

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 CO_2 to cause pores and fissures to form (activation)

1. Creates carbon to which organic chems will sorb,

2. Increases surface area available for sorption



Source: NIOSH, 2003. Guidance for Filtration and Air-Cleaning Systems to Protect Building Environments from Airborne Chemical, Biological, or Radiological Attacks. DHHS (NIOSH) Pub No. 2003-136. National Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio. April 2003. <http://www.cdc.gov/niosh/docs/2003-136/2003-136c.html>. Accessed February 21, 2006.

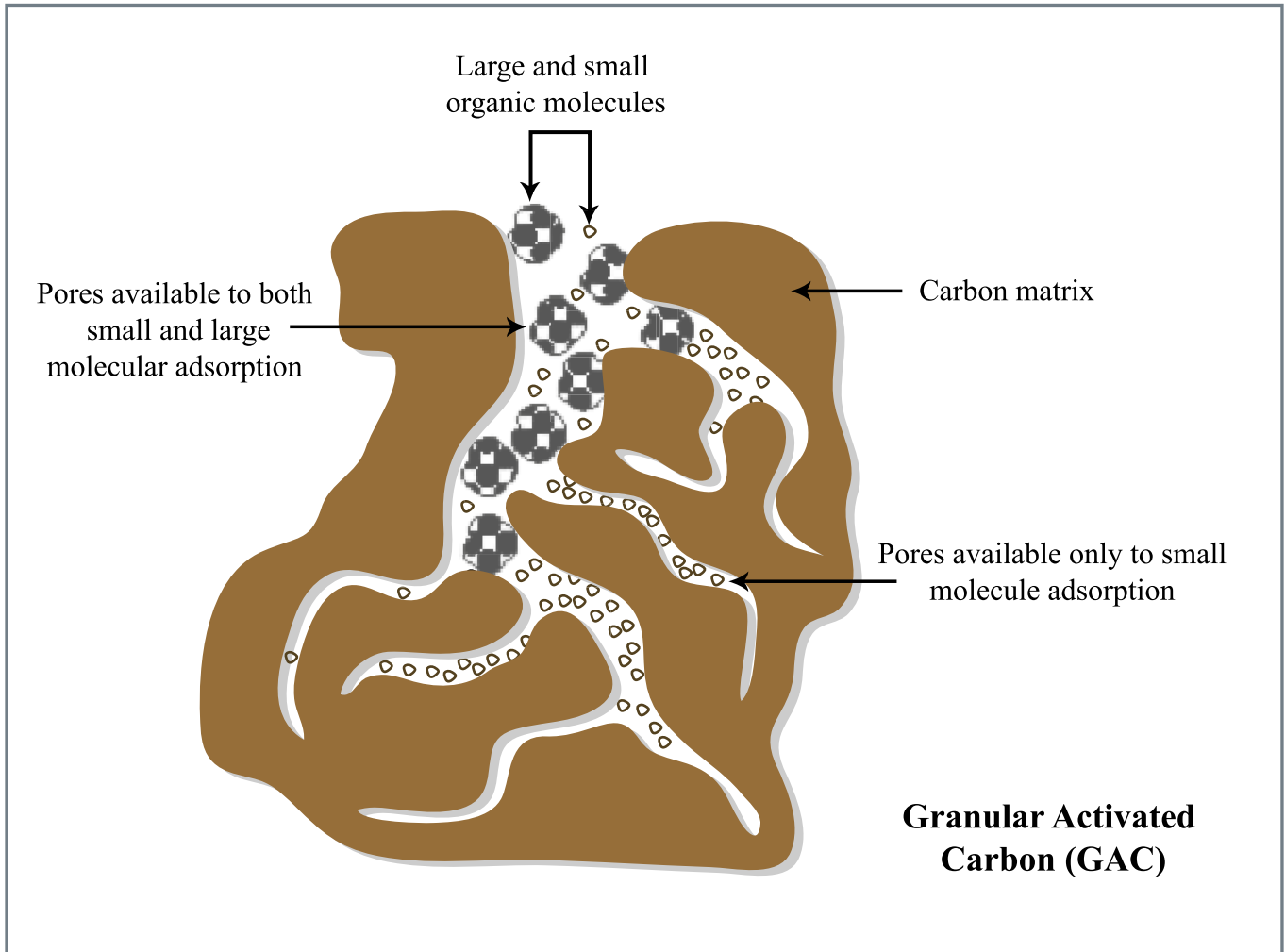


Figure by MIT OCW.

