

# Cyclic Adsorption Processes

## Liquid Phase Separation Processes

### Simulated Moving Bed: Enantiomers Separation

**KEYWORDS:** Simulated Moving Bed (SMB) Chromatography/ Fixed-Bed Chromatography / Multicomponent Chiral Separations / Optimization of Mobile Phase Composition / Chiral and Achiral Adsorbents

**During this report, the research group focused on identifying and implementing novel global strategies for the complete preparative separation of nadolol chiral quaternary mixture into its single stereoisomers. Several experimental preparative separations of nadolol were implemented using Fixed-Bed and Simulated Moving Bed strategies. Additionally, the preparative separation of guaifenesin enantiomers by simulated moving bed process with four operation modes was also studied.**

#### Introduction

Preparative chiral separations using adsorption-based processes are traditionally hard and complex tasks since they are based on a solute-adsorbent-solvent composition compromise optimization that allows better process performance parameters, usually productivity, solvent consumption, recovery, and purity. When leading with multicomponent chiral mixtures there is a clear increase in complexity due to the rise of adsorption competition between solute molecules for the chiral adsorbent, under high concentrations, mandatory for the industry wanted high operation performances. Extensive work has been developed inside our group to identify and implement a global strategy for the complete separation using simulated moving bed and fixed-bed chromatography of all the components present in a nadolol chiral quaternary mixture.

Nadolol is a nonselective beta-adrenergic receptor antagonist pharmaceutical drug that represents a very interesting case study of multicomponent chiral separation since it is composed of four stereoisomers and two pairs of enantiomers. In this way, it introduces the possibility of alternative separation strategies, using different kinds of separation sequences and techniques, the use of different packings (chiral and achiral stationary phases), and the correspondent mobile phase optimization at both normal and reversed-phase modes. It is important to notice that the marketing of less safe pharmaceutical drugs based on mixtures of enantiomers remains an important drawback for the pharmaceutical industry.

The preparative chiral liquid chromatography separation of nadolol stereoisomers was first reported by our group in 2013, using a Chiralpak® AD adsorbent with a particle size diameter of 20 µm, and an 80%ethanol:30%heptane:0.3%diethylamine solvent composition. In 2016, we reported the same preparative separation but using the Chiralpak® IA stationary phase and a 100%methanol:0.1diethylamine solvent mixture. Later, in 2019, we presented another relevant improvement in the performance parameters of the preparative separation by SMB chromatography of the RSR-nadolol stereoisomer, using the same Chiralpak® IA and changing the solvent composition to 25%methanol:75%acetonitrile:0.1diethylamine.

The first global strategy for the complete preparative separation of nadolol was introduced by our team in 2020, reporting an extensive screening of the adsorbent to be used on the first achiral step using C18 adsorbents. In that work, the preparative separation of nadolol racemates under high pH reversed-phase chromatography conditions is referred to. The Water XBridge C18 adsorbent and a 30-40%ethanol:70-60%water:0.005-0.1%diethylamine solvent composition

combination was identified as a good option for the implementation of the first achiral step using SMB and/or FB chromatography. In 2022, we reported the implementation of the first achiral step with the separation of nadolol racemates by high pH reversed-phase FB and SMB chromatography using the findings referred to in previous work published in 2019. More recently, we implemented the second step of the global strategy selected for the complete separation of the four nadolol stereoisomers. In this second step, the two feed solutions for SMB and FB operation were obtained using the two outlet streams collected during the SMB operation with the achiral adsorbent used in the first step. After the first achiral step, racemate B containing a racemic mixture of nadolol stereoisomers 2 and 3, was collected in the extract outlet stream, and racemate A, a racemic mixture of nadolol stereoisomers 1 and 4, was collected in the raffinate outlet stream. After SMB operation, the mass present in both racemic solutions was obtained by solvent evaporation using a rotary evaporator and freeze-drying equipment. The two obtained nadolol solids were then used to prepare new feed solutions for SMB and FB operations. After the screening for the solvent composition, we concluded that for the separation of racemate A, the solvent composition is a 25%methanol:75%acetonitrile mixture, which is the same solvent already used to separate the more retained stereoisomer (4) from the mixture of (1+2+3) in the previous work presented in 2016. We also concluded, from the solvent screening, that for the more hard chiral separation of racemate B, a binary separation of stereoisomer 2 from 3, the better values for preparative performance parameters are obtained using a 5:95 or 10:90 %methanol:%acetonitrile composition. Then, for the three chiral separations, the experimental measure and modeling of equilibrium adsorption isotherms are presented. The final selection of solvent composition to be used on the SMB separation for racemate B separation, a 5%methanol:95%acetonitrile mixture, was done by comparison of productivity and solvent consumption. The final results presented that are presented in this work clearly define a complete and global strategy that can be used for the complete preparative separation of all four stereoisomers present in the nadolol quaternary mixture. After this work, the four pure stereoisomers can now be used by the pharmaceutical industry for running important studies to identify the individual pharmacological and therapeutical properties of each nadolol stereoisomer.

#### Current Development

The first experimental pseudobinary preparative separation of nadolol stereoisomers was performed by simulated moving bed chromatography (SMB). Using the Chiralpak IA adsorbent, a new 25:75:0.1 (v/v/v) methanol-acetonitrile-diethylamine solvent composition was selected to perform the experimental SMB separation. Using a 2 g/L total feed concentration of an equimolar mixture of the four stereoisomers of nadolol, the more retained component was fully recovered (100% purity and 100% recovery), with a system productivity of 0.77 g/(Lhour) and a solvent consumption of 9.62 L/g. Comparing these results with the ones previously reported using 100:0.1 methanol-diethylamine solvent composition, this work shows



that the 25:75:0.1 methanol-acetonitrile-diethylamine is a better alternative for the preparative separation of nadolol stereoisomers by SMB chromatography.

The second experimental preparative separation of nadolol racemates under high pH reversed-phase preparative chromatography was presented for the first time. Three Waters C18 adsorbents (XBridge, Shield, and XSelect) were compared for the separation of nadolol racemates using ethanol:water:diethylamine solvent mixtures. The Waters XBridge C18 adsorbent and ethanol:water:diethylamine solvent mixture were selected as a good option for the preparative separation of nadolol racemates. This work introduced the potential of using an initial achiral separation step in the global strategy for the complete multicomponent separation of the four nadolol stereoisomers.

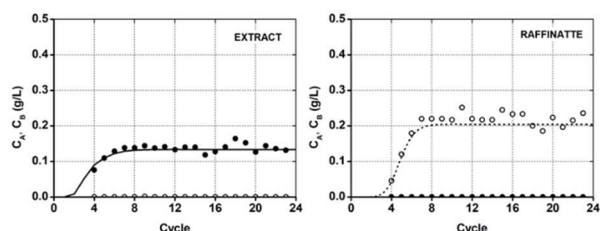


Fig 1. Experimental (points) and predicted (lines) transient evolution (24 full cycles) of the nadolol racemate concentrations in the extract and raffinate SMB outlet streams. Closed circles for the more retained racemate A, open circles for less retained racemate B, for a 2 g/L nadolol feed solution.

The third experimental separation of nadolol racemates under high pH reversed-phase using both the fixed-bed (FB) and the simulated moving bed (SMB) preparative chromatographic techniques was done using the Waters XBridge C18 adsorbent and an ethanol:water:diethylamine solvent mixture. In this work, the experimental preparative separations using one commercial fixed-bed preparative HPLC Azura system equipped with one sole column of preparative dimensions (30 mm ID  $\times$  250 mm L) and one lab-scale SMB apparatus (the FlexSMB-LSRE pilot unit) equipped with six semi-preparative columns (19 mm ID  $\times$  100 mm L) were presented.

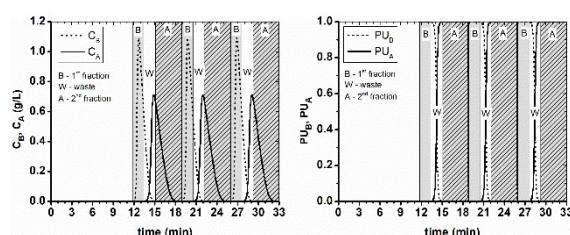


Fig 2. Simulated fixed-bed chromatograms of three consecutive pulses (left plot, dashed line for the less retained racemate B, solid line for more retained racemate A) and purities of B and A (right plot, dashed line for purity of B, solid line for purity of A) of a 9 g/L nadolol feed solution.

Both systems used the Waters XBridge C18 adsorbent of 10  $\mu$ m particle diameter and a 30:70:0.1 (v/v/v) ethanol:water:diethylamine solvent mixture. For FB, using a feed concentration of 9 g/L of an equimolar mixture of the two nadolol racemates, both were recovered almost pure (at least 99.9 %), with a global system productivity of 3.06 gfeed/(Lbed.hr) and a solvent consumption of 4.21 Lsolvent/gfeed. For SMB, the pilot unit's pressure drop limits imposed a maximum internal flow-rate of only 5 mL/min and, for a nadolol feed concentration of 2 g/L, both racemates were recovered 100 % pure, with a system productivity of 0.13 gfeed/(Lbed.hr) and a solvent consumption of 6.19 Lsolvent/gfeed. Additional simulation results showed that an

SMB preparative unit can perform the 9 g/L nadolol racemate separation with a system productivity of 3.61 gfeed/(Lbed.hr) and a solvent consumption of only 1.95 Lsolvent/gfeed using the same average internal flow-rate as in FB operation. Even better SMB productivity can still be obtained using the same feed or solvent flow-rates as in FB operation if the internal SMB flow-rates are allowed and not limited by the system pressure drop.

