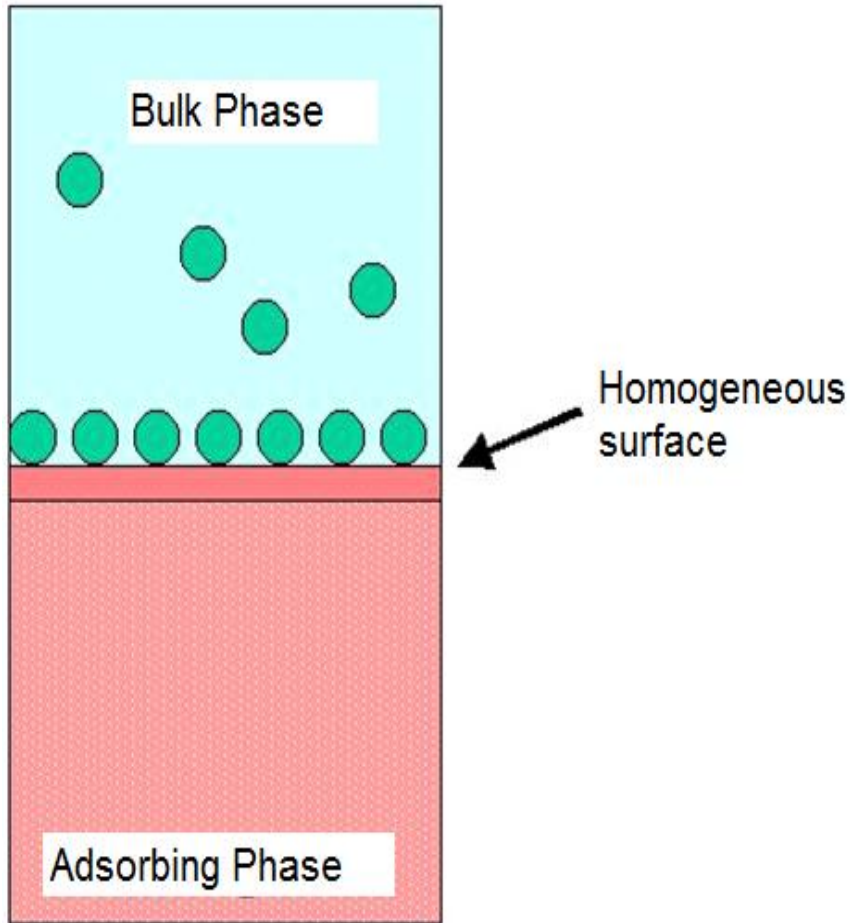


# Adsorption Equilibria

Ref: [faculty.washington.edu/.../Adsorption%20...](http://faculty.washington.edu/.../Adsorption%20...)  
Adsorption Equil Principles\_483



If the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by **adsorption isotherms**.

# Adsorption Equilibria

An **adsorption isotherm** is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent,  $q_e$ , to the concentration of the solute in the liquid,  $C_e$ , with which it is in contact.

The adsorption isotherm is also an **equation** relating the **amount of solute adsorbed onto the solid** and the **equilibrium concentration of the solute in solution** at a given temperature.

$q_e$  = amount of solute adsorbed per unit weight of solid at equilibrium. Unit is either  $\frac{g}{g}$  or  $\frac{mg}{g}$

$C_e$  = equilibrium concentration of solute remaining in solution when amount adsorbed equals  $q_e$ .

$q_e/C_e$  relationships depend on the type of adsorption that occurs, multi-layer, chemical, physical adsorption, etc.

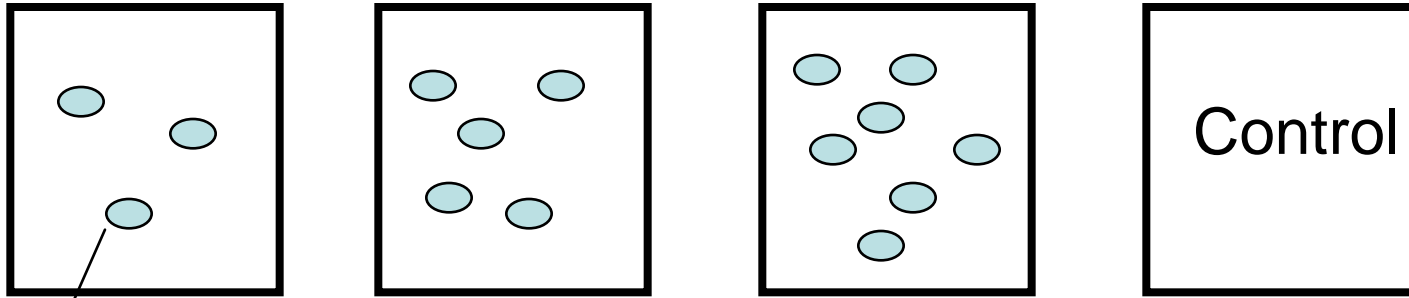
# Adsorption Equilibria

The adsorption capacity of activated carbon may be determined by the use of an **adsorption isotherm** which can take multiple forms.