Adapted from Culp, G.L., and R.L. Culp. *New Concepts in Water Purification*. New York, NY: Van Nostrand Reinhold Co. 1974

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

$$q_A = \text{solid phase conc} = \frac{\text{mass of adsorbate}}{\text{mass of adsorbent}} = X \text{ in R/R}$$

C_A = liquid phase conc of adsorbate

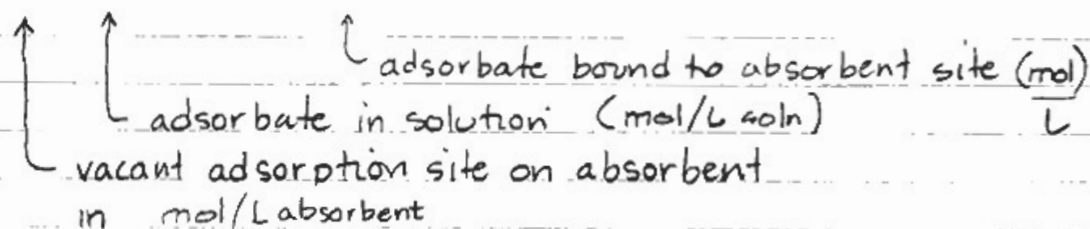
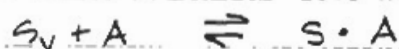
Very simplest is linear isotherm =

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

$$K_d = \text{partition coeff} \frac{\text{mg/kg}}{\text{mg/L}} = \frac{\text{L}}{\text{kg}}$$

Another possible isotherm is the Langmuir

Assumes reaction:



At equilibrium

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

K_{ad} in L/mg
 $[A]$ in mg/L

Consider total number of sites to be fixed:

$$S_T = [S_v] + [S \cdot A] \quad (\text{moles/m}^2)$$

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

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

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

\uparrow
 surface area
 per gm adsorbent
 m^2/g

\uparrow
 molecular wt of
 adsorbate
 g/mol

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

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

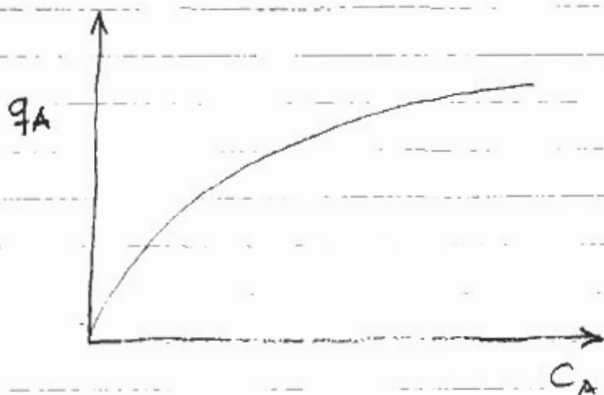
Q_M = max. adsorbent-phase conc of adsorbate, occurs when all sites ($S_T A_{ad}$) are saturated with adsorbate

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

$\frac{C_A}{q_A}$ plots as straight line vs C_A

slope = $1/Q_M$

intercept = $1/K_{ad} Q_M$



Another alternative isotherm is BET (Brunauer-Emmett-Teller) assumes several molecular layers involved

$$\frac{q_A}{Q_M} = \frac{B_A C_A}{(C_{S,A} - C_A) [1 + (B_A - 1)(C_A / C_{S,A})]}$$

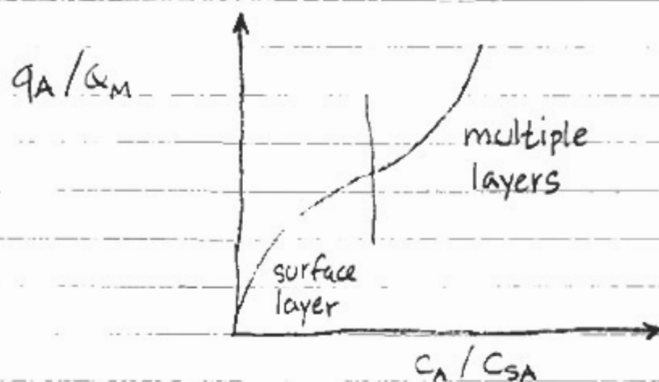
q_A equilibrium adsorbate/adsorbent conc

Q_M max q_A at saturation

C_A equilibrium aqueous conc

$C_{S,A}$ saturation C_A

$$B_A = \frac{K_{1,ad}}{K_{i,ad}} = \frac{\text{eq. const for first layer}}{\text{eq. const for subsequent layers}}$$



