ADVANCING BIOREFINERIES: DOWNSTREAM AND FERMENTATION INTEGRATION FROM COMPLEX WASTE

Paula R. F. Rosa[1,2], Diego A. Lemos, [1]Daniel R. Noguera [2]

[1] Departure of Chemical Engineering, University of São Carlos, São Carlos, Brazil.
[2] Wisconsin Energy Institute, University of Wisconsin Madison, Madison, USA.
** Corresponding author's email address: paularosa@ufscar.br*

ABSTRACT

In the realm of the carboxylate platform, carboxylic acids stand out as crucial components for the chemical industry, though their extraction poses significant hurdles. Predominantly generated through the fermentation of carbohydrates sourced from lignocellulosic biorefineries, starch ethanol plants, and the dairy sector, these acids underscore the potential for economic and environmental advancements. This research investigates the production and extraction of carboxylic acids from ultra-filtered milk permeate (UFMP), tapping into real-world industrial effluents. Utilizing a Upflow Anaerobic Sludge Blanket (UASB) system, the study achieved a liquid retention time of 1.4 days at a maintained temperature of 35℃ and a pH of 5.5, leading to the predominant production of lactic, acetic, and butanoic acids. A critical aspect of this study was the assessment of the COSMO-RS method to determine the partition coefficients for carboxylic acids across 12 solvent pairs, ranging in polarity. The investigation also explored the impact of solvent type, pH levels, and solvent-to-UFMP ratios on the extraction efficiency. Notably, a one-to-one ratio proved most effective for acid recovery, with butanoic and hexanoic acids showing recovery efficiencies of up to 89% and 97%, respectively, highlighting the potential for efficient carboxylic acid recovery processes beyond petrochemical methodologies.

Keywords: Carboxylic acids. Fermentation. COSMO-RS method. Sustainable development. Recovery efficiency.

1 INTRODUCTION

Within the carboxylate platform, carboxylic acids are important building-blocks for the chemical industry, but their processes and recovery are challenging. Many carboxylic acids are currently produced by fermentation of carbohydrates, such as residues from lignocellulosic biorefineries, starch ethanol plants (thin stillage), and the dairy industry (ultra-filtered milk permeate, UFPM) and are examples of economic and environmental sustainability.

Since numerous types of microorganisms are available to be used for fermentation, a wide variety of chemicals can be produced by fermentation, ranging from commodity chemicals to pharmaceutical intermediates[1]. Rather than directing these intermediates to methane, the carboxylate platform harnesses microbiomes to convert these intermediates to other organic acids, such as lactic, acetic, butyric, pentanoic, hexanoic, heptanoic, and octanoic acids [2].

In addition to optimized production strains and fermentation processes, efficient separation of carboxylic acid from the aqueous fermentation broth is indispensable to compete with the current petrochemical production processes. The present study focused on carboxylic acid production and recovery from UFMP, real industrial wastewater by extraction with different solvents.

2 MATERIAL & METHODS

The selection of potential extractants for the separation and purification was evaluated by the conductor-like screening model for real solvents (COSMO-RS)[3].The ultra-filtered milk permeate (UFMP) was collected through Babcock Dairy Plant is located at the University of Wisconsin -Madison, Madison, USA. The reactor used in the assays was inoculated with the acid sludge used to seed the ultra-filtered milk permeate fed reactor derives from a mesophilic, acid-phase digester at Nine Springs Wastewater Treatment Plant (Madison, WI).The UASB with a height of 54 cm, a diameter of 4.1 cm, and a total volume was 1.4L was fed with UFMP (52 g/L COD). Influent rate (using the milk permeate amended with 400 N-NH4Cl mg/L) was 1 L/ day, and the recirculation rate was 110 liters per day. The liquid retention time was 1.4 days. The temperature was controlled at 35℃ using a water bath and pH was 5.5. Carboxylic acids were produced from UFMP by mixed culture, for the extraction. Samples were taken periodically.

