Contents lists available at ScienceDirect

Separation and Purification Technology



Separation and Purification Technology

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Production and purification of organic acids from partially oxidised waste activated sludge



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A R T I C L E I N F O Editor: Luo Guangsheng

Hydrothermal treatments

Liquid-liquid extraction

Membrane filtration

Waste valorisation

Keywords:

Fouling

ABSTRACT

Short-chain organic acids (SCFAs) are widely used in the chemical and food industries. However, their conventional production relies heavily on fossil raw materials, necessitating sustainable alternatives. Waste activated sludge (WAS) can serve as a renewable feedstock for SCFA production through oxidative hydrothermal pretreatment. Thus, the aim of this work was to optimize the production and recovery of SCFAs from partially oxidised WAS. To achieve this, WAS was treated by wet oxidation (WO) at different temperatures (160–200 °C) and ultrafiltered using ceramic membranes (50 and 1 kDa) to pre-purify the SCFAs. Subsequently, these acids were extracted with different combinations of trioctylamine (TOA), tributylphosphate (TBP) and octan-1-ol in the temperature range 25–50 °C.

WO at 160 $^{\circ}$ C for 240 min maximized the SCFA production, obtaining a concentration of 6.07 g/L, with acetic acid as the main component (28.2 %).

Membrane ultrafiltration operating in total recycle mode achieved rejections of 39% for TOC and 73% for colour, with a low SCFA rejection (4%) effectively pre-purifying the SCFAs present in the WAS. The main fouling mechanism was cake formation.

The highest extraction yields of SCFAs at room temperature were achieved with a mixture of TOA and TBP at 10 % in octan-1-ol, extracting 34 % of the total SCFAs present in the 1 kDa permeate. Lower extraction yields were obtained with the pre-purified WAS compared to synthetic solutions of SCFAs, showing the detrimental effect of the matrix in liquid–liquid extraction. Increasing the temperature within the range of 25–50 °C generally had a favourable effect on the SCFA extraction.

1. Introduction

As global efforts to reduce the impact of human activity have gained importance over the years [1,2], the concept of circular economy has become a promising strategy to achieve a sustainable economy/society. Circular economy can be defined as a closed-loop material flow within the entire economic system, where it is aimed to maintain all the materials at their highest utility value [3,4]. This stands in contrast to the traditional linear economy, where raw materials are transformed into products and eventually discarded as residues at the end of their lifespan.

The circularization of the economy involving urban wastewaters is of particular significance. The production volumes of these wastewaters and the restrictions on their discharge are increasing due to the global population growth and the rise on the environmental concerns [5,6]. Moreover, wastewater treatment plants themselves contribute to

adverse environmental effects through material and energy consumption, as well as the release of various emissions into the environment. In this sense, significant amounts of waste activated sludge (WAS) are generated daily, necessitating subsequent treatment [7]. This sludge has been traditionally discarded in landfills or used as a low-value product, fuel or fertilizer [8]. However, this residue, mainly composed of microorganisms, their debris and extracellular polymeric substances, represents a promising source of valuable biological products like enzymes, proteins, humic acids, saccharides and lipids, along with short-chain fatty acids (SCFAs) [8,9]. This offers an interesting opportunity to valorise WAS and obtain high-value products through their recovery. In particular, SCFAs, due to their high industrial importance, are produced in large volumes and find wide-ranging applications across industries including food, chemical, biochemical, biofuel, textile, cosmetic, and pharmaceutical [10-12]. Traditional methods of SCFAs production, such as methanol carboxylation, have high energetic demands [13],

https://doi.org/10.1016/j.seppur.2024.126815

Received 21 December 2023; Received in revised form 12 February 2024; Accepted 14 February 2024 Available online 18 February 2024

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employ non-renewable fossil sources and produce large chemical waste discharges [14].

While SCFAs are not abundant in WAS, its organic matter can be transformed into organic acids through mild wet oxidation (WO), a hydrothermal technique that, in addition to SCFA production using a renewable source, also solubilises and sterilises the sludge, helps to precipitate heavy metals; turns up to 99 % of toxic organics into harmless end products, also not generating nitrous oxide, sulfur dioxide, hydrochloric acid, dioxins, furans, and fly ash [15,16]. The optimisation of the production of SCFAs using WO requires careful consideration of both operation time and temperature [17].

The treatment of the WAS by mild WO results in a complex matrix comprising a solid [18] and a liquid phase containing the solubilised organic and inorganic matter [19] as well as the SCFAs. As a result, separation and purification processes are necessary for their recovery. Membrane separation proves to be a very suitable technology for the pre-purification of these acids. It is considered a green technology since it can be continuously conducted under mild conditions without the need for additional chemicals, with high selectivity and low energy consumption, and it can be easily coupled with other operations [20]. In addition, affinity based methods, such as resin adsorption or liquid–liquid extraction (LLE), are normally employed for the purification of SCFAs due to low energy and temperature requirements [9,11]. After the LLE, the remaining liquid fraction, which is easily degradable, could be treated at a wastewater treatment plant [21] or anaerobically fermented to obtain energy in the form of methane [21] or hydrogen [22].

Both membrane filtration and LLE are conditioned by several factors. In the case of membrane filtration, factors such as geometry, material composition and, especially, molecular weight cut-off (MWCO), significantly impact selectivity and permeability [23,24]. On the other hand, the election of the solvent is critical for LLE, with the most suitable option depending on the nature of the desired compounds and the phase in which it is dissolved (the stationary phase). In particular, reactive extraction has gained relevance for the extraction of carboxylic acids, and has proven to be highly effective for their in-situ recovery [25,26]. A reactive solvent typically consists of a diluent, which is immiscible with the stationary phase, and acts as a transport phase; and an extractant, which forms a reversible complex with the carboxylic acid [27]. While both polar and non-polar diluents can be employed in reactive extraction, it has been reported that polar diluents are more effective, particularly for carboxylic acids [28]. In such cases, the optimal extraction yield of SCFAs is determined by the ratio between the diluent and the extractant. On one hand, the polar diluent provides additional solvating power to the relatively low polar extractants, allowing for higher levels of SCFA-extractant complexes to be formed in the transport phase. On the other hand, increasing the proportion of diluent reduces the number of extractant molecules available for forming complexes [29]

Works studying the production of SCFAs from WAS have mainly focused on bioproduction via fermentation [30]. However, fermentation has several disadvantages compared to WO, such as higher reaction times, requirement of higher reactor volumes, or high sensibility to inhibition by organics present in the WAS or generated during its digestion [31]. Few of them studied physicochemical methods [32,33], and, to the best of our knowledge, none of them has focused on the recovery process of SCFAs.

Taking into account these considerations, this study was focused on evaluating the process for the production, separation and purification of SCFAs from WAS. To achieve this, the study aimed to: i) optimize the production of SCFAs through partial WO, ii) analyse the impact of the pre-purification by membrane filtration on partially oxidised WAS, and iii) assess the effect of LLE on the recovery of SCFAs.

2. Material and methods

2.1. Waste activated sludge

The thickened WAS was collected from a wastewater treatment plant in Baíña, Asturias, Spain, and then stored at 4 °C until it underwent partial oxidation, a process that took place within no more than three days after collection. Its physical–chemical characteristics are shown in Table 1.

2.2. Production of organic acids by partial wet oxidation

Different conditions of time and temperature were studied to optimize the production of SCFAs from WAS. Partial WO tests were performed in a 1 L 316 SS batch reactor (Parr Instrument Co., Moline, IL) equipped with pressure and temperature controllers, indicators, a sampling system, and a heating jacket. The reactor content (loaded up to the 70 % of its capacity for safety purposes) was stirred at 150 rpm by two six-bladed magnetically driven turbine agitators. A constant flow of 1600 mL/min of oxygen, previously saturated with water by a humidifier, was provided from a compressed bottle throughout the operation, and the pressure was set at 40 bar. A detailed scheme of the experimental setup can be found in [34]. The reaction was carried out without pH adjustment nor addition of catalyst. Temperatures of 160 °C, 180 °C and 200 °C were tested for a total reaction time of 5 h, taking samples at different intervals to analyse the evolution of SCFAs and their degradation throughout the partial oxidation.

After the partial WO, 0.1 % (w/v) sodium azide was added to prevent microbiological growth. The oxidised sludge was then stored at 4 $^\circ C$ for further usage.

