
Adsorption properties and process performances relationship: Application to the screening of adsorbents for xylene isomers separation

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ABSTRACT

This work aims to study the adsorption behavior of different adsorbents prepared experimentally in the *para*-xylene separation process under conditions representative of the industrial process to provide insight into the performances of these materials when they are implemented in the process.

For a first analysis of these solids, it is performed a classification based on their experimental selectivities values, which allows to observe, among other things, the affinity of the adsorbents for the different isomers and the corresponding adsorption strength of the desorbent.

Critical selectivities of the *para*-selective adsorbents in two points of the process are then analyzed and compared to those obtained for a reference adsorbent to verify which solids present the highest potential to be implemented industrially. A first prediction of the process performances obtained with the use of these solids is obtained through a theoretical approach based only on thermodynamic considerations.

Simulations are performed for the tested adsorbents with the most appealing thermodynamic characteristics and also for an industrial solid with the use of two simplified thermodynamic models in order to calculate the process performances obtained for these adsorbents. It was found that the use of the tested adsorbents FAU 1 and FAU 2 result in better performances than those obtained currently in the industrial process. Thus, both solids appear to be good candidates to replace the industrial adsorbent used nowadays, being FAU 1 the solid which results in the most satisfying values of productivity and desorbent consumption.

Keywords: *para*-xylene; adsorption; Faujasite; Simulated Moving Bed; Optimization

1. Introduction

The demand of mixed xylenes, the second most important aromatic products in terms of world consumption (1), has suffered a significant growth over the years due to the constant increase of *para*-xylene consumption, result of the expansion in the polyethylene terephthalate (PET) market, driven by the demand in polyesters fibers and by the increasing application in carbonated soft drinks (CDS) packaging as well as rising consumption of packaged, frozen and other processed foods.

The sources used for xylene production (catalytic reformat, pyrolysis gasoline and toluene disproportionation/transalkylation) contain a mixture where *para*-xylene is found along with the remaining isomers and ethylbenzene, making it necessary to purify this compound through a separation process (2). Due to the proximity of boiling points of these aromatic compounds, it is not possible to separate them by conven-

tional distillation. As such, three different methods to separate *para*-xylene from the remaining compounds are used industrially: Crystallization, adsorption and a hybrid crystallization/adsorption process (3).

Since commercialized, the adsorption process of Simulated Moving Bed (SMB) chromatography became the world's most used technology for *para*-xylene recovery (4). The SMB is a continuous countercurrent process which exploits the differences in affinity of a molecular sieve for the different xylenes. The countercurrent flow of solid and liquid phases is simulated by the periodic shifting of the inlet and outlet streams. In this process, the adsorbents used are usually Faujasite X or Y type containing exchangeable cations, which give specific adsorption properties to the material (5).

The adsorption sites of both water and xylene molecules in these zeolites are mainly located near the exchanged cations that are normally localized in three types of sites, identified in Figure 1(5). Site *I* is situated at the center of the hexagonal prism, site *I'* located in the

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sodalite cage in front of the six-ring window connected to the hexagonal prism and site II is found in the supercage in front of the six-ring connected to the sodalite cage.

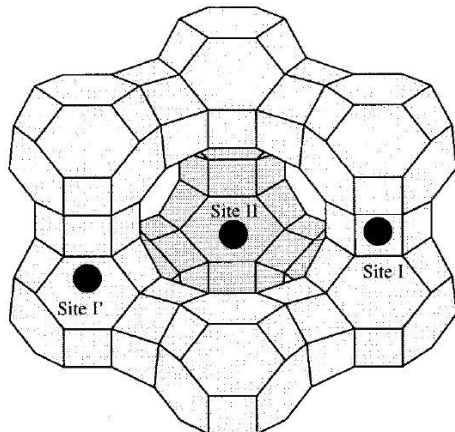


Figure 1 - Structure and cationic sites of the faujasite zeolites (5)

It was found that the adsorption sites for *para* and *meta*-xylene are located in site II, near to the Barium cation. Regarding *para*-xylene, it was also found an extra, less favorable non-cationic adsorption site, located in the plane of the 12-ring window (5).

The TMB process is a limiting case of a SMB process with an infinite number of columns and an infinitely small switching time of the inlet and outlet ports. Thus, the principle of Simulated Moving Bed operation can be described by reference to the equivalent True Moving Bed unit (6). In the TMB unit (Figure 2), two inlet (feed and desorbent) and two outlet (extract and raffinate) ports are fixed along the bed, dividing the process in four distinct zones.

For a more understandable explanation of the process, it is considered that the feed injected in the process is a mixture with two components: **A** (which corresponds to *para*-xylene) and **B** (which corresponds to the remaining isomers). Therefore, **A** is the more strongly adsorbed component while **B** is the one with lowest affinity for the adsorbent. The desorbent (**D**) used is a component that can displace the feed components from the adsorbent and the opposite also happens depending on the liquid and solid flow rates on a certain zone (7). The extract outlet, located between zones 1 and 2, contains the more adsorbed component (**A**) mixed with desorbent while the raffinate outlet, located between zones 3 and 4, contains the less adsorbed component **B** mixed with desorbent. The different inlets and outlets fixed along the bed divide the unit in four zones in which distinct adsorption-desorption phenomena occur.

