EWC 105
Environmental Chemistry

Lecture 14

Instructor
Maj Kazi Shamima Akter, Ph.D, Engrs
Department of EWCE, MIST

Lecture Outlines

Topics	Sub-Topics	References
Adsorption of metal ions	• Metal ions in aqueous solutions • Metal toxicity • Adsorption at solid-water interface • Adsorption isotherms	**1. *Chemistry for Environmental Engineering*** Authors: Clair N. Sawyer, Perry L. McCarty and Gene F. Parkin

Metal Ions in Aqueous Solutions

- The chemical behavior of any element, esp heavy metals, depends on the nature of its chemical form.

- For example, biological availability and toxicity of metal ions depend on its chemical form.

Metal Toxicity

Thumb rule of metal toxicity:

- Some metals (Cu^{2+}, Pb^{2+} etc) are more toxic to aquatic life, while complexed metals are much less toxic.

- For example: $CuHCO_3^+$, $CuCO_3$, $Cu(CO_3)_3^{2-}$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$ are much less toxic compared to Cu^{2+}.

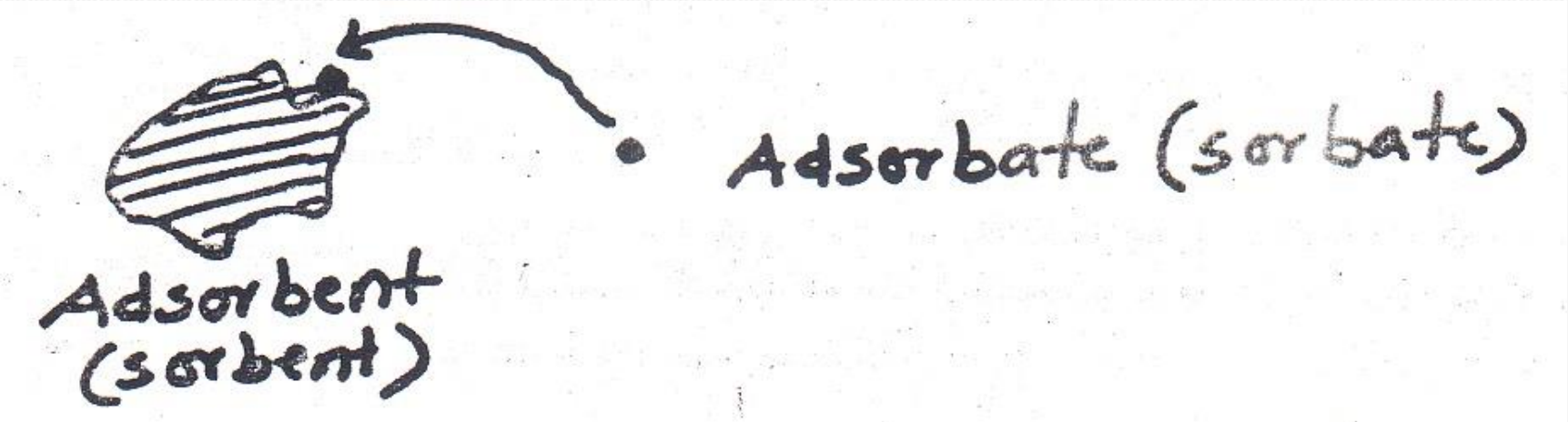
- Cu is important in view of its toxicity to aquatic life, but not so harmful to human.

- Sometimes $CaSO_4$ is added to lakes to suppress the growth of algae.

Adsorption

- Adsorption is the process by which ions (molecules) present in one phase (e.g., water) tend to condense or concentrate on the surface of another phase (e.g., solid).

- Adsorption often dictates the fate of trace inorganic or organic pollutants in aquatic system.



Significance of Adsorption

- Adsorption processes are very important
  ✓ to the fate and transport of contaminants in the environment and
  ✓ for the removal of contaminants in engineered reactors.

- Adsorption of contaminants in air or water onto activated carbon is frequently used for purification of air or water.

Types of Adsorption Processes

1. Physical Adsorption

- Is due to the operation of weak forces of attraction or van der Waal's forces between molecules.

- Generally reversible, i.e., with a decrease in concentration, the adsorbed material is desorbed to the same extent that it was originally adsorbed.

