Volatile fatty acids concentration in real wastewater by forward osmosis

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A B S T R A C T

Forward osmosis (FO) was studied as a concentration step for volatile fatty acids (VFA, especially acetic acid) to optimise downstream microbial desalination cell (MDC). First, it was demonstrated that water concentration factor (WCF) of wastewater (WW) above 10 (15–30) is achievable with seawater or brine as draw solution and similar flow for feed and draw solution. It was also observed that VFA rejection by FO membrane is highly connected to pH. At pH = 7.5 rejection rates above 80% are achievable working with domestic WW and therefore concentration of VFA by FO process is realistic. Nevertheless, concentration of VFA present in pre-treated real domestic WW proved to be more challenging with regards to fouling /biofilm formation which favours the biodegradation of VFA. Thanks to fouling mitigation (WW pre-filtration with microfiltration membrane and interbatch osmotic backwashing) and biodegradation strategies implemented (by applying N2 sparging and avoiding air contact with the WW), VFA concentration (and especially acetic acid) from 60–80 up to 300–400 mg L\textsuperscript{−1} is possible. Maintaining high permeation flux, high VFA recovery and concentration factor of VFA during 20 batches of operation was achieved, being more difficult the stable operation of the FO concentration process at high WCF and VFA concentration.

1. Introduction

In the overall growing context of water scarcity, alternative methods to safely produce water at the lowest costs from seawater desalination or wastewater (WW) reuse are highly studied \cite{1–4}. Moreover, integrating WW treatment and desalination in one plant can also result in potential economic benefits by synergistically lowering water intake costs and optimising energy efficiency of water treatment \cite{5,6}. In that context, salinity gradient technologies such as forward osmosis (FO) have been studied to take advantage of the osmotic difference of both streams and proved to be beneficial both from the energetic side but also to produce high quality water and to lower operational costs \cite{7–9}. Similar concepts of salinity gradient based processes were applied to the co-location of desalination and WW treatment streams using pressure retarded osmosis (PRO) or reverse electro-dialysis (RED) towards energy and water harvesting \cite{6,10,11}. In the meantime, another innovative process called microbial desalination cell (MDC), has been developed by modifying microbial electrolysis synthesis cell (MEC) to take advantage of the energy content from WW, where electricity is produced thanks to the degradation of organic matter by bioelectrogenic bacteria in the anode chamber \cite{12–14}. The electric current obtained is used to promote ions migration through ion exchange membranes in a self-sustained desalination system. In MDC, in comparison with MEC, a third channel fed with the saline stream is coupled in-between cationic and anionic compartments separated by ionic exchange membranes. During MDC process, ions are removed from seawater and the resulting low salinity effluent can be further polished in a downstream RO system operated at low pressure and energy consumption.

Nowadays, upscaling of MDC is one of the technical challenges that are under evaluation in water desalination. Using MDC as pre-treatment of RO, the EU funded MIDES project aims at producing safe drinking water at energy consumption below 0.5 kWh·m\textsuperscript{−3} \cite{15}, and demonstrate the feasibility of this technology in different demonstration sites after process optimisation, design and development of electrodes and membranes. Another technical barrier of MDC implementation is to provide sufficient biodegradable organic matter from the WW stream to the bacteria growth in the anodic chamber. In order to optimise the availability of easily utilizable organic matter by bioelectrogenic bacteria, WW can be pre-treated in hydrolytic anaerobic bioreactor, where

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the hydrolysis of organic matter takes place to break it down to highly biodegradable volatile fatty acids (VFA), such as acetic acid, to be used as feed in the MDC. However, the VFA concentration achieved depends on the WW source, which is insufficient for an optimal operation of the MDC (> 300 mg/L VFA, acetic acid).

Forward osmosis has proven to be of interest for the treatment of complicated streams [16] and could be adapted to such environment where a saline stream is locally available [17]. Thanks to its low operating pressure and high rejection, FO exhibits low fouling propensity while allowing the production of high water permeate quality and concentration of most other feed components (or contaminants) [18–20]. Potential application in many WW streams such as raw WW with the implementation for example of osmotic membrane bioreactor, concentration of activated sludge, treatment of landfill leachate and concentrate of anaerobic digester or for potable water reuse are envisioned [7,16,19,21–27]. Still, recent works proved that higher fouling rate is expected when operating at increasing flux [28]. Therefore further work is requested regarding fouling and its mitigation especially using real WW streams.