The function of zone 1, situated between the desorbent and extract ports, is to desorb component **A** to ensure that it leaves the process through the extract outlet. In this zone, the desorbent is highly concentrated in order to guarantee the desorption of **A**. For the occurrence of this desorption phenomena, it is necessary to have a low A/D selectivity. In zone 2, situated between the extract and the feed ports, it is necessary to ensure that the component with lower affinity, **B**, does not reach the

extract node and contaminate this outlet (7). Thus, the objective in this zone is to guarantee the desorption of **B** from the adsorbent and that the component **A** is adsorbed and carried out with the solid phase. As such, it is necessary to have a high A/B selectivity in this zone to ensure that **B** is gradually displaced from the adsorbent and replaced by **A**. The purpose of Zone 3, situated between the feed and raffinate ports, is to prevent that component **A** does not reach the end of this section and contaminates the raffinate outlet. It is then necessary to guarantee that this component is adsorbed from the liquid phase (7). Since the solid phase coming from zone 4 carries only **B**, it is necessary to have high A/B and A/D selectivities in zone 3 to ensure that **B** is gradually displaced from the adsorbent and replaced only by **A**. In zone 4, situated between the raffinate and the desorbent ports, it is necessary to ensure the regeneration of the desorbent, ensuring that the liquid that reaches the end of this zone has only **D** and can be recycled to zone 1 as pure desorbent (7). For this purpose, it is necessary to have a high B/D selectivity in this zone in order to ensure that **B** is adsorbed in the solid phase to be sent to the raffinate port.

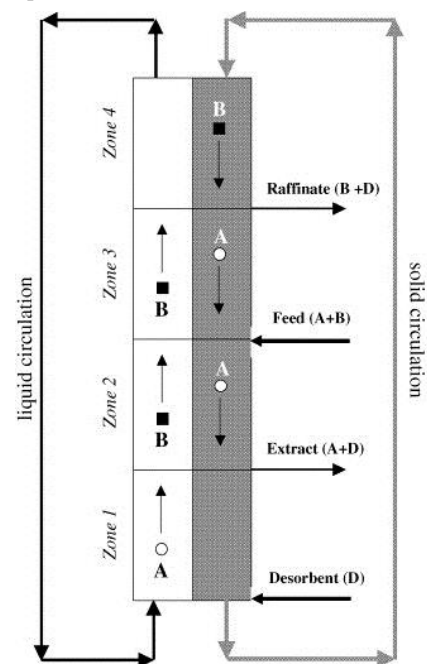


Figure 2 - Schematic diagram of the Simulated Moving Bed (SMB) unit (7)

Difficulties in ensuring homogeneous motion of the solid phase, mechanical erosion of the adsorbent and back-mixing made impossible to implement the True Moving Bed Process commercially (7). These problems have been overcome by the Simulated Moving Bed technology. In a SMB unit, the adsorbent is found in a finite number of interconnected conventional fixed bed chromatographic columns (7). The countercurrent movement of the solid phase is simulated through switching the inlet and outlet ports one column forward in the direction of the fluid flow at constant time intervals.

The modeling of a SMB unit for *para*-xylene separation from mixed xylenes can be made through the True Moving Bed (TMB) and the Simulated Moving Bed (SMB) approaches (7). The main difference between them is that the stationary regime of the SMB is a cyclic steady state, in which in each zone there is an identical transient during the switching period (7). This cyclic state is reached after several cycles, however, the system state continues to vary over the time due to the periodic movement of the inlet and outlet ports along the columns.

In a previous work by Minceva and Rodrigues, it was confirmed that the performance of an industrial scale SMB units with 24 columns for *para*-xylene separation could be reasonably predicted with the equivalent True Moving Bed modeling strategy (7). As such, it is preferable to use this model instead of the SMB approach due to the different level of difficulty involved in the solution of the two models and the required computation time (8). Also, a True Moving Bed unit operates in steady state and so its stationary behavior can be described by a set of ordinary differential and algebraic equations.

The mathematical model created for the simulation of an equivalent TMB system takes into account axial dispersion flow for the liquid phase, plug flow for the solid phase and linear driving force (LDF) for the intraparticle mass transfer rate (8). The multicomponent adsorption equilibrium is described through the Langmuir Isotherm.

Performances parameters

The modeling and optimization of a Simulated Moving Bed unit for the *para*-xylene separation process is evaluated by the performances parameters obtained, which can be divided in two different categories, the separation and process performance parameters. *Para*-xylene, as the more strongly adsorbed component, is recovered in the extract outlet while the remaining components are recovered in the raffinate. Therefore, the only product stream of interest that has to satisfy the separation specifications is the extract outlet (9). As such, it is necessary to guarantee that this stream respects the constraints defined for the two separation parameters, the purity and recovery of *para*-xylene.

The purity of *para*-xylene is defined by the demand of this compound in the market (8). This performance parameter is expressed through the ratio between the concentration of *para*-xylene and the sum of the concentration of all xylenes in the extract outlet.

$$P_E (\%) = \frac{c_{PX,E}}{(c_{PX,E} + c_{MX,E} + c_{OX,E} + c_{EB,E})} \quad (1)$$

The *para*-xylene recovery is defined as the amount of this desired compound obtained in the extract stream relative to the injected in the feed inlet:

$$R_E (\%) = \frac{c_{PX,E} Q_E}{c_{PX,F} Q_F} \quad (2)$$

Being the flow rates in the feed injection and in the extract withdrawal points calculated through the mass balances on the connecting nodes of zones 1, 2 and 3:

$$Q_F = Q_3 - Q_2 \quad (3)$$

$$Q_E = Q_2 - Q_1 \quad (4)$$

Once the separation parameters are determined, the choice of the specific optimal operating conditions can be performed on the basis of economic considerations (9). For the evaluation of this process two performance parameters are used: Productivity of the process and desorbent consumption.

The productivity of the process, the most important economic parameter of the process, is defined through the following equation:

$$PR = \frac{c_{T,F} Q_F}{(1-\varepsilon) \rho_s V_T} \quad (5)$$

The desorbent consumption is expressed through the ratio between the desorbent and the xylenes inlet flow rates, calculated through the following expression:

$$\frac{S}{F} = \frac{Q_D}{Q_F} \quad (6)$$

The flow rate in the desorbent injection point is calculated through the mass balance on the connecting node between zones 1 and 4:

$$Q_D = Q_1 - Q_4 \quad (7)$$

2. Experimental section

The aim of this work is to evaluate the thermodynamic performances of new adsorbents in the *para*-xylene separation process through the Simulated Moving Bed technology. For this purpose, different Faujasite adsorbents were created and tested on a laboratory scale in IFPEn by coworkers. The experimental work made is divided into two parts, the adsorbents preparation and the thermodynamic parameters measurement.

