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CO_2-enhanced extraction of acetic acid from fermented wastewater

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The industrial process of recovering fermentation-based volatile fatty acids (VFAs) utilizes H_2SO_4 to acidify the fermentation broth containing VFA-salts [e.g. $Ca(CH_3COO)_2$] to enable formation of molecular VFAs. Molecular VFAs are then recovered by liquid-liquid extraction. However, acidification with H_2SO_4 results in production of large quantities of salts (e.g. $CaSO_4$). Using CO_2 rather than mineral acids for acidification of fermentation broth is an environmentally benign alternative which eliminates salt formation. In this study, CO_2 was applied in pressures up to 40 bar to enhance the efficiency of extraction of acetic acid (HAc) from fermented wastewater. HAc extraction at atmospheric conditions was also investigated to obtain benchmarks. The ionic liquid $[P_{666,14}]$[Phos] and trioctylamine (TOA) dissolved in n-octanol were applied as solvents to extract HAc from fermented wastewater model solutions containing HAc (1 wt%) and various salts resulting in pH ranging from 2.8 to 6. A more pronounced increase in extractability of HAc, expressed as HAc distribution ($D = [HAc]_{solvent}/[HAc]_{aqueous}$), was observed for $[P_{666,14}]$[Phos] with increasing CO_2 pressure. A mathematical model taking into account carbonic acid equilibria and dissociation of HAc and salts showed that the measured influence of CO_2 cannot be explained by the effect of CO_2 on aqueous phase pH. Thus, it may be concluded that the pressurized CO_2 has altered the fluid properties of the solvents and made them more accessible for HAc. This suggests that applying pressurized CO_2 may enhance extraction efficiency of processes other than those involving extraction of volatile fatty acids.

Keywords: liquid-liquid extraction, volatile fatty acids, pressurized liquid-liquid extraction, carbon dioxide, ionic liquids

1. Introduction

Rising concerns on depletion of easily recoverable petroleum resources over the next decades together with rising awareness of the need for more sustainable processes in industry has resulted in significant attention for production of bio-based chemicals in both academia and industry. Several strategies to obtain bio-based chemicals have been proposed including thermochemical routes such as pyrolysis[1-3] and gasification followed by gas-to-liquid techniques[4-6], and fermentative routes.[7]

Various approaches for fermentative routes have been examined in the literature. Steinbusch et al. developed a method to produce medium chain fatty acids (MCFAs) from residual biomass streams via fermentation.[8] Fermentative production of MCFAs from municipal solid waste has also been reported.[9] Another fermentative route is production of volatile fatty acids (VFAs) from waste streams.[10, 11] Bio-based VFAs have been used as platform chemicals to produce plastics.[12] They are also utilized in bio-energy.[13] The advantage of VFA platform is its versatility in downstream conversions.[7] However, producing chemicals from waste through VFAs in an economically viable operation is not straightforward.

An important limitation for commercializing VFA production from wastewater is the low VFA concentration in fermented wastewater (see Table 1 for typical composition of fermented wastewater), which is mainly due to the limited carbon content of wastewater before undergoing fermentation. Therefore, effective separation methods must be developed to recover VFAs from dilute fermented wastewater.

Table 1: Typical composition of fermented wastewater

Component	Chemical formula	Concentration [g/L]	pK_a
Acetate	CH_3COOH	2.5 – 10	4.76
Propionate	CH_3CH_2COOH	2.5 – 10	4.88
Butyrate	$CH_3(CH_2)_2COOH$	2.5 – 10	4.82
Lactate	$CH_3CH(OH)COOH$	2.5 – 10	3.86
Sodium	Na^+	1 – 5	
Potassium	K^+	1 – 5	
Chloride	Cl^-	1 – 10	
Phosphate	$H_2PO_4^-/HPO_4^{2-}$	1 – 10	
Sulphate	SO_4^{2-}	1 – 10	
Sulphide	S^{2-}	0.3	
Magnesium	Mg^{2+}	0.3	
Calcium	Ca^{2+}	0.3	
Ammonium	NH_4^+	0.1	
Trace elements (cations)	Co, Fe, Ni	10^{-4}	
Inert COD		1	
Microbes			

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Separation of VFAs from aqueous solutions can be performed using various methods. Most commercialized processes use distillation.[14] However, due to the low concentration of VFAs in fermented wastewater, the amount of water to evaporate is extremely large and therefore, distillation is not economical. Other separation methods reported for VFA recovery include azeotropic or extractive distillation[15], membrane filtration[16, 17] and crystallization[18, 19]. Affinity separation techniques make use of physical and/or chemical interactions to form intermolecular complexes with VFA molecules. Adsorption and liquid-liquid extraction are the most common affinity separation techniques. They are considered as suitable techniques to separate VFAs from dilute solutions in an energy efficient manner.[20]

