

The Islamic University of Gaza- Environmental Engineering Department
Water Treatment (EENV- 4331)

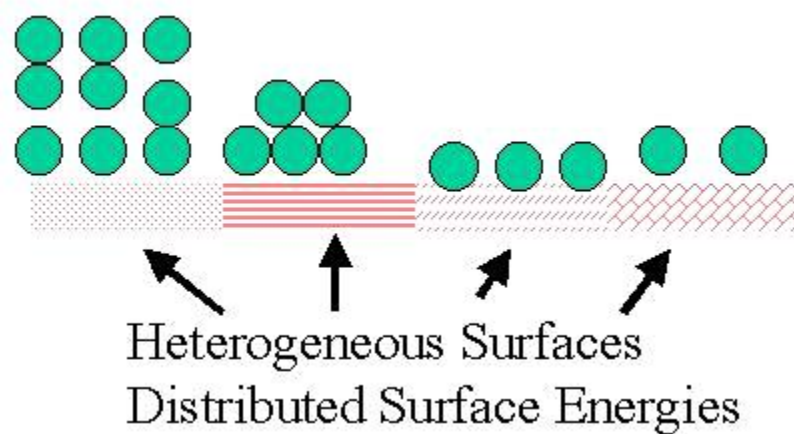
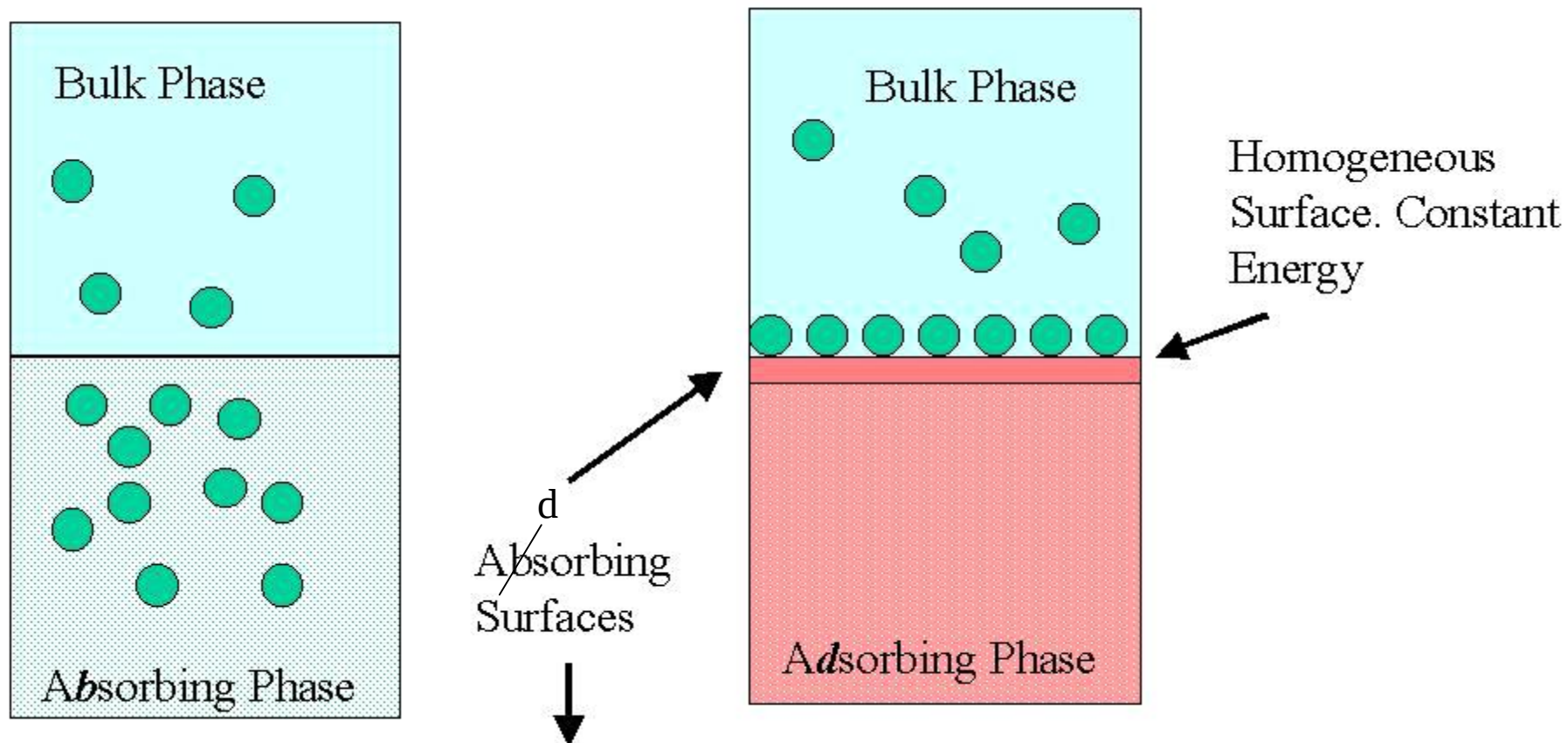
Lecture 4: Adsorption

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ADSORPTION

Adsorption 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.



To remove soluble material from the solution phase, but the material is neither volatile nor biodegradable, adsorption processes is employ.

adsorbate: material being adsorbed

adsorbent: material doing the adsorbing.

Adsorption Isotherm: the mass of adsorbate per unit mass of adsorbent **at equilibrium & at a given temperature**

Surface Energy

An explanation of why material accumulates at the interface is based on the excess energy associated with particles at interfaces.

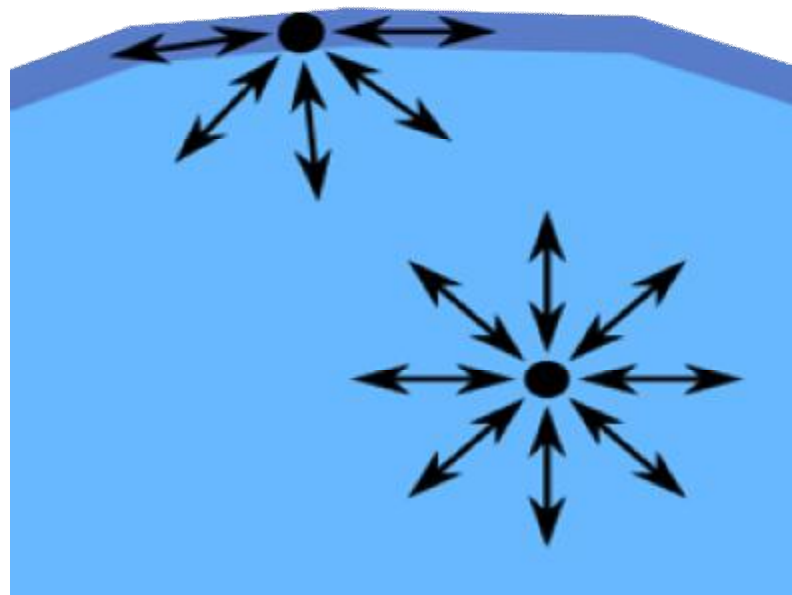
For example, in the case of pure water and air, the water molecules at the air-water interface have higher energy than water molecules in the interior of the water phase.

The reason that these surface molecules have higher energy is that, unlike the interior molecules, they have an unbalanced force component (on the airside of the molecule).

These surface molecules have additional energy to balance the forces.

This excess energy is called *surface tension*.

Since it takes energy to create interfacial surfaces, the system will try to minimize the total interfacial surface area. Hence we see spherical droplet.



Thermodynamics of surface adsorption

In solutions certain particles tend to concentrate at the surface.

These particles are those that have low affinity for the solvent.

These are **hydrophobic molecules**. Because they have low affinity for the solvent they can get to the surface easily since they have low bond energy in the bulk phase.

The water system prefers to have these molecules at the surface because the placement at the surface requires less energy than a water molecule -- hydrophobic molecules decrease surface energy (surface tension) relative to a pure water system.

On the other hand if a particle has a high affinity for the solvent phase **(hydrophilic)** it will tend to remain in the bulk solution because of its strong bond with water.

In fact, this bonding makes the water bonding stronger and, therefore, there is a larger energy required to get water molecules to the surface-- therefore, hydrophilic molecules increase surface tension, e.g. salts such as NaCl.

Hydrophilic substances are those that can enter into a charged interaction with water molecules

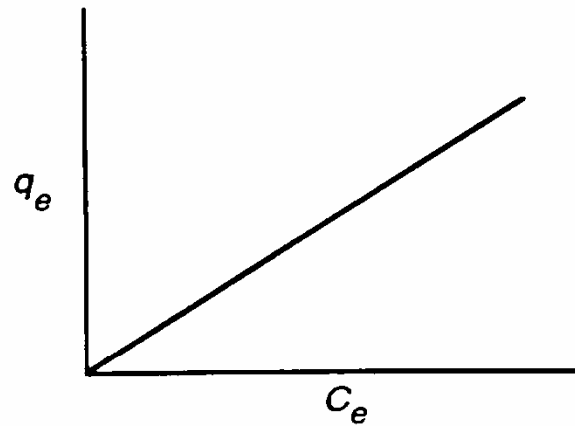
- Exchange adsorption (ion exchange)– electrostatic due to charged sites on the surface. Adsorption goes up as ionic charge goes up and as hydrated radius goes down.
- Physical adsorption: Van der Waals attraction between adsorbate and adsorbent. The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface. This is relatively weak, reversible, adsorption capable of multilayer adsorption.
- Chemical adsorption: Some degree of chemical bonding between adsorbate and adsorbent characterized by strong attractiveness. Adsorbed molecules are not free to move on the surface. There is a high degree of specificity and typically a monolayer is formed. The process is seldom reversible.

