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Silicone membrane contactor for selective volatile fatty acid and alcohol separation

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ABSTRACT

The effect of pH and extraction temperature on flux, recovery, mass transfer coefficient and separation factor of volatile fatty acids (VFAs) and alcohols from synthetic solutions and cheese whey fermentate was investigated using a silicone membrane contactor with water as extractant. The silicone membrane allowed extraction of undissociated acids only, resulting in substantially higher recovery efficiencies at pH 3 than at pH 5. Furthermore, the non-porous silicone membrane favoured extraction of longer chain over shorter chain acids. Caproic acid was extracted with the highest flux of 1.30 (± 0.02) g m^{-2} h^{-1} in short time (32 h), with a 41.5 % recovery efficiency at pH 3 and 20 °C, indicating the feasibility of its selective separation from the VFA mixture. A similar trend was observed for alcohols, with butanol being extracted with a 39 % recovery efficiency at 40 °C, against 32 % and 19 % of propanol and ethanol, respectively, while the mass transfer coefficients were not affected by temperature. When applying the silicone membrane contactor to real cheese whey fermentate at pH 3, butyric and acetic acid were extracted with 21.5 % and 7% recovery efficiency, respectively, suggesting the feasibility of the contactor for VFA recovery from real fermentate.

1. Introduction

Waste valorisation plays a key role in circular economy that relies on the transformation of value chains from linear to closed loop (Maina et al., 2017). This is necessary to achieve EU's long-term goal of a low carbon economy by 2050 (Scarlat et al., 2015). Biological processes such as dark and photo fermentation (Yuan et al., 2019) have the potential to partially replace fossil fuel-based refineries to produce platform chemicals such as volatile fatty acids (VFAs) and alcohols. Hence, waste processing is moving towards a biorefinery approach, in which a combination of physico-chemical and biological processes is used to obtain marketable products from waste. Separation and recovery of these valuable products is still a major bottleneck due to low concentrations and complex physiochemical nature of the fermentate and digestate (Zacharof and Lovitt, 2014). *In-line* recovery of these products from biological processes would be advantageous as continuous harvesting of VFAs and alcohols would facilitate their efficient and stable operation (Trad et al., 2015).

Several separation methods have been reported in the literature, i.e. solvent extraction, adsorption, and membrane processes, including electrodialysis, reverse osmosis/nano-filtration and membrane extraction (Atasoy et al., 2018), each having its own benefits and drawbacks. Solvent extraction is a method used to separate compounds or complexes based on their relative solubilities in two different immiscible liquids. Different extractants such as trioctylamine (TOA), trioctylphosphine oxide (TOPO), Alamine 336 or N,N-didodecylpyridin-4-amine are reported in the literature with TOA being the most used (Li et al., 2002; Alkaya et al., 2009; Reyhanitash et al., 2016). However, such chemicals are expensive and require a regeneration step. Furthermore, the extractants are non-selective, and extraction of other compounds than VFAs (e.g. salts and alcohols) can result in low purity. These extractants are also mostly toxic to microorganisms and can thus not be applied *in-line* in combination with the biological processes (Playne and Smith, 1983).

Adsorption is a surface phenomenon in which the molecules from a gaseous or liquid medium adhere to a solid surface. Ion-exchange resins are used as adsorbents for VFA adsorption (Bertin et al., 2016; Cabrera-Rodríguez et al., 2017; Reyhanitash et al., 2017) with a maximum reported recovery yield of 85 % from synthetic mixtures (Rebecchi et al., 2016). A desorption step is however

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required to obtain the final products, which results in deterioration over time (Aktij et al., 2020), thereby increasing the process costs. Furthermore, adsorption is not selective towards VFAs, resulting in products contaminated with anions such as phosphates, sulphate and chloride, commonly found in biological processes.

Membrane processes are well documented in the literature and have been previously used for VFA separation (Aktij et al., 2020). Membranes facilitate in separation while avoiding contact between the bulk solution and the permeate. Typically, membrane processes involve application of high pressure (e.g. nanofiltration and reverse osmosis; pressure range: 3.5–20 bar) or an electric field (e.g. electrodialysis) across a semi-permeable or ion exchange membrane, respectively, that separates solutes such as salts or organic molecules from the solvent and other compounds (Aktij et al., 2020). Nanofiltration and reverse osmosis membranes have been investigated for VFA separation from different matrices, and a separation of 75–90 % have been reported under operating conditions of pH 3.5 and 5 bar, and pH 2.93 and 50 bar, respectively (Xiong et al., 2015; Zhou et al., 2013). Jonas et al. (2015) applied electrodialysis for VFA separation from a synthetic solution and showed 99 % recovery within 60 min of operation (Jones et al., 2015), whereas Zhang and Angelidaki (2015) recovered 98.3 % of VFAs from digested pig manure via bipolar membrane electrodialysis. However, both processes are energy intensive and still require considerable research to make them cost-effective, particularly for recovery of products from waste streams, due to problems such as inhomogeneity and fouling.

Another type of membrane based VFA separation process is the vapour permeation membrane contactor that works on vapour pressure difference and concentration gradient (Aydin et al., 2018). Yesil et al. (2014) studied VFAs extraction from organic solid waste leachate solutions using hydrophobic polytetrafluoroethylene (PTFE) membranes with NaOH as extractant for VFA diffusion and precipitation as sodium salts. Integration of a membrane contactor with a leach bed reactor demonstrated separation of acetic, butyric and caproic acid from the leachate (Yesil et al., 2014). Aydin et al. (2018) extended the idea and studied the application of extractant filled membranes (PTFE membrane with air and two tertiary amine (trioctylamine (TOA) and tridodecylamine (TDDA)) for VFAs separation from a synthetic mixture and a fermentation broth of municipal organic solid waste, anaerobic landfill leachate and chicken manure digestate. TOA-filled PTFE membranes showed high removal efficiencies for all VFAs present in the fermentation broth and landfill leachate, with a maximum removal efficiency of 86–95 % for propionic, butyric, valeric and caproic acid (Aydin et al., 2018).

Outram and Zhang (2018) reported solvent free separation of VFAs using silicone membranes with water as an extractant. The advantages of using water include lower cost (than solvents such as NaOH or TOA with octanol) and recovery of VFAs in the undissociated form, thereby eliminating the requirement for a counter-ion removal process as in the case of other reported studies (Aydin et al., 2018; Yesil et al., 2014; Tugtas, 2014). Furthermore, fouling did not occur on the silicone membrane and the process requires a large membrane surface area due to the low mass transfer coefficients of VFAs. However, the study did not look at the diffusion of caproic acid at high concentrations nor at organic solvents such as alcohols. These are vital to understand the separation characteristics while treating a multicomponent solution such as fermentate which can affect the performance and economic scalability of the system.

The present study investigated the applicability of silicone membranes for VFA and alcohol separation from synthetic solutions and a model anaerobic fermentate, i.e. cheese whey, with water as the extractant. A synthetic mixture of concentrated VFAs and alcohols, and cheese whey fermentate were examined for VFA separation at different temperatures (20, 30 and 40 °C) and pH (3 and 5). The VFAs and alcohols diffusion through the silicone membranes and their flux, mass transfer coefficients, recovery and separation factor were investigated. This study provides insights in VFA separation from a synthetic solution and cheese whey, and reports for the first-time the alcohol extraction through a silicone membrane, in view of utilising the silicone membrane separation process for *in-line* VFA and alcohol extraction from anaerobic fermentates.

2. Materials and methods

2.1. Source of feed solution

In view of understanding the separation of carboxylic acids and alcohols in a multicomponent solution, a synthetic VFA solution containing equal amounts of acetic, propionic, butyric, valeric and caproic acids (5 g L^{-1} each) and alcohol solutions containing ethanol, propanol and butanol (5 g L^{-1} each) were prepared in RO water (resistivity 13 MΩ cm^{-1}). Equal concentrations of VFAs and alcohols were chosen to avoid the concentration related changes in flux and separation factor. Cheese whey from cow milk was obtained from the dairy industry (Dairygold, Mitchelstown, Ireland) and the fermentate, rich in VFAs, was obtained after fermentation of cheese whey at 35 °C and pH 5 for 7–8 days (Dessì et al., 2020). Preliminary analysis of the VFA content showed the predominance of butyric and acetic acid with an average concentration of, respectively, 4.6 and 4.0 g L^{-1} in the cheese whey fermentate.

