



Universidade de São Paulo
Instituto de Química



L1 - Adsorção de ácido acético sobre carvão ativo

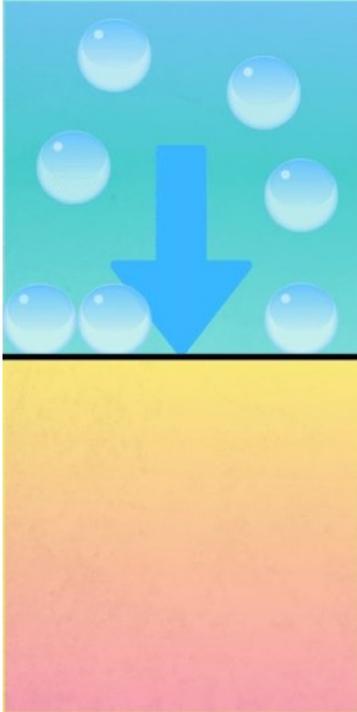
Prof. Vitor Leite Martins

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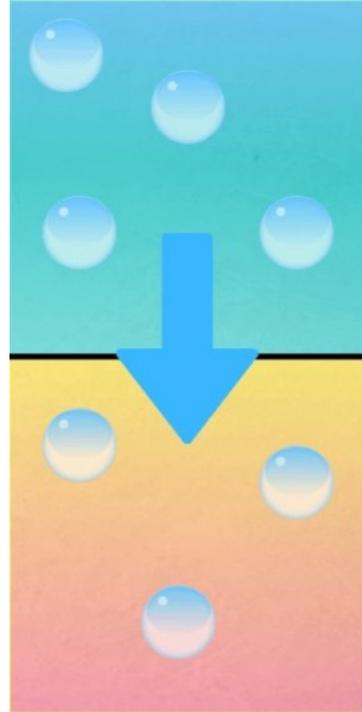
QFL1444 - 2023

Adsorção

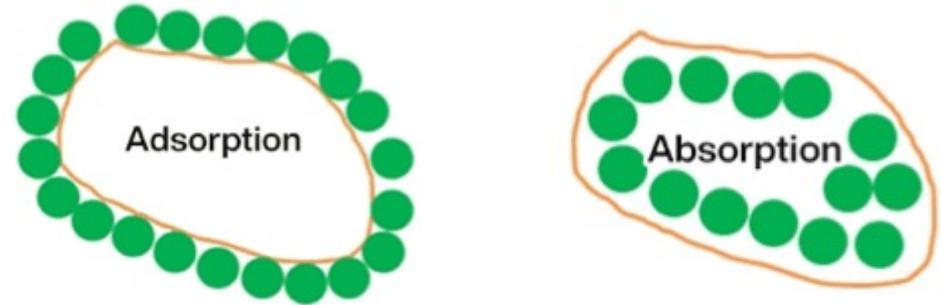
É um processo de interação entre espécies de um meio com uma **superfície**



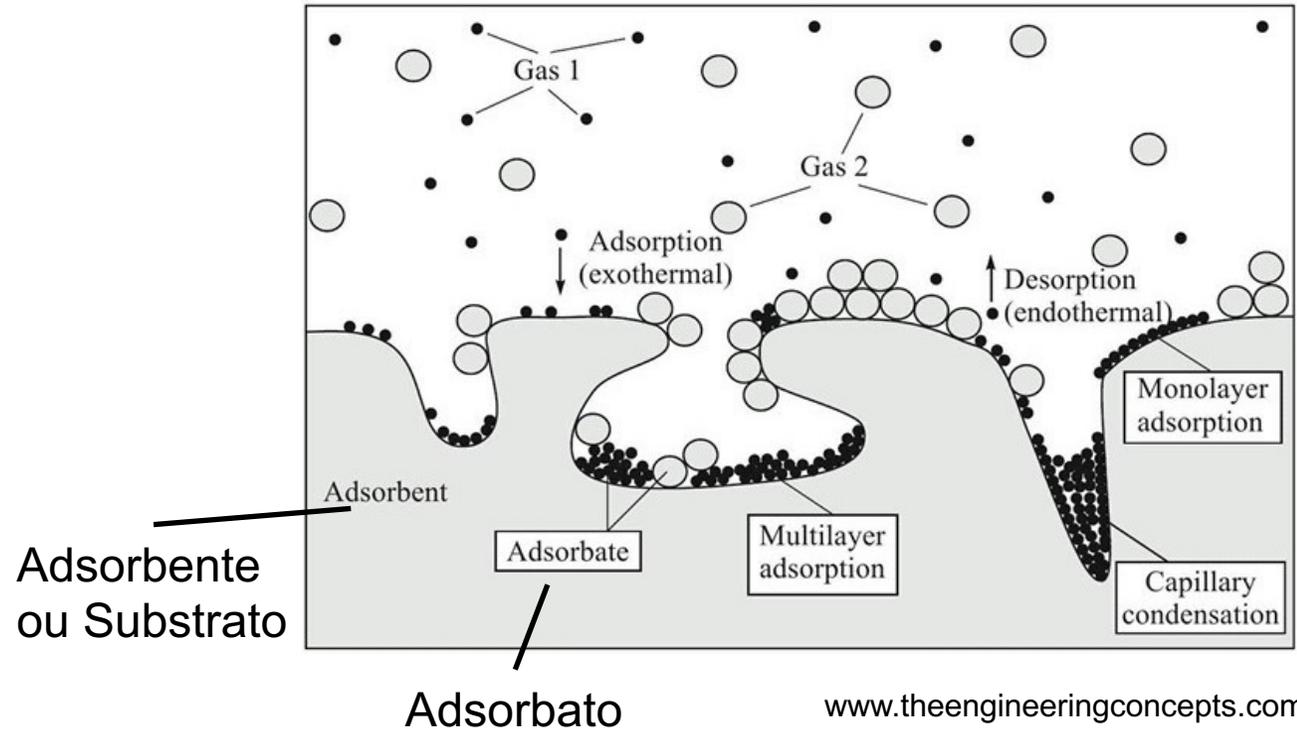
Fenômeno de superfície



Não confundir com absorção, um fenômeno bulk

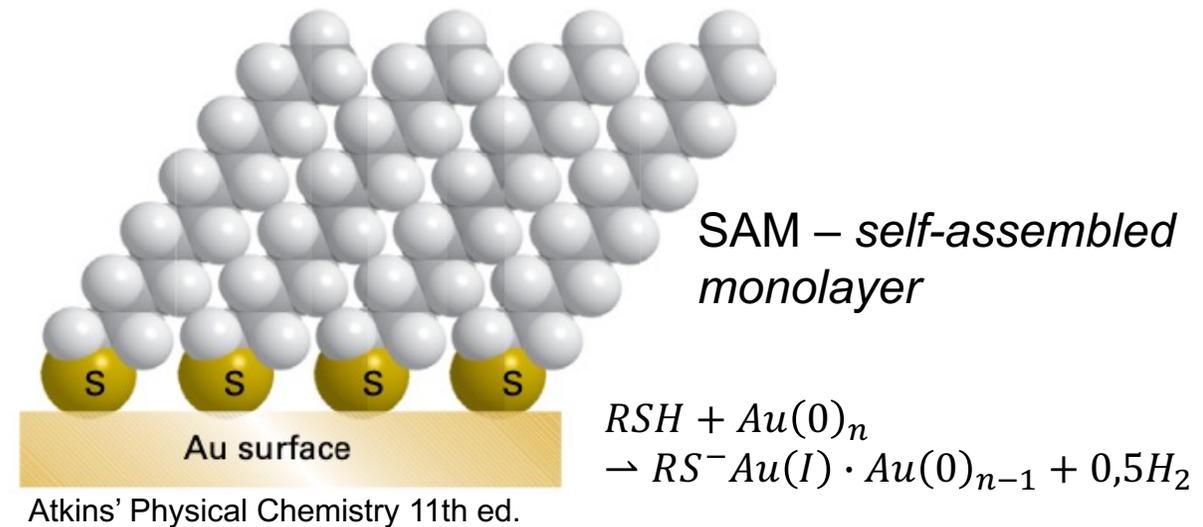
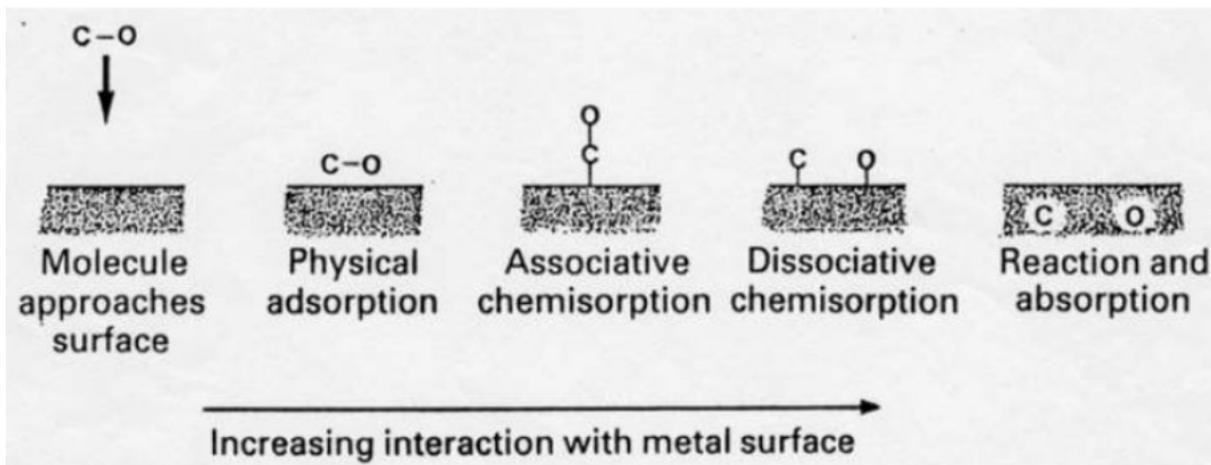


