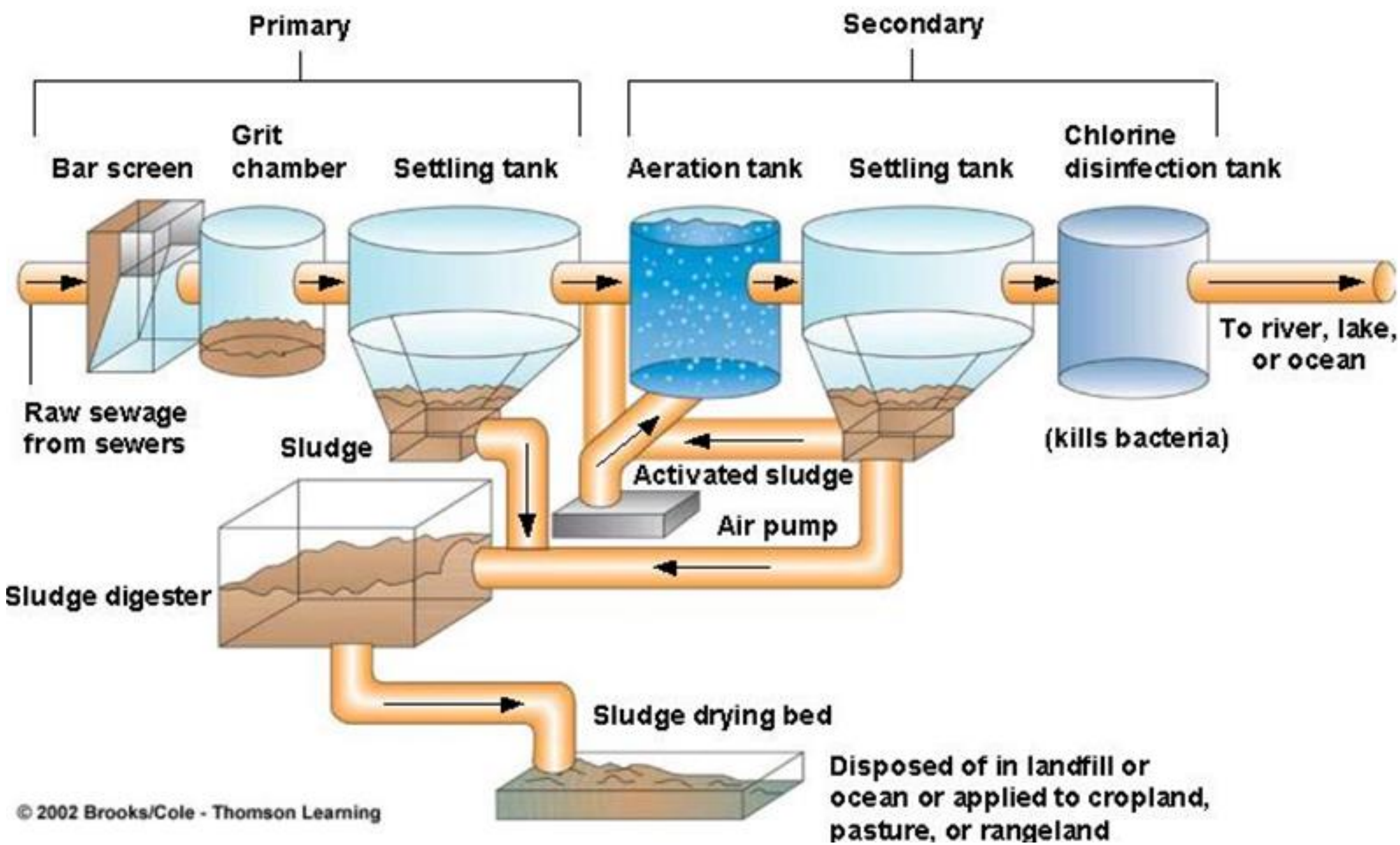
Methods of pollution control and waste management

Lecture 4

Sewage treatment methods

(Part 2)

The main stages of sewage treatment process



Tertiary (advanced) wastewater treatment

Secondary treatment removes 85 to 95 percent of BOD and TSS and minor portions of nitrogen, phosphorus and heavy metals

Contaminants removed by tertiary step

(final or advanced treatment) :

- Dissolved organic compounds
- Dissolved inorganic compounds

Sludge disposal methods

Tertiary wastewater treatment

Removal of dissolved organics

Adsorption on activated carbon (AC) which has affinity for organic compounds. Two general types:

- granulated activated carbon consisting of particles 0.1-1 mm in diameter (GAC)
- powdered activated carbon consisting of particles 50-100 μm in diameter (PAC)

Phenol value – amount of carbon in milligrams required to reduce by 90% the phenol in 1 l of a solution containing 100μg/l. Commercial activated carbon 15-30 .