Isotherms are found by doing lab tests.

# Adsorption Isotherms

Add same initial target chemical concentration,  $C_{init}$ , in each



Different activated carbon dosage,  $C_{solid}$ , in each

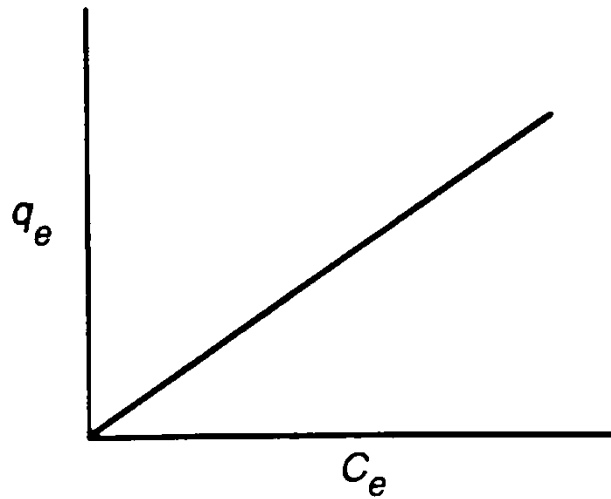
$$q_e \left( \frac{\text{mg}}{\text{g}} \right) \text{ or } \left( \frac{\text{g}}{\text{g}} \right) = \frac{C_o - C_e \text{ (mg/L)}}{C_{solid} \text{ (g/L)}} \text{ or } = \frac{(C_o - C_e) \cdot V}{X} = \frac{\text{mass}}{\text{mass}}$$

An adsorption 'isotherm' is a  $q_e$  vs.  $C_e$  relationship at equilibrium.

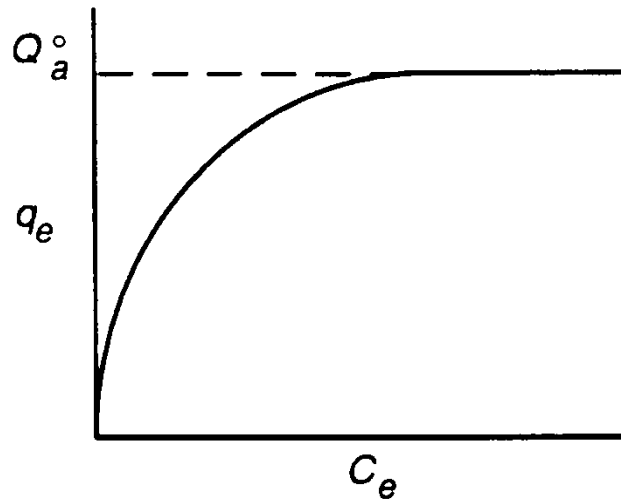
## **Isotherm models**

There are several models for predicting the equilibrium distribution.

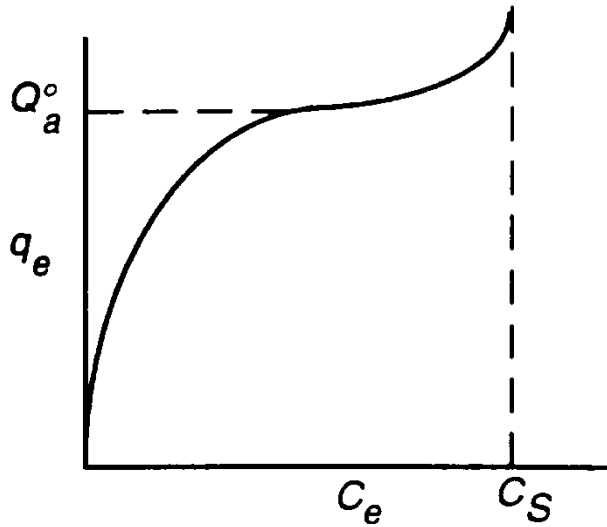
However, the following four models are most commonly observed.