Adsorbents preparation (Design and making)

The preparation of ion-exchanged adsorbents is made by percolation, where a salt solution containing the desired cation(s) is injected in a packed column filled with a zeolite previously hydrated. Zeolites NaX and NaY with spherical shape are used as the original solids in this experimental work.

The process of cations exchange takes places in five different steps:

- Hydration of the solid;
- Cation exchange;
- Washing of the columns;
- Drying of the adsorbent;

Thermodynamic parameters measurement

After the preparation of the different adsorbents, it is necessary to measure their thermodynamic parameters in mixtures with similar compositions to the ones of critical points of the SMB column in order to characterize and evaluate the adsorbents regarding the thermodynamic performances. These tests are performed under the operating conditions of temperature and pressure of the industrial process.

These experimental tests are made for two set of mixtures. While the first set, containing three different mixtures is tested for all the adsorbents created, the second set is tested only for the two adsorbents that demonstrated the greatest potential for implementation at industrial level. Both tests are performed similarly but in different units with slight modifications.

The mixtures used for the experimental tests contain the xylene isomers to separate, the industrial desorbent (PDEB) and a tracer compound which is not adsorbed in the micropores of the adsorbent in the presence of aromatics. Since PDEB is present in the mixtures tested with the objective of measuring the selectivities between the xylenes and the industrial desorbent, it is chosen to use toluene as the desorbent in this experimental work.

The methods used for the measurement of the thermodynamic parameters are different for both sets of mixtures. For the first set, it is calculated from a breakthrough curve obtained through a Raman online analysis and from simplified reverse breakthrough, while for second set of mixture it are obtained by simplified breakthrough and reverse breakthrough.

3. Adsorbents classification

Of the adsorbents prepared, only the ones that presented characteristics of interest for the *para*-xylene separation process are of interest to study in detail. As such, it is created a classification of the adsorbents using different criteria in order to evaluate the interest of the solids. This classification is based on the nomenclature adapted by Mazzoti et al. (10) which considers that in a countercurrent adsorption process, the mixtures can be divided in two different groups, the components which are collected in the extract outlet and the ones found in the raffinate. Regarding the isomers separation, it is pretended to separate the four aromatic compounds and the desorbent, obtaining only the isomer with highest affinity for the adsorbent in the extract outlet and the remaining in the raffinate. Therefore, in this particular process, the first group is only constituted by one component, titled as the strong key (*sk*), whereas the second group is constituted by three compounds, the weak key (*wk*) a weak (*ww+I*) and the weakest (*ww*) components.

To perform this classification, it is created a *macro* in the software *Visual Basic for Application* (VBA) that defined, for each adsorbent, which xylene corresponded to *sk*, *wk*, *ww+I* and *ww* components in a chosen mixture used in the thermodynamic parameters measurement. This association is obtained through the use of the

selectivities between the xylenes and the desorbent with the objective of obtaining for each the adsorbent the following sequence:

$$\alpha_{sk/D} > \alpha_{wk/D} > \alpha_{ww+1/D} > \alpha_{ww/D} \quad (8)$$

In the adsorbent classification, each xylene is assigned to a specific number (PX-1; EB-2; MX-3 and OX-4), which allowed to obtain, using the same *macro*, a simple four number classification for each solid considering a certain mixture.

Limit flow rate approach

The adsorbents performances are obtained through the use of a *FORTRAN* simulator which requires significant calculations time. As such, before running the simulations, it is applied a simplified theoretical approach titled as Limit Flow Rate Approach (created previously in IFPEn) that allows the study of the thermodynamic impact in the process and a first guess of the process performances.

In this approach, the chosen variables that describe in the different zones, the behavior of the process, are titled as reduced flow rate and are expressed as a ratio between the liquid and the adsorbed phases flow rates. The limits of these flow rates in each zone are determined based solely on thermodynamic considerations that are dependent on the feed composition, geometric characteristics (porosity) and physico-chemical properties (capacity, selectivities) of the adsorbent. The expressions used for the calculation of these flow rates are based on inequations imposed in each zone of the process to guarantee that the compounds move in the pretended directions.

Simulation

The process performances of a given adsorbent in the *para*-xylene separation process are obtained through the use of a *FORTRAN* simulator created previously in IFPEn. The simulations can be performed with different modeling approaches such as the Simulated Moving Bed and the True Moving Bed. For this work, all the simulations were performed using the last approach, in an Intel(R) Core (CPU 2,83 GHz, 4 GB RAM).

In order to perform the simulations of the different adsorbents in this work, it is necessary to first define certain parameters related to the Simulated Moving Bed process and to the adsorbent. The operating and geometrics parameters of the SMB unit are chosen in order to obtain similar conditions to those observed at the industrial level, with only the number of beds reduced from the typical used twenty four to fifteen so as to reduce the computation time of the simulations.

Optimization of the simulated moving bed

The optimization of a Simulated Moving Bed unit considers the selection of the operating conditions and/or the geometric parameters that minimize/maximize a given objective function(s) (8).

The optimization procedure used in the present work is based on the two-level optimization process created by Minceva and Rodrigues (8), with the objective of maximizing the productivity of the process and minimizing the desorbent consumption with imposed constraints of *para*-xylene yield (97,0%) and purity (99,8%) in the extract outlet. The procedure comprises two consecutive levels, being that in each it is considered a single objective function of a process performance parameter. In the first level, the productivity of the process is maximized for given flow rates in zones **1** and **4** and in the second level it is calculated the minimum desorbent consumption needed to achieve this productivity (8). The global solution of the optimization process results in the optimal operating conditions (flow rates in the four zones of the SMB unit) required to achieve the maximum productivity with a corresponding minimum desorbent requirement for the imposed purity and recovery constraints.