Based on the existing experimental data for the preparative separation of guaifenesin enantiomers using the Chiralcel OD CSP, we make a further investigation for the effect of operation modes on the separation performance of SMB unit, including the asynchronous shifting of inlet/outlet ports (VariCol mode), varying feed flow rate (PowerFeed mode), and varying feed concentration (ModiCon mode) within the switching interval. The mathematical models of the multicolumn SMB process are established, and the separation performances of SMB units with four operation modes are compared at similar operation conditions. Compared with the conventional six-column SMB process at the purity criterion of single enantiomer in products up to 99%, ModiCon 1 with feed concentration adjusting "First low last high" within the switching interval is the best one with the productivity increasing 27.5% and the solvent consumption decreasing 21.7%; PowerFeed mode also has some improvement with the productivity increasing 10.6% and solvent consumption decreasing 8.7%; five-column VariCol mode has the improvement on the productivity increasing 26% due to the benefit to save one packed column with the expensive chiral stationary phase.

#### Future Perspectives

The ongoing project includes the use of different SMB modes of operation, such as the asynchronous port shift (Varicol), variable feed concentration (ModiCon), or Japan Organo (JO) operation for ternary mixtures, among others, to study the improvement of preparative performance parameters of productivity, recovery and solvent consumption. The implementation of some of these non-conventional SMB modes of operation will imply the change of LSRE-FlexSMB unit hardware and software. It is also understudying the use of the developed methodology for the preparative separation of multicomponent mixtures obtained from different extracts of natural products.

#### Related Sustainable Development Goals



#### Outputs

##### PhD Theses

[1] Rami Sami Arafah, Multicomponent Chiral Separation by Preparative and Simulated Moving Bed Chromatography, PDEQB, FEUP, 2023

##### Selected Publications

- [1] Y. Yang *et al.*, Adsorption 25, 1227 (2019)
- [2] R.S. Arafah *et al.*, Chirality 31, 62 (2019)
- [3] R.S. Arafah *et al.*, Sep. Pur. Technol. 233, 116018 (2020)
- [4] R.S. Arafah *et al.*, Sep. Pur. Technol. 305, 122529 (2023)

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FCT Scholarships: SFRH/BD/137966/2018



# Cyclic Adsorption Processes

## Liquid Phase Separation Processes

### Expanded Bed and Simulated Moving Bed: proteins capture and separation

**KEYWORDS:** Simulated moving bed / Expanded bed adsorption/ Proteins/ Mixed mode chromatography/ Size Exclusion / Ion Exchange

**This topic is divided into two different parts: 1) Expanded bed adsorption and 2) simulated moving bed separation. Expanded bed adsorption was used for the capture and separation of two blood serum proteins, immunoglobulin (IgG) and Human Serum albumin (HSA). Simulated moving bed was used for the separation of two model proteins, bovine serum albumin (BSA) and myoglobin (Mb).**

#### Introduction

Proteins are present in many products, so they are essential for many industries, such as pharmaceuticals, food processing, cosmetic products, and others. Therefore, proteins must be produced and purified industrially at a large scale.

Separation by chromatography is one of the most relevant processes for purifying biological molecules. Depending on protein properties, such as molecular size, charge, or binding affinity, different types of chromatographic methods can be used including, affinity chromatography, gel filtration or size exclusion, ion exchange, hydrophobic interaction, and reserved-phase chromatography.

Therefore, the current work presents distinct types of protein separations, first based on expanded bed adsorption (EBA) technology and then simulated moving bed technology (SMB). The expanded bed technology provides advantages over traditional separation methods as eliminating contaminants from the column without the risk of blockage and minimizing pressure drop problems. On the other hand, a simulated moving bed (SMB) has a continuous countercurrent operation which increases productivity and reduces the eluent consumption.

#### Current Development

Regarding the EBA separation, it was possible to study the separation of the two blood serum proteins HSA and IgG on a mixed-mode adsorbent, MabDirect MM, which is designed for EBA processes. The expanded bed behavior was characterized by RTD experiments with different columns, Streamline 50 for the HSA study, Omnifit 66/20, and XK 16/20 for the IgG study. For HSA, four breakthrough experiments were conducted at pH5 without NaCl. The elution stage was optimized by lowering the flow rate and changing the buffer solution pH and NaCl concentration. It obtained a dynamic binding capacity of 8.9, 9.7, 7.5, and 7.0  $\text{mg} \cdot \text{g}_{\text{dry}}^{-1}$  at 10% of breakthrough, corresponding to 41, 39, 38, and 30% of the saturation capacity for runs 1–4, respectively. These adsorption experiments under various conditions were compared with simulation results using a mathematical model.

Concerning IgG adsorption, breakthrough experiments were conducted at pH 5.0 with 0.4 M NaCl and it was obtained a dynamic binding capacity of 3.3  $\text{mg} \cdot \text{g}_{\text{dry}}^{-1}$  at 10% of breakthrough, corresponding to 22% of saturation capacity.

Then, binary experiments were also performed in batch, fixed bed, and expanded bed adsorption. Competitive adsorption isotherm was measured by batch experiment at the binding condition of pH 5.0 without salt where it was found that increasing the IgG concentration present in the solution ( $0\text{--}3 \text{ g dm}^{-3}$ ) the HSA adsorption capacity decreases significantly (from 29.32 to 3.17  $\text{mg g}_{\text{dry}}^{-1}$ ) as a result of IgG competitive adsorption with HSA on MabDirect MM. Fixed bed adsorption experiments with binary mixture of HSA and IgG were

performed at two flowrates. There is no roll-up in the adsorption breakthrough curves even when it was increased the experiment timescale (from 2 to 0.7 mL/min at the adsorption stage) which suggests that they are both adsorbed also on different sites at the binding condition, 20 mM citrate buffer pH 5.0 with 0.4 M NaCl. The adsorption capacity for both proteins is in agreement with their respective single adsorption isotherms. Displacement experiments were carried out and showed that some amount of protein is released when the other protein is being fed to the column. Expanded bed breakthrough experiment with binary mixture of HSA and IgG shows an adsorption capacity (14.2  $\text{mg}_{\text{HSA}} \text{ g}_{\text{dry}}^{-1}$  and 6.3  $\text{mg}_{\text{IgG}} \text{ g}_{\text{dry}}^{-1}$ ) in good agreement with single protein batch experiments and also fixed bed adsorption for similar conditions. Regarding HSA and IgG desorption, it was obtained an HSA recovery of 62% and an IgG recovery of 39%.

The second type of studied separations was based on SMB technology. Here, three separations were performed with the two model proteins BSA and Mb, presented in Fig.1.



Fig.1. BSA and Mb lyophilized powder.

The first separation was achieved by Size-Exclusion Simulated Moving Bed (SE-SMB) and performed experimentally in the FlexSMB-LSRE unit, an SMB unit designed and built in the LSRE laboratory (schematic diagram in Fig.2).

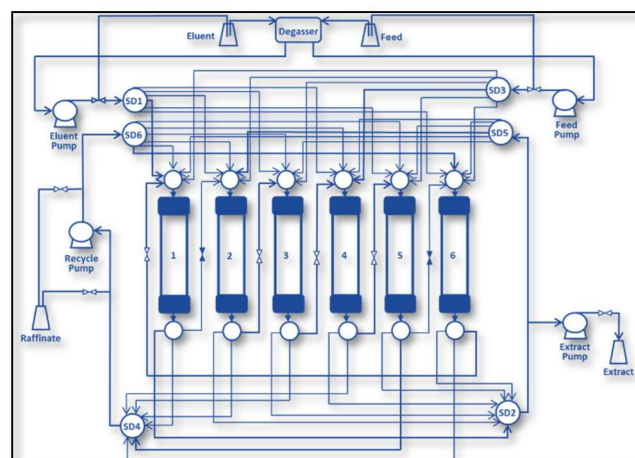


Fig.2. Schematic diagram of The FlexSMB-LSRE setup.

Before accomplishing the separation experiments in the mentioned unit, separation regions were computed by simulation based on a phenomenological mathematical model to determine appropriate operating conditions. The developed



model was validated in advance, against fixed-bed dynamic adsorption experimental results, for pure component and binary mixtures. Then the SMB experiments were carried out, and purities of the Mb on the extract and BSA on the raffinate streams were 98% and 96%, respectively. The achieved recoveries were 80% of Mb on the extract and 94% of BSA on the raffinate. Lastly, productivities of  $6.4 \text{ g}_{\text{protein}} \cdot \text{lads}^{-1} \cdot \text{day}^{-1}$  for the extract and  $28.8 \text{ g}_{\text{protein}} \cdot \text{lads}^{-1} \cdot \text{day}^{-1}$  for the raffinate were obtained.

Then, another separation was achieved, in this case with an anion exchange resin, Q Sepharose FF using a salt step elution in an SMB bench-scale unit. The BSA adsorption equilibrium at different salt concentrations was determined by frontal analysis. A phenomenological mathematical model, *i.e.*, the general rate model coupled with steric mass action equilibrium, was used and validated against fixed-bed dynamic adsorption experiments at different salt concentrations. The separation region was computed, and the operating conditions for an SMB experiment were selected within the obtained region. The chosen operating point was experimentally tested, and purity, recovery, and productivity of the BSA on the extract were 96%, 99%, and  $4.93 \times 10^{-3} \text{ mol}_{\text{protein}} \cdot \text{kg}_{\text{ads}}^{-1} \cdot \text{day}^{-1}$  and for the Mb on the raffinate were 99%, 96%, and  $4.77 \times 10^{-3} \text{ mol}_{\text{protein}} \cdot \text{kg}_{\text{ads}}^{-1} \cdot \text{day}^{-1}$ , respectively.

