



Volatile fatty acids recovery from the effluent of an acidogenic digestion process fed with grape pomace by adsorption on ion exchange resins



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HIGHLIGHTS

- Volatile fatty acids (VFA) were separated from anaerobic digestion effluent.
- Tertiary amino resin featured low cost and high ion exchange (IE) performances.
- Highest IE recovery were obtained for the high added value long-chain VFAs.
- Basified ethanol leads to complete VFA desorption.
- VFA IE model includes anion competitive effect and $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffering effect.

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ABSTRACT

The purpose of this work was to perform the preliminary development and optimization of a volatile fatty acid (VFA) separation process from an actual effluent of grape pomace acidogenic anaerobic digestion by ion exchange (IE) resins. Batch IE and desorption tests were performed with acetic acid, VFA synthetic mixtures and an actual digestate. The comparison of four amino IE resins led to the selection of Amberlyst A21, a tertiary amino resin characterized by a relatively low price and high IE performances. The latter increased by increasing VFA chain length, this suggesting a relevant contribution of physical adsorption for high molecular weight VFAs. The best IE performances were obtained at pH 3–4.5 in the presence of acetic acid alone, and at pH 6.5 with the actual digestate. Basified ethanol allowed a complete desorption of all the adsorbed VFAs. Solvent recovery by evaporation, obtained with negligible losses of the desorbed VFAs, allowed the production of a highly concentrated water solution of the recovered VFAs. This result represents a crucial feature for the development of innovative VFA-fed biotechnological processes such as polyhydroxyalkanoate production ones. A model taking into account VFA IE, the competitive effect exerted by other anions and the $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffering effect that characterizes actual digestates led to a satisfactory prediction of the experimental data, and represents an effective tool to identify the optimal operational conditions. Overall, Amberlyst A21 represents an effective candidate for the development of an adsorption/desorption process for VFA recovery from the effluents of acidogenic fermentations.

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1. Introduction

Volatile fatty acids (VFAs) are important bio-based chemicals, which can be produced through anaerobic digestion (AD) processes carried out under acidogenic conditions [1]. VFAs can represent precursors for the production of biopolymers, biofuels and chemicals such as esters, ketones, aldehydes, alcohols and alkanes. Thus, their recovery from liquid effluents of anaerobic acidogenic

digestion (AAD) processes becomes attractive in the perspective of approaching the so called “carboxylate platform” [2]. The AAD of agro-industrial waste could represent an effective and competitive approach for the production of VFAs. Therefore, the production of highly concentrated VFAs effluents from biowastes and their subsequent separation is of interest in the perspective of obtaining valuable products from wastes [3,4].

Grape pomace (GP) is the most plentiful solid waste originated by the winemaking process. 3.2 Mtons of GPs were produced in Europe in 2013 [5]. In the past they were mostly used for ethanol production in distilleries. Recently, alternative disposal methods

