Lecture 10: Chemical Removal - Adsorption and Ion Exchange

Definitions:

Adsorption - 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

Adsorbent - adsorbing phase

Adsorbate - chemical being adsorbed

Adsorption is used in drinking water treatment to remove organic contaminants:
- taste and odor-causing chemicals
- synthetic organic chemicals
- color forming organics
- some disinfection by-product precursors (but not THMs)

Adsorbent of choice is activated carbon

Made in two-step process:

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

2. Carbonized material is exposed to steam or hot CO₂ to cause pores and fissures to form (activation)

1. Creates carbon to which organic chems will sorb,
2. Increases surface area available for sorption
Figure by MIT OCW.

Adsorption depends on properties of activated carbon, chemistry of adsorbate, pH and temp. of water — each application requires development of adsorption isotherm.

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

Some bonding is chemical and is generally irreversible.

Adsorption process is quantified via an adsorption isotherm which can take multiple forms.

Isotherm relates $q_A$ to $C_A$.

$$q_A = \text{solid phase conc} = \frac{\text{mass of absorbate}}{\text{mass of absorbent}} = x$$

in $\text{R/R}$

$$C_A = \text{liquid phase conc of absorbate}$$

Very simplest is linear isotherm:

$$q_A = K_d C_A = K C e \text{ in } \text{R/R}$$

$$K_d = \text{partition coeff} \quad \frac{\text{mg/kg}}{\text{mg/L}} = \frac{L}{\text{kg}}$$
Another possible isotherm is the Langmuir

Assumes reaction:

$$S_v + A \underset{\text{adsorbate bound to absorbent site (mol)}}{\overset{\text{adsorbate in solution (mol/mL solution)}}{\rightleftharpoons}} S \cdot A$$

vacant adsorption site on absorbent

in mol/L absorbent

At equilibrium

$$K_{ad} = \frac{[S \cdot A]}{[S_v][A]}$$

in L/mg

K_{ad} in mg/L

Consider total number of sites to be fixed:

$$S_T = [S_v] + [S \cdot A]$$

(moles/m²)

$$S_T = \frac{[S \cdot A]}{K_{ad} [A]} + [S \cdot A]$$

Solve for [S \cdot A] and use $C_A = [A]$

$$[S \cdot A] = \frac{S_T}{1 + 1/K_{ad} C_A} = \frac{K_{ad} C_A S_T}{1 + K_{ad} C_A}$$

Need expression for $q_A$, mg adsorbate/g adsorbent

$$q_A = \frac{[S \cdot A] \cdot A_{ad} \cdot M_{N_A}}{ \text{surface area per gm adsorbent}}$$

m²/g

molecular wt of adsorbate

$g$/mol
\[ q_A = [S \cdot A] \cdot A_{ad} \cdot MW_A \]

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

\( Q_M \) = max. adsorbent-phase conc of adsorbate, occurs when all sites (\( S_T \cdot A_{ad} \)) are saturated with adsorbate

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

\( \frac{C_A}{q_A} \) plots as straight line vs. \( C_A \)

slope = \( \frac{1}{Q_M} \)

intercept = \( \frac{1}{K_{ad} \cdot Q_M} \)
Another alternative isotherm is BET (Brunauer-Emmett-Teller) which assumes several molecular layers involved.

\[
\frac{q_A}{q_M} = \frac{B_A c_A}{(c_{SA} - c_A)[1 + (B_A - 1)(c_A/c_{SA})]}
\]

- \(q_A\): equilibrium adsorbate/adsorbent conc
- \(q_M\): max \(q_A\) at saturation
- \(c_A\): equilibrium aqueous conc
- \(c_{SA}\): saturation \(c_A\)

\[
B_A = \frac{k_{1,ad}}{k_{2,ad}} = \text{eq. const for first layer}
\]
\[
\frac{k_{1,ad}}{k_{2,ad}} = \text{eq. const for subsequent layers}
\]

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.
Isotherms are found by doing lab tests

Mass of carbon put in bottle (M)