2.3. Membrane filtration

In order to pre-purify the oxidised WAS prior to the LLE of SCFA, different filtration experiments were conducted. The filtrations were carried out with a laboratory-scale filtration device manufactured by Addefi (Spain). The equipment, built in AISI316 high-pressure stainless steel and connected with high-pressure fittings, consisted of a jacketed 10 L feed tank equipped with a heating resistance. From there, the feed was pumped into the gasketed membrane using an IEC 60034 three-phase pump (AEG, Germany). The equipment was equipped with a temperature controller, pressure gauges before and after the ultrafil-tration module, as well as flow and temperature sensors. Transmembrane pressure (cros) was regulated by a pressure valve located in the retentate line. The permeate line was built in rubber, and directed to a PS750R2 (Radwag, Poland) weighting scale for flux determination. A scheme of the device is shown in Fig. 1.

Tubular mono-channel ZrO_2 -TiO₂ membranes of 50 and 1 kDa (TAMI Industries, France) were used for the experiments. The permeate obtained after the filtration with the 50 kDa membrane was used as the feed for the filtration with the 1 kDa membrane. The membranes had a length of 604 mm and an internal diameter of 6 mm. All filtration experiments were performed at 50 °C, with a TMP of 4 bar, and a cross-flow velocity (CFV) 3.2 m/s.

Two modes of filtration were tested:

Table 1

Physical-chemical parameters of the thickened waste activated sludge.

Parameter	Value
pH Total chemical oxygen demand (mg O ₂ /L) Soluble chemical oxygen demand (mg O ₂ /L) Total organic carbon (mg C/L) Total suspended solids (g/L)	$\begin{array}{c} 6.6 \pm 0.2 \\ 22030 \pm 40 \\ 350 \pm 150 \\ 6100 \pm 800 \\ 33 \pm 1 \\ 26.8 \pm 0.4 \end{array}$
Volutile Subpended Solids (8/2)	



Fig. 1. Filtration setup used in the pre-purification experiments of the oxidised WAS.

- Total recycle (TR) mode: the retentate and permeate were returned to the feed tank to maintain a constant feed composition. This mode allowed for the evaluation of membrane fouling evolution over time. TR experiments were conducted for a total of 300 min.
- Volume concentration (VC) mode: only the retentate was returned to the feed tank, concentrating the feed composition. This mode allowed for the assessment of the effect of concentration on fouling development. VC experiments were performed until a volume concentration ratio (VCR) of 3 was reached with the 50 kDa membranes; and of 1.5 with the 1 kDa membrane, due to the slow flux rate obtained. VCR is calculated as follows:

$$VCR = \frac{V_f}{V_r}$$

Where V_f is the initial feed volume, and V_r is the retentate volume.

In both modes, retentate and permeate samples were taken periodically and frozen until further use. Rejection coefficients (R_i) were determined using the following equation:

$$R_i = 1 - \frac{C_{P_m,i}}{C_{R_t,i}}$$

Where $C_{P_{m,i}}$ and $C_{R_{t,i}}$ represent the concentration of the compound "i" in the permeate and the retentate, respectively.

After each filtration, the membrane was rinsed with distilled water until attaining a stable flux value. Subsequently, it was cleaned at moderate temperature (70 °C) with a Diversey basic detergent (0.5 % v/v). Cycles of chemical cleaning were performed as needed, until the final flux was over 90 % of the initial water flux [35]. All experiments were performed in duplicate.

In order to understand the occurring fouling mechanisms, membrane fouling was modelled with Hermia models [36] (Eq. (4):

$$\frac{\mathrm{dJ}}{\mathrm{dt}} = -K_{j} \cdot (\mathrm{J} - \mathrm{J}_{0}) \cdot \mathrm{J}^{2-n} \tag{4}$$

Where t stands for time (min), K_j is the model constant that depends on the occurring fouling, J_0 is the limiting flux (m·s⁻¹), and n is a constant that varies for the fouling mechanism: n = 2 for complete pore blocking (CPB) (K_b in min⁻¹), n = 1.5 for internal pore blocking (IPB) (K_i in m⁻¹), n = 1 for particle pore blocking (PPB) (n = 1, K_p in m⁻¹), and n = 0 for cake filtration (CF) (n = 0, K_c in min·m⁻²) [37].

In order to obtain the model curves, the difference between the predicted fluxes and the experimental data as the sum of residuals (SR) was minimized by adjusting the value of K_js for every fouling mechanism model. The lowest SR indicated the main fouling mechanism.

2.4. Liquid-liquid extraction

Tributyl phosphate (TBP) (99.9 %, VWR) and trioctylamine (TOA)

(97 %, Acros Organics) were used as extractants, and octan-1-ol (99 %, Sigma) as diluent. Octan-1-ol was selected due its polar character, which, as previously stated, favours the extraction of SCFAs. Additionally, it is totally immiscible with water; and presents a low latent heat of vaporization (65 kJ/mol). The tested solvents were prepared by dissolving TOA, TBP and a 50:50 (v/v) TOA/TBP mixture at concentrations of 10 %, 25 % and 40 % (v/v) in octan-1-ol. They were designated based on the employed extractant and its concentration (e.g., TBP40 represents TBP at 40 % in octan-1-ol).

Firstly, the extractions were performed at 25 °C by mixing the 1 kDa permeate with the solvent in a 1:1 (v/v) proportion and stirred overnight to ensure the equilibrium was reached. The aqueous phase was then analysed to determine the SCFA content.

After this initial screening, the effect of temperature on the extraction yields of SCFAs was also studied. The TOA, TBP and TOA/TBP mixtures that delivered the highest yields at room temperature were tested at 40 and 50 $^{\circ}$ C following the same procedure described above. Additionally, these extractions were performed using a synthetic solution prepared dissolving the studied SCFAs at the same concentrations present in the oxidised WAS, in order to study the effect of the WAS matrix on the LLE yield.

The extraction yield (Y_i) was determined as follows:

$$Y_i(\%) = \left(1 - \frac{C_{R,SCFA_i}}{C_{F,SCFA_i}}\right) \cdot 100$$

Where
$$C_{R,SCFA_i}$$
 represents the concentration of the SCFA "i" in the raf-
finate, and $C_{F,SCFA_i}$ the concentration of the SCFA "i" in the feed solution.

The distribution constants (K_D) were determined by the following equation:

$$K_D = \frac{C_{SCFA_i,org}}{C_{SCFA_i,aq}}$$

Where $C_{SCFA_i,org}$ and $C_{SCFA_i,aq}$ represent the concentrations of the SCFA "i" in the organic and aqueous phase respectively, after reaching the equilibrium.

2.5. Analytical methods

Density and kinematic viscosity were measured at 50 °C and room temperature with a pycnometer and a Cannon-Fenske inversed-flow viscometer (Proton, UK), respectively. pH was determined using a Basic 20 pH meter (Crison, Spain). Spectral absorbance coefficients (SAC) were measured at 436, 525 and 620 nm using a Helios Alpha UV–Vis spectrophotometer (Thermo Scientific, USA) to calculate the colour number (CN). Both SAC and CN have units of cm⁻¹. CN was calculated as follows:

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}}$$

Total organic carbon (TOC) was determined using a TOC analyzer (Shimadzu TOC- V_{CSH}). The concentration of SCFAs were determined by HPLC Agilent Technologies 1200 Series, using an ICSep ICE-ION-300 column (Teknokroma, Spain) as the stationary phase and with H₂SO₄ 0.45 mM (with pH adjusted to 3.2–3.3) as the mobile phase.

A refractive index detector was used to measure SCFAs. Standard curves of oxalic, maleic, pyruvic, lactobionic, malic, lactic, formic, acetic and propionic acids were elaborated to properly identify and quantify these SCFAs.

2.6. Statistical analysis

To analyse significant differences among experimental groups, including the total production of SCFAs by partial oxidation, the rejection coefficients in TR and VC modes, distribution constants, and

extraction yields for each of the SCFAs, analysis of variance (ANOVA) with a confidence level of 95 % was performed using the statistical software Jamovi (version 2.3.26). Tukey's HSD *post hoc* test was employed to identify and assess significant differences between the specific experimental groups for each parameter studied.

3. Results

3.1. Optimization of SCFAs production by partial WO

The production of SCFAs by partial oxidation of WAS is shown in Fig. 2.

In all cases, the concentration of SCFAs presented a consistent pattern over time. Initially, the SCFA concentrations increased with time, as the sludge was solubilised, and the released biocompounds into the reaction media were oxidised into these acids. The concentration values eventually reached either a peak or a plateau, after which they began to decrease. This can be attributed to the SCFA degradation rate, which started to be faster than its production rate (Fig. 2). This behaviour was in accordance with other studies that have analysed the degradation pathways of organic matter. These studies indicated that the process involved the successive formation and degradation of peroxides, alcohols, ketones, and organic acids, consecutively, until their ultimate degradation to CO_2 , H_2O and ash [38].