Used in packed beds or columns in a series or parallel operation

Adsorption on activated carbon (AC)

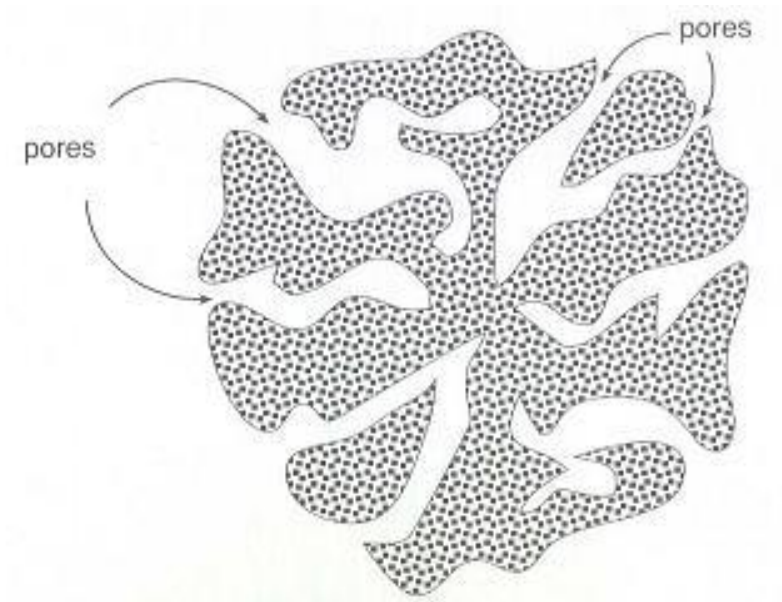
Adsorption –process for the removal of one phase of material, and its concentration on the surface of another phase. Accumulation at an interface.

Raw materials for AC preparation: coal – most common, nut shells, wood, bone, resins

Preparation: 1) dehydratation (170^{o}C), 2) carbonization (400-700^{o}C in absence of O_2), 3)activation pyrolysis (400-1200 ^{o}C in steam and O_2)

$$1\ g \cong 500\ m^2$$

AC is a material with an exceptionally high surface area and a high degree of micro-porosity



During water *filtration* through activated carbon, contaminants adhere to the surface of these carbon granules or become trapped in the small pores of the activated carbon

A typical carbon particle has numerous pores that provide a large surface area

Source: LEMLEY et al. (1995)

GAC

PAC


Waste Water
Water Treatment by
Activated Carbon
Purifying Water by
Activated Carbon

Tertiary wastewater treatment

- Bacteria growth on the **activated carbon** in wastewater plants increases effectivity of removal organic compounds.

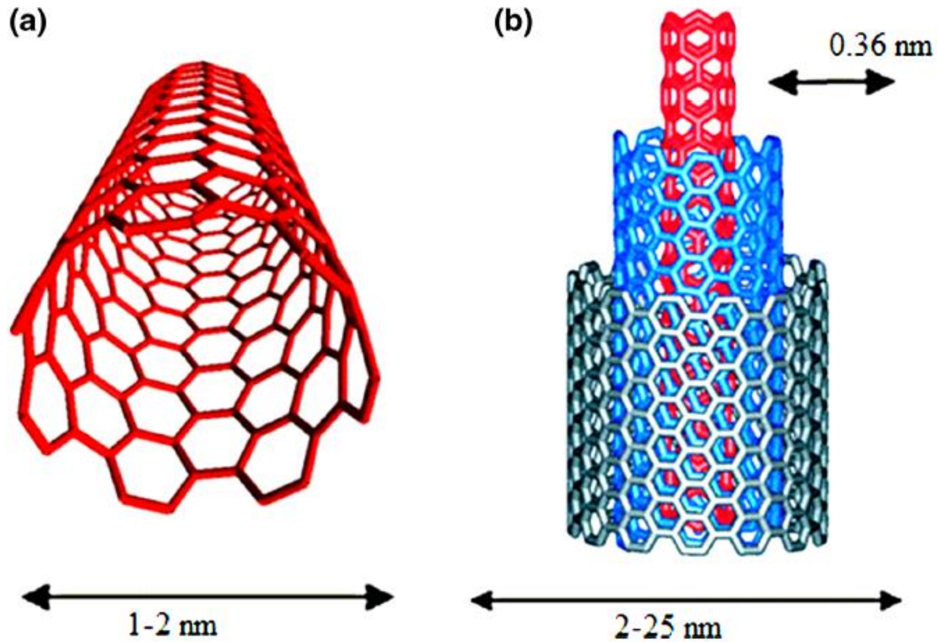
- Regeneration - heating to 950^0C under low oxygen conditions in the presence of steam (loss is about 5-15% for each regeneration). Adsorbed organics are volatalized and oxidized during the regeneration.

- Adsorption on **synthetic polymers** such as Amberlite which strongly attract organic compounds such as chlorinated pesticides, these polymers have hydrophobic surface porosity is up 50% by volume, surface area is very high. They are readily regenerated by organic solvents by extraction using such solvents as isopropanol, acetone.

