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

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1	Contents	
2		
3	1. Introduction	4
4	2. Production methods of VFAs	5
5	3. Applications of VFAs	7
6	4. Non-membrane based methods for recovery and purification of VFAs	13
7	5. Membrane-based methods for recovery and purification of VFAs	18
8	5.1. Pressure-driven membrane processes	19
9	5.1.1. Clarification of the fermented effluents using MF and UF	19
10	5.1.2. VFAs recovery with NF/RO processes	21
11	5.2. Non pressure-driven membrane processes	23
12	5.2.1. Forward Osmosis	23
13	5.2.2. Membrane Distillation	26
14	5.2.3. Electrodialysis	27
15	5.2.4. Membrane Contactor	31
16	5.2.5. Pervaporation	33
17	6. Future perspective and challenges	35
18	7. Conclusions	37
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		

1 **Abstract**

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

19

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

21

22

1 **1. Introduction**

2 Volatile fatty acids (VFAs) are saturated or unsaturated carboxylic acids consisting of short chains
3 of carbon (usually six or fewer carbon atoms), e.g., acetic, formic, propionic, butyric acid [1].
4 VFAs are water-soluble organic acids “capable of being distilled at atmospheric pressure” [2].
5 These chemicals are inaccurately called short-chain fatty acids (SCFAs) in various reports [3,
6 4]. VFAs are commonly produced via engineered biochemical degradation of agricultural and
7 food products, e.g., agro-industrial lignocellulosic wastes, and as a by-product of petrochemical
8 processes [1, 5-8]. Moreover, VFAs are naturally produced through microbial fermentation of
9 organic matter in landfill leachate, food and water wastes, and generally in all environmental
10 systems [9]. These compounds are important intermediates and metabolites of biological processes
11 and accordingly, their presence in the environment ascertains the presence of bacterial activity.
12 Numerous materials, including antimicrobials, alcohols, aldehydes, ketones, esters, and olefins,
13 are synthesized using VFAs [10, 11]. Applications of VFAs are thus widespread, including feed
14 for microbial fuel cells [12, 13], cosmetics and textiles [14, 15], fermentation feed for hydrogen
15 [16] and biofuel production [17, 18], carbon resource alternatives for wastewater treatment plants
16 [19] and phosphorous removal processes [20], synthesis of biopolymer and bioplastics [21, 22].
17 Therefore, the production, purification, and recovery of VFAs are critical for several industrial
18 applications, such as those related to renewable energy, fuel production, and water and wastewater
19 treatment. While organic wastes have great potential to be utilized as feeds in biological process
20 for VFAs production [5], the presence itself of VFAs may inhibit these fermentation- based
21 technologies [23]. Aggregation of produced VFAs may alter the process, transformation pathways,
22 and render some reaction thermodynamically unfavorable [23]. To control the efficient and stable
23 production of VFAs, their continuous harvesting from the fermentation medium is critical [24].

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

18

19 **2. Production methods of VFAs**

20 Nowadays, most of the VFAs required for industrial applications are produced via chemical routes
21 [42]. However, due to issues related to the availability and price of global petroleum resources, as
22 well as to increasing awareness of their environmental effects in terms of pollution and climate
23 change, the interest in alternative methods of VFAs production has renewed [43-45]. Biological