Volatile SFCAs (propionic, acetic, and formic acids) were produced in larger quantities than the non-volatile ones (oxalic, maleic, pyruvic, lactobionic, malic and lactic acids). This trend was more pronounced at higher temperatures (180 °C and 200 °C) and longer reaction times (from 180 min onwards), in which the average concentration of volatile SCFAs represented 70 % of the total concentration of SCFAs. Among these, acetic acid showed at the highest concentration, reaching a maximum value of 2.83 \pm 0.08 g/L at 200 $^\circ\text{C}$ after 240 min of oxidation. Furthermore, it was observed that increasing the temperature favoured the formation of acetic acid. Specifically, a concentration of 1.28 ± 0.07 g/L was obtained at 160 °C for 180 min, while the value was 1.65 times higher at 180 °C for the same time. This finding is consistent with the studies of Chung et al. [29], who reported that acetic acid was the most produced SCFA due to its stability among the low molecular SCFAs obtained as intermediates.[39]. Moreover, the production of acetic acid as a final compound of the WO of sludge has been described by several other authors [39-42]. A similar behaviour was also observed for the non-volatile lactic, lactobionic and malic acids, which achieved

maximum concentrations at 200 °C that were 1.3, 2.3 and 1.8 times higher than those obtained at 160 °C (0.75 \pm 0.02 g/L, 0.16 \pm 0.05 mg/L; 0.11 \pm 0.01 g/L, respectively). As for propionic acid, the increase in concentration with higher temperatures was more significant within 45 min of reaction. Specifically, the values were 3 times and 3.8 times higher at 180 °C and 200 °C for 45 min, compared to that of at 160 °C for the same reaction time (0.106 \pm 0.003 g/L). Chung et al. [29] reported a similar increase in propionic acid concentration when oxidising sewage sludge at temperatures ranging from 200 to 240 °C.

However, the opposite behaviour was observed for oxalic, pyruvic, and formic acids, as their degradation rate accelerated with increasing temperature, although it was less pronounced for formic acid. Particularly, the maximum concentration of oxalic acid decreased from 1.3 \pm 0.1 g/L at 160 °C, to 0.243 \pm 0.004 g/L at 200 °C. For pyruvic acid, the concentration dropped from 0.700 \pm 0.006 mg/L at 160 °C to 0.20 \pm 0.01 mg/L at 200 °C, and for formic acid decreased from 1.19 \pm 0.08 mg/L at 160 °C to 0.7 \pm 0.1 mg/L at 200 °C.

Increasing the temperature resulted in a decrease in the maximum concentration of total SCFAs generated. Specifically, the concentrations were 6 % and 18.3 % lower at 180 °C and 200 °C compared to that of at 160 °C (6.07 g/L). This reduction can be attributed to a greater mineralization of the organic matter, where the oxidation routes leading to CO_2 formation are more favoured than those leading to acetic acid at higher temperatures (Fig. 3). This can be supported based on the data reported by Prince-Pike et al. [33] related to the oxidation of the "fast



Fig. 3. Proposed model for the oxidation of WAS adapted from [43]. sOM: soluble organic matter. DON: dissolved organic nitrogen. AA: acetic acid. VFA: volatile fatty acids without including AA. f, s and nr subscripts stand for fast reacting, slow reacting, and non-reacting, respectively.



Fig. 2. Evolution of the concentrations of oxalic (■), maleic (■), pyruvic (■), lactobionic (■), malic (■), lactic (■), formic (■), acetic (■) and propionic (■) over time in the range 160–200 °C. Different letters indicate significant differences (p < 0.05).

reacting" and "slow reacting" soluble organic matter to CO_2 , acetic acid and other volatile fatty acids. At low temperatures, "slow reacting" soluble organic matter was predominant, with higher kinetic constants for its oxidation to acetic acid (varied from $4.9 \ 10^{-4} \ s^{-1}$ for 160 °C to $1.5 \cdot 10^{-3} \ s^{-1}$ for 200 °C) and other volatile fatty acids (varied from $3.7 \ 10^{-4} \ s^{-1}$ for 160 °C to $8.9 \cdot 10^{-.4} \ s^{-1}$ for 200 °C) compared to its oxidation to CO_2 (ranged from $4.8 \ 10^{-8} \ s^{-1}$ for 160 °C to $6.0 \cdot 10^{-.7} \ s^{-1}$ for 200 °C). However, at higher temperatures, "fast reacting" soluble organic matter is more favoured, resulting in higher kinetic constant for its oxidation to CO_2 (varied from $9.7 \ 10^{-2} \ s^{-1}$ for 160 °C to $2.2 \cdot 10^{-.1} \ s^{-1}$ for 200 °C) compared to that obtained for the oxidation to acetic acid (varied from $3.810^{-5} \ s^{-1}$ for 160 °C to $1.6 \cdot 10^{-.4} \ s^{-1}$ for 200 °C) and other volatile fatty acids (ranged from $1.1 \cdot 10^{-22} \ s^{-1}$ for 160 °C to $8.0 \cdot 10^{-21} \ s^{-1}$ for 200 °C).

These results followed the trend reported by other authors [39,43], who observed an increase in the concentration of SCFAs with reaction time. However, their experiments were only performed within 60–80 min, and stopped them while SCFAs were still being generated. Additionally, these studies did not analyse the concentration of non-volatile SCFAs. This is why they reported SCFA concentrations ranging from approximately 1 g/L to 4 g/L for the oxidation of sewage sludge at temperatures between 180 °C and 240 °C, and pressures from 20 bar to 60 bar.

The highest concentration of total SCFAs (6.07 g/L) was reached at 160 $^{\circ}$ C after 240 min. Therefore, the subsequent experiments were performed with the WAS partially oxidised at these conditions.

Moreover, ANOVA analysis was performed for the total production of SCFAs, considering reaction temperature and time as factors, with the total concentration of SCFAs as dependent variable. Three levels were considered for the reaction temperature: i) 160 °C, ii) 180 °C and iii) 200 °C, and ten levels for time: i) 0 min, ii) 15 min, and iii) 30 min, iv) 45 min, v) 60 min, vi) 90 min, vii) 120 min, viii) 180 min and ix) 240 min and x) 300 min. Statistically significant differences (p-value < 0.05) were observed for both reaction temperature, time and the interaction between temperature and time for the total production of SCFAs. Subsequent Tukey's HSD post hoc tests were conducted between temperature pairs, time pairs, and temperature and time pairs. Statistically significant differences (p-value < 0.05) were found between all pairs of temperature (160-180 °C, 160-200 °C, and 180-200 °C). Additionally, no statistically significant differences (p-value < 0.05) were observed among time pairs 0–15 min, 0–30 min, 0–45 min, 15–30 min, 15–45 min and 30–45 min, while significant differences (p-value < 0.05) were found in the remaining pairs. Regarding, temperature and time pairs, the main conclusion drawn was that no statistically significant differences (p-value < 0.05) were observed among all temperatures (160 °C, 180 °C and 200 °C) with short reaction times (up to 45 min) for the total production of SCFAs. All the results are presented in Fig. 2.

Finally, an energy evaluation of the WO process was included in the Supplementary Material. The evaluation of energy consumption was conducted for the reaction described in this work. The calculation basis was 700 mL of WAS (0.686 kg), representing the amount of sludge loaded into the reactor for each WO reaction. In terms of energy consumption, industrial production of SCFAs occurs under similar conditions of temperature and pressure to those used in the WO employed in this study (160 °C and 40 bar). For instance, the most common process for acetic acid production, which is the main SCFA produced by WO, is methanol carboxylation, typically carried out at temperatures ranging from 150 to 200 °C and pressures from 30 to 50 bar [13]. It is worthy noting that this traditional technology relies on non-renewable fossil sources and generates large chemical waste discharges [14], whereas WO is considered a clean technology. WO does not involve the use of any toxic chemical reagents, and no harmful species, such as NOx, SO₂, HCl, dioxins, furans or fly ashes are produced [44].

It should be noted that, for this energy evaluation, a start-up condition regime was assumed, where the majority of the consumed energy is used to heat the reactor. This is the reason why the cost here obtained is around 10 times higher than those reported in the methanol carboxylation [45]. Therefore, if operated in continuous mode, the energy expenditure would not be as intensive as calculated. Furthermore, the heat generated during the WO process [46] can even render the process energetically self-sufficient above 200 °C [16].

3.2. Pre-purification of the SCFAs by sequential ultrafiltration

WO of WAS results in a complex aqueous matrix, with many compounds besides SCFAs [47]. In order to pre-purify these acids, and to avoid undesired antagonistic interactions during the LLE [48,49], two sequential ultrafiltrations with membranes of 50 and 1 kDa were performed to separate compounds of greater molecular size from the SCFAs.

3.2.1. Flux

The obtained fluxes for all filtration experiments are shown in Fig. 4.

