



APLICAÇÕES DE ADSORÇÃO

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Simposio sobre Adsorción, Adsorbentes y sus Aplicaciones

San Luis, Fev 2009

DEFINIÇÕES IMPORTANTES

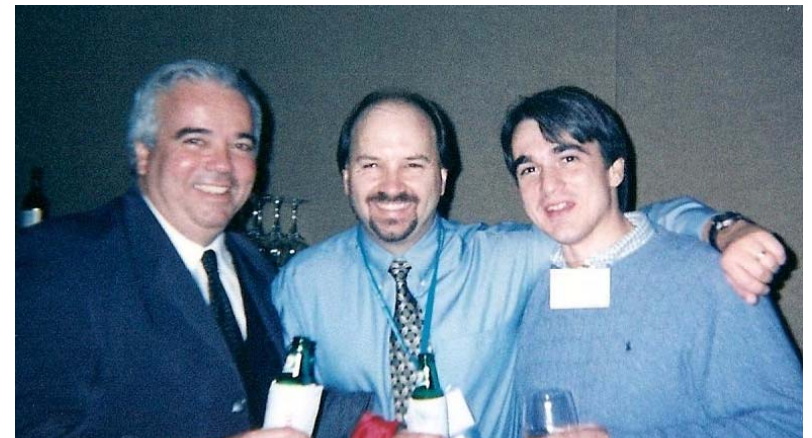
Simposio: “drink together”!!!



Porto de Galinhas



Sicilia



San Francisco



DEFINIÇÕES IMPORTANTES

***O que é um
Engenheiro Químico ?***



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DEFINIÇÕES IMPORTANTES

Alguém que fala de química com os engenheiros...



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DEFINIÇÕES IMPORTANTES

Alguém que fala de engenharia com os químicos...



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DEFINIÇÕES IMPORTANTES

***Alguém que fala de “futebol” com
outro engenheiro químico!!!***



DEFINIÇÕES IMPORTANTES

E por falar de futebol...



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DEFINIÇÕES IMPORTANTES

Qual o melhor jogador de futebol do mundo em toda a história ?



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DEFINIÇÕES IMPORTANTES

Na minha opinião, MARADONA !!!



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DEFINIÇÕES IMPORTANTES

***Especialmente quando veste
assim...***



DEFINIÇÕES IMPORTANTES

Óbvio que PELÉ está acima de qualquer classificação...



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DEFINIÇÕES IMPORTANTES

Em Brasil, as pessoas acima de qualquer qualificação são chamadas de “Pelés”, na sua especialidade !!!



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DEFINIÇÕES IMPORTANTES

Um “Pelé” da academia !!!



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DEFINIÇÕES IMPORTANTES

O que é Adsorção ?



LIVROS DE REFERÊNCIA

- PRINCIPLES OF ADSORPTION AND ADSORPTION PROCESSES, Douglas M. Ruthven (1984).
- GAS SEPARATION BY ADSORPTION PROCESSES, Ralph T. Yang (1997).
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- ADSORPTION ANALYSIS: EQUILIBRIA AND KINETICS, Duong D. Do (1998).
- GAS ADSORPTION EQUILIBRIA: EXPERIMENTAL METHODS AND ADSORPTIVE ISOTHERMS, Jürgen Keller and Reiner Staudt (2004).
- PRESSURE SWING ADSORPTION, Douglas M. Ruthven, S. Farooq, and K. S. Knaebel (1993).
- DIFFUSION IN ZEOLITES AND OTHER MICROPOROUS SOLIDS, Jorg Kärger and Douglas M. Ruthven (1992).
- ENCYCLOPEDIA OF SEPARATION TECHNOLOGY, Douglas M. Ruthven (1997).
- EQUILIBRIA AND DYNAMICS OF GAS ADSORPTION ON HETEROGENEOUS SOLID SURFACES (*Studies in Surface Science and Catalysis*), W. Rudzinski, W.A. Steele, and G. Zgrablich (1996).

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EXEMPLOS DE APLICAÇÕES:

- REMOÇÃO DE POLIAROMÁTICOS EM LEITO FIXO*
- PURIFICAÇÃO DE HIDROGÊNIO POR PSA*
- SEPARAÇÃO DE XILENOS POR LEITO MÓVEL SIMULADO (SMB)*
- TRANSESTERIFICAÇÃO DE ÓLEOS VEGETAIS PARA OBTENÇÃO DE BIODIESEL*

COMENTÁRIOS FINAIS



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INTRODUÇÃO

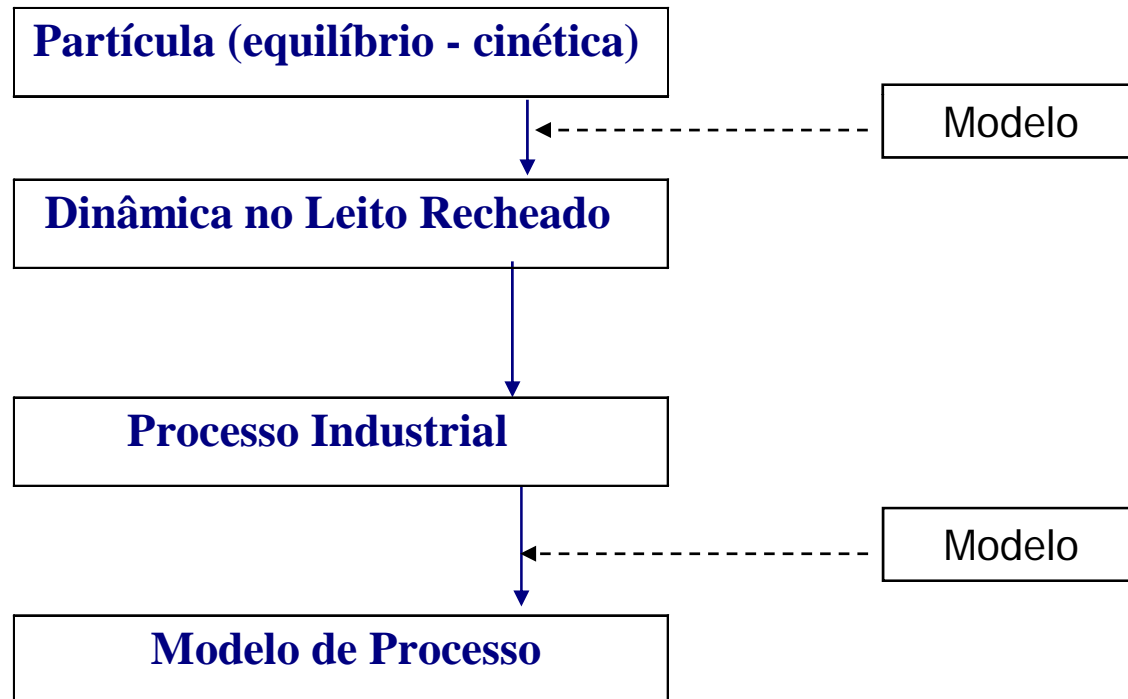
O fenômeno da adsorção se apresenta de modo importante em diversas aplicações, em variadas escalas, tais como:

- ***caracterização de sólidos porosos,***
- ***armazenamento de gases,***
- ***catálise,***
- ***eletroquímica,***
- ***refrigeração,***
- ***processos de separação ou purificação (tanto em fase gás como em fase líquido).***



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“...utilizando parâmetros termodinâmicos e cinéticos fundamentais, modelar e simular unidades contínuas de processamento”

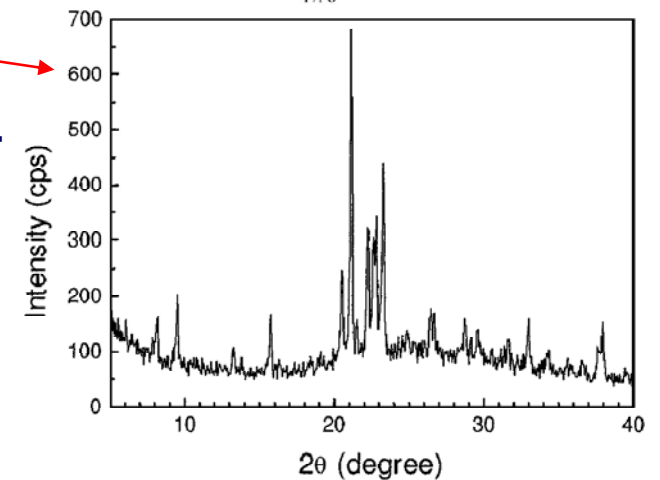
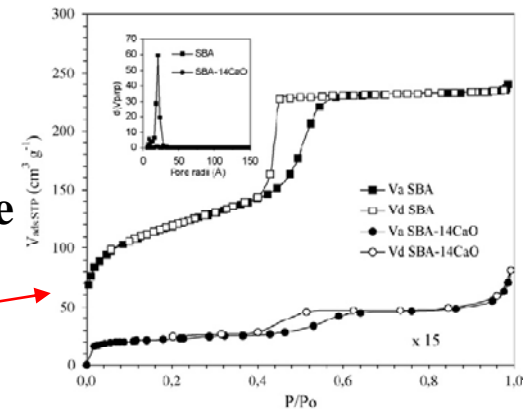


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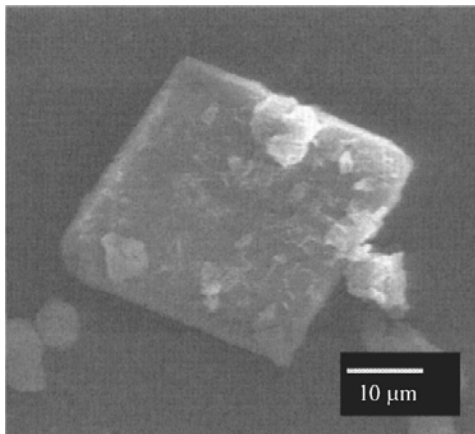
Introdução

CARACTERIZAÇÃO DO ADSORVENTE

- Propriedades texturais: área superficial, volume de poros, tamanho médio de poros, distribuição de tamanho de poros (adsorção de N₂).
- Difração de raios-X
- FTIR
- Acidez superficial (TPD amônia, volumetria n-butilamina, etc.)
- SEM / TEM
- Composição química, XPS, etc.



SEM



FTIR

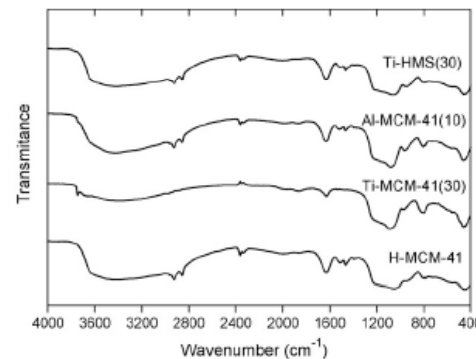


Fig. 4. ATR-FTIR spectra of the samples: MCM-41, Al-MCM-41(10), Ti-MCM-41(30) and Ti-HMS(30) after calcination.

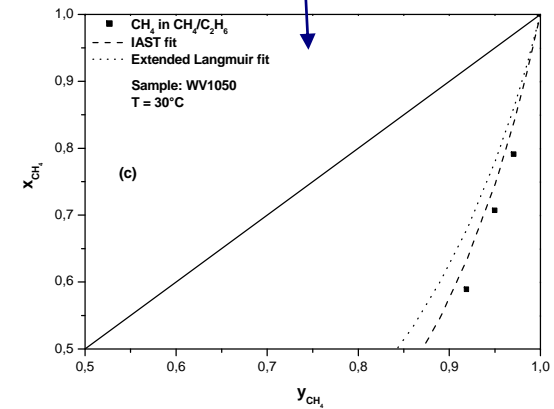
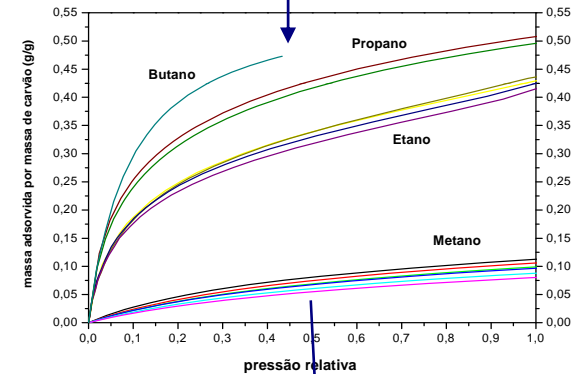
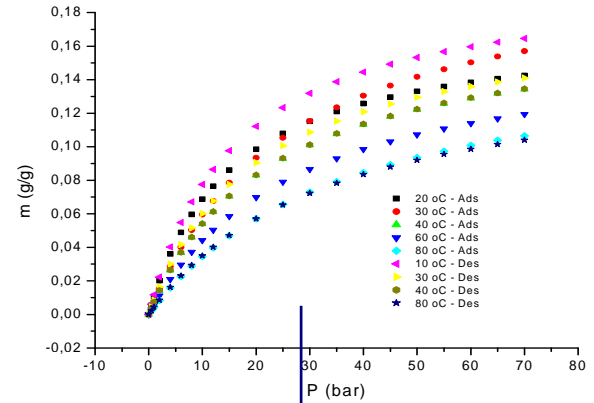
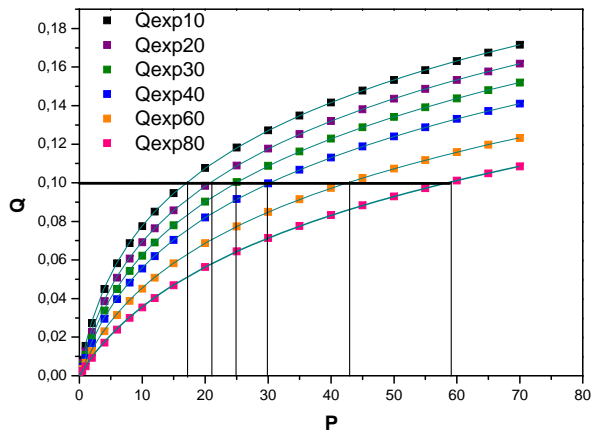


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Equilíbrio:

- isothermas monocomponentes
(medidas e modelos)
- isothermas multicomponentes
(medidas e modelos)
- calores de adsorção

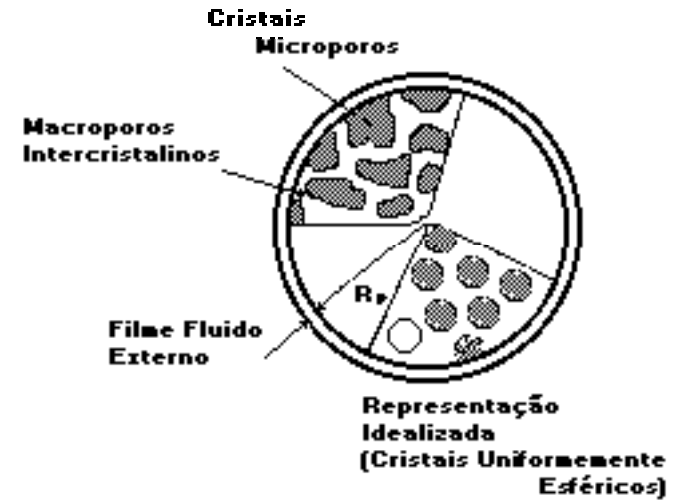
$$\left(\frac{\partial \ln P}{\partial T}\right)_{q_{ex}} = \frac{-\Delta H_{Ads}}{RT^2} \Rightarrow \Delta H_{Ads} = R \cdot \left(\frac{\partial(\ln P)}{\partial(1/T)}\right)_{q_{ex}}$$



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Cinética na partícula:

- modelos de difusão
- difusão macroporos
- difusão microporos
- modelos agregados (LDF)



$$D_0 = D_0^* \exp\left(\frac{-E_a}{RT}\right)$$

$$\frac{\partial c}{\partial t} = -K_L(c_e - c_\infty)$$

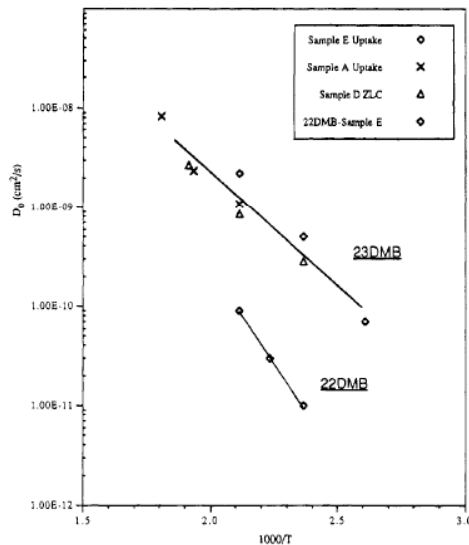
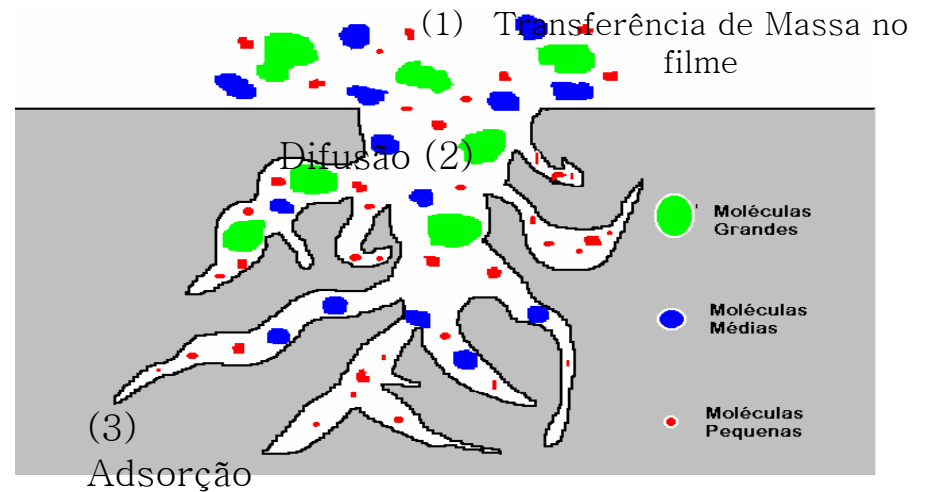
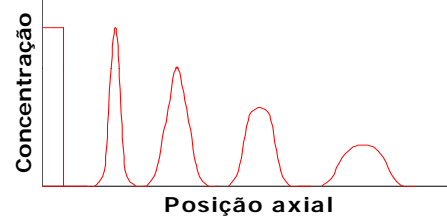


Figure 8. Arrhenius plot showing temperature dependence of intracrystalline diffusivities of 2,3-dimethylbutane and 2,2-dimethylbutane in silicalite.



Dinâmica no leito recheado:

- dispersão axial



Alargamento dos perfis de concentração em uma coluna de leito fixo devido a dispersão axial

- Efeitos extra-coluna
- Distribuição do fluido na coluna
- Não idealidade do empacotamento
- Todos efeitos hidrodinâmicos podem ser resumidos no termo de dispersão axial (D_L)

Correlações (p.ex., Chung e Wen, 1968):

$$Pe = \frac{0,2}{\varepsilon} + \frac{0,011}{\varepsilon} (\varepsilon Re)^{0,48}$$

$$Pe = \frac{ud_p}{D_L}$$

$$Re = \frac{ud_p \rho}{\eta}$$

Dinâmica no leito recheado:

- perda de carga

Influência da qualidade do empacotamento e tamanho de partícula para a Δp no interior de uma coluna

- Pequenas partículas promovem maior Δp
- Δp aumenta com o aumento da vazão de escoamento
- Geralmente, segue a Lei de Darcy

Equação de Kozeny-Carman:

$$\frac{\Delta p}{L} = \frac{\eta}{\left(\frac{d_p^2 \varepsilon^3}{36\beta(1-\varepsilon)} \right)} u = \frac{\eta}{\kappa} u$$

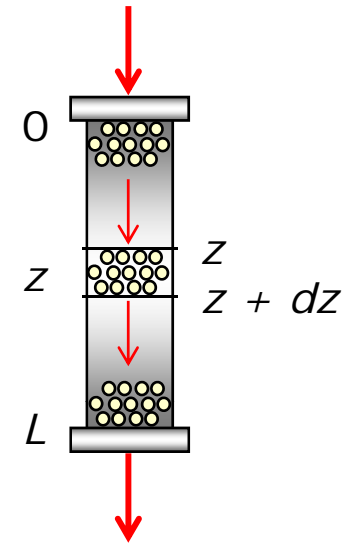
κ - permeabilidade do leito; β - coeficiente de Kozeny

Dinâmica no leito recheado:

- modelo (mais simples: equilíbrio)

- Operação isotérmica
- Equilíbrio é atingido instantaneamente em cada ponto do leito $\bar{q}_i = q_i^*$
- Escoamento em fluxo pistonado
- Perda de carga desprezível

Efeitos de dispersão e de transferência de massa são negligenciados



$$(\varepsilon A)v c_i|_z - (\varepsilon A)v c_i|_{z+dz} + \varepsilon(Adz) \frac{\partial c_i}{\partial t} + (1 - \varepsilon)(Adz) \frac{\partial q_i^*}{\partial t} = 0$$

$$\varepsilon v \frac{\partial c_i}{\partial z} + \varepsilon \frac{\partial c_i}{\partial t} + (1 - \varepsilon) \frac{\partial q_i^*}{\partial t} = 0$$

$$v \frac{\partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + \left(\frac{1 - \varepsilon}{\varepsilon} \right) \frac{\partial q_i^*}{\partial t} = 0$$

$$q_i^* = f(c_i)$$

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OBTENÇÃO DE BIODIESEL*



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CLASSIFICAÇÃO DE PROCESSOS

TIPO DE PRODUTO:

- *purificação*
- *separação “bulk”*

MODO DE OPERAÇÃO:

- *batelada*
- *bateladas cíclicas*
- *contínuo*

MÉTODO DE REGENERAÇÃO DO ADSORVENTE:

- *TSA*
- *PSA*
- *purga com inerte*
- *purga com dessorvente*



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Tipo de produto

Purificação:

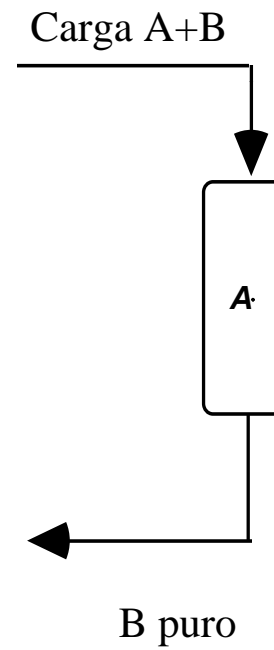
- quando se quer apenas um dos componentes em maior pureza
- remoção de contaminantes ou de um produto de alto valor
- exemplos: purificação de água (metais, orgânicos) / remoção de água de correntes de processo / remoção de H₂S

Separação “bulk”:

- quando se quer mais de um dos componentes
- quando as concentrações não são muito baixas nem muito altas
- exemplos: separação do ar / separação de xilenos / separação de olefinas / separação de açúcares / separação de enantiômeros

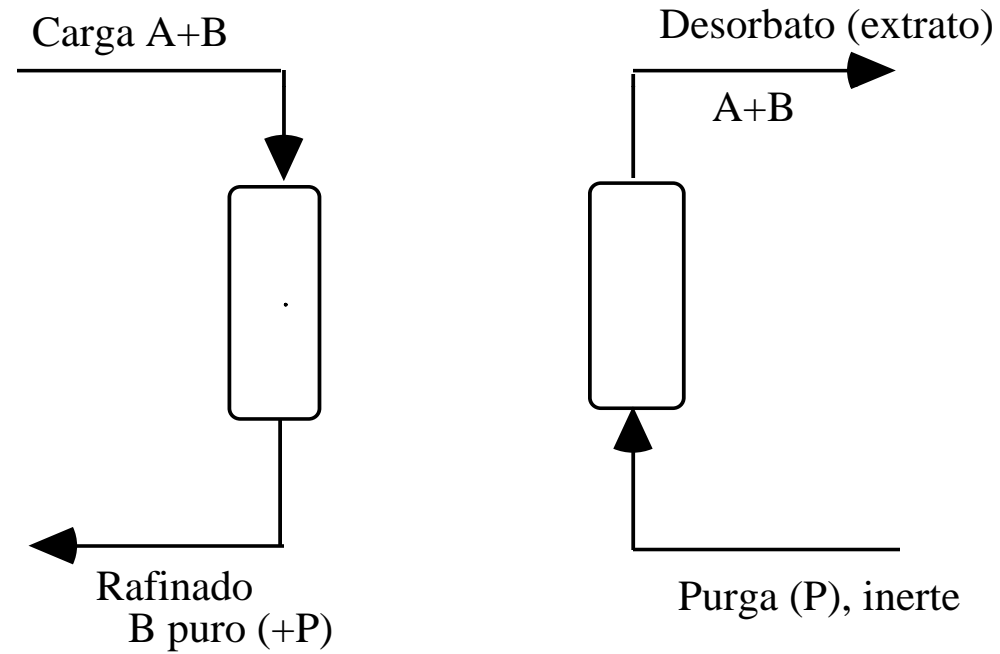
Modo de Operação

Batelada



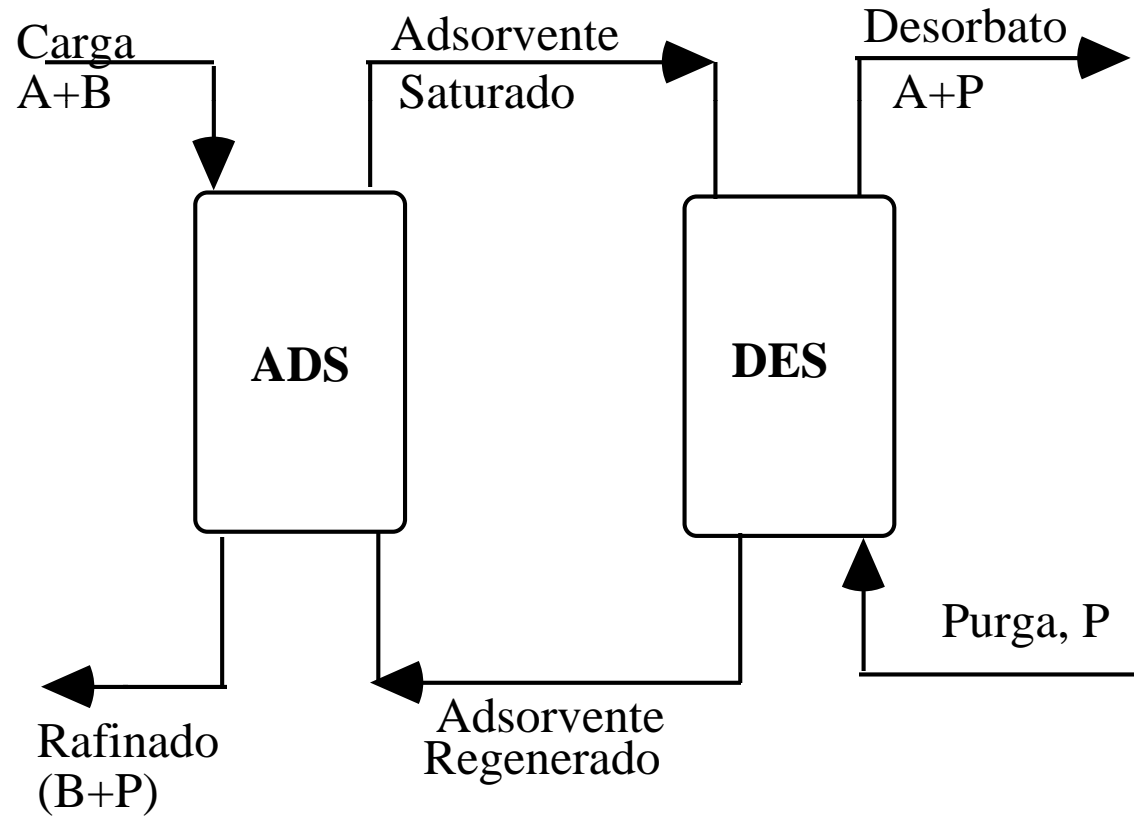
Modo de Operação

Bateladas cíclicas



Modo de operação

Contracorrente contínuo



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

- ✓ TSA (mudança de temperatura)
- ✓ PSA (Mudança de pressão)
- ✓ Purga com inerte
- ✓ Purga com gás inerte quente
- ✓ Dessorção por substituição

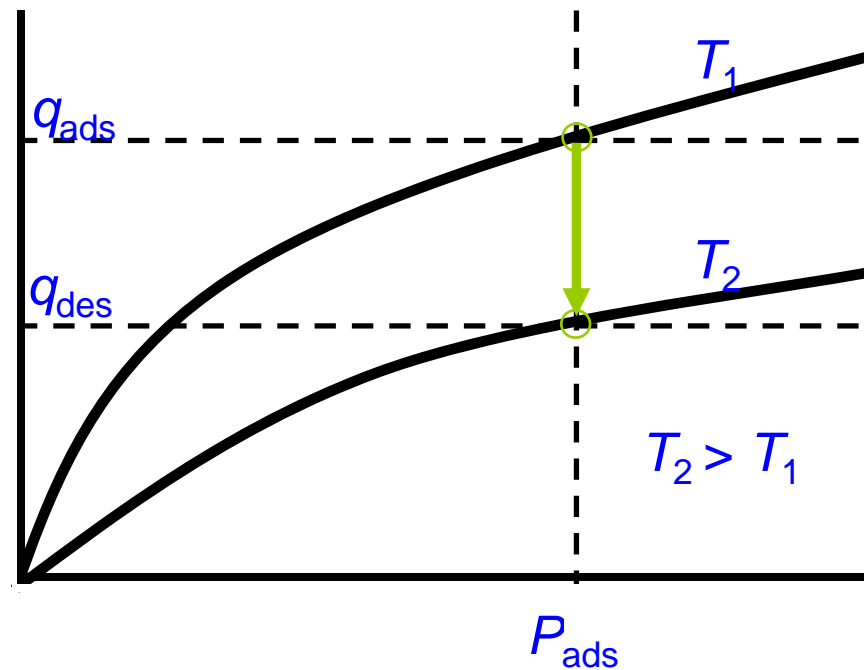


MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

TSA (mudança de temperatura)

O leito é regenerado por aquecimento a pressão constante.

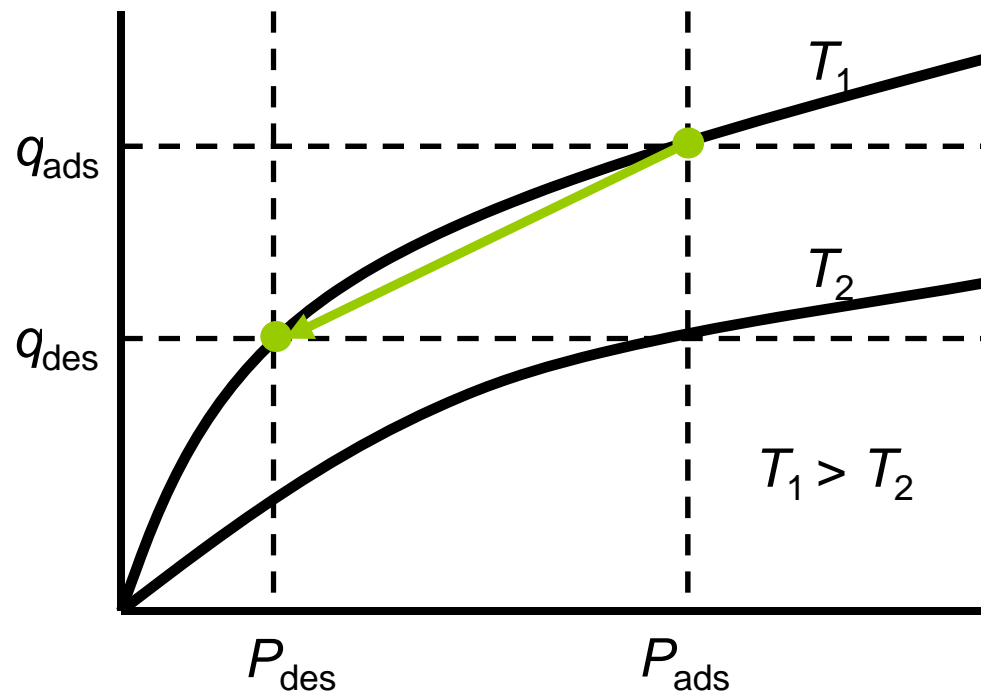
Em geral, utiliza-se um gás quente ao invés da troca indireta de calor.



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

PSA (Mudança de pressão).

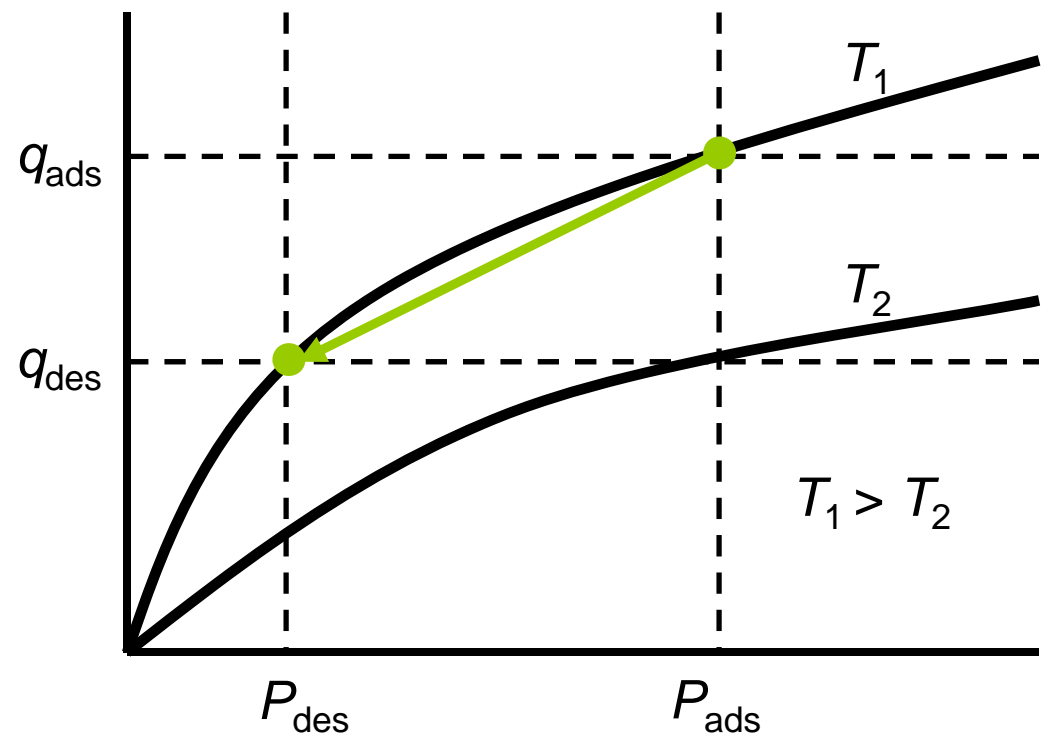
A regeneração ocorre por redução da pressão, mantendo a temperatura essencialmente constante



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

Purga com inerte.

