uses in flavorings and in food products (such as fishing bait additive and animal feed supplement) owing to its butter-like texture and taste, as a component of some anti-

cancer drugs and also in perfumes because of its fruity aroma [116, 117]. The market of butyric acid was estimated to be roughly $124.6 million in 2014, with a predicted growth rate of 15.1% (the highest growth among bio-based chemicals) until 2020 [111].

Lactic acid is also a remarkably versatile material with many applications in the food, cosmetic, chemical, textile and pharmaceutical industry, as a preservative, flavoring, bacteria inhibitor, acidulant, and as an intermediate for numerous other products [118-120]. It is used in the production of acrylic acid, ethyl lactate, pyruvic acid, and 1, 2-propane diol, and as a feedstock monomer for the polymerization of poly-lactic acid (PLA) [121, 122]. Furthermore, lactic acid polymerization is of growing interest due to the specific characteristics of this polymer, such as its biocompatibility in the manufacturing of human prostheses for bone substitution, and its suitable use in food packaging [123]. The lactic acid world demand is raising annually at the rate of 5-8%, while its production was estimated as roughly 370,000 metric tons in 2017 [123].

Finally, formic acid is a major chemical feedstock in the organic chemical industry, with important applications in rubber processing, leather tanning, manufacturing of pharmaceuticals, and processing of textiles and paper [109, 124]. Other applications of formic acid are as antibacterial preservative and as pesticide, due to its intrinsic antibacterial properties [109, 125]. Additionally, this acid is used as a food additive commonly added to silage and animal feed. Here, it provides the dual function of antibacterial agent while allowing silage to initiate fermentation at a lower temperature, thus leading to increased nutritional value of the finished product [109]. Moreover, formic acid is used to improve the flavor in the food industry and to create synthetic scents in perfumes [126, 127].

4. Non- membrane-based methods for the recovery and purification of VFAs

Mixed VFAs is less valuable in comparison with the pure form of individual acids; therefore, it is desirable to convert the mixture into value-added chemicals or to separate it to obtain each component in its pure form [115]. However, this separation and purification is challenging, since VFAs form an azeotropic mixture with H_2O [128]. Multiple-stage separation and purification processes are often necessary to obtain cost-effective and marketable VFAs, in their pure of mixed form [129]. Specifically, VFAs recovery from complex aqueous solutions can be achieved through a variety of physical/chemical techniques consisting of precipitation [130], distillation [131], adsorption [132, 133], ion exchange [31, 133], liquid-liquid extraction, reactive extraction [32, 134], and/or membrane processes [27, 135]. The selection of the most suitable techniques depends on various parameters, such as the nature and properties of the fermentation media, the concentration of VFAs, and the presence of different ions in the fermented stream (e.g., Na^+, Cl^-, K^+, SO_4^{2-} and $H_2PO_4^-/HPO_4^{2-}$). A summary of the main methods used for VFAs separation and purification from aqueous solutions and their advantages and disadvantages is presented in Table 1.

Distillation is a conventional technique to separate components from a solution based on their volatility differences. The carbonyl group (carboxyl) in the structure of VFAs is an electrophile, therefore VFAs have a higher boiling point than water [136]. The reactive and extractive distillations are effective to recover VFAs [137]. Vacuum distillation is also applied to recover VFAs as a potentially more cost-effective method among the various distillation methods [138]. Generally, the distillation process is efficient when the VFAs concentration in the fermentation media is low, while at high concentration, especially close to the azeotropic point, distillation is largely inefficient [139]. A reactive distillation process was studied by Kumar et al. [136] to

recover lactic acid. In their continuous process, methanol was added to the aqueous solution to break the azeotrope by forming methyl lactate. Blahušiak et al. [138] used short path distillation with a phosphonium ionic liquid to separate butyric acid with a yield of about 90%.

Precipitation is another conventional method, consisting of different steps to separate the VFAs based on the type of precipitant. For example, precipitation with calcium consists of four stages. (1) adding $Ca(OH)_2$ or $CaCO_3$ to the filtered fermentation liquid under mixing, (2) filtering away the calcium salts of VFAs from the aqueous solution, (3) treating the calcium salt with sulfuric acid to release the desired VFA, and (4) further purification to obtain the pure VFA as final product [140]. The calcium lactate to sulfuric acid molar ratio was found to be a significant factor in the isolation of lactic acid by precipitation [141]. Ammonia or ammonia-based titration agents can also be used as precipitants to separate the VFAs [142]. Although this latter method has some advantages, such as high selectivity and no phase transition, finding proper precipitants is challenging; the consumption and the unfeasibility of regeneration of the precipitants render this process relatively expensive.

