Treatment of Sludges

❖Fundamentals of Cleanup Reactions

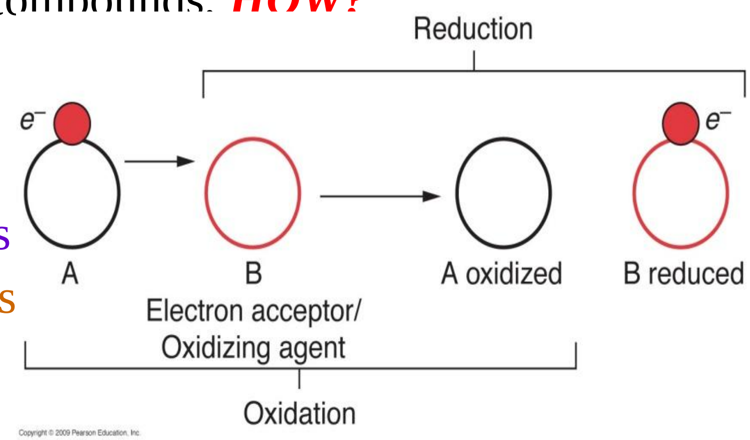
- •Microbes can convert many chemicals into harmless compounds. ***HOW?***
  - •Aerobic or anaerobically
  - • Through oxidation and reduction reactions

❖ ***Oxidation and Reduction Reactions takes place:***

a) Oxidation involves the removal of one or more electrons

b) Reduction involves the addition of one or more electrons

* Oxidizing agents gain electrons and reducing agents lose electrons



c) The rxns are usually coupled and the paired rxns are known are **redox reactions.**

Aerobic and Anaerobic Biodegradation

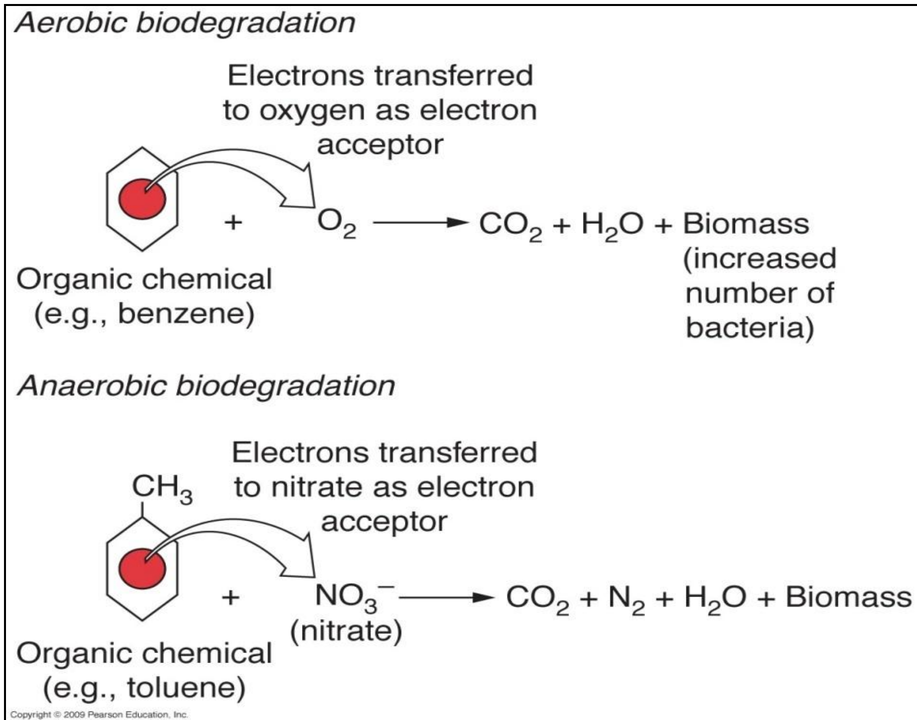
a) Aerobic

Oxygen is reduced to water and the organic molecules (e.g. petroleum, sugar) are oxidized

b) Anaerobic

An ***inorganic compound*** is ***reduced*** and the ***organic molecules*** are ***oxidized*** (e.g. nitrate is reduced and sugar is oxidized)

❖ Many microbes can do both aerobic and anaerobic respiration; the process which produces the most ATP is used first!



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What is sludge?

❖ The treatment of sewage results in the production of solids commonly referred to as **sludge.**

- ***Sludge*** is produced from the treatment of wastewater in on-site (e.g. septic tank) and off-site (e.g. activated sludge) systems.
- ***Sludge*** is also produced from the treatment of storm water, although it is likely to be less organic in nature compared to wastewater sludge.

❖ Sludge can be contaminated with heavy metals and other pollutants, especially when industrial wastes are disposed into the sewer.

