

Universidade de São Paulo
Instituto de Química



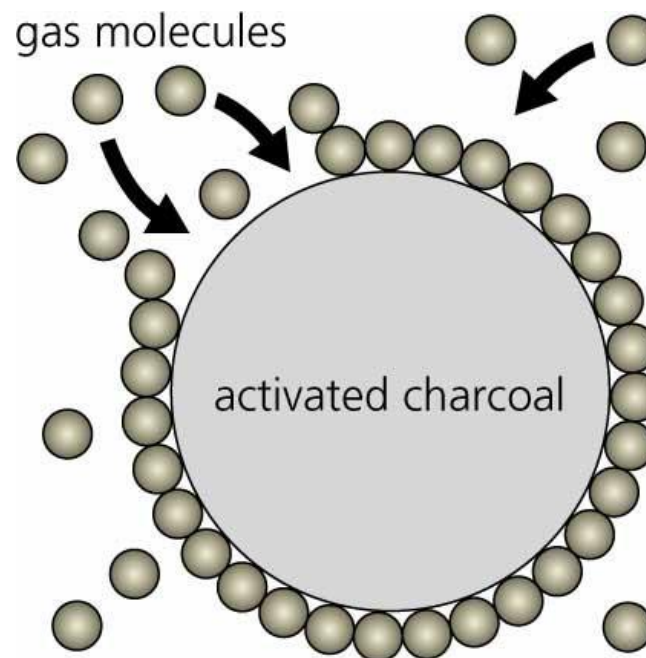
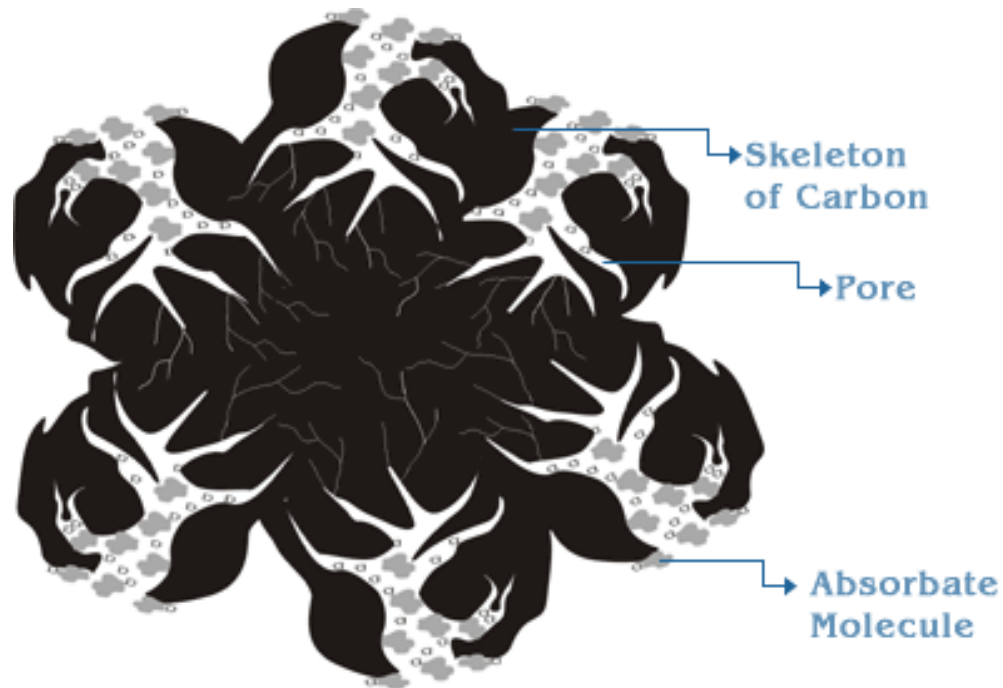
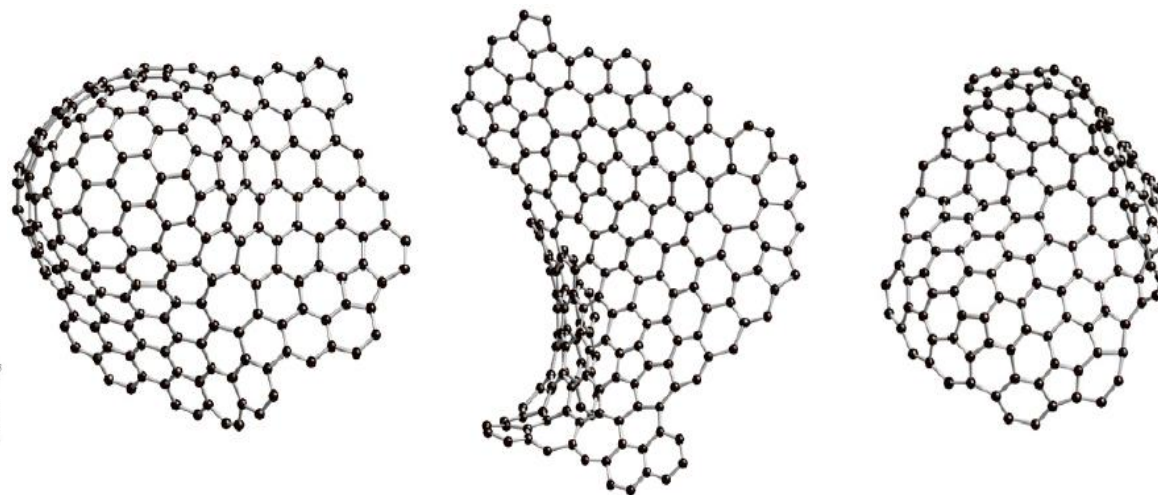
Colóquio – Adsorção de ácido acético sobre carvão ativo

QFL1444

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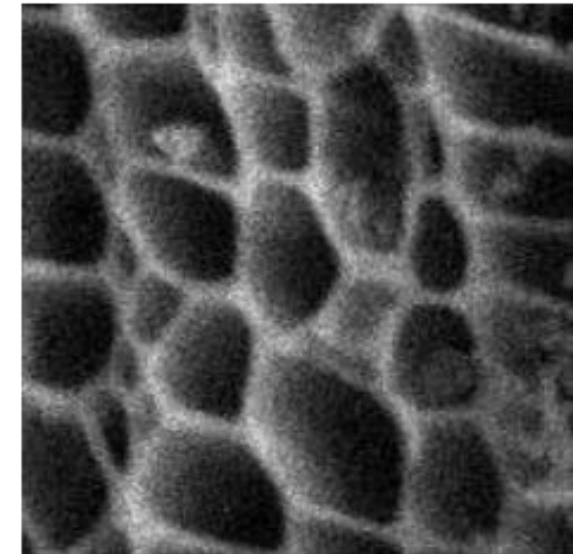
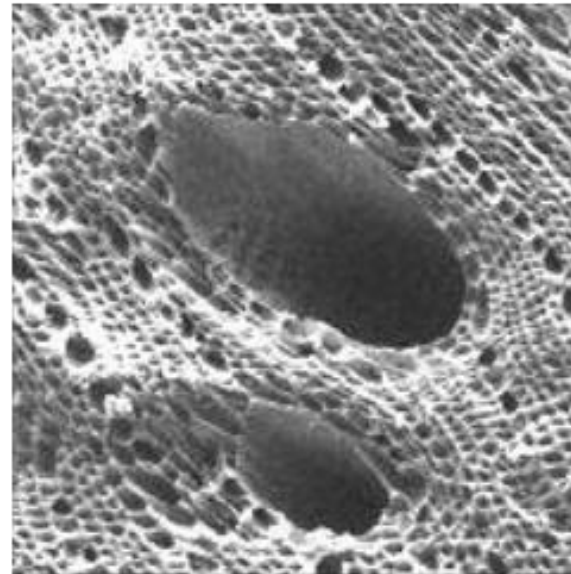
Carvão ativo: estrutura



Área superficial:

- 600 a 4000 m² (piscina olímpica aprox. 1250 m²)
- Possui heteroátomos ligados aos carbonos (principalmente oxigênio)

Carvão ativo: estrutura



Aumento

Carvão ativo - aplicações cotidianas



CARVÃO EM CÁPSULAS



<https://www.cliquefarma.com.br/>

Usos - amostras gas./líq.

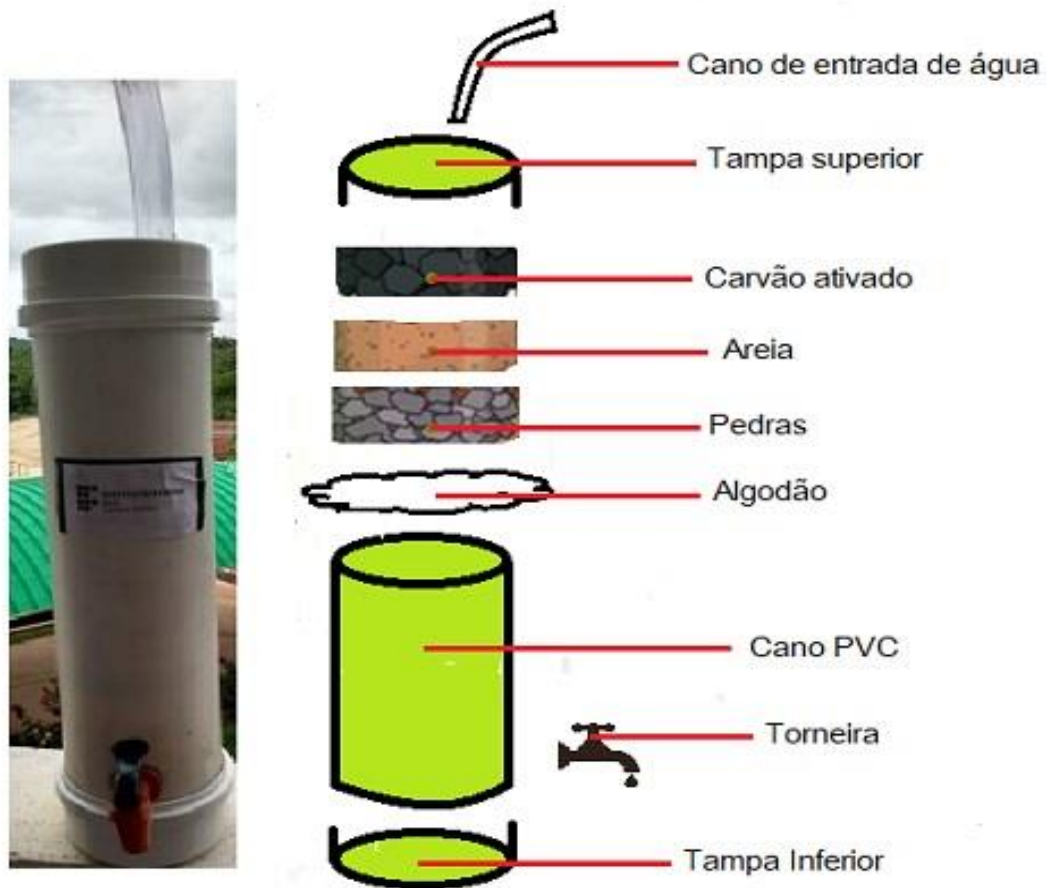
- Recuperação de espécies químicas
- Remoção: comp. orgânicos, metais e contaminantes em geral.
- Purificação
- Suporte sólido para catalisadores

Desvantagens?