Adsorption is a reliable method for the physical capture of the neutral form of protonated VFAs from dilute and complex aqueous solutions. Adsorption may be combined with ion exchange to promote an ionic bond between the ionized acid and the functional group of the ion exchange material [143]. Various types of materials have been suggested for the adsorption of VFAs, such as neutral polymeric resins, crosslinked poly(4-vinyl pyridine), zeolite molecular sieves, titanium dioxide (TiO_2), activated carbon, and iron oxide nanoparticles [132]. The most reactive functional groups on these adsorbents are usually amines type I to III, and quaternary ammonium moieties. The adsorbents containing quaternary ammonium reactive sites provide strong adsorption through anion exchange [144], while tertiary amines mostly adsorb VFAs in the uncharged state. Very few

studies have explored the integrated process of adsorption/desorption to recover single VFAs or mixtures of them. For instance, the adsorption ability of Purolite A133S and activated carbon was studied and compared by Silva and Miranda [133]. It was found that n-propanol was an appropriate eluent for the desorption process. In most circumstances, a chemical addition and a demanding processing are required in the desorption stage (as shown in Fig. 2), and the VFAs achieved after the regeneration process is not necessarily pure (it often contains a significant mineral impurity from the desorption chemicals). This technology for the separation and purification of VFAs from fermentation broths is still poorly developed.

Table 1. Non-membrane based conventional methods for recovery of VFAs

Methods	Procedure	Advantages	Disadvantages	Ref.
Distillation	Acids are usually neutralized by using ammonia and then the achieved ammonium carboxylate is mixed with alcohol to produce esters that can be separated easily by distillation.	- Easy to install - Products of high purity - Possibility of direct use of the products as fertilizer	- High energy demand - High capital costs of process	[137, 145]
Precipitation	To neutralize the organic acids, calcium-based salts are added to the solutions; evaporation is usually applied to concentrate the resulting calcium carboxylate solutions. Crystallization or further separation needs then to be carried out.	- Easy to install - High yields of product - High purities of products - Low capital costs	- Undesired solid waste production - High energy demand	[130, 141]
Adsorption (physical and/or chemical)	Adsorbent and/or ion exchange materials are used to capture carboxylate ions or the protonated form of the VFA compounds.	- Easy to install and operate - Relatively high selectivity	- High costs and energy demand - Low adsorption capacities	[133, 143]
Electrodialysis	Negatively charged dissociated species of VFAs move through an anion exchange membrane towards the anode in the electrodialyzer thanks to the electric field.	- High concentration of carboxylate usually obtained - No need to adjust the pH by acid treatment	- Need for further purification - Hard to scale-up - High energy demand - High membrane fouling	[130]
Solvent extraction	Organic solvents with or without extractant additives are utilized to extract carboxylic acids from the aqueous solution.	- High yield of product - Low cost - High selectivity achievable	- Acidification of the feed is required - Further process needed to regenerate the extractants	[10, 134]
Membrane separation	Membrane first retain and concentrate a portion of the mixed effluents; then, the concentrate or the permeate are further fractionated/purified to obtain the desired substances.	- High yields of product - Easy to scale up - Reliable - Low energy demand	- High membrane fouling - Unknown potential for the most complex solutions	[27, 135]

Fig. 2. Schematic of the adsorption process for separation and purification of VFAs [132].

Extraction is another useful process to separate and purify VFAs based on their different affinity/solubility to two immiscible solvents. Three main aspects should be considered in designing an extraction process [10]: (i) regulating the pH of the solution to achieve the dissociated form of the acids for easier extraction, (ii) using extraction solvents (usually organic in nature) with high partition coefficient of VFAs, leading to high selectivity, and (iii) choosing a solvent with high reversibility and likelihood of regeneration. The process may be accomplished in three different ways, namely, solvent extraction, reactive extraction, and ionic liquid extraction. Solvent extraction is effective and economical, deploying available solvents, such as alcohols, ethers, ketones, organophosphates, aliphatic hydrocarbons, or aliphatic amines, all with an interesting potential for the extraction of VFAs from aqueous solutions [146]. Fig. 3 presents a possible scheme of extraction process for the recovery of acids and ethanol produced by acidogenic fermentation, which is based on the transfer of the acids and ethanol to a glycerol phase via an intermediate solvent phase [147]. In the first step, Tri-n-octylamine-based solvents preferentially extract acids and in the second (as re-extraction step), the acids are extracted from the intermediate solvent using glycerol. As opposed to simple solvent extraction, reactive extraction isolates the VFAs from aqueous streams using various chemical extractants in the organic phase [134]. For example, Huh et al [10] adopted a reactive extraction system containing tri-n-octylamine(TOA)/1-octanol and TOA/oleyl alcohol to recover succinic acid and lactic acid from fermentation broths. They achieved a purity of about 99.8% and yield of 73.1% for succinic acid. In another research, Rasrendra et al [134] used tri-n-octylamine to reactively extract acetic acid from the aqueous phase of a pyrolysis oil. In this process, the functional groups, polarity of the solvent, and stability of the

complex between the amine groups and the acid all played an important role in influencing the yield of recovery. Finally, ionic liquid (IL)-assisted extraction is a promising method in which IL organic salts are used as extractants. ILs are non-volatile, chemically stable, nonflammable, and in liquid form in a wide range of temperatures, with low viscosity and high density. Imidazolium [148], quaternary ammonium salts [149], or quaternary phosphate [150] are the most important ILs used in extraction processes for organic compounds. The application of phosphonium-based hydrophobic ILs in the recovery of organic acids (L-malic, L-lactic, and succinic acids) from aqueous solutions has great potential over conventional solvent extraction processes [150]. Phosphonium-based ILs were used by Martak and Schlosser [151] in the high-performance separation of lactic acid from aqueous solutions. Reyhanitash et al. [152] showed that trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate [P666,14][Phos] had suitable performance for the separation of acetic acid from aqueous solutions. An important issue in the IL-based extraction of VFAs is the choice of the solvent, whose desired properties include high selectivity, high coefficient of distribution, and high stability. Another issue is related to the toxicity or inhibitory activity of some solvents used for in-line separation of organic acids.

