Adsorption

ChE 392 Chemical Engineering Laboratory I
Experiment No: 4b

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ADSORPTION

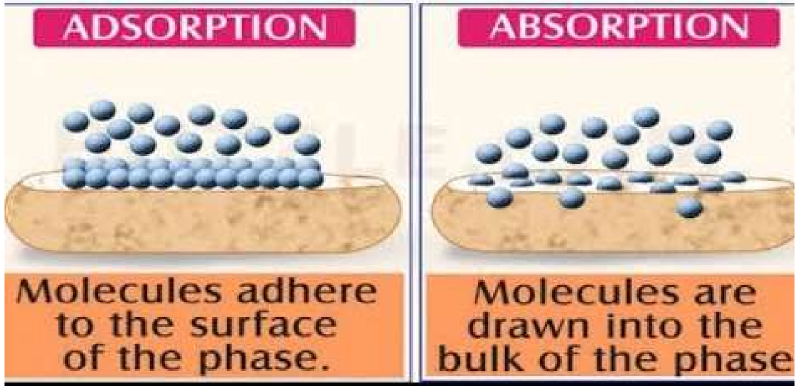
A**d**sorption is the process in which matter is extracted from one phase and concentrated at the surface of a second phase. (Interface accumulation). This is a surface phenomenon as opposed to absorption where matter changes solution phase, e.g. gas transfer. This is demonstrated in the following schematic.

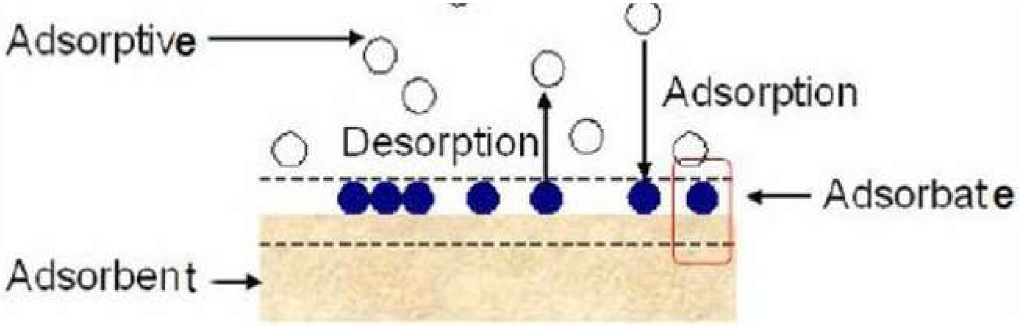
If we have to remove soluble material from the solution phase, but the material is neither volatile nor biodegradable, we often employ adsorption processes.

adsorbate: material being adsorbed

adsorbent: material doing the adsorbing. (examples are activated carbon or ion exchange resin).

In a typical adsorption process, a gaseous, liquid or solid molecule (the *adsorptive)* attached to a solid or liquid surface, the *adsorbent,* and forms the *adsorbate,* a complex between *adsorptive* and *adsorbent.*





Classification of adsorption

Physical adsorption (physisorption)

- The bonding interaction between adsorbate and adsorbent is long range but weak and is associated with van der Waals-type interactions.

- Chemical adsorption (chemisorption)

- ➢ chemical bonds are formed between the molecules (atoms) and the surface.

- ***Physical Adsorption***

The adsorbed material is held on the surface by weak van der Walls forces. The process is reversible and by changing the process conditions, the adsorbed material can be easily removed from the surface. Physical adsorption is an exothermic phenomenon. It is characterized by a low adsorption heat of about 10 000 calories per molecule adsorbed. In contrast to physical adsorption, it is frequently encountered with "negative adsorption" which shows decrease of concentration on the surface. This process is called "desorption".

Generally, components or process conditions (adsorbed material, T, P, concentration) that cause an increase in surface free energy lead to negative adsorption. Both types of surface events (increase and decrease of surface concentration) are expressed by the term "sorption".

- ***Chemical Adsorption***

Chemical adsorption is the adsorption of particles by chemical bonding. The strength of the chemical bond varies. However, the bonds formed are stronger than the bonds in the physical adsorbent. Chemical adsorption is usually encountered in solid-catalyzed reaction systems. Adsorption energy is between 20 000 and 100 000 calories per mole of adsorbed material. This value is also about the same as the reaction heat in chemical reactions - depending on whether it is exothermic or endothermic. Chemical adsorption is also referred to as "active adsorption" and usually occurs as a result of interaction with heterogeneous catalysts.