2.2. Experimental set-up

A system consisting of two beakers, a silicone tube membrane (peroxide cross-linked, with internal diameter of 3 mm and external diameter of 5 mm, and 2 m length, VWR Ltd), a peristaltic pump (Masterflex) and a system of non-permeable tubes (Masterflex L/S Tygon E-Lab E-3603) connecting the feed and the draw was used for the experiments (Fig. 1). The feed beaker contained 400 mL of synthetic VFA/alcohol solution or cheese whey fermentate, whereas the draw beaker contained 400 mL RO water. The peristaltic pump was operated at 55 mL min^{-1}. The draw solution was stirred at 150 rpm by a magnetic stirrer with temperature control, inside which the silicone membrane was immersed for extraction tests. An active internal membrane area of 0.0125 m^2 was in contact with the RO water in the draw beaker. All experiments were performed in duplicates and membranes were changed after each experiment.

The details of individual experiments are summarised in Table 1. Experiments were conducted for at least 70 h with samples taken at periodic intervals from both beakers for VFA/alcohol analysis. The temperature of the draw solution was maintained at 20, 30 or 40 °C using a hot plate. The experiments with synthetic VFA fermentate were performed at pH 3 and 5 at three different extraction temperatures (20, 30 and 40 °C). The pH values chosen were below and slightly above the pKa of the acids. Before the start of each experiment, if necessary, the feed pH was adjusted using H_2SO_4 or NaOH. The synthetic alcohol solution had a pH of 2 and was used as such for the experiments, since alcohol does not dissociate at low pH. For the experiments on VFA recovery from cheese whey fermentate, the first sample was collected after 10 min. (to ensure the cheese whey fermentate was able to flow through the membrane without any blockage/clogging).

2.3. Analytical methods

The pH and conductivity for the draw and feed solution was monitored using an accumet® pH and conductivity meter (AB200)

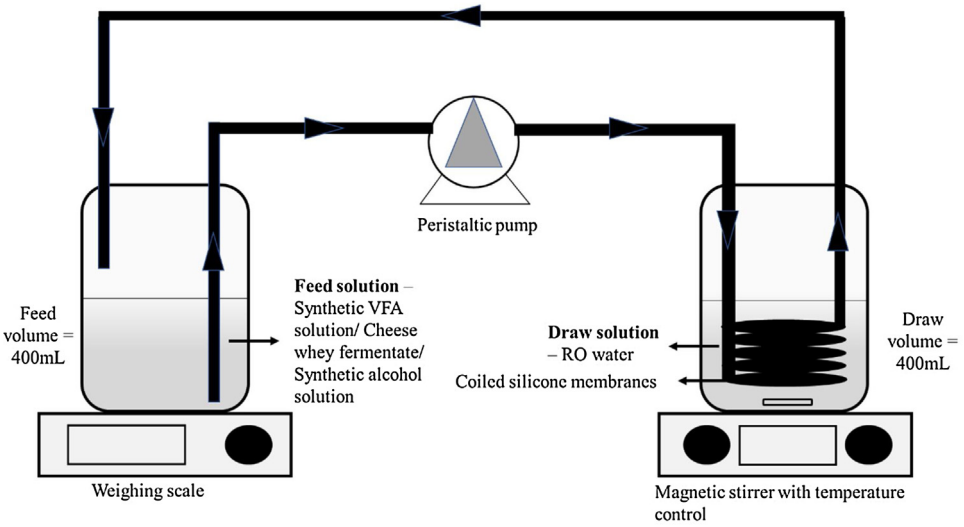

Fig. 1. Schematic representation of the experimental set-up.

Table 1
Overview of the experimental conditions applied to the silicone membrane contactor.

Experiment	Feed solution	Feed solution pH	Temperature of draw solution (°C)
1	Synthetic VFA solution	3 and 5	20, 30 and 40
2	Cheese Whey fermentate	3 and 5	20, 30 and 40
3	Synthetic alcohol solution	2	20, 30 and 40

throughout the course of the experiment. The change in mass of the feed was monitored using a weighing scale (Ohaus Scout® SKX).

VFA concentrations were measured using a Varian 450 gas chromatograph (GC) equipped with a flame ionisation detector and an SGE BP-21 column (30 m long, internal diameter 0.25 mm and film thickness 0.25 μm). Helium was used as a carrier gas at a flow rate of 1 mL min^{-1}. The GC oven temperature was increased from 60 °C to 110 °C at a rate of 30 °C min^{-1} and from 110 °C to 200 °C at a rate of 10 °C min^{-1}. The injector and detector temperatures were 250 °C and 300 °C (Nzeteu et al., 2018). Prior to GC analysis, cheese whey fermentate samples were centrifuged at 11,000 rpm for 6 min (Eppendorf non-IVD Centrifuge 5430 G) and the supernatant was filtered (0.2 μm) and diluted appropriately. The alcohol concentration was measured using liquid chromatography (LC) (1260 Infinity II, Agilent, USA) equipped with a refractive index detector (RID) and a Hi-Plex H column. The mobile phase was H_2SO_4 (5 mM) at a flow rate of 0.7 mL min^{-1}.

2.4. Calculations

The flux (J) or permeation rate of individual VFA or alcohol was calculated using Eq. 1:

$$J = \frac{1}{A}\frac{\Delta m}{\Delta t} \tag{1}$$

where Δm is the mass of VFA or alcohol permeated through the membrane (g), A is the membrane surface area (m^2) and Δt is the time interval (h).

The overall mass transfer coefficient, K, was estimated using Eqs. 2 and 3 (Outram and Zhang, 2018):

$$J_i = AK\left(C_{i,D} - C^*_{i,D}\right) \tag{2}$$

$$\ln\left(\frac{C_{i,Dt} - C^*_{i,D}}{C_{i,D0} - C^*_{i,D}}\right) = \frac{AKt}{V_F} \tag{3}$$

where $C_{i,D0}$ is the initial concentration at t = 0, $C_{i,Dt}$ is the concentration at time, $C^*_{i,D}$ denotes the equilibrium concentration, V_f is the initial volume of the VFA solution, t is time (h) and A is the surface area (m^2). The values were calculated using the draw VFA or alcohol concentration.

The membrane separation factor (β_{VFA}) was estimated using Eq. 4 (Aydin et al., 2018):

$$\beta_{VFA/Water} = \frac{\frac{VFA\ or\ alcohol\ weight\ fraction\ in\ permeate}{VFA\ or\ alcohol\ weight\ fraction\ in\ the\ feed}}{\frac{Water\ weight\ fraction\ in\ the\ permeate}{Water\ weight\ fraction\ in\ the\ feed}} \tag{4}$$

The water weight fraction in the permeate and feed is calculated using Eq. 5 (Aydin et al., 2018):

$$W_{water,i} = \frac{\rho_i \mathrm{x}\, V_i - (\sum m_{VFA,i})}{\rho_i \mathrm{x}\, V_i} \tag{5}$$

where ρi is the density of the solution (g L^{-1}), V_i is the volume of the solution (L) and $m_{VFA,i}$ is the mass of individual VFA (g).

The recovery percentage was calculated using Eq. 6:

$$Recovery\ (\%) = \left(\frac{Concentration\ of\ VFA\ or\ Alcohol\ in\ draw\ solution\ (t_n)}{Concentration\ of\ VFA\ or\ Alcohol\ in\ feed\ solution\ (t_0)}\right) * 100 \tag{6}$$

where t_0 and t_n represent the start and the end time (h) of experiment. For few experiments, the feed concentration of individual VFAs at the start was observed to be less than 5 g L^{-1} and the observed values were used to calculate the recovery percentage.

The vapour pressure was calculated using Eq. 7:

$$P_s = P_{S,t} \times X_{s,t} \tag{7}$$

where P_s is the vapour pressure of the VFA in solution, $P_{s,t}$ is the vapour pressure of the individual VFA at a given temperature and $X_{s,t}$ is the mole fraction of the individual VFA at a given temperature.

