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Journal

Journal of Environmental Chemical Engineering, 11(5)

ISSN

2213-3437

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Publication Date

2023-10-01

DOI

10.1016/j.jece.2023.110507

Peer reviewed

1 **Adsorptive Recovery of Volatile Fatty Acids from Wastewater Fermentation Broth**

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9 Keywords: Adsorption, Ion-exchange resin, Volatile fatty acids, Wastewater, Resin reuse,
10 Fermentation broth.

11 **Abstract**

12 This work developed an adsorptive separation and recovery process for anaerobically generated
13 volatile fatty acids (VFAs) from swine wastewater fermentation. Batch adsorption studies were
14 conducted using several weak anion exchange resins and synthetic adsorbent resins to identify a
15 suitable candidate. Relite RAM2 with a tertiary amine functional group showed the highest
16 adsorption (over 98%) of hexanoic acid. Under the different pH values (1.8- 7.5) and extraction
17 temperatures (30- 50 °C), the highest adsorption was observed at a pH of 3.2, which is below the
18 pKa of hexanoic acid, at all the evaluated temperatures. A Full Factorial Design was used to
19 optimize the resin and VFA concentrations, wherein over 99% adsorption could be achieved
20 when the ratio of resin to VFA was below 0.23 (g/g) for model solution (VFAs in water). The
21 adsorption equilibrium could be achieved within 30 min of contact time and 0.5% w/v NaOH
22 was identified as a suitable desorption agent. Under the optimal conditions, 65- 72% of VFAs
23 present in fermentation broth have been adsorbed, which was increased to 72- 76% by using
24 fresh resins. The VFAs adsorption and recovery efficiency were maintained for 9 successive
25 cycles without requiring extensive resin washing and regeneration for both model solution and
26 fermentation broth. Overall, the work presents a comprehensive study for resin adsorption to

1 recover VFAs and provides a potential industrial relevant process to recover VFAs from
2 fermentation broth.

3 **1. Introduction**

4 Volatile fatty acids (VFAs), short-chain carboxylic acids containing two to six carbon atoms are
5 important building blocks and can be used for the production of biopolymers, biochemicals, and
6 biofuels. Among the VFAs, acetic acid and propionic acid have the highest market size and were
7 envisioned to reach 11.85 billion USD [1] and 1.6 billion USD [2] by 2026, respectively.
8 Similarly, the global butyric acid market was expected to surpass 170 million USD by 2026 [3]
9 and capric acid was projected to reach 252 million USD by 2027 [4]. Conventionally, VFAs can
10 be obtained from petroleum resources in high yields [5]. To improve sustainability, anaerobic
11 fermentation of organic feedstocks including manure, sewage sludge, industrial and household
12 waste, and agricultural residues for VFA production has been reported [6,7].
13 Pure cultures of *Clostridium*, *Acetobacter* have been reported to obtain individual VFAs.
14 However, using pure culture necessitates aseptic working conditions and refined substrates. To
15 overcome these drawbacks, mixed cultures of two or more microbes have been used to produce a
16 mixture of VFAs from waste carbon-rich streams [8,9]. Recovery of microbially produced VFAs
17 is challenging due to the high volume/ low VFA concentrations and the complex nature of the
18 fermentation broth. Several techniques including gas stripping and absorption using calcium
19 carbonate slurry [10,11], resin adsorption [12,13], solvent extraction [14–16], electrodialysis
20 [17,18], and membrane filtration [19,20] have been reported for VFA recovery.

21 The ion exchange adsorption process offers ease of scale-up, resin reusability, and relatively high
22 selectivity compared to other processes and hence has been reported for recovery of microbially
23 produced VFAs [21,22]. A weakly basic resin, Purolite A133S, was compared with granular
24 activated carbon (mean particle size of 1.9 mm) for its adsorption capacity of acetic, propionic,
25 and butyric acid. The author observed a 35% higher adsorption capacity using resin compared to
26 activated carbon [23] Among the evaluated resins containing primary, tertiary, or quaternary
27 amines as functional groups, Amberlyst A21, a weak tertiary amine based resin, showed higher
28 adsorption efficiency for acetic acid. A caproic acid adsorption of 85% for a synthetic mixture
29 and 62% for real grape pomace digestate, was observed, respectively [14]. Similarly, using a

1 synthetic VFA solution basic Lewatit VP OC 1065 resin showed 86-96% adsorption of
2 individual VFAs; however, the adsorption decreased to 40% with a VFA mixture [21].
3 Functionalized and nonfunctionalized primary, secondary, and tertiary amine- resins have been
4 compared for VFA adsorption from model solution containing VFAs and salts. It was observed
5 that nonfunctionalized resins showed higher adsorption capacity [13]. Solvents including
6 ethanol, aqueous NaOH have been reported for desorption of VFAs. It has been shown that 70-
7 90% desorption of the VFAs was achieved with 1 M NaOH solution [21].

8 One of the key factors determining the full scale application of resin adsorption for VFA
9 recovery from wastewater fermentation broth pertains to sustainable regeneration and reuse of
10 resins. However, very limited studies reported resin reuse especially with actual wastewater
11 fermentation broths. Amberlyst A21 was used for 3 successive cycles of adsorption and
12 desorption using a synthetic solution (Rebecchi et al., 2016). Using nitrogen stripping for VFA
13 recovery, the adsorption capacity of Lewatit VP OC 1064 MD PH resin was observed to
14 significantly decrease over 3 successive cycles [13]. The decrease was attributed to salt
15 deposition inside the pores on the adsorbent. Although the loss of adsorption capacity could be
16 avoided by a water-wash step, the extra step resulted in a 5-20 wt% loss of VFAs.

17 This work aimed to develop an efficient adsorptive process to recover VFAs from the
18 fermentation broth produced using a bioreactor fed with swine wastewater, augmented with
19 synthetic VFAs, and develop an optimized process for the adsorptive recovery of VFA from
20 fermentation broth. A Full Factorial Design (FFD) was used to optimize the experimental
21 conditions including resin and VFA concentration. Further, the resin reusability was determined
22 over nine successive cycles of adsorption-desorption of VFA using both model solution and
23 fermentation broth.

24 **2. Materials and Methods**

25 Ion exchange resins such as Diaion WA20, Diaion WA30, Relite RAM2, and adsorbent resins
26 including Diaion HP20, Sepabeads SP70, and Sepabeads SP700 were generously provided by
27 ITOCHU Chemicals America Inc (NY, USA). The properties of resin used in this study is
28 summarized in Table 1. The resins were used without further processing. Glacial Acetic acid (\geq

1 99.7%), propionic acid ($\geq 99.5\%$), butyric acid ($\geq 99\%$), hexanoic acid ($>99\%$), and sodium
2 hydroxide pellets (anhydrous) were procured from Millipore Sigma (Wisconsin, USA).

3 **2.1.Preliminary adsorption study**

4 To identify a suitable resin, the adsorption capacity of hexanoic acid (predominant VFA
5 observed in the fermentation broth) on several anion exchange resins (AERs) and adsorbent
6 resins was measured. Briefly, a known amount of resin (10 % w/v) was contacted with 10 ml of a
7 1% w/v aqueous hexanoic acid solution (pH: 3.2) at 30°C for 4 h at 150 rpm. At the end of
8 incubation, the residual hexanoic acid was quantified. The difference between the initial and
9 final hexanoic acid concentration was used to calculate the adsorption capacity (q , mg/g) using
10 equation 1.

$$11 \quad q = \frac{(C_{\text{initial}} - C_{\text{final}}) V}{W} \quad (1)$$

12 where, C_{initial} and C_{final} are the initial and final concentrations, respectively, (g/L) in the aqueous
13 phase, V is the volume of solution (L), and W is the mass of adsorbent (g).

14 The resin with the highest adsorption capacity for hexanoic acid was selected and subsequently
15 used to determine the effect of temperature (30, 40, 50°C) and pH (1.8, 3.2, 4.5, 6, 7.5) on
16 adsorption capacity.

