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Flow-based recovery of acetic acid from aqueous solutions using bio-derived terpenes as extracting solvents

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ABSTRACT

The ability to recover acetic acid and related byproducts from wastewater treatment plants would unlock a sustainable source of important building block-chemicals that are currently derived from fossil fuels. We report here a two-stage flow-based procedure for the extraction and alkaline back-extraction of acetic acid from an aqueous feed solution, using geraniol or eucalyptol as bio-derived organic solvents. In the first stage, acetic acid is extracted from the feed solution into the organic solvent; and, in the second stage, acetic acid is back-extracted into a 2-M $NaOH_{aq}$ solution, leaving a regenerated solvent that may be used for further extractions. Recovery efficiencies of up to 51 % and 37 % were obtained using geraniol and eucalyptol, respectively. By back-extracting acetic acid into a smaller volume of NaOH than the feed solution from which it was extracted, more than three-fold enhancements in acetic acid concentration were achieved with respect to the feed solution. Overall acetic acid recovery efficiencies of 57 ±1% and 46 ±2% were obtained for geraniol and eucalyptol, respectively. Both solvents were successfully used for multiple extraction/back-extraction cycles, with geraniol giving a stable concentration of back-extracted acetic acid over the course of ten cycles.

1. Introduction

In wastewater treatment plants, volatile fatty acids (VFAs) are produced as a byproduct of the anaerobic digestion of organic matter. Wastewater VFAs could potentially be used as “building-block” chemicals for the production of plastics, pharmaceuticals and other high value chemicals if methods could be found to recover them efficiently from wastewater effluent [1]. This would have the effect of transforming treatment plants into biorefineries, consistent with the principles of a circular economy [2]. VFAs are conventionally produced from petrochemical sources, with acetic acid being one of the most important due to its extensive use in industrial chemistry [3]. Bio-derived VFAs offer a sustainable alternative, and significant efforts are currently underway to optimise anaerobic digesters for their efficient production [4–6].

In addition to increasing the volume of VFAs produced in the effluent, it is also necessary to develop effective methods for extracting them from the effluent [7]. A variety of potential processes for VFA extraction have been reported, including adsorption onto solid frameworks [8], membrane-based technologies [9], and liquid–liquid extraction (LLE) [10–12]. LLE has several advantages – including simplicity and convenience – and has been successfully used to recover VFAs and other acids, such as lactic [13] and formic acid [14]. However, there is a need to find sustainable, low toxicity solvents to replace the hazardous, fossil-fuel derived solvents that are currently used for their extraction [15].

Terpenes and terpenoids are nature’s most diverse plant-derived compounds [16]. They have several properties that make them attractive as solvents. They are non-toxic, biodegradable, renewable, and have good solvating properties [17,18]. They are also inexpensive and widely available, making them a cost-effective alternative to many synthetic solvents [17,18]. Because of their hydrophobic nature, they have been employed for the extraction of a wide variety of biomolecules from aqueous solutions, including lipids, carotenoids, phenolic compounds derived from food products [19,20], microalgae [21,22], alcohols [23,24], pharmaceuticals [25,26], pesticides [27], phenols [28,29], and VFAs [11,30]. Terpenes and terpenoids can also be combined to form eutectic solvents [11,18,20,31–38] that offer a broadened range of operating temperatures.

Following the transfer of the VFA to the extracting organic solvent, it is necessary to return it to the aqueous phase and restore the extracting

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solvent to its original form so it may be used for further extractions. This may be achieved in a number of ways, including distillation [39], temperature swing [40], and reactive back-extraction (RBE) using, for example, alkaline solutions [12,41]. RBE has the advantage of being efficient (in terms of both materials recovery and energy usage), requiring only mild reaction conditions that do not damage sensitive materials, and being applicable to a broad range of solutes and solvents [42]. When alkaline solutions are used to extract VFAs, carboxylates are formed that pass into the aqueous phase due to their higher polarity, leaving a purified solvent that can be used for further extraction [12,13,43].

Liquid-liquid extraction offers valuable advantages regarding short cycle and efficient mass transfer. However, the prudent selection of environmentally friendly solvents with low toxicity remains critical to this extraction process [44,45]. In this regard, terpenes emerge as a promising option due to their inherent stability and extraction capabilities, rendering them highly suitable candidates for consideration. In this work we investigate the use of two specific terpenes – geraniol and eucalyptol – as solvents to extract acetic acid – one of the most abundant VFAs in the effluent of anaerobic digesters but also one of the most challenging to extract because of its high polarity [10–12]. Geraniol was selected on the basis of earlier work where we found it to be an excellent extractant for VFAs [30]. Eucalyptol – which to our knowledge has not previously been used for VFA extraction – was chosen following an initial screening of terpenes as solvents for acetic acid using the COSMO-RS method [46,47].

We also report here a two-stage microfluidic flow-reactor that incorporates acetic extraction using geraniol or eucalyptol (stage 1) with reactive back-extraction of acetic acid by aqueous NaOH and simultaneous regeneration of the terpene solvent (stage 2). The application of microfluidics to LLE processes has great potential, offering several advantages over traditional batch processes, such as improved mass transfer between phases and the ability to operate in a closed-cycle format with continuous regeneration of the extracting solvents [48,49]. Microfluidic formats also allow for rapid and extensive screening of extraction conditions due to the small sample volumes needed, and hence can be used to improve the efficiency and cost-effectiveness of extraction processes [50].

The separation of the (immiscible) aqueous and organic liquid streams in the extraction and back-extraction steps can be performed using membrane-based liquid–liquid separators, exploiting differences in the wettability of the two phases to the membrane to spatially divide the liquids [51,52]. In the set-up used here, one separator is used to separate the (acetic-acid-containing) terpene from the feed solution after the initial extraction, while a second separator is used to separate the regenerated terpene from (carboxylate-containing) aqueous NaOH following back-extraction.

When considering the choice between direct, single-stage distillation and extraction-distillation, the decision depends on the concentration of acetic acid. Distillation alone is economically feasible for streams containing >50 wt% acetic acid. However, for concentrations below this threshold, a preliminary separation process, such as liquid–liquid extraction, is required [44]. Different simulation processes for organic acid extraction encounter elevated recovery costs when operating at 1 wt% or lower concentrations [44]. Therefore, a preliminary concentration stage can be effectively employed to obtain more concentrated streams, thus mitigating the cost implications. Although there are already design proposals and simulations for the extraction of lactic acid [11,13], and extraction-distillation systems for VFAs [53], to the authors' knowledge, this is the first time that a continuous process for the extraction and alkaline back-extraction of acetic acid has been experimentally realised.

2. Methods and materials

2.1. Chemicals

The suppliers, purities, CAS numbers, structures, and physical properties of the chemicals used in this work are listed in Table S1 of the Supplementary Material. The aqueous solutions were prepared using ultrapure water from a Purelab Flex Elga Veolia water purification system.

2.2. Fluidic setup for extraction and back-extraction of acetic acid

All experiments were carried out at room temperature. The fluidic system was based on a small number of fluidic components, linked together by PTFE tubing of Ø1mm × Ø2 mm. Injection of liquids into the system was achieved using Kd Scientific LEGATO210 syringe pumps and Hamilton Gastight #1015 precision glass syringes of volume 50, 20, or 10 mL (depending on the flow-rates of the experiments). Immiscible liquid streams were combined into droplet flows using Y-shaped mixers based on a previously reported design [54]. Droplet flows were separated into discrete organic and aqueous flow streams, using liquid–liquid phase-separators based on a short segment of porous, extruded PTFE tubing with ID 0.70 ± 0.02 mm, OD 0.098 ± 0.02 mm, and average pore size 20 µm (Aeos ePTFE).

The pore size and its distribution, along with the viscosities, densities, interfacial tensions, and flow rates of the incoming liquids within the porous capillary, as well as the fluidic resistance of the downstream flow components, all contribute to the determination of the optimal pressure for the through-outlet adjusted with the needle valves. Generally, a smaller pore size is required when the interfacial tension is lower. However, it is important to note that reducing the pore size limits the maximum viscosity that the membrane can handle. Additionally, a smaller pore size leads to a decrease in the overall throughput of the device [52,55–57]. The pore size chosen for this study has proven effective in intermediate viscosity systems, including water-chloroform [55], water-toluene [52], and water-fluorous oil [54], with flow rates ranging from 10 to 1000 µL/min. The literature provides varying pore sizes for liquid–liquid separators, depending on the specific application and system under investigation. For instance, in separations involving low interfacial tension systems such as (water + methanol)-ethyl acetate, a pore size as small as 0.1 µm is necessary [58]. Conversely, membrane pore sizes increase to approximately 1 µm in systems like water-sulfonated kerosene [59] or water-toluene [60]. Moreover, in highly viscous systems employing ionic liquids, even larger pore sizes are required to achieve adequate phase separation [56,61].