Generally some combination of physical and chemical adsorption is responsible for activated carbon adsorption in water and wastewater.

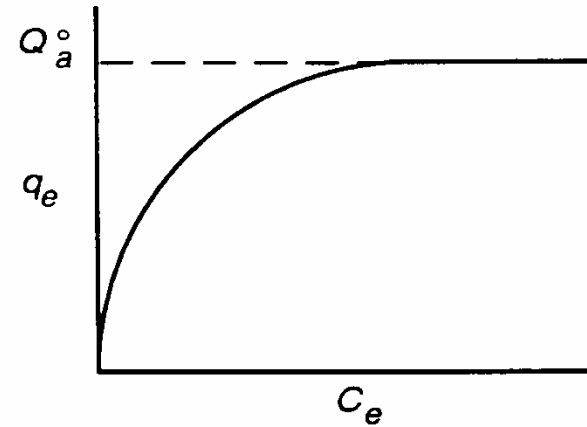
ADSORPTION EQUILIBRIA

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 isotherms.

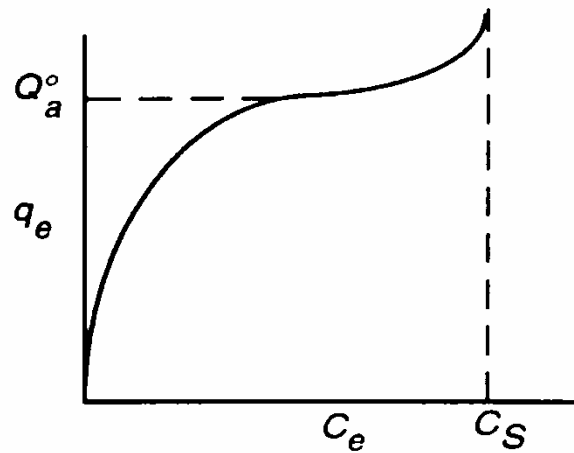
Isotherm models: There are four common models for isotherms



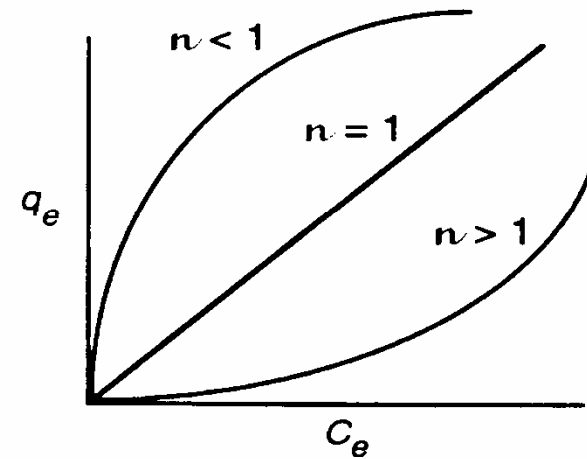
(a) Linear



(b) Langmuir

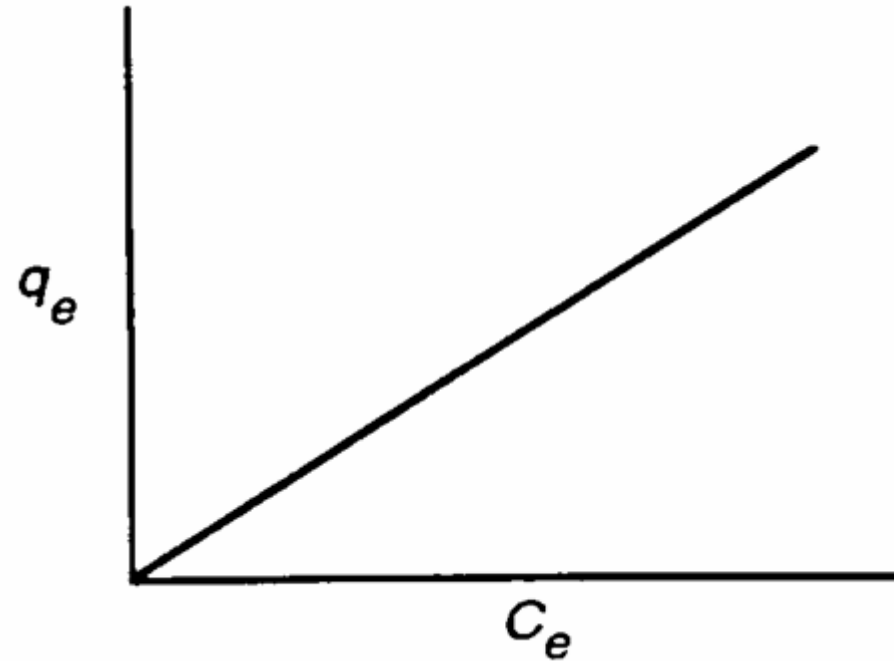


(c) BET



(d) Freundlich

a. Linear



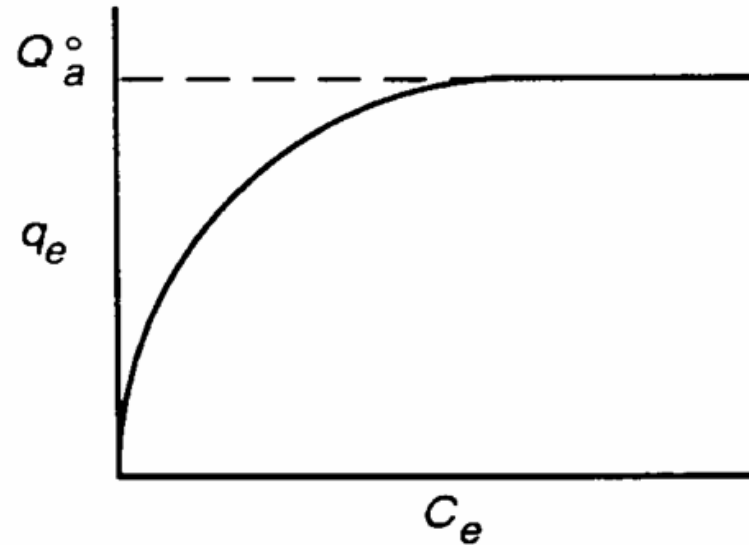
q_e = mass of material adsorbed (at equilibrium) per mass of adsorbent.

C_e = equilibrium concentration in solution when amount adsorbed equals q_e

b. Langmuir Isotherm: This model assumes monolayer coverage and constant binding energy between surface and adsorbate.

The model is:

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



q_e = mass of material adsorbed (at equilibrium) per mass of adsorbent.

Q_a^0 : represents the maximum adsorption capacity (monolayer coverage) (g solute/g adsorbent).

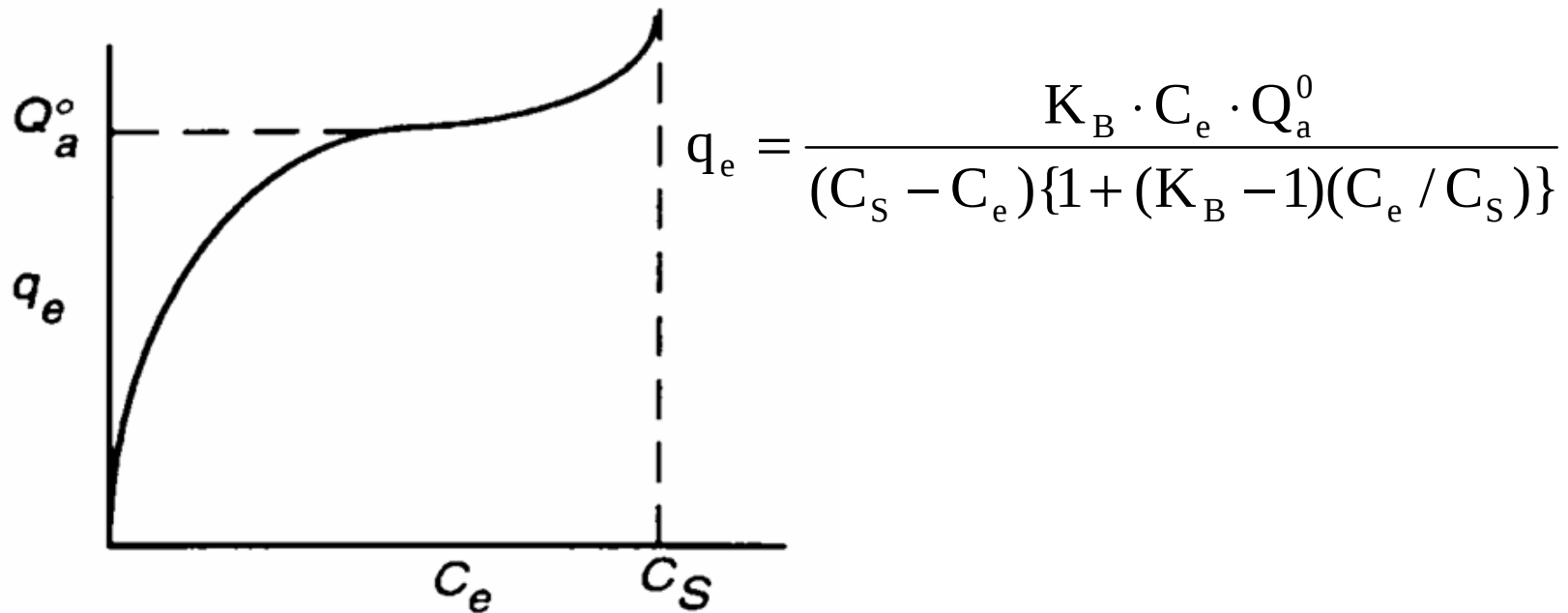
C_e = equilibrium concentration in solution when amount adsorbed equals q_e .