- Pre-treatment of industrial sludge wastes are therefore essential before discharge to the sewer.
- ***Options for sludge treatment include stabilization, thickening, dewatering, drying and incineration.***

➢ ***All non-biodegraded compounds extracted from wastewater are found in the sludge.***

- **Thus, *further removal of suspended and dissolved contaminants, not normally removed by conventional treatment should be needed.***

Composition of Sludge

- *Predominantly water*
- Microbes including viruses and pathogens
- Organic compounds and particles, heavily bio-degradable and adsorpted to sludge flocs
- Heavy metals
- Micro-pollutants, pharmaceuticals, endocrine disrupters, etc.

Types of Sludge

- ***Primary sludge-*** consist of organic solids, grit, inorganic fines, gray, greasy, odorous slurry and includes ***4-6% solid concentration and 60 to 80% of VSS.***
- ***Waste activated sludge*** (secondary sludge) – consist of active microbial mass, dark brown suspension, inoffensive at first, can rapidly become odorous.
- Its concentration includes ***0.5 -1.5% solid concentration***, whereas **70 to 80% of VSS**.
- ***Trickling filter sludge-*** similar to waste activated sludge with **4-5% solid**, with **45-70%VSS**.
- ***Anaerobically digested sludge-*** dark brown, thick slurry, smells like garden soil, with **30-60% VSS**.
- ***Aerobically digested sludge-*** dark brown, more difficult to process than anaerobicallly digested sludge due to flocculent nature with **35-40% VSS**.
- ***Mechanically dewatered sludge-*** consistency of wet mud to chunky solid with **15-40% solid**.

Estimation of Solid Production

$W_s = W_{sp} + W_{ss}$

W_s = total dry solids [M/T]
W_{sp} = raw primary solids [M/T]
W_{ss} = raw secondary solids [M/T]
$W_{sp} = f \cdot SS \cdot Q$

f = fraction of suspended solids removed in primary settling
$f \approx 0.4$ to 0.6 – use 0.5 for domestic wastewater
SS = suspended solids conc. in wastewater [M/L³]
Q = flow rate [L³/T]

$W_{ss} = K \cdot BOD \cdot Q$

K = fraction of influent BOD that becomes excess biomass

$K \approx 0.3$ to 0.5 (for $F/M = 0.05$ to $0.5 \ \frac{kg\ BOD}{kg\ MLVSS \cdot d}$)

K is lower for extended aeration AST and RBC's

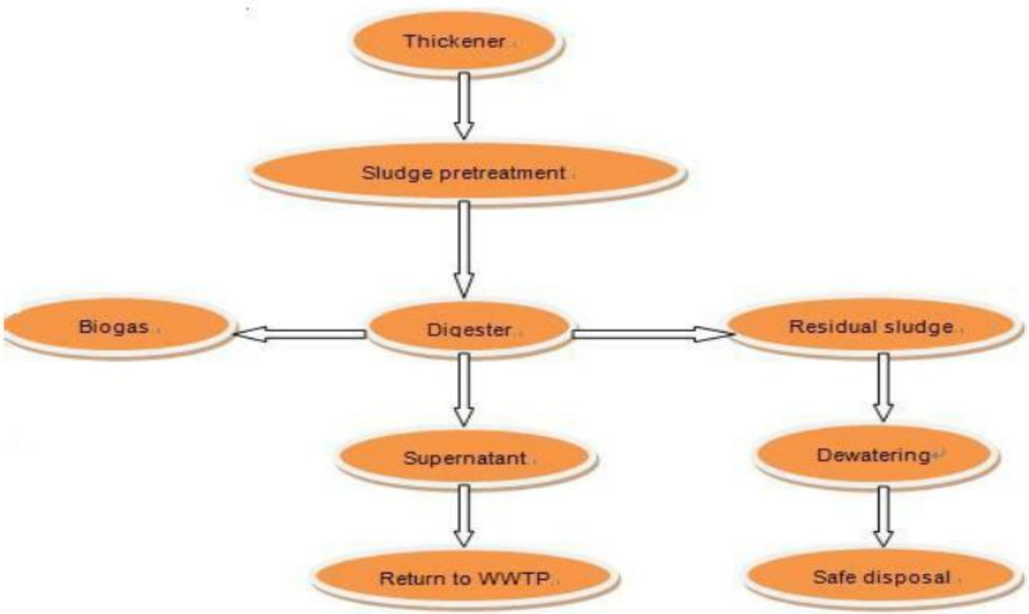
Why sludge treatment?

- To reduce the volume through thickening and dewatering and cost reduction
- To eliminate pathogenic organisms
- To stabilize the organic substances through gas production for energy, reduction of dry content, improvement of dewatering and reduction of odour.
- To recycle the substances through composting to serve as bio-fertilizer and biogas production

Factors affecting the selection of treatment processes:

- The nature of the wastewater
- The potential use of the treated effluent
- The compatibility of the various operations and processes
- The available means to dispose of the ultimate contaminants, and
- The environmental and economic feasibility of the various systems

❖ This figure shows the process flowchart of the sludge processing steps.