A description of the construction, design and operation of the phase-separators has been given in a previous paper [51], and a schematic of the assembled separator is presented in Fig. 1. In brief, injection of a mixed organic/aqueous flow stream into the porous capillary causes the organic phase to permeate the porous capillary wall due to preferential wetting to PTFE, leaving a continuous stream of the aqueous phase to emerge from the end of the capillary (the "through-outlet", **T**). The organic phase floods a hollow jacket surrounding the porous capillary, where it is coerced into a continuous stream and is directed to a second outlet (the "side-outlet", **S**).

There are four separate steps in the extraction/back-extraction procedure. In the first step, the aqueous feed solution is brought into intimate contact with the organic solvent (geraniol or eucalyptol) using a Y-mixer, allowing the VFA molecules to transfer to the organic phase. In the second step, the feed solution and the organic phase containing extracted VFA molecules are separated by means of a phase-separator. In the third step, the (VFA-containing) organic phase is brought into intimate contact with an alkaline solution (2-M $NaOH_{aq}$) using a second Y-mixer, which leads to reactive back extraction of the extracted molecules into the aqueous phase. And, in the final step, the organic phase and the alkaline solution are separated by means of a second phase-separator,

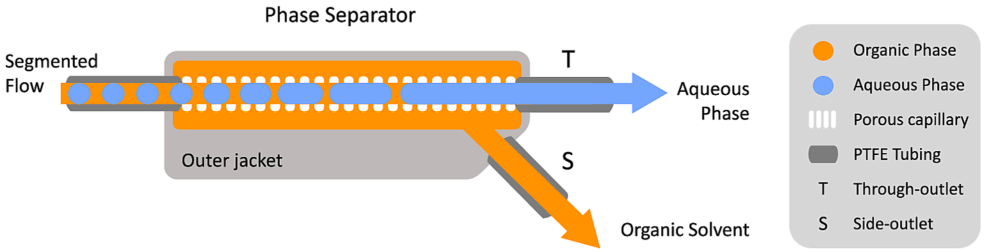

Fig. 1. Schematic of capillary-based liquid–liquid separator, comprising a short length of porous PTFE tubing inside an aluminium jacket. When an organic/aqueous two-phase flow is injected into the separator from the left, the organic phase preferentially wets the walls of the porous capillary and permeates the walls, filling a small chamber surrounding the capillary and leaving a continuous stream of the aqueous phase inside the capillary. The organic phase emerges as a continuous stream from the side-outlet S, while the aqueous phase emerges as a continuous stream from the through-outlet T.

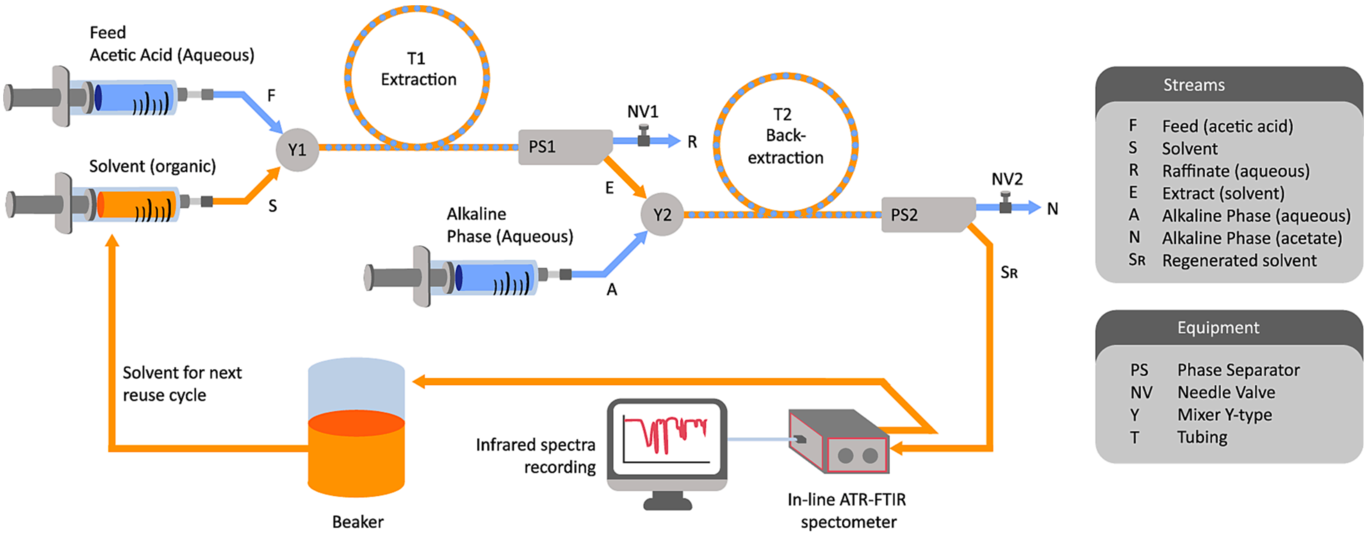

Fig. 2. Schematic of the setup used for the extraction and back-extraction of acetic acid, using geraniol or eucalyptol as the extracting solvent **S**.

leaving an alkaline solution of the VFA molecules and a “scrubbed” organic solvent that can be used for further VFA extraction.

The complete fluidic set-up is shown in Fig. 2. The feed solution (**F**) of acetic acid and the solvent (**S**) were separately injected into the system at constant volumetric flow rates and combined using the first mixer (**Y1**), generating a droplet flow with a high interfacial area to enhance solute exchange [62]. The extraction process was allowed to occur by passing the resulting droplet stream through an extended length of PTFE tubing **T1** that connected the outlet of **Y1** to the input of the first phase-separator (**PS1**). The efficiency of mass transfer in **T1** depends on the residence time inside this tubing, and could be controlled by changing the tubing length and/or the solvent flow rates, with longer tubing and slower flow rates providing more time for mass transfer to occur. For the work reported here, a fixed 1-m length of tubing was used between **Y1** and **PS1** for all experiments. Following phase separation inside **PS1**, two outlet streams were obtained – the extract stream (**E**) containing successfully extracted acetic acid molecules and the raffinate stream (**R**) containing residual (unextracted) acetic acid molecules.

To induce back-extraction of the acetic acid into water (and simultaneous regeneration of the solvent), **E** was combined with an alkaline phase (**A**) consisting of 2-M NaOH using a second Y-mixer (**Y2**). The resulting segmented flow was then passed through a 1-m tube (**T2**) to allow time for solute transfer to occur. The segmented flow was then passed into a second phase separator (**PS2**), yielding separate output streams that contained the aqueous phase with VFA-based acetate (**N**) and the regenerated solvent (**S$_R$**). Adjustable needle valves (**NV1**) and (**NV2**) were used to control the phase separation at the outlets of the aqueous phases **R** and **N**, respectively as described in Ref. [51].

The regenerated solvent was collected in a beaker at the outlet. At each subsequent solvent reuse cycle, the collected solvent was reloaded into syringe **S**. For some measurements, an in-line Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectrometer (Arcoptix) was placed immediately before the beaker to monitor the chemical composition of the regenerated solvent stream.

The overall extraction/back-extraction process was visualised using a dye in the aqueous feed, as shown in Figure S1 and Video S1 of the Supplementary Material attached to this work.

2.3. *Experimental tests*

To assess the performance of the experimental set-up, we investigated experimental factors that affect: (i) the efficiency with which acetic acid is extracted from the feed solution **F** into the solvent **S**; and (ii) the final concentration of back-extracted acetic acid in the alkali phase **N**. The feasibility of re-using the terpene solvents for multiple extractions and back-extractions was also investigated.