Through liquid-liquid extraction, VFA molecules are transferred into an extracting solvent due to the affinity between them and the solvent. With increasing affinity strength, the distribution of VFAs (defined as the ratio of VFAs concentration in the extract phase to that in the raffinate phase) increases. Since a further recovery step is needed to retrieve extracted VFAs from the solvent and regenerate the solvent, extremely high affinities must be avoided to make solvent regeneration feasible. Next to affinity for VFAs, affinity for water and other accompanying compounds is also an important factor, and preferentially, the solvent must have a high affinity for VFAs, but a limited affinity for water and other species accompanying VFAs (i.e. the solvent should be highly selective). Very hydrophobic solvents limit water co-extraction, but on the other hand, they often show limited VFA distribution. In the literature, many different solvents are proposed to extract VFAs from aqueous solutions including alcohols, ketones, ethers, aliphatic hydrocarbons, organophosphates, and aliphatic amines.[14, 21-24] Furthermore, in recent years, ionic liquids have gained interest for extraction of carboxylic acids, as they are considered as "green" solvents.[25-29] Contrary to non-ionic solvents, for some ionic liquids, VFA distribution is reported to continuously increase with decreasing VFA concentration in raffinate.[27, 28] This behaviour is particularly interesting for this study, as the VFA concentration in fermented wastewater is low due to the limited carbon content of the feedstock.

Another challenge for extraction of VFAs from fermented wastewater streams is the presence of salts (see Table 1) which results in a pH of 4.5 – 6. Due to the low concentration of VFAs and relatively high pH, VFAs are present predominantly in their dissociated form. Since the reported solvents (e.g. tertiary amines) extract carboxylic acids in their molecular form,[23, 30] extraction of VFAs from fermented wastewater is challenging.

Production of large quantities of salts through the industrial process of recovering volatile fatty acids from fermentation broth poses environmental problems.[31, 32] The alternative technique reported in the literature to avoid salt production utilizes CO_2 rather than H_2SO_4 to reversibly acidify fermentation broth. [33,34,35,36] Urbas demonstrated that the concentration of molecular HAc in an aqueous solution can be increased by applying high pressure or atmospheric CO_2 which results in enhanced extraction of HAc.[33] This technique was later improved by Eggeman and Verser.[34] Reversible acidification with CO_2 was also used to facilitate recovery of lactic acid by Baniel et al..[35] Recently, Peterson and Daugulis showed that sparging CO_2 through a butyric acid containing fermentation broth increases the amount of recovered butyric acid.[36]

In this study, reversible acidification with pressurized CO_2 was combined with the use of an ionic liquid ([$P_{666,14}$][Phos]) as solvent to enhance extraction of VFAs from fermented wastewater in which VFA concentration is much lower than that in a typical VFA-containing fermentation broth. In order to compare the performance of [$P_{666,14}$][Phos] with that of conventional molecular solvents, 20 wt% TOA in n-octanol solution was also applied for extraction of HAc from fermented wastewater model solutions. These systems were chosen based on the literature. 20 wt% TOA in n-octanol has been the best traditional solvent for extraction of carboxylic acids[23, 30], and recently the use of [$P_{666,14}$][Phos] has been shown to be very promising due to high distributions obtained at very low carboxylic acid concentrations in raffinate.[27] The applied CO_2 pressure was up to 40 bar. Since the fermented wastewater model solutions prepared for this study are not previously examined in the literature, HAc extraction at atmospheric conditions was also studied.

2. Experimental and analysis

2.1. Chemicals

Acetic acid (HAc, >99.7%), n-octanol (>99%), trioctylamine (TOA, 98%), potassium chloride (>99%), anhydrous sodium phosphate dibasic (>99%), and anhydrous sodium sulphate (>99%) were purchased from Sigma-Aldrich. Potassium hydroxide (1 M) was supplied by Merck, and [$P_{666,14}$][Phos] (Cyphos IL104, >95%) was purchased from io-li-tec. Fermented wastewater model solutions were prepared by adding the desired amounts of HAc and salts to demi water (see Table 2).