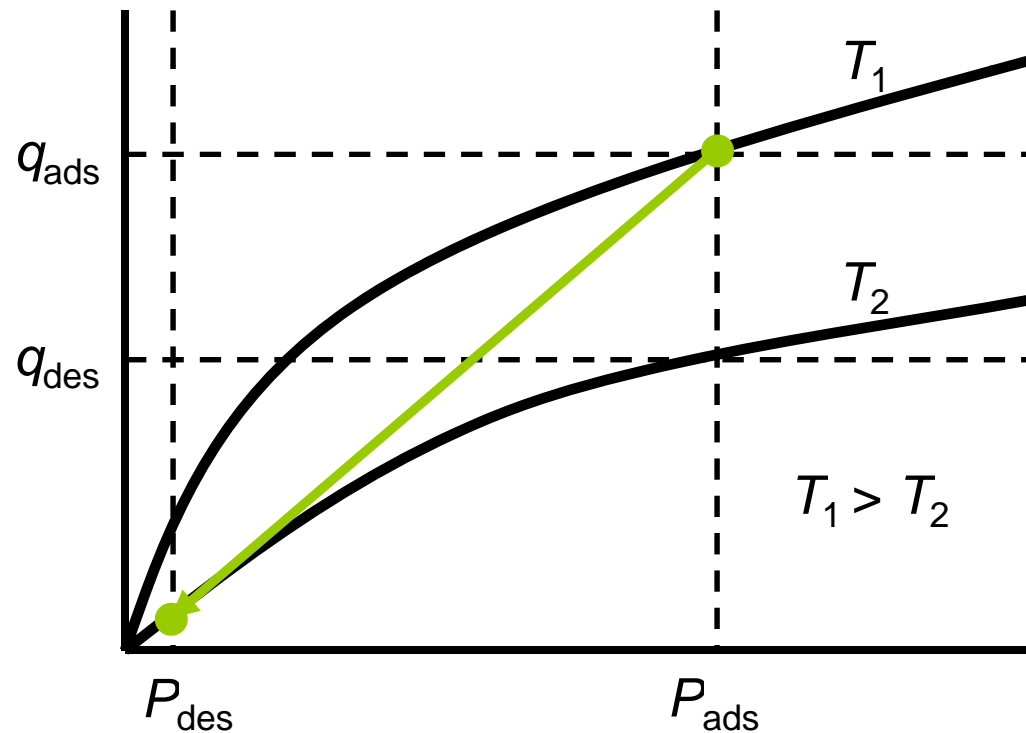
A regeneração ocorre com a introdução de um gás inerte, mantendo a temperatura e pressão constantes, varia-se a pressão parcial, em vez da pressão total.



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

Purga com gás inerte quente.

É a combinação do TSA com uma purga inerte



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

Purga com adsorvente.

T e P são mantidos constantes, como na regeneração com purga, mas a purga inerte é substituída por uma corrente contendo um componente que é mais fortemente adsorvido.



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

Método	Vantagens	Desvantagens
Módulação térmica	Bom quando adsorção é forte; pequena variação de T produz variação grande de q	Envelhecimento térmico do adsorvente
	O produto pode ser recuperado em concentração elevada	Perdas térmicas significam uso ineficiente de energia
		Não é adequado para ciclos rápidos; o adsorvente não pode ser usado com eficiência máxima
	Gases e líquidos	Em sistemas líquidos tem que se adicionar um calor latente elevado ao líquido intersticial



MÉTODOS DE REGENERAÇÃO DE ADSORVENTES

Método	Vantagens	Desvantagens
Módulação de pressão	Bom para purificação de substâncias com potencial de adsorção reduzido	Pode ser necessário trabalhar a uma pressão muito baixa
		Energia mecânica é mais dispendiosa do que a energia térmica
	Ciclos rápidos – uso eficiente do adsorvente	Desorvente é recuperado com baixa pureza
Desorção por substituição	Bom para espécies fortemente adsorvidas	Necessita de separação e recuperação do produto (a selecção do desorvente é crucial)
	Impede o risco de reacções de craqueamento durante a regeneração	
	Impede o envelhecimento térmico do adsorvente	



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APLICAÇÕES

1) Remoção de Poli-aromáticos em Materiais Mesoporosos

2) Purificação de H₂ por PSA

3) Separação de Xilenos por SMB

4) Transesterificação de óleos vegetais para obtenção de biodiesel

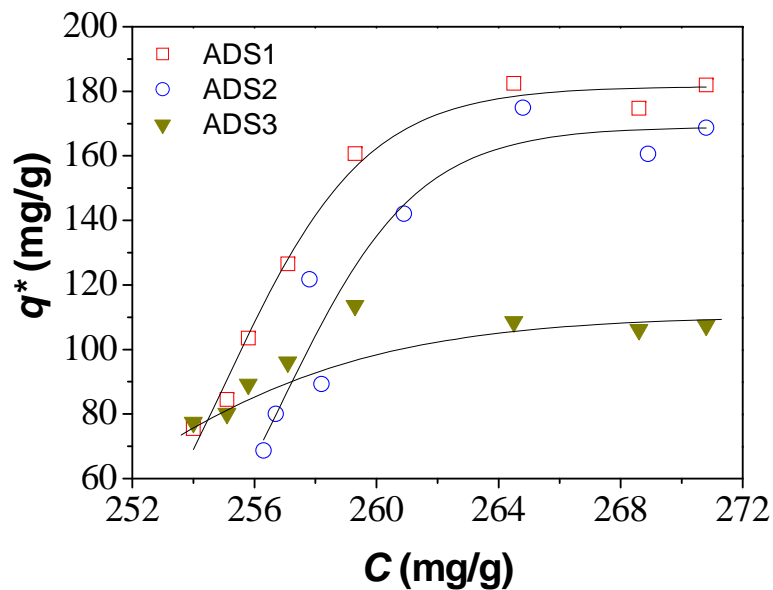


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Adsorção de poli-aromáticos em materiais mesoporosos

Óleo Mineral Naftênico (MNO)

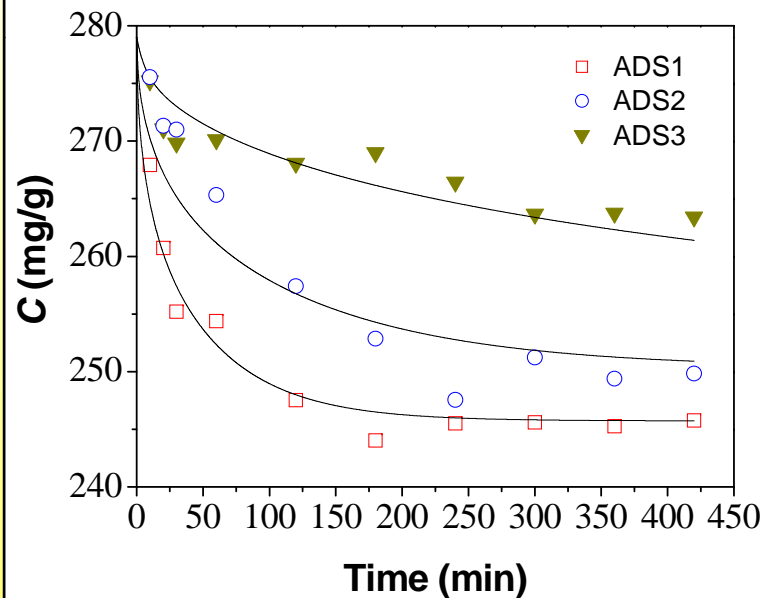
Isotermas de adsorção de aromáticos totais de MNO a 25 °C usando diferentes adsorventes (carbono ativado, zeolito Y)



Adsorventes	b (g / mg)	q_m (mg/g of ads.)
Carbono 1	4.48	181
Carbono 2	2.05	168
Zeolito Y	1.15	113

Adsorção de poli-aromáticos em materiais mesoporosos

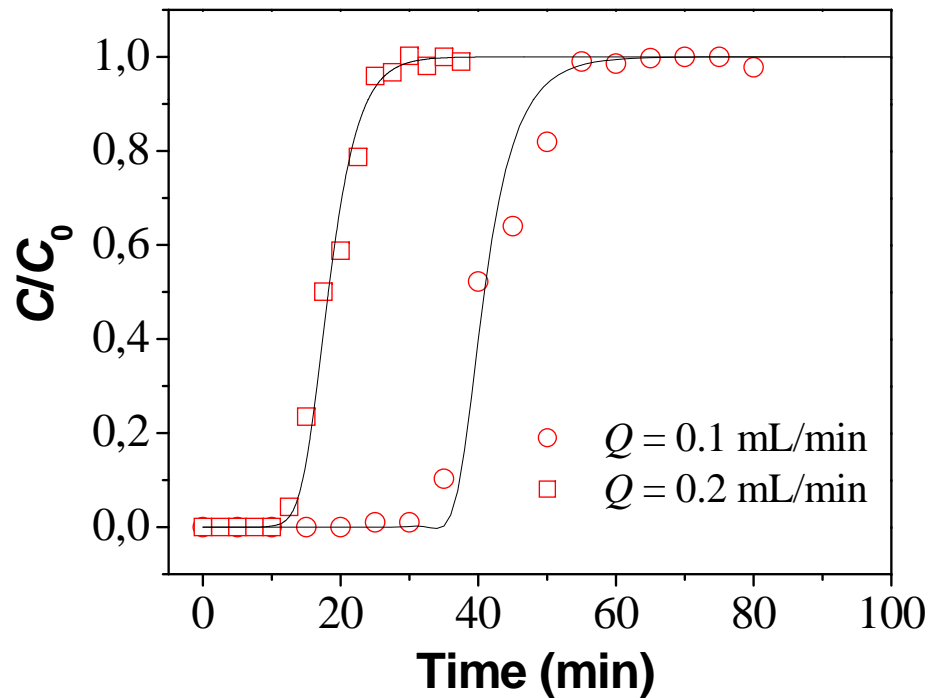
Cinética de adsorção de aromáticos totais a 25 °C



Adsorbents	$k_{f,b}$ (cm/min)	D_p (cm ² /min)
ADS1	1.004	$9.35 \cdot 10^{-6}$
ADS2	1.000	$3.64 \cdot 10^{-6}$
ADS3	0.516	$7.62 \cdot 10^{-8}$

Adsorção de poli-aromáticos em materiais mesoporosos

Carbons - Column



Luna et al., IEC Res, 2008

Adsorção de poli-aromáticos em materiais mesoporosos

Carbons - Column

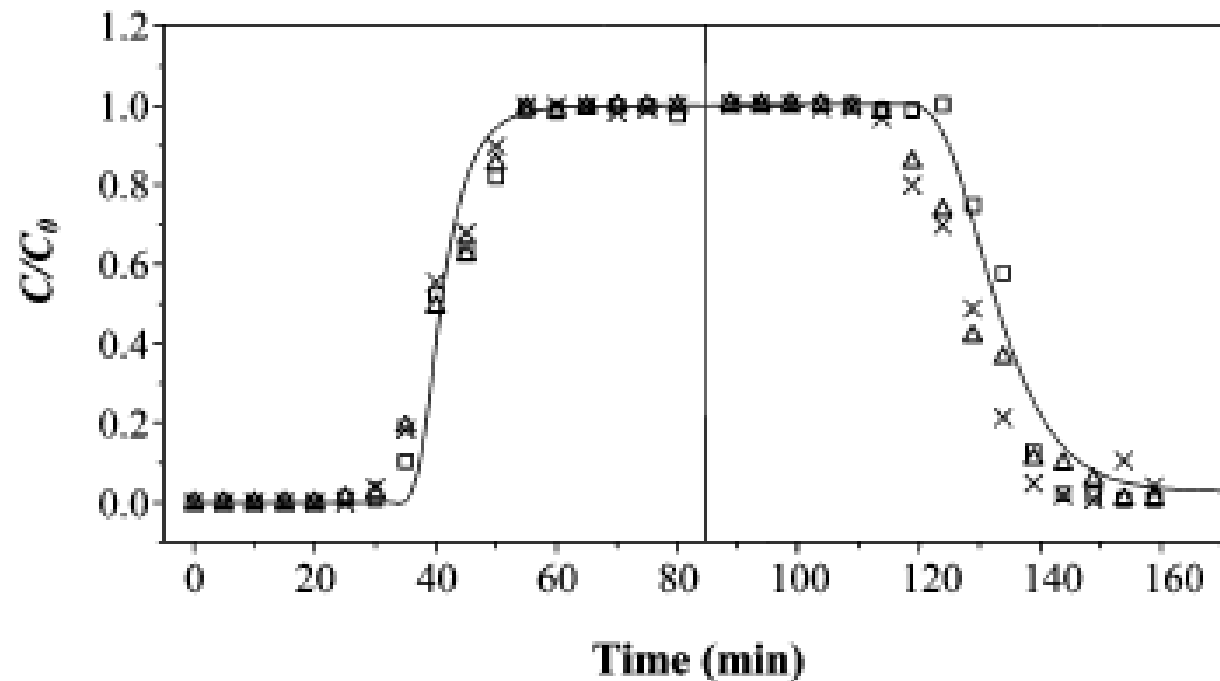


Figure 6. Adsorption/desorption steps of MNO on ADS1 at 25 °C. (□) First cycle, (Δ) second cycle, (×) third cycle. Full line is model representation for the first cycle.

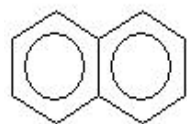
Adsorção de poli-aromáticos em materiais mesoporosos

Mesoporous MCM-41 with Pure PAH

MCM-41

Al-MCM-41 (Si/Al=10)

Al-MCM-41 (Si/Al=30)



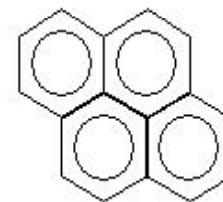
$D_c = 7,3 \text{ \AA}$

Naftaleno



$DC = 7,3 \text{ \AA}$

Antraceno

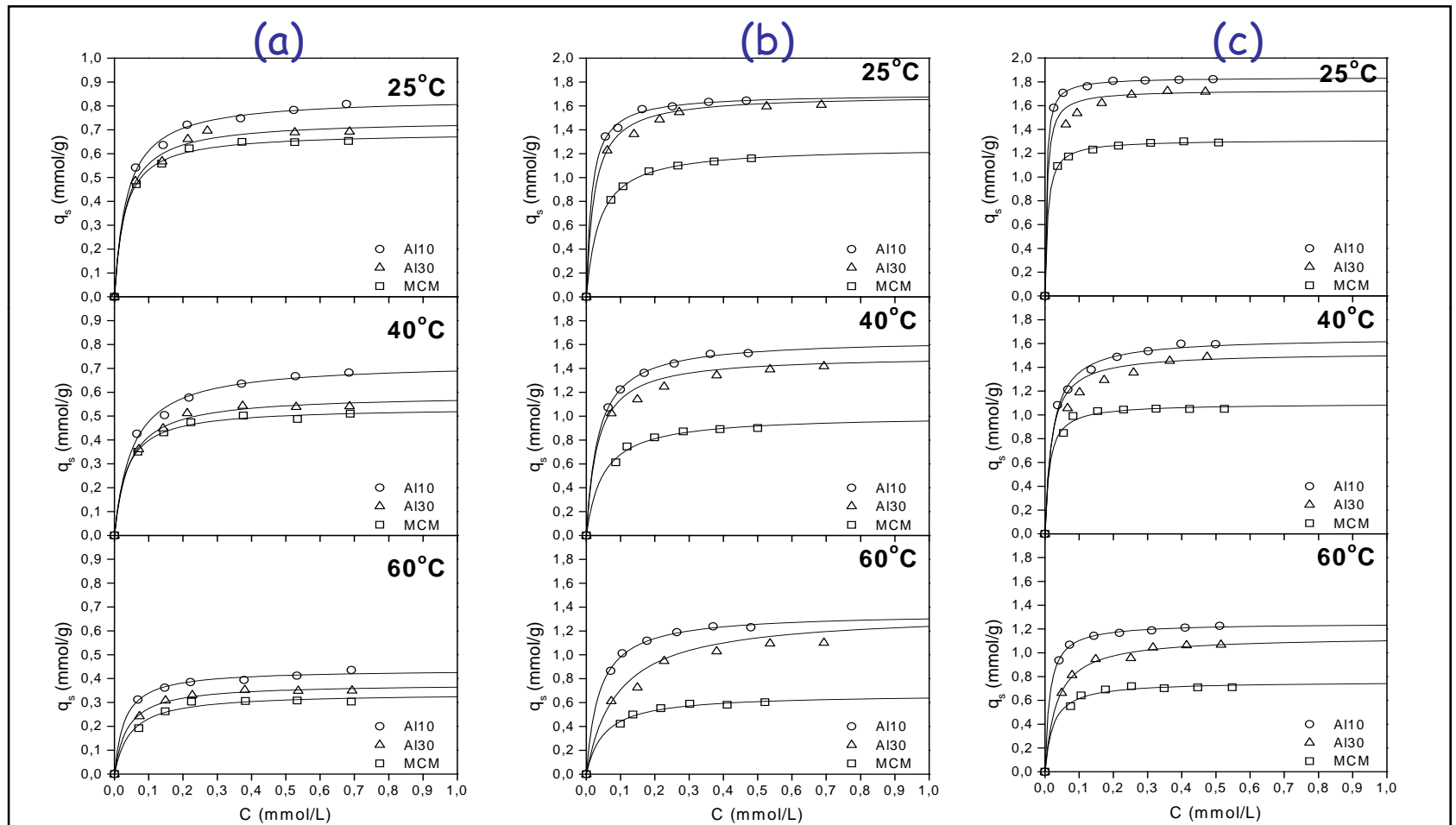


$DC = 8,9 \text{ \AA}$

Pireno

(Araujo et al., Microporous and Mesoporous Materials, 2008)

Equilibrium adsorption isotherms (MCM-41)

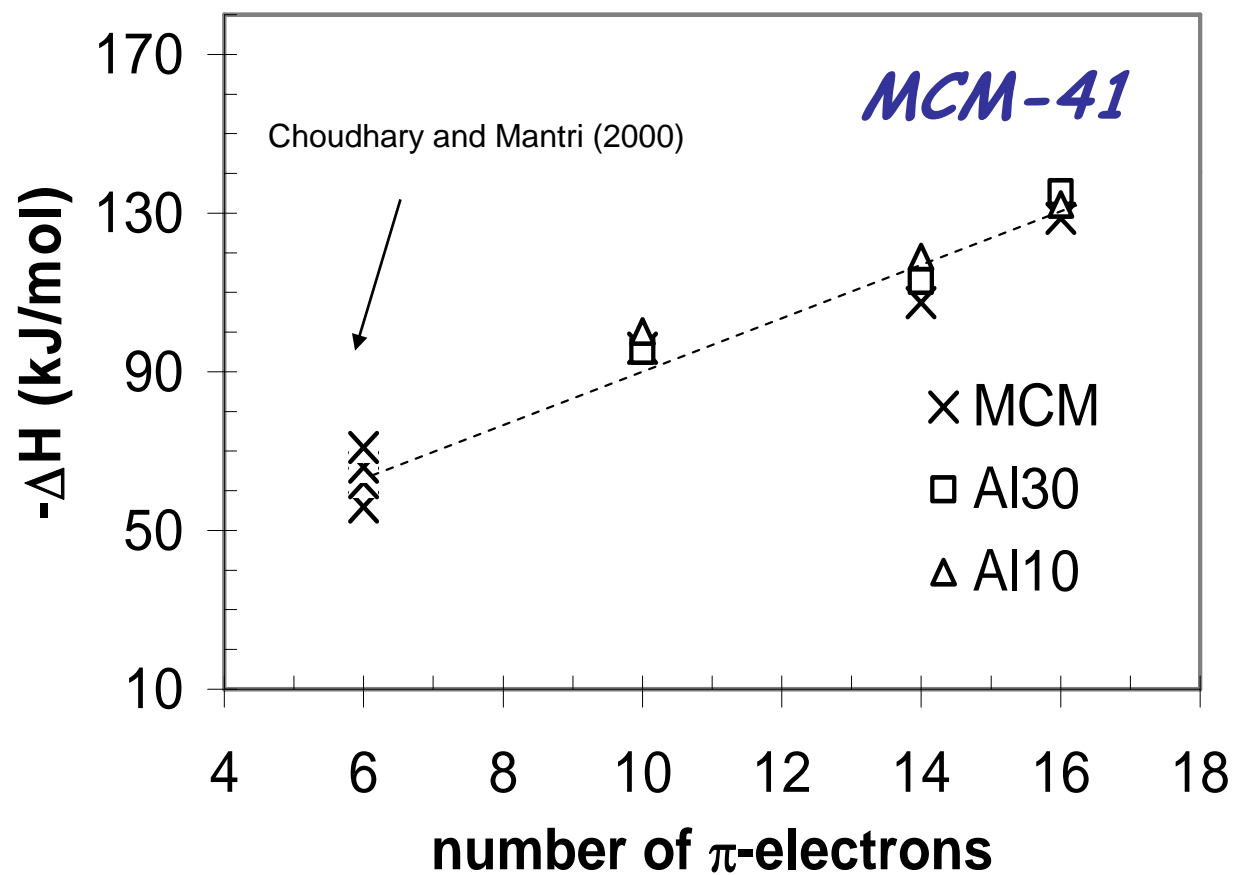


Isotherms of Naphthalene (a), Anthracene (b) and Pyrene (c). Symbols represent experimental points and lines are Langmuir fittings.

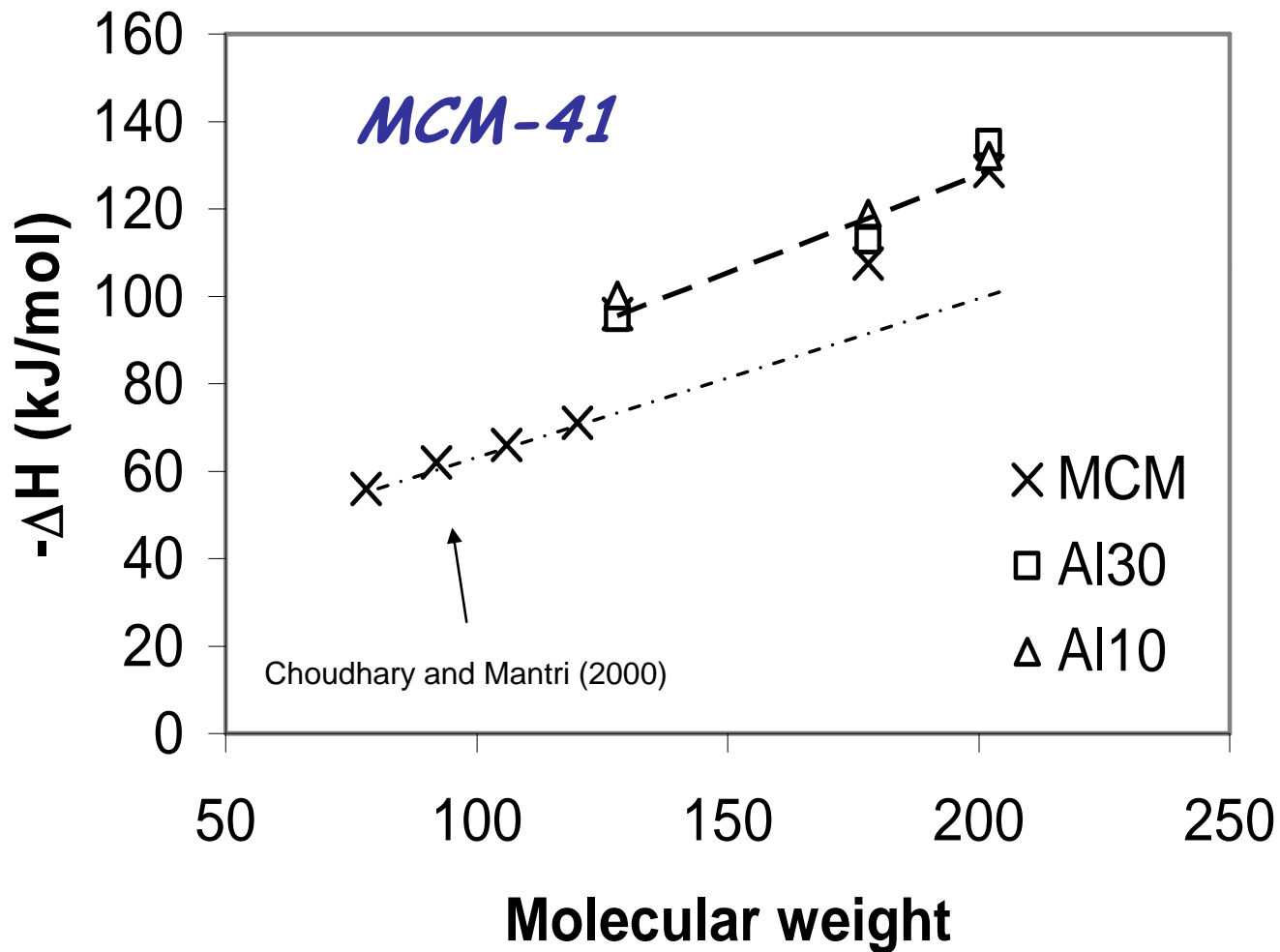
Heats of adsorption for each PAH at each of the synthesized mesoporous adsorbents

Adsorbent	$-\Delta H(\text{kJ/mol})$		
	Naphthalene	Anthracene	Pyrene
MCM-41	95.9	107.5	128.6
Al-MCM-41(30)	95.2	112.8	135.2
Al-MCM-41(10)	100.2	118.9	132.1

Adsorção de poli-aromáticos em materiais mesoporosos



Adsorção de poli-aromáticos em materiais mesoporosos



APLICAÇÕES

1) Remoção de Poli-aromáticos em Materiais Mesoporosos

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Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

Hidrogênio praticamente não é adsorvido. A capacidade de determinados adsorventes em adsorver praticamente todas as impurezas permite que se possa produzir hidrogênio com elevada pureza. (> 99.9 % vol).

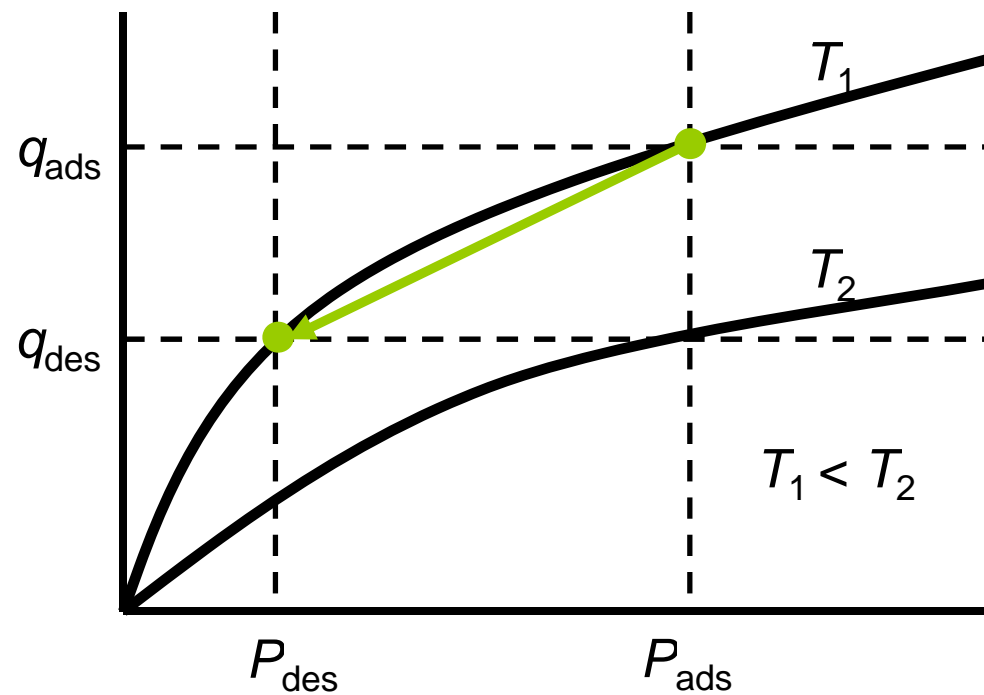
A **utilização** de um sistema PSA depende de se poder **regenerar o adsorvente** por **abaixamento de pressão**.

Em virtude dos **ciclos** poderem serem **rápidos**, pode ser usado tanto para remover **grandes quantidades** de impurezas com também para remoção de **pequenas quantidades** de impurezas.



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

Sistema PSA → regeneração do adsorvente durante a dessorção é feita reduzindo a pressão total e purgando o leito em baixa pressão com uma pequena fração do produto puro.



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

Adsorção: produz uma fase gasosa mais rica nos componentes menos adsorvidos;

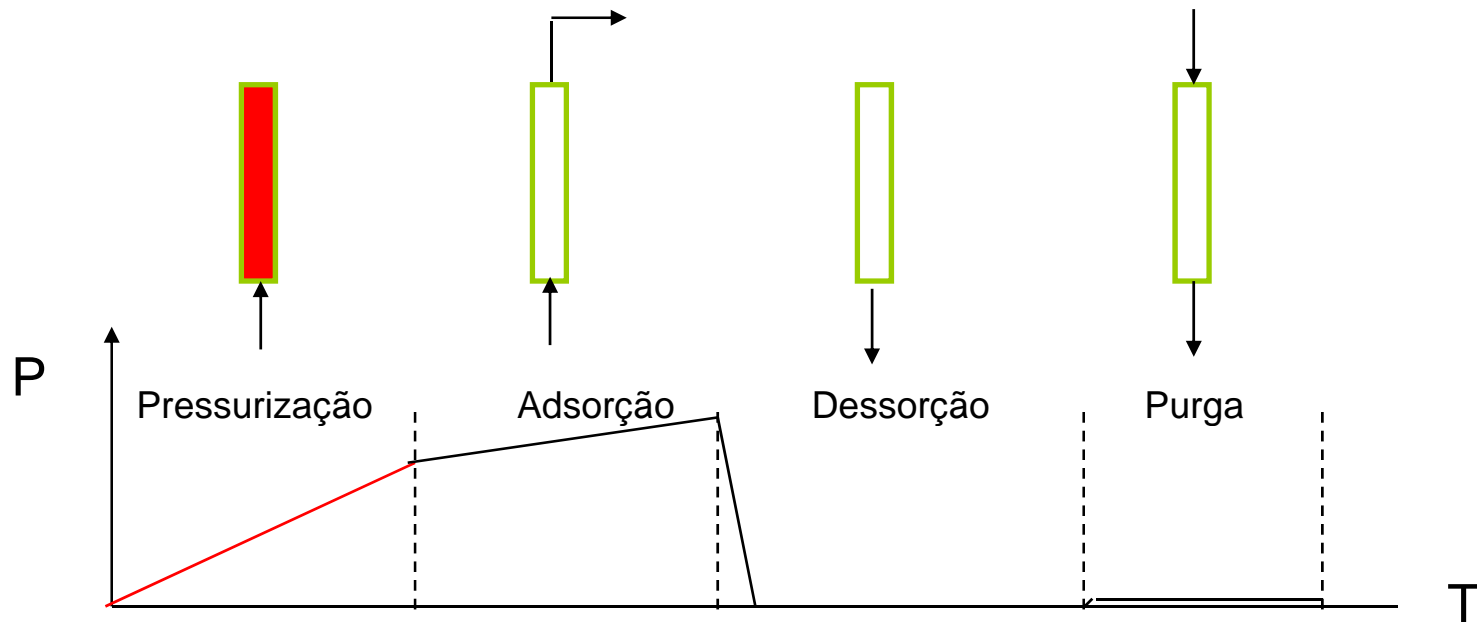
Dessorção dos componentes mais fortemente adsorvidos:

- Produz uma fase gasosa enriquecida nos componentes mais adsorvidos;
- Limpa o adsorvente para a sua reutilização

Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

- **Pressurização**

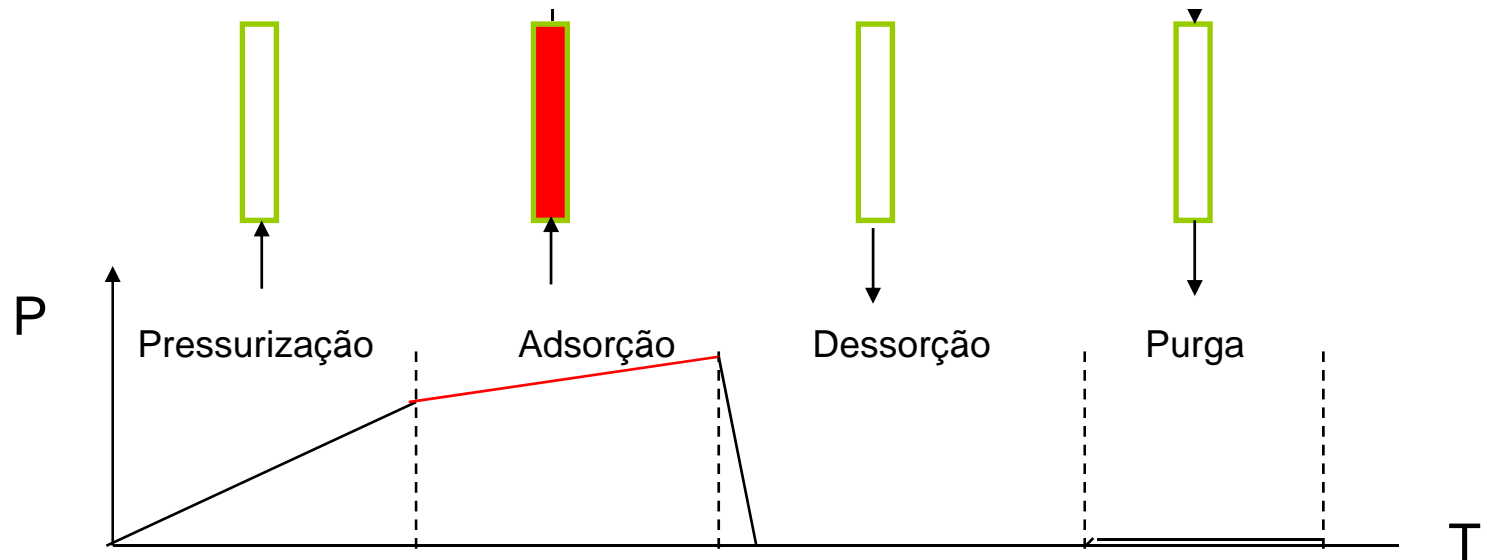
- A coluna é pressurizada desde P_{baixa} até P_{alta} com a mistura gasosa de alimentação através de uma das extremidades da coluna (co-corrente) mantendo a outra extremidade fechada.