The extractions were performed with octanol and toluene, at Erlenmeyer with a volume ratio of solvent/effluent of 1:1, 1:2 and 1:3 with a time from 1 min until 330 min. Different pH (1; 1.7; 2.5 and 4) were evaluated. The samples from effluents, aqueous phase, and organic phase were collected for chemical analyses. End products and 7 organic compounds from GC and HPLC were analyzed in accordance with Scarborough et al. (2019).

3 RESULTS & DISCUSSION

Carboxylic acids were produced by UASB from UFMP by mixed culture, for the extraction. Lactic acid (6.7 g/L), acetic acid (12.8 g/L) and butanoic acid (4.7 g/L) were the major metabolites. Moreover, small amounts of pentanoic acid and hexanoic acid were found. The main metabolic pathway is of ethanol-acetate with ethanol. This occurs with a higher amount of ethanol and acetate than 47% of the soluble metabolites.

Utilizing COSMO*therm* software, this study predicted suitable extractants for carboxylic acid separation, focusing on log P values in biphasic systems of water and organic solvents, such as alcohols and hydrocarbons. Log P ranged from -3.10 in heptane (C2) to 3.11 in diethyl ether (C8), indicating a preference for solvents with higher log P for optimal acid extraction. For mixed acids, a balance between highest log P and differential log P (Δlog P) was essential. Certain solvents were excluded due to toxicity, volatility, and environmental concerns, with hydrocarbons also showing low yields. Despite these challenges, octanol and toluene emerged as viable solvents, supported by previous empirical evidence of octanol's effectiveness. This selection process underscores the importance of balancing extraction efficiency with environmental and safety considerations in solvent selection for carboxylic acid recovery.

Figure 1 shows the results extraction efficiency for different ratios (1:1; 1:2 and 1:3). For octanol as a solvent, butanoic acid range from 63% to 89%, and hexanoic acid about 92% shows the greatest extraction efficiency. For Toluene as a solvent, butanoic acid range of from 20% until 46% percent and hexanoic acid from 70% until 97% shows the greatest extraction efficiency. Hexanoic acid had the best recovery was achieved when one to one solvent to solution ratio was used. So, the efficiency of carboxylic acid extraction decreases with a reduction in the amount of solvent, the rate of 1:1 was the most efficient for both solvents, except for hexanoic acid using octanol (the same extraction efficiency).

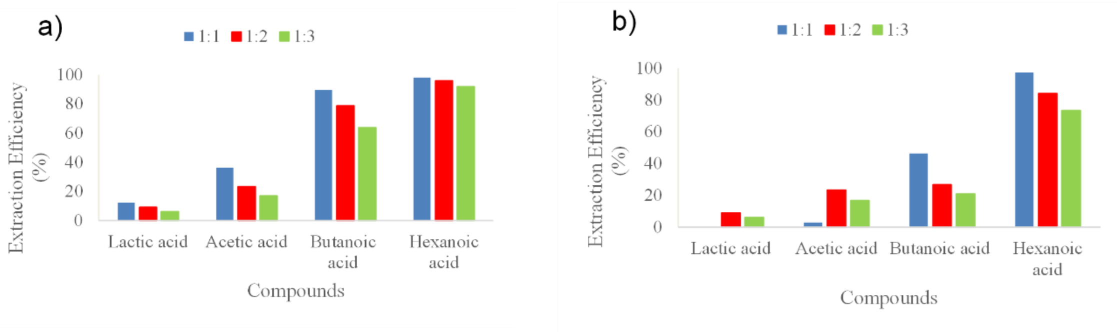

Figure 1 Extraction equilibrium for different ratios (1:1; 1:2 and 1:3) with use of (a) octanol as extractant (b) toluene as extractant.

One of the most important factors for effectively extracting carboxylic acids is pH. In the extraction, only the protonated form of the acid is extracted and consequently, the extraction is more efficient at low pH [4]. So, the effect of different pH (1; 1.7; 2.5 and 4) on the partition coefficient was evaluated. The best rate in the study previous (1:1) was used, with a time of 3 h. Octanol and toluene were used as a solvent.