2.2. Experimental equipment

The setup used to perform liquid-liquid extraction under high CO_2 pressures consisted of an autoclave (Büchi, V = 1 L, P_{max} = 60 bar) coupled to a CO_2 supply vessel (Swagelock, V = 1 L, P_{max} = 120 bar). The CO_2 supply vessel was connected to a CO_2 cylinder (via Valve 1 in Figure 1) to allow refilling the vessel. Figure 1 shows a schematic view of the setup. The autoclave was kept at the operating temperature (20 ± 0.1 ºC) using a heating/cooling jacket.

2.3. Single stage liquid-liquid extraction at atmospheric pressure

Atmospheric pressure liquid-liquid extraction experiments were performed using 5 mL of a fermented wastewater model solution (see Table 2) and 3 mL of a solvent. The volumetric solvent to feed ratio (S/F) of 3:5 was chosen to keep the obtained results comparable with those obtained from high pressure experiments, as the location of the autoclave sampling ports were adjusted to the liquid heights associated with 500 mL of a feed and 300 mL of a solvent. The liquid mixtures were magnetically stirred at 500 rpm or more at room temperature (20 ± 1 ºC) for 1 h, as it was experimentally verified that the time needed to reach equilibrium is less than 1 h for every pair of feed and solvent.

After 1 h of stirring, the mixtures were centrifuged at 8000 rpm for 5 minutes. After centrifugation, samples were taken from both of the phases for analysis.

Table 2: Composition of fermented wastewater model solutions

Model solution	Concentration [mol/L]				pH
	HAc	KCl	Na_2SO_4	Na_2HPO_4	
pH 2.8 solution	0.17 (1 wt%)				2.8
pH 4.8 solution	0.17 (1 wt%)	0.05	0.05	0.1	4.8
pH 6.0 solution	0.17 (1 wt%)			0.2	6.0

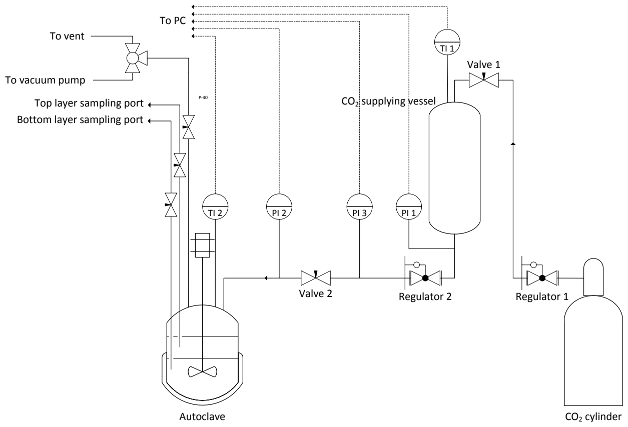

Figure 1: High pressure liquid-liquid extraction setup

2.4. Multistage cross-current liquid-liquid extraction at atmospheric pressure

Atmospheric multistage cross-current liquid-liquid extraction experiments were carried out to monitor the accumulation of HAc in $[P_{666,14}]$[Phos] and in 20 wt% TOA in n-octanol with increasing the number of extraction stages. The volumetric solvent to feed (pH 4.8 solution) ratio was 3:5. After every extraction stage (following the same procedure described in the previous section), the solvent phase was separated from the raffinate phase, and without further treatment, it was exposed to fresh feed in another extraction stage. After every extraction stage, the HAc content of the obtained raffinate phase was measured. Additional extraction stages were performed until the HAc concentration in the raffinate phase did not change anymore. The final concentration of HAc in the solvent phase was measured via washing the solvent phase with KOH (1 M) followed by analysis of the alkaline phase with HPLC.

2.5. Single-stage liquid-liquid extraction at high pressure

In each high pressure liquid-liquid extraction experiment, 500 mL of a fermented wastewater model solution and 300 mL of a solvent was loaded into the autoclave. The autoclave was then sealed and any residual air was removed from inside the autoclave using a vacuum pump. A leak test was performed with CO_2 at the intended pressure of experiment (up to 40 bar) for 5 min. If no leak was detected, stirring started while the autoclave was already at the intended pressure and 20 ± 0.1 ºC. The stirring speed for every experiment was 620 rpm, and during the experiments, CO_2 pressure was controlled and kept constant by continuously supplying CO_2 from the vessel. After 1 h, (enough for reaching equilibrium, validated experimentally), stirring was stopped to let the liquid phases settle for 30 minutes. To avoid disturbing equilibrium, the autoclave was kept pressurized while taking samples from both phases.