Types of Adsorption Processes

2. Chemical Adsorption / Chemiosorption

- Is the result of much stronger forces, comparable with those leading to the formation of chemical compounds.

- Is seldom reversible. The adsorbent must generally be heated to higher temperatures to remove the adsorbed materials.

Types of Adsorption Processes

3. Exchange Adsorption

- Characterized by electrical attraction between the adsorbate and the surface.

- Example includes ion exchange. Here, ions of a substance concentrate at the surface as a result of electrostatic attraction to sites of opposite charge on the surface.

- Ions with greater charges (trivalent ions) are attracted adsorbed more strongly than those with lesser charges (monovalent ions).

Adsorption of Gases

- At a given temperature and pressure, a sample of activated carbon (AC) will absorb a definite quantity of gas.
- If the pressure is increased, AC will absorb more gases and vise versa.

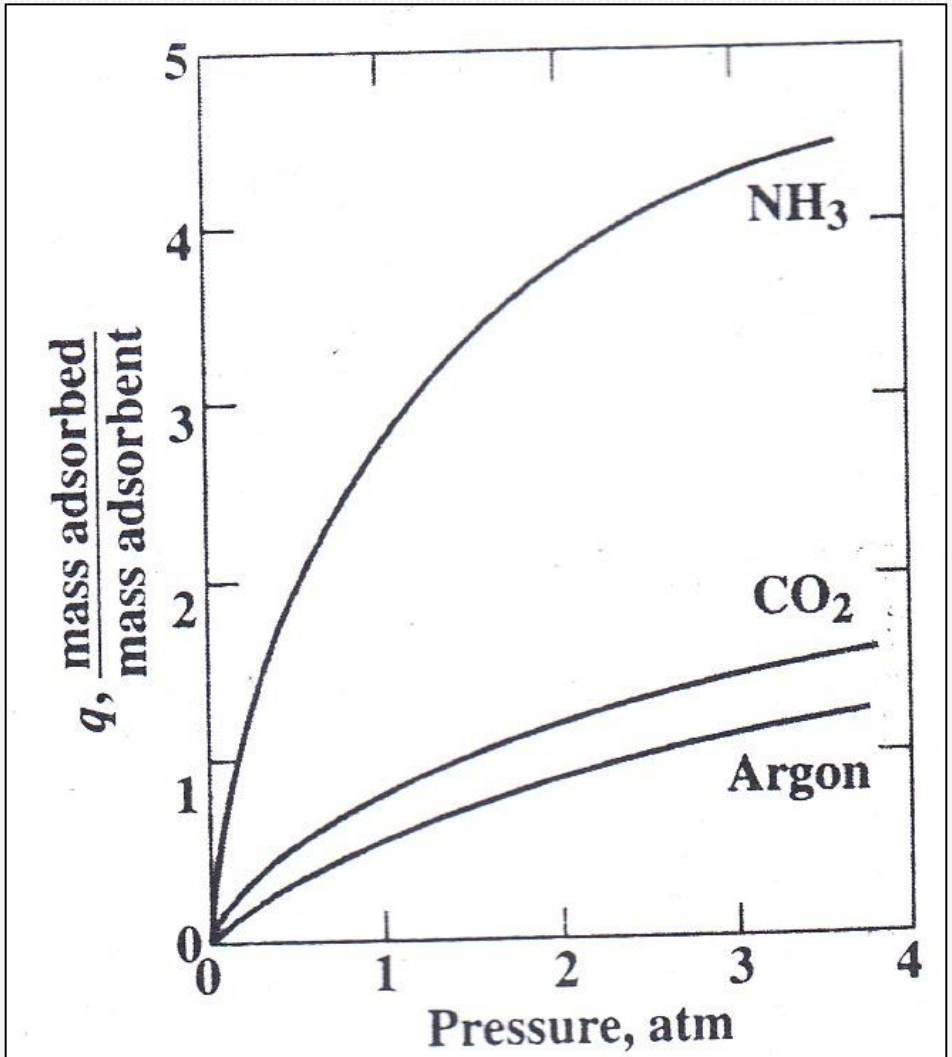


Figure 3.12
Adsorption of gases on charcoal in relation to pressure at constant temperature.

