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VFA RECOVERY FROM ANAEROBIC FERMENTATE: FOCUSING ON ADSORPTION AND DESORPTION PERFORMANCES

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ABSTRACT

Volatile Fatty Acids (VFAs) are valuable products from acidogenic fermentation, whose separation from digestor's effluents and subsequently concentration represent the key step for their usage at industrial grade. In this study different batch adsorption tests were performed both on the single VFA, using 0.5 g of three solid matrices (Powdered Activated Carbon (PAC), Lewatit VP OC 1065, Amberlyst A21), and on VFA mixtures using Lewatit and Amberlyst as adsorbents. Adsorption yields around 70% for PAC and 86-96% for Lewatit and Amberlyst, were achieved for the single VFA tests at an initial concentration of 5 g/L. The VFA mixture tests at 25 g/L (5 g/L for each VFA) showed lower yields (40% and 27% for Lewatit and Amberlyst, respectively), but a higher selectivity for long-chain VFAs, especially n-caproic with adsorption yield of 74% (Lewatit) and 51% (Amberlyst). Batch desorption tests were performed adopting 2 desorbents (ethanol and water) at various NaOH concentration (1, 0.1, 0.01 M) on Lewatit and Amberlyst. The VFA desorption was almost complete at 1M NaOH on the two matrices both in ethanol and water solutions. This condition was further studied using different volumes of desorbent (5, 3 and 2 mL) with the aim to reduce the desorbent's amount and increase the VFA concentration. An average desorption yield of about 85% were met at 1 NaOH ethanol and water solutions on Lewatit, allowing a final VFA concentration of 40 g/L, 1.6 times more than initial concentration.

KEYWORDS: Volatile Fatty Acids; adsorption; desorption; Ion Exchange resins; Dark Fermentation; powdered activated carbon.

1. Introduction

Volatile Fatty Acids (VFAs) are short-chain carboxylic acids, commonly used as biological precursors in pharmaceutical, cosmetic, food, plastic industries and bio-fuel production.[1], [2] Thus, VFAs are a high-demand chemicals, with values ranging from 800 €/ton for acetic acid, to 1,650 and 2,500 €/ton for butyric and propionic acids, respectively.[3] VFAs are mainly produced via non-renewable resources and fossil-oil; however, the rising concerns about environmental safety and the progressive depletion of petroleum reserves have increased the interests in ecological-based production of VFAs, such as acidogenic fermentation of household, industrial and agricultural wastes.[4]

VFA production from food wastes has been largely investigated in the last years because of the relatively high VFA production capacity. It was demonstrated that the best operative conditions for the acidogenic fermentation are: neutral pH range (6.0 – 7.0); Hydraulic Retention Time (HRT) lower than 10 days; temperatures between 40°C and 60°C (thermo- and hyperthermophilic range); 10 kgVS/m^{3}d of organic loading rate; mineral acid addition (0.5 – 3.0%) and thermal pretreatment (140-170°C).[5]

The main challenge for fermentative VFAs production is the separation step from the fermentation medium and their concentration. Many techniques have been proposed: i) VFA precipitation, ii) liquid-liquid extraction, where VFAs are separated by organic solvents; iii) membrane separation, using electro-dialysis, where a voltage difference promotes the VFAs passage through the membrane; iv) nanofiltration, where the passage is driven by size or pressure's gradient and v) adsorption, where VFAs are separated through the VFA interactions with the activated sites of a solid matrix.[6]

Precipitation and liquid-liquid extraction are easy to install and scale-up, and have a high yield of extraction, but the production of solid wastes and the usage of organic solvents made them dangerous and non-environmentally friendly.[3] Membrane methods, such as electrodialysis, nanofiltration and reverse-osmosis, permits to obtain high yield of acids, but application on real bioreactor's effluents may be cumbersome due to high membrane fouling.[7] Ion exchange adsorption, based on interactions between the negative-charged carboxylic group with a positive-charged group of a solid matrix, usually an amine, is easy to operate and grants a relatively high selectivity.[8] For these reasons, Ion exchange adsorption could be an interesting method for industrial-grade VFAs extraction, especially for wastewater and fermentation effluents.

In the last years, some researchers investigated the performances of different solid matrices on the VFA adsorption.[6] Da Silva and Miranda[1] confronted the adsorption of single- and multicomponent mixture of VFAs (Acetic, Propionic and Butyric) of Purolite A133S (a tertiary amine functionalized resin) and Granular Activated Carbon (GAC), finding that the resin gave ~35% higher adsorption yields than GAC. Rebecchi et al.[9] studied the VFAs adsorption from a real grape pomace digestate, confronted by a synthetic VFAs mixture, on various resins, finding Amberlyst A21 (tertiary amine) as an effective candidate for adsorption/desorption studies, with adsorption yield of ~61% and ~11% for acetic acid and real grape pomace digestate respectively; desorption achieved ~99% yield with NaOH addition on ethanol and water. Reyhanitash et al.[8] tested the influence of the amine functionalization type of the resins on a VFAs mix, finding that the nonfunctionalized resin was more selective than the functionalized ones (primary, secondary, tertiary).