2.6. Analysis

The concentrations of HAc, HPO_4^{2-} in aqueous phases were measured with HPLC [Agilent 1200 series HPLC system equipped with Agilent Hi-plex H column (300*7.7 mm) and Agilent 1200 series refractive index detector]. Cl^- and SO_4^{2-} concentrations were quantified with IC (Metrosep A Supp 4 - 250/4.0 column and Metrohm 732 IC detector coupled to Metrohm 733 IC Separation Center). The water contents of solvent phases were measured with Karl-Fischer titration (Metrohm 787 KF Titrano). Na^+ and K^+ concentrations were measured with a flame photometer (BWB Flame Photometer XP).

3. Results and discussion

3.1. Liquid-liquid extraction at atmospheric pressure

HAc extraction at atmospheric pressure was studied (see Table 3) and used as benchmark for HAc extraction under high CO_2 pressure. Because in many previous studies ideal model solutions containing only a VFA and water were used, a model solution containing only HAc (1 wt%) and water (pH = 2.8) was also examined in this study for comparison.

As can be seen in Table 3, all the HAc distribution coefficients significantly decreased when the pH of fermented wastewater model solution increased from 2.8 to 4.8 or 6.0. For 20 wt% TOA in n-octanol, this trend matches the previously suggested extraction mechanism by which carboxylic acids are extracted only in their molecular form.[23, 30] Due to the increase in pH, less HAc was available in molecular form, and as a result, HAc distribution dropped significantly for pH 4.8 and 6.0 solutions compared to pH 2.8 solution. The decrease in the HAc distribution coefficient of $[P_{666,14}]$[Phos] suggests that it also extracts HAc in its molecular form. In a set of additional experiments, presented in the Supporting Information, measuring the concentrations of both the cations Na^+ and K^+ and the anions present in the aqueous solutions before and after extraction revealed that the cations are not extracted by $[P_{666,14}]$[Phos] which confirms that $[P_{666,14}]$[Phos] indeed extracts HAc in its molecular form.

Comparing the HAc distribution coefficients obtained for $[P_{666,14}]$[Phos] with those obtained for 20 wt% TOA in octanol, it can be seen that although the HAc distribution coefficient of $[P_{666,14}]$[Phos] was twice that of 20 wt% TOA in octanol for pH 2.8 solution, it significantly decreased for pH 4.8 and pH 6.0 solutions resulting in values similar to those of 20 wt% TOA in octanol.

In order to identify the major phenomenon responsible for this significant decrease, the experiments in the Supporting Information were executed and the concentrations of the anions present in the extraction systems (Cl^-, SO_4^{2-} and HPO_4^{2-}) were also measured using HPLC and IC. It was observed that Cl^-, SO_4^{2-} and HPO_4^{2-} were extracted by both of the solvents, but not their counter ions Na^+ and K^+. Thus, HCl, H_2SO_4 and H_3PO_4 were the extracted species with distributions in the order HCl > H_2SO_4 > H_3PO_4.

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Table 3: HAc distribution coefficients and water co-extraction. Volumetric S/F = 3/5, T = 20 ± 1 ºC.

	pH 2.8 solution			pH 4.8 solution			pH 6.0 solution		
Solvent	$[HAc]_{raff}$ [wt%]	D_{HAc} [wt%/wt%]	Water co-extraction [wt%]	$[HAc]_{raff}$ [wt%]	D_{HAc} [wt%/wt%]	Water co-extraction [wt%]	$[HAc]_{raff}$ [wt%]	D_{HAc} [wt%/wt%]	Water co-extraction [wt%]
20 wt% TOA in n-octanol	0.18	8.9	3.7	0.73	0.8	3.7	0.84	0.3	3.3
$[P_{666,14}][Phos]$	0.09	17.5	14.1	0.81	0.6	14.9	0.80	0.5	15.7

As a result, the pH of the aqueous phase increased significantly resulting in much lower HAc distributions. Co-extraction of HCl, H_2SO_4 and H_3PO_4 was much more remarkable for $[P_{666,14}][Phos]$ than 20 wt% TOA in n-octanol which led to a stronger decrease in HAc distribution for pH 4.8 and pH 6.0 solutions.

Both $[P_{666,14}][Phos]$ and 20 wt% TOA in octanol have been previously studied for extraction of carboxylic acids from aqueous solutions similar to pH 2.8 solution. Extraction of lactic acid by $[P_{666,14}][Phos]$ resulted in distribution coefficients up to 40.[27, 37] Using 20 wt% TOA in n-octanol, lactic acid distribution coefficients up to 30 were obtained.[24] Therefore, although HAc distribution is in the same order of magnitude, its value is lower which may be due to the higher pK_a of HAc (4.76 vs 3.86 for lactic acid).

