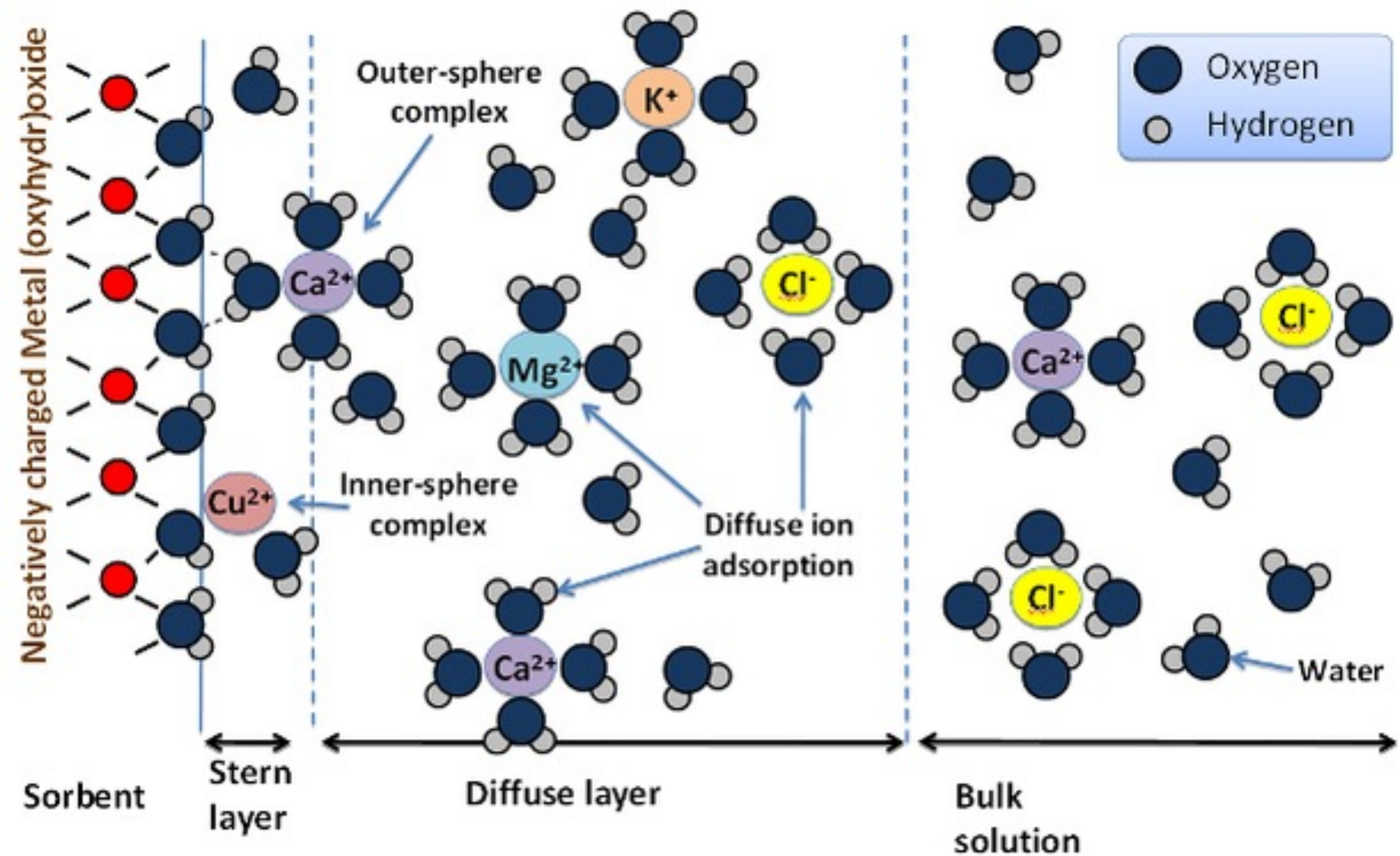
Surface Chemistry and Adsorption

EAR 419/619 Environmental Aqueous Geochemistry

Adsorption: attachment of a solute to the surface of a solid or the accumulation of solutes in the near vicinity of a surface



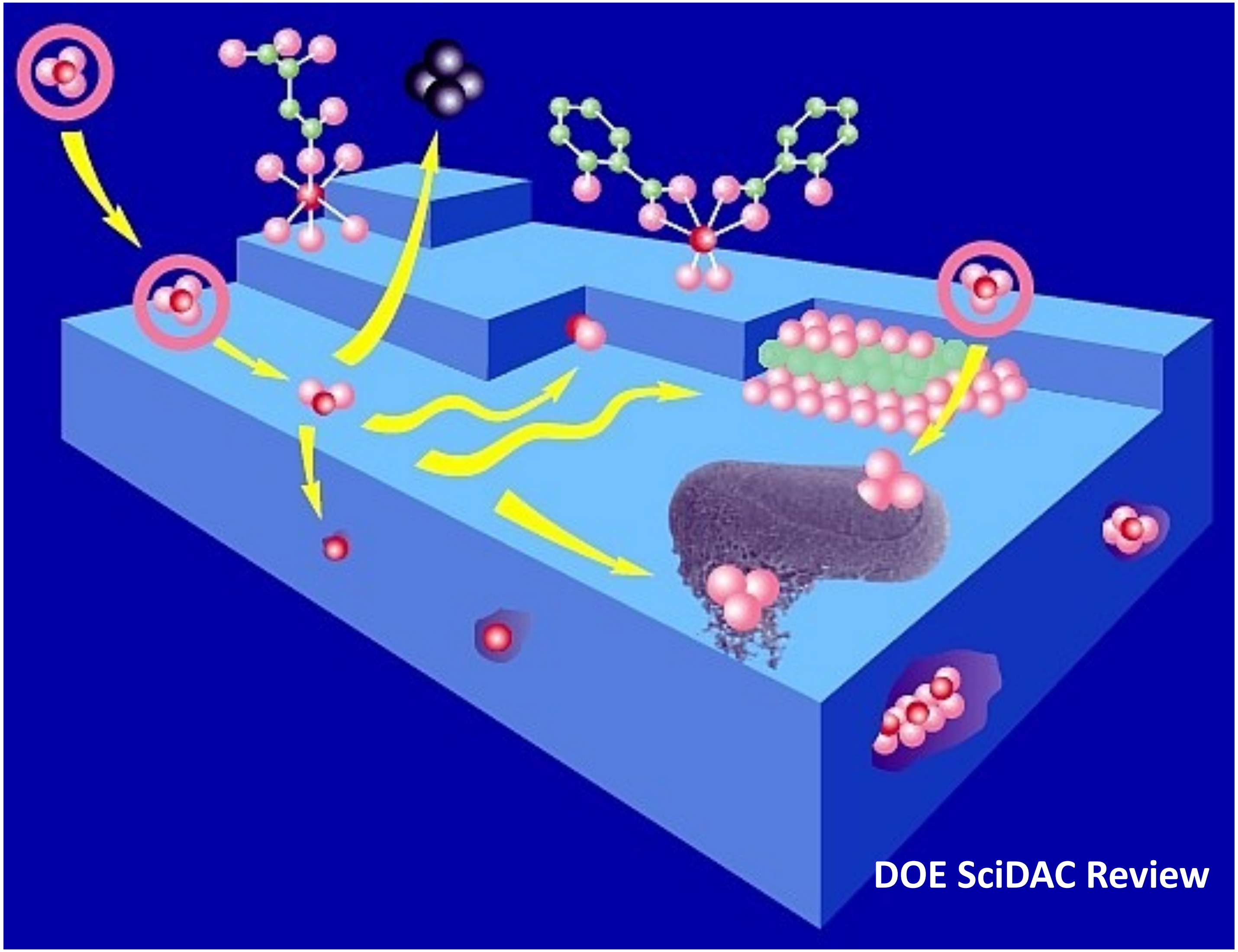
Nature Education

Factors that influence adsorption

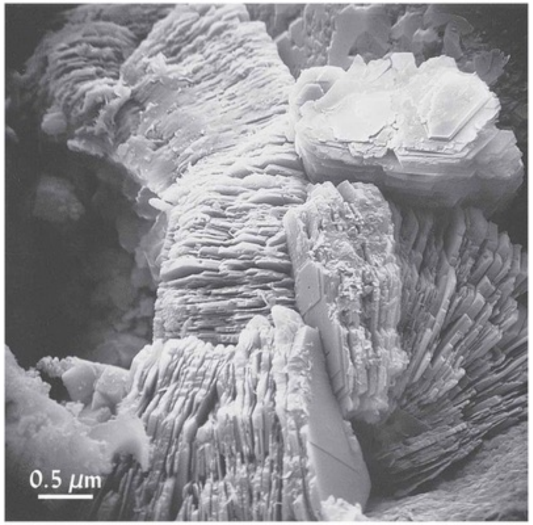
1. Surface charge – f(pH, mineralogy, surface site density)
2. Solute charge – f(pH, solute)
3. Surface area
   - Small particles → high SA → more adsorption

Mineral surface are not homogeneous!