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

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

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

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

13

14 **3. Applications of VFAs**

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

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

8 VFAs can also be utilized as substrates under anaerobic conditions in order to produce biogas,
9 which is suitable for power and heat generation due to its high content of methane (65–70 v/v %)
10 [69]. Additionally, VFAs can be converted to hydrogen by electrohydrolysis [70], photo
11 fermentation [71] or in microbial electrolysis cells [72]. There, the protons produced from the
12 electrohydrolysis of VFAs can combine with electrons released from the metal electrode (e.g.,
13 copper electrode) by application of direct current voltage to produce hydrogen [70]. In photo
14 fermentation, hydrogen is instead produced by the activity of non-sulfur bacteria consuming VFAs
15 in the presence of light [73]. As dark fermentation produces VFAs in addition to hydrogen, the
16 photo fermentation is commonly combined with dark fermentation as a process of two-stage
17 hydrogen production [74], whereby the VFA-rich effluent deriving from dark fermentation is
18 consumed in downstream photo fermentation to improve the overall hydrogen production [1].
19 Finally, microbial electrolysis cells are systems in which the protons coming from the microbial
20 oxidation of VFAs at the anode, are reduced at the cathode through the application of an external
21 power supply to yield hydrogen [75, 76]. Since the anodic microorganisms favor simpler VFAs,
22 acetate is consumed at higher rates compared to other VFAs in the fermentation liquid;

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

3 Moving away from processes utilizing VFAs as an indirect source of energy, these valuable acids
4 are also applied in the production of many chemicals. For example, heterotrophic microbial cells
5 can consume acids to produce various copolymers with diverse properties [77, 78]. In particular,
6 VFAs can be used as a carbon source and precursor for polyhydroxyalkanoates (PHA) ,
7 biodegradable polymers with a wide range of applications , for instance, as additives of
8 polyvinylchloride and packaging materials [17, 79]. Traditional carbon substrates are costly,
9 representing roughly 30% of the total operating costs in PHA production and thus restricting the
10 implementation of these polymers as replacements for conventional petrochemical-based plastics
11 [80]. The PHA polymer production by microbial fermentation of VFAs may improve the
12 economics of this process [81]. To this purpose, the composition of VFAs should be tweaked
13 through acidogenic fermentation, since the chain length of the VFAs has a great effect on the
14 composition and properties of the final PHA [82, 83]. For instance, acetic and butyric acids
15 promote the production of 3-hydroxybutyrate (3HB), while propionic and valeric acids are usually
16 consumed to yield 3-hydroxyvalerate (3HV) [84, 85]. Ethyl 3-ethoxybutyrate is a new fuel
17 oxygenate with high cetane number and associated with lower emission of pollutants; this
18 compound can be obtained by conversion of PHAs [86]. As another example, the incorporation of
19 3HV into poly(3HB) leads to the formation of copolymer P(3HB-co-3HV) [87], utilized as food
20 packaging material due to its flexibility and toughness [88]. Valuable chemicals, such as esters,
21 ketones, 1-alcohols, and 2-alcohols can also be produced by converting VFAs [89]. Usually, VFAs
22 are produced through biomass fermentation, which is already pretreated with suitable chemicals
23 to improve digestibility [90]. Then, CaCO_3 , NaHCO_2 , or NH_4HCO_3 is added as neutralizing agent

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

6 Another valuable application of VFAs is in the biological removal of nutrients in wastewater
7 treatment units, a necessary step to avoid nutrient enrichment or eutrophication of aquatic
8 ecosystems [94, 95] and a preferred route to physicochemical methods of nutrient removal [96,
9 97]. Ammonia/ammonium is transformed into nitrates and then into nitrogen through aerobic
10 nitrification followed by anoxic denitrification, while phosphorus removal can be accomplished
11 through enhanced biological phosphorus removal (EBPR) processes [98-101]. The practical range
12 of carbon to nitrogen ratio for combined nitrification/denitrification is 5–10 mg COD/mg N;
13 instead, to remove 1 mg of phosphorus, COD is needed in the range 7.5–10.7 mg [102, 103]. The
14 carbon substrate necessary to perform these transformations is frequently inadequate in typical
15 wastewaters and external carbon substrate is added to achieve an effective biological nutrient
16 removal (BNR) [104]. VFAs are highly appropriate sources of carbon to assist the biological
17 removal of phosphorus and nitrogen from wastewater [19, 105]. VFAs produced directly on site
18 through the anaerobic acidogenesis of organic wastes can be directly applied for BNR [105]. Zheng
19 et al. found that using VFAs produced from waste activated sludge fermentation led to phosphorus
20 and nitrogen removal efficiencies of 82% and 95%, respectively [106]. In nitrogen removal
21 processes, denitrifying bacteria favor VFAs with lower molecular weight and easier metabolic
22 pathways, thus promoting the consumption of acetate as the first VFA, followed by propionate,
23 butyrate, and lastly valerate [51].