The Differences between Chemical Adsorption and Physical Adsorption

- Although the chemical adsorption may be only one layer, the physical adsorption can be a layered or multi-layered.
- Physical adsorption is usually a reversible action and desorption occurs by changing the processing conditions (concentration, P, T, etc). Chemical adsorption is an irreversible process because of the strong bond formation.
- While physical adsorption is usually reduced by increasing the temperature, the chemical adsorption may show an increase or decrease with increasing temperature depending on the exothermic or endothermic of the adsorption and the activation energy.

Frequently used adsorbents;

- Activated carbon
- Alumina
- Silica gel
- Polymers
- Zeolites
- Molecular sieves
- Soil, clay, etc…

Adsorption Isotherms

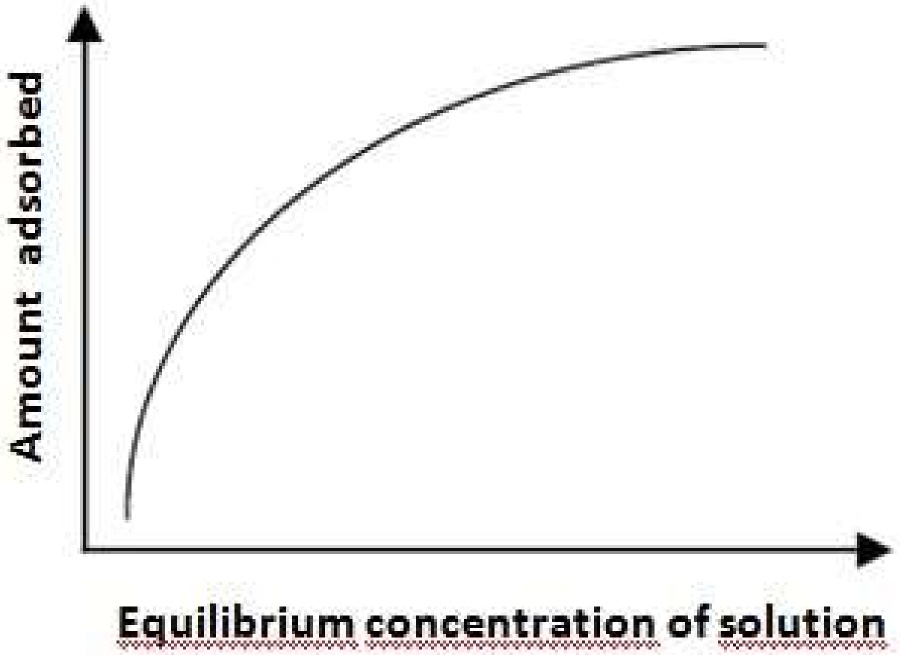
Data relating adsorbed concentration (g/g of bed weight) to equilibrium gas phase concentration (g/ml of stream) is given in terms of adsorption isotherms.