The final VFA loading of a solvent after a single extraction stage is always lower than that when the loaded solvent leaves a counter-current extraction process, and to study the highest HAc loading achievable with the pH 4.8 model solution, cross-current extraction was continued until no more HAc extraction was observed. At this point, the solvents were in equilibrium with the fresh pH 4.8 model solution. Figure 2 shows the gradual increase in the HAc content of the solvents with increasing the number of extraction stages. The HAc loading of every extraction stage is the summation of extra loading achieved after the current stage and the loading existed in the solvent from previous extraction stages. The total HAc loadings of the solvents after they reached equilibrium with fresh pH 4.8 solution were experimentally determined by washing the solvent phases with KOH (1 M) and analysis of the alkali phases. The obtained values are presented with "KOH-wash loading" lines in Figure 2. They are well in agreement with the final accumulative loadings obtained by analysis of the raffinate phases after extraction.

As can be seen in Figure 2, HAc loadings as high as 4.5 wt% in $[P_{666,14}][Phos]$ can be achieved in cross-current extraction with the pH 4.8 solution, while the maximum loading achieved in 20 wt% TOA in n-octanol was only 1.7 wt%. Based on the maximum loading of the solvents, a mass-balance for a counter-current extraction column was performed at minimum S/F. At these conditions, the pH 4.8 solution is in equilibrium with the loaded solvents. The calculated composition of the streams leaving the columns is depicted in Figure 3.

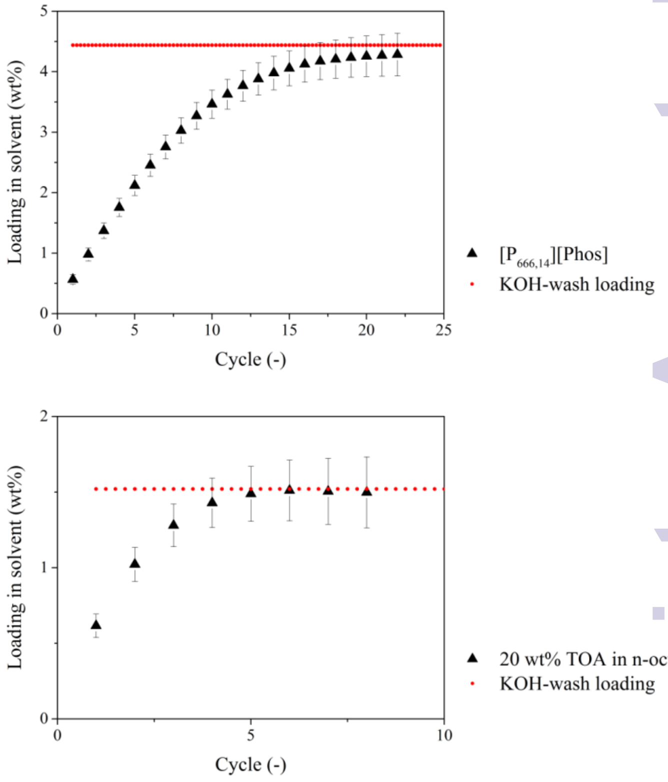


Figure 2: HAc loading in solvent phase during cross current extraction using pH 4.8 solution. Volumetric S/F = 3/5, T = 20 ± 1 ºC, $[P_{666,14}][Phos]$ (top), 20 wt% TOA in n-octanol.

The water content of each HAc-saturated solvent was also measured, and the values in equilibrium with the feed are also included in Figure 3. The water content of $[P_{666,14}][Phos]$ decreases as its HAc content increases, which was previously observed by Schlosser et al.[27, 38] This suggests that (a part of) the co-extracted water by is interacting with $[P_{666,14}][Phos]$ in a competitive way with HAc. The calculation of the $(S/F)_{min}$ is based on mass balance and assuming 90 wt% removal of the initial HAc content of pH 4.8 solution through the columns. Since the $(S/F)_{min}$ needed to use $[P_{666,14}][Phos]$ in the counter-current column described above is rather low, it may be practical to impregnate [$P_{666,14}$][Phos] in solid particles.[39]