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

- **Adsorção**

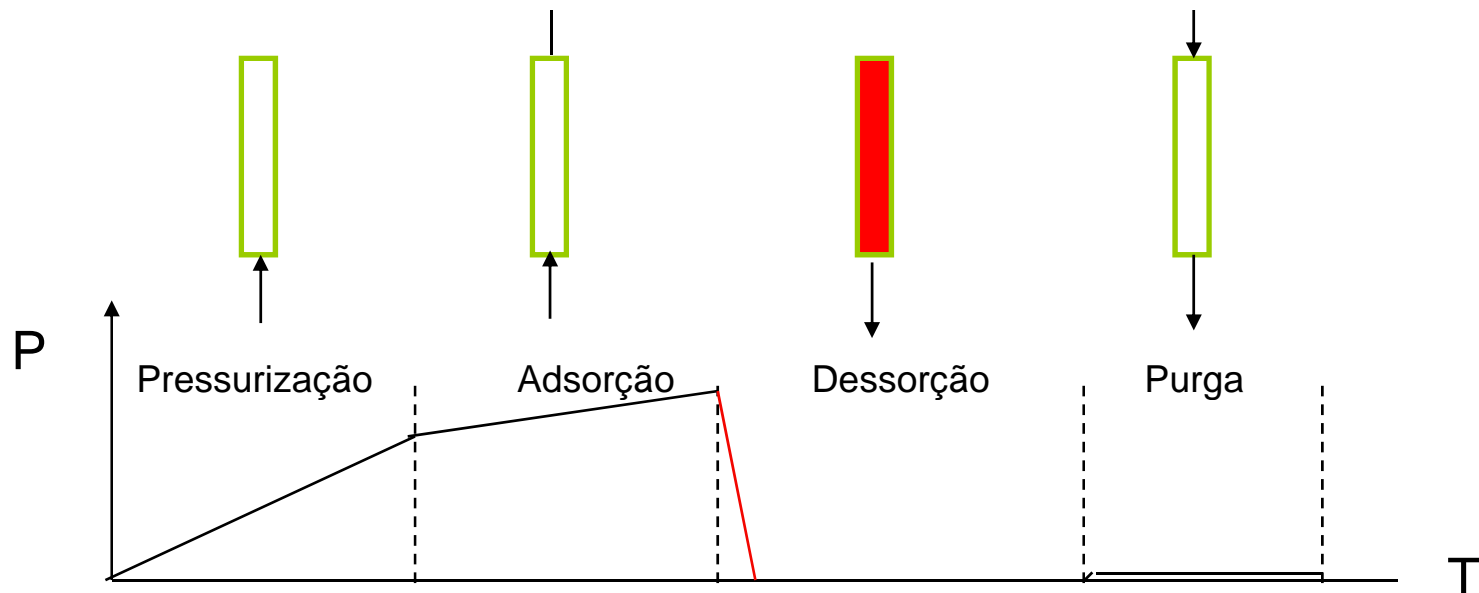
- A coluna continua a ser alimentada com o gás de alimentação à pressão constante P_{alta} , obtendo-se no outro extremo um produto gasoso rico no componente menos adsorvido



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

- **Dessorção (despressurização)**

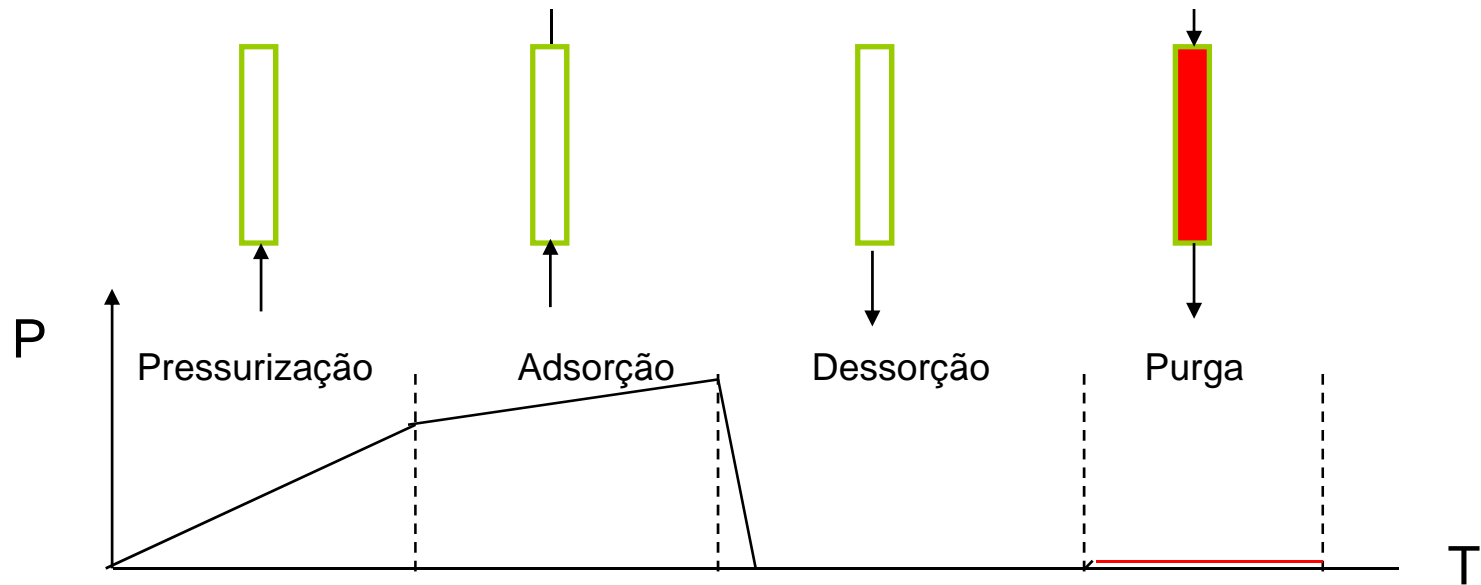
- A pressão na coluna é diminuída até ao seu valor mais baixo P_{baixa} por remoção do gás pelo extremo da coluna onde esta foi alimentada (contra-corrente)



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

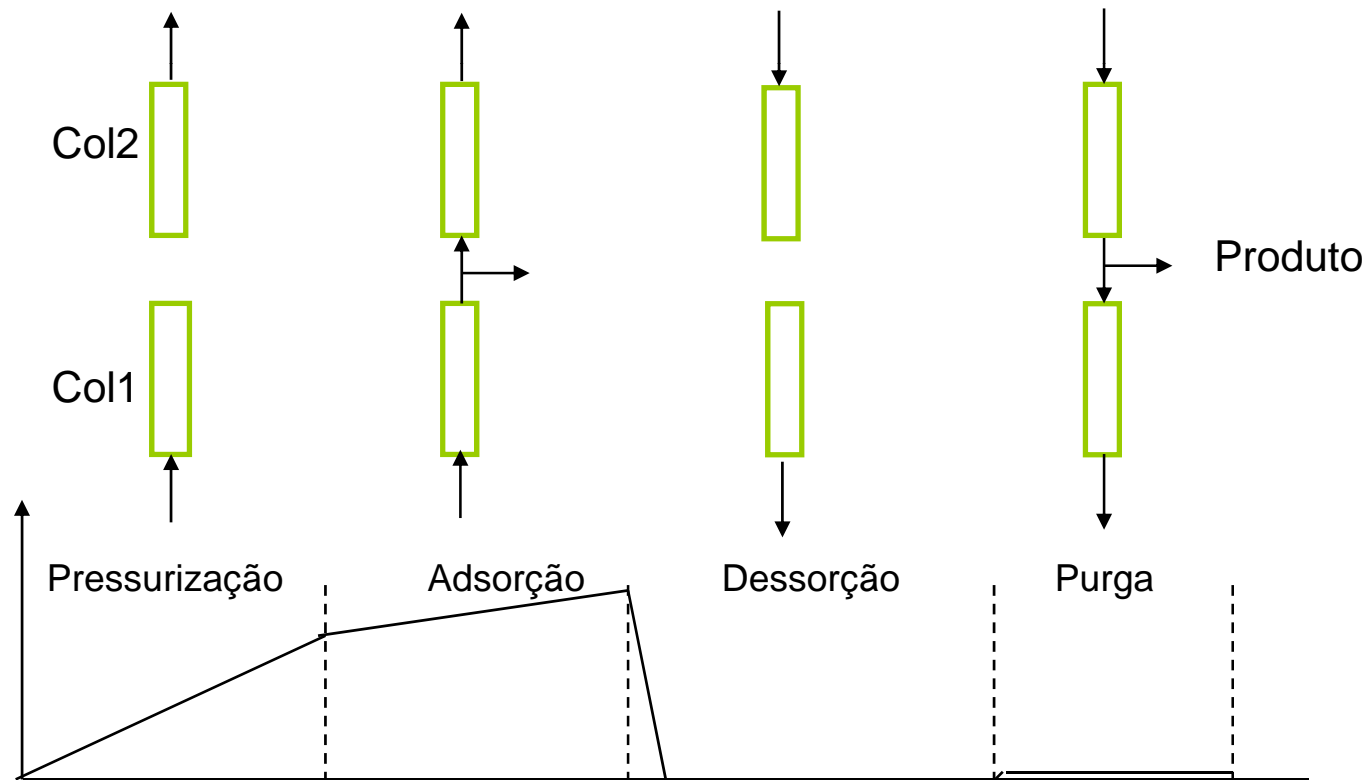
▪ *Purga*

- A coluna é purgada em contra-corrente a P_{baixa} com um gás rico no componente menos adsorvido
- Normalmente, na purga utiliza-se parte do gás produzido na etapa de adsorção



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

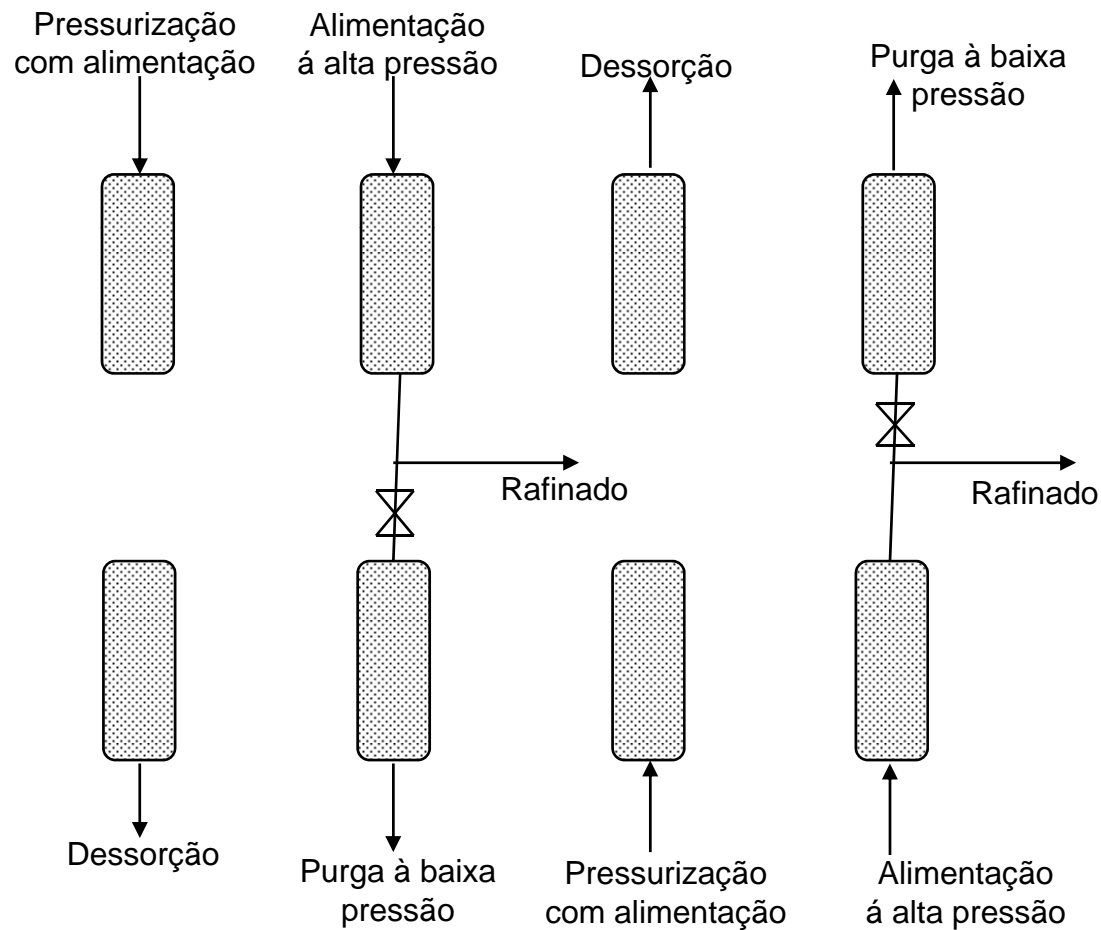
- **Produção contínua – múltiplos leitos**
 - Duas colunas são pressurizadas e despressurizadas alternadamente para originar um processo contínuo



2	1
DE	PR
PU	ADS
PR	DE
ADS T	PU

Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

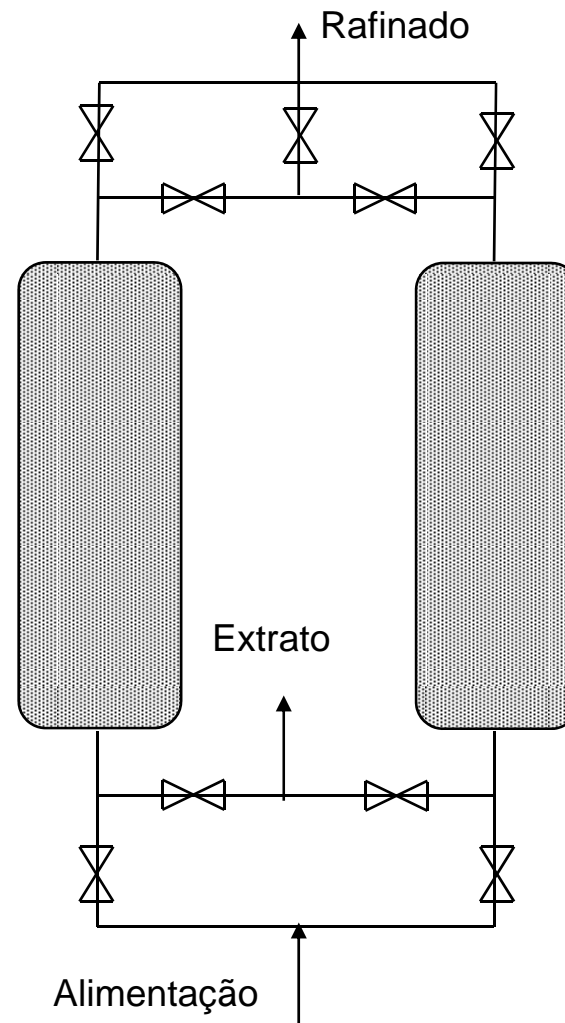
Processo PSA (Skarstrom)



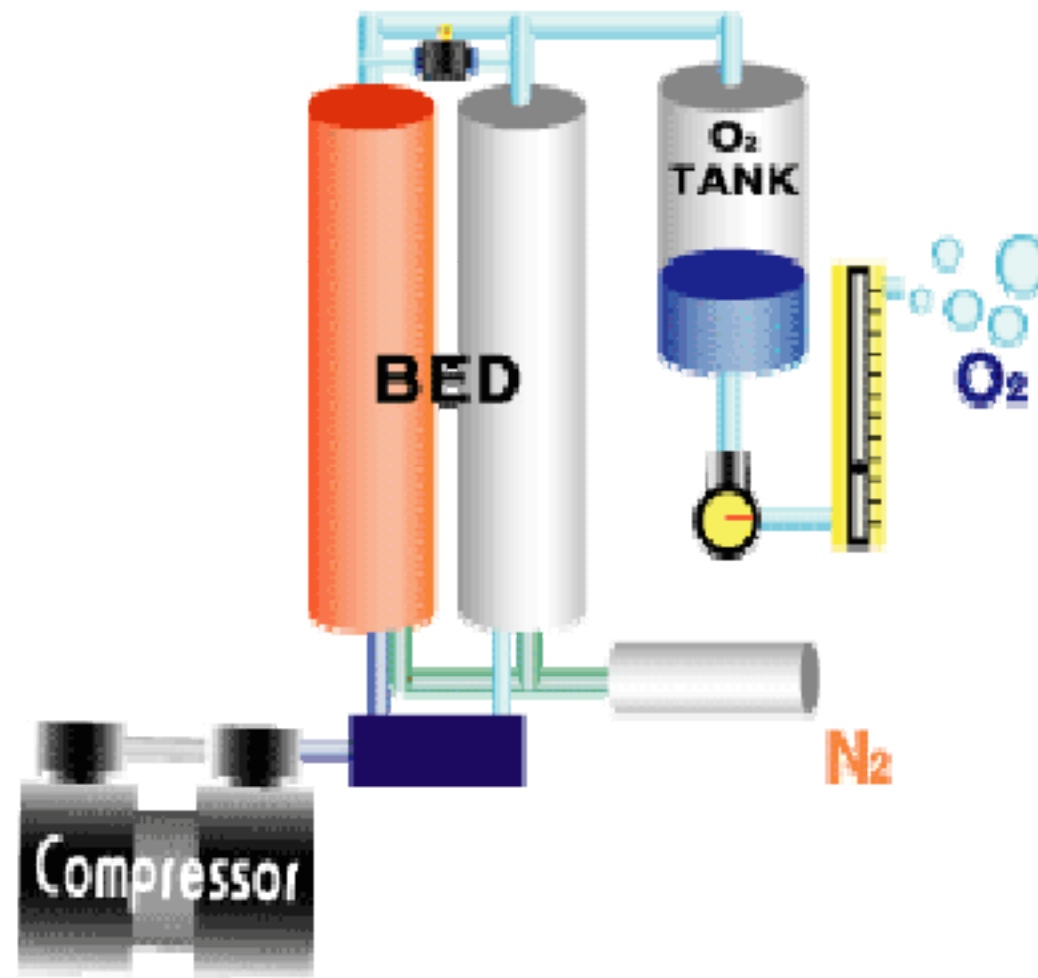
Ciclo de Skarstrom para purificação de gases

Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

**Processo PSA
(Skarstrom):**

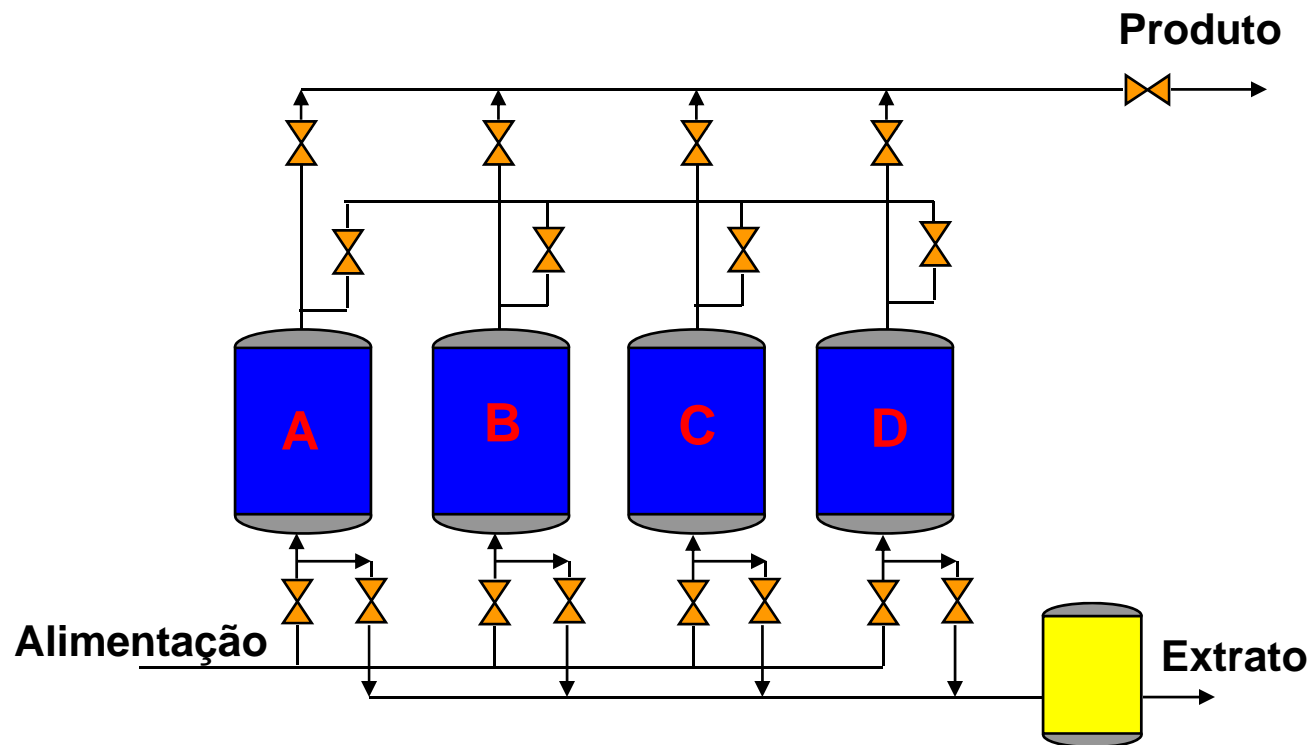


PSA com duas colunas - separação de ar



Purificação de Hidrogênio por PSA – Pressure Swing Adsorption

PSA com quatro leitos (UOP/Lubnor)



APLICAÇÕES

1) Remoção de Poli-aromáticos em Materiais Mesoporosos

2) Purificação de H₂ por PSA

3) Separação de Xilenos por SMB

4) Transesterificação de óleos vegetais para obtenção de biodiesel

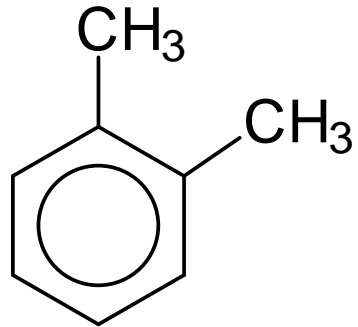


UFC

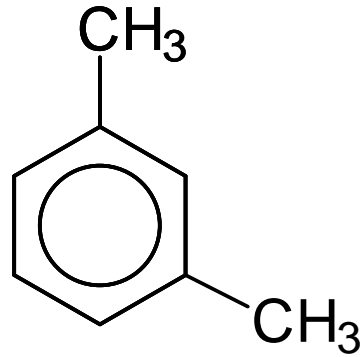
Separação de xilenos por SMB

Aromáticos C8

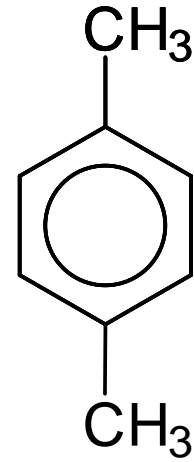
o-xileno



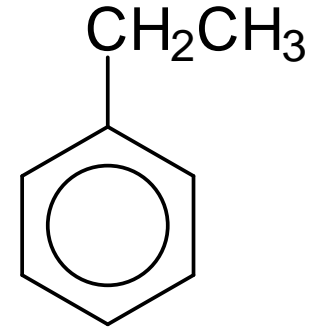
m-xileno



p-xileno



etilbenzeno



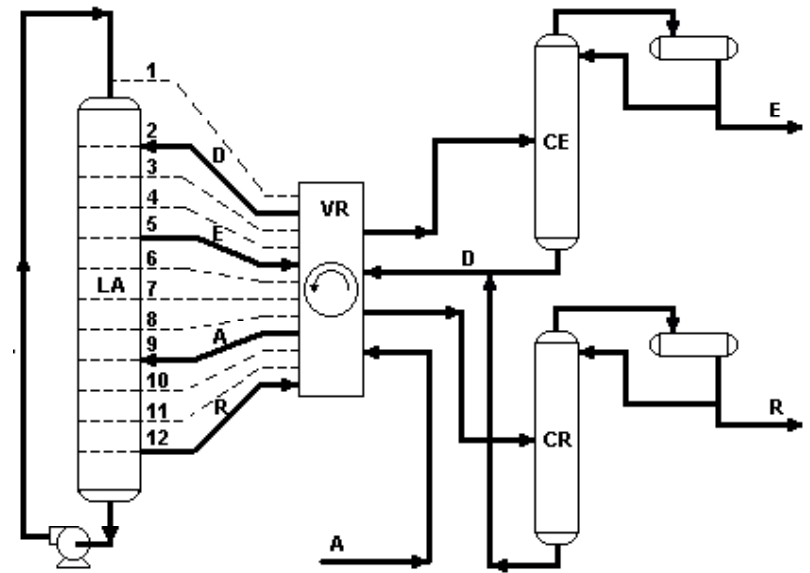
Separação de xilenos por SMB

Separação de C₈ Aromatics Separation

- Distilação x Cristalização x Adsorção

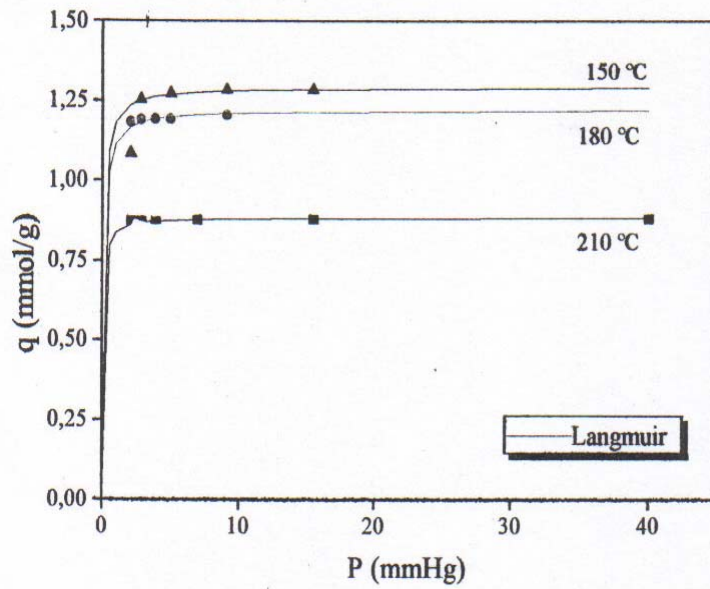
Industrial Process

- UOP Parex
- *Pellets Y Zeolite*
- P-Diethylbenzene
- Pressões e temperaturas moderadas

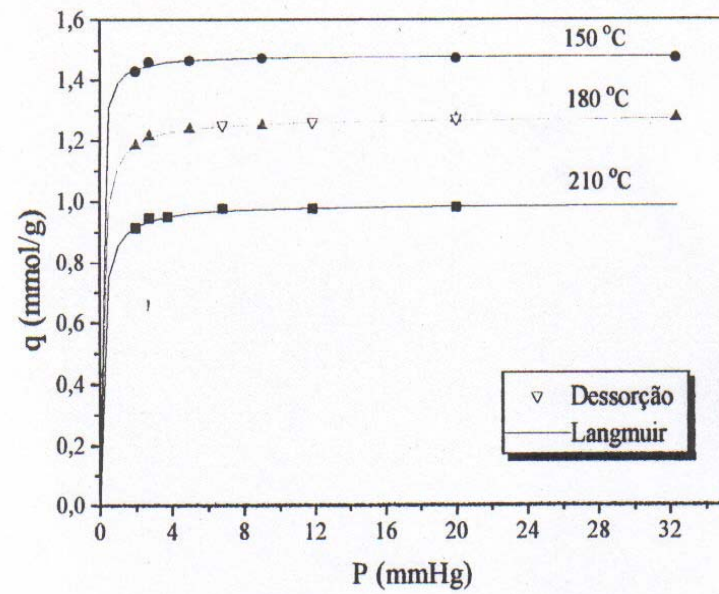


Separação de xilenos por SMB

Isotermas zeolite Y

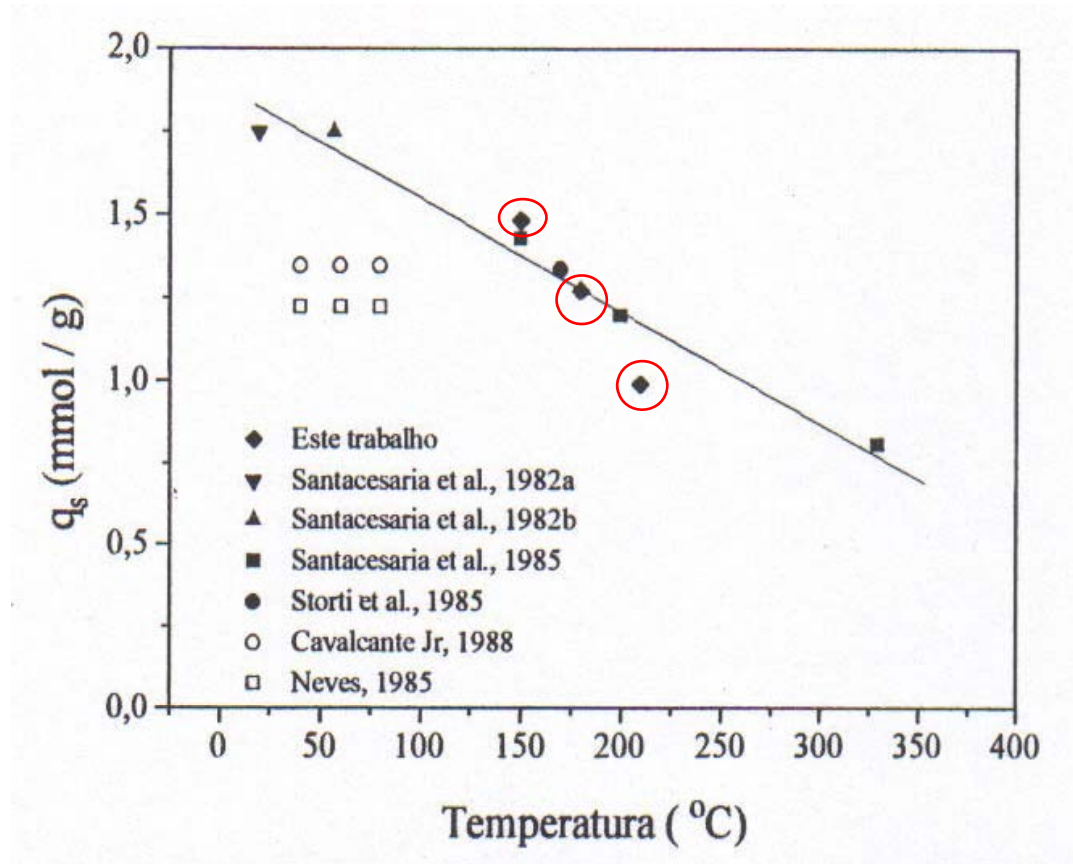


oX



pX

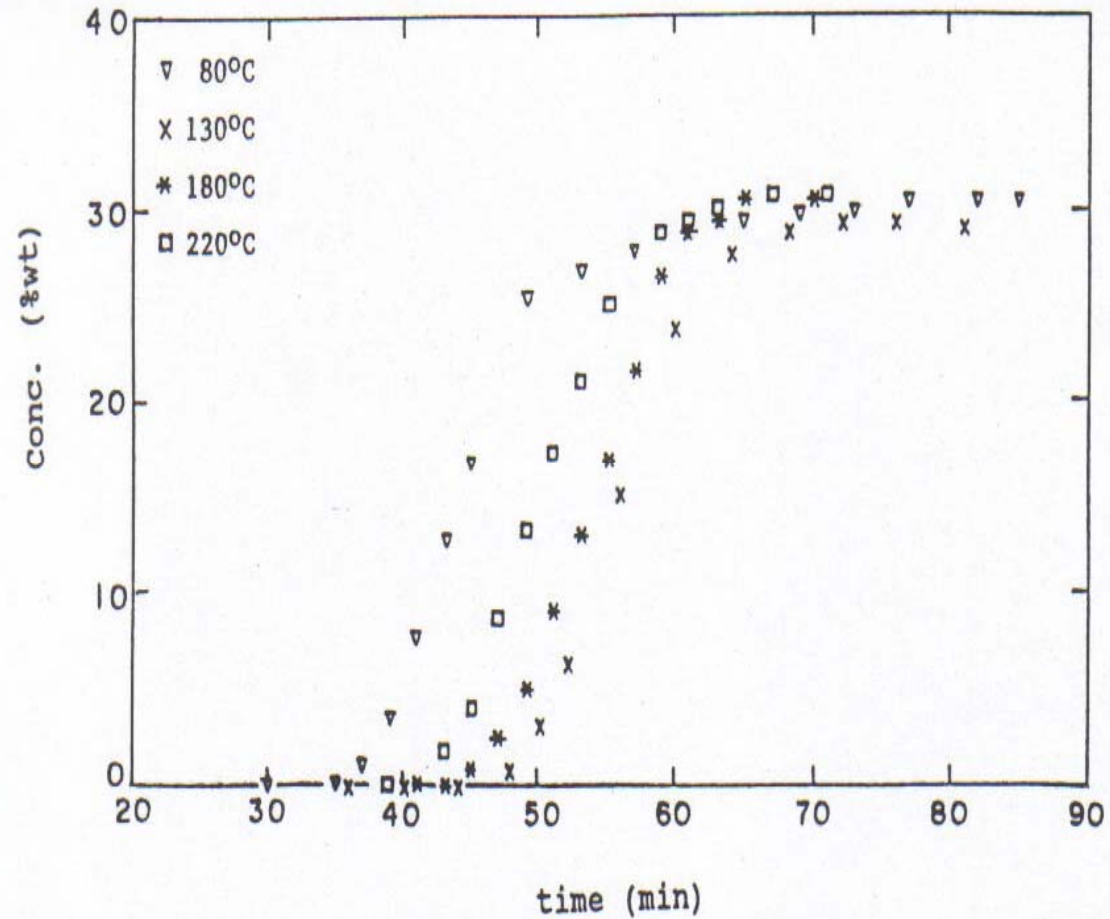
Separação de xilenos por SMB



Variação do limite de saturação do p-xileno em zeólito Y comercial com a temperatura

Separação de xilenos por SMB

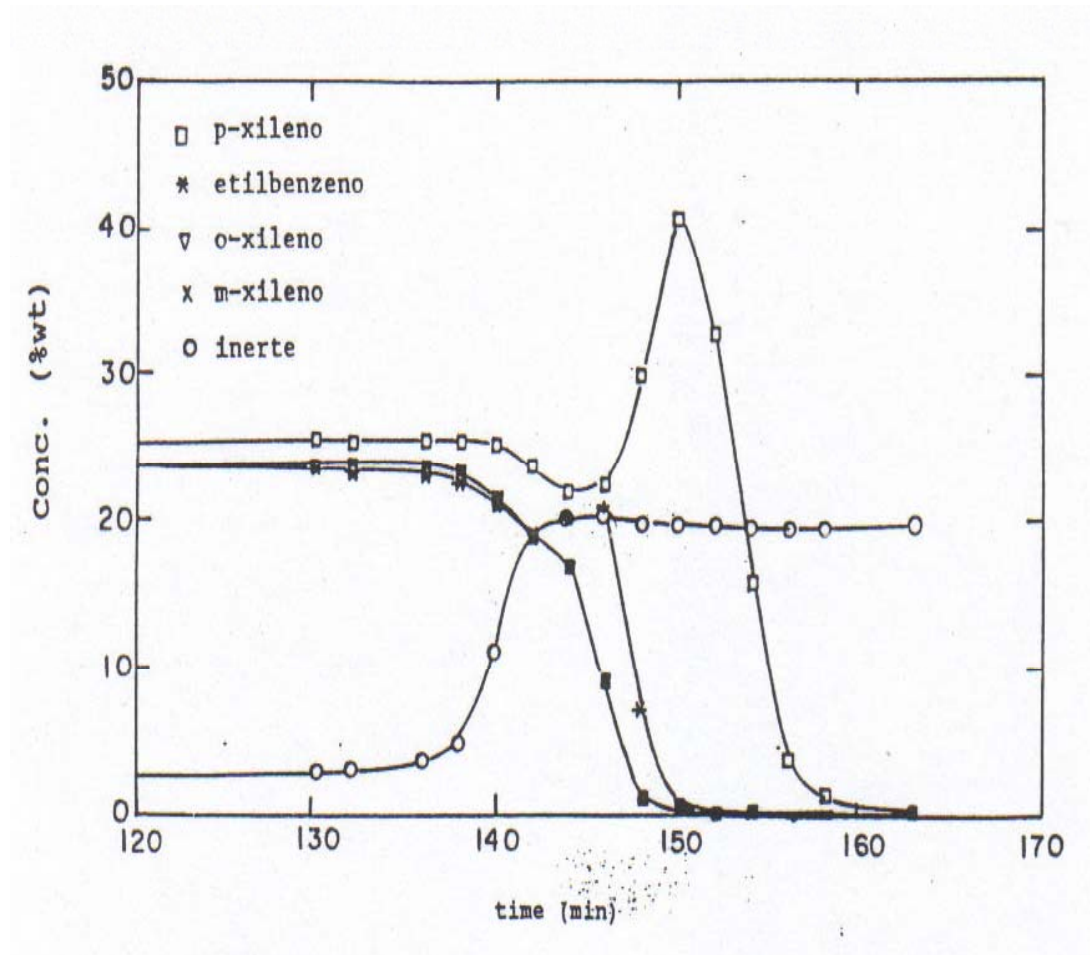
Curvas Breakthrough



p-Xylene Breakthrough in Y zeolite: different temperatures

Separação de xilenos por SMB

Multicomponente



Multicomponent Xylenes Breakthrough in Y zeolite

Separação de xilenos por SMB

Capacidade Total de Adsorção:	1.16 mmol/g
Seletividade pX/mX:	3.04
Seletividade pX/oX :	3.04
Seletividade pX/EB :	2.60