High rejection of organic compounds is commonly accepted with FO membranes and therefore would make it an adapted technology to VFA concentration. However, most studies were dedicated to emerging organic contaminants [29] while only few information is related to VFA recovery and concentration. Among the few studies dedicated to FO and VFA, one demonstrated that sludge pre-concentration (10 times) by FO allowed for 4.4 times more production of VFA during downstream anaerobic digestion but significant amount of COD was lost during aeration [30] and, in that case, FO concentration was upstream VFA production and therefore VFA rejection by FO was not assessed. Another more specific study evaluated VFA rejection by FO membranes [31]; rejection above 90% was achieved but only for pH above 5 (above pKa of dissociation of tested VFA). Whilst the results are promising, a mixed solution of VFA was used and therefore specific rejection of each VFA has not been defined so far.

To act as an efficient process to concentrate VFA in WW for downstream MDC process optimisation, FO should achieve (1) high water concentration factor (WCF), (2) high rejection of VFA and (3) sustainable operation with real WW to avoid fouling and VFA biodegradation. The aim of this study was to assess all those aspects through a step by step methodology. In a first step, FO potential to extract water from WW (WCF) was assessed using different feeds and draw salinities. VFA rejection by FO membrane was then evaluated using synthetic VFA solutions and for different pH. Concentration factor, VFA rejection, fouling propensity as well as fouling mitigation and adapted cleaning procedures were assessed then using real domestic WW. Finally, long term operation test (20 batches) was performed using real domestic WW and applying optimised operating conditions from previous steps.

2. Materials and method

2.1. FO concentration setup

It has been decided to operate the system using similar initial feed and draw volume (flow) as a first option as it is a realistic hypothesis in the context of combining water reuse and desalination and in the specific context of the study. Also, the system was operated in batch mode (i.e. draw dilution with time; not constant draw concentration as in other studies) as it is more representative of the tested application and allows for an estimation of the achievable concentration rate.

Similar setups and operating conditions were used as in our former studies [28,32]. New generation of thin film composite (TFC) commercially available FO membranes obtained from Porifera Inc. (Hayward, CA, USA) was used with active layer facing the feed solution [33]. The filtration cell was provided by Metacrilats Futura, (Banyoles, Spain) following our requested design and featured a membrane surface area of 82 cm² Peristaltic pump Model LabM3 from Baoding Schenchen precision pump (Baoding city, China) with double pump head that could be operated in the range of 100–1000 mL min⁻¹ was used for both feed and draw circulation. 1.2 mm thickness diamond-type polypropylene mesh spacer were used both in feed and draw channels, pump flowrate of 0.3 L min⁻¹ (i.e. cross flow velocity of 0.1 m s⁻¹) for both feed and draw channels operated in co-current flow. Due to the specificity of the concentration and to avoid dead volumes, a 1 L decantation cone was used as feed container (Fig. 1). 1 L of feed and draw solution were prepared and the system was operated in batch until no permeation flux was observed (osmotic equilibrium).

The water flux (Jw) crossing the membrane from the feed to the draw was determined by measuring the increase of mass of the draw solution over time, using a Kern PCB 6000-1 balance (Balingen, Germany). Salt content of the feed solution as a function of time was determined from the feed solution conductivity measured with a Crison conductimeter probe obtained from Hach lange Spain (L’Hospitalet de
Llobregat, Spain) using a NaCl-conductivity calibration curve and was used to calculate reverse salt diffusion (RSD, J_s) [32]. All data were recorded using a Bluetooth based system provided by Instrument works (Waterloo, Australia); the conductivity sensor was connected to a Bluetooth Arduino Controller and the balance to a Bluetooth-RS232 Adaptor. Visualization, acquisition and storage of all data was realised thanks to the Dataworks data app installed on an Apple Ipod (Cupertino, CA, USA).