- Ineficaz para espécies como ânions alcalinos, nitratos, metais pesados, etc.
- Vida curta, precisa ser trocado com frequência
- Tempo de filtragem pode ser um problema
- Algumas bactérias conseguem se desenvolver nos poros

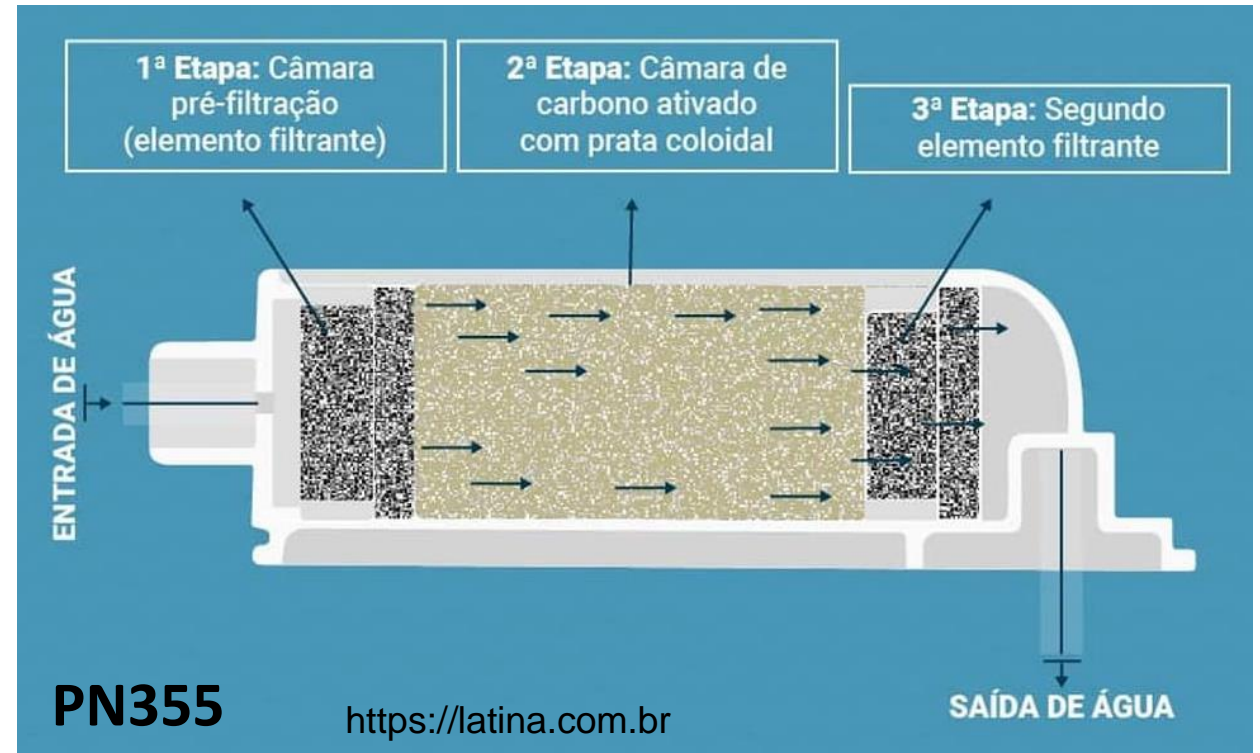


<https://lifestraw.com/>



<http://www.abq.org.br/cbq/2019/trabalhos/12/606-12804.html>

CBQ-2019 - Pinheiro et. al (IFPA)



Raramente empregado com único sistema de filtragem e/ou precisa de tratamentos específicos

Aplicações diversas – Carvão ativo

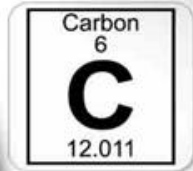


ACTIVATED CARBON

For Industrial Use/Applications



Carbon Based Water Treatment Plant



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Mail us: sales@nanoshel.com

Aplicações diversas – Carvão ativo

ACTIVATED CARBON MARKET

Global Activated Carbon Market Size, 2018-2026 (USD Billion)

**\$2.73
Billion** in 2018 & **\$4.09
Billion** by 2026

Global Activated Carbon Market Share, By Application, 2018

Air & Gas Purification 31.2%

Water Treatment | Food & Beverage | Others

North America Activated Carbon Market Size, 2018

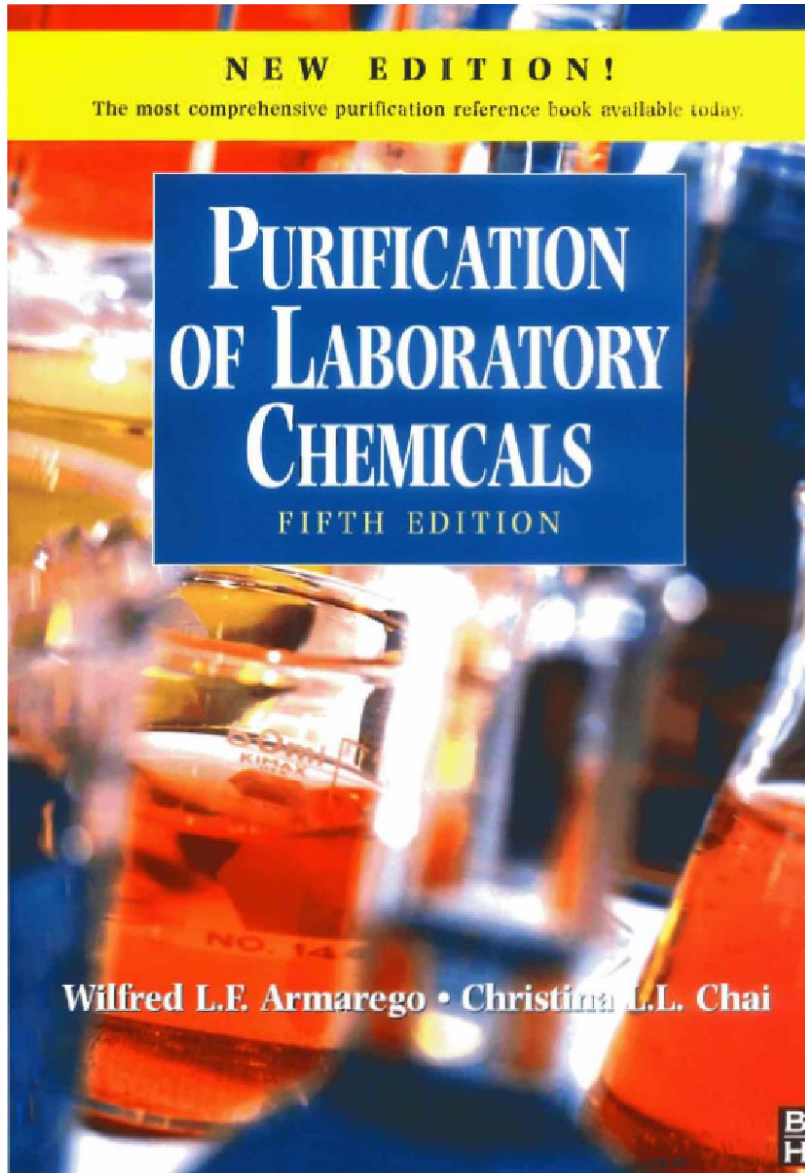
\$709.7 Million



 Copyrights © Fortune Business Insights | www.fortunebusinessinsights.com

<https://www.prnewswire.com/news-releases/activated-carbon-market-size-to-reach-usd-4-09-billion-by-2026-rising-urgency-to-curb-emissions-from-industries-worldwide-to-favor-market-growth-fortune-business-insights-301005902.html>

Aplicações diversas – Carvão ativo



Purificação de compostos químicos

RECRYSTALLISATION

Techniques

The most commonly used procedure for the purification of a solid material by recrystallisation from a solution involves the following steps:

- (a) The impure material is dissolved in a suitable solvent, by shaking or vigorous stirring, at or near the boiling point, to form a near-saturated solution.
- (b) The hot solution is filtered to remove any insoluble particles. To prevent crystallisation during this filtration, a heated filter funnel can be used or the solution can be diluted with more of the solvent.
- (c) The solution is then allowed to cool so that the dissolved substance crystallises out.
- (d) The crystals are separated from the mother liquor, either by centrifuging or by filtering, under suction, through a sintered glass, a Hirsch or a Büchner, funnel. Usually, centrifugation is preferred because of the greater ease and efficiency of separating crystals and mother liquor, and also because of the saving of time and effort, particularly when very small crystals are formed or when there is entrainment of solvent.
- (e) The crystals are washed free from mother liquor with a little fresh cold solvent, then dried.

If the solution contains extraneous coloured material likely to contaminate the crystals, this can often be removed by adding some activated charcoal (decolorising carbon) to the hot, but not boiling, solution which is then shaken frequently for several minutes before being filtered. (The large active surface of the carbon makes it a good adsorbent for this purpose.) In general, the cooling and crystallisation steps should be rapid so as to give small crystals which occlude less of the mother liquor. This is usually satisfactory with inorganic material, so that

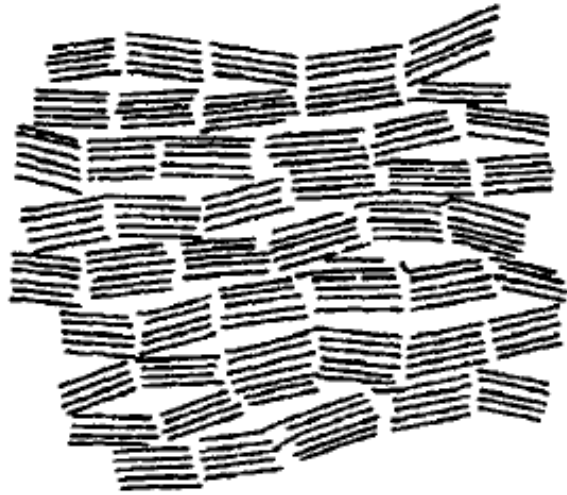


Philips Carbon, Inc.

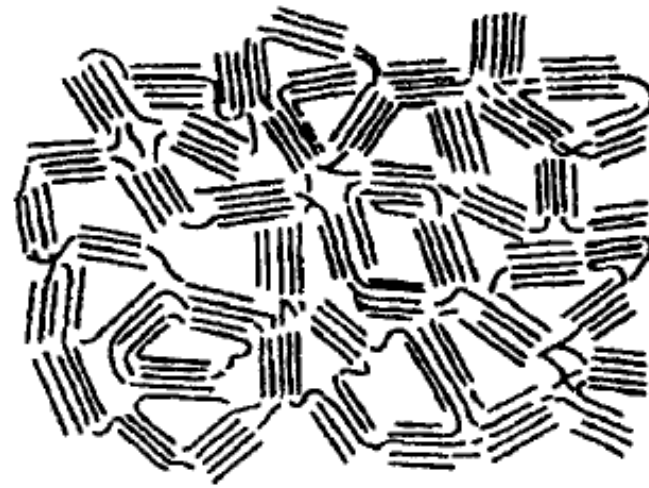
Your Professional Activated Carbon Source



Estrutura – Carvão ativo



(a) Graphitizable carbon



(b) Non-graphitizable carbon

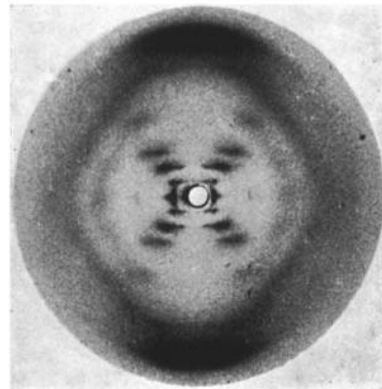
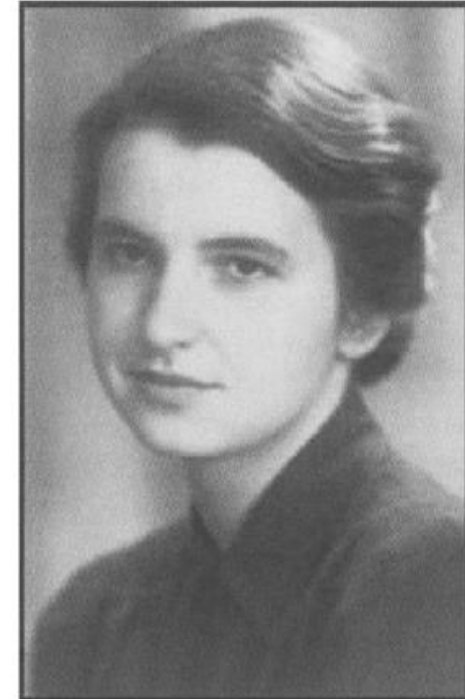