In the first level of optimization, productivity of the SMB unit is defined as the objective function to be maximized. The objective is to find the values of the flow rates in zones **2** and **3** that result in the maximum productivity, which implies at the same time maximum feed flow rate. The optimization procedure starts by fixing the values of flow rates in zones **1** and **4**. The flow rate of zone **2** is then decreased along with the increase of the flow rate in zone **3**, the productivity is at the maximum value when the constraints reach the imposed values.

In the second level of optimization, the objective function, desorbent consumption, is minimized for a given feed flow rate. The optimization procedure starts by fixing the value of flow rate in zone **1** and increasing the flow rate in zone **4** until the separation requirements begin to be violated, this result in the decrease of desorbent consumption without affecting the productivity. After the optimized flow rate of zone **4** is found, this variable is fixed and the flow rate in zone **1** is decreased. The second level of optimization is stopped externally by the user when defined the constraints cease to display the imposed values. The global solution of the

optimization procedure that provides maximum SMB unit productivity with a minimum possible desorbent consumption is then achieved.

The flow sheet of the optimization procedure used is shown in Figure 3.

4. Results and discussion

In order to evaluate the possibility of implementing new adsorbents in the *para*-xylene separation process at industrial level, experimental thermodynamic parameters measurement are performed for a total of 60 ion exchange faujasite-type zeolite adsorbents.

It is chosen to perform these tests for three mixtures with different compositions. The first mixture, titled as desorbent point, is representative of zones **1** and **4** of the SMB unit, where the liquid phase is mainly composed of *para*-diethylbenzene, a second one with a similar composition of a typical feed injection point and a third one with a quaternary concentration of the mixed xylenes without the presence of *para*-diethylbenzene.

Classification of adsorbents

Since it is not of interest to study in detail all of the adsorbents tested experimentally, it is use a classification using different criteria to verify which are of interest to study. The numerical classification of the adsorbents is made for the feed injection point due to its importance for the proper functioning of the process, being necessary to ensure that only the *sk* component is adsorbed in preference to the remaining xylenes and is consequently driven towards the extract outlet by the solid phase, while the remaining components are transported to the raffinate outlet by the liquid phase.

In the feed injection point, it is important to ensure that *sk/wk* selectivity is the highest possible to guarantee a proper separation between the components with higher affinity for the solid, while the desorbent point is used to assess the separation performances in zones **1** and **4** of the process. As such, regarding zone **1**, it is necessary to ensure a *sk/D* selectivity as low as possible. Considering

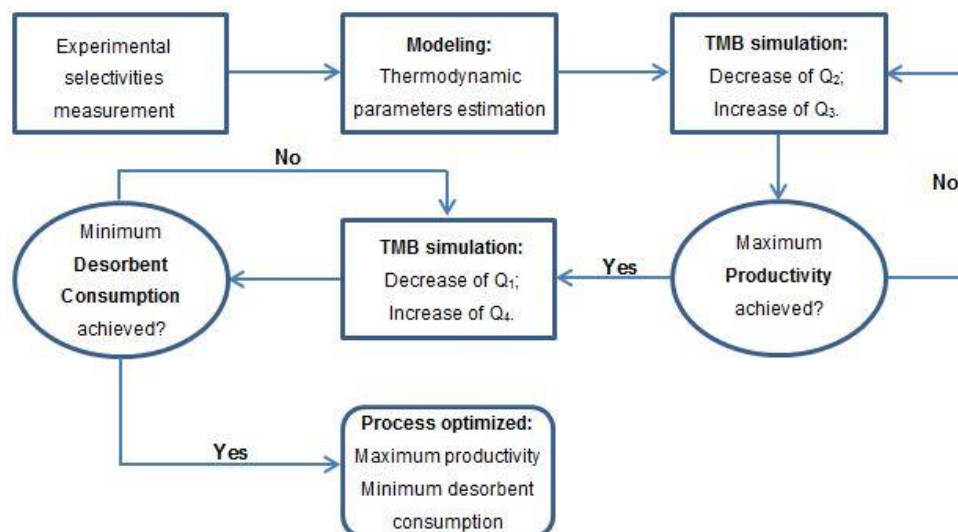


Figure 3 - Flow sheet of the optimization procedure

zone 4, it is necessary to ensure a *ww/D* selectivity as high as possible.

After the calculation of the numerical classification in the feed injection point and the analysis of the selectivities in the two different mixtures, the classification of the different adsorbents is made. It is possible to conclude that, of the 60 adsorbents tested experimentally, 38 are *para*-selective, 9 *ethylbenzene*-selective, 5 *meta*-selective and 8-*ortho* selective. It is also observed that there were nine *para*-selective adsorbents with a numerical classification identical to the obtained industrially, 1234.

Para-xylene selective adsorbents

The utilization of an adsorbent for the *para*-xylene separation process at industrial level requires that the solid display certain thermodynamic parameters at different points in the SMB column. Experimentally, the two mixtures representative of the four zones of the SMB unit are the desorbent point (representative of zones 1 and 4) and the feed injection (representative of zones 2 and 3). To verify which of these *para*-selective adsorbents should be studied in further detail, it is necessary to compare their thermodynamic parameters with the ones of an adsorbent used industrially (titled as Faujasite 4) in the mixtures mentioned above.

To guarantee the proper performance of the process, it is necessary to ensure the separation between *para*-xylene and the remaining isomers in the feed injection point (mixture 2). To this end, it is necessary that the adsorbents had, in this point of the process, high PX/EB and PX/MOX selectivities to guarantee that *para*-xylene is the only isomer adsorbed in these zones. It is then possible to state, in a first instance that, of the adsorbents tested, those who presents PX/EB and PX/MOX selectivities higher than the reference adsorbent (FAU 4) are of interest to study in greater detail.