17 **2.2.Optimization of VFA adsorption**

18 A general Full Factorial Design (FFD) experiment was used to optimize the adsorption of VFAs
19 onto the selected resin. For optimization, a model solution of VFA consisting of a mixture of
20 acetic acid, propionic acid, butyric acid, and hexanoic acid in water was used. The adsorption
21 process was optimized by evaluating the effect of the independent variables i.e. resin
22 concentration (X_1) and VFA concentration (X_2). Low, medium, and high levels of the resin
23 concentrations at 1.75, 3.5, and 7.5% w/v and the VFA concentrations at 0.2, 0.4, and 0.8% w/v
24 were studied. The highest VFA concentration was limited to 0.8% v/v due to limited solubility of
25 hexanoic acid. As 10% w/v resin concentration was observed to adsorb over 90% of hexanoic
26 acid, the resin concentration range of 1.75 – 7.5% w/v was selected targeting to obtain maximum
27 adsorption at the lowest resin concentration. For the optimization study, a model solution was
28 prepared containing the selected concentration of each acid (acetic, propionic, butyric, and

1 hexanoic) in water. Thus, 0.2% w/v VFA concentration denotes 0.2% w/v of each of the four
2 organic acids. A total of 27 experiments were performed in random order at a fixed temperature
3 of 30 °C for 4 h at 150 rpm. An aliquot was withdrawn at the end of 4 h to analyze the residual
4 VFA concentrations, which were used to estimate the adsorption capacity.

5 **2.3.Fermentation broth preparation**

6 A lab-scale Anaerobic Membrane Bioreactor (AnMBR) equipped with Zeeweed 500D
7 ultrafiltration membranes was operated under methanogenic mode (no accumulation of VFAs)
8 with swine wastewater as the primary substrate [25]. The chemical composition of the broth was
9 reported in the prior publication [26]. Broth obtained from the lab-AnMBR unit was filtered and
10 volatile fatty acids were added externally. The VFA-added broth was used for adsorption study.

11

12 **2.4.Recovery of adsorbed VFA and resin reusability**

13 After adsorption, the resin was recovered from the solution and incubated with different solvents
14 such as water, ethanol, and aqueous NaOH solution (0.5% w/v and 1% w/v) to identify a suitable
15 desorption agent to recover the VFAs. Briefly, the resin containing adsorbed VFA was incubated
16 with desorption solvent at 30°C for 4 h at 150 rpm. At the end of incubation, an aliquot of the
17 solution was used to quantify the VFAs and estimate the recovery of adsorbed VFAs. Further, to
18 evaluate the reusability, the resin obtained after desorption was used for successive cycles
19 without extensive washing or regeneration. For subsequent cycles, the used resin was contacted
20 with fresh VFA solution (both model solution and fermentation broth) and desorption solvent.
21 The adsorption capacity and recovery were measured at the end of each cycle and used to
22 determine the reusability of the resin.

23 **2.5. Improvement of VFA adsorption from fermentation broth**

24 To increase VFA adsorption from the broth, several approaches were attempted: scenario 1
25 wherein pH of the fermentation broth was adjusted to 2.6; scenario 2 where the spent broth was
26 contacted with fresh resin; and scenario 3 where the pH of spent broth was adjusted to 2.6 and
27 then contacted with fresh resin. The VFA adsorption efficiency for all approaches were
28 determined using the protocol described in section 2.1.

29 **2.6.Analysis**

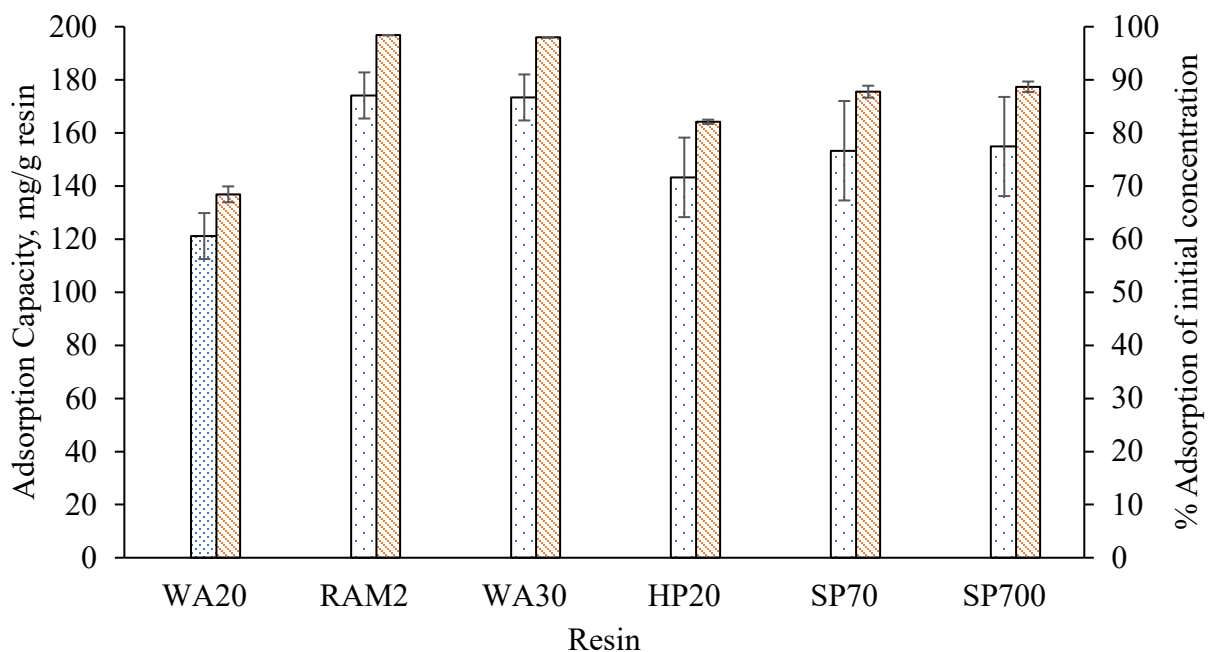
1 The HPLC analysis was conducted using a Dionex Ultimate 3000 equipped with a refractive
2 index detector (RID) (Thermo Fisher, MA, USA). The VFAs were eluted using 4 mM sulfuric
3 acid solution at 0.6 ml/min through Aminex HPX-87H column (Biorad, CA, USA) held at 60°C
4 and detected using RID (50°C). The VFAs were quantified through calibration curves made with
5 pure VFA compounds.

6 The FFD, ANOVA, Main plot, interaction plot and contour plot were performed and obtained
7 using Minitab Statistical Software, Version 16 (Pennsylvania State University, USA).

8 3. Results and Discussion

9 3.1. Preliminary resin selection study for VFA adsorption

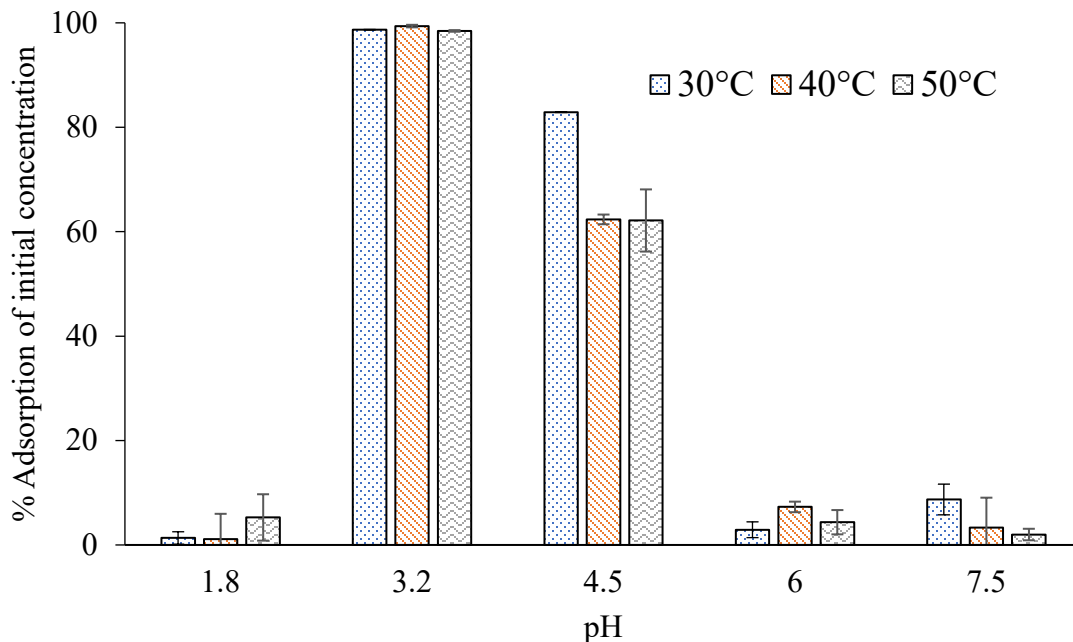
10 To identify a suitable resin, the adsorption capacity of resins for hexanoic acid was measured and
11 presented in Figure 1. Relite RAM2 and Diaion WA30 adsorbed $98.40 \pm 0.02\%$ and 97.98 ± 0.03
12 % of hexanoic acid, corresponding to adsorption capacity of 174.10 ± 8.69 and 173.36 ± 8.67 mg
13 of hexanoic acid/ g of resin, respectively. The synthetic adsorbent resins (HP20, SP70, and SP
14 700) could adsorb between 82 to 89% of hexanoic acid. The % adsorption increased as the
15 specific surface area of the synthetic resin increased from $590 \text{ m}^2/\text{g}$ for Diaion HP20 to 1100
16 m^2/g Sepabeads SP700. The lowest adsorption ($68.44 \pm 1.49 \%$) was observed for Diaion WA20
17 with a polyamine functional group.