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 V w/contaminant conc C_0 added

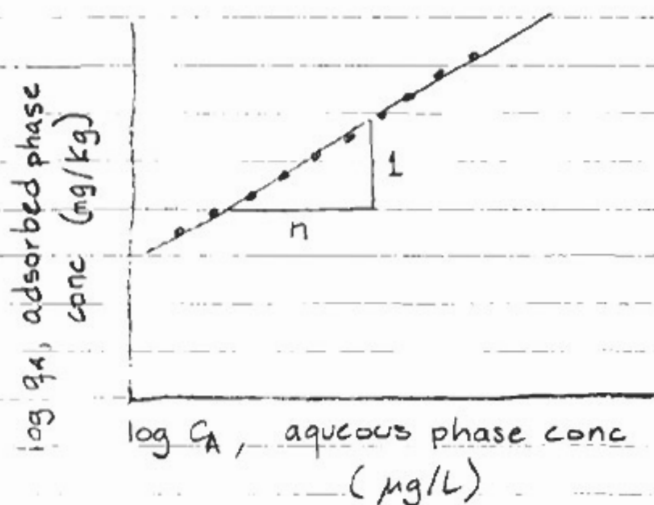
Tumbled gently for 6 days to get equilibrium

Equilibrium C_A in water measured

Compute $q_A = \frac{V}{M} (C_0 - C_A)$

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 $\frac{\text{mg}}{\text{kg}}$

C_A is $\frac{\mu\text{g}}{\text{L}}$

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

Example: Assume $1/n = 1/3$

If q_A is $\frac{\text{mg}}{\text{kg}}$

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

what is conversion factor for K_F to units above?

$$\frac{\left(\frac{\text{mg}}{\text{kg}}\right)}{\left(\frac{\text{mg}}{\text{L}}\right)^{1/n}} \cdot \frac{\left(\frac{\text{mg}}{\text{L}}\right)^{1/n}}{\left(\frac{\mu\text{g}}{\text{L}}\right)^{1/n}} = \frac{\left(\frac{\text{mg}}{\text{kg}}\right)}{\left(\frac{\mu\text{g}}{\text{L}}\right)^{1/n}}$$

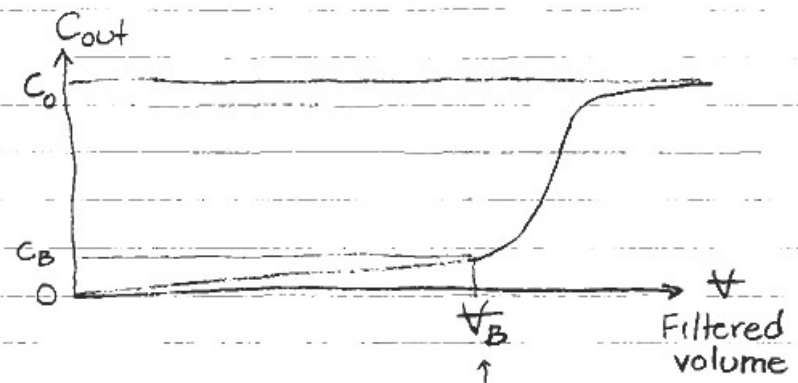
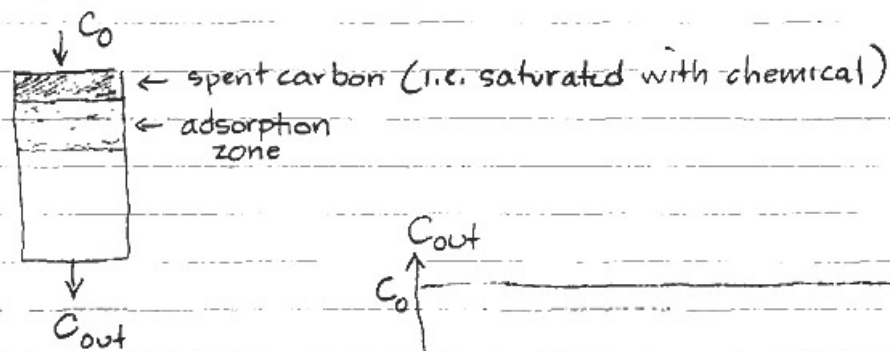
$$\uparrow = \left(\frac{\text{mg}}{\mu\text{g}}\right)^{1/n} = 1000^{1/3} = 10$$

Activated carbon comes in two main forms:

PAC - powdered activated carbon ($\approx 24 \mu\text{m}$)
 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_B is based on regulatory std.

breakthrough

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

GAC Tank

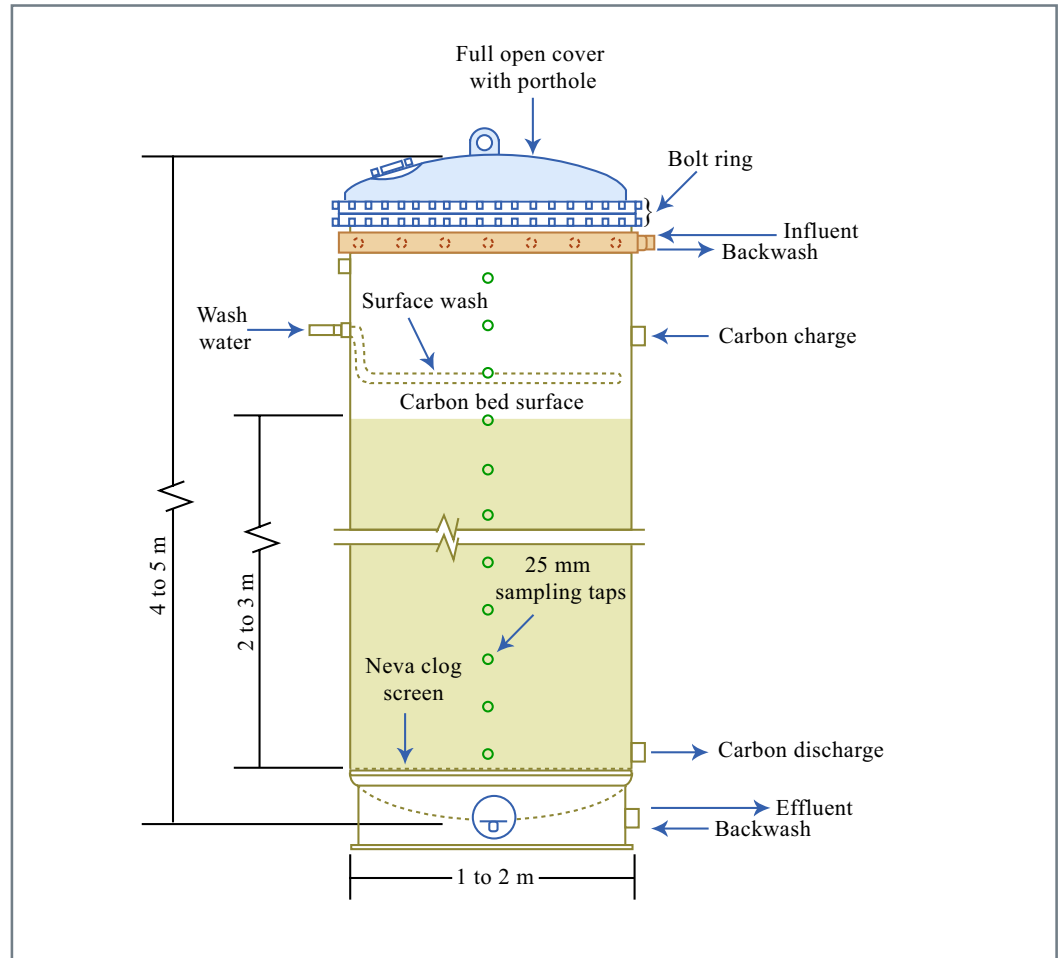


Figure by MIT OCW.
Source: Metcalf & Eddy Inc.
Wastewater Engineering: Treatment, Disposal, Reuse. McGraw-Hill, New York, 1979.

Granular activated carbon tanks at MMR



Source: MMR, undated. Extraction, treatment and reinjection. Air Force Center for Environmental Excellence, Installation Restoration Program, Massachusetts Military Reservation. <http://www.mmr.org/community/guide/extraction.htm>. Accessed March 7, 2004.