Even if desorption is the effective challenging step, as it serves in the achievement of industrial-grade concentration of VFA (70-100 g/L), few articles on the topic are currently present in the scientific literature, at the best authors' knowledge. The desorbents must have low price and high efficiency and, possibly, have to be non toxic and environmentally friend. Da Silva and Miranda[1] proposed the adoption of ethanol and n-Propanol for the desorption stage of VFA from Purolite

A133S, observing that ethanol and n-propanol gave ~99% desorption yield and the latter needed less volume to achieve it. After desorption, further operations to increase the VFA concentration are often needed. Rebecchi et al.[9] used basified ethanol for desorption, suggesting a distillation for recovering the extractant while minimizing VFAs loss. [9] Reyhanitash et al.[8] used N_2 flux to regenerate the adsorbent matrix by stripping, recovering VFAs extracted by a condenser.

This work has the main objective to individuate the best solid matrix and the operational conditions to optimize the VFA adsorption. The goal was achieved through various sequential steps, starting the investigation on single VFA and on a synthetic mixture. Firstly, the VFA adsorption performances were compared on three solid matrices: a) powdered activated carbon, b) Lewatit (primary amine) and c) Amberlyst (tertiary amine). The adsorption tests were performed both on all the single VFA (acetic, propionic, butyric, valeric and caproic acids) at different concentrations (1-20 g/L) and on a VFA mixture, simulating the typical VFA concentration in a real food wastes fermentation medium. By this way, it was evaluated simultaneously the performances of the three adsorbents on the single VFA at different concentrations and their VFA affinity in a mixture including all the acids. The best matrices in terms of adsorption yields were tested for the evaluation of the VFA desorption. In particular, basic aqueous solutions and basic ethanol solutions have been used as eluents with the scope to obtain the highest desorption performances with the minimal eluents' volume and to maximize the concentration of the VFA.

2. Materials and Methods

The IEX matrices, the single VFAs (Acetic, Propionic, Butyric, Valeric and Caproic Acids), NaOH and ethanol were purchased by Merck.

2.1 VFA adsorption on three solid matrices

2.1.1 Description of the tests

The adsorption of VFA was studied on three solid matrices: a) powdered activated carbon (PAC) and two Ion Exchange (IEX) resins, b) Lewatit VP OC 1065 (primary amine) and c) Amberlyst A-21 (tertiary amine). They were chosen for the different chemical and physical properties, which are summarized in Table 1. By this way, the influence of the different chemical-physical features on the adsorption of the single VFA and on their mixture can be evaluated.

	PAC	**Lewatit VP OC 1065**	**Amberlyst A-21**
Chemical composition	Carbon	Styrene-divinylbenzene Primary amine (Benzyl amine)	Styrene-divinylbenzene Tertiary amine (Not specified in the technical sheet)
Particles size (mm)	0.001- 0.150	0.47 - 0.57	0.49 - 0.69
Approx pore volume (cm^3/g)	0.65	0.27	0.10
Approx surface area (cm^2/g)	0.12	50.00	35.00

Table 1. Characteristics of PAC, lewatit VP OC 1065, amberlyst A-21

The adsorption tests were conducted on the single VFA (acetic, n-propionic, n-butyric, n-valeric, n-caproic acids) in a concentration range 1-20 g/L and on a VFA mixture at 25 g/L (5 g/L for each VFA). The pH of the different tests was not edited and was in the range 3.0 -6.0, condition which assures the VFA dissociation and the consequent interaction between the VFA and the activated sites of the solid matrices[9].

The tests were performed at batch mode in 15 mL falcons with a working volume of 10 mL and 0.5g (50 g adsorbent/L) of solid matrices, following the procedure of some previous works (Eregowda et al.[4] ,Yousuf et al.[10]). The operative temperature of the adsorption tests was 30°C. The tests were shacked for 3 h on a laboratory shaker at 150 rpm to favor the VFA diffusion in the falcons and their adsorption on the solid matrices. Considering the lower performances obtained from PAC, the adsorption tests on the 25 g/L VFA mixture (5 g/L for each VFA) were performed only on Lewatit and Amberlyst.

As above, the choice to perform the adsorption tests with 0.5 g of adsorbent was taken to obtain to compare the results with the ones obtained by previous works. Moreover, the 0.5 g of adsorbent were adopted to observe the appearing of the solid matrix's saturation by the increasing of the initial VFA concentration. The 0.5 g adsorbent's amount, in fact, was over-estimated to assure a complete adsorption for low initial VFA concentration, but was not enough to adsorb all the VFA in the 25 g/L VFA mixture tests.

All the different tests were conducted in triplicate.

2.1.2 Evaluation of the VFA adsorption and definition of the isothermal kinetic parameters

The experimental data from VFA adsorption tests were used for the determination of the single VFA adsorption isotherms according the Langmuir model, whose equations are reported both in the differential and linear forms (Equations 1 and 2, respectively).[4]

$$q_e = \frac{Q_0 b\, C_e}{1 + b\, C_e} \qquad \text{(Equation 1)}$$

$$\frac{C_e}{q_e} = \frac{1}{b\, Q_0} + \frac{C_e}{Q_0} \qquad \text{(Equation 2)}$$

The adsorption yields of the three IEX matrices were calculated for the single acids at 5 g/L (Equation 3). Being the maximal water solubility of the caproic acid of 10.3 g/L (PubChem[11]), the concentration of 5 g/L can assure an easy and complete solubilization of the VFA in water and, consequently it was chosen to compare the adsorption yields of all the single VFA on the three solid matrices (Equation 3).

$$\text{Adsorption yield (\%)} = \frac{C_0 - C_e}{C_0} \cdot 100 \qquad \text{(Equation 3)}$$

The equilibrium adsorption capacity (q_e) of each solid matrix was also evaluated as below (Equation 4):

$$q_e = \frac{c0 - ce}{m} \cdot V \qquad \text{(Equation 4)}$$

Where:

C_0 is the initial concentration of each VFA (mg/L), C_e is the equilibrium concentration of each VFA in the solution (mg/L), V is the volume of the solution (L), m is the mass of the adsorbent (g), q_e is the amount of adsorbate in the adsorbent under equilibrium conditions (mg/g), Q_0 is the maximum monolayer coverage capacities (mg/g), b is the Langmuir's isotherm constant (L/mg).