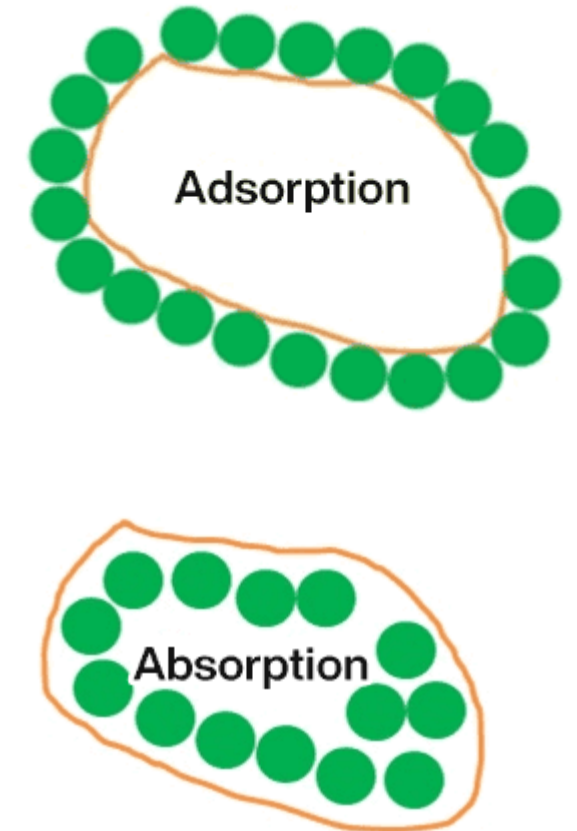
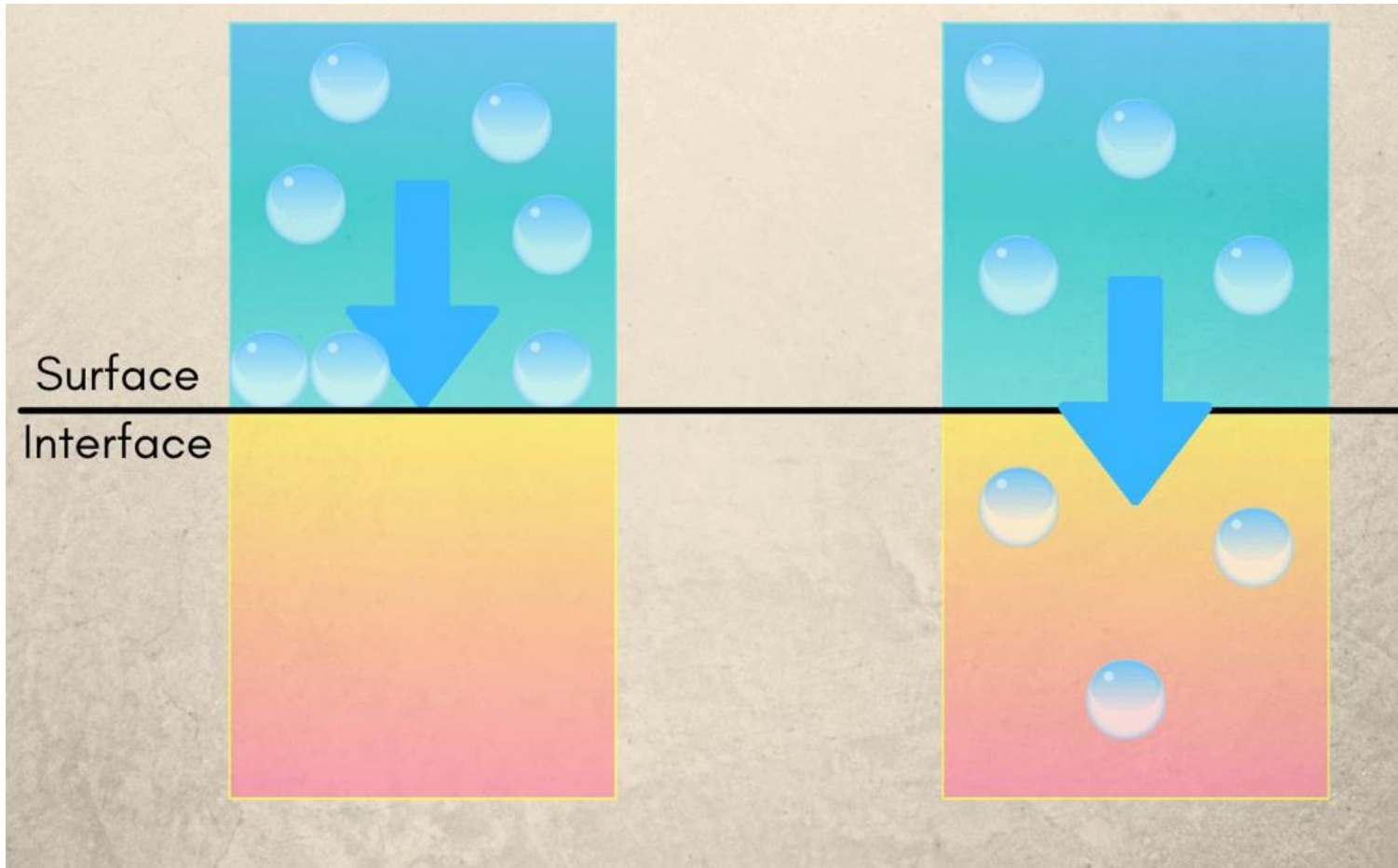
Photo 51



Rosalind Franklin (1920 – 1958)