Separação de xilenos por SMB

Estudos Binários OX/PX (60°C)

$$\alpha_{PX/OX} = \frac{z_{PX} / z_{OX}}{x_{PX} / x_{OX}} = 5.7$$

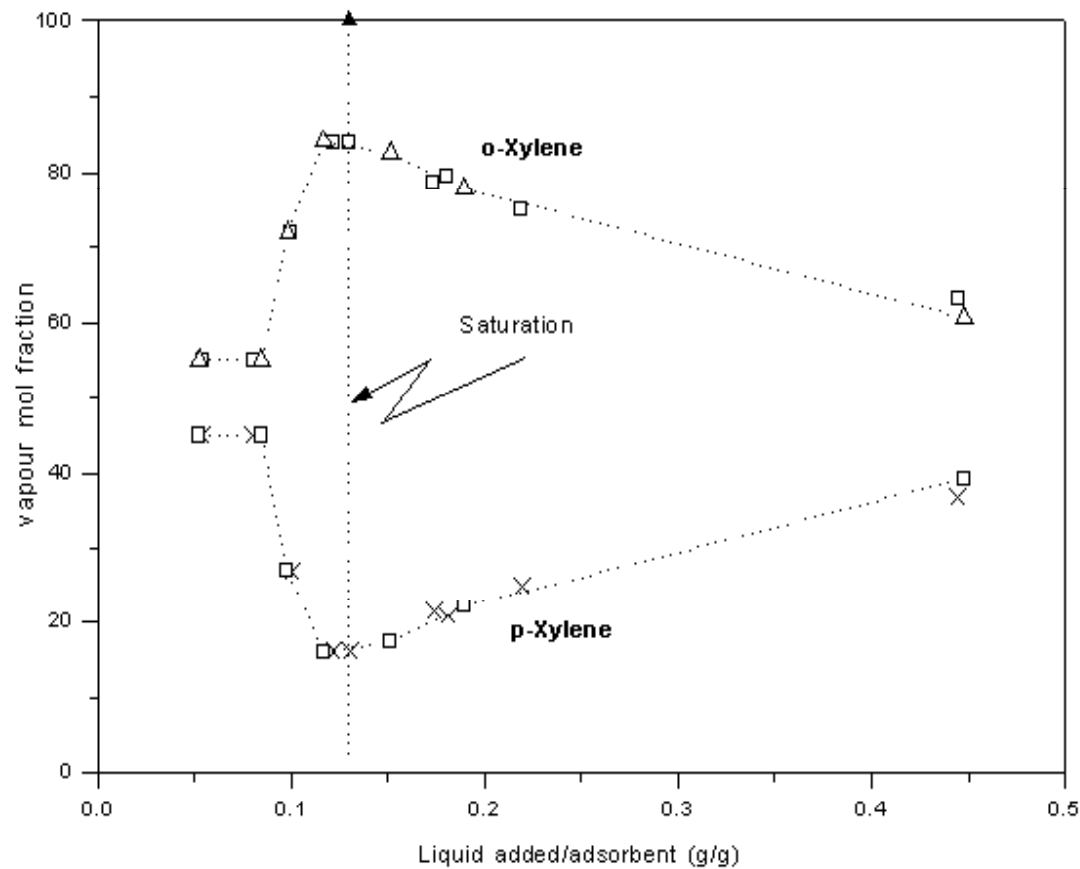
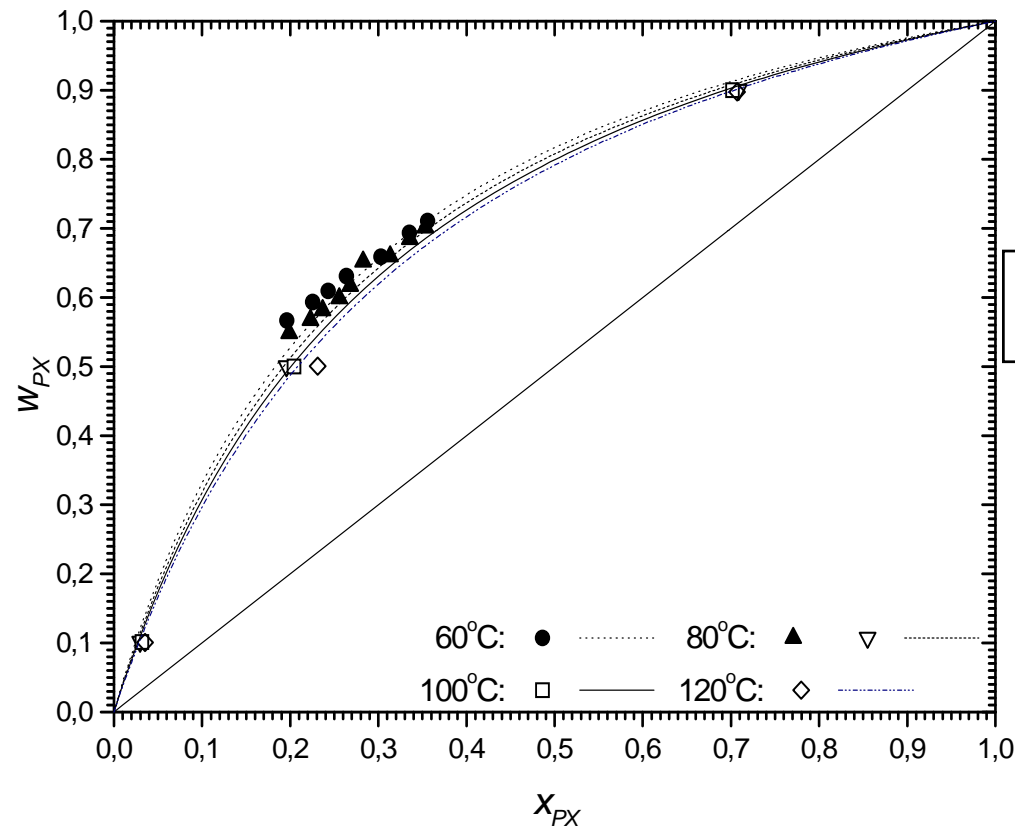


Figure 2: Results of headspace measurements for an equimolar mixture of *p*-xylene/*o*-xylene adsorbed on BaY zeolite pellets at 60°C. Note the coincidence between replicate experiments.

Separação de xilenos por SMB

Equilíbrio binário

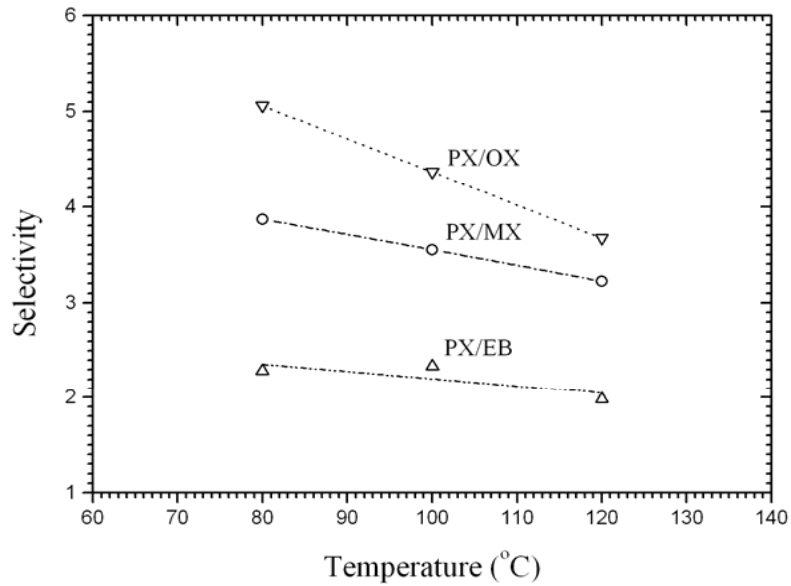


Buarque et al.,
Sep. Sci. Tech., (2005)

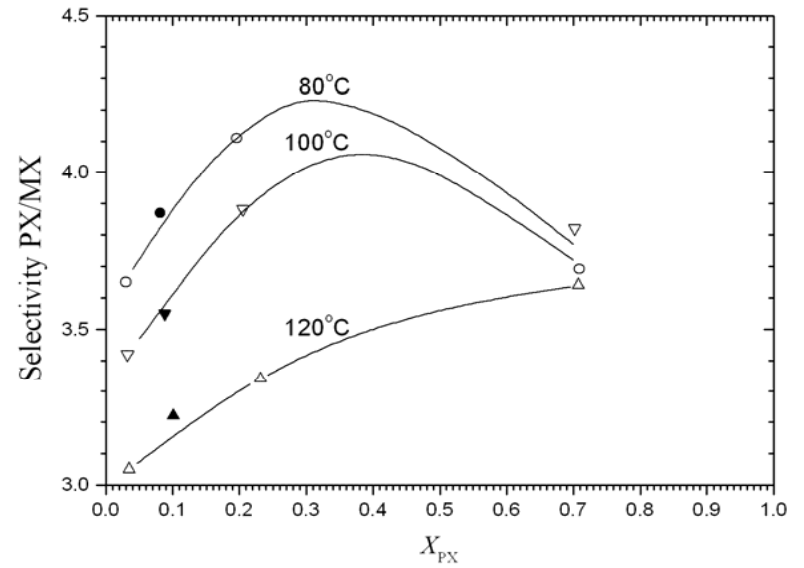
Dados binários PX/MX. Open symbols are experimental data from this work; solid symbols are experimental data from Neves (1995); lines are multicomponent Langmuir fittings

Separação de xilenos por SMB

Xylene Binários



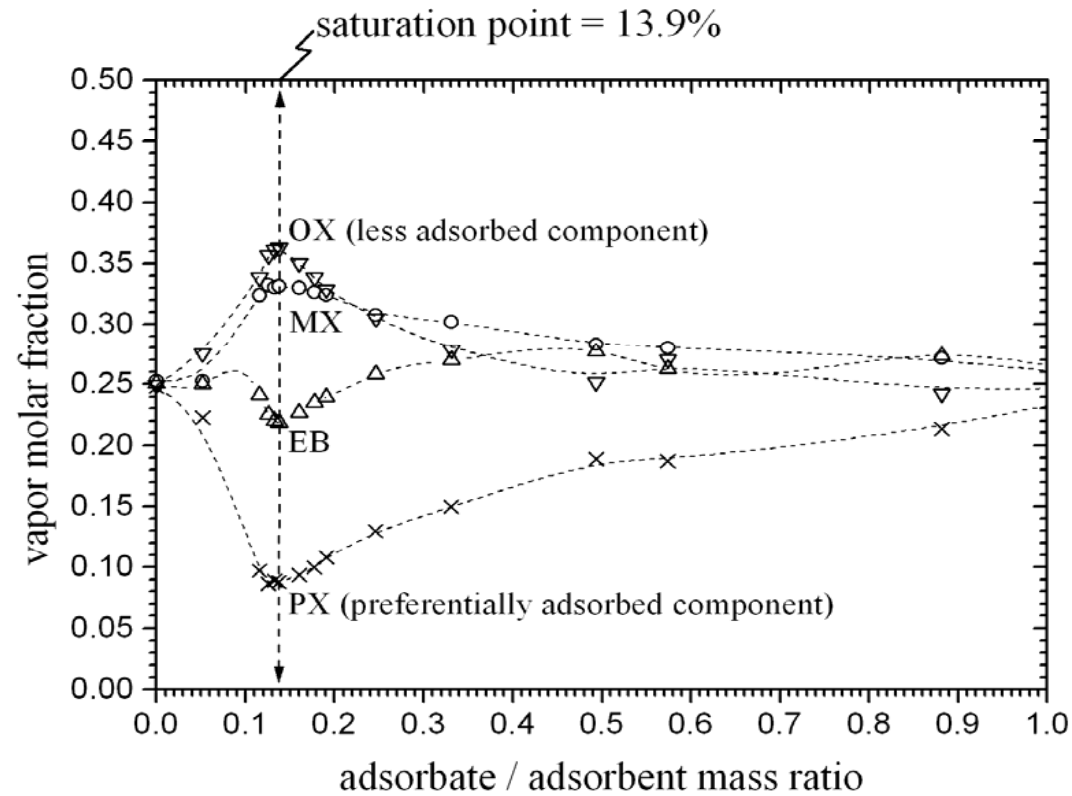
Influência da temperatura



Influência da Composição

Separação de xilenos por SMB

Headspace - Quaternário



Buarque et al., *Sep. Sci. Tech.*, (2005)

Separação de xilenos por SMB

Headspace - Seletividades

Table 6. Experimental selectivities of C₈ aromatics on Y zeolite at different temperatures

T [°C]	X_{PX}	X_{MX}	X_{OX}	W_{PX}	W_{MX}	W_{OX}	α_{PX-MX}	α_{PX-OX}	α_{PX-EB}
80	0.030	0.970	—	0.101	0.899	—	3.65	—	—
	0.196	0.804	—	0.500	0.500	—	4.11	—	—
	0.709	0.291	—	0.900	0.100	—	3.69	—	—
	0.081	0.317	0.413	0.248	0.250	0.250	3.87	5.06	2.29
100	0.032	0.968	—	0.101	0.899	—	3.42	—	—
	0.205	0.795	—	0.500	0.500	—	3.88	—	—
	0.702	0.298	—	0.900	0.100	—	3.82	—	—
	0.088	0.316	0.387	0.248	0.250	0.250	3.55	4.37	2.34
120	0.035	0.965	—	0.101	0.899	—	3.05	—	—
	0.231	0.769	—	0.5016	0.499	—	3.34	—	—
	0.707	0.293	—	0.898	0.102	—	3.64	—	—
	0.101	0.326	0.371	0.250	0.250	0.250	3.22	3.67	1.98

Separação de xilenos por SMB

Difusividades por ZLC

Gás de Arraste	Vazão de Purga (ml/min)	D_m (cm ² /s)	$\epsilon_p D_p$ (cm ² /s)	τ_p
Nitrogênio	34	0.156	0.079	2.0
Nitrogênio	68	0.156	0.131	1.2
Nitrogênio	102	0.156	0.189	0.8
Hélio	34	0.474	0.114	4.1
Hélio	102	0.474	0.317	1.5
				τ_p médio $\cong 2.0$

Separação de xilenos por SMB

Dinâmica em Leito Fixo

Linear Driving Force – LDF (all resistances coupled in a lumped coefficient K_L)

$$u \frac{\partial c_{e,j}}{\partial z} + \varepsilon_e \frac{\partial c_{e,j}}{\partial t} - D_L \varepsilon_e \frac{\partial^2 c_{e,j}}{\partial z^2} = -K_{L,j} (c_{e,j} - c_{i,j}) \frac{3}{r_p} (1 - \varepsilon_e)$$

$$\varepsilon_i \frac{\partial c_{i,j}}{\partial t} = K_{L,j} \frac{3}{r_p} (c_{e,j} - c_{i,j}) - \rho_s (1 - \varepsilon_i) \frac{dq_j}{dt}$$

$$\frac{\partial q_j}{\partial t} = \sum_{l=1}^{NC} \frac{f_{eq}(c_{i,l})}{\partial c_{i,l}} \frac{\partial c_{i,l}}{\partial t}$$

equilibrium:
$$f_{eq}(c_{i,j}) = \frac{q_{m,j} K_j c_{i,j}}{1 + \sum_{l=1}^{NC} K_l c_{i,l}}$$

(Langmuir multicomponent)

Determination of K_L :

$$\frac{1}{K_L} = \frac{1}{k_e} + \frac{1}{k_i \varepsilon_i}$$

$$k_i = \frac{5D_m / \tau}{r_p}$$

Separação de xilenos por SMB

Dinâmica em Leito Fixo

Boundary Conditions:

$$uc_{e,j}^F = uc_{e,j} - \varepsilon_e D_L \left. \frac{\hat{a}_{e,j}}{\hat{z}} \right|_0 \quad \text{for } z = 0, t > 0$$

$$\left. \frac{\hat{a}_{e,j}}{\hat{z}} \right|_L = 0 \quad \text{for } z = L, t > 0$$

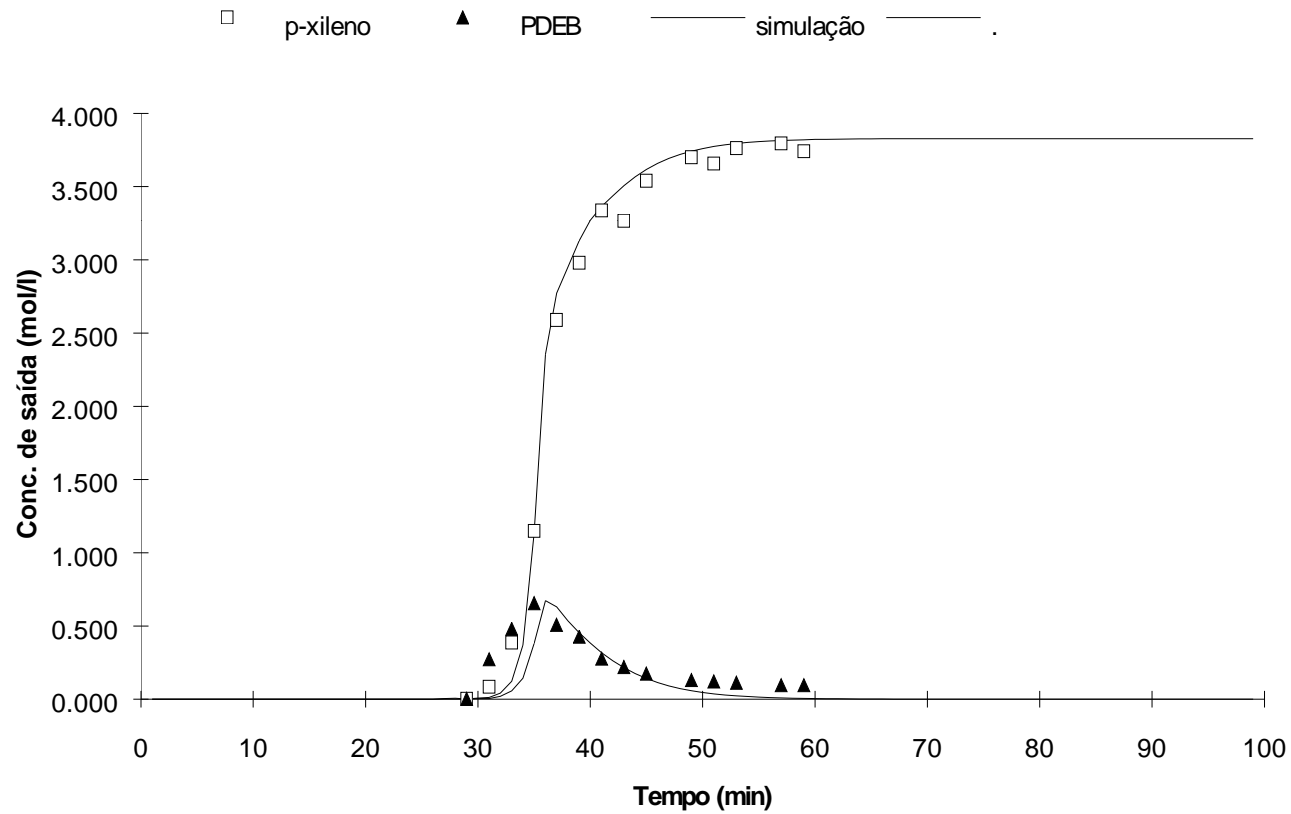
$$c_{e,j}(z,0) = c_{e,j}^0(z) \quad \text{for } t = 0, z > 0$$

$$c_{i,j}(z,0) = c_{i,j}^0(z) \quad \text{for } t = 0, z > 0$$

$$q_j(z,0) = q_j^0(z) \quad \text{for } t=0, z > 0$$

Separação de xilenos por SMB

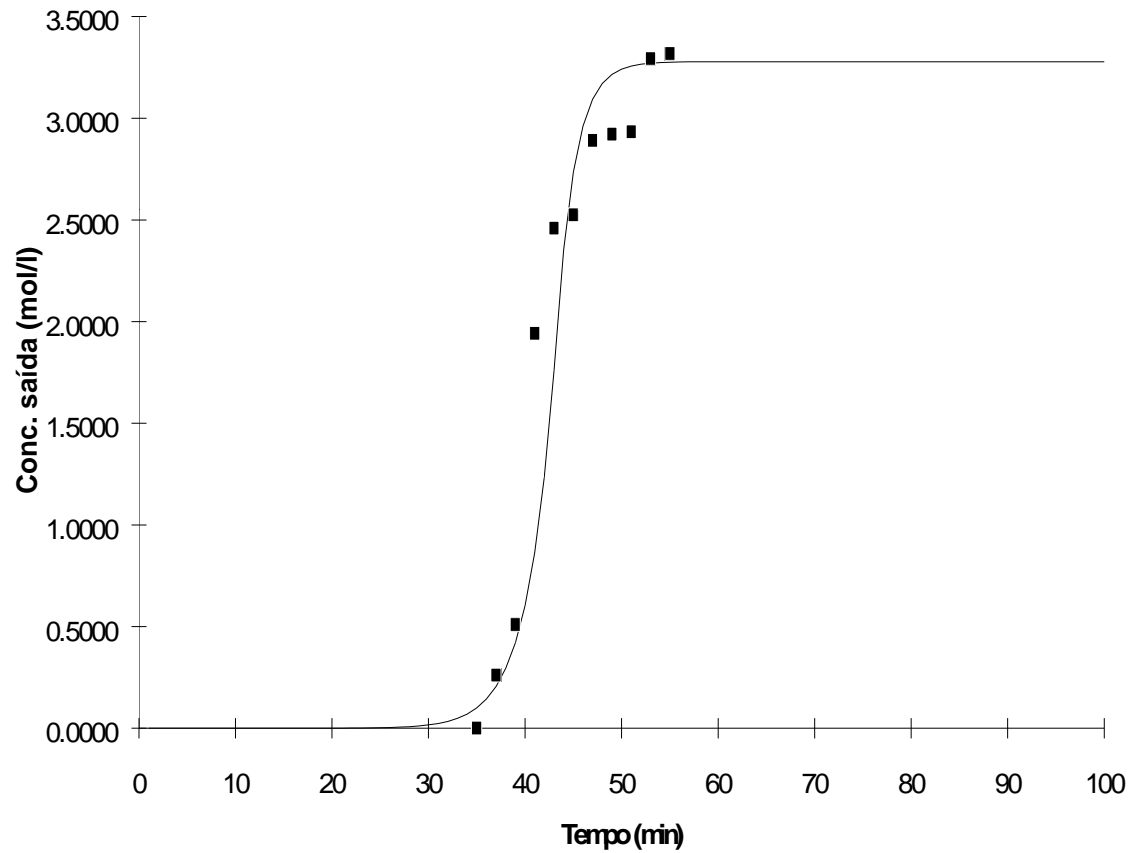
Dinâmica em Leito Fixo



Model and experimental: p-xylene at 80°C.

Separação de xilenos por SMB

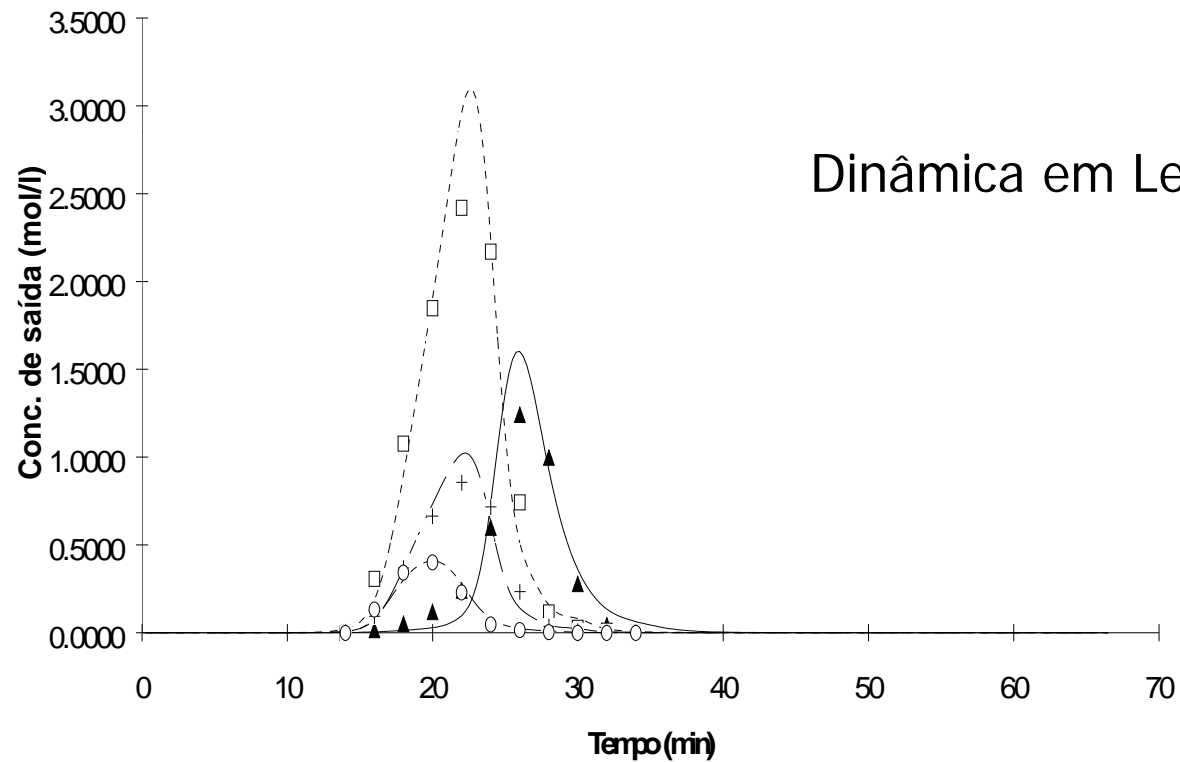
Dinâmica em Leito Fixo



Model and experimental: p-xylene at 180°C.

Separação de xilenos por SMB

▲ p-xileno ——— . □ m-xileno - - - - .
+ o-xileno — — — . ○ n-octano - - - - .

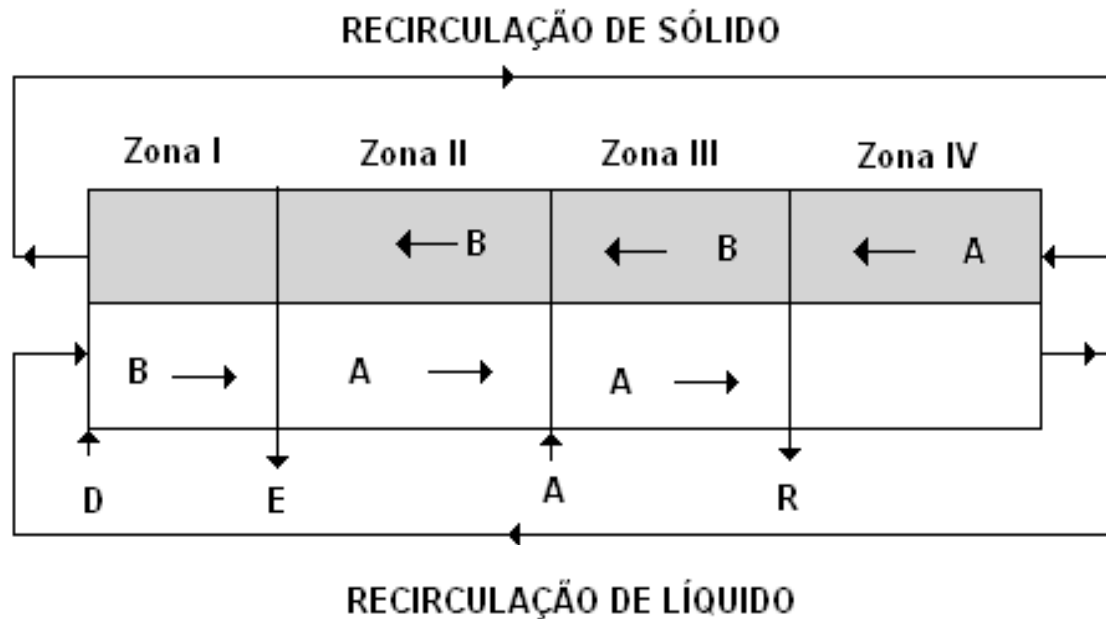


Model and experimental: multicomponent pulse at 180°C.

Separação de xilenos por SMB

Processo Industrial

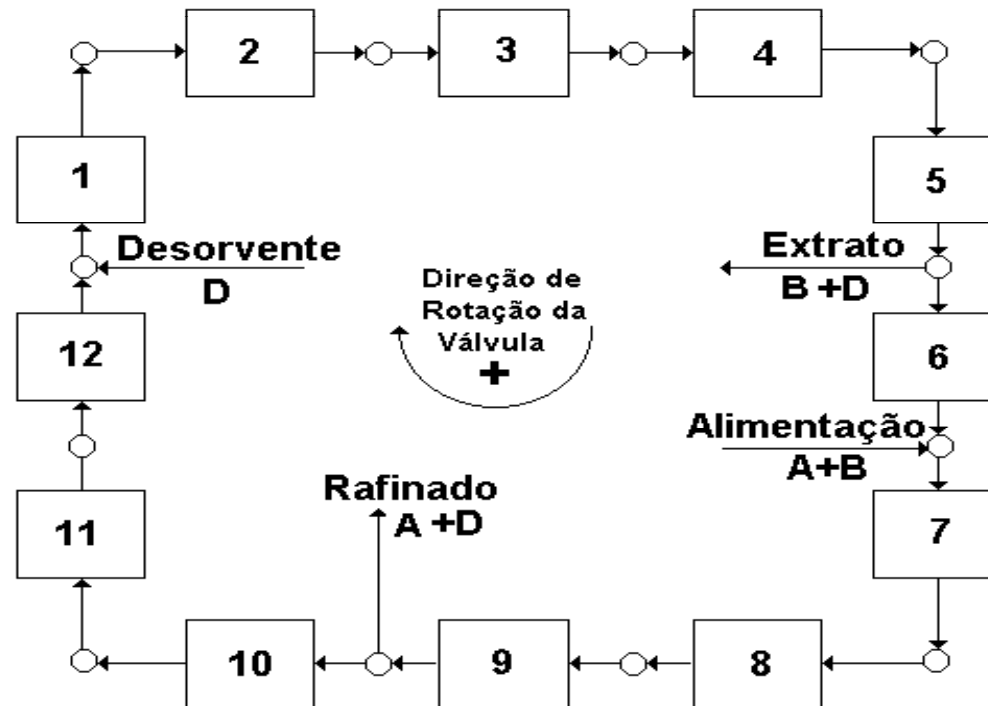
True Moving Bed



Separação de xilenos por SMB

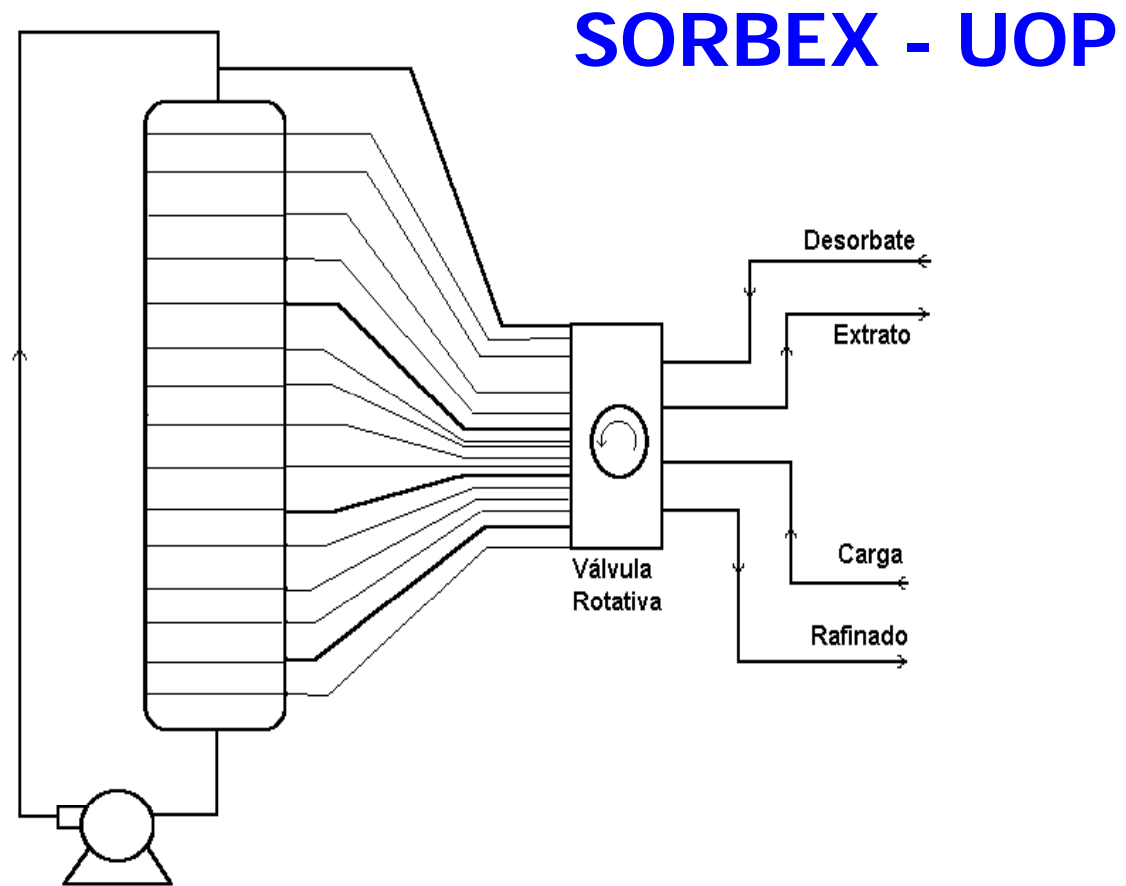
Processo Industrial

Simulated Moving Bed



Separação de xilenos por SMB

Processo Industrial



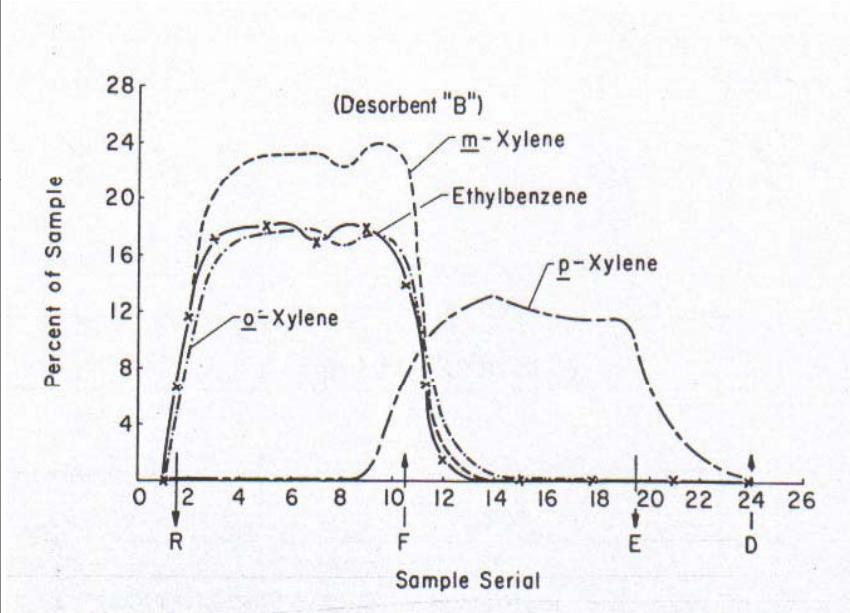
Separação de xilenos por SMB

Processo Industrial (SORBEX)

