

# Methacrylonitrile-based adsorbents for recovery of VFAs from fermentation broth

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## Abstract

**BACKGROUND:** Adsorption is a promising affinity separation technique to target a sorbate in extremely dilute solutions. In this work, methacrylonitrile (MAN)-functionalized resins were investigated to recover volatile fatty acids (VFAs) from a mimicked fermentation broth as an alternative for the already known amine-based resins and non-functionalized poly(styrene-divinylbenzene) (PS-DVB), aiming for high VFA capacity and selectivity.

**RESULTS:** Next to comparison with commercial PS-DVB resin, also several PS-DVB resins were synthesized as non-functionalized analogues for the new MAN-functionalized resins. For MAN-functionalized resins, the maximum equilibrium VFA loading of about 153 (g acid/kg adsorbent) was found, which is higher than the 125 (g acid/kg adsorbent) for the PS-DVB non-functionalized resins. The water uptake of the PS-DVB resins was with 0.53–0.87 (g water/g adsorbent) significantly lower than for the MAN-DVB resins taking up 0.99–1.85 (g water/g adsorbent).

**CONCLUSION:** Overall, the MAN-functionalized adsorbents retained higher loading capacity for corresponding acid, compared to the PS-DVB resins, while also taking in more water. Acid uptake is due to the hydrogen bonding between the nitrile groups of the resins with carboxyl group of the acids. Moreover, none of the adsorbents displayed an affinity towards the salts present in the fermentation broth.

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**Keywords:** adsorption; volatile fatty acids; methacrylonitrile-functionalized resins; fermentation broth

## NOMENCLATURE

BET	Brunauer–Emmett–Teller
BPO	benzoyl peroxide
DVB	divinylbenzene
HAc	acetic acid
HBu	butyric acid
HLa	lactic acid
HPLC	high pressure liquid chromatography
HPr	propionic acid
IC	ion chromatography
LLE	liquid–liquid extraction
MAN	methacrylonitrile
PEG	polyethylene glycol
PS	polystyrene
PVA	polyvinyl alcohol
S	styrene
THF	tetrahydrofuran
VFAs	volatile fatty acids
Δ	solubility parameter

## INTRODUCTION

Valorizing a waste/wastewater is an interesting approach to the circular economy model, allowing to recover valuable chemicals from waste.<sup>1–7</sup> Over the last decades, researchers have been

focused on converting a waste/wastewater to value-added chemicals by fermentation. Various organic-enriched wastes have potential to be anaerobically fermented into Volatile fatty acids (VFAs) which are short carboxylic acids with a wide range of applications in industry.<sup>1,4,8–11</sup> Every year, 50.3 M tons of waste are produced at the urban level in EU-27 with the organic fractions of municipal solid and sewage sludge being the predominant wastes.<sup>8</sup> Anaerobic digestion of these carbon-rich waste/wastewater towards VFAs have been well studied.<sup>8,11–14</sup> Indeed, the bio-based pathways through fermentation of inexpensive feedstocks appears to be a feasible approach to produce such essential platform chemicals.<sup>15</sup> However, a robust recovery technique is still necessary to recover the produced VFAs from the

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fermentation broth. Anaerobic fermentation of a waste/wastewater results in extremely dilute aqueous solution of VFAs (~1 wt%) due to their low carbon content.<sup>16</sup> Thus, affinity separation techniques such as liquid–liquid extraction (LLE) and adsorption, targeting the VFAs rather than water can be economic routes to recover the VFAs.<sup>16–20</sup> LLE using ionic liquids (ILs) has also been investigated to recover the carboxylic acids.<sup>21–23</sup> From the extraction point of view, ILs appear to be an interesting solvent class to recover the acids from the broths with limited acid content.<sup>22–24</sup> However, the regeneration of ILs remains still challenging.<sup>24</sup>