Tertiary wastewater treatment

- The nanomaterials as novel kind of adsorbents investigated in wastewater treatment

Fig. 2 Schematics of SWCNTs (a) and MWCNTs (b) (copied form Ref. [22])



The CNTs exhibit exceptionally high adsorption capacities

H. Sadegh, G. AM Ali, V. K. Gupta, A. S. Hamdy Makhlouf, R. Shahryari-ghoshekandi, M. N Nadagouda, M. Sillanpää, E. Megiel, Journal of Nanostructure in Chemistry, 2017, 1, 28.

Tertiary wastewater treatment

Removal of dissolved inorganics

- Inorganic nutrients phosphorus and nitrogen (eutrophication downstream)

Precipitation, ion-exchange method, reverse osmosis

Total phosphorus in wastewater

Phosphorus compounds are present in wastewater almost solely as phosphates, which come from three sources:

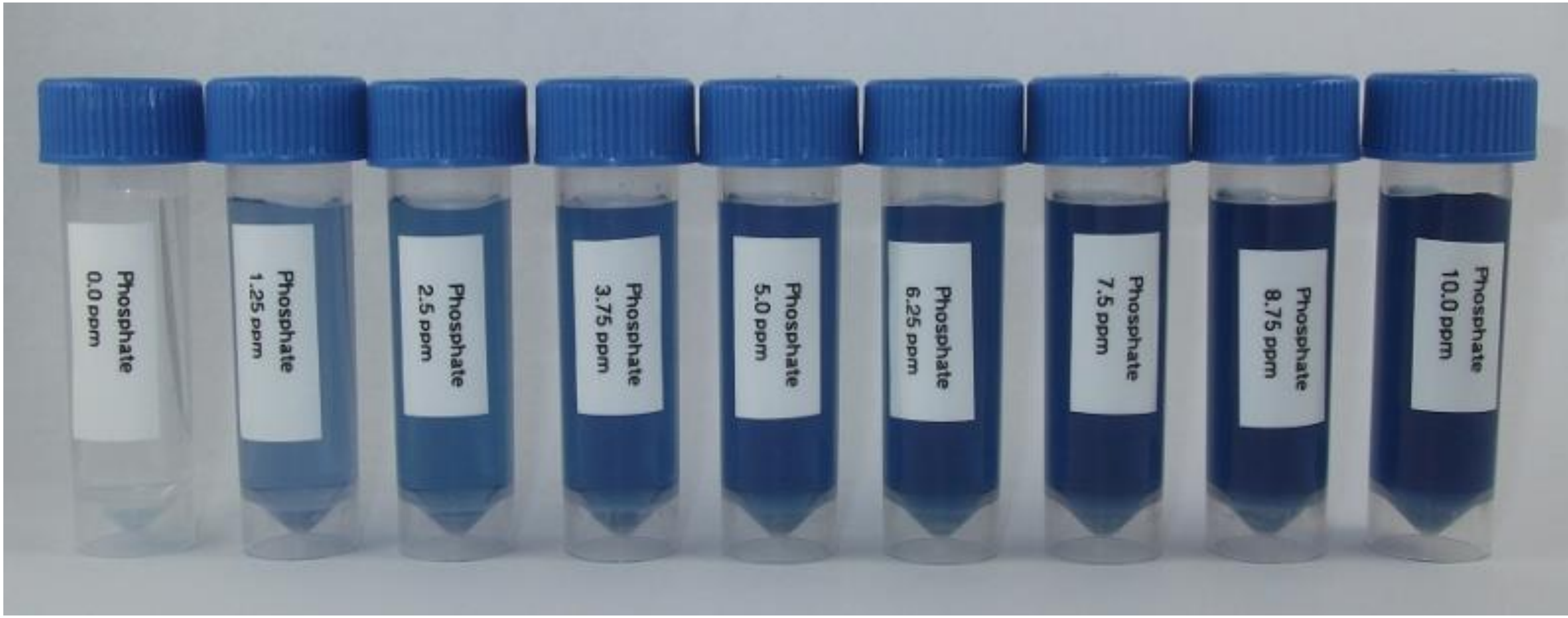
- Cleaning solutions
- Fertilizers
- Biological waste

Phosphorous compounds must be removed to prevent the growth of harmful bacteria

Total phosphorus analysis

- Phosphorus compounds levels are measures colorimetrically by converting these compounds to a highly coloured complex known as „molybdenium blue”

1. All the different phosphates are oxidized to orthophosphates (PO_4^{3-}) using 1:5 mixture H_2SO_4 and HNO_3
2. Orthophosphates are reacted with ammonium molybdate and potassium antimonyl tartrate to yellow complex
3. The obtained complex is reduced with ascorbic acid to molybdenum blue.
4. The absorption at λ_{max} is measured and compare with standard calibration curve



Maximum of absorption: 625 nm.

This method for measuring phosphate is based on APHA Standard Method 4500-P E
Also called ascorbic acid method.