<https://www.carbotecnica.info>

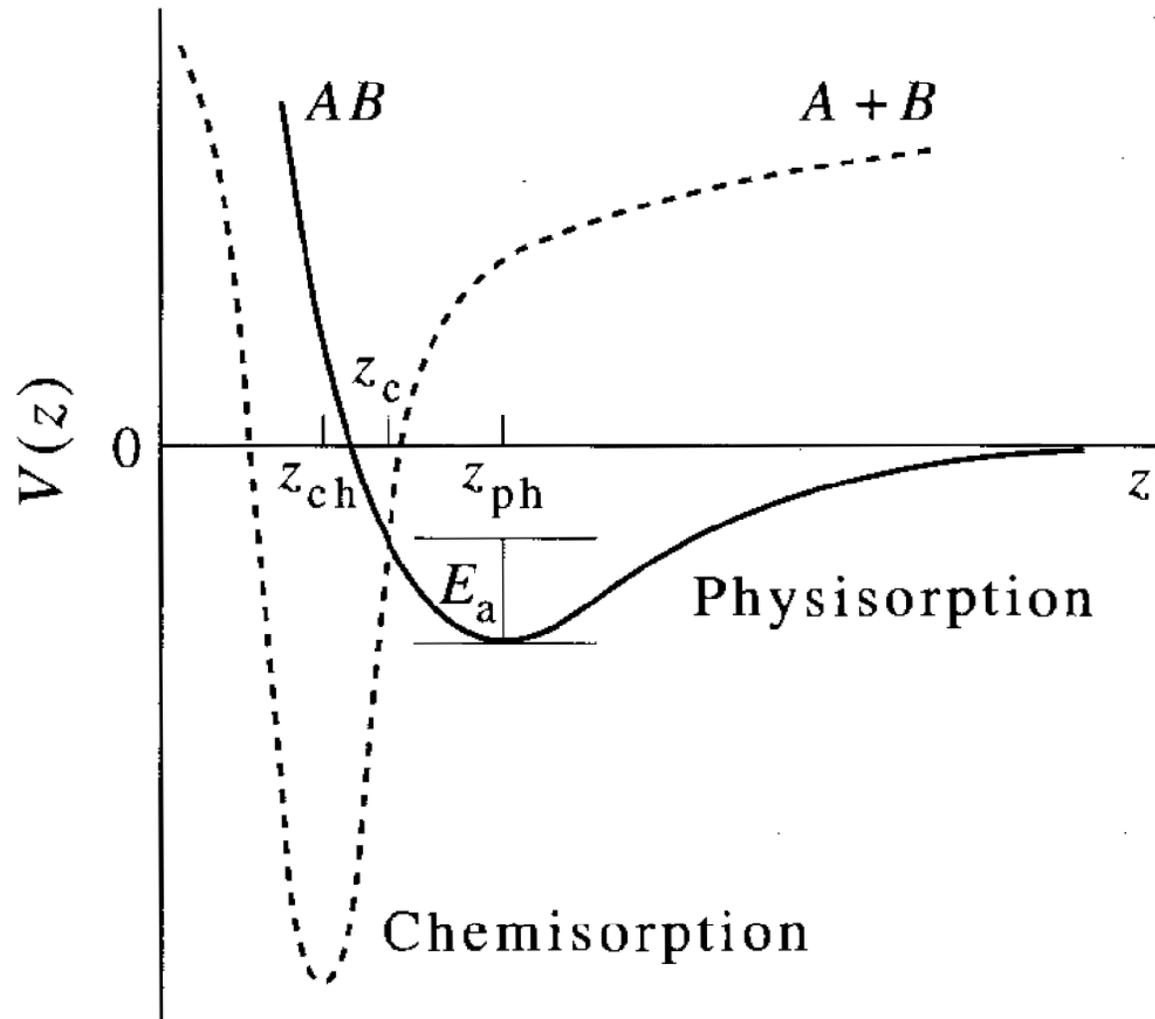


Tipos de Adsorção

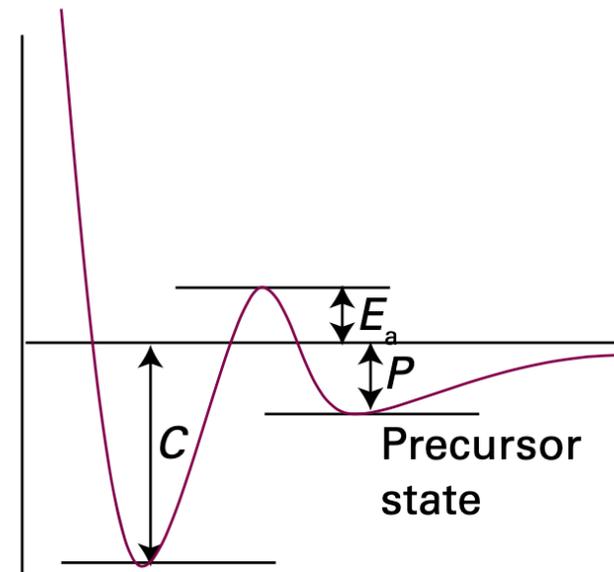
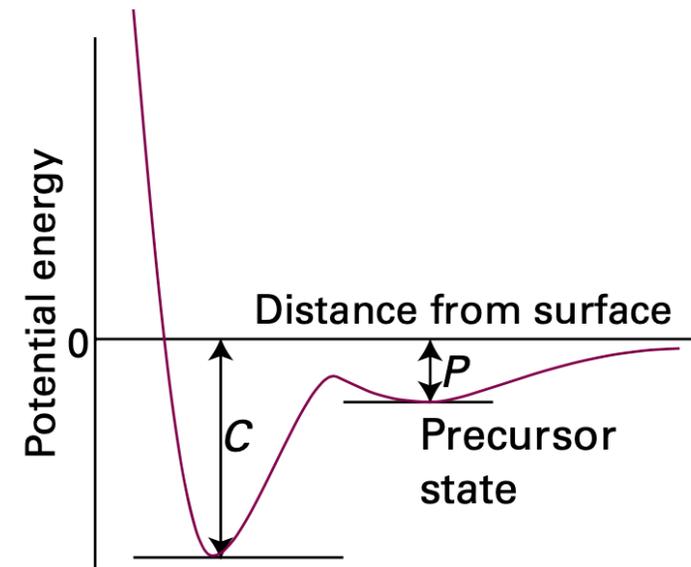
| Propriedade | Fisissorção | Quimissorção |
|-------------------|---|---------------------|
| Tipo de Ligação | van der Waals (dispersão de London, dipolo-dipolo, etc.) | covalente ou iônica |
| Entalpia | 20 a 40 kJ/mol | 80 a 240 kJ/mol |
| Tipo de cobertura | 1 ou mais camadas | 1 camada |
| Reversível?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



Tipos de Adsorção



McQuarrie and Simon



Por que é importante?

Estudo de interação espécies – superfícies.

Muitas técnicas de análise e processos (físico)-químicos são baseados em interação com superfícies.

Catálise heterogênea.

Eletroquímica.