1 **Figure 1:** Adsorption of hexanoic acid on different resins. Primary axis represents adsorption
2 capacity, mg of hexanoic acid/ g of resin and secondary axis provides % adsorption of hexanoic
3 acid based on the initial concentration.

4 Compared to the literature, Lewatit VC OP 1065 could adsorb 182.20 ± 25.40 mg/g of acetic acid,
5 153.37 ± 22.96 mg/g of propionic acid, 207.55 ± 30.44 mg/g of butyric acid and 217.16 ± 31.80
6 mg/g of valeric acid, at 5 g/L VFA concentration [21]. For a VFA mixture containing 1 g/L of
7 acetic acid, propionic acid, butyric acid, isobutyric acid, isovaleric acid and valeric acid, Amberlite
8 IRA-67 (50 g/L) and Dowex Optipore L-493 (75 g/L) had a total equilibrium adsorption capacity
9 of 119.6 mg/g and 54.39 mg/g, respectively (Eregowda et al., 2020). Using a 1 wt % total VFA
10 concentration (model solution), a total VFA adsorption capacity of 114 mg/g was observed for
11 nonfunctionalized resin (Reyhanitash et al., 2017). Thus, adsorption capacity of hexanoic acid onto
12 resin are comparable to reported values.

13 Figure 2 shows the adsorption of hexanoic acid on Relite RAM2 under different temperatures
14 and pHs. The highest adsorption (above 98%) was obtained at pH of 3.2 and at all the evaluated
15 temperatures.



16
17 **Figure 2:** Effect of temperature and pH on adsorption of hexanoic acid on Relite RAM2

18 The proposed primary mechanism for adsorption on weak anion exchange resin includes
19 physical interaction between the undissociated form of volatile fatty acids and the adsorbent [27].

1 Weak AERs having secondary or tertiary amine functional groups are preferred for VFA
2 recovery as they can interact with the carboxylic group of VFAs in their charge-neutral form to
3 maintain the charge neutrality [12,13,22]. As the pKa of VFAs is 4.8, most of the VFAs would
4 be in the undissociated form at pH 3.2, thus favoring interaction with the tertiary amine groups of
5 the resin. The pH of VFAs in model solution (2.2-2.6) and in the fermentation broth (3.1-4.0) at
6 different concentration of VFAs was observed to be below the pKa of VFAs. On the other hand,
7 adsorption efficiency was similar at all the evaluated temperature (Figure 2) and hence 30°C was
8 selected as optimal which is also aligned with fermentation temperature (30°C). Based on
9 obtained results, Relite RAM2 was selected as the resin of choice and further adsorption studies
10 were conducted at 30°C.

11 **3.2.Optimization of adsorption process**

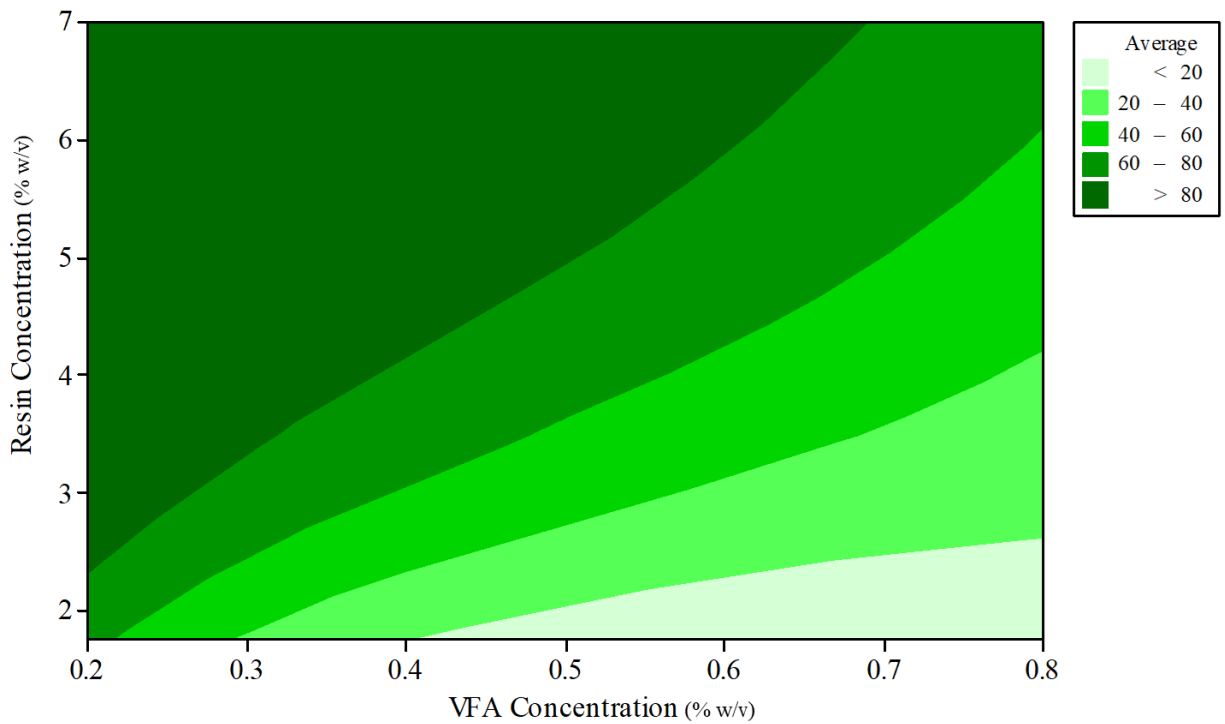
12 The adsorption process was optimized using FFD to predict a suitable resin concentration for a
13 given VFA concentration in the fermentation broth. The pH of model solution of VFAs at 0.2%
14 w/v, 0.4% w/v and 0.8% w/v were ca 2.6, 2.3 and 2.2, respectively. Since the pH values were
15 below the pKa of VFAs, the model solutions were used without further pH adjustment to avoid
16 the need for additional chemical use in the process. The results of FFD and ANOVA are shown
17 in Table 2 and Table 3, respectively. Both the resin and VFA concentrations (alone & in
18 combination) had significant influence on the VFA adsorption ($p < 0.05$). The VFA adsorption at
19 a fixed resin concentration decreased as the VFA concentration increased from 0.2 to 0.8% w/v.
20 This could be attributed to the saturation of the active sites on the resin. The highest adsorption
21 (above 99% w/w) was observed at the lowest VFA concentration (0.2% w/v), when the resin
22 concentration was 3.5% w/v or 7% w/v. In other words, the ratio of VFA to resin amount below
23 0.23 allowed over 99% VFA adsorption. With an increase in the ratio to 0.46, the % VFA
24 adsorption decreased to 64-68% w/w. The regression equation to calculate VFA adsorption at a
25 given VFA and resin concentration is shown in equation 2. Oakland, CA, US

$$26 \quad \% \text{ VFA Adsorption} = 58.7 + 10.4 * \text{Resin Concentration} - 84.1 * \text{VFA Concentration} \quad (2)$$

27 The R^2 and adjusted R^2 from ANOVA were 0.9961 and 0.9937 indicating a good fit between the
28 experimental value and model predicted value. The contour plot presented in Figure 3a can be
29 used to predict the average VFA adsorption capacity at a given VFA and resin concentration.
30 The steep main effects plot (Figure 3b) suggests both resin and VFA concentrations have a

1 significant impact for VFA adsorption. The VFA adsorption increases with an increase in resin
2 concentration, whereas VFA concentration has the opposite effect. As seen from Figure 3c, an
3 interaction could be observed either at the lowest VFA concentration (0.2% w/v) or at highest
4 resin concentration (7% w/v). When the VFA concentration was 0.2% w/v, using 3.5% or 7%
5 resin gave similar VFA adsorption. Similarly, at 7% w/v resin concentration, similar adsorption
6 could be observed when 0.2% or 0.4% w/v VFA was used.