Watson e Crick, Nobel 1962 - Dupla hélice

Adsorção vs. absorção

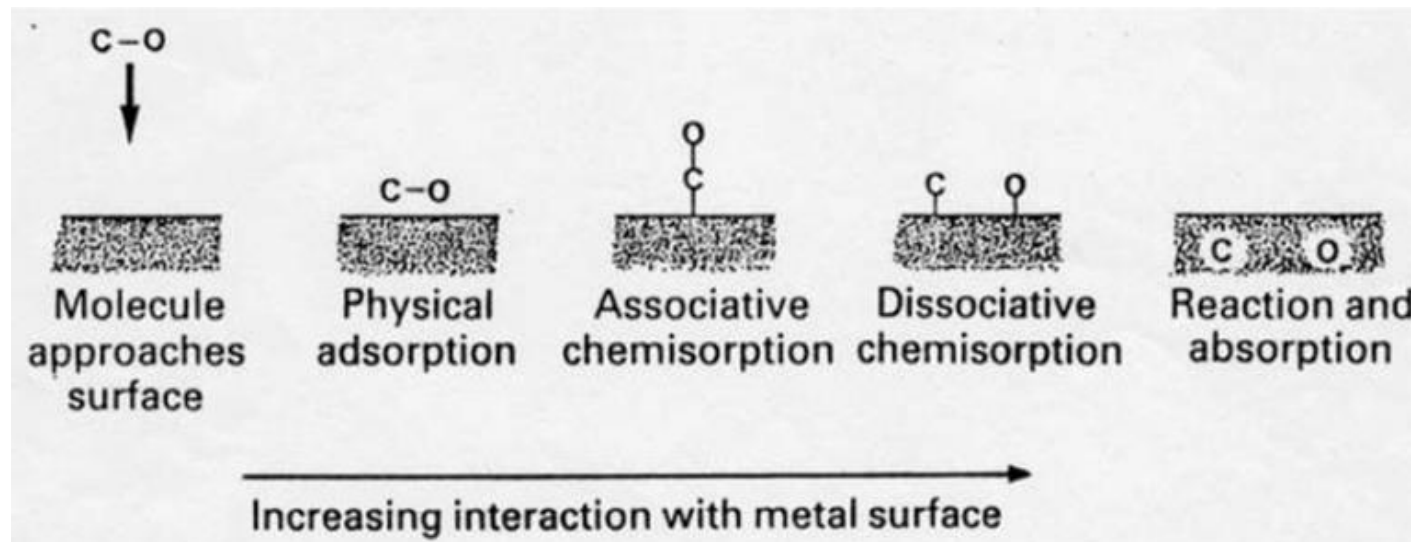


Fenômeno de **superfície** vs. Fenômeno do **“bulk”**

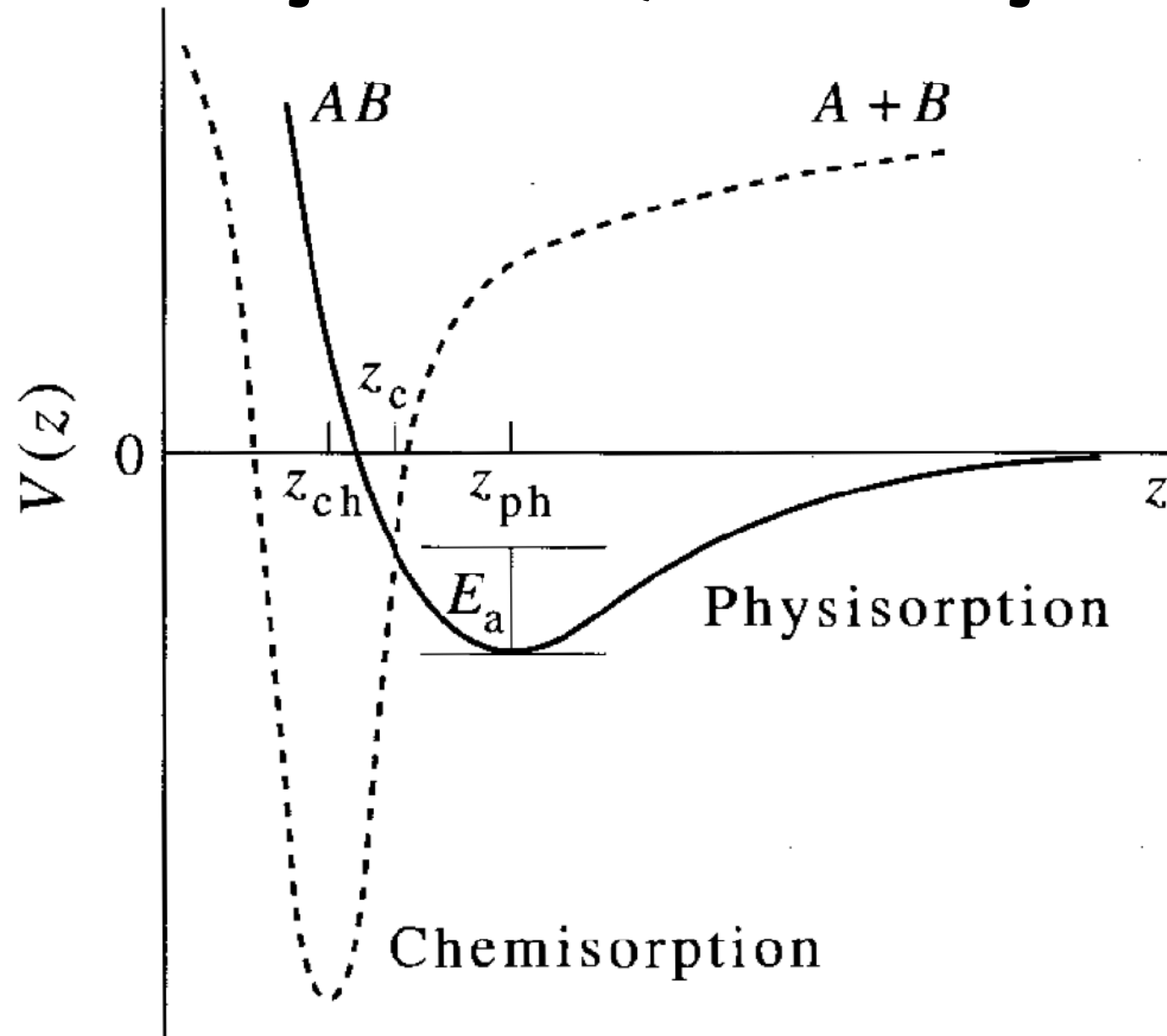
sciencenotes.org

Tipos de adsorção: Fisissorção vs. Quimissorção

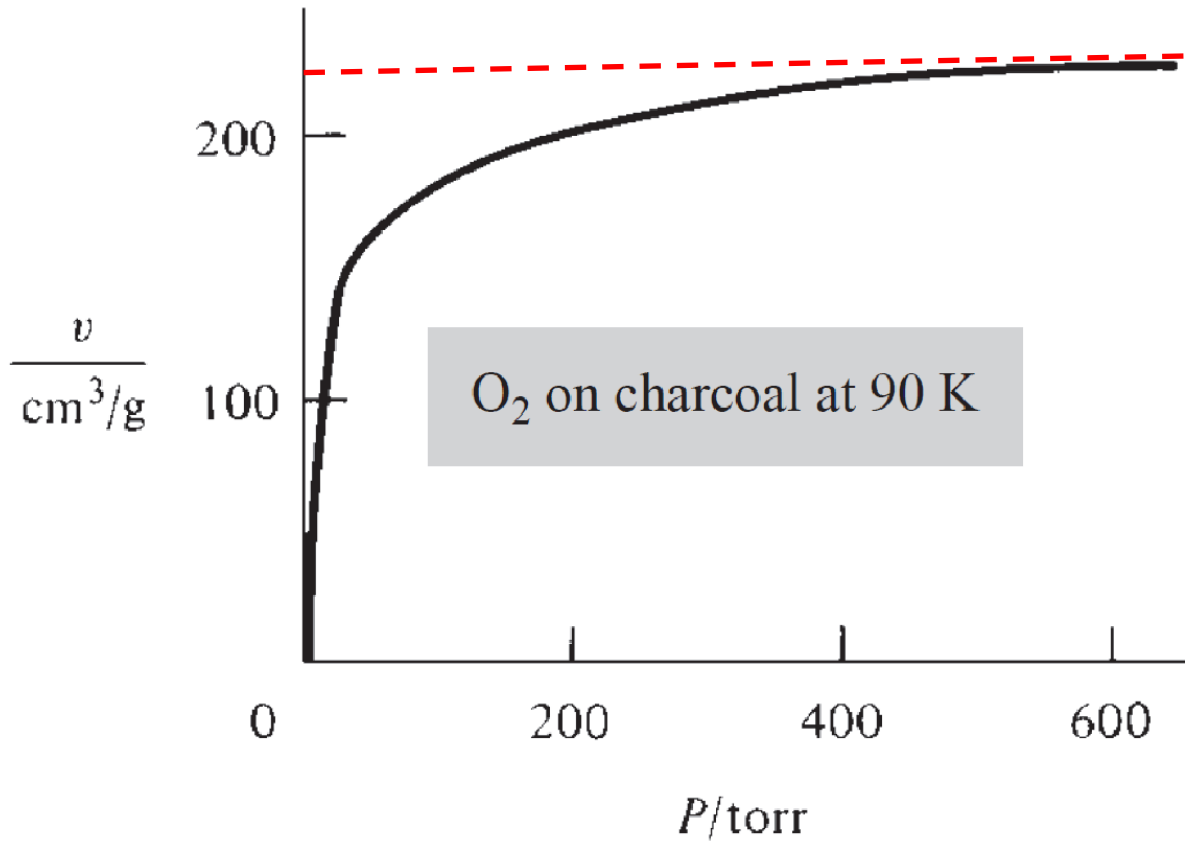
Propriedade	Fisissorção	Quimissorção
Tipo de Ligação	van der Waals (dispersão de London, dipolo-dipolo, etc.)	covalente ou iônica
Entalpia	20 a 40 kJ/mol	80 a 240 kJ/mol
Tipo de cobertura	1 ou mais camadas	1 camada
Reversível?	sim	não (geralmente)



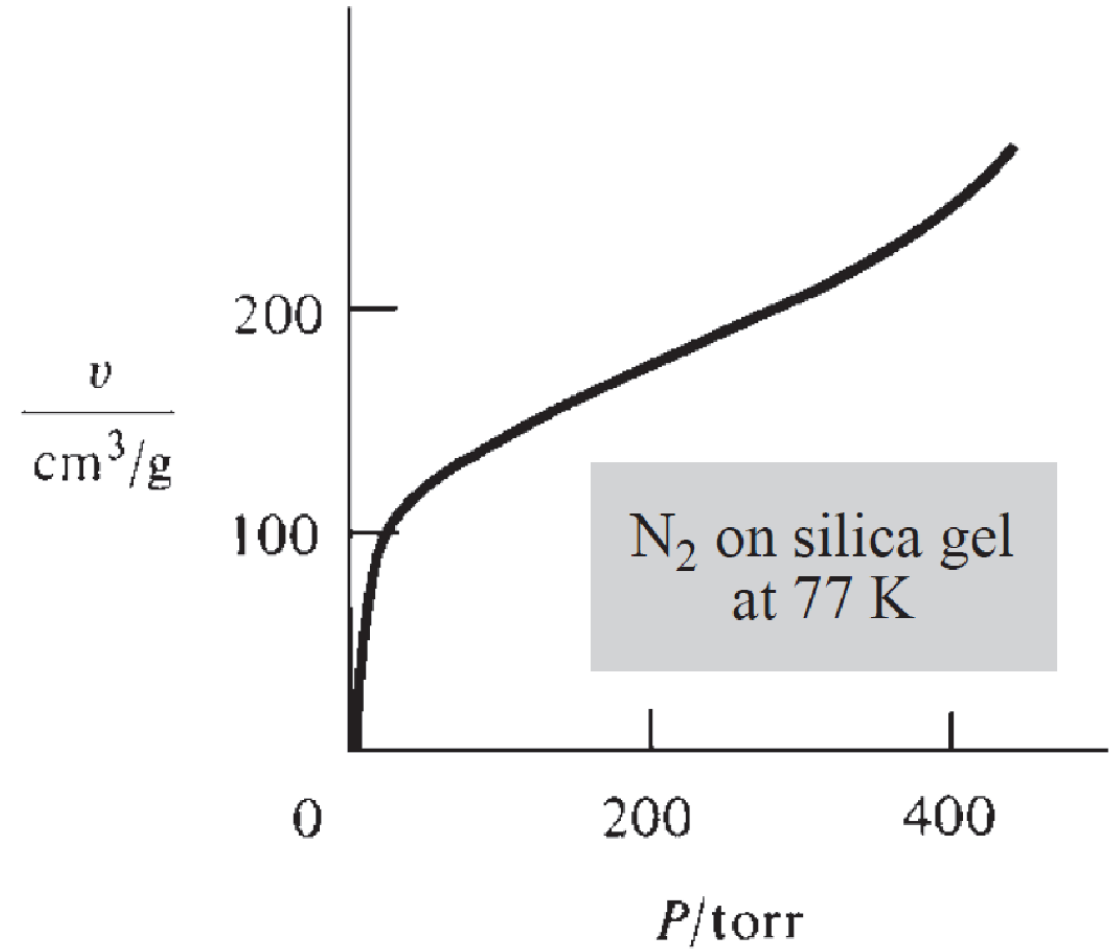
Fisissorção vs. Quimissorção



Exemplos – Adsorção de O₂ em carvão ativo e N₂ em sílica



Tipo I



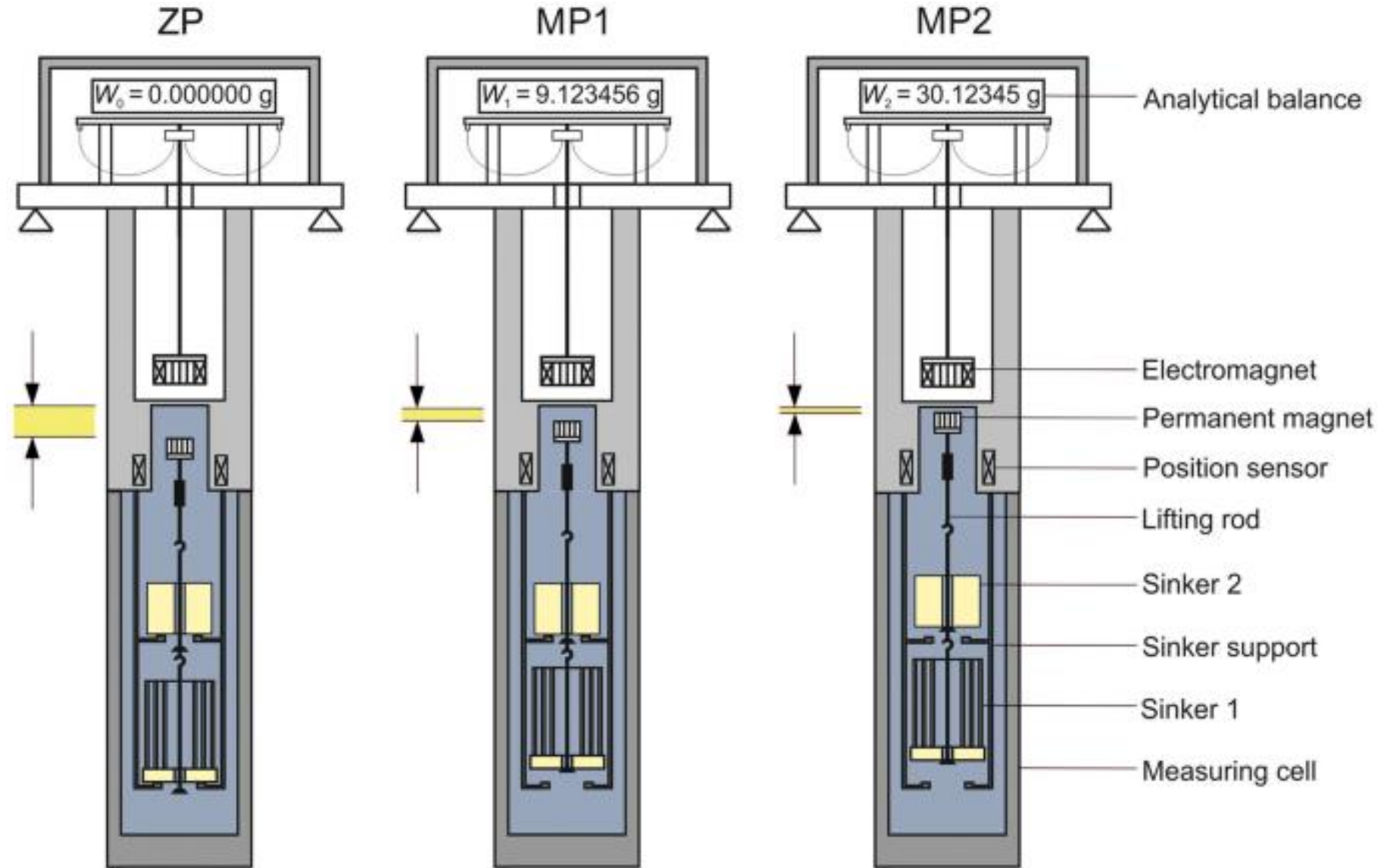
Tipo II

Como determinar esses diagramas?