Tertiary wastewater treatment

Phosphorus Removal

Domestic sewage contain high concentration of phosphorus from detergents .

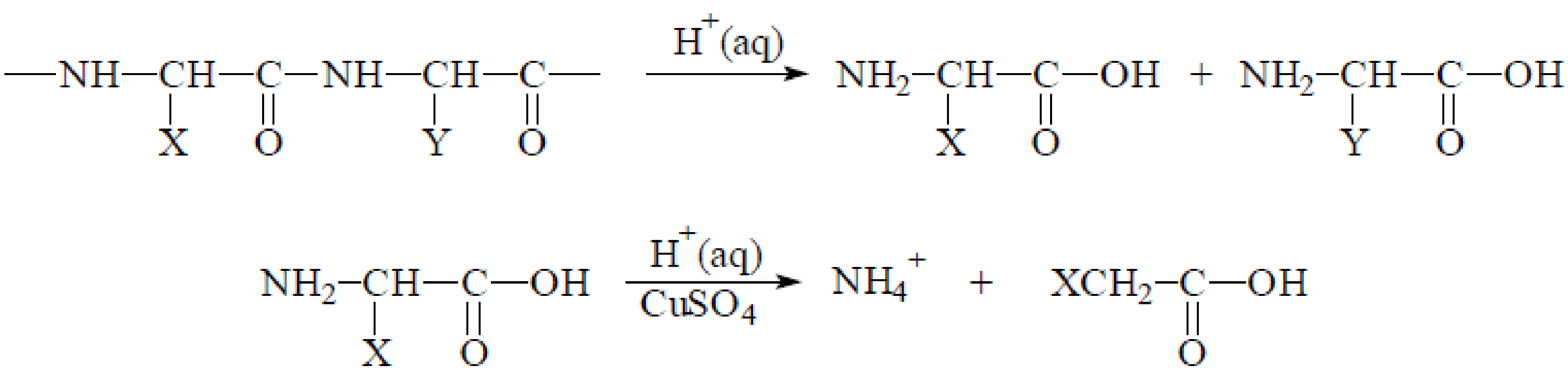
Chemical precipitants for phosphate and their product

Precipitant (s)	Product
$Ca(OH)_2$	$Ca_5OH(PO_4)_3$ (hydroxyapatite)
$Ca(OH)_2$ + NaF	$Ca_5F(PO_4)_3$(fluoroapatite)
$Al_2(SO_4)_3$	$AlPO_4$
$FeCl_3$	$FePO_4$
$MgSO_4$	$Mg_3(PO_4)_2$

Total nitrogen in wastewater

Total nitrogen (TN) – organic from proteins, free amino acids and inorganic from nitrites, nitrates, ammonia

Amount of organic nitrogen determination



$$NH_3 + H^+ \longrightarrow NH_4^+$$

The ammonium ions are then converted with base to ammonia:

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

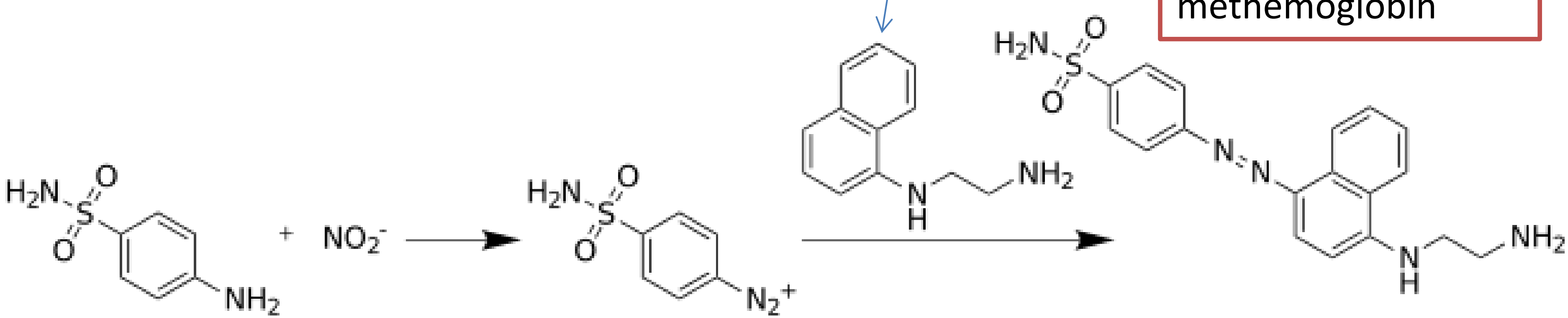
NH_3 concentration is determined by titration against H_2SO_4 using combined indicators.