Contour Plot of Average vs Resin Concentration, VFA Concentration

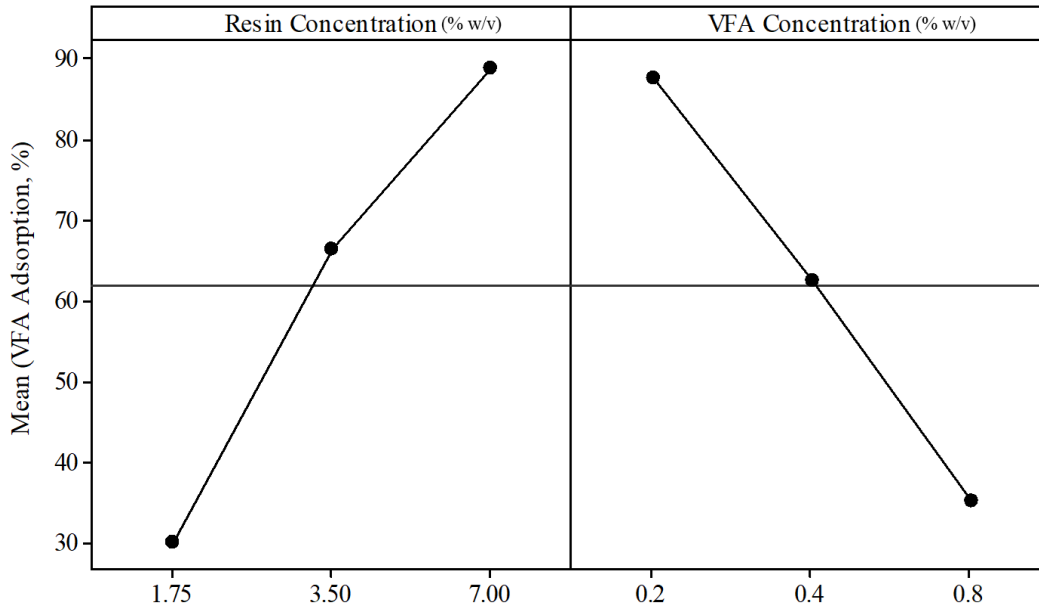


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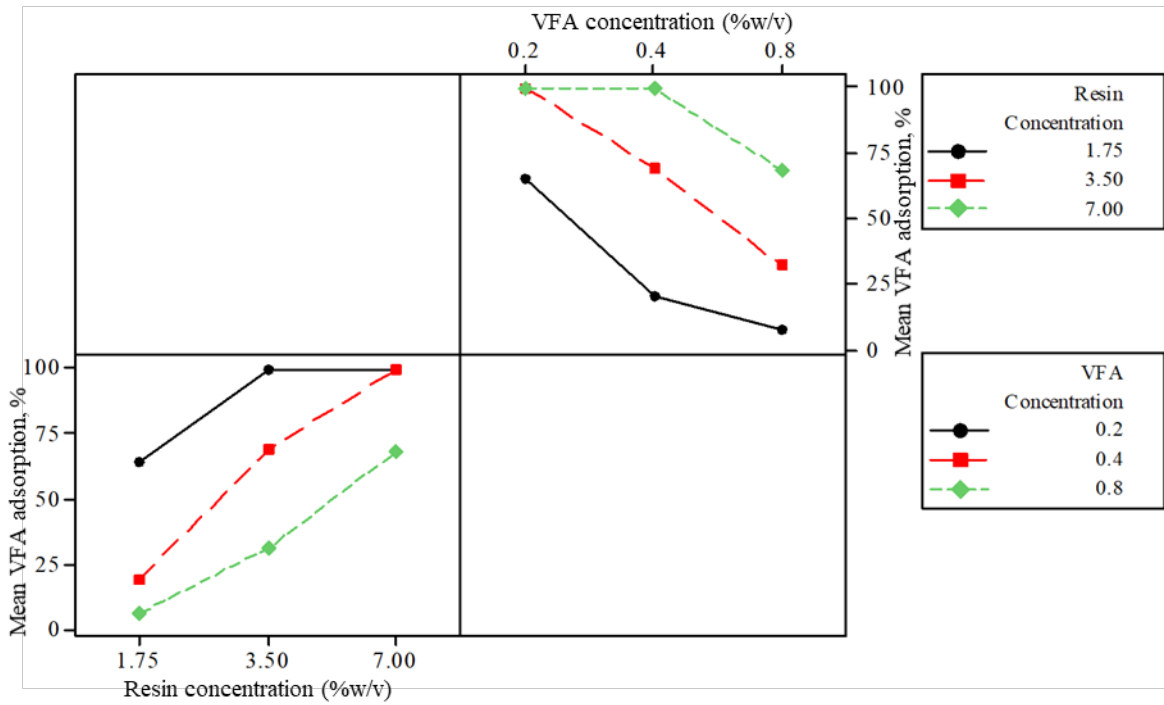
(a)

Main Effects Plot for Average Data Means



1
2

(b)



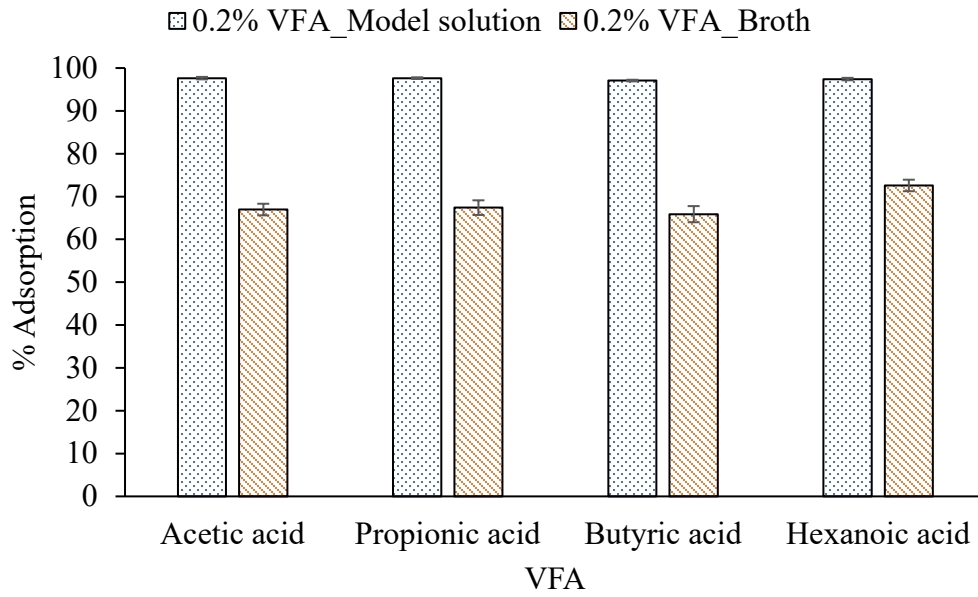
3
4

(c)

5 **Figure 3:** Full Factorial Design analysis of VFA adsorption on Relite RAM2 (a) Contour plot