Finally, the separation of these model proteins was performed using HAp as an adsorbent and by performing a buffer step-elution in the SMB unit. Concerning this material, it was necessary to obtain granules with the provided powder to pack a fixed bed column. Granules were produced in a lab extruder, binder-free. Batch experiments determined the BSA and Mb adsorption equilibrium using pH 7 at different buffer concentrations. Then, fixed bed experiments were also performed for both proteins using the same buffer concentration. Here, it was used the same mathematical model mentioned above, the general rate model. The validity of

general rate model combined with steric mass action equilibrium, the same used above, but in this case using buffer concentration as a variable, was confirmed through experimental validation using fixed bed dynamic adsorption tests at various buffer concentrations. Based on the results, a separation region was computed, and suitable operating conditions for an SMB experiment were chosen from within this region. Experimental verification was performed to validate the selected operating point, and purity, recovery, and productivity of Mb on the extract were 92%, 87%, and  $1.04 \times 10^{-3} \text{ mol}_{\text{protein}} \cdot \text{kg}_{\text{ads}}^{-1} \cdot \text{day}^{-1}$ , and for BSA on the raffinate were 95%, 98%, and  $1.24 \times 10^{-3} \text{ mol}_{\text{protein}} \cdot \text{kg}_{\text{ads}}^{-1} \cdot \text{day}^{-1}$  respectively. Results are presented in Fig.3.

### Future Perspectives

Regarding future work considerations, our group can study different perspectives about protein separation and purification. Other types of SMB configurations can be tested, for example pseudo-SMB concept can be used to study ternary separations. Another concept of an integrated process can also be tested which is an expanded bed SMB process.

Different adsorbent materials, including shaped materials, can be used for protein separation.

### Related Sustainable Development Goals



### Outputs

#### PhD Theses

[1] Pedro Gomes, Proteins Separation by Expanded Bed Chromatography Technology, PDEQB, FEUP, 2018.

[2] Albertina Rios, Protein Separation and Purification by Cyclic Adsorption Processes, PDEQB, FEUP, 2023.

#### Selected Publications

[1] P. F. Gomes, *et al.*, Adsorption 24, 745–755 (2018)

[2] P. F. Gomes, *et al.*, Adsorption 24, 293–307 (2018)

[3] A. Rios, *et al.*, Journal of Chromatography A 1628, 461431 (2020)

[4] A. Rios *et al.*, Separation and Purification Technology 326, 124779 (2023)

[5] A. Rios, *et al.*, Ind. Eng. Chem. Res. 62, 13932–13942 (2023)

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FCT Grant: SFRH/BD/137891/2018, 2018-2022

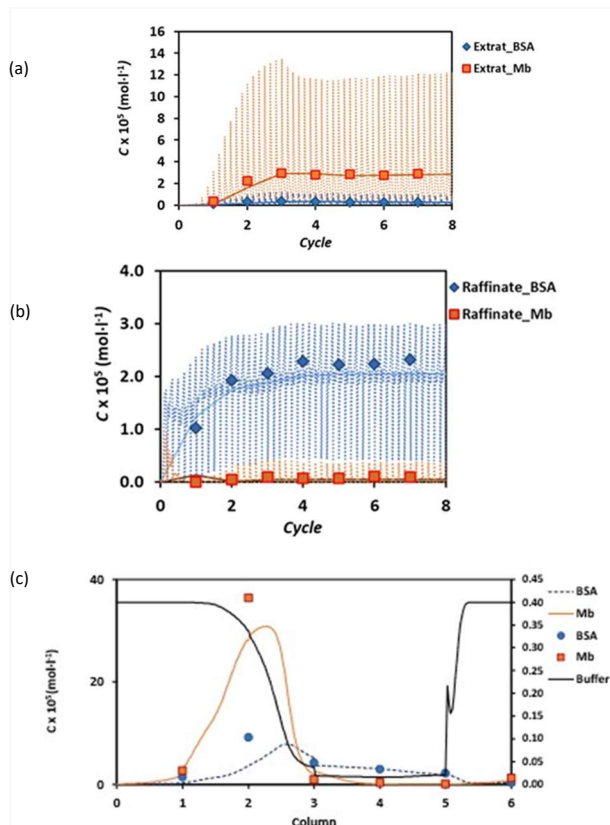


Fig.3. Extract (a) and Raffinate (b) concentration histories, and concentration profile at 50% of the time switch (c).

a phenomenological mathematical model, specifically the



# Cyclic Adsorption Processes

## Liquid Phase Separation Processes

### Simulated Moving Bed: Xylene Isomers Separation

**KEYWORDS:** Xylenes / Simulated Moving Bed / Metal-organic Frameworks / Adsorption / Optimization

The separation of xylenes was studied over MIL-125(Ti)<sub>2</sub>NH<sub>2</sub> at different temperatures to evaluate its influence on the selectivity towards *p*-xylene.

A current aromatics complex was studied, and several modifications to improve the production of *p*-xylene were analyzed through optimization of the simulated moving bed considering the most significant operating costs of the complex.

#### Introduction

Mixed xylenes is a term that defines a mixture that includes *p*-xylene (pX), *m*-xylene (mX), *o*-xylene (oX), and ethylbenzene (EB).

Metal-organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials that can have extended 1D-3D pore networks, combining high chemical and thermal stability, large surface areas, and tuneable surface properties. Functionalization of MOFs is an easy way to tune the physicochemical properties of MOFs, modulating for instance their adsorption properties.

#### Current Development

The separation of xylene isomers feedstock containing ethylbenzene is still a relevant industrial challenge. The increase in *p*-xylene consumption worldwide promotes the search for more efficient separation processes. One possible way to achieve such a goal is to upgrade the existing SMB units with selective adsorbents operating at lower temperatures. Therefore, new adsorbents such as the functionalized metal-organic framework MIL-125(Ti)<sub>2</sub>NH<sub>2</sub> appear as strong candidates. The MIL-125(Ti)<sub>2</sub>NH<sub>2</sub> was tested for the selective adsorption and separation of xylene isomers, including ethylbenzene, in the liquid phase and using *n*-heptane as an eluent. For this, an experimental study of binary and multicomponent adsorption equilibrium of xylene isomers in MIL-125(Ti)<sub>2</sub>NH<sub>2</sub>, at three temperatures (299 K, 313 K and 343 K) in the liquid phase, was performed.

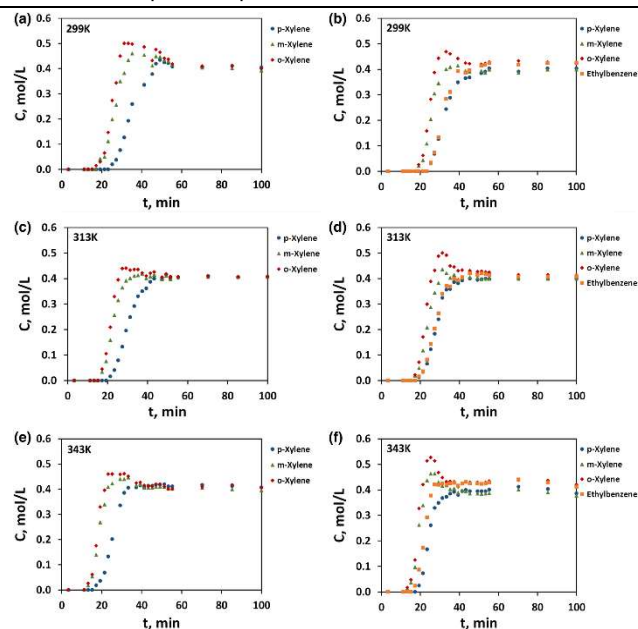


Fig 1. Breakthrough curves for a feed solution containing: (a) 5 wt% of pX, mX and oX in n-heptane at 299 K; (b) 5 wt% of pX, mX, oX and EB in n-heptane at 299 K; (c) 5 wt% of pX, mX, and oX in n-heptane at 313 K; (d) 5 wt% of pX, mX, oX and EB in n-heptane at 313 K; (e) 5 wt% of pX, mX and oX in n-heptane at 343 K; (f) 5 wt% of pX, mX, oX and EB in n-heptane at 343 K.

Ternary breakthrough experiments indicate competitive adsorption between *p*-xylene over the two other isomers. Indeed the selectivity values range from 1.4 to 1.9 and 1.5 to 2.3 for the *p*-xylene/*m*-xylene and *p*-xylene/*o*-xylene pairs, respectively, increasing with the temperature. Similar trends are observed for the quaternary mixtures, where *p*-xylene and ethylbenzene are adsorbed preferentially. However, the MIL-125(Ti)<sub>2</sub>NH<sub>2</sub> does not discriminate between the two more linear molecules at lower temperatures. Yet, when the temperature is increased to 343 K, the adsorption of *p*-xylene becomes more favorable than ethylbenzene, presenting a selectivity of 1.3. Therefore, within the studied temperature range a temperature, 343 K is the most favorable temperature to operate the SMB process, for the *p*-xylene production from mixtures containing ethylbenzene.

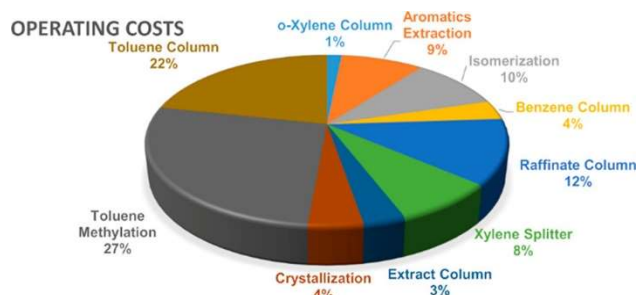


Fig 2. Operating costs of an aromatics complex.

The aromatics complex is a petrochemical facility where the main products are benzene and *p*-xylene. The xylene isomer is produced through an energy-intensive cycle loop in which the



*p*-xylene separation unit plays a significant role. Many works have focused on improving the efficiency of the separation unit; however, optimizations aiming to reduce the energy consumption of the whole complex are very scarce.