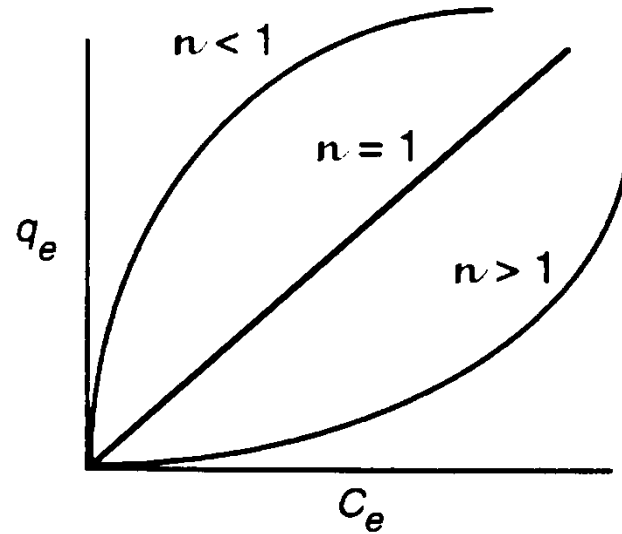
(a) Linear



(b) Langmuir



(c) BET



(d) Freundlich

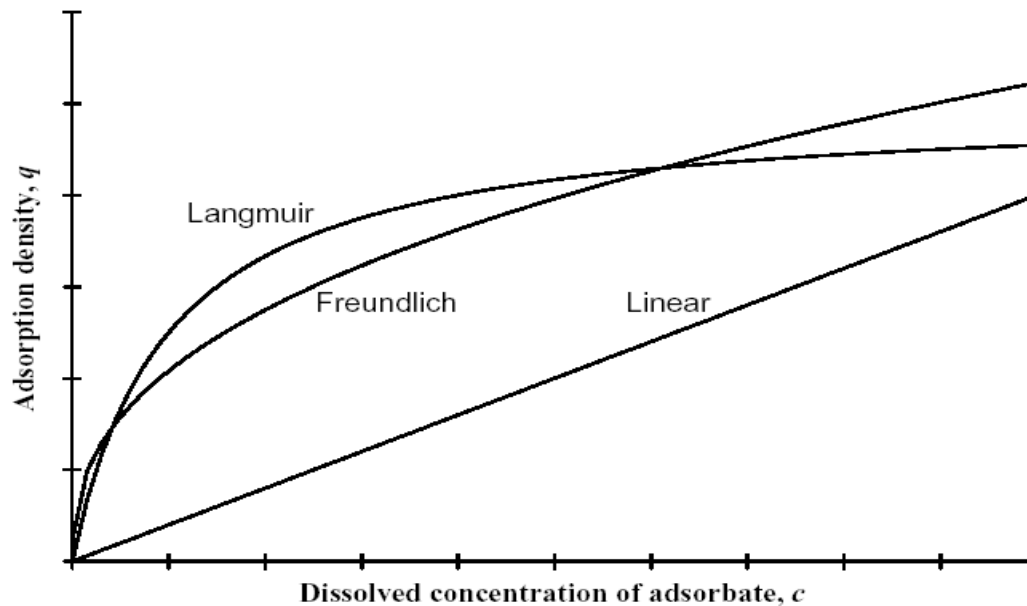
# Commonly Reported Adsorption Isotherms

Linear:  $q = k_{\text{lin}} c$

Langmuir:  $q = q_{\text{max}} \frac{K_L c}{1 + K_L c}$

Freundlich:  $q = k_f c^n$

where  $k_{\text{lin}}$ ,  $K_{\text{Lang}}$ ,  $q_{\text{max}}$ ,  $k_f$ , and  $n$  are all empirical constants.<sup>2</sup>





# Adsorption Equilibria

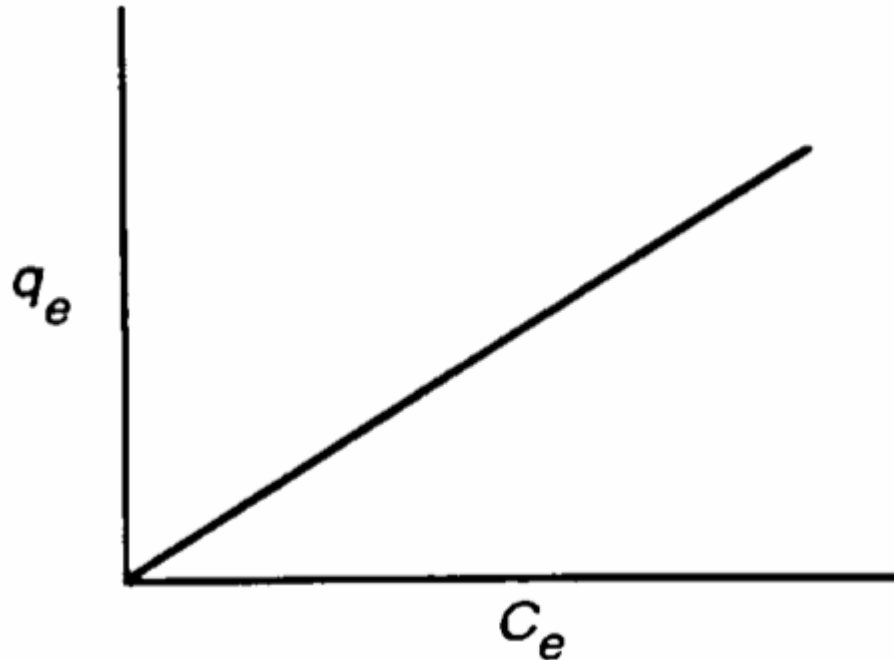
- i. Linear
- ii. Langmuir
- iii. Freundlich
- iv. Brunauer, Emmet, and Teller (BET)

The most commonly used isotherms for the application of activated carbon in water and wastewater treatment are the **Freundlich** and **Langmuir** isotherms.

Freundlich isotherm is an empirical equation.

Langmuir isotherm has a rational basis.