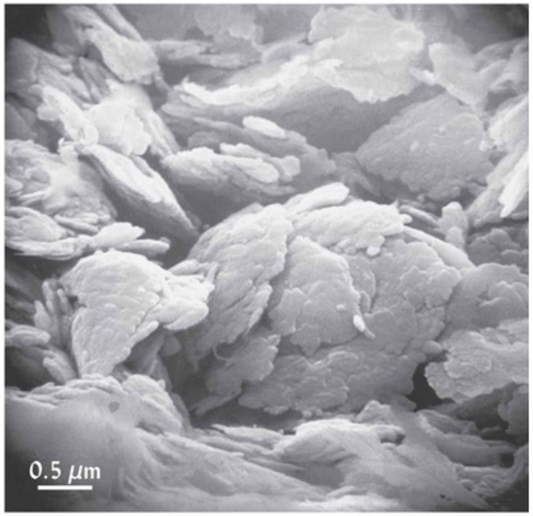
They have topographic and chemical variability that create high energy sites where reactions can occur



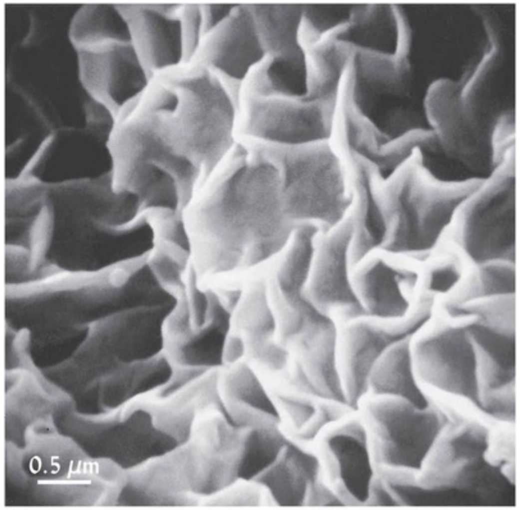
Surfaces of mineral grains



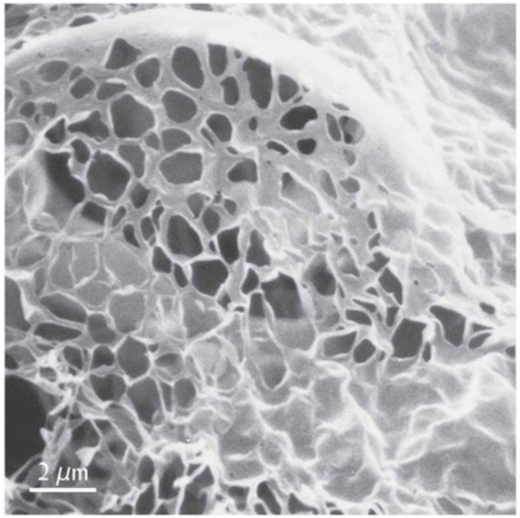
kaolinite



mica



Montmorillonite



fulvic acid

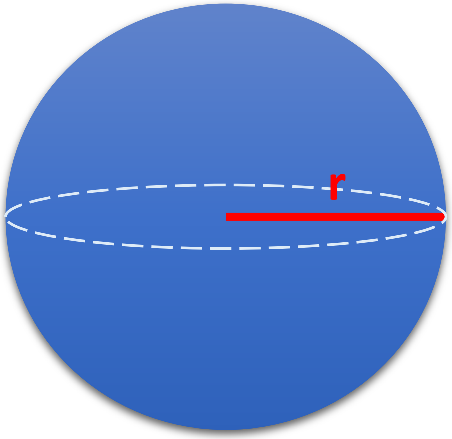
Surfaces of mineral grains

https://www.youtube.com/watch?v=NV-ZKG2uCaA

Calcite Dissolution

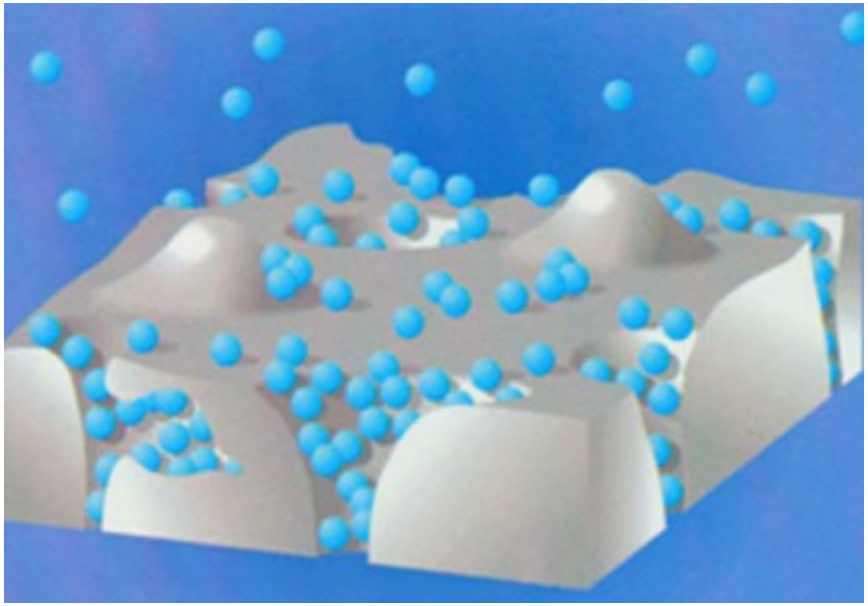
Measuring specific surface area ($S_{A,}$ m^2/g)

