Lecture 6 – Part 2

The Pollution and Purification of Water

(Chapter 14)

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Purification of Drinking Water

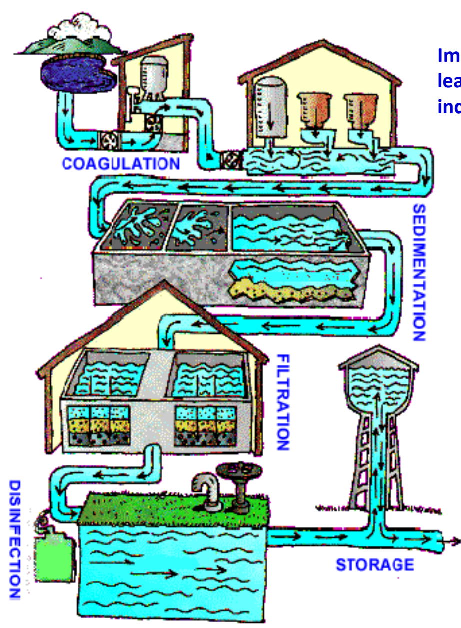

Image available at http://water.epa.gov/learn/kids/drinkingwater/watertreatmentplant_index.cfm

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Tour a municipal water and a wastewater treatment plant in seven minutes
by Wally Waterdrop

http://vimeo.com/1973831

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Steps involved in purification of drinking water

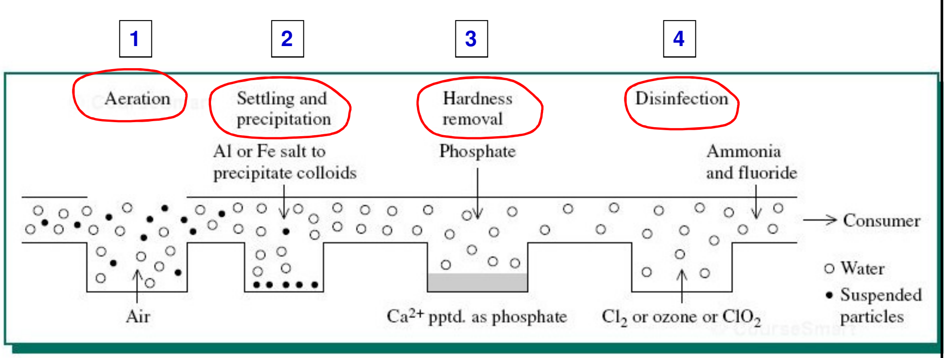

FIGURE 14-1 The common stages of purification of drinking water.

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Steps involved in water purification:

1. **Aeration** - involves bubbling of air

- Removes dissolved gases
  - Foul smelling H_2S and organosulfur
  - **VOCs**
- Oxidizes some organics to $CO_{2\,(g)}$
  - Could affect odor of water
- Oxidizes Fe^{2+} to insoluble Fe^{3+}, which is easier to remove

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Steps involved in water purification (*Cont.*):

2. **Coagulation and precipitation**

- Removes tiny suspended solids or colloids
- ***Alum*** (aluminum salt) or iron sulfate salt is added
  - Converts colloidal particles into a larger mass, which precipitate out

Settles faster

3. **Hardness removal**

- Only if water is excessively "hard," like calcareous water
  - Precipitates Ca^{2+}, Mg^{2+} and other M^{n+} ions that cause "hardness"

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Hardness removal – Cont.

Common removal processes:

- Precipitation of Ca^{2+} as $CaCO_{3\,(s)}$ and Mg^{2+} as $Mg(OH)_{2\,(s)}$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_{3\,(s)}$$

- Added as Na_2CO_3, or
- Produced from naturally present HCO_3^- through reaction with OH^-

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$$

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Hardness removal (Cont.)

- The added OH^- also precipitates Mg^{2+}

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_{2\,(s)}$$

Problem 14-1, p. 465. Ironically, Ca^{2+} is often removed from water by adding hydroxide ion in the form of $Ca(OH)_2$. Deduce a balanced chemical equation for the reaction of $Ca(OH)_2$ with dissolved calcium bicarbonate, $Ca(HCO_3)_2$, to produce insoluble calcium carbonate. What molar ratio of $Ca(OH)_2$ to dissolved calcium should be added to ensure that almost all the calcium is precipitated.