Feed solutions **F** of acetic acid had concentrations of 1, 5, or 10 g/L, which is typical of the range of concentrations found in effluents and those used in similar studies [2,6]. The alkaline solution **A** was 2-M NaOH$_{aq}$, and the extracting solvent (**S**) was geraniol or eucalyptol. The key experimental parameters used to control the extraction and back-extraction processes were the volumetric flow-rate ratio of solvent to feed-stock α_{SF} and the volumetric flow-rate ratio of solvent to alkaline solution α_{SA}:

$$\alpha_{SF} = \frac{\mathscr{F}_S}{\mathscr{F}_F} \tag{1}$$

$$\alpha_{SA} = \frac{\mathscr{F}_S}{\mathscr{F}_A} \tag{2}$$

Extraction tests were performed at a fixed total flow rate of $\mathscr{F}_S + \mathscr{F}_F = 200$ μL/min, corresponding to a residence time of approximately four minutes in **T1**. Preliminary testing using an acetic acid loading of 10 g/L acetic acid in **F** and balanced flow rates of 100 μL/min each for the feed solution and solvent ($\alpha_{SF} = 1.0$) indicated four minutes was sufficient to achieve effective transfer of acetic acid from the aqueous feed solution to the extracting solvent, see Fig. S2.

2.3.1. *Influence of $\boldsymbol{\alpha_{SF}}$ on the extraction efficiency.*

Tests to determine the influence of α_{SF} on the extraction efficiency were carried out using α_{SF} ratios of 0.5, 1.0, and 2.0, with acetic acid concentrations of 1, 5, and 10 g/L in the feed solution. A fixed solvent-to-alkali ratio of $\alpha_{SA} = 1$ was maintained for these experiments by adjusting the volumetric flow-rate of the alkaline phase **A** to match that of the solvent **S**. For each set of flow conditions, the needle valves **NV1** and **NV2** were adjusted to achieve complete phase separation in the separators, and the system was then allowed to stabilise for two hours before commencing measurements. 1-mL samples of the raffinate (**R**), alkaline solution (**N**), and regenerated solvent ($\mathbf{S_R}$) were then collected every 30 min for a total of five replicates to assess the reproducibility of the results.

2.3.2. *Influence of $\boldsymbol{\alpha_{SA}}$ on the concentration of acetic acid in N*

Tests to determine the influence of α_{SA} on the concentration of acetic acid in **N** were carried out at an initial acetic acid concentration of 5 g/L and a fixed α_{SF} ratio of 2.0, adjusting the flow rate of the alkaline phase **A** to obtain α_{SA} ratios of 2, 4, 10, 20, and 40, and taking sample volumes of **A** of 1, 1, 0.4, 0.2, and 0.2 mL, respectively. For each flow condition, a total of five samples were taken. The interval between samples was 30 min for α_{SA} ratios of 2, 4 and 10 and 60 min for α_{SA} ratios of 20 and 40. 1-mL samples of of **R** and $\mathbf{S_R}$ were also taken at each time. The system was allowed to stabilise for two hours after each adjustment of the flow conditions before collecting any samples.

2.3.3. *Effect of reusing solvent on the extraction and back extraction performance*

The effect of reusing solvent on the extraction and back extraction performance was investigated using a fixed acetic acid concentration of 5 g/L in the feed solution **F**, a fixed α_{SF} ratio of 2.0, and a fixed α_{SA} ratio of 10. The separated solvent stream ($\mathbf{S_R}$) from phase separator **PS2** was passed through an in-line ATR-FTIR spectrometer as shown in Fig. 2 before being collected in a beaker. The initial volume of solvent in the syringe was 15 mL, so system was allowed to stabilise for 37.5 min before starting the cycles (5 mL of solvent has passed through). The extraction and back-extraction were performed for 75 min. During this time, 1.0-mL and 0.5-mL samples of **A** and **N** were collected in triplicate every 15 min, leaving an initial 30-min delay after starting the flow. After 75 min, 10 mL of the solvent in the syringe (**S**) had been depleted, so the syringe was refilled with 10 mL of regenerated solvent ($\mathbf{S_R}$) collected in the beaker, and the procedure was repeated. 10 cycles were carried out in this way, with each cycle involving the re-use of collected solvent from the previous stage. Three infrared spectra were recorded with a delay of 5 min in each sample collection, with a total of 9 in each cycle stage (3 spectra for each sample). Subsequently, they were processed to an average spectrum in each cycle stage.

2.4. *Samples analysis*

The aqueous samples were analysed by high performance liquid chromatography (HPLC), see Table S2 of Supplementary Material for further details. Alkaline phase samples were diluted by a factor of two, and neutralised with 2-M H_2SO_4 before HPLC analysis.

Solvent samples were analysed using a Karl Fischer Mettler Toledo C10S Coulometric KF Titrator to determine their water content.

3. Results and discussion

3.1. *Effect of acetic acid loading and α_{SF} on extraction efficiency*

3.1.1. *Extraction efficiency*

The efficiency η_{ex} with which acetic acid is extracted from the feed solution is given by the equation:

$$\eta_{ex} = \frac{m_0 - m_R}{m_0} \tag{3}$$

where m_0 is the mass of acetic acid injected from the feed-solution and m_R is the mass of acetic acid collected in the raffinate in a time Δt. In the ideal situation, where there is no mixing of water with the solvent and liquid–liquid separation is perfect, the injected volume V_0 of feed solution will equal the volume V_R of the raffinate, and we can write

$$\eta_{ex}^{I} = \frac{m_0 - m_R}{m_0} = \frac{C_0 V_0 - C_R V_R}{C_0 V_0} = \frac{C_0 V_0 - C_R V_0}{C_0 V_0} = \frac{C_0 - C_R}{C_0} \tag{4}$$

where C_0 and C_R are the measured concentrations of acetic acid in the feed solution and raffinate (determined by HPLC), and the superscript I indicates we have assumed equal volumes for the feed solution and raffinate, i.e. no intermixing of the aqueous phase with the solvent phase.

It is common in the literature to calculate extraction efficiencies using Eq. (4) [63,64]. However, for the solvents used here, there is a small net flow of liquid from the aqueous phase to the organic phase due to partial miscibility between the two terpenes and water, meaning η_{ex}^{I} is a biased estimate that is lower than the true extraction efficiency η_{ex} – see Supplementary Material. (For a net flow of liquid from the organic phase to the aqueous phase, Eq. (4) would overestimate the extraction efficiency).

Fig. 3 shows the estimated extraction efficiency η_{ex}^{I} determined from Eq. (4), using a fixed total flow-rate of $\mathscr{F}_S + \mathscr{F}_F = 200$ μL/min with acetic acid loadings of 1, 5 and 10 g/L and α_{SF} ratios of 0.5, 1.0 and 2.0. The estimated extraction efficiencies were found to be broadly independent of the acetic acid loading in agreement with previous reports for

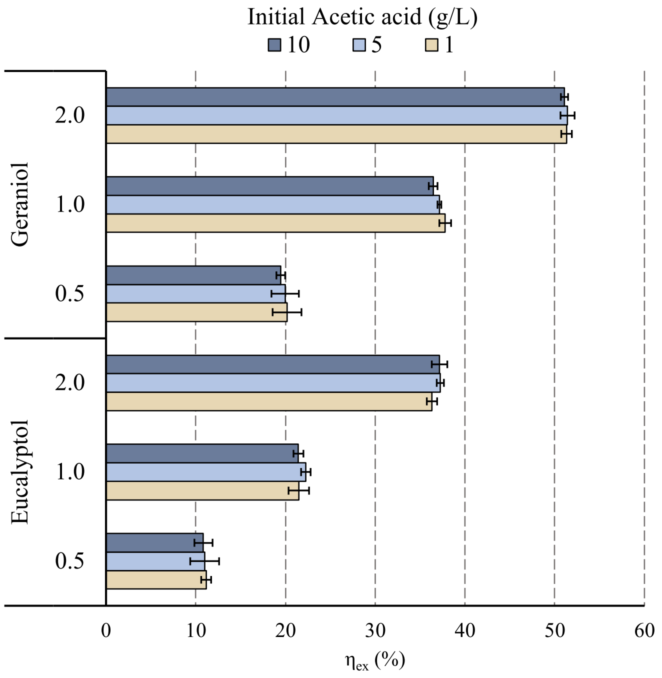

Fig. 3. Estimated acetic acid extraction efficiencies η_{ex}^{I} determined from Eq. (4) at a fixed total volumetric flow rate in **T1** of $\mathscr{F}_S + \mathscr{F}_F = 200$ μL/min, using α_{SF} ratios of 0.5, 1.0 and 2.0 and initial acetic acid loadings C_0 of 1, 5 and 10 g/L with geraniol or eucalyptol as the extracting solvent.

batch extraction of acetic acid into menthol: lauric acid, where the extraction efficiency was found to be constant in the range 1–10 g/L. [10,65].