Fig. 3. TOA-based extraction and glycerol-based re-extraction process for the separation of volatile fatty acids.

5. Membrane-based methods for the recovery and purification of VFAs

Using membranes in separation and purification of chemicals and biofuels may potentially reduce the number of steps of the overall recovery scheme, often while improving the overall efficiency of the production and shortening the residence time, thus resulting in a more economical process

[153-155]. Membrane processes with separation purposes may be divided in two general categories; (i) pressure-driven processes, for instance, microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)/reverse osmosis (RO), (ii) non-pressure-driven processes, such as pervaporation (PV), electrodialysis, membrane distillation (MD), membrane contactor, and forward osmosis (FO) [154].

5.1. Pressure-driven membrane processes

5.1.1. Clarification of the fermented effluents using MF and UF

Pressure-driven membrane systems offer an opportunity for cost-effective purification, fractionation, and recovery of VFAs [37, 156, 157]. The fermented effluent is often quite complex, comprising various VFAs and different kinds of impurities, such as residual sugars, proteins, colloids, or pigments. Impurities cause membrane fouling, which restricts the process efficiency and performance [37, 158, 159] and obliges a certain pretreatment of the fermented effluent. Micro- (MF) and ultrafiltration (UF) can clarify the fermented effluent to alleviate its fouling potential [160]. Since the fouling agents should also be separated from VFAs as part of their recovery, this pretreatment step results in a primary step of recovery.

As a first instance, UF was applied in a system to recover short chain VFAs from sewage sludge [26]. This process clarified the fermented sewage sludge successfully, resulting in a permeate stream containing a low amount of suspended solids and a high content of VFAs. A reduction in the filtration performance was observed with time, due to the deposition of soluble and insoluble substances, especially fibrous materials, onto the UF membrane surface. In general, high pH values were also found to negatively affect the UF productivity [161]. Zacharof and Lovitt [27] treated waste effluents from anaerobic digesters of agricultural waste for the enrichment and concentration

of acetic and butyric acids. They applied a crossflow microfiltration unit as pretreatment, employing a Membralox ceramic filter element (α-Al_2O_3) with pore size and effective surface area of 0.2 μm and 0.22 m^2, respectively. A sterile and particle-free solution with a concentration of 21.08 mM of acetic acid and 15.81 mM of butyric acid was obtained using MF, and was then further processed via NF. In another study, Kim et al. [162] applied microfiltration ceramic membranes with a pore size range of 0.1-5 μm for the recovery of volatile fatty acids from liquid organic sludge. They found that the appropriate pH range of suspension was 5.0-6.0 for the best recovery of organic materials as well as to achieve a high permeation flux. Additionally, the optimal membrane pore size for the recovery of dissolved organics from fermented liquid was around 1μm. Tao et al. [130] used MF with modified polyethersulfone (mPES MiniKros) membrane modules with an effective length of 65 cm, a housing diameter of 1.9 cm and pore size of 0.2 μm to recover VFAs and nutrients from the production of biodegradable polyhydroxyalkanoates. Around 90% of all organic acids were recovered; confirming that MF is an effective strategy to recover VFAs from fermentation broths. Longo et al. [26] studied the application of UF in the pilot scale production of short chain fatty acids from sewage sludge through alkaline fermentation. Two tubular polyvinylidene fluoride UF modules with internal diameter of 8 mm and molecular weight cutoff of 15 kDa were installed after the fermentation process to separate the fermentation liquid from the sludge. A semi-continuous configuration system coupled with a UF system was applied by separating and recirculating the solids fraction of the fermented sludge to the fermentation reactor, leading to improving the organic loading rate (OLR) as well as maintaining the SRT higher than the HRT.

5.1.2. VFAs recovery with NF/RO processes

As reported in several previous studies, NF and RO can effectively separate VFAs from other components in aqueous solutions [163-165]. The separation efficiency of NF and RO membranes in the treatment of VFAs is determined by a combination of size and charge effects [166-168]. For relatively loose RO membranes and for all NF membranes, the charge interactions between the membrane surface and the solution components appear to have a dominant effect over the molecular weight and size [169-171]. On the other hand, dense RO membranes remove molecules mostly based on size effects and are less affected by the physico-chemical characteristics of the feed solution. For example, M.I. González et al. applied NF to recover lactic acid (LA) from fermentation broths already clarified by UF [166]. They found that the feed solution pH had a significant influence on LA transport through the NF membranes. Specifically, increasing the pH enhanced the LA rejection while the water flux was reduced. A significant increase in organic acid retention was also observed as pH increased in other NF experiments [172]. In other investigations, commercial thin-film polyamide NF and RO membranes were employed to separate acetic acid from monosaccharides [165]. The results suggested that the transport of acetic acid was controlled by the Donnan effect resulting from the electrostatic interaction between the acetic acid and the membrane surface [165, 173]. The NF membranes could not retain the acid at low pH value, while RO membranes were generally less influenced by this parameter and separation factors of 348.7 and 223.2 were achieved for acetic acid over glucose and xylose, respectively [173, 174]. Because of the different transport mechanisms characterizing the membranes based on their properties and on their interactions with VFAs, it is ideally possible to select the recovery place of the desired organic acid either in the concentrate stream or in the permeate stream. These factors are especially important to control the retention efficiency of VFAs in NF [175].