The permeability of the clean 50 kDa membrane (581 \pm 1 LMH) was over 10 times higher than that of the clean 1 kDa membrane (54.8 \pm 0.1 LMH). It should be noted that the oxidised WAS filtered with the 1 kDa membrane was previously pre-filtered with the 50 kDa membrane, thus showing the importance of a pre-filtration stage. The concentration of the feed also significantly influenced the resulting flux, this effect being more pronounced with the 1 kDa membranes (excluding the clean fluxes in VC mode with 50 kDa and 1 kDa membranes (excluding the clean fluxes) were approximately 1.85 times and 2 times lower, respectively, than those obtained in the TR mode (60 \pm 40 LMH and 14 \pm 5 LMH, respectively) in both cases.

In terms of flux loss during filtration, higher relative losses (compared to the initial flux) were measured during the filtration with the 50 kDa membrane in both TR and VC modes (93.9 % and 98.5 %, respectively) than those achieved with the 1 kDa membrane (78 % and 94.3 %, respectively). This can be explained by considering that the stream filtered with the 1 kDa membrane had already undergone pre-filtration with the 50 kDa membrane.

The measured fluxes were generally lower compared to those obtained in ultrafiltration and nanofiltration studies with different polymeric and ceramic membranes, which reported values from 300 to 30 LMH (50 kDa) and from 40 to 20 LMH (1 kDa) [50–61]. This difference can be attributed to the high complexity of the solubilised WAS. For instance, Cassini et al. [53] achieved fluxes of around 300 LMH with a 50 kDa ceramic membrane, which approximately 5 times higher than the fluxes obtained in this study with the 50 kDa membrane under similar operation conditions when treating soy protein wastewaters. Optimize CFV and TMP parameters to operate at critical flux conditions could minimize the flux loss during the ultrafiltration [62,63].

Fluxes obtained in TR mode were also modelled with Hermia models in order to determine the main fouling mechanism (Fig. 5). Knowing this can facilitate the optimization of the cleaning cycles of the membrane, improving its performance and expanding its lifespan. Hermia models contemplate four different fouling mechanisms: complete pore blocking (CPB), where particles are larger than the pore size and reduce the active membrane area; internal pore blocking (IPB), where the particles are smaller than the pore and reduce the pore size itself; partial pore blocking (PPB), where particles may bridge pores without completely seal them, resulting in similar effects to CPB but less severe; and cake formation (CF), where fouling particles form a layer on the top of the membrane without entering the pores. The main fouling mechanism of both 50 and 1 kDa membranes was CF, which is primarily reversible, and can be removed by physical methods such as backwashing, backpulsing, sponge ball cleaning and air sparging [64].

As shown in Table 2, hardly any retention of SCFAs was observed with the 50 kDa membrane operating in TR mode, and even negative retentions occurred for some SCFAs. These negative retentions can be attributed to the Donnan effect: CN in organic matter (NOM) is produced by compounds rich in aromatic C=C bonds [65], such as humic acids (the main biopolymer found in the studied WAS) or melanoidin, which



Fig. 4. Flux evolution during the filtration of the oxidised WAS with the 50 kDa membrane in TR (a) and VC (b) mode; and with the 1 kDa membrane in TR (c) and VC (d) mode.



Fig. 5. CPB [—], IPB [—], PPB [—] and CF [—] flux models, and experimental fluxes (**●**) for 50 kDa (a) and 1 kDa (b) membranes.

are a group of large, negatively charged, coloured, refractory, nitrogenous molecules produced by Maillard reaction from the heating of amino acids and carbohydrates [66], and thus generated during the WO of the WAS. Humic acids and melanoidin are strongly negatively charge at the operational pH [67]. With the high rejection values for CN, it is likely that these negatively charged molecules were concentrated in the retentate side. Consequently, SCFAs were compelled to pass through the membranes to reach charge equilibrium [68]. Furthermore, negative charges would be attracted to the solution-membrane surface interface, as ZrO_2 -TiO₂ has been reported to be positively charged at pH levels below ~6.5 [69], which facilitated the permeation of the SCFAs through the membrane. Negative retentions of SCFAs have already been reported by several authors [70,71].

In contrast with the SCFAs rejections, TOC rejection of around 50 % was obtained with the 50 kDa membrane in TR mode, indicating that a partial purification of the SCFAs was achieved after membrane filtration. However, a slightly lower TOC rejection (39 ± 3 %) was observed during the filtration with the 1 kDa membrane in TR mode. This can be due to the removal of a significant portion of larger molecules by the 50 kDa filtration. The high TOC rejections obtained are consistent with the considerable CN rejections achieved in all cases, ranging from 53 to 73 %. Operating in VC mode significantly increased the CN rejections when filtering with the 50 kDa membrane, but made no significant difference filtering with the 1 kDa membrane.

Additionally, a one-way ANOVA with membrane treatment as a factor with 4 levels was conducted. The levels were: i) TR mode with 50 kDa membrane (TR 50 kDa), ii) VC mode with 50 kDa membrane (VC 50 kDa), iii) TR mode with 1 kDa membrane (TR 1 kDa) and iv) VC mode with 1 kDa membrane (VC 1 kDa). The analysis included the retention of CN, TOC, theoretical COD from SCFAs, total SCFAs, and each individual SCFA (oxalic, maleic, pyruvic, lactobionic, malic, lactic, formic, acetic and propionic acids) as dependent variables. Statistically significant differences (p-value < 0.05) were observed for CN, TOC, and theoretical COD from SCFAs. Subsequent Tukey's HSD *post hoc* tests were conducted for CN, TOC and theoretical COD (Table 1). It was found that, in the

Table 2

Average rejection coefficients with 50 kDa and 1 kDa membranes during the operation in TR and VC modes.

R	TR 50 kDa	VC 50 kDa	TR 1 kDa	VC 1 kDa
CN	0.53 ± 0.09^{b}	0.73 ± 0.07^a	$0.73 \pm 0.06^{\rm a}$	$\begin{array}{c} 0.86 \pm \\ 0.06^a \end{array}$
Total SCFAs	$\begin{array}{c} -0.08 \pm \\ 0.2^{\rm a} \end{array}$	0.1 ± 0.3^a	0.04 ± 0.1^a	$\begin{array}{c} 0.2 \pm \\ 0.2^{\rm a} \end{array}$
Oxalic	0.03 ± 0.2^a	0.3 ± 0.2^{a}	0.3 ± 0.3^a	$\begin{array}{c} 0.47 \pm \\ 0.09^a \end{array}$
Maleic	0.002 ± 0.191^{a}	0.2 ± 0.5^a	0.2 ± 0.2^a	$\begin{array}{c} 0.42 \pm \\ 0.06^a \end{array}$
Pyruvic	0.07 ± 0.44^{a}	0.4 ± 0.5^a	-0.3 ± 1^a	$\begin{array}{c} 0.45 \pm \\ 0.09^a \end{array}$
Lactobionic	-0.2 ± 0.3^a	0.3 ± 0.4^{a}	0.4 ± 0.4^{a}	0.4 ± 0.1^{a}
Malic	-0.010 ± 0.285^{a}	0.2 ± 0.3^{a}	$0.002 \pm 0.4^{\mathrm{a}}$	0.05 ± 0.2^{a}
Lactic	-0.03 ± 0.2^{a}	-0.2 ± 0.7^{a}	-0.1 ± 0.3^{a}	0.05 ± 0.4^{a}
Formic	-0.03 ± 0.3^{a}	0.1 ± 0.3^{a}	$0.2\pm0.2^{\mathrm{a}}$	0.3 ± 0.4^{a}
Acetic	$-0.2\pm0.3^{\mathrm{a}}$	-0.01 ± 0.5^a	-0.04 ± 0.1^{a}	0.2 ± 0.2^{a}
Propionic	-2 ± 4^a	-0.5 ± 1^a	$-0.2 \pm 0.7^{\mathrm{a}}$	0.3 ± 0.2^{a}
Total TOC	$\textbf{0.48} \pm \textbf{0.07}^{b}$	0.61 ± 0.06^a	$0.39 \pm 0.03^{\rm b}$	0.47 ^b
Theoretical COD from SCFAs	$\begin{array}{c} -0.18 \ \pm \\ 0.05^{b} \end{array}$	$\begin{array}{l} 0.0280 \pm \\ 0.0003^{ab} \end{array}$	-0.01 ± 0.02^{ab}	$\begin{array}{c} 0.20 \ \pm \\ 0.20^a \end{array}$

Different letters in the same row indicate significant differences (p < 0.05).

terms of CN retention, significant differences at p-value <0.05 were observed between pairs TR 50 kDa-VC 50 kDa, TR 50 kDa-TR 1 kDa, and TR kDa-VC 1 kDa. For TOC retention, statistically significant differences (p-value <0.05) were observed between pairs VC 50 kDa-TR 50 kDa, VC 50 kDa-TR 1 kDa, and VC 50 kDa-VC 1 kDa. Regarding the retention of the theoretical COD from SCFAs, statistically significant differences (p-value <0.05) was observed between pair TR 50 KDa-VC 1 kDa.