In order to analyze these thermodynamic parameters, the selectivities between the xylene isomers in the feed injection point obtained for the *para*-selective adsorbents are plotted in the figure shown below.

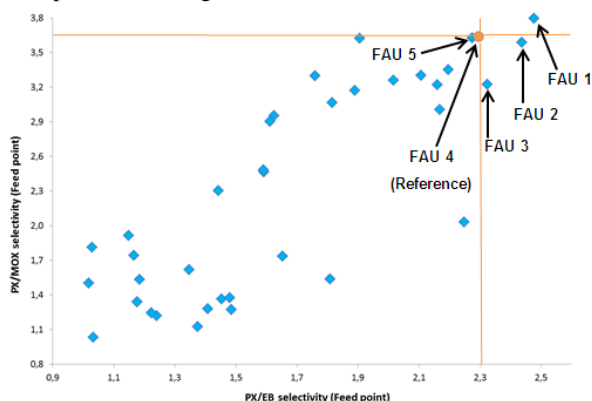


Figure 4 - Selectivities between the xylene isomers in the feed injection point obtained for the *para*-selective adsorbents

It is possible to verify that only one of the adsorbents studied, FAU 1, presents PX/EB and a PX/MOX

selectivities higher than the reference adsorbent (FAU 4). However, since the selectivity between isomers that has greater impact on the xylene separation in this zone of the process is the PX/EB, FAU 2 and FAU 3, despite having a PX/MOX selectivity lower than the one of the reference, appeared to have appealing characteristics regarding the productivity of the process. Since FAU 5 presented similar selectivities values to FAU 4, it is also chosen to analyze the remaining thermodynamics characteristics of this adsorbent. No further study is conducted for the remaining *para*-selective adsorbents

Regarding this point of the process, it is also necessary to ensure that *para*-xylene is adsorbed in detriment of *para*-diethylbenzene. As such, it is necessary that the adsorbents tested exhibit also a high PX/PDEB selectivity.

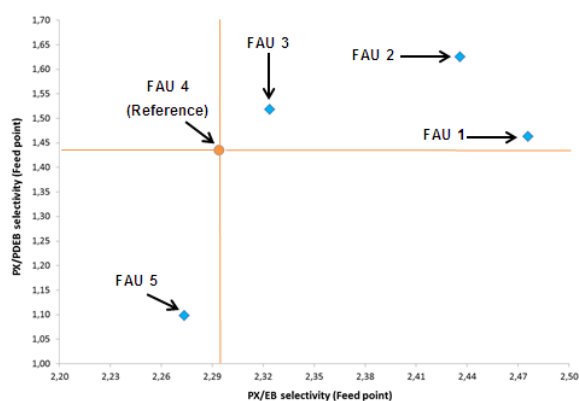


Figure 5 - PX/PDEB and PX/EB selectivities obtained for interesting *para*-selective adsorbents in the feed injection point

As it is possible to observe in Figure 5, three adsorbents exhibit higher PX/PDEB and PX/EB selectivities than the reference Faujasite: FAU 1, FAU 2 and FAU 3. Regarding the thermodynamic parameters in the feed injection point, it appears that FAU 1 is the best candidate of the adsorbents studied. However, it is also considered that the utilization of FAU 2 and FAU 3 would result in a gain of productivity since only the PX/MOX selectivity is lower than the obtained for the reference adsorbent. The use of FAU 5 is discarded once the values for all its critical selectivities are lower than those obtained with FAU 4.

It is still necessary to analyze the critical thermodynamic parameters of these adsorbents in the desorbent point, mixture used for studying the behavior of the solids regarding zones 1 and 4 of the process. To guarantee that *para*-xylene in zone 1 is desorbed from the solid, it is necessary that the adsorbent exhibit a low PX/PDEB selectivity in this mixture. Regarding zone 4, it is necessary to ensure that the components with lowest affinity are adsorbed in the solid. As such, it is necessary that the adsorbents tested also exhibit a high MOX/PDEB selectivity in the desorbent mixture.

It is then possible to affirm that the adsorbents that present higher MOX/PDEB and lower PX/PDEB selectivities than the reference would provide a gain in desorbent consumption.

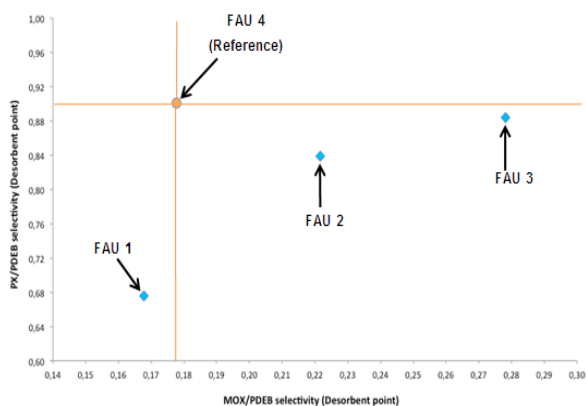


Figure 6 - PX/PDEB and MOX/PDEB selectivities obtained for the more interesting *para*-selective adsorbents in the desorbent point

It is possible to observe in Figure 6 that the three adsorbents exhibit PX/PDEB selectivities in the desorbent point lower than the reference solid, which indicates that their utilization would result in gain of desorbent consumption regarding zone 1. Considering the adsorption phenomena that occur in zone 4, it is possible to observe that FAU 2 and FAU 3 present higher MOX/PDEB selectivities than FAU 4, which consequently results in the pretended adsorption of the weakest components in this zone. However, the selectivity obtained for FAU 1 is lower than the one of FAU 4, meaning that regarding this zone, the use of this adsorbent would not result in a gain of desorbent consumption.