Geometric



S_A (sphere) = $4\pi r^2$

BET

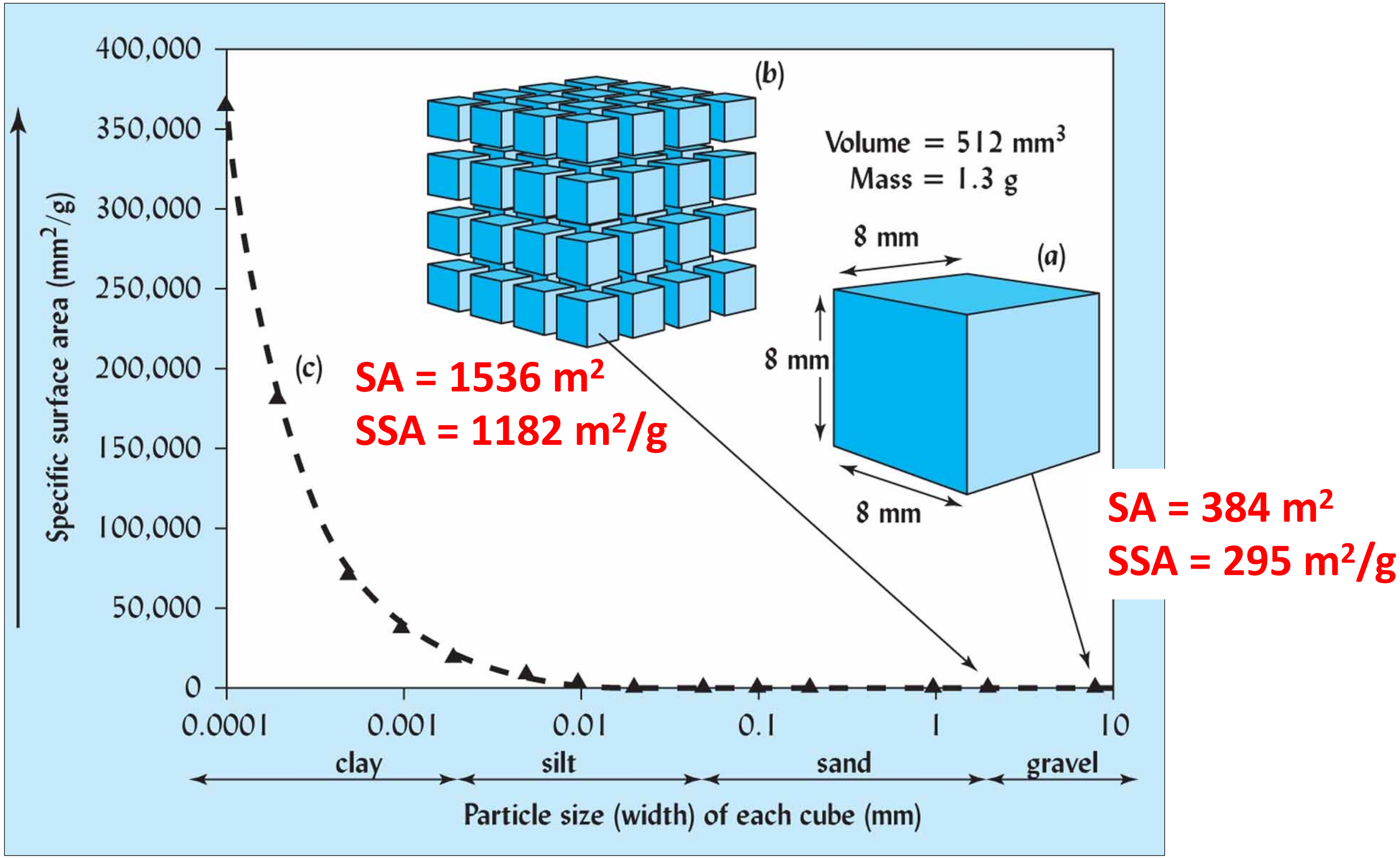


Adsorption of gas to a surface

Surface area increases with decreasing particle size

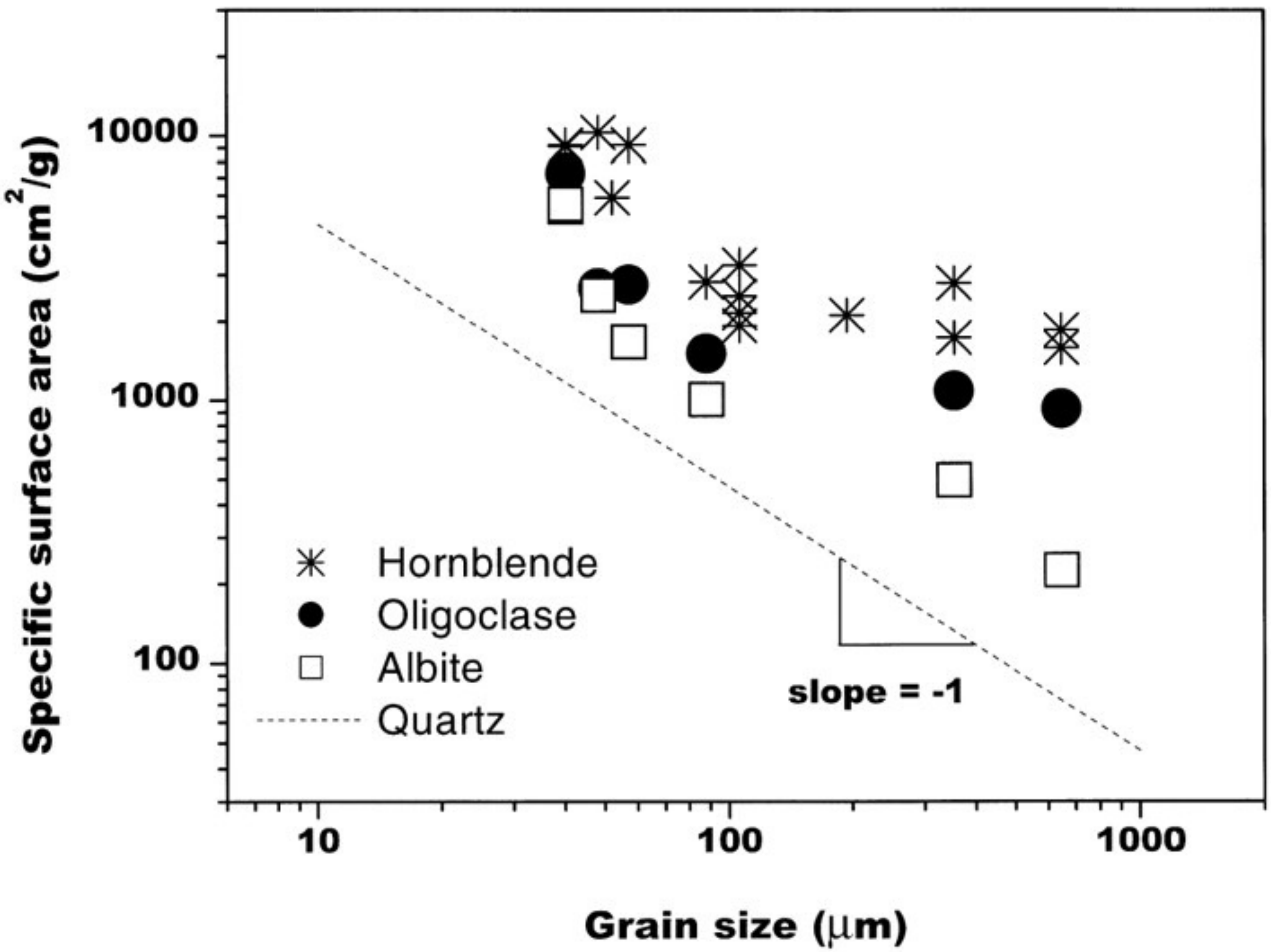
Specific surface area (SSA; m^2/g): the total surface area per unit mass of solid material

- The graph below assumes smooth, geometric shapes



Brady&Weil: FIGURE 4.4

S_A generally increases with decreasing grain size

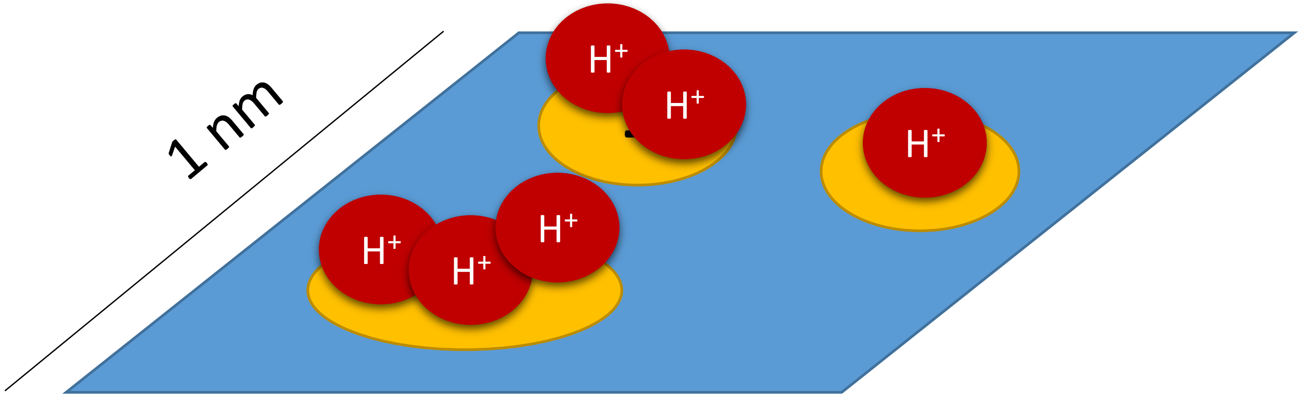


Brantley and Mellott 2000 Am. Mineral.