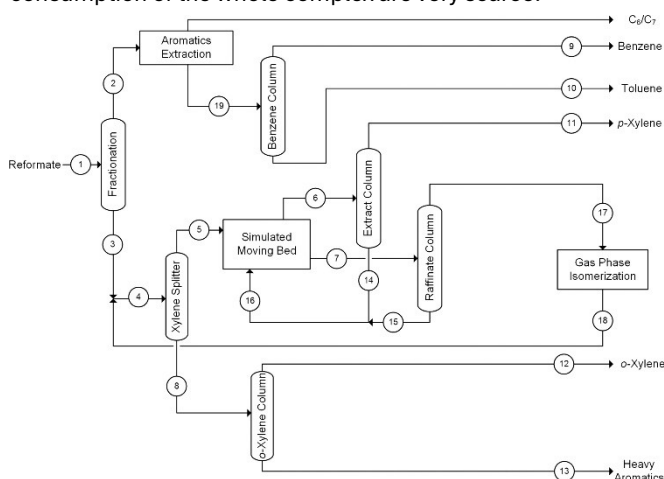


Fig 3. Current aromatics complex.

Based on the aforementioned, an existing aromatics complex was studied, and the *p*-xylene separation unit, that is the simulated moving bed (SMB) unit, was optimized in the framework of several modifications to the complex. The changes consisted of the addition of a crystallization unit, operating at two different temperatures, and a toluene methylation unit. The objective function included the revenue from the final products and the major operating costs from the units of the complex.

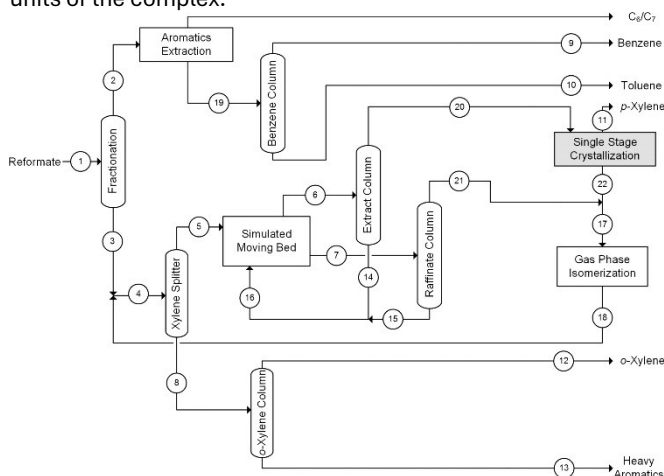


Fig 4. Proposed aromatics complex with crystallization.

Because of the complexity of the optimization problem, simplified models were used but validated against reported data. For almost all the cases studied, the optimum SMB consisted of more columns in zones I and IV and switching times of 180 s; when the feed of the SMB increased around 40%, the optimum switching time was 112 s. The crystallization unit alone did not improve the efficiency of the complex; however, *p*-xylene production doubled with the addition of the toluene methylation unit, which constituted the best proposal among the cases studied. Optimum toluene conversion and *p*-xylene selectivity were about 20 and 95%, respectively. The results also showed that it is more profitable to operate the crystallization unit at higher temperatures and send the mother liquor, with a *p*-xylene fraction above the thermodynamic equilibrium, back to the SMB.

#### Related Sustainable Development Goals



#### Outputs

##### Selected Publications

- [1] M. A. Moreira et al., Adsorption 24, 715-724 (2018)
- [2] J. C. Gonçalves et al., Ind. Eng. Chem. Res. 59, 11570-11581 (2020)

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## Cyclic Adsorption Processes

### Liquid Phase Separation Processes

#### Simulated Moving Bed: Purification of Glycerol Oxidation Derivatives

**KEYWORDS:** SMB separation / Glycerol valorization / Dihydroxyacetone purification / Organic Acids

A green DHA production process, involving glycerol catalytic oxidation and DHA purification via SMB separation, was developed, marking the first publication of this separation study in open literature. The separation process was validated on the FLEXSMB-LSRE® unit, using a cascade of two SMBs with a strong cationic exchange resin. DHA was obtained with 98.6% purity and a recovery of 77.5%. Additionally, the separation of tartronic acid and glyceric acid was experimentally studied on a single SMB unit, producing a pure GCA stream and a TTA stream with 80% purity. The SMB model exhibited excellent agreement with experimental data, offering valuable insights for dynamic process behavior and enabling confident process optimization.

##### Introduction

In response to the global effort to mitigate climate change included in this energy transition era, the biodiesel industry has emerged as a viable alternative to fossil fuel energies. Noteworthy for its renewability, biodegradability, and non-toxic nature, biodiesel serves as a direct substitute for fossil diesel. Biodiesel production more than doubled from 20 Mm<sup>3</sup> in 2010 to 45 Mm<sup>3</sup> in 2022, and projections from the International Energy Agency indicate it is expected to keep growing until 2050.

The expansion of biodiesel production has led to a significant accumulation of the main reaction by-product, crude glycerol, posing economic challenges. Its valorization is crucial for enhancing the sustainability and competitiveness of the biodiesel industry. Among the various glycerol valorization routes, catalytic oxidation emerges as an attractive and sustainable solution.

The catalytic oxidation of glycerol yields several high-added-value products, with dihydroxyacetone (DHA) standing out due to its diverse applications, particularly as it is the active compound in sunless skin tanning lotions, making it a high-demand product by the cosmetics industry. The current industrial production of DHA through bio-fermentation faces limitations such as long fed-batch processes and operation limitations, creating space for alternative processes.

However, the catalysts with moderate and high activity are not completely selective to DHA, and organic acids such as Tartronic Acid (TTA) and Glyceric Acid (GCA) are also obtained by glycerol catalytic oxidation. While TTA finds applications in pharmaceuticals for treating osteoporosis and obesity, its commercial viability is hindered by current pricing. GCA, on the other hand, lacks commercial applications so far.

The reaction selectivity may be tuned by adjusting the reaction conditions, and the catalyst properties. Pt-based and Pd-based catalysts, particularly those supported in carbon materials exhibit high yields for GCA and TTA, especially under basic conditions. By doping the catalyst with Bismuth and changing to base-free conditions the reaction selectivity shifts to DHA production. Promising catalysts for high DHA yield processes include Pt-Bi and Pt-Sb nanoparticles supported in carbon and mesoporous materials, as well as Au nanoparticles supported by late transition metal oxides like Au/CuO and Au/ZnO.

Focusing on DHA production three commercial Pt-based catalysts supported in activated carbon were tested for

glycerol oxidation in a batch reactor under base-free conditions. Focusing on a sustainable approach, mild operation conditions were employed, using water as the solvent and oxygen as the oxidant agent. The Pt5%-Bi1.5%/AC catalyst showed superior performance for DHA production, with a maximum DHA yield of 36% after two hours of reaction.

The main challenge is to design and experimentally validate a separation process to separate DHA from the remaining compounds, as the final step of a complete alternative process for DHA production via a catalytic route. Continuous chromatographic separation processes were proposed based on the simulated moving bed unit. The binary separation of TTA from GCA on an SMB unit was also studied.

##### Current Development

A green DHA production process, comprehending a glycerol catalytic oxidation step and a DHA purification by continuous chromatographic step was found to be feasible.

The purification of DHA from the reactional mixture obtained during GLY aerobic oxidation with Pt-based catalysts was successfully designed and experimentally validated using a lab-scale SMB unit, the FLEXSMB-LSRE®, with six columns packed with a strong cationic exchange commercial resin, the DOWEX 50WX-2. The composition of the solution obtained by glycerol aerobic oxidation using a Pt-Bi/AC catalyst was considered as the feed solution.

Kinetic and equilibrium data were obtained by frontal analysis on a fixed-bed column packed with the resin in acidic form and 5 mM H<sub>2</sub>SO<sub>4</sub> as mobile phase.

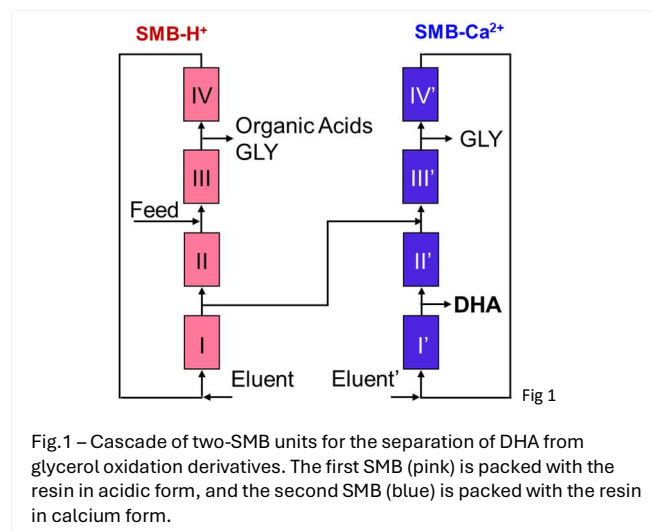


Fig. 1 – Cascade of two-SMB units for the separation of DHA from glycerol oxidation derivatives. The first SMB (pink) is packed with the resin in acidic form, and the second SMB (blue) is packed with the resin in calcium form.

The adsorption data of glycerol, dihydroxyacetone, and the organic acids (tartronic acid, glyceric acid, and glycolic acid) was well described by a linear adsorption isotherm, except oxalic acid which was better described by the Freundlich isotherm. Dihydroxyacetone was the most retained species. Furthermore, kinetic and equilibrium adsorption data were determined for DHA and GLY in the same resin but in calcium form, using water as the mobile phase. Again, both species showed a linear adsorption isotherm, with DHA being the most retained compound. For the resin in the calcium form, the study was not extended to organic acids since their protons



would exchange with the calcium cations in the resin matrix, which would return to their acidic form over the operation time.

Multicomponent adsorption breakthrough experiments were conducted in the resin in acidic form using a six-component mixture, and in the resin in calcium form using a binary mixture of DHA and GLY. The experimental data were well described by the model, validating the suitability of using linear isotherms to describe the adsorption phenomena for the concentrations of interest.

The pseudo-binary separation of DHA from the remaining species (OXA, TTA, GCA, GCO, and GLY) was not considered due to the very low separation selectivity of DHA from GLY of 1.04. In contrast, DHA separation from GLY may be more easily performed over the resin in calcium form as the separation selectivity sharply increased to 1.28.