GAC Breakthrough

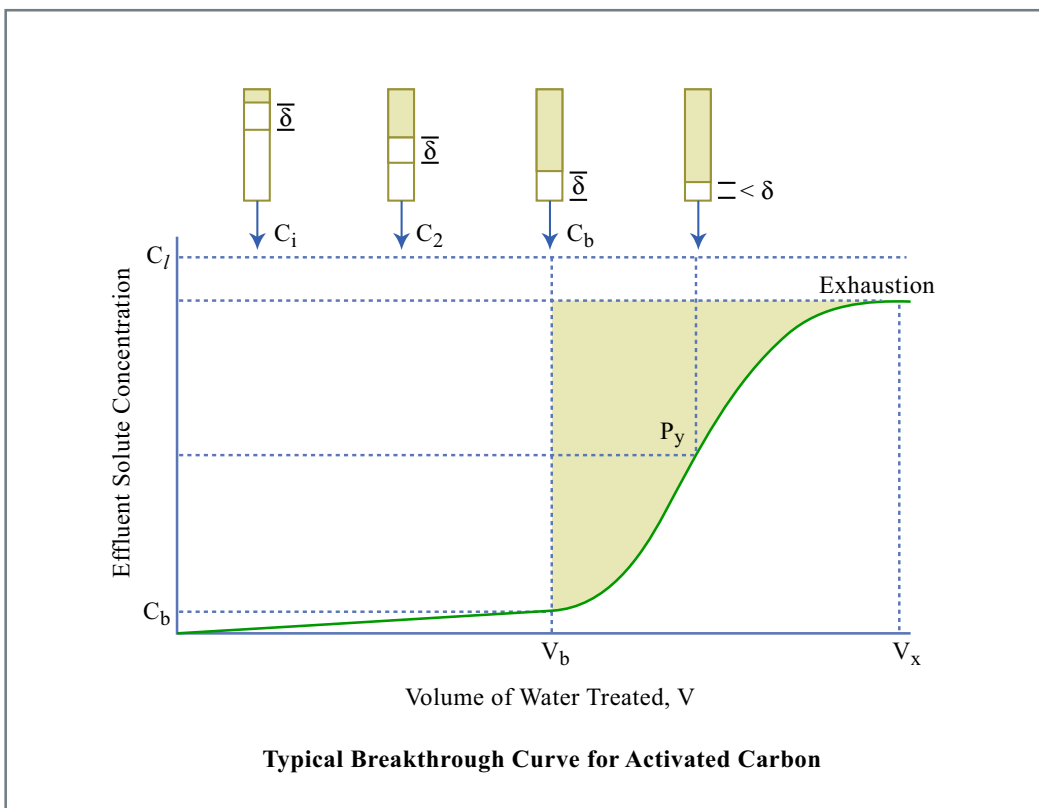
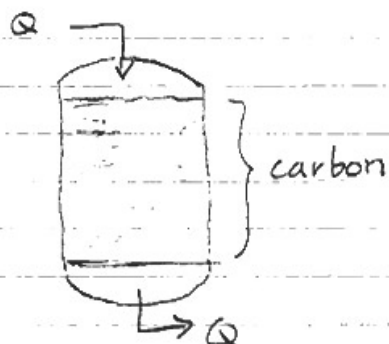


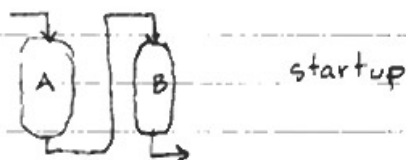
Figure 10 MIT W

Source: Metcalf & Eddy Inc.
Wastewater Engineering: Treatment, Disposal, Reuse. McGraw-Hill, New York, 1979.

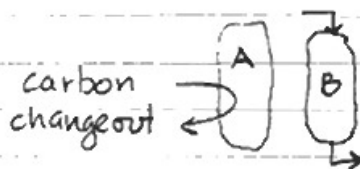
Carbon typically used in pressure vessels much like pressure filtration tanks:



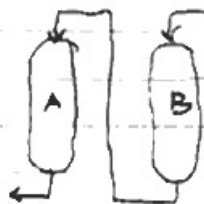
tanks are often placed in series with piping and valving to change order of tanks =



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}

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

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

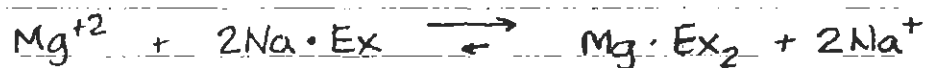
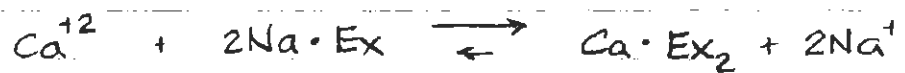
Similar in many ways to adsorption treatment, but chemical mechanism is ion exchange rather than adsorption.