Instead, the adsorption performance on the VFA mixture was evaluated considering both the adsorption yield of each and all the VFA (Equation 3).

For a complete understanding of the adsorption phenomenon on the different solid matrices, another parameter was introduced with the aim to express the affinity between adsorbents and the VFAs. This parameter was rearranged from the "water-octanol partition coefficients (Kow)", which is defined as the ratio of the concentrations of a solute between two solvents: a hydrophobic solvent (octanol) and a hydrophilic one (water). Consequently, Kow expresses a measure of lipophilicity or hydrophobicity of the compounds. Negative Kow values are typical of very hydrophilic molecules, while Kow positive value of lipophilic compounds. Close to zero Kow demonstrates the double nature (hydrophilic and lipophilic) of the solvent.[12]

Nielsen et al.[13] edited Kow to determine the adsorption potential of a solute on a specific solid matrix. They defined the "equilibrium resin-VFA partition coefficient" ($K_{r/VFAi}$), which could be expressed as:

$$K_{r/VFAi} = \frac{LVFA,i}{[VFA,i]} \qquad \text{(Equation 5)}$$

Where $L_{VFA,i}$ is the specific amount of VFA_i on resin at equilibrium (mmol/kg) and $[VFA,_i]$ (mM) is the concentration at equilibrium of the specific VFA in the aqueous phase. Since the mechanism of adsorption is driven by hydrophobic interactions between the solute molecules and the resin surface, the greatest overall adsorption will occur on the most hydrophobic resins, as well as by those resins with high specific surface areas. Likewise, the more highly hydrophobic solutes should experience the strongest interactions with the resin phase and thus be subject to the greatest adsorption.[13]

2.2 Desorption of VFA

2.2.1 Description of the tests

The desorption study was tested on the VFA mixture at 25 g/L (5 g/L each acids) on the two matrices which demonstrated the best adsorption yields in the previous part of the work, lewatit and amberlyst. The concentration of 25 g/L was chosen because it is close to the VFA concentration of a real fermentation broth from food wastes (Strazzera et al., 2018).

After the adsorption phase, the equilibrium VFA solution was separated from the solid matrices by a filtration operation (mesh size 0.45 μm). Then, the VFA desorption from the selected matrices (lewatit and amberlyst) was performed with different desorbents. A first round of tests was carried out using: i) distilled water; ii) NaOH aqueous solutions at 1M, 0.1M and 0.01 M and iii) NaOH solutions (1M, 0.1 M and 0.01 M) in ethanol. The desorption operation was conducted keeping all the samples in agitation at 150 rpm for 2 hours.

The eluent desorbents' volume for all these tests was of 5 mL, the half of the initial VFA solution's volume used for the adsorption tests. Then, a second round of tests was conducted with lower amounts of desorbents (3.0 and 2.0 mL) in order to increase the VFA concentration as much as possible. The desorbents adopted in this last stage of desorption tests were ethanol (1 M NaOH) and water (1 M NaOH) solutions, the ones with the highest desorption yield in the previous tests conducted at 5 mL of volume.

2.3 Analytical methods

The VFA equilibrium concentrations in the solution were determined by ion chromatography system (Dionex ICS 1100 with AS23 column). pH was measured through Mettler Toledo Five Easy pH meter. All the VFA concentrations were expressed in terms of Chemical Oxygen Demand (COD).

3. Results and discussions

3.1 VFA adsorption on three solid matrices

3.1.1 Adsorption tests on the single VFA

The adsorption performance of the three matrices was tested on the single VFA at different concentration ranges (1-20 g/L).

Figure 1 shows the adsorption yields of the matrices (Equation 3) for the single VFA tests at 5 g/L.

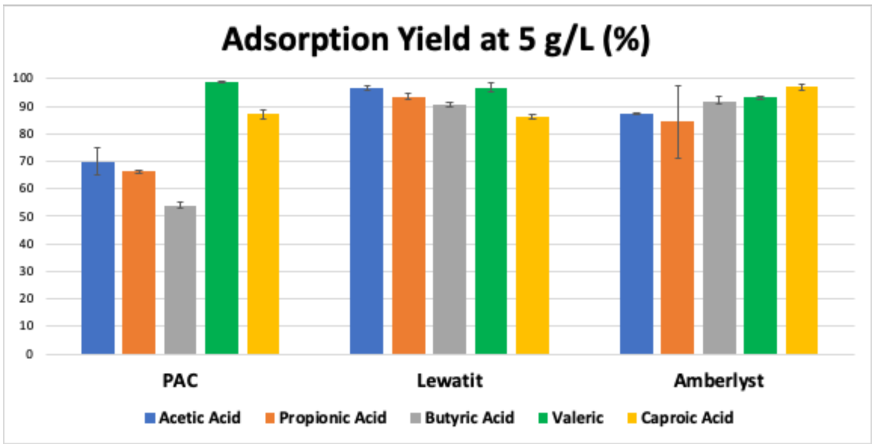

Figure 1. Adsorption yields of the matrices for single VFA at 5 g/L.

