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

## AIM OF THIS WORK

Aim of this work is the investigation on the conditions optimizing the purification and concentration of Volatile Fatty Acids from anaerobic fermentate by sequential adsorption/desorption operations.

The investigation has started studying the adsorption/desorption processes of synthetic VFA



#### Adsorption of single synthetic VFA NaOH in ethanol NaOH in water 0,5 g VFA solution **Activated Carbon** 1 to 20 g/L Lewatit VP OC 1065 5 3 2 mL Amberlyst A-21 mL mL 3h*,* 30°C 10 mL 04 Lewatit VP OC 1065 Amberlyst A-21 Activated Carbon **Concentrated VFA**

#### Adsorption on single VFA mix (1 to 20 g/L)



Lewatit Adsortpion's Performance





#### Amberlyst Adsorption's Performance

- Figure 2. Specific adsorption capacity of the IEX matrices
  - 2a. Specific adsorption on PAC
  - 2b. Specific adsorption on lewatit
  - 2c. Specific adsorption on amberlyst



#### Specific capacity (q<sub>e</sub>) and Langmuir's constant (b)

|           | PAC                   |          | Lewatit VC OP 1065    |          | Amberlyst A 21        |          |
|-----------|-----------------------|----------|-----------------------|----------|-----------------------|----------|
|           |                       |          |                       |          |                       |          |
|           | q <sub>e</sub> (mg/g) | b (L/mg) | q <sub>e</sub> (mg/g) | b (L/mg) | q <sub>e</sub> (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    |

#### Physical properties of solid matrices

|                      | PAC          | Lewatit VP OC 1065     | Amberlyst A-21                |  |
|----------------------|--------------|------------------------|-------------------------------|--|
|                      |              | Styrene-divinylbenzene | Styrene-divinylbenzene        |  |
| Chemical             |              | Primary amine (Benzyl  | Tertiary amine (Not specified |  |
| composition          | Carbon       | amine)                 | in the technical sheet)       |  |
| Particles size (mm)  | 0.001- 0.150 | 0.47 - 0.57            | 0.49 - 0.69                   |  |
| Approx pore volume   |              |                        |                               |  |
| (cm <sup>3</sup> /g) | 0.65         | 0.27                   | 0.10                          |  |
| Approx surface area  |              |                        |                               |  |
| (cm²/g)              | 0.12         | 50.00                  | 35.00                         |  |

#### Adsorption of a synthetic VFA mixture



## Adsorption Yields at 25 g/L VFA multi-solution

|           | LEWATIT VP OC 1065     | AMBERLYST A-21         |  |  |
|-----------|------------------------|------------------------|--|--|
|           | Adsorption Yield (%)   | Adsorption Yield (%)   |  |  |
| VFA       | from VFA Mixture tests | from VFA Mixture tests |  |  |
| Acetic    | $26.21 \pm 1.04$       | $23.26 \pm 2.93$       |  |  |
| Propionic | $15.56\pm0.48$         | $16.42\pm0.71$         |  |  |
| Butyric   | $18.90\pm0.62$         | $17.53\pm0.39$         |  |  |
| Valeric   | $49.35 \pm 2.59$       | $23.63 \pm 1.98$       |  |  |
| Caproic   | $74.20\pm3.14$         | $51.26 \pm 2.03$       |  |  |
| Overall   | $40.85 \pm 6.05$       | 27.72 ± 5.83           |  |  |

- VFA mix composition: 5 g/L each VFA (C2 to C6) for a total of 25 gVFAs/L;
- After ~10 gVFAs/L the matrices saturates, thus leading to reduced yields;
- Lewatit VP OC 1065 has the best yields overall, as it has better Langmuir's costants and specific capacity than PAC and Amberlyst;
- Longer the chain, better the yields.

## Chemical-Physical properties of VFAs

|                |                |         | Ка                        |           | Vapor        |  |
|----------------|----------------|---------|---------------------------|-----------|--------------|--|
|                | Molecular      |         | (at 25°C, 10 <sup>-</sup> | рКа       | Pression (at |  |
|                | formula        | log Kow | <sup>5</sup> )            | (at 25°C) | 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           |  |
|                |                |         |                           |           |              |  |

- Valeric and Caproic Acids have the best log Kow values, indicating a high affinity for the resin;
- pKa values higher than the pH of solution (~3.50), indicates a physical-type adsorption.

# Adsorption step highlights

- Lewatit VP OC 1065 and Amberlyst A-21 showed the best performance on single and multi VFAs solutions;
- Powdered Activated Carbon was excluded from further trials for poor performance;
- On multi solution, longer chain VFAs are better adsorbed.

# **Desorption Step**



#### Desorption Step Yields at 5mL of desorbent



Lewatit VP OC 1065



## Desorption Step Yield at 2mL of desorbent



- Desorption yields at 2 mL of desorbent are lower but consistent with the 5 mL desorption assay, at 1M NaOH;
- This allows to concentrate x5 the VFA volume: from 10 mL to 2 mL;
  - VFAs concentration rises from 25 g/L to ~95 g/L.

Adsorption and Desorptions overall results

- Best adsorption matrix: Lewatit VP OC 1065
- Best desorption conditions: 2 mL ethanol + NaOH 1M

# On the next weeks, the best conditions will be applied on a real fermentate.

## THANK YOU FOR THE ATTENTION!