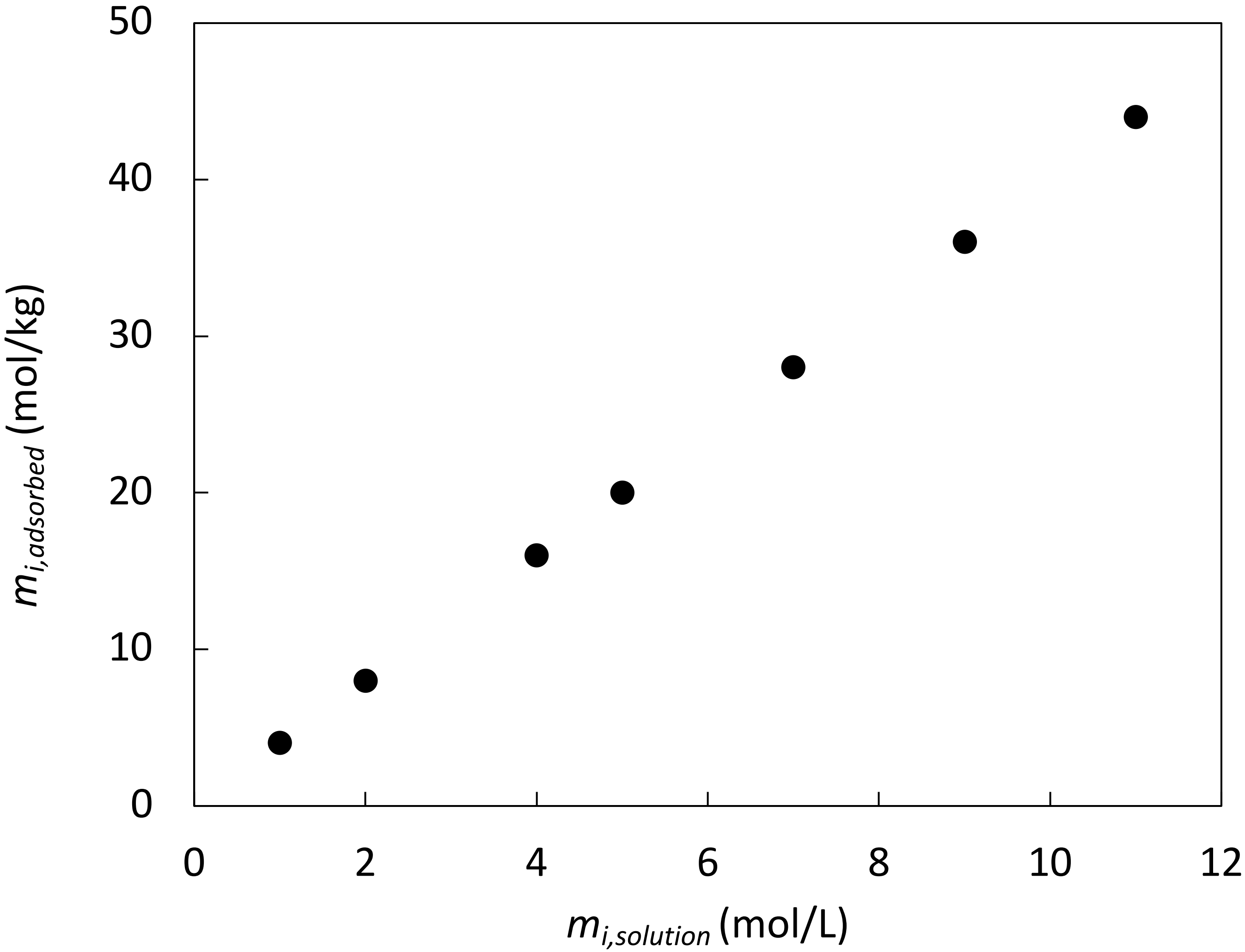
Measuring surface site density (N_S)

Adsorption of a reactive sorbate to a surface:

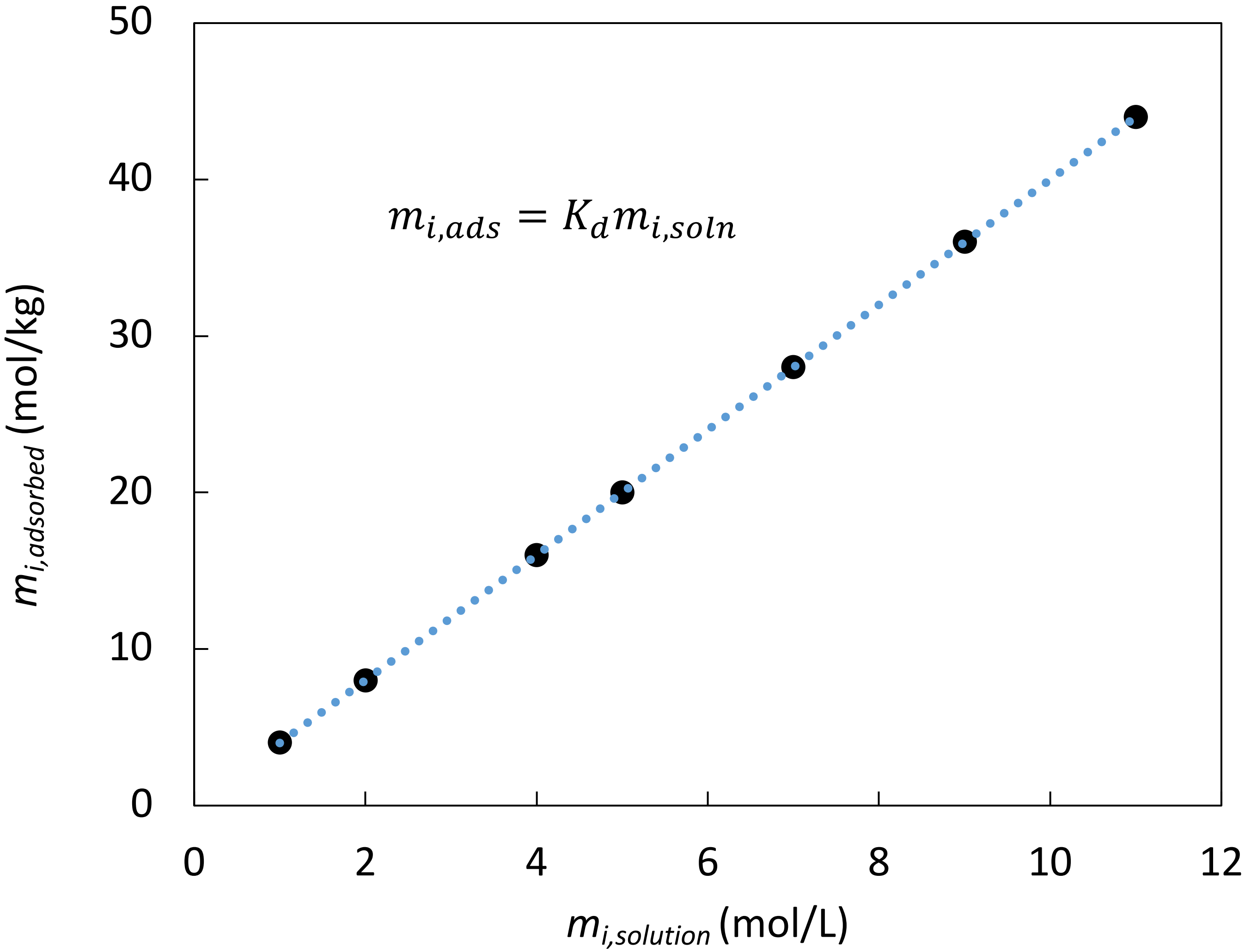
- Protons (H^+, e.g., mineral titration)
- Fluoride ions (F^-)