1 Fig. 1 presents the main commercial and industrial applications of various pure VFAs [107]. What
2 follows is thus a brief discussion of the main uses of each of the VFAs. One of the most
3 commercially significant VFAs is acetic acid, which is consumed worldwide with almost one-third
4 of its consumption occurring in the United States [108]. Other than in the applications described
5 just above, acetic acid has important applications in the food industry as a solvent [109], as well
6 as in the preparations of some food products [110]. Additionally, it is applied in the production of
7 acetic anhydride, which is used in the manufacturing of dyes, explosives, perfumes, and
8 antibiotics, as well as in the production of vinyl acetate for further polymerization into polyvinyl
9 acetate, which is in turn applied in paper coatings, latex paint, textile finishing, and adhesives
10 [109, 111]. Acetic acid is also utilized in the production of purified terephthalic acid (PTA), an
11 alternative raw material for manufacturing polyester fibers; in the production of monochloro acetic
12 acid used in bacteriostats, herbicides, preservatives, and finally to obtain carboxy methyl cellulose,
13 glycine, and other laboratory chemicals, such as EDTA [111].

14
15 **Fig. 1.** Commercial and industrial applications of various pure VFAs.

16
17 Propionic acid has several applications in the preservation of animal fodder and food grains, the
18 production of herbicides, esters, and flavors [112, 113], in the chemical industry manufacturing
19 plastics and petrochemicals, and finally in the pharmaceutical industry [114, 115]. According to
20 market research estimations, the value of the propionic acid market was \$935.7 million in 2012,
21 and this number was anticipated to increase by 7.8% as of 2018 [111].

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

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

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

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

22

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 H₂O [128]. Multiple-stage separation and purification processes are often necessary to obtain cost-effective and marketable VFAs, in their pure or 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⁺, SO₄²⁻ and H₂PO₄⁻/HPO₄²⁻). 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

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

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

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

1 studies have explored the integrated process of adsorption/desorption to recover single VFAs or
2 mixtures of them. For instance, the adsorption ability of Purolite A133S and activated carbon was
3 studied and compared by Silva and Miranda [133]. It was found that n-propanol was an appropriate
4 eluent for the desorption process. In most circumstances, a chemical addition and a demanding
5 processing are required in the desorption stage (as shown in Fig. 2), and the VFAs achieved after
6 the regeneration process is not necessarily pure (it often contains a significant mineral impurity
7 from the desorption chemicals). This technology for the separation and purification of VFAs from
8 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.	<ul style="list-style-type: none"> - Easy to install - Products of high purity - Possibility of direct use of the products as fertilizer 	<ul style="list-style-type: none"> - 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.	<ul style="list-style-type: none"> - Easy to install - High yields of product - High purities of products - Low capital costs 	<ul style="list-style-type: none"> - 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.	<ul style="list-style-type: none"> - Easy to install and operate - Relatively high selectivity 	<ul style="list-style-type: none"> - 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.	<ul style="list-style-type: none"> - High concentration of carboxylate usually obtained - No need to adjust the pH by acid treatment 	<ul style="list-style-type: none"> - 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.	<ul style="list-style-type: none"> - High yield of product - Low cost - High selectivity achievable 	<ul style="list-style-type: none"> - 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.	<ul style="list-style-type: none"> - High yields of product - Easy to scale up - Reliable - Low energy demand 	<ul style="list-style-type: none"> - High membrane fouling - Unknown potential for the most complex solutions 	[27, 135]

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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