Based on the flux loss and the increase in SCFA rejections observed in VC mode, this operating mode can be considered inadequate for the treatment of oxidised WAS. Thus, the latter LLE experiments to recover the SCFAs were performed using the permeate collected during the filtration under TR mode.

An energy evaluation of the membrane filtration step was included in the Supplementary Material.

3.3. Recovery of SCFAs by liquid-liquid extraction

3.3.1. Solvent screening

First, a solvent screening was carried out at 25 $^{\circ}$ C to select the best performing one. Initial concentrations in the permeate before the LLE are shown in Table 3.

Distribution constants (K_D) and extraction yields (Y) obtained during the solvent screening of the 1 kDa permeates are displayed in Tables 4–5 and A.3–A.4. To ensure clarity, the SCFAs were divided into non-volatile SCFAs (NVAs) (oxalic, maleic, pyruvic, lactobionic, malic and lactic

 Table 3

 SCFA concentrations in the raffinate before extraction.

SCFA	Concentration (g/L)
Oxalic	0.68 ± 0.02
Maleic	0.020 ± 0.002
Pyruvic	0.51 ± 0.07
Lactobionic	0.08 ± 0.01
Malic	0.120 ± 0.001
Lactic	0.91 ± 0.02
Formic	0.54 ± 0.02
Acetic	1.89 ± 0.07
Propionic	0.23 ± 0.06

acids) and volatile SCFAs (VAs) (formic, acetic and propionic acids).

The effect of the extractant on the yield obtained for the different SCFAs varies depending on the nature of the extractant. In the case of TBP, which is a phosphorous-based extractant, its complexation mechanism with SCFAs primarily relies on the hydrophobicity of SCFAs due to hydrogen bond formation [72]. As a result, the complexation is more pronounced when the SCFA is less hydrophobic. The octanol-water partition coefficient (log P) is the parameter commonly employed to quantify hydrophobicity. The lower the log P value, the lower the hydrophobicity of the SCFA [72]. In this context, polar and hydrophilic compounds may even exhibit negative log P values. As for the complexation with amines like TOA, the mechanism is more intricated, involving different factors such as acid concentration, the nature of the diluent and the number of carboxyl groups [73]. However, the pKa value can serve as an indicator for monocarboxylic acids: pyruvic, lactobionic, lactic, formic, acetic and propionic acids. In this sense, the strongest acids (i.e., those with lower pKa values) are more strongly complexed and, consequently, more efficiently extracted.

The values of LogPs and pKas of the studied SCFAs are shown in Table 6.

Some deviations from the theoretically expected extraction order were observed. After the extraction with TOA, all monocarboxylic acids were recovered in the expected order except for pyruvic and propionic. In this sense, pyruvic acid exhibited the lowest extraction efficiency, with a maximum value of 12.9 %, whereas it was anticipated to be the most efficiently extracted monocarboxylic SCFA. Conversely, propionic acid presented an average yield of 53.4 %, despite being expected to be the least efficiently extracted acid. Lactobionic acid was also less extracted than expected when using TOA10 and TOA40 as solvents, although it could not be detected in the raffinate after extracting with TOA25. Regarding the extractions with TBP, slight deviations from the expected order were observed for most of the acids, with significant deviations noted for propionic, lactobionic and pyruvic acids. Consequently, propionic acid, which was expected to be the least extracted acid, yielded an average of 50.3 %. On the other hand, lactobionic acid, which was expected to be the acid extracted more efficiently, exhibited an average yield of 29.8 %, while malic acid obtained the highest average value at 82.1 %. In the case of pyruvic acid, higher values were expected, but the maximum observed was 5.2 %. This behaviour can be attributed to differences between the concentrations of the different acids or to interferences between the SCFAs or with other elements of the matrix. Similar results were obtained by Morales et al. when they studied the extraction of butyric, propionic, formic, acetic and lactic acids with TBP in dodecane and with TOA in decane-1-ol and dodecane [28]. They reported extraction yields that differed from what was expected. Thus, propionic and butyric acids, which were expected to be the least complexed, turned out to be the most extracted SCFAs with both TOA and TBP. Similarly, formic acid, with the lowest pKa among the extracted SCFAs, was the least extracted with TOA, contrary to expectations [28]. These deviations from the theoretical extractions were also observed in other studies [49], although some authors have been able to observe a rough correlation between log K and log P [73].

The effect of extractant concentration also varied between SCFAs. As explained before, the optimization of the solvent composition while using a polar diluent relies on a compromise between the concentration of diluent and of extractant. On viewing the results, no clear trends were observed, and the optimal choice of extractant and the ideal diluent: extractant ratio differed for nearly every acid. The combination of TOA and TBP seemed to enhance the extraction in most cases, except for malic acid. Similar synergistic effects between TBP and TOA have been reported by other authors [73,85]. Matsumoto et al., in particular, observed an enhancement in the extraction efficiency for all acids, thus showing that the complex matrix of the oxidised WAS can alter the extraction equilibria.

Regarding K_D values, high values indicate that the extraction process was efficient. In the case of pyruvic acid, low K_D values were obtained

Table 4

Distribution constants (K_D) of NVAs.

NVAs	K _D								
	TOA 10	TOA 25	TOA 40	TBP 10	TBP 25	TBP 40	T/T 10	T/T 25	T/T 40
Oxalic Maleic Pyruvic Lactobionic Malic Lactic	$\begin{array}{c} 0.14 \pm 0.01^c \\ 0.6 \pm 0.1^c \\ \textbf{n.d.}^1 \\ 0.09 \pm 0.01^b \\ 4.7 \pm 0.4^b \\ 0.35 \pm 0.04^c \end{array}$	$\begin{array}{c} 0.14 \pm 0.05^c \\ 0.4 \pm 0.1^c \\ 0.10 \pm 0.01^c \\ \textbf{n.d.}^1 \\ 3.80 \pm 0.06^b \\ 0.55 \pm 0.09^c \end{array}$	$\begin{array}{c} 0.18\pm 0.02^c\\ 0.32\pm 0.04^c\\ 0.22\pm 0.02^b\\ 0.12\pm 0.01^b\\ 2.2\pm 0.1^b\\ 0.42\pm 0.09^c \end{array}$	n.d. ¹ 0.20 ± 0.02^{c} n.d. ¹ 0.49 ± 0.04^{a} 3.8 ± 0.4^{b} 0.10 ± 0.01^{cd}	$\begin{array}{l} 0.006 \pm 0.001 \ ^{de} \\ 0.24 \pm 0.01^c \\ 0.067 \pm 0.007^c \\ 0.38 \pm 0.03 \ ^{a} \\ 11 \pm 11 \ ^{a} \\ 0.09 \pm 0.01 \ ^{cd} \end{array}$	$\begin{array}{c} 0.27 \pm 0.03^{b} \\ \textbf{n.d.}^{1} \\ 0.12 \pm 0.02^{c} \\ 0.40 \pm 0.06^{a} \\ 3 \pm 3^{b} \\ 0.027 \pm 0.003^{cd} \end{array}$	$\begin{array}{l} 0.36 \pm 0.06 \ ^{ab} \\ 0.054 \pm 0.004 ^{b} \\ \textbf{n.d.}^{1} \\ 0.7 \pm 0.8 \ ^{a} \\ \textbf{n.d.}^{1} \\ \textbf{8} \pm 1 ^{b} \end{array}$	$\begin{array}{l} 0.45\pm 0.07\ ^{a}\\ 0.1\pm 0.1^{b}\\ \textbf{n.d.}^{1}\\ 0.4\pm 0.4\ ^{a}\\ \textbf{n.d.}^{1}\\ 17\pm 3\ ^{a} \end{array}$	$\begin{array}{l} 0.015\pm 0.002\ ^{e}\\ 4\pm 4^{a}\\ 1\pm 1\ ^{a}\\ 0.47\pm 0.06\ ^{a}\\ \textbf{n.d.}^{1}\\ 10\pm 3^{b} \end{array}$

¹ n.d.: not detected. Different letters in the same row indicate significant differences (p < 0.05).

Table 5

Distribution constants (K_D) of VAs.