Adsorption has displayed a promising potential to separate VFAs from extremely dilute solutions.<sup>16,25,26</sup> Various adsorbents have been employed to recover the VFAs from the fermentation broth.<sup>18,27</sup> Ahasa Yousef *et al.*<sup>27</sup> reported 42.68 g/kg adsorption capacity with activated carbon to separate butyric acid from a broth obtained by dark fermentation of food waste, containing 6.6 g/L butyric acid. A total VFA capacity of 76 g/kg is reported for non-functionalized styrene-divinylbenzene based adsorbent with commercial name of Lewatit VP OC 1064 MD PH (called ‘Lewatit’ in this work).<sup>16</sup> Lewatit is a macroporous hydrophobic resin with high surface area and large pore volume. Its high thermal stability and remarkable capacity towards VFAs made it as a promising adsorbent to separate VFAs from the aqueous solutions, followed by thermal regeneration of the resin and recovering the acids in highly concentrated solution.<sup>16</sup> After this initial work,<sup>16</sup> it was realized that developments towards more energy efficient adsorption–desorption cycles may proceed through two routes, an alternative regeneration using for example magnetic nano-heaters,<sup>28</sup> or by lowering the pore volume while keeping pore surface as much as possible. This latter subject is what is reported in this work, where it is realized that the hydrophobic interaction between the carbon chain of the acids and the aromatic ring of the resin is the main affinity responsible for separation of VFAs from water using Lewatit while water physically fills the pores. Therefore, to limit the water up-take during adsorption and consequently obtain acids in concentrated solution in final thermal regeneration step, pore volume reduction was one of the aspects of resins that was investigated. Another interesting development was electrochemical adsorption,<sup>29</sup> but due to the high costs of a gold adsorbent, this approach in the investigated form was deemed not suitable for large scale application.

Considering thus polymeric resins most cost-effective, variations on polystyrene may be considered. Next to the polystyrene-based adsorbents reported by Reyhanitash *et al.*,<sup>16</sup> various amine functionalized ion exchange resins have also been proposed to extract carboxylic acids from the fermentation broth.<sup>25,30–34</sup> Quaternary ammonium based adsorbents attract the carboxylates *via* anion exchange. Whilst the primary, secondary and tertiary amines can form either hydrogen bonding with the acids or transfer proton with the carboxylates to maintain the charge neutrality of the resin.<sup>35</sup> These ion exchangers are interesting adsorbents, since the pH of the fermentation broth is usually between 5 and 7 and consequently the VFAs are in their dissociated form.<sup>31</sup> However, the regeneration of the ion exchangers requires another ion exchange reaction using an extra agent (e.g., mineral acids) to protonate them and recover the VFAs which produces a stoichiometric amount of salts.<sup>32</sup> Moreover, these resins can attract not only the acids, but also the minerals (salts) present in the fermentation broth *via* ion exchange reaction.<sup>16</sup> Therefore, we aimed to apply resins functionalized with nitrile instead of amines, where it is aimed to prevent ion exchange reactions while introducing another interaction

mechanism between the acids and the adsorbent to enhance the recovery yield and the acid selectivity. The nitrile based active sites can form hydrogen bonding with the carboxyl group of the acids, but proton transfer is not expected.

In this work, the main goal was to explore whether the possible adsorbents based on nitrile functionality can perform similar to amine functionalized Lewatit in terms of adsorption capacity, but without co-adsorption of mineral acids. Next to the acid adsorption capacity, also the uptake of water was investigated. Different adsorbents with either methacrylonitrile (MAN) or styrene (S) crosslinked with divinylbenzene (DVB) were synthesized. The MAN-functionalized adsorbents were aimed to enhance VFA recovery by hydrogen bonding between the carboxyl group of the acids and nitrile group of the resins. The PS-DVB resins were synthesized, aiming to control the morphology and possibly reduce the water up-take with introducing small pore volumes while maintaining a reasonable internal surface area. The performance of MAN-functionalized resins were compared to the PS-DVB adsorbents by conducting batch adsorption experiments using a mimicked fermentation broth.