For each of the acetic acid loadings tested, a substantial increase in η_{ex}^{I} was observed when the α_{SF} ratio was increased from 0.5 to 2.0. For geraniol η_{ex}^{I} increased by a factor of 2.5 from 20 % to > 50 %, while for eucalyptol, it increased by a factor of 3.6 from 10 % to 36 %. Increasing α_{SF} for a fixed total volumetric flow-rate has two effects: firstly, it decreases the size of the feed solution droplets (since a smaller volume of feed solution is injected per unit time); and, secondly, it increases the volume of solvent relative to feed solution. Both effects lead to increased transfer of solute from the feed solution to the solvent, increasing the extraction efficiency. (Note, increasing α_{SF} beyond 2.0 to further enhance the extraction efficiency is possible, but was not pursued here as – for a fixed total flow-rate of 200 µL/min – higher α_{SF} ratios correspond to lower flow-rates of feed solution and a lower concentration of acetic acid in the extracting solvent, which in turn leads to a lower concentration of acetic acid after back-extraction).

From Fig. 3 it is evident that in all cases η_{ex}^{I} for geraniol is substantially higher than η_{ex}^{I} for eucalyptol. For instance, at an α_{SF} ratio of 2.0 and an acetic acid loading of 1 g/L, the extraction efficiency was 51.3 % for geraniol compared to 36.3 % for eucalyptol.

Table 1 summarises key literature results for acetic acid extraction at a feed concentration of 10 g/L and a solvent-to-feed ratio of one, using a variety of solvent systems. In contrast to the flow-based work described here, the literature results in Table 1 were obtained in a batch format.

The highest acetic acid extraction efficiencies (of up to 60 %) have typically been obtained using co-mixtures of trioctylphosphine oxide (TOPO) and various organic solvents, although Liu et al. [11] recently reported an extraction efficiency of 62 % using a eutectic solvent based on a 2:1 mixture of n-di-n-butylacetamide (DBA) and geraniol. The estimated single-stage extraction efficiencies of 36 % and 21 % for geraniol and eucalyptol reported here are lower than the values using TOPO and DBA/geraniol. However, neither TOPO, DBA or any of the other solvent systems listed in the upper section of Table 1 is considered to be a sustainable solvent, and several of the solvents are incompatible with alkali back-extraction. For instance, poor solvent stability has been reported when using NaOH to back-extract acetic acid from eutectic solvents formed from medium-chain fatty acids due to the solvents becoming deprotonated [65], while using amides under alkaline conditions carries a high risk of hydrolysis during the back-extraction process [68]. For this reason, Liu et al. attempted without success to carry out back-extraction of acetic acid from a DBA/geraniol solvent mixture using ultrapure water (although they did report successful back-extraction of lactic acid using water) [11]. Geraniol and eucalyptol by contrast are compatible with alkali back extraction.

3.1.2. Extraction partition coefficients

We define the mass partition coefficient P_i for the division of a species i between the extract and raffinate as:

$$P_i = m_i^{E} / m_i^{R} \tag{5}$$

where m_i^E and m_i^R are the mass fractions of that species in the Extract (**E**) and Raffinate (**R**), respectively. The acetic acid, water and solvent partition coefficients – P_{aa}, P_{H_2O} and P_{sol} – influence the efficacy of the extraction and back-extraction process (although we note they are not equilibrium values as they depend on the kinetics of the mass transfer processes within the flow reactor and hence depend on the selected flow conditions).

Table 1
Single-stage acetic acid extraction efficiencies reported in the literature and in this work, using a solvent-to-feed ratio of 1.0, an acetic acid loading of 10 g/L in the feed solution and a temperature of approximately 298 K.

Solvent	η_{ex}(%)	Ref
TOPO (20 %) in Kerosene	≈ 60[a]	[66]
C_6OOH	27.3	[63]
C_8OOH	22	[63]
$C_{10}OOH$:methyltrioctylammonium chloride (2:1)	38	[64]
TOPO:$C_{10}OOH$ (1:1)	≈ 22[b]	[65]
TOPO:menthol (2:1)	46.5	[67]
N-di-n-butylacetamide:geraniol (2:1)	≈ 62[a]	[11]
Eucalyptol	21.4	This Work
Geraniol	36.5	This Work

[a] Approximated from graphical illustration.
[b] Calculated from partition coefficient.

Fig. 4 shows P_{aa} values obtained at α_{SF} ratios of 0.5, 1.0 and 2.0, and acetic acid loadings of 1, 5 and 10 g/L. For geraniol at all acetic acid loadings P_{aa} was largest at an α_{SF} ratio of 1.0, while for eucalyptol a progressive increase in P_{aa} was observed as α_{SF} was increased from 0.5 to 2.0.

The water partition coefficients P_{H_2O} were broadly independent of the chosen α_{SF} ratios and acetic acid loadings, with geraniol and eucalyptol yielding partition coefficients of approximately 0.03 and 0.005, respectively (see Figure S3 of the Supplementary Material), indicating a net transfer of water into the solvent phase during the course of the one-stage extraction process due to partial miscibility between the two phases. The higher P_{H_2O} value for geraniol indicates that water dissolves in it more readily than eucalyptol.

The solvent partition coefficients P_{sol} for geraniol and eucalyptol were broadly independent of the α_{SF} ratio with values of around 300 and 1300, respectively, implying minimal loss of solvent to the raffinate in both cases (see Fig. S4). The higher value P_{sol} for geraniol indicates it is less soluble in water than eucalyptol.

3.1.3. Recovery of acetic acid

From simple mass-balance considerations, it may be shown that under conditions of perfect liquid–liquid separation in the two separators and perfect back-extraction in **T2**

$$C_{\mathbf{R}} + C_{\mathbf{N}}^{*} = C_0 \tag{6}$$

where $C_{\mathbf{N}}^{*} = (\alpha_{SF}/\alpha_{SA})C_{\mathbf{N}}$ corresponds to a corrected concentration of acetic acid in output stream **N** that compensates for differences in the flow-rate of the feed-stock **F** and the alkaline stream **A**, with $C_{\mathbf{N}}^{*}$ reducing

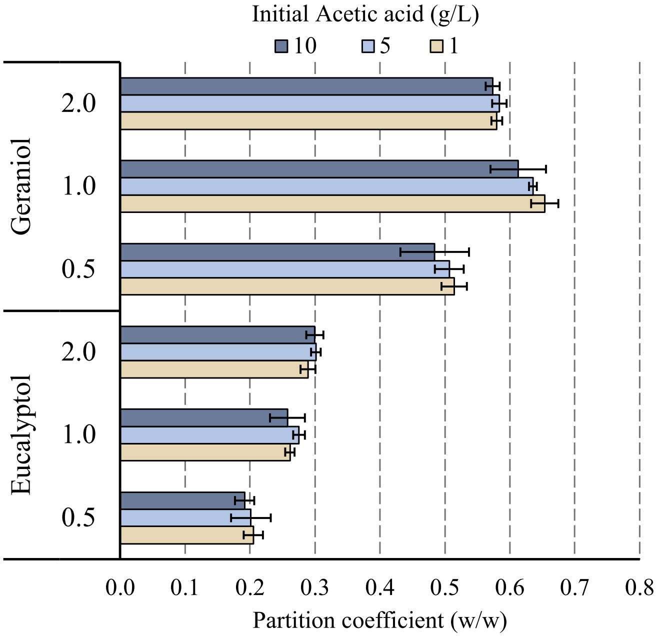

Fig. 4. Measured mass partition coefficients for acetic acid, using α_{SF} ratios of 0.5, 1.0 and 2.0, acetic acid loadings of 1, 5 and 10 g/L and a total flow-rate in **T1** of $\mathscr{F}_S + \mathscr{F}_F =$ 200 µL/min.

to $C_{\mathbf{N}}$ when $\mathscr{F}_{\mathrm{A}}$ is equal to $\mathscr{F}_{\mathrm{F}}$ (see Supplementary Material).