VAs	K _D								
	TOA 10	TOA 25	TOA 40	TBP 10	TBP 25	TBP 40	T/T 10	T/T 25	T/T 40
Formic Acetic Propionic	$\begin{array}{l} 1\pm1^{b} \\ 0.25\pm0.05^{b} \\ 1.1\pm0.4^{a} \end{array}$	$\begin{array}{c} 0.4 \pm 0.3^{b} \\ 0.38 \pm 0.07 \ ^{a} \\ 1.15 \pm 0.09 \ ^{a} \end{array}$	$\begin{array}{c} 0.4\pm 0.3^{b}\\ 0.26\pm 0.04^{b}\\ 1.2\pm 0.2^{a} \end{array}$	$\begin{array}{l} 0.4\pm 0.2^{b}\\ 0.15\pm 0.02^{b}\\ 1.1\pm 0.2^{a} \end{array}$	$\begin{array}{c} 0.3 \pm 0.1^{b} \\ 0.20 \pm 0.03^{b} \\ 1.07 \pm 0.07 \ ^{a} \end{array}$	$\begin{array}{c} 0.10 \pm 0.04^{b} \\ 0.07 \pm 0.01^{c} \\ 0.9 \pm 0.2^{a} \end{array}$	$\begin{array}{l} 5\pm3 \;^{a} \\ 0.24\pm0.03^{b} \\ 1.1\pm0.1 \;^{a} \end{array}$	$\begin{array}{c} 0.3 \pm 0.1^{b} \\ 0.29 \pm 0.04 \ ^{ab} \\ 1.0 \pm 0.2 \ ^{a} \end{array}$	$\begin{array}{c} 1.8 \pm 0.9^{b} \\ 0.19 \pm 0.03^{b} \\ 0.9 \pm 0.2^{a} \end{array}$

Different letters in the same row indicate significant differences (p < 0.05).

 Table 6

 Values of the pKa and LogP of the studied SCFAs.

SCFAs	рКа	Ref	Log P	Ref
Oxalic ¹	рКа ₁ = 1.46; рКа ₂ = 4.40	[74]	-0.688	[75]
Maleic ¹	рКа ₁ = 1.90; рКа ₂ = 6.07	[76]	-0.650	[77]
Pyruvic	2.39	[78]	-0.38	[79,80]
Lactobionic	3.28 ± 0.35^2	[81]	-4.847	[82]
Malic ¹	$pKa_1 = 3.51; pKa_2 = 5.03$	[83]	-1.474	[84]
Lactic	3.86	[29]	-0.413	[29]
Formic	3.75	[29]	-0.538	[29]
Acetic	4.75	[29]	-0.313	[29]
Propionic	4.87	[29]	0.290	[29]

¹ Dicarboxylic acid.

² Predicted value.

with TOA extractant, ranging from 0.1 \pm 0.01 to 0.22 \pm 0.02. These values are in line with those reported Marti et al. (2011) [86], who obtained a K_D value of 0.10, when they extracted pure pyruvic acid using concentrations of TOA ranging from 0.1 M to 0.4 M in 1-octanol at pH 4. For oxalic acid, a significant increase (25 %) in K_D value was observed when TOA concentration increased from 25 % to 40 %. Qin et al. (2001) [87] also reported that an increase in TOA from 10 % to 50 % resulted in an increase in K_D values when pure oxalic acid was extracted in TOA:noctanol mixtures. In the case of TBP:1-octanol mixtures, K_D values (varied from 0.006 \pm 0.001 to 0.27 \pm 0.03) were lower than that reported by Barnes et al. (1999) [88] for the extraction of aqueous solutions of oxalic acid with pure TBP (1.275). In the case of malic acid, the values obtained for TOA25 (3.80 \pm 0.06) and TOA40 (2.2 \pm 0.1) were 4 and 1.5 times higher than those reported by Uslu and Kırbaşlar [89]. This difference can be due to the effect of the matrix and the initial acid concentration, as pure malic acid with a concentration of approximately 107 g/L was used, while in this study the concentration was 0.12 g/L. For lactic acid, K_D values ranging from 0.027 \pm 0.003 to 0.10 \pm 0.01 were achieved with TBP:1-octanol mixtures. Labbaci et al. (2010) [90] also obtained similar K_D values, varying between 0.03 and 0.08, when extracting pure lactic acid using TBP:dodecane mixtures at similar concentrations.

Considering VAs, when TOA:1-octanol mixtures were used, the K_D values for formic acid ranged from 0.4 ± 0.3 to 1 ± 1 , for acetic acid from 0.25 ± 0.05 to 0.38 ± 0.07 , and for propionic acid from 1.1 ± 0.4 to 1.2 ± 0.2 . These values were higher compared to those obtained with TBP:1-octanol mixtures, which varied from 0.10 ± 0.04 to 0.4 ± 0.2 for formic acid, from 0.07 ± 0.01 to 0.20 ± 0.03 for acetic acid, and from

 0.9 ± 0.2 to 1.1 ± 0.2 for propionic acid. This difference may be attributed to 1-octanol exhibiting an acid interaction functional group, resulting in higher specific and general solvation to the acid-TOA complexes, leading to a greater distribution than the TBP mixtures (Keshav et al., 2008) [91].

By comparing the extraction yields obtained for each SCFA using different combinations of extractant-diluent, the most effective process was found to be the one involving n-octanol as diluent and a combination of TOA and TBP at 10 % (v/v) as extractant. Both extractants synergised when combined, as indicated in the previous section. Under these conditions, the total extracted SCFAs consisted mainly of formic (14 \pm 2 % of total SCFAs weight in feed) and acetic (10.4 \pm 0.1 % of total SCFAs weight in feed) acids, followed by propionic and lactic acids (4.0 \pm 0.2 % and 3.77 \pm 0.01 % of total SCFAs weight in feed each). Altogether, a maximum of 34 % of total SCFAs weight in feed was extracted under these conditions.

Additionally, ANOVA analysis was performed for each of the SCFAs, considering the type of extractant and its concentration as factors, with the KD values as dependent variable. Three levels were considered for the type of extractant: i) TOA, ii) TBP and iii) T/T and for their concentrations: i) 10 %, ii) 25 % and iii) 40 %.

In the case of oxalic and lactic acids, statistically significant differences (p-value < 0.05) of both type of extractant, concentration and the interaction between extractant and concentration were observed. Subsequent Tukey's HSD *post hoc* tests were performed between the type of extractant pairs, concentration pairs and the type of extractant and concentration pairs. For oxalic acid, statistically significant differences (p-value < 0.05) were found between all pairs of extractants (TOA-TBP, TOA-T/T and TBP-T/T). For lactic acid, statistically significant differences (p-value < 0.05) were found between extractants pairs TOA-T/T and TBP-T/T, and concentration pairs 10–25 % and 25–40 %. The results are presented in Table 4.

For maleic, pyruvic, formic and acetic acids, statistically significant differences (p-value < 0.05) were observed for the type of extractant and concentration. Subsequent Tukey's HSD *post hoc* tests were performed between the type of extractant pairs and concentration pairs. For maleic, pyruvic and formic acids, statistically significant differences (p-value < 0.05) were found between extractant pairs TOA-T/T and TBP-T/T. For acetic acid, statistically significant differences (p-value < 0.05) were found between all extractant pairs (TOA-T/T, TOA-TBP and TBP-T/T) and concentration pairs 10–25 % and 25–40 %. The results are presented in Tables 4 and 5.

For lactobionic and malic acids statistically significant differences (p-

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value < 0.05) were observed for the type of extractant. Subsequent Tukey's HSD *post hoc* tests were performed between the type of extractant pairs. For lactobionic acid, statistically significant differences (p-value < 0.05) were found between extractant pairs TOA-T/T and TOA-TBP. For malic acid, statistically significant differences (p-value < 0.05) were found between extractant pair TOA-TBP. The results are presented in Table 4.

For propionic acid no statistically significant differences (p-value < 0.05) were observed.

3.3.2. Effect of temperature on organic acid extraction

Based on the results obtained, TOA25, TBP25 and T/T10 were the chosen solvents for the temperature study. Additionally, synthetic solutions containing the same quantities of SCFAs as those found in the pre-purified WAS were prepared and subjected to extraction to evaluate

the effect of the matrix. The extraction yields obtained for total, NVAs and VAs are shown in Fig. 6.

As it can be seen in Fig. 6, temperature had a generally positive effect on the extraction of both NVAs and VAs from pre-purified WAS in the range 25 °C–50 °C. It is important to note that a further increase in temperature could lead to a loss of extractables caused by thermal degradation [49,92]. Higher yields were observed for total NVAs, ranging from 18.8 % to 72.6 %, compared to total VAs, in which the values varied from 22.7 % to 46.1 %. These results are in agreement with those reported by other authors when SCFAs from oxidised Kraft black liquor was extracted with 30 % TOA in heptane in the range 25–55 °C, who obtained extraction yields for NVAs and VAs, which varied from 28 % to 72 %, and from 15 % to 45 %, respectively [56]. Additionally, the influence of temperature was more pronounced for TOA25 and T/T10 in comparison to TBP25. Thus, in the temperature range of 25 °C–50 °C,



Fig. 6. Effect of temperature in extraction yields of total (\blacksquare), non-volatile SCFAs (\blacksquare) and volatile SCFAs (\blacksquare) from WAS (a) and synthetic SCFAs solution (b). Different letters in total SVFAs, non-volatile SCFAs, and volatile SCFAs indicate significant differences (p < 0.05).