C_e : has units of mg/l.

K : has units of l/mg

C. 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.



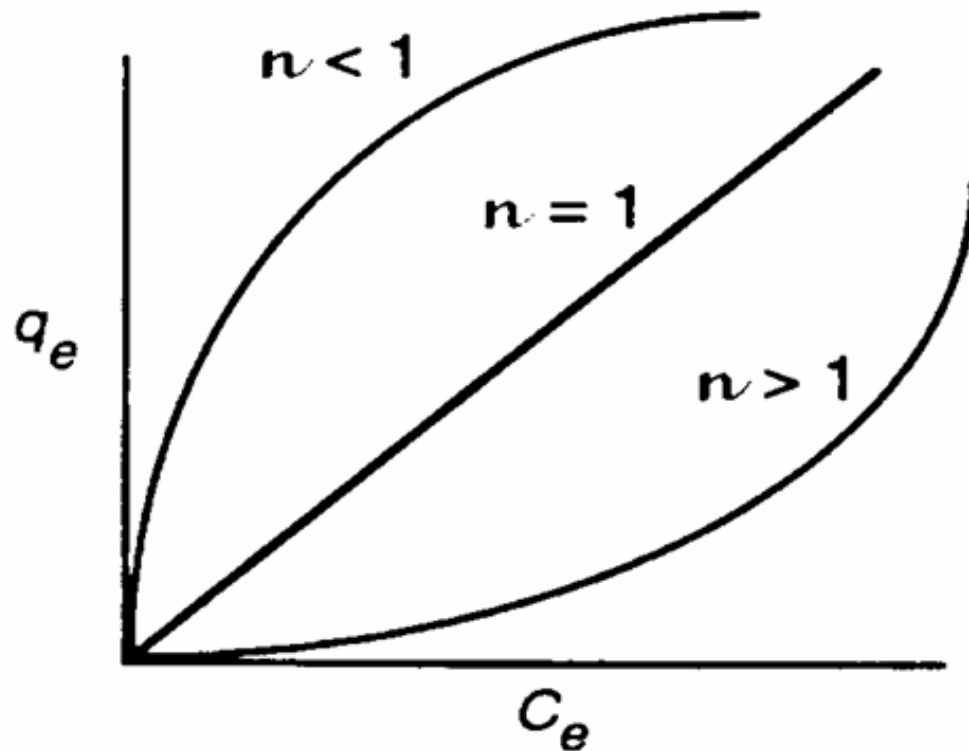
C_S =saturation (solubility limit) concentration of the solute. (mg/liter)

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 $K = K_B/C_S$ BET isotherm approaches Langmuir isotherm.

d. Freundlich Isotherm:

For the special case of heterogeneous surface energies (particularly good for mixed wastes) in which the energy term, “ K_F ”, varies as a function of surface coverage we use the Freundlich model.



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

n and K_F are system specific constants.

Competitive adsorption: If more than one solute is competing for the same adsorption site the isotherm must be modified. For example, the multi-solute Langmuir isotherm would look like:

$$q_{e,i} = \frac{Q_{a,i}^0 \cdot K_i \cdot C_{e,i}}{1 + \sum_i K_i \cdot C_{e,i}}$$

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:

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

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

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

and slope: $\frac{1}{Q_a^0}$ Or: $\frac{1}{q_e} = \frac{1}{Q_a^0} + \frac{1}{K \cdot Q_a^0} \cdot \frac{1}{C_e}$

Here a plot of $1/q_e$ versus $1/C_e$ should give a straight line with intercept $1/Q_a^0$ and slope $\frac{1}{K \cdot Q_a^0}$

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 $1/n$.

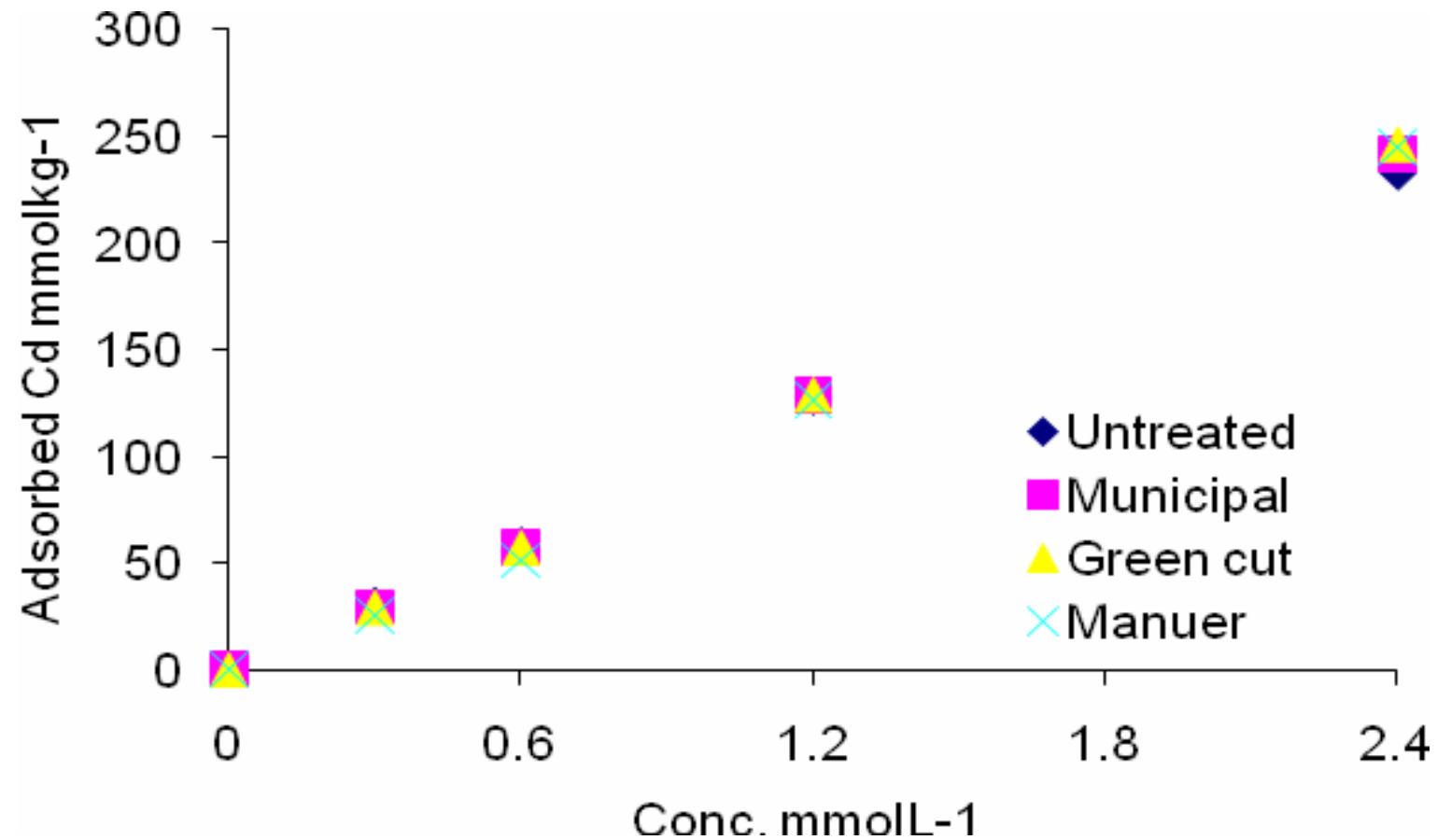
For the **BET isotherm** we can arrange the isotherm equation to get:

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

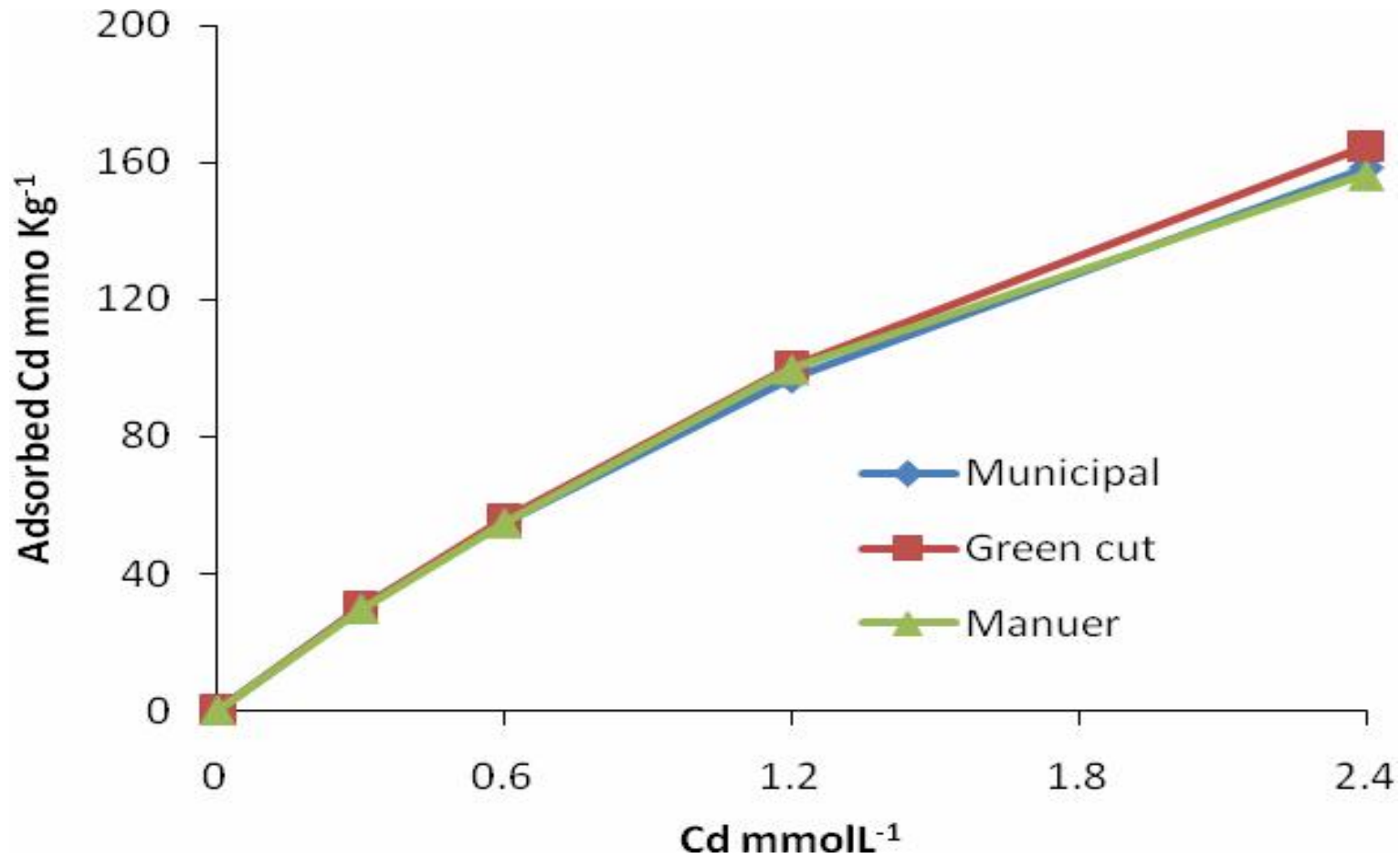
$$\text{Intercept} = \frac{1}{K_B \cdot Q_a^0}$$

$$\text{Slope} = \frac{K_B - 1}{K_B \cdot Q_a^0 \cdot C_S}$$

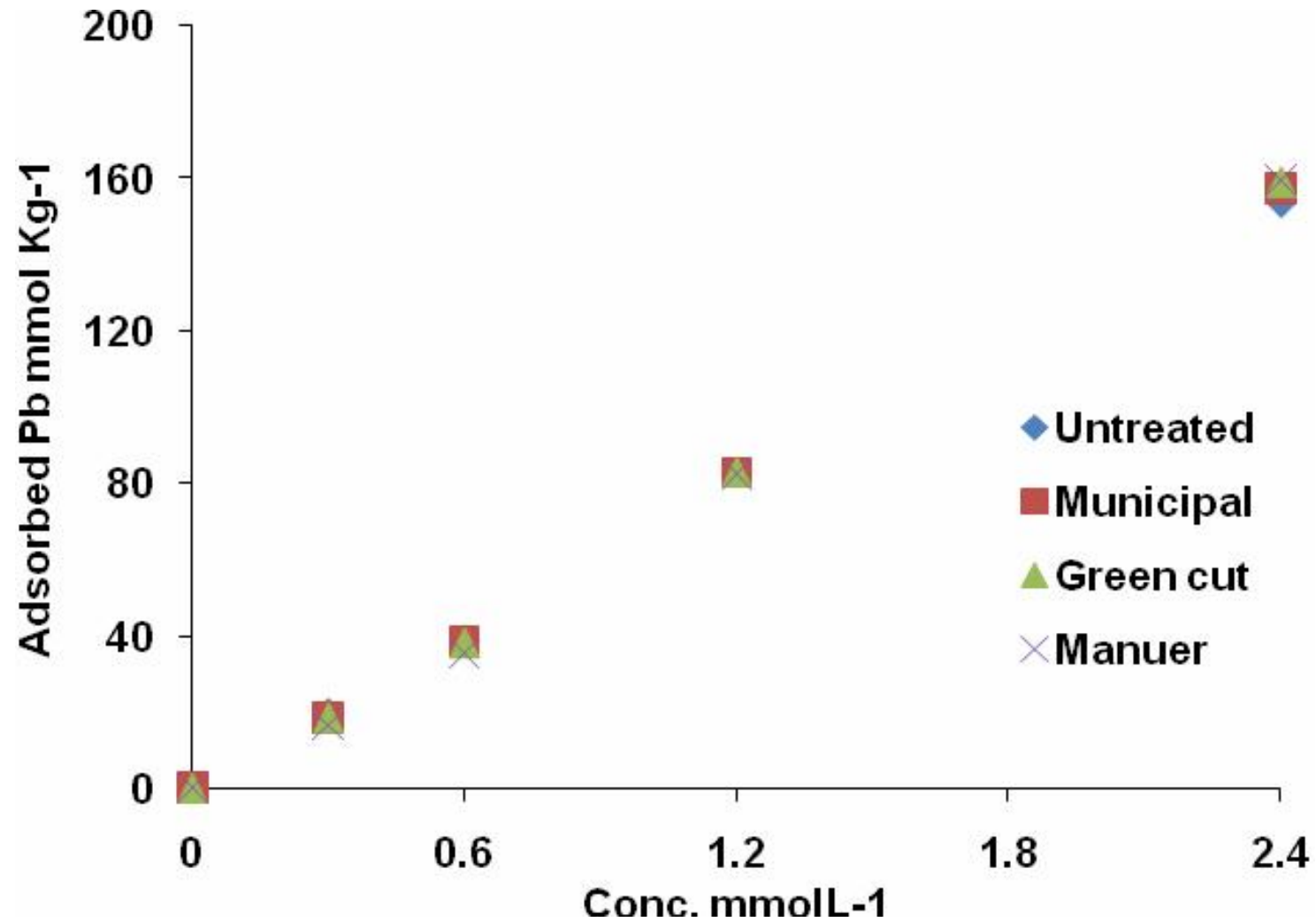
Cd sorption by Montmorillonite and HS (municipal, green cut and manuer)
from single –metal solution



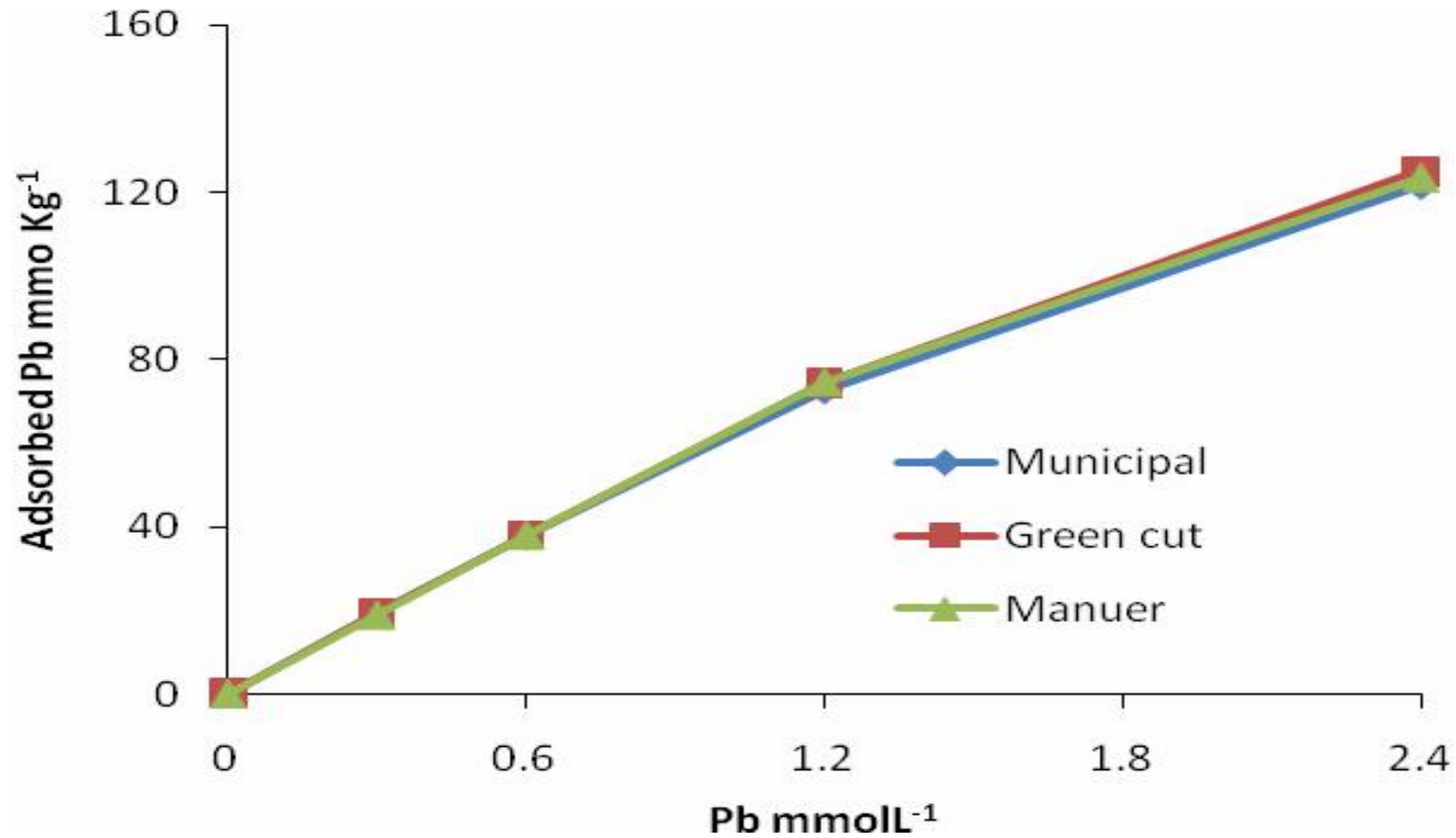
Cd sorption by Montmorillonite and HS from municipal, green cut and manuer (Multi metal-aqueous solution)