The experimentally determined sum C_{tot} of $C_{\mathbf{R}}$ and $C^*_{\mathbf{N}}$ may be greater or smaller than C_0 due to partial intermixing of water and the extracting solvent or loss of acetic acid to the solvent, i.e. incomplete back-extraction. For perfect back-extraction and a net flow of liquid from the aqueous phase to the solvent phase (as implied by the partition coefficients obtained in §3.1.2), C_{tot} is expected to be greater than C_0.

Fig. 5a,b,c show experimentally determined plots of $C_{\mathbf{R}}$, $C_{\mathbf{N}}$, $C^*_{\mathbf{N}}$ and C_{tot} versus C_0 for α_{SF} ratios of 0.5, 1.0 and 2.0, using geraniol as the extracting solvent, with the dotted line showing the ideal case of Eq. (6) in which there is no intermixing of the two phases and back-extraction is perfect. For all α_{SF} values the lines of C_{tot} versus C_0 lie slightly above the ideal line, with slopes of 1.06 ± 0.03, 1.03 ± 0.03 and 1.05 ± 0.03 for $\alpha_{\mathrm{SF}} = 0.5$, 1.0 and 2.0, respectively, indicating a small net-flow of liquid from the aqueous phase to the organic phase, resulting in an underestimation of the extraction efficiency by Eq. (4) as discussed above.

As the α_{SF} ratio is increased from 0.5 to 2.0, there is a decrease in the slope of $C_{\mathbf{R}}$ vs C_0 and a corresponding increase in the slopes of C_{N} and $C^*_{\mathbf{N}}$ vs C_0, corresponding to improved extraction of acetic acid by the solvent phase. By differentiating Eq. (4) with respect to C_0, we obtain:

$$\eta^{\mathrm{I}}_{\mathrm{ex}} = 1 - \left(\frac{dC_{\mathbf{R}}}{dC_0}\right) \tag{7}$$

where the slope $dC_{\mathbf{R}}/dC_0$ is an (over)estimate of the retention efficiency η_{ret}, i.e. the fraction of acetic acid molecules retained in the raffinate after extraction:

$$\eta^{\mathrm{I}}_{\mathrm{ret}} = \frac{dC_{\mathbf{R}}}{dC_0} \tag{8}$$

Alternative estimates of the extraction and retention efficiencies may (for the specific case $\alpha_{SA} = 1$) be obtained from the slope $dC^*_{\mathbf{N}}/dC_0$ of the $C^*_{\mathbf{N}}$ vs C_0 line

$$\eta^{\mathrm{II}}_{\mathrm{ex}} = \left(\frac{dC^*_{\mathbf{N}}}{dC_0}\right) \tag{9}$$

and

$$\eta^{\mathrm{II}}_{\mathrm{ret}} = 1 - \eta^{\mathrm{II}}_{ex} \tag{10}$$

which apply under the assumption that there is no intermixing of the solvent and alkaline phases and there is perfect recovery of acetic acid molecules from the solvent during back extraction (see Supplementary Material). High NaOH concentrations increase immiscibility between water and organic solvents due to "salting-out" behaviour, inhibiting the transfer of water to the organic solvent or transfer of organic solvent to the water [69]. However, dissolved water in the solvent (from the initial extraction) may return to the aqueous phase, reducing the concentration of acetic acid in **N**. Water transfer from solvent to **N** and/or a back-extraction efficiency η_{back} less than 100 % would result in an underestimate of η_{ex} (see Eq. 16 of Supplementary Material).

Fig. 5d,ef and Fig. 5g,h,i show the calculated extraction and retention efficiencies for geraniol, obtained using Eqs. (7), (8) and (9), (10) respectively. The two sets of estimates show the same general trends with $\eta^{\mathrm{I}}_{\mathrm{ex}}$ and $\eta^{\mathrm{II}}_{\mathrm{ex}}$ both increasing as α_{SF} increases, but with method II yielding consistently higher estimates of η_{ex} than method I.

Fig. 5j,k,l shows the concentration enhancement factor (CEF) for the output stream **N**

$$\gamma_{\mathrm{N}} = \left(\frac{dC_{\mathbf{N}}}{dC_0}\right), \tag{11}$$

which represents the concentration of acetic acid in **N** relative to the concentration of acetic acid in the feed-solution. From mass-balance considerations (see Supplementary Material) under conditions of perfect solvent/alkali separation and a back extraction efficiency η_{back}:

$$\gamma_{\mathrm{N}} = \eta_{\mathrm{ex}}\eta_{\mathrm{back}}\left(\frac{\alpha_{\mathrm{SA}}}{\alpha_{\mathrm{SF}}}\right) \tag{12}$$

where the product $\eta_{\mathrm{ex}}\eta_{\mathrm{back}}$ corresponds to the overall recovery efficiency η_{rec} of acetic acid from the feed solution.

We may also define an equivalent CEF for the raffinate:

$$\gamma_{\mathrm{R}} = \left(\frac{dC_{\mathbf{R}}}{dC_0}\right) \tag{13}$$

which from Eq. (8) is identical to $\eta^{\mathrm{I}}_{\mathrm{ret}}$.

From Fig. 5d,e,f and 5 g,h,i it is evident that increasing α_{SF} from 0.5 to 2.0 has the beneficial effect of increasing the (estimated) extraction efficiency from ca. 20 % to ca. 50 %. However, it also increases the volume of water in the alkaline stream by a factor of two since α_{SA} is kept

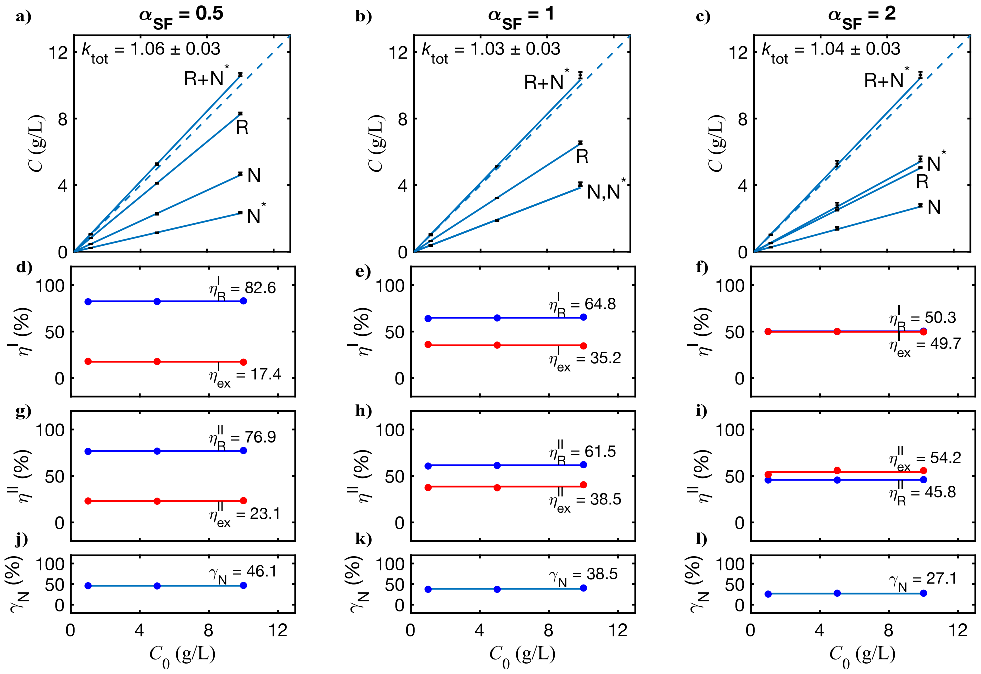

Fig. 5. **(a,b,c)** $C_{\mathbf{R}}$, $C_{\mathbf{N}}$, $C^*_{\mathbf{N}}$ and $C_{\mathrm{tot}} = C_{\mathbf{R}} + C^*_{\mathbf{N}}$ versus C_0, obtained using geraniol as the extracting solvent. Data were obtained using a total flow-rate in **T1** of $\mathscr{F}_{\mathrm{S}} + \mathscr{F}_{\mathrm{F}} = 200$ μL/min at α_{SF} ratios of 0.5, 1.0 and 2.0 and a fixed α_{SA} ratio of 1.0. **(d,e,f)** estimated extraction efficiencies $\eta^{\mathrm{I}}_{\mathrm{ex}}$ obtained from the data in (a,b,c) using Eq. (7). **(g,h,i)** estimated extraction efficiencies $\eta^{\mathrm{II}}_{\mathrm{ex}}$ obtained from the data in (a,b,c) using Eq. (8). **(j,k,l)** Concentration enhancement factors γ_{N} (in %) for acetic acid in the alkali output stream obtained from the data in (a,b,c).