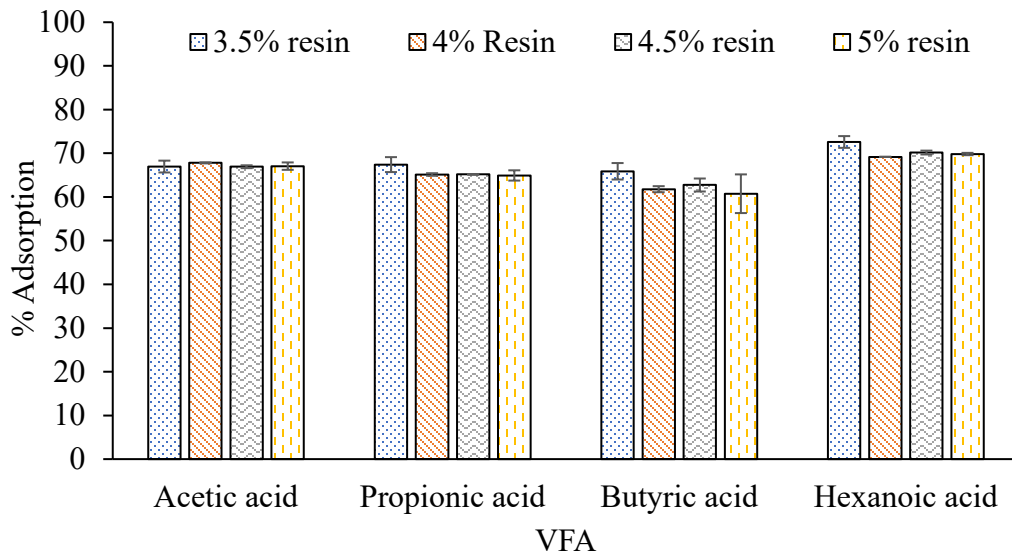
6 (b) Main plot and (c) Interaction plot

1 As shown in Figure 4a, the VFA adsorption was compared between the model solution and
2 fermentation broth obtained from fermentation under the optimal experimental conditions (0.2%
3 w/v VFA concentration, 3.5% w/v resin concentration, 30°C). When the substrate is changed to
4 actual fermentation broth, maximum adsorption of VFAs was 67.0 % for acetic acid, 67.4% for
5 propionic acid, 65.9% for butyric acid, and 72.6 % for hexanoic acid, which was significantly
6 lower than that obtained using the model solution. The higher adsorption of hexanoic acid can be
7 attributed to its lower solubility in water, allowing for increased interaction with the adsorbent
8 surface [28]. At optimal conditions, Relite RAM2 showed an adsorption capacity of 280.4 mg
9 VFA/g resin for the model solution and 154.2 mg VFA/g resin for broth. Furthermore, no
10 increase in VFA adsorption from broth was observed even when resin concentration was
11 increased from 3.5% to 5% w/v (Figure 4b). Weak AERs are suggested to adsorb unionized form
12 of VFAs. Upon adsorption of unionized VFAs, a shift in equilibrium between ionized and
13 unionized forms may increase concentration of unionized VFA in solution. Therefore, an
14 increase in the resin concentration could improve VFA adsorption. However, increased
15 adsorption was not observed with an increase in the resin concentration. The VFA adsorption
16 was also evaluated at different incubation times to estimate the time required to reach adsorption
17 equilibrium. It was observed that 96-97% VFAs were adsorbed within 0.5 h of contact time. The
18 adsorptions were slightly increased to 97-99% with an increase of adsorption time to 1 h and
19 above. Therefore, 0.5 h of contact time was considered suitable to achieve high VFA adsorption
20 and further adsorption study were conducted at 0.5 h of contact time.



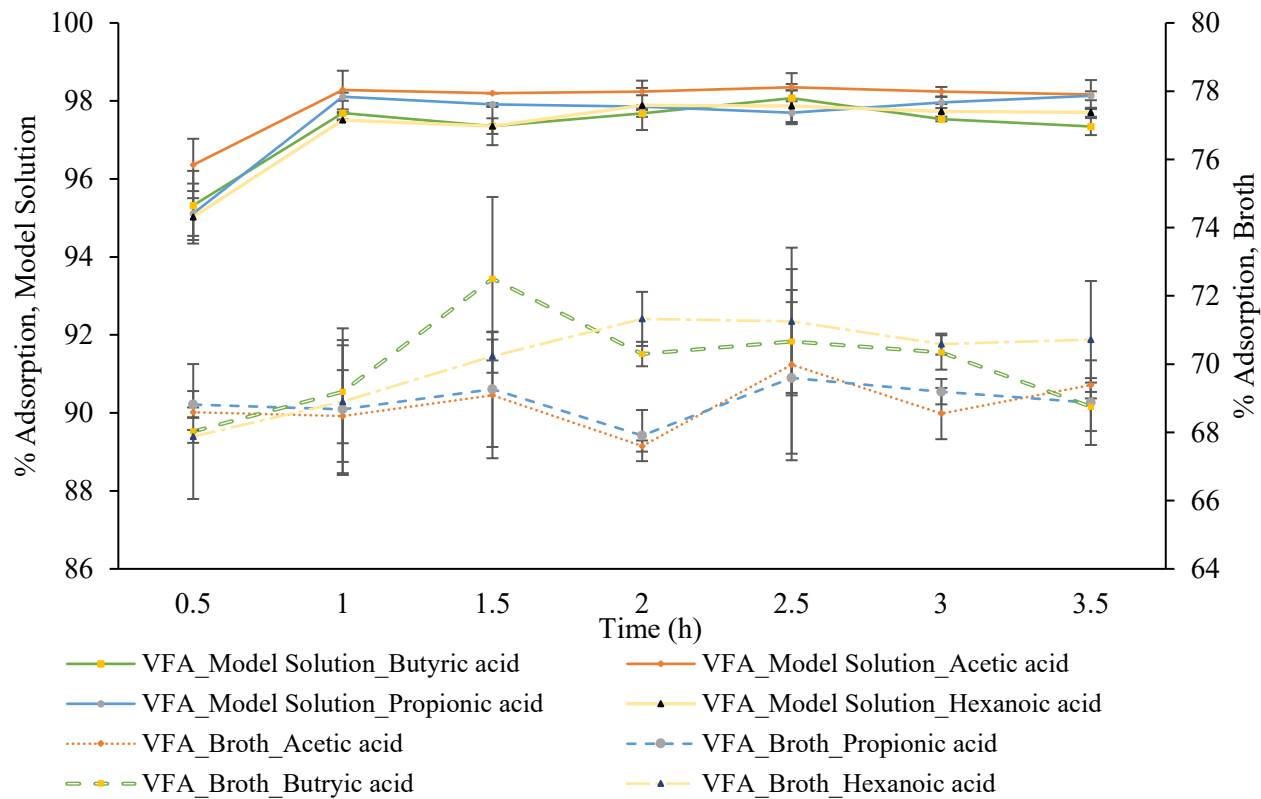
1
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(a)



3
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(b)



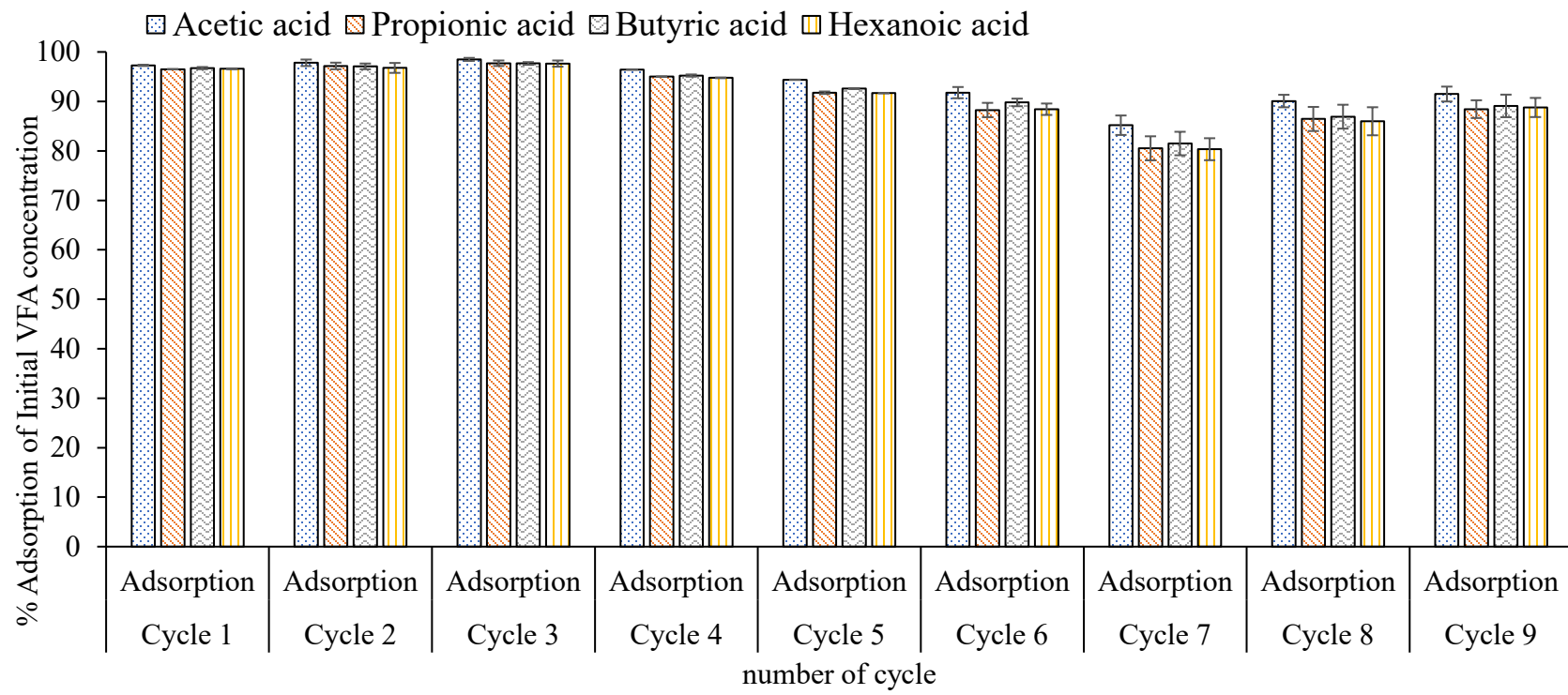
1
2
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(c)