## MATERIALS AND METHODS

### Chemicals

Butyric acid (HBU, >99%), Acetic acid (HAc, >99.7%), propionic acid (HPr, >99.5%), anhydrous sodium phosphate dibasic (>99%), anhydrous sodium sulfate (>99%), potassium chloride (>99%), methacrylonitrile (MAN) styrene (S), divinylbenzene (80%) (DVB), benzoyl peroxide (BPO), poly(vinyl alcohol) 88% hydrolyzed (PVA), poly(ethylene glycol) (PEG,  $M_w = 2000$  Da), polystyrene (PS,  $M_w = 35\,000$  Da) were purchased from Sigma-Aldrich. Crystalline lactic acid (HLA, >98%) was provided by Corbion. Potassium hydroxide (1 M) was supplied by Merck. Lewatit VP OC 1064 MD PH adsorbent was purchased from Lenn-teck. Sodium chloride, sodium hydroxide, magnesium sulfate, copper sulfate, potassium sulfate, sulfuric acid, boric acid, hydrochloric acid, toluene, tetrahydrofuran (THF) and octanol were obtained from POCH, Poland. S and DVB were purified by extraction with 5% NaOH solution and dried with  $MgSO_4$  before use. The water used was ultrapure (Milli-Q, with a resistance of  $18.2\ \mu\Omega\ cm$  at  $25\ ^\circ C$ ).

### Synthesis of polymer adsorbent by radical suspension polymerization

The polymers were synthesized by radical suspension polymerization in order to obtain the sorbent in the form of spherical grains. The continuous water phase comprised 2 wt% sodium chloride and 1 wt% PVA. The dispersed organic phase contained monomers (MAN or S), crosslinker (DVB), initiator (BPO) (0.5 wt%) and porogens. Various types of porogens were used at each experiment. Toluene, octanol and the 6 wt% solutions of linear polymers PS and PEG in toluene or THF were used as a porogen agent. The ratio of monomers to porogen was 1:1 (w/w) and the ratio of the water phase to the organic phase was 2:1 (w/w). The polymerization was carried out for 9 h with continuous stirring at 300 rpm. The porogens of the obtained polymers were extracted with toluene in a Soxhlet apparatus for 12 h.

### Determination of water up-take for the synthesized resins

Water up-take,  $W$  (g/g) of the adsorbent was determined using the centrifugation method and calculated using Eqn (1):

$$W = \frac{(m_w - m_d)}{m_d} \quad (1)$$

where  $m_w$  (g) is the weight of wet polymer after centrifugation in a small column with fritted-glass bottom and  $m_d$  (g) is the weight of polymer after drying at 100 °C overnight.

### Nitrile groups content determination for MAN-functionalized resins

The content of nitrile groups was determined by nitrogen elemental analysis using a Büchi K-314 set of equipment for the Kjeldahl method. 0.2 g of dried polymer was placed in a flask and then 0.4 g of copper sulfate, 0.8 g of potassium sulfate, and 20 mL of concentrated sulfuric acid (96–98%) were added. The flask was heated to sample mineralization. After the cooling, 40 mL of distilled water and 33% NaOH solution were added to the flask in sufficient quantities to change the color of the solution from blue to brown, followed by subjecting it to steam distillation for about 5 min (Büchi K-314 distiller). During this time, the ammonia evolved and was absorbed by a 2.0% solution of boric acid containing a mixture of indicators (bromocresol green and methyl red), placed in a conical flask (receiver). Then, the solution was titrated with 0.1 mol/dm<sup>3</sup> of HCl until the color changed from green to grey.

The nitrogen content was determined based on Eqn (2):

$$N = \frac{C_{\text{HCl}}(V_{\text{HCl}} - V_0)}{m} \quad (2)$$

where  $N$  – the amount of nitrogen in the polymer sample (mol/g),  $C_{\text{HCl}}$  – concentration of HCl solution (mol/dm<sup>3</sup>),  $V_{\text{HCl}}$  – HCl solution volume used for titration of the tested sample (cm<sup>3</sup>),  $V_0$  – HCl solution volume used for the blank titration (cm<sup>3</sup>),  $m$  – the mass of weighed polymer (g).