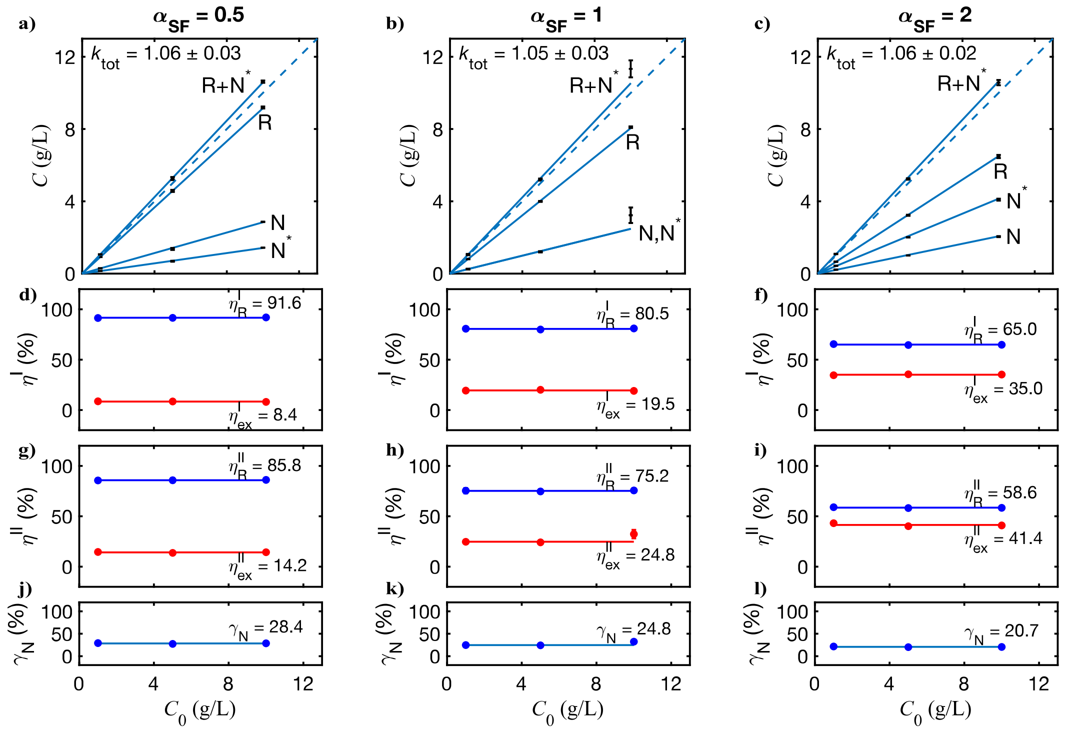

Fig. 6. **(a,b,c)** $C_{\mathbf{R}}$, $C_{\mathbf{N}}$, $C^{*}_{\mathbf{N}}$ and $C_{\text{tot}} = C_{\mathbf{R}} + C^{*}_{\mathbf{N}}$ versus C_0, obtained using eucalyptol as the extracting solvent. Data were obtained using a total flow-rate in **T1** of $\mathscr{F}_{S} + \mathscr{F}_{F} = 200$ µL/min at α_{SF} ratios of 0.5, 1.0 and 2.0 and a fixed α_{SA} ratio of 1.0. **(d,e,f)** estimated extraction efficiencies η^{I}_{ex} obtained from the data in (a,b,c) using Eq. (7). **(g,h,i)** estimated extraction efficiencies η^{II}_{ex} obtained from the data in (a,b,c) using Eq. (8). **(j,k,l)** Concentration enhancement factors γ_{N} (in %) for acetic acid in the alkali output stream obtained from the data in (a,b,c).

at a constant value of one. Hence, the overall effect of increasing α_{SF} from 0.5 to 2.0 is to reduce γ_{N} from 46.1 % to 27.2 %, corresponding to a substantially lower concentration of acetic acid in the output than the feed solution.

The corresponding results obtained with eucalyptol are shown in Fig. 6. The C_{tot} vs C_0 lines were again seen to lie close to but slightly above the ideal line, indicating some loss of water to the solvent phase as before. The estimated extraction efficiencies – as determined by both methods I and II – were somewhat lower than those obtained with geraniol, with method II again yielding higher η_{ex} values than method I. η^{II}_{ex} increased from > 14.2 % to > 41.5 % as α_{SF} increased from 0.5 to 2.0 (compared to an increase from > 23.0 % to > 54.3 % for geraniol). The overall effect of increasing α_{SF} was to reduce γ_{N} from 28.5 % to 20.8 %. Hence, in terms of both estimated extraction efficiencies and measured γ_{N} concentration enhancement factors, the performance of eucalyptol was substantially worse than geraniol.

3.2. *Enrichment of the acetate concentration through back-extraction*

For the data shown in Figs. 5 and 6, there was a substantial dilution of the acetic acid concentration in the output stream **N** compared to the feed solution **F**. However it follows from Eq. (12) that an enhancement in the concentration could be achieved if α_{SA} were much larger than $\alpha_{SF}/\eta_{ex}\eta_{back}$, which may be achieved by setting $\mathscr{F}_{A} \ll \mathscr{F}_{F}$, while still ensuring there is sufficient alkali for efficient back-extraction.

Fig. 7a shows γ_{R} and γ_{N} versus the solvent-to-alkali ratio α_{SA} for geraniol, using a total flow rate in **T1** of $\mathscr{F}_{S} + \mathscr{F}_{F} = 200$ µL/min, an α_{SF} ratio of 2.0 and an acetic acid concentration in the feed solution of 5 g/L. γ_{R} was as expected unaffected by changes in α_{SA} (since α_{SA} should affect only the back-extraction process), while γ_{N} increased from 0.52 ± 1 % to 6.70 ± 52 % as α_{SA} was increased from 2 to 40. Likewise for eucalyptol (Fig. 7b), γ_{R} did not vary with α_{SA}, while γ_{N} increased from 0.42 ± 1% to 5.66 ± 27 %. In both cases, for $\alpha_{SA} \leq 4$, γ_{N} showed a near-linear dependence on α_{SA} in agreement with Eq. (11). For higher α_{SA} values, γ_{N} showed a sub-linear dependence on α_{SA} due mainly to the dilutery effect of water in the Extract **E** transferring back to the aqueous phase **N** during the back-extraction of acetic acid in **T2** (see Supplementary Material). For large values of α_{SA} – i.e. low flow-rates of alkali – the dilutery effect is substantial, leading to a significant reduction in γ_{N}. C_{N} may be fitted by a weighted non-linear least squares procedure to an equation of the form

$$C_{N} = \eta_{rec} C_0 \left(\frac{\alpha_{SA}}{\alpha_{SF} + \lambda \alpha_{SA}} \right) \tag{14}$$

where λ is the fraction of water from the feed solution **F** that enters **N** via the solvent **S** (see Supplementary Material). Fitting the data in Fig. 7a and 8a to Eq. (14), we obtain recovery efficiencies η_{rec} of 57 ± 1 %for geraniol and 46 ± 2 % for eucalyptol. The corresponding λ values are 7.4 ± 0.4 %and 4.2 ± 1 %. The data for$\alpha_{SA} = 40$ was characterised by a high standard deviation due to non-uniform droplet flow in **T2**, and was excluded from the fit, although including it within the fit did not substantially change the extracted parameter values.

To achieve uniform flow and consistent acetic acid concentrations in the output stream **N**, it was necessary to limit α_{SA} to a maximum value of 20, under which conditions γ_{N} values of approximately 3.2 were obtained for both geraniol and eucalyptol. Although eucalyptol has a lower recovery efficiency than geraniol, it also has a smaller λ value due to the lower solubility of water in eucalyptol (see Table S3 of Supplementary Material). Hence, the dilutery effect is weaker in eucalyptol, resulting in similar γ_{N} values at$\alpha_{SA} = 20$.