# Linear Isotherm



$$q_e = K \cdot C_e$$

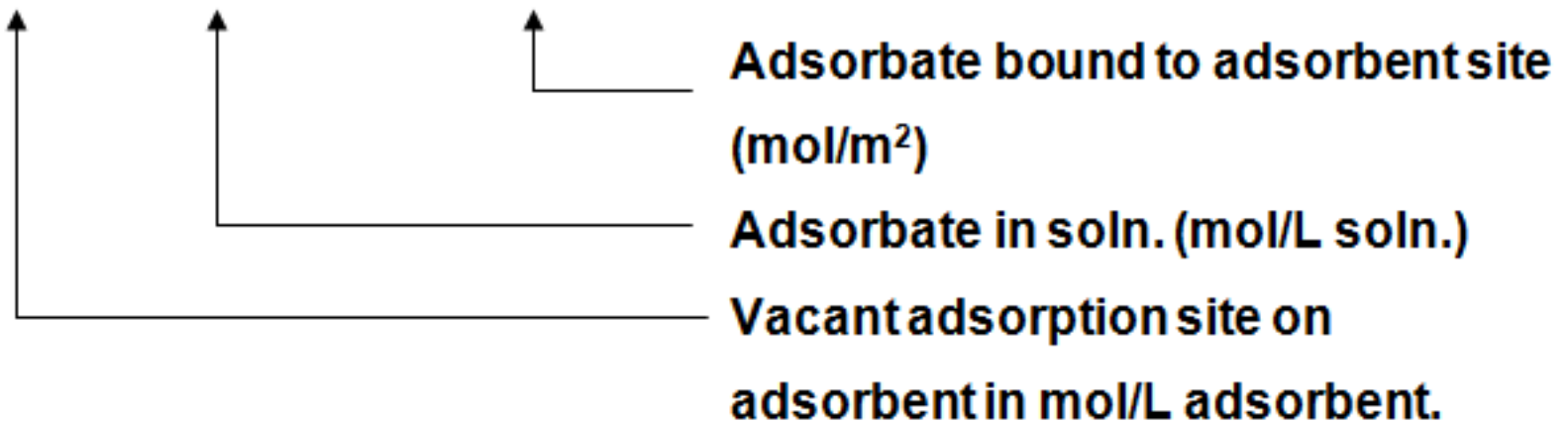
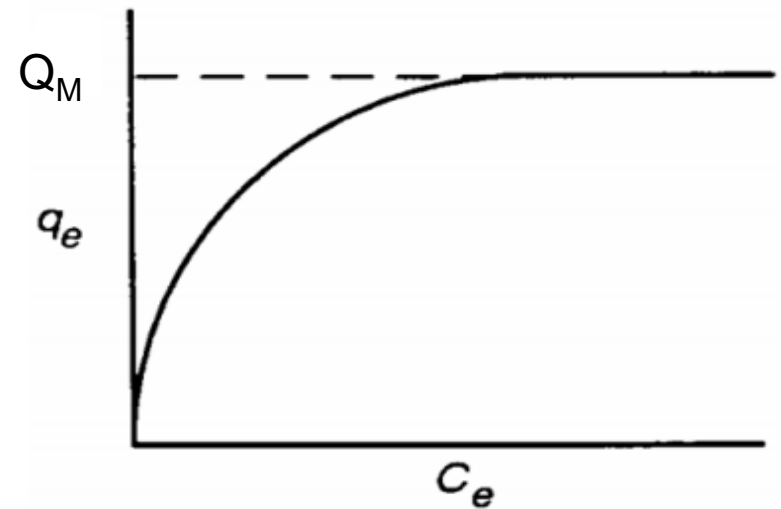
$q_e$  = amount of solute adsorbed per unit weight of solid at equilibrium. Unit is either  $\frac{g}{g}$  or  $\frac{mg}{g}$

$C_e$  = equilibrium concentration of solute remaining in solution when amount adsorbed equals  $q_e$ .

# Langmuir Isotherm

It assumes

1. Monolayer coverage,
2. Equilibrium model,
3. All adsorption sites are equally probable,
4. A second order reaction.



At equilibrium  $K_{ad} = \frac{[S.A]}{[S_v][A]}$  Eq'n 1

Consider total number of sites,  $S_T$ , to be fixed :  
(possible if monolayer coverage is assumed)

$$S_T = [S_v] + [S.A] \quad (\text{moles/m}^2) \quad \text{Eq'n 2}$$

*Combining Eq'n.s 1 & 2*

$$S_T = \frac{[S.A]}{K_{ad}[A]} + [S.A]$$

Solve for [S.A] and use  $C_A = [A]$

$$[S.A] = \frac{S_T}{1 + \frac{1}{K_{ad} \cdot C_A}} = \frac{K_{ad} \cdot C_A \cdot S_T}{1 + K_{ad} \cdot C_A}$$

Need expression for  $q_A$ , which is  $\frac{\text{mg adsorbate}}{\text{g adsorbent}}$

$$q_A = [S.A] \cdot A_{ad} \cdot MW_A$$

↑  
Surface area per g adsorbent, m<sup>2</sup>/g

↑  
Molecular weight of adsorbate, g/mol

$$q_A = [S.A].A_{ad}.MW_A$$

$$q_A = \frac{K_{ad}.C_A.S_T}{1+K_{ad}.C_A}.A_{ad}.MW_A$$

$$q_A = \frac{Q_M.K_{ad}.C_A}{1+K_{ad}.C_A}$$

*or*

$$q_A = \frac{b.C_e.Q^0}{1+b.C_e}$$

*where*

$Q_M$  or  $Q^\circ$  = maximum adsorption capacity for forming single layer.