The most relevant result consists in the lower adsorption performances of PAC than lewatit and amberlyst. The acetic, propionic and butyric acids' adsorption yields on PAC were of about 70%, 67% and 54%, respectively, with a decreasing trend. Instead, the adsorption of valeric and caproic acids (99% and 87%, respectively) was similar to the performances achieved by the other matrices. This trend can be explained considering the solubility of the VFA, which decrease with the number of the C atoms in the chain. Solubility represented one of the main factors, influencing the VFA adsorption on PAC: it is favored when the solubility decreases as VFA become more and more hydrophilic, thus, more similar to the solid matrices than to the aqueous phase.[14] This consideration explains the higher adsorption of valeric and caproic acids (solubility values of 20 and 10.8 g/L at 20°C, respectively) than acetic[15], propionic[16] and butyric[17] acids, which have a solubility superior to 100 g/L (20°C).

Lewatit and Amberlyst demonstrated a very high adsorption capacity with yields in the range of 86-96% for all the VFAs. But, a different behavior of these IEX matrices emerged from the analysis of Langmuir adsorption's curves, showing the specific equilibrium adsorption yields (mg_{VFA}/g dry resin) of the single VFA tests at different initial concentrations (Figure 2).

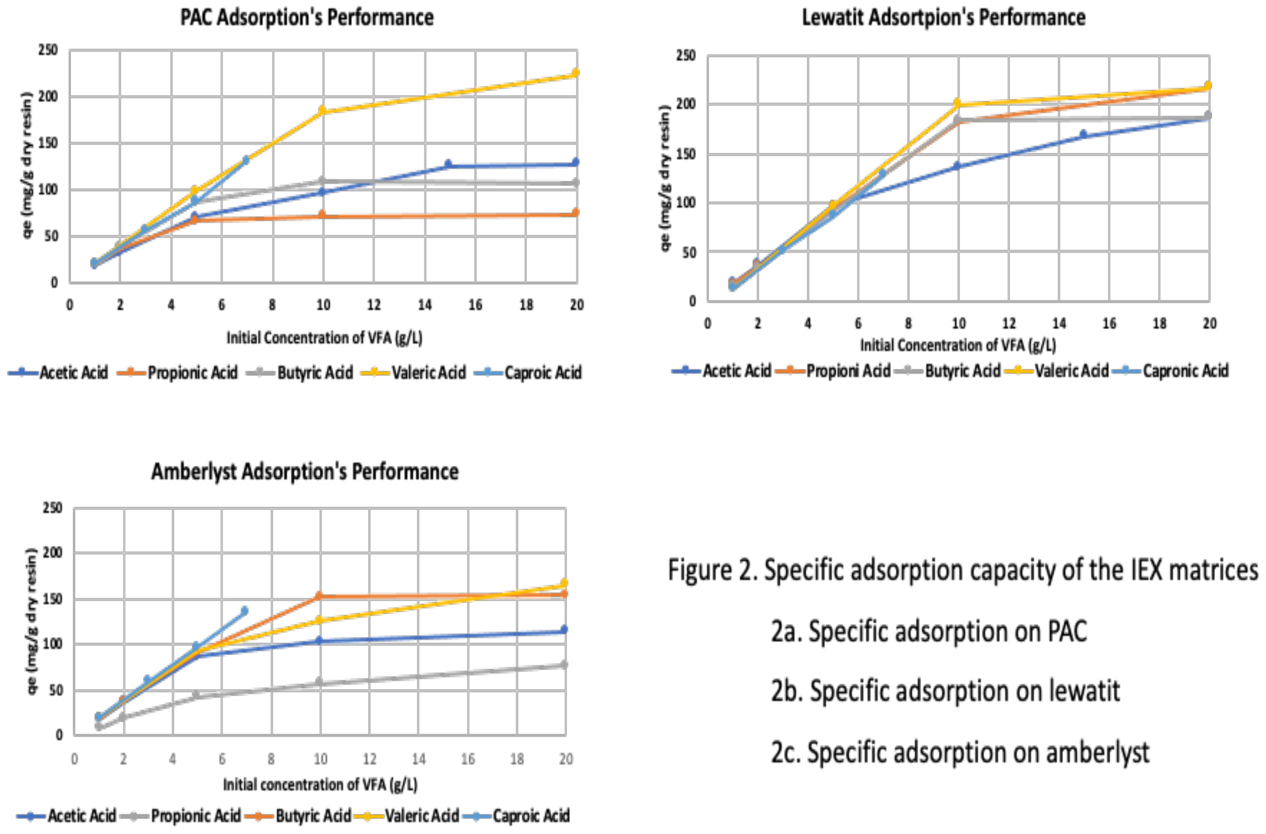

Figure 2. Specific adsorption capacity of the IEX matrices

2a. Specific adsorption on PAC

2b. Specific adsorption on lewatit

2c. Specific adsorption on amberlyst

Figure 2. Langmuir curves for each VFA on the considered IEX resins.