<u>Processo</u>	<u>Separação</u>	<u>Unidades licenciadas</u>
Parex	p-xileno/C8 aromáticos	70
Molex	Parafinas lineares/Hidro-carbonetos cíclicos e ramificados	30
Olex	Olefinas/Parafinas	5
Sarex	Frutose/Dextrose	5
Outros	Outros	5
		TOTAL: 115

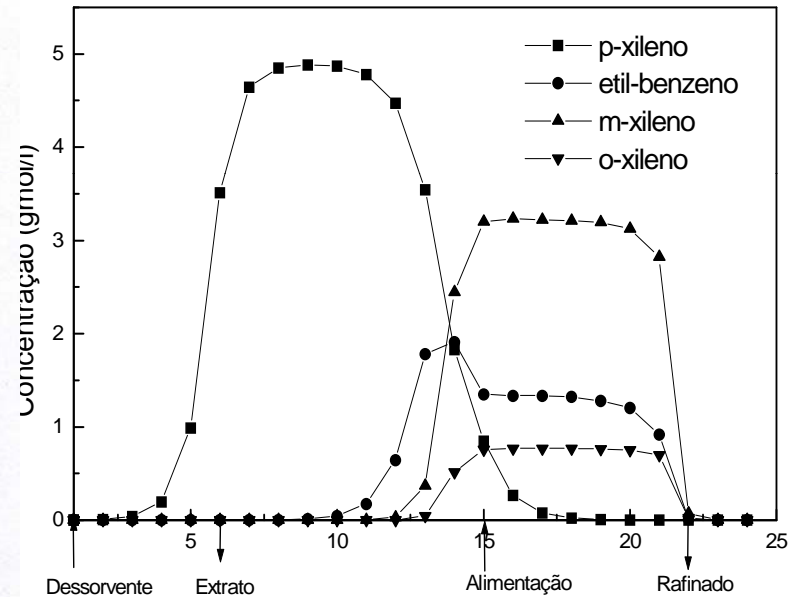
Separação de xilenos por SMB

Pilot Plant (UOP)



Perfil Interno de Concentrações Experimental, obtidos em Planta Piloto *Sorbex* para C8 Aromáticos em Zeolitos Y

Model
w/ exp'l data from our lab



Perfil interno de concentrações em regime permanente para um SMB com xilenos

APLICAÇÕES

- 1) Remoção de Poli-aromáticos em Materiais Mesoporosos*
- 2) Purificação de H₂ por PSA*
- 3) Separação de Xilenos por SMB*
- 4) Transesterificação de óleos vegetais para obtenção de biodiesel***



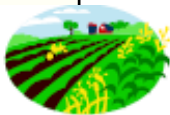
UFC

PROCESSOS COM BIODIESEL

- Fonte renovável de energia
- *Mais lubricidade => melhora vida útil dos motores*
- *Menos poluente => menos enxofre e aromáticos compounds*
- *Menor dependência externa de combustíveis fósseis*
- *Benefícios sociais, especialmente na área rural*



Fontes de óleo vegetal



Palma / Soja



Babaçu-Mamona-Palma



**Soja-Mamona-
Algodão (caroço)**



Soja-Algodão-Girassol

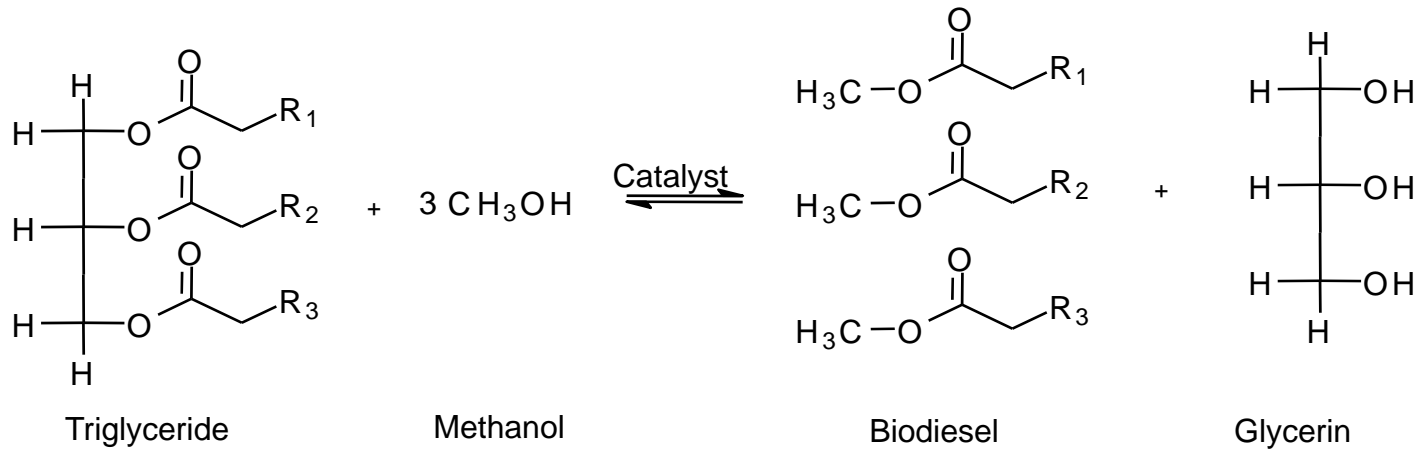
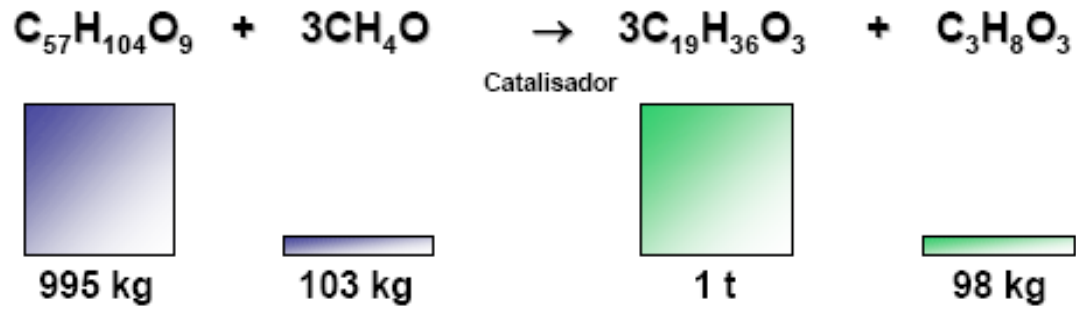


Soja-Algodão-Girassol

MAMONA



Óleo vegetal + Metanol → Esters + Glicerol



Óleo vegetal + Etanol



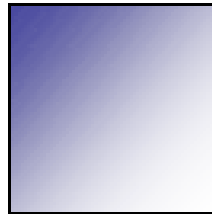
Esters

+

Glicerol



Catalisador

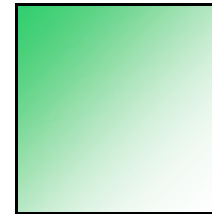


954 kg



140 kg

Batelada



1 t



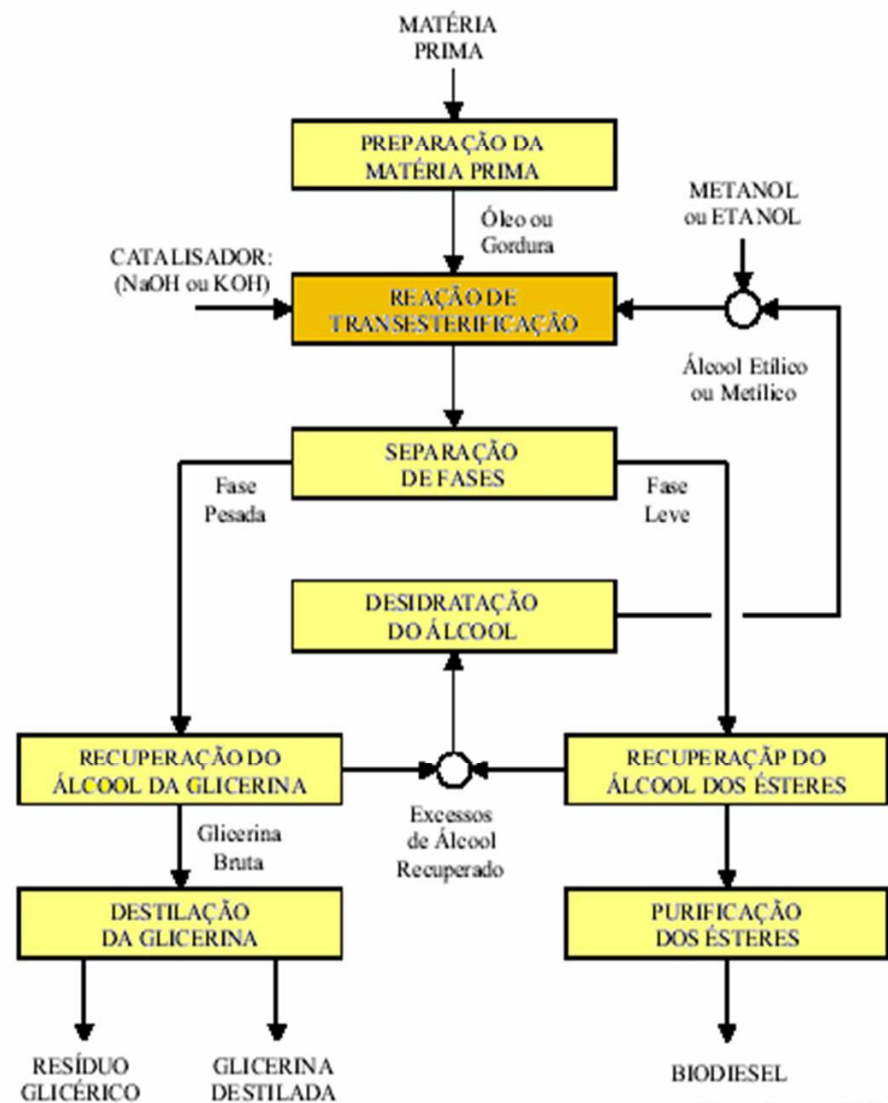
94 kg

- Ethanol is preferred because it can be locally produced, mainly from sugarcane;
- Ethanol brings more phase separation difficulties compared to methanol.

PROCESSO INDUSTRIAL HOMOGÊNEO

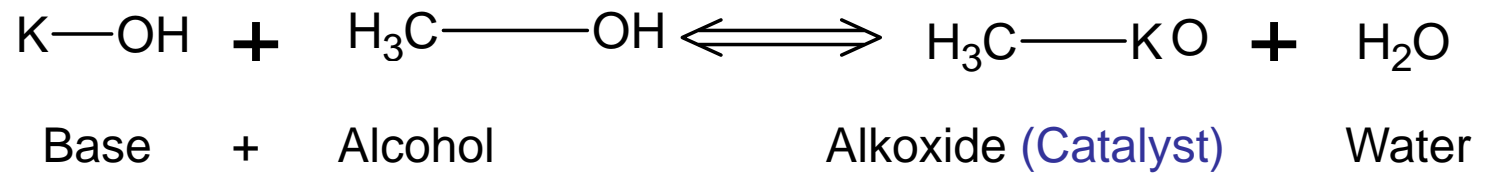
Etapas:

- Preparação catalisador
- Reação transesterificação
- Separação de fases
- Remoção de álcool e sab



Fonte: Parente, E. J. S.

Preparação do catalisador In situ

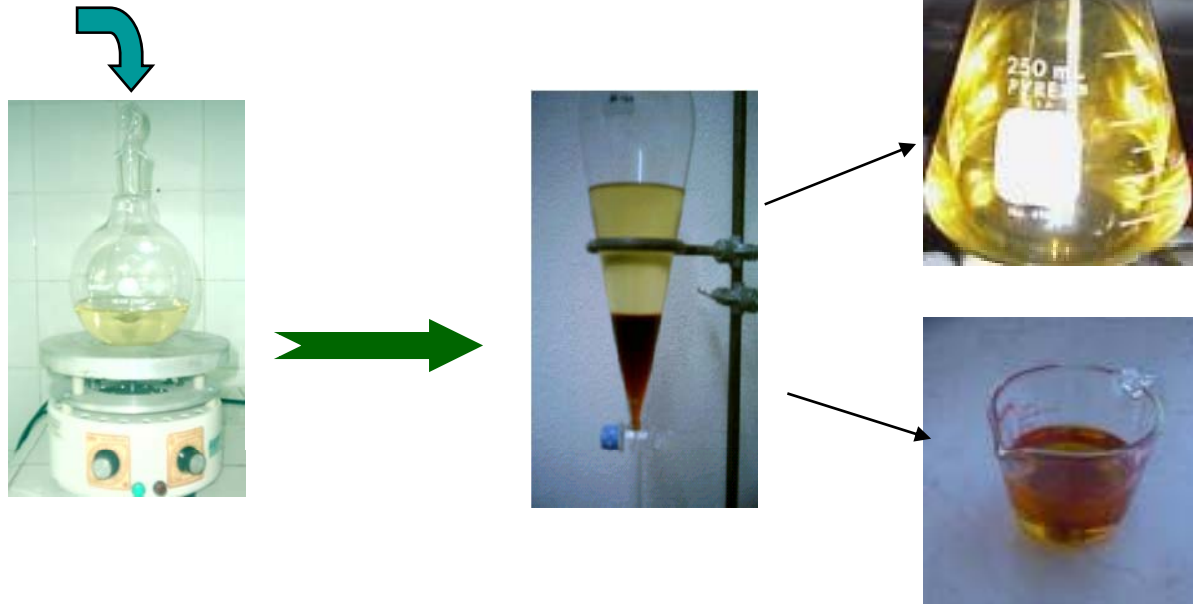


- Reação reversível: remoção de água favorece a formação do catalisador.
- Zeolite A pode ser usado para remoção de água.

Separação de fases

Separação extrativa (light and heavy phases)

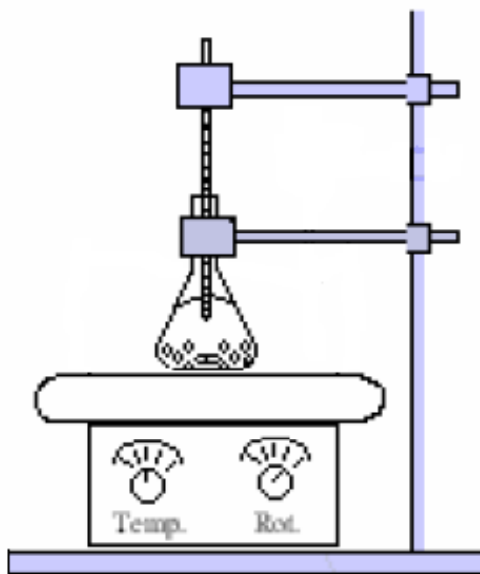
- Vegetable Oil
- Alcohol
- Catalyst



- Fase leve: ester + alcool (etanol/metanol)
- Fase pesada: glicerol + alcool (etanol/metanol)

REMOÇÃO DE ÁGUA USANDO ZEOLITO 3A

- Zeolito 3A adicionado na etapa de formação do catalisador
- Zeolito 3A adicionado na etapa de reação de transesterificação
- Razão (alcalinidade livre/alcalinidade total) => indica a quantidade de catalisador ativo ainda presente na reação.



Albuquerque et al., Energy and Fuels, in press (2009)

REMOÇÃO DE ÁGUA USANDO ZEOLITO 3A

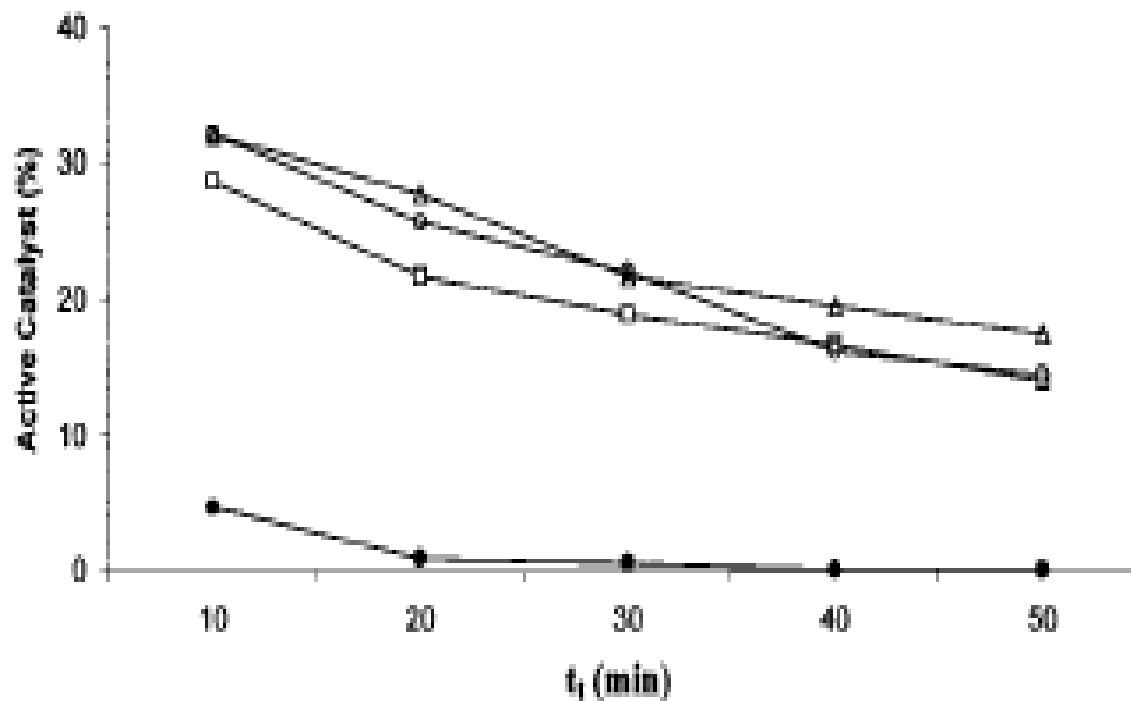


Figure 2. Effect of the adsorbent contact time during catalyst formation (t_1) [(●) Homogeneous catalyst only; using adsorbent in both steps ($W_c = 0.5$ and $W_t = 0.3$), (□) 60 min, (△) 120 min, and (○) 180 min].

REMOÇÃO DE ÁGUA USANDO ZEOLITO 3A

Case	Experiment	Catalyst formation	Transesterification reaction	Conversion (% wt)
Only homogeneous catalyst	1	$W_c = 0.0;$ $t_c = 180\text{min}$	$W_t = 0.0;$ $t_t = 50\text{min}$	44.6
	2	$W_c = 0.3;$ $t_c = 180\text{min}$	$W_t = 0.0;$ $t_t = 50\text{min}$	54.7
	3	$W_c = 0.4;$ $t_c = 180\text{min}$	$W_t = 0.0;$ $t_t = 50\text{min}$	52.3
	4	$W_c = 0.5;$ $t_c = 180\text{min}$	$W_t = 0.0;$ $t_t = 50\text{min}$	52.1
Case 1	5	$W_c = 0.5;$ $t_c = 60\text{min}$	$W_t = 0.3;$ $t_t = 50\text{min}$	56.2
	6	$W_c = 0.5;$ $t_c = 120\text{min}$	$W_t = 0.3;$ $t_t = 50\text{min}$	72.2
	7	$W_c = 0.5;$ $t_c = 180\text{min}$	$W_t = 0.3;$ $t_t = 50\text{min}$	64.3

Albuquerque et al., Energy and Fuels, accepted (2009)

COMENTÁRIOS FINAIS



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OUTRAS APLICAÇÕES EM ESTUDO NO GRUPO

- *Armazenamento de gás natural*
- *Dióxido de carbono*
- *Desulfurização de combustíveis*
- *Difusão de hidrocarbonetos em zeolitos*
(Beta, mordenita, silicalita)
- *Adsorventes alternativos para separação de xilenos*
- *Separação de açúcares (caju)*
- *Óleos lubrificantes ou óleos mais pesados*
- *Materiais mesoporosos para separação e catálise em biocombustíveis e biolubrificantes*
- *Separação de produtos biotecnológicos (ácido hialurônico, enzimas)*



UFC



Financiadores

CAPES

CNPq

FUNCAP

ANP

FINEP

PETROBRAS

COPENE / BRASKEM

etc.

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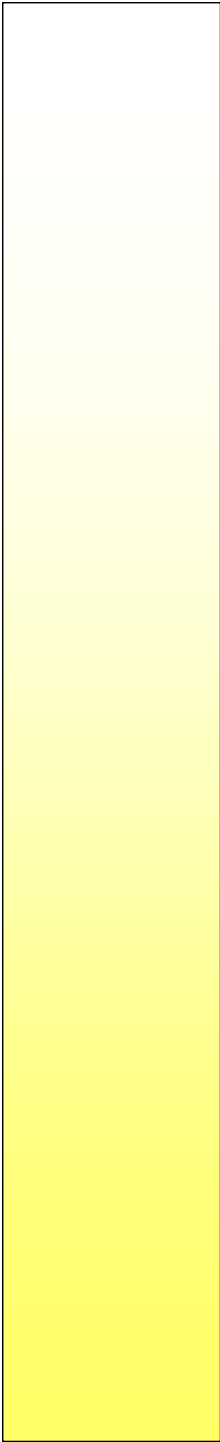
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Mardonio Lucena

Ivanildo Silva

Monica Albuquerque

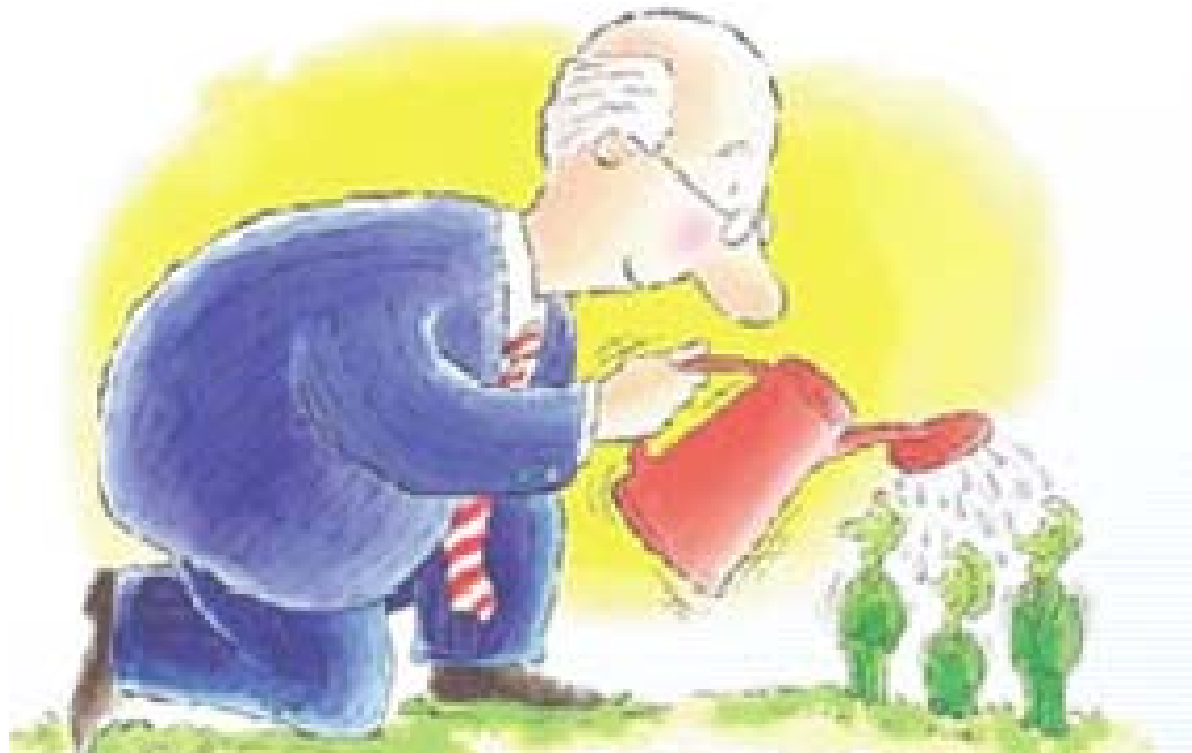
Rodrigo Vieira



Cerca de 100 estudantes que já
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A LITTLE HISTORY BOOK

extract from
*Jim Ritter's talk at the
AIChE Centennial Meeting
Philadelphia, Nov 2008*

I. Langmuir, JACS 40 (1918) 1361-1403

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM.

BY IRVING LANGMUIR.

Received June 25, 1918.

In his studies of the continuous change from the liquid to the vapor state, at temperatures above the critical, van der Waals developed the theory that at the boundary between a liquid and its vapor there is not an abrupt change from one state to the other, but rather that a transition layer exists in which the density and other properties vary gradually from those of the liquid to those of the vapor.

This idea of the continuous transition between phases of matter has been applied very generally in the development of theories of surface phenomena, such as surface tension, adsorption, etc.

Eucken,¹ for example, in dealing with the theory of adsorption of gases, considers that the transition layer is a sort of miniature atmosphere, the molecules being attracted to the surface by some kind of "action at a

¹ Eucken, *Verh. deut. physik. Ges.*, 16, 345 (1914).

PROCESSES OF ADSORPTION AND DIFFUSION
ON SOLID SURFACES.

BY J. E. LENNARD-JONES (*Bristol*).

Received 4th January, 1932.

§ 1.

The literature pertaining to the sorption of gases by solids is now so vast¹ that it is impossible for any, except those who are specialists in the experimental technique, rightly to appraise the work, which has been done, or to understand the main theoretical problems which require elucidation. The author has been fortunate in this respect in having the benefit of the experience of Professor Garner, who has brought to his attention from time to time many of the problems relating to sorption and has sifted the experimental material for this purpose. The ideas in this paper have been stimulated by these discussions and it seemed appropriate to bring them forward tentatively for discussion at this meeting.

As the author understands it, one of the main problems which recent work has emphasised is the nature of the cohesion which holds gases to solid surfaces, and whether molecules are held as molecules or dissociated into atoms. The same gas and the same solid appear in certain cases to interact in a different way according to the temperature. In the case of hydrogen and certain metals, for instance, there is considerable adsorption at very low temperatures, then the adsorption diminishes to a minimum at temperatures between -180° and 0° , increases to a maximum and then diminishes again at high temperatures.² Garner³ has found in some cases evidence that there is still another increase of adsorption at very high temperatures. There appear to be at least

ADSORPTION AND DIFFUSION IN ZEOLITE CRYSTALS

ARNE TISELIUS

University of Upsala, Upsala, Sweden

Received June 20, 1935

Zeolites are silicates of calcium, sodium, or potassium together with some aluminum in the anion structure. They occur as minerals in certain volcanic rocks and often form very large and beautiful crystals. Artificial zeolites are made technically for use in water-softening processes, but these substances are not nearly as well defined or well crystallized as the natural minerals.

It has been known for a long time that zeolite crystals show some very unusual properties. (For complete literature references see ref. 2.) They are capable of exchanging reversibly both the cations in the structure against others (for example, Ca against 2Na, and so on), and the water of crystallization against other substances, like ammonia, carbon dioxide, and hydrogen. The cation exchange is the basis of the technical use of zeolites in water-softening. It is quite remarkable that the exchange processes, if performed carefully, leave the crystal lattice unspoiled, as x-ray measurements have shown. Only slight modification of the parameters may occur, corresponding to shrinking or expansion of the lattice. Even the

THEORY OF CHROMATOGRAPHY

PART 10.—FORMULÆ FOR DIFFUSION INTO SPHERES AND THEIR APPLICATION TO CHROMATOGRAPHY

BY E. GLUECKAUF

Atomic Energy Research Establishment, Harwell, Nr. Didcot, Berks.

Received 1st December, 1954; in final form, 17th May, 1955

A method is shown which permits a test of various empirical diffusion equations giving the rate of the mean internal concentration change $d\bar{q}/dt$ as function of the mean internal concentration \bar{q} and the surface concentration q .

$$\frac{d\bar{q}}{dt} = \frac{\pi^2 D}{r^2} (q - \bar{q}) + \left(1 - \frac{\pi^2}{15}\right) \frac{dq}{dt} \quad (\text{A})$$

$$= \frac{15D}{r^2} (q - \bar{q}) \quad (\text{B})$$

$$= \frac{\pi^2 D}{r^2} \frac{(q^2 - \bar{q}^2)}{2\bar{q}} \quad (\text{C}) \quad (\text{Vermeulen } 2)$$

$$= \frac{\pi^2 D}{r^2} (q - \bar{q}) \left(\frac{3}{4}q + \frac{1}{4}\bar{q}\right) / \bar{q} \quad (\text{D})$$

It is shown that, under the conditions occurring in chromatographic columns with substances following linear or moderately curved adsorption or exchange isotherms ($K_d < 3$), where conditions are maintained close to equilibrium, eqn. (A) is almost perfect,

Thermodynamics of Mixed-Gas Adsorption

A. L. MYERS and J. M. PRAUSNITZ

University of California, Berkeley, California

A simple technique is described for calculating the adsorption equilibria for components in a gaseous mixture, using only data for the pure-component adsorption equilibria at the same temperature and on the same adsorbent. The proposed technique is based on the concept of an ideal adsorbed solution and, using classical surface thermodynamics, an expression analogous to Raoult's law is obtained. The essential idea of the calculation lies in the recognition that in an ideal solution the partial pressure of an adsorbed component is given by the product of its mole fraction in the adsorbed phase and the pressure which it would exert as a pure adsorbed component at the same temperature and spreading pressure as those of the mixture. Predicted isotherms give excellent agreement with experimental data for methane-ethane and ethylene-carbon dioxide on activated carbon and for carbon monoxide-oxygen and propane-propylene on silica gel. The simplicity of the calculation, which requires no data for the mixture, makes it especially useful for engineering applications.

Adsorption equilibria are required in the design of heterogeneous chemical reactors and in certain types of separation equipment. In many cases the desired equilibria are for a mixed rather than for a pure gas, and it is therefore of considerable practical interest to develop a technique for estimating the adsorption equilibria of a gaseous mixture from the known adsorption isotherms of the pure components. Such a technique is described here. The principal idea on which the proposed technique is based is the proper definition of an ideal adsorbed solution in a manner analogous to that used for liquid-phase solutions. As shown towards the end of this work, the equations developed from the ideal-solution concept predict adsorption isotherms which are in excellent agreement with experimental adsorption data for gaseous mixtures.

A complete review of the current status of mixed-gas adsorption is given in the excellent monograph by Young and Crowell (12). The usual procedure for the interpretation of experimental adsorption equilibria for a gaseous mixture is to compare the experimental data with the prediction of some theoretical model. Most models for physical adsorption contain two or three parameters, and it is usually assumed that the parameters for mixture adsorp-

The thermodynamics of physical adsorption has been thoroughly discussed by Hill (4). The validity of the usual thermodynamic equations for the adsorbed phase rests upon three assumptions:

1. The adsorbent is assumed to be thermodynamically inert; that is the change in a thermodynamic property of the adsorbent, such as internal energy, during an adsorption process at constant temperature is assumed to be negligible compared with the change in the same property for the adsorbing gas.
2. The adsorbent possesses a temperature-invariant area which is the same for all adsorbates. This assumption would not be valid, for example, for a molecular sieve adsorbent, where the area available for adsorption depends on the size of the adsorbate molecule.
3. The Gibbs definition of adsorption applies; this definition corresponds to the usual volumetric technique of obtaining experimental adsorption isotherms. In most practical cases, the volumetric technique gives the same experimental results as other methods (the gravimetric measurement of adsorption, for example).

The above assumptions are implicit in almost all theories of physical adsorption. These details have been empha-

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE LINDE AIR PRODUCTS COMPANY, A DIVISION OF UNION CARBIDE AND CARBON CORPORATION]

Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A

BY T. B. REED AND D. W. BRECK

RECEIVED APRIL 23, 1956

The new synthetic zeolite, Type A, is cubic, $a_0 = 12.32 \text{ \AA}$, and X-ray data are consistent with space group $O^1\text{-Pm}\bar{3}m$. The unit cell composition is $\text{Me}_{12/n} [(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot N\text{H}_2\text{O}$ where Me is an exchangeable cation of charge n , and N varies from 20 to 30. The unit cell dimension varies slightly with the cation present. The aluminosilicate framework consists of 24(Si,Al)- O_4 tetrahedra which are joined to form 8-membered oxygen rings in the faces and distorted 6-membered rings on the 3-fold axes. A large cavity 11.4 \AA in diameter occupies the center of the cell and smaller 6.6 \AA cavities are located on the 3-fold axes. Probable positions of the cations in the lithium, sodium, thallium and calcium forms are indicated, and correlation of the structure with the adsorptive and ion-exchange properties of the Type A zeolite is discussed.

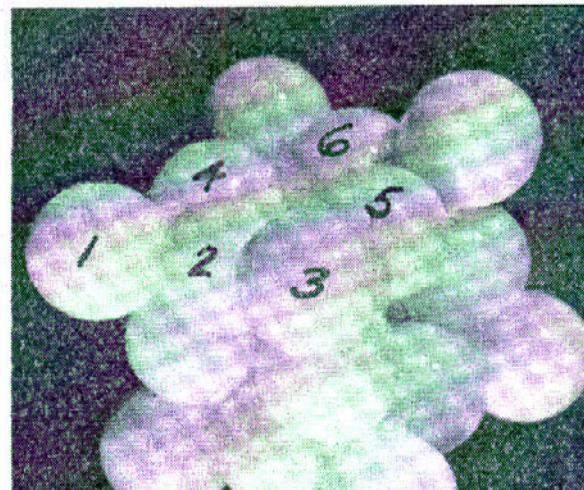
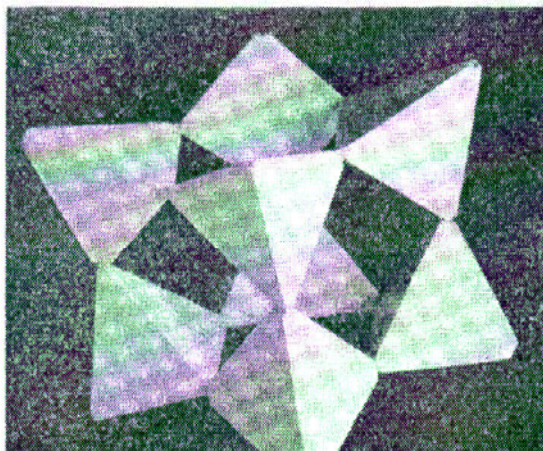
Introduction

A new synthetic crystalline zeolite, not known to exist in nature, has been reported recently and its properties described.¹ The novel adsorptive properties of certain zeolites after dehydration have been the subject of many investigations and are intimately related to their open crystal structure and pores of uniform dimensions.^{2,3} In order to

Experimental

The composition of the Type A zeolite is expressed by the structural formula $\text{Me}_{12/n} [(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot N\text{H}_2\text{O}$ where Me represents exchangeable cations of charge n . The aluminosilicate framework, $[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$, will be designated by [A].