Y.H. Cho et al. pursued the goal of recovering butyric acid in the permeate side of NF and RO membranes [176]. They took advantage of the naturally acidic pH in the fermentation broth to selectively promote the passage of negatively charged butyric acid through the neutral or positively charged NF and RO membranes. The butyric acid permeation did not occur through RO membranes as much as through NF membranes, thus causing an inefficient recovery [176]. On the other hand, the RO membranes provided a stream with high purity butyric acid [176]. Various studies determined that the optimum pH for the permeation of VFAs through NF membranes is roughly 3 [164, 165]. Likewise, Xiong et al. applied NF membranes to recover VFAs in the permeate stream and achieved the recovery rate of 86% along a 21-day digestion run [177]. They succeeded to reduce the concentration of VFAs in the digestate of over 90% compared to the control experiment without acid removal.

Zacharof et al. aimed instead to recover VFAs from agricultural waste in the concentrate side of the NF membrane. They recovered 69% of butyric acid and 72% of acetic acid at high pH values [178]. Masse et al. used RO membranes and observed a higher rejection for VFAs compared to NF membranes [28]. While pH has a lower effect on RO compared to NF, other parameters may influence the VFA retention from a fermentation broth in RO: previous studies showed that increasing the applied pressure enhanced the retention of acetic acid, while an increase in the temperature of the feed solution had an opposite effect [179]. To summarize, acidic pH values usually allow the recovery of VFAs in the permeate side of nanofiltration membranes. RO can provide permeate streams of higher purity but with challenges related to the overall recovery rate, as the separation of dense membranes is less tunable by adjusting the pH and other physico-chemical conditions of the feed solution. Oppositely, high pH values commonly result in higher VFAs rejection by the membranes and their recovery in the concentrate stream. The existence of

numerous diverse types of NF and RO membranes with different surface properties, pore size, and MWCO virtually allow the separation of individual VFAs from a mixed VFA solution [180].

5.2. Non pressure-driven membrane processes

5.2.1. Forward Osmosis

Forward osmosis (FO) has interesting potential in the VFAs recovery due to its unique mass transfer properties, the low hydraulic pressures involved, and the existence of reverse draw solute diffusion [181-183]. The driving force of the FO process is the osmotic pressure gradient between the feed side and a concentrated draw solution side, separated by a semipermeable membrane [40, 184, 185]. FO exhibits a lower fouling tendency and higher fouling reversibility compared to pressure-driven membrane processes [186, 187]. The FO process may be run in two different modes, FO and pressure retarded osmosis (PRO) modes, based on the orientation of the membrane active layer with respect to the feed stream. In the FO mode, the selective layer of the membrane faces the feed solution (ALFS), while in the PRO mode, the membrane active layer faces the draw solution (ALDS). FO technology is currently in the early industrial stage of development; several pilot scale systems exist and are applied in different fields, while only a few large-scale plants are being implemented.

As depicted in Fig. 4, in the FO system the water passes through the FO membrane from the feed stream to the draw stream. The VFAs are rejected by the membrane, as this has similar selective properties of dense RO membranes, and thus they remain within the feed solution during the dewatering process. Accordingly, the VFAs concentration of the feed solution is increased with the overall system recovery rate. In FO, the water permeated through the membrane from the feed solution to the draw solution dilutes the draw solution. To be recycled, the draw solutes need to be

regenerated and hybrid systems can be applied to this purpose [188]. Also, reverse draw solute flux induces the passage of the draw solute into the feed solution during the process [189].

Fig. 4. Conceptual illustrations of the FO membrane process for VFA recovery.

Increasing the concentration of VFAs in the feed solution caused a lower FO water flux as well as lower reverse draw salt flux. This is attributed to the higher osmotic pressure in the feed solution, causing a reduction in the FO driving force. The change in orientation from FO to PRO mode did not have a considerable effect on the FO water flux but reduced the reverse salt flux. This is not entirely consistent with previous studies that showed that the water flux in the PRO mode was higher than that in the FO mode [190, 191]. This phenomenon is related to membrane fouling influencing the deposition and accumulation of VFA on the membrane. In the FO mode, the deposition of VFAs takes place at the active layer/solution interface, while in PRO mode, the VFAs accumulate within the porous structure of membrane support layer [192, 193]. Accordingly, more severe VFAs fouling was observed in PRO mode [194]. Increasing the VFAs concentration in the feed solution can also reduce their rejection rates in both the orientations. A higher rejection rate means an enhanced recovery of VFAs in the process.

