



Wastewater Design - Granular Activated Carbon Systems

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Module 1: Introduction to Adsorption Processes

Learning Objectives

By the end of this section, you will be able to:

- **Define** the fundamental thermodynamic principles governing adsorption, including the distinction between physisorption and chemisorption.
- **Differentiate** between adsorption, absorption, and sorption in the context of water treatment.
- **Select** appropriate adsorbents (activated carbon, oxidic adsorbents, etc.) based on specific water treatment objectives.
- **Analyze** the mechanisms of natural attenuation (geosorption) in bank filtration and groundwater recharge.

Executive Summary: Adsorption is a surface-based phase transfer process governed by thermodynamics. It is generally an exothermic process ($\Delta H < 0$) resulting in a decrease in entropy ($\Delta S < 0$). Success in water treatment design relies on understanding the interplay between the adsorption equilibrium (capacity), kinetics (rate), and dynamics (column performance), whether utilizing engineered adsorbents like GAC or natural geosorbents in bank filtration.

Basic Concepts and Definitions

Adsorption as a Surface Process

Adsorption is the enrichment of chemical species from a fluid phase (gas or liquid) onto the surface of a liquid or solid. In water treatment, this is a primary method for removing solutes by binding molecules or ions to solid surfaces characterized by active, energy-rich sites.

Key Definitions

- **Adsorbent:** The solid material providing the surface.
- **Adsorbate:** The species being absorbed.
- **Desorption:** The reverse process where adsorbed species are released back into the liquid phase due to changes in conditions (e.g., pH, temperature, concentration).

Engineered adsorbents are typically highly porous with internal surface areas ranging from **100 to 1,000 m²/g**. The external surface area is often negligible (e.g., $< 1 \text{ m}^2/\text{g}$ for powdered activated carbon).

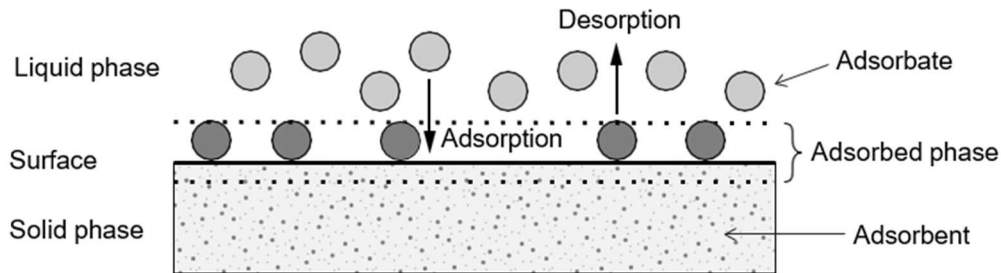


Figure 1.1: Basic terms of adsorption.

Thermodynamic Considerations

The state of the system is described by the Gibbs free energy (G). In surface processes, G is a function of temperature (T), pressure (p), composition (n_i), and surface area (A).

Equation 1:1

$$dG = -S dT + V dp + \sum_i \mu_i dn_i + \sigma dA$$

Where:

- S = Entropy
- V = Volume
- μ = Chemical potential
- σ = Surface free energy (surface tension)

The surface free energy (σ) is defined as the partial derivative of Gibbs free energy with respect to surface area at constant temperature, pressure, and composition.

Equation 1:2

$$\sigma_{ws} - \sigma_{as} = \pi > 0$$

When adsorption occurs, the surface tension at the water-solid interface (σ_{ws}) reduces to the value at the adsorbate solution-solid interface (σ_{as}). This difference is the spreading pressure (π).

Equation 1:3

$$\sigma_{ws} - \sigma_{as} = \pi > 0$$

Heat of Adsorption


For adsorption to occur spontaneously, the change in free energy (ΔG_{ads}) must be negative.

Equation 1:4

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T * \Delta S_{\text{ads}} < 0$$

Entropy (ΔS_{ads}): Typically negative ($\Delta S_{\text{ads}} < 0$) because immobilizing the adsorbate decreases disorder.

Enthalpy (ΔH_{ads}): Since ΔH_{ads} must be negative and the $-\Delta S_{\text{ads}}$ term is positive, the enthalpy change (ΔH_{ads}) must be negative. Therefore, adsorption is an exothermic process.

 **Design Tip:** Because adsorption is exothermic, adsorption capacity generally decreases as water temperature increases.