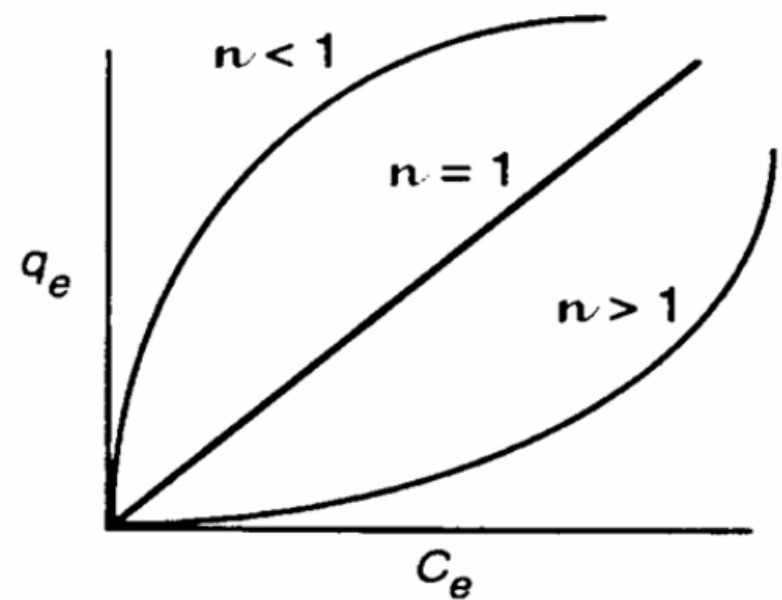
$C_e$  has units of mg/L.

$K_{ad}$  or  $b$  has units of L/mg.

## Freundlich Isotherm

It is empirical and very widely used.

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



$K_F$  is an indicator of adsorption capacity.

Higher the maximum capacity, higher the  $K_F$ .

$1/n$  is a measure of intensity of adsorption.

Higher the  $1/n$  value, more favorable is the adsorption.

$$\text{Generally, } n < 1 \quad \frac{1}{n} > 1$$

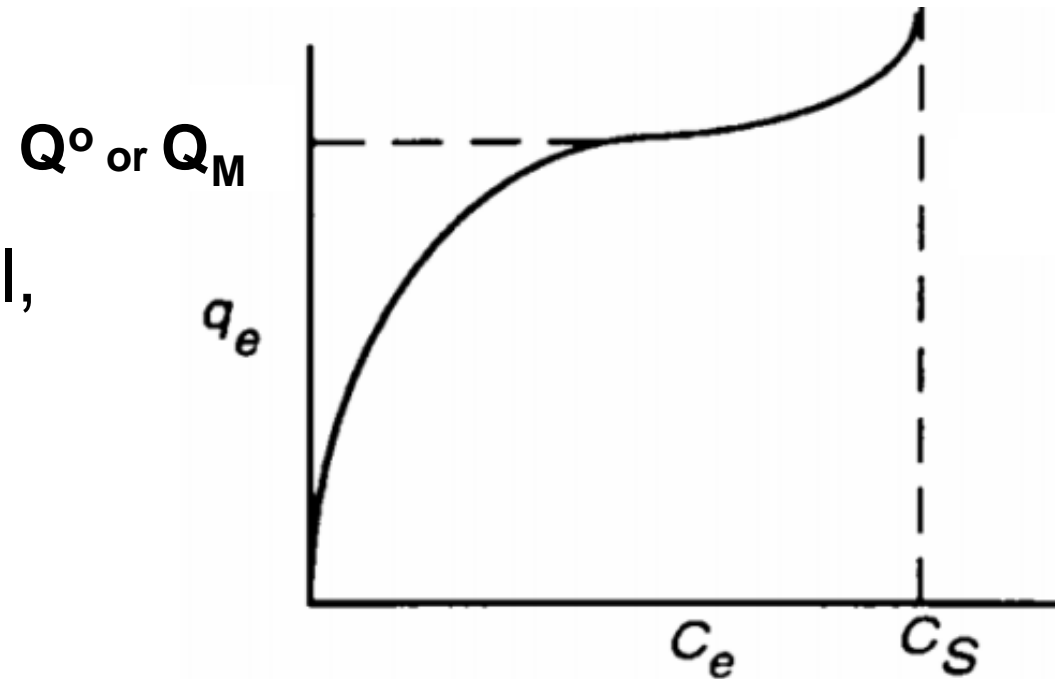
$n$  and  $K_F$  are system specific constants.



# BET (Brunauer, Emmett and Teller) Isotherm

This is a more general, multi-layer model. It assumes that a Langmuir isotherm applies to each layer

and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer.