The results presented by the K. Jung et al. suggest that VFAs recovery in the FO systems should be operated in ALFS mode due to a more effective process performance in this orientation [194]. The existence of reverse draw solute diffusion in the FO process may be exploited as a way to increase VFAs recovery: in a previous study, the reverse salt flux limited the forward diffusion of the VFAs and it also prevented their adsorption on the membrane surface [195]. K. Jung et al. also investigated the effects of pH on the FO performance during the VFA recovery process [194] and

obtained the results summarized in Fig. 5. The pH value had a significant influence on the VFA rejection rate and reverse salt flux while it had a moderate effect on the FO water flux. Increasing the VFA solution pH resulted in a lower FO water flux and a more severe reverse salt diffusion. Instead, the VFAs rejection and recovery were improved, similarly to what stated above for NF membranes. Though the water flux was the lowest at the highest investigated pH, the final concentration of VFAs at the end of the process was increased of over 60% compared to the tests conducted at the lowest pH value [194]. This can be explained by the fact that at high pH levels, the VFAs exist mostly as negatively charged ions. Hence, the VFAs rejection is improved by both electrostatic repulsion with the membrane active layer negative charges and as the hydrated ions are bulkier than their neutral counterparts [196, 197]. Likewise, methodologies based on pH adjustment, such as the use of alkali, are reported to increase VFA production from sludge [198, 199]. Actually, alkaline conditions increase both hydrolysis and acidification rates as well as the solubilization of the main components of the sludge, causing a higher VFAs production [200]. Therefore, processing the FO dewatering at alkaline pH directly in the sludge or fermentation broth can enhance the final VFAs concentration [201]. Some authors suggested that the pH level should be adjusted in the range of 7-8 to maximize VFAs production from fermentation broths, using NaOH as a preferred pH adjustment agent [194].

Although the pH value mostly influences the VFAs rejection and reverse salt flux, the temperature, type and concentration of the draw solution affect more directly the FO water flux [194]. Calcium-based draw solutes are characterized by a higher reverse salt flux and lower VFAs rejection, leading to a recovery of the VFAs with a lower purity [194]. On the other hand, $MgCl_2$ draw solute provided both high osmotic pressure and a low reverse salt flux compared to NaCl [197, 201]. C. Cagnetta et al. applied FO to recover VFAs from the organics of domestic wastewater, high-rate

activated A-sludge, and secondary sludge [201]. They concentrated the feeds containing VFAs 10-fold via an FO process in batch mode. The FO water flux decreased over time because of fouling and reverse salt flux, which also increased the salinity of the VFAs concentrated solution. They observed that the retained organics at high concentration extensively deposited on the membrane surface, causing a significant decline in the FO dewatering performance. In this regard, they suggested using recirculation and air scouring by gas bubbling (N_2: CO_2 (9:1)) as a physical technique to control the properties of the sludge in the feed solution and minimize fouling, but at the expense of higher operating costs [201].

Fig. 5. The pH effect on (a) FO water flux, reverse salt flux, (b) VFAs rejection, and final concentration of VFAs in the concentrated feed. FO membrane: cellulose triacetate (CTA), draw solution: 5 M NaCl [194].

5.2.2. Membrane Distillation

Membrane distillation (MD) is a thermally-driven membrane technique that utilizes low-grade heat to concentrate/separate the target components from the aqueous phase [202, 203]. In MD, a hydrophobic membrane separates the feed solution from the distillate phase (Fig. 6). The hydrophobic nature of the MD membrane prevents the transport of liquid while allowing gases and vapor to move across the membrane pores [204]. Mass transport is initiated as the feed solution is heated to produce the vapor pressure gradient between the two phases. The more volatile components tend to become gaseous, are transported in this phase through the membrane, and accumulate in the permeate side [205]. The desired components may be concentrated either in the feed side or permeate side, based on their vapor pressure. MD is not yet implemented at large scale, mostly due to issues related to the construction of efficient membrane modules with high

packing density. However, the technology readiness level of this process is rapidly increasing due to some potential advantages of MD over other membrane-based separation processes, such as the possibility to exploit renewable sources to supply energy to these systems.

Fig. 6. Conceptual illustration of the MD process for VFAs recovery.

Given the volatility of short-chain fatty acids, their recovery in MD is suitable in the distillate phase, with the potential of obtaining high-purity streams if water and VFAs may be the only distillable components of the feed solution. Virtually, various VFAs may be separated from each other by working at different temperatures of the feed solution. In truth, very few studies exist on the application of MD to recover VFAs. The main investigations were provided by M. Gryta et al. for the purification of fermenting glycerol solutions [206, 207]. The application of MD facilitated the removal of mainly acetic acid from the fermentation broth and its passage into the distillate, which improved bacterial growth and increased productivity. Fouling accelerated the process of membrane wetting, causing a reduction in the module efficiency [208]. However, polypropylene membranes demonstrated fair resistance against wettability [206]. Accordingly, the fabrication of MD membranes with omniphobic or superhydrophobic property would mitigate the membrane fouling and wetting, thus leading to improved VFAs recovery efficiency [209].

5.2.3. Electrodialysis

Electrodialysis (ED) is another technology in the early stages of industrial development that could be applied to selectively recover charged components from mixed streams to obtain high-quality products. The ED arranges ion-exchange membranes in an electrical field [210, 211]. Hence, the

anions and cations migrate towards the anodes and cathode, respectively [212]. The anion or cation-exchange membranes applied in conventional ED (CED) prevent the passage of co-ions via Donnan repulsion (Fig. 7). Bipolar membranes containing both anion and cation exchange layers may also be used in an ED process. However, bipolar membranes are usually expensive compared to those used in CED [29, 213, 214].

Fig. 7. Conceptual illustration of the CED process for VFAs recovery.