The largest crystals of the Type A zeolite that have been prepared are about 25 μ in diameter, so that most of the structural work was done from X-ray powder diffraction data obtained on a geiger-counter spectrometer as previously



United States Patent Office

3,130,007
Patented Apr. 21, 1964

1

3,130,007
CRYSTALLINE ZEOLITE Y

Donald W. Breck, Tonawanda, N.Y., assignor to Union Carbide Corporation, a corporation of New York
No Drawing. Filed May 12, 1961, Ser. No. 109,487
30 Claims. (Cl. 23-113)

This invention relates to a synthetic, crystalline, zeolitic sodium aluminosilicate of the molecular sieve type which is useful as an adsorbent, and to a method for making the composition.

It is an object of this invention to provide a novel, synthetic, crystalline, zeolitic, sodium aluminosilicate of the molecular sieve type which is suitable for use as an adsorbent.

Another object of the present invention is to provide a method of making the novel adsorbent of the invention.

Other objects will be apparent from the subsequent disclosure and appended claims.

Naturally-occurring, crystalline, hydrated, metal aluminosilicates are called zeolites. The synthetic, crystalline, sodium aluminosilicate described herein will be designated hereinafter as "zeolite Y" to distinguish it from other materials.

Certain adsorbents, including zeolite Y, selectively adsorb molecules on the basis of the size and shape of the adsorbate molecule and are called molecular sieves. Molecular sieves have a sorption area available on the inside of a large number of uniformly sized pores of molecular dimensions. With such an arrangement, molecules of a certain size and shape enter the pores and are adsorbed, while larger or differently-shaped molecules are excluded. Not all adsorbents behave in the manner of molecular sieves. The common adsorbents, charcoal and silica gel, for example, do not exhibit molecular sieve action.

The crystals of zeolite Y are basically three-dimensional frameworks of SiO_4 and AlO_4 tetrahedrons cross-linked by the sharing of oxygen atoms. The electrovalence of each tetrahedron containing aluminum is balanced by the presence in the aluminosilicate framework of a cation such as an alkali metal ion. The void spaces

2

TABLE A

	hkl	$h^2+k^2+l^2$	$d, \text{A.}$	Relative Intensity
5	111	3	14.37-14.15	VS
	220	8	8.80-8.67	M
	311	11	7.50-7.39	M
	331	19	5.71-5.62	S
	333, 511	27	4.79-4.72	M
	440	32	4.46-4.33	M
10	531	35	4.29-4.16	W
	600, 442	36	4.13-4.09	W
	620	40	3.93-3.88	W
	533	43	3.79-3.74	S
	631	46	3.66-3.62	M
	711, 551	51	3.48-3.43	VW
	642	56	3.33-3.28	S
15	733	67	3.04-3.00	M
	822, 660	72	2.93-2.89	M
	751, 555	75	2.87-2.83	S
	840	80	2.78-2.74	M
	911, 753	83	2.73-2.69	W
	664	88	2.65-2.61	M
	844	96	2.54-2.50	VW
20	10, 0, 0; 860	100	2.49-2.45	VW
	10, 2, 0; 862	104	2.44-2.40	VW
	10, 2, 2; 666	108	2.39-2.36	M
	10, 4, 0; 864	116	2.29-2.25	VW
	11, 1, 1; 775	123	2.24-2.21	VW
	880	128	2.20-2.17	W
	11, 3, 1; 971; 955	131	2.18-2.14	VW
	11, 3, 3; 973	139	2.11-2.08	W
25	12, 0, 0; 884	144	2.07-2.04	VW
	11, 5, 2; 10, 7, 1; 10, 5, 5	150	2.03-2.00	VW
	10, 8, 2	168, 171	1.92-1.89	VW
	13, 1, 1; 11, 7, 1; 11, 5, 5; 993			
	13, 3, 1; 11, 7, 3; 977			
	13, 3, 3; 995	187, 192	1.82-1.79	VW
	838			
30	13, 5, 1; 11, 7, 5	195	1.78-1.76	VW
	14, 2, 0; 10, 10, 0; 10, 8, 6	200	1.76-1.73	W
	13, 5, 4; 11, 8, 5	210	1.71-1.69	W

In producing zeolite Y, representative reactants are activated alumina, gamma alumina, alumina trihydrate and sodium aluminate as a source of alumina. Silica may be obtained from sodium silicate, silica gels, silicic acid, aqueous colloidal silica sols and reactive amorphous solid silicas. The latter two groups are preferred when zeolite Y products having molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios above about 4.5 are to be produced; however, these silica sources may

1

2

3,306,922

MOLECULAR SIEVE ADSORBENTS

Richard M. Barrer, Bromley, Kent, and Patrick J. Denny, Caversham, Reading, England, and Edith M. Flanigen, Buffalo, N.Y., assignors to Union Carbide Corporation, a corporation of New York

No Drawing. Filed Mar. 22, 1961, Ser. No. 97,474

20 Claims. (Cl. 260—448)

This invention relates to synthetic adsorbent materials and more particularly to synthetic crystalline forms of nitrogenous aluminosilicate zeolites, derivatives thereof and methods of making these adsorbent materials.

The term "zeolite," in general refers to a group of rigid, three-dimensional crystalline, hydrated metal aluminosilicates; some of these occur in nature and some have been synthesized. The synthetic zeolite materials of this invention exhibit significant differences in properties over naturally occurring zeolites and other synthetic zeolites. For convenience and distinguishability, the synthetic materials of this invention will be referred to hereinafter as zeolite N-A, zeolite N-X, zeolite N-Y and zeolite N-B wherein the term "N" designates an ammonium or alkyl ammonium substituted cationic species, such as tetramethylammonium ion and lower derivatives thereof, and the letters A, X, Y and B designate various types of zeolitic structures containing the tetramethylammonium cation or derivative thereof.

open three-dimensional framework of SiO_4 and AlO_4 tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms, so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal to two, or $\text{O}/(\text{Al}+\text{Si})=2$. The negative electrovalence of tetrahedra containing aluminum is conventionally balanced by the inclusion of alkali metal or alkaline earth metal ions within the crystal in the ratio of $2 \text{ Al}/(2\text{Na}, 2 \text{ K}, 2 \text{ Li}, \text{Ca}, \text{Ba}, \text{Sr}, \text{etc.})=1$. Moreover it has been found in the zeolite art that in some compositions one

within the crystal structure. The existence of a number of zeolites having similar but distinguishable properties advantageously permits the selection of a particular member having optimum properties for a particular use.

The present invention has as its prime object the provision of novel, synthetic, crystalline zeolites of the molecular sieve type. Another object is to provide novel, synthetic, crystalline zeolites having useful ion-exchange and adsorption properties. A further object is to provide a convenient and efficient process for preparing the novel materials of this invention. Additional objects and advantages will be apparent from the ensuing disclosure and appended claims.

Heretofore the electrovalent balance within the framework of silica and alumina tetrahedra during synthesis was thought to be only attainable by having present in the reactant mixture a substantial quantity of metal cations, such as sodium. Once the metal cation ion had been included in the reactant mixture and the synthesis reaction completed, the metal ions which occupy the cationic sites of the crystal could then be replaced by a wide variety of other metallic cations using ion exchange techniques. For the first time in the synthetic zeolite art we have prepared crystalline zeolites containing a substantial weight percent of a cation other than sodium or other metal cation. The incorporation of cations other than metal cations directly into the crystal structure in high concentrations during synthesis has not heretofore been accomplished. Substitution could in some cases be accomplished by ion-exchange methods applied to the crystalline product.

In the novel process of the present invention, nitrogenous aluminosilicate zeolites of the molecular sieve type are produced. An embodiment of the process of the present invention comprises heating a suitable aqueous reactant mixture containing tetramethylammonium hydroxide $(\text{CH}_3)_4\text{NOH}$, for the preparation of zeolites N-A, N-X, and N-Y, and containing ammonium tetra-

articles

Silicalite, a new hydrophobic crystalline silica molecular sieve

E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton & R. M. Kirchner

Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591

J. V. Smith

Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637

A new polymorph of SiO₂ (silicalite, refractive index 1.39, density 1.76 g cm⁻³) has a novel topologic type of tetrahedral framework. This encloses a three-dimensional system of intersecting channels defined by 10-rings wide enough to adsorb molecules up to 0.6 nm diameter. Silicalite is hydrophobic and organophilic, and selectively adsorbs organic molecules over water.

A MAJOR scientific and technological achievement since 1949 has been the discovery and development of synthetic crystalline, aluminosilicate zeolites as molecular sieve adsorbents and catalysts. We now report the synthesis, crystal structure, and properties of silicalite, a new microporous crystalline silica with remarkable sieve properties. Unlike aluminosilicate zeolites which are hydrophilic, silicalite is hydrophobic and organophilic, and selectively adsorbs organic molecules in the presence of water.

The crystal structure is a new topologic type of tetrahedral framework, which contains a large fraction of five-membered

rings of silicon-oxygen tetrahedra. The framework outlines a three-dimensional system of intersecting channels defined by 10-rings of oxygen ions in all three directions. Organic quaternary ammonium ions which occupy the channels in the precursor obtained by hydrothermal synthesis, are removed by heating to yield silicalite. The resulting void occupies about 33% of the crystal volume, and the three-dimensional channel is wide enough to adsorb molecules up to about 6 Å in diameter. Silicalite can be heated to near 1,300 °C where it degrades to a glass.

Synthesis

The silicalite precursor is crystallised hydrothermally in a closed system containing alkylammonium cations (for example, tetrapropylammonium), hydroxyl ions, and a reactive form of silica at 100–200 °C. The organic-containing precursor crystals have a typical empirical composition (TPA)₂O · 48SiO₂ · H₂O, mean refractive index 1.48, and measured density 1.99 g cm⁻³. The organic cation is larger than the pore and therefore must be removed by chemical or thermal decomposition (usually calcination in air at 500–600 °C) to yield the microporous silicalite

July 12, 1960

C. W. SKARSTROM
METHOD AND APPARATUS FOR FRACTIONATING
GASEOUS MIXTURES BY ADSORPTION

2,944,627

Filed Feb. 12, 1958

9 Sheets-Sheet 1

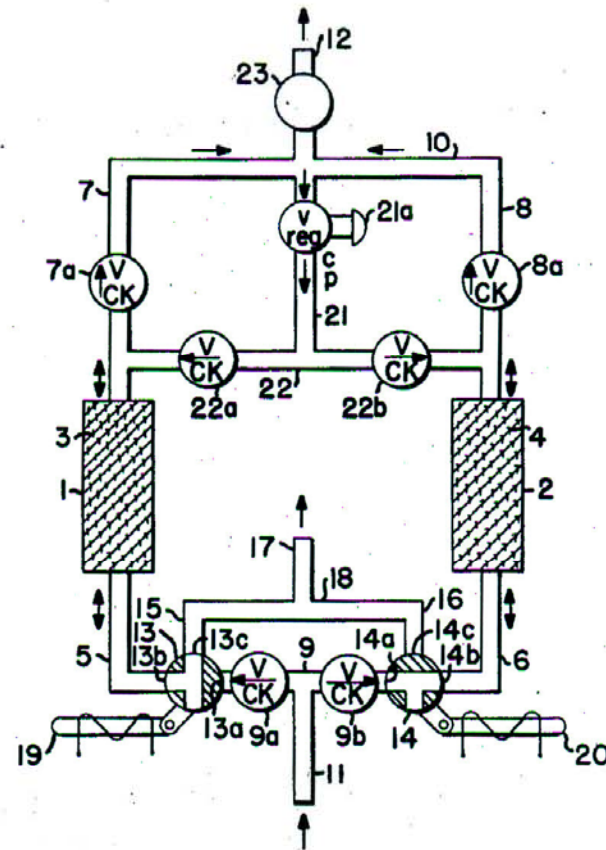


FIG. 1

May 23, 1961

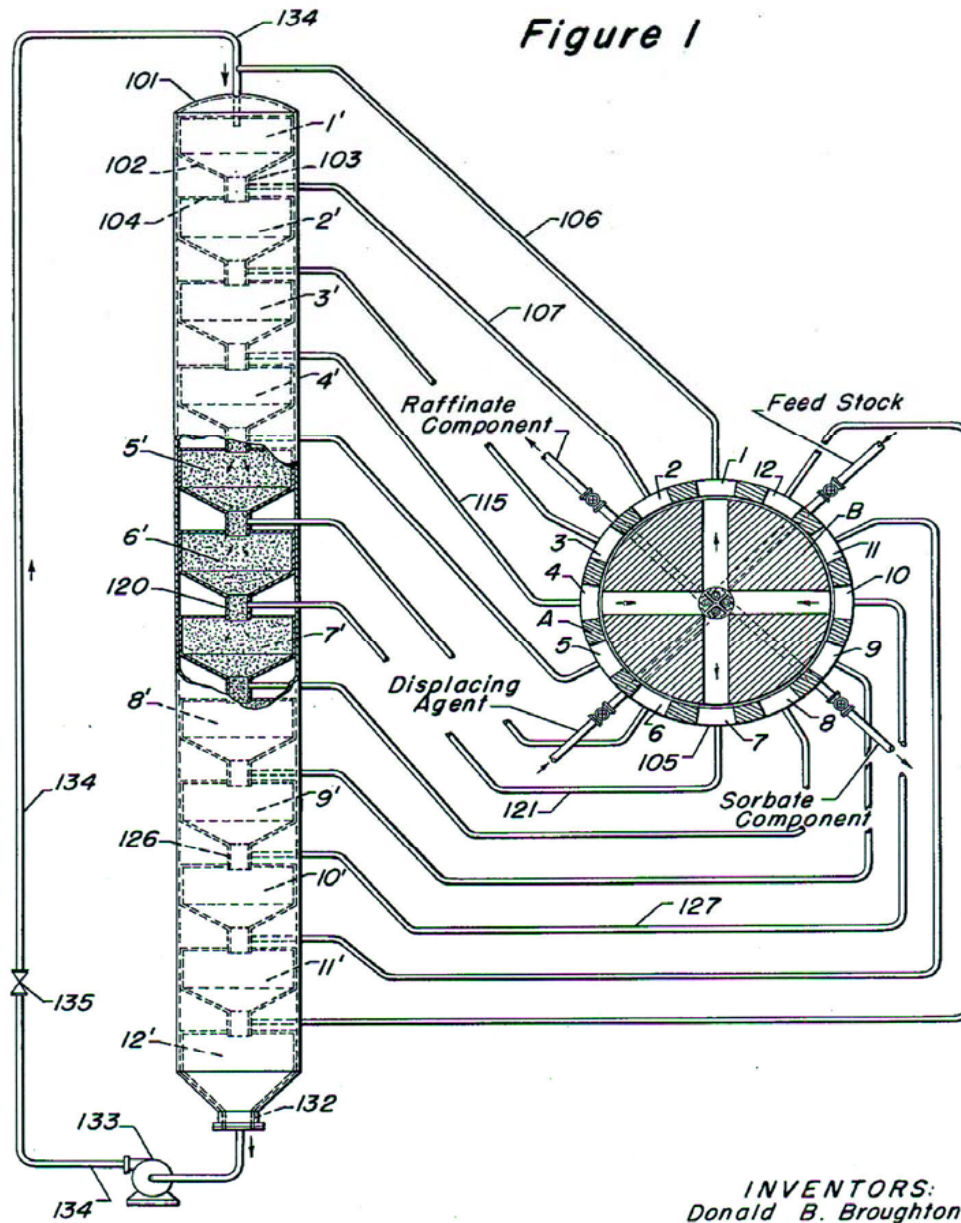
D. B. BROUGHTON ET AL
CONTINUOUS SORPTION PROCESS EMPLOYING FIXED BED
OF SORBENT AND MOVING INLETS AND OUTLETS

2,985,589

Filed May 22, 1957

2 Sheets-Sheet 1

Figure 1



INVENTORS:
Donald B. Broughton
Clarence G. Gerhold

BY



Simposio sobre Adsorção, Adsorbentes y sus Aplicaciones

GRACIAS !!!



UFC

celio@gpsa.ufc.br
<http://www.gpsa.ufc.br>



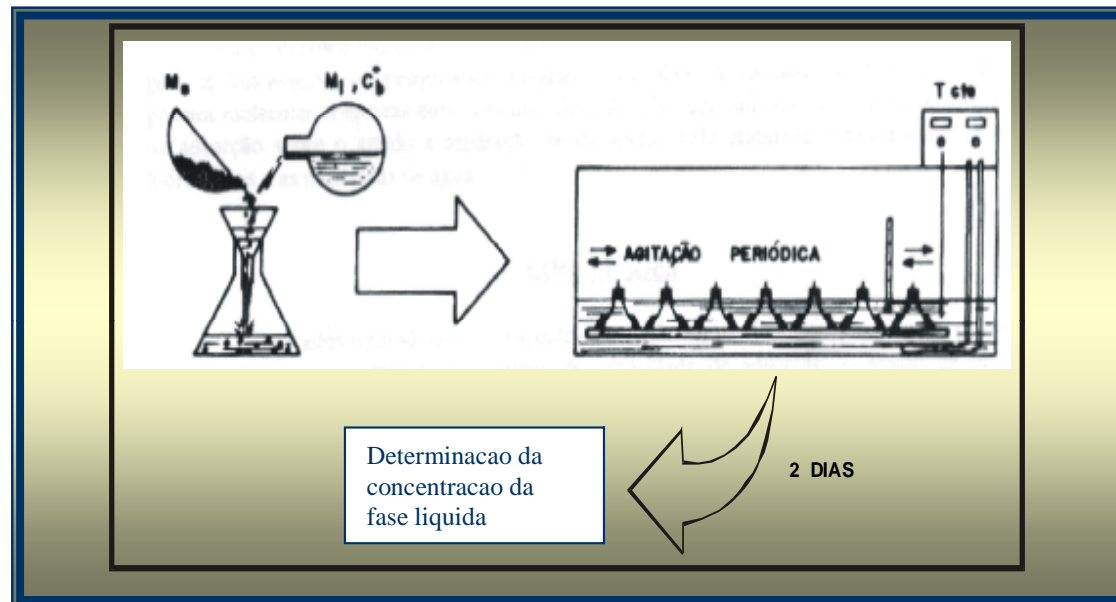
Métodos Experimentais

Métodos utilizados no GPSA:

- *Batelada*
- *Gravimétrico*
- *Cromatográfico*
- *Volumétrico*
- *Headspace*
- *ZLC (Zero-Length Column)*

Métodos Experimentais

Método Batelada



Cálculo do equilíbrio por balanço:

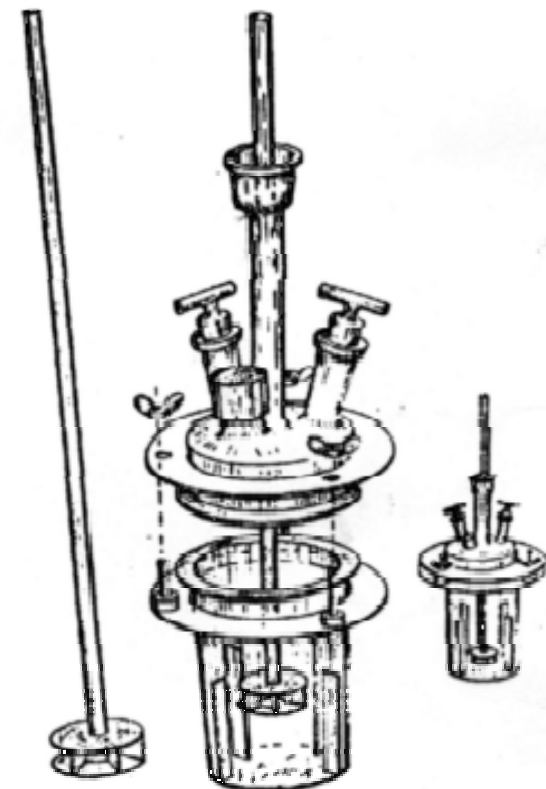
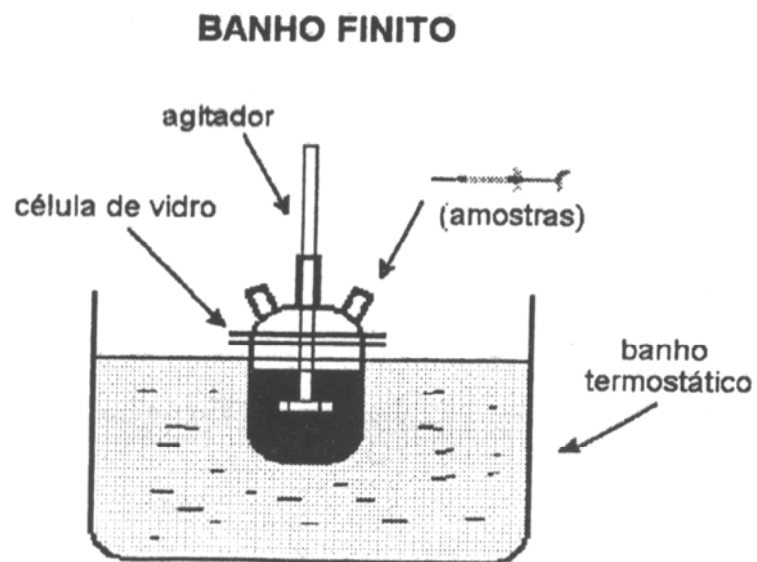
- diferença de concentrações inicial e final;
- supõe presença de inerte.

Métodos Experimentais

Método Batelada

Estudos difusivos:

- Banho finito;
- Efeitos de filme.



Métodos Experimentais

Método Batelada

Modelo Difusivo:
$$\frac{\partial .q}{\partial .t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial .r} \left(r^2 D \cdot \frac{\partial .q}{\partial .r} \right)$$

para partículas esféricas, T constante, e D constante:

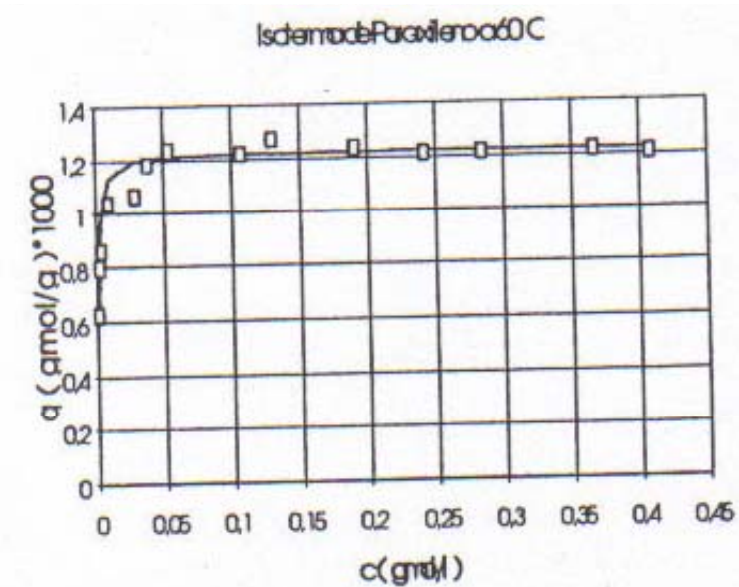
$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6(1 + \alpha)}{9\alpha(1 + \alpha) + P_n^2} \text{EXP} \left(- P_n^2 D t / r^2 \right)$$

$$\tan P_n = P_n / (1 + 3 P_n^2 \alpha)$$

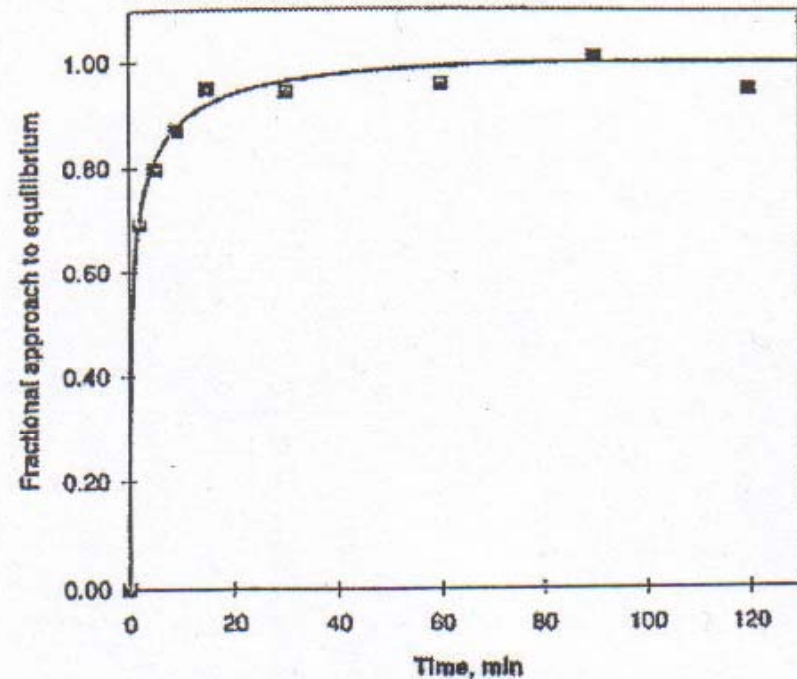
$$\alpha = V_s q_\infty / V_g \cdot C_\infty$$

Métodos Experimentais

Método Batelada



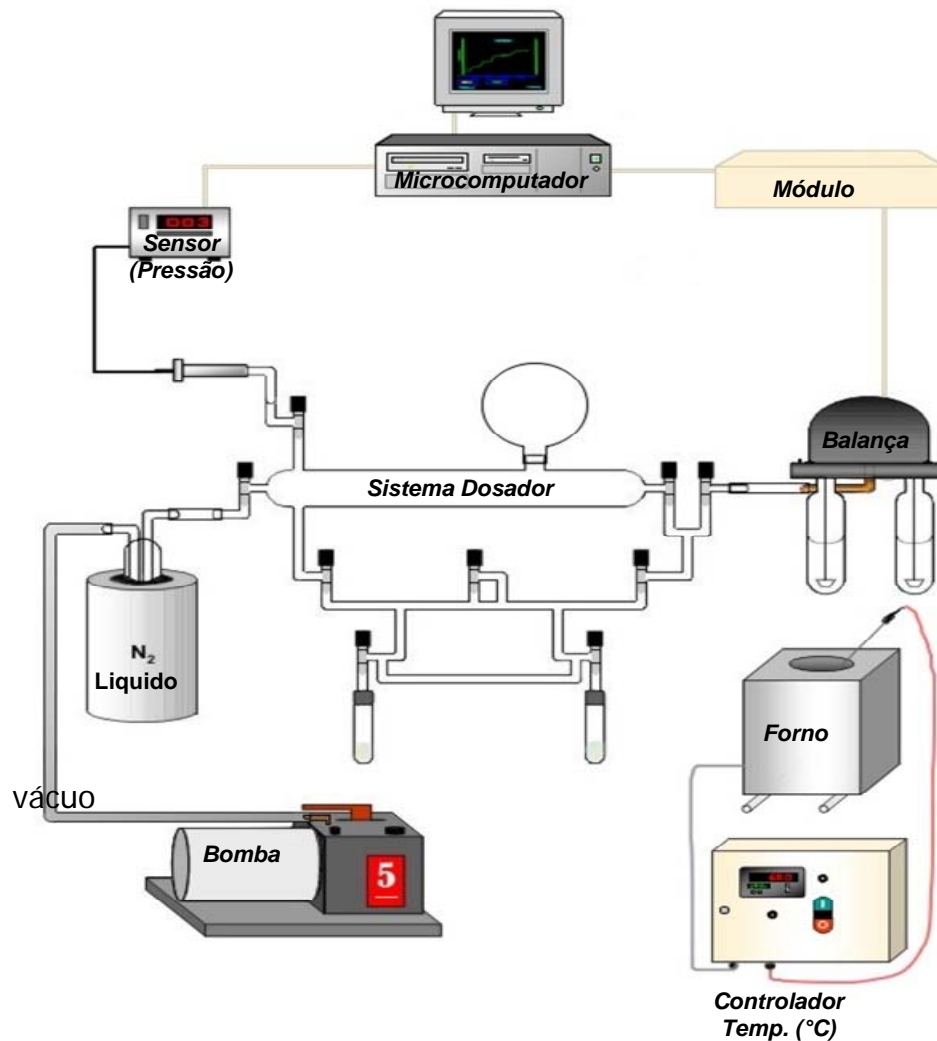
Isoterma de adsorção do p-xileno em zeolito Y comercial (Neves, 1995)



Cinética da adsorção de Sb em Resina Duolite C-467 (Gabai et al., 1997)

Métodos Experimentais

Método Gravimétrico



- Medidas diretas de aumento do peso em virtude da quantidade adsorvida.
- Medidas de quantidade adsorvida em função da pressão parcial.
- Adsorção e Dessorção

Métodos Experimentais

Método Gravimétrico - Cinética

Modelo de Fick, difusividade constante:

$$\frac{q(t) - q_0}{q_\infty - q_0} = \frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp\left(\frac{-n^2 \pi^2 D t}{r^2}\right)$$

Para tempos curtos e $\gamma < 0.3$, a solução da equação 3.27 pode ser escrita como:

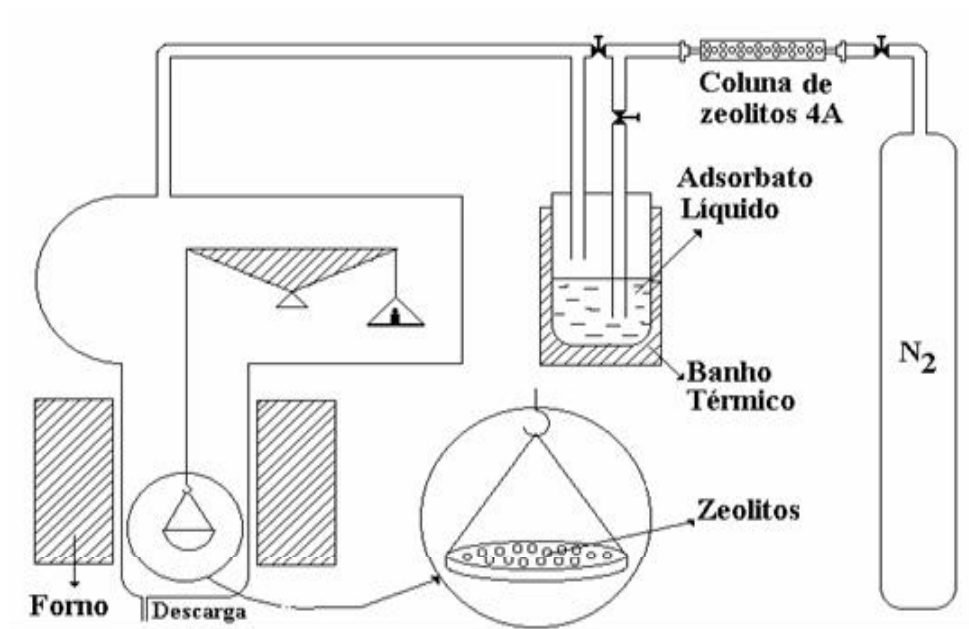
$$\frac{m_t}{m_\infty} = \frac{6}{\sqrt{\pi}} \left(\frac{D}{r^2}\right)^{1/2} \sqrt{t}$$

Para tempos maiores, onde $\gamma \geq 0,7$

$$\ln\left(1 - \frac{m_t}{m_\infty}\right) = \ln\frac{6}{\pi^2} - \frac{\pi^2 D t}{r^2}$$

Métodos Experimentais

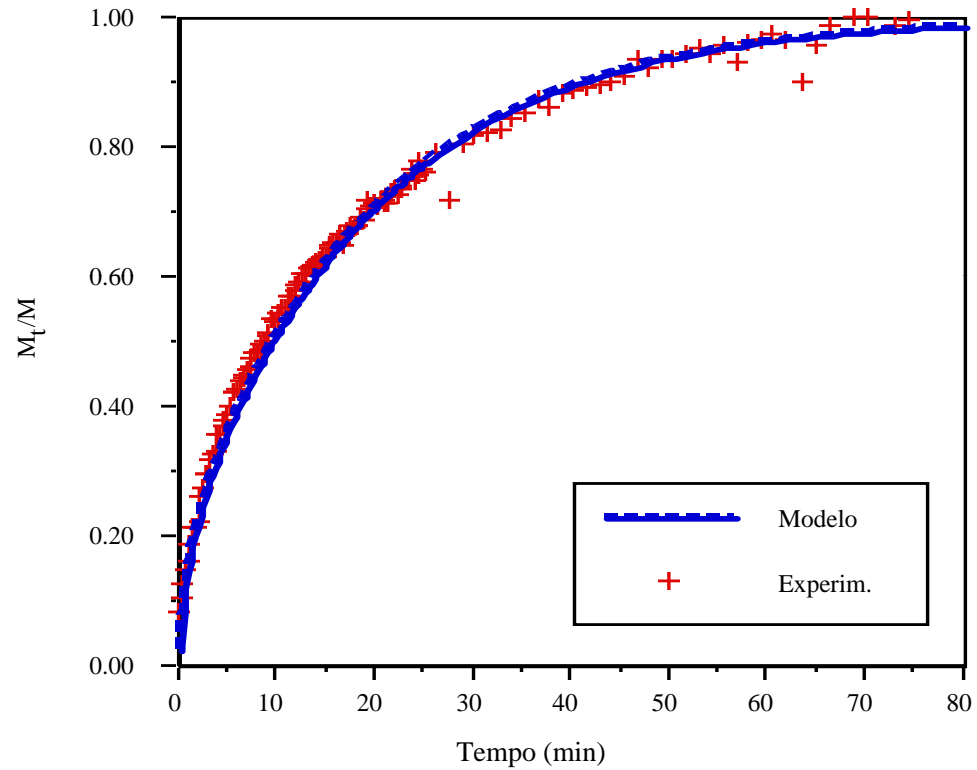
Método Gravimétrico – “alternativo” (com fluxo de inerte)



- Medidas diretas de aumento do peso em virtude da quantidade adsorvida.
- Medidas de quantidade adsorvida em função da pressão parcial.
- Adsorção e Dessorção

