CHEMICAL REMOVAL

ADSORPTION AND ION EXCHANGE

Definitions

Adsroption- Mass transfer of chemicals in liquid phase onto solid phase.

Adsorption- Chemicals adhere to surface of solid(dominant mechanism).
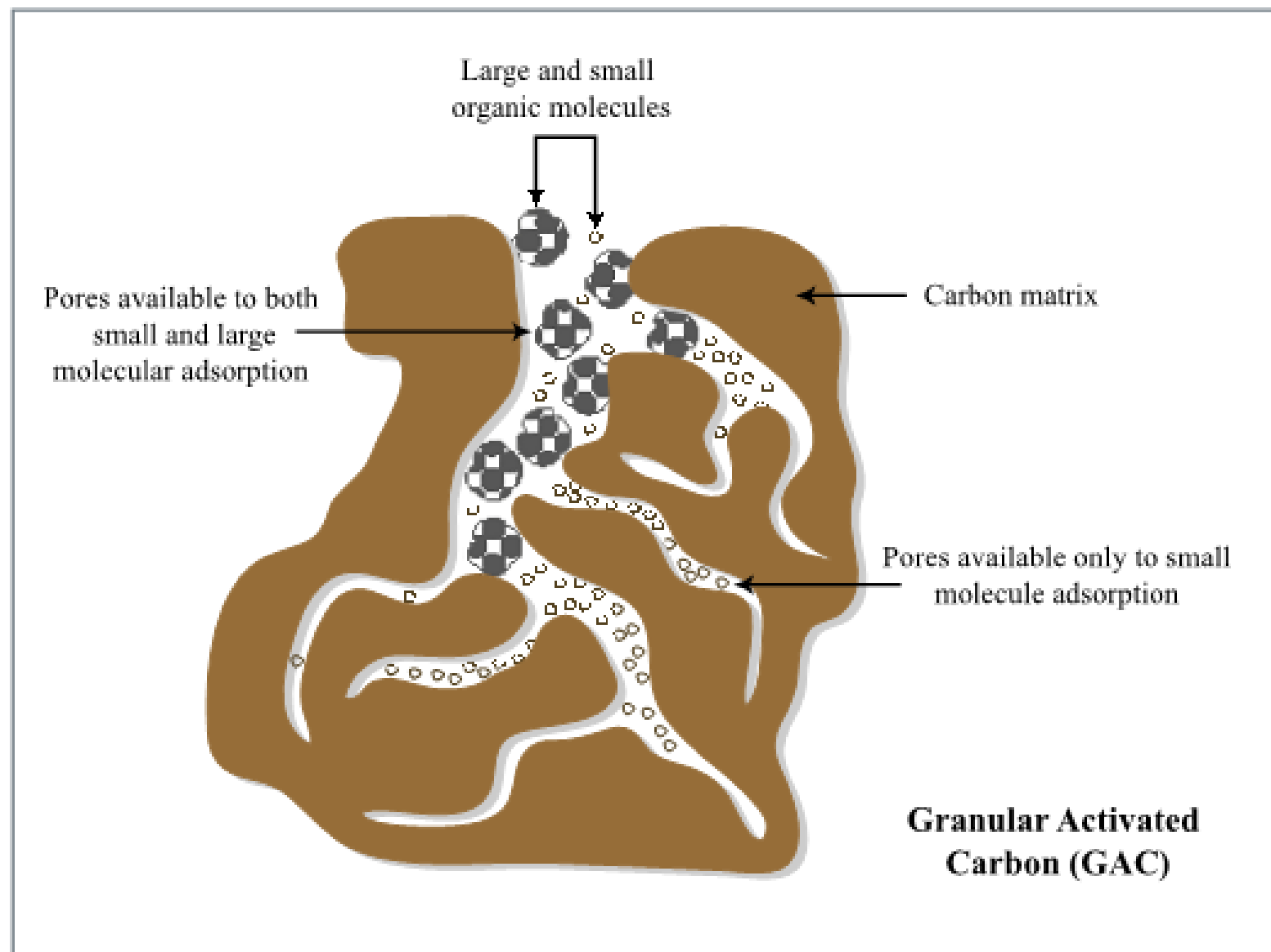
Absorption- Chemicals penetrate into solid, forming solid solution.