### Adsorbent screening to recover VFAs from fermentation broth

Following the method described by Reyhanitash *et al.*,<sup>16</sup> the batch adsorption experiments were performed for each resin to determine their equilibrium loading using a model solution as a feed. The composition of the feed is given in Table 1. 0.5 g of each adsorbent was contacted with 11 g feed for 1 h at >500 rpm. Afterwards, a sample was taken from the eluent and analyzed by high pressure liquid chromatography (HPLC) and ion chromatography (IC) to determine the concentration of the acids and salts, respectively.

The capacity of the adsorbent was calculated using Eqn (3):

$$q = \frac{(C_0 - C_e) \times F}{m} \quad (3)$$

where  $q$  is the amount of adsorbate adsorbed by the adsorbent (g of Acid/kg of Adsorbent),  $F$  is the mass of feed (g),  $m$  is the mass

of resin (kg) used for batch adsorption,  $C_0$  (wt%) is the initial concentration of each acid in the feed and  $C_e$  (wt%) is the equilibrium concentration of corresponding acid in the eluent.

### Analysis

#### The Brunauer–Emmett–Teller (BET)

Specific surface area of commercial Lewatit was obtained using N<sub>2</sub> adsorption isotherms determined at 77 K using a Micromeritics Gemini VII 2390a. First, the commercial resins were washed with water and dried using N<sub>2</sub> at 100 °C and 0.2 L/min. Afterwards, the sample was degassed at 180 °C for 15 h and analyzed by BET equipment. For the synthesized resins MAN-DVB and PS-DVB, pore size and surface area were obtained by examining nitrogen adsorption at 77 K using Micromeritics ASAP 2020 analyzer. The total pore volume was estimated from a single point adsorption at the relative pressure of 0.988.

#### High performance liquid chromatography (HPLC)

The concentrations of HPr, HBU, HAc and HLa were measured with an inaccuracy of <0.5% using a HPLC [Agilent Hi-Plex H column (300 × 7.7 mm) using a refractive index detector on an Agilent 1200 series HPLC system; mobile phase, 5 mM H<sub>2</sub>SO<sub>4</sub> solution; column temperature of 65 °C at a flow rate of 0.6 mL/min].

#### Ion chromatography (IC)

Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations were quantified with IC (Metrosep A Supp 16–150/4.0 column on a Metrohm 850 Professional IC; mobile phase, 7.5 mM Na<sub>2</sub>CO<sub>3</sub> + 0.75 mM KOH solution; column temperature, 45 °C; flow rate, 0.8 mL/min). Na<sup>+</sup> and K<sup>+</sup> concentrations were measured with IC as well (Metrosep C6-150/4.0 column on a Metrohm 850 Professional IC; mobile phase, 1.7 mM HNO<sub>3</sub> + 1.7 mM dipicolinic acid solution; column temperature, 20 ± 1 °C; flow rate, 1.0 mL/min).

#### pH measurement

pH values were measured with a Metrohm pH probe (6.0234.100) connected to a Metrohm 780 pH-meter.

## RESULTS AND DISCUSSION

### Characterization of the adsorbents

The MAN-functionalized and PS-DVB polymeric sorbents were synthesized by radical suspension polymerization method. A series of copolymers of methacrylonitrile and divinylbenzene (MAN-DVB) or styrene and divinylbenzene (S-DVB) were synthesized using various porogens to differentiate their porous structures. They are cross-linked with divinylbenzene, which nominal content is 50 wt%. The polymerization reaction schemes are shown in Fig. 1.