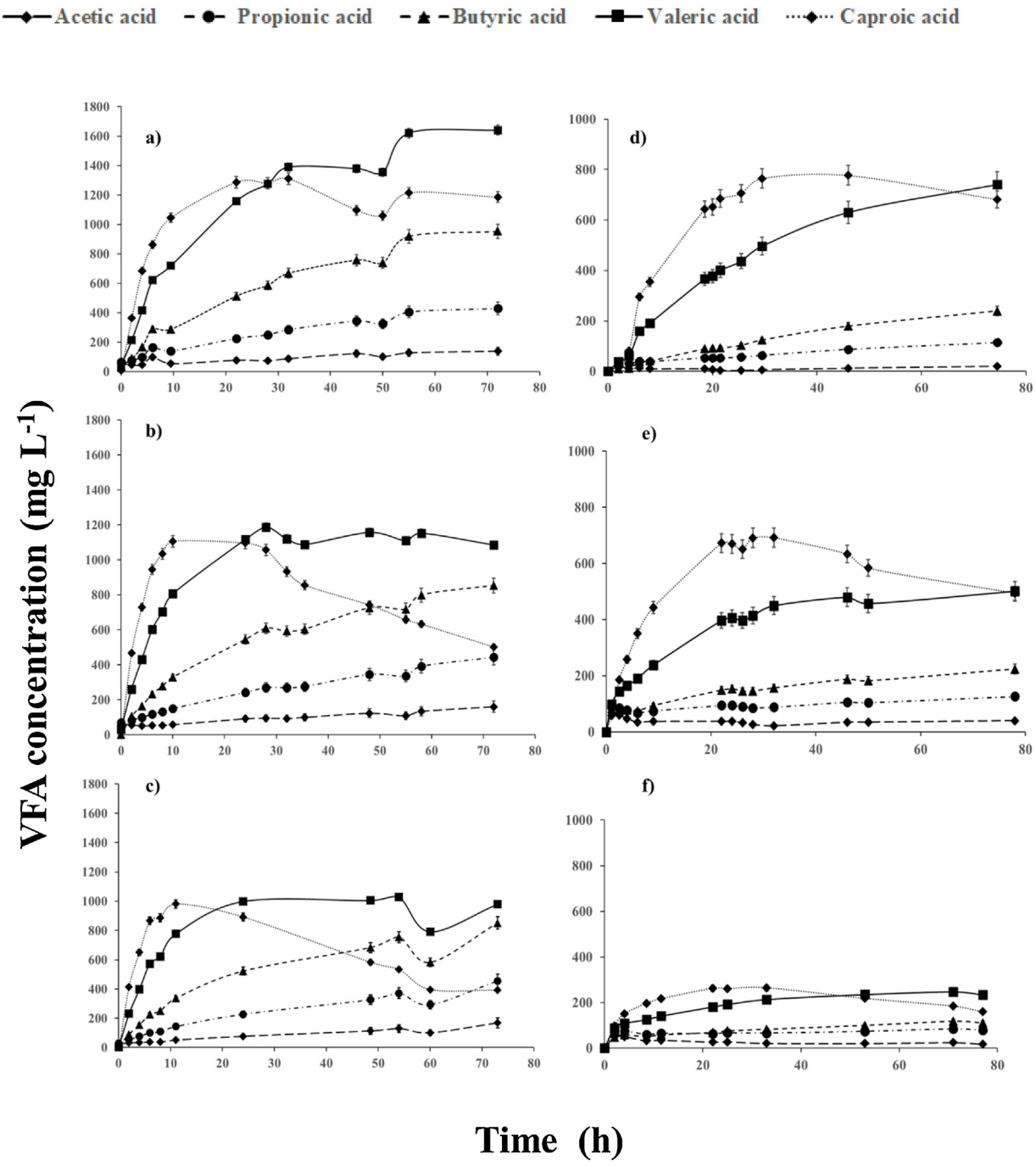

Fig. 2. Draw solution VFA concentrations with synthetic VFA mixture as feed at pH 3 **a)** 20 °C, **b)** 30 °C, **c)** 40 °C, and pH5 **d)** 20 °C, **e)** 30 °C and **f)** 40 °C. *(Note the different y-axis scale for different* pH *conditions).*

3. Results and discussion

3.1. VFA recovery from synthetic VFA solution

Fig. 2 shows the concentration profile of VFAs in the draw solution. At the end of 70 h operation, the draw solution had more valeric acid as compared to other VFAs regardless of pH and temperature. The VFA concentration in the draw solution increased with time, except for caproic acid, which initially increased and then decreased for all the conditions (Fig.2). Analysis of the feed side caproic acid concentration showed it did not diffuse back to the feed compartment. At pH 3, the caproic acid concentration increased rapidly in the draw solution in a short time (10–30 h depending on the temperature) and started to decrease over time after 32, 24 and 11 h at 20, 30 and 40 °C, respectively, suggesting the possibility of evaporative loss or formation of an immiscible layer on top of the draw solution due to the low solubility as opposed to other VFAs in water (Khor et al., 2017). This trend was also noticed at pH 5 for all temperatures tested, with decreasing caproic acid concentrations in the draw solution after 46, 22 and 22 h at 20, 30 and 40 °C, respectively. The present study used the highest caproic acid concentration (5 g L^{-1}) in the synthetic solution compared to other model solutions reported in the literature (Aydin et al., 2018; Yesil et al., 2014; Outram and Zhang, 2018; Tugtas, 2014). Nonetheless, the rapid increase in caproic acid concentration in a short time (20

h) can be used for its selective extraction from a VFA mixture even at such high initial concentrations.

Feed composition, pH and temperature affected mass transfer from the feed to the draw solution, resulting in different overall mass flux values (Table 2). At both pH 3 and 5, the flux values of the fatty acids generally decreased with increase in extraction temperature. This was a result of the higher net vapour pressure in the draw side, resulting in a resistance to diffusion and hence reduction in the flux. At pH 3, the calculated vapour pressure of individual acids in the draw solution was higher compared to the feed side (Table S1), with an exception being acetic acid, where the flux did not change (Table 2). As the majority of the acids (about 60 %) is dissociated at pH 5 (pKa ~ 4.7–4.8), the vapour pressure data for individual acids in feed side was not calculated. However, the individual vapour pressure of the acids in the draw solution (where pH < 4) was calculated (Table S1, Fig S1) and can be expected to be higher than the feed side with pH 5 (Bandini and Gostoli, 1992). Valeric acid showed the highest overall flux after 70 h of operation (0.70 (±0.07) g m^{-2} h^{-1}) at pH 3 and 20 °C, followed by caproic acid (0.52 (±0.06) g m^{-2} h^{-1}). However, at the first 32 h of operation at pH 3 and 20 °C, caproic acid was extracted with a maximum flux of 1.3 (±0.02) g m^{-2} h^{-1}, with an overall recovery of 41.5 %.

Aydin et al., (2018) conducted a study with a microporous PTFE and PTFE-TOA composite membrane for VFAs separation (at pH 3.9 for 21, 30 and 38 °C) from a synthetic VFA solution using NaOH as extractant for a 7 h period. The study reported that the mass flux of individual VFAs was not significantly different at 21 °C and 30 °C, but slightly increased at 38 °C for separation using the PTFE membrane. The mass fluxes obtained for PTFE-TOA membranes were comparable with temperature (at 21, 30 and 38 °C) with slightly lower flux observed for valeric and caproic acid when the temperature was increased from 21 °C to 30 °C. Yesil et al. (2014) conducted a VFA separation study using hydrophobic PTFE membranes with synthetic mixed VFA solution at pH 3 and 30 °C with 1 N NaOH as draw solution for 30 h. Propionic acid had a maximum flux of 14.21 g m^{-2} h^{-1} followed by acetic acid at 13.12 g m^{-2} h^{-1}. Caproic acid had the lowest flux of 2.13 g m^{-2} h^{-1} (Yesil et al., 2014). This was due to the high acetic and propionic acid concentrations (6 g L^{-1}) compared to that of caproic acid (1 g L^{-1}) in the synthetic feed VFA mixture.

The flux values obtained in the present study under similar operating conditions (pH 3 and temperature 30 °C with water as draw solution) (Table 2) were rather low compared to those reported with similar extraction methods (Aydin et al., 2018; Yesil et al., 2014). This can be attributed due to the non-porous property of the silicone membrane that resists mass transfer as opposed to the porous PTFE membranes (Aydin et al., 2018; Yesil et al., 2014) which facilitate solute transport. Generally, non-porous membranes are used to separate molecules with sizes in same order of magnitude (Mulder, 2012). The flux of organic liquids or vapours through non-porous membranes depends on concentration gradients with diffusivities increasing with concentration (Mulder, 2012). Higher mass fluxes of 7.34 g m^{-2} h^{-1} and 5.4 g m^{-2} h^{-1} were reported for acetic acid at 25 °C when using respectively, porous hydrophobic hollow fibre membranes (Qin et al., 2003) and TOA impregnated hydrophobic membranes, in pervaporation units (Thongsukmak and Sirkar, 2007). These studies reporting higher mass flux (Aydin et al., 2018; Yesil et al., 2014; Qin et al., 2003; Thongsukmak and Sirkar, 2007) of VFAs however, require either a chemical extractant or a high energy investment as opposed to the present work.