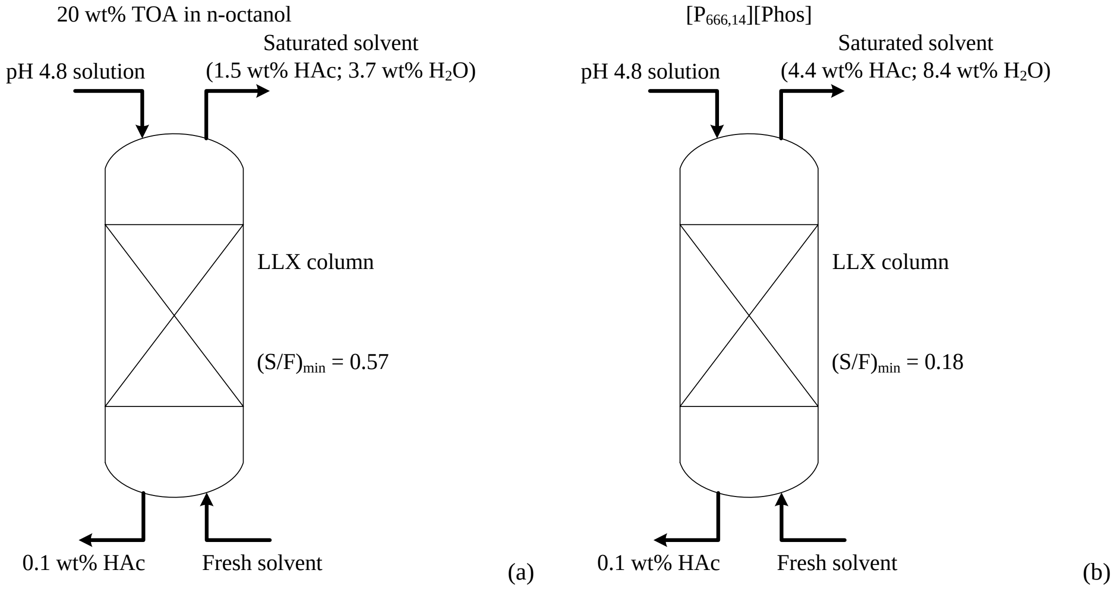


Figure 3: Counter-current extraction columns at minimum S/F for the pH 4.8 solution: 20 wt% in n-octanol (a), [$P_{666,14}$][Phos] (b)

Considering the ratio of the extracted HAc to the co-extracted water in the solvents, as shown in Figure 3, it can be concluded that [$P_{666,14}$][Phos] is superior to 20 wt% TOA in n-octanol in terms of extraction capacity and selectivity. Starting with a solution containing 1 wt% HAc and obtaining a ratio of 4.4 wt% HAc to 8.4 wt% water (34 % HAc) in the solvent implies that when both water and HAc are fully recovered from the ionic liquid, a 34 times more concentrated solution can be obtained. Although 34 times more concentrated, there is still a large amount of water and the HAc concentration in the solvent is not very high. A method that may improve this, is to use pressurized CO_2.

3.2. Liquid-liquid extraction at high pressure

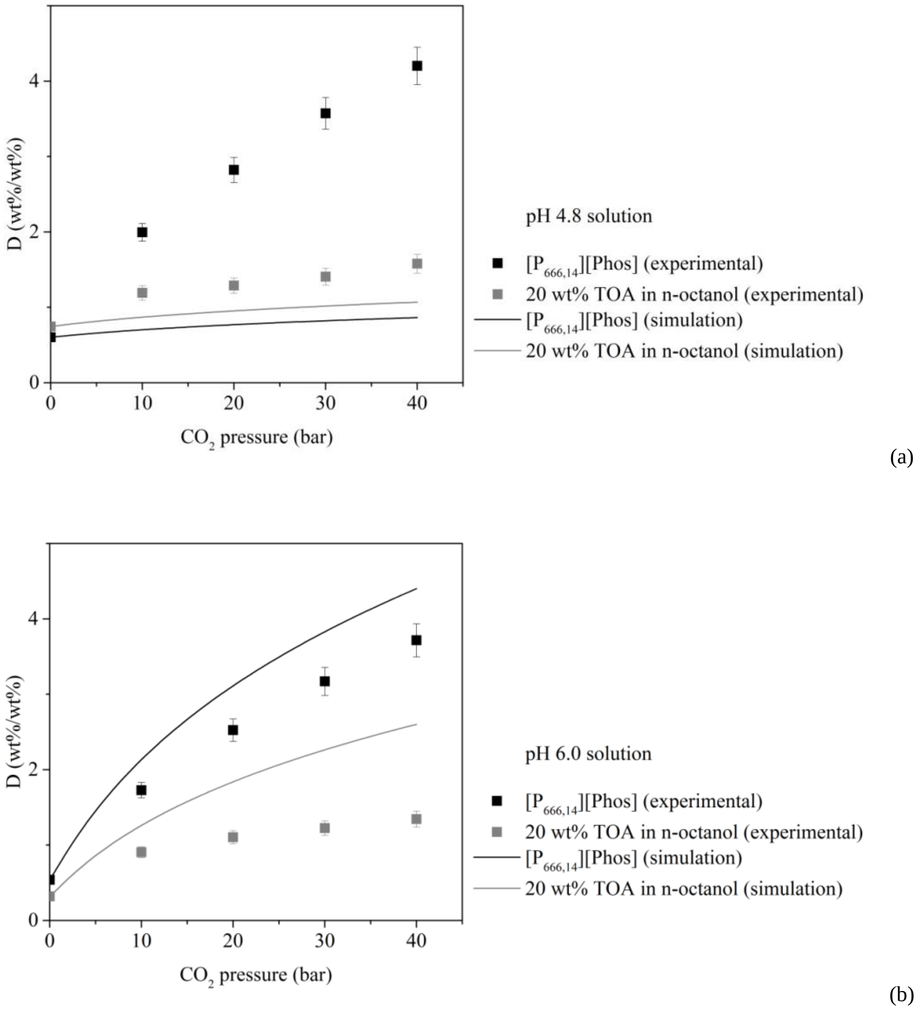
The high pressure extraction experiments were performed using the apparatus depicted in Figure 1 at 10, 20, 30 and 40 bar of CO_2 pressure. The obtained HAc distribution coefficients are presented in Figure 4. The data points at 0 bar of CO_2 pressure represent the distribution coefficients obtained at atmospheric conditions (see Table 3).