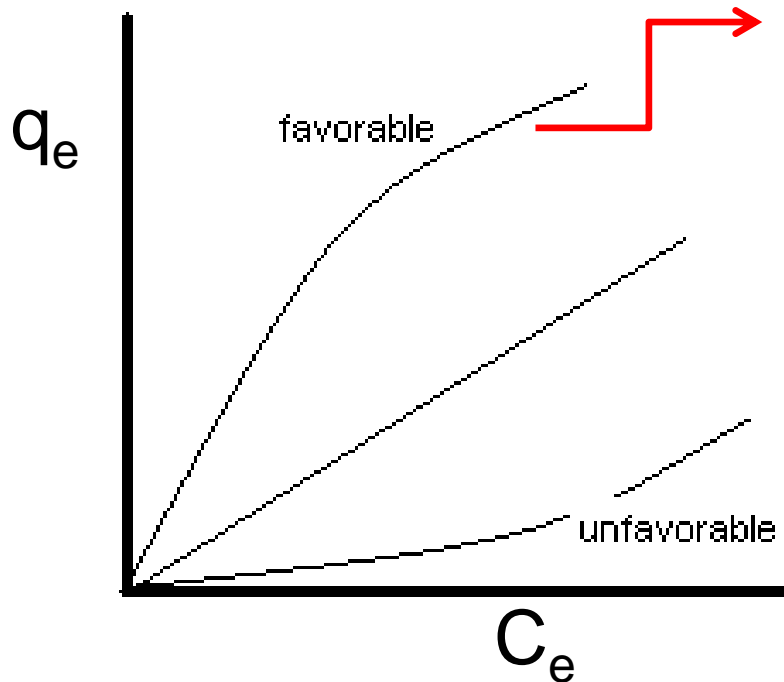
## BET (Brunauer, Emmett and Teller) Isotherm

$$q_e = \frac{K_B \cdot C_e \cdot Q^0}{(C_S - C_e) \{1 + (K_B - 1)(C_e / C_S)\}}$$

$C_S$  =saturation (solubility limit) concentration of the solute. (mg/liter)

$K_B$  = a parameter related to the binding intensity for all layers.

Note: when  $C_e \ll C_S$  and  $K_B \gg 1$  and  $K_{ad} = K_B/C_S$   
BET isotherm approaches Langmuir isotherm.

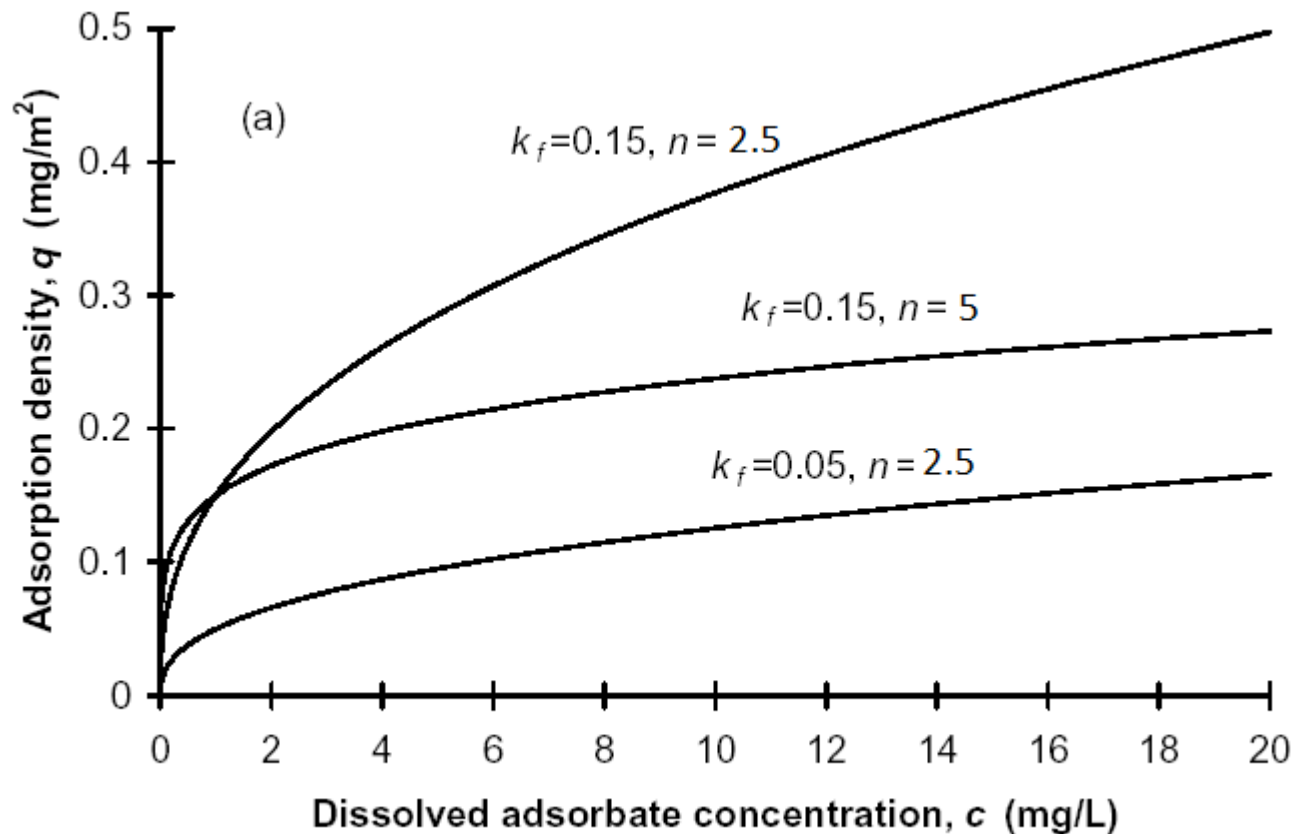


Most favorable one because even at low concentrations you can load your surface with high amounts of material.