1 complex between the amine groups and the acid all played an important role in influencing the
2 yield of recovery. Finally, ionic liquid (IL)-assisted extraction is a promising method in which IL
3 organic salts are used as extractants. ILs are non-volatile, chemically stable, nonflammable, and in
4 liquid form in a wide range of temperatures, with low viscosity and high density. Imidazolium
5 [148], quaternary ammonium salts [149], or quaternary phosphate [150] are the most important
6 ILs used in extraction processes for organic compounds. The application of phosphonium-based
7 hydrophobic ILs in the recovery of organic acids (L-malic, L-lactic, and succinic acids) from
8 aqueous solutions has great potential over conventional solvent extraction processes [150].
9 Phosphonium-based ILs were used by Martak and Schlosser [151] in the high-performance
10 separation of lactic acid from aqueous solutions. Reyhanitash et al. [152] showed that
11 trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate [P666,14][Phos] had
12 suitable performance for the separation of acetic acid from aqueous solutions. An important issue
13 in the IL-based extraction of VFAs is the choice of the solvent, whose desired properties include
14 high selectivity, high coefficient of distribution, and high stability. Another issue is related to the
15 toxicity or inhibitory activity of some solvents used for in-line separation of organic acids.

16

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

19

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

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

1 [153-155]. Membrane processes with separation purposes may be divided in two general
2 categories; (i) pressure-driven processes, for instance, microfiltration (MF), ultrafiltration (UF)
3 and nanofiltration (NF)/reverse osmosis (RO), (ii) non-pressure-driven processes, such as
4 pervaporation (PV), electrodialysis, membrane distillation (MD), membrane contactor, and
5 forward osmosis (FO) [154].

6

7 **5.1. Pressure-driven membrane processes**

8 **5.1.1. Clarification of the fermented effluents using MF and UF**

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

17 As a first instance, UF was applied in a system to recover short chain VFAs from sewage sludge
18 [26]. This process clarified the fermented sewage sludge successfully, resulting in a permeate
19 stream containing a low amount of suspended solids and a high content of VFAs. A reduction in
20 the filtration performance was observed with time, due to the deposition of soluble and insoluble
21 substances, especially fibrous materials, onto the UF membrane surface. In general, high pH values
22 were also found to negatively affect the UF productivity [161]. **Zacharof and Lovitt [27] treated**
23 **waste effluents from anaerobic digesters of agricultural waste for the enrichment and concentration**

1 of acetic and butyric acids. They applied a crossflow microfiltration unit as pretreatment,
2 employing a Membralox ceramic filter element (α -Al₂O₃) with pore size and effective surface area
3 of 0.2 μ m and 0.22 m², respectively. A sterile and particle-free solution with a concentration of
4 21.08 mM of acetic acid and 15.81 mM of butyric acid was obtained using MF, and was then
5 further processed via NF. In another study, Kim et al. [162] applied microfiltration ceramic
6 membranes with a pore size range of 0.1-5 μ m for the recovery of volatile fatty acids from liquid
7 organic sludge. They found that the appropriate pH range of suspension was 5.0-6.0 for the best
8 recovery of organic materials as well as to achieve a high permeation flux. Additionally, the
9 optimal membrane pore size for the recovery of dissolved organics from fermented liquid was
10 around 1 μ m. Tao et al. [130] used MF with modified polyethersulfone (mPES MiniKros)
11 membrane modules with an effective length of 65 cm, a housing diameter of 1.9 cm and pore size
12 of 0.2 μ m to recover VFAs and nutrients from the production of biodegradable
13 polyhydroxyalkanoates. Around 90% of all organic acids were recovered; confirming that MF is
14 an effective strategy to recover VFAs from fermentation broths. Longo et al. [26] studied the
15 application of UF in the pilot scale production of short chain fatty acids from sewage sludge
16 through alkaline fermentation. Two tubular polyvinylidene fluoride UF modules with internal
17 diameter of 8 mm and molecular weight cutoff of 15 kDa were installed after the fermentation
18 process to separate the fermentation liquid from the sludge. A semi-continuous configuration
19 system coupled with a UF system was applied by separating and recirculating the solids fraction
20 of the fermented sludge to the fermentation reactor, leading to improving the organic loading rate
21 (OLR) as well as maintaining the SRT higher than the HRT.