Métodos Experimentais

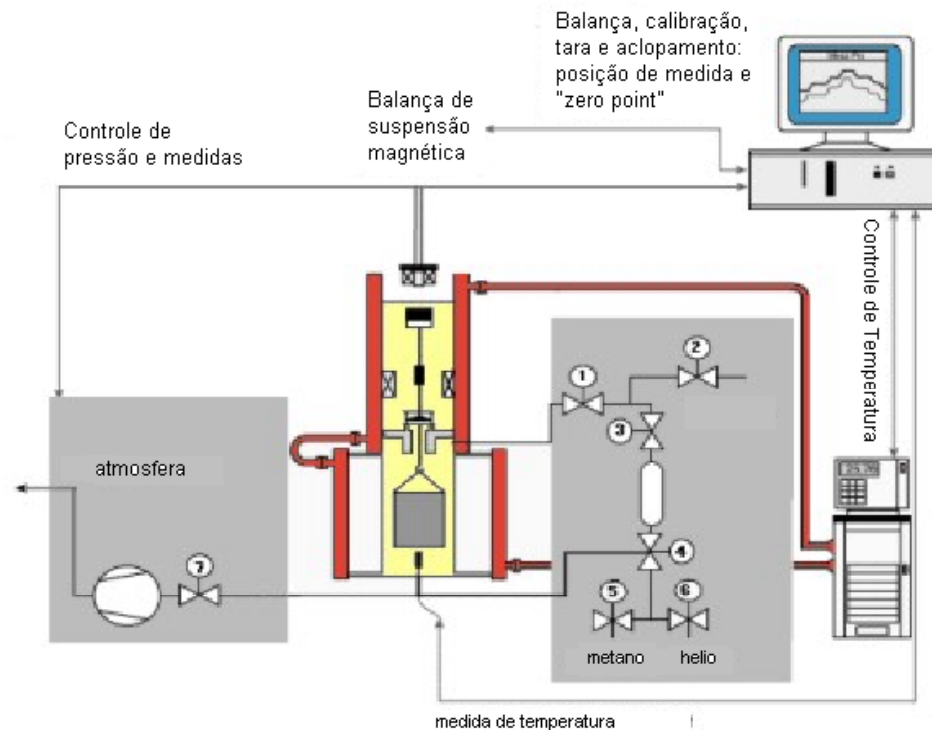
Método Gravimétrico - Cinética



Adsorção de Ciclohexano em Silicalita (Cavalcante Jr. e Ruthven, 1995)

Métodos Experimentais

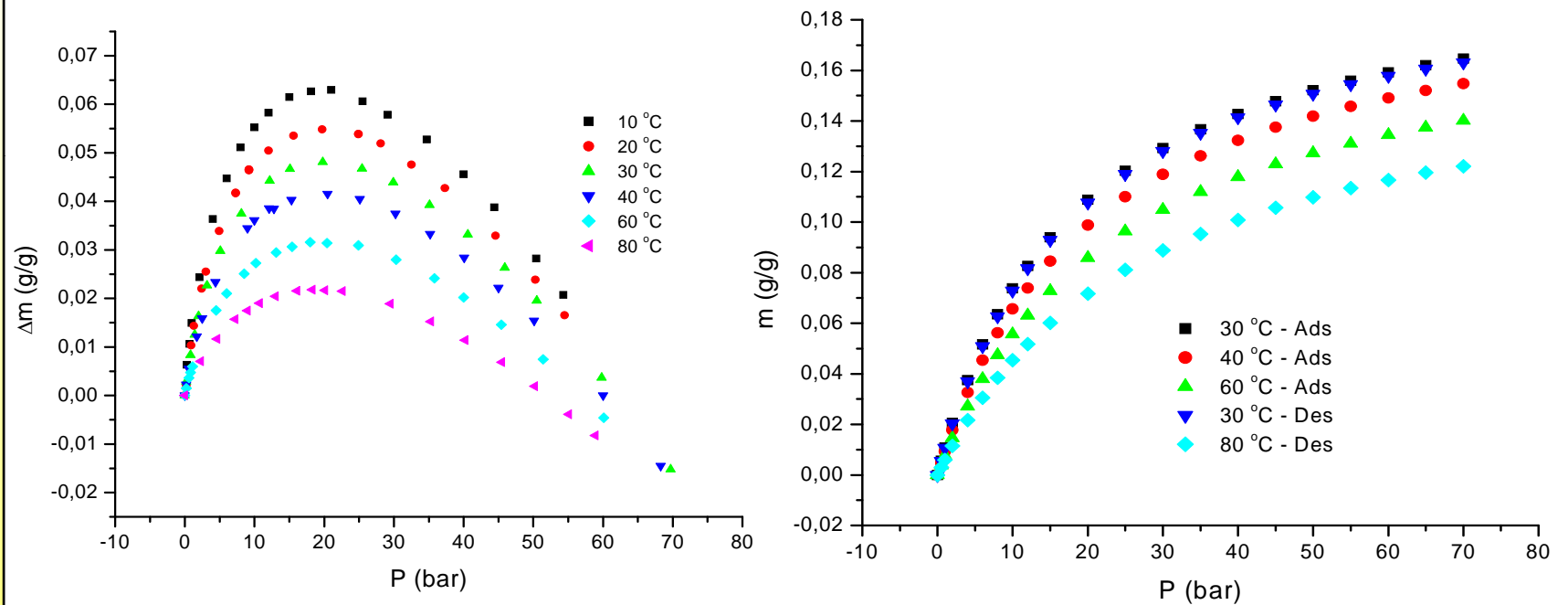
Método Gravimétrico – medidas em pressões elevadas



- **Medidas diretas de aumento do peso em virtude da quantidade adsorvida;**
- **Deve ser considerado o efeito do empuxo.**

Métodos Experimentais

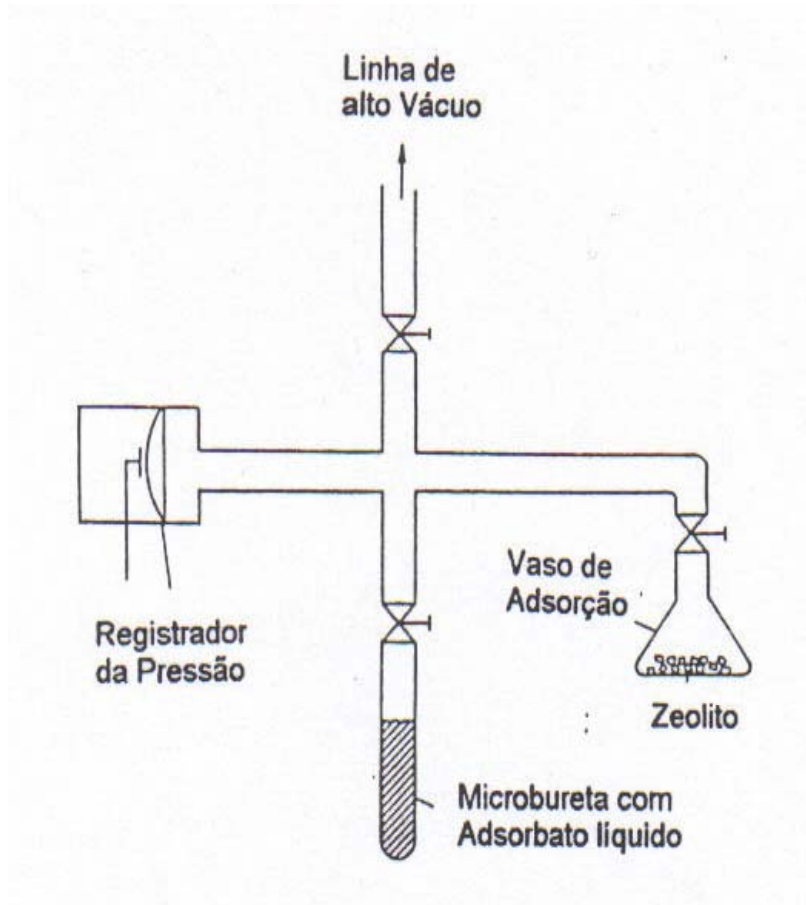
Método Gravimétrico – medidas em pressões elevadas



Metano em carvão ativado

Métodos Experimentais

Método Volumétrico



- **Variação de volume a T constante e P final conhecida**

Métodos Experimentais

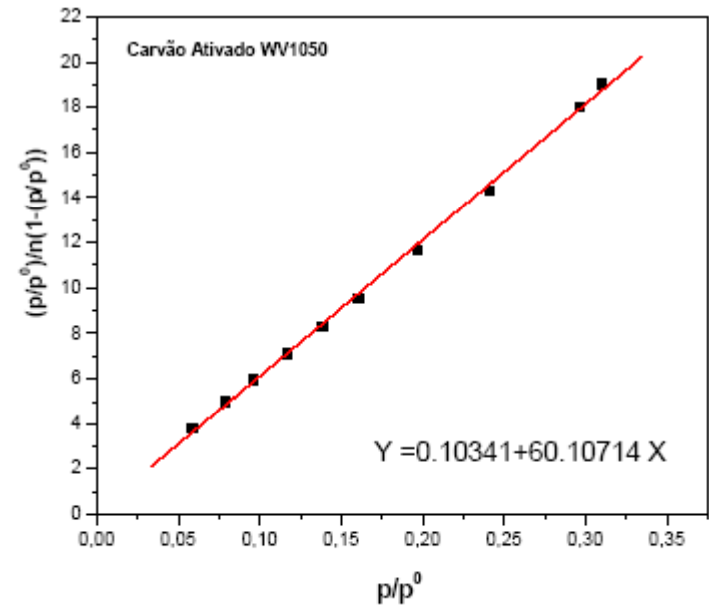
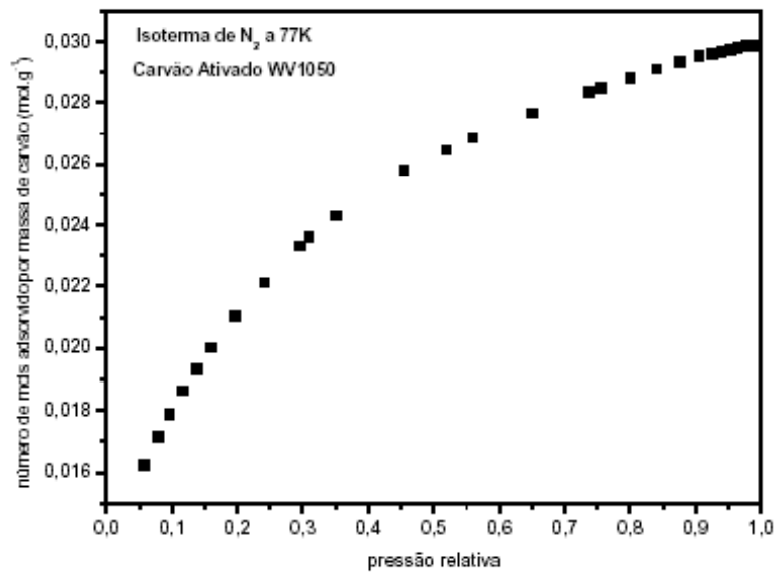
Autosorb



- **Medidas de volumes adsorvido por equações de estado e medidas de pressão e temperatura;**
- **Muito utilizado na caracterização de adsorventes, com moléculas padrão**

Métodos Experimentais

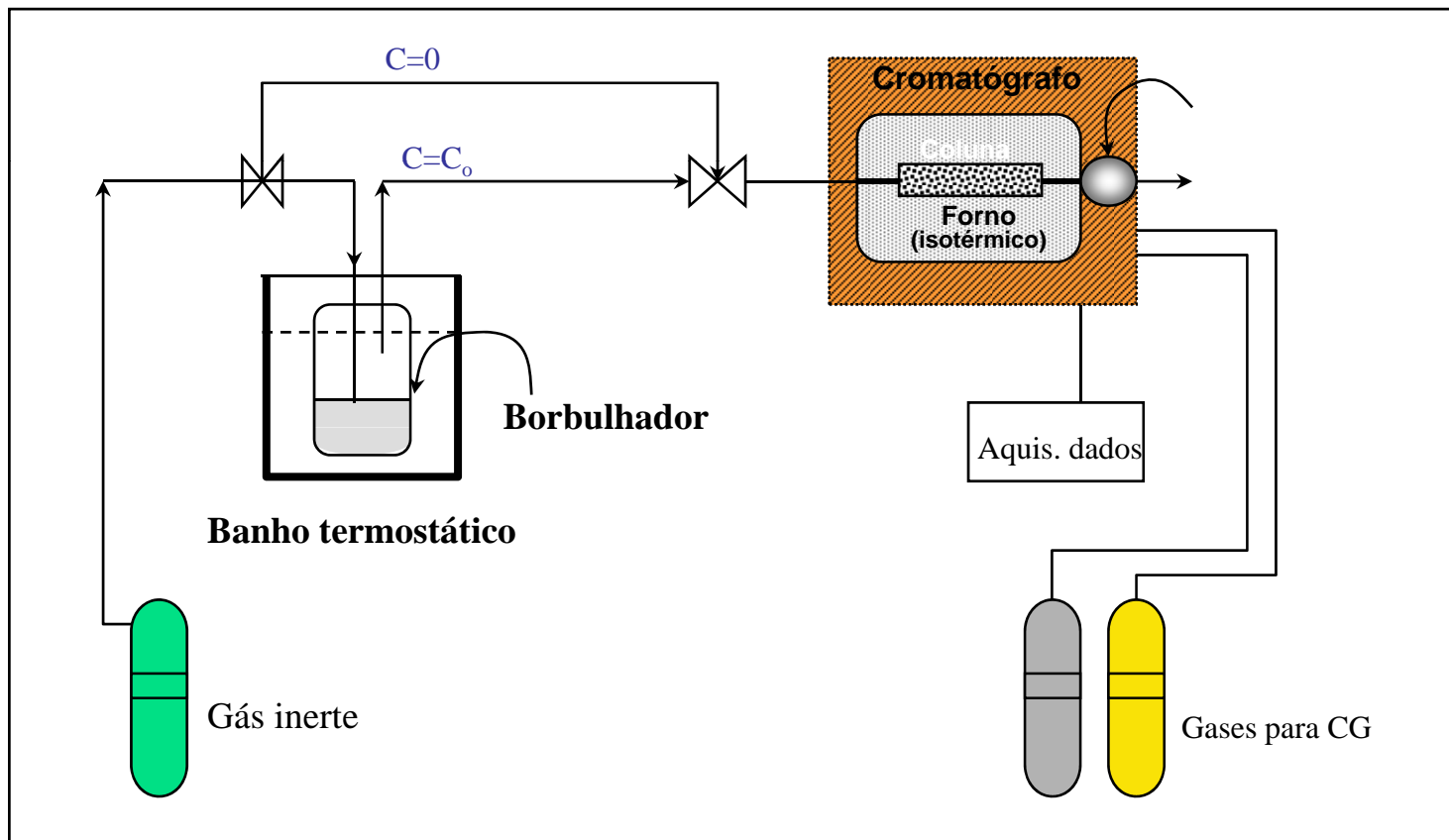
Método Volumétrico Autosorb



Métodos Experimentais

Método Cromatográfico

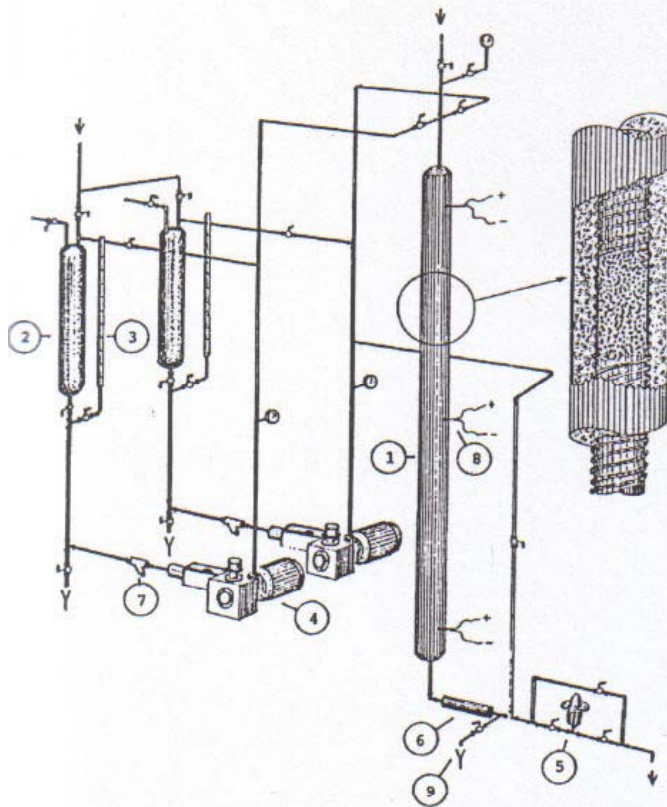
Fase Gás



Métodos Experimentais

Método Cromatográfico

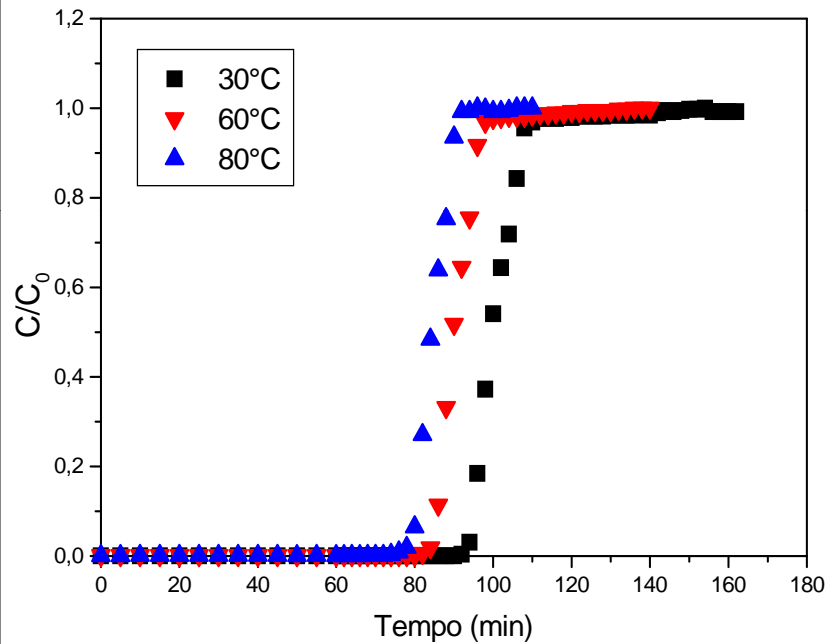
Fase líquida



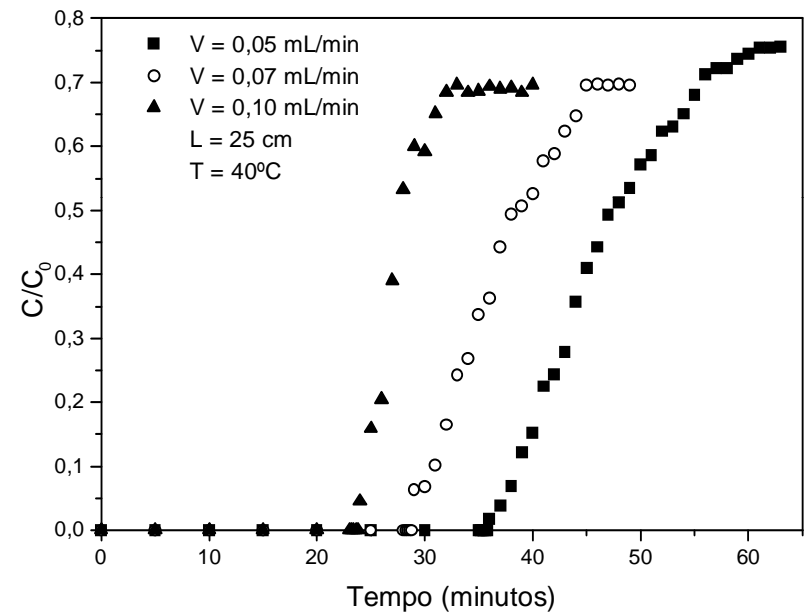
- (1) Coluna de adsorção
- (2) Reservatório
- (3) Medidor de nível e vazão
- (4) Bomba de pistão
- (5) Válvula reguladora de pressão
- (6) Resfriador
- (7) Filtro
- (8) Termopares
- (9) Válvula de amostragem

Métodos Experimentais

Método Cromatográfico



Tolueno em Carvão ativado
(gás)

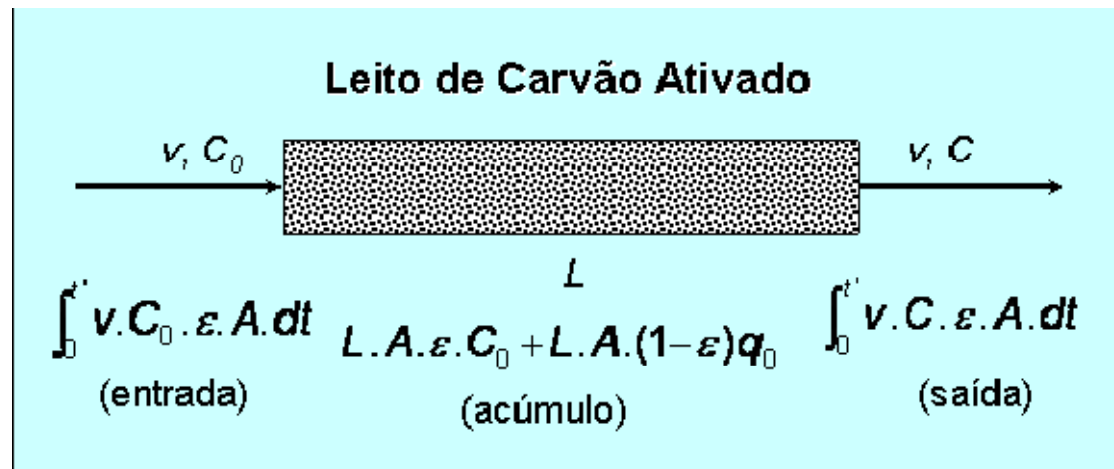


Naftaleno em Y
(líquido)

Métodos Experimentais

Método Cromatográfico

Balanço de Massa:



Equação final do balanço de massa no leito:

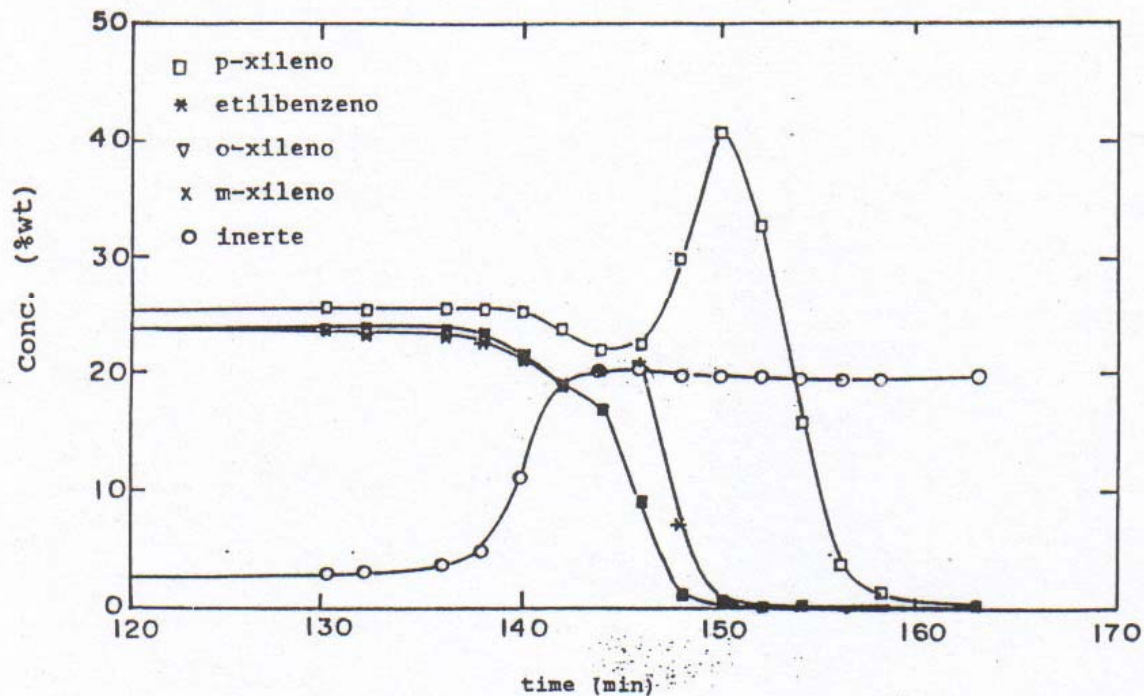
$$\int_0^{t'} v_i C_0 \cdot \epsilon \cdot A \cdot dt = \int_0^{t'} v_i C \cdot \epsilon \cdot A \cdot dt + [L \cdot A \cdot \epsilon \cdot C_0 + L \cdot A \cdot (1 - \epsilon) q]$$

$$\frac{v_i}{L} \int_0^{t'} \left(1 - \frac{C}{C_0} \right) dt = 1 + \frac{(1 - \epsilon)}{\epsilon} \frac{q_0}{C_0}$$

ponto da isoterma

Métodos Experimentais

Método Cromatográfico - seletividade

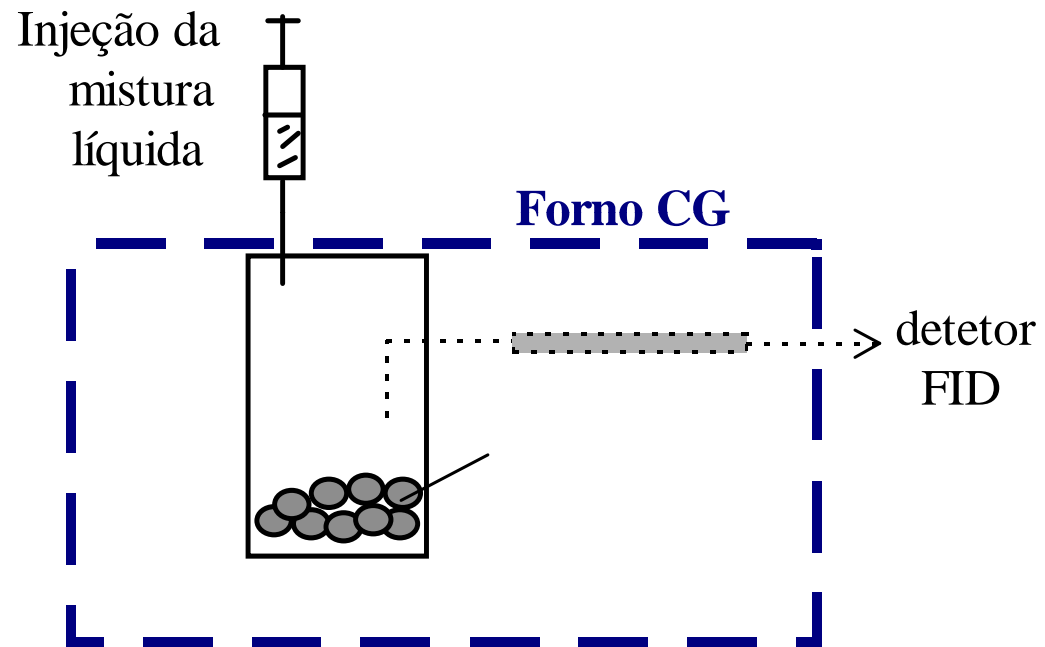


PX em Y

Capacidade de Adsorção Total:	1,16 mmol/g
Seletividade p-xileno/m-xileno:	3,04
Seletividade p-xileno/o-xileno:	3,04
Seletividade p-xileno/etilbenzeno:	2,60

Métodos Experimentais

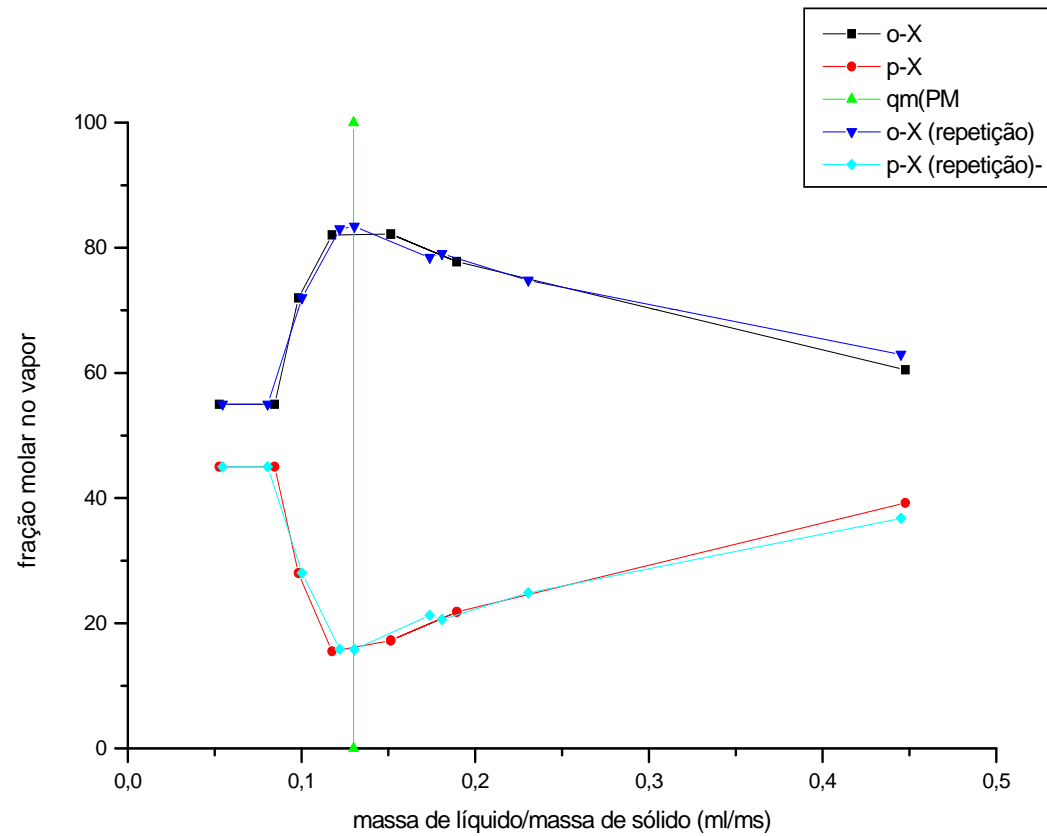
Método Headspace



Avaliação de seletividade na saturação

Métodos Experimentais

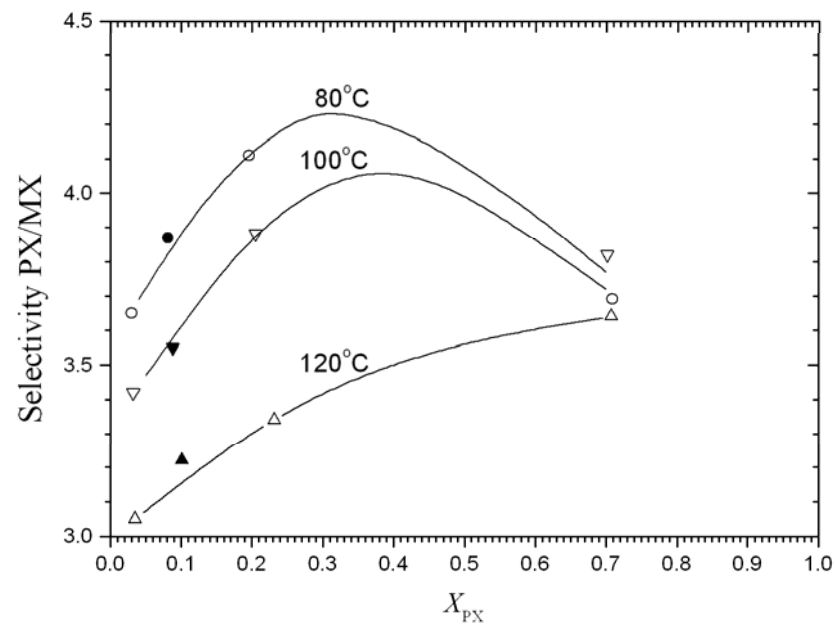
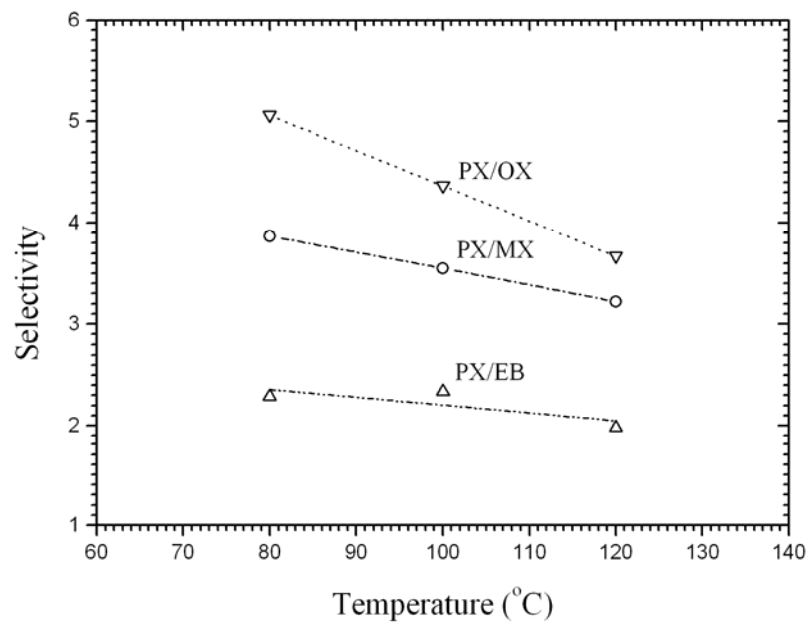
Método Headspace



Resultados experimentais para a seletividade p-xileno/o-xileno sobre zeólito Y comercial a 60°C.
(Torres et al., 1998)

Métodos Experimentais

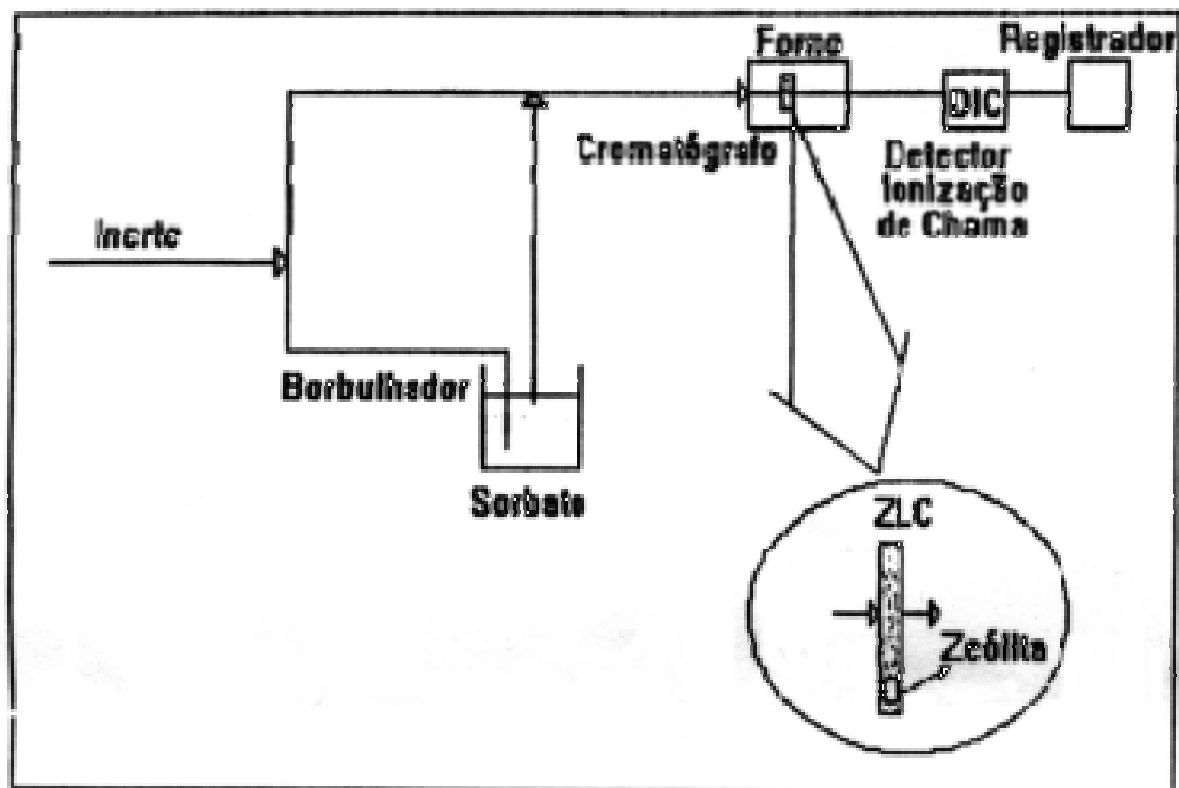
Método Headspace



Seletividade versus temperatura e concentração – xilenos em Y (Buarque et al., 2005)