Types of Adsorptions

1. **Physisorption (Physical Adsorption):** Caused by weak van der Waals forces. Adsorption enthalpy is typically < 50 kJ/mol.
2. **Chemisorption (Chemical Adsorption):** Based on chemical reactions between adsorbate and surface sites. Interaction energies are > 50 kJ/mol.

Adsorption vs. Absorption vs. Sorption

- **Adsorption:** Enrichment on the surface.
- **Absorption:** Transfer of a substance from one bulk phase to another bulk phase (enrichment *within* the phase).
- **Sorption:** A general term used when distinguishing between adsorption and absorption is difficult, particularly in natural systems involving soils, sediments, or aquifers (geosorbents). It also covers ion exchange.

Describing Adsorption Processes

While surface concentration (Γ , mol/m²) is theoretically sound, practical engineering uses adsorbent loading (q) because adsorbent mass is easier to measure than surface area

Equation 1:6

$$q = n_a / m_A$$

Where:

- q = Adsorbent loading (mass adsorbed / mass adsorbent)
- n_a = Adsorbed amount
- m_A = Adsorbent mass

The Three Pillars of Adsorption Theory

1. **Equilibrium:** Dependence of loading on concentration and temperature ($q = f(c, T)$). At constant temperature, this is the Adsorption Isotherm.
2. **Kinetics:** Time dependence of the process ($q = f(t)$). Rate is typically limited by mass transfer.
3. **Dynamics:** Spatiotemporal dependence in fixed-bed adsorbers ($q = f(t, z)$).

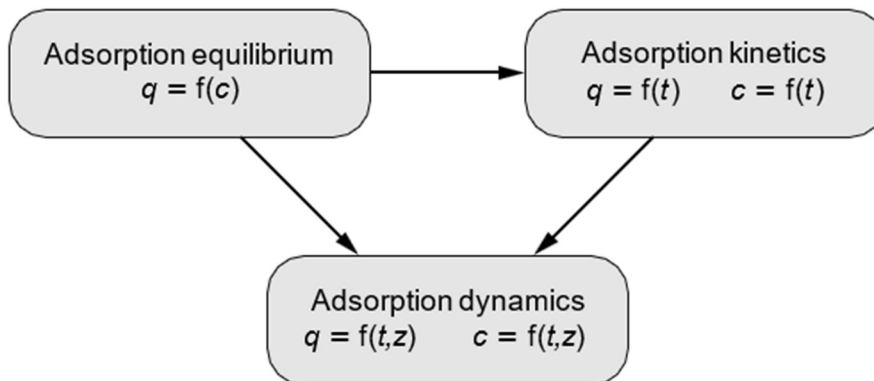


Figure 1.2: Elements of the adsorption theory.

Engineered Adsorption Processes

Adsorption is versatile in water treatment, removing both organic substances and inorganic ions.

Overview of Applications

Table 1.1: Adsorption processes in water treatment

Application field	Objective	Adsorbent
Drinking water treatment	Removal of dissolved organic matter	Activated carbon
	Removal of organic micropollutants	Activated carbon
	Removal of arsenic	Aluminum oxide, iron hydroxide
Urban wastewater treatment	Removal of phosphate	Aluminum oxide, iron hydroxide
	Removal of micropollutants	Activated carbon
Industrial wastewater treatment	Removal or recycling of specific chemicals	Activated carbon, polymeric adsorbents
Swimming-pool water treatment	Removal of organic substances	Activated carbon
Groundwater remediation	Removal of organic substances	Activated carbon
Treatment of landfill leachate	Removal of organic substances	Activated carbon
Aquarium water treatment	Removal of organic substances	Activated carbon

Specific Treatment Applications

Drinking Water

Activated carbon has been used for nearly 100 years, initially for taste and odor, and now for micropollutants (pesticides, pharmaceuticals).

- **Competition:** Natural Organic Matter (NOM) competes with micropollutants for sites, reducing capacity.
- **DBP Control:** Removing NOM reduces the formation of Disinfection By-Products (DBPs).
- **Arsenic:** To meet WHO limits (10 µg/L), oxidic adsorbents like ferric hydroxide or aluminum oxide are used.

Wastewater

- **Tertiary Treatment:** Adsorption removes nutrients (phosphate) and persistent micropollutants not degraded by activated sludge.
- **Phosphate Recycling:** Phosphate adsorbed onto oxides can potentially be recycled for fertilizer.



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