1 **5.1.2. VFAs recovery with NF/RO processes**

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

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

12 Zacharof et al. aimed instead to recover VFAs from agricultural waste in the concentrate side of
13 the NF membrane. They recovered 69% of butyric acid and 72% of acetic acid at high pH values
14 [178]. Masse et al. used RO membranes and observed a higher rejection for VFAs compared to
15 NF membranes [28]. While pH has a lower effect on RO compared to NF, other parameters may
16 influence the VFA retention from a fermentation broth in RO: previous studies showed that
17 increasing the applied pressure enhanced the retention of acetic acid, while an increase in the
18 temperature of the feed solution had an opposite effect [179]. To summarize, acidic pH values
19 usually allow the recovery of VFAs in the permeate side of nanofiltration membranes. RO can
20 provide permeate streams of higher purity but with challenges related to the overall recovery rate,
21 as the separation of dense membranes is less tunable by adjusting the pH and other physico-
22 chemical conditions of the feed solution. Oppositely, high pH values commonly result in higher
23 VFAs rejection by the membranes and their recovery in the concentrate stream. The existence of

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

3

4 **5.2. Non pressure-driven membrane processes**

5 **5.2.1. Forward Osmosis**

6 Forward osmosis (FO) has interesting potential in the VFAs recovery due to its unique mass
7 transfer properties, the low hydraulic pressures involved, and the existence of reverse draw solute
8 diffusion [181-183]. The driving force of the FO process is the osmotic pressure gradient between
9 the feed side and a concentrated draw solution side, separated by a semipermeable membrane [40,
10 184, 185]. FO exhibits a lower fouling tendency and higher fouling reversibility compared to
11 pressure-driven membrane processes [186, 187]. The FO process may be run in two different
12 modes, FO and pressure retarded osmosis (PRO) modes, based on the orientation of the membrane
13 active layer with respect to the feed stream. In the FO mode, the selective layer of the membrane
14 faces the feed solution (ALFS), while in the PRO mode, the membrane active layer faces the draw
15 solution (ALDS). FO technology is currently in the early industrial stage of development; several
16 pilot scale systems exist and are applied in different fields, while only a few large-scale plants are
17 being implemented.

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

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

3

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

5

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

18 The results presented by the K. Jung et al. suggest that VFAs recovery in the FO systems should
19 be operated in ALFS mode due to a more effective process performance in this orientation [194].

20 The existence of reverse draw solute diffusion in the FO process may be exploited as a way to
21 increase VFAs recovery: in a previous study, the reverse salt flux limited the forward diffusion of
22 the VFAs and it also prevented their adsorption on the membrane surface [195]. **K. Jung et al.** also
23 investigated the effects of pH on the FO performance during the VFA recovery process [194] and

1 obtained the results summarized in Fig. 5. The pH value had a significant influence on the VFA
2 rejection rate and reverse salt flux while it had a moderate effect on the FO water flux. Increasing
3 the VFA solution pH resulted in a lower FO water flux and a more severe reverse salt diffusion.
4 Instead, the VFAs rejection and recovery were improved, similarly to what stated above for NF
5 membranes. Though the water flux was the lowest at the highest investigated pH, the final
6 concentration of VFAs at the end of the process was increased of over 60% compared to the tests
7 conducted at the lowest pH value [194]. This can be explained by the fact that at high pH levels,
8 the VFAs exist mostly as negatively charged ions. Hence, the VFAs rejection is improved by both
9 electrostatic repulsion with the membrane active layer negative charges and as the hydrated ions
10 are bulkier than their neutral counterparts [196, 197]. Likewise, methodologies based on pH
11 adjustment, such as the use of alkali, are reported to increase VFA production from sludge [198,
12 199]. Actually, alkaline conditions increase both hydrolysis and acidification rates as well as the
13 solubilization of the main components of the sludge, causing a higher VFAs production [200].
14 Therefore, processing the FO dewatering at alkaline pH directly in the sludge or fermentation broth
15 can enhance the final VFAs concentration [201]. Some authors suggested that the pH level should
16 be adjusted in the range of 7-8 to maximize VFAs production from fermentation broths, using
17 NaOH as a preferred pH adjustment agent [194].