The concept of the adsorption isotherm is very important, because how much you load the surface at equilibrium depends on how much is left in water.

# Shape of Freundlich Isotherm

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



## **Determination of appropriate model**

To determine which model to use to describe the adsorption for a particular adsorbent/adsorbate isotherms experiments are usually run. Data from these isotherm experiments are then analyzed using the following methods that are based on linearization of the models.

For the Langmuir model linearization gives:

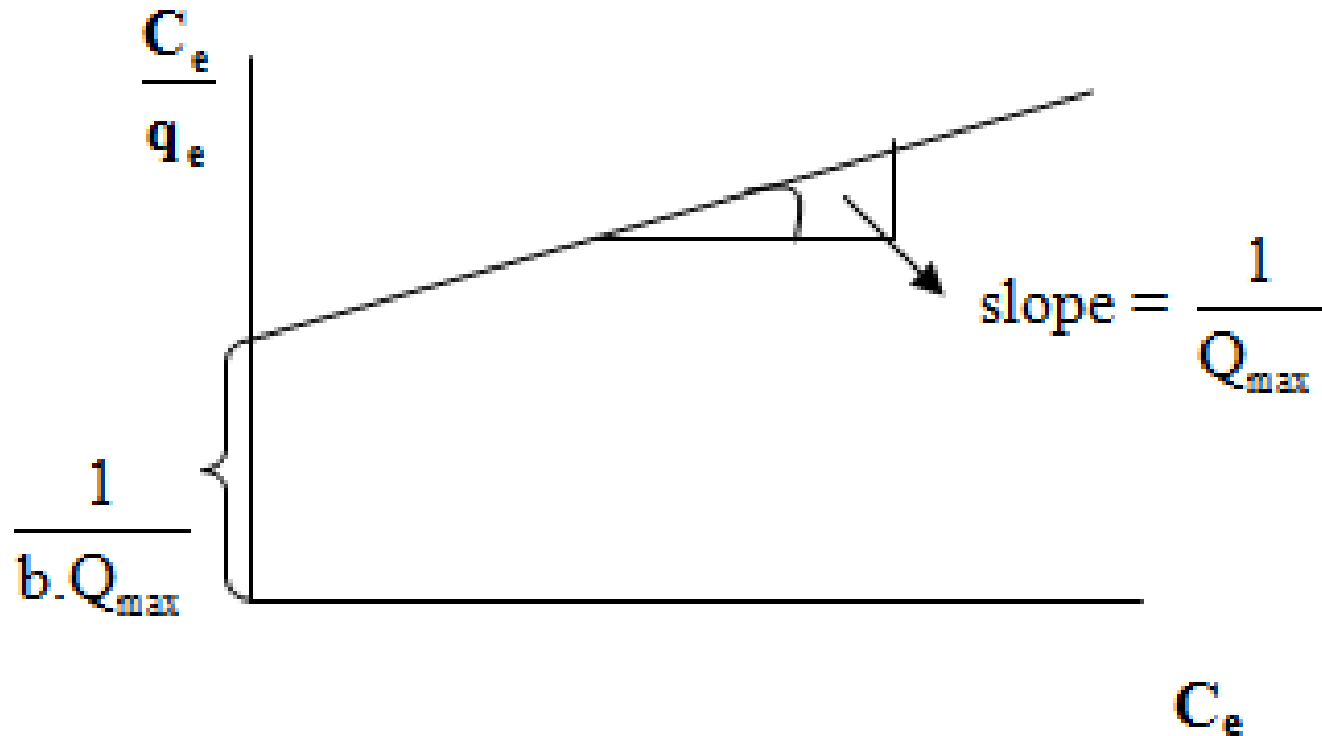
$$\frac{C_e}{q_e} = \frac{1}{K \cdot Q^0} + \frac{C_e}{Q^0}$$

A plot of  $C_e/q_e$  versus  $C_e$  should give a straight line with intercept :

$$\frac{1}{K \cdot Q^0}$$

and slope:  $\frac{1}{Q^0}$

If you obtain a straight line, determine constants from slope and intercept.





