Adsorption

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Definition of Adsorption

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by *accumulation at the interface* between that phase and a separate (solid) phase.

In principle adsorption can occur at any solid-fluid interface. Examples include:

- gas-solid interface (as in the adsorption of a VOC on activated carbon);

- liquid-solid interface (as in the adsorption of an organic pollutant on activated carbon).

Definitions

- **Adsorbate or solute: the material being adsorbed (e.g., 2,4,6-trichlorophenol).**

- **Adsorbent: the solid material being used as the adsorbing phase (e.g., activated carbon).**

Driving Force for Adsorption

- The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid.

- The surface or interfacial tension, s, is the change in free energy, G, resulting when the area between two phases, A, is increased. The definition of s is:

$$s = \left(\frac{\partial G}{\partial A} \right)_{T,P,n_j}$$

Adsorption vs. Absorption

A**b**sorption is the process through which a substance, originally present in one phase, is removed from that phase by *dissolution* in another (typically a liquid), as opposed to the accumulation at the interface as in the case of a**d**sorption.

Motivation for the Use of Adsorption Processes in Wastewater Treatment

Many industrial wastewaters contain substances that:

- are difficult to remove via conventionally secondary treatment

- are toxic or hazardous

- are volatile and cannot be transferred to the atmosphere

- have the potential for creating noxious vapors or odors, or for imparting color to the wastewater

- are present is very small concentrations that make their removal via other methods difficult

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Adsorption in Wastewater Treatment

- Adsorption is typically used in wastewater treatment to remove toxic or recalcitrant organic pollutants (especially halogenated but also non-halogenated), and to a lesser extent, inorganic contaminants, from the wastewater.

- Adsorption finds applications in tertiary wastewater treatment as a polishing step before final discharge.

- Adsorption is commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary (biological) treatment or toxic.

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Adsorption as a Physical Process

- In any adsorption process the material being adsorbed (e.g., a pollutant) is simply but effectively removed from one phase (e.g., a wastewater) and transferred to another phase (e.g., activated carbon).

- This means that adsorption is a *physical separation process* in which the adsorbed material is <u>not</u> chemically altered.

- Since the chemical characteristics of the adsorbed material are not changed the use of adsorption in wastewater treatment is associated with the removal of hazardous material(s) from the wastewater and its transfer to the activated carbon

Adsorption as a Physical Process (continued)

- This implies that the activated carbon now contains the hazardous material. Therefore, appropriate actions must then be taken to treat the spent activated carbon at the end of a cycle. The carbon can be:

  - regenerated (i.e., the hazardous material may be removed via stripping)

  - disposed of (together with the pollutants it contains) in a landfill

  - destroyed (together with the pollutants it contains) in an incinerator

Common Adsorbents

- **Activated carbon - a char-like material with high surface area.**

- **Silica gel - hard, granular, porous material made by precipitation from sodium silicate solutions treated with an acid.**

- **Activated alumina - aluminum oxide activated at high temperature and used primarily for moisture adsorption.**

- **Aluminosilicates (molecular sieves) - porous synthetic zeolites used primarily in separation processes.**

Activated Carbon as an Adsorbent

- Activated carbon is by far the most common adsorbent used in wastewater treatment.

- Since, during adsorption, the pollutant is removed by accumulation at the interface between the activated carbon (absorbent) and the wastewater (liquid phase) the adsorbing capacity of activated carbon is always associated with very high surface area per unit volume.

Production of Activated Carbon

The high surface area per unit volume characteristic of activated carbon is obtained with a two-step process used in carbon manufacturing:

- pyrolysis of raw material (typically a high carbon source such as coal, wood, nut shells) to drive off (distill) the lighter fraction producing a charred, highly carbonaceous solid residue;

- activation of the charred residue via oxidation (typically with air or steam) to form a network of pores and passages with high surface area.

Pore Structure in Activated Carbons

- **Pores in activated carbon typically range from 10 to 10,000 Å in diameter.**

- **Pores having a diameter larger than 1000 Å are called *macropores.***

- **Pores having a diameter smaller than 1000 Å are called *micropores.***

- **Micropores are primarily responsible for the adsorption characteristics of activated carbon.**

- **Typical surface areas in activated carbons range from 500 to 1500 m²/g of carbon.**

Sizes of Activated Carbon Particles

- Activated carbon is produced in particle sizes up to a few millimeters.

- The total surface area available for adsorption is not significantly affected the by particle size since the micropore structure responsible for adsorption does not change appreciably with particle size.

- This implies that the total adsorption capabilities of small and large particles are not too different although the time to achieve equilibrium can vary significantly because of diffusional effects.

Sizes of Activated Carbon Particles

- Carbon having larger particle sizes (of the order of 1 mm or more) is termed "<u>granular</u>". This material can be packed in columns through which a liquid can be passed, and can be regenerated after use.

- Carbon having smaller particle sizes (of the order of tens of mm) is termed "<u>powdered</u>". This material can only be used by direct addition to a liquid and must be removed after use (e.g., by filtration) and disposed of.

- In general, the larger the particle size the more expensive is the carbon.

Activated Carbon in Wastewater Treatment

Two sizes of activated carbon are typically used in wastewater treatment:

- **Granular Activated Carbon (GAC)**. Particle size: larger than 0.1 mm (100 μm). Typical range: 0.4-2.5 mm. This material is commonly used in *adsorption columns*;

- **Powered Activated Carbon (PAC)**. Particle size: smaller than 200 mesh (74 μm). Typical range: 10-50 μm. This material is commonly used by direct addition.

Densities of Activated Carbons

- Bulk dry (apparent) density (GAC): 0.22-0.5 kg/L.

- Bulk dry (apparent) density (PAC): 0.34-0.74 kg/L.

- Real density: 2-2.1 kg/L.

Factors Affecting Adsorption

The most important factors affecting adsorption are:

- *Surface area of adsorbent.* Larger sizes imply a greater adsorption capacity.

- *Particle size of adsorbent.* Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained). However, wastewater drop across columns packed with powdered material is too high for use of this material in packed beds. Addition of powdered adsorbent must be followed by their removal.

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Factors Affecting Adsorption (continued)

- *Contact time or residence time.* The longer the time the more complete the adsorption will be. However, the equipment will be larger.

- *Solubility of solute (adsorbate) in liquid (wastewater).* Substances slightly soluble in water will be more easily removed from water (i.e., adsorbed) than substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the latter have a greater affinity for water.

Factors Affecting Adsorption (continued)

- ***Affinity of the solute for the adsorbent (carbon).*** **The surface of activated carbon is only slightly polar. Hence non-polar substances will be more easily picked up by the carbon than polar ones.**

- ***Number of carbon atoms.*** **For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence formic-acetic-propionic-butyric acid).**

Factors Affecting Adsorption (continued)

- *Size of the molecule with respect to size of the pores.* Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.

- *Degree of ionization of the adsorbate molecule.* More highly ionized molecules are adsorbed to a smaller degree than neutral molecules.

- *pH.* The degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption.

Adsorption Equilibrium

- **Upon contacting an amount of activated carbon with a wastewater containing an adsorbable substance adsorption will take place. Adsorption will continue until *equilibrium* will be established between the substance in solution and the same substance in the adsorbed state.**

- **At equilibrium a relationship exists between the concentration of the species in solution and the "concentration" of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent).**

Adsorption Isotherm

The adsorption equilibrium relates *q* to *C*. The equilibrium is a function of the temperature. Therefore, the adsorption equilibrium relationship <u>at a given temperature</u> is typically referred to as *adsorption isotherm*, i.e.:

$$q = f(C)$$

where:

q = mass of species adsorbed/mass of adsorbent (i.e., equilibrium concentration of adsorbable species in solid adsorbent)

C = equilibrium concentration of adsorbable species in solution

Experimental Determination of an Adsorption Equilibrium Point

To determine the relationship between the concentration of an adsorbate in solution (C) and the amount of adsorbate adsorbed per unit mass of adsorbent (q) one can proceed as follows:

- a bottle is filled with a solution of the adsorbate and a carbon pellet is added;

- enough time should be allowed to elapse to achieve equilibrium;

- the solution is sampled and analyzed for the adsorbate.

Experimental Determination of an Adsorption Equilibrium Point

A mass balance for the adsorbate in the bottle is:

$$V\left(C_o - C\right) = M\left(q - q_o\right)$$

from which a relationship between a value of C and the corresponding <u>equilibrium</u> value of q can be established.