As shown in Table 2, the polymerization yield varies from 90 to 98% for various resins. The water up-take of the investigated copolymers is due to the retention of water in the pores of the polymer. MAN-based copolymers have relatively high water up-take

**Table 1.** The composition of the concentrated mimicked fermentation broth

Solution	Concentration (wt%)				Concentration (mol/L)			pH
	HAc	HPr	HBU	HLa	KCl	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	
Feed	1.25	1.25	1.25	1.25	0.25	0.25	0.5	4.98

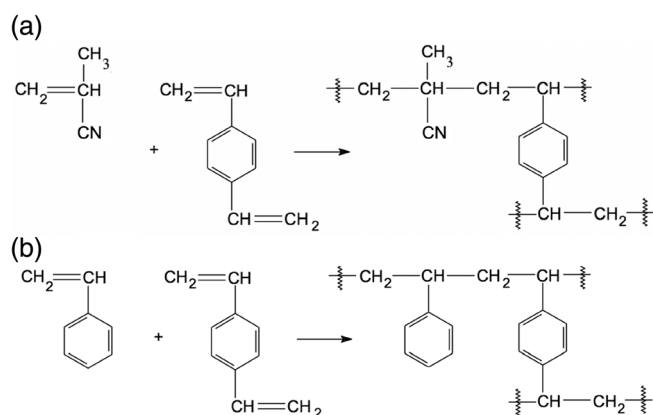
(0.99–1.85 g/g) which is almost twice greater water up-take than PS-DVB resins. This is because of the more polar nature of MAN compared to S. Moreover, the water up-take of the synthesized PS-DVB is lower than commercial Lewatit due to their small pores volumes. The determination of nitrogen content by the Kjeldahl method enables to determine the content of nitrile groups, presented in the MAN-based co-polymers structure. They can play a key role in sorption intensification due to the possibility of forming hydrogen bonds. The nitrogen present in this group as a strongly electronegative atom is a proton acceptor. The number of nitrile groups in synthesized MAN-based particles are also presented in Table 2. They contain 4.68–5.19 mmol/g nitrogen, which indicates the satisfactory amount of the nitrile groups in the adsorbents structure. These groups can increase the adsorption capacity by creating specific interactions between the sorbent and sorbate.

The separation efficiency of an adsorption process depends on the physicochemical properties of both the adsorbate and the adsorbent, as well as on the fluid phase properties. Surface chemistry, pore size and internal surface area are the relevant characteristics of an adsorbent which directly influence its capacity. These properties have been determined, and are summarized in Table 2. In total, 8 resins have been synthesized, of which five MAN-functionalized and three PS-DVB-based resins. The PS crosslinked with DVB resins

have been synthesized using various porogens to vary the porosity in the particles. Toluene ( $\delta = 18.3 \text{ MPa}^{1/2}$ ), octanol ( $\delta = 20.9 \text{ MPa}^{1/2}$ ), and solutions of poly(ethylene glycol) (PEG, oligomer;  $\delta = 20.8 \text{ MPa}^{1/2}$ ) and polystyrene (PS, polymer;  $\delta = 18.3 \text{ MPa}^{1/2}$ ) have been applied to produce the resins which are examined in the present work.