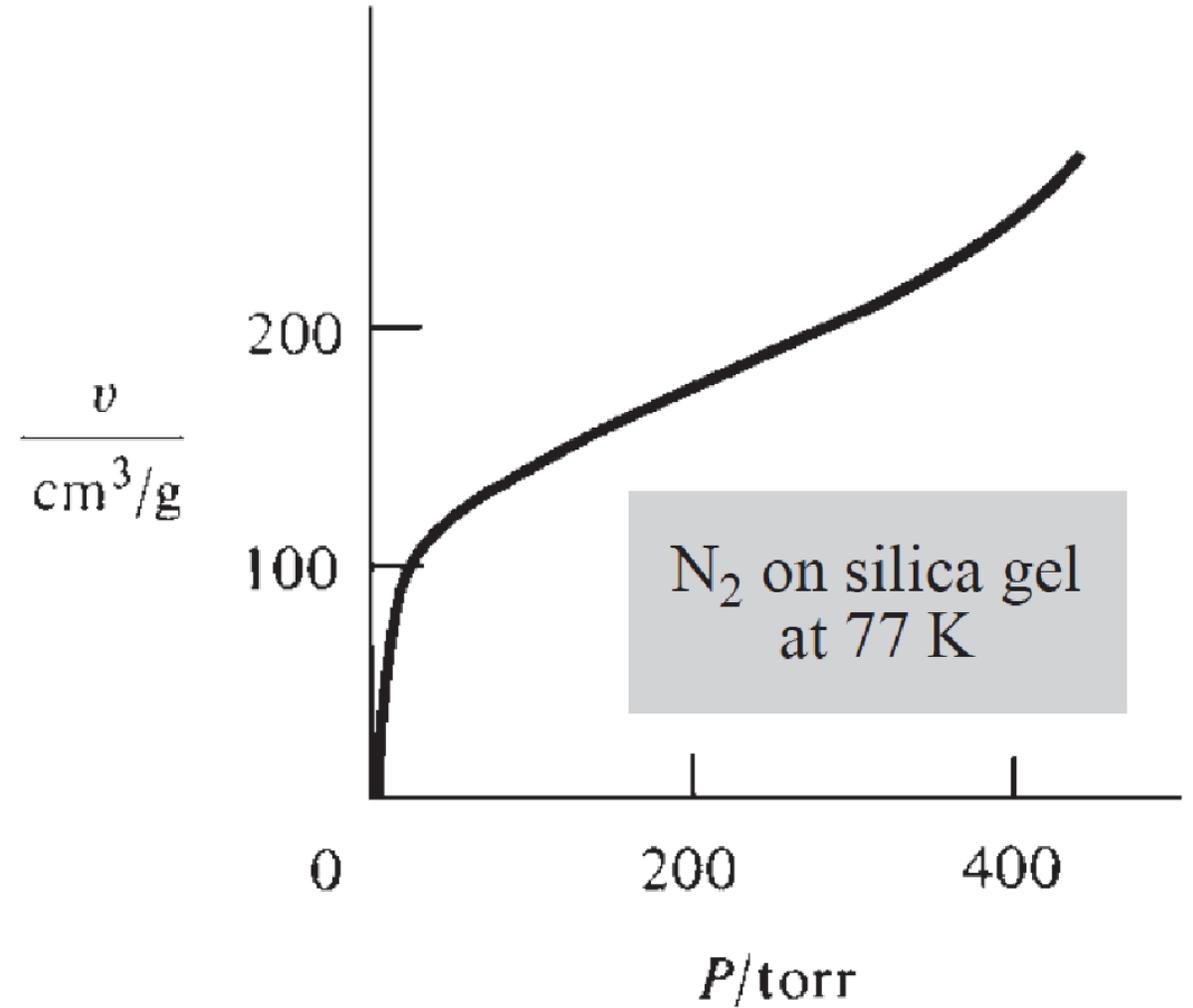
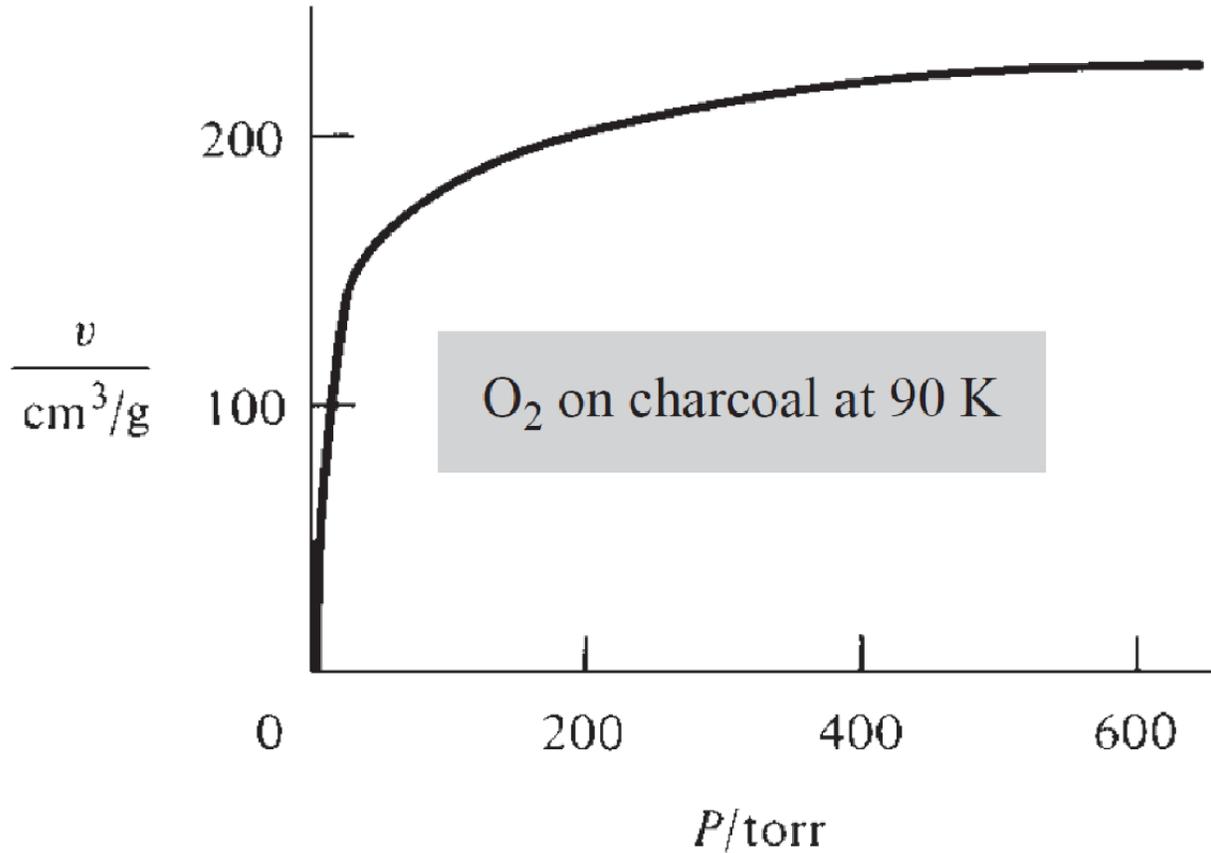
Processos de purificação

Fatores de influência

- 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.

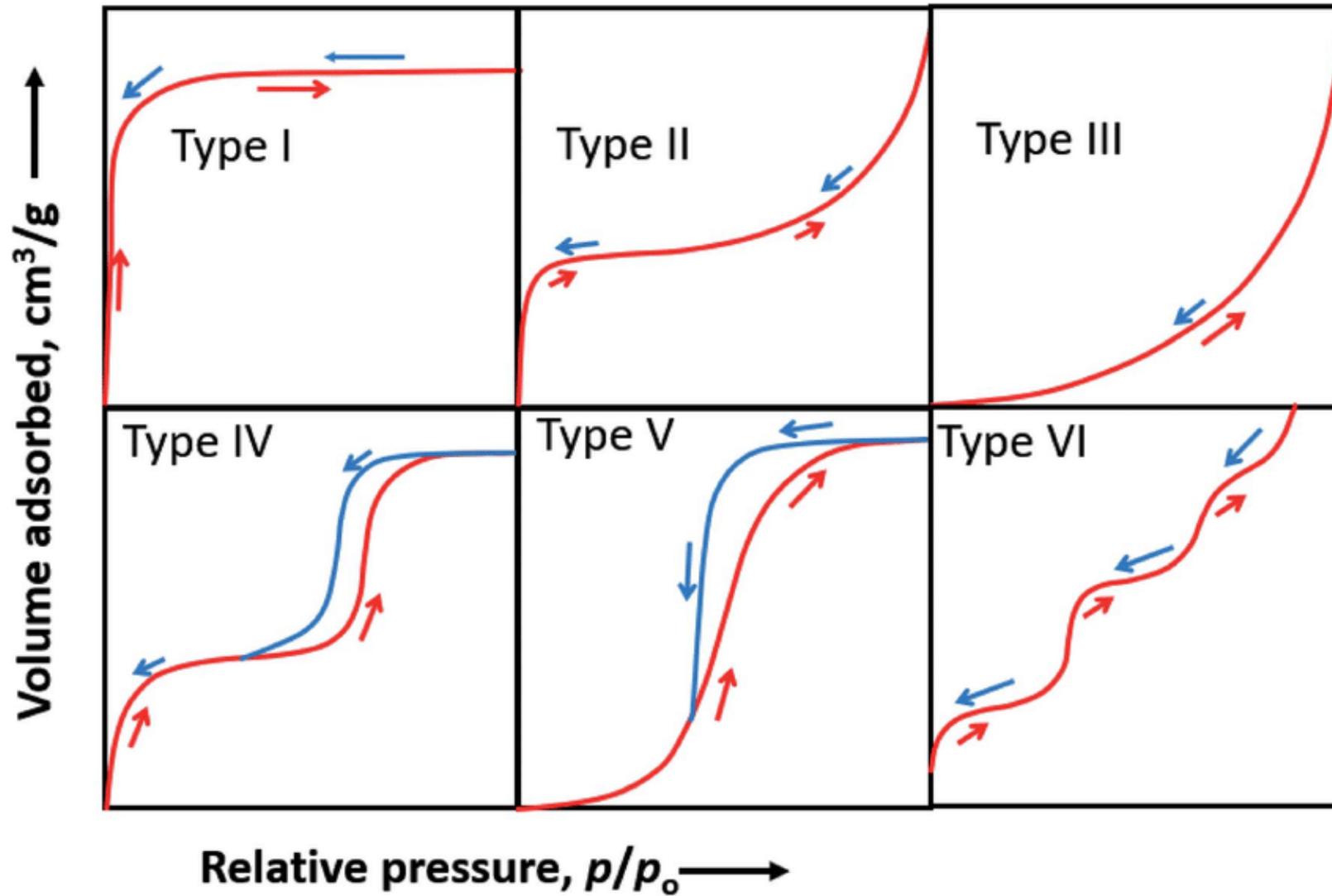
No equilíbrio, o estudo quantitativo das relações entre as quantidades no meio e adsorvidas, a dada temperatura, podem ser definidas por uma **isoterma**