2.2. Water concentration factor

Given the specific need of this study, dedicated indicators were used with regards to achievable concentration and associated filtration time. The first indicator is the WCF that represents the concentration of the feed solution over time and is calculated using the following equation:

\[ \text{WCF} = \frac{V_0}{V(t)} \]  

(1)

With \( V_0 \) the feed initial volume and \( V(t) \) the feed volume at any moment (t) during the filtration. WCF at the end of the filtration (when osmotic equilibrium was reached) was especially of interest. Also, given the fact that the initial goal of this study was to concentrate VFA to a factor of 5, it is a requirement to concentrate water by a factor of 5, therefore the time to achieve a WCF of 5 (WCF = 5) was also used as a comparative filtration indicator.

The impact of feed and draw solution salinities on permeation flux, achievable WCF and on time to reach WCF = 5 were first assessed using clean feed and draw solutions. Achieved WCF were experimentally obtained when osmotic equilibrium was reached; i.e. no more permeation flux. DI water, tap water, 0.5 g L\(^{-1}\) and 1 g L\(^{-1}\) salinity (0-1500 µS cm\(^{-1}\) conductivity range) were tested as feed solution (with 35 g L\(^{-1}\) SW as draw) and then 5, 20, 35 and 70 g L\(^{-1}\) as draw solution and tap water as feed. All saline solutions were prepared using sea salts (> 99.4% NaCl) provided by Vicens i Batllori S.L. (Banyoles, Spain).

2.3. Wastewater

All filtration tests with WW were carried out using real domestic WW pre-treated in an hydrolytic anaerobic reactor working in a domestic WW treatment plant operated by FCC Aqualia in Spain. These samples were received and tested through the duration of the study and will be named as (real) WW from now on. On the received samples, a pre-treatment with microfiltration was also tested; Microfiltration was achieved using submerged plates obtained from Kubota (MF cartridges 203). All samples were stored in a fridge after reception and until further use for FO filtration.

2.4. Fouling tests

Draw solution of 70 g L\(^{-1}\) synthetic seawater, mimicking seawater brine, was used following recommendations of concentration tests and given that such stream is available in seawater RO desalination plant.

Fouling behaviour was assessed following a methodology described in former study by operating the system for 4 consecutive batches [28,34]. Each time, 1 L of feed and draw solution were prepared and the system was operated until no permeation flux was observed (osmotic equilibrium). Then new feed and draw solution were prepared. Longer filtration time and initial flux decrease over batches attest for potential fouling behaviour. In addition, cleaning procedure was evaluated; it consisted in osmotic backwashing [34,35] (DI water as draw, 35 g L\(^{-1}\) seawater as feed during 1 h, co-current flow, cross flow velocity = 0.1 m s\(^{-1}\)) followed by a flushing of both feed and draw channel at high cross flow velocity (0.3 m s\(^{-1}\)) during 1 min with DI water. Osmotic backwashing was evaluated either as final treatment (after 4 batches) or implemented in between batches (intermediate backwashing). Flushing allows for removal of particles that were dissociated from the membrane during osmotic backwashing as well as cleaning of both channels where salinity was reversed [28]. The efficiency of the cleaning procedure was evaluated by measuring the flux before and after cleaning using clean solutions (i.e., DI water as feed and 70 g L\(^{-1}\) SW as draw) and comparing it with the initial flux of the new membrane before fouling. As alternative to cleaning in place, manual cleaning was also tested and consisted in removing the membrane from the filtration cell and rinsing it with a spray of water and slight scrub by hand wearing laboratory gloves.

2.5. VFA analysis

VFA (and especially acetic acid) concentration is the objective of the FO pre-concentration step of this study. Typically, it is expected to increase the VFA concentration of the treated domestic WW from 60 to 80 to > 300 mg L\(^{-1}\).

For all tests, samples were first filtered at 0.2 µm; then 85 µL of crotonic acid (standard) and 100 µL phosphoric acid (stabilisation) were added to 1.5 mL of filtered sample and stored in the fridge. VFA analyses were performed by the analytical service of the university of Girona (STR) using an Agilent 7890A (Agilent Technologies, US) gas chromatograph (GC) equipped with a DB-FFAP column and a flame ionisation detector (FID). The concentration of VFA in the liquid phase is given in mg L\(^{-1}\). Even if no VFA biodegradation has been noticed in the prepared samples even after several weeks, all samples were typically analysed within 3 days.