Volume of water & w/contaminant conc C₀ added

Tumbled gently for 6 days to get equilibrium

Equilibrium $C_A$ in water measured

Compute $q_A = \frac{V}{M} (C₀ - C_A)$

Plot $q_A$ vs $C_A$ on log-log graph

If Freundlich isotherm applies plot will be linear:

Get $n$ from slope

Substitute to solve for $K_A$

Tests are often done by carbon manufacturers (e.g., Calgon carbon)
Freundlich Isotherm

\[ q_a = K_F C_A^{1/n} \]

if \( q_a \) is \( \frac{mg}{kg} \)

\( C_A \) is \( \frac{mg}{L} \)

then \( K_F \) is in units of \( \frac{\left( \frac{mg}{kg} \right)}{\left( \frac{mg}{L} \right)^{1/n}} \)

Example: Assume \( 1/n = 1/3 \)

If \( q_a \) is \( \frac{mg}{kg} \)

and \( C_A \) is \( \frac{mg}{L} \) (1000x larger than above)

what is conversion factor for \( K_F \) to units above?

\[ \frac{\left( \frac{mg}{kg} \right)}{\left( \frac{mg}{L} \right)^{1/n}} \cdot \frac{\left( \frac{mg}{L} \right)^{1/n}}{\left( \frac{mg}{L} \right)^{1/n}} = \frac{\left( \frac{mg}{kg} \right)}{\left( \frac{mg}{L} \right)^{1/n}} \]

\[ \downarrow \]

\[ \left( \frac{mg}{(mg)} \right)^{1/n} = 1000^{1/3} = 10 \]
Activated carbon comes in two main forms:

PAC - powdered activated carbon (\(\approx 24\ \mu m\)) which is suspended in water/wastewater 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 "breaks through".

\[ C_0 \quad \downarrow \quad C_0 \quad \text{spent carbon (i.e. saturated with chemical)} \]
\[ \text{adsorption zone} \]

\[ C_{out} \quad \downarrow \quad C_B \]

\( C_B \) is based on regulatory std. breakthrough

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

Figure by MIT OCW.
Granular activated carbon tanks at MMR

Typical Breakthrough Curve for Activated Carbon

Source: Metcalf & Eddy Inc.
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:

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

  Then operation resumes in reverse order, B then A.

  Continues until breakthrough at B.

Second tank is essentially always "fresh", acts as backup to ensure fully treated water even when there is premature breakthrough.
Spent carbon can be sent back to manufacturer for regeneration - heat treatment to remove adsorbed organics.

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/wastewater and used to predict breakthrough volume $V_B$ for certain mass of GAC, $M_{GAC}$.

$$\text{carbon usage rate} = \frac{M_{GAC}}{V_B} = \text{CUR}$$

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.
Ion exchange.

Similar in many ways to adsorption treatment, but chemical mechanism is ion exchange rather than adsorption.

An ion exchanger is a material to which certain ions are sorbed in exchange for ions already bound to exchanger.

For example: water can be softened by an ion exchanger that adsorbs Ca and Mg, releasing Na in exchange. Zeolite is a natural mineral that softens water by ion exchange.

Reaction looks like:

\[
\begin{align*}
\text{Ca}^{12+} + 2\text{Na} \cdot \text{Ex} & \rightleftharpoons \text{Ca} \cdot \text{Ex}_2 + 2\text{Na}^+ \\
\text{Mg}^{12+} + 2\text{Na} \cdot \text{Ex} & \rightleftharpoons \text{Mg} \cdot \text{Ex}_2 + 2\text{Na}^+ \\
\text{exchanger} & \quad \text{solid}
\end{align*}
\]

Exchanger is regenersted using strong brine:

\[
\begin{align*}
\text{Ca} \cdot \text{Ex}_2 + 2\text{Na}^+ & \xrightarrow{\text{strong brine}} 2\text{Na} \cdot \text{Ex} + \text{Ca}^{12+} \\
\text{Mg} \cdot \text{Ex}_2 + 2\text{Na}^+ & \xrightarrow{\text{strong brine}} 2\text{Na} \cdot \text{Ex} + \text{Mg}^{12+}
\end{align*}
\]
Most exchangers are now synthetic resins

\[ \begin{align*}
\text{e.g.} & \quad -\text{CH}_2-\text{CH} - \text{CH}_2 - \text{CH} - \ldots \\
 & \quad \text{sulfonic group } -\text{SO}_3\text{H} \text{ is an ion exchanger} \\
 & \quad \text{H}^+ \text{ swaps with cations}
\end{align*} \]