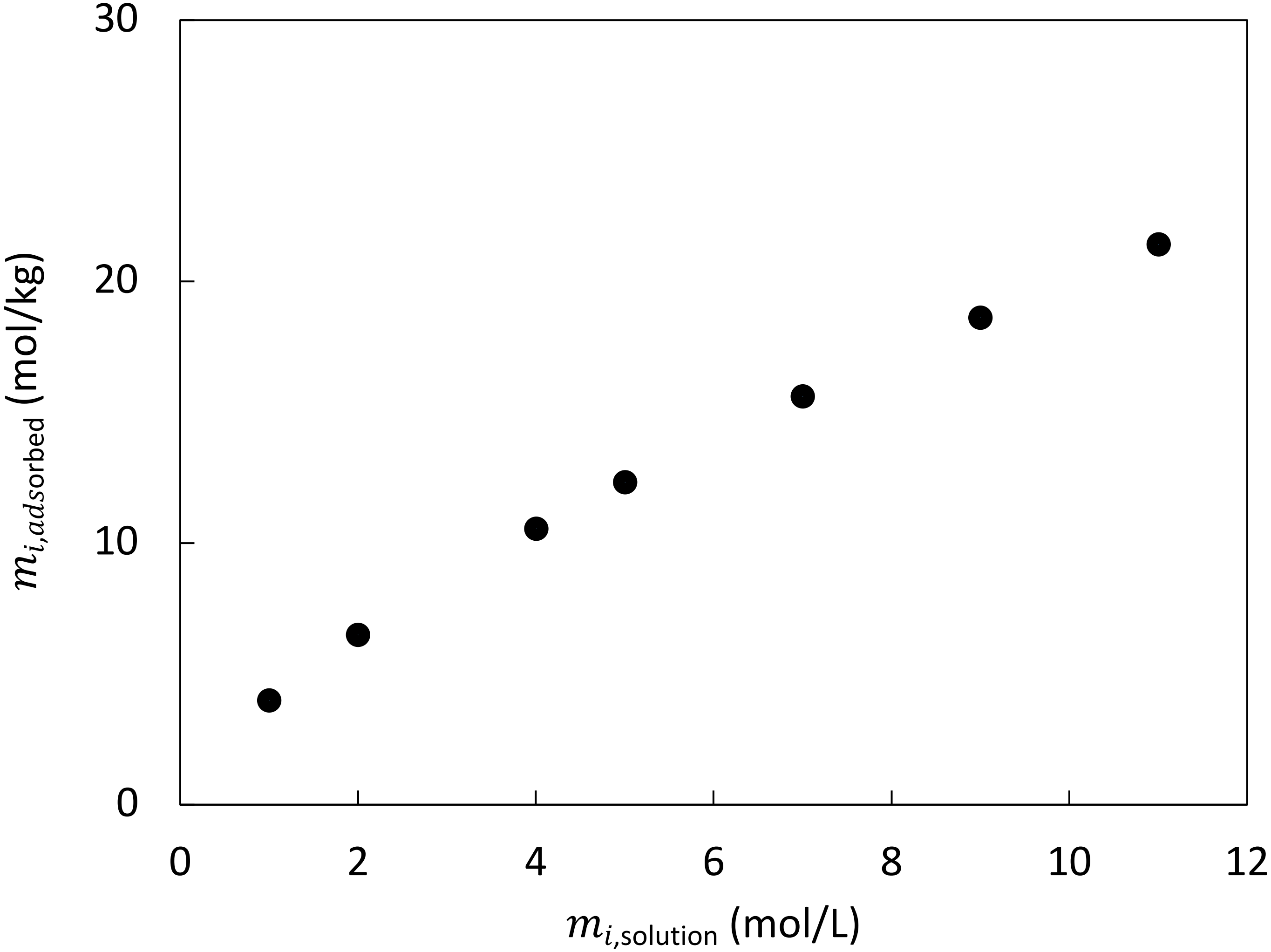
Linear Distribution Coefficient



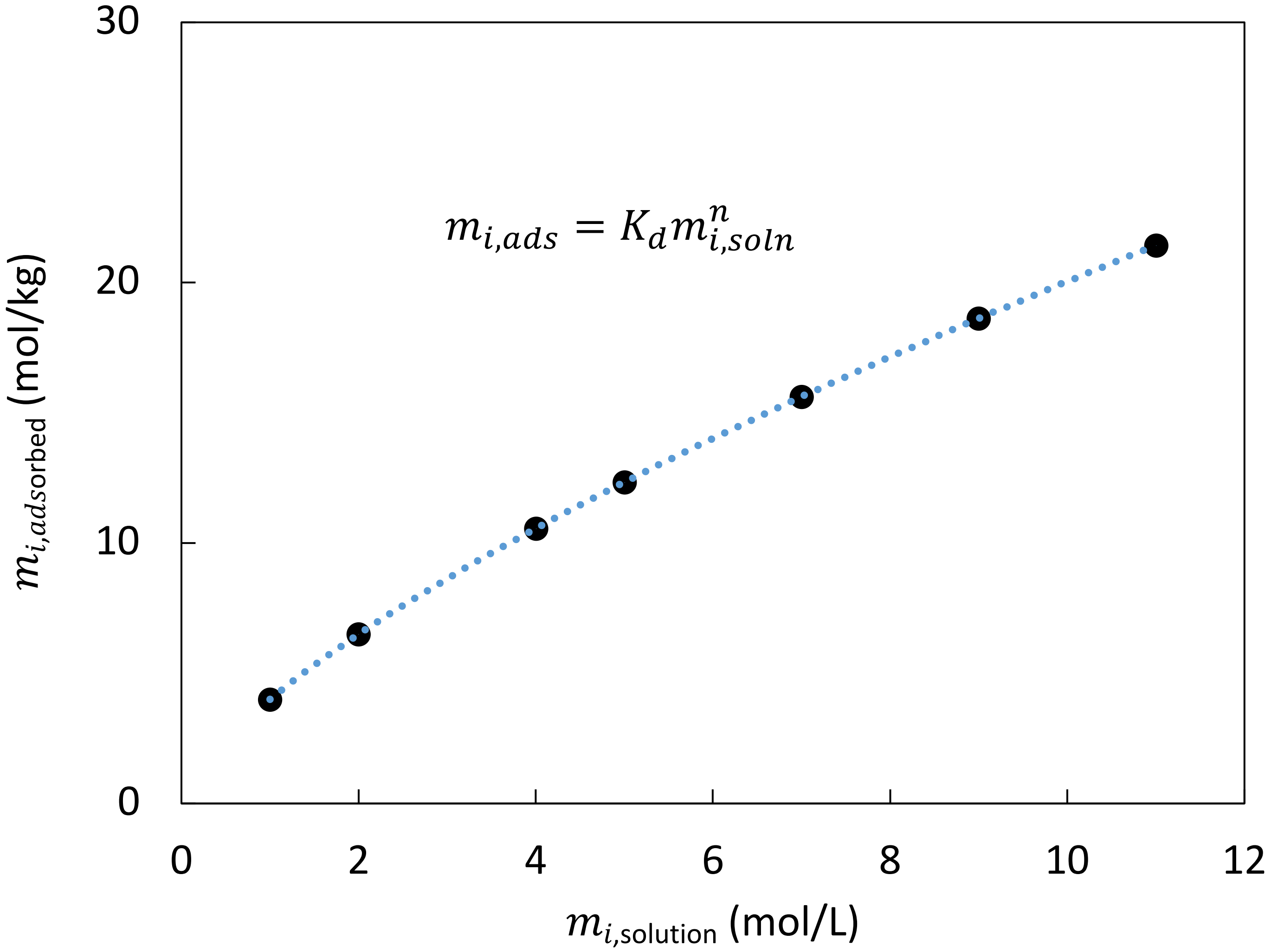
Linear Distribution Coefficient



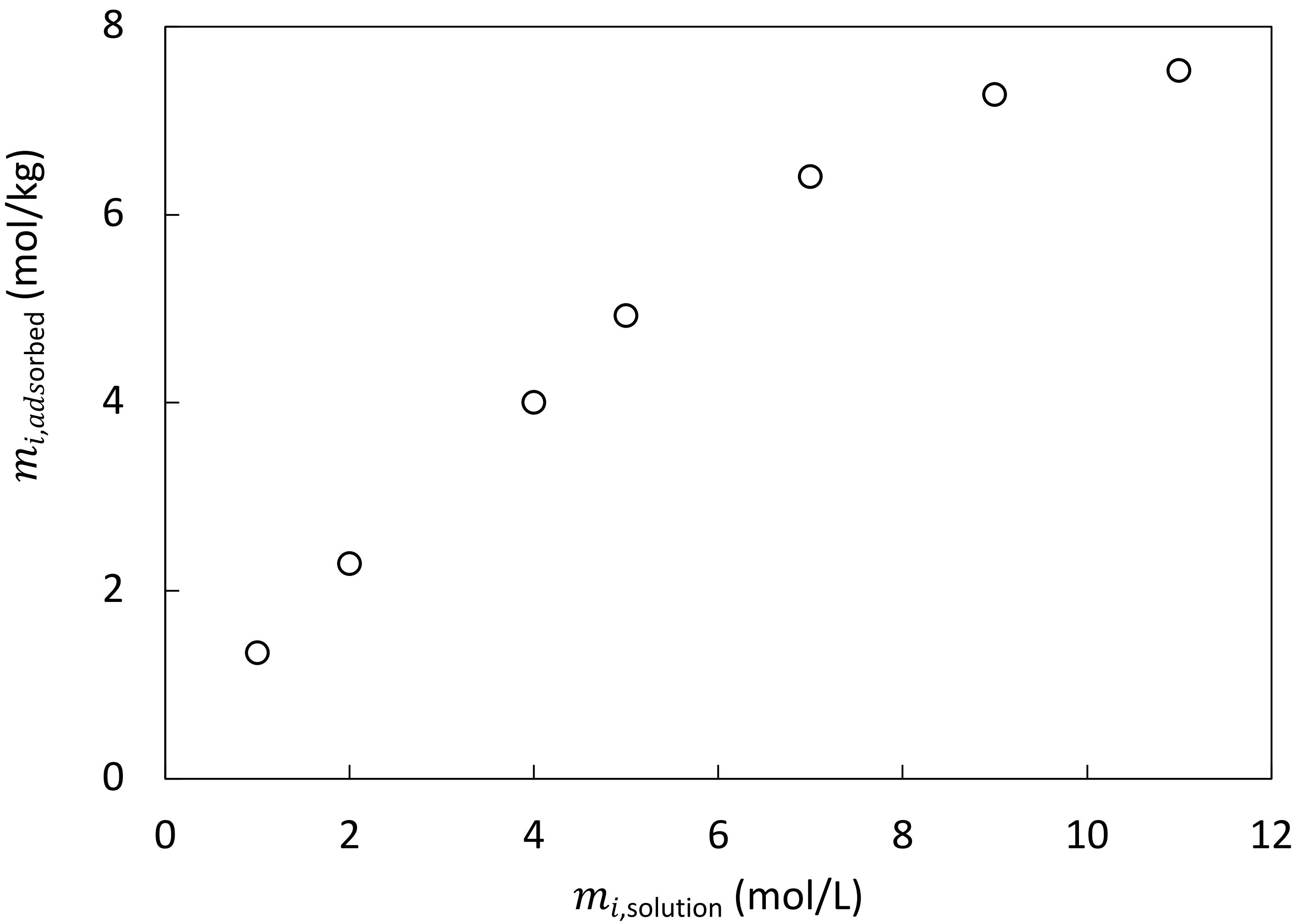
