

Chapter 12. Approaches to Hazardous Waste Minimization, Remediation, Treatment, and Disposal

1. Concepts of Waste Minimization and Pollution Prevention (p. 547)

- a) hazardous waste management (Fig. 12.1)
 - source reduction
 - volume reduction
 - recycling
 - treatment and disposal
- b) shift in paradigm
 - from "end-of-pipe treatment"
 - to "waste minimization (reduction)", "pollution prevention (P2)"

2. Concepts in Hazardous Waste Remediation and Treatment (p. 551)

- a) Ex situ and in situ processes
- b) removal or treatment of source materials
 - Fig. 12.5
- c) effect of sorption
 - sorbed contaminants are physically unavailable (but not always)
 - therefore, desorption rate limits the treatment efficiency
 - desorption rate is a function of a mass transfer coefficient and a concentration gradient

$$- \frac{dC}{dt} = K(C_s - C)$$

$$- \frac{dC}{dt}; \text{ contaminant degradation rate (mg/L-sec)}$$

K; a mass transfer coefficient (sec^{-1})

C_s : contaminant saturation conc. in aqueous phase (mg/L)

C; measured contaminant conc. (mg/L)

- two possible cases (Fig. 12.6)
 - . slowly desorbed contaminants
 - . slowly degraded contaminants
- rebound effect (Fig. 12.7)
 - . pump-and-treat system
 - . usually due to the presence of DNAPLs

3. Reactor Analysis Applied to Hazardous Waste Systems (p. 557)

4. Classification of Remediation and Treatment Processes (p. 560)

4.1. Sorption processes (p. 560)

- 1) Granular activated carbon (GAC)
 - a) an excellent sorbent
 - high surface area (1000-1400 m²/g)
 - hydrophobic surfaces
 - highly porous; macropores and micropores (Fig. 12.12 & Fig. 13.3)
 - b) gravity-flow GAC system (Fig. 12.13)

- 2) Ion exchange
 - a) usually for metal removal
 - b) types of exchange resins
 - for cation exchange; acidic resins (e.g., SO₃⁻, COO⁻)
 - for anion exchange; basic resins (e.g., NH₃⁺)

- 3) Stabilization
 - a) addition of materials to hazardous wastes -> less mobile and less toxic
 - b) stabilization; addition of reagents to reduce the potential contaminant migration and toxicity
 - c) solidification; modification of a liquid or slurry waste to a solid material by adding solids or other reagents
 - portland cement
 - organoclays
 - d) vitrification; melting and entrapment

- 4) Soil washing and thermal desorption
 - a) methods to enhance desorption
 - b) soil washing
 - ex situ process
 - generally use water-surfactant solution
 - . surfactant micelles sorb hydrophobic contaminants (Fig. 12.14)
 - need to collect and treat washed-out (desorbed) contaminants
 - . bioremediation or other transformation processes
 - soil flusing; in situ soil washing
 - c) thermal desorption
 - use heat (<550°C) to enhance desorption (and volatilization)
 - need to collect and treat the volatilized contaminants
 - . biofiltration or other transformation processes

4.2. Volatilization processes (p. 564)

- 1) Air stripping
 - a) effective for volatilized contaminants
 - remove ammonia, sulfur dioxide, hydrogen sulfide from water
 - b) not strippable compounds

- contaminants less volatile than water; dieldrin, benzo(a)pyrene,...
- highly water-soluble contaminants; acetone,...
- c) Henry's law constant is a good predictor
 - H' (dimensionless; H/RT) \geq 0.01 \rightarrow air stripping effective

2) Soil vapor extraction (SVE)

- a) widely used to remove VOCs from the vadose zone (Fig. 12.16)
- b) place a vacuum on the soil to promote the volatilization of contaminants
- c) need to collect and treat the volatilized contaminants
- d) important variables
 - soil permeability/porosity
 - contaminant volatility

4.3. Abiotic transformation processes (p. 567)

- hydrolysis, photolysis, oxidation-reduction
- Advanced Oxidation Processes (AOPs)
 - . ozone
 - . UV + ozone
 - . hydrogen peroxide + ozone
 - . UV + hydrogen peroxide
 - . Fenton's reagent (hydrogen peroxide + Fe²⁺)
 - . titanium dioxide-mediated photocatalysis
 - . "cost" is the primary disadvantage in AOPs