At first, concentration tests were run using DI water spiked with 80 mg L\(^{-1}\) of 5 selected VFA (acetic acid, propionic acid, butyric acid, isobutyric acid and valeric acid) and 35 g L\(^{-1}\) draw solution. Rejection and concentration tests were realised first without pH adjustment (pH = 4) and then after pH adjustment (pH = 7.5, which corresponds to the typical pH range of the real WW). 4 samples were collected through the duration of the rejection/concentration tests; rejection average values and standard deviation are reported. Permeation flux was maintained at 15 ± 2 L m\(^{-2}\) h\(^{-1}\) during the test.

VFA analyses performed in all received WW samples were highly variable and generally lower than expected (Acetic acid concentration from 15 to 95 mg L\(^{-1}\)) possibly as a result of initial concentration variation and/or (different degree of) biodegradation during transport of WW samples from the full scale plant to the lab. Therefore, it has been decided to spike systematically all the samples with a mix of each VFA at a concentration of 80 mg L\(^{-1}\) to allow for normalised operation and to study the behaviour of VFA (not just acetic acid). VFA concentration of all samples was analysed after spiking and before each filtration tests.

In parallel, we observed that VFA were also partly consumed even after spiking in WW and storage in the fridge leading probably also to some bacterial development. VFA (and acetic acids especially) are highly appreciated by microorganisms and therefore a great care has to be put to limit conditions of bacterial growth that can on one side lead to degradation of VFA and on the other side to the development of microorganisms during the storage that can then after consume VFA during the filtration. Thus for further tests with VFA in WW the following procedure has been implemented: (1) MF filtration of WW samples after reception of the samples to remove s before each filtration test solids, (2) sparging with nitrogen in the filtered WW to remove oxygen, (3) storage of the samples in the fridge, (4) spiking with VFA just before filtration tests, (5) coverage of the feed tank to limit contact with air.

VFA rejection (RVFA) has been calculated based on feed concentration and as described in Eq. (2).

\[ R_{\text{VFA}} = \frac{C_{\text{VFA}(f)} WCF(f)}{C_{\text{VFA}(i)}} \]  

(2)

With \( C_{\text{VFA}(f)} \) the VFA concentration and WCF (f) the WCF at the moment of sampling time \( t \), and \( C_{\text{VFA}(i)} \) the initial VFA concentration in the feed
solution. Also, similarly to WCF the VFA concentration factor (VFA CF) was calculated using Eq. (3):

\[
\text{VFA CF} = \frac{C_{\text{VFA(f)}}}{C_{\text{VFA(i)}}}
\]

3.2. Evaluation tests with real domestic WW

3.2.1. Fouling propensity and mitigation strategies

Fouling tests were performed with received pre-treated in a hydrolytic anaerobic reactor domestic WW (1) as is, (2) on MF pre-filtered WW and (3) MF pre-filtered WW and implementation of osmotic backwashing in between each batches as explained in Section 2.6.
Normalised initial flux over batches and after fouling and cleaning procedure are presented in Fig. 4.

Non pre-filtered WW caused a severe membrane fouling during the first batch which led to a reduction of the initial flux by 50% on the 2nd batch (Fig. 4a). Important fouling behaviour was confirmed through the 4 successive fouling batches (Fig. 4a), leading to a severe 80% overall loss of initial flux. Cleaning procedure and flux evaluation with clean solutions allowed to compare flux before and after four batches of operation and confirmed the severe flux decline observed during fouling batches (Fig. 4b) but to a lower extend (only 60% flux loss). This indicates that flux decline during batches with tested WW is not only due to fouling; most likely salts accumulation in the fouling layer also occurs, leading to enhance concentration polarization phenomenon and affecting the actual osmotic pressure driving force \([53,54]\). Also, osmotic backwashing allowed a limited partial recovery of the initial flux. It attests of the high fouling propensity of the tested WW used in this study and that the applied cleaning strategy did not show sufficient efficiency for stable process operation.