Adsorption of Solutes

- Adsorption of solutes from solution follow the same general laws as gases.
- The quantity of substances adsorbed by a given sample of adsorbent depends on the nature of the material and its concentration.
- It also depends on temperature (not discussed here).

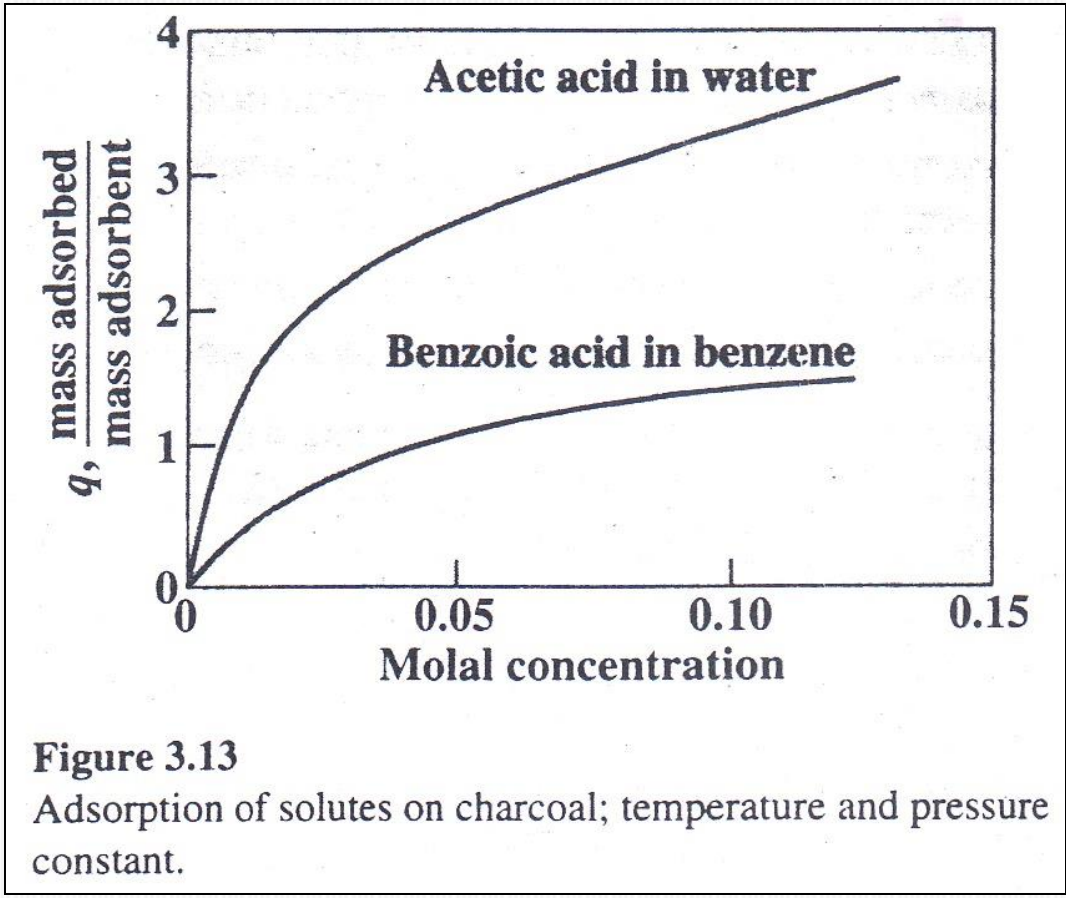


Figure 3.13
Adsorption of solutes on charcoal; temperature and pressure constant.

Adsorption Isotherms

- An adsorption isotherm is a quantitative relationship describing the equilibrium between –

  ✓ the concentration of adsorbate in solution (mass/ volume) and

  ✓ its adsorbed concentration (mass adsorbate/ mass adsorbent).

- The term “Isotherm” is used to signify that the relationship is for a given temperature.