Since the extraction process through silicone is driven by a concentration gradient, a maximum of half the initial concentration in the feed solution can be theoretically obtained in the draw solution. Based on the initial VFA concentration in feed and final VFA concentration in draw solution, the recovery of individual VFAs was calculated for the experimental conditions (Fig. 3.). The increase in temperature considerably decreased the VFAs mass transfer from the synthetic VFA solution and hence reduced the VFA recovery at both pH values investigated. At pH 3, the recovery trend after 70 h was valeric > caproic > butyric > propionic > acetic acid. However, caproic acid recovery could be enhanced when extracting at a shorter extraction time of 32, 24 and 11 h at 20, 30 and 40 °C, respectively, where its concentration was higher as compared to 70 h (Fig. 2). A maximum recovery of 5, 15, 29, 45 and 38 % was obtained at pH 3 and 20 °C for acetic, propionic, butyric, valeric and caproic acid, respectively. At pH 5, the VFA recovery followed a similar trend as observed at pH 3. Digestates with high concentration of caproic acid, viz. 3.2 and 4.5 g L^{-1} (values compared closely to this work) present in leachate of a fermented organic waste and chicken manure digestate showed low recoveries of 8.5 and < 10 % for an experimental duration of 15 days and 7 h, respectively, when using PTFE and PTFE-TOA membrane contactors (Aydin et al., 2018; Yesil et al., 2014). Shorter extraction times could have led to a better caproic acid recovery as observed in the present study.

The recovery of VFAs was lower than the theoretical equilibrium concentration of 2.5 g L^{-1}, which could possibly be due to the adsorption of VFAs on the silicone membrane due to its high hydrophobicity. A similar observation of concentrations below the predicted equilibrium concentration is reported for a synthetic VFA solution and was attributed to the distribution of VFAs in the membranes (Outram and Zhang, 2018).

The overall mass transfer coefficients of VFAs extracted at different temperatures and pH (Table 3) were calculated considering the maximum concentration obtained in the draw solution as the equilibrium concentration. The overall mass transfer coefficients of VFAs followed the order of the carbon chain length (caproic > valeric > butyric > propionic > acetic) for both pH values investigated, irrespective of the temperature. The longer chain acids, indeed, have a higher affinity to the silicone membrane due to their higher hydrophobicity (Yesil et al., 2014). The coefficients were lower at pH 5 as compared to pH 3 (Table 3), although the effect of temperature on the overall mass transfer coefficients was not observed (Table 3).

The mass transfer coefficient values were comparable to those reported by Outram and Zhang (2018). The study reported that iso-valeric acid had the highest mass transfer coefficient (0.14 μm s^{-1}) followed by butyric (0.082 μm s^{-1}) and acetic (0.02 μm s^{-1}) acid at 25 °C. Yesil et al. (2014) also reported a higher mass transfer coefficient for caproic acid (2.07 μm s^{-1}) as opposed to other fatty acids (acetic, propionic, butyric and valeric having mass transfer coefficients of 0.56, 0.71, 0.97 and 1.21 μm s^{-1}, respectively) using a cross-flow membrane contactor with a PTFE membrane. The mass transfer coefficients reported by Aydin et al. (2018) were also higher in magnitude, ranging between 0.61–2.3, 1.16–3.3, 2.7–7.5, 4.4–16.3 and 5.8–19.7 μm s^{-1} for acetic, propionic, butyric, valeric and caproic acid, respectively. This is due to the use of porous membranes along with NaOH as extractant which creates a stronger driving force for VFA transfer. The mass transfer coefficient strongly depends on the hydrodynamics of the system and can therefore be varied and optimised. In the present system, the movement of VFAs through the silicone membrane is through absorption, diffusion, and desorption into the extractant, which is a slow process (Outram and Zhang, 2018). Further research on the mass transfer resistance is needed to elucidate which of these components is limiting the transfer. However, reducing the thickness or increasing the flow velocity could further improve the mass transfer coefficient of the silicone membrane contactor system studied, though negatively affecting the selectivity towards longer chain acids (Outram and Zhang, 2018).

pH and electrical conductivity were monitored for the feed and draw solution, which in this experiment was an indicator of the VFA migration. Fig. S1 and S2 shows the variations in pH and conduc-

Table 2
Flux of VFAs across a silicone membrane for different feed composition and temperatures.

	Flux ($g\ m^{-2}\ h^{-1}$)											
VFAs	Synthetic VFA solution						Cheese whey fermentate					
	pH 3			pH 5			pH 3			pH 5		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Acetic acid	0.04 ± 0.00	0.04 ± 0.00	0.03 ± 0.02	0.01 ± 0.00	0.02 ± 0.02	0.01 ± 0.01	0.04 ± 0.02	0.06 ± 0.04	0.09 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
Propionic acid	0.16 ± 0.01	0.16 ± 0.02	0.10 ± 0.04	0.05 ± 0.00	0.06 ± 0.05	0.04 ± 0.00	–	–	–	–	–	–
Butyric acid	0.40 ± 0.03	0.38 ± 0.03	0.20 ± 0.08	0.10 ± 0.00	0.09 ± 0.00	0.05 ± 0.00	0.25 ± 0.08	0.28 ± 0.02	0.25 ± 0.02	0.02 ± 0.00	0.07 ± 0.00	0.09 ± 0.00
Valeric acid	0.70 ± 0.07	0.47 ± 0.07	0.23 ± 0.10	0.32 ± 0.03	0.20 ± 0.00	0.12 ± 0.16	–	–	–	–	–	–
Caproic acid	0.52 ± 0.06	0.22 ± 0.06	0.09 ± 0.04	0.30 ± 0.06	0.20 ± 0.02	0.10 ± 0.02	–	–	–	–	–	–

Table 3
Mass transfer coefficient values of VFAs through a silicone membrane with synthetic and cheese whey fermentate as the feed.

	Mass transfer coefficient ($\mu m\ s^{-1}$)											
VFAs	Synthetic fermentate						Cheese whey fermentate					
	pH 3			pH 5			pH 3			pH 5		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Acetic acid	0.12 ± 0.02	0.06 ± 0.02	0.10 ± 0.00	0.02 ± 0.00	0.04 ± 0.00	0.06 ± 0.04	0.06 ± 0.04	0.03 ± 0.01	0.09 ± 0.04	0.12 ± 0.09	0.12 ± 0.08	0.14 ± 0.01
Propionic acid	0.15 ± 0.01	0.08 ± 0.03	0.13 ± 0.00	0.05 ± 0.03	0.04 ± 0.01	0.08 ± 0.07	–	–	–	–	–	–
Butyric acid	0.17 ± 0.01	0.13 ± 0.06	0.16 ± 0.00	0.07 ± 0.02	0.06 ± 0.01	0.18 ± 0.06	0.14 ± 0.02	0.13 ± 0.02	0.08 ± 0.01	0.17 ± 0.03	0.07 ± 0.01	0.20 ± 0.04
Valeric acid	0.23 ± 0.02	0.33 ± 0.20	0.30 ± 0.07	0.11 ± 0.05	0.16 ± 0.08	0.16 ± 0.07	–	–	–	–	–	–
Caproic acid	0.49 ± 0.17	0.92 ± 0.76	0.73 ± 0.49	0.35 ± 0.23	0.46 ± 0.35	0.55 ± 0.32	–	–	–	–	–	–

Acids were not present in cheese whey fermentate.

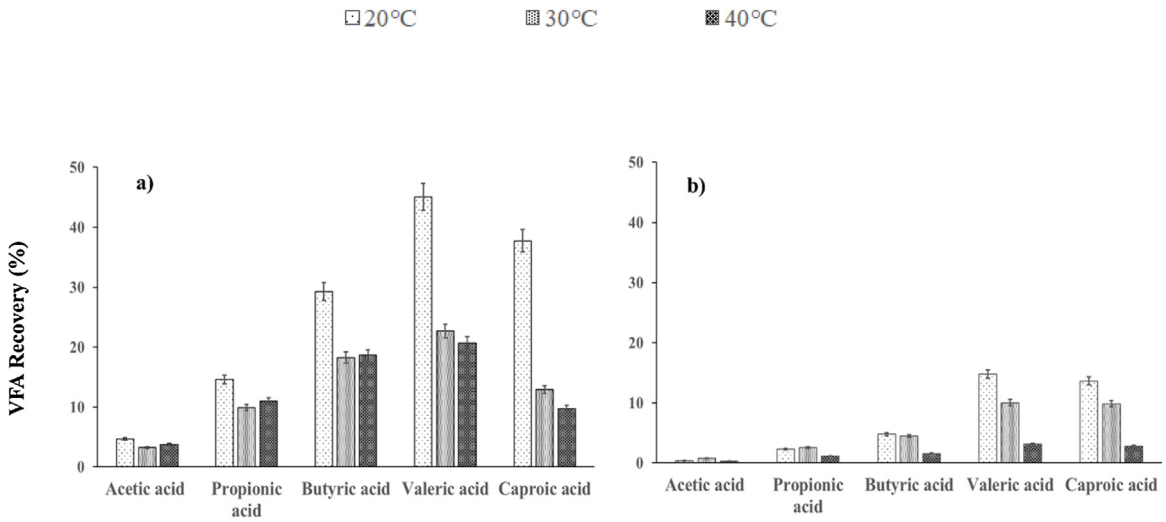

Fig. 3. VFA recovery through the silicone membrane from synthetic feed at **a)** pH 3 and **b)** pH 5. *It should be noted that a maximum VFA recovery of* 50 % *is achievable because the extraction is a concentration gradient driven process.*

tivity of the feed and draw solutions at the different experimental conditions of VFA and alcohol extraction. The draw solution showed a sharp decrease during the initial 2 h (for all conditions), indicating a rapid diffusion of VFA or alcohol across the silicone membrane (Fig. S1). The conductivity profiles of the feed solutions (Fig. S2) decreased with time, while that of the draw solution increased, further confirming the VFA or alcohol migration.