As shown in Table 2, using PEG dissolved in toluene as a porogen resulted in the highest BET surface area for both MAN and PS-DVB-based resins. Whilst PS solution in THF yields resins with remarkably low surface area and small mesopores. The function of each diluent depends mainly on their solubility parameters. The Hildebrand solubility parameters ( $\delta$ ) for MAN, S and DVB are  $21.9 \text{ MPa}^{1/2}$ ,  $19.0 \text{ MPa}^{1/2}$  and  $18.2 \text{ MPa}^{1/2}$ , respectively. Solvents having a solubility parameter ( $\delta$ ) similar to the  $\delta$  of the monomer (good solvents) yield into small pores (inducing micropores) and a high surface area. The non-solvating diluents result in worse solvation of monomer and consequently, the average pore size becomes large (inducing macropores or mesopores), and the surface area decreases.<sup>36</sup> Usually, the pore sizes are designed using different types of solvent mixtures.<sup>37–39</sup> Another possibility is to use porogens, containing large size molecules, such as oligomers.<sup>40</sup> Using oligomer as co-porogen with a good solvent can induce phase separation in two stages: an early event in which the oligomer phase separates to produce macropores and a late event in which the solvent phase separates to produce micropores. Optimally a bimodal pore size distribution might be achieved. This increase in surface area arises from the increase in the population of mesopores in these polymers, which probably make previously inaccessible or closed micropores accessible, while also contributing directly to the surface area themselves.<sup>40</sup> Polymer solutions, such as a toluene solution of polystyrene, can generate pores in polymers with diameters usually greater than 50 nm (i.e., macropores).<sup>36,41</sup> In the case of MAN-DVB 5 sorbent, a much larger BET surface area was expected as a good solvent of octanol was used as a porogen which should lead to the development of micropores. However, the conducted BET analysis (nitrogen adsorption at the liquid nitrogen temperature) did not indicate their presence. The explanation may be that the resulting micropores have a size less than 0.7 nm and are therefore not measurable by the used method. It should also be emphasized that this material shows the highest water regain.

Overall, the average pore size and pore volume of the synthesized particles are smaller than the ones for the commercial resin



**Figure 1.** Scheme of copolymer synthesis: (a) methacrylonitrile and divinylbenzene (MAN-DVB) and (b) poly(styrene-divinylbenzene) (PS-DVB).

**Table 2.** Summary of the characterization of the various adsorbents

Resins	Polymerization yield (%)	Water up-take (g/g)	N content (mmol/g)	BET Surface area (m <sup>2</sup> /g)	Mesopores		Micropores		Porogen
					Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	
MAN-DVB 1	98	1.38	5.14	550	0.88	6.41	0.08	0.69	PEG in toluene
MAN-DVB 2	97	1.17	4.83	412	0.29	2.78	0.07	0.69	PS in toluene
MAN-DVB 3	98	0.99	4.68	2	0.004	7.10	-	-	PS in THF
MAN-DVB 4	97	1.19	5.19	526	0.87	6.64	0.08	0.69	Toluene
MAN-DVB 5	97	1.85	4.93	327	0.54	6.63	-	-	Octanol
PS-DVB 1	90	0.60	-	502	0.55	4.39	0.07	0.72	PEG in toluene
PS-DVB 2	98	0.87	-	429	0.31	2.93	0.07	0.69	PS in toluene
PS-DVB 3	94	0.53	-	6	0.009	6.00	-	-	PS in THF
Lewatit	-	1.00	-	931	-	-	1.50	8.74	N/A

Abbreviations: BET, Brunauer–Emmett–Teller; MAN-DVB, methacrylonitrile and divinylbenzene; PS-DVB, poly(styrene-divinylbenzene); PEG, polyethylene glycol; PS, polystyrene; THF, tetrahydrofuran.

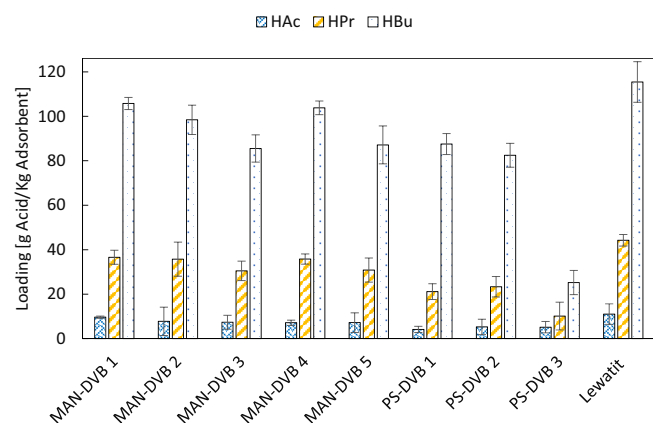


Lewatit. Unfortunately, there is no information available about the polymerization mechanism and the type of the diluent used in the synthesis of Lewatit.