Exemplos de Isotermas de Adsorção

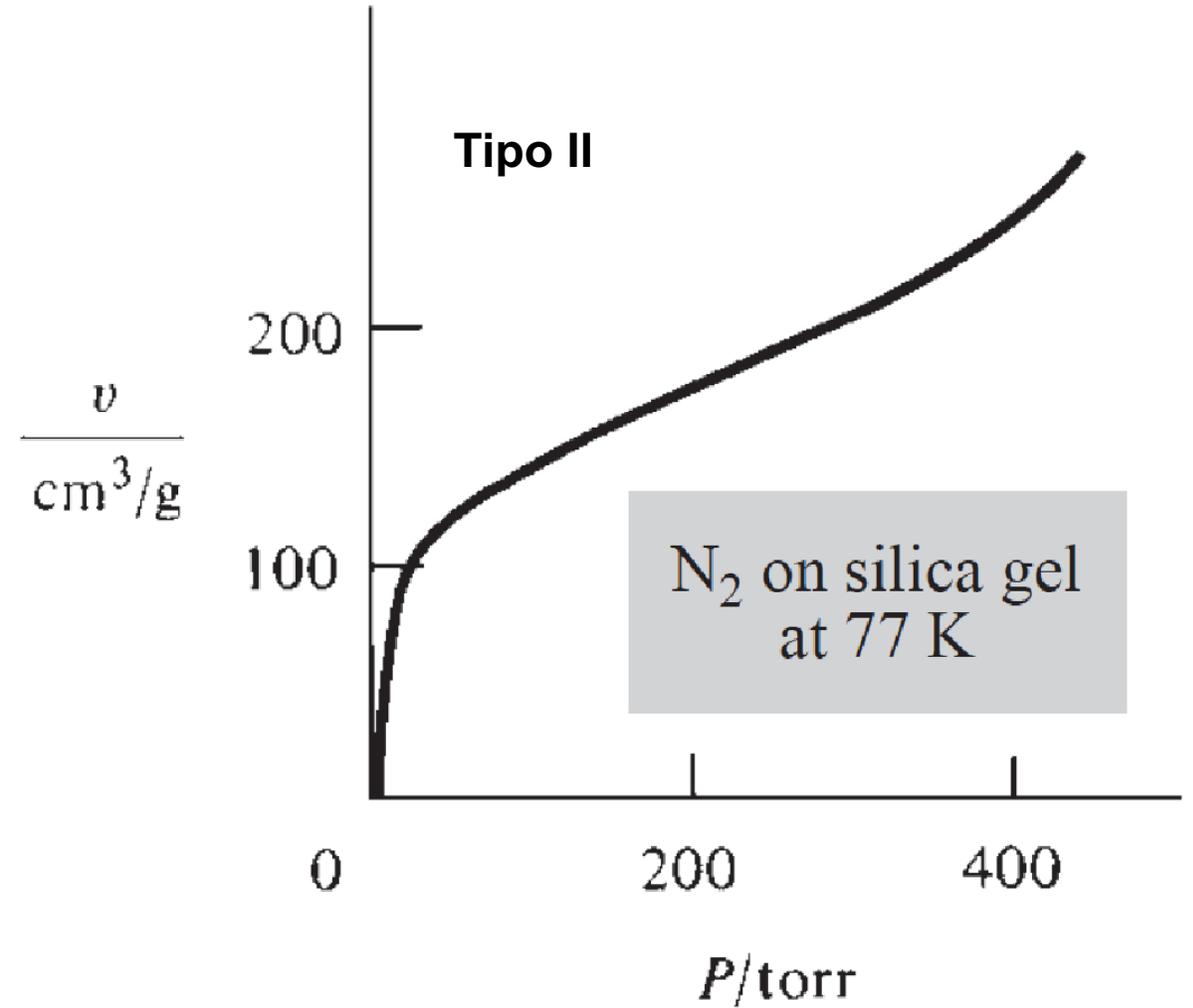
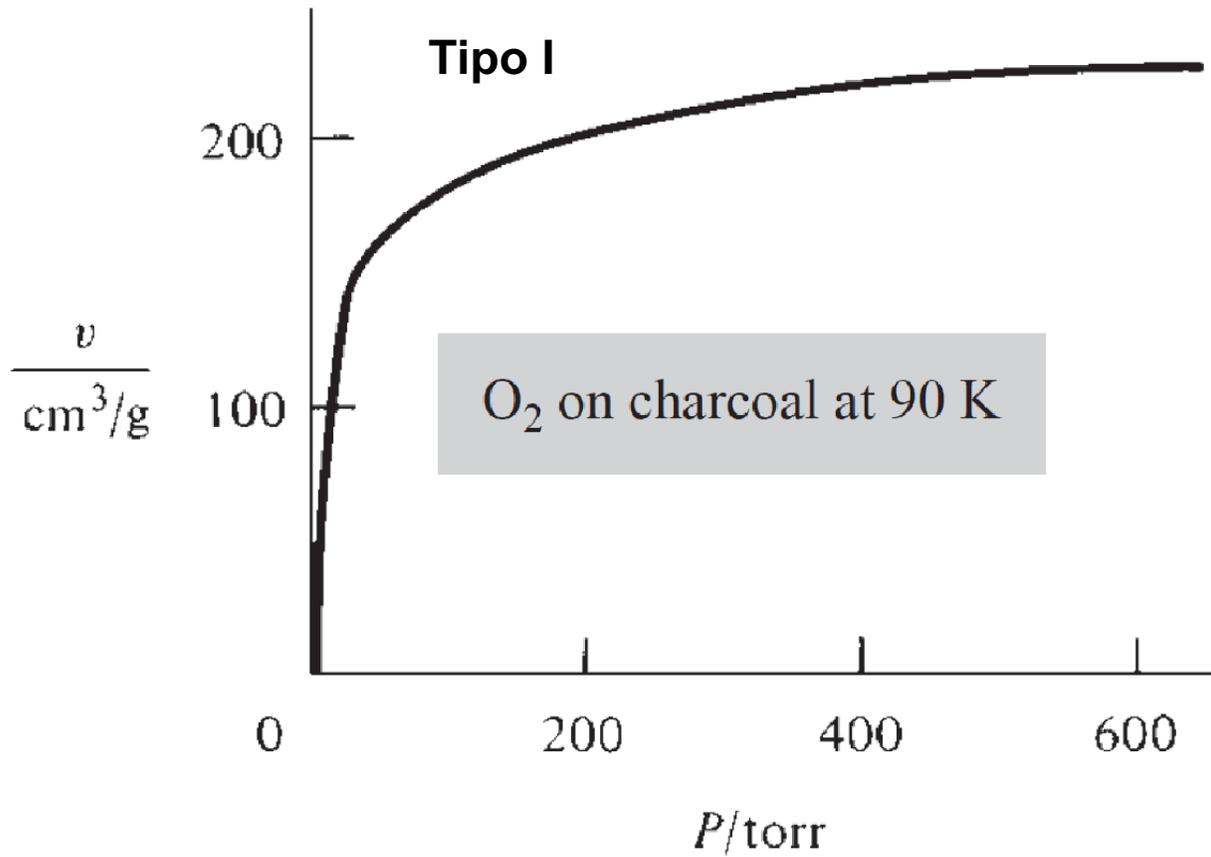


São diferentes!

Tipos de Isotermas



Exemplos de Isotermas de Adsorção



Isotermas de Adsorção

Diferentes abordagens e diferentes modelos



Irving Langmuir



"for his discoveries
and investigations in
surface chemistry."