3.2. VFA recovery from cheese whey fermentate

Fig. 4 shows the VFA concentration profiles of draw solutions, extracted from the cheese whey fermentate. For all experimental conditions tested, butyric acid concentrations in the draw solution increased faster than the acetic acid concentration (Fig. 4). A substantially higher VFA extraction was achieved at pH 3 than 5, and at both pH values, a higher temperature favoured VFA extraction. This effect of temperature on VFA extraction through the membrane can be understood through the relationship between penetration and temperature established by the Van't Hoff–Arrhenius relationship:

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) \quad (8)$$

where P is the penetration, P_o is a pre-exponential factor, R is the molar gas constant, T is the temperature and E_p is the apparent activation energy of permeation required for VFA into the membrane and the opening between the polymeric chains of membrane to allow the VFA to diffuse (Han et al., 2001).

Eq. 8 shows that for a given membrane and a penetrant (VFA), penetration (P) increases with temperature resulting in a higher extraction efficiency (Han et al., 2001). Although the temperature should improve the VFA extraction, for the synthetic solution (see section 3.1), the higher net vapour pressure in the draw side resulted in lower recovery for longer carbon chain acids with increased temperature (Table S1).

The cheese whey fermentate contained different ions (NO_2^-, NO_3^- and SO_4^{2-}) with predominance of Ca^{2+}, K^+, Na^+, PO_4^{3-}, Cl^- and NH_4^+ of 210, 2297, 694, 124, 270 and 462 mg L^{-1}, respectively. The presence of proteins in cheese whey fermentate was measured to be in the range of 0.15–0.65 g L^{-1}. The high conductivity of around 10 mS cm^{-1} confirmed the presence of these ions in the cheese whey fermentate, which further increased to 16 mS cm^{-1} at pH 3 upon addition with H_2SO_4.

The maximum recovery efficiency for acetic and butyric acid after 70 h operation at 40 °C amounted to, respectively, 7 and 21.5 % for pH 3, and 3.5 and 7% for pH 5 (Fig. 5). The lower removal efficiency observed compared to the synthetic VFA solution can be attributed to the presence of the solids and ions present in the cheese whey fermentate (Aydin et al., 2018). For example, the presence of calcium and phosphate ions in the fermentate can result in their precipitation when the $Ca_3(PO_4)_2$ solubility product is exceeded, resulting in a decline of the permeation flux and selectivity of the membrane (Chandrapala et al., 2015). Furthermore, the ions can result in concentration polarisation, forming a boundary layer which can induce in precipitation of salts and thus impede the VFA transfer across the membrane (Bellman, 2012). The solids or other suspended particles, including proteins, present in the cheese whey fermentate may have formed a layer on the silicone membranes, limiting the transfer of VFAs, even though fouling was not visually observed. Similar recovery efficiencies of 3.3 and 7.2 % for, respectively, acetic, and butyric acid have been reported from organic waste leachate at pH 6.6 using a counter-current flow membrane extraction system with NaOH as extractant (Yesil et al., 2014). In contrast, acetic acid was recovered with a greater than 45 % efficiency from three different organic wastes (fermentation broth, landfill leachate and chicken manure digestate) (Aydin et al., 2018) using a TOA-filled PTFE porous membrane in a contactor. Plácido and Zhang (2018) looked at VFA recovery from slaughterhouse blood anaerobic fermentate using a porous hydrophobic hollow membrane system with Octanol/TOA as extract solution. Unacidified slaughterhouse broth (where pH was unmodified) showed a VFA recovery of < 5%, confirming the necessity of low pH for VFA recovery (Plácido and Zhang, 2018). Upon acidification (exact value not reported) of the slaughterhouse anaerobic fermentate, the overall VFA recovery increased to 80 %, with valeric, butyric, propionic and acetic acid showing 100, 94, 80 and 42 % recovery, respectively.

Table 2 shows the VFAs flux through the silicone membrane at different pH and temperature. Butyric acid had a higher flux as compared to acetic acid at all conditions tested. At pH 3, the maximum flux obtained for both butyric and acetic acid was 0.28 (± 0.02) g m^{-2} h^{-1} (at 30 °C) and 0.09 (± 0.00) g m^{-2} h^{-1} (at 40 °C), respectively. Yesil et al. (2014) conducted experiments for VFA separation from organic waste leachate using a PTFE membrane contactor. The leachate solution had a pH of 6.6 at 30 °C and contained fatty acids including acetic (14,277 mg L^{-1}), propionic (846 mg L^{-1}), butyric (3926 mg L^{-1}), valeric (428 mg L^{-1}) and caproic (3223 mg L^{-1}) acid. The maximum flux was obtained for acetic (0.240 g m^{-2} h^{-1}), followed by butyric (0.150 g m^{-2} h^{-1}) and caproic (0.140 g m^{-2}