$$\theta = \frac{\text{Sítios ocupados}}{\text{Sítios totais}}$$

$$q_e = \frac{m_{\text{adsorbato}}}{m_{\text{adsorvente}}}$$

$$q_e = \frac{X}{m}$$

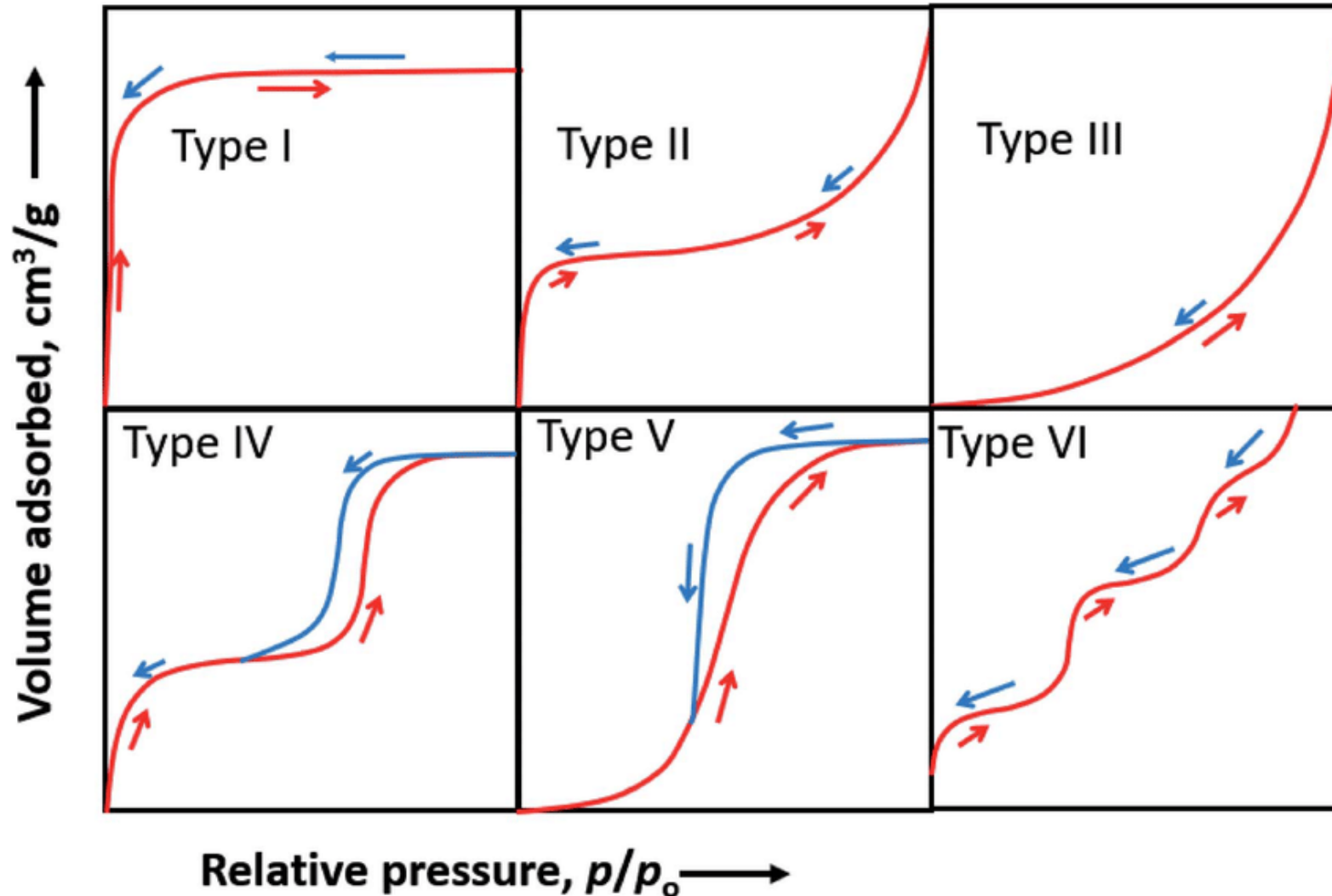


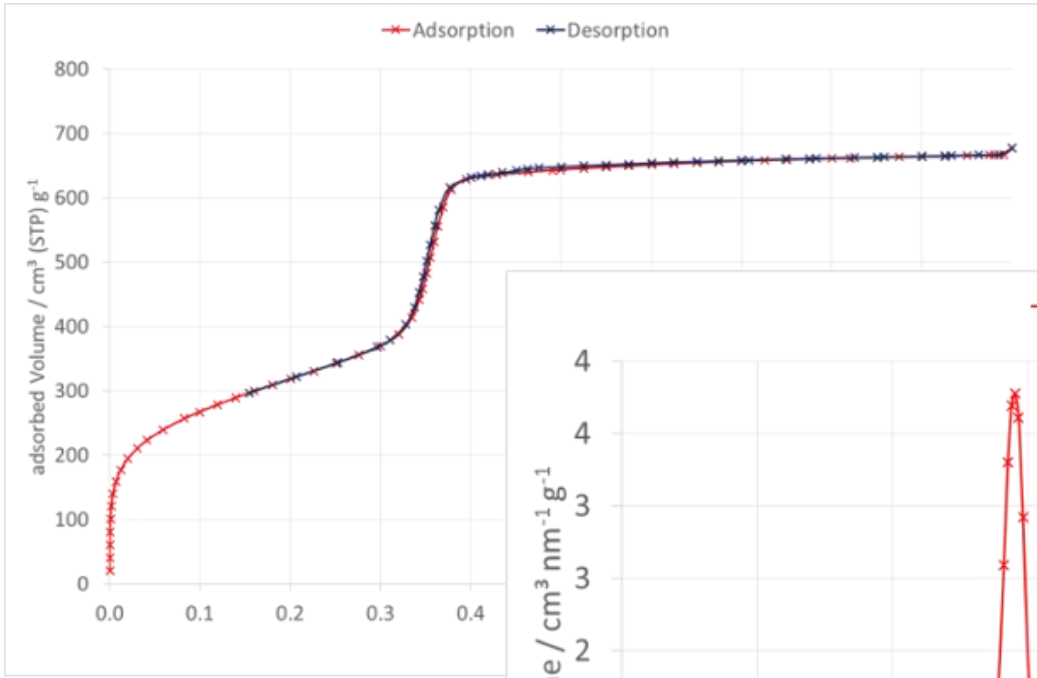
O que pode influenciar a adsorção?

- Área superficial do adsorvente
- Grupos funcionais na superfície do adsorvente
- Temperatura
- Solubilidade do adsorbato
- Natureza química do adsorbato.
- Tempo suficiente para ser estabelecido um **equilíbrio** entre o adsorbato em solução e adsorvido.

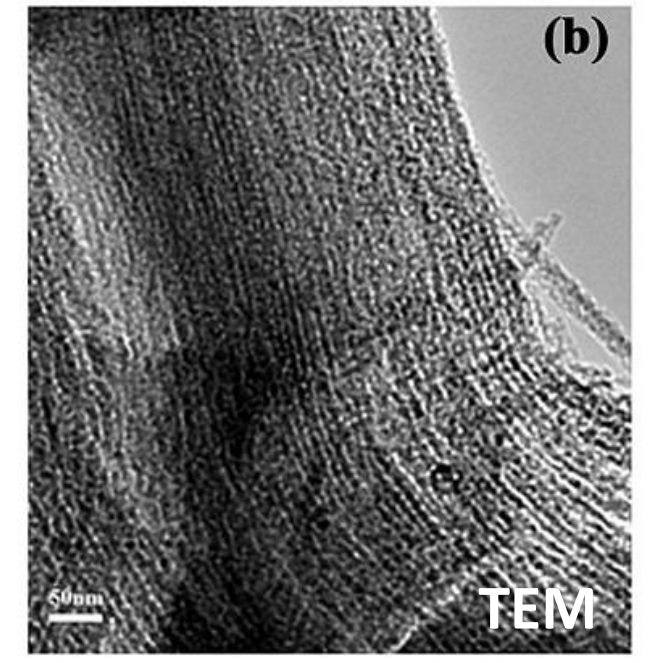
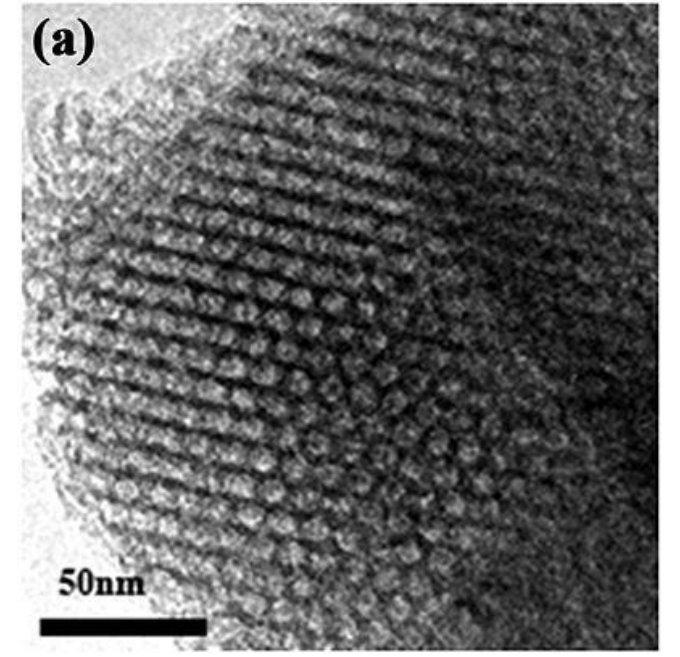
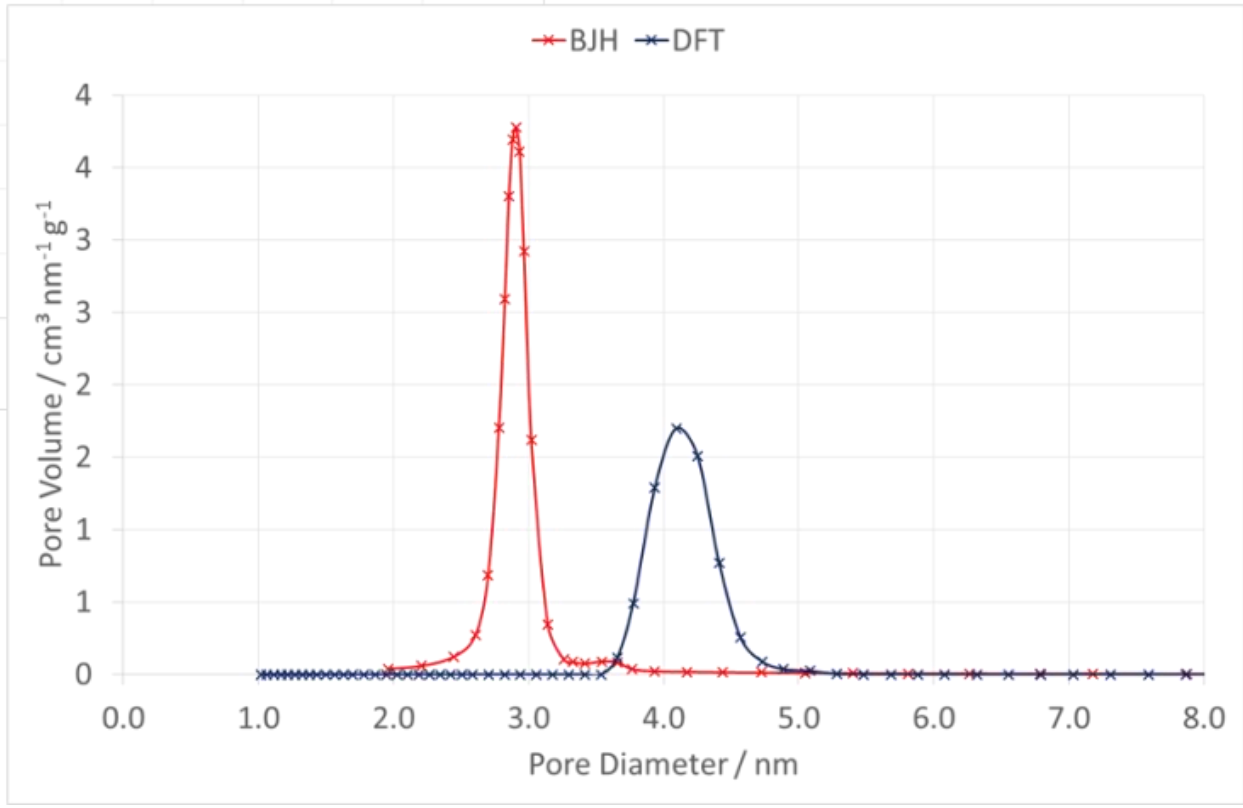
No equilíbrio, o estudo quantitativo das relações entre as quantidades no meio e adsorvidas, a dada temperatura, podem ser definidas por uma **isoterma**

Tipos de adsorção classificados pela IUPAC





MCM-41



<https://www.3p-instruments.com/measurement-methods/gas-adsorption/>
https://en.wikipedia.org/wiki/File:Mesoporous_carbon_TEM.jpg

Isotermas de adsorção

Diferentes modelos



I. Langmuir



1932

"for his discoveries and investigations in surface chemistry."

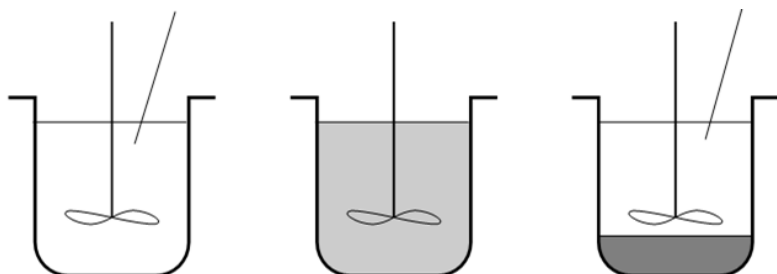


H. Freundlich

Outras isotermas:

- BET*
- Temkin
- Dubinin-Radushkevich
- ...