So, a two SMB unit cascade was considered for the separation purification of DHA, represented in Fig.1. DHA was separated from the organic acids, selectivity of 1.06 on the first

global productivity of  $21.7 \text{ kg}_{\text{DHA}} (\text{m}^3_{\text{adsorbent}} \cdot \text{day})^{-1}$  and an eluent consumption of  $5.7 \text{ m}^3_{\text{eluent}} \text{ kg}_{\text{DHA}}^{-1}$ .

The mathematical model used to describe the SMB experiments was validated and demonstrated good agreement with the experimental SMB data, along with the kinetic and equilibrium data obtained from single fixed-bed column experiments.

Additionally, the purification of the binary mixture of tarttronic acid and glyceric acid was designed and experimentally validated using the FLEXSMB unit packed with the resin in acidic form and 5 mM  $\text{H}_2\text{SO}_4$  as mobile phase. In cyclic steady-state conditions, TTA was collected in the raffinate stream with a purity of 80%, and GCA was collected in the extract with a purity of 100%. The productivities of TTA and GCA were 79 and  $115 \text{ kg} (\text{m}^3_{\text{adsorbent}} \cdot \text{day})^{-1}$ , respectively, consuming only  $0.50 \text{ m}^3_{\text{eluent}} \text{ kg}_{\text{product}}^{-1}$ . Optimization improved the productivity by 30% and the eluent consumption by 20%.

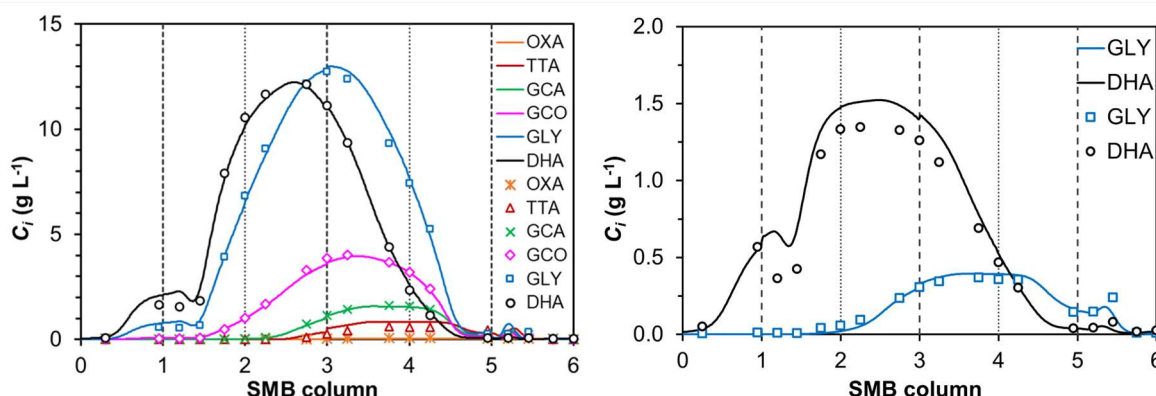


Fig.2 – Internal concentration profiles at half-time of the first switching time under cyclic steady state conditions, with a 1-2-2-1 column configuration: Left) Pseudo-binary separation of DHA from the organic acids in the SMB-H<sup>+</sup> unit; and Right) separation of DHA from GLY in the SMB-Ca<sup>2+</sup> unit.

SMB unit packed with the resin in acidic form, neglecting the extract stream contamination with GLY. This stream was fed to a second SMB unit packed with the resin in calcium form, separating DHA from GLY. DHA was collected in the extract stream while GLY was collected in the raffinate stream, which could be recycled to the oxidation reactor and further converted into DHA.

The separation process was implemented and studied in the gPROMS model builder software, using the axial dispersive flow model with the LDF approximation to represent the dynamic behavior of the fixed-bed column alone and within the FlexSMB unit. The separation regions for both SMB units were determined considering mass transfer limitations and the design and dead volumes of the FlexSMB unit.

The separation of DHA from the main organic acids (OXA, TTA, GCA, and GCO) was performed in the SMB-H<sup>+</sup>, and CSS conditions were achieved after 30 cycles, with an experimental DHA recovery of 87.0%, and an extract purity in glycerol free basis of 96.8%. The internal concentration profiles are represented in Fig.2.

The extract stream from the first SMB was then fed into the second SMB unit, SMB-Ca<sup>2+</sup>, with the same design but packed with the resin in calcium form. The separation of DHA from GLY was carried out, and CSS conditions were achieved after 30 cycles, with experimental DHA recovery of 89.0% and an extract purity of 98.6%. The internal concentration profiles are represented in Fig.2.

The model described well the history of the average concentration of the species in the outlet streams and the SMB internal concentration profiles at cyclic steady state conditions for both SMBs. The two-unit SMB cascade produced DHA with a concentration of 0.50 g/L and 98.6 % of purity, showing a

## Future Perspectives

Optimization of the SMB cascade for DHA production should be performed, as well as further studies are still required to evaluate the economic potential of the chromatographic separation process. The purification of the organic acids collected from the raffinate stream of the first SMB cascade, or an SMB with up to eight sections may be studied to solve the separation of the organic acids.

## Related Sustainable Development Goals



## Outputs

### Selected Publications

- [1] Walgode, P. *et al.*, Chemical Engineering Journal, 476, 146447, (2023).
- [2] MWalgode, P. *et al.*, Industrial & Engineering Chemistry Research, 60, 10551-10565, (2021).
- [3] Coelho, L. *et al.*, Journal of Chromatography A, 1563, 62-70, (2018).
- [4] Walgode, P. *et al.*, Catalysis Reviews, 63, 422-511, (2021).

### Team

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### Funding

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# Cyclic Adsorption Processes

## Liquid Phase Separation Processes

### Hybrid Separation Processes: Purification of Aqueous Solutions

**KEYWORDS:** Selective Adsorption / Wastewater treatment / Dyes / Graphene oxide biocomposite / Chloroquine diphosphate

This topic is about hybrid separation processes, and it includes different separation processes for water and wastewater treatment. Different compounds, dyes, and chloroquine were used as pollutants for water and wastewater purification using different adsorbent materials.

#### Introduction

Water pollution is a serious problem worldwide. Anthropogenic activities from the pharmaceutical and textile industries have led to the release of dyes and pharmaceutical drugs into water bodies. Dyes are used in many kinds of industries such as textiles, paper, food, cosmetics, and plastics. The produced effluents, often with a high chemical oxygen demand and toxicity, require treatment before their discharge into the hydrosphere.

Therefore, the potential for remediating environmental problems, such as water pollution, has also increased because of nanotechnological improvements. Biologic, chemical, or physical methods may be used for water treatment. Among the available water treatment techniques, adsorption can be pointed out as one of the most attractive techniques for the removal of organics because it is considered cheap, versatile, and simple to operate. Different adsorbent materials can be used for the removal of these kinds of pollutants.

The work here presents three different cases of water treatment using different adsorbent materials and different adsorbates.

Silica can be used for dye removal. Therefore, it is reported a work with mesoporous structured silica for dye removal.

Activated carbons are commonly used for organics removal from wastewater. With the improvements in nanotechnology, the use of carbon nanocomposites for the uptake of pharmaceuticals and synthetic dyes has been explored. So, here it is presented two works with a hydrogel biocomposite using graphene oxide and agar biopolymer.

#### Current Development

Regarding the first work, the adsorption of Basic Blue 41 (BB41), Methylene Blue (MB), and Basic Red 18 (BR18), three known basic dyes, was studied in shaped mesoporous adsorbent MCM-41. The granules were obtained by extrusion of the powder adsorbent and were analyzed by nitrogen adsorption, SEM-EDS, XRD, mercury porosimetry, and helium picnometry. Adsorption equilibrium isotherms, kinetics, and breakthrough curves were performed with the selected adsorbent and dyes. The experimental results indicated that the Sips model better describes the equilibrium than the Langmuir and Freundlich isotherm models. Additionally, the co-adsorption equilibrium of two dyes was well predicted by the extended form of the Sips model. The kinetics results showed that the adsorption of Basic Blue 41 onto the selected adsorbent is faster than with the other studied dyes. The obtained adsorbed equilibrium amounts through the breakthrough curves were 308 mg·g<sup>-1</sup>, 55 mg·g<sup>-1</sup> and 106 mg·g<sup>-1</sup> for the Basic Blue 41, Methylene Blue, and Basic Red 18 dyes, respectively. The dye is concentrated during the regeneration step, since the volume of regenerating solution, eluted during the regeneration, is considerably lower (about two orders of magnitude) when compared with the volume of effluent treated until the breakthrough point. This fact

demonstrates the feasibility of a potential adsorption-based process to treat dyed effluents, with the shaped MCM-41.

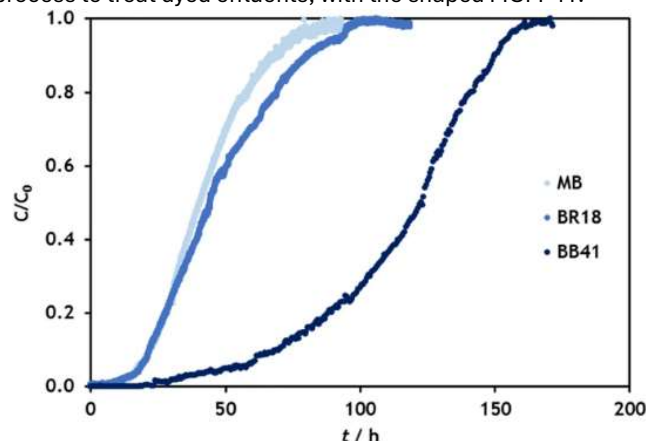


Fig.1. Breakthrough curves for adsorption of Basic Blue 41, Basic Red 18, and Methylene Blue.