Selection of adsorbents for further study: Two parameter selectivity model

With regard to the industrial implementation of an adsorbent, it is necessary that its thermodynamic characteristics translate into a satisfactory process performance, otherwise there is no interest in its implementation. As such, to evaluate in a first instance the performances obtained for the different adsorbents, it is applied the Limit Flow Rate Approach. This theoretical approach allows the prediction of the feed and desorbent flow rates of the process, indicators of productivity and desorbent consumption.

Having only three mixtures tested experimentally, it is not possible to build a very complex and precise selectivity model. As such, it is opted to build a simplified model with two parameters, titled as **2P2M** model, where it is considered that the variation of the xylenes selectivities are dependent only of the PDEB composition along the column, as it is possible to observe through the following equation:

$$\alpha_{i/PDEB} = a_i x_{PDEB} + b_i \quad (9)$$

In order to build this model, it is applied a linear regression to the PX/PDEB, EB/PDEB and MOX/PDEB selectivities in function of *para*-diethylbenzene composition in the desorbent and feed injection mixtures. Although it is recognized the importance of the quaternary mixture in assessing the behavior of the isomers selectivities, it is decided to consider only these

two mixtures for the model constructed so as to have the lowest associated error for the selectivities near these two critical points of the process.

After the construction of this model, it is applied the Limit Flow rate Approach in order to obtain Ω_F (indicator of productivity) and Ω_D / Ω_F (indicator of desorbent consumption) parameters for the three appealing adsorbents (FAU 1, FAU 2 and FAU 3) and the reference solid (FAU 4).

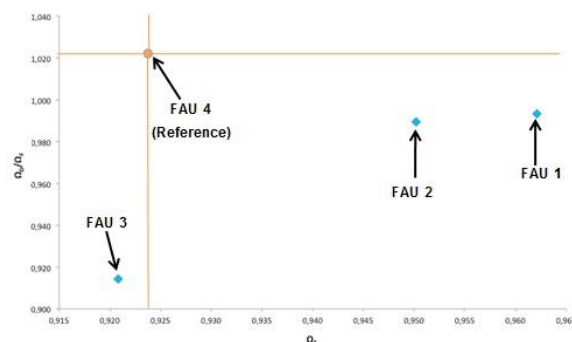


Figure 7 - Ω_F and Ω_D/Ω_F parameters obtained for appealing *para*-selective adsorbents

Figure 7 shows that, of the three appealing adsorbents, only FAU 1 and FAU 2 present more attractive values of Ω_F and Ω_D/Ω_F than the reference solid, while FAU 3, despite having the lowest desorbent consumption, presents a lower productivity than FAU 4. In this figure it is also possible to observe that, of the adsorbents studied, FAU 1 is the one that presents higher productivity, and since the desorbent consumption obtained for this solid and for FAU 2 are similar, it is concluded that, in a first analysis with a theoretical approach, FAU 1 is, of all adsorbents studied, the one that presents the most appealing characteristics. It is then decided to carry out a more detailed study on the two solids with more satisfying process performances, FAU 1 and FAU 2.

Four parameter selectivity model

For the more detailed study of FAU 1 and FAU 2, it is decided to conduct further experimental tests on these adsorbents with an additional set of mixtures, which consist of four points that correspond to typical compositions of the feed injection (mixture **A**), extract withdrawal (mixture **B**), raffinate withdrawal (mixture **C**) and a mixture with equal composition of all the isomers and *para*-diethylbenzene.

Since the **2P2M** model is built through a linear regression between only two points of the process and considers that the behavior of the xylenes selectivities is only described by the variation of the composition of only one component (PDEB), it may present significant errors in the description of the thermodynamic parameters of a such complex process. As such, it is built a four parameters model, titled as **4P4M**, to estimate the thermodynamic *para*, *meta/ortho*-xylene and ethylbenzene parameters of the xylene isomers through the use of the selectivities obtained for the new set of mixtures. This model considers that the behavior of the

xylene selectivities is described by the compositions of through the following expression:

$$\alpha_{i/PDEB} = a_i + b_i x_{PX} + c_i x_{EB} + d_i x_{MOX} \quad (10)$$

This thermodynamic model is built with the use of the least square method.

FAU 0

The study concerning the potential of FAU 1 and FAU 2 for the *para*-xylene separation process is done through the comparison between the performances obtained upon the utilization of these adsorbents with the ones of the adsorbent currently used industrially, titled as FAU 0. The performance parameters are obtained through a simulator based on FORTRAN that was developed in *IFPE*n which requires the thermodynamic parameters of the used adsorbent as input.

In order to perform this comparison, it is necessary to obtain firstly the thermodynamics parameters of the 2P2M and 4P4M thermodynamic models for the industrial solid, FAU 0.

It is not performed experimental measures of the thermodynamic parameters of FAU 0 for the set of mixtures used in the 2P2M and 4P4M models. Instead, it is used a complete thermodynamic model, titled as Full model (FM), already built in *IFPE*n for this adsorbent, based on a large number of selectivity measurements obtained for different compositions representative of a profile obtained on a pilot plant. This model, described by a quadratic correlation, allows the calculation of the xylene isomers selectivity along the SMB column without associated errors. Through the use of this quadratic correlation, the selectivities concerning the six mixtures used to build the models 2P2M and 4P4M are calculated for FAU 0. Through these values it is then possible to obtain the thermodynamic parameters of these models for FAU 0.

Simulations of FAU 0: Validation of the simplified models

Before running simulations on the adsorbents tested experimentally with the simplified models, it is first necessary to conduct a set of simulations with the reference solid (FAU 0) to assess the validation of these models.

The simulation performed with the solid FAU 0 using the FM model is defined as the reference case. In order to initialize this simulation, it is necessary to have an initial estimation of the four process zones flow rates. As such, the reduced flow rates obtained through the Limit Flow Rate approach for FAU 0 using the FM model are used as initial design variables after being converted into volumetric flow rates.