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Steps involved in water purification *(Cont.)*:

4. **Disinfection**

- Elimination of microorganisms that can cause sickness (i.e. pathogenic)
- These pathogens are present in raw water due to contamination by human and animal ***feces***

Examples of these pathogens include:

Bacteria, such as *Salmonella* (causes ***typhoid***) - includes *E. coli* O1567:H17

Can cause death

Viruses, including those that cause ***polio*** and ***hepatitis-A***

Protozoans, including *Crystoporidium* and *Giardia lambia* (can cause ***diarrhea***; ***death***)

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Disinfection (Cont.)

Common disinfection methods

1. **Chemical methods** - use of chlorine (as hypochlorous acid, HOCl, or chlorine dioxide gas, ClO_2) or ozone, O_3 (pp. 616-617)
2. **Irradiation with UV light** (pp. 609-610)
3. **Filtration** - using membrane technology (pp. 606-609)

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Chemical disinfection methods

(1) Chlorination => using hypochlorous acid, HOCl

- Most common disinfection method in North America

Surface water (~ 50 % of U.S. population)

Groundwater (~ 25 % of U.S. population)

- How does HOCl disinfect water?
  - HOCl is a small, weak acid molecule --- could pass through cell membranes
  - Once inside, HOCl ***oxidizes*** biochemical species, causing the cell to burst

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How is HOCl generated?

- HOCl is formed by dissolving chlorine (Cl_2) gas in water

$$Cl_{2\,(g)} + H_2O \rightleftharpoons HOCl_{(aq)} + H^+$$

Chlorine gas **Hypochlorous acid**

  - At moderate pHs, the forward reaction is favored (more HOCl produced)

- NOTE: For disinfecting swimming pools, the source of HOCl is calcium hypochlorite, $Ca(OCl)_2$, or sodium hypochlorite, NaOCl, not Cl_2 gas. WHY?
  - Read page 612. In addition answer the question "Why is pH control of water important in swimming pools?"

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Chlorination

Advantages

- Effective
- Relatively inexpensive
- Long-lasting (if a small excess of HOCl is added)

  Protects water from subsequent bacterial contamination

Disadvantages

- Formation of chlorinated organic compounds (as disinfection by-products)

  Some are toxic; probable human carcinogens

  Ex. Chloroform, $CHCl_3$, a suspected carcinogen; Other trihalomethanes, THMs

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Chemical disinfection methods (Cont.)

(2) Disinfection with **Ozone (O_3) or Chlorine Dioxide (ClO_2)**

- Both gases have to be generated on-site. WHY?

  O_3 is short-lived (Cannot be stored)

  ClO_2 is explosive at high levels (Cannot be stored either)

- O_3 is generated by passing *electrical discharge* through dry air

Generation of ozone:

$$2O_{2\,(g)} \xrightarrow{\text{20,000 volts}} O_{3(g)} + O_{(g)}$$

- ClO_2 is generated from the oxidation of aqueous sodium chlorite, $NaClO_2$

Generation of chlorine dioxide:

$$ClO_2^-{}_{(aq)} \longrightarrow ClO_{2(aq)} + e^-$$

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Disinfection with O_3 or ClO_2

Advantages

- Effective
- ClO_2 produces less chlorinated organic by-products than chlorination

Disadvantages

- Not as long-lasting as HOCl = need for more frequent disinfection
- More costly than chlorination. WHY?
  - Frequent disinfection also adds to the cost
  - Both O_3 and ClO_2 have to be generated on-site (= added cost)

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Disadvantages – Cont.

- Also produces disinfection by-products, such as ***formaldehyde*** (toxic) and ***bromate ions*** (probable human carcinogen)

From reactions of O_3 with naturally-occurring Br^- ions

From oxidation of organics by O_3

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Common disinfection methods (Cont.)