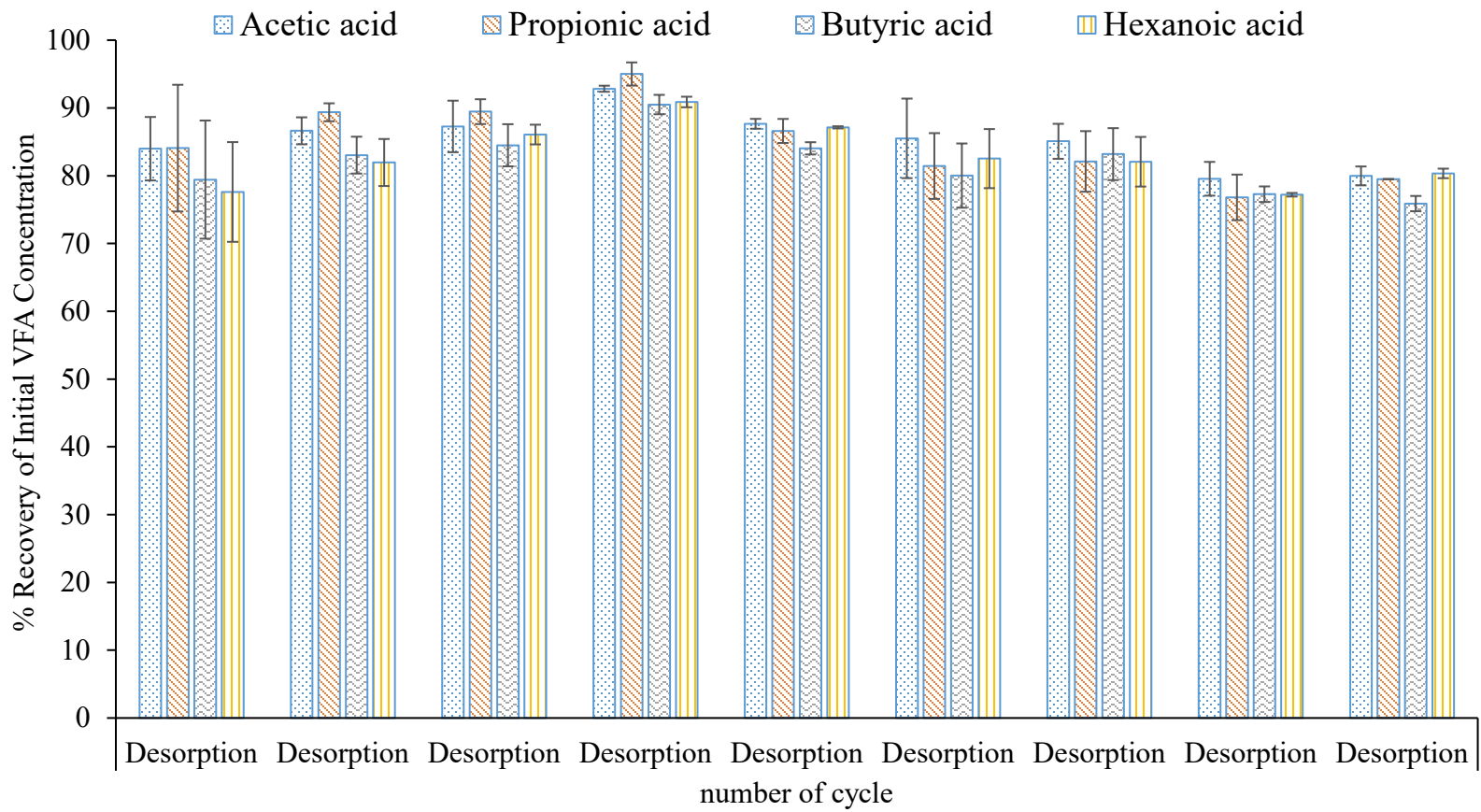
Figure 4: VFA adsorption using Relite RAM2 (a) comparison between model solution and broth (b) effect of resin concentration on VFA adsorption using broth and (c) effect of contact time on VFA adsorption