Other separations with cationic dyes were performed. In this case, hydrogel biocomposite using graphene oxide and agar biopolymer (agar-GO) was synthesized to treat textile wastewater through fixed-bed adsorption. After characterization, batch experiments were conducted to evaluate the pH effect in the adsorption process, adsorption isotherms, and kinetics for four cationic dyes – Nile Blue A (NB), Methylene Blue (MB), Malachite Green (MG), and Basic Fuchsin (BF). Adsorption equilibrium isotherms were fitted to Freundlich, Langmuir, and Sips models, and kinetic data were adjusted to Driving Force models, and the Fickian Diffusion equation. The influence of the initial pH in the adsorptive capacity was tested and it is presented in Fig2. In this figure, it is also presented the adsorption equilibrium data for all dyes.

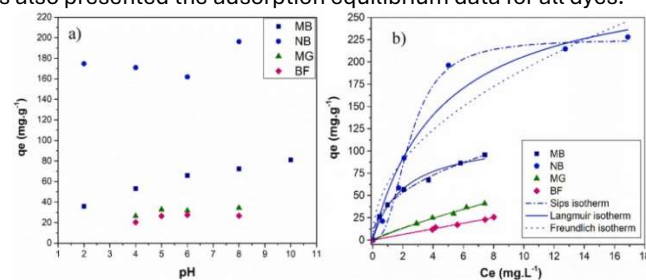


Fig.2. (a) Influence of the initial pH in the adsorptive capacity of agar-GO in the removal of the dyes with  $C_0 = 10 \text{ mg} \cdot \text{L}^{-1}$  (MB, MG, BF), and  $20 \text{ mg} \cdot \text{L}^{-1}$  (NB); (b) adsorption isotherms for MB, NB, MG, BF adsorption onto agar-GO hydrogel on a dry basis.

Fixed-bed experiments were carried out, and the adsorption capacities on a dry basis were 226.46 mg·g<sup>-1</sup> (NB), 79.51 mg·g<sup>-1</sup> (MB), 58.25 mg·g<sup>-1</sup> (MG), 38.11 mg·g<sup>-1</sup> (BF). LDF model was fitted with the experimental breakthrough curves. The column packed with the agar-GO hydrogel was tested for the treatment of synthetic textile wastewater. Color and total organic carbon (TOC) were evaluated and there was an indication of the adsorbent selectivity for the separation of the dyes, which can facilitate dye recovery. Agar-GO proved to be a viable and eco-friendly alternative since a small amount of material was used to treat over 6 L of wastewater, most of the composite



biodegradable. Moreover, the material exhibited remarkable regenerative capacity, proving its effectiveness for applications in industrial textile wastewater treatment.

Then, this material was also used for other separation processes. Chloroquine diphosphate and the cationic dye Safranin-O were selectively removed from water using the agar-graphene oxide (A-GO) hydrogel. The morphology of the A-GO biocomposite was characterized and batch experiments were performed, with adsorption isotherms satisfactorily fitting ( $R^2 > 0.98$ ) Sips (Safranin-O) and Freundlich (Chloroquine) isotherms. Driving force models and Fick's diffusion equation were applied to the modeling of kinetic data, and a satisfactory fit was obtained. Selective adsorption carried out in batch indicated that competitive adsorption occurs when both components are mixed in water solution - the adsorptive capacities dropped  $\sim 10 \text{ mg}\cdot\text{g}^{-1}$  for each component, remaining  $41 \text{ mg}\cdot\text{g}^{-1}$  for safranin-O and  $31 \text{ mg}\cdot\text{g}^{-1}$  for chloroquine. Fixed-bed breakthrough curves were obtained, and the process diagram of these experiments is given in Fig.3.

In an adsorption column the selected adsorbent showed adsorption capacities over  $63 \text{ mg}\cdot\text{g}^{-1}$  and  $100 \text{ mg}\cdot\text{g}^{-1}$  for chloroquine and safranin-O, respectively, also exhibiting outstanding regenerative potentials. Overall, the biocomposite produced using graphene oxide proved to be a viable and eco-friendly alternative to continuously remove both contaminants from water.

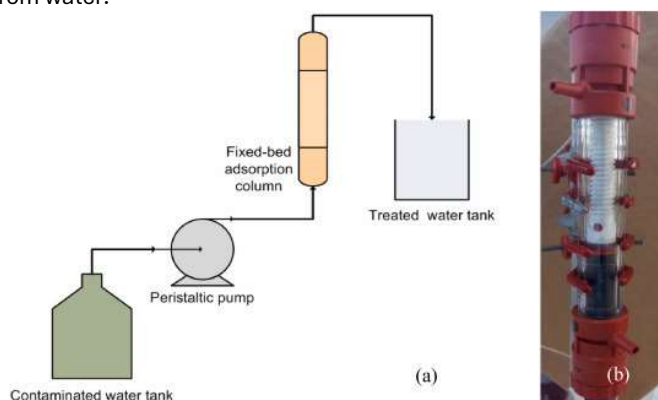


Fig.3. Process flow diagram depicting the experimental setup for fixed-bed adsorption experiments (a); photograph of the column packed with A-GO hydrogel (b).

There are other two studies about a selective adsorption process for the removal of a compound, 4-hydroxy-TEMPO, from a liquid industrial effluent, from the PVC production industry. Two different adsorbent materials were tested for the removal of this compound to reuse the water stream, and consequently, to reduce the amount of water used in the industrial process. The materials tested were BPL activated carbon and Dowex 50WX2 resin. Both batch and fixed bed experiments were performed, and higher adsorption capacity was obtained for the activated carbon using lower concentrations of the compound.

#### Future Perspectives

Regarding future work considerations, our group could study different adsorption techniques that can be used for wastewater treatment, for example, parametric pumping could be implemented as a continuous method for dye removal.

Different adsorbent materials, including other shaped materials, can be used for dye adsorption.

#### Related Sustainable Development Goals



#### Outputs

##### PhD Theses

[1] Caroline Araújo, Water and wastewater treatment using recyclable agar-graphene oxide biocomposite hydrogel in batch and fixed-bed adsorption column: bench experiments and modelling for the selective removal of organics. Dissertation in Chemical Engineering, UFPE, Brazil, 2022.

##### Master Dissertations

[1] Marta Sousa, Tratamento seletivo de um efluente industrial por adsorção., MIEQ, FEUP, 2019.

[2] Rita Almeida, Tratamento seletivo de um efluente industrial por adsorção., MIEQ, FEUP, 2020.

##### Selected Publications

[1] A.G. Rios *et al.*, Adsorption 26, 75–88 (2020)

[2] C.M.B. de Araujo *et al.*, Colloids and Surfaces A: Physicochemical and Engineering Aspects 639, 128357 (2022)

[3] C.M.B. de Araujo *et al.*, Environmental Research 216, 114425 (2023)

##### Team

**Alírio E. Rodrigues**, Emeritus Professor; **José M. Loureiro**, Associate Professor; **Alexandre Ferreira**, Assistant Professor / Group Leader, **Ana Mafalda Ribeiro**, Assistant Professor; **Caroline Araújo**, Visiting Ph.D. student; **Albertina Rios**, M.Sc. student, **Marta Alves**, M.Sc. student; **Rita Almeida**, M.Sc. student.

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LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019

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ALiCE, LA/P/0045/2020, 2021-2023



# Cyclic Adsorption Processes

## Liquid Phase Separation Processes

### Hybrid Separation Processes: Sustainable effluent processing

**KEYWORDS:** Electrocoagulation/Adsorption/Water treatment/Sustainable mineral processing/Lithium recovery

The application of different processes for treating effluents containing potentially hazardous compounds has been studied. Additionally, the possible ways to valorize the effluents / urban mining were investigated. Another aspect considered in the research work was the improvement of the sustainability of the processes. The research work includes the study of the adsorption of the of Pb(II) and Hg(II) ions on bentonite-alginate composite (BAC); lithium recovery in flat sheet supported liquid membranes (FSSLMs); the use of both discontinuous and continuous EC processes for the removal of several contaminants from water; and the use of alternative leaching reagents for sustainable gold extraction.

#### Introduction

In the current context of increasing concern about water scarcity worldwide, the sustainable use of water resources should be one of the main priorities of different industries. Additionally, releasing untreated effluents to natural water bodies significantly impacts the environment and potentially human health. Therefore, the mitigation of the impact of those effluents on natural water resources is an urgent issue that requires a generalized application of alternative decentralized effluent treatment systems in large and small industries.

The electrocoagulation (EC) process is a possible simple, cost-effective alternative to conventional effluent treatment methods. The basic principle of EC is the electro-dissolution of a sacrificial anode (typically iron or aluminum) to generate the coagulant species. There is no need to add any chemical coagulant in this process, thus reducing the amount of sludge produced. Additionally, there is the possibility of operating the EC process using sustainable energy sources, such as solar cells, windmills, and fuel cells.

Adsorption is another attractive way of treating effluents due to the potential of using low-cost and environmentally friendly adsorbents. Due to its high surface area and well-developed pore structure, activated carbon is the most used adsorbent in wastewater treatment systems. However, several low-cost adsorbents such as biochar, peanut shells, coal fly ash, rice husk, and bagasse fly ash are alternatives for effluent treatment.

Another critical aspect of the different effluent processing methods is their sustainability and economic viability. Therefore, finding ways to extract value from those processes is an important research topic. Using the sludge resulting from the EC process operation to produce fertilizers, pigments, construction materials, adsorbents, and catalysts is a possible way to valorize this by-product. Another example is lithium recovery from the leaching solution resulting from the lithium-ion batteries (LIBs) recycling processes using membrane technology. Using low-cost and sustainable materials in the processes is also a critical factor in improving the processes. An example is using low-cost materials such as agricultural and industrial wastes as adsorbents. Another example is the use of sustainable leaching reagents in mineral processing.

#### Current Development

Batch EC was used to remove arsenic, fluoride, and iron from drinking water. The experiment outcomes demonstrated that arsenic might be readily eliminated even in the presence of other pollutants. Even though the rate of arsenic removal is

slightly slower when fluoride is present, the entire amount of arsenic can be removed in less than 30 minutes of EC operation. Conversely, the presence of iron positively impacts the rate at which arsenic is removed. It appears that having both fluoride and iron removal in the EC operation is beneficial. Furthermore, the presence of arsenic has no discernible effect on eliminating either component. In less than an hour, batch EC can remove the three contaminants simultaneously.