All the curves show an asymptote of the specific adsorption capacity for the VFA concentrations higher than 15-20 g/L, which can be easily explained with the reaching of the saturation capacity of the resins. Adsorption is a chemical-physical phenomenon, leading to the instauration of interactions between the molecules in the fluid and the solid matrices, which have some specific points (activated sites), able to react with the functional group of the molecules.[18] Clearly, there is maximum equilibrium adsorption capacity, beyond all the other molecules do not find free activated sites, remaining in the aqueous solution.

The equilibrium adsorption capacity was different for the IEX matrices: PAC had q_e in the range 70-125 mg_{VFA}/g dry resin, with the exception of valeric acid which was adsorbed more (223 mg_{VFA}/g dry resin). Then, q_e values of Amberlyst were in the range 114-165 mg_{VFA}/g dry resin, except for propionic acid, whose adsorption was lower (76 mg_{VFA}/g dry resin). Lastly, Lewatit had the best performances with q_e value in the range of 185-220 mg_{VFA}/g dry resin with all the VFA.

The equilibrium adsorption capacity of the resins is influenced by their physical properties, summarized in Table 1. The number of the activated sites, responsible of the adsorption phenomenon, depends on the particles' sizes, on their porosity and mainly on the superficial area. Higher is the surface, higher are the activated sites installed on it.[19], [20] Lewatit is the resin with the highest surface area of 50 cm^2/g, while PAC the lower one (0.12 cm^2/g). Porosity of the particles is also important as the void degree is directly correlated to the surficial area.[21] From this point of view, PAC has the highest internal porosity (0.65 cm^3/g) among all the other matrices, but its particles, being in powered status, are the smallest ones (Table 1). This characteristic decreases strongly the porosity between the different PAC particles (external porosity), affecting negatively the transport phenomenon of the VFA on the PAC (Battista et al., 2018).[21]

The different behavior of the three solid matrices were confirmed by the isothermal kinetic parameters too (Table 2). The parameters have not been calculated for caproic acid, in consideration of its low solubility in water which not allowed to reach saturation condition with 0.5 g of matrices.

Table 2. qe and B values for the different single VFA's adsorption tests.

	PAC		Lewatit VC OP 1065		Amberlyst A 21	
	q_e (mg/g)	b (L/mg)	q_e (mg/g)	b (L/mg)	q_e (mg/g)	b (L/mg)
Acetic	153.76	11.66	182.20	24.12	114.91	23.44
Propionic	73.30	14.44	153.37	19.12	97.36	16.18
Butyric	107.96	16.86	207.55	27.81	146.92	23.39
Valeric	227.56	21.29	217.16	28.77	165.43	25.78

Higher qe values belong to IEX matrices having a bigger activated surface, as commented above. It is consistent with the meaning of the Langmuir constant (b), which represents the sorption/desorption equilibrium constant between the adsorbates (VFA) and the binding sites of the IEX matrices. It is correlated to the adsorption capacity: a variation of the suitable area and of the adsorbent's porosity can be expresses with b constant, implying the fact that higher adsorption capacity can be resulted from large surface area and pore volume.[22] Thus, higher b constants indicate a bigger affinity between VFA and the IEX matrices. Lewatit VC OP 1065 has the highest b constants of the IEX matrices for all the acids, while PAC the lowest ones, confirming the existing correlation between the physical characteristics of the matrices and their ability to adsorb the VFA.

3.1.2 Adsorption tests on the VFA mixture

Lewatit and Amberlyst, the IEX matrices with the better adsorption performances, were selected for the adsorption tests on the VFA mixture at a total concentration of 25 g/L, 5 g/L for each VFA. Table 3 shows the VFA adsorption yields from VFA mixture tests on 0.5 g of the two matrices.

	LEWATIT VP OC 1065		AMBERLYST A-21	
VFA	q_e (mg/g)	Adsorption Yield (%) from VFA Mixture tests	q_e (mg/g)	Adsorption Yield (%) from VFA Mixture tests
Acetic	36.97 ± 2.16	26.21 ± 1.04	26.61 ± 1.40	23.26 ± 2.93
Propionic	12.45 ± 3.49	15.56 ± 0.48	12.14 ± 1.70	16.42 ± 0.71
Butyric	15.12 ± 5.18	18.90 ± 0.62	14.02 ± 1.49	17.53 ± 0.39
Valeric	39.48 ± 5.69	49.35 ± 2.59	15.70 ± 2.38	23.63 ± 1.98
Caproic	59.36 ± 7.69	74.20 ± 3.14	41.01 ± 1.37	51.26 ± 2.03
Overall	163.38 ± 24.21	40.85 ± 6.05	109.48 ± 17.27	27.72 ± 5.83

Table 3. Adsorption yields from VFA mixture tests (25 g/L) on 0.5g of Lewatit and Amberlyst.

The adsorption yields on the two matrices from VFA mixture tests revealed the presence of a competition between the different VFA to form chemical bonds with the activated sites of the resins. In particular, caproic, acetic and valeric were adsorbed more than propionic and butyric acids. This phenomenon was more marked on Lewatit (74.20%, 26.21 and 49.35, respectively, corresponding to q_e values of about 60, 37 and 40 mg/g, respectively) than in Amberlyst, where the adsorption yields were lower with all the VFA. This different behavior of VFA on the resins was already explained, considering their physical and chemical properties (Table 1).