3.3.VFA recovery and resin reusability

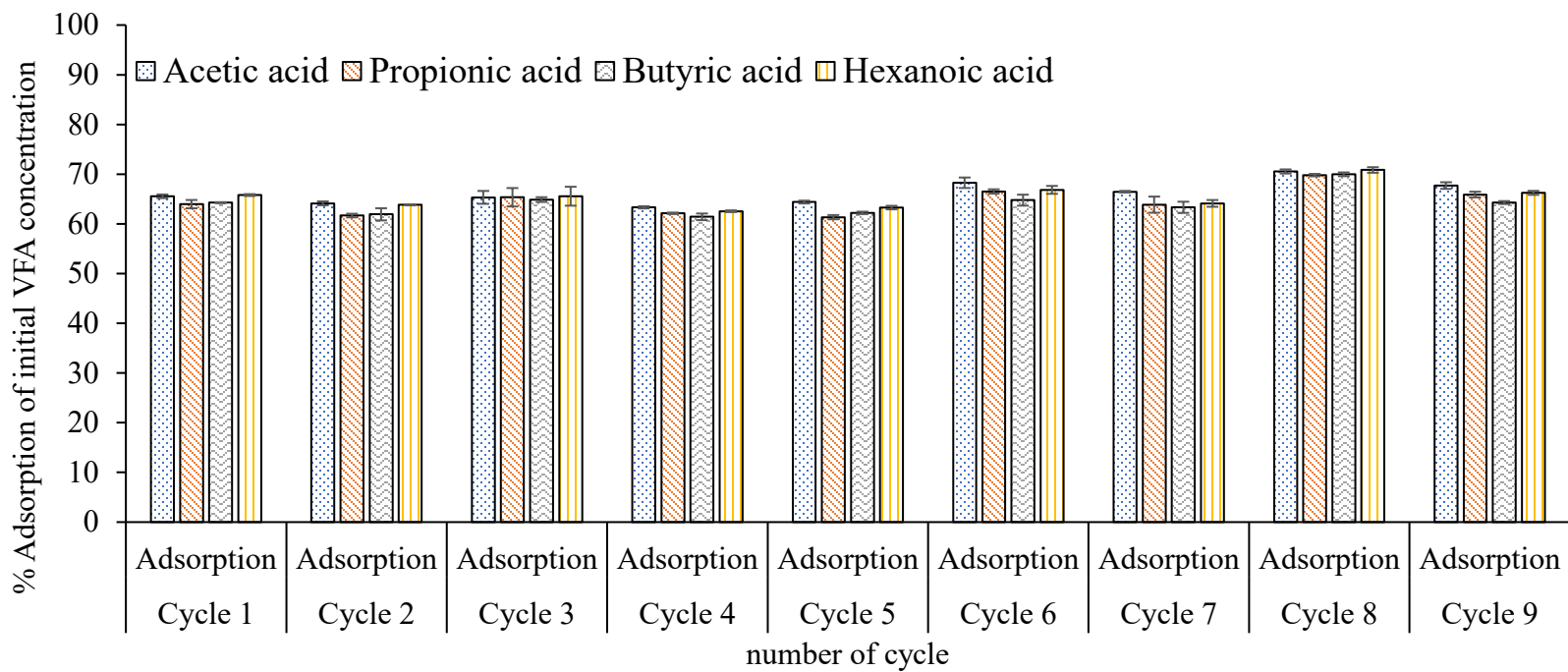
Among the evaluated desorption solvents, 0.5% w/v NaOH solution achieved nearly complete desorption of adsorbed VFAs with 0.5 h of contact time, and desorption efficiency remained similar when NaOH concentration was raised to 1% w/v. Only 9 to 14% of the adsorbed VFAs can be desorbed using water. Similarly, ethanol can desorb 6 to 16% of adsorbed acetic acid, propionic acid, and butyric acid. A recovery of 37% was observed for hexanoic acid using ethanol. Thus, 0.5% w/v NaOH was selected as the desorption solvent for further study. Our results corroborate with VFA desorption study using Lewatit VP OC 1065 resin, where about 95% of acetic acid could be desorbed using 1 M NaOH solution, whereas less than 10% was achieved with water [21]. Similarly, over 98% VFA desorption was achieved with 0.1 M NaOH, and the desorption decreased with a decrease in NaOH concentration (Eregowda et al., 2020). The results of adsorption and recovery of VFA from model solution and fermentation broth using 0.5% w/v NaOH are shown in Figure 5. As shown in Figure 5a, above 90% VFA adsorption has been achieved for 5 successive cycles using the model solution. The adsorption was reduced to 85-90% in cycle 6-9. Overall, adsorption of over 85% could be maintained for up to 9 cycles. As shown in Figure 5b, 80% VFA recovery was achieved for 9 successive cycles of the same batch of resin using 0.5% w/v NaOH as a desorption agent. Similarly, adsorption (Figure 5c) and recovery (Figure 5d) efficiencies were maintained for 9 successive cycles using broth. Although over 90% of adsorbed VFA could be recovered, the recovery rate (considering both adsorption and desorption) was significantly lower for broth than that observed for the model solution. A 1.75 M NaOH is suggested to regenerate Relite RAM2 (vendor recommended). The use of 0.5% w/v NaOH (0.125 M) NaOH as a desorption solvent also assisted in the desorption and regeneration of the resin active group. The applied NaOH concentration is significantly lower, which has a positive impact on the economics of the process. It was reported that the adsorption capacity for acetic acid (85-88%) was maintained over 3 successive cycles using Amberlyst A21 and synthetic solution (Rebecchi et al., 2016). Similarly, nonfunctionalized resin was stable over four successive cycles, however a short water-wash stage had to be included between cycles [13]. To our knowledge, this is the first report showing the reusability of resin for 9 successive adsorption and desorption cycles using both model solution and broth. The robustness of the process shows great potential for industrial application of VFA recovery from dilute fermentation broth.



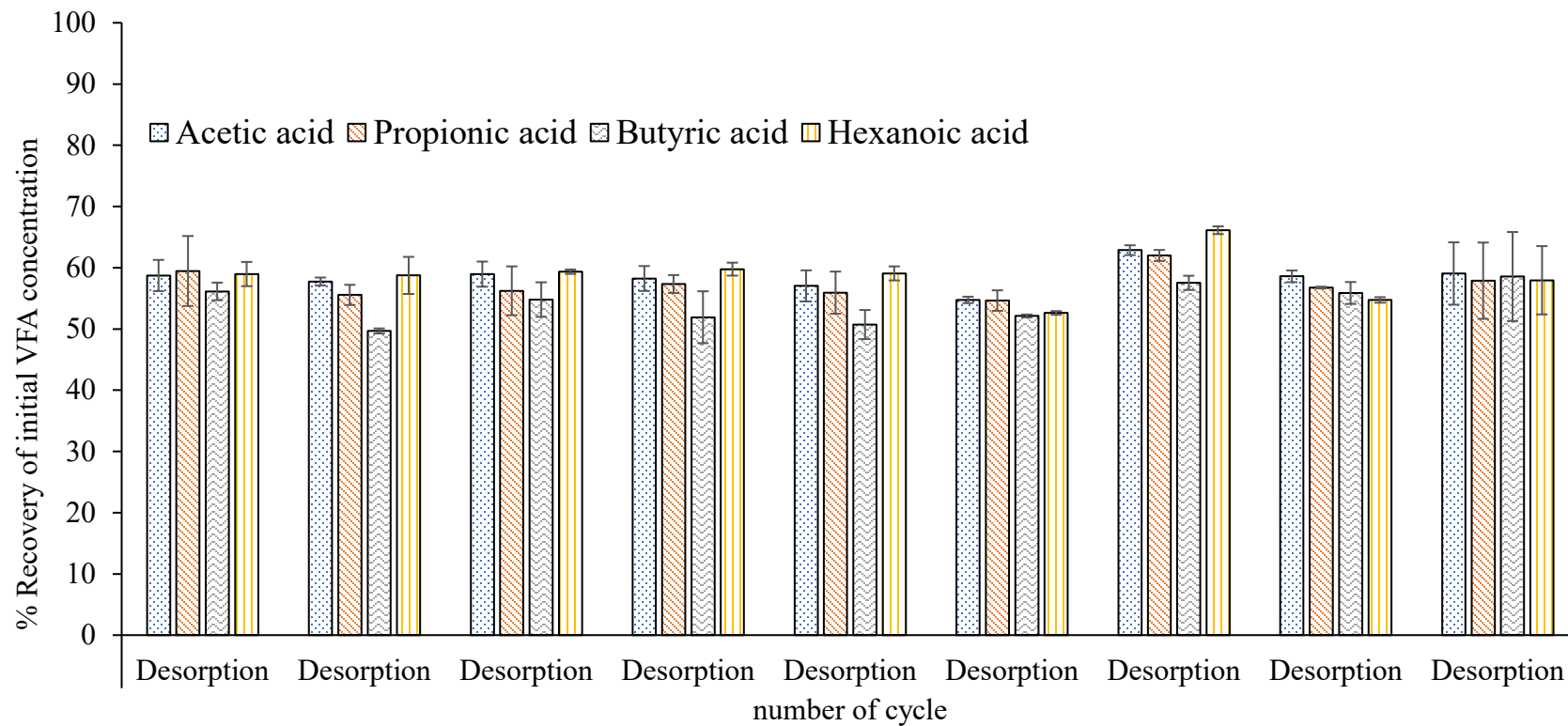
(a)



(b)



(c)



(d)

Figure 5: Resin reusability for successive cycles of VFA adsorption and recovery (a) VFA adsorption from model solution, (b) VFA desorption using model solution, (c) VFA adsorption from broth and (d) VFA desorption using broth. % Adsorption and % Recovery for each cycle are calculated based on starting VFA concentration for each cycle

3.4.Improvement of VFA adsorption from fermentation broth

The pH of 0.2% w/v VFA in water was 2.6 compared to pH 4.0 noted for the same concentration of VFA added to broth. As VFAs have a pKa of ca. 4.8, the percentage ionization would vary depending on the pH of the solution. Weak basic resins adsorb unionized form of acids; hence adsorption capacity would vary with different pH. Therefore, several approaches were attempted to test the hypothesis and further improve the adsorption efficiency (Figure 6). When the pH of broth was adjusted to 2.6 using sulfuric acid, the % adsorption increased to about 70% compared to 65% without pH adjustment (Figure 5c). When the spent broth containing residual VFAs was contacted with fresh resin, the adsorption was observed to increase from 65% to 72-76%. Whereas, when the pH of spent broth was adjusted to 2.6 and contacted with fresh resin, the adsorption remained to be 72 - 76%. Therefore, no significant difference ($p < 0.05$) was observed upon using fresh resin with spent broth with or without pH adjustment. Acidification of broth to shift the equilibrium towards unionized form of VFAs did result in improvement of adsorption, however, the maximum adsorption was obtained by using fresh resin with spent broth. This process is similar to the usage of multiple resin beds at industrial scale and avoids the need of using additional chemicals.