Total nitrogen in wastewater

Nitrite ions are detected and analyzed by formation of a red pink color upon treatment of a NO_2^--containing sample with the Greiss reagent

naphthylethylenediamine

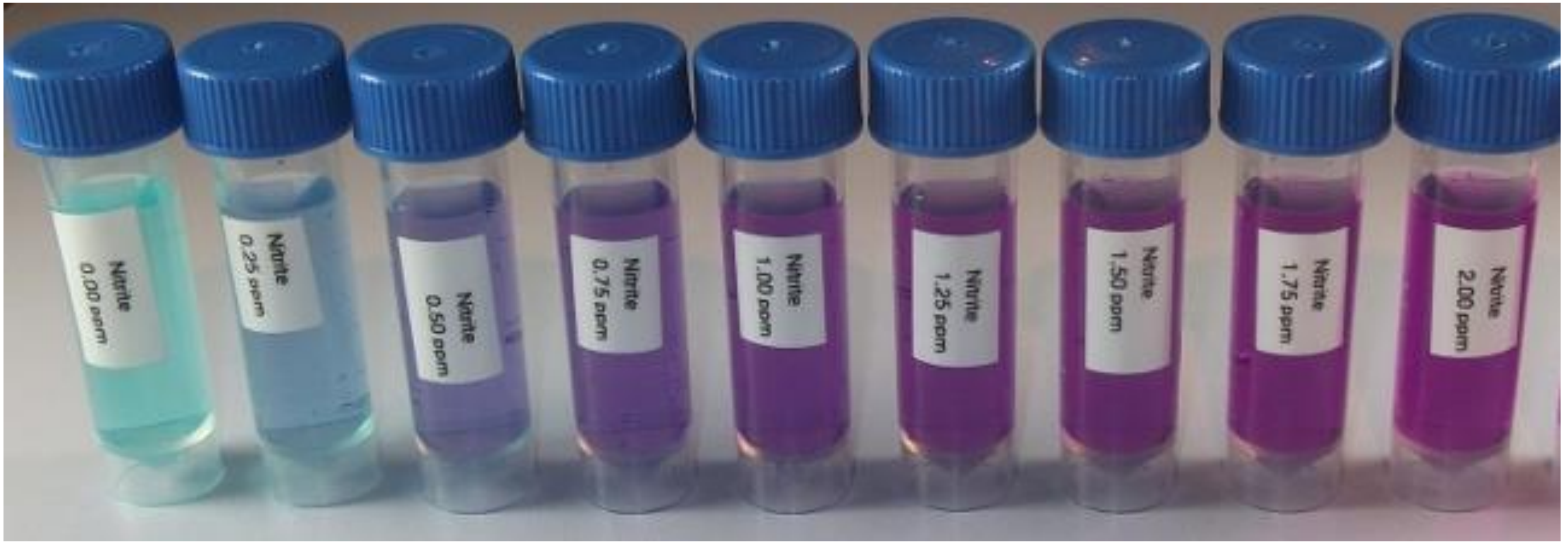
NO_2^- changes the normal form of hemoglobin to methemoglobin



Sulphanilamide

Highly coloured azo dye which can be determined spectrophotometrically

Nitrite-Greiss colorimeter assay



Maximum absorption 540 nm

Total nitrogen in wastewater

Nitrate (NO_3^-)

The amount of nitrate is determined by measuring the amount of nitrite in a sample, reducing the nitrate to nitrite, measuring the nitrite again and calculating the difference. The nitrite is determined using the method described above, and the nitrate is reduced to nitrite with copper in a Cu/Cd column:

$$NO_3^- + 2H^+ + Cu \rightarrow NO_2^- + Cu^{2+} + H_2O$$

Tertiary wastewater treatment

Nitrogen Removal

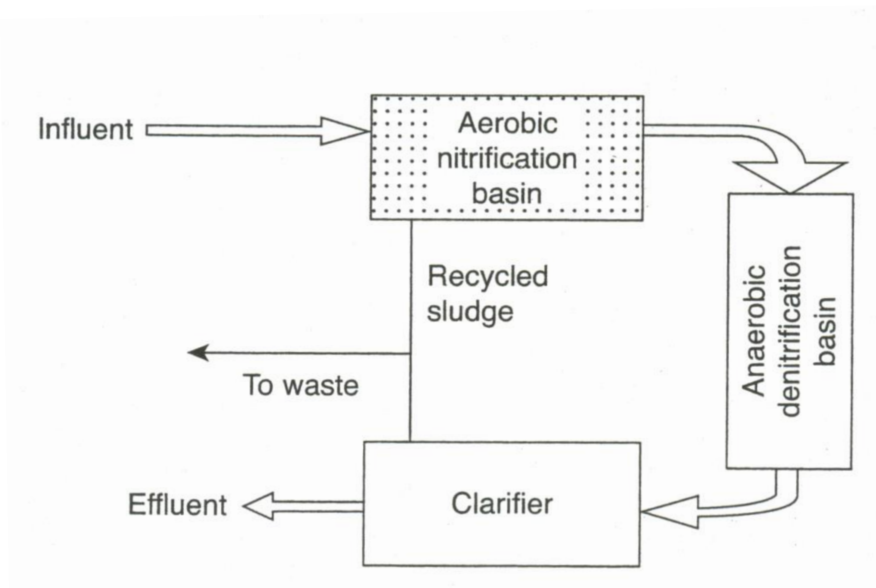
Common processes for the removal of nitrogen from wastewater