Instead, the bigger tendency of caproic and valeric acids to be more adsorbed on both the resins can be explained from their chemical properties: the vapor pressure, the Kow and pKa (Table 4). According Lama (2013)[14], in presence of a mixture the adsorption is favored with VFA having lower vapor pression, as valeric and caproic acids. Moreover, the better adsorption of valeric and caproic acids is expected also considering the Kow, value of 1.40 and 1.90, respectively. As commented, Kow express the affinity between VFA and the aqueous phase: higher is Kow, lower is the affinity with water. This means that VFA have a higher tendency to form an interaction with the resins.[12], [14], [23]

	Molecular formula	**log Kow**	**Ka (at 25°C, 10^{-5})**	**pKa (at 25°C)**	**Vapor Pression (at 20°C), Pa**
Acetic Acid	$C_2H_4O_2$	-0.20	1.76	4.74	1,540
Propionic Acid	$C_3H_6O_2$	0.30	1.34	4.87	390
Butyric Acid	$C_4H_8O_2$	0.79	1.54	4.82	57
Valeric Acid	$C_5H_{10}O_2$	1.40	1.52	4.81	20
Caproic Acid	$C_6H_{12}O_2$	1.90	1.31	4.88	27

Table 4. Physical and chemical properties of the VFA.

VFA are monocarboxylic acids with -COOH as functional group, which interact with the activated sites of the solid matrices. Depending on the pH, these acids can be in dissociated and un-dissociated forms. Ka (or pKa, in alternative form) represents the dissociation constant, defined as the ratio between the VFA concentration in dissociated and un-dissociated form. In particular, when the solution's pH is below the pKa, the VFA is mainly in undissociated form, whereas above pKa value, the VFA is mainly undissociated. The mechanism of the adsorption process changes depending on the resin basicity.[24], [25] With a weak basic resin, the mechanism is mainly based on the adsorption of the undissociated forms of acid on the resin, beside the ion exchange.[9] On the other hand, with a strong basic one, it becomes an anion-exchange process between the dissociated form of the target acid in the solution and the functional group of the resin.[26] Lewatit VP OC 1065 and Amberlyst A21, are both classified as weak resins having a primary (benzyl amine) and tertiary amine (not explicit in the technical sheet), respectively, as functional group (https://moodle2.units.it). The pH of the VFA mixture tests is 3.21± 0.02, lower than the pKa of the VFA (Table 4). It means that VFA are mainly in undissociated form, condition which favors the physical adsorption, rather than ion exchange.[9] However, the different adsorption yields (Table 3) demonstrate the existence of a different basicity potential between lewatit and amberlyst, which can be predict through the $K_{r/VFAi}$ (Equation 5), whose values are reported in Table 5.

VFA	**Lewatit**	**Amberlyst**
Acetic	17.59	7.96
Propionic	23.61	12.38
Butyric	17.42	10.89
Valeric	47.48	14.26
Caproic	not determined	not determined

Table 5. Kr/VFAi values for the different VFA. Caproic acid's Kr/VFAi was not calculated as it is not soluble at 15-20 g/L, when equilibrium was reached with 0.5g of resins.

Lewatit had all the $K_{r/VFAi}$ higher than Amberlyst which is consistent with the overall VFA adsorption yield of about 40%, higher than the one achieved by amberlyst (27%). It demonstrated the better affinity of lewatit with the VFA, which have been more adsorbed than on Amberlyst (Table 3). The adsorption mechanism was explained by Reyhanitash et al. (2017)[8], which worked with Lewatit and Amberlyst on Styrene-divinylbenzene support too. In particular, the VFA molecules interact with the polymeric matrix of the IEX resin through the hydrogen bond─π interactions between their carboxyl groups and the adsorbent's aromatic rings, and the hydrophobic interactions between the hydrocarbon chain and the adsorbent surface. They also confirmed this hydrophobic interaction was higher on Lewatit than in Amberlyst.

3.2 Desorption tests on VFA mixture

Desorption with 5 mL of desorbent, 1/2 of adsorption volume, has been tested on the two matrices which achieved the best adsorption yields, lewatit and amberlyst, using ethanol and water as solvents at various NaOH concentrations (1, 0.1, 0.01 M). Figure 3 and 4 show desorption yields for Lewatit VP OC 1065 and Amberlyst A-21, respectively.

At 1M NaOH, desorption is high (~95%) on both matrices with the two desorbents, for all the acids with the only exception of acetic acid. The decreasing of NaOH concentration, led to the desorption yields' reductions. At 0.1M NaOH, it was of about 45% and 30% for ethanol and water, respectively, on lewatit, while Amberlyst showed higher yield: 80-90% on ethanol and 40-75% on water. Finally, at 0.01 NaOH desorption dropped even more with average values around 30% on ethanol and ~15% on water on Lewatit. The behavior seemed to be different on Amberlyst, where desorption remains high on ethanol (~80%) and drops to ~45% on water.

Desorption was also tested using distilled water as desorbent, but its performances were low: >10% on Lewatit and >15% on Amberlyst.