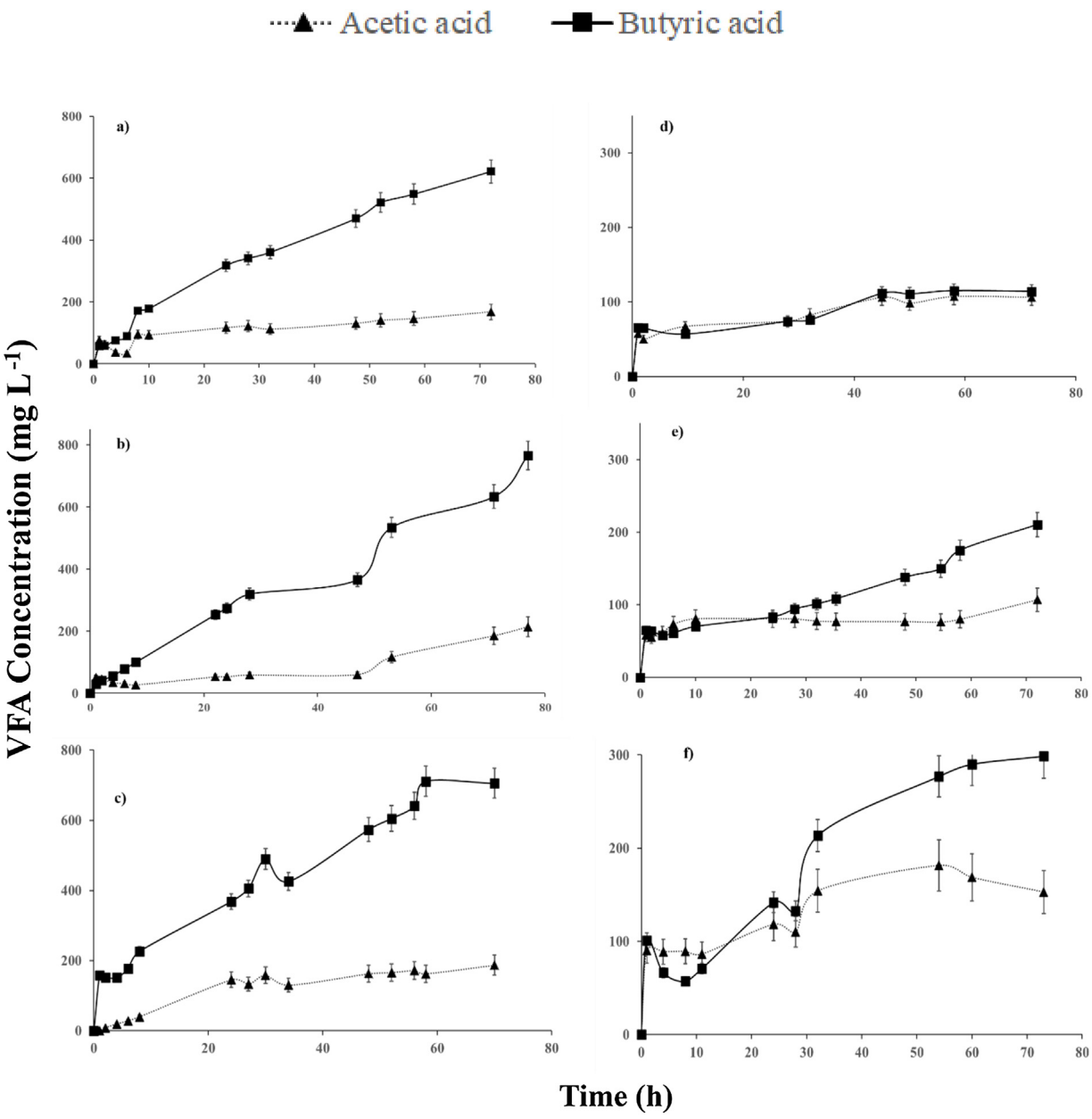

Fig. 4. Draw solution VFA concentrations with cheese whey fermentate as feed at pH 3 **a)** 20 °C, **b)** 30 °C, **c)** 40 °C and pH5 **d)** 20 °C, **e)** 30 °C and **f)** 40 °C *(Note the different y-axis scale for different* **pH** *conditions).*

h^{-1}) acid, suggesting higher VFA concentrations favoured a greater flux, which was facilitated by the concentration gradient across the porous PTFE membranes. In the present study, the average butyric acid concentration (4.6 g L^{-1}) was slightly higher than that of acetic acid (4.0 g L^{-1}), and the longer chain acids migrated faster through the silicone membrane.

The mass transfer coefficient of butyric acid was comparatively higher than acetic acid for most conditions investigated (Table 3). Acetic and butyric acid showed maximum mass transfer coefficients of 0.14 (± 0.01) and 0.20 (± 0.04) μm s^{-1} at pH 5. Overall, the coefficients obtained from cheese whey fermentate are similar to those obtained for the synthetic fatty acid solution for the majority of the conditions tested, confirming the net driving force for separation is the free acid concentration. The mass transfer coefficient of butyric acid from a fish fermentation broth (pH 7) using a silicone membrane extraction system was reported to be 0.157 μm s^{-1} (Outram and Zhang, 2018). Yesil et al. (2014) reported a slightly higher mass transfer coefficient of 0.022 μm s^{-1} for butyric acid extracted from organic leachate of a leach bed reactor at pH 6.6 using a hydrophobic polytetrafluoroethylene (PTFE) membrane with NaOH as extractant. Plácido and Zhang (2018) reported a butyric acid mass transfer coefficient of 0.291 μm s^{-1} obtained from slaughterhouse anaerobic fermentate under acidified conditions with a porous polypropylene membrane and TOA+1-Octanol as extractant. Table 6 compares VFA extraction using different membrane contactors reported in the literature.

3.3. Alcohol recovery from synthetic alcohol solution

Depending on the operation pH or prevailing conditions in the fermenter, the cheese whey fermentation pathway can shift to solventogenesis, producing alcohols rather than VFAs (Calero et al., 2018). Therefore, preliminary tests of alcohol extraction across the silicone membrane were performed. All the alcohols tested moved from the feed to the draw solution across the silicone membrane, with butanol showing the maximum concentration at the end of

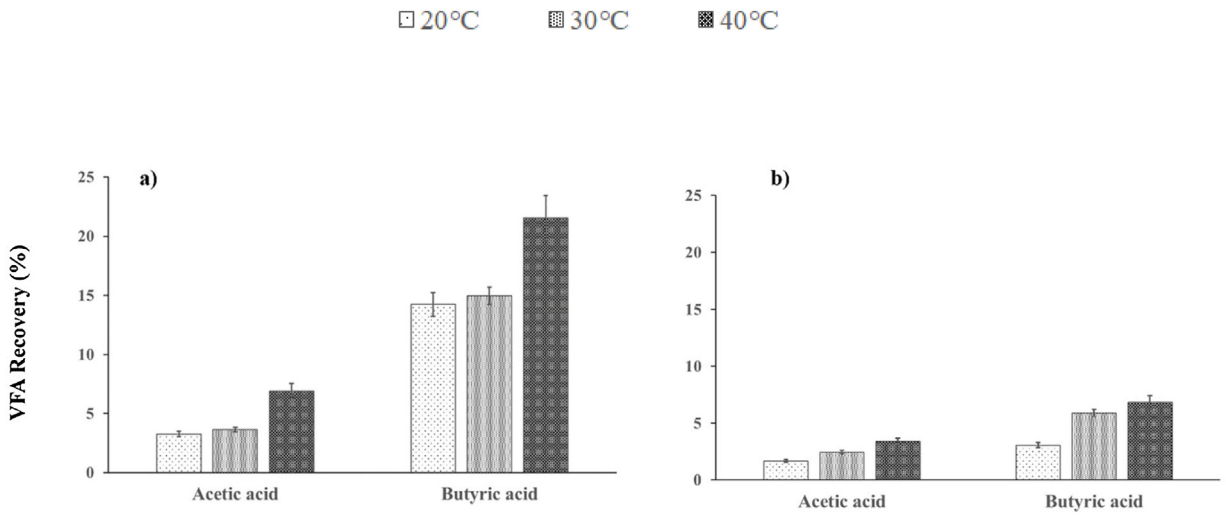

Fig. 5. VFA recovery by the silicone membrane from cheese whey fermentate at **a)** pH 3 and **b)** pH 5. *It should be noted that a maximum VFA recovery of* 50 % *is achievable because the extraction is a concentration gradient driven process.*

operation, followed by propanol and ethanol (Fig. 6). Similarly, to the observation noted with VFAs, this can be ascribed to the higher hydrophobicity of longer chain alcohols that have more affinity for the silicone membrane.

The alcohol recovery increased with temperature (Fig. 6), with an exception for butanol due to the decrease in its solubility in water at 40 °C (Stephenson and Stuart, 1986). The maximum recovery of 42 % was observed for butanol at 30 °C, whereas the highest propanol and ethanol recoveries of 32 and 19 %, respectively, were achieved at 40 °C (Fig. 7). Butanol had a higher flux as compared to propanol and ethanol (Table 4). Higher temperature improved the flux of all alcohols resulting in a maximum flux of 0.25 (± 0.01), 0.33 (± 0.03) and 0.42 (±0.07) g m^{-2} h^{-1} for ethanol, propanol and butanol, respectively, at 40 °C. Thongsukmak and Sirkar (2007) reported butanol and ethanol separation from the feed solution containing 1.5 wt% butanol, 0.8 wt% acetone and 0.5 wt% ethanol using pervaporation with TOA immobilised on hollow fibre membranes. Butanol and ethanol had a flux of 11 and 1.2 g m^{-2} h^{-1}, respectively at 54 °C. The lower flux values reported in the present work are due to the inherent nature of the process (non-pressure driven) where the concentration gradient is the driving force for alcohol separation. However, the use of a non-porous silicone membrane contactor enables selective recovery of longer chain alcohols and is cheaper than pervaporation processes.

The overall mass transfer coefficients of alcohols followed the order butanol > propanol > ethanol for all temperatures investigated (Table 4). As observed for VFAs, the increase in temperature did not substantially affect the alcohol mass transfer coefficients. Butanol had the highest mass transfer coefficient of 0.16 (± 0.00) μm s^{-1} at 40 °C, whereas propanol and ethanol had the highest coefficient of 0.13 (±0.00) and 0.12 (± 0.03) μm s^{-1}, respectively, at 20 °C. Li et al. (2011) investigated *in-situ* butanol separation from acetone-butanol-ethanol fermentation broth using PDMS composite membranes through a pervaporation process. The overall mass transfer coefficients of butanol during the separation from a binary (butanol/water), a model and a fermentation culture solution were 0.41, 0.35, and 0.3 μm s^{-1}, respectively (Li et al., 2011).