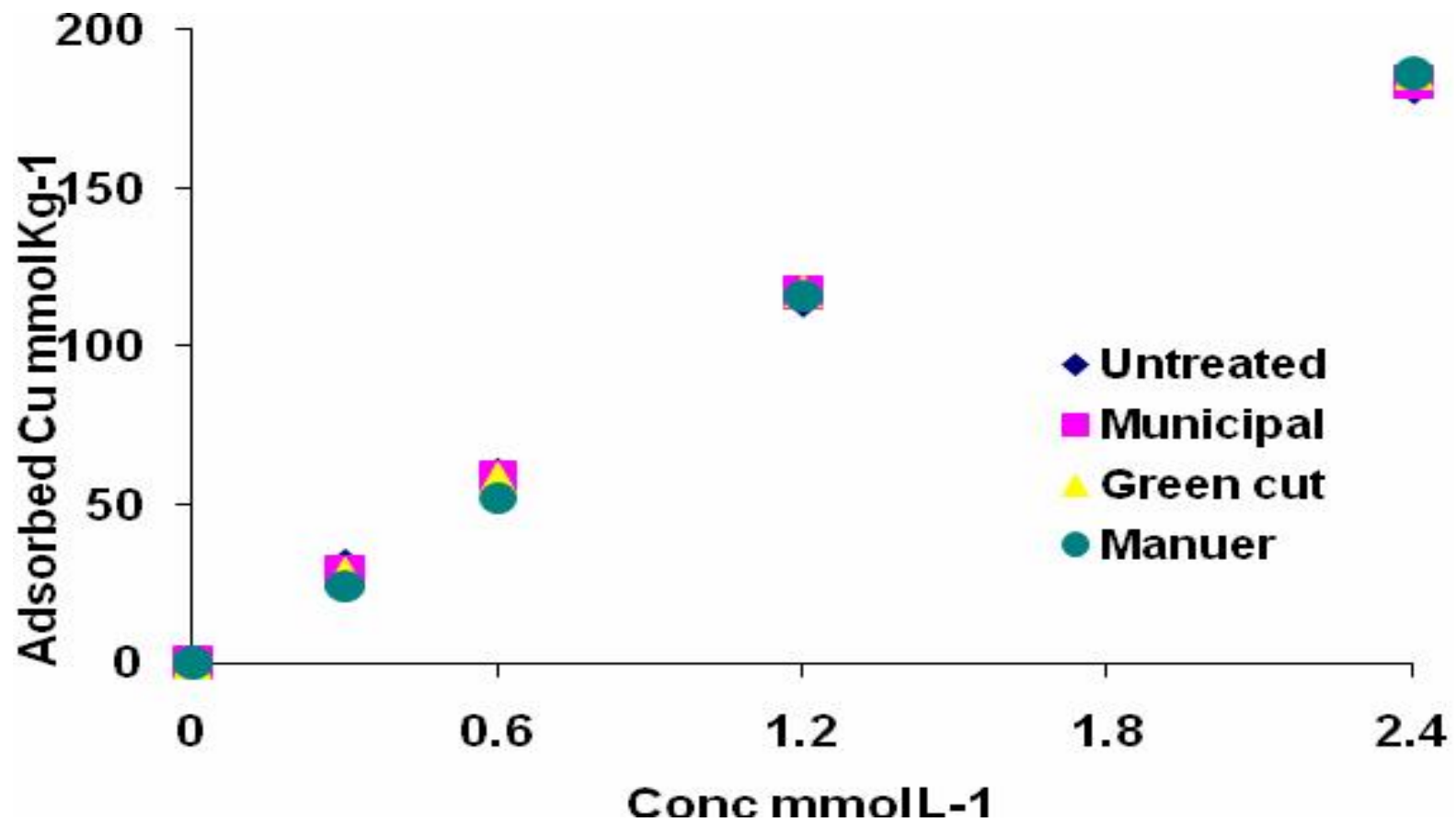
Pb sorption by Montmorillonite and HS (municipal, green cut and manuer)
from single –metal solution



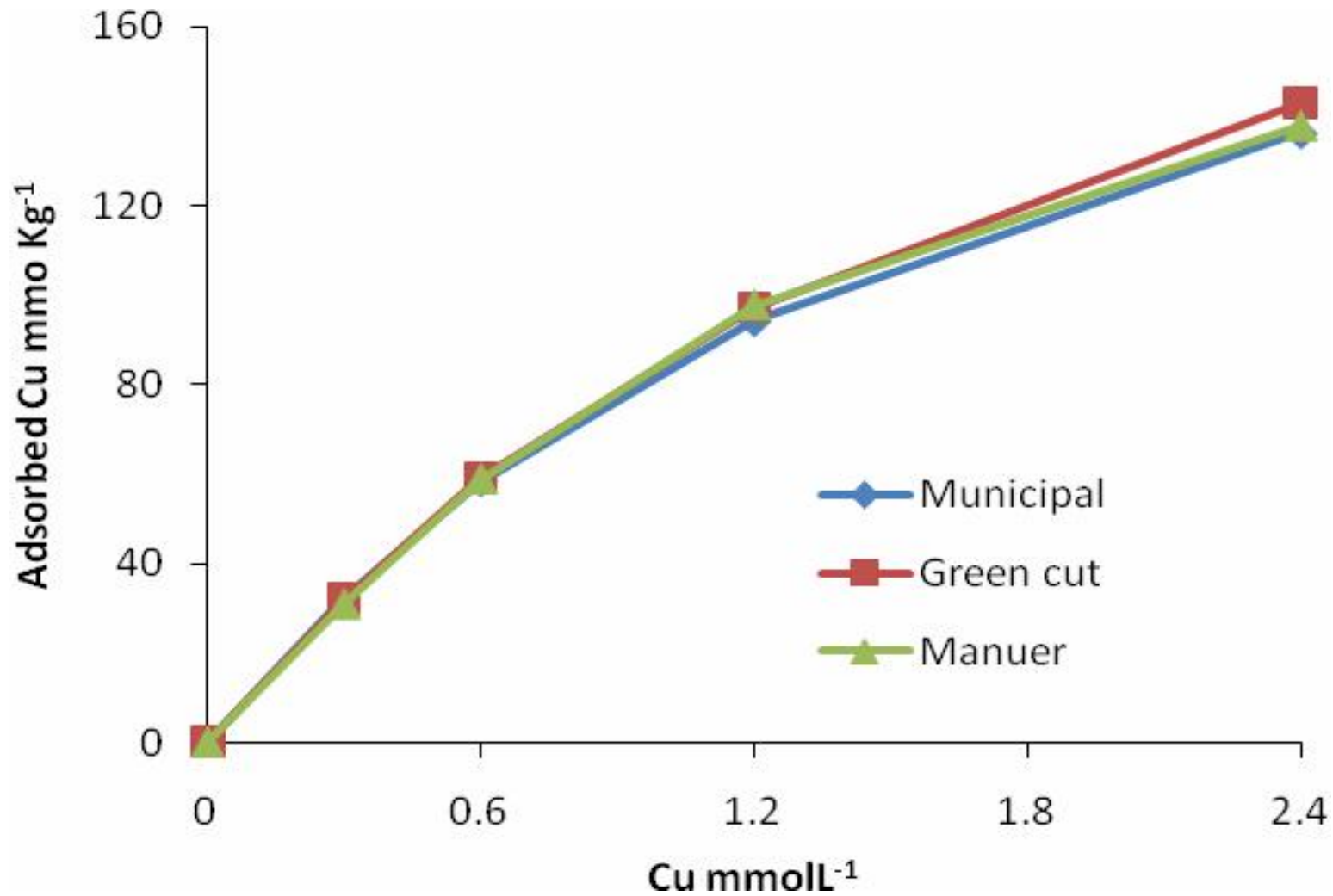
Pb sorption by Montmorillonite and HS from municipal, green cut and manuer
(Multi metal-aqueous solution)



Cu sorption by Montmorillonite and HS (municipal, green cut and manuer)
from single –metal solution



Cu sorption by Montmorillonite and HS from municipal, green cut and manuer
(Multi metal-aqueous solution)



Factors which affect adsorption extent (and therefore affect isotherm) are:

Adsorbate:

Solubility

In general, as solubility of solute increases the extent of adsorption decreases.

Factors which affect solubility include:

molecular size (high MW- low solubility),

Ionization (solubility is minimum when compounds are uncharged),

polarity (as polarity increases get higher solubility because water is a polar solvent).

pH

pH often affects the surface charge on the adsorbent as well as the charge on the solute. Generally, for organic material as pH goes down adsorption goes up.