$$W_{\mathrm{ads}} = f(P,T)$$

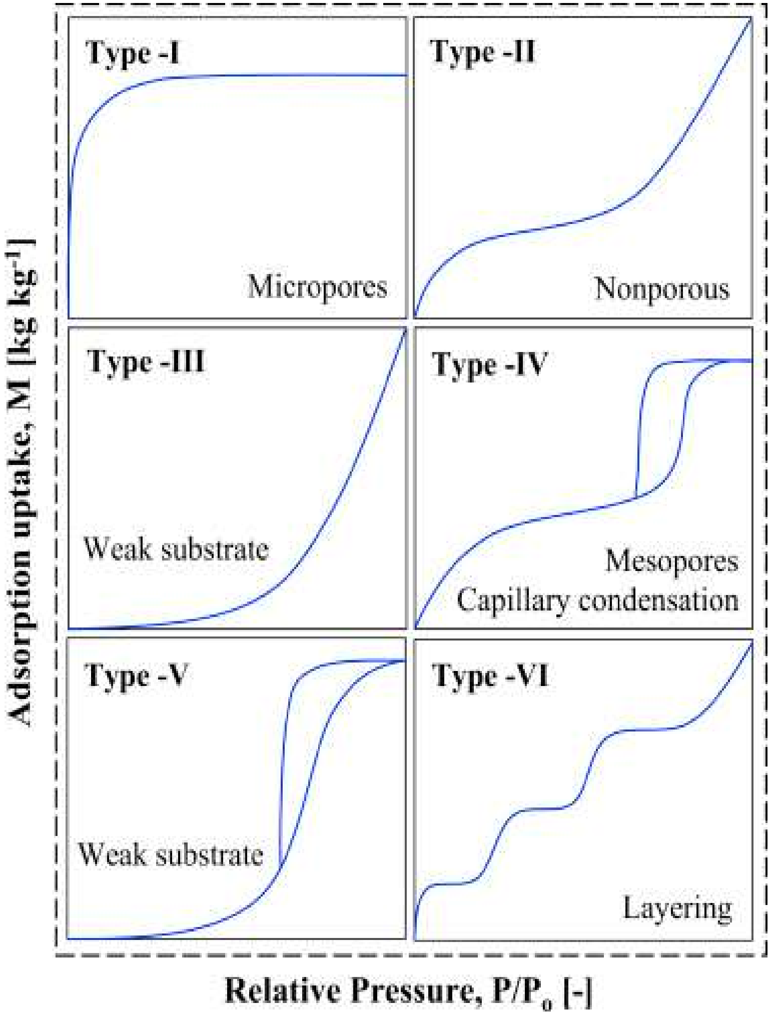
Three common types of isotherms:

- **Langmuir**
- **Freundlich**
- **BET**

The relation between the amount of adsorbed material by the unit amount of adsorbent and the equilibrium concentration (or pressure) at constant temperature is called an “adsorption isoterm”.



The IUPAC Classification of Adsorption Isotherms:



TYPE-1: Adsorption isotherm in microporous solids is similar to TYPE-I curve. It is the type of isotherm that appears when the surfaces of microporoses with high adsorption power are coated as a single layer.

TYPE-II: The adsorption isotherm in macroporous solids is similar to the TYPE-II curve.

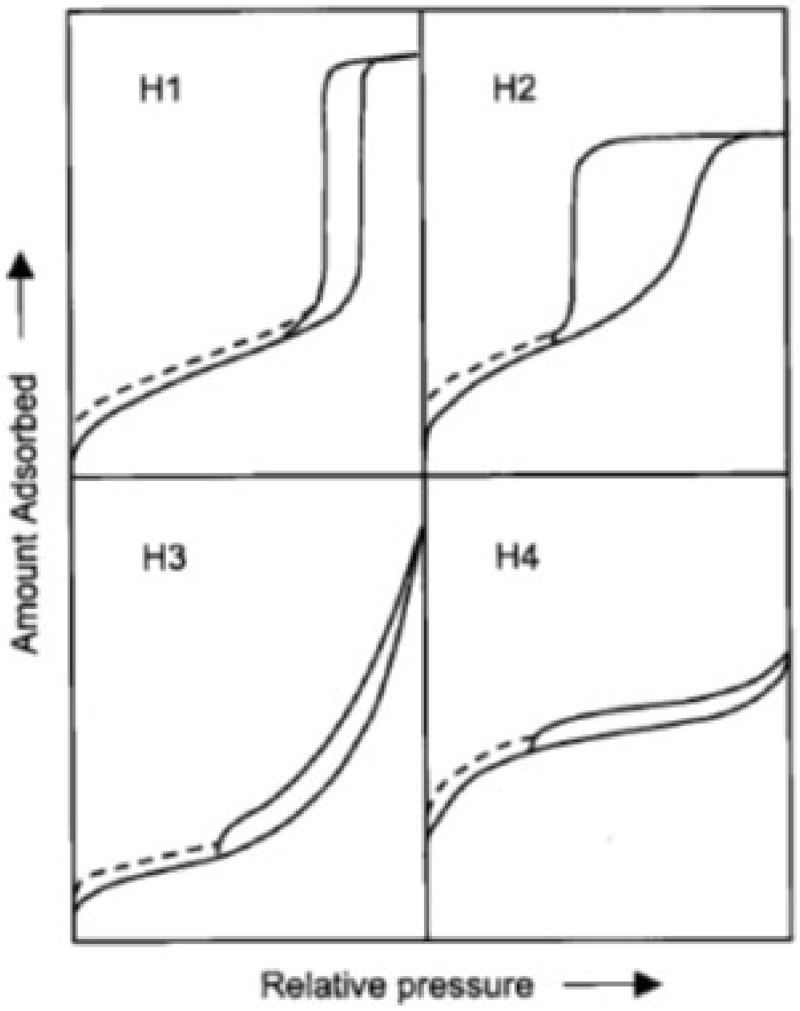
TYPE-III: It is caused by weak adsorbent-adsorbate interaction. It is observed in porous solids where irregular adherence is involved.