(3) Disinfection by **Irradiation with Ultraviolet (UV) Light**

- Use of lamps containing **mercury** (Hg) vapor

Immersed in water

Emits UV-C (~254 nm), which disrupts microorganism's DNA

↓

No replication

↓

Inactive cells

- 10 s irradiation kills pathogenic microorganisms, including *Cryptosporidium*, which can be resistant to chlorination

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Disinfection by Irradiation with Ultraviolet (UV) Light

Advantages

- Technology can be employed in small units (to serve small population bases)
- Gets rid of microorganisms that are resistant to chlorination

Disadvantages

- Effectiveness is reduced by the presence of the following, which absorb or scatter UV light:

Reduces amount available for disinfection

- Dissolved iron (Fe^{2+})
- Humic substances
- Suspended solids

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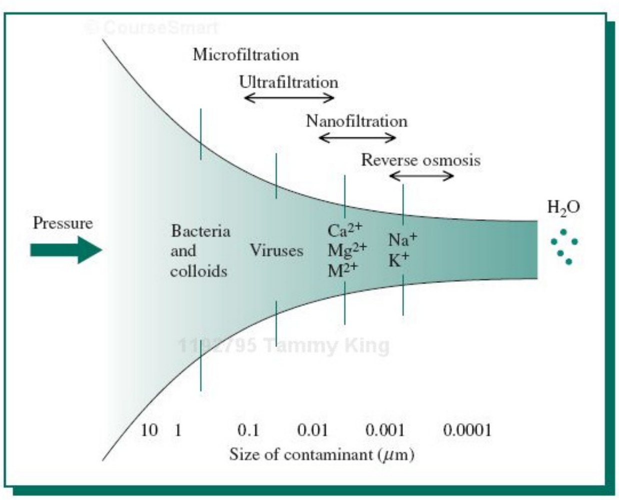
Common disinfection methods (Cont.)

(4) Disinfection by ***Membrane Technology***

- A membrane is a semi-permeable material that contains tiny individual holes (called *pores*)
- These microscopic pores are of uniform size
- A membrane works by acting as a barrier, trapping contaminants whose ***size is bigger than the pore size***
  - Ions
  - Molecules
  - Viruses
  - Bacteria

Disinfection by Membrane Technology (Cont.)

Figure 14-2. Filtration of contaminants by various methods



➢ Application of pressure forces the water through the membrane, leaving behind particles larger than the pore size

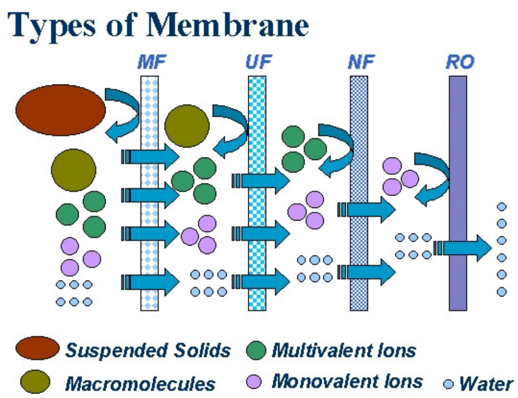


Image available at http://www.yale.edu/env/elimelech/index_research.htm

Membrane Technology (Cont.)

Recall from Figure 14-2 the ***range of sizes of various contaminants in water***:

Bacteria & colloids > Viruses > Small molecules > Large ions > Small ions

Membrane filtration techniques based on pore size: (Recall that smaller pore size = better filtration efficiency)

Microfiltration > Ultrafiltration > Nanofiltration > Hyperfiltration (or Reverse Osmosis, RO)

Microfiltration	Ultrafiltration	Nanofiltration	Hyperfiltration
Removes bacteria & colloids	**Also removes viruses**	**Also removes large ions**	**Removes all of the above**

Membrane Technology (Cont.)

Reverse Osmosis, RO

- The ultimate in membrane filtration - Why?

  = Most efficient

- Uses ***organic polymeric membrane*** material

  Ex. Cellulose acetate or triacetate

- Widely used in the Middle East to desalinate seawater

  How is salt removed by RO?

  Practical question: Why is it necessary to pretreat polluted water by other methods before subjecting it to RO?