Temperature

Adsorption reactions are typically exothermic. Here heat is given off by the reaction therefore as **T increases extent of adsorption decreases.**

Presence of other solutes

In general, get competition for a limited number of sites therefore get reduced extent of adsorption or a specific material.

Adsorbent:

Virtually every solid surface has the capacity to adsorb solutes. From the wastewater/water treatment point of view activated carbon (AC) is the adsorbent of choice. AC prepared from many sources: Wood- Lignite (الفحم الحجري)- Coal- Nutshells- Bone

These raw materials are prepared at high temperature under low oxygen conditions (so we don't get complete combustion). This forms a "char". The char is then activated by heating to 300 – 1000 °C in the presence of steam, oxygen or CO₂. Result: "Activated carbon" which is highly porous, micro-crystalline material which resembles graphite plates with some specific functional groups (e.g. COOH, OH)

Most of the surface area is in pores of molecular sized dimensions.

This results in slower mass transfer during the adsorption process but also results in greater binding capacity of the adsorbate.

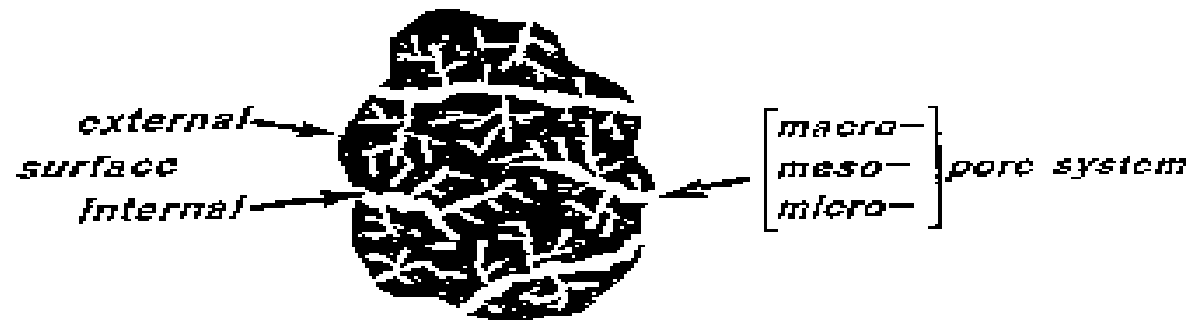
Adsorption behavior is related in part to the nature of the functional groups on the carbon surface. In general carbon manufactured at:

<500 °C is weakly acidic

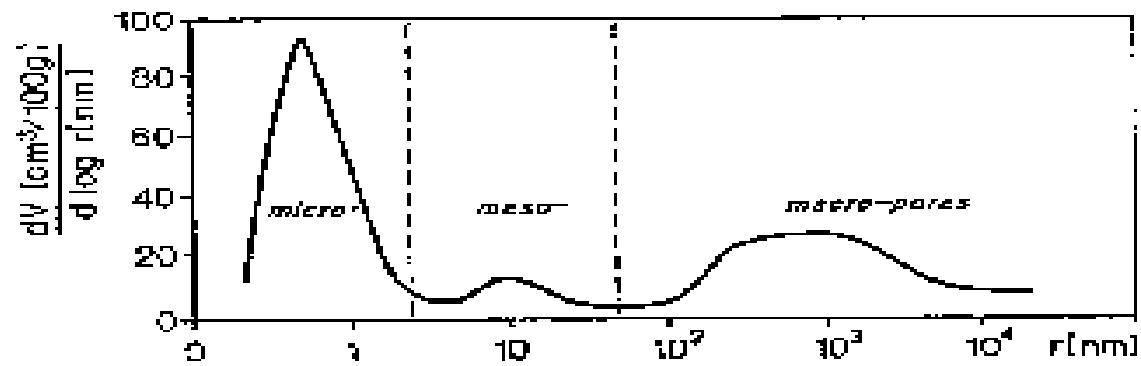
> 500 °C is weakly basic

Spent AC can be regenerated at high temperatures (roughly a maximum of fifteen times).

Activated Carbon



Pore size distribution



CARBON CONTACTORS

Activated carbon reactors are usually called carbon contactors because the waste stream is “contacted” with the carbon. Many times the contactor is of the columnar fluidized or fixed-bed type. Sometimes (less often) the contactor is in a slurry form.

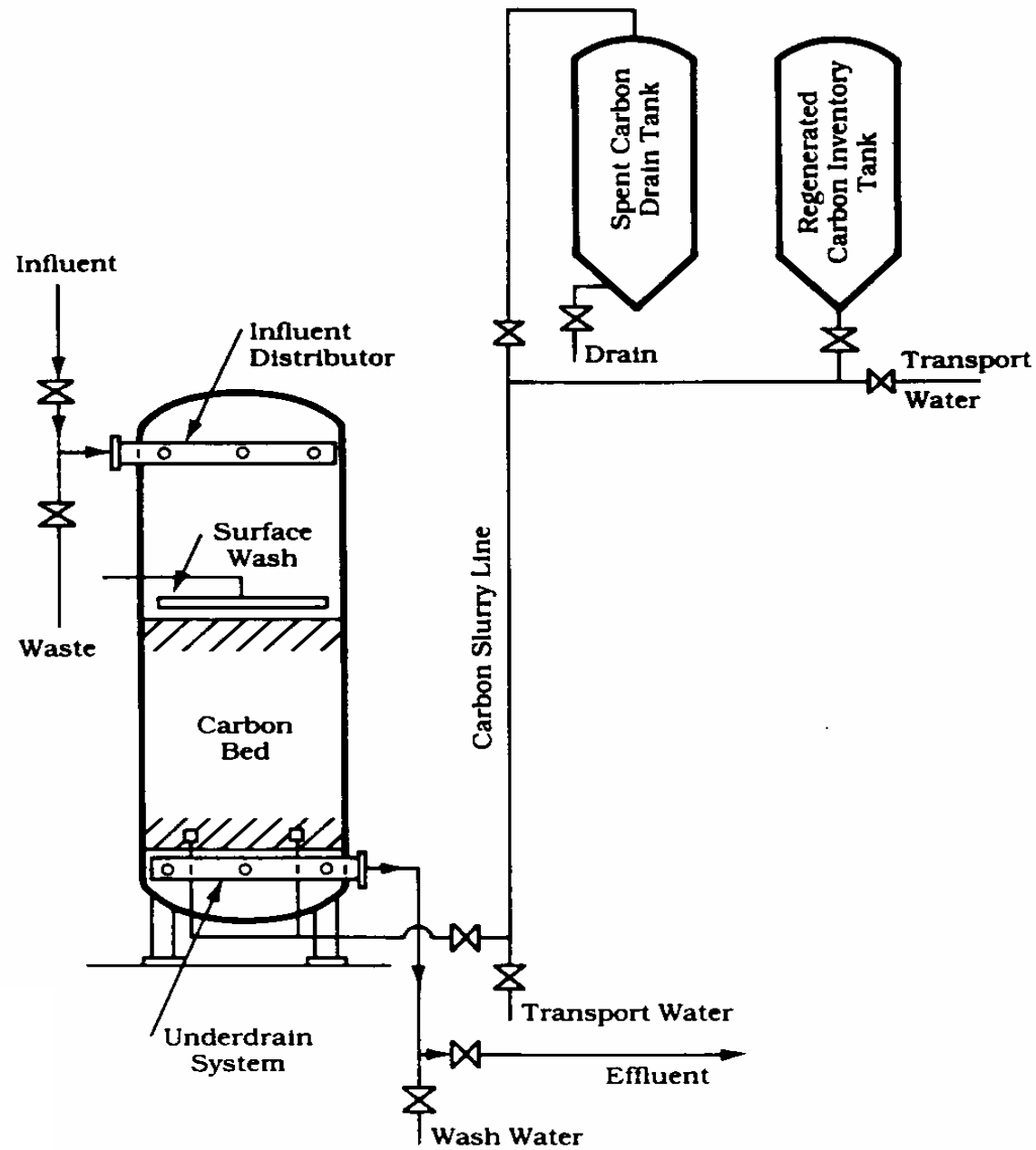
Fixed or fluidized (مميع) beds have the advantage of not having to separate the carbon from the liquid stream after the contact period.