Freundlich Isotherm



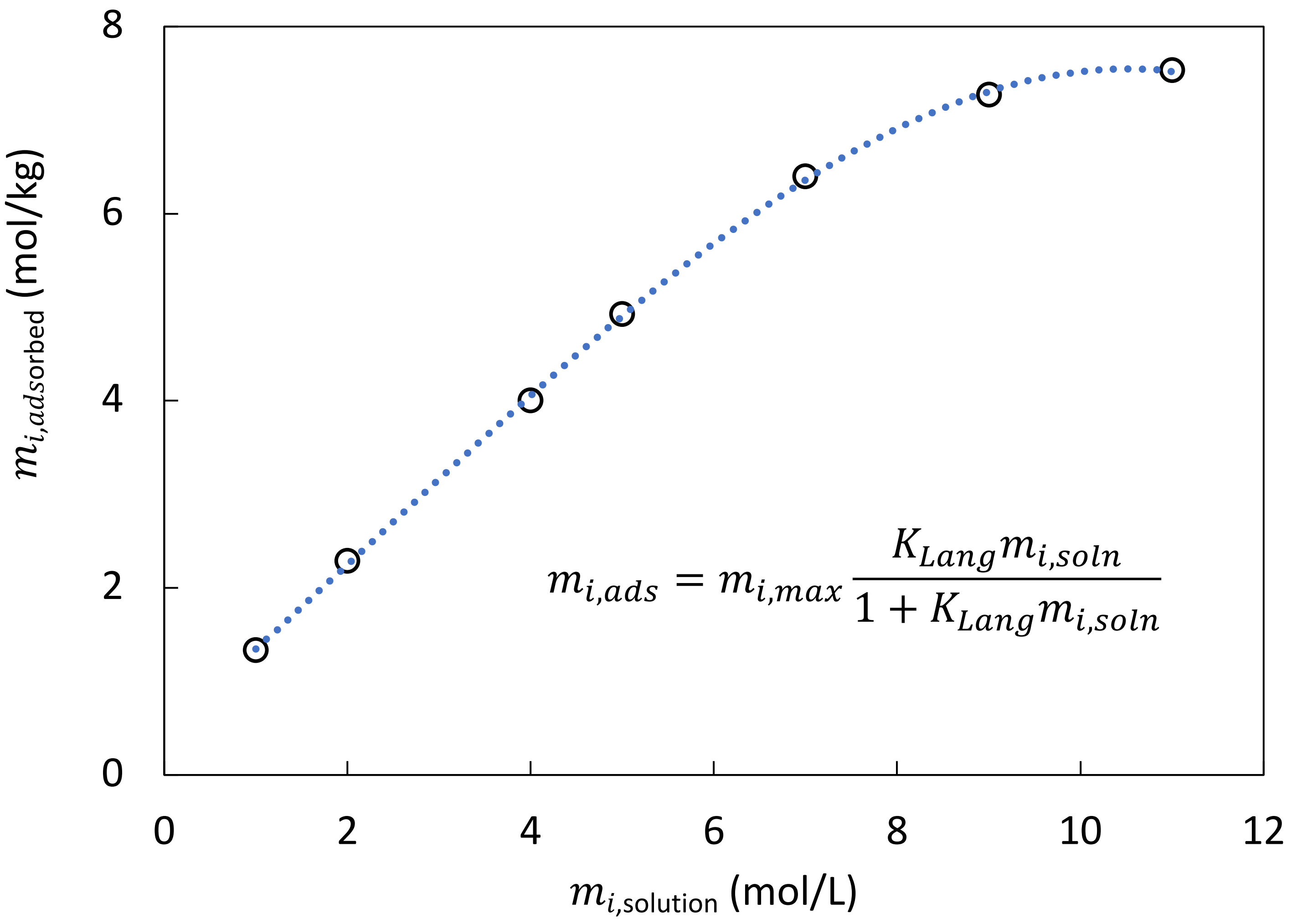
Freundlich Isotherm



Langmuir Isotherm

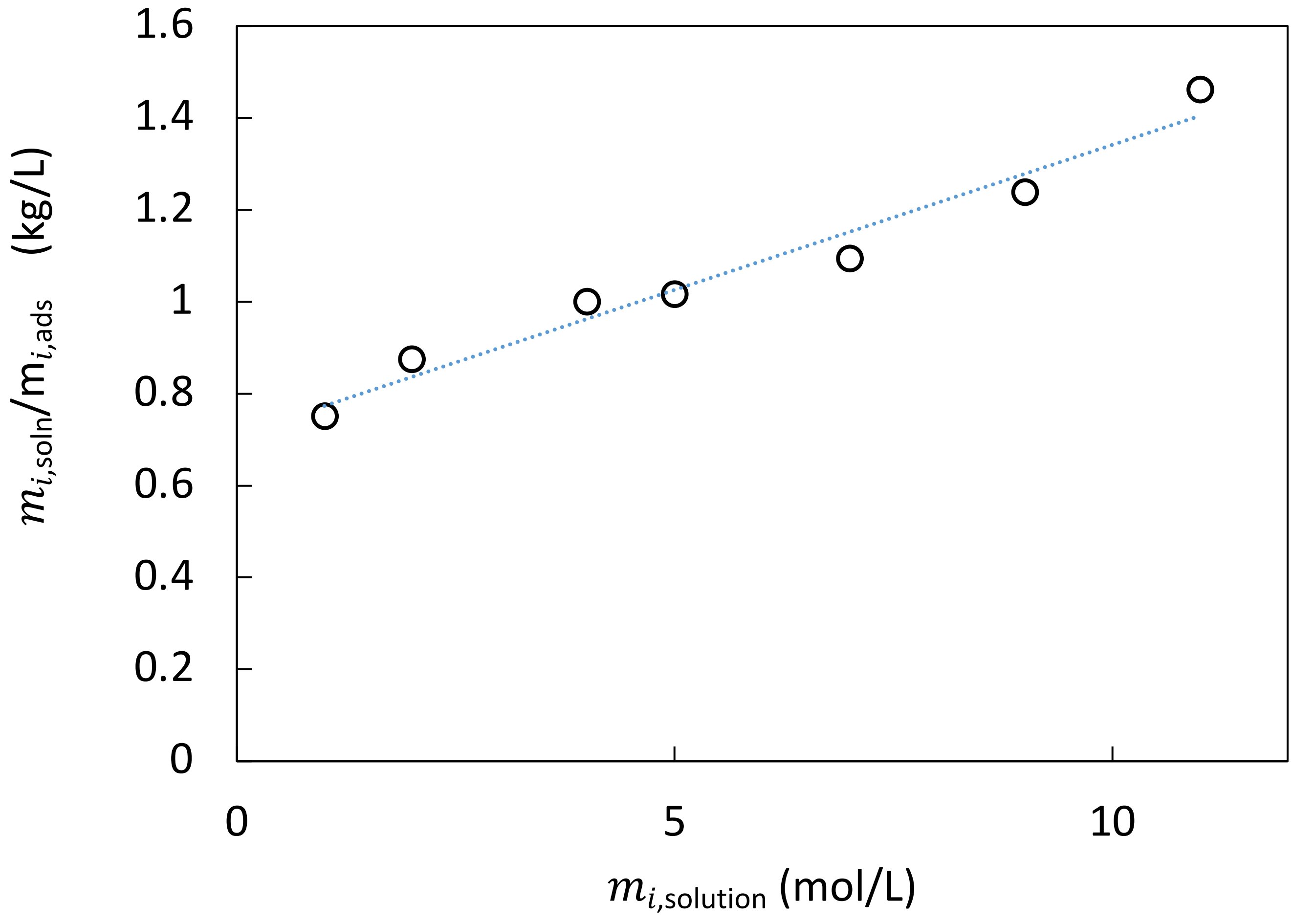


Langmuir Isotherm