Regarding extraction efficiency with different pH (Figure 2), using octanol as a solvent, lactic acid ranges from 4% to 19%, acetic acid from 27% to 43%, butanoic acid from 84% to 90%, and hexanoic acid about 98%. Lactic acid presented the lowest extraction ability at pH=4 (4.5 %). Hexanoic acid presented better extraction ability, with 97%, no significant changes with different pH.

Regarding extraction efficiency using toluene as a solvent, acetic acid showed the lowest recovery rates in all cases (up to 2.7%), followed by lactic acid (up to 3.0%) With a decrease in pH from 4 to 2.5, there was a decrease in the efficiency of extraction for butanoic and hexanoic acid. Generally, the best carboxylic recovery was achieved when pH was 2.5 using the rate of 1:1. The highest recovery efficiency of hexanoic acid (96%, pH= 2.5).

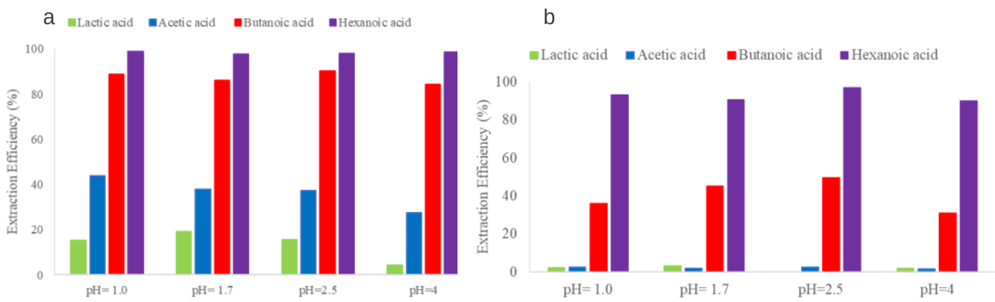

Figure 2 Effect of pH on the extraction efficiency using: (a) octanol as solvent (b) toluene as solvent after equilibrium.

4 CONCLUSION

This study successfully demonstrated the viability of producing carboxylic acids from ultra-filtered milk permeate (UFMP), with the ethanol-acetate pathway emerging as predominant, accounting for over 47% of soluble metabolites in the form of ethanol and acetate. Additionally, substantial levels of lactic acid were extracted from dairy waste residue, highlighting the potential of such waste as a resource. Experimental findings from batch extractive tests indicated that the solvent-to-effluent ratio significantly impacts extraction efficiency, particularly for butanoic and hexanoic acids, where high efficiencies were achieved. A 1:1 ratio was found to be optimal for maximizing extraction efficiency across solvents, with octanol performing equally well for hexanoic acid. However, the study also revealed that both tested solvents were less effective in recovering shorter-chain acids like lactic and acetic acid, which showed a tendency to remain in the aqueous phase. These insights underscore the complexity of extracting specific acids based on their chemical characteristics and highlight the need for tailored approaches in the recovery process to optimize efficiency and sustainability in carboxylic acid production from waste streams.

REFERENCES

[1] REYHANITASH, R.; BROUWER, T. KERSTEN, S.R.A.; VAN DER HAM, A.G.J.; SCHUUR. B. Liquid-liquid extraction-based process concepts for recovery of carboxylic acids from aqueous streams evaluated for dilute streams. Chemical Engineering Research and Design, 137, 2018, 510-533.

[2] SCARBOROUGH, M.J. Harnessing microbiomes to close the carbon cycle: production of beneficial chemicals from complex renewable feedstocks. Dissertation at the University of Wisconsin Madison, 2019.

[3] KHAN, A.V.B.; NASEF, M.M.E.; BUSTAM, M.A.; GOTO, M.; MONIRUZZAMAN, M. Screening of ionic liquids for the extraction of biologically active compounds using emulsion liquid membrane: COSMO-RS prediction and experiments. Journal of Molecular Liquids , 309 , 2020, 113122.

[4] NELSON, R. S.; PETERSON, D. J.; KARP, E, M.; BECKHAM, G. T.; SALVACHÚA,D. Mixed Carboxylic Acid Production by Megasphaera elsdenii from Glucose and Lignocellulosic Hydrolysate. Fermentation ,2017, 3, 10.

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