TYPE-IV: Hysteresis occurs due to the fact that adsorption and desorption isotherms occur in different ways. It is generally observed in micropore and mesoporous solids.

TYPE-V: It is observed in mesoporous solids with low adsorption power.

TYPE-VI: These isotherms that occur in steps are very rare. Besides micropore, it is observed in solids containing different sizes of mesopore groups.

Adsorption hysteresis occurs when adsorption and desorption isotherms follow different paths. Figure shows the types of adsorption hysteresis:



THE AIM OF THE EXPERIMENT

The objectives of the experiment can be listed as follows;

1. To create an experimental adsorption isotherm that characterizes the adsorption of acetic acid on activated carbon for monolayer formation,
2. Determination of suitable isotherm from adsorption models for experimental data,
3. Determination of the surface area of the activated carbon with the amount of adsorbed for monolayer formation after the appropriate adsorption model is found.

EXPERIMENTAL PROCEDURE

1. Dilute the 0.6 M acetic acid stock solution to prepare a sufficient number of 100 mL acetic acid solutions in different concentrations as indicated in the above range of concentrations.
2. Weigh 0.5 grams of moisture removed activated coal at a temperature of 100 ± 5°C (0.01 mg accuracy) and place it in a dry erlenmeyer flask. In this way, prepare a sufficient number (equal to number of acetic acid solution) of erlenmeyers containing 0.5 g of activated coal.
3. Pour 100 mL of the acetic acid solution prepared at the concentrations you determined (item 1) into the erlenmeyers with activated coal.

4. Record the time of addition of the acid solutions to the activated coal.

5. Rinse the erlenmeyers regularly for 30 minutes with the mouth closed. Then, allow sufficient time for room temperature to reach adsorption equilibrium.

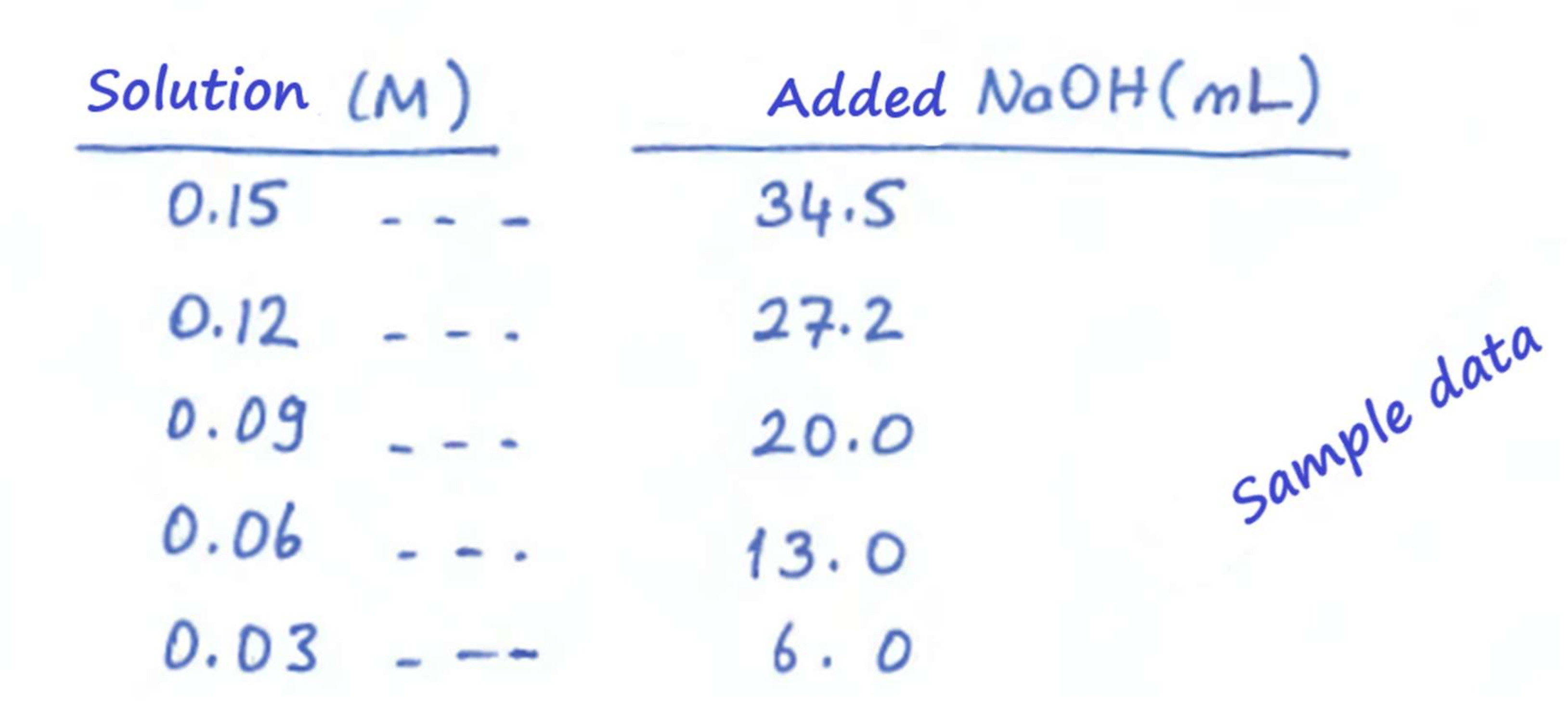
6. Once the equilibrium has been reached, start filtering the solutions. Discard the first 10 mL of filtrate. Titrate using a few drops of phenolphthalein indicator with 0.1 M NaOH on a sufficient amount of filtrate. If you have enough time, repeat each titration.