Tang et al. studied ED using a bipolar membrane to recover acetic acid from fermentation broths [215]. They recovered about 93% of acetic acid in relatively quick experiments. CED was applied to recover valuable VFAs and increased the yield of hydrogen from a dark fermentation reactor at a potentially low cost [213]. The concentrations of individual acids in dilute compartments were reduced gradually during a 60 min of process, while the VFAs were simultaneously concentrated and recovered in the opposite compartments. In the case of acetic acid, the system allowed around 98% of recovery from a synthetic solution. Fig. 8 reports the results obtained by Tang et al. in the concentration of acetic acid and n-butyric acid from a real fermentation broth using low-cost membranes in CED [215]. The VFAs concentrations were increased significantly in the concentrate circuits during the initial 30 min of process, and their concentrations accordingly decreased by up to 96% in the dilute circuits. Back diffusion of the acetic acid levels in the dilute stream was observed after 50 min of CED process, due to the significant concentration gradient overcoming the electrical gradient [216]. The rate of acid transport was found to relate to its initial concentration gradient [213]. B. Tao et al. applied the CED process to effectively enrich VFAs from thermally hydrolyzed waste activated sludge [130]. MF was used as a pretreatment, allowing the recovery of roughly 80% of the VFAs in the permeate stream. Approximately 92% of this

VFAs content was then recovered in the downstream CED process. The results suggested that the various acids behave differently, with the small molecular weight acids showing better transfer performance. Accordingly, acetic acid had the highest recovery efficiency while n-valeric acid the lowest one of about 85%. X.-R. Pan et al. studied different VFAs in terms of migration flux through the ED process [217], revealing comparatively higher transport potential of smaller-molecule VFAs across the ED membrane. Analogous results were also reported by another study [213]. VFAs transfer across the CED membranes is also highly correlated to their different ionization in solution. CED promotes the progressive ionization of the weak organic acids in the dilute solution, by selective removal of the ionized ions. On the contrary, increased proton levels in the concentrate compartments inhibits ionization, and the VFAs are more likely to be found there in their free acid form. High levels of free acids may lead to their loss by evaporation owing to the high volatility of VFAs.

Fig. 8. Acetic acid and n-butyric acid concentration flux during the CED of hydrogen fermentation broths (more than 90% recovery of the VFAs during 30 min of CED). The slope of the graphs, denoting the VFA transport rate, is correlated to the initial concentration gradient [213].

Further studies investigated changes in the current during the CED process: an initial quick decrease associated to fast transfer of VFAs caused by a lower concentration difference between the streams was followed by a more gradual decrease in the subsequent stages of the process. To avoid this undesired phenomenon, the CED process may be terminated based on the information gained from the current curves [130]. L. Shi et al. used ED through a bipolar membrane to recover nutrients and VFAs from pig manure hydrolysate [212]. They observed unfavorable fluxes of ions from the acid compartment to the base compartment, which contributed to low current efficiencies

and undesirable product purity [212]. They successfully minimized these fluxes via a two-stage operation of ED, improving both the recovery and the purity of the target products. Over 87% of VFAs were recovered in the acid compartment in the second stage. The effect of applied voltage on the VFAs recovery ratio during the ED process was investigated by P. Wei et al. [217]. Higher voltage resulted in a better recovery rate for both acetate and butyrate. When the voltage was set to 0 V (no applied electric field), around 45% of the acetate and 48% of butyrate were recovered in 96 hours of operation. Applying 2 V enhanced the recovery efficiency of butyrate and acetate to about 73% and 74%, respectively [218, 219]. Voltages of 4 V and 6 V allowed the same recovery in much shorter experiments with duration of 40 h and 20 h, respectively, with rates correlating almost linearly with the magnitude of the electric field. After 96 hours, the acetate and butyrate removal efficiency improved to 96% and 95% at higher voltages [217].

Removal of the VFAs from the fermentation broth can simultaneously improve hydrogen production [220, 221]. In this regard, Noblecourt et al. used a submerged membrane anaerobic bioreactor to control the VFAs level and avoid their accumulation in solution [222]. They successfully limited the VFAs concentration, but at the expense of losing other small molecules, such as amino acids and monosaccharides, which are favorable substrates for hydrogen-producing bacteria. To address this issue, P. Wei et al. [217] introduced a novel three-chamber in-situ ED, which simultaneously recovered VFAs and controlled their level in the fermentation reaction zone [217]. Using single chamber fermentation without ED (control test) resulted in a rapid increase in the acetate and butyrate concentrations in the broth (Fig. 9). On the other hand, the three-chamber ED process promoted the passage of acetate and butyrate from the fermentation chamber to the anode chamber, resulting in an overall higher hydrogen production. Higher voltage (4 and 6 V)

caused a more rapid initial movement of VFAs toward the anode chamber, further improving the VFAs recovery and the hydrogen production.

Fig. 9. VFAs removal during fermentation using three-chamber in-situ ED. (a) Acetate concentration in the fermentation chamber; (b) Butyrate concentration in the fermentation chamber; (c) Acetate concentration in the anode chamber; (d) Butyrate concentration in the anode chamber. Thanks to the rapid transport of VFAs, their concentration in the fermentation chamber was maintained at a low level, which can enhance the hydrogen production [217].