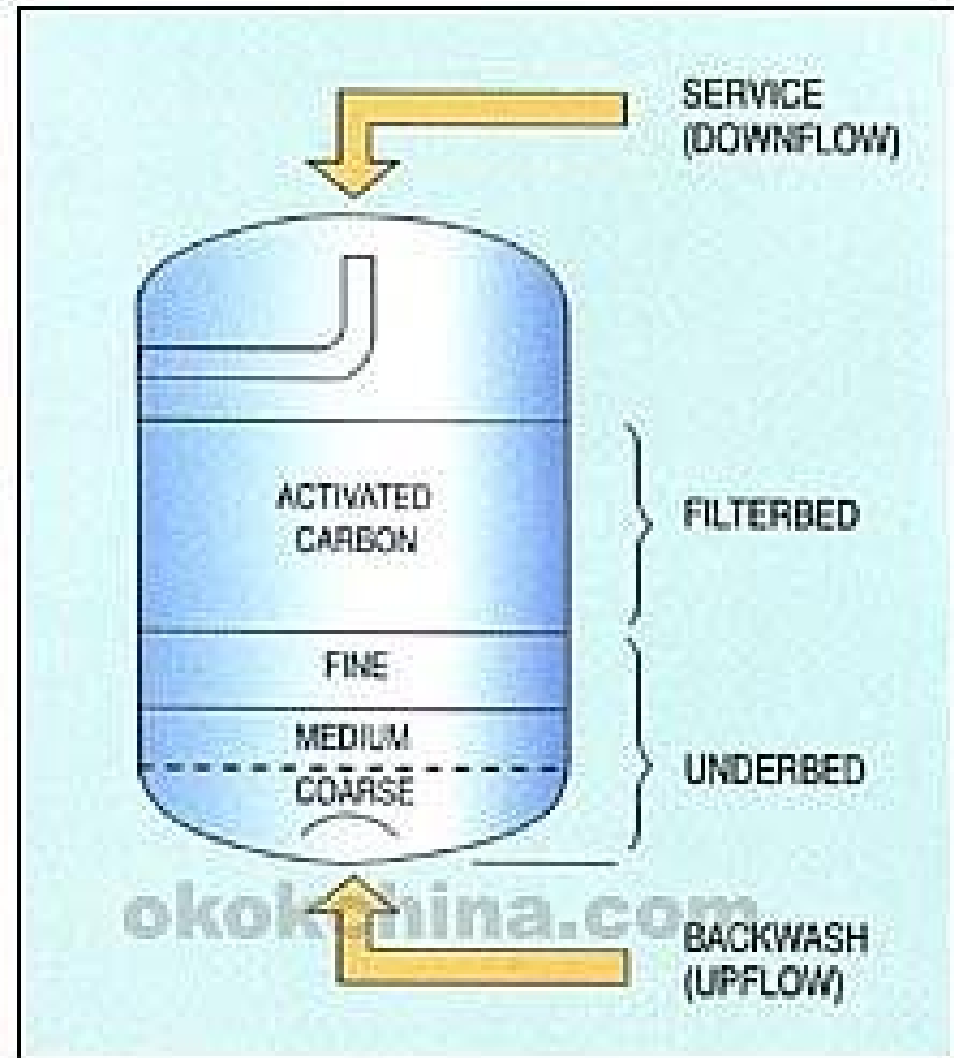
Slurry systems need some sort of activated carbon removal process to separate the AC from the liquid stream.

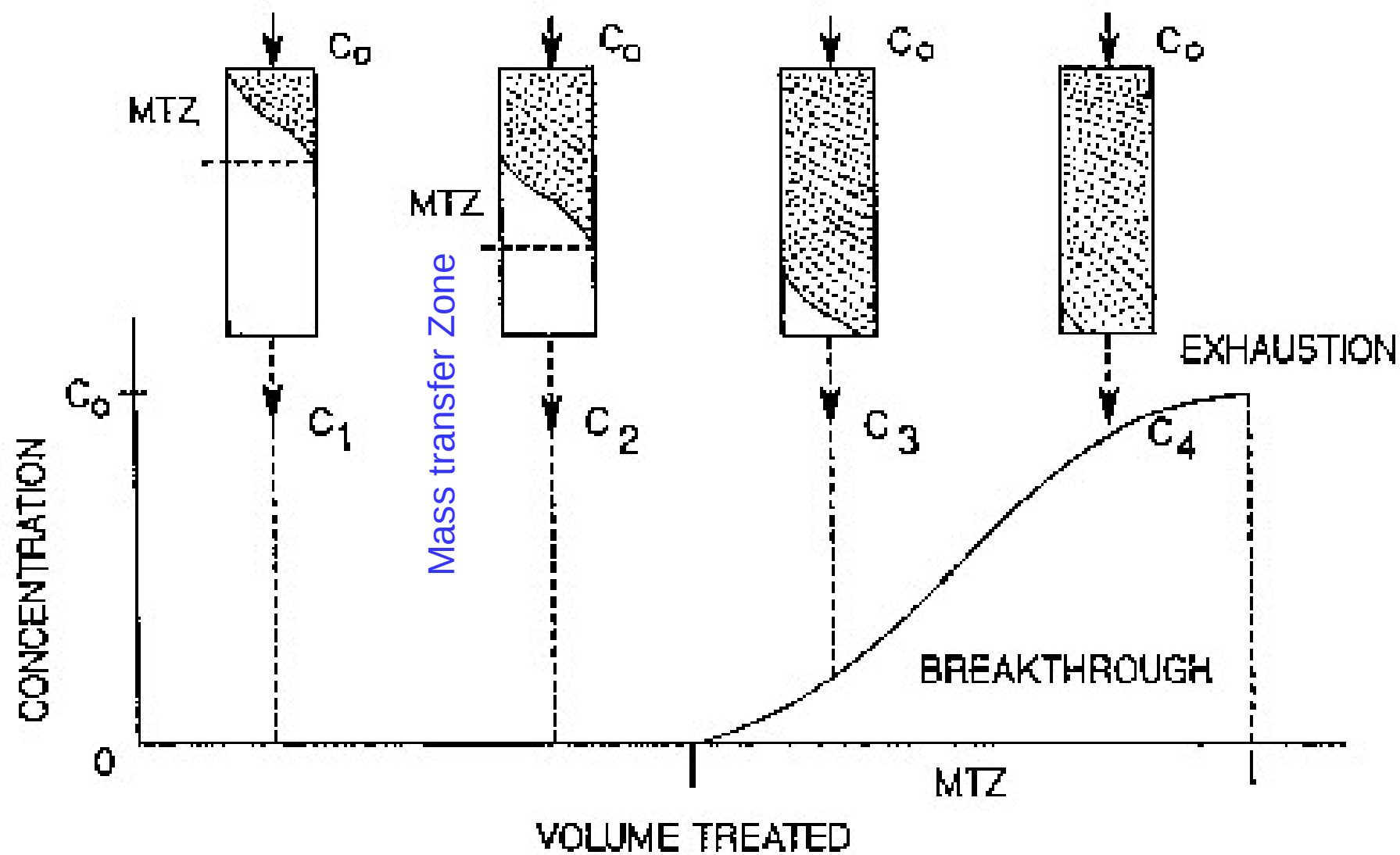
Packed bed (fixed carbon bed)

contactors provide filtration as well as adsorption so they have to be periodically backwashed or cleaned.

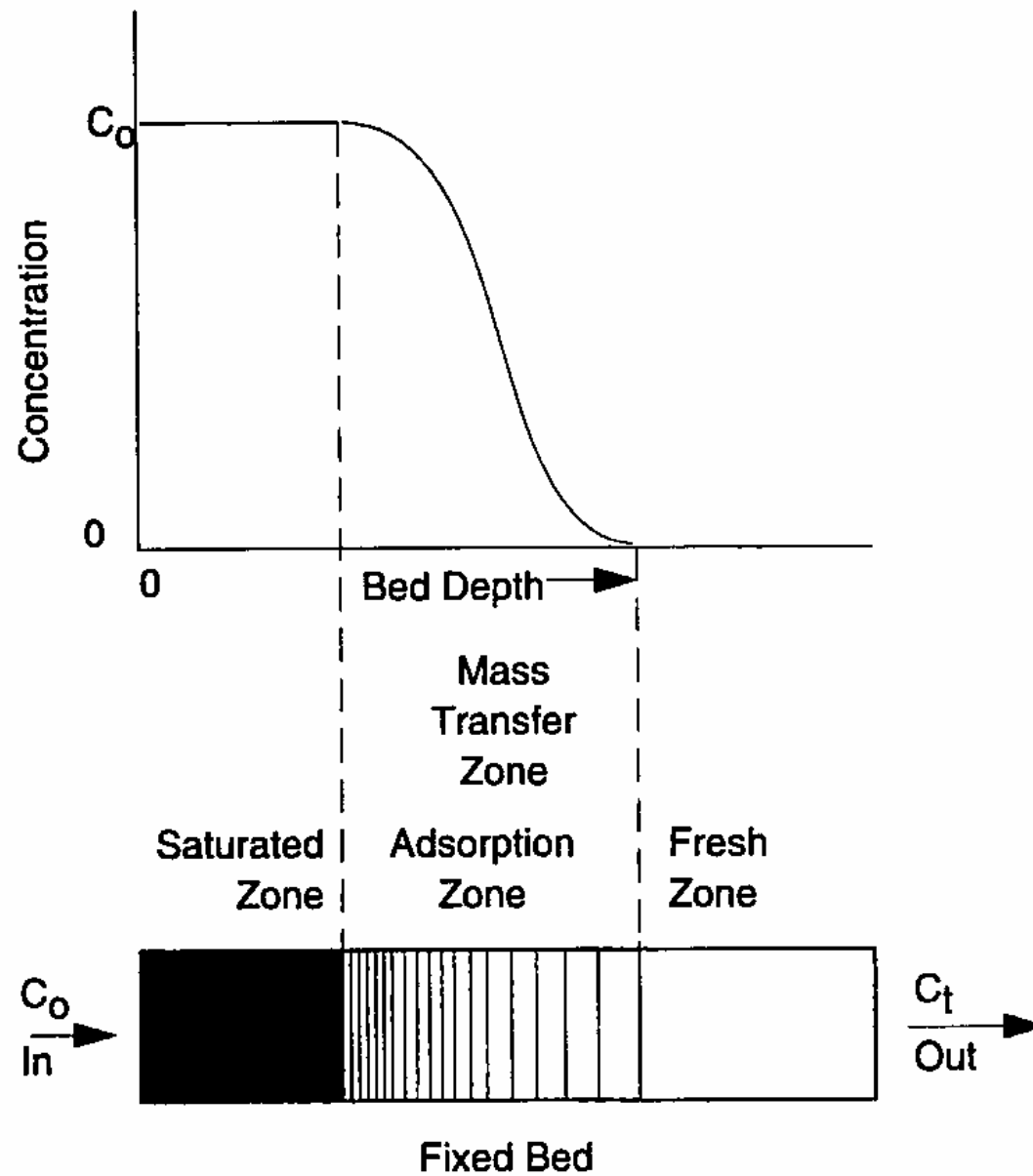
This is one reason why we only want to run soluble material through a contactor.