Langmuir Isotherm

- Assumptions –
  ✓ a single adsorbate binds to a single site on the adsorbent

  ✓ all surface sites on the adsorbent have the same affinity for the adsorbent

- Langmuir isotherm is given by

$$q = q_m \frac{K_{ads} C}{1 + K_{ads} C} \quad \ldots\ldots\ldots (1)$$

Langmuir Isotherm

Langmuir isotherm -

$$q = q_m \frac{K_{ads} C}{1 + K_{ads} C}$$

where,

q = adsorbed concentration
(often called adsorption density)
(expressed as mass adsorbate/ mass adsorbent)

q_m = maximum capacity of adsorbent for adsorbate
(expressed as mass adsorbate/ mass adsorbent)

C = aqueous concentration of adsorbate (mass/ volume)

K_{ads} = measure of affinity of adsorbate for adsorbent

Langmuir Isotherm

Langmuir isotherm -

$$q = q_m \frac{K_{ads} C}{1 + K_{ads} C} \quad \ldots\ldots\ldots (1)$$

- As C gets larger and larger-
  - ✓ adsorption sites become filled and
  - ✓ q approaches q_m.

Langmuir Isotherm

Langmuir isotherm -

$$q = q_m \frac{K_{ads} C}{1 + K_{ads} C} \quad \ldots\ldots (1)$$

- Equation (1) can be linearized as follows –

$$\frac{1}{q} = \frac{1}{q_m K_{ads}} \left(\frac{1}{C} \right) + \frac{1}{q_m} \quad \ldots\ldots (2)$$

- Evaluation of the coefficients q_m and K_{ads} can be obtained using equation (2).

$$q = q_m \frac{K_{ads} C}{1 + K_{ads} C}$$

$$\Rightarrow \frac{1}{q} = \frac{1 + K_{ads} C}{q_m K_{ads} C}$$

$$= \frac{C\left(\frac{1}{C} + K_{ads}\right)}{q_m K_{ads} C}$$

$$= \frac{1}{C q_m K_{ads}} + \frac{K_{ads}}{q_m K_{ads}}$$

$$\Rightarrow \frac{1}{q} = \frac{1}{q_m K_{ads}} \left(\frac{1}{C}\right) + \frac{1}{q_m}$$

Langmuir Isotherm

$$\frac{1}{q} = \frac{1}{q_m K_{ads}}\left(\frac{1}{C}\right) + \frac{1}{q_m} \quad \ldots\ldots (2)$$

y = mx + C

- Evaluation of the coefficients q_m and K_{ads} can be obtained using equation (2).
- Here, equation (2) represents a straight line with the slope of $1/q_m K_{ads}$, in the plot of 1/q vs 1/C,