In the case of simulations performed for the models 2P2M and 4P4M for the same solid, it is used the flow rates obtained with the optimized simulation of the reference case as a first guess for the design variables. The models validation is made by the comparison of the performances obtained for these models with the

reference case. In order to facilitate the understanding of the analysis, the values obtained for the feed and desorbent flow rates, parameters used for this comparison, are normalized with the values obtained with the reference simulation.

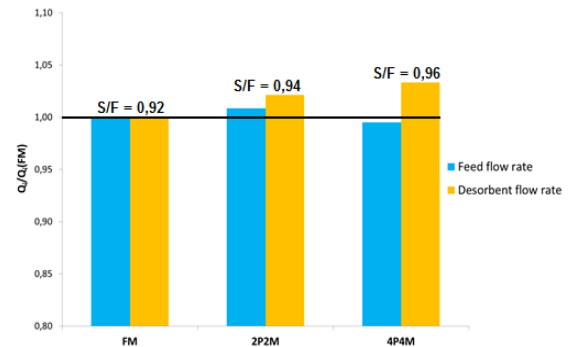


Figure 8 - Normalized feed and desorbent flow rates obtained for the optimized simulations of FAU 0 with the different models

As shown in Figure 8, the utilization of the 2P2M and 4P4M models for the solid FAU 0 result in similar performances to those obtained with the FM model. Considering the 2P2M thermodynamic model, it is obtained a feed flow rate 0,9% higher than the obtained with the FM model, which indicates that this model is slightly non-conservative in regard to the productivity. With the use of this model it is also obtained a desorbent flow rate 2,2% higher than the obtained for the reference case, indicating that this model is conservative in terms of desorbent consumption.

With the utilization of the 4P4M model it is obtained a feed flow rate 0,5% lower than the obtained for the reference simulation, which indicates that the model is slightly conservative in regard to the productivity of the process. It is also obtained a desorbent flow rate 3,3% higher than the value obtained with the FM model, which allows the conclusion that this model is also conservative in respect to the desorbent consumption.

Since the use of the 2P2M and 4P4M thermodynamic models result in similar process performances to those obtained for the reference case, it is not possible to identify which model result in more realistic performances. Therefore, it is opted to perform simulations of FAU 1 and FAU 2 with both thermodynamic models.

Performances of FAU 1 and FAU 2: 2P2M model

Firstly, Simulations for the solids FAU 1 and FAU 2 are performed with the use of the 2P2M thermodynamic model. The performances obtained for FAU 1 and FAU 2 are compared with those obtained for FAU 0, the reference adsorbent, since there is only an interest in these solids if their use results in superior performances to the obtained with the adsorbent currently used industrially. For this purpose, the feed and desorbent flow rates obtained for FAU 1 and FAU 2 are normalized with the values obtained for FAU 0.

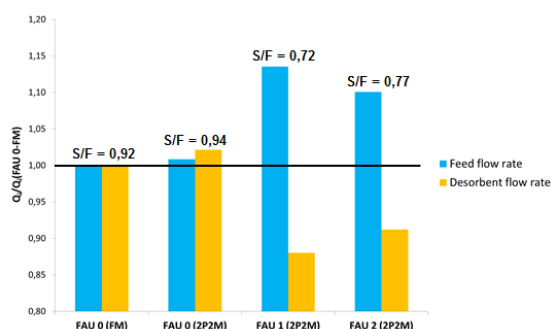


Figure 9 - Normalized feed and desorbent flow rates obtained for the optimized simulations of FAU 1 and FAU 2 with the 2P2M thermodynamic model

As shown in Figure 9, the simulations of FAU 1 and FAU 2 with the 2P2M model result in superior performances to those obtained with the reference adsorbent, FAU 0, which indicates that both solids are good candidates to replace the reference solid for the *para*-xylene separation process.

Considering FAU 1, it is obtained a feed flow rate 13,6% higher and a desorbent flow rate 12% lower than the obtained for the reference case. While the use of FAU 2 resulted in a feed flow rate 10,1% higher and a desorbent flow rate 8,8% lower than the values obtained with FAU 0. It is then possible to state that both solids exhibited superior performances than the obtained for industrial adsorbent and that between the two solids, FAU 1 is the one that shows a superior performance.

Performances of FAU 1 and FAU 2: 4P4M model

Lastly, simulations for the solids FAU 1 and FAU 2 are performed with the use of the 4P4M thermodynamic model in order to verify if the results obtained with the 2P2M model are reproducible. In order to compare performances obtained with FAU 1 and FAU 2 with the reference solid, the feed and desorbent flow rates obtained for FAU 1 and FAU 2 are normalized with the values obtained for FAU 0.

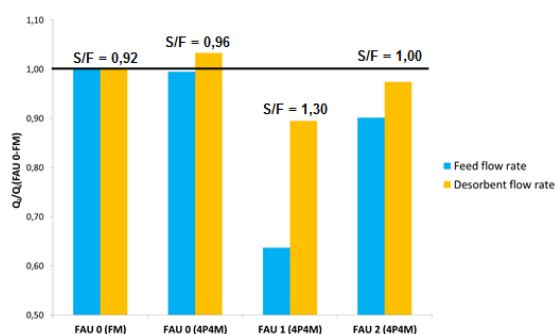


Figure 10 - Normalized feed and desorbent flow rates obtained for the optimized simulations of FAU 1 and FAU 2 with the 4P4M thermodynamic model

As shown in Figure 10, the simulations of FAU 1 and FAU 2 with the 4P4M model result in inferior performances to those obtained with the reference adsorbent, FAU 0, the opposite of what is indicated with the 2P2M model. Considering FAU 1, it is obtained feed and desorbent flow rates 36,3% and 10,5% lower than the

ones for the reference case. While the use of FAU 2 results in feed and desorbent flow rates 9,9% and 2,6% lower than the values obtained with FAU 0. It is possible to conclude that, despite showing lower desorbent flow rates than FAU 0, both adsorbents exhibit worse performances than the obtained for the industrial adsorbents.