Loss of initial flux was limited to 36% after the fourth batch for the WW pre-treated by MF, attesting for the efficiency of MF to mitigate fouling (Fig. 4a). Implementing interbatch backwashing further helped to maintain a high initial flux with a loss below 30% after the fourth batch. Positive impact of fouling mitigation techniques was confirmed during the cleaning evaluation procedure (Fig. 4b). However, maximum flux recovery was limited to about 80% of the initial values in all cases even after manual cleaning (tested only for pre-filtered WW and pre-filtered WW combined with interbatch cleaning). Additional in place cleaning techniques such as chemical cleaning with different agents: i) NaOCl (to remove organic fouling), ii) citric acid (to remove scaling) and, iii) ethanol (in case of membrane drying) were performed but no beneficial effect was observed with neither of those. The membrane appeared slightly coloured but no fouling layer formed on the membrane surface was observed. This fact suggests that this incomplete flux recovery can be caused by some irreversible fouling within the membrane or a modification of the membrane properties. This phenomenon should be further studied as it can affect long term /full scale operation of the process. Also, NaOCl was tested but is not recommended since, as for RO membranes, the polyamide active layer of

Fig. 2. Impact of (a) draw concentration (tap water as feed) and (b) initial feed conductivity (35 g L\(^{-1}\) SW as draw) on initial permeation flux (Jw), achieved WCF and filtration time required to reach WCF = 5.

Fig. 3. (a) Acetic acid concentration as function of WCF and pH in the feed and draw solution and (b) VFA rejection as function of feed pH (pH = 4 and 7.5, DI water as feed, 35 g L\(^{-1}\) SW as draw solution).
Fig. 4. Comparison of initial flux during (a) filtration batches (real WW as feed, 70 g L\(^{-1}\) SW as draw) and (b) recovery with cleaning (DI water as feed, 70 g L\(^{-1}\) SW as draw) for WW, pre-filtered WW and pre-filtered WW combined with interbatch cleaning.

Fig. 5. (a) VFA rejection in WW and DI water and VFA concentration: (b) % recovery of VFA at the end of the batches with WW spiked with VFA, VFA CF in function of WCF during (c) batch 1 and (d) batch 4 spiked samples (real WW as feed, 70 g L\(^{-1}\) SW as draw).
FO membrane is not highly tolerant to chlorine; cleaning in place solutions such as alkaline treatment, chelating agents, surfactants used in RO and tested for osmotic processes will be preferred in the future for organic fouling removal [55–57].

As an alternative to pre-treatments or more intensive cleaning, operating at lower flux has proven to be beneficial for fouling mitigation in FO [28]. In the tested application, achievable WCF and initial flux are both dependent from the available draw concentration and limit the flexibility to operate at lower flux. However, as mentioned earlier and considering large scale operation, counter flow can allow not only to reach higher WCF but also lower (but more constant) flux [43] and consequently will limit fouling issues.

3.2.2. VFA concentration and recovery

In order to standardize the initial VFA concentration in the feed, samples were spiked with a mix of all VFA at a concentration of 80 mg L\(^{-1}\) as in Section 3.1.2 (followed by pH adjustment at pH = 7.5 to balance the acidification that occurred with VFA addition). High rejection of all VFA by FO (around 90% at pH = 7.5) was confirmed for real domestic WW (Fig. 5a) [31]. VFA concentration controlled on the draw solution at the end of the filtration batches remained below the detection limit (< 5 mg L\(^{-1}\)). VFA recovery was calculated as the ratio of the VFA concentration at the beginning and the end of each batch.

Then, VFA were spiked to WW sample and concentration of VFA was followed during the 4 consecutive batches of fouling tests (filtered WW, no intermediate backwashing, Fig. 5). High VFA recovery values were observed during batch 1 for all VFA (from 85% for acetic acid and up to 92% for valeric acid). However, VFA recovery sharply decreased over batches; acetic and propionic acid were no longer found already on the second batch, butyric and valeric acid disappeared fully on the third batch as shown by the poor recovery (Fig. 5b). Only isobutyric acid was found at the end of the concentration step during the four batches but showing also a decrease of recovery over batches. VFA concentration kinetic during filtration was then analysed for batch 1 (clean membrane) and batch 4 to get further insight of concentration process; VFA CF as function of WCF is reported in Fig. 5c&d. In batch 1 with the clean membrane (Fig. 5c), a linear increase of VFA CF with WCF was observed, indicating high rejection and concentration rate. This confirms that VFA concentration by FO is a feasible solution, even with real WW. Totally different behaviour was observed in batch 4 with a membrane partly fouled. Increase of VFA CF was initially observed up to WCF of about 1.5 (i.e. during the 3 first hours of filtration) but then CF of butyric, propionic and acetic decreased, lowering down to 0 when WCF reaches 4.5. Valeric acid followed the same trend but delayed in time (higher WCF). Only isobutyric acid CF kept increasing with time until WCF of 4.5. However, as shown in (Fig. 5b) at the end of the batch 4 when WCF reached 10, isobutyric acid also disappeared.