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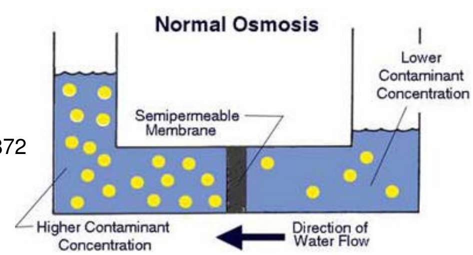
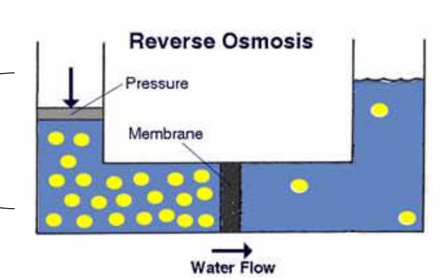
Reverse Osmosis, RO (Cont.)

The Water Quality Association : What Is...Reverse Osmosis?

http://www.wqa.org/sitelogic.cfm?ID=872



Water flows from a concentrated solution to a more dilute (usually just pure H_2O) solution



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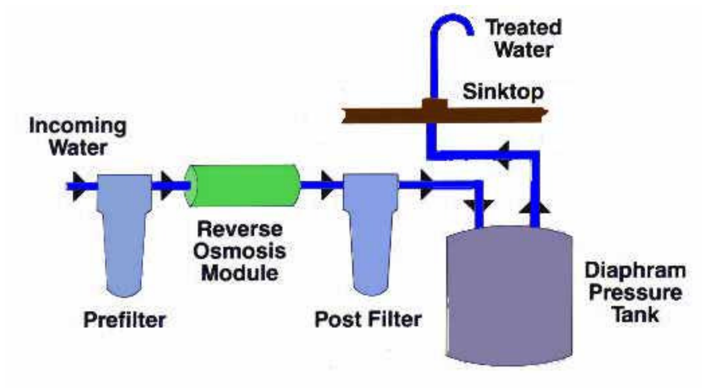
Reverse Osmosis, RO (Cont.)



The Water Quality Association : What Is...Reverse Osmosis?
Image available at http://www.wqa.org/sitelogic.cfm?ID=872

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Drinking Water

Water Quality Regulation in the U.S. (Spiro and Stigliani, "Chemistry of the Environment." 2nd ed., 2003)

Two basic laws:

- **Clean Water Act** (CWA) of 1972
- **Safe Drinking Water Act** (SDWA) of 1974

Both have been amended many times

What is regulated under the CWA and SDWA?

- Discharges of ***point source*** pollutants => subject to a permitting process
- **Industries** => advised w.r.t. best available pollution control technologies
- **Municipal treatment plants** => resources are provided for their construction

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Under the **SDWA, standards*** have been set for the following drinking water pollutants:

1. Microorganisms

Ex. *Fecal coliform* and *E. coli*; Viruses (enteric)

2. Inorganic chemicals (14)

Ex. Heavy metals such as Cd, Hg, Pb; *Anions* such as F^-, CN^-, NO_2^-/NO_3^-
Metalloids such as arsenic (As)

3. Organic chemicals (54)

Ex. Pesticides (insecticides and herbicides); Acrylamide (from sewage/wastewater treatment); Dioxin (from waste incinerators); Disinfection by-products (chlorinated organics)

4. Radionuclides

* SDWA standards are set as ***maximum contaminant levels*** (MCL), which are as close as is technologically feasible to the ***maximum contaminant level goal*** (MCLG).

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MCLG = level of contaminant below which there is no known or expected risks to human health

Examples: **MCLG** = **0** for each of the following:

- Benzene (a carcinogen)
- Dioxin (a carcinogen)
- PCBs (a carcinogen)
- Lead (toxic)
- Total coliform; Giardia lamblia (pathogenic)

MCL for some common contaminants

Contaminant	MCL, mg/L	Health Effect
Heavy metals ▪ Cadmium, Cd ▪ Copper, Cu ▪ Lead, Pb	 0.005 1.3 (action level) 0.015	▪ Kidney damage ▪ From gastrointestinal distress to kidney damage ▪ Delayed physical and mental dev't (children); Kidney problems; High B.P.
Inorganic anions ▪ Fluoride ▪ Nitrate, NO_3^-	 4 10	 ▪ Kidney problems; High B.P. ▪ Blue baby syndrome (shortness of breath, etc.)