3.4. Membrane separation factor

The separation factor is defined as the ability of a membrane to separate a target compound and is a crucial parameter when selecting membranes (Luis, 2018). The separation factor calculated in the

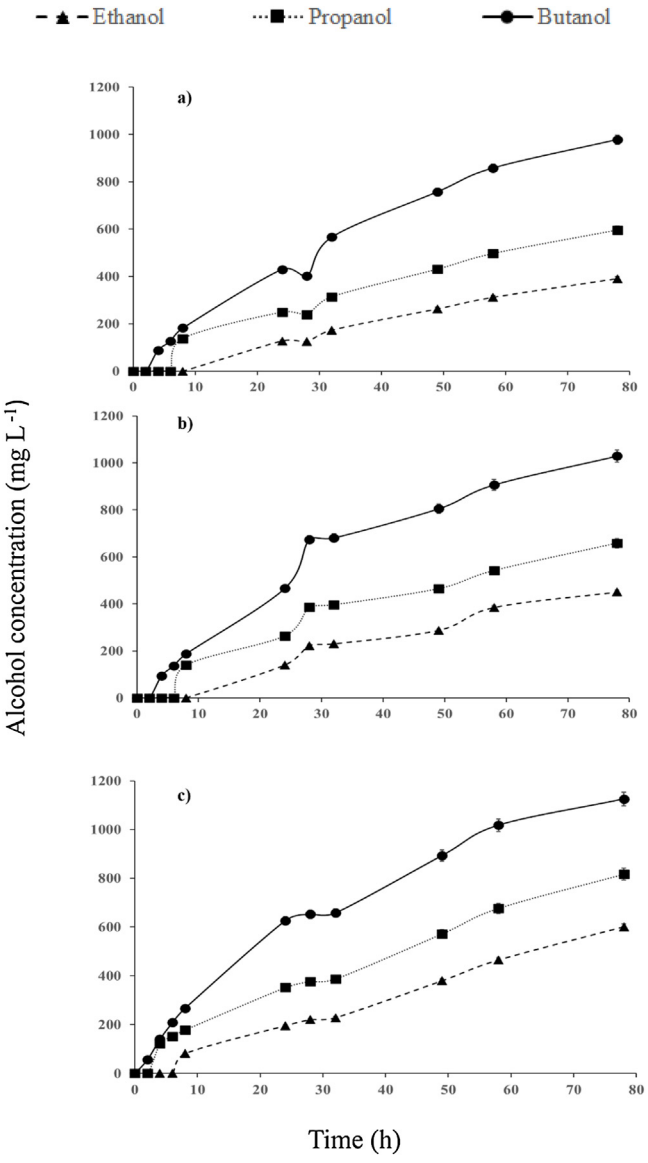

Fig. 6. Draw solution concentration of alcohols extracted using a silicone membrane contactor from a synthetic alcohol mixture (pH 2) at **a)** 20 °C, **b)** 30 °C and **c)** 40 °C.

Table 4
Flux and mass transfer coefficients of alcohols across a silicone membrane at pH 2 for different temperatures.

Alcohol	Flux (g m^{-2} h^{-1})			Mass transfer coefficient (μm s^{-1})		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Ethanol	0.16 ± 0.00	0.18 ± 0.01	0.25 ± 0.01	0.12 ± 0.03	0.08 ± 0.02	0.10 ± 0.01
Propanol	0.24 ± 0.012	0.27 ± 0.02	0.33 ± 0.03	0.13 ± 0.00	0.10 ± 0.00	0.12 ± 0.00
Butanol	0.40 ± 0.034	0.40 ± 0.05	0.42 ± 0.07	0.15 ± 0.00	0.14 ± 0.01	0.16 ± 0.00

Table 5
Separation factor of VFAs and alcohols from synthetic solutions and cheese whey fermentate.

Synthetic VFA solution						
VFA	pH 3			pH 5		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Acetic acid	0.17 ± 0.01	0.25 ± 0.01	0.28 ± 0.01	0.06 ± 0.00	0.13 ± 0.00	0.16 ± 0.00
Propionic acid	0.53 ± 0.02	0.74 ± 0.01	0.83 ± 0.01	0.38 ± 0.00	0.47 ± 0.00	0.62 ± 0.00
Butyric acid	1.06 ± 0.00	1.34 ± 0.00	1.41 ± 0.00	0.70 ± 0.00	0.80 ± 0.00	0.85 ± 0.00
Valeric acid	1.63 ± 0.02	1.64 ± 0.02	1.56 ± 0.02	1.55 ± 0.00	1.64 ± 0.00	1.71 ± 0.00
Caproic acid	1.37 ± 0.00	0.94 ± 0.00	0.74 ± 0.01	1.78 ± 0.01	1.87 ± 0.01	1.58 ± 0.00
Cheese whey fermentate						
VFA	pH 3			pH 5		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Acetic acid	0.39 ± 0.01	0.40 ± 0.01	0.38 ± 0.01	0.77 ± 0.01	0.65 ± 0.01	0.68 ±- 0.01
Butyric acid	1.68 ± 0.01	1.68 ± 0.01	1.68 ± 0.01	1.32 ± 0.02	1.33 ± 0.02	1.28 ± 0.02
Synthetic Alcohol solution						
Alcohol		pH 2				
	20 °C	30 °C	40 °C			
Ethanol	0.61 ± 0.00	0.61 ± 0.00	0.65 ± 0.00			
Propanol	0.95 ± 0.00	0.89 ± 0.00	1.13 ± 0.00			
Butanol	1.41 ± 0.00	1.66 ± 0.00	1.34 ± 0.00			

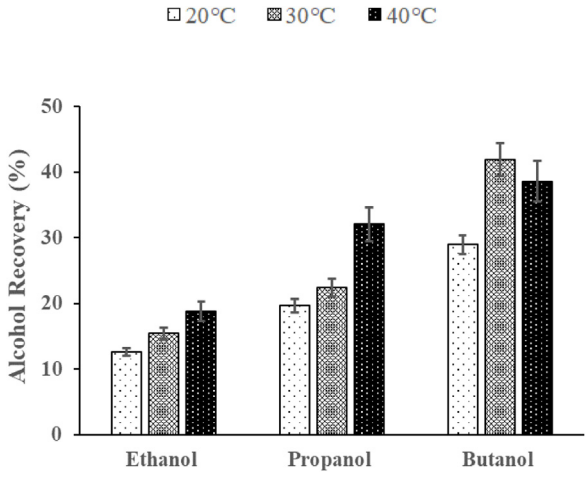

Fig. 7. Alcohol recovery through a silicone membrane from a synthetic solution at pH 2. *It should be noted that a maximum alcohol recovery of 50 % is achievable because the extraction is a concentration gradient driven process.*

present work shows the selectivity of VFA/alcohol over water. The non-porous silicone membrane used in this study does not support water transfer and the separation of fatty acids depends solely on the concentration gradient that acts as the driving force. Valeric and caproic acid had a higher separation factor from the synthetic solution as compared to other fatty acids at both pH 3 and 5 (Tables 5,6). As the separation factors were calculated based on the final concentrations in the draw solution, caproic acid, due to its low solubility, showed a lower separation factor compared to valeric and butyric acid at pH 3 and 30 as well as 40 °C. However, the separation factor for caproic acid increased at pH 5, which is due to the lower separation of acetic, butyric and propionic acid at pH 5 as opposed to pH 3 (Table 5). The separation factor increased for acetic, propionic and butyric acid with increase in temperature at both pH values investigated. High separation factor values (>1) indicate a better selectivity, suggesting the suitability of the membrane. For separation of volatile organic carbons (VOCs), such as acetic acid, ethylene glycol and dimethyl acetamide (DMAC) from water, the separation factor typically ranges from 1–5 for silicone membranes (Luis, 2018). An increase in separation factor beyond 5 provides very little additional benefits for VFA separation (Baker, 2012). When cheese whey fermentate was used as the feed, butyric acid had a higher separation than acetic acid at both pH 3 and 5 (Table 5). The increase in temperature had a negligible effect on the separation factor of both acids, indicating butyric acid had a better selectivity over acetic acid regardless of the temperature.

The effect of temperature on the VFAs separation factor using PTFE and PTFE + TOA membranes was investigated using synthetic solutions (Aydin et al., 2018). The carboxylic acid separation factor increased with the alkyl chain length increased at all temperatures assessed (Aydin et al., 2018). The separation factor was higher for the PTFE + TOA membrane at 30 °C, being 0.74, 7.05, 171.2 for acetic, propionic, butyric, respectively and >1250 for both valeric and caproic acid (Aydin et al., 2018). The present study found a similar selectivity order as well, showing higher selectivity for longer alkyl chain lengths from both the synthetic solution and cheese whey fermentate (Table 5). Similarly, the separation factor of alcohols in the present work indicated that butanol had the highest separation factor followed by propanol and ethanol for all temperatures investigated (Table 5). The temperature did not show any effect on alcohol selectivity (Table 5), signifying that a longer carbon chain had a better extraction selectivity regardless the extractant temperature. Typically for alcohols, the separation factor ranges between 5–20 for silicone membranes (Li et al., 2011).