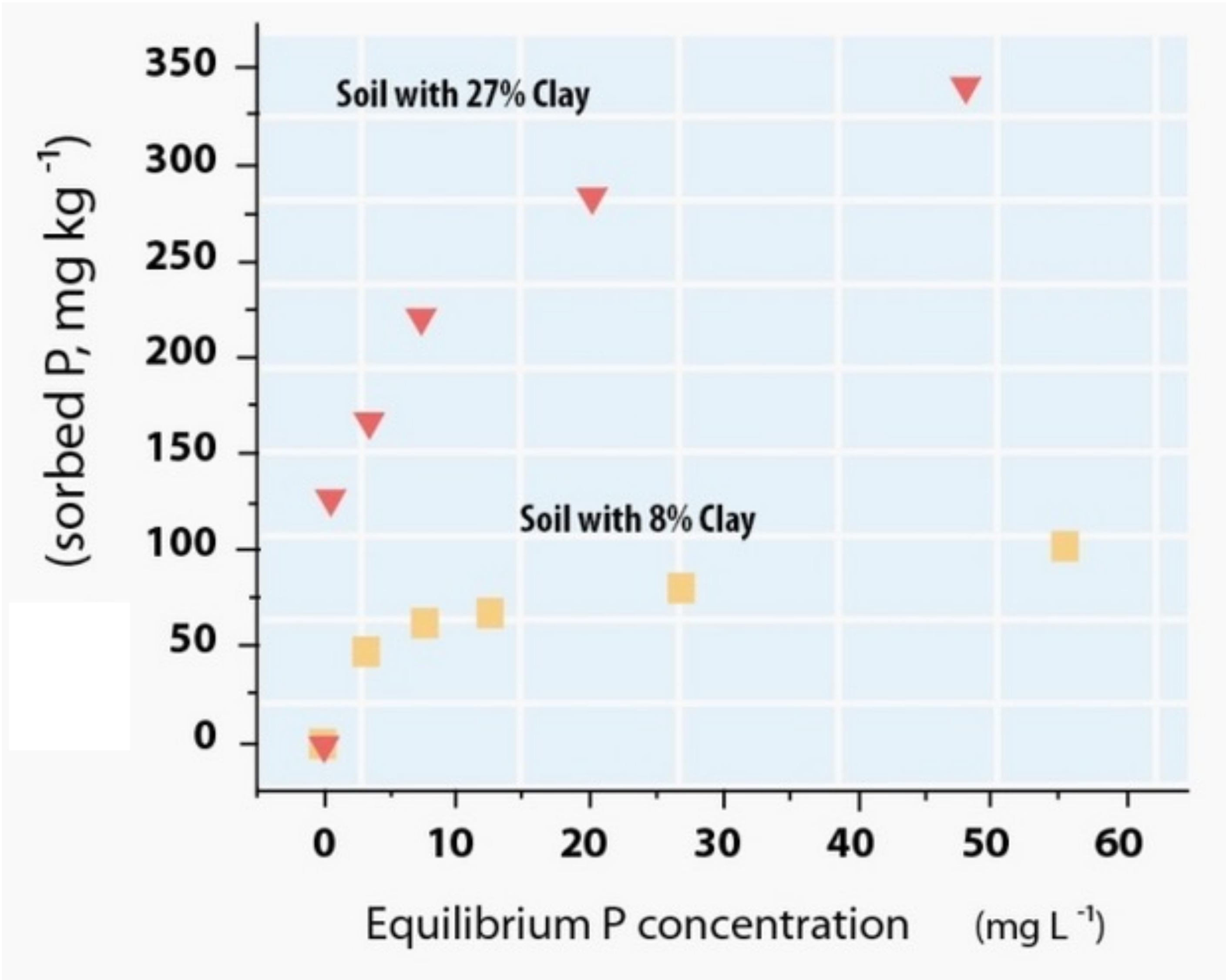


Langmuir Isotherm

$$\frac{m_{i,soln}}{m_{i,ads}} = \frac{1}{K_{Lang} m_{i,max}} + \left(\frac{1}{m_{i,max}}\right) m_{i,soln}$$