Concentration Profile Along a Column



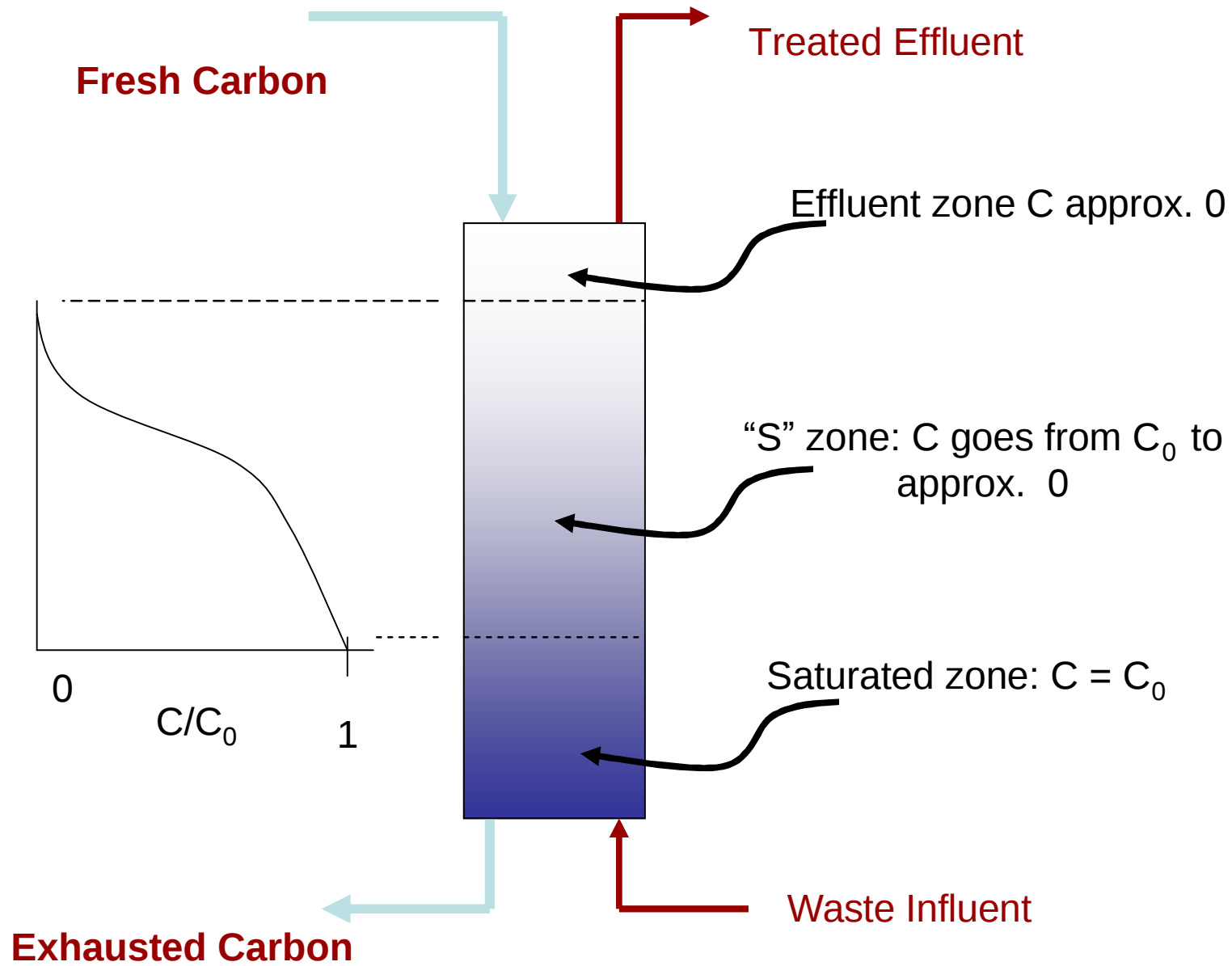
Fluidized Bed Contactors:

however, do not filter and we can employ continuous supply of fresh carbon while removing spent carbon.

In a fluidized bed mode (upflow) carbon can be continuously removed from the bottom of the contactor as it's exhausted.

Fresh make-up carbon can then be added to the top of contactor at the same rate.

Upflow fluidized beds also minimize clogging and unintentional filtration.



Carbon Regeneration

Since activated carbon is relatively expensive, adsorption would not be feasible unless the carbon can be regenerated after exhaustion.

Spent carbon is usually regenerated at 500 °C under low oxygen conditions in the presence of steam.

Activated carbon loss is about 5-15% for each regeneration. Adsorbed organics are volatilized and oxidized during the regeneration process.

Activated carbon is mostly applied in water treatment for:

- The removal of taste and odor producing compounds
- the elimination of inconvenient or toxic often-non polar compounds.
- additional efforts are the removal of heavy metals, if present.

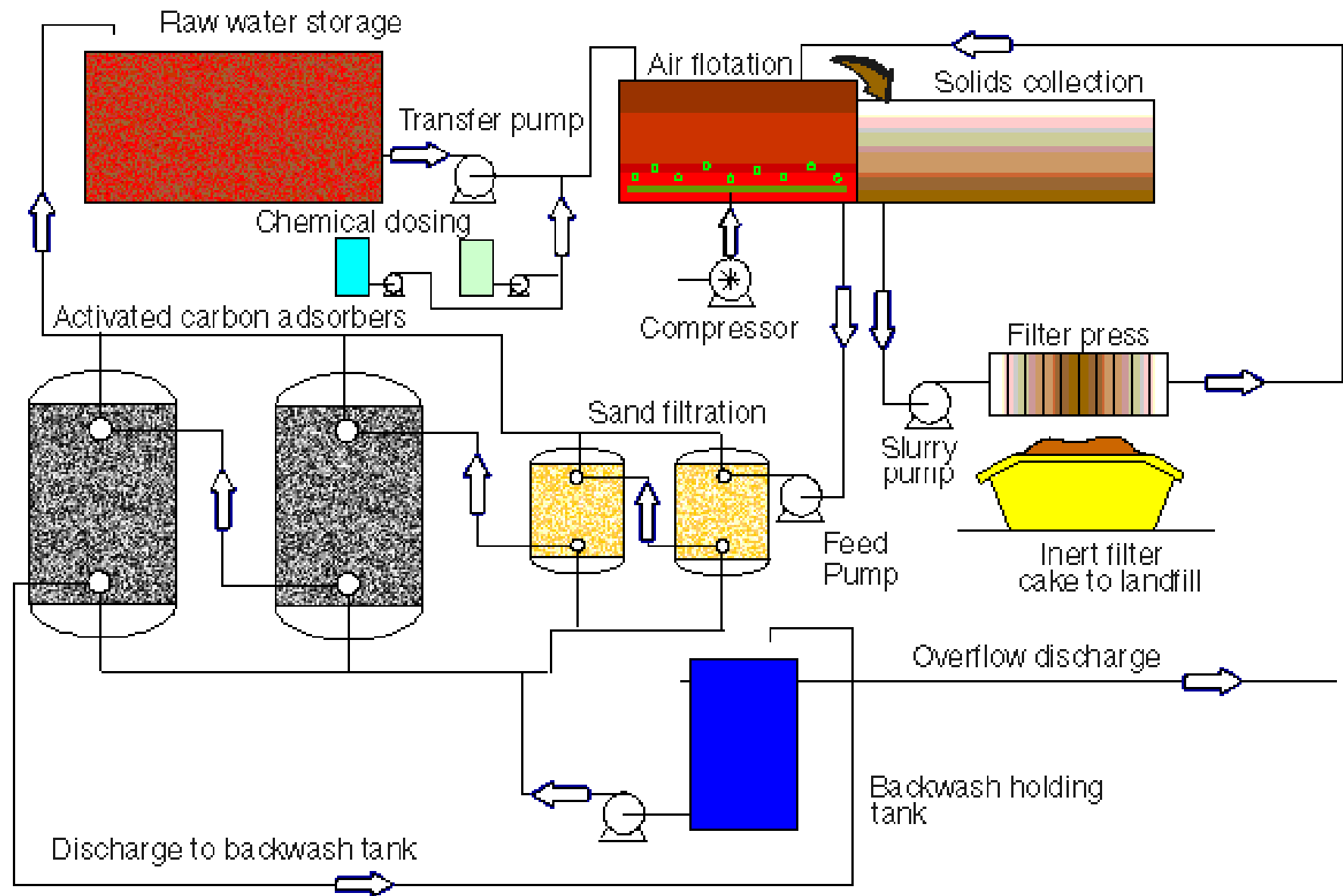
The application of AC in powder form is specially suitable in cases low dosage are needed or intermittent use (removal of taste originated from an algae-bloom)

Common apparent contact times are in dependence of the goal between 5 and 30 minutes; bed thickness up to 2-3 m are applied in water treatment.

Proper application of activated carbon needs experiments to decide for the proper type (adsorption isotherm) and the proper dose.

Applications in water treatment usually involve adding AC as a media to the filtration unit.

In some cases a contactor is added just before the final chlorination step.



El-Mansoura Water Treatment Plant, Egypt