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

1 activated A-sludge, and secondary sludge [201]. They concentrated the feeds containing VFAs 10-
2 fold via an FO process in batch mode. The FO water flux decreased over time because of fouling
3 and reverse salt flux, which also increased the salinity of the VFAs concentrated solution. They
4 observed that the retained organics at high concentration extensively deposited on the membrane
5 surface, causing a significant decline in the FO dewatering performance. In this regard, they
6 suggested using recirculation and air scouring by gas bubbling (N₂: CO₂ (9:1)) as a physical
7 technique to control the properties of the sludge in the feed solution and minimize fouling, but at
8 the expense of higher operating costs [201].

9

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

13

14 **5.2.2. Membrane Distillation**

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

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

4

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

6

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

19

20 **5.2.3. Electrodialysis**

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

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

6
7 **Fig. 7.** Conceptual illustration of the CED process for VFAs recovery.

8
9 Tang et al. studied ED using a bipolar membrane to recover acetic acid from fermentation broths
10 [215]. They recovered about 93% of acetic acid in relatively quick experiments. CED was applied
11 to recover valuable VFAs and increased the yield of hydrogen from a dark fermentation reactor at
12 a potentially low cost [213]. The concentrations of individual acids in dilute compartments were
13 reduced gradually during a 60 min of process, while the VFAs were simultaneously concentrated
14 and recovered in the opposite compartments. In the case of acetic acid, the system allowed around
15 98% of recovery from a synthetic solution. Fig. 8 reports the results obtained by Tang et al. in the
16 concentration of acetic acid and n-butyric acid from a real fermentation broth using low-cost
17 membranes in CED [215]. The VFAs concentrations were increased significantly in the
18 concentrate circuits during the initial 30 min of process, and their concentrations accordingly
19 decreased by up to 96% in the dilute circuits. Back diffusion of the acetic acid levels in the dilute
20 stream was observed after 50 min of CED process, due to the significant concentration gradient
21 overcoming the electrical gradient [216]. The rate of acid transport was found to relate to its initial
22 concentration gradient [213]. B. Tao et al. applied the CED process to effectively enrich VFAs
23 from thermally hydrolyzed waste activated sludge [130]. MF was used as a pretreatment, allowing
24 the recovery of roughly 80% of the VFAs in the permeate stream. Approximately 92% of this

1 VFAs content was then recovered in the downstream CED process. The results suggested that the
2 various acids behave differently, with the small molecular weight acids showing better transfer
3 performance. Accordingly, acetic acid had the highest recovery efficiency while n-valeric acid the
4 lowest one of about 85%. X.-R. Pan et al. studied different VFAs in terms of migration flux
5 through the ED process [217], revealing comparatively higher transport potential of smaller-
6 molecule VFAs across the ED membrane. Analogous results were also reported by another study
7 [213]. VFAs transfer across the CED membranes is also highly correlated to their different
8 ionization in solution. CED promotes the progressive ionization of the weak organic acids in the
9 dilute solution, by selective removal of the ionized ions. On the contrary, increased proton levels
10 in the concentrate compartments inhibits ionization, and the VFAs are more likely to be found
11 there in their free acid form. High levels of free acids may lead to their loss by evaporation owing
12 to the high volatility of VFAs.