### VFAs recovery using the synthesized resins

Figure 2 represents the capacity of each resin to recover VFAs from a mimicked fermentation broth. The maximum loading capacity is observed for HBU in all the resins applied in batch adsorption. It indicates the hydrophobic interaction between the carbon chain of the acids and aromatic rings of the resins. The longer the carbon chain, the higher the capacity of the resins.<sup>16,42</sup> Lewatit has the highest equilibrium loadings of  $115 \pm 9$  and  $44 \pm 3$  (g Acid/kg Adsorbent) for HBU and HPr, respectively. The equilibrium capacity of Lewatit has previously been reported to be 65.2 (g Acid/kg Adsorbent) and 26.5 for HBU and HPr, respectively.<sup>16</sup> The difference might be because of using different batches of Lewatit with possibly differ in the surface area.

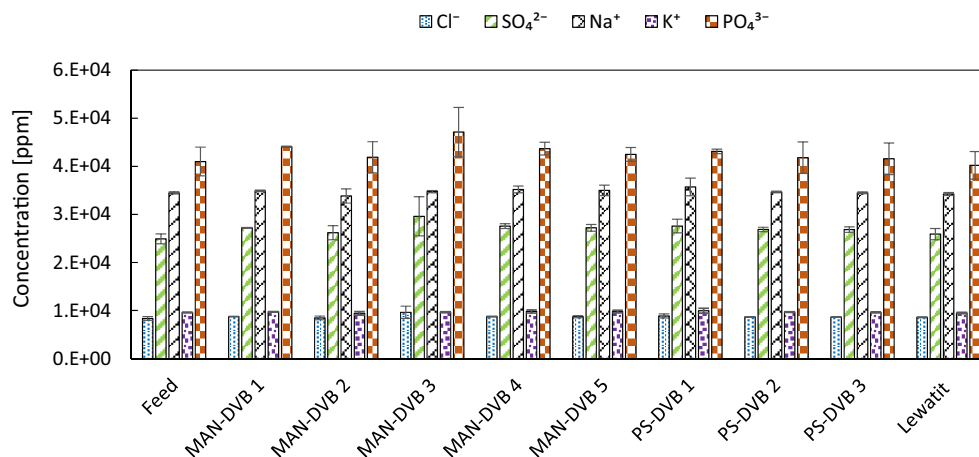
The maximum loadings of  $106 \pm 3$ ,  $98 \pm 7$  and  $104 \pm 3$  (g Acid/kg Adsorbent) were achieved for MAN-DVB 1, MAN-DVB 2 and



**Figure 2.** Measured capacity of various hydrophobic resins to recover the volatile fatty acids (VFAs) from a concentrated mimicked fermentation broth, the concentration of each acid in the feed is 1.25 wt%, batch adsorption is performed with resin to feed mass ratio of 0.5:11 at room temperature, contact time of 1 h and >500 rpm. MAN-DVB, methacrylonitrile and divinylbenzene; PS-DVB, poly(styrene-divinylbenzene).

MAN-DVB 4, respectively. Considering the difference in the BET surface area of Lewatit and these MAN-based resins, their capacity for HBU and HPr is significant, indicating extra affinity between the acids and the adsorbents. The nitrile groups in the structure of MAN-based resins enable forming hydrogen bond with the acids. Whilst the capacity of the PS-DVB resins is relatively low with PS-DVB 3 having the lowest loading of 25 (g Acid/kg Adsorbent) as well as the lowest surface area. In terms of HPr and HAC adsorption capacity, it is approximately in the same order of magnitude for all MAN-based resins and Lewatit. Generally, MAN-based adsorbents have higher loading values than non-functionalized PS-DVB-based resins for the corresponding acid. In the case of functionalized sorbents such as MAN-DVB, specific sorption (hydrogen bonds interactions, donor-acceptor interactions) and non-specific sorption (van der Waals or London interactions) are responsible for their sorption capacity. Non-specific sorption is directly proportional to the development of the specific surface area of the sorbent. The results obtained for MAN-DVB3 indicate the significant role of specific interactions in the tested sorption systems, and therefore we do not observe, as for the S-DVB series, dependence on the development of the specific surface area. The general trend observed for all VFAs is that with increasing hydrocarbon chain the adsorption capacity increases. This is due to the increasing hydrophobicity at increasing hydrocarbon chain length. Itself not a VFA, lactic acid was not adsorbed at any significance on any of the resins, which is explained by the extra hydroxy group and the lower pKa, making it extremely hydrophilic. The VFAs all have a pKa of 4.8, and since the acidity is equal, the only discerning factor for their adsorption capacity is the hydrophobicity correlated with their hydrocarbon chain length.