Métodos Experimentais

Método ZLC – Zero Length Column



- pequenas quantidades de amostra
- curva concentração versus tempo

Métodos Experimentais

Método ZLC

Modelo difusivo, baixas concentrações de sorbato:

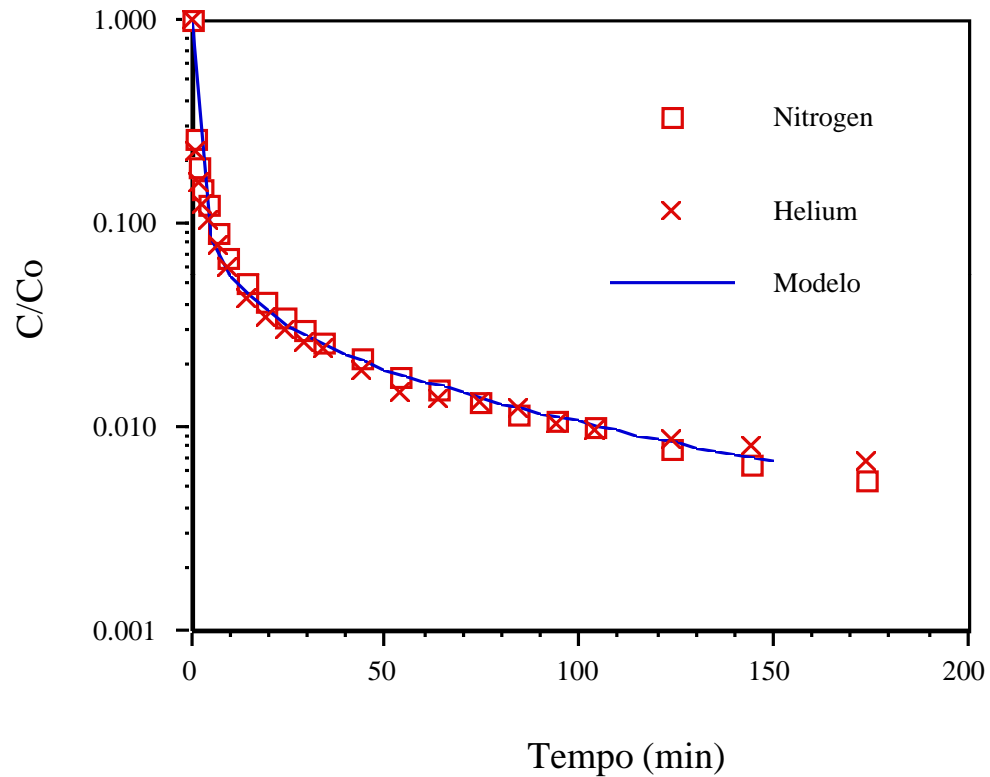
$$\frac{C}{C_0} = 2L \cdot \sum_{n=1}^{\infty} \left\{ \frac{\exp(-\beta_n^2 D_c t / r_c^2)}{[\beta_n^2 + L(L-1)]} \right\}$$

$$L = \frac{1}{3} \frac{F_p}{V_c} \frac{r_c^2}{K D_c}$$

$$\beta_n \cdot \cot \beta_n + L = 1$$

Métodos Experimentais

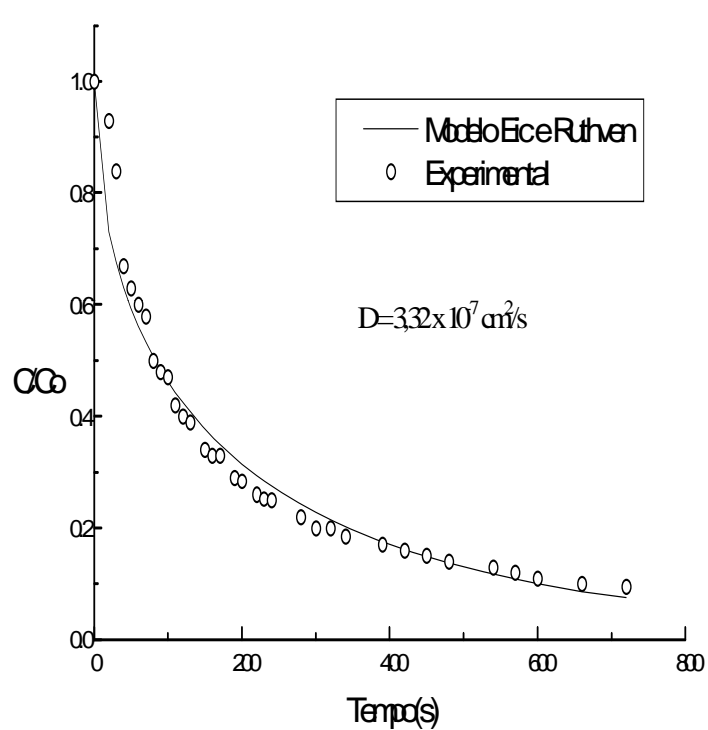
Método ZLC



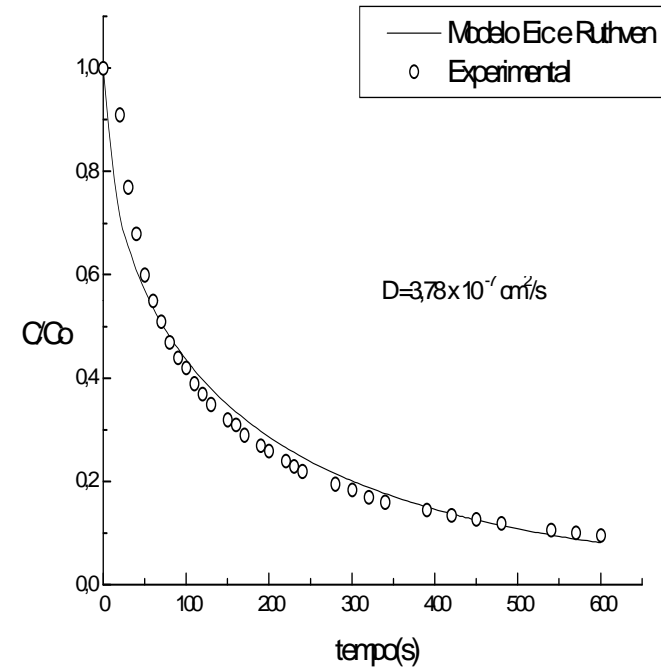
Modelo Teórico da Difusão em ZLC e Resultados Experimentais da difusão de n-dodecano em Peneira Molecular Erionita a 150oC (Cavalcante Jr. et al., 1995)

Métodos Experimentais

Método ZLC



PX - pellets Y, 150C, Helio, 34 ml/min



PX - pellets Y, 150C, N2, 68 ml/min

Resultados Experimentais ZLC da difusão de p-xileno em Peneira Molecular Y a 150oC



COMENTÁRIOS FINAIS

Comentários Finais

Comportamento da fase adsorvida

- A fase adsorvida, independente da natureza da fase fluido (se gás ou líquido), tem comportamento semelhante ao comportamento do líquido “livre” no estado saturado.
- Apesar dos valores absolutos das densidades na fase adsorvida e como líquido saturado serem diferentes, a relação entre elas permanece aproximadamente constante com o aumento da temperatura.
- Esta observação permite a extrapolação, sem perda de precisão significativa, de dados obtidos em condições experimentais com fase fluido gás (mais comuns) para condições operacionais em fase fluido líquido (maioria dos processos industriais de grande porte).

Densidades (g/cm^3) de 3-Metilpentano na fase adsorvida e em fase líquida saturada [38]

Temp. ($^{\circ}\text{C}$)	Fase Adsorvida (A)	Líquido Saturado (S)	Relação (A/S)
100	0,357	0,568	0,63
125	0,315	0,539	0,58
150	0,321	0,507	0,63
200	0,285	0,421	0,68



Comentários Finais

Difusão macroporos

P-xileno em Y:

Gás de Arraste	Vazão de Purga (ml/min)	D_m (cm ² /s)	$\epsilon_p D_p$ (cm ² /s)	τ_p
Nitrogênio	34	0.156	0.079	2.0
Nitrogênio	68	0.156	0.131	1.2
Nitrogênio	102	0.156	0.189	0.8
Hélio	34	0.474	0.114	4.1
Hélio	102	0.474	0.317	1.5
				τ_p médio \cong 2.0

Diferentes vazões e inertes:

- tortuosidade appx.constante
- Controle difusivo no microporo



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Comentários Finais

Força Motriz Linear na transferência de massa (LDF)

Resistências em série:

$$\frac{1}{Kk} = \frac{R_p}{3k_f} + \frac{R_p^2}{15\varepsilon_p D_p} + \frac{r_c^2}{15KD_c}$$

Coef. global Filme externo macroporo microporo

Se o efeito de difusão no microporo é desprezível, podemos escrever:

$$\frac{1}{K_L} = \frac{1}{k_e} + \frac{1}{k_i \varepsilon_i}$$

Coef. global Filme externo macroporo

onde: $k_i = \frac{5D_m / \tau}{r_p}$ (Glueckauf, 1955)

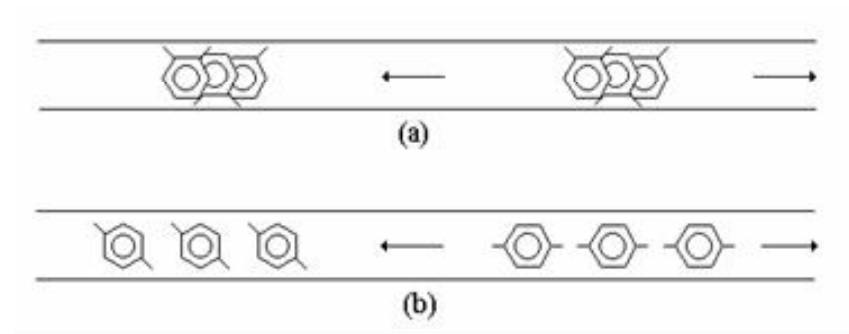


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Comentários Finais

Peneiras Moleculares aluminofosfatadas (AlPO's)

- orto-seletividade



Equilíbrio (AlPO₄-11):

Table 2. Parameters from equilibrium data of xylenes in AlPO₄-11.

	Temp. (°C)	Langmuir model		
		b (mm Hg ⁻¹)	q_s (%g/g)	K (dimensionless)
<i>o</i> -Xylene	60	2.205	4.250	31,200
	80	3.662	3.543	45,800
	100	1.653	2.597	16,000
<i>p</i> -Xylene	60	1.946	3.791	24,600
	80	2.202	2.783	21,600
	100	2.887	2.488	26,800

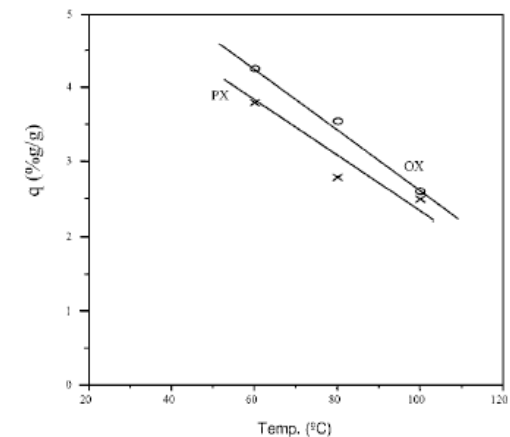


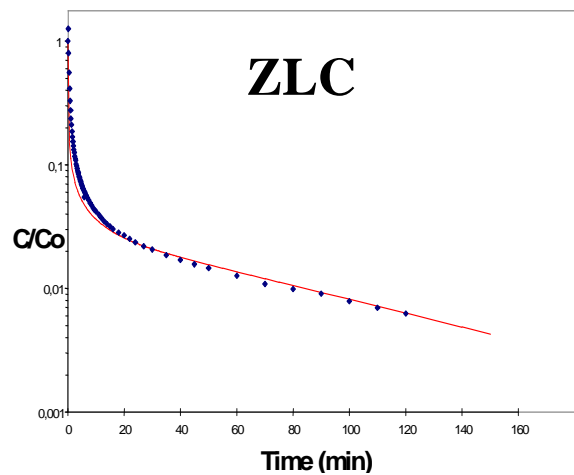
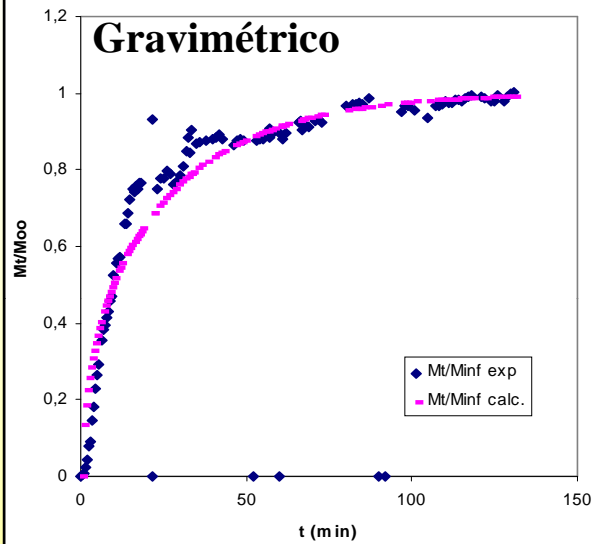
Figure 7. Temperature dependence of saturation capacities of *p*-xylene and *o*-xylene in AlPO₄-11.



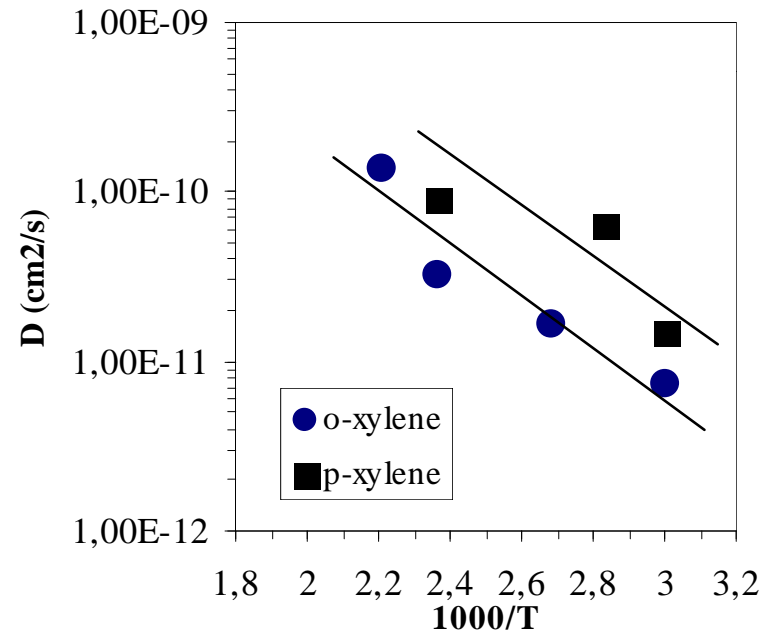
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Comentários Finais

Peneiras Moleculares aluminofosfatadas (AlPO's)



P-xileno difunde mais rapidamente

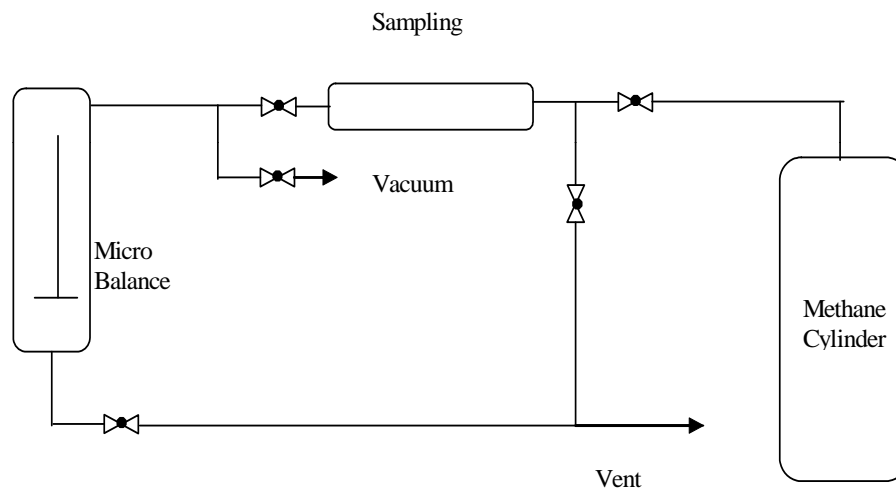


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Comentários Finais

Armazenamento de Gás natural

Medidas de Parâmetros Fundamentais

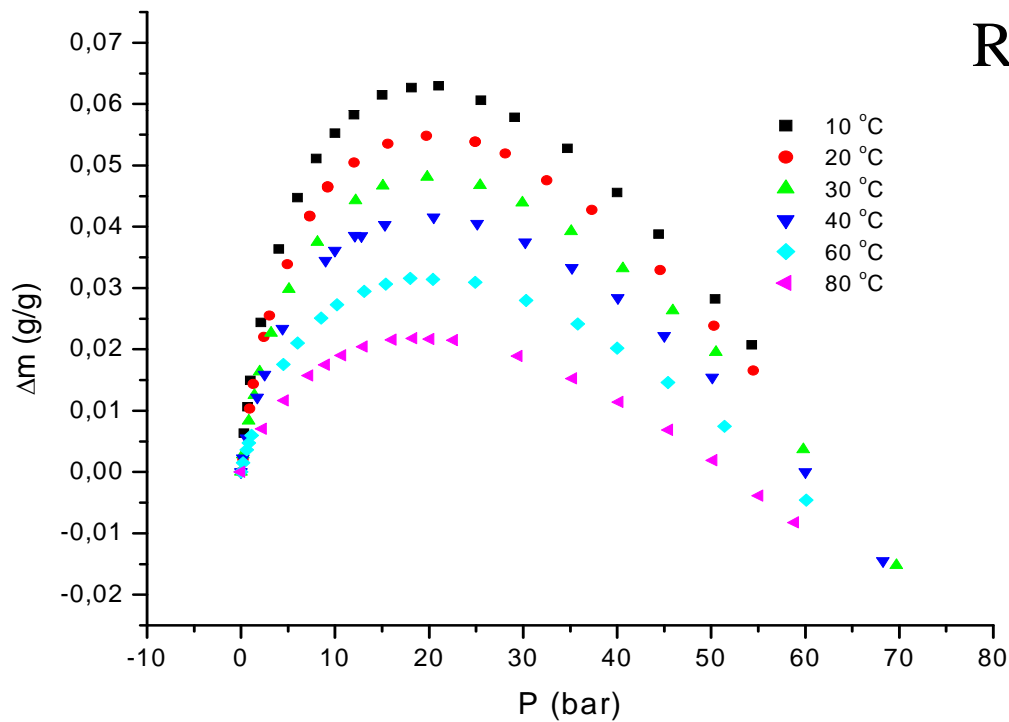


- Microbalance Rubotherm
- Pressures: vacuum to 150 atm
- Temperatures up to 500°C
- Capacity: 25g ± 0.01 mg



Comentários Finais

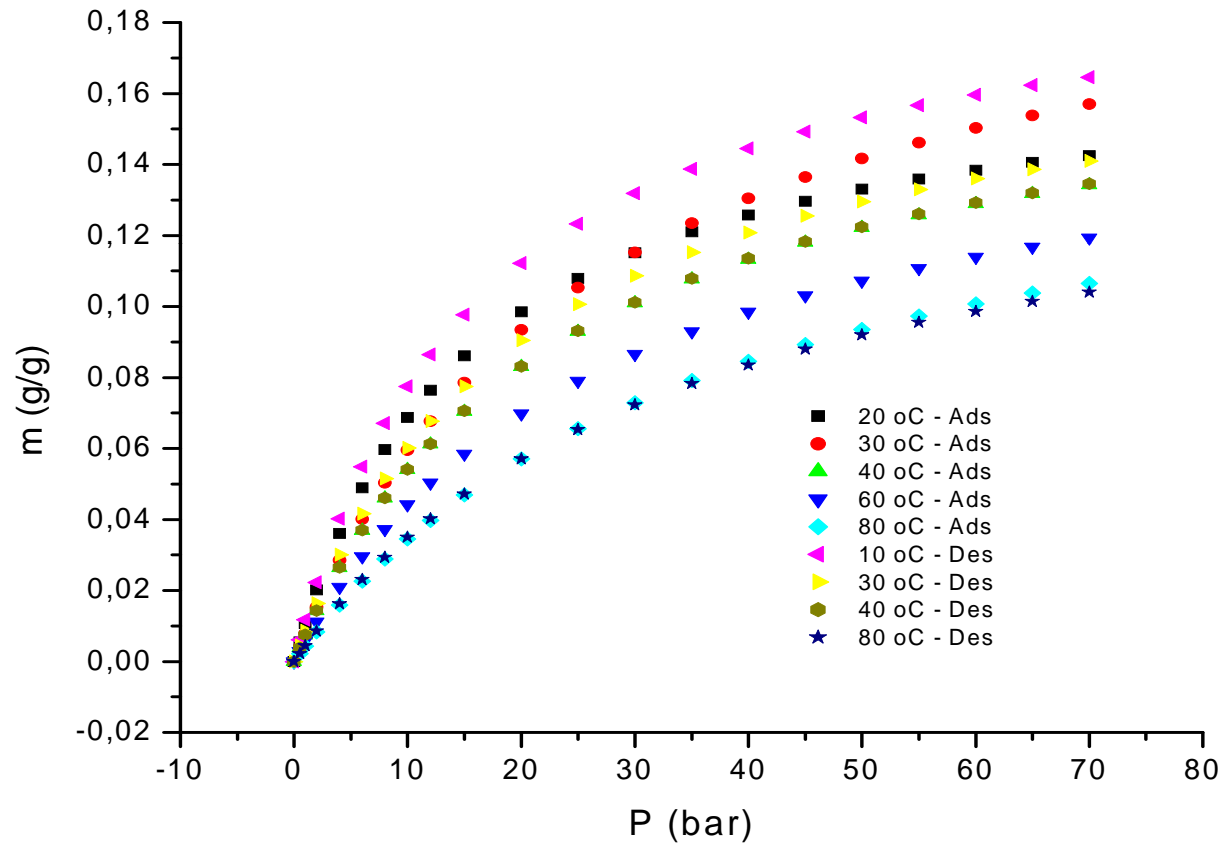
Dados dos Experimentos da Balança



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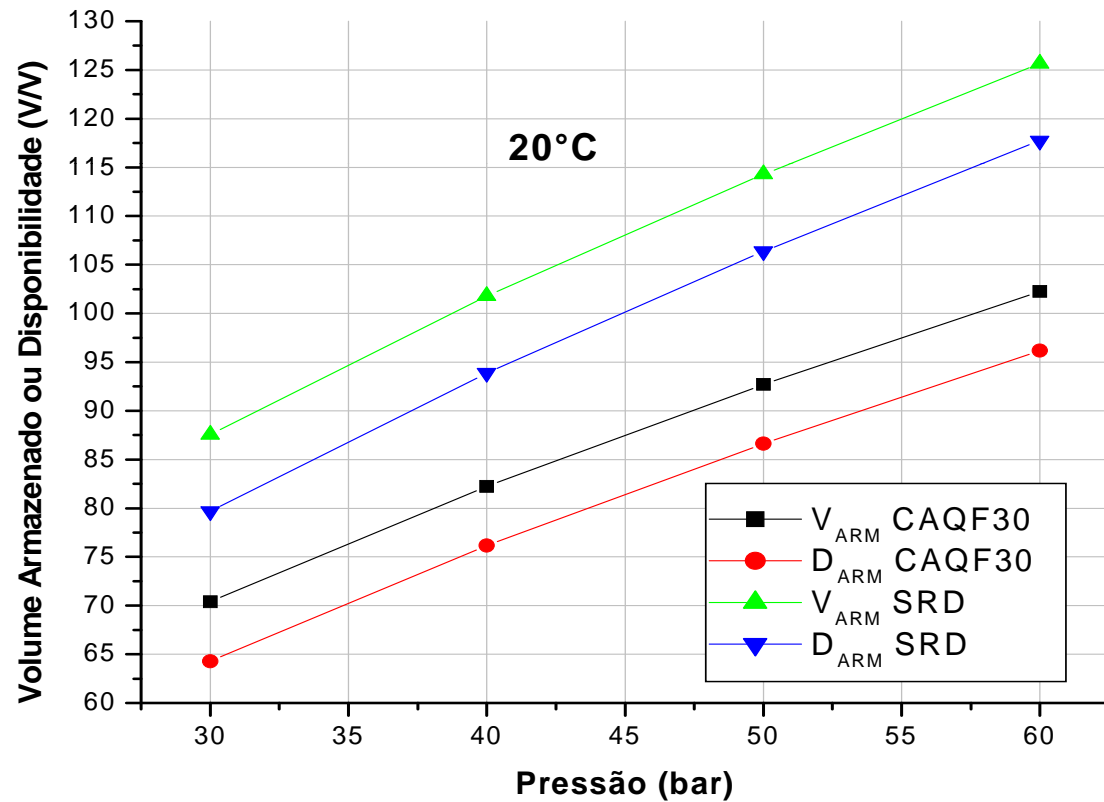
Comentários Finais

Resultados



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Densidade de Armazenamento e Disponibilidade



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Comentários Finais

Protótipo



Comentários Finais

Modelo Matemático

Eq. continuidade:

$$\frac{\partial}{\partial t} (\varepsilon_T c + \rho_b q) + \nabla \cdot \mathbf{G} = 0 \quad \mathbf{G} = \vec{v} \cdot c \quad \vec{v} = -\frac{1}{\alpha} \nabla P \quad \alpha = \frac{150 \cdot (1 - \varepsilon_L)^2 \cdot \mu}{4 \cdot \varepsilon_L^3 \cdot R_p^2}$$

Eq. energia:

$$\frac{\partial}{\partial t} ((\varepsilon_T c + \rho_b q) C_{pg} T) + \rho_b \Delta H \frac{\partial q}{\partial t} - \varepsilon_T \frac{\partial P}{\partial t} + \rho_b C_{ps} \frac{\partial T}{\partial t} + \nabla \cdot (\mathbf{G} C_{pg} T - \lambda_e \nabla T) = 0$$

$$\frac{P}{q} = \exp\left(\left(k_1 + \frac{k_2}{T}\right) + \left(k_3 + \frac{k_4}{T}\right)q\right)$$

EQUILÍBRIO

Conds. iniciais e de fronteira:

$$P = P_i, \quad T = T_i, \quad q = q_i \quad \text{para } R_i \leq r \leq R_0, \quad t = 0$$

$$\lambda_e \frac{\partial T}{\partial r} + e_w \cdot C_w \frac{\partial T}{\partial t} = h_w (T - T_{amb}) \quad \text{para } r = R_0$$

$$\left. \frac{\partial P}{\partial r} \right|_r = 0 \quad \text{para } r = R_0$$

$$\lambda_e \frac{\partial T}{\partial r} = c \cdot \frac{K}{\mu} \cdot \frac{\partial P}{\partial r} \cdot C_{pg} \cdot (T_w - T) \quad \text{para } r = R_i$$

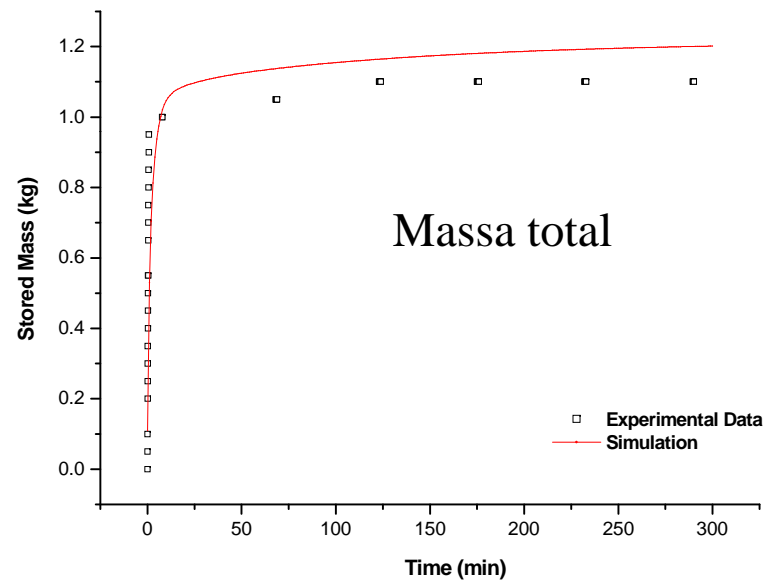
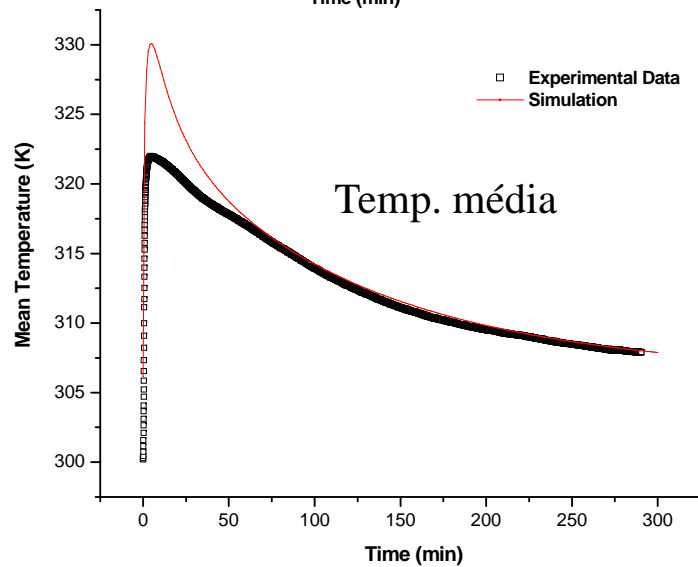
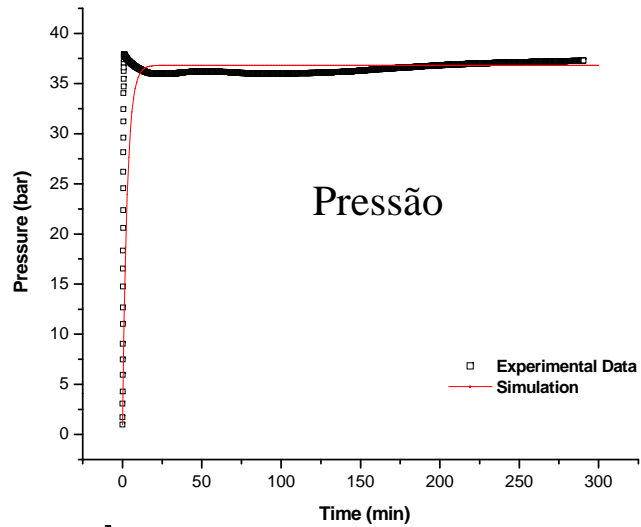
$$P = P_0, \quad \text{para } r = R_i$$



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Comentários Finais

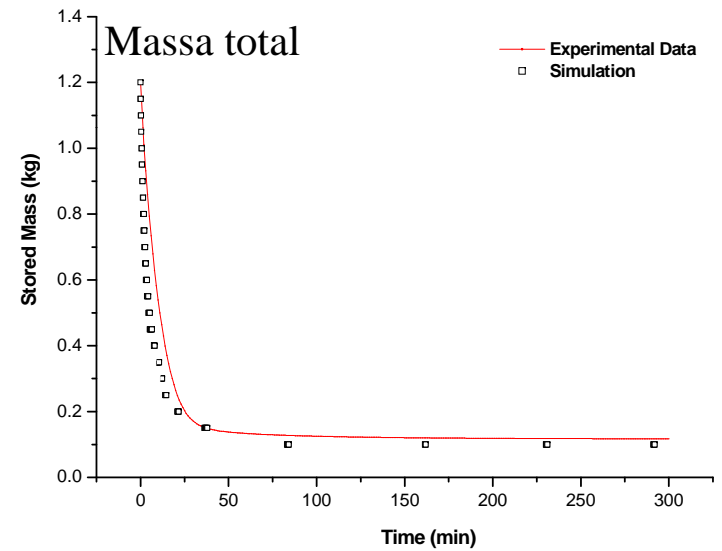
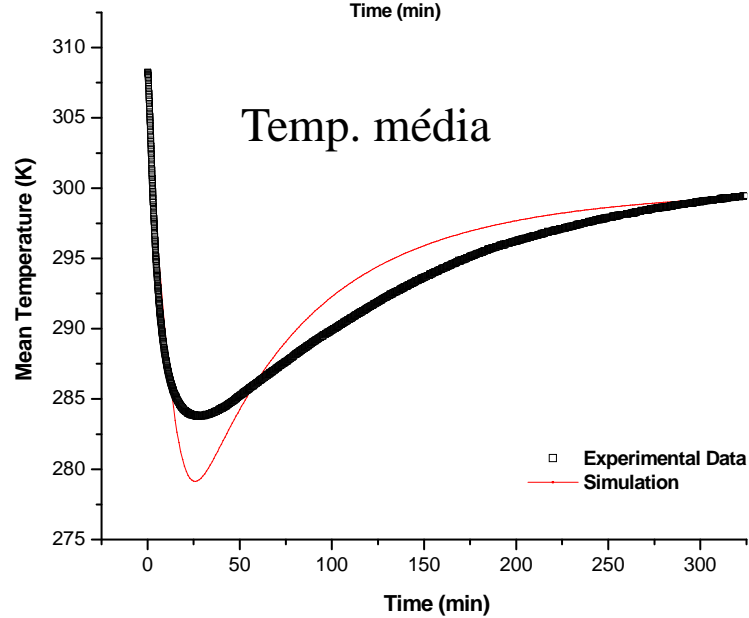
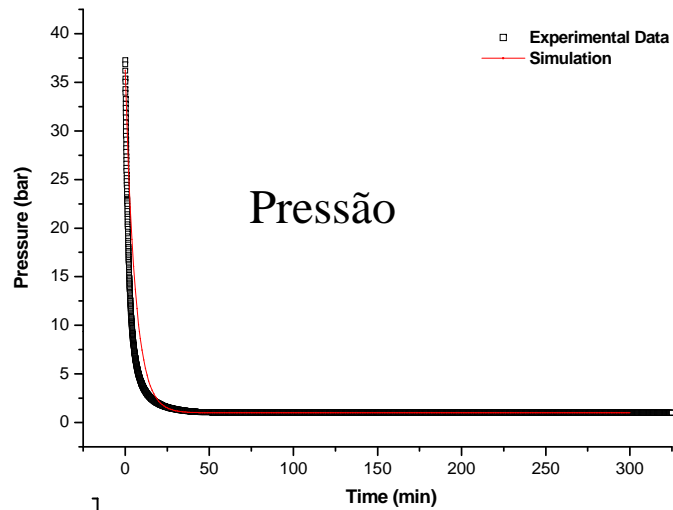
Simulação carga



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Comentários Finais

Simulação descarga



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