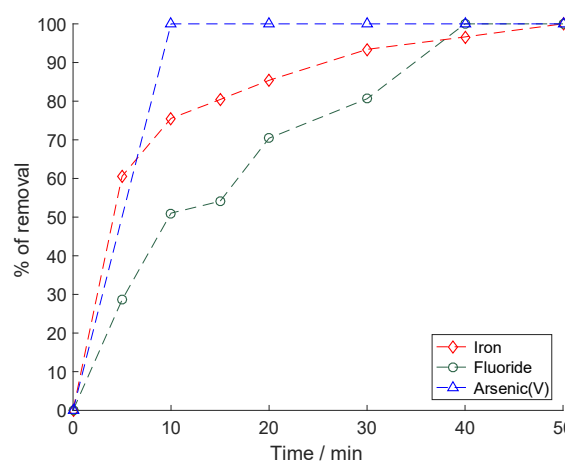


Fig 1. Simultaneous removal of iron, arsenic and fluoride.

Both total and dissolved aluminum concentrations were experimentally measured during the batch EC process. The total aluminum concentration was fitted with Faraday's equation and was obtained as 1.6 of current efficiency, indicating a super-faradaic behavior of the electrochemical process at the given operating conditions. A mathematical model was also developed considering the electrochemical dissolution of the aluminum anode, water electrolysis, hydrolysis of dissolved aluminum, and water dissociation reaction involved in the EC process. The simulated results showed a good prediction of the evolution of dissolved aluminum and pH concentration during the batch EC process operation. The model was also employed to simulate the removal of arsenic from water by electrocoagulation, showing a good prediction of the experimental results at the operating conditions considered.

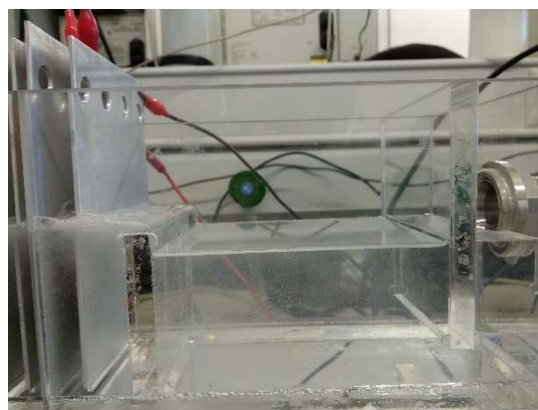


Fig 2. Continuous electrocoagulation experimental setup.



An experimental continuous EC experimental setup was constructed and used to remove fluoride from water using aluminum electrodes. The experimental results showed that the proposed process can remove 97% of fluoride from 5 L of water with a 15 mg F/L concentration. Additionally, it was verified that the applied voltage during the operation remains almost constant, indicating that this experimental setup overcomes the increase of the electrical resistance due to the electrode passivation. The experimental setup was tested for the treatment of 20 L of water. The results showed that the total removal of fluoride for 20 L of water could be achieved with an energy consumption of 506 kWh m<sup>-3</sup>.

The continuous electrocoagulation (CEC) process for removing fluoride from the water was modeled using an artificial neural network (ANN). After the ANN training, the sum of the squared errors (MSE) and the determination coefficient (R<sup>2</sup>) of the testing set model predictions were 0.0088 and 0.999, respectively, showing a good generalization and the model's predictive capacity. The optimization of the process cost using the genetic algorithm (GA) showed that the optimal conditions are highly dependent on the feed concentration and the fluoride removal requirements. For 5 L of water containing 10 mg/L of fluoride, the optimal conditions to reduce the fluoride concentration below the permissible limit (1.5 mg/L) are 88.3 mA of current intensity, a flow rate of 73.6 mL/min, and the use of a series monopolar (SM) electrode configuration, corresponding to a fluoride removal of 85% and an operating cost of 0.05 €/L.

The treatment of carpet cleaning wastewater was studied for electrocoagulation-flotation (ECF) followed by sedimentation. Response surface methodology (RSM) under central composite design (CCD) was employed to optimize the process. The operating cost was calculated at the optimum operating conditions as 0.673 USD/m<sup>3</sup>. The study's results indicated that the electrocoagulation-flotation followed by sedimentation was a cost-effective treatment for removing target pollutants from the carpet cleaning wastewater.

The adsorption of Pb(II) and Hg(II) ions on bentonite-alginate composite (BAC) was studied in both single-compound and binary systems at three different temperatures. A simple examination of all adsorption equilibrium isotherms shows that the bentonite-alginate composite is more effective for Pb (II) adsorption than for Hg (II), and the adsorption capacity is reduced in a binary system, reflecting a competitive effect between the Pb (II) and Hg (II). Hill and competitive Hill models are applied to explain the single and binary processes and the corresponding mechanisms. The adsorption geometry can be determined at different temperatures by estimating the number of ions captured per BAC adsorbent site. These models show that the affinity sequence in all adsorption systems is Pb (II) - Hg (II). An energetic analysis deduced from these models can explain and corroborate this behavior. Finally, to deepen the interpretation of single-compound and binary adsorption, the conductor-like screening model (COSMO-RS) was tested and applied to calculate the total interaction energies between heavy metals and BAC adsorbent. The evaluation of energies deduced from the COSMO-RS model indicated that the electrostatic misfit interaction energy might play the primary role in the heavy metal ion's adsorption in tested systems.

The lithium recovery from the leaching solution from the LIBs recycle process was studied. Two models were used for flat sheet-supported liquid membranes (FSSLMS) to estimate the behavior of ion concentrations during lithium recovery operation. Applying the simplified model, predicting the system's behavior is possible based on a few experiments.

A comprehensive review of potential sustainable leach reagents in the gold mining sector was performed. In addition to extraction, the application of these reagents in the gold processing, pre-treatment, and purification stages was explored. The main objective was to discuss how the gold extraction process can be more sustainable and develop greener leaching reagents.

### Future Perspectives

The process integration methodology will be explored to improve efficiency, sustainability, and economic viability. Wastewater treatment processes combining EC with adsorption to remove target pollutants are examples of process integration that can be explored. Despite both processes' great potential for treating various wastewater, using each method separately has drawbacks. Combining the strengths of both processes to create a hybrid process is one way to get around these constraints while maximizing their potential.

Furthermore, the combined process has several qualities that make it appropriate for a decentralized wastewater treatment method and in a zero-waste circular economy model. Finding a good balance between the effectiveness of the treatment and its operating costs is one of the main challenges when developing this kind of treatment. Therefore, more studies should be conducted on this subject to broaden the applicability of those processes.

### Related Sustainable Development Goals



### Outputs

#### Selected Publications

- [1] J. F. A. Silva *et al.*, Separation and Purification Technology 197, 237-243, (2018)
- [2] N. S. Graça *et al.*, Ind. Eng. Chem. Res. 58, 5314–532 (2019)
- [3] N. S. Graça *et al.*, Chemical Engineering Science 197, 379-385 (2019)
- [4] N. S. Graça *et al.*, Water Supply 22, 643–658 (2022)
- [5] N. S. Graça and A. E. Rodrigues, Clean Technol. 4, 1020–1053 (2022)
- [6] L. Sellaoui *et al.*, Journal of Molecular Liquids 253, 160-168 (2018)
- [7] E. Shakeri *et al.*, Desalination and Water Treatment 227, 163-176 (2021)
- [8] M. J. Regufe *et al.*, Chemical Engineering and Technology 45, 595-600 (2022)
- [9] R. Sousa *et al.*, The Extractive Industries and Society 9, 101018 (2022)

### Team

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 Inn-INDIGO, Project Inn-INDIGO/0003/2014.  
 ERA-NET LIMEX, ERA-MIN-2018\_57



# Cyclic Adsorption Processes

## Liquid Phase Separation Processes

### Hybrid Separation Processes: Volatile fatty acids separation

**KEYWORDS:** Permeation / Nanofiltration / Reverse Osmosis / Retention / Permeate flux / Adsorption equilibrium / Adsorption kinetics / Fixed-bed / Mathematical modelling

**Separation of volatile fatty acids was studied through two methods: 1) permeation, where different nanofiltration and reverse osmosis membranes were tested and analyzed at different operating conditions (pressure, feed concentration and pH) with single-component solutions, and 2) adsorption, where adsorption equilibrium and kinetics were determined at batch mode, where single-site Langmuir and linear driving force models were adjusted to the experimental results of adsorption equilibrium and kinetics, respectively. Fixed-bed experiments were also performed to validate the mathematical model.**

#### Introduction

Volatile fatty acids (VFAs) are carboxylic acids with short chains of carbon, usually six or fewer carbon atoms, such as formic, acetic, propanoic, butyric, valeric, and hexanoic acids. They are usually used as intermediates in the production of different products, in a variety of industries (e.g., food, pharmaceuticals, chemicals, cosmetics, bioenergy, materials), making them attractive and valuable compounds in the market.

Typically, VFAs are produced by chemical routes, specifically from petroleum-based components. However, due to the negative health and environmental effects of petrochemical production, the interest in developing sustainable processes for volatile fatty acids production has increased. An alternative and more sustainable VFAs production method is via biological means, like acidogenic fermentation of wastewater. The resulting stream contains VFAs in a not-processed and mixed form, which have very little value. Therefore, separating the acids into a more worthy form is needed to be used for their intended purpose. Several methods have already been studied for this end, such as precipitation, distillation, adsorption, and membrane-based technologies (e.g., electrodialysis, nanofiltration, reverse osmosis, and vapor permeation membrane contactors). Adsorption and pressure-driven membrane-based (specifically nanofiltration, and reverse osmosis) approaches are the most promising ones, due to their economic and environmental advantages, relatively easy operation, and wider diversity in materials. Therefore, these were the methods implemented in this work to separate volatile fatty acids.