Experimento de adsorção de ácido acético em carvão ativado

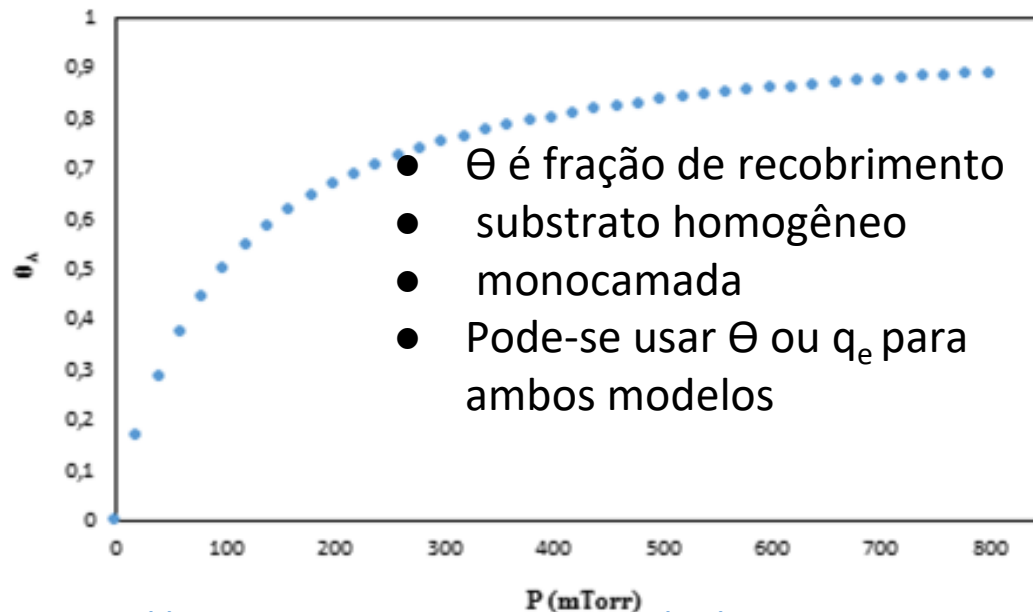


Modelos de adsorção

Langmuir:

$$\theta = \frac{K_L P}{1 + K_L P}$$

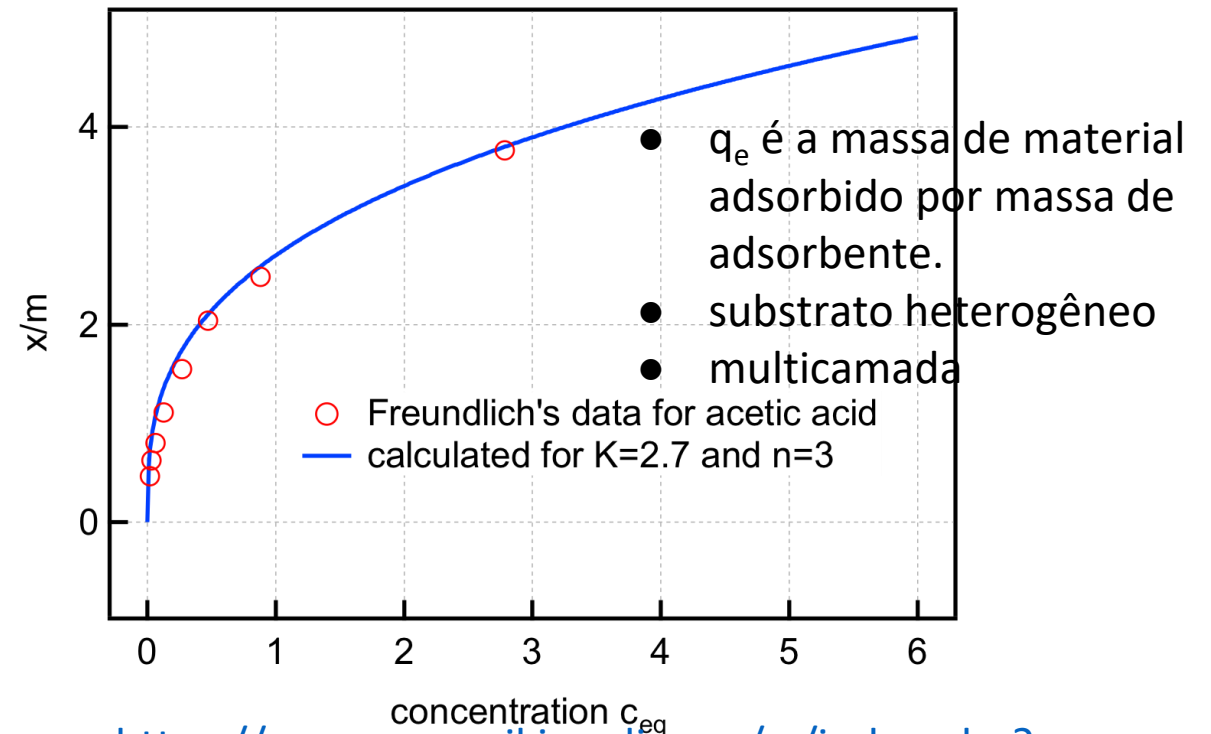
Surface coverage



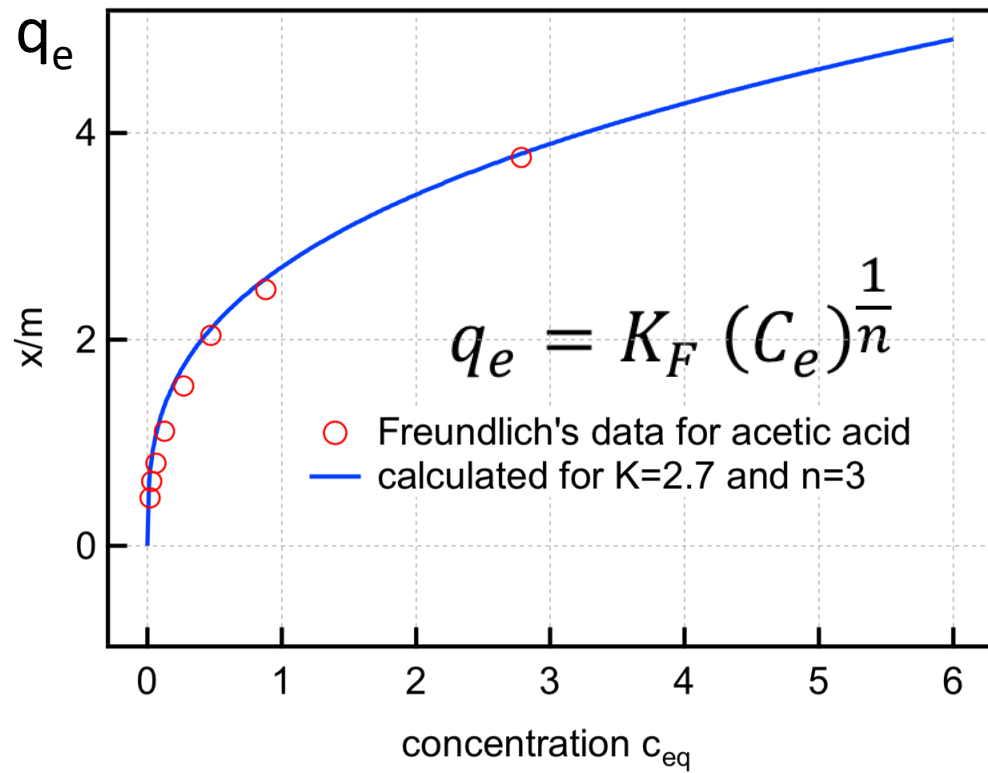
<https://commons.wikimedia.org/w/index.php?curid=51208299>

Freundlich:

$$q_e = K_F (C_e)^{\frac{1}{n}}$$



<https://commons.wikimedia.org/w/index.php?curid=59075650>



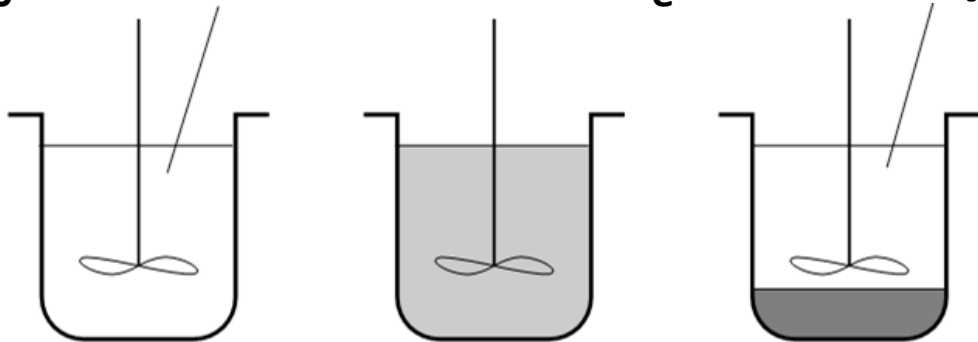
Construção da isoterma

$$q_e = \frac{(C_0 - C_e)V}{m}$$

$q_e = x/m$ = massa adsorbato/massa do adsorbente (mg/g)

C_0 = conc. inicial

C_e = conc. equil.



Agitação e tempo para equilíbrio

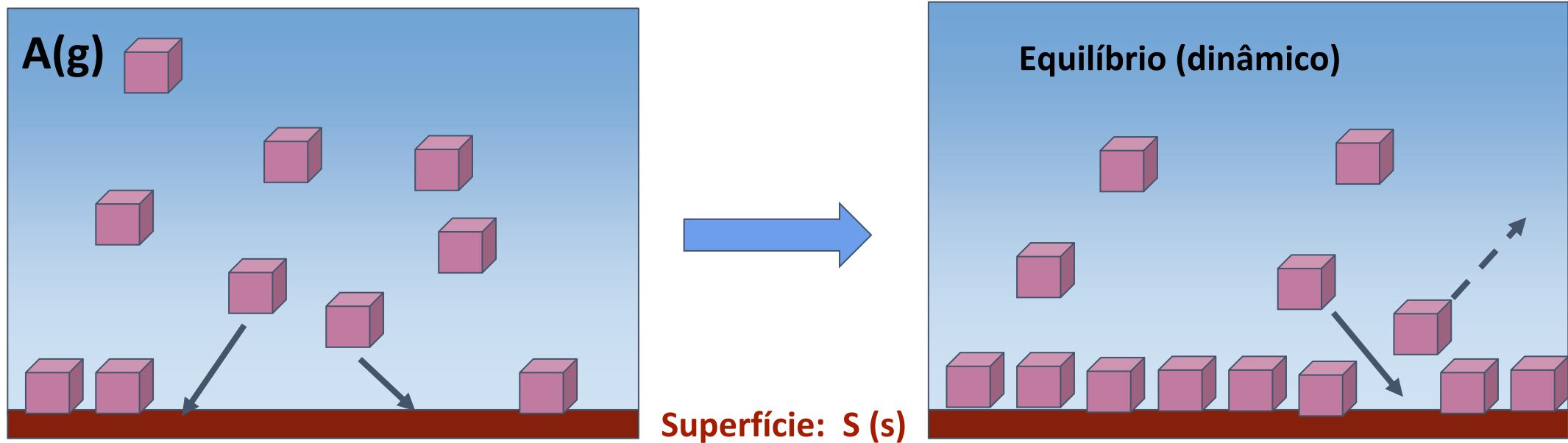
C_0 = conc. inicial de adsorbato (mg/L)