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the extraction yields for NVAs and VAs with TOA25 and T/T10 were notably higher, showing increases of 2.4 times and 1.5 times, respectively, at 50 °C compared to 25 °C forTOA25, and of 2.8 and 1.4 times, respectively, in the case of T/T10. T/T10 was the most efficient solvent for total SCFAs at all temperatures, with slightly higher yields than TOA25. The extraction yields for NVAs were higher with TOA25, while they were higher for VAs using T/T10.

The extraction of SCFAs from the synthetic solution showed that the components present in the sludge matrix hindered the LLE. As a result, the extraction yields of NVAs and VAs were significantly higher than those of WAS for every solvent and temperature. Besides, the synergistic effect of both extractants was more significant in synthetic solution for both NVAs and VAs, achieving complete separation with T/T10 at 50 °C. Additionally, the theoretical extraction order was neither observed in the synthetic solution. Therefore, it can be concluded that the presence of multiple SCFAs can also alter the theoretical distribution constants, presumably due to competition influenced by the different concentrations in which the SCFAs are present [93].

In this case, a positive effect of temperature was also observed for the extraction of VAs from synthetic solution when temperature increased from 25 $^{\circ}$ C to 50 $^{\circ}$ C. The most marked influence was obtained with

TBP25 in which the yield increased 1.6 times at 50 °C compared to 25 °C (44.9 %). However, in the case of TOA25, a slight detrimental effect of temperature was observed for NVAs, where the yield decreased from 94.8 % at 25 °C to 89.1 % at 50 °C.

Besides, the highest extraction yields were obtained with the T/T10 solvent at all temperatures. This showed the beneficial synergistic effect of TOA and TBP for both real and synthetic solutions. TBP25 exhibited the lowest extraction efficiency for WAS at 40 and 50 $^{\circ}$ C, although it yielded slightly better results than TOA25 at 25 $^{\circ}$ C. In the case of synthetic solutions, TBP25 consistently produced the lowest yields across all temperatures.

Furthermore, ANOVA analysis was conducted for the extraction yields of the total SCFAs, NVAs and VAs in both WAS and synthetic solution. The analysis considered the type of extractant and temperature as factors, with the yields as the dependent variable. Three levels were considered for the type of extractant: i) TOA, ii) TBP and iii) T/T and for temperature: i) 25 °C, ii) 40 °C and iii) 50 °C. For both WAS and synthetic solution, significant differences (p-value < 0.05) in total SCFAs, NVAs and VAs were observed for both the type of extractant and temperature, as well as for the interaction between extractant and temperature. Subsequent Tukey's HSD *post hoc* tests were performed between

Table 7

K_D values for non-volatile and volatile SCFAs using TOA25, TBP25 and T/T10 as solvent mixtures in the temperature range 25 °C-50 °C.

WAS									
T (°C)	Oxalic			Maleic			Pyruvic		
	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10
25 40 50	$\begin{array}{c} 0.14 \pm 0.05^{b} \\ 1.8 \pm 0.3^{a} \\ 2.4 \pm 0.9^{a} \end{array}$	$\begin{array}{c} 0.006 \pm 0.001^b \\ 0.32 \pm 0.9^b \\ 0.6 \pm 0.4^b \end{array}$	$\begin{array}{c} 0.36 \pm 0.06^{b} \\ 1.1 \pm 0.3^{a} \\ 1.8 \pm 0.9^{a} \end{array}$	$\begin{array}{c} 0.4 \pm 0.1^c \\ 2.4 \pm 0.3^b \\ 4.8 \pm 0.3^a \end{array}$	$\begin{array}{c} 0.24 \pm 0.01^c \\ 0.64 \pm 0.09^c \\ 0.8 \pm 0.5^c \end{array}$	$\begin{array}{l} 0.054 \pm 0.004 \ ^{cd} \\ 1.0 \pm 0.4^{c} \\ 3.0 \pm 0.4^{b} \end{array}$	$\begin{array}{c} 0.10 \pm 0.01^c \\ 2.2 \pm 0.3^a \\ 2.6 \pm 0.3^a \end{array}$	$\begin{array}{c} 0.067 \pm 0.007^c \\ 0.4 \pm 0.2^c \\ 0.4 \pm 0.3^c \end{array}$	$\begin{array}{c} \text{n.d}^1 \\ 1.0 \pm 0.3^b \\ 1.1 \pm 0.3^b \end{array}$
T (°C)	Lactobionic			Malic			Lactic		
	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10
25 40 50	n.d ¹ * *	0.38 ± 0.03 ^a * *	0.7 ± 0.8 ^a *	$\begin{array}{c} 3.80 \pm 0.06^{a} \\ 1.9 \pm 0.3^{a} \\ 2.8 \pm 0.8^{a} \end{array}$	$\begin{array}{c} 11 \pm 11^{a} \\ 1.1 \pm 0.2^{a} \\ 0.9 \pm 0.2^{a} \end{array}$	$\begin{array}{c} n.d^{1} \\ 1.6 \pm 0.1^{a} \\ 2.2 \pm 0.5^{a} \end{array}$	$\begin{array}{c} 0.55 \pm 0.09^{b} \\ 0.8 \pm 0.4^{b} \\ 1.2 \pm 0.1^{b} \end{array}$	$\begin{array}{c} 0.09 \pm 0.01^{b} \\ 0.8 \pm 0.3^{b} \\ 0.5 \pm 0.3^{b} \end{array}$	$\begin{array}{c} 8\pm1^a\\ 1.0\pm0.4^b\\ 1.0\pm0.4^b\end{array}$
T (°C)	Formic			Acetic			Propionic		
	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10
25 40 50	$\begin{array}{c} 0.4 \pm 0.3^{c} \\ 1.2 \pm 0.1^{c} \\ 1.5 \pm 0.3^{c} \end{array}$	$\begin{array}{c} 0.3 \pm 0.1^c \\ 0.46 \pm 0.08^c \\ 0.6 \pm 0.3^c \end{array}$	$\begin{array}{l} 5\pm3^{b}\\ 2.2\pm0.2^{bc}\\ 5.6\pm0.4^{a} \end{array}$	$\begin{array}{c} 0.38 \pm 0.07^b \\ 0.5 \pm 0.1^a \\ 0.6 \pm 0.1^a \end{array}$	$\begin{array}{c} 0.20 \pm 0.03^b \\ 0.35 \pm 0.04^b \\ 0.30 \pm 0.02^b \end{array}$	$\begin{array}{c} 0.24 \pm 0.03^{b} \\ 0.45 \pm 0.08^{a} \\ 0.6 \pm 0.1^{a} \end{array}$	$\begin{array}{c} 1.15 \pm 0.09^{a} \\ 1.0 \pm 0.5^{a} \\ 2 \pm 1^{a} \end{array}$	$\begin{array}{c} 1.07 \pm 0.07^{a} \\ 1.1 \pm 0.6^{a} \\ 1.4 \pm 0.5^{a} \end{array}$	$\begin{array}{c} 1.1 \pm 0.1^{a} \\ 1.9 \pm 0.9^{a} \\ 2.1 \pm 0.8^{a} \end{array}$

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T (°C)	Oxalic			Maleic			Pyruvic		
	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10
25	*	0.3 ± 0.1	*	11.2 ± 0.7^{a}	0.524 ± 0.009^d	5 ± 1^{b}	*	*	*
40	*	*	*	*	0.4 ± 0.1^{d}	*	*	*	*
50	*	*	*	4.7 ± 0.3^{c}	$1.2\pm0.2^{\rm d}$	*	*	*	*

T (°C)	Lactobionic			Malic			Lactic	Lactic		
	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	
25	2.4 ± 0.3^a	2.3 ± 0.2^{a}	2.0 ± 0.2^{a}	*	$2.2\pm0.2^{\rm a}$	*	*	*	7 ± 3^{a}	
40	$2.0\pm0.2^{\rm a}$	$0.2\pm0.1^{\rm c}$	*	*	*	*	5 ± 2^{a}	*	*	
50	0.58 ± 0.04^{c}	$1.8\pm0.2^{ m b}$	*	*	$2.1\pm0.9^{\mathrm{a}}$	*	*	*	*	

T (°C)	Formic			Acetic			Propionic		
	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10	TOA25	TBP25	T/T10
25 40 50	$\begin{array}{c} 5.2 \pm 0.3^{d} \\ 5.2 \pm 0.5^{d} \\ \ast \end{array}$	0.69 ± 0.07^{e} * 7.1 ± 0.9 ^c	$\begin{array}{c} 16\pm1^{b} \\ 19.8\pm0.8^{a} \\ \ast \end{array}$	$\begin{array}{l} 7\pm1^b\\ 6.0\pm0.8^b\\ 7.9\pm0.6^{ab} \end{array}$	$\begin{array}{c} 1.1 \pm 0.2^d \\ 0.91 \pm 0.05^d \\ 1.6 \pm 0.1^d \end{array}$	$\begin{array}{c} 4.4 \pm 0.8^c \\ 3.5 \pm 0.9^c \\ * \end{array}$	n.d. n.d. 1.0 ± 0.4^{a}	n.d. n.d. 1.5 ± ^a 0.3	n.d. n.d. *

* Large: SCFA not detected in aqueous phase.