Comparison between the results obtained with the simplified models

In order to evaluate the results obtained for the simulations performed for the three solids with different thermodynamics, the normalized feed and desorbent flow rates obtained for the different simulations are summarized in Table 1.

Table 1 - Summary of the normalized feed and desorbent flow rates obtained for the three adsorbents with different thermodynamic models

Adsorbent	Feed flow rate			Desorbent flow rate		
	FM	2P2M	4P4M	FM	2P2M	4P4M
FAU 0	1,00	1,01	1,00	1,00	1,02	1,03
FAU 1	-	1,14	0,64	-	0,88	0,89
FAU 2	-	1,10	0,90	-	0,91	0,97

Regarding the reference adsorbent, FAU 0, it is observed that the performances obtained with both simplified thermodynamic models are similar to the one obtained for the reference simulation, which indicates that the use of these models for the simulations of remaining adsorbents should result in similar performances. However, as it is observed in this table, the results obtained for the tested adsorbents with the two models are quite distinct, mainly in regard to the feed flow rate, where it is obtained a gain of productivity with the 2P2M model and a loss with the 4P4M. Concerning the desorbent flow rate, in spite of obtaining slightly different values, it is obtained for both models a gain of desorbent consumption. Therefore, it is concluded that the difference between the performances obtained is not due to the thermodynamic models but to the selectivities used for the calculation of their parameters.

In order to confirm this hypothesis, new experimental measurements were conducted with a new FAU 1 for the feed injection point (mixture A) used in the estimation of the parameters of the 4P4M model. The selectivities obtained for the different measurements are found in Table 2.

Table 2 - Selectivities obtained for mixture A (feed injection) with FAU 1

Measurement	$\alpha_{PX/PDEB}$	$\alpha_{EB/PDEB}$	$\alpha_{MX/PDEB}$	$\alpha_{OX/PDEB}$
Original	1,25	0,63	0,39	0,39
Repetition	1,49	0,61	0,41	0,41

It is observed that the PX/PDEB selectivity obtained for the original measurement is significantly lower than

the obtained for the repetition measurement made with a new FAU 1, while the remaining remained constant. The PX/PDEB selectivity obtained for the original measurement explains the lower feed flow rates obtained with the use of the 4P4M model since this is a critical selectivity for the productivity of the process.

The difference between the PX/PDEB selectivities obtained for the two measurements is explained by the higher hydration of the FAU 1 solid used in the original measurement, which result from the multiple tests conducted on this original adsorbent. Between each test performed the unit is stopped and the temperature of the column where the adsorbent is found along with a given mixture is decreased to the room temperature, which favors the adsorption of water molecules in the solid. The co-adsorption of water is known to lead to the decrease of *para*-xylene adsorption, which explains the consequent decrease of PX/PDEB selectivity in the subsequent experimental tests. The repetition measurements were made with an FAU 1 with a similar water content to the one used at industrial level, which makes the selectivities obtained for this solid to be more close to those found in the industrial process.

In respect to the 2P2M thermodynamic model, the selectivities used for obtaining the parameters for the adsorbent FAU 1 are similar to those obtained for the repetition measurement of mixture A, which leads to the conclusion that the simulations performed with the 2P2M model result in the most reliable performance between the two models. As such, it is possible to affirm that both FAU 1 and FAU 2 are good candidates to replace FAU 0 at industrial level and that between both solids, being the best performance obtained with the use of FAU 1.

5. Conclusions

The objective of this study is to analyze the adsorption behavior of new adsorbents prepared experimentally in IFPEN under conditions representative of the industrial application to provide insight into the performance of these materials when they are implanted in the *para*-xylene separation process.

Through the comparison of critical selectivities obtained for the tested *para*-selective adsorbents and a reference (FAU 4) in two distinct points of the SMB process, it is found that the use of FAU 1, FAU 2, and FAU 3 could result in more satisfying performances than the obtained with the reference solid. To confirm this hypothesis, the Limit Flow Rate approach is applied for these adsorbents. The comparison of the results obtained with the ones of FAU 4, allows the conclusion that two adsorbents, FAU 1 and FAU 2, appear to be good candidates to replace the reference adsorbent at industrial level since their use result in gains of productivity and desorbent consumption.

Simulations are performed for FAU 1 and FAU 2 with the use of both 2P2M and 4P4M. With the first, it is obtained better performances for FAU 1 and FAU 2 than for the industrial adsorbent FAU 0, in respect to both productivity and desorbent consumption, while the use of

the 4P4M model result in worst performances of FAU 1 and FAU 2 than for FAU 0 in respect to both parameters.

New experimental selectivities measurements were conducted with a new FAU 1 for the feed injection mixture used in the estimation of the 4P4M model parameters. When compared the selectivities values obtained for the original and repetition measurements, it is observed that the PX/PDEB selectivity obtained for the first measurement is significantly lower than the one obtained for the repetition while the other parameters remained constant. Therefore, it is concluded that the FAU 1 used for the estimation of 4P4M parameters had higher water content than the used industrially and as such, the use of this model is not representative of the performances obtained industrially. Through the comparison between the selectivities used for the estimation of the 2P2M model parameters and those obtained for the repetition measurement it is observed that their values were similar and therefore, it is possible to conclude that this model was obtained with more reliable selectivities.

Finally, it is possible to conclude that, since the performances obtained with the 2P2M are the most reliable, the use of the two tested adsorbents result in better performances than those obtained currently industrially and therefore, these desorbents appear to be good candidates to replace FAU 0, being FAU 1 the adsorbent which results in the most satisfying values of productivity and desorbent consumption.

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