❑ High expenditures associated with solids management at a wastewater treatment facility can also be a direct result of a lack of emphasis to provide the most efficient and effective solids handling process.

Aerobic and Anaerobic Sludge Stabilization

❖ ***Digestion*** is a commonly used biological process for the stabilization of sludges from wastewater treatment plants.

▪ ***The stabilization of sludges*** results in the ***destruction of pathogens and reduction in volatile solids, odors, toxics and heavy metals***.

❖ From the bioengineering and biotechnological point of view, the aerobic and anaerobic sludge treatment process involves,

a) the microorganisms and

b) degradation biocatalysts and composition of the sludge,

c) the process bacteria mediate the bio-degradation process that occur and utilize the resultant product produced from lysis of the bed microbe and of process bacteria.

➢ ***Biodegradation*** is the use of living organisms by enzymatically process and otherwise attack numerous organic chemicals and break them down to lesser toxic chemical species.

▪ Biodegradation with MOs is the most frequently occurring bioremediation option, since MOs can break down most compounds for their growth and energy with or without need of air.

➢ ***Thus, sludge treatment by bioremediation and the success of bioremediation depends on:***

(1) the growth and survival of microbial populations: sufficient numbers of microorganisms to make bioremediation successful;

(2) the ability of these organisms to come into contact with the substances that need to be degraded into less toxic compounds;

(3) the microbial environment must be habitable for the microbes to thrive.

Aerobic Sludge Stabilization

- ***Aerobic digestion*** is a solids stabilization process that ***provides a limited supply of oxygen*** to microorganisms in order to ***promote competition as well as facilitate oxidation*** of organic matter ***and convert it into carbon-dioxide and water.***
- ***Aerobic digestion system*** typically consists of *two or more aerated tanks* used to ***process*** and ***store waste activated sludge*** (WAS) generated from the liquid treatment process and/or primary sludge (PS) from primary sedimentation tanks.
- The WAS and PS in aerobic digestion system can be processed either separately or in combined into one product.
- **Air** is introduced to the tank(s) from an aeration system typically coarse or fine bubble diffuser equipment with the air being supplied by a positive displacement or centrifugal blower.

- While in general aerobic digestion is a relatively simple process, there are many design and operational parameters to be considered such as:
  * *temperature and pH control, oxygen transfer and mixing,*
  * *nitrification and denitrification,*
  * *solids retention time, sludge loading characteristics, and*
  * *tank configuration that must be considered in order to achieve a sustainable process.*

- Enyzme activity data showed that during aerobic digestion, polysaccharide degradation activity decreased to near zero and this was consistent with the accumulation of polysaccharides in aerobic digesters.
- DO conditions under **0.3 mg/L** in aerobic digestion systems do not adversely impact volatile solids reduction or pathogen removal performance and that ***high DO causes low pH*** which can be detrimental since mesophilic bacteria are sensitive to pH conditions (Enviroquip, 1999).
- ***Endogenous respiration*** should be created to achieve biomass and volatile solids reduction.

- Thus, main ***objectives of aerobic digestion processes*** are to ***produce biosolids*** that are ***stable*** and ***amenable*** to various beneficial uses such as ***land application***, ***reduce pathogens*** (disease causing organisms), and ***control odors***.

- The performance of an aerobic digestion system is typically based on ***volatile solids and pathogen destruction*** which is an indicator of sludge stabilization.
- The microorganisms utilized in aerobic digestion processes are ***mesophilic facultative bacteria*** which mean they thrive in temperatures between **25°C and 37 °C** and ***live under aerobic (presence of oxygen) and anoxic (no oxygen but presence of nitrates) conditions***.

- An aerobic digestion process is a decay process operated under different range of DO conditions.
- Aerobic digestion systems are operated at a DO ranging typically between 0.5 mg/L to 1.0 mg/L in order to promote competition of microorganisms for a limited oxygen supply.
- ***Study showed that***
  - * High DO causes low pH which can be detrimental since mesophilic bacteria are sensitive to pH conditions (Enviroquip, 1999).
- The microorganisms that are out competed for oxygen must consume a portion of their cellular protoplasm in order to obtain energy for cell maintenance.
- However, only about 75% to 80% of the cell tissue can be oxidized while the remaining 20% to 25% is composed of inert and organic compounds that are not biodegradable (Metcalf and Eddy, 1991).
- ***This process is known as endogenous respiration and is help biomass or volatile solids destruction to be achieved.***

❖ ***The following table below shows stoichiometric equations