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Wastewater and **Sewage**

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Purification of Wastewater Water

Bridgewater Wastewater Treatment Plant
Photo by Jonathan Xavier, 2002

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Once collected, sewage water flows into a multi-step treatment facility.

Goals of water treatment:

- Remove solids (sludge and scum) so they don't accumulate in rivers where the water is discharged,
- Prevent organics from entering rivers – Why?
  - Decomposition uses up DO; suffocates fish
- Prevent odors created in water that lacks DO, and
- Remove potential disease-causing bacteria and viruses (pathogens)

http://dnr.metrokc.gov/wtd/homepage/process.htm

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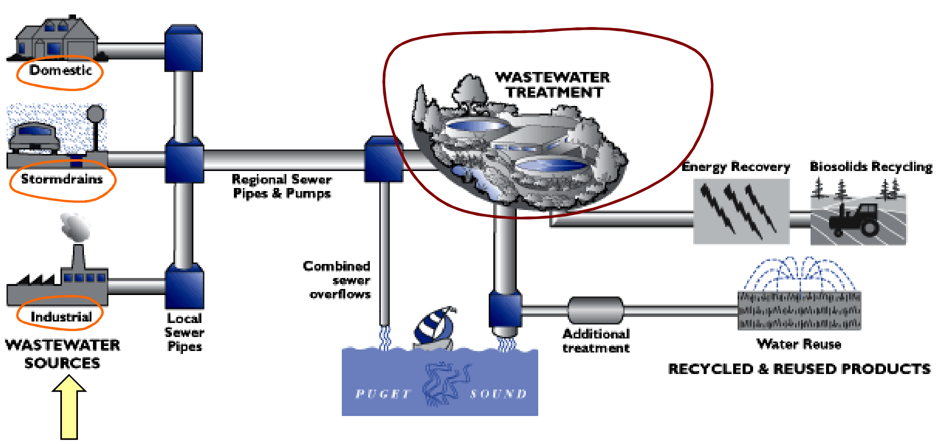
Wastewater and Sewage



Sources of raw sewage

Source: http://dnr.metrokc.gov/wtd/homepage/process.htm

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Materials typically found in municipal sewage:

- O_2-demanding materials, such as OM
- Sediment, oil and grease
- Disease-causing microorganisms
- *Inorganics*: Salts, algal nutrients and heavy metals
- *Organics*: Pesticides (herbicides and insecticides), other potentially harmful organics

Thus, **sewage treatment involves**:

- Removal of solids (***primary treatment***)
- Removal of OM and reduction of BOD (***secondary treatment***)
- Removal of inorganics, such as algal nutrients (***tertiary treatment***)

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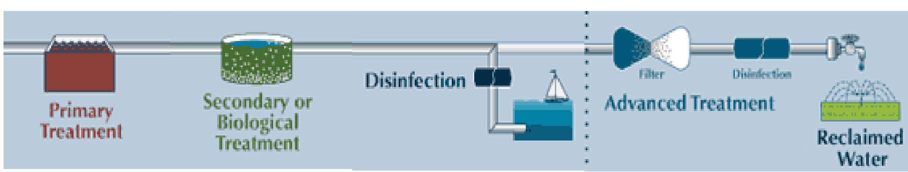
Overview of Standard and Advanced Wastewater Treatment Processes



Wastewater Treatment Processes

1. Primary treatment - removes

- Solids
- Grease
- Scum

by filtration (***screening***) and settling (***sedimentation***).

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Wastewater and Sewage

Primary screen

Primary clarifiers

Photos courtesy Falke Bruinsma

- Primary treatment is very simple -- it involves a screen followed by a set of pools or ponds that let the water sit so that the solids can settle out.
- The ***solids are allowed to settle out*** of the water while the ***scum rises***. The system then collects the solids for disposal (either in a landfill or an incinerator).