The most important factors to be considered in adsorption studies

- The effect of temperature
- The initial pH of the solution
- Initial adsorbate concentration
- Shaking speed
- Shaking time

CALCULATIONS

1. Calculation of equillibrium concentrations



Solution (M)	Added NaOH(mL)
0.15	34.5
0.12	27.2
0.09	20.0
0.06	13.0
0.03	6.0

Sample data

Calculation for 0.15 M acetic acid solution (C_e: equillibrium concentration)

M_{acid} x V_{acid} = M_{base} x V_{base}

M_{acid} (25 ml) = (0.1 M) (34.5 ml)

M_{acid} = 0.138 M = C_e

The amount of acidic acid adsorbed

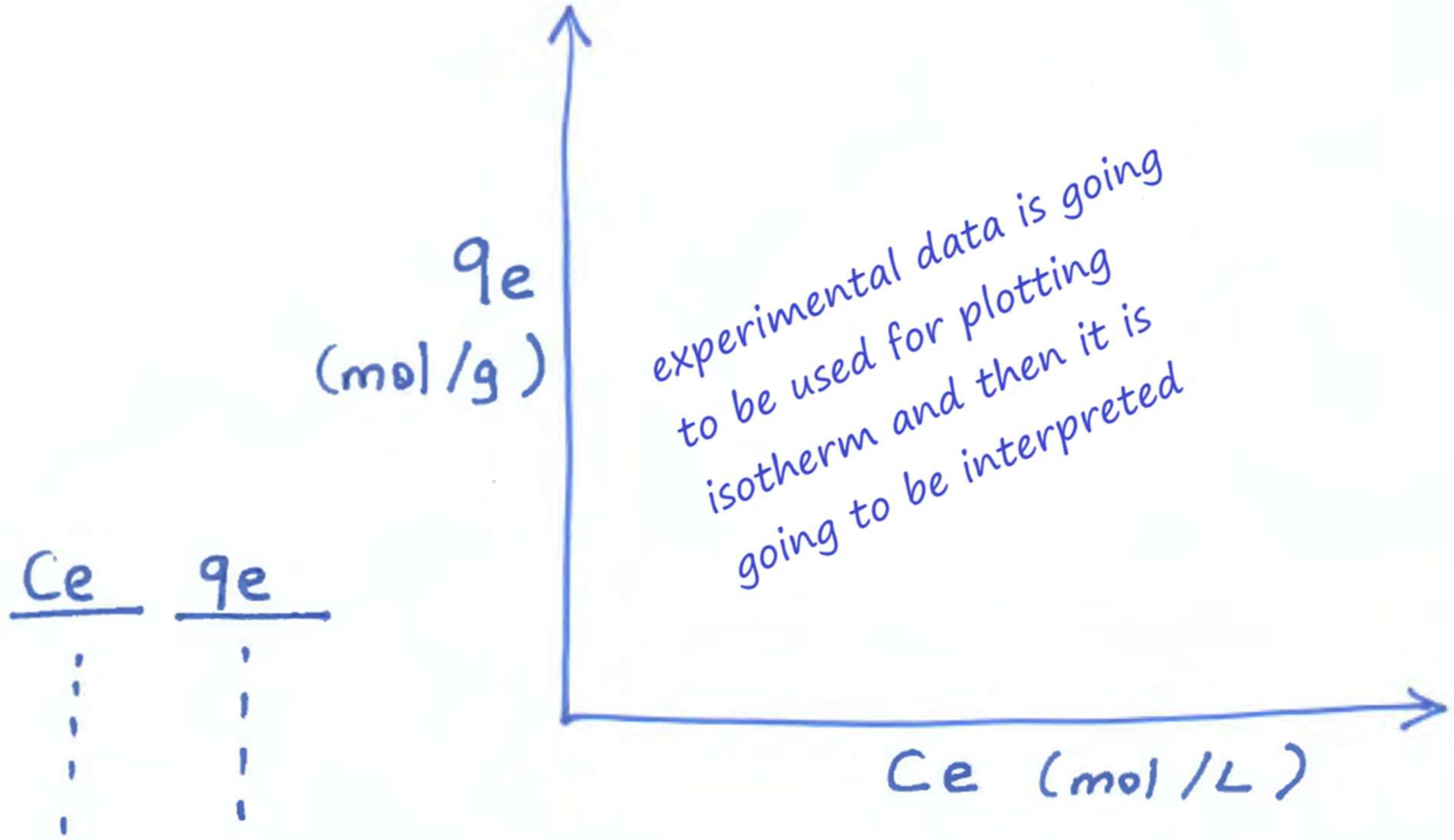
$$N_{ads} = (0.15\,M)(0.1\,L) - (0.138\,M)(0.1\,L)$$

$$= 1.2 \times 10^{-3}\ mol$$

m_{coal} =0.5 g

$$q_e = \frac{N_{ads}}{m_{coal}} = \frac{1.2 \times 10^{-3}}{0.5} = 0.0024\ mol/g$$

q_e values will be determined for all concentrations

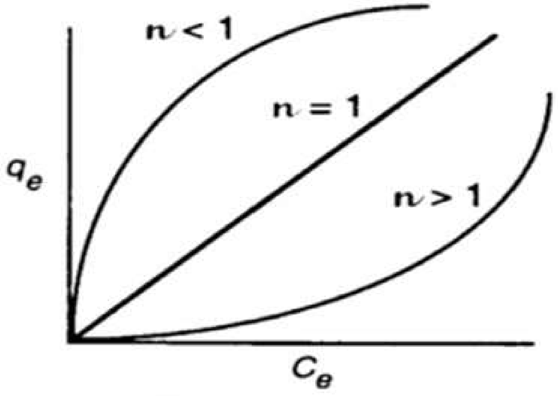


experimental data is going to be used for plotting isotherm and then it is going to be interpreted

Freundlich Isotherm

It is emprical 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.