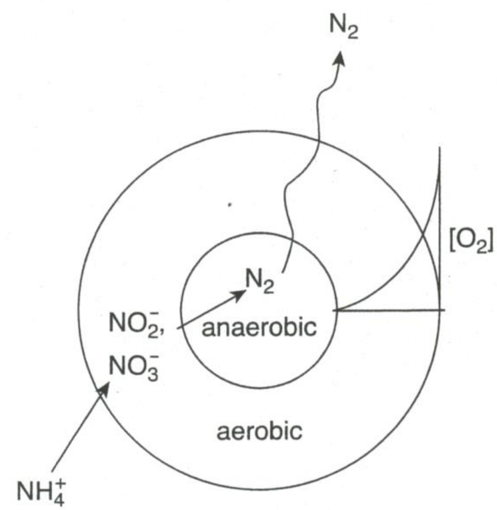
Process	Principles and conditions
Air stripping ammonia (NH_3)	Raising the pH to 11 with lime and stripping ammonia gas from water by air
Ammonium ion-exchange	Natural zeolite selective for ammonia ion, regenerate with sodium or calcium salts
Biosynthesis	The production of biomass and its subsequent removal from the sewage effluent
Denitrification	Reduction of nitrate to nitrogen bacterially catalyzed

Tertiary wastewater treatment

Nitrogen Removal

Denitrification - anaerobic microbiological process



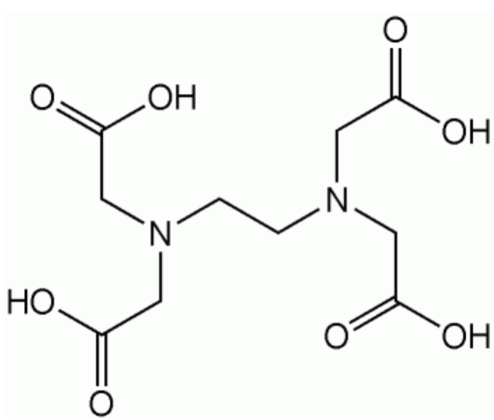


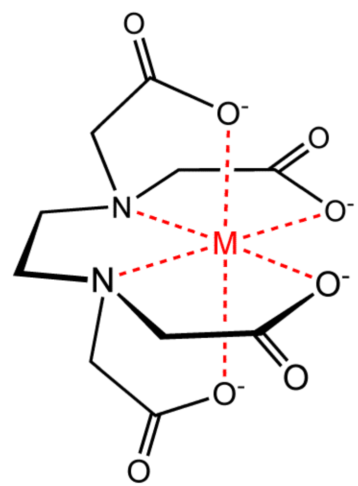
$$6NO_3^- + 5\,CH_3OH + 6H^+ \xrightarrow[\text{bacteria}]{\text{Denitrifying}} 3N_2 + 5CO_2 + 13\,H_2O$$

Tertiary wastewater treatment

Removal of heavy metals

- Lime treatment removes heavy metal as insoluble hydroxides, basic salts, does not completely remove mercury, cadmium, lead
- Addition of sulfide $Cd^{2+} + S^{2-} \longrightarrow CdS$
- Solvent extraction using organic-soluble chelating substances e.g. EDTA *(**e**thylene**d**iamine**t**etra**a**cetate)*





Sludge disposal

‘Sludge’ = wastes from screens, primarily clarifiers and biosolids from bioreactors

Disposal: land application, landfills, incineration

Sludge processing: key process is thickening – helps transportation, digestion, drying and combustion

Sludge can often be digested anaerobically (more common) or aerobically. Digested sludge can be composted for further stabilization (pathogen removal).

Sludge Treatment Processes

Thickening (water removal)

⇩

Digestion (pathogen inactivation and odor control)

⇩

Conditioning (improved dewatering with alum and high temp, 175-230° C)

⇩

Dewatering (pathogen inactivation and odor control)

⇩

Incineration (volume and weight reduction)