3.5. Practical implication

Although the results indicate the feasibility of extracting VFAs and alcohols from fermentate without the requirement of chemical extractants and with little energy (non-pressure driven process), only a maximum recovery of 50 % can be obtained with the present technology (where using solely the concentration gradient as the driving force for extraction). Integration of the present system for

Table 6
Comparative studies on VFA extraction using membrane contactors.

Stock solution	Membrane	Operating conditions		Parameter					Reference
		pH, Time and Temperature	Extractant	VFA concentration (g L^{-1})	Mass transfer coefficient($\mu m\ s^{-1}$)	Flux(g m^{-2} h^{-1})	Selectivity /separation factor	Recovery (%)	
Organic municipal leachate	PTFE	6.6, 15 d and 30 °C	1 N NaOH	AA- 14.27, PA- 0.84, BA- 3.9, VA- 0.42, and CA- 3.2	AA- 0.003, PA- 0.004, BA- 0.021, VA- 0.020, and CA- 0.021	AA- 0.240, PA- 0.008, BA- 0.150, VA- 0.023, and CA- 0.140	AA- 0.03, PA- 0.02, BA- 0.06, VA- 0.08, and CA- 0.11	AA- 3.3, PA- 1.8, BA- 7.2, VA- 10.8, and CA- 8.5	21
Synthetic solution	PTFE	3, 30 h and 30 °C	1 N NaOH	AA- 6, PA- 6, BA- 2, VA- 2, and CA- 1	AA- 0.56, PA- 0.71, BA- 0.97, VA- 1.21, and CA- 2.07	AA- 13.12, PA- 14.21, BA- 5.25, VA- 5.27, and CA- 2.13	AA- 0.9, PA- 1.10, BA- 1.70, VA- 2.20, and CA- 5.60	Not reported	21
Synthetic solution	PTFE	3, 24 h and 25 °C	0.5 N NaOH	AA- 6, PA- 6, BA- 5.5, and VA- 1,	AA- 0.7, PA- 0.91, BA- 0.947, and VA- 1.64	AA- 11.65, PA- 13.16, BA- 12.015.25, and VA- 2.99	AA- 1.20, PA- 1.75, BA- 1.79, and VA- 4.42	Not reported	23
Leachate of fermented organic wastes	PTFE	3.03, 24 h and 25 °C	0.5 N NaOH	AA- 6, PA- 6, BA- 2, VA- 2, and CA- 1	AA- 0.64, PA- 0.75, BA- 1.4, VA- 0.64, and CA- 0.86	AA- 12.93, PA- 6.77, BA- 12.94, VA- 3.57, and CA- 2.03	AA- 1.23, PA- 0.87, BA- 0.93, VA- 1.61, and CA- 1.37	Not reported	23
Synthetic solution	PTFE	2.9, 7 h and 38 °C	0.5 N NaOH	AA- 1.25, PA- 1.25, BA- 1.25, VA- 1.25, and CA- 1.25	AA- 2.33, PA- 3.33, BA- 3.88, VA- 4.44, and CA- 5.83	~ *AA- 8, PA- 11, BA- 12.5, VA- 13, and CA- 14.5	~* AA- 3.1, PA- 6.51, BA- 6.51, VA- 15.05, and CA- 21.5	AA- 54, PA- 64, BA- 69, VA- 72, and CA- 74	20
Synthetic solution	PTFE	2.9, 7 h and 38 °C	0.5 N NaOH	AA- 1.25, PA- 1.25, BA- 1.25, VA- 1.25, and CA- 1.25	AA- 0.61, PA- 2.55, BA- 7.5, VA- 16.4, and CA- 19.7	~ *AA- 3, PA- 9, BA- 17.5, VA- 23, and CA- 24	~* AA- 0.75, PA- 4, BA- 60, VA- 1300, and CA- 1350	AA- 34, PA- 85, BA- 98, VA- 99, and CA- 99	20
Landfill leachate	PTFE-TOA	4, 7 h and 38 °C	0.5 N NaOH	AA- 4.3, PA- 0.48, BA- 7.1, VA- 0.14, and CA- 0.756	Not reported	Not reported	Not reported	AA- >45, PA- >86, BA- >86, VA- >86, and CA- >86	20
Chicken manure digestate	PTFE-TOA	4, 7 h and 38 °C	0.5 N NaOH	AA- 2.66, PA- 1.98, VA- 0.189, and CA- 4.53	Not reported	Not reported	Not reported	*AA- >45, PA- 78, VA- 30, and CA- 8	20
Fermentation broth	PTFE-TOA	4, 7 h and 38 °C	0.5 N NaOH	AA- 4.2, PA- 1.0, BA- 7.8, VA- 0.13, and CA- 0.89	Not reported	Not reported	Not reported	AA- >45, PA- >95, BA- >95, VA- >95, and CA- >95	20
Slaughterhouse blood	Polypropylene	Acidified, and 6 h	TOA + 1 -Octanol	Not reported	AA- 0.058, PA- 0.170, BA- 0.291, VA- 0.00, and CA- 0.145	Not reported	Not reported	AA- 42, PA- 80, BA- 94, and VA-100	34
Slaughterhouse blood	Polypropylene	Un-acidified, and 2 h	TOA + 1 -Octanol	Not reported	AA- 0.099, PA- 0.121, BA- 0.091, VA- 0.027, and CA- 0.091	Not reported	Not reported	Total VFA recovery < 5	34
Fish fermentate	Silicone membrane	3, 200 h and 25 °C	Water	**AA- 11.4, PA- 3.5, BA- 12.8, VA- 0.4, and CA- 0.3	AA- 0.0, PA- 0.114, BA- 0.157, VA- 0.209, and CA- 0.144	Not reported	Not reported	Not reported	22
Fish fermentate	Silicone membrane	6.6, 200 h and 25 °C	Water	**AA- 11.8, PA- 3.6, BA- 14, VA- 0.5, and CA- 0.5	AA- 0.00, PA- 0.00, BA- 0.00, VA- 0.00, and CA- 0.00	Not reported	Not reported	Not reported	22
Synthetic solution	Silicone membrane	2.5, 200 h and 25 °C	Water	AA- 6, PA- 6, BA- 2, VA- 2, and CA- 1	AA- 0.0017, PA- 0.0075, BA- 0.016, VA- 0.053, and CA- 0.199	Not reported	Not reported	Not reported	22
Synthetic solution	Silicone membrane	3&5, 70 h, 20, 30 & 40 °C	Water	AA- 5, PA- 5, BA- 5, VA- 5, and CA- 5	Refer Table 3	Refer Table 2	Refer Table 5	Refer Fig. 3	*This study*
Cheese whey fermentate	Silicone membrane	3&5, 70 h, 20, 30 & 40 °C	Water	AA- 4, and BA- 4.6	Refer Table 3	Refer Table 2	Refer Table 5	Refer Fig. 5	*This study*

Note: D- days; h- hours; AA- Acetic acid, PA- Propionic acid, BA- Butyric acid, VA- Valeric acid and CA- Caproic acid; *Approximate values obtained from bar graphs or ratios in the manuscript; ** Averaged from two fish fermentates used in the study.

concurrent hydrogen production through fermentation and butyric acid extraction from fermentate demonstrated good separation of butyric acid with high purity (over 90 % on carbon content basis) without affecting the hydrogen production rates (Dessì et al., 2020). However, in view of achieving a sustainable extraction process, further research is still required to advance the technology readiness level of the silicone membrane contactor. Coupling the contactor with a membrane distillation unit can separate the individual VFAs from the mixture at different temperatures with the potential to obtain pure VFAs while maintaining the concentration gradient for extraction (Aktij et al., 2020). The selectivity of membrane for VFAs/alcohols can also be improved through membrane modification (filling extractants in the membrane pores) (Aydin et al., 2018), thereby improving the overall recovery efficiency from the fermentate.

4. Conclusion

VFAs and alcohol recovery from concentrated synthetic solutions and cheese whey fermentate through a silicone membrane contactor using water as the extractant was demonstrated. A maximum of 45 % and 41.5 % recovery of valeric and caproic acid, respectively, as well as 42 % recovery of butanol, was achieved from synthetic solutions. Maximum recovery of caproic acid occurred within 20 h of experimental operation. Acetic and butyric acid extraction from cheese whey fermentate (pH 3; 40 °C) was achieved with 7% and 21.5 % recovery efficiency, respectively, showcasing the feasibility of the silicone membrane contactor for concentration driven VFA separation from cheese whey fermentate. The separation factor values indicate longer carbon chain VFAs/alcohols had better selectivity through silicone membrane. Further research on membrane modification or downstream processing coupling the membrane contactor with better selectivity of VFAs/alcohols can improve the overall recovery efficiencies and evolve into a mature technology for *in-line* separation of VFAs/alcohols from real fermentate.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.psep.2020.09.052.

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