VFA concentration was controlled in the draw solution but no VFA were found (below detection limit) demonstrating that the loss of VFA in the feed solution was not due to a lack of membrane selectivity. Loss of VFA in the feed can only be explained by biodegradation. The fact that the phenomenon occurred in the batch 4 and not in batch 1 indicates that biodegradation can be connected to the development of biofilm on the membrane (and even in the pipes). Additionally, the fact
that isobutyric acid was still present at WCF = 4.5 (Fig. 5d) but disappeared at the end of batch 4 (Fig. 5b) can be explained by longer residence time. VFA biodegradation was demonstrated in a former study and kinetic proved to be dependent on the substrate content [58]. In line with former studies, acetic acid proved to be the most biodegradable compounds being consumed first [58,59]. Slower degradation of iso-butyric was also observed in several works [58–61]; the slower degradation of isomeric form versus normal form was explained as a consequence of structural differences of components and possibly as an isomerisation from the normal to the isomeric form [60]. Our results are also in line with observation from where n- form butyric, propionic proved to be consumed before isobutyric acid (when glucose pre-grown inoculum was used) [58]. Faster degradation of butyrate than propionate was observed in [61] as a consequence of low concentration of propionate degrading bacteria. However, most of those studies were realised in the late 90’s, with consideration of anaerobic digestion conditions and pointed out various degradation effect depending on the inoculum and interactions in-between VFA.

Further studies are required with regards to the specific context of VFA degradation during concentration and storage after anaerobic digestion to fully explain VFA degradation mechanisms and should consider the influence of other organics in the WW to be concentrated. More generally, the presence of concentrated VFA favours the development of biofilm that further enhances VFA consumption in repeated batches. It confirms that fouling mitigation has a crucial role to play not only to mitigate water flux losses but even more to avoid VFA biodegradation by the biofilm developed.

3.3. Long term evaluation with real wastewater

Long term evaluation was finally conducted through 20 consecutive batches and considering all former observations so to limit fouling (and biofilm development) and to optimise VFA concentration (i.e. MF pre-filtration, interbatch osmotic backwashing, sparging with nitrogen in the filtered WW to remove oxygen, spiking with VFA just before filtration tests and coverage of the feed tank to limit contact with air).

3.3.1. Flux and water concentration factor

Water permeation fluxes, time to reach WCF = 5 and permeation flux during osmotic backwashing were monitored (Fig. 6).

A slight decrease of initial flux with batches was observed but flux remained high (above 14 L m⁻² h⁻¹) even for batch 20 (Fig. 6a). It demonstrates the efficiency of the MF pre-treatment and cleaning strategy (interbatch osmotic cleaning and flushing) to mitigate fouling. When looking at the time to reach WCF = 5, a higher sensitivity was observed, with filtration time multiplied by 2 (from 400 min to around 800 min) when initial flux is in the lowest range (Fig. 6b). It can be explained by a generally lower permeation flux leading to extended
filtration time especially when WCF gets high. The loss of performance over batches is also seen on osmotic backwash flux (Fig. 6c, values are negative since the flux is reversed). In fact it was observed that flux during the osmotic backwash (after the initial stabilisation of 10 min) remained constant over time (i.e. no flux improvement) and therefore it may indicate that osmotic backwash in this case is efficient only during the first minutes. Consequently reducing osmotic backwashing time below 1 h may be possible in order to reduce downtime operation [28,35]. In general, monitoring backwash flux is a potentially interesting control tool that should be further developed so to (1) monitor loss of performances in normal operation and (2) to adjust backwash duration time [35]. Fouling was expected to be responsible of flux reduction but in fact minimal fouling was observed after batch 8 and 20 (Fig. 6d) and as already mentioned in Section 3.2.1, no further flux recovery was obtained even after manual cleaning, chemical cleaning, ethanol treatment. Also, the change of membrane (after batch 8, following damage during manual cleaning test) demonstrated significant increase of flux, back to initial level. Thus it reinforces the hypotheses of irrecoverable fouling, change in membrane properties or damages during cleaning that should be further evaluated.