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"Urban Wastewater Systems" at http://people.howstuffworks.com/sewer3.htm

Wastewater Treatment Processes (Cont.)

2. Secondary treatment

- Reduces **BOD** by removing dissolved and suspended organics

(a) ***Activated sludge treatment*** = harnesses bacteria to convert biodegradable OM into bacterial biomass and CO_2

- Organic N is converted to ammonium, NH_4^+ or nitrate, NO_3^-
- Organic P is converted to orthophosphate, HPO_4^{2-}
- Reduces BOD by as much as 90%
- Prevents anoxic condition in the receiving water

(b) ***Clarification*** = sedimentation of remaining solids, including microbes

= sludge

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Secondary treatment removes organic materials and nutrients. This is done with the help of bacteria -- the water flows to large, aerated tanks where bacteria consume the organic matter in water. Bacterial growth is speeded up by vigorous mixing of air (aeration) with the concentrated microorganisms (activated sludge) and the wastewater.

Aeration tank

Photo courtesy Falke Bruinsma

"Urban Wastewater Systems" at http://people.howstuffworks.com/sewer3.htm

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Secondary treatment – Cont.

- Wastewater then flows to settling tanks where the bacteria settle out

Secondary clarifier, or

Final settling basin

Photo courtesy Falke Bruinsma

http://www.gocolumbiamo.com/PublicWorks/Sewer/wwtppg_4.html#SECONDARY
http://people.howstuffworks.com/sewer3.htm

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Secondary treatment – Cont.

Q: What happens to the sludge?

1) ***Incineration***

- provides energy for heating, electricity

2) Conversion to ***methane***, CH_4 (i.e. fuel)

- done by anaerobic bacterial digestion

3) Disposal in ***landfills***

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Wastewater Treatment Processes (Cont.)

3. Tertiary treatment (also called ***advanced waste treatment***)

- Removes inorganics not eliminated by 1^0 and 2^0 treatments

→ NH_4^+, NO_3^-, PO_4^{3-}

(a) **Liming** – addition of CaO; makes water basic (high pH)

- Removes phosphate, PO_4^{3-}, by precipitation with ***lime***
- Converts NH_4^+ into volatile ammonia, NH_3 (called ***ammonia stripping***)

(b) **Recarbonation** = injection of CO_2

- Lowers the pH to ~ 7 to recover (reprecipitate) lime

(c) **Filtration** (activated charcoal)

- Removes remaining organics

(d) **Disinfection**

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The third stage, known as ***tertiary treatment***, varies depending on the community and the composition of the wastewater. Typically, the third stage will use chemicals to remove phosphorous and nitrogen from the water, but may also include filter beds and other types of treatment. ***Chlorine*** added to the water kills any remaining bacteria, and the water is discharged.

Final clarifier

Chlorination tank

Photos courtesy Falke Bruinsma

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Measuring the Effectiveness of a Treatment Plant

Based on the following scale:

- **pH**
  - Should match the pH of the receiving river or lake
- **BOD**
  - Ideal value is zero
- **Dissolved oxygen (DO)**
  - Zero DO could kill any aquatic life
  - DO should be ***as high as possible*** and needs to cover the BOD

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Measuring the Effectiveness of a Treatment Plant – *Cont.*

- **Suspended solids**
  - Ideal value is zero
- **Total nitrogen and phosphorous (TNP)**
  - Measures nutrients remaining in the water
- **Chlorine**
  - Needs to be removed so it does not kill beneficial bacteria in the environment
  - Ideally, chlorine should not be detectable

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Measuring the Effectiveness of a Treatment Plant – Cont.

- **Coliform bacteria count**
  - Measures fecal bacteria remaining in the water
  - Ideally, this number would be zero.

Note that water in the environment is not totally free of fecal bacteria – Why?

- Birds and other wildlife introduce some

These indicators need to be watched closely because any community produces a huge quantity of wastewater.

- **Discharge levels** ranging from ***10 million to 100 million gallons per day*** (38 million to 380 million liters) are common for a wastewater treatment plant.

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