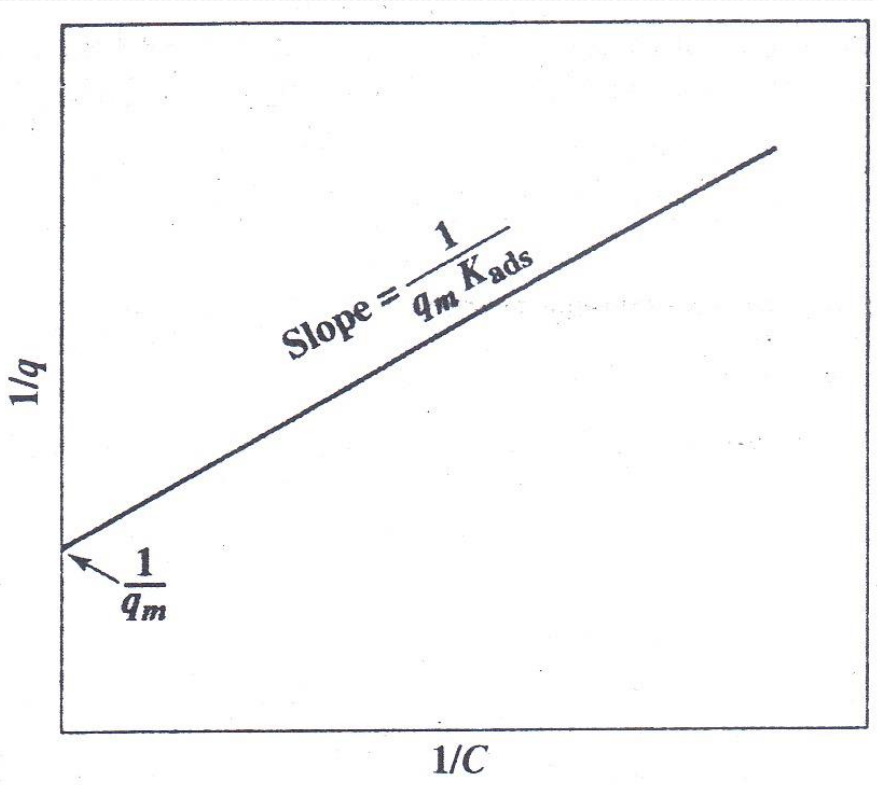


Figure 3.14
Straight-line form of the Langmuir isotherm.

Freundlich Isotherm

- The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates, with each site behaving according to the langmuir isotherm.

- The Freundlich isotherm is given by :

$$q = K C^{1/n} \ldots\ldots (3)$$

where,

K = measure of capacity of the adsorbent
(mass adsorbate/ mass adsorbent)

n = measure of how affinity for the adsorbate changes with changes in adsorbtion density.

Freundlich Isotherm

- The Freundlich isotherm is given by :

$$q = K C^{1/n} \ldots\ldots (3)$$

- When n =1, the Freundlich isotherm becomes a linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbates.

- Values of n>1 indicates that affinities decrease with increasing adsorption capacity.

Freundlich Isotherm

- The Freundlich isotherm is given by :

$$q = K C^{1/n} \quad \ldots\ldots (3)$$

- Evaluation of K and n can be accomplished from

$$\log q = \log K + 1/n \log C \quad \ldots\ldots (4)$$

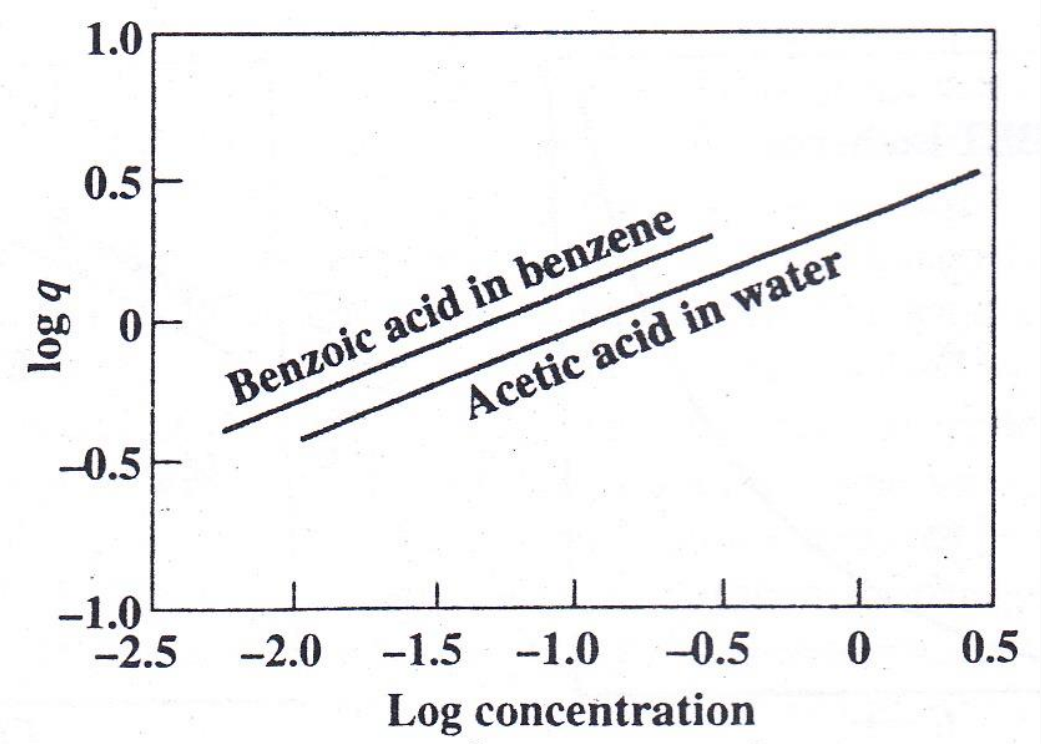


Figure 3.15
Logarithmic plot of adsorption data.