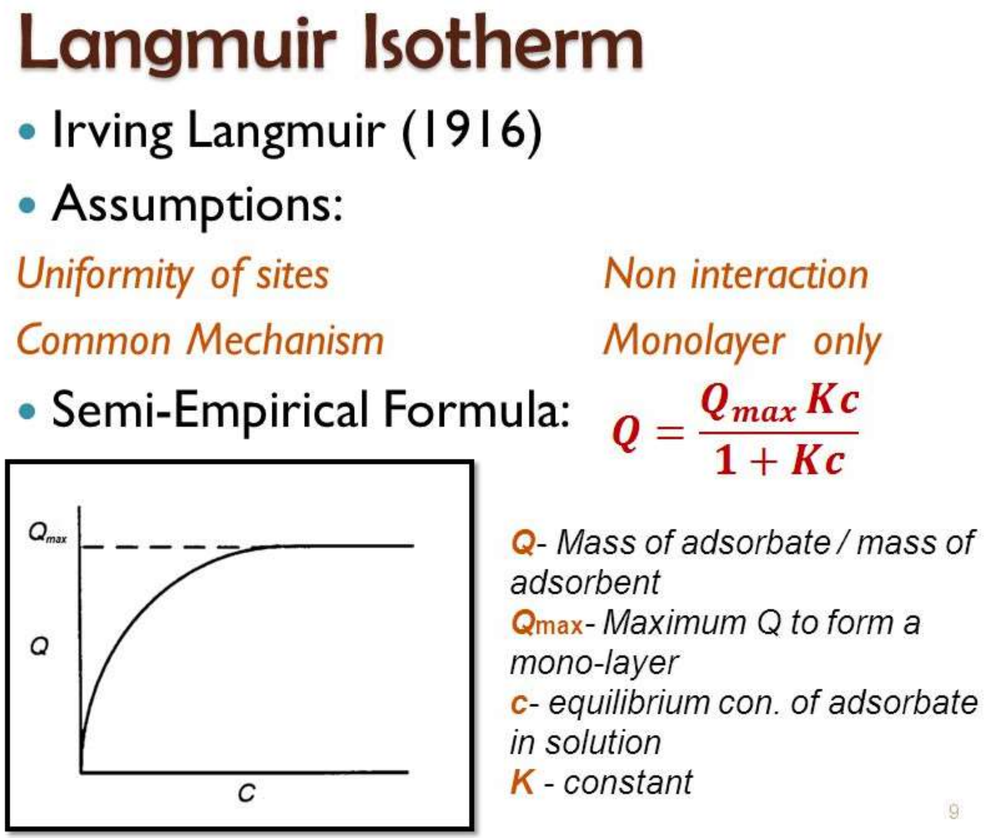
1/n is a measure of intensity of adsorption.
Higher the 1/n value, more favorable is the adsorption.

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

n and K_F are system specific constants.
q_e = amount of solute adsorbed per unit weight of solid at

The linear form of this isotherm is expressed as;

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



Langmuir Isotherm

- Irving Langmuir (1916)
- Assumptions:

Uniformity of sites	*Non interaction*
Common Mechanism	*Monolayer only*

- Semi-Empirical Formula: $Q = \frac{Q_{max} Kc}{1 + Kc}$

Q- *Mass of adsorbate / mass of adsorbent*
Qmax- *Maximum Q to form a mono-layer*
c- *equilibrium con. of adsorbate in solution*
K - *constant*

The Langmuir equation is applicable to homogeneous adsorption where the adsorption of each adsorbate molecule on to the surface has equal sorption activation energy.