¹ n.d.: not detected. Different letters in K_D values of each SCFAs indicate significant differences (p < 0.05).

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the type of extractant pairs, temperature pairs and the type of extractant and temperature pairs. All the results are presented in Fig. 6.

For WAS, statistically significant differences (p-value <0.05) were found between all pairs of temperatures (25–40 °C, 25–50 °C, and 40–50 °C) and all pairs of extractants (TOA-TBP, TOA-T/T and TBP-T/T) for total SCFAs, NVAs and VAs.

For synthetic solution, statistically significant differences (p-value < 0.05) were found between all temperature pairs (25–40 °C, 25–50 °C, and 40–50 °C) and extractant pairs TOA-TBP and TBP-T/T for total SCFAs. In the case of NVAs, statistically significant differences (p-value < 0.05) were found between temperature pairs 25–50 °C, and 40–50 °C, and extractant pairs TOA-TBP and TBP-T/T. For VAs, statistically significant differences (p-value < 0.05) were found between all temperature pairs 25–50 °C, and 40–50 °C, and extractant pairs TOA-TBP and TBP-T/T. For VAs, statistically significant differences (p-value < 0.05) were found between all temperature pairs (25–40 °C, 25–50 °C, and 40–50 °C) and extractant pairs TOA-TBP and TBP-T/T.

The values of K_D for the extraction from pre-purified WAS and synthetic solutions are shown in Table 7.

The K_Ds observed were in line with those reported by other authors [28,94]. Türk et al. [95] obtained K_Ds in the range of 0.638–1.609 for acetic acid and of 0.496–1.502 for formic acid extracting with TBP diluted in cyclopentyl methyl ether and 2-methyltetrahydrofuran at similar extractant concentrations. Nonetheless, the K_Ds for oxalic, pyruvic, and propionic acids were lower than those found in the literature [29,86,96,97]. For instance, Keshav et al. [98] achieved K_Ds in the range of 5.72–10.11 for propionic acid while extracting TOA 30 % in oleyl alcohol, while in our case it could only be extracted at 50 °C with a K_D of 1.0 \pm 0.4. It should be noted than these studies analysed the extraction of the pure acid, without the hindering effects of a complex matrix or the competition with other SCFAs for the formation of complexes with the solvent.

Besides, ANOVA analysis was performed for each of the SCFAs in both WAS and synthetic solution. The analysis considered the type of extractant and temperature as factors, with the K_D values as the dependent variable. Three levels were considered for the type of extractant: i) TOA, ii) TBP and iii) T/T and for temperature: i) 25 °C, ii) 40 °C and iii) 50 °C.

For WAS, significant differences (p-value < 0.05) were observed in oxalic, maleic, pyruvic, lactic, formic and acetic acids for both the type of extractant and temperature, as well as for the interaction between extractant and temperature. However, no statistically significant differences (p-value < 0.05) were observed for lactobionic, malic and propionic acids.

Subsequent Tukey's HSD post hoc tests were specifically conducted for the SCFAs with significant differences, considering the type of extractant pairs, temperature pairs and the type of extractant and temperature pairs. For oxalic and acetic acids, significant differences (pvalue < 0.05) were presented between temperature pairs 25–40 °C and 25-50 °C, and extractant pairs TOA-TBP and TBP-T/T. For maleic acid, significant differences (p-value < 0.05) were presented between all temperature pairs (25-40 °C, 25-50 °C and 40-50 °C) and all extractant pairs (TOA-TBP, TOA-T/T and TBP-T/T). For pyruvic acid, significant differences (p-value < 0.05) were presented between temperature pairs 25-40 °C and 25-50 °C, and all extractant pairs TOA-TBP, TOA-T/T and TBP-T/T. For lactic acid, significant differences (p-value < 0.05) were presented between temperature pairs 25-40 °C and 25-50 °C and extractant pairs TOA-T/T and TBP-T/T. For formic acid, significant differences (p-value < 0.05) were presented between temperature pair 40–50 °C, and extractant pairs TOA-T/T and TBP-T/T. All the results are presented in Table 7.

For the synthetic solution, statistically significant differences (p-value < 0.05) were observed for maleic, lactobionic, formic and acetic acids in terms of the type of extractant, temperature, and interaction between extractant and temperature. Conversely, no statistically significant differences (p-value < 0.05) were observed for malic, lactic, and propionic acids. Subsequent Tukey's HSD *post hoc* tests were specifically conducted for the SCFAs with significant differences, considering the

type of extractant pairs, temperature pairs and the type of extractant and temperature pairs.

For maleic and formic acids, significant differences (p-value < 0.05) were presented between all temperature pairs (25–40 °C, 25–50 °C and 40–50 °C) and all extractant pairs (TOA-TBP, TOA-TT and TBP-T/T). For lactobionic acid, significant differences (p-value < 0.05) were presented between temperature pairs 25–40 °C and 25–50 °C, and all extractant pairs (TOA-TBP, TOA-TT and TBP-T/T). For acetic acid, significant differences (p-value < 0.05) were presented between temperature pairs 25–50 °C, and all extractant pairs (TOA-TBP, TOA-TT and TBP-T/T). For acetic acid, significant differences (p-value < 0.05) were presented between temperature pairs 25–50 °C, and all extractant pairs (TOA-TBP, TOA-TT and TBP-T/T). All the results are also presented in Table 7.

4. Conclusions

WO proved to be an efficient treatment for the valorisation of WAS, converting a significant portion of the natural organic matter into valueadded SCFAs. Optimal conditions involved lower temperatures and longer reaction times (160 °C, 240 min), resulting in a peak SCFAs concentration of 6.07 g/L.

Membrane filtration effectively pre-purified the SCFAs present in the oxidised WAS, facilitating the subsequent extraction. Operating in TR mode resulted in average rejections of 53 % of CN and 48 % of TOC and also negative rejections of the SCFAs (-15 %) due to the Donnan effect. Subsequent filtration of the 50 kDa permeate with the 1 kDa membrane in TR mode further purified the SCFAs, achieving rejections of 73 % for CN and 39 % for TOC, with a low SCFAs rejection of 4 %. Concentrating the oxidised WAS was considered impractical due to the substantial flux loss and the increased rejection of SCFAs. In all cases, the main fouling mechanism was cake formation, indicating that non-aggressive cleaning protocols can be applied to maintain membrane efficiency.

LLE extraction with a mixture of TOA and TBP at 10 % in octan-1-ol was found to be the most suitable for the recovery of both NVAs and VAs, obtaining a total yield of 34 %. This proved the synergistic effect of the two extractants during the extraction of SCFAs. Lower extraction yields were obtained with the pre-purified WAS compared to synthetic solutions of SCFAs, thus showing the detrimental effect of the matrix in LLE. Increasing the temperature within the range of 25–50 °C generally had a favourable effect on the extraction of SCFAs.

CRediT authorship contribution statement

Daniel Núñez: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Martina Zabatta: Writing – original draft, Investigation. Paula Oulego: Writing – review & editing, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. Sergio Collado: Data curation. Francisco A. Riera: Funding acquisition. Mario Díaz: Supervision, Project administration, Funding acquisition.

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.

Data availability

Data will be made available on request.

Acknowledgements

The authors are grateful for the financial support from the Spanish Ministry of Science and Innovation through the projects MCIU -19-RTI2018-094218-B-I00 and MCIU-22-PID2021-125942OB-I00. Authors also want to acknowledge the Employment, Industry and Tourism Office of the Principality of Asturias, Spain, for their financial support through the project AYUD/2021/51041. The author Daniel Núñez thanks the Principality of Asturias, Spain, for their financial support through the Severo Ochoa scholarship n^{o} BP19-093.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.126815.

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