13

14 **Fig. 8.** Acetic acid and n-butyric acid concentration flux during the CED of hydrogen
15 fermentation broths (more than 90% recovery of the VFAs during 30 min of CED). The slope of
16 the graphs, denoting the VFA transport rate, is correlated to the initial concentration gradient
17 [213].

18

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

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

12 Removal of the VFAs from the fermentation broth can simultaneously improve hydrogen
13 production [220, 221]. In this regard, Noblecourt et al. used a submerged membrane anaerobic
14 bioreactor to control the VFAs level and avoid their accumulation in solution [222]. They
15 successfully limited the VFAs concentration, but at the expense of losing other small molecules,
16 such as amino acids and monosaccharides, which are favorable substrates for hydrogen-producing
17 bacteria. To address this issue, P. Wei et al. [217] introduced a novel three-chamber in-situ ED,
18 which simultaneously recovered VFAs and controlled their level in the fermentation reaction zone
19 [217]. Using single chamber fermentation without ED (control test) resulted in a rapid increase in
20 the acetate and butyrate concentrations in the broth (Fig. 9). On the other hand, the three-chamber
21 ED process promoted the passage of acetate and butyrate from the fermentation chamber to the
22 anode chamber, resulting in an overall higher hydrogen production. Higher voltage (4 and 6 V)

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

3

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

9

10 **5.2.4. Membrane Contactor**

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

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

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

12

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

14

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

1 [227]. These results were corroborated by another study, in which a TOA-filled membrane was
2 observed to be highly selective toward valeric and caproic acids, moderately selective toward
3 butyric acid, and least selective toward acetic acid. This process resulted in the near complete
4 recovery of caproic acids [230]. These authors highlighted that filling the membrane pores with
5 the extractant may be economical and environmentally friendly, due to the small amount of
6 extractant required for the separation [227]. For feed containing suspended particles and inorganic
7 precipitates, these substances were observed to accumulate on the membrane surface to create an
8 extra resistance to mass transfer [135]. This phenomenon resulted in a lower separation efficiency
9 of a real feed containing mixed VFAs compared to that of a synthetic VFAs mixture in the absence
10 suspended particles. Issues associated with the interference of suspended matter must be
11 considered when designing a membrane contactor process for VFAs recovery.

12

13 **5.2.5. Pervaporation**

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

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

1 framework (MOF) [235]. The authors aimed to dehydrate the feed stream and recover acetic acid
2 in the concentrate side of the membrane. The results showed that an appropriate loading of MOF
3 resulted in a significant enhancement in water permeability and selectivity, translating into
4 improved flux and separation factor during operation. The authors also investigated the effect of
5 acetic acid concentration, feed temperature, and flow rate on the PV performance [235]. The water
6 flux increased significantly by increasing the feed temperature, while the separation factor
7 decreased considerably. This result was attributed to a reduced diffusion resistance of the PV
8 membrane for both acetic acid and water due to the higher operating temperature. Moreover, as
9 the temperature increased, the vapor pressure difference between the two sides of the membrane
10 was enhanced, thus improving the driving force for mass transport [235]. As the acetic acid
11 concentration increased in the feed solution, the swelling degree of the membrane decreased. In
12 turn, this phenomenon reduced the free volume of the membrane, leading to an enhancement of
13 the separation factor at the expense of a reduction in permeate flux [235]. As other researchers
14 reported, there is a trade-off which usually observed in the PV process [236, 237]. Increasing the
15 feed flow rate caused a turbulent flow at the membrane/solution interface, reduced the boundary
16 layer thickness, and resulted in a lower mass transfer resistance as well as concentration
17 polarization, overall translating into a larger value of the permeate flux but lower separation factor
18 [235].

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

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

5

6 **6. Future perspective and challenges**

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

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

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

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

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

10

11 **7. Conclusions**

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

1

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