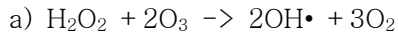
1) Reactants in AOPs

- a) major reactants; hydrogen peroxide, ozone, UV light
- b) hydrogen peroxide
 - relatively stable (stabilized form available also)
 - produces hydroxyl radicals
- c) ozone
 - unstable (must be generated on site)
 - reacts more slowly than hydroxyl radicals

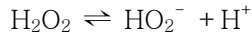
© oxidation mechanism by ozone

- direct reaction; O₃ directly oxidize organics
- indirect reaction; free radicals reaction (O₃ decomposes to hydroxyl radicals at higher pH, catalyzed by OH⁻)
 - $O_3 + OH^- \rightarrow O_3^- + OH\cdot$
 - $OH\cdot + RH \rightarrow R\cdot + H_2O$
 - $R\cdot + O_2 \rightarrow RO_2\cdot$
 - $RO_2\cdot + RH \rightarrow ROOH + R\cdot$

2) Hydrogen peroxide/ozone



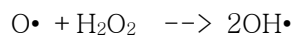
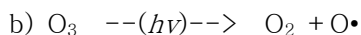
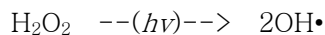
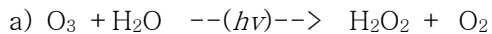
b) primary initiator of ozone decomposition; HO_2^- (hydroperoxide ion)



c) hydroperoxide ion reacts rapidly with ozone to produce hydroxyl radicals



3) UV/ozone



c) mechanism b) is predominant than mechanism a) since the photochemical decomposition of hydrogen peroxide is slow

© **Example 12.1**

4) Supercritical water oxidation

a) supercritical water

- generated at temperatures and pressures above the critical point (374.2°C and 218.4 atm)

- no phase boundary exists between liquid water and water vapor (a single phase with properties of both liquid water and water vapor)

b) supercritical water acts as an organic solvent

- organic contaminants are highly solubilized and partition into it

c) *"The same conditions that promote the formation of supercritical water also enhance the potential for molecular oxygen to oxidize organic contaminants"*

- thermodynamically, molecular oxygen can oxidize organics, but not easily observed because the reaction rate is too slow (kinetic reason)

- in supercritical water, kinetics of oxygen molecules become rapid, and most contaminants are oxidized within minutes

4.4. Biotic processes (p. 572)

1) In situ bioremediation (Fig. 12.19)

a) "microbial degradation is the major removal mechanism from the env."

b) by promoting microbial growth and metabolism

c) low cost, complete biodegradation (mineralization)

d) difficult to control, mass transfer limitation

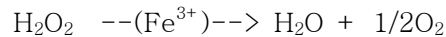
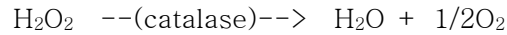
e) intrinsic bioremediation vs. engineered bioremediation

f) bioaugmentation; inoculates degrading microorganisms

g) biostimulation; provides nutrients (organics, inorganics)

h) terminal electron acceptor

- O₂ for aerobic, most common and efficient
- delivery through injection well
 - . compressed air, compressed pure oxygen, oxygenated water
 - . stabilized hydrogen peroxide



- i) in most cases, organic contaminants themselves are electron donors
- exception) for TCE treatment through cometabolism in groundwater

4.5. Bioventing (p. 574)

- a) a process similar to SVE, but different in many ways
- aerobic biodegradation (SVE is just a desorption process)
 - minimal contaminants emissions
- b) highly effective for hydrocarbons (e.g., BTEX), ineffective for highly oxidized contaminants such as PCE, PCBs

4.6. Landfarming (p. 575)

- bioremediation of surface soils
- develops a high microbial biomass by supplying nutrients and oxygen
- organic contaminants serve as the carbon and energy source

4.7. Thermal processes—incineration (p. 575)

- high operation and capital cost, but effective means
- incomplete burning → harmful chemicals (e.g., dioxins)

4.8. Other treatment operations and processes

- a) air sparging; in situ volatilization process, applied to groundwater
- b) phytoremediation; use vascular plants, applied to heavy metals, nitroaromatics (e.g., TNT),...
- c) Permeable Reactive Barrier (PRB)
- in situ process in groundwater
 - zero valent iron
- d) Monitored Natural Attenuation (MNA)
- intrinsic bioremediation
 - monitored by geochemical indicators
- e) treatment processes in series
- Example 12.2

5. Ultimate Disposal—Hazardous Waste Landfills (p. 578)

-The End-