3.3.2. VFA concentration and recovery

Follow up of acetic acid concentration over batches demonstrated that the objective of concentration from 80 up to 300 mg L\(^{-1}\) can be reached; up to 500 mg L\(^{-1}\) was even obtained (Fig. 7a). Very interestingly also, a trend of decrease of concentration (biodegradation) over batches resulting from biofilm development as observed in Section 3.2.2 (Fig. 5) was not detected during long term experiments (Fig. 7a). As such, it confirms that the pre-treatment and cleaning procedure implemented were successful to avoid biofilm formation on the membrane so to avoid biodegradation of acetic acid. However, very high variability in acetic acid final concentration was experienced from one batch to the other (1–7 and 14–19). Low final concentration were typically observed during batches operated overnight (2, 4, 6, 15, 17, 19, 20) when the system was operated with higher filtration time (12–15 h) and higher WCF (7–18). Due to such variability and despite very low recovery in some batches, an overall average final concentration of 265 mg L\(^{-1}\) was reached for acetic acid with average recovery of 45% (Fig. 7b). Important variation of final concentration of other VFA were also observed but overall final concentration was less sensible to operation conditions during the FO concentration process, reaching final VFA concentration above 400 mg L\(^{-1}\) and recovery rates of 70–80% (Fig. 7b&c).

To get further insight of the high variability of acetic acid (and other VFA) recovery and final concentration, monitoring of VFA concentration during FO filtration and as function of WCF was carried out (Fig. 8).

A linear increase of all VFA concentration and recovery rates were achieved at increasing WCF values up to 4.5. Higher WCF values led to a severe decrease of recovery, which was particularly significant for acetic acid whose recovery rate dropped down to 34% for WCF of 10 (Fig. 8a and b). Analysis of % recovery of acetic acid for all batches (from 10 to 20) which featured different WCF completely confirm this observation (Fig. 8c). On one hand, with lower WCF (4–5) which corresponds to shorter filtration time (7–10 h, day operation), 70–80% of acetic acid recovery is achieved. On the other hand very low recovery is obtained when WCF is in-between 10 and 20 (12–15 h, overnight operation). In line with results from Section 3.2.2, recovery of other VFA remains in all cases higher than that of acetic acid, confirming the highest biodegradability of the latter while isobutyric acid proved to be less sensitive in our conditions and with the WW used. Longer residence
time certainly favours VFA biodegradation. Additionally, at high recovery, (1) feed tank level is very low (and possibly pump cavitation can happen) bringing air to the feed solution, (2) intense recirculation is occurring exposing the feed intensively to the biolnit that potentially starts to develop and finally (3) higher WCF also means higher concentration of VFA that will promote biological development and may decrease apparent rejection as mentioned in Section 3.1.2. Towards full scale implementation as well as for further laboratory scale studies, the design of process limiting residence time and avoiding contact with air even at high WCF will be a key challenge. Alternatively, operating at WCF = 5 avoids producing WW with very high VFA concentration allowing for more flexibility in the design and limit biofilm formation and associated biodegradability issues.

4. Conclusions

WCF above 10 (15–30) is largely achievable with pre-treated real domestic WW using seawater or brine as draw solution. VFA concentration can be largely affected by pH (poor rejection at acidic pH) and biodegradation. As such, VFA concentration using real WW proved to be more challenging with regards to fouling mitigation and VFA biodegradation. It is possible to reach VFA concentration (and especially acetic acid) up to 300–400 mg/L thanks to the application of operation strategies to mitigate fouling and biodegradation but still remains very sensitive to biological development that is potentially very intense in such environment. Further studies should be conducted to optimise this process especially with regards to industrial application at full scale; full scale operation using FO modules in counter flow will also be in favour of reaching higher WCF, can allow for operating with lower salinity draw solutions, lower (but more constant) flux and consequently will limit fouling issues. High permeation flux above 14 L m⁻² h⁻¹ was maintained during long term operation tests (20 batches) but loss of flux despite intense cleaning of the membrane was noticed. Longer operation, dedicated tests, membrane characterization and autopsy may help improving the understanding of mechanisms involved.

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References