Figure 4 shows that the HAc distribution of both solvents significantly increases with increasing CO_2 pressure, which was expected as result of acidification with pressurized CO_2 on extractability of VFAs. The expected increase as result of shifting the dissociation equilibrium of HAc with decreasing pH due to increasing CO_2 pressure was calculated. Since considerable amounts of ions are present in both of the solutions, the calculations were performed including a Debye-Hückel approximation for ion activity coefficients in electrolytes.[20, 40] Since it was shown that only molecular HAc is extracted by the solvents, the effect of acidification with pressurized CO_2 on HAc distribution can be expressed using equation 1:

$$D_{calculated} = D_0 \frac{\left(\frac{[HAc]}{[HAc]+[Ac^-]}\right)_P}{\left(\frac{[HAc]}{[HAc]+[Ac^-]}\right)_{P_0}} \qquad (1)$$

where D_0 is the distribution coefficient experimentally obtained at atmospheric conditions (see Table 3), and [HAc] and [Ac^-] are the calculated concentrations of molecular HAc and acetate anion respectively.

As can be seen in Figure 4, independent of the initial pH of the aqueous solution, the HAc distribution of [$P_{666,14}$][Phos] and 20 wt% TOA in n-octanol increased from ~ 0.5 to ~ 4 and ~ 1.5 respectively. The increase in HAc distribution was more substantial for [$P_{666,14}$][Phos]. Due to the higher $\frac{[Ac^-]}{[HAc]}$ in the pH 6.0 solution than in the pH 4.8 solution, a more pronounced increase in HAc distribution due to acidification of aqueous phase was expected for the pH 6.0 solution. The expected increase is shown by the model lines, and by comparing the calculated distributions with the experimental values, it can be concluded that the influence of CO_2 on the equilibria in the aqueous phases is not the major phenomenon governing HAc distribution under high CO_2 pressure.



(a)

(b)

Figure 4: HAc distribution coefficient as a function of CO$_2$ pressure. pH 4.8 solution (a), pH 6.0 solution (b), volumetric S/F = 3/5, T = 20 ± 0.1 ºC.

Pressurized CO$_2$ has likely altered the fluid properties of the solvents and made them more accessible for HAc fragments, and this effect is more pronounced for the ionic liquid than the molecular solvent. Supporting this statement, in the literature, CO$_2$ solubility in [P$_{666,14}$][Phos] is reported to be significant, mole fraction of 0.587 at 40 bar and 60˚C[41], and it is expected to be even higher at 25˚C. This will significantly affect physical properties of [P$_{666,14}$][Phos]. To confirm that the effect is of physical nature, and the ionic liquid has not changed chemically, a ^{31}P-NMR study was performed. The full results of this study are presented in the Supporting Information from which it can be concluded that sparging CO$_2$ through [P$_{666,14}$][Phos] does not chemically change the ionic liquid. Adding water to [P$_{666,14}$][Phos] changes the chemical shift of the anion whic is attributed to aggregates of water.[42] However, both in the samples without water and in those with water, sparging CO$_2$ does not affect the chemical shift of [P$_{666,14}$][Phos] significantly. This finding suggests that using pressurized CO$_2$ may also be beneficial for other extraction systems in which acidification of an aqueous phase is not intended.