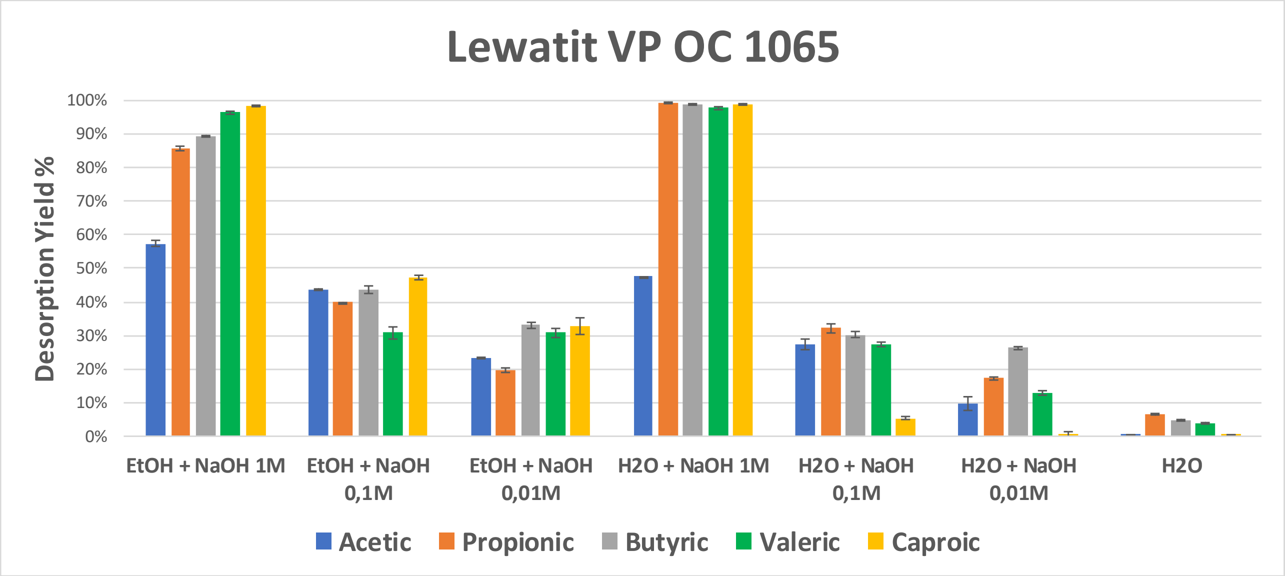

Figure 3. Desorption yields on Lewatit VP OC 1065.

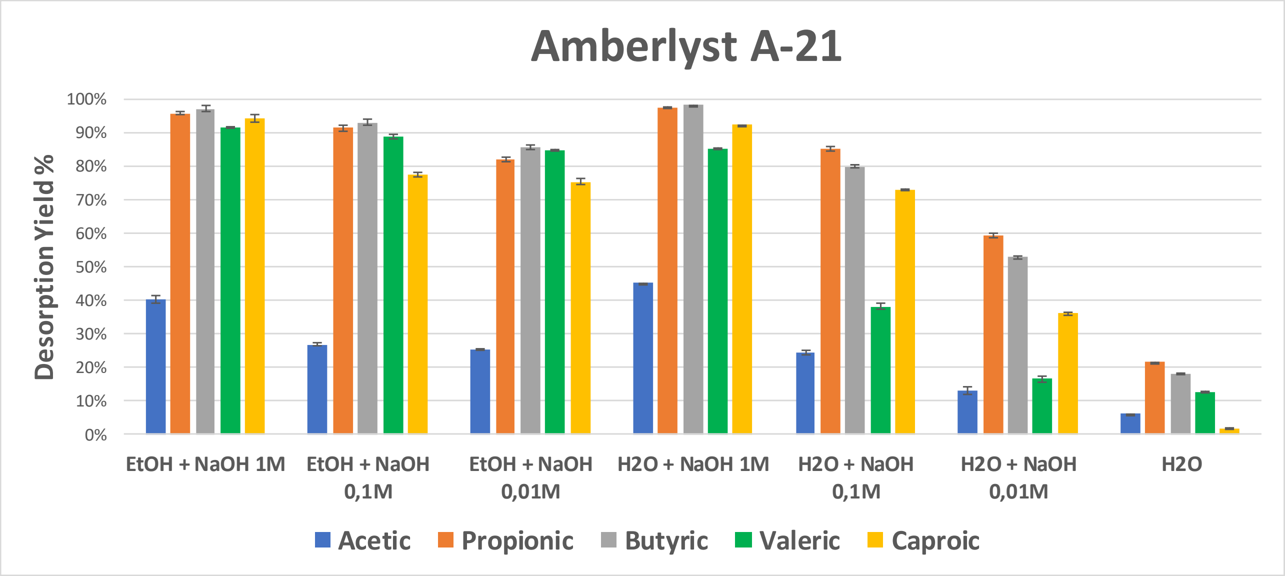

Figure 4. Desorption yields on Amberlyst A-21.

The previous results can be summarized as following: i) almost all of the VFAs absorbed were removed using desorbents (ethanol or water) at 1M NaOH; ii) lowering hydroxide concentration to 0.1 and 0.01 reduces the desorption yields; iii) Amberlyst had high desorption yields also at lower NaOH concentrations, which can be explained simply because of the lower amount of adsorbed VFA. Finally, iv) by lowering the NaOH concentration, the adoption of ethanol as desorbent leads to higher yield of desorption than water. However, at the highest pH value, the desorption capacity of ethanol and water were comparable. Thus, the lower OH ions, at 0.1 and 0.01 NaOH solutions, are enough to assure desorption of VFA on Amberlyst, where the VFA adsorption yield was of 27%, but not in Lewatit as it had a higher adsorption yield of 40% (Table 3). Finally, iv) the adoption of ethanol as desorbent leads to higher yield of desorption than water. It can be explained because ethanol is more hydrophobic than water, thus more competitive for the matrices' active sites.[1] The pH played a fundamental role in the desorption mechanism. The regenerants' pH was measured before and after the desorption step (Table 6) at the different NaOH concentrations for the ethanol and water solution and on the two matrices.