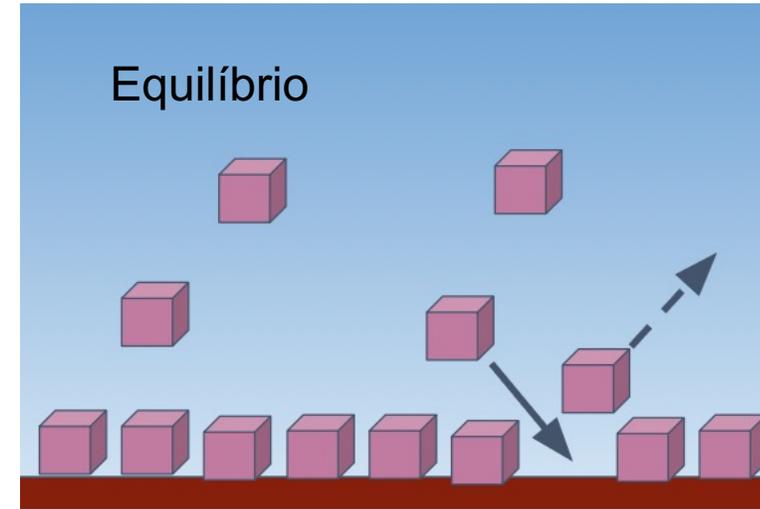
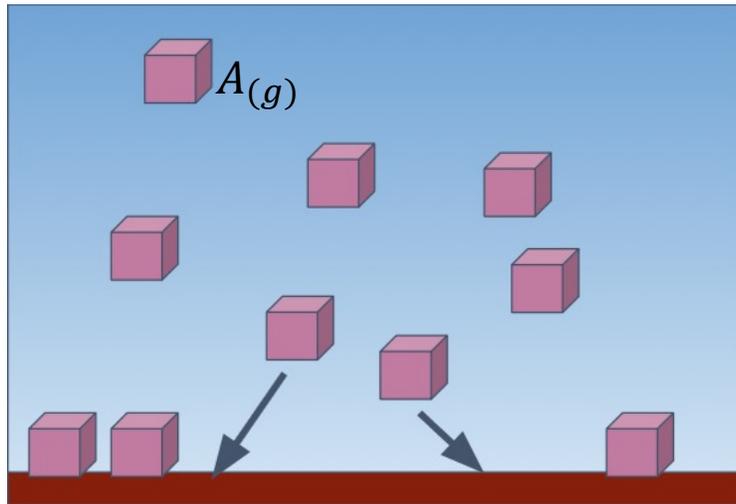
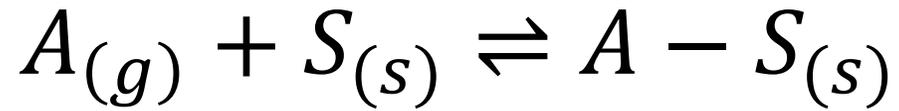


Herbert Freundlich

Outras isotermas:

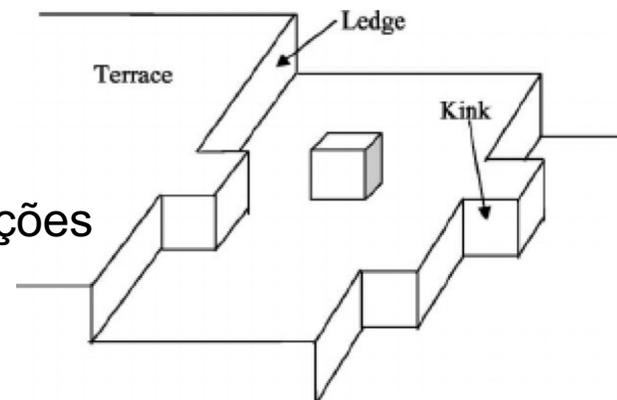
- BET
- Temkin
- Dubinin-Radushkevich
- e mais

Isoterma de Langmuir (1918)



Superfície $S_{(s)}$

- Sistema modelo ideal (gás perfeito)
- Todos os sítios são idênticos
- Distribuição homogêna dos adsorbatos
- Mesma energia envolvida em todas adsorções
- Partículas não-interagentes
- Monocamada de adsorbatos



https://my.eng.utah.edu/~lzung/images/Lecture_7_STM_surface_structure.pdf

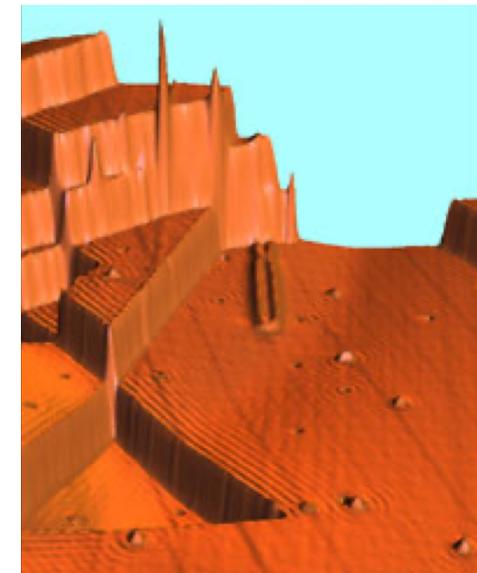
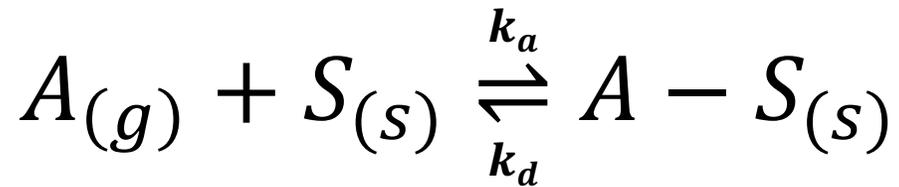


Imagem de cobre por STM

Isoterma de Langmuir (1918)



Equilíbrio: $v_a = v_d = \frac{d\theta}{dt}$

$$k_a \cdot [A][S] = k_d \cdot [A - S]$$

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

θ = fração de sítios ocupados

σ_0 = sítios (m^{-2})

$\theta \cdot \sigma_0$ = [sítios ocupados]

$\sigma_0 - (\theta \cdot \sigma_0)$ = [sítios vazios]

$$v_a \propto [A] \text{ ou } P_A$$

$$v_a \propto \sigma_0 - (\theta \cdot \sigma_0) \quad v_d \propto \theta \cdot \sigma_0$$

$$v_a = k_a(1 - \theta)\sigma_0 P_a \quad v_d = k_d \theta \cdot \sigma_0$$

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

$$\frac{k_a}{k_d} (1 - \theta) P_a = \theta \quad \Rightarrow \quad K_c (1 - \theta) P_a = \theta$$

$$\frac{(1 - \theta)}{\theta} = \frac{1}{P_A K_c}$$

$$\boxed{\frac{1}{\theta} = 1 + \frac{1}{P_A K_c} \Rightarrow \theta = \frac{K_c P_A}{1 + K_c P_A}}$$

Isoterma de Langmuir (1918)

Transformando em unidade de massa (q):

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

Equação anterior

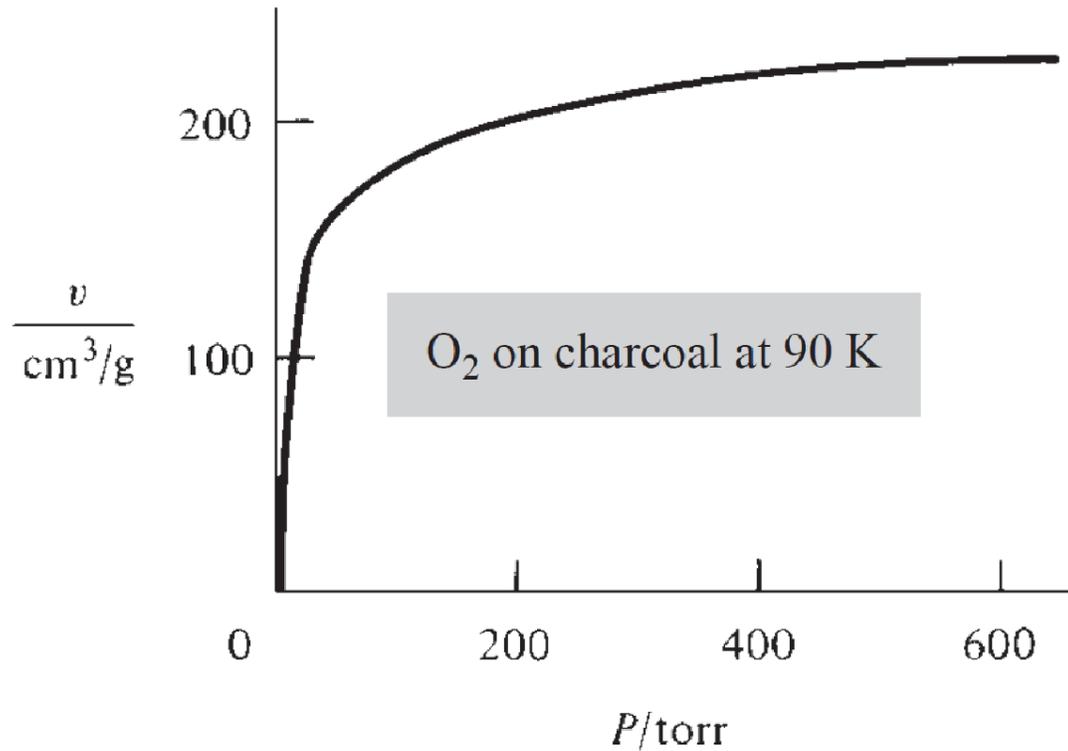
$$\theta = \frac{K_c P_A}{1 + K_c P_A} \Rightarrow \frac{q}{q_{max}} = \frac{K_c P_A}{1 + K_c P_A}$$

Linearizando a expressão:

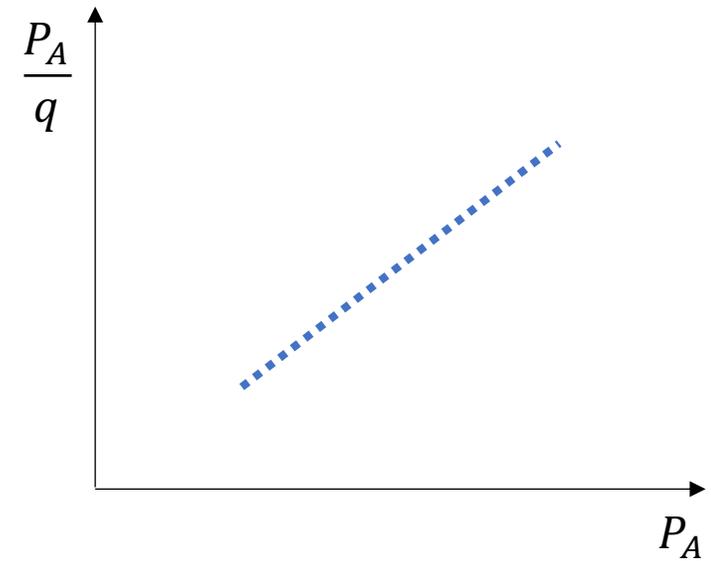
$$\frac{1}{q} = \frac{1 + K_c P_A}{q_{max} + K_c P_A} \Rightarrow \frac{P_A}{q} = \frac{1}{K_c q_{max}} + \frac{P_A}{q_{max}} \Rightarrow \frac{P_A}{q} = \frac{1}{K_L q_{max}} + \frac{P_A}{q_{max}}$$

$$K_L P^0 = K(\text{sem unidade}) \quad [A] = \frac{P_A}{k_B T}$$

Adsorção de O₂ em carvão ativo



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



$$\frac{1}{K_L q_{max}}$$

Coef. linear

$$\frac{1}{q_{max}}$$

Coef. angular

Entalpia de adsorção

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

Como o processo de adsorção é **espontâneo**:

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

Raramente um processo de adsorção tem aumento de entropia:

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

Portanto: $\Delta_{ads}H < 0 \Rightarrow$ **processo exotérmico**

$\Delta G^\circ = -RT \ln K$ e $K = K_L P^\circ$ Podemos construir isotermas variando T, e usando Gibbs-Helmoltz:

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

Como K_L é relacionado com P, quando θ é constante, podemos escrever:

$$\left(\frac{d \ln(P/P^\circ)}{d(1/T)}\right)_\theta = \frac{\Delta_{ads}H^\circ}{R}$$

Isoterma de Freundlich

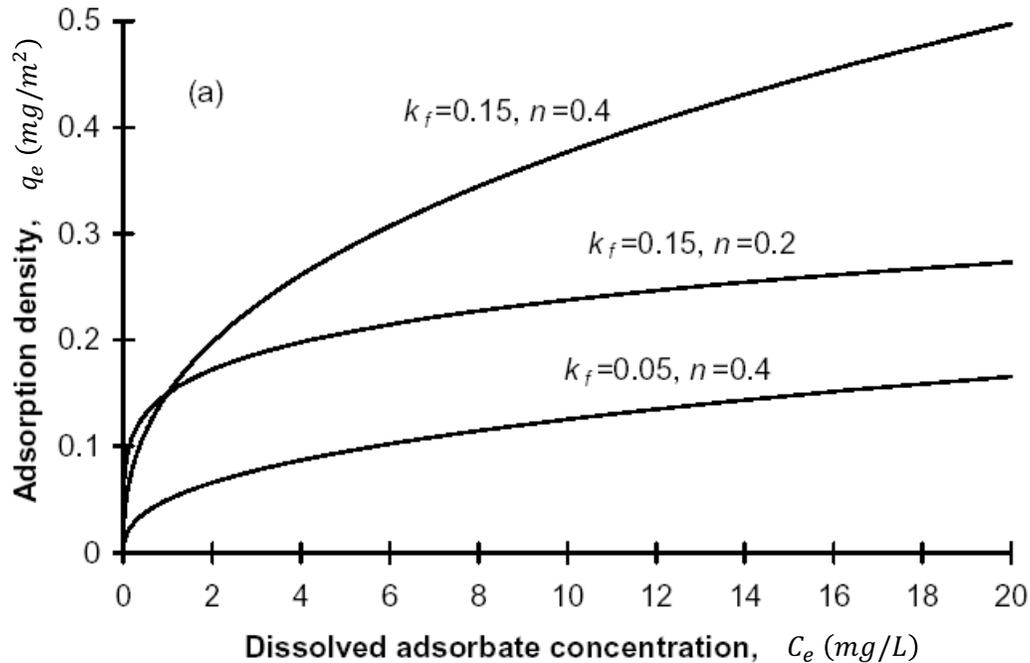
Modelo empírico e não-linear em função da pressão (tipo 1)

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

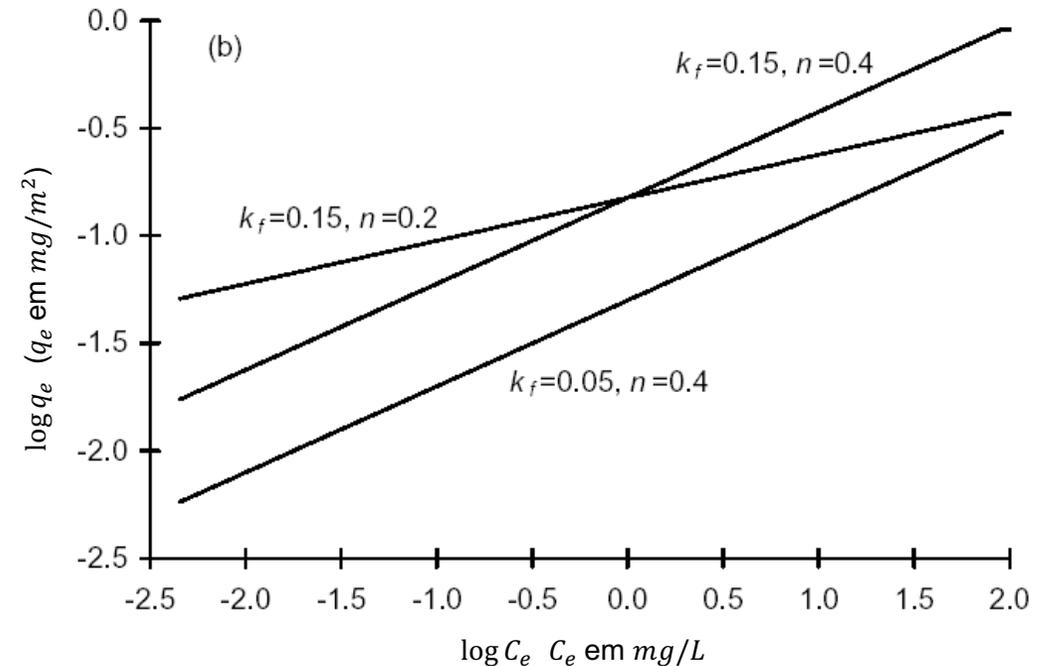
K_F é a constante de Freundlich (mg/g) – capacidade de adsorção

n é parâmetro que reflete heterogeneidade e intensidade de adsorção

- K_F e n dependem de T (n aumenta e K_F diminui com T)
- Menor n , maior a heterogeneidade
- $1 < n < 10$ favorece adsorção

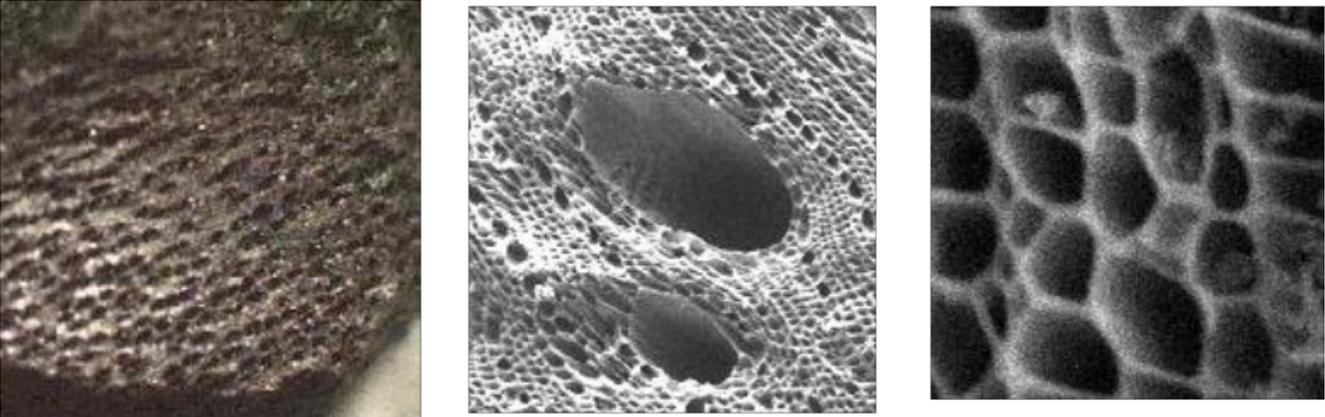
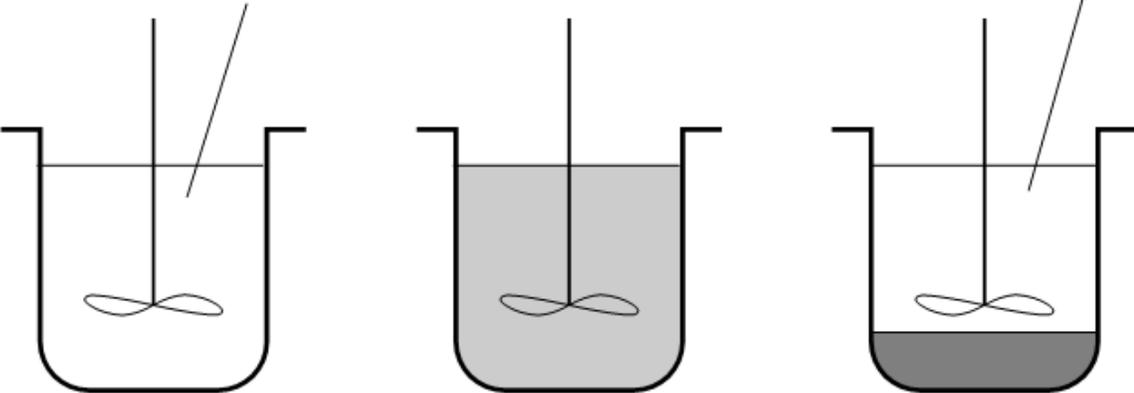