Sorption- Includes both adsorption and absorption.

Adsorbent- Adsorbing phase.

Adsorbate- Chemical being adsorbed.

WD16 0mm 25.0kV x800 50um

Large and small organic molecules

Pores available to both small and large molecular adsorption

Carbon matrix

Pores available only to small molecule adsorption

Granular Activated Carbon (GAC)

Adsorption is used in drinking water treatment to remove organic contaminants

1) Taste and odor causing chemicals.

2) Synthetic organic chemicals.

3) Color forming organics.

4) Some disinfection by-product precursors.

Adsorbent of choice is **ACTIVATED CARBON**

Made in two step.

1) Carbonaceous material (wood, coal, coconut shells) is heated in oxygen starved environment to liberate oxygen (CARBONIZATION).

2) Carbonized material is exposed to steam or hot CO_2 to cause pores and fissures to form (ACTIVATION).

Step1 creates carbon to which organic chemicals will get adsorb.

Step2 increases surface area available for sorption.

Adsorption depends on properties of activated carbon, chemistry of adsorbate, pH and temperature of water. Each application requires development of adsorption isotherm.

In adsorption,

Most bonding is physical, occurring by various mechanisms such as van der Waals force.

Some bonding are chemical and generally irreversible.

Adsorption process is quantified via an adsorption isotherm which can take

multiple forms.

Isotherm relates q_A to C

q_A = solid phase concentration = $\dfrac{\text{mass of adsorbate}}{\text{mass of adsorbent}}$ X in R/R

C_A = liquid phase concentration of adsorbate

Very simplest is linear isotherms.

$q_A = K_d C_A = K C_e$ in R/R

K_d = partition coefficient $\dfrac{\text{mg/Kg}}{\text{mg/L}}$ = L/Kg

Langmuir Adsorption Isotherm

Assumes reaction

$$S_v + A \rightleftharpoons S.A$$

Where,
S_v = vacant adsorption site on absorbent in mol/L absorbent
A = Adsorbate in solution (mol/L)
S.A = adsorbate bound to absorbent site.(mol/L)

At equilibrium,

$$K_{ad} = \frac{[S.A]}{[S_v][A]} \qquad K_{ad} \text{ in L/mg and}$$

[A] in mg/L

Consider total number of sites to be fixed:

$$S_T = [S_v] + [S.A]$$

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

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

$$[S.A] = S_T / [1 + 1/K_{ad} C_A] = K_{ad} C_A S_T / [1 + K_{ad} C_A]$$

Need expression for q_A mg adsorbate /g adsorbent
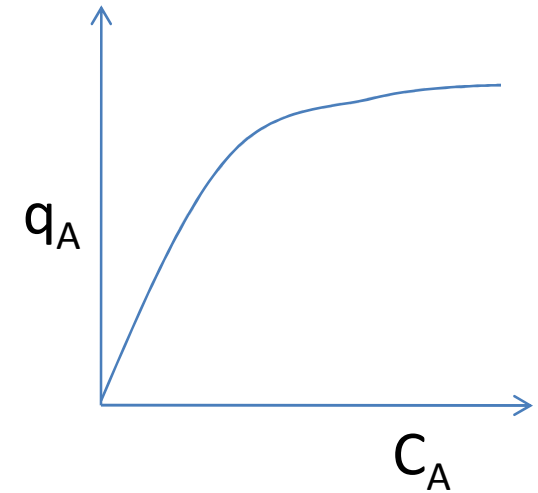
$$q_A = [S.A] . A_{ad} . MW_A$$

A_{ad} = surface area per gm adsorbent m^2/g

MW_A = molecular weight of adsorbate g/mol

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

$$q_A = K_{ad} C_A S_T / [1 + K_{ad} C_A] \cdot A_{ad} \cdot MW_A$$

$$= K_{ad} C_A Q_M / [1 + K_{ad} C_A]$$

Q_M = maximum adsorbent phase concentration of adsorbate occurs

when all sites ($S_T A_{ad}$) are saturated with adsorbate.