C_o = initial adsorbate concentration in solution (mg/L)

q_o = initial amount of adsorbate per unit mass of adsorbent (mg/g carbon)

M = mass of carbon pellet (g)

Experimental Determination of an Adsorption Equilibrium Point

Since, in most cases, virgin carbon pellets are used to determine equilibrium relationship it is:

$$q_o = 0 \quad \Rightarrow \quad q = \frac{V(C_o - C)}{M}$$

Note that this experiment results in just <u>one</u> equilibrium point (*C; q*). If an equilibrium curve is required the same experiment must be repeated with different initial concentrations and/or different additions of carbon pellets so as to produce other *C-q* equilibrium points.

Types of Adsorption Isotherms

- **Different adsorbates-adsorbents exhibit different types of equilibrium relationships (i.e., the function $q = f(C)$ may take different mathematical forms)**

- **It has been found that for most of the cases of importance in wastewater treatment the function $q = f(C)$ takes the form of one of the following isotherms:**

  - **Langmuir isotherm**

  - **Brauner-Emmet-Teller (BET) isotherm**

  - **Freundlich isotherm**

Adsorption Model for Langmuir Isotherm

The assumptions made in the derivation of the Langmuir model are:

- adsorption is a reversible process

- the adsorbed layer is made up of a single layer of molecules

- the adsorbed molecules do not move on the surface of the adsorbent. However, they can be lost back to the solution

- the enthalpy of adsorption is the same for all molecules independently of how many have been adsorbed

Derivation of Langmuir Isotherm

In the Langmuir model (1918) adsorption is assumed to be a dynamic process. At equilibrium the number of molecules being adsorbed will be equal to the number of molecules leaving the adsorbed state, i.e.:

rate of adsorption $\propto$

$$\propto (\text{conc. in solution}) \cdot (\text{available area for adsorption})$$

$$\propto C\left(A_{total} - A_{occupied}\right) \propto C\left(k_1' q_m - k_1' q\right) \propto k_1' C\left(q_m - q\right)$$

$$= k_1 C\left(q_m - q\right)$$

Derivation of Langmuir Isotherm

Similarly:

rate of desorption $\propto$ (amount already adsorbed)

$$\propto A_{occupied} \propto k_2^{'} q = k_2 q$$

At equilibrium it is:

rate of adsorption $=$ rate of desorption

i.e.:

$$k_1 C \left(q_m - q \right) = k_2 q$$

Langmuir Isotherm

The previous equation can be rewritten as:

$$q = \frac{q_m \, k_1 \, C}{k_2 + k_1 \, C}$$

which, with the substitution: $K_A = k_1/k_2$, becomes the final expression for the *Langmuir isotherm*:

$$\boxed{q = \frac{q_m \, K_A \, C}{1 + K_A \, C}}$$

where:

q_m = maximum adsorbable value of q

K_A = constant (function of enthalpy of adsorption and temperature)

Langmuir Isotherm

q_m

q (g solute/g adsorbant)

Langmuir
Isotherm

C (g/L)
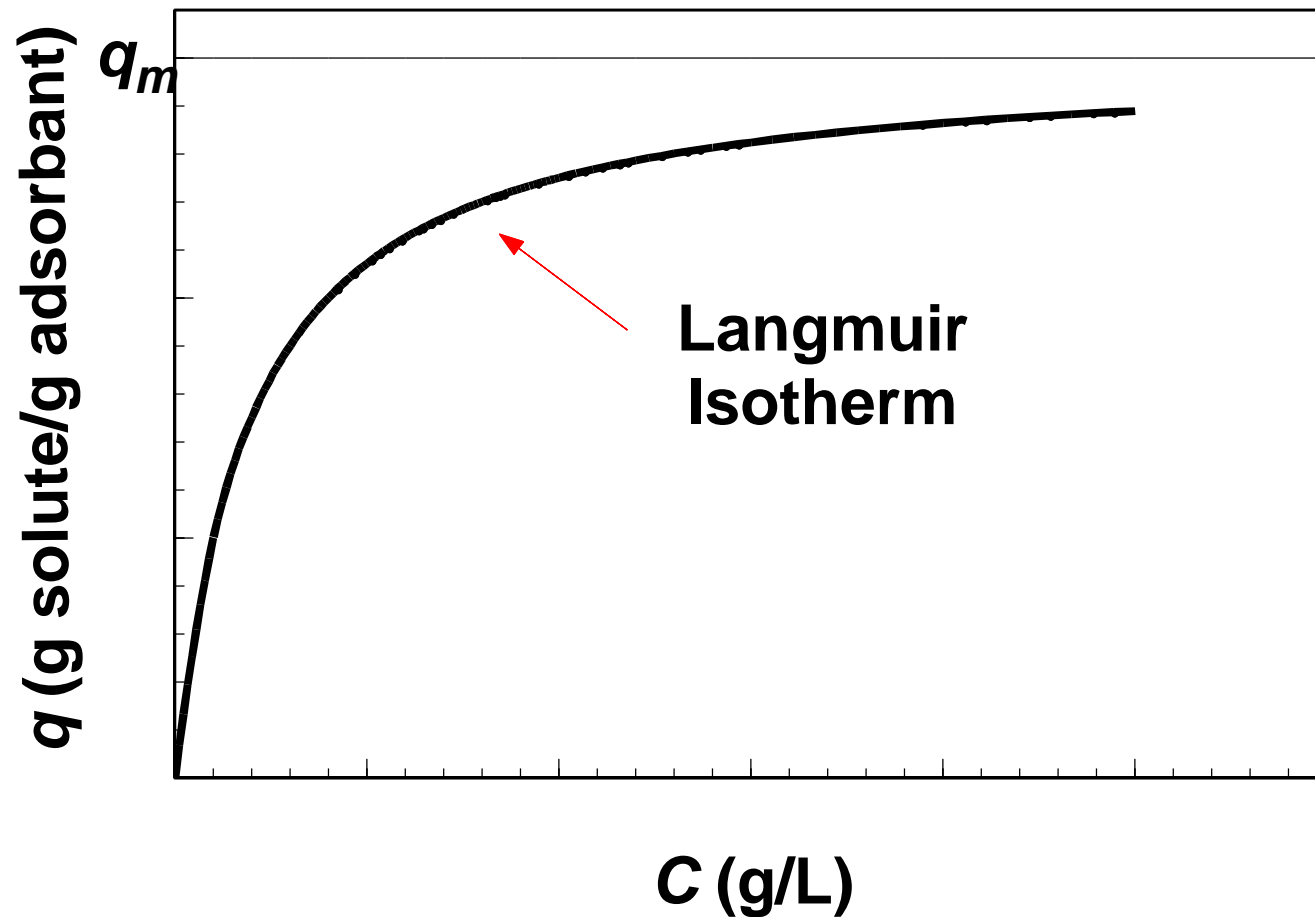
Determination of Parameters in Langmuir Isotherm

The Langmuir isotherm can be rearranged to give:

$$\frac{C}{q} = \frac{1}{K_A q_m} + \frac{1}{q_m} C$$

Accordingly, a plot of *C/q* vs. *C* should produce a straight line with:

$$\text{slope} = \frac{1}{q_m}$$

$$\text{intercept} = \frac{1}{K_A q_m}$$

Determination of Parameters in Langmuir Isotherm
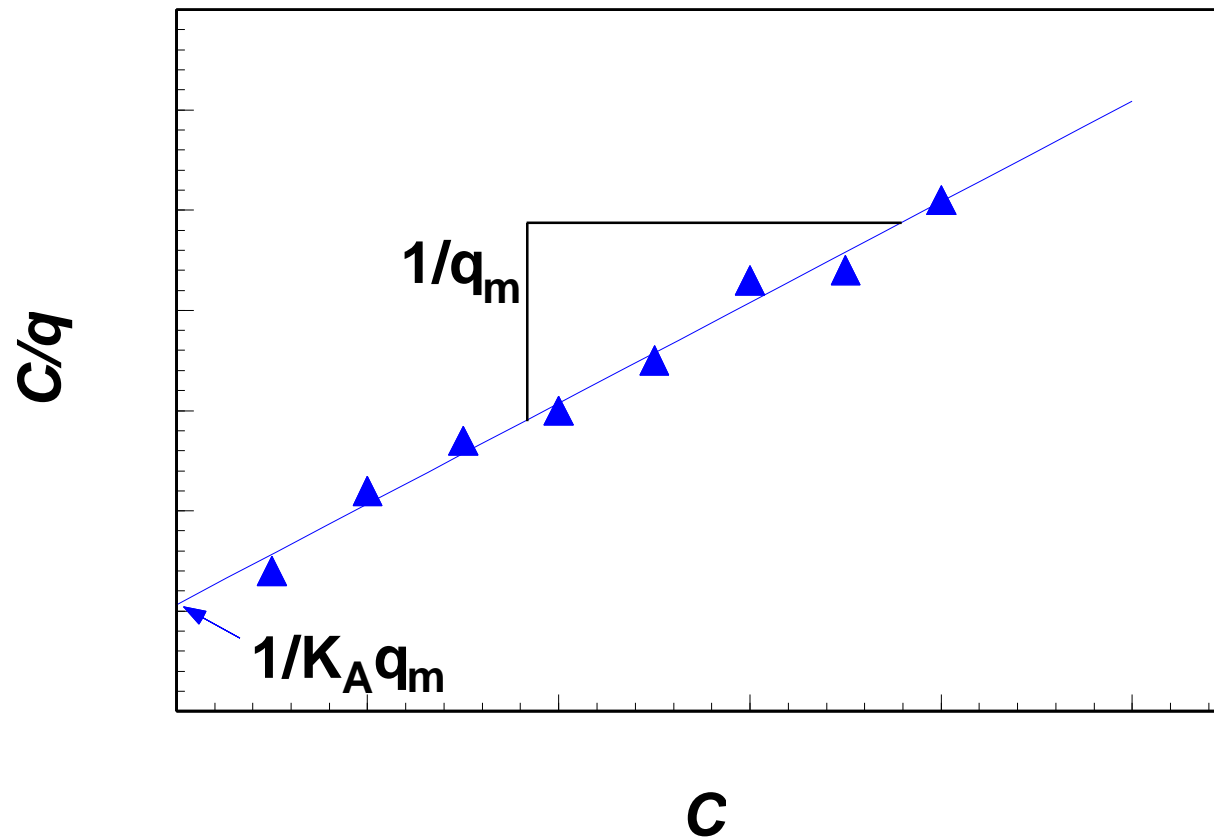
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Alternative Determination of Parameters in Langmuir Isotherm

The Langmuir isotherm can also be rearranged to give:

$$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{K_A\,q_m}\right)\frac{1}{C}$$

from which a plot of *1/q* vs. *1/C* gives:

$$\text{slope} = \frac{1}{K_A\,q_m}$$

$$\text{intercept} = \frac{1}{q_m}$$

Alternative Determination of Parameters in Langmuir Isotherm

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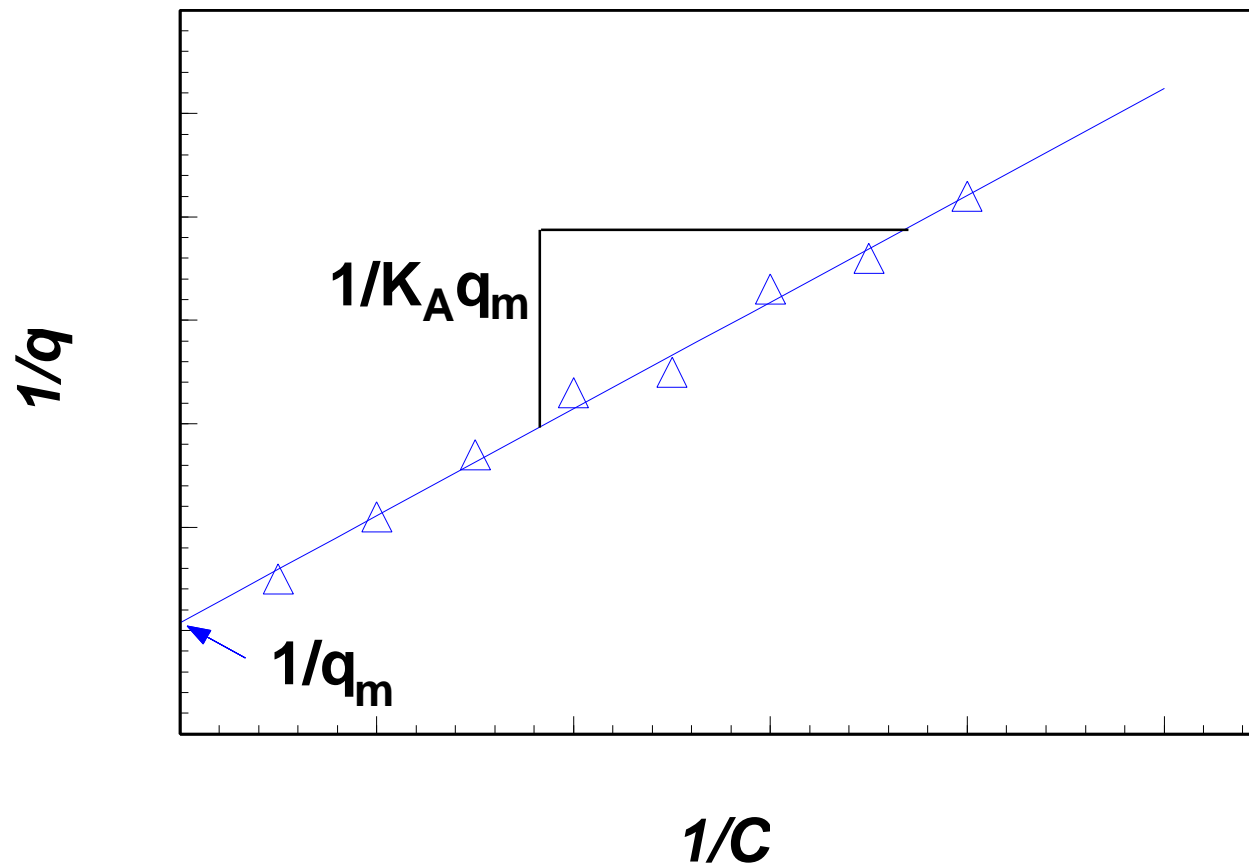
Adsorption Model for BET Isotherm

The assumptions made in the derivation of the BET model are:

- the adsorbed molecules are arranged in multiple layers on the surface of the adsorbent

- the adsorbed molecules do not move on the surface of the adsorbent

- a layer does not need to be completed before the next layer starts to fill up

- the enthalpy of adsorption is the same for all molecules in a given layer

- all molecules in layers other than the first have the same adsorption energy

BET Isotherm

The BET equation can be mathematically represented by:

$$q = \frac{q_m\, K_B\, C}{\left(C_s - C\right)\left[1 + \left(K_B - 1\right)\cdot\dfrac{C}{C_s}\right]}$$
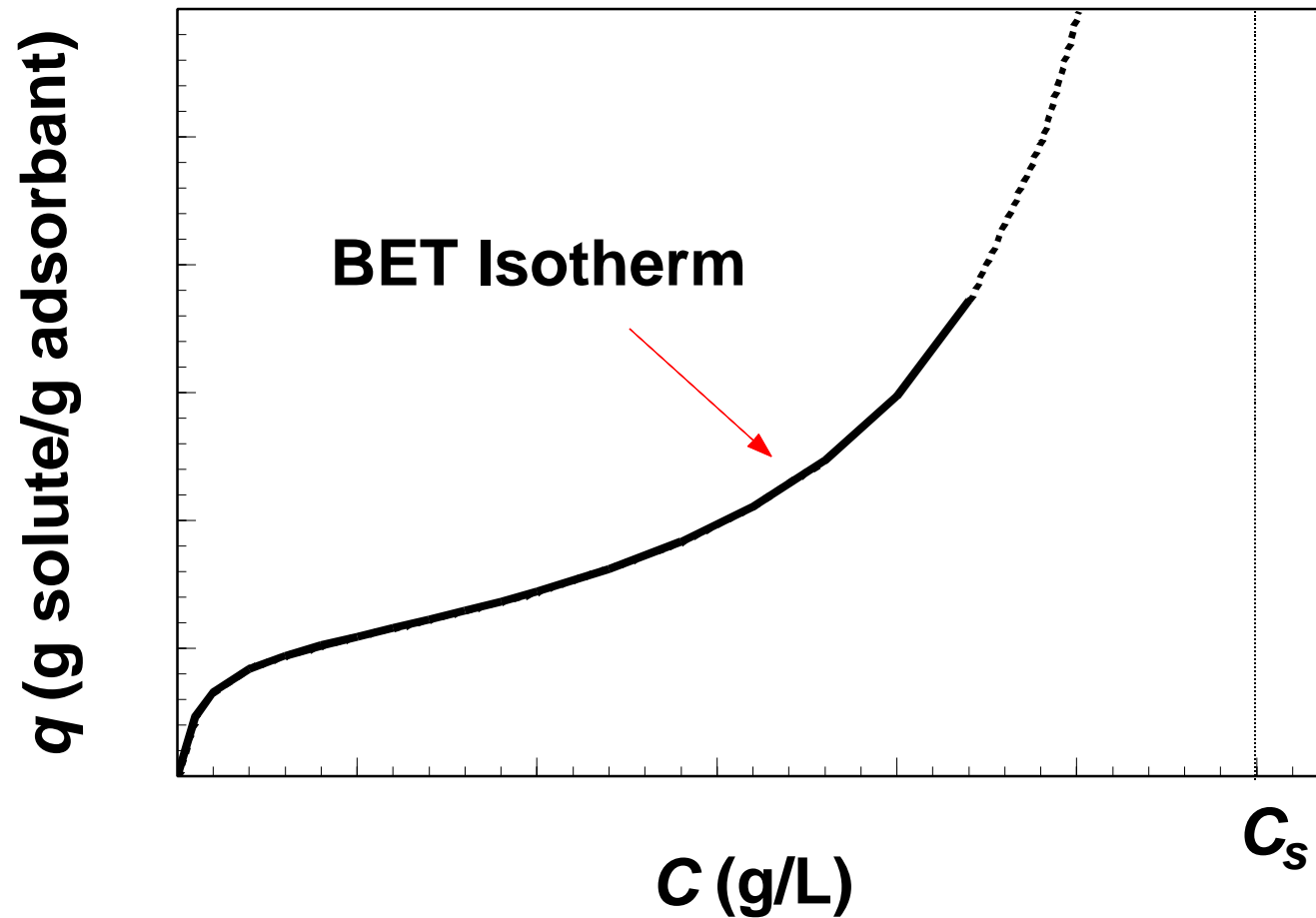
where:

q_m = maximum adsorbable value of q

K_B = constant (function of energy of adsorption and temperature)

C_s = concentration of solute when all layers are saturated

BET Isotherm

BET Isotherm

q (g solute/g adsorbant)

C (g/L)

C_s

Determination of Parameters in BET Isotherm

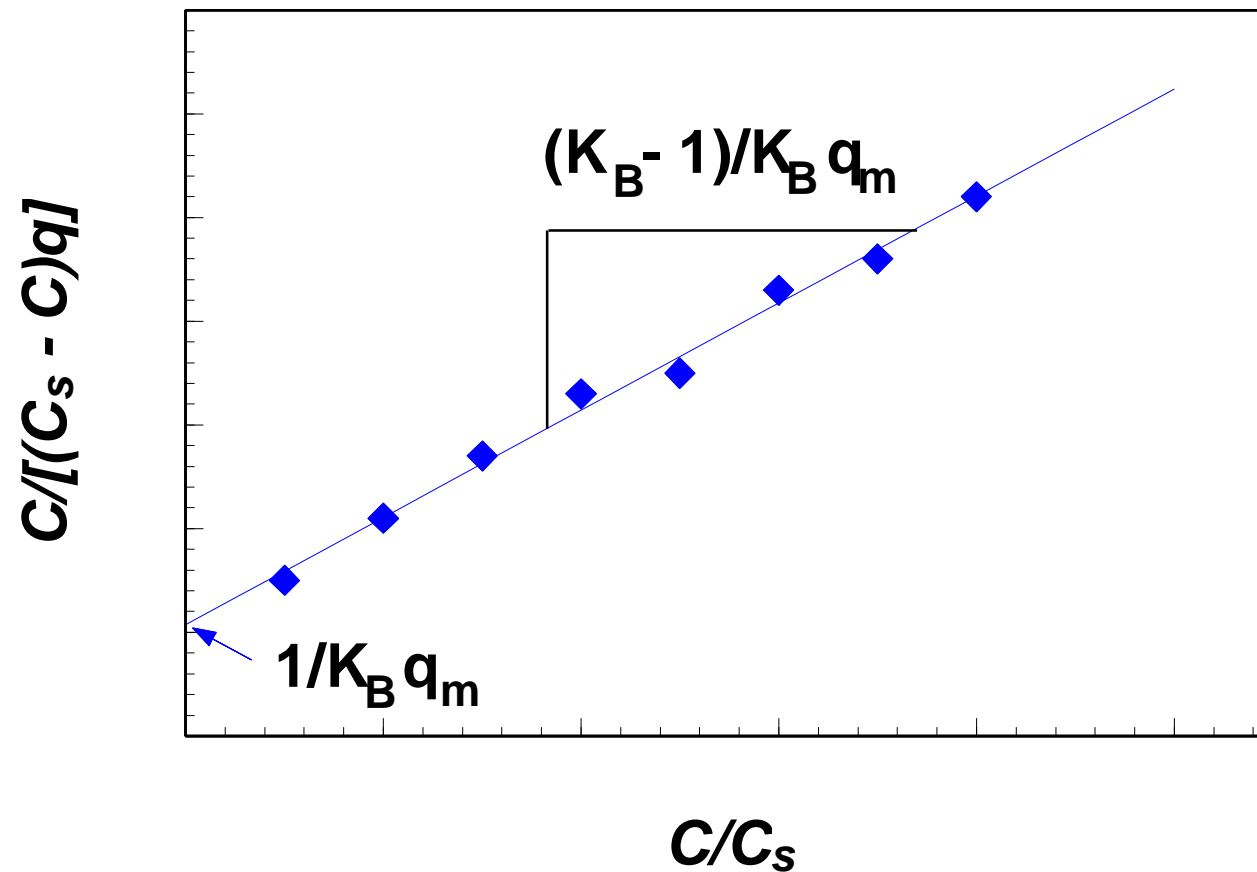**The BET isotherm can be rearranged to give:**

$$\frac{C}{\left(C_s - C\right)q} = \frac{1}{K_B\,q_m} + \left(\frac{K_B - 1}{K_B\,q_m}\right)\frac{C}{C_s}$$

Accordingly, a plot of $C/[(C_s - C)\,q]$ vs. C/C_s should produce a straight line with:

$$\text{slope} = \frac{K_B - 1}{K_B\,q_m}$$

$$\text{intercept} = \frac{1}{K_B\,q_m}$$

Determination of Parameters in BET Isotherm

The plot shows data points with a linear fit. The y-axis is labeled $C/[(C_s - C)q]$ and the x-axis is labeled C/C_s. The slope is labeled $(K_B - 1)/K_B q_m$ and the y-intercept is labeled $1/K_B q_m$.