The objectives of this work are to report a complete analysis of the adsorption/desorption process on VFAs, and characterize and design a continuous permeation process, to acquire the acids in a more refined and pure form (more worthy form).

#### Current Development

The study of VFAs recovery and separation was integrated within the scope of the project CONSERVAL, in which the main goal was to develop different technologies for the valorization of wastewater from the fish canning sector, as well as the optimization of the separation processes needed. In the wastewater valorization process, acetic, propanoic, and butyric acids are produced in higher quantities, which makes them the target compounds to isolate.

Seven volatile fatty acids were used in all of this work: acetic, propanoic, butyric, isobutyric, valeric, isovaleric, and hexanoic acids.

#### Part 1 – Permeation process

Pure water permeation was analyzed in 5 different nanofiltration and reverse osmosis membranes (nanofiltration DK and MPF-34 membranes, and reverse osmosis RO90, RO98pHt, and SE membranes). Fig. 1 displays pure water permeate flux as a function of pressure difference. From those results, water permeance was determined for each membrane, obtaining 12.32, 7.10, 4.47, 2.86, and 1.47 L.m<sup>-2</sup>.h<sup>-1</sup>.bar<sup>-1</sup> for DK, RO90, RO98pHt, MPF-34 and SE membranes, respectively.

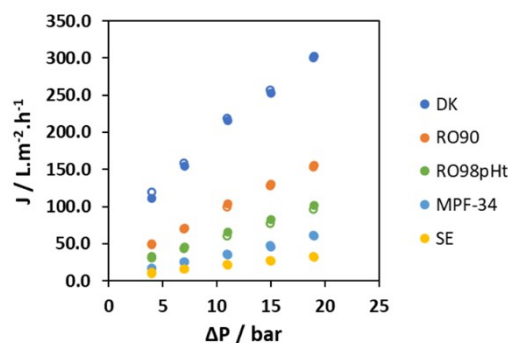
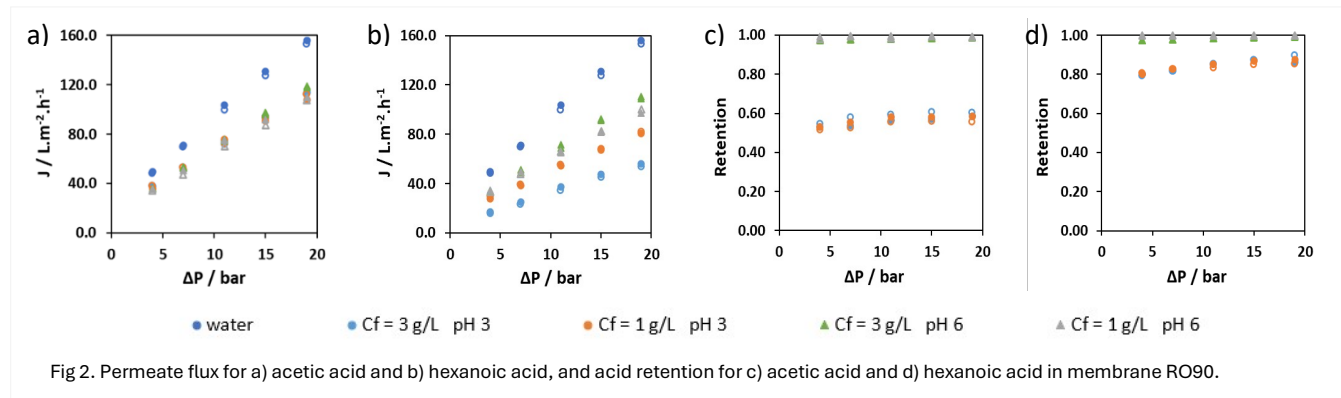


Fig 1. Pure water permeate flux in function of the transmembrane pressure for the 5 membranes tested.

DK, RO90 and SE membranes were selected to study VFAs permeation. A series of experimental tests with single-component solutions were performed to evaluate the pressure, feed concentration, and pH effect on the permeate flux and acids retention. Experimental results for acetic and hexanoic acids in the RO90 membrane are presented in Fig. 2, as an example of the results obtained.

The results obtained indicated an insignificant effect of feed concentration and pH in the permeate flux. Increasing pressure applied in the system, the permeate flux also increased since solvent flux is directly proportional to the transmembrane pressure. A decrease in the permeate flux with an increase acid aliphatic chain was also observed. As for the acid retention tendencies, it was concluded that feed concentration did not affect considerably the retention. An increased retention of VFAs was noticed for higher pH, due to the change of the membrane surface charge and the degree of ionization of the acid, creating repulsion, and also for higher applied pressure since it increases water permeation and reduces acid concentration in the permeate side. Acids retention also increases with increasing of the acids' alkaline chain (smaller acids permeate more easily through the membrane).



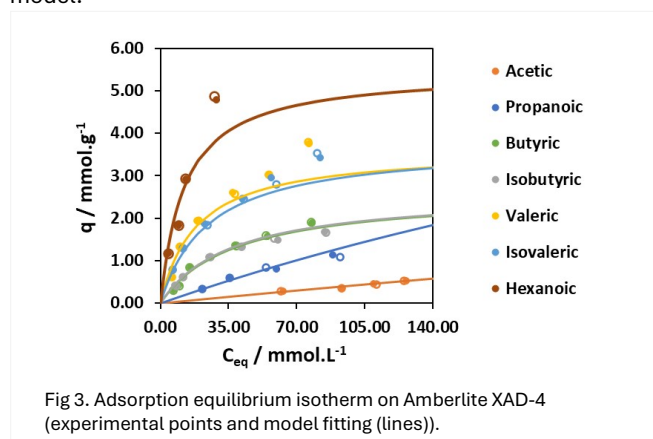


Finally, a comparative analysis was made of the separation performance of nanofiltration and reverse osmosis membranes. In the nanofiltration membrane (DK), low retentions (between 30-50% for pH 6 and zero for pH 3) and high permeate fluxes (reaching around 270 L.m<sup>2</sup>.h<sup>-1</sup> for 20 bar) were obtained, which is in agreement with nanofiltration membranes characteristics – pores size lose and bigger than the VFAs that allow components to passage easily through the membrane and not be retained in the feed side. Donnan effect was the only transfer mechanism that promoted some retention in the nanofiltration membranes. Reverse osmosis membranes are practically dense/homogeneous membranes, making the solution permeation more difficult, which decreases the permeate flux and increases acid retention in comparison to the nanofiltration membranes.

From the results acquired, RO90 membrane showed a better potential for concentrating and/or separating the VFAs due to the high permeate flux and acids retention that can achieved.

#### Part 2 – Adsorption process

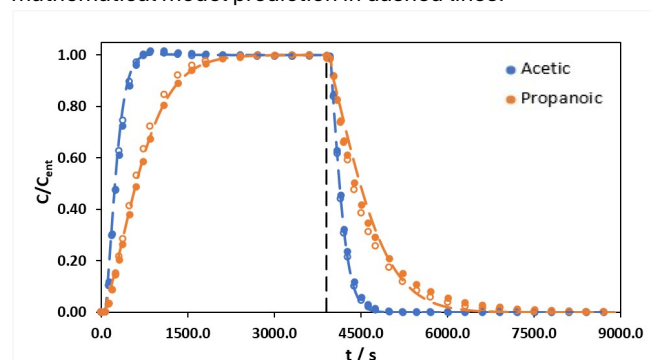
The adsorption equilibrium on four different adsorbents (Amberlite XAD-4, Amberlyst A21, Amberlite IRA-67 and Dowex Marathon MSA) was studied in batch mode, at room temperature. Fig. 3 shows the adsorption equilibrium for all the acids in the Amberlite XAD-4 resin, which was the adsorbent that displayed more potential to separate the volatile fatty acids since the adsorption capacity is different for each acid. The experimental points were fitted by the single-site Langmuir model.



Moreover, adsorption kinetics was also analysed for the seven VFAs in study and on the four adsorbents, at batch mode and room temperature. Linear driving force (LDF) model was adjusted to the experimental results, to determine the mass transfer coefficient in the adsorbent particle, exhibiting an order of magnitude of 10<sup>-3</sup> s<sup>-1</sup>.

Then, fixed-bed experiments were performed with the Amberlite XAD-4 adsorbent. Single-component breakthrough curves were obtained for all the acids. Binary-component breakthrough curves were also acquired, for the following

binary solutions: acetic acid with all the other acids, propanoic acid with all the other acids, butyric and isobutyric acids, and valeric and isovaleric acids. Finally, a breakthrough curve using a mixture with all the 7 VFAs in study (acetic, propanoic, butyric, isobutyric, valeric, isovaleric and hexanoic acids) was as well determined. Stoichiometry time and adsorption capacity were calculated for every case and the values were compared with the data given by the adsorption isotherms, being in agreement with each other. A mathematical model composed of the mass balance to the column, LDF model, and isotherm model was applied to predict the experimental results, which achieved the goal. Fig. 4 presents the binary breakthrough curve of acetic and propanoic acids with the mathematical model prediction in dashed lines.



#### Future Perspectives

Volatile fatty acids permeation will continue to be studied with multicomponent solutions and mathematical models will be implemented to determine permeation parameters, such as mass transfer coefficients and permeances, and predict experimental results. A continuous permeation system will be designed and optimized to achieve the separation of the acids.

In the VFAs adsorption, a Simulated Moving Bed will be simulated, and operating conditions will be defined to apply in the pilot unit of the laboratory (FlexSMB) and separate the acids. A final goal is to achieve an integrated process with VFA concentration with a membrane unit followed by a separation process by SMB.

#### Related Sustainable Development Goals



#### Outputs

##### PhD Theses

[1] Cristiana Andreia Vieira Gomes, Valorization and treatment of wastewater from the canning industry, PDEQB, FEUP, ongoing.

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