K_{ad} = Langmuir adsorption constant (L/mg)

C_A/q_A plots as straight line vs C_A

Slope = $1/Q_M$ Intercept = $1/K_{ad} C_A Q_M$

Limitations of Langmuir adsorption isotherm

1. It does not consider the in-homogenity of the surfaces, multiple site-type available for adsorption.

2. Ignores adsorbate-adsorbate interactions

Another alternate isotherm is BET (Brunauer-Emmett-Teller) assumes several molecular layers involved.

$$q_A/Q_M = B_A C_A /(C_{SA}-C_A)[1 + (B_A-1)(C_A/C_{SA})$$
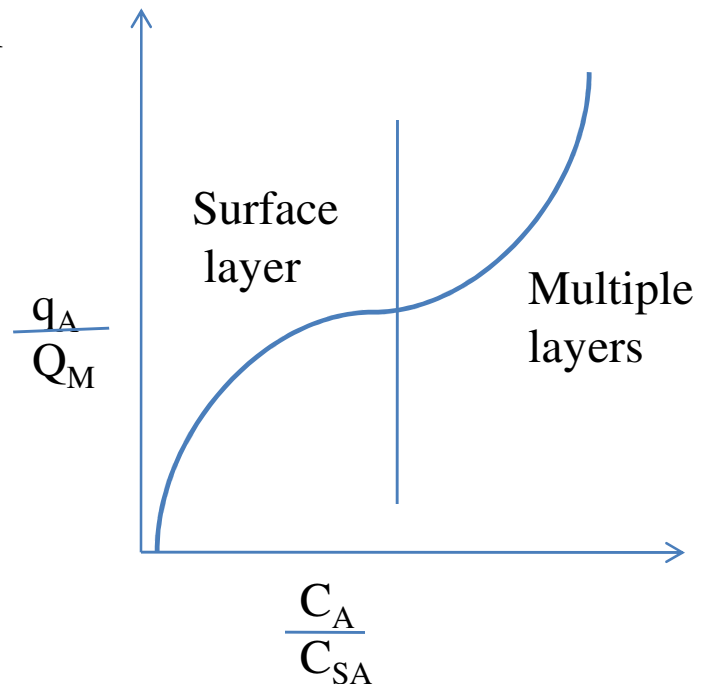
Where,

q_A = equilibrium adsorbate /adsorbent layer

Q_M = max q_A at saturation

C_A = equilibrium aqueous concentration

C_{SA} = saturation C_A

B_A = $K_{1,ad} /K_{i,ad}$

= eq. constant for layer first layer/
 eq. constant for subsequent layers

Alternative most used for activated carbon is Freundlich isotherm (empirically derived)

$$q_A = K_F \, C_A^{\,1/n}$$

Can be shown consistent with Langmuir adsorption by heterogeneous sites with distribution of energy of adsorption.

$q_A = K_F C_A^{1/n}$

if q_A is mg/Kg

C_A is µg/L

Then K_F is in units of $\dfrac{mg/Kg}{(µg/L)^{1/n}}$

Example Assume $1/n = 1/3$

If q_A is mg/Kg and C_A is mg/L (1000X larger than above).What is the conversion factor for
K_F to units above?

$$\dfrac{mg/Kg}{(mg/L)^{1/n}} \cdot \dfrac{(mg/L)^{1/n}}{(µg/L)^{1/n}} = \dfrac{mg/Kg}{(µg/L)^{1/n}} = (mg/µg)^{1/n} = 1000^{1/3} = 10$$