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Freundlich Isotherm

The Freundlich equation can be mathematically represented by:

$$q = K_F \, C^{1/n}$$

where:

K_F = constant (function of energy of adsorption and temperature)

n = constant

Freundlich Isotherm

Freundlich Isotherm

q (g solute/g adsorbant)

C (g/L)
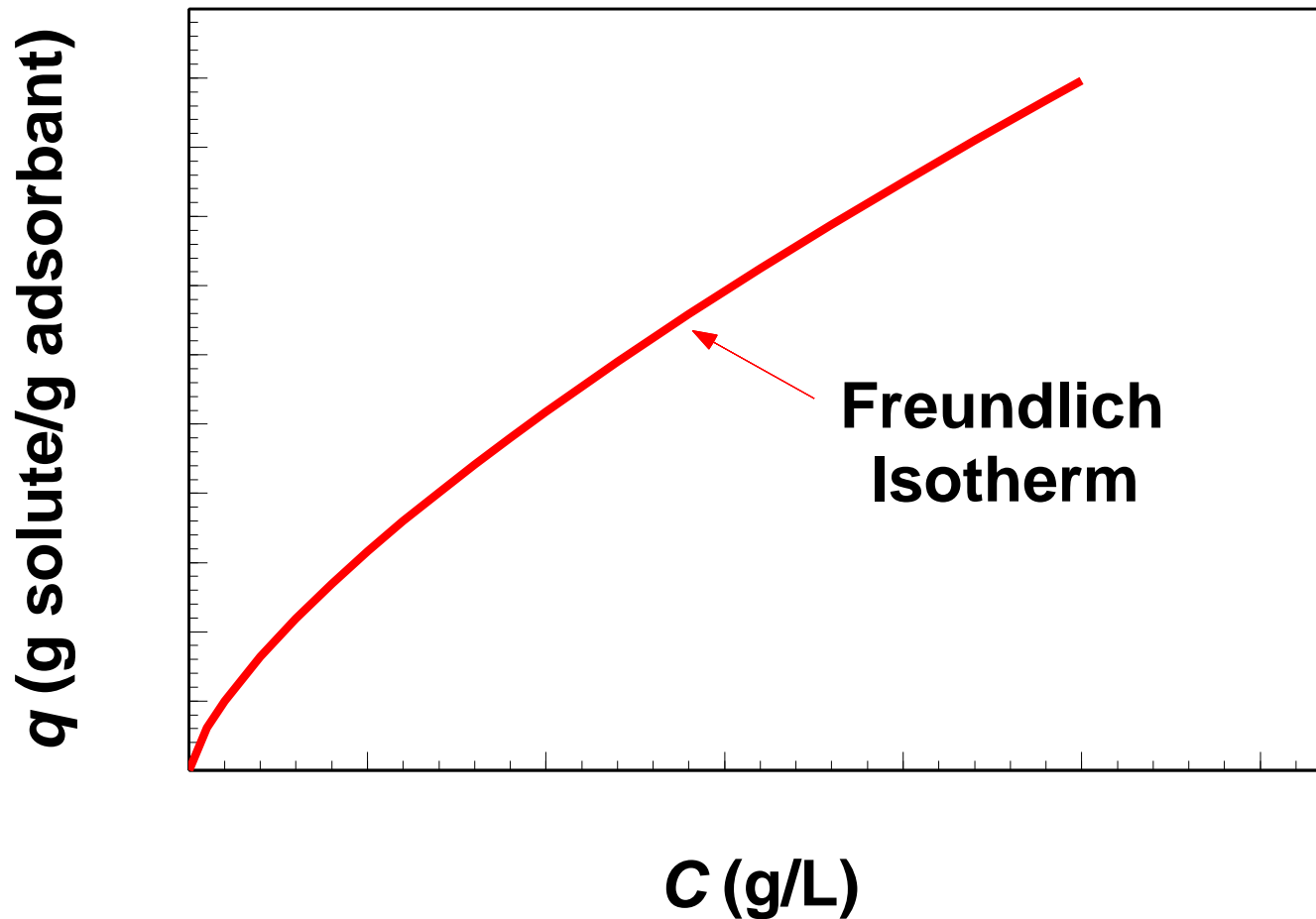
Determination of Parameters in Freundlich Isotherm

The Freundlich isotherm can be rearranged to give:

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

Accordingly, a plot of log *q* vs. log *C* should produce a straight line with:

$$\text{slope} = \frac{1}{n}$$

$$\text{intercept} = \log K_F$$

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Determination of Parameters in Freundlich Isotherm
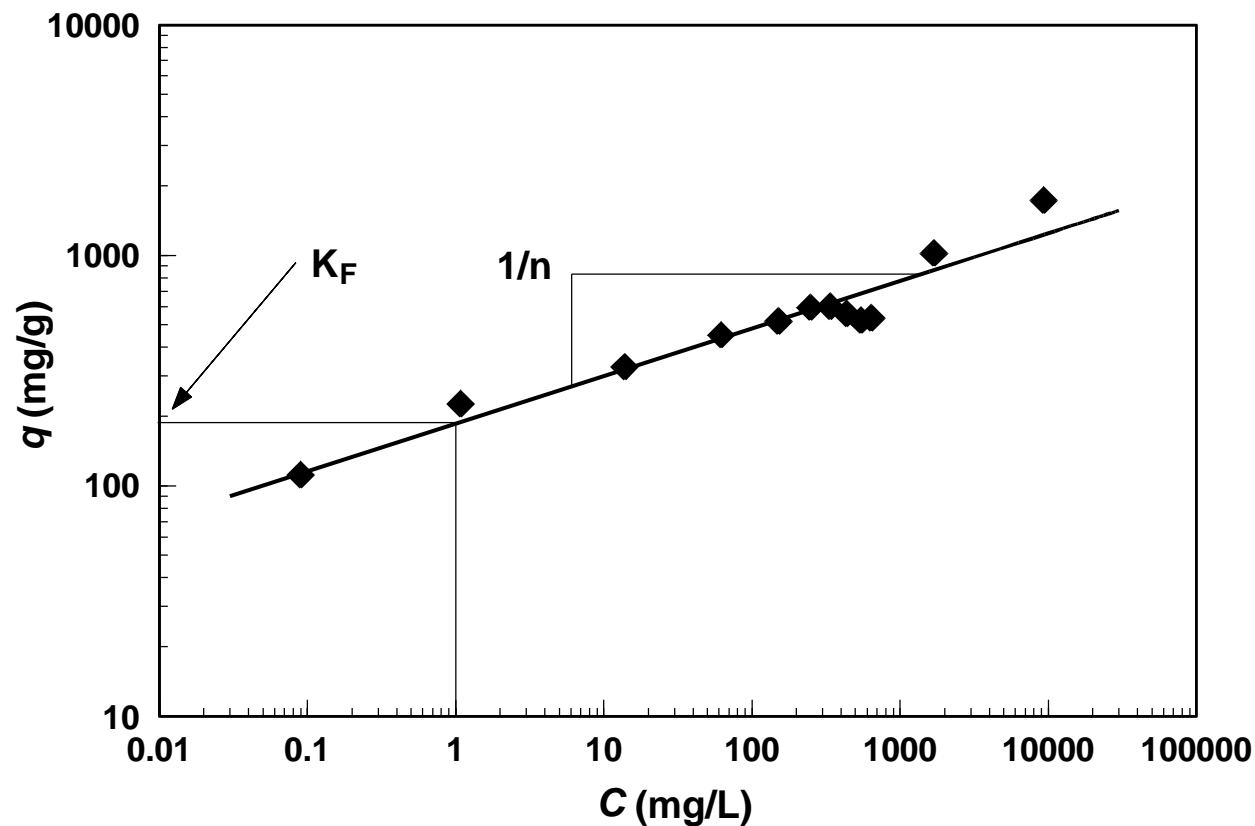
Freundlich Parameters at Neutral pH

Compound	K_F	1/n
Hexachlorobutadiene	360	0.63
Anethole	300	0.42
Phenyl mercuric acetate	270	0.44
p-Nonylphenol	250	0.37
Acridine yellow	230	0.12
Benzidine dihydrochloride	220	0.37
n-Butylphthalate	220	0.45
N-Nitrosodiphenylamine	220	0.37
Dimethylphenylcarbinol	210	0.33
Bromoform	200	0.83
b-Naphthol	100	0.26
Acridine orange	180	0.29
a-Naphthol	180	0.31
a-Naphthylamine	160	0.34
Pentachlorophenol	150	0.42
p-Nitroaniline	140	0.27
1-Chloro-2-nitrobenzene	130	0.46
Benzothiazole	120	0.27
Diphenylamine	120	0.31
Guanine	120	0.40
Styrene	120	0.56
Dimethyl phthalate	97	0.41
Chlorobenzene	93	0.98
Hydroquinone	90	0.25
p-Xylene	85	0.16
Acetophenone	74	0.44
1,2,3,4-Tetrahydronaphthalene	74	0.81
Adenine	71	0.38
Nitrobenzene	68	0.43
Dibromochloromethane	63	0.93

$q = K_F\, C^{1/n}$ **with *q* in mg/g and *C* in mg/L**

After Eckenfelder, Industrial Water Pollution Control, 1989, p. 266.