⇩

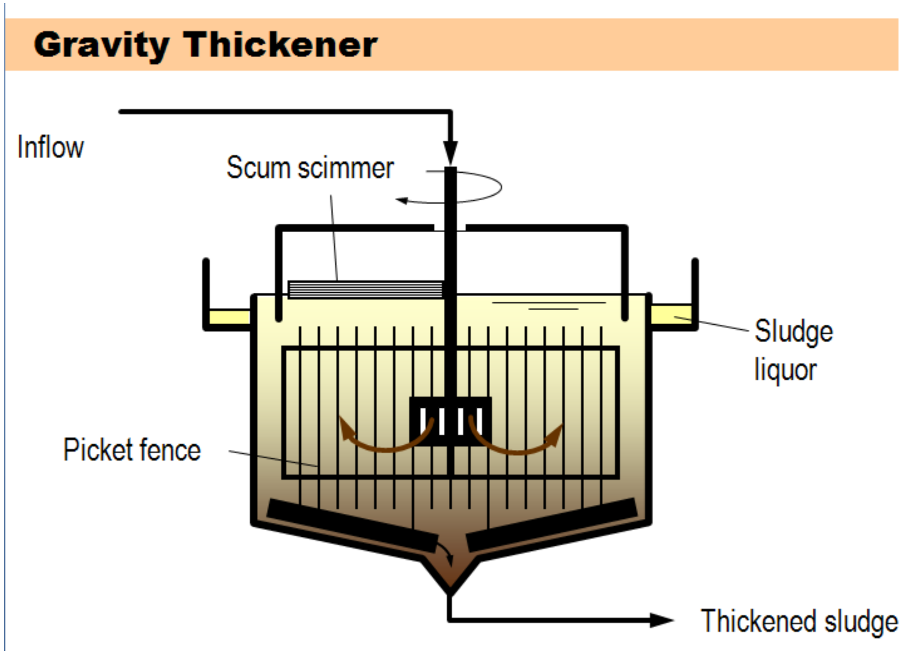
Final disposal

*S. E. Manahan „Environmental Chemistry" Brooks/Cole Publishing Company , 1984

Sludge treatment and disposal

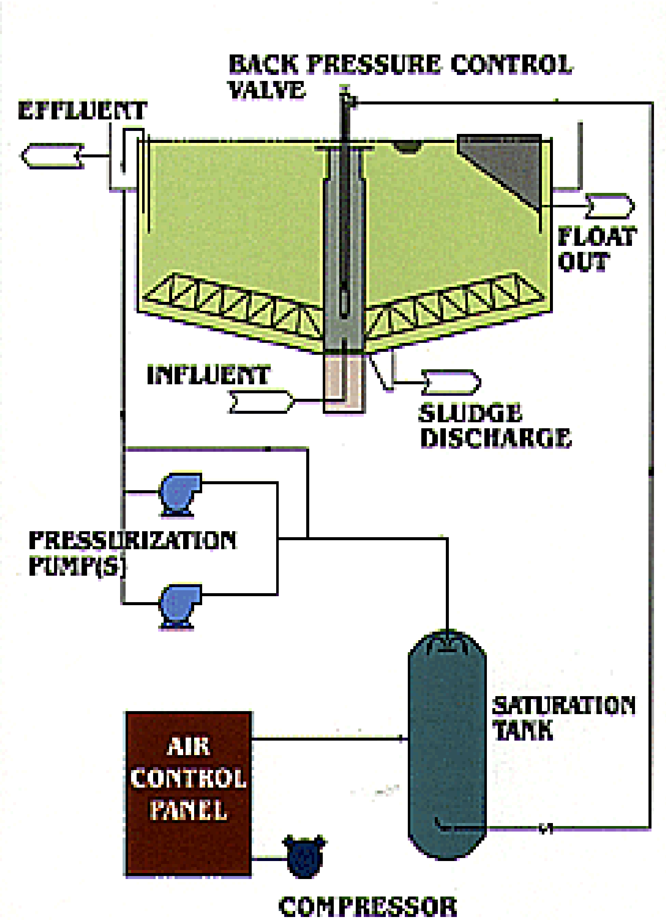
The thickening of sludge

Gravity – sedimentation basins where solids separate to scum, sludge liquor and thickened sludge



P. Krebs, Technische Universität Dresden, lecture materials

Sludge treatment and disposal



Thickening by flotation - sludge is placed in contact with air-saturated water, air bubbles attach to solid particles, floating sludge bubble composite is collected at the surface

P. Krebs, Technische Universität Dresden, lecture materials

Sludge treatment production of biogas

Anaerobic digestion mesophilic sludge stabilisation

35^0C

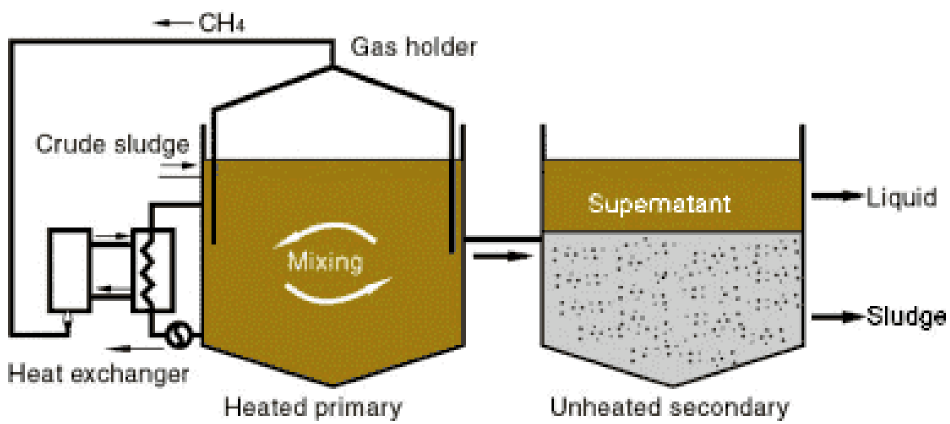


Figure 33: Simple anaerobic digestion process

Digester

Storage unit

Bacterial decomposition process that stabilises organic waste and produces a mixture of methane and carbon dioxide gas (biogas). After digestion sludge is passed to a sedimentation tank where the sludge is thickened. Biogas is collected from the digester.