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List of symbols

$[A^-]$	ion acetate concentration at the equilibrium (mol/L)	$C_{S,A}$	sorbed concentration of acetic acid (mmol/g _{dry resin})
$[A]_0$	acetic acid concentration initially supplied to the batch system (mol/L)	$C_{S,A,\infty}$	sorbed acetic acid concentration at saturation, in the Langmuir model (mmol/g _{dry resin})
$[Cl^-]$	chloride ions concentration at the equilibrium in the liquid (mol/L)	$C_{S,A,eq}$	sorbed acetic acid concentration in the solid at equilibrium (mmol/g _{dry resin})
$[CO_2]$	absorbed CO ₂ concentration in the liquid (mol/L)	$C_{S,VFA,eq}$	VFA concentration in the solid at equilibrium (mmol/g _{dry resin})
$[CO_3^{2-}]$	carbonate concentration in the liquid (mol/L)	H_{CO_2}	Henry constant for the absorption of CO ₂ in water (29.76 atm L/mol)
$[H^+]$	protons in solution concentration the equilibrium in the liquid (mol/L)	$k_{a,A}$	acetic acid dissociation constant ($1.8 \cdot 10^{-5}$ mol/L)
$[H_2CO_3]$	carbonic acid concentration in the liquid (mol/L)	k_{a1,CO_2}	first dissociation constant of carbonic acid ($2.52 \cdot 10^{-4}$ mol/L)
$[HA]$	acetic acid concentration at the equilibrium (mol/L)	k_{a2,CO_2}	second dissociation constant of carbonic acid ($5.64 \cdot 10^{-11}$ mol/L)
$[HCO_3^-]$	bicarbonate concentration in the liquid (mol/L)	$k_{b,R}$	basic equilibrium constant of the resin (mol/L)
$[Na^+]$	sodium ions concentration at the equilibrium in the liquid (mol/L)	k_{h,CO_2}	CO ₂ hydration constant = $1.70 \cdot 10^{-3}$ (–)
$[OH^-]$	hydroxy groups concentration at the equilibrium in the liquid (mol/L)	$k_{s,RA}$	equilibrium constant of the resin-acetic acid salt (L/mol)
$[R_3N]$	resin amino groups concentration at the equilibrium in the liquid (mol/L)	k_W	dissociation constant of water (10^{-14} mol ² /L ²)
$[R_3N]_0$	resin amino groups concentration initially supplied to the batch system (mol/L)	$mol_{VFA,initial}$	moles of VFAs in the liquid before the adsorption test
$[R_3NAH]$	group amino-ion acetate concentration at the equilibrium in the liquid (mol/L)	$mol_{VFA,sorbed}$	moles of VFAs sorbed by the resin
$[R_3NH^+]$	protonated resin amino groups concentration at the equilibrium in the liquid (mol/L)	m_{resin}	dry resin mass (g _{dry resin})
$C_{calc,i}$	i th calculated concentration, for the calculation of the correlation coefficient (mol/L)	P_{CO_2}	CO ₂ partial pressure in the gas phase (atm)
$C_{exp,i}$	i th experimental concentration, for the calculation of the correlation coefficient (mol/L)	$V_{L,added}$	liquid volume added to the resin (mL)
$C_{exp,m}$	average value of the experimental concentrations in a given test, for the calculation of the correlation coefficient (mol/L)	$V_{L,final}$	final liquid volume (mL)
$C_{L,A}$	acetic acid concentration in the liquid (mol/L)	X_p	vector of the simulated equilibrium concentrations in the Gauss Newton method
$C_{L,A,eq}$	total acetic acid concentration in the liquid at equilibrium (mol/L)	y	vector of the experimental data, in the Gauss Newton method
$C_{L,VFA,0}$	initial VFA concentrations in the liquid (mmol/L)	Y_{ads}	adsorption yield, calculated as $mol_{VFA,sorbed}/mol_{VFA,initial}$ (–)
$C_{L,VFA,eq}$	final VFA concentrations in the liquid (mmol/L)	ϑ_A	adsorption equilibrium constant of acetic acid in the Langmuir model (mol/L)
		ϕ	vector of the experimental conditions used for the best fit of the proposed model
		θ	vector of unknowns in the best fitting

and applications started to be applied, such as thermovalorisation [6] or the production of animal feed [7], compost and fertilizers [8,9]. Furthermore, GP carries a particularly high concentration of tannins and phenolic compounds, whose antioxidant features make their recovery industrially attractive and widely studied [4,10]. GP is characterized by a significant amount of organic carbon, mainly composed by cellulose ($14\% \pm 3\%$), hemicellulose ($13\% \pm 7\%$) and lignin ($33\% \pm 8\%$) [3]. GP AD is an interesting way to convert the organic carbon into energy. However, low specific biomethanization yields were generally obtained ($120\text{--}270$ NL_{CH₄}/kg_{VS} [11,12]). Several explanations were proposed for this evidence, such as the high amounts of slowly-fermentable lignin and the inhibitory effects due to the occurrence of alcohols and polyphenols [12]. While biomethane production from GP appears to be not competitive, its anaerobic digestion could be of interest if it is truncated before methanogenesis, so as to produce a VFA mixture. In order to curb methane production and to promote VFA accumulation, high organic loading rates in the $5\text{--}15$ kg_{COD}/(m³ d) range are required, whereas the optimal retention time are in the $1\text{--}7$ d range [13].

VFA recovery from the acidogenic broth is the main obstacle to their utilization. In fact, a multiple phase separation and enrichment process is generally required in order to obtain marketable products from effluents of biomass transformation processes. In particular, a well-established “5-Stages Universal Recovery Process” was proposed for the recapture of valuable compounds from

food waste [14]. Many VFA recovery methods have been evaluated. Liquid-liquid extraction, based on the use of specific anionic extracting agents (such as organophosphates and aliphatic amines) in solvents, is characterized by high efficiencies and easy application, but it is not environmentally friendly [15]. In electrodialysis (ED), VFAs are carried across a membrane, from a solution to another, thanks to the application of a voltage difference between two electrodes [16]. High membrane cost, high energy demand, membrane fouling, back diffusion and polarization represent the main problems of the ED approach. Nanofiltration, a pressure-driven membrane separation based on size and electrical interactions, shows a high selectivity towards VFA. However, it is characterized by high membrane cost and energy demands, and it does not lead to the production of highly concentrated VFA solutions [17].

VFA adsorption and ion exchange (IE) are based on the interaction between the carboxylate groups of solved VFAs and the active sites of a solid matrix. In particular, while adsorption is based on a physical interaction between the adsorbent and the protonated neutral form of the VFA, IE is based on the formation of ionic bond between the ionized acid and a cation, such as an ammonium salt, which represents the functional group of the commonly used anionic IE resin. This technology represents an interesting approach for VFA recovery, since the adsorbent can be directly applied into the effluent and easily separated from it. Adsorption can be effectively applied for the recovery not only of VFAs [18] but also of other

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