Preference series shows which ions exchange:

\[ \begin{align*}
\text{Ba}^{2+} & > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \\
\text{Cu}^{2+} & > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Ag}^{2+} > \\
\text{Cs}^+ & > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{H}^+
\end{align*} \]

For strong acid resins (e.g. sulfonates with \(-\text{SO}_3\text{H}\) group)

More preferred ions are swapped for less preferred — e.g. \text{Ca}^{2+} for \text{H}^+

For anion exchangers (use carboxylic group \(-\text{COOH}\))

\[ \begin{align*}
\text{SO}_4^{2-} & > \text{I}^- > \text{NO}_3^- > \text{CrO}_4^{2-} > \text{Br}^- > \\
\text{Cl}^- & > \text{OH}^-
\end{align*} \]

(Preference varies with the resin)
Design

Design procedure and treatment systems are very similar to those for activated carbon.

Bench-scale column tests are used to develop curves of breakthrough (C vs. t).

Resin is generally placed in pressure tanks similar to those for GAC.

Overflow rates = 6-8 gpm/ft².
Iron and manganese removal

Iron II ($Fe^{2+}$) and Manganese II ($Mn^{2+}$) exist in acidic and reducing environments (e.g. wetlands and in aquifers below wetlands) – see Eh-pH diagrams pp. 14-15.

$Fe^{2+}$ and $Mn^{2+}$ are soluble and remain in water following conventional treatment but precipitate at the point of use, causing stains on plumbing fixtures and in laundry.
Also support growth of iron bacteria (iron slime) in well screens, distribution systems.

$Fe$ and $Mn$ can be addressed in variety of ways:

1. In-situ treatment – injection wells around water supply wells to precipitate $Fe$ and $Mn$ in the ground

2. Sequestration – phosphate chemicals added to water to bind with and "sequester" $Fe$ and $Mn$, preventing later precip

3. Ion exchange treatment with Greensand (glauconite) – Natural ion exchanger with $Fe$ and $Mn$

Removal reaction:

$$E - MnO_2 + \{ Fe^{2+} \}_{Mn^{2+}} \rightarrow E - Mn_2O_3 + \{ Mn^{2+} \}_{Mn^{4+}}$$

$L$ Mn-coated glauconite

Regeneration with potassium permanganate

$$E - Mn_2O_3 + KMnO_4 \rightarrow E - MnO_2$$
Forms of Iron in Water as Function of Redox Potential Versus pH Constructed with Total Iron Activity $10^{-7}$ M or 5.6 μg/L, 96 mg/L SO$_4^{2-}$, CO$_2$ Species at 1000 mg/L HCO$_3^-$, Temperature at 25°C, and Pressure of 1 atm.

Figure by MIT OCW.
Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous.
Forms of Manganese in Water as Function of Redox Potential Versus pH at a Water Temperature of 25°C.

Figure by MIT OCW.

4. Oxidation

Goal is to oxidize Mn^{2+}, Fe^{2+} to get precipitates

Aeration (works for Fe, not for Mn)

\[ 2\text{Fe}^{2+} + 4\text{HCO}_3^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 s + 4\text{CO}_2 \]

Precipitated iron is then settled and filtered.

(most removal by filtration)

Chemical oxidation

Addition of strong oxidizer - chlorine or KMnO_4.

Precipitated iron settled and filtered

Reaction with permanganate:

\[ 3\text{Fe}^{2+} + 6\text{HCO}_3^- + \text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_3 s + \text{MnO}_2 + 3\text{KCO}_3 + 4\text{CO}_2 \]

\[ 3\text{Mn}^{2+} + 6\text{HCO}_3^- + 2\text{KMnO}_4 \rightarrow 5\text{MnO}_2 + 2\text{KCO}_3 + 2\text{H}_2\text{O} + 4\text{CO}_2 \]

5. Lime-soda ash softening

Fe and Mn removed during softening

If pH is raised above 9.8