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Langmuir Isotherm vs. Freundlich Isotherm

- **The Langmuir isotherm has a theoretical justification. The Freundlich isotherm represents an empirical model**

- **The Langmuir isotherm assumes reversible adsorption and desorption of the adsorbate molecules. No assumption is made for the Freundlich isotherm**

- **The Langmuir isotherm typically represents well data for single components. The Freundlich isotherm can be used also for mixtures of compounds**

Isotherms for Multiple Adsorbates

When more than one adsorbate is present in solution modified adsorption isotherms can be used. For example, for the case of two adsorbates, A and B, the Langmuir equations are:

$$q_A = \frac{a_A\, b_A\, C_A}{1 + a_A\, C_A + a_B\, C_B} \quad \text{and} \quad q_B = \frac{a_B\, b_B\, C_B}{1 + a_A\, C_A + a_B\, C_B}$$

where the constants for each compound can be obtained from experiment with pure solutions.

A number of other equilibrium equations based on other models (e.g., Freundlich) have also been developed.

Adsorption with Powdered Activated Carbon (PAC)

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Adsorption Processes Utilizing Powdered Activated Carbon (PAC) for Wastewater Treatment

In all these processes powdered activated carbon (PAC) is added to the wastewater for a given period of time to allow pollutants to be adsorbed. This process can be carried out once (*single stage*) or repeated (in several *stages*). The possible processes using PAC can be classified as:
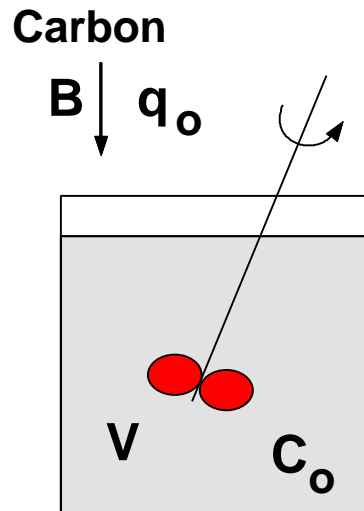
- Batch adsorption (single stage)

- Multistage crosscurrent adsorption

- Multistage countercurrent adsorption

Batch Adsorption

- Batch adsorption consists of contacting finely divided activated carbon with the wastewater for a given period of time in a mixing vessel

- The activated carbon used in this process is typically supplied in a powdered form (PAC) to maximize surface area for mass transfer and minimize agitation for suspension. Typical carbon particle size: 10 - 50 μm

- After the process is complete (typical contact time: 10 - 60 minutes) the spent carbon is separated from the wastewater (e.g., by filtration) and regenerated or disposed of

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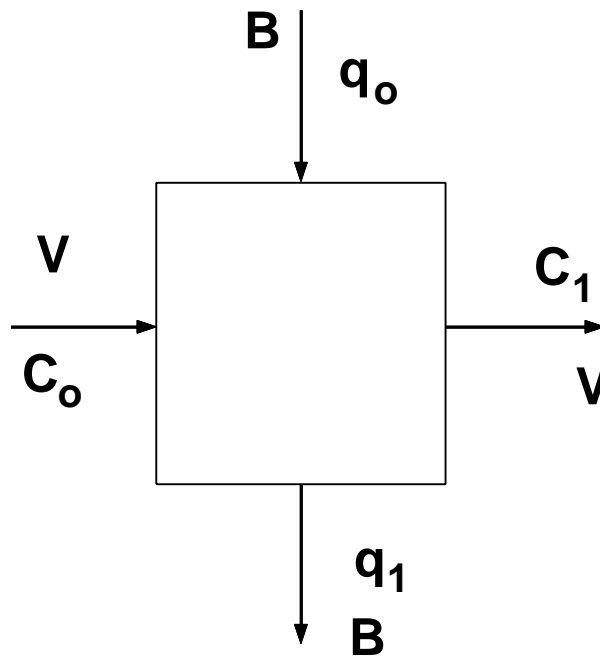# Unsteady State Mass Balance for Batch Adsorption

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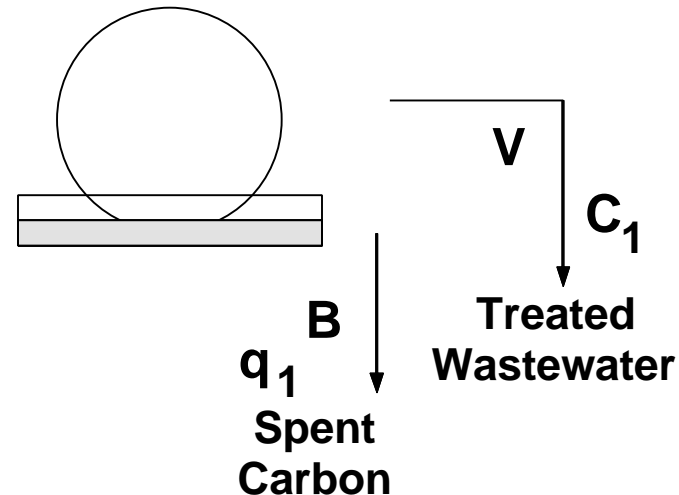
Unsteady State Mass Balance for Batch Adsorption

The previous diagram can be seen as a stage operation, i.e.:

Unsteady State Mass Balance for Batch Adsorption

At a given time *t* when the carbon is separated the following mass balance can be written:

$$V\left(C_o - C\right) = B\left(q - q_o\right)$$

where: *V* = wastewater volume (» constant)

B = mass of activated carbon

q = q_o at t=0

C_o = initial   concentration   of   pollutant   in   wastewater

Unsteady State Mass Balance for Batch Adsorption

At the generic time *t* it is:

$$C = C_o - \frac{B}{V}\left(q - q_o\right)$$

This equation represents an *operating line* (from a mass balance) for the system.

If the time elapsed is long enough for equilibrium to be established then this equation becomes:

$$C_{eq} = C_o - \frac{B}{V}\left(q_{eq} - q_o\right)$$

Unsteady State Mass Balance for Batch Adsorption

A mass balance for a pollutant in an differential time interval, *dt*, during a batch adsorption operation is:

$$V \, dC = -K \, A_p \left(C - C^* \right) dt$$

where: V = volume of wastewater (m³)

K = mass transfer coefficient between carbon particle and wastewater (m/s)

A_p = cumulative surface area of carbon particles (m²)

C = pollutant concentration (g/L)

C^* = pollutant concentration in equilibrium with concentration q in the particle at time t (g/L)

Unsteady State Mass Balance for Batch Adsorption

The previous equation can be integrated to give:

$$t = -\frac{1}{K\,a_p} \int_{C_o}^{C} \frac{dC'}{C'-C'^*}$$

where: a **= surface area of particles/liquid volume**

This equation can be integrated if the equilibrium isotherm is known and by knowing that the mass balance at a generic time, t**, is given by:**