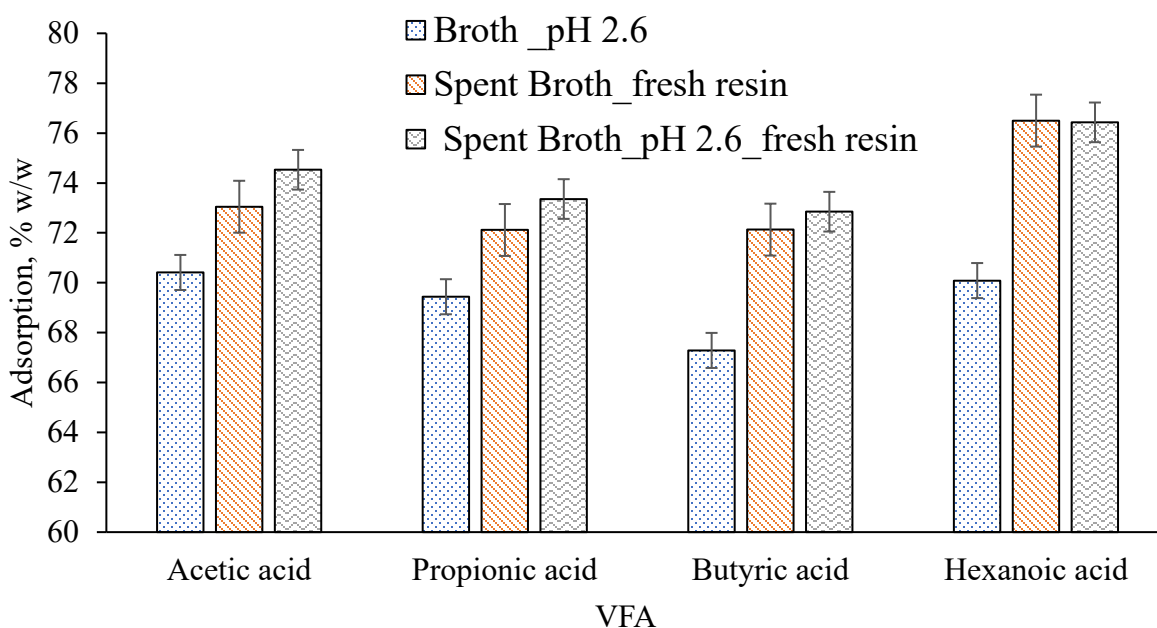


Figure 6: Impact of pH adjustment of VFA broth to pH 2.55 and re-contacting the spent broth with fresh resins on VFA adsorption

4. Conclusion

Several weak anion exchange resins and adsorbent resins were evaluated for their ability to adsorb VFAs derived from a swine wastewater matrix. Relite RAM2 having tertiary amine groups on a gel copolymer acrylate-DVB matrix was identified to have the best performance. The adsorption process was optimized using a full factorial design wherein over 99% VFA adsorption was observed when the VFA: resin ratio was less than 0.23 (g/g) using model solution (VFA in water). The optimal adsorption condition was observed to be 3.5% w/v resin, and 0.2% w/v VFA at 30°C with 30 min of contact time. The % VFA adsorption efficiency from wastewater fermentation broth (65 - 72%) was lower compared to model solution (~97%), due to difference in pH and adsorption of colored impurities present in the broth. The adsorption efficiency was further improved to 72-76% by passing the spent broth with fresh resins. Among the evaluated desorption solvent, 0.5% w/v NaOH showed the highest VFA desorption and recovery. Further, it was observed that the resin could be reused for at least 9 successive cycles without a loss of VFA adsorption or recovery efficiency for both model solution and broth. Thus, an efficient adsorptive VFA recovery process has been demonstrated for further VFA upgrading and application.

5. Authors contribution:

Ramkrishna Singh: Conceptualization; Methodology; Data Curation; Formal Analysis; Writing, review and editing-original draft.

Skye Palar, Amy Kowalczewski and Caitlin Swope: Methodology; review& editing.

Ning Sun and Prathap Parameswaran: Conceptualization; Funding acquisition; Supervision; Writing- review & editing.

6. Funding source

This work was supported by the Advanced Manufacturing Office (AMO) within the US DOE's Office of Energy Efficiency and Renewable Energy (DE-EE0009504). ABPDU would also like to thank the support from The Bioenergy Technologies Office (BETO) within the US DOE's Office of Energy Efficiency and Renewable Energy.

7. Acknowledgement

The authors would like to thank Itochu Chemicals America Inc for providing the resins for this study.

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Table 1: Properties of resins used in this study

| Resin | Matrix | Type | Functional group | Effective size (mm) | Ionic form | Total exchange capacity | Total swelling (%) | Max operating temperature (°C) | Regenerant |
|------------------|-----------------------------|---------------------|-------------------------|----------------------------|-------------------|--------------------------------|-----------------------------|---------------------------------------|--------------------------|
| Diaion WA20 | Styrene-DVB, porous | Weak base | Polyamine | 0.4 | Free base | 2.5 (meq/ml) | 19 (FB to Cl ⁻) | 100 | NaOH |
| Relite RAM2 | Copolymer Acrylate-DVB, gel | Weak base | Tertiary amine | 0.4 | Free base | 1.6 (eq/l) | 20 (FB to Cl ⁻) | 40 | NaOH, NH ₄ OH |
| Diaion WA30 | Styrene-DVB, highly porous | Weak base | Tertiary amine | 0.4 | Free base | 1.5 (meq/ml) | 21 (FB to Cl ⁻) | 100 | NaOH |
| Diaion HP20 | Polystyrene-DVB, porous | Synthetic adsorbent | | 0.25 | | | | 130 | Bases |
| Sepabeads SP 70 | PolyDVB/ EVB, highly porous | Synthetic adsorbent | | 0.25 | | | | 130 | Bases |
| Sepabeads SP 700 | PolyDVB/ EVB, highly porous | Synthetic adsorbent | | 0.25 | | | | 130 | Bases |

*all resin had a uniformity coefficient of 1.6 (maximum). The values are provided by vendor.

Table 2: Full Factorial Design and result for optimization of VFA adsorption on Relite RAM2

| Resin Concentration (% w/v) | VFA Concentration (% v/v) | Ratio (VFA: Resin) | % Average VFA adsorption | |
|-----------------------------|---------------------------|--------------------|--------------------------------------|-----------------|
| | | | Experimental value (mean \pm s.d.) | Predicted value |
| 1.75 | 0.2 | 0.16 | 64.68 \pm 7.67 | 64.86 |
| 1.75 | 0.4 | 0.91 | 19.76 \pm 0.29 | 19.95 |
| 1.75 | 0.8 | 1.83 | 7.11 \pm 0.95 | 7.29 |
| 3.5 | 0.2 | 0.23 | 99.43 \pm 0.14 | 99.62 |
| 3.5 | 0.4 | 0.46 | 69.07 \pm 1.35 | 69.25 |
| 3.5 | 0.8 | 0.91 | 31.51 \pm 0.31 | 31.69 |
| 7 | 0.2 | 0.11 | 99.02 \pm 0.03 | 99.21 |
| 7 | 0.4 | 0.23 | 99.40 \pm 0.03 | 99.60 |
| 7 | 0.8 | 0.46 | 68.19 \pm 1.74 | 68.37 |

Table 3: ANOVA for VFA adsorption on Relite RAM2

| Source | Degree of Freedom | Sequential SS | Adjusted SS | Adjusted MS | F-value | P-value |
|---|-------------------|---------------|-------------|-------------|---------|---------|
| Resin Concentration | 2 | 15618.3 | 15618.3 | 7809.1 | 1066.23 | 0.000 |
| VFA Concentration | 2 | 12226.2 | 12226.2 | 6113.1 | 834.66 | 0.000 |
| Resin Concentration* VFA Concentration | 4 | 2137.8 | 2137.8 | 534.4 | 72.97 | 0.000 |
| Error | 16 | 117.2 | 117.2 | 7.3 | | |
| Total | 26 | 3011.9 | | | | |

*SS= sum of squares, MS: Mean sum of squares; F-value determines whether the term is associated with response, higher F value indicates the term or model is significant; p-value represents significance at 95% confidence interval