Next to the acid loading, it is also relevant to study the impact of the salts on the capacity of the resins, as these salts are usually presented in the wastewaters. The ions namely  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}/\text{PO}_4^{3-}$  are representing the salts as they are the dissociated form of their corresponding salts in the aqueous solution. Therefore, comparing their concentration before and after adsorption can provide more information of whether or not there is a competitive adsorption between the VFAs and the salts. Figure 3 shows the concentration of the ions, determined by IC. The concentration of the ions in the 'Feed' represents



**Figure 3.** Determination of the capacity of various hydrophobic resins to adsorb salts from the concentrated mimicked fermentation broth during volatile fatty acids (VFA) recovery, batch adsorption is performed with resin to feed mass ratio of 0.5:11 at room temperature, contact time of 1 h and >500 rpm. MAN-DVB, methacrylonitrile and divinylbenzene; PS-DVB, poly(styrene-divinylbenzene)

their concentration before starting batch adsorption. As can be clearly seen from the graph, the concentration of all the ions remains constant before and after adsorption for each adsorbent. It illustrates that there is no interaction between the resins and the salts which is a benefit to have high capacity for the VFAs. This observation is highly interesting, since it was previously reported that amine-based adsorbents have high affinity towards the mineral acids, originating from the salts.<sup>16</sup> In fact, the amine-based ion exchange resins attract the salts via ion exchange reaction with their corresponding mineral acid form to comply to the charge neutrality constraint.<sup>16</sup> For example, the competitive adsorption capacity of amine-functionalized resins for H<sub>3</sub>PO<sub>4</sub> is reported to be about 200 (g Acid/kg Adsorbent), reducing the VFAs loading capacity significantly.<sup>16</sup> In the present work, the nitrile-based particles did not attract the mineral acids which can be explained by lower basicity of the nitrile groups than amine groups.<sup>43,44</sup> It implies the higher selectivity of the nitrile-based adsorbents towards VFAs rather than minerals (salts). Since also a higher adsorption was measured for the VFAs than with non-functionalized PS-DVB, the use of nitrile functionality for VFA adsorption appears to represent a new direction for future research and application of adsorption technology in VFA recovery from diluted broths.

## CONCLUSION

The recovery of the VFAs from a mimicked fermentation broth was studied by adsorption technique. The loading capacity of various adsorbents were examined by performing batch experiments. The maximum equilibrium VFA loading of about 153 (g Acid/kg Adsorbent) was obtained using MAN-based resins. While having a comparable surface area to MAN-based resins, the non-functionalized PS-DVB-based adsorbents exhibited lower adsorption capacity. It is because of the extra attraction mechanism between the acids and the MAN-based particles which is hydrogen bonding between carboxyl group of the VFAs and the nitrile group of the adsorbents.

In this study, low water up-take was the great feature of the synthesized PS-DVB due to their high hydrophobicity and small pore volume. They displayed 3–4 times lower water-up take, compared to MAN-functionalized resins. Moreover, their water up-take was less than commercial Lewatit. The low water loading implies PS-DVB resins with small pore volume and high surface area can also be an appropriate candidate to selectively separate the acids from a dilute aqueous solution, followed by thermal regeneration to effectively recover the VFAs at high concentration.

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## DATA AVAILABILITY STATEMENT

Data available upon reasonable request from corresponding author.

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