$$q_e = K_F(C_e)^{1/n}$$



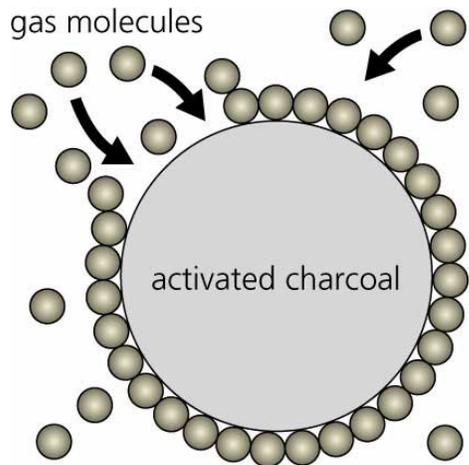
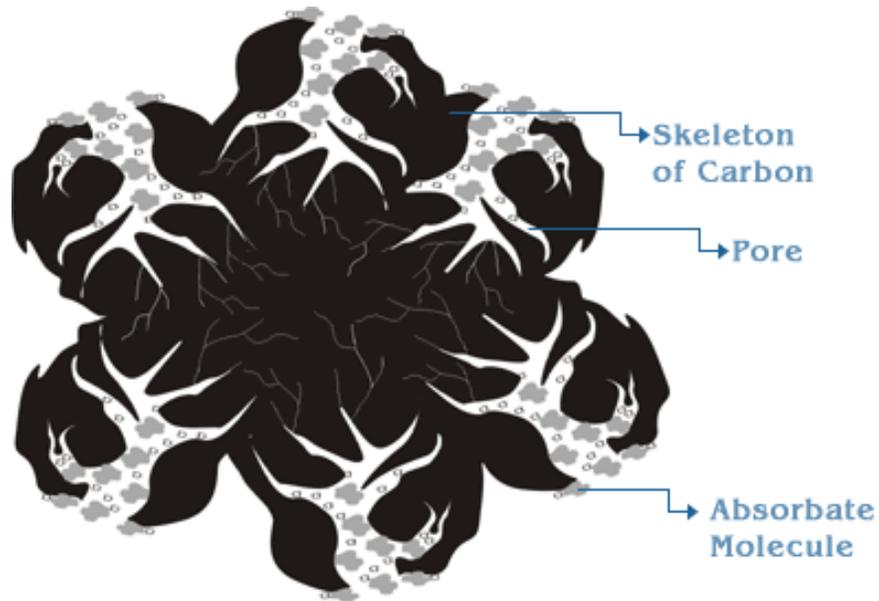
$$\log q_e = \log K_F + \frac{1}{n} \log(C_e)$$

Adsorção de ácido acético em carvão ativo



Aumento

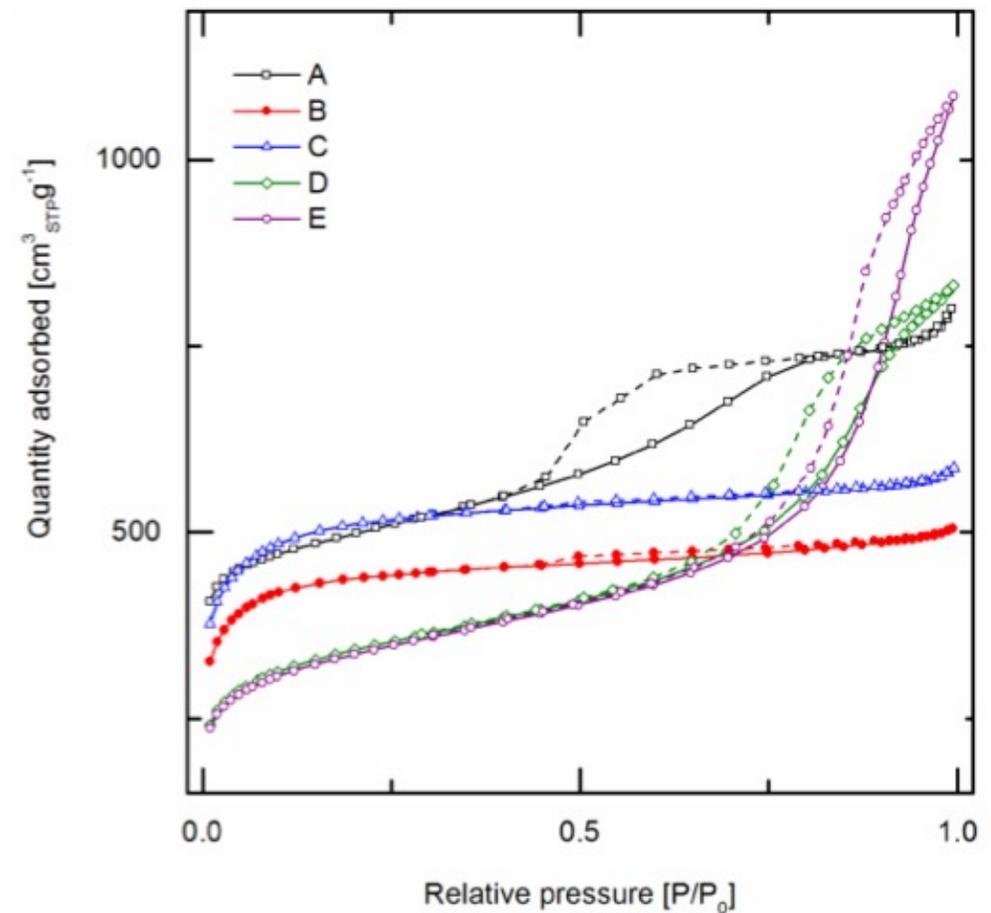
Carvão Ativo



Academy Artworks

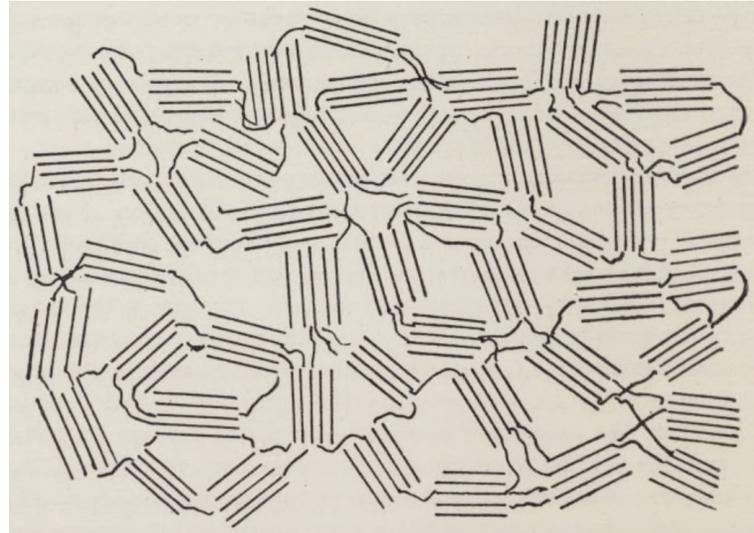
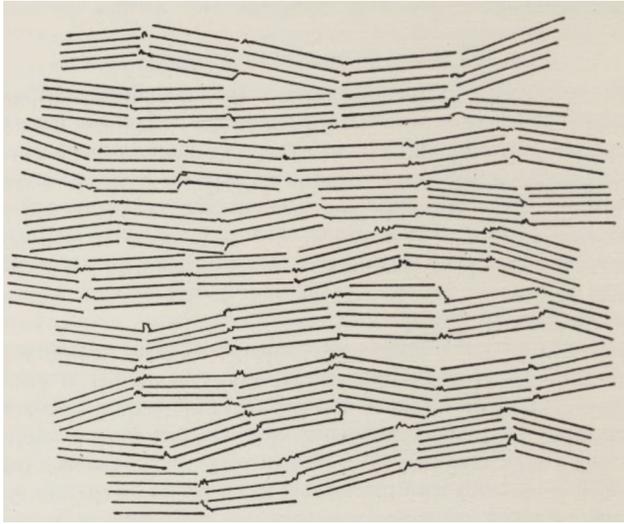
Área superficial:

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

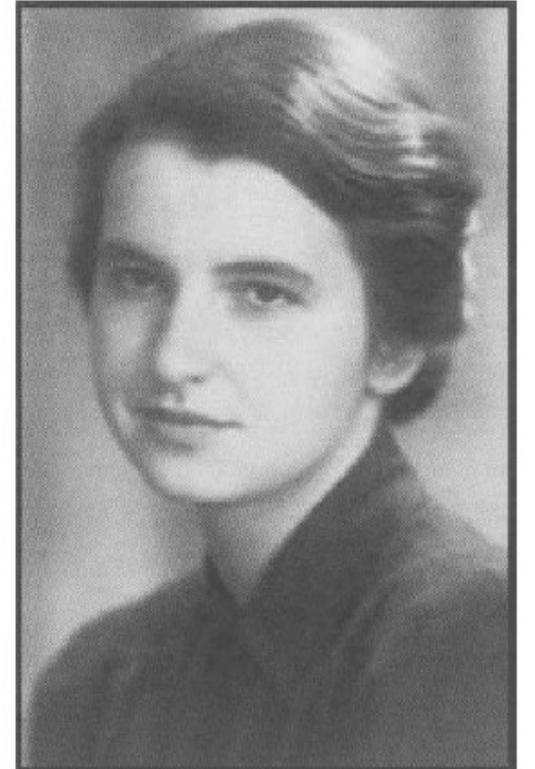
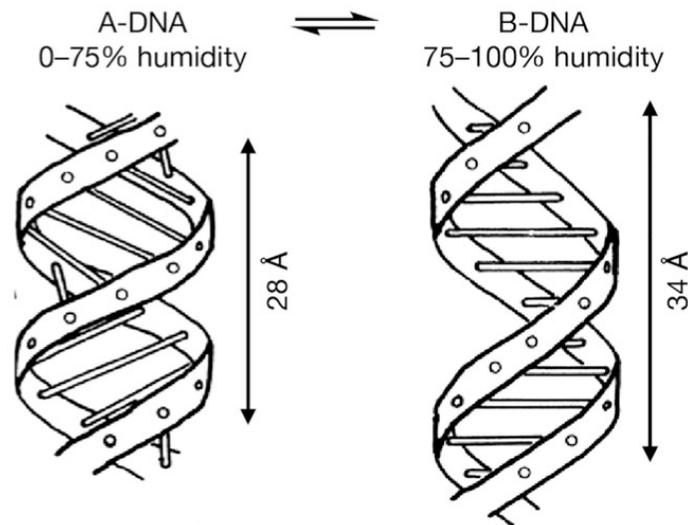
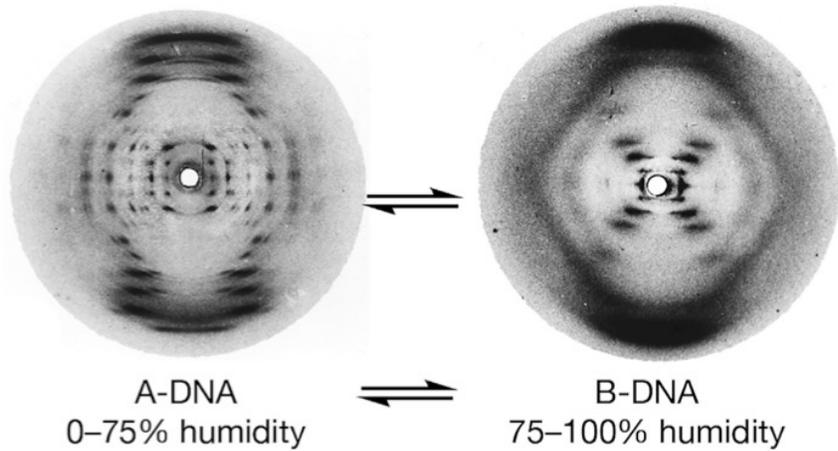


Electrochimica Acta 270, 453-460

Estrutura do Carvão ativo



Franklin R. E. Crystallite growth in graphitizing and non-graphitizing carbons, PROCEEDINGS OF THE ROYAL SOCIETY A 209, p196, 1951.



Rosalind E. Franklin (1920 - 1958)

Uso de Carvão Ativo



ACTIVATED CARBON

For Industrial Use/Applications



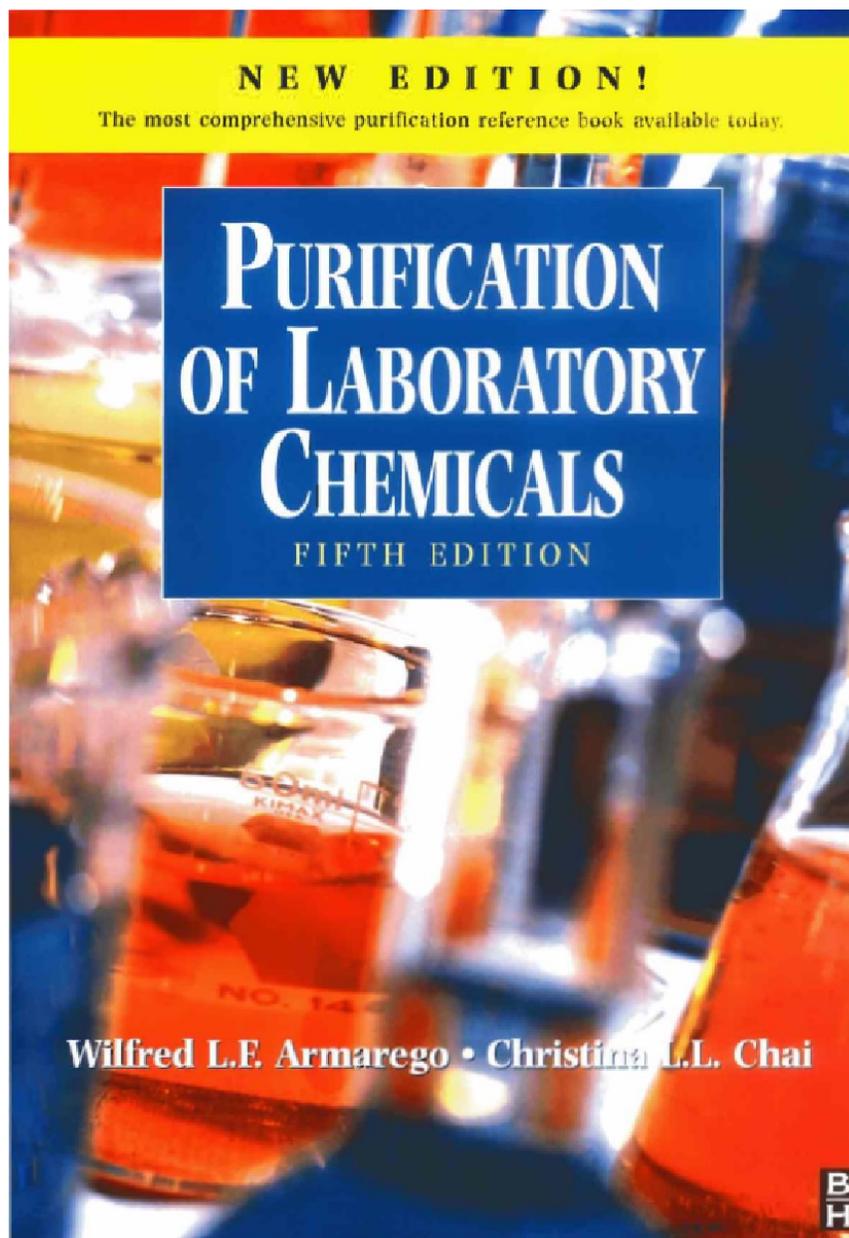
Carbon Based Water Treatment Plant



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Uso de 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:

- 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.
- 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.
- The solution is then allowed to cool so that the dissolved substance crystallises out.
- 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.
- 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

Procedimento Experimental

Medir temperatura da sala no início e fim do experimento

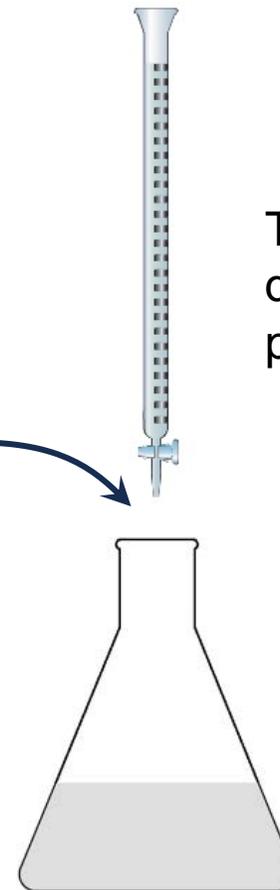


Procedimento Experimental

Após 40 min., lavar o papel de filtro com a solução que será filtrada, com auxílio de pipeta de pauster, da mais diluída para a mais concentrada, filtre.



5 ou 25 mL
(pipeta volumétrica)



Titule com a solução de NaOH com a bureta pequena

| Volume de HAc na solução / mL | Volume da alíquota / mL | Volume médio de NaOH / mL | Massa de carvão ativado / g |
|-------------------------------|-------------------------|---------------------------|-----------------------------|
| 20.00 | 5.00 | | |
| 16.00 | 5.00 | | |
| 12.00 | 5.00 ou 25.00 | | |
| 8.00 | 25.00 | | |
| 4.00 | 25.00 | | |