Since it is known that amines can react with CO$_2$,[43] and the ammonium carbonate might leach to the aqueous phase more easy than the neutral tertiary amine, the aqueous phase was analysed afte sparging biphasic samples of water and 20 wt% TOA in n-octanol.

Although the conductivity with 0.122 mS/cm was about five times higher than sparged water (0.0235 mS/cm), it is still orders of magnitude lower than regular electrolyte solutions, and in the ion chromatograph, no peak was observed, indicating a maximum concentration in the order of ppm's of any leachate.

The solvent loadings obtained after single extraction stages under high CO_2 pressure are comparable to those obtained at atmospheric conditions after multiple extraction stages. This implies that applying pressurized CO_2 to the counter-current extraction columns depicted in Figure 3 can significantly improve the efficiency of HAc removal from fermented wastewater.

4. Conclusions

In this study, high pressure CO_2 was utilized to enhance extraction of HAc from fermented wastewater model solutions with pH ranging from 2.8 to 6. [$P_{666,14}$][Phos] and 20 wt% TOA in n-octanol were used as solvents. The obtained results showed that with increasing CO_2 pressure the HAc distribution of the solvents increases significantly, and the increase in HAc distribution was more substantial for [$P_{666,14}$][Phos] than for 20 wt% TOA in n-octanol. The difference between the experimentally obtained HAc distribution coefficients and those obtained by simulating the aqueous phases under CO_2 pressure implies that acidification of aqueous phase is not likely the only consequence of pressurizing the extraction system with CO_2. The change in the physical properties of the solvents caused by pressurized CO_2 has likely made them more accessible for HAc molecules. This suggests that applying pressurized CO_2 to other extraction systems in which acidification of aqueous phase is not intended may also be beneficial.

5. Nomenclature

MCFAs: Medium chain fatty acids
VFAs: Volatile fatty acids
HAc: Acetic acid
TOA: Trioctylamine
[$P_{666,14}$][Phos]: trihexyl(tetradecyl)phosphonium bis-2,4,4 (trimethylpentyl) phosphinate

6. Acknowledgement

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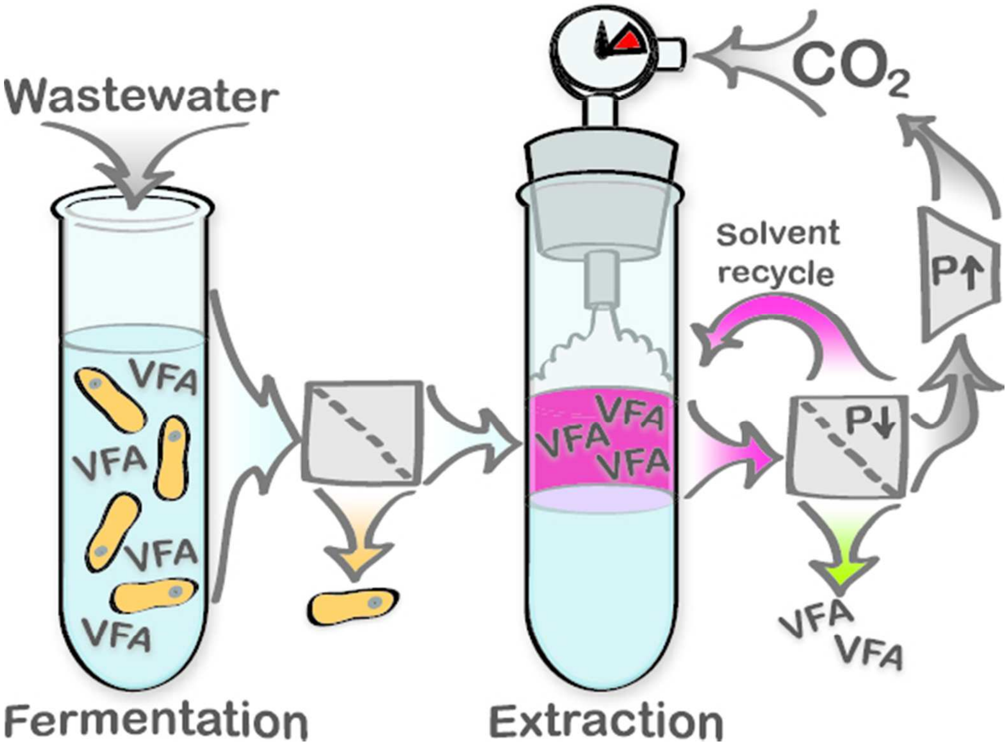

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