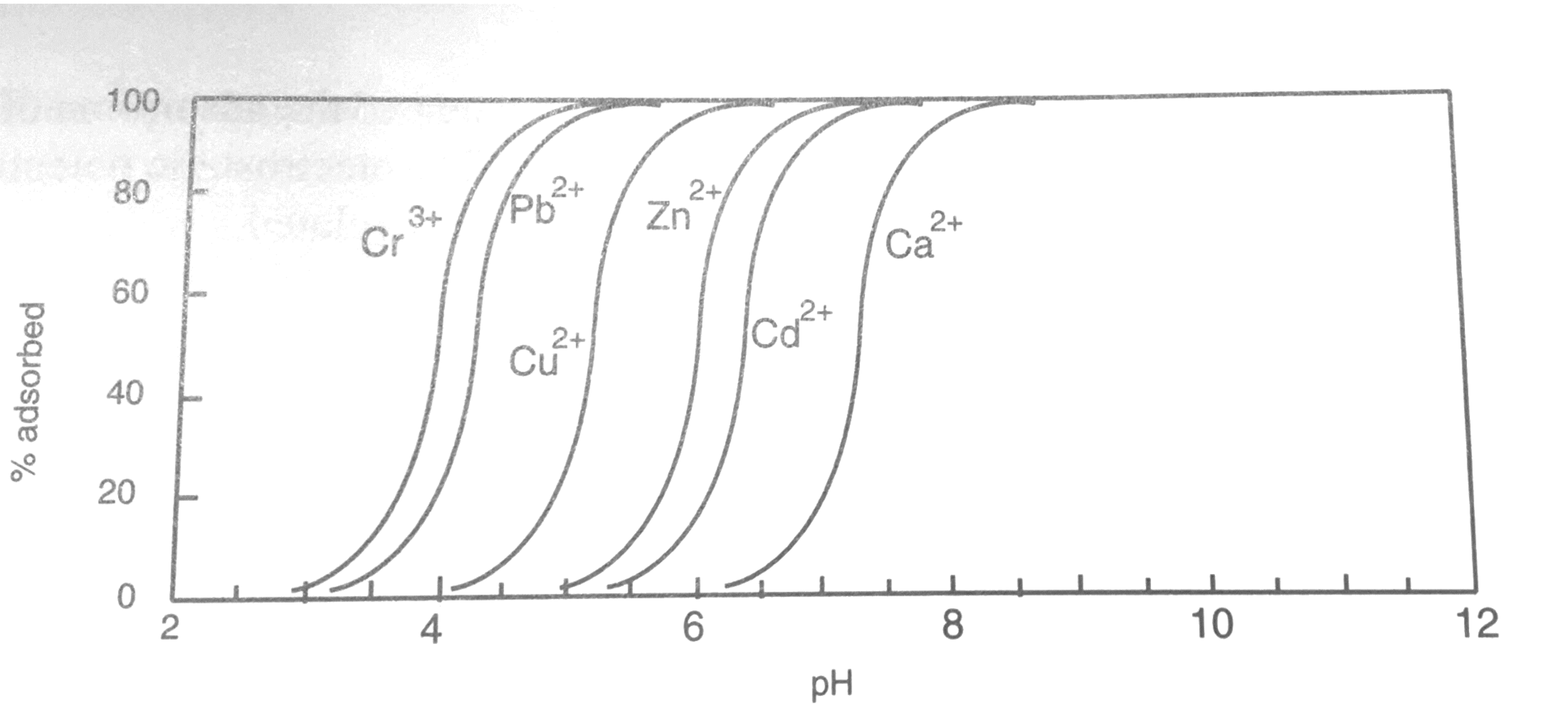
Phosphate sorption to clay-rich and clay-poor soils



Surface chemistry and adsorption

Cation adsorption: Cations (e.g., M^{2+}) compete with H^+ for negatively charged binding sites

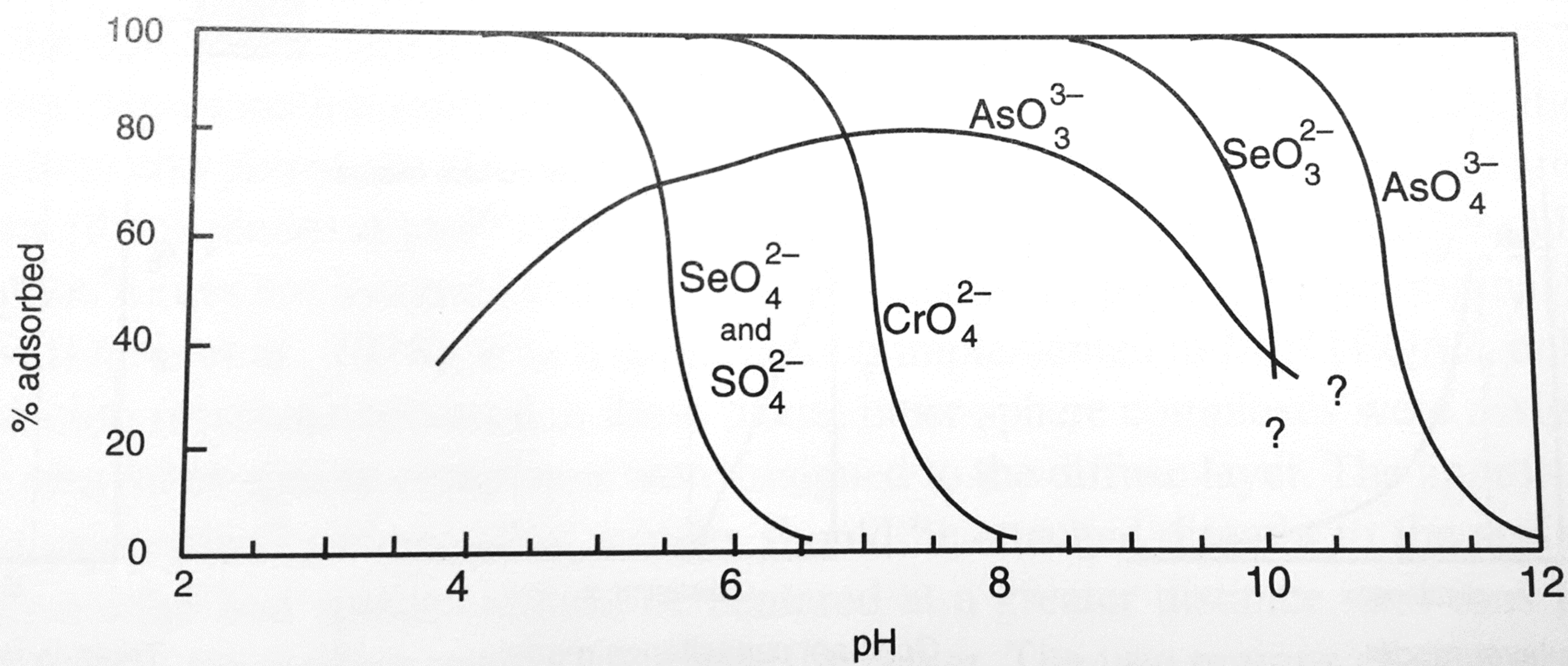
Adsorption of cations (M^{2+}) on ferric oxide



Surface chemistry and adsorption

Anion adsorption: Anions (e.g., L^-) compete with OH^- for binding sites

Adsorption of anions (L^-) on ferric oxide



Solute charge can vary as a function of pH:

$$H_3AsO_4 \rightarrow H_2AsO_4^{-} \rightarrow HAsO_4^{2-} \rightarrow AsO_4^{3-}$$