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

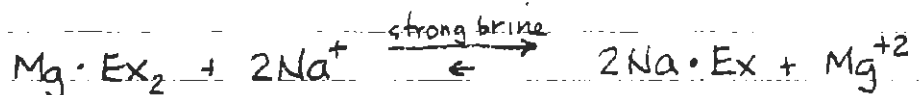
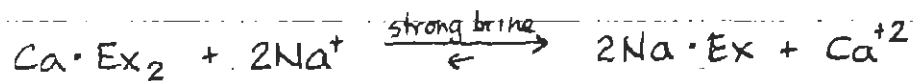
Zeolite is a natural mineral that softens water by ion exchange

Reaction looks like =

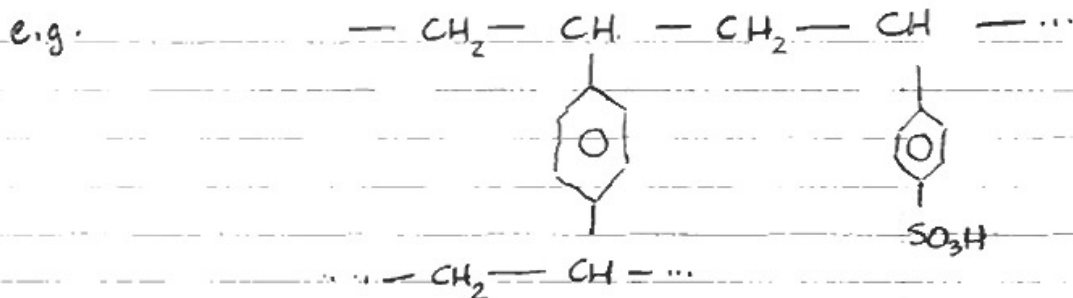


↑ exchanger
solid

Exchanger is regenerated using strong brine =



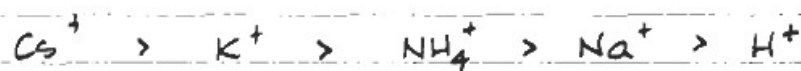
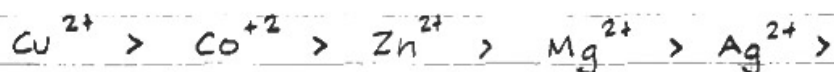
Most exchangers are now synthetic resins



sulfonic group $\text{--- SO}_3\text{H}$ is ion exchanger

H^+ swaps with cations

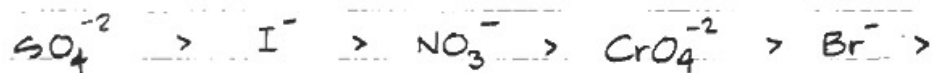
Preference series shows which ions exchange:



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

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

For anion exchangers (use carboxylic group --- COOH)



(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. V)

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

Overflow rates \sim 6-8 gpm/ft²

Iron and manganese removal

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

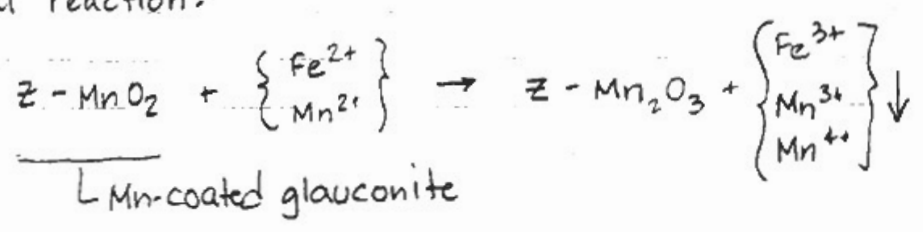
Fe^{2+} and Mn^{2+} are soluble and remain in water following conventional treatment but precipitate at the point of use, causing stains on plumbing fixtures and in laundry.

Also support growth of iron bacteria (iron slime) in well screens, distribution systems

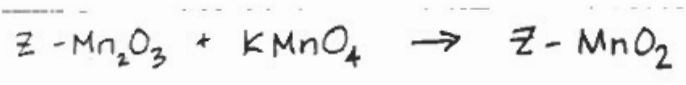
Fe and Mn can be addressed in variety of ways:

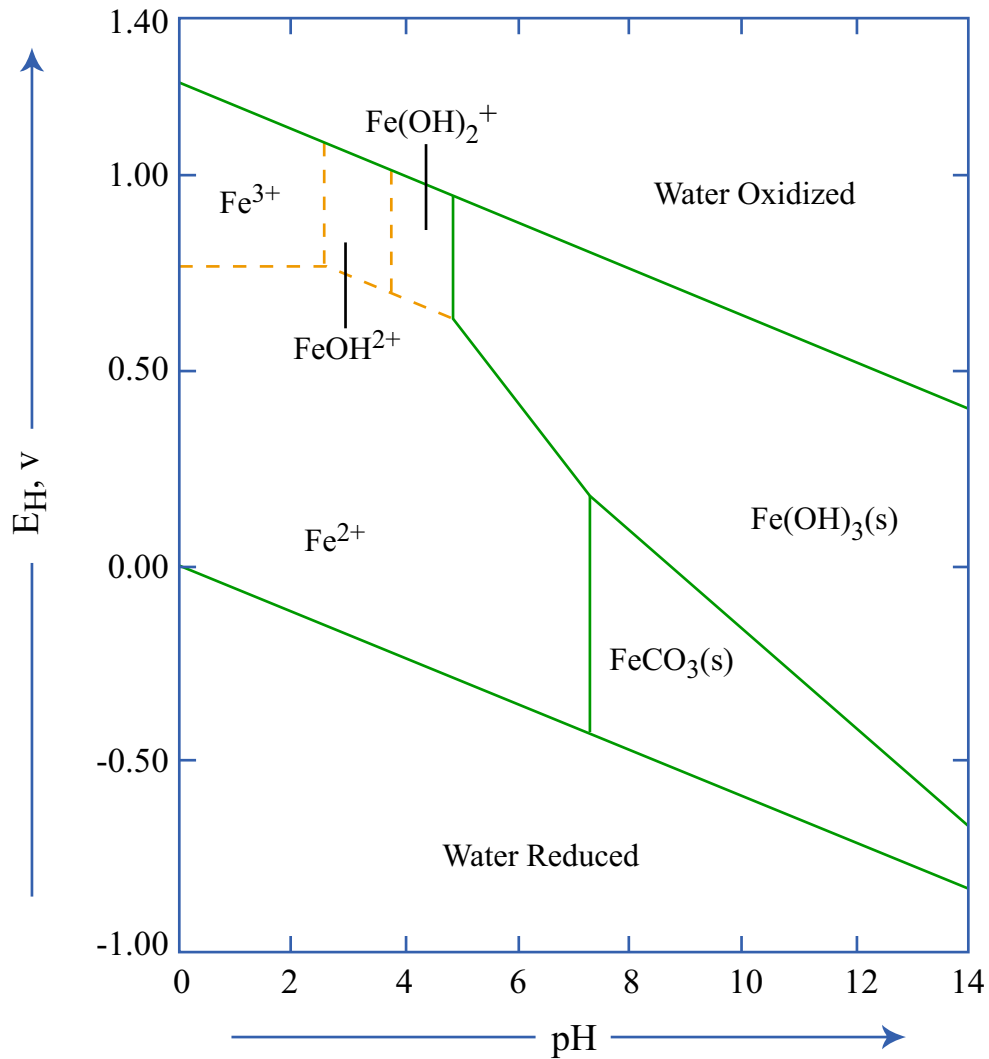
1. In-situ treatment - injection wells around water supply wells to precipitate Fe and Mn in the ground
2. Sequestration - phosphate chemicals added to water to bind with and "sequester" Fe and Mn, preventing later precip
3. Ion exchange treatment with Greensand (glauconite) - natural ion exchanger with Fe and Mn

Removal reaction:



Regeneration with potassium permanganate

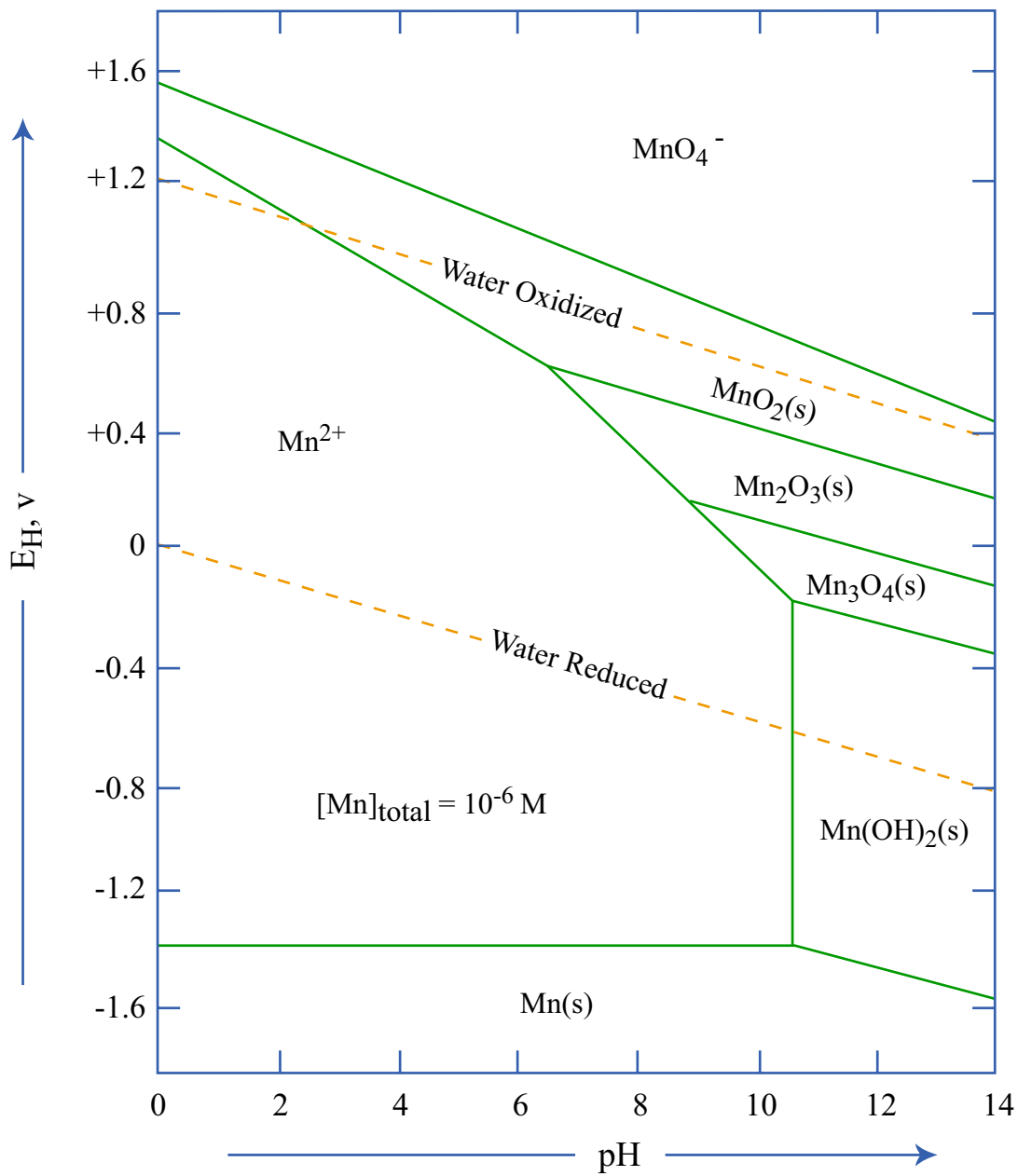




Forms of Iron in Water as Function of Redox Potential Versus pH Constructed with Total Iron Activity $10^{-7}M$ or $5.6 \mu g/L$, $96 mg/L SO_4^{2-}$, CO_2 Species at $1000 mg/L HCO_3^-$, Temperature at $25^\circ C$, and Pressure of 1 atm.

Figure by MIT OCW.

Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous. *Water Treatment: Principles and Design*. 2nd ed. Hoboken, NJ: John Wiley & Sons, 2005, p. 1571.



Forms of Manganese in Water as Function of Redox Potential Versus pH at a Water Temperature of 25°C.

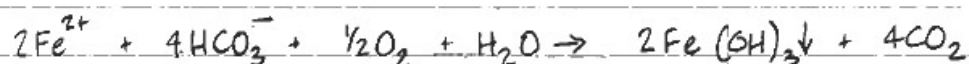
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4. Oxidation

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

Aeration (works for Fe, not for Mn)



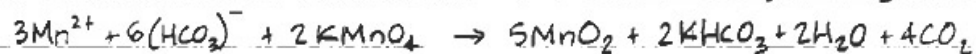
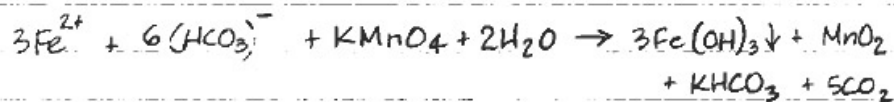
Precipitated iron is then settled and filtered
(most removal by filtration)

Chemical oxidation

Addition of strong oxidizer - chlorine
or $KMnO_4$

Precipitated iron settled and filtered

Reaction with permanganate =



5. Lime-soda ash softening

Fe and Mn removed during softening
if pH is raised above 9.8