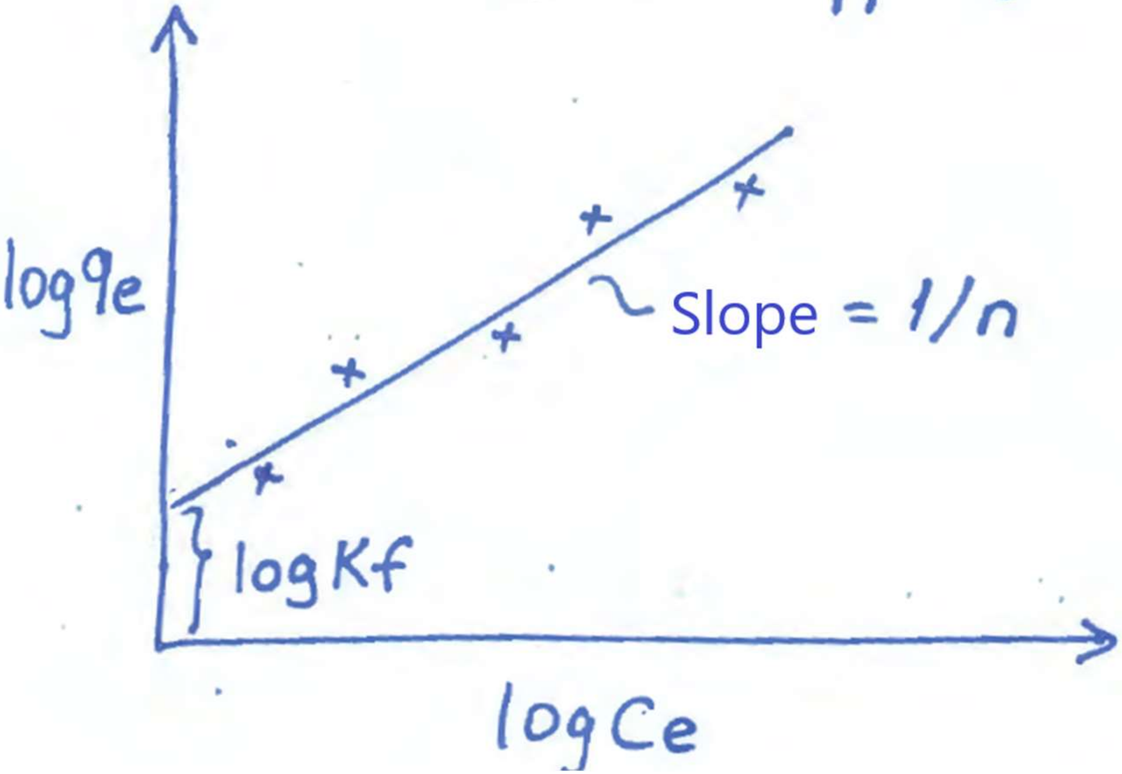
The linear form of this isotherm is represented:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$

Freundlich Isoterm

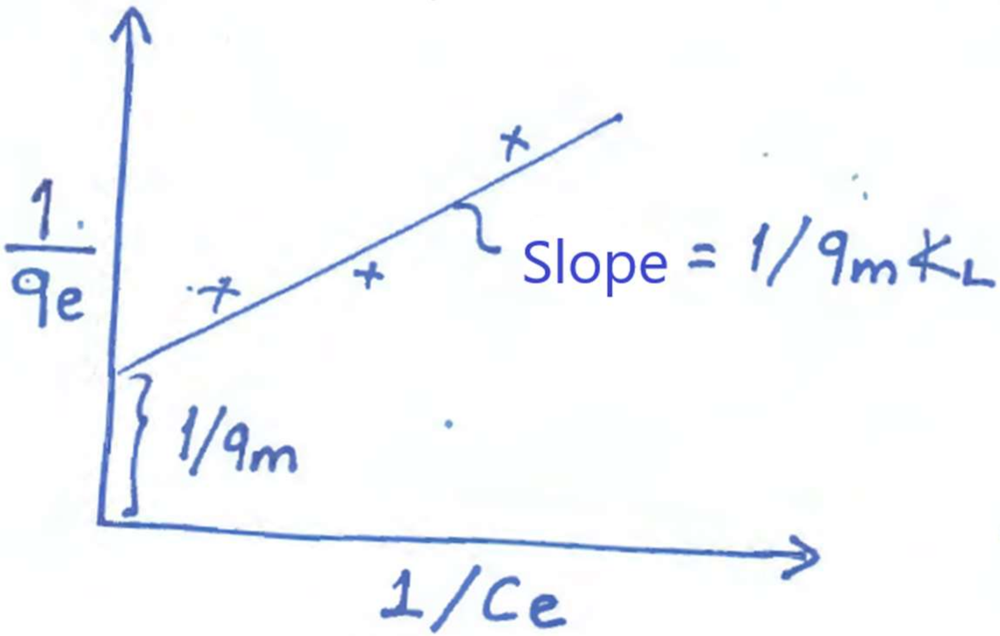
$$q_e = K_f \, C_e^{1/n}$$

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



Langmuir Isotherm

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \longrightarrow \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e}$$



Calculating Surface Area

It is calculating by using the q_m value belongs to the suitable isotherm.
For example;

$q_m = 0.00254$ mol/g;

$$A = 0.00254\,\frac{\text{mol}}{\text{g}}\;\frac{6.02\times10^{23}\ \text{molecules}}{1\ \text{mole}}\cdot\frac{21\,\mathring{A}^2}{1\ \text{molecule}}\;\frac{10^{-20}\ \text{m}^2}{1\,\mathring{A}^2}$$

$$A \cong 321\cdot \text{m}^2/\text{g}$$