Note, the above analysis assumes there is no reduction in η_{back} as α_{SA} increases, but the possibility of such a reduction cannot be ruled out. If η_{back} does decrease with α_{SA}, the extracted η_{rec} values would be correct only in the range $\alpha_{SA} < 10$ where C_{N} varies approximately linearly with C_0. (In addition, the λ values would be smaller than those determined here).

To further enhance the acetate concentration in stream N without

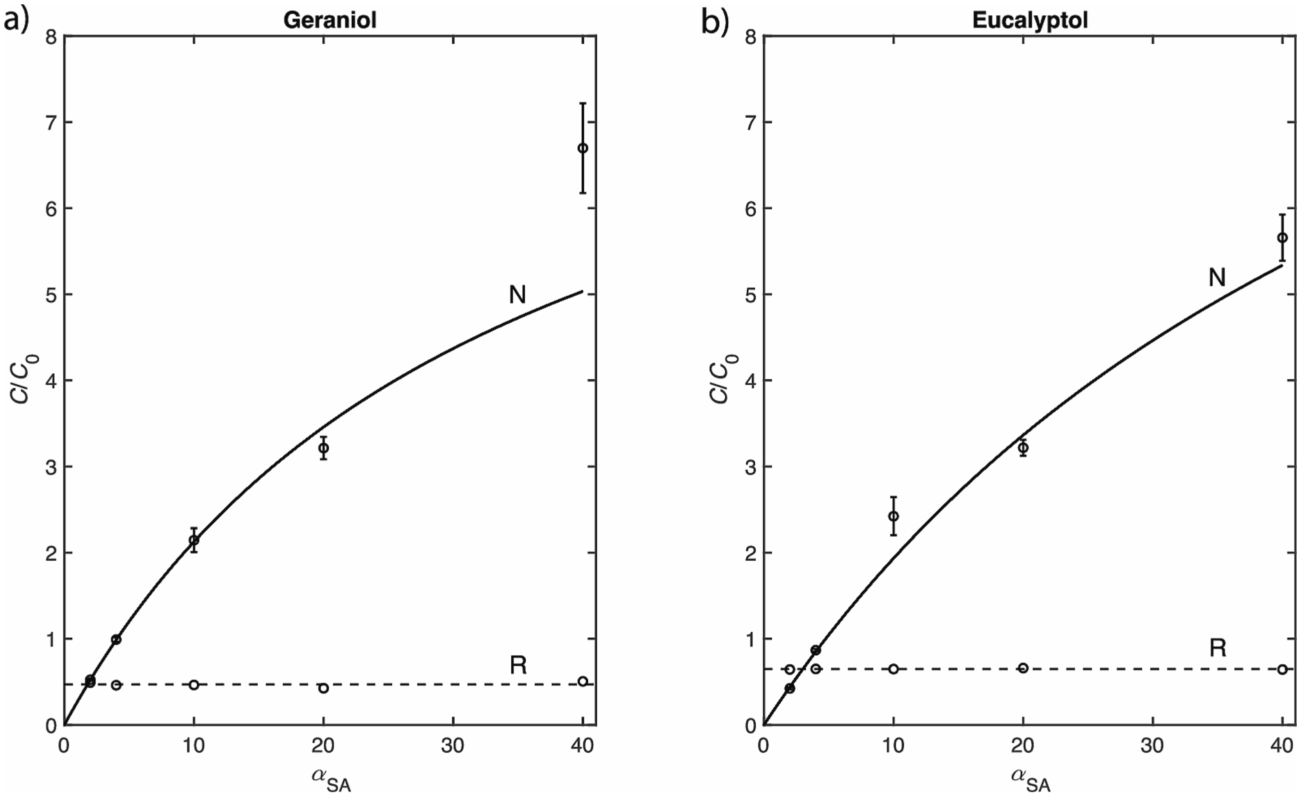

Fig. 7. $\gamma_{\mathbf{R}}$ and $\gamma_{\mathbf{N}}$ versus α_{SA}, obtained using geraniol **(a)** and eucalyptol **(b)** as the extracting solvent. Data were obtained at a total flow-rate in **T1** of $\mathscr{F}_S + \mathscr{F}_F =$ 200 μL/min, with $\alpha_{SF} = 2.0$ and a C_0 of 5 g/L. The solid black line represents a weighted non-linear least squares fit to Eq. (14), omitting the data for $\alpha_{SA} = 40$ due to poor reliability caused by non-uniform droplet flow.

compromising the phase separation, a cyclic reincorporation of stream N into the extraction cycle as stream A proves beneficial. This process enables the accumulation of successive acetate loadings in the alkaline phase, progressively increasing the α_{SA} ratio in a discontinuous manner.

3.3. Solvent reuse

The regenerated solvent obtained from the back-extraction process may in principle be used for further extractions. Fig. 8a,b shows for geraniol and eucalyptol γ_R and γ_N versus the number N of times the solvent has been used to carry out an extraction, with $N = 1$ corresponding to the use of fresh solvent. The data were obtained using an acetic acid loading of 5 g/L, a total flow rate in **T1** of $\mathscr{F}_S + \mathscr{F}_F = 200$ μL/min, and α_{SF} and α_{SA} ratios of 2.0 and 10.0, respectively. $\alpha_{SF} = 2$ was chosen to ensure a high extraction efficiency and$\alpha_{SA} = 10$ was chosen to ensure a high back-extraction efficiency (since from Fig. 7 it is in the linear range where for fresh solvent, the back-extraction efficiency is highest) and$\alpha_{SA} = 10$ was chosen to ensure a γ_N value >1.

For geraniol, γ_R showed a very slight increase with cycle number from 49.3 % at the first extraction using fresh solvent to 54.96 % at the 10th cycle, implying from Eq. (4) a small reduction in η_{ex}. γ_N by contrast remained at an approximate value of 2.0 (albeit with significant scatter in the data), implying an approximately constant recovery efficiency. For eucalyptol, γ_R remained at a fixed value of 0.66 over ten cycles,

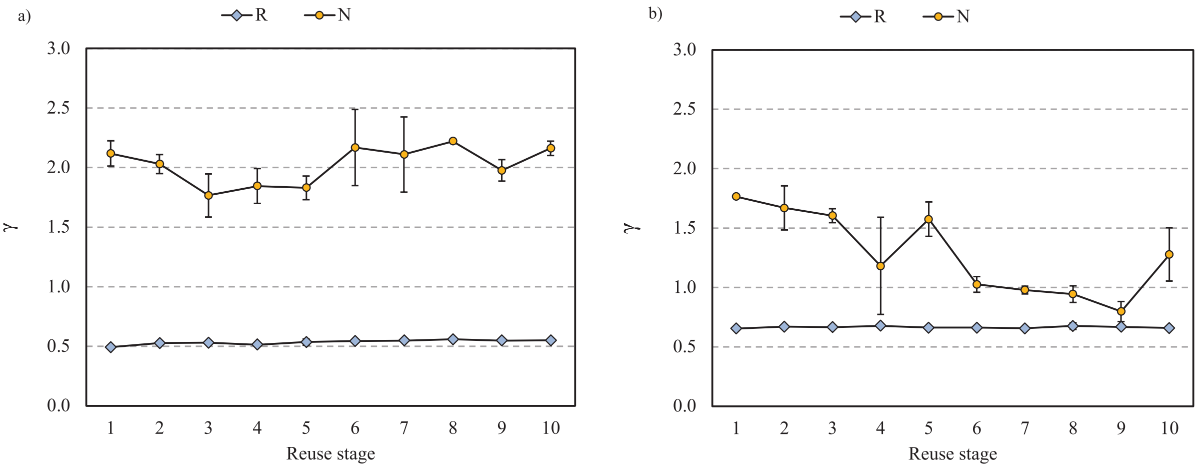

Fig. 8. $\gamma_{\mathbf{R}}$ and $\gamma_{\mathbf{N}}$ versus cycle number N, obtained using geraniol **(a)** and eucalyptol **(b)** as the extracting solvent. Data were obtained at a total flow-rate in **T1** of $\mathscr{F}_S + \mathscr{F}_F = 200$ μL/min, with $\alpha_{SF} = 2.0$, $C_0 = 5$ g/L, and $\alpha_{SA} = 10$.