	Initial pH	Lewatit VP OC 1065		Amberlyst A21	
		EtOH	H_2O	EtOH	H_2O
NaOH 1M	14.00	13.95	13.75	13.80	13.65
NaOH 0.1M	13.00	8.00	6.80	7.40	6.20
NaOH 0.01M	12.00	6.85	4.55	6.35	4.35
No NaOH	7.00	n.d.	3.80	n.d.	3.45

Table 6. pH values of desorbent solvent on starting and equilibrium conditions.

It was observed that at 1M NaOH, the pHs were only slightly lower than the initial one of 14. At this concentration there is a very high excess of OH^- ions, which are able to deprotonate the amines, constituting the matrices' functional groups, favoring the complete VFAs desorption.[9] With the decreasing of the NaOH concentration, the final pH moved towards neutral and acidic conditions. It demonstrated an early exhaustion of the OH^- which reduces desorption yield too. Lastly, the desorption yields with distilled water were even poor. In this case, the VFA desorption was probably due to the only instauration of a new matrix/solvent equilibrium hypothesis, which could be confirmed by the desorption yields values which were complementary to the adsorption yields on both matrices (Figure 1).

Considering the very high desorption performances, ethanol and water at 1M NaOH were tested at lower volumes of 3 and 2 mL, in order to favor the VFA concentration.

The desorption yields with a desorbent volume of 3mL were not shown being very similar to the ones obtained at 5 mL.

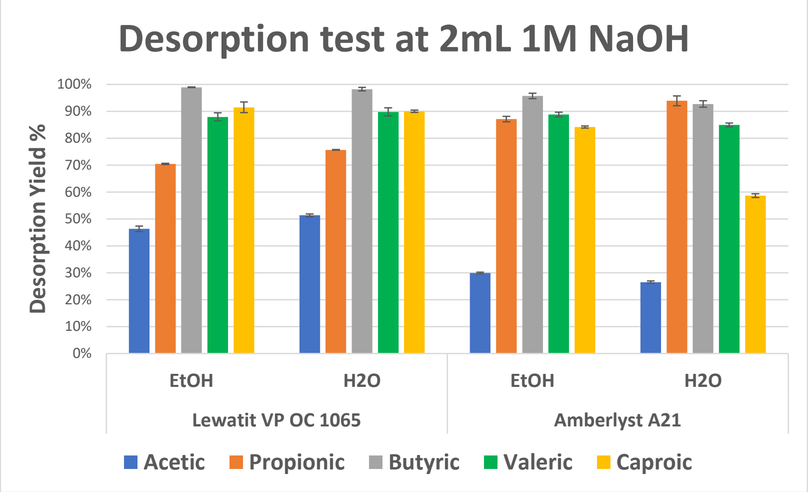

Figure 5. Desorption test with 2 mL of desorbent at 1 M NaOH.

The desorption performances with 2 mL with ethanol and water at NaOH concentration of 1M (Figure 5) were similar to the ones achieved with 5 mL of desorbent's volume too. In particular the desorption yields were in the range 87-96% for butyric, valeric and caproic, when ethanol was adopted as desorbent. The yields were slightly lower with water, especially for caproic acid on amberlyst.

The loss of desorption performances was more evident for acetic acid, which achieved lower yields at all the considered volumes' desorbent (5, 3 and 2 mL). This trend was already observed by Eregowda et al. (2020)[4], who justified this behavoiur supposing a specific desorption mechanism, which is different to the other VFA. In fact, they hyphotyzed that, being the more hydrophilic VFA, the acetic acid's desorption was mainly led by the eluent molecules transport to the surface of the resin rather than the exchanges of the electron at the resin surface.

Conclusions

The main aim of the research was the investigation of the best operational conditions for VFA adsorption/desorption process in order to concentrate VFA from 15-25 g/L, the conventional VFA concentrations after a dark fermentation step, to 50-100 g/L. Batch adsorption tests were conducted on three IEX matrices. Lewatit and Amberlyst achieved high adsorption yield (>90%) on the single VFA tests at 5 g/L, while the adsorption yield on PAC was lower. Thus, only Lewatit and Amberlyst were tested for adsorption tests with VFA mixture at 25 g/L. At this condition, the overall VFA adsorption yields were lower: 40 and 27% for Lewatit and Amberlyst, respectively, as consequence of the activated sites' saturation. Desorption tests were conducted at different desorbents' volumes and at different NaOH concentrations in ethanol and water solutions. It emerged the 1M NaOH concentration allowing the achievement of high desorption yields (70-95%) for Lewatit both in ethanol and water. Considering the yields of adsorption and desorption tests, a final VFA concentration of 40 g/L, 1.6 times the initial concentration, which was obtained with a desorbent' s volume of 2 mL (5 times lower than the initial one) at 1M NaOH both in ethanol and water. This preliminary work will be further researched to improve the VFAs concentration, in order to be viable for industrial use or commercialization.

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