C_e = conc. equilíbrio (mg/L); massa adsorbida = q_e

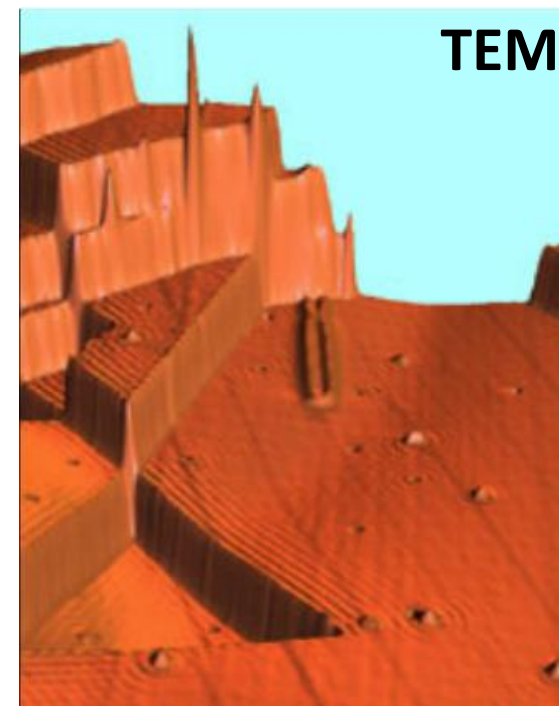
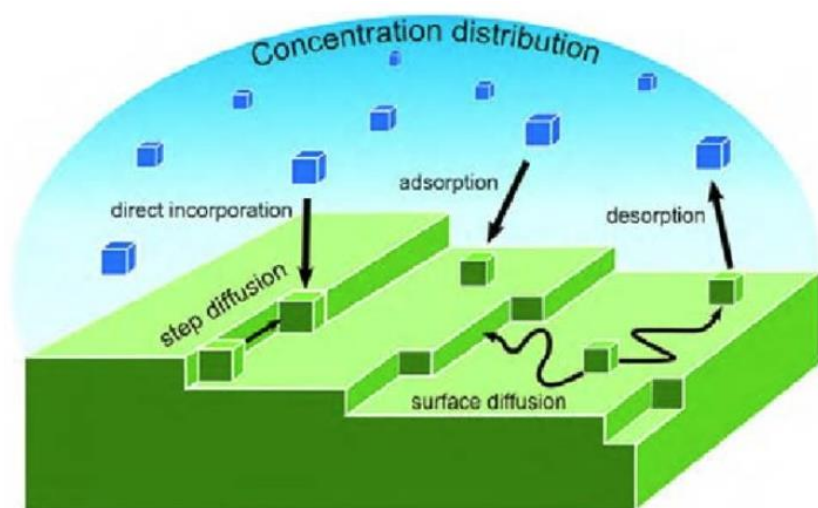
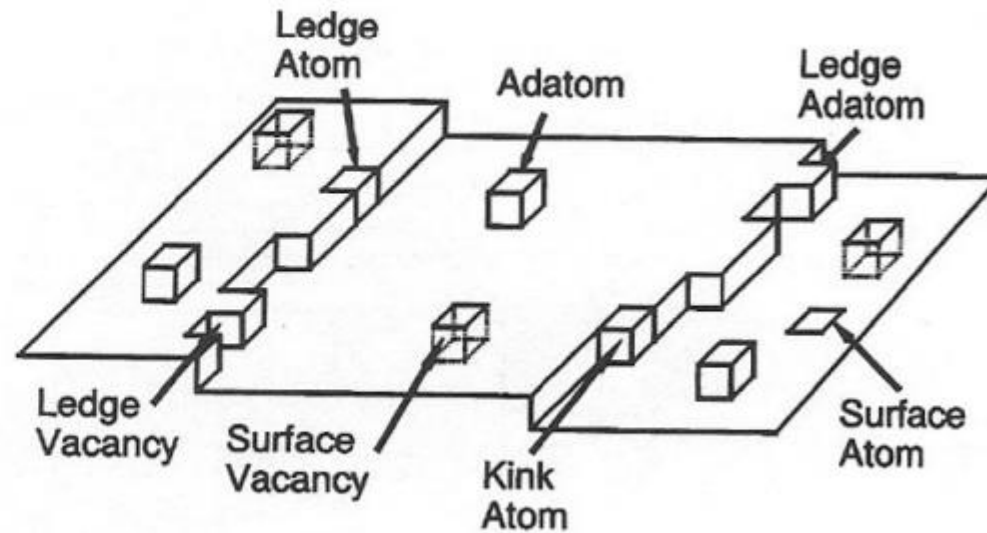
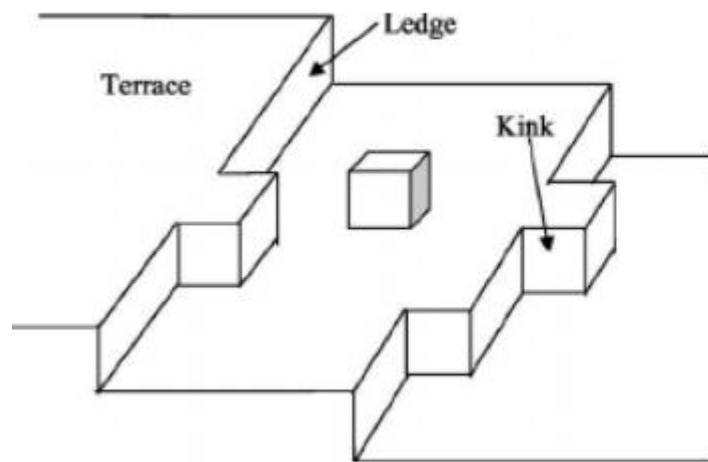
V = volume da solução (L)

m = massa do adsorbente (g)

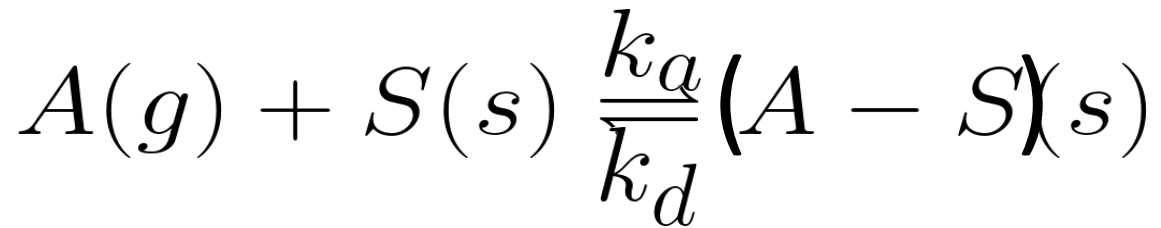
Isoterma de Langmuir (1918)



- Sistema modelo ideal (gás perfeito)
- Distribuição dos poros de maneira homogênea
- Distribuição homogênea dos adsorbatos
- Mesma energia envolvida em todas adsorções
- Partículas não-interagentes
- Monocamada de adsorbatos



Isoterma de Langmuir (1918)



Equilíbrio: $v_{ads} = v_{des}$

$$\frac{k_a}{k_d} = K_c = \frac{[A - S]}{[A][S]}$$

$$\sigma_0 = [\textit{sitios}]m^{-2}$$

θ = fracao sitios ocupados

$\theta\sigma_0$ = conc. sitios ocupados

$\sigma_0 - \theta\sigma_0$ = conc. sitios vazios

$$v_{des} \propto \theta\sigma_0$$

$$v_{ads} \propto \sigma_0 - \theta\sigma_0$$

$$v_{ads} \propto [A] \text{ ou } P_A$$



$$v_{des} = k_d\theta\sigma_0$$

$$v_{ads} = k_a(1 - \theta)\sigma_0 P_A$$

Isoterma de Langmuir (1918)

$$k_a(1 - \theta)\sigma_0 P_A = k_d\theta\sigma_0 \quad \text{Equilíbrio: } v_{ads} = v_{des}$$

$$k_a(1 - \theta)\cancel{\sigma_0} P_A = k_d\theta\cancel{\sigma_0}$$

$$\frac{k_a}{k_d}(1 - \theta)P_A = \theta \quad \Longrightarrow \quad K_L(1 - \theta)P_A = \theta$$

$$\frac{1 - \theta}{\theta} = \frac{1}{P_A K_L}$$

$$\frac{1}{\theta} = 1 + \frac{1}{K_L P_A}$$

$$\theta = \frac{K_L P_A}{1 + K_L P_A}$$

Isoterma de Langmuir (1918)

Transformar em unidades de massa (q)

$$\theta = \frac{q}{q_{max}}$$

$$\frac{q}{q_{max}} = \frac{K_L P_A}{1 + K_L P_A}$$

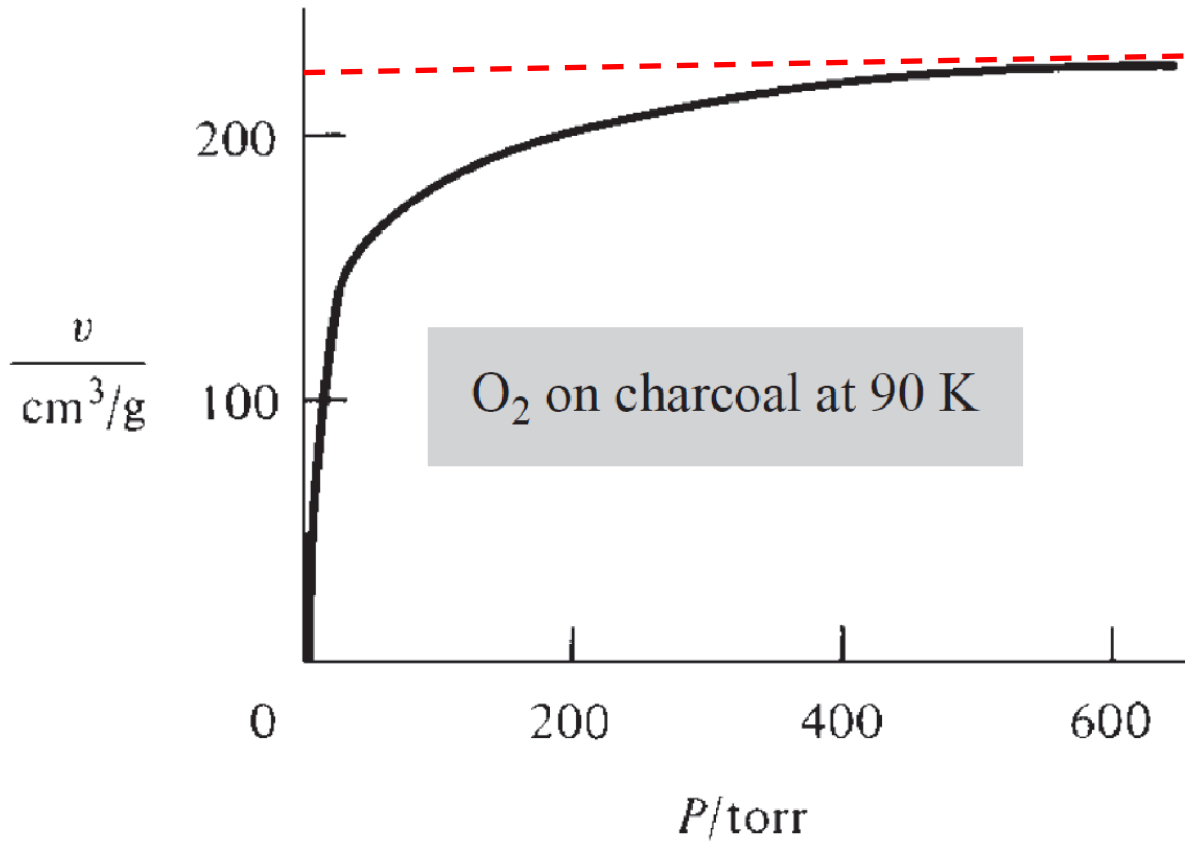
$$\frac{1}{q} = \frac{1 + K_L P_A}{q_{max} K_L P_A} \quad \longrightarrow \quad \frac{P_A}{q} = \frac{1}{K_L q_{max}} + \frac{P_A}{q_{max}}$$

$$K_L P^0 = K \text{ (sem unidade)}$$

$$[A] = \frac{P_A}{k_B T}$$

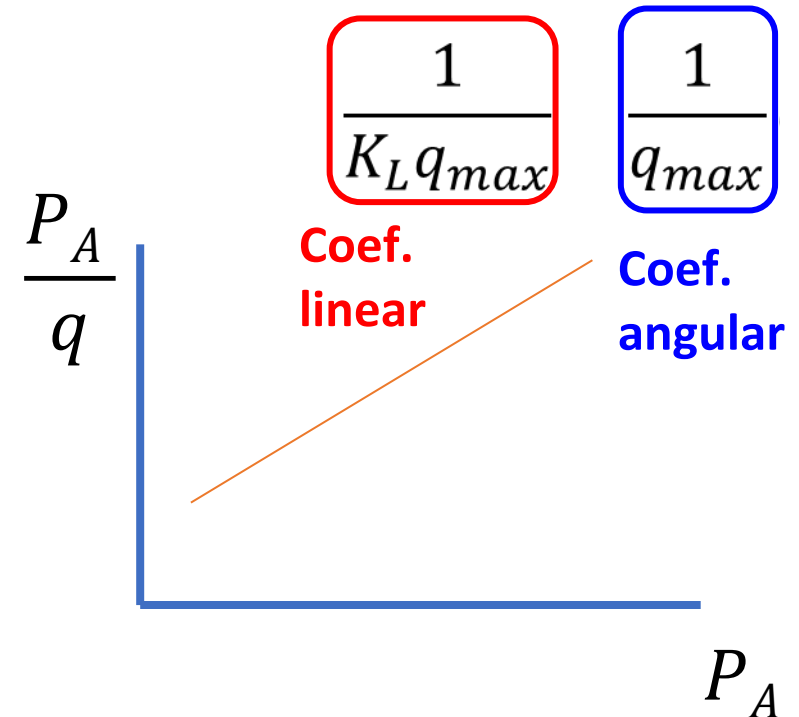
- Substituindo na expressão anterior:
- Vamos linearizar a expressão:

Exemplos – Adsorção de O₂ em carvão ativo e N₂ em sílica



Tipo I

$$\frac{P_A}{q} = \frac{1}{K_L q_{max}} + \frac{P_A}{q_{max}}$$



Entalpia de adsorção

$$\Delta_{ads}G = \Delta_{ads}H - T\Delta_{ads}S$$

$$\Delta_{ads}S < 0$$

$$\Delta_{ads}H < 0$$

$$\Delta_{ads}G < 0 \quad (\textit{espontaneo})$$

$$\Delta G^{\circ} = -RT \ln K \quad K = K_L(p^{\circ})$$

Construir isotermas com várias T, usando a equação de **Gibbs-Helmoltz**

$$\frac{\ln(K_L P^{\circ})}{dT} = \frac{\Delta_{ads}H^{\circ}}{RT^2} \rightarrow \frac{d \ln(K_L P^{\circ})}{d(1/T)} = -\frac{\Delta_{ads}H^{\circ}}{R}$$

Entalpia de adsorção

$$\frac{d \ln(K_L P^0)}{d(1/T)} = - \frac{\Delta_{ads} H^0}{R}$$

K_L é diretamente relacionado a P , o que facilita a construção do gráfico de $\ln P$ por $1/T$. Com Θ fixo, podemos escrever:

$$\left(\frac{d \ln(P/P^0)}{d(1/T)} \right)_0 = - \frac{\Delta_{ads} H^0}{R}$$

Isoterma de Freundlich

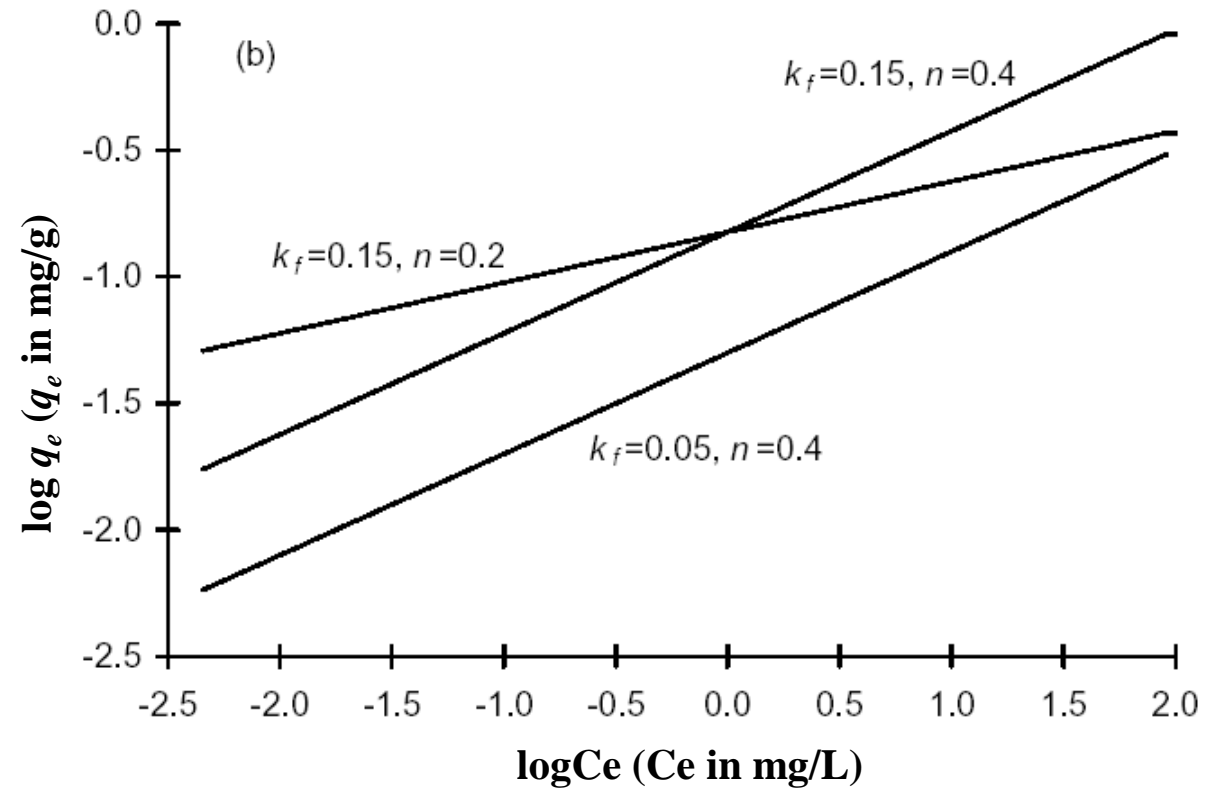
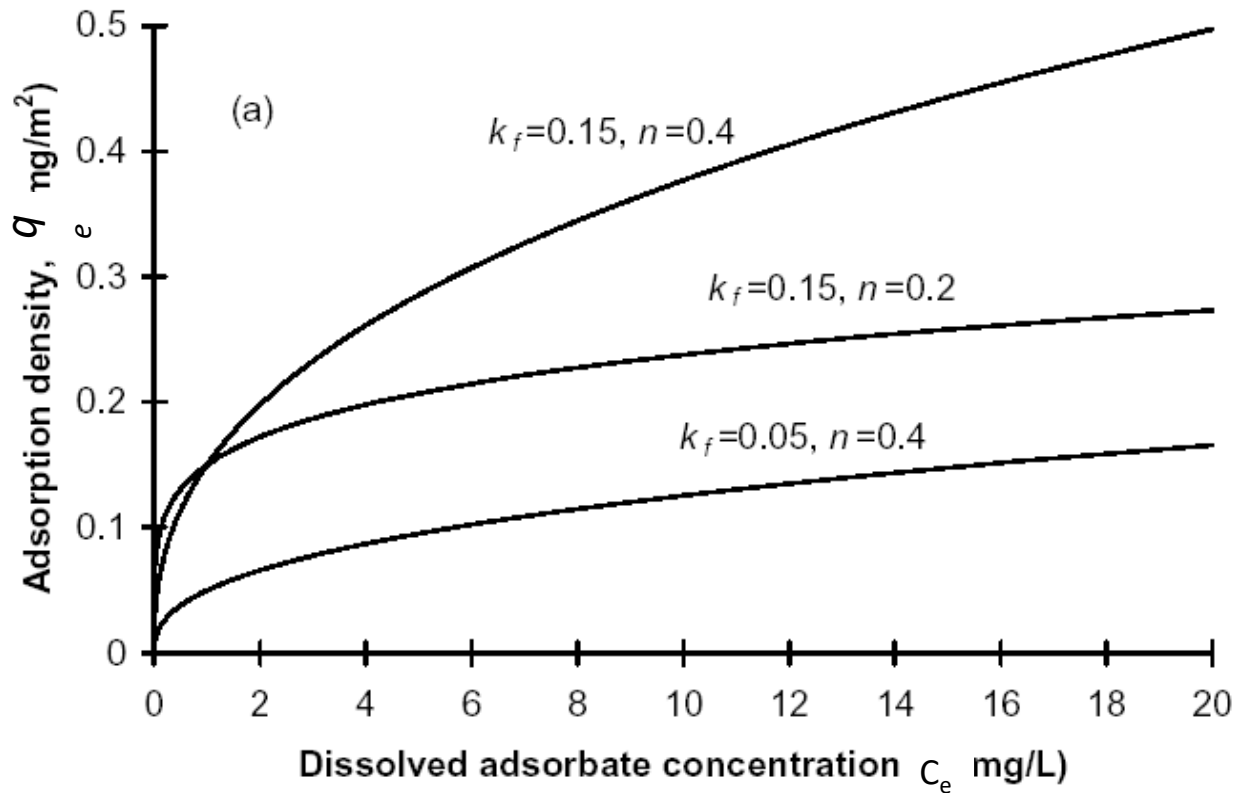
- Modelo empírico para superfície heterogênea e com entalpia de adsorção não uniforme

$$q_e = K_F (C_e)^{1/n}$$

- K_F = const. Freundlich (mg/g) - capacidade de adsorção
- n = parâmetro que reflete a heterogeneidade e intensidade de adsorção
- K_F e n dependem da T (n aumenta com T , e K_F diminui)
- Menor n , maior heterogeneidade.
- $1 < n < 10$ leva à adsorção favorável.
- Para linearizar, apliquemos o logaritmo

$$\log q_e = \log K_F + \frac{1}{n} \log(C_e)$$

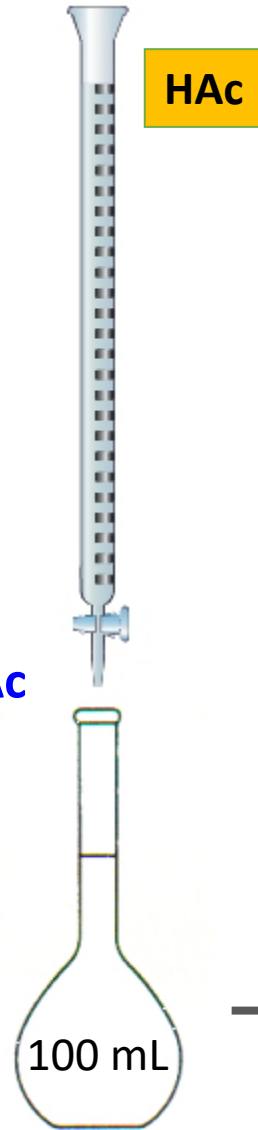
Isoterma de Freundlich



$$q_e = K_F (C_e)^{1/n}$$

$$\log q_e = \log K_F + \frac{1}{n} \log(C_e)$$

Experimento



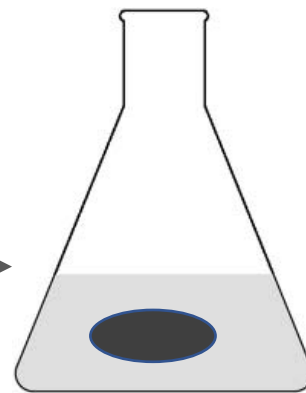
HAc

100 mL

Preparar 5 soluções de HAc

4,0 mL, 8,0 mL, 12,0 mL, 16,0 mL e 20 mL de HAc, completando com água destilada

Medir a temperatura no início e fim do experimento



1,0 g



40 min no shaker



Experimento

Volume de HAc na solução / mL	Volume da alíquota / mL	Volume médio de NaOH (0,09825 M) na titulometria / mL	Massa de carvão ativado / g
20.00	5.00	9.35	1.04
16.00	5.00	7.60	1.04
12.00	25.00	28.50	1.03
8.00	25.00	9.30	1.07
4.00	25.00	9.65	1.02

$$q_e = \frac{C_0 - C_e}{m} \times V$$

- Apresentar os gráficos de $q_e \times C_e$ e comparar os pontos experimentais com os gráficos segundo os modelos linearizados (Langmuir e Freundlich)
- Apresentar uma tabela comparativa com os parâmetros de ajuste obtidos (q_{\max} , K_L , n , K_F , R^2) com as respectivas unidades

Modelos de adsorção

Langmuir:

$$\theta = \frac{K_L P}{1 + K_L P}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e$$

**Coef.
linear**

**Coef.
angular**

Freundlich:

$$q_e = K_F (C_e)^{\frac{1}{n}}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

**Coef.
linear**

**Coef.
angular**

Referências

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- http://www.biospektrum.de/blatt/d_bs_pdf&id=1008995