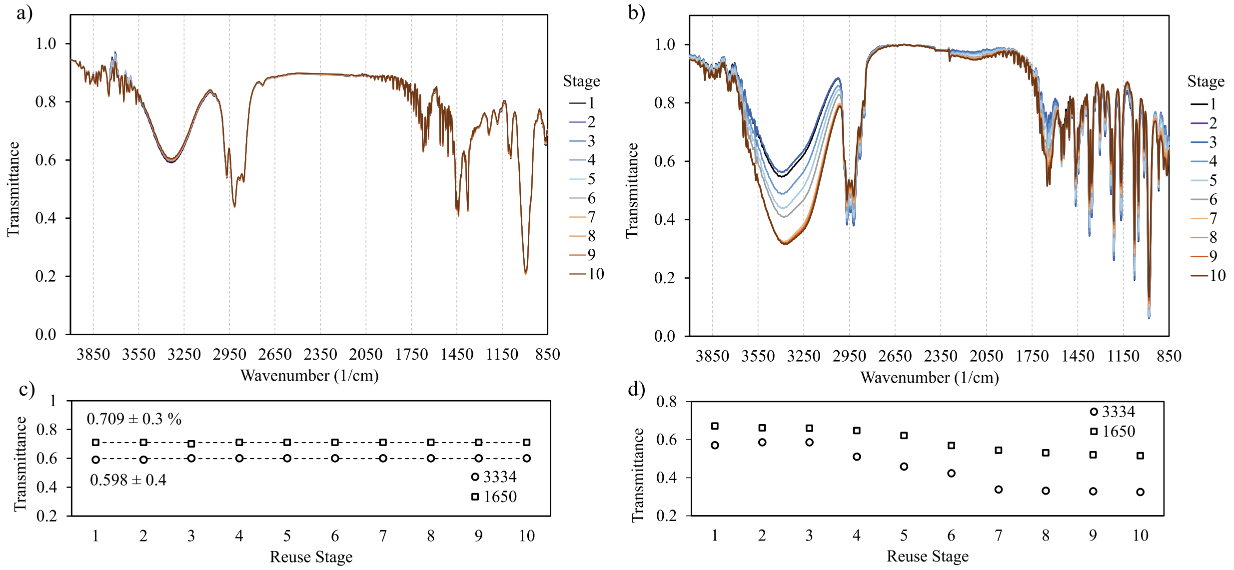

Fig. 9. IR transmittance spectra of $\mathbf{S_R}$ recorded after each complete extraction/back-extraction cycle, using geraniol **(a)** and eucalyptol **(b)** as the extracting solvent. Transmittance at 3334 cm^{-1} and 1650 cm^{-1} versus cycle number N for geraniol **(c)** and eucalyptol **(d)**, extracted from the data in (a, b).

indicating a constant value of $\eta_{ex}\ \gamma_N$, by contrast, showed a downward trend over the first six cycles from approximately 1.8 at $N = 1$ to 1.0 at $N = 6$ (although there was again significant scatter in the data), implying a reduction in the recovery efficiency caused by a reduction in the back-extraction efficiency.

Fig. 9a,b show infrared (IR) transmittance spectra for geraniol and eucalyptol collected after each cycle using an inline IR spectrometer. The main vibrational peaks of fresh geraniol and eucalyptol are identified in Figures S5 and S6 of the Supplementary Material, following the IR vibrational group identifying guidelines from Ref. [70]. The IR transmittance spectra of geraniol did not change significantly with cycle number, while substantial water-related dips appeared in the transmittance spectra of eucalyptol between 3550 and 3200 cm^{-1} and between 1750 and 1600 cm^{-1} over the first six cycles. Fig. 9c,d show the transmittance T versus cycle number N at 3334 cm^{-1} and 1650 cm^{-1}, which correspond to the OH stretch and scissor bend of water, respectively [71]. For geraniol, the transmittance at 3334 cm^{-1} and 1650 cm^{-1} remained approximately constant, which implies that after an initial uptake of water in cycle one, there was no further uptake during subsequent cycles. For eucalyptol, by contrast, the transmittance fell substantially at both 3334 cm^{-1} and 1650 cm^{-1} from $N = 1$ to $N = 6$, indicating progressive uptake of water by eucalyptol during each of the first six cycles. The drop in transmittance correlates with the observed fall in γ_N over the first six cycles (Fig. 8b), implying the reduction in η_{back} is due to water uptake by the eucalyptol.

4. Conclusions

We have described a simple flow-based procedure for the extraction and alkaline back-extraction of acetic acid from an aqueous feedstock, using geraniol and eucalyptol as sustainable bio-derived green solvents. The initial extraction was achieved by merging a stream of an aqueous feed-solution with a stream of the extracting solvent in a Y-shaped mixer, resulting in a two-phase flow. Following mass-transfer of acetic acid to the solvent, the two phases were separated by a porous-capillary-based separator. Compositional comparison of the aqueous raffinate with the feed solution indicated single-stage extraction efficiencies of >54.2 % and >41.4 % for geraniol and eucalyptol, respectively. To enhance the extraction yields obtained in this work, a multi-stage countercurrent extraction configuration, inspired by the scheme proposed by Weeranoppanant et al. [72], could be employed. This approach involves the incorporation of additional phase separators and extractions, thereby improving and increasing the efficiency of the extraction step. A practical demonstration of this concept can be seen in the synthesis of methyl oximino acetoacetate, where a configuration consisting of 3 Multistage Counter-Current extraction stages was utilized [73].

The solvent stream from the separator was merged with an aqueous stream of 2-M NaOH, resulting in a second two-phase flow. Following mass transfer of acetic acid back to the aqueous phase, the two phases were separated by a second porous-capillary based separator. For both geraniol and eucalyptol, concentration enhancement factors of approximately three were obtained at a solvent-to-alkali flow rate of 20:1.

The feasibility of using the regenerated solvent from back-extraction for further extractions was demonstrated. Using geraniol in combination with 2-M NaOH, it was found the extracting solvent could be used at least ten times with an approximately constant concentration enhancement factor γ_N of around 2.0. Using eucalyptol, γ_N decreased from around 1.8 at the first cycle to around 1.0 at the sixth cycle, remaining at around 1.0 up to the 10th cycle. IR analysis of the regenerated geraniol immediately after back extraction indicated a stable level of absorbed water from the first cycle onwards, while analysis of the regenerated eucalyptol indicated increasing uptake of water from cycles 1 to 6, leading to a reduction in the back-extraction efficiency and a drop in γ_N.

Overall, the work reported here confirms the feasibility of using geraniol and (to a lesser extent) eucalyptol as reusable bio-derived solvents for extracting acetic acid from aqueous feed solutions and subsequently returning it to the aqueous phase via reactive back-extraction with 2–M NaOH. The flow set-up used here to carry out extraction and back-extraction may be readily adapted to continuous extended closed-loop operation – with the regenerated solvent obtained after back extraction being directly recirculated through the flow reactor to carry out further extractions – as we have previously shown for metal extraction in Ref. [52]. The system could also be expanded through the use of parallel channels [74–76] to reach the higher flow-rates needed for industrial applications.

The process engineering design necessitates comprehensive deliberation on several key aspects. i) The incorporation of a solvent makeup stream to account for losses encountered in the aqueous phase. ii) Deliberate reduction of NaOH concentration ensuring an effective back-extraction process while minimizing the alkali required. iii) Exploration of the potential for alkaline stream recirculation to enable subsequent acetic acid back-extraction. Consideration should be given to implementing a NaOH makeup procedure. iv) Rigorous assessment of pumping costs. The pressure applied in the membranes should be considered to evaluate associated expenses, ensuring optimal phase separation and balancing membrane longevity.

In order to obtain more concentrated streams, an additional recovery process is required for the output stream N, such as the utilization of a distillation method [13,44]. The implementation of an additional process to achieve a more concentrated current requires careful consideration of the associated efforts and costs when designing an industrial-scale process.

CRediT authorship contribution statement

Diego Rodríguez-Llorente: Supervision, Investigation, Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization. **Yu Liu:** Methodology, Investigation. **John C. de Mello:** Supervision, Methodology, Funding acquisition, Project administration, Writing – review & editing. **Juan García:** Funding acquisition, Project administration, Writing – review & editing. **Marcos Larriba:** Supervision, Funding acquisition, Project administration, Writing – review & editing, Methodology.

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.

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Appendix A. Supplementary Material

Chemicals. Experimentation set-up. HPLC analysis. Influence of flow-rates in extraction efficiencies. Water and solvent partition coefficients. Water loading. Identified FTIR vibrational groups. Mass-balance analysis. Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.124524.

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