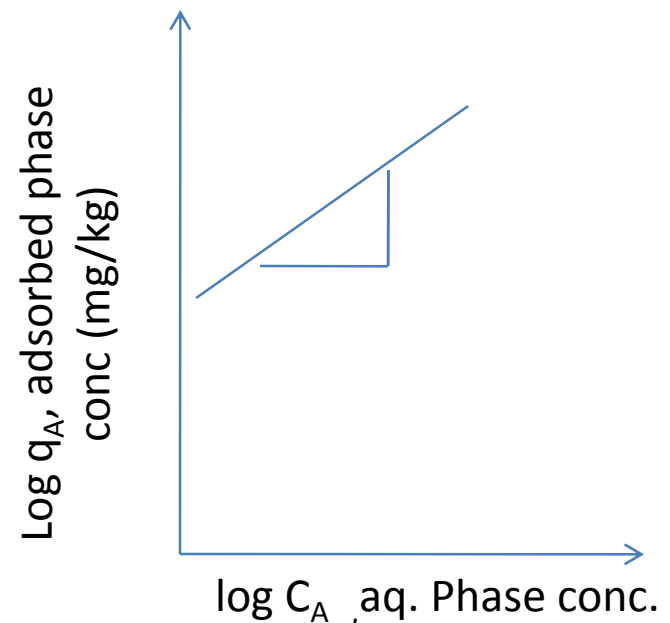Isotherms are found by doing lab tests.

Mass of carbon put in bottle (M).

Volume of water V with contaminant concentration C_0 added.

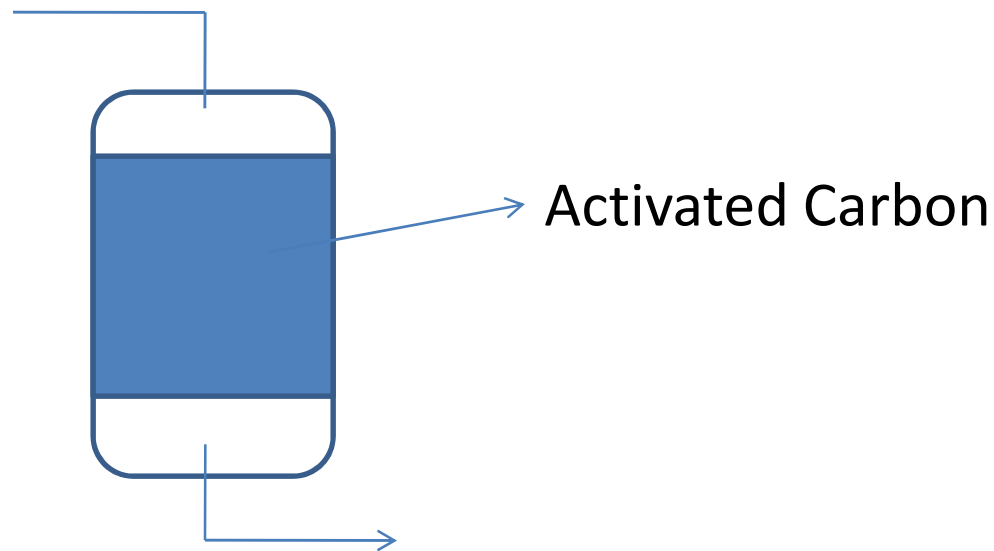Tumbled gently for 6 days to get equilibrium.

Compute $\qquad q_A = \qquad V/M \, (C_0 - C_A)$

Plot q_A vs C_A on log-log graph

Log q_A, adsorbed phase conc (mg/kg)

log C_A, aq. Phase conc.

Carbon typically used in pressure vessels much like pressure filtration tanks. Tanks are often placed

in series with piping and valving to change order of tanks.

Activated Carbon

At tank A breakthrough, Tank A goes off-line for carbon change out. Fresh Tank B operates alone.

Regenerated carbon is not as effective as virgin carbon- some applications specify virgin Carbon only.

Isotherms are custom developed for type of carbon and water/waste water and used to predict

Breakthrough volume V_B for certain mass of GAC, M_{GAC}

Carbon usage rate = M_{GAC} / V_B = CUR

CUR tells how much carbon is needed to treat certain volume of water.

In practice, Effluent from GAC tank is monitored to also watch for breakthrough.

Activated carbon comes in two main forms:

PAC – Powdered Active Carbon (≈24μm) which is suspended in water/waste water to be treated.

       PAC is then settled/filtered out and may be recycled.

GAC -   Granular Activated Carbon (0.6 to 2.4 mm)

       placed in packed beds usually in pressure tanks.

Carbon has fixed adsorption capacity, so chemical eventually 'break through'

Contact time is 7 to 20 minutes in typical water treatment plant.