5.2.4. Membrane Contactor

Membrane contactor (MC) applies microporous hydrophobic membranes to separate two aqueous phases and inhibit their mixing [223, 224]. Vapor permeation membrane contactor (VPMC) is the most common configuration for VFAs recovery (Fig. 10). In VPMC, the driving force is induced by the partial pressure difference or concentration gradient between the two sides of the membrane. The separation is not attributed to size exclusion and also there is no convective flow through the pores. In isothermal batch operation, volatile components including VFAs are transferred from the feed to the permeate side until the chemical potential equilibrium of the two sides is restored [225]. Membrane contractors are receiving increased attention as emerging processes for the recovery of VFAs from waste due to development of hydrophobic membrane with suitable thermal stability and chemical resistance [226].

A.E. Tugtas investigated the performance of an MC system to recover acetic acid and studied the influence of the stripping solution concentration, feed solution pH, and recirculation rate, using a flat hydrophobic polytetrafluoroethylene (PTFE) membrane [135]. The increase of stripping solution concentration or recirculation rate resulted in improvements of both the VFAs permeate flux and the selectivity. On the other hand, increasing the feed solution pH caused a reduction in

the VFAs flux and selectivity. Since the main driving force was the concentration gradient of VFAs, the system was more efficient as the boundary conditions for diffusion improved. When using a mixture of VFAs as feed solution, the mass transfer coefficient of each VFA relates to the individual solubility. As the alkyl chains get longer, the solubility of VFAs decreases. Hence, it is not surprising to see that the mass transfer coefficient of valeric acid is higher than that of acetic acid. While some authors observed that MC systems may provide a cost-effective and environmental alternative for VFA recovery because of the absence of organic extractants, other researchers underline that the VFAs selectivity can be improved by filling the membrane pores with extractants [227]. The extractant-filled pores block the diffusion of water vapor, alcohols, ammonia, and other volatile species [228, 229]. Candidate extractants include tridodecylamine (TDDA), trioctylphosphine oxide (TOPO), and trioctylamine (TOA) [134, 228].

Fig. 10. Conceptual illustration of the VPMC process for VFAs recovery.

When comparing three VPMC systems, one comprising an air-filled PTFE membrane and the others deploying PTFE membranes filled with two different extractants (TOA or TDDA), authors observed comparable recovery percentages for acetic, propionic, butyric, valeric, and caproic acids through the air-filled PTFE membrane [227]. In contrast, the recovery efficiencies of VFAs by extractant-filled PTFE membranes improved for the VFAs of larger alkyl chain length, thus allowing the selective separation of the VFAs, in correlation with their different mass transfer coefficients. The mass transfer resistance generally decreased in extractant-filled membranes compared to air-filled membranes, except for acetic acid. Accordingly, systems comprising extractants resulted in an improvement in the VFAs recovery, except for the case of acetic acid

[227]. These results were corroborated by another study, in which a TOA-filled membrane was observed to be highly selective toward valeric and caproic acids, moderately selective toward butyric acid, and least selective toward acetic acid. This process resulted in the near complete recovery of caproic acids [230]. These authors highlighted that filling the membrane pores with the extractant may be economical and environmentally friendly, due to the small amount of extractant required for the separation [227]. For feed containing suspended particles and inorganic precipitates, these substances were observed to accumulate on the membrane surface to create an extra resistance to mass transfer [135]. This phenomenon resulted in a lower separation efficiency of a real feed containing mixed VFAs compared to that of a synthetic VFAs mixture in the absence suspended particles. Issues associated with the interference of suspended matter must be considered when designing a membrane contactor process for VFAs recovery.

5.2.5. Pervaporation

Pervaporation (PV) is a membrane-based separation process relying on the difference in solubility and diffusivity of different components through a dense membrane [231, 232]. In PV, the driving force is induced by the chemical potential gradient across the membrane, which can be created by applying a vacuum or gas purge on the permeate side to keep the permeate vapor pressure lower than the partial pressure of the feed liquid [233]. It is potentially economical and environmentally friendly in comparison to other VFAs separation techniques [234]. Pervaporation has no adverse effects on the microorganisms present in the feed solution and may be directly coupled with an anaerobic digestion chamber to unceasingly remove the inhibitory products from the broth.

In order to improve the dewatering performance of acetic acid in PV, Su et al. developed sodium alginate mixed matrix membranes by incorporating an amine-functionalized metal-organic

framework (MOF) [235]. The authors aimed to dehydrate the feed stream and recover acetic acid in the concentrate side of the membrane. The results showed that an appropriate loading of MOF resulted in a significant enhancement in water permeability and selectivity, translating into improved flux and separation factor during operation. The authors also investigated the effect of acetic acid concentration, feed temperature, and flow rate on the PV performance [235]. The water flux increased significantly by increasing the feed temperature, while the separation factor decreased considerably. This result was attributed to a reduced diffusion resistance of the PV membrane for both acetic acid and water due to the higher operating temperature. Moreover, as the temperature increased, the vapor pressure difference between the two sides of the membrane was enhanced, thus improving the driving force for mass transport [235]. As the acetic acid concentration increased in the feed solution, the swelling degree of the membrane decreased. In turn, this phenomenon reduced the free volume of the membrane, leading to an enhancement of the separation factor at the expense of a reduction in permeate flux [235]. As other researchers reported , there is a trade-off which usually observed in the PV process [236, 237]. Increasing the feed flow rate caused a turbulent flow at the membrane/solution interface, reduced the boundary layer thickness, and resulted in a lower mass transfer resistance as well as concentration polarization, overall translating into a larger value of the permeate flux but lower separation factor [235].