$$2\,C_5H_7NO_2 + 8\,H_2O \rightarrow 5\,CH_4 + 3\,CO_2 + 2\,NH_4^+ + 2\,HCO_3^-$$

http://www.unep.or.jp/ietc/publications/freshwater

History of Biogas

- **First digestion plant was built in 1859 in Bombay, India for a leper colony**
- **Exeter, England, in 1895: biogas used to power street lamps**
- **1920's and 30's interest in anaerobic digestion increased**
- **Interest in Biogas has been cyclical**

Biogas

Biogas production: 63% CH_4
35% CO_2 → **electricity and heating**
2% other gases (N_2, H_2, H_2S)

Degradation of organic substances in 50%

Mean residence time of sludge

Small units, badly mixed > 30 d

Medium size units with mixing 20 d

Large plants with mixing 12-16 d

Biogas production related to degradation of organic substances 0.9 m^3 / kg

Digester tanks in WWTP

Widok typowych komór fermentacyjnych (WKF)

Stages of methane fermentation

•**Hydrolysis** to amino acids, fatty acids, and sugars

•**Acidogenesis** to form three, four, and five-carbon volatile fatty acids, such as lactic, butyric, propionic, and valeric acid

•**Acetogenesis**, bacteria consume these fermentation products and generate acetic acid, carbon dioxide, and hydrogen.

•**Methanogenic** organisms consume the acetate, hydrogen, and some of the carbon dioxide to produce methane.

Stages of methane fermentation

Three biochemical pathways are used by methanogens to produce methane gas

- Acetotrophic methanogenesis:

$4\ CH_3COOH \rightarrow 4\ CO_2 + 4\ CH_4$

- Hydrogenotrophic methanogenesis:

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$

- Methylotrophic methanogenesis:

$4\ CH_3OH + 6\ H_2 \rightarrow 3\ CH_4 + 2\ H_2O$

Methane fermentation

- The optimal conditions for anaerobic digestion of organic matter are near-neutral pH, constant temperature (thermophilic or mesophilic), and a relatively constant feeding rate.

- Mesophilic and thermophilic microbes are adapted to roughly 30-40 °C (86-104 °F) and 50-60 °C (122-140 °F) respectively.

Sludge treatment

Dewatering (drying) **Water content in stabilised sludge > 95%**

mechanically using a filter press (employing pressure or vacuum), or a centrifuge. It can also be done using **drying beds**. A drying bed consists of a bed of sand with an under-drainage.

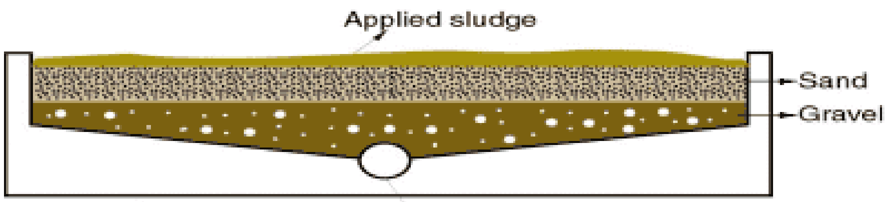


Figure 35: Sludge drying bed

First dewatered by drainage then air-dried through evaporation

http://www.unep.or.jp/ietc/publications/freshwater

Sludge disposal

Use in agriculture

Land spreading - recycling of nutrients, from stabilised sludge

Disadventages: presence of toxic substances is possible

Composting

Aerobic biological degradation of organic substances

> **Requirements are more demanding than for sludge use as fertiliser**

Incineration

Mono incineration (expensive), co-incineration
(solid waste incinerator, coal power station)

Sludge components and disposal

- Before use in agricultre, composting or disposal in incineration sludge should be analysed in detail
- If undesirable /dangerous compounds are presence the another methods of utilization must be performed additionally (RO, NF, ED)

Industrial wastewater treatment

Removal inorganic matter:

- Neutralization
- Reduction and oxidation of inorganic compounds (such as chromic salt, chromates or cyanate to cyanide)
- Precipitation of cations and anions in the form of insoluble compounds (for example barium chromate)

Removal organic matter:

- Extraction: phenol can be extracted from wastewater with butyl acetate, cumene or diisopropylether. The remaining concentration is between 20 and 500 mg/l which is not toxic for the bacteria in the activated sludge tank. Phenol and the extraction solvent are separated in a following distillation process.
  Acetic acid can be extracted with ethyl acetate, again the extraction solvent is recycled for the process and acetic acid is a valuable substance.