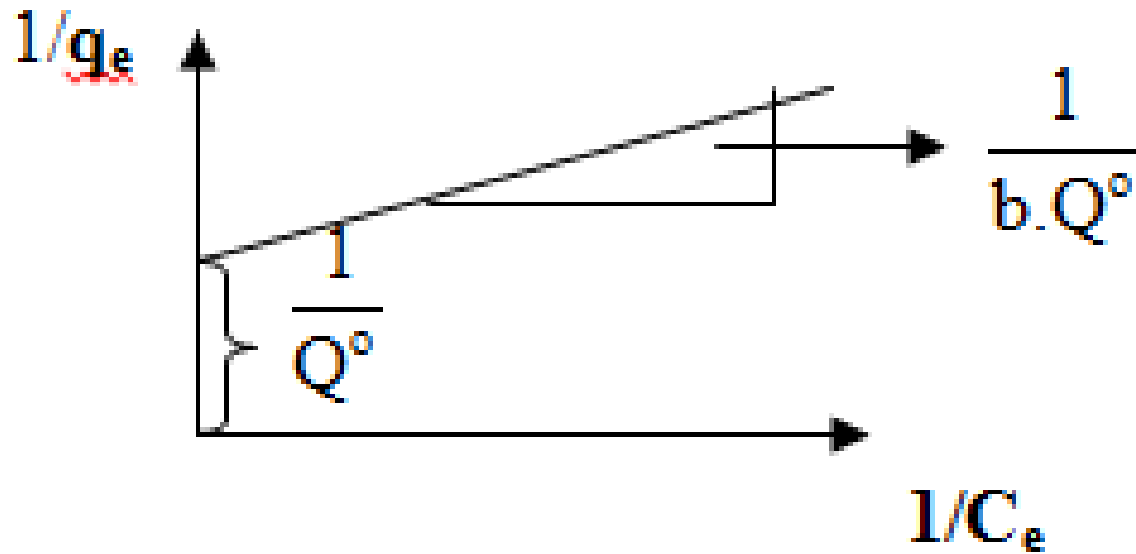
or:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{K \cdot Q^0} \cdot \frac{1}{C_e}$$

Here a plot of  $1/q_e$  versus  $1/C_e$  should give a straight line with intercept :  $1/Q^0$

and slope :  $\frac{1}{K \cdot Q^0}$

If you obtain a straight line, determine constants from slope and intercept.



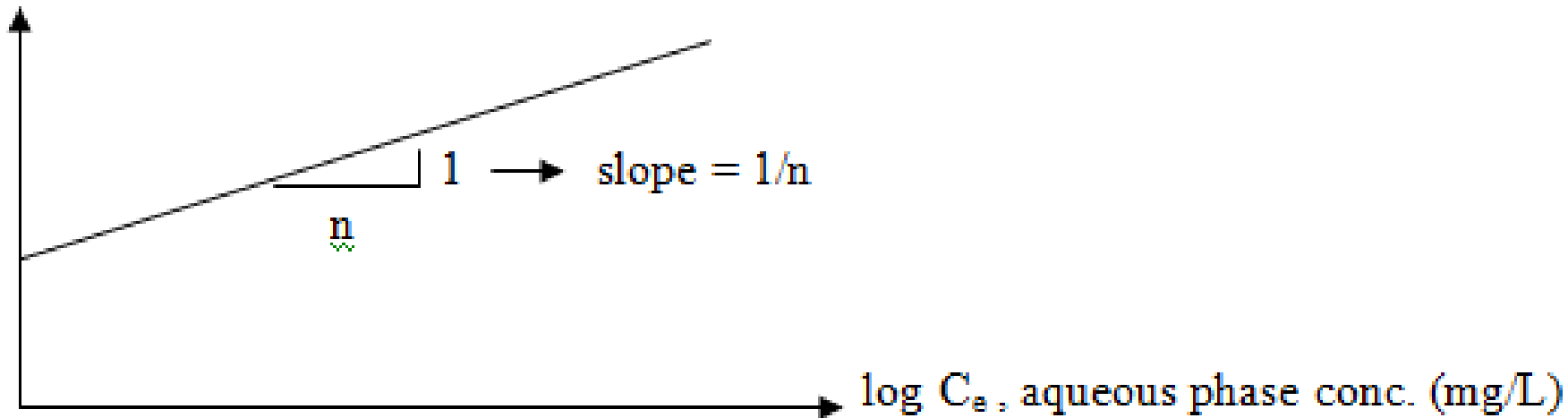
For the Freundlich isotherm use the log-log version :

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

A log-log plot should yield an intercept of  $\log K_F$  and a slope of  $1/n$ .

If Freundlich isotherm applies plot will be linear:

$\log q_e$ , adsorbed phase conc. (mg/kg)



Get  $n$  from slope.

Substitute to solve for  $K_F$ .

Tests are often done by carbon manufacturers ( e.g. Calgon carbon)

For the BET isotherm we can arrange the isotherm equation to get:

$$\frac{C_e}{(C_s - C_e) \cdot q_e} = \frac{K_B - 1}{K_B \cdot Q^0} \cdot \frac{C_e}{C_s} + \frac{1}{K_B \cdot Q^0}$$

$$\text{Intercept} = \frac{1}{K_B \cdot Q^0}$$

$$\text{Slope} = \frac{K_B - 1}{K_B \cdot Q^0 \cdot C_s}$$