S.K. Choudhari et al. dispersed two-dimensional layered structures, such as graphene-based nanomaterials, within a polyether block amides (PEBA) matrix to prepare PEBA composite membranes [234]. The membranes were investigated in the PV process to separate butyric acid produced by anaerobic digestion. Unlike the example discussed above, these authors aimed to recover butyric acid in the permeate side of the PV membranes. Incorporating graphene in the PV

membrane matrix resulted in an improved overall performance, attributed to the enhanced hydrophobicity of the membrane and increased transport resistance to water. The authors also reported that increasing the feed pH reduced the butyric acid separation due to its higher solubility in water in the dissociated state.

6. Future perspective and challenges

The membrane-based processes reviewed above show the potential to advance VFAs recovery by maximizing the concentration factors and improving the selectivity. However, progress in this field is necessary to achieve scalable and economical recovery methods. The VFAs are recovered from a complex stream containing impurities that require removal or careful control in order to reduce membrane fouling and contaminations. Fouling is a major operational challenge, limiting the process efficiency and performance [238, 239]. Back-flushing and chemical cleaning are common methodologies to remove foulants from the membrane surface and alleviate their detrimental effects, at the expense of some operational cost, as well as increased chemical and energy requirements [240-243]. Pretreatment of the fermented effluent is a favorable and often necessary strategy to prevent fouling in both membrane-based and non-membrane based methods [28]. In the case of membrane-based methods, the MF and UF systems can pretreat the stream and alleviate its fouling potential, as described in section 5.1.1. The key advantage of membrane methods is their capability to be integrated with the conventional VFAs recovery systems. However, the VFAs may loosely bind to the solids contained in waste effluents and be lost with them during pretreatment [244]. Fortunately, the denser or hydrophobic membranes applied in the downstream VFAs recovery system can also be engineered to reduce fouling. Membrane and module

manufacturing require more studies focusing on effective and low-cost antifouling properties that minimize the loss of VFAs during treatment.

Hybrid membrane processes are promising solutions to enhance the overall efficiency of in-site VFAs recovery. For instance, in an FO process, the diluted draw solution is re-concentrated to be successfully reused within the draw loop. The resulting integration of the FO step with another downstream separation process complements the VFAs recovery with the production of high-quality product water. In several cases, the downstream separation stage may be effectively performed with other membrane processes, such as RO, MD, and ED [240, 245, 246]. In FO hybrid processes, FO act as a high-performance pretreatment for the following membrane process and it may result in a reduced operating cost by alleviating fouling. This is the result of the lower tendency of the FO process to foul compared to the typical downstream processes [247, 248]. Moreover, MD systems may also be driven via solar energy, thus lessening the overall operating costs of combined VFAs recovery and freshwater production [249, 250]. Likewise, in an FO-ED hybrid system, ED may be powered using solar photovoltaic energy to re-concentrate the draw solution [240]. Despite the potential advantages of hybrid systems for VFAs recovery, there are some challenges and limitations. Contaminants in the feed stream may pass through the FO membrane and accumulate in the draw solution. These pollutants are highly rejected in the RO or MD process, thus accumulating in the draw solution [251, 252]. In this regard, the current FO membranes require improvement in terms of selectivity to guarantee high performance of the hybrid system.

Most of the recovery methods described in section 5 can enrich all the VFAs together. Nonetheless, a major challenge exists in cases where the various components of VFAs should be recovered separately. Some of the membrane processes reviewed above have the potential to recover and

separate the various VFAs, which opens numerous opportunities for new research. The cost of VFAs recovery will unavoidably be added to the overall VFAs production costs. Although some of the recovery methods, such as high voltage electrodialysis and reverse osmosis, have the potential to recover VFAs with high purity, they are high-cost techniques. Accordingly, when a cost-effective recovery method guaranteeing relatively low purity is appropriate for a certain application, using a high-cost method becomes unfeasible even though VFAs with higher purity can be produced in this way [253]. Therefore, a cost-benefit analysis of the VFAs recovery methods for each different application is necessary, ultimately helping in the selection of the most appropriate technique.

7. Conclusions

In general, membrane-based processes can potentially enhance the VFAs recovery in a scalable way. Among the operating conditions, the pH of the VFAs feed solution has the most important influence in the recovery of VFAs as the dissociation degree of these acids influence their final fate in the concentrate or in the permeate stream. Three emerging membrane systems, ED, FO, and MD, may advance the field of VFAs recovery due to their unique properties. ED promotes the ionization of the weak organic acids in the diluted solution, promoting their transport through the membrane, resulting in high concentration efficiency. FO has low fouling tendency and may be engineered to maximize VFAs recovery also with the help of draw solute reverse flux. MD, driven by a vapor pressure difference, is capable to achieve a high concentration factor in the distillate stream. In addition, integration of different membrane processes could considerably improve VFAs recovery efficiency at reduced operating costs. For the future, detailed analyses of the integrated membrane processes in VFAs recovery should be carried out, both experimentally and by means of modeling tools.

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