$$V(C_o - C) = B(q - q_o)$$

Unsteady State Mass Balance for Batch Adsorption
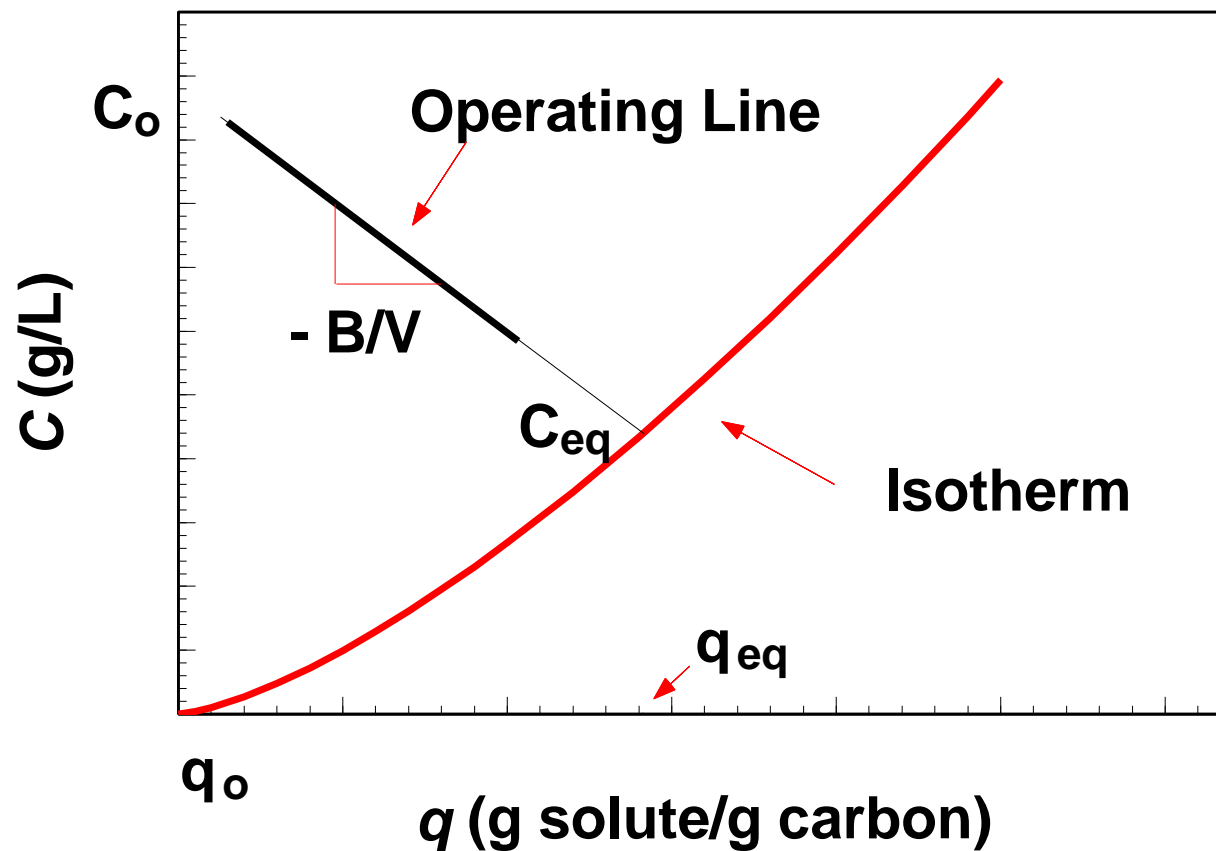
During the initial stages of the process it is:

$$C >> C*$$

Then:

$$t \cong -\frac{1}{Ka_p}\int_{C_o}^{C}\frac{dC'}{C'} = \frac{1}{Ka_p}\ln\frac{C_o}{C}$$

This equation can be used to approximately estimate the time required for the pollutant concentration in the wastewater to drop to a desired level.

Unsteady State Mass Balance for Batch Adsorption

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Unsteady State Mass Balance for Batch Adsorption

If the adsorption follows a known adsorption model (e.g., Freundlich isotherm) then:
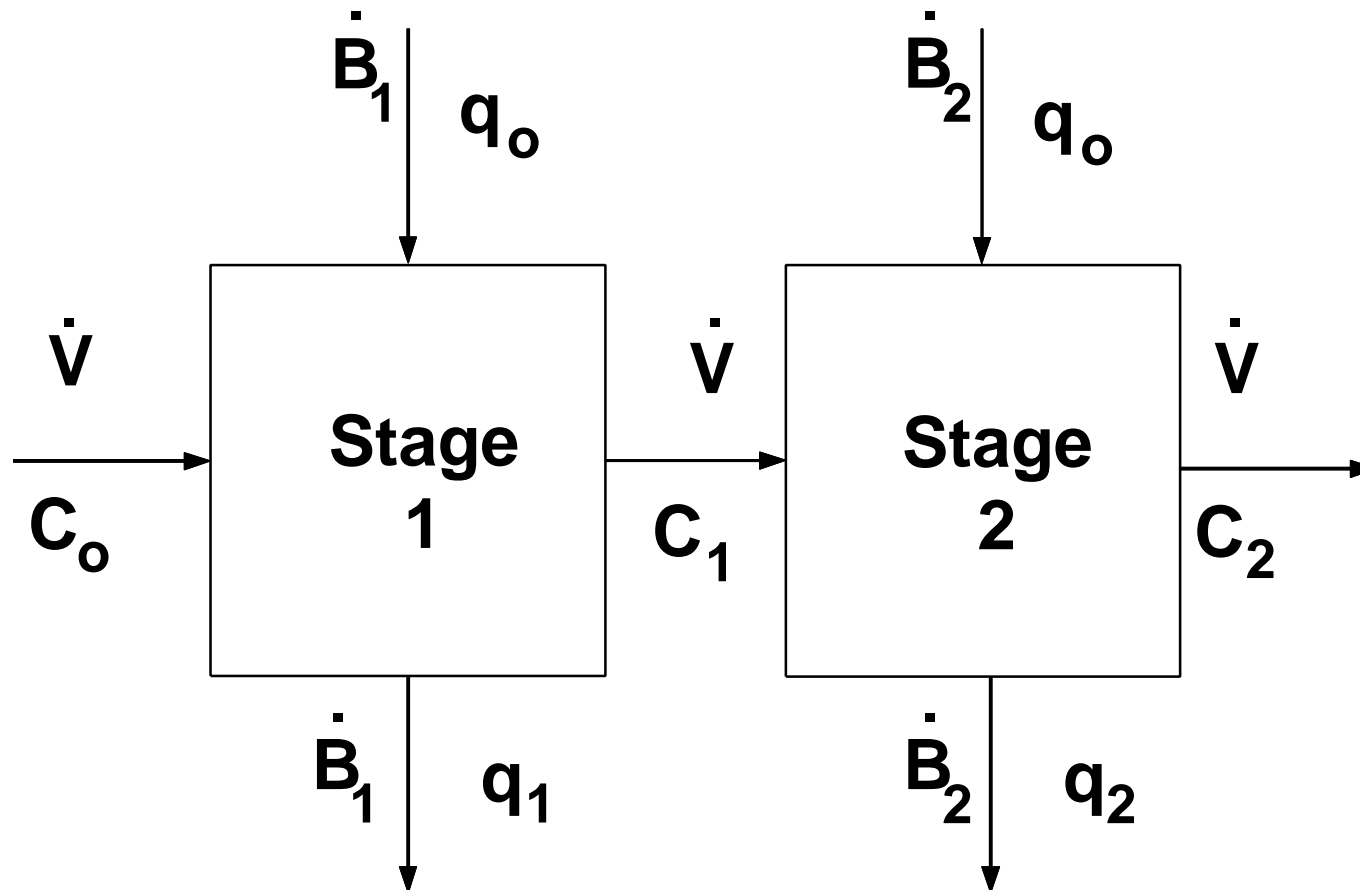
$$q_{eq} = K_F \, C_{eq}^{1/n}$$

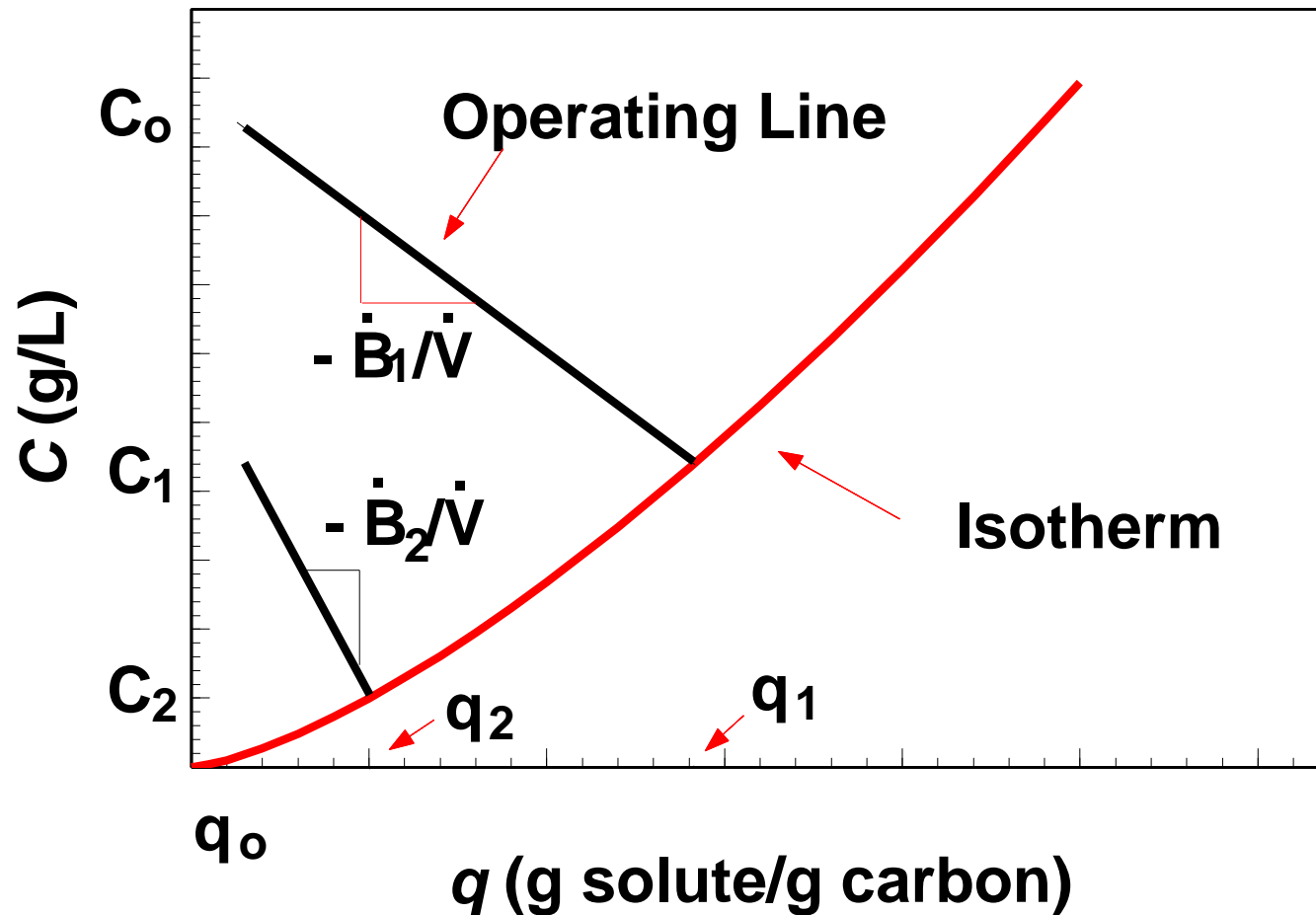combined with:

$$C_{eq} = C_o - \frac{B}{V}\left(q_{eq} - q_o\right)$$

gives:

$$C_{eq} = C_o - \frac{B}{V}\left(K_F \, C_{eq}^{1/n} - q_o\right)$$

which can be solved to find C_{eq} for the case in which enough time is allowed for *equilibrium* to be reached.

Multistage Crosscurrent Adsorption

Multistage Crosscurrent Adsorption

Multistage Crosscurrent Adsorption

In this case fresh carbon is added to each stage of the adsorption process.

If equilibrium is assumed to be achieved in each stage then one can write:

$$\dot{V}\left(C_o - C_1\right) = \dot{B_1}\left(q_1 - q_o\right) \qquad \text{for Stage 1}$$

$$\dot{V}\left(C_1 - C_2\right) = \dot{B_2}\left(q_2 - q_o\right) \qquad \text{for Stage 2}$$

Multistage Crosscurrent Adsorption

If the adsorption follows a known adsorption model (e.g., Freundlich isotherm) then:

$$q_{eq} = K_F C_{eq}^{1/n}$$

then the previous mass balances can be rewritten as:

$$\frac{\dot{B}_1}{\dot{V}} = \frac{C_o - C_1}{K_F C_1^{1/n} - q_o} \qquad \text{for Stage 1}$$

$$\frac{\dot{B}_2}{\dot{V}} = \frac{C_1 - C_2}{K_F C_2^{1/n} - q_o} \qquad \text{for Stage 2}$$

Multistage Crosscurrent Adsorption

The total amount of carbon used per volume of liquid treated is:

$$\frac{\dot{B}_{tot}}{\dot{V}} = \frac{\dot{B}_1 + \dot{B}_2}{\dot{V}} = \frac{C_o - C_1}{K_F C_1^{1/n} - q_o} + \frac{C_1 - C_2}{K_F C_2^{1/n} - q_o}$$

Note that the amount of carbon needed for a given process is a function of the initial, intermediate and final concentration in the wastewater (C_o, C_1, and C_2, respectively), the equilibrium constant K_F, and the level of pollutant already present in the carbon (if the carbon is fresh $q_o = 0$)

Multistage Countercurrent Adsorption
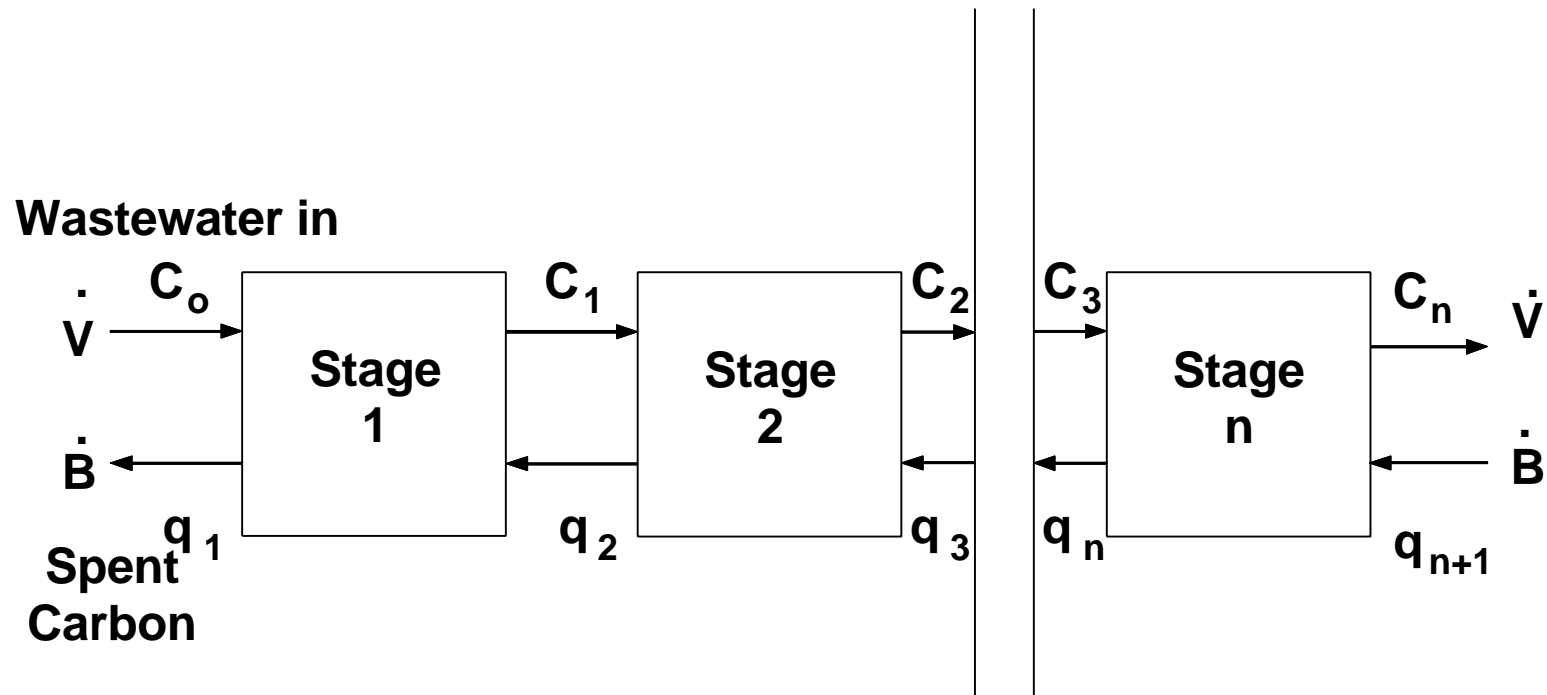
Multistage Countercurrent Adsorption

- The streams leaving each stage are assumed to be in equilibrium with each other

- The numbers attached to the streams leaving any stage are the same as the number of the stage the streams are leaving

- The rates of wastewater and activated carbon moving from stage to stage are constant

- In wastewater applications typically no more than two (2) stages are used

Multistage Countercurrent Adsorption

From a mass balance around the first *j* stages it is:

$$\dot{V}\left(C_o - C_j\right) = \dot{B}\left(q_1 - q_{j+1}\right)$$

From an overall mass balance for the entire process it is:

$$\dot{V}\left(C_o - C_n\right) = \dot{B}\left(q_1 - q_{n+1}\right)$$

from which the operating line can be obtained as:

$$C_j = C_o - \frac{\dot{B}}{\dot{V}}\left(q_1 - q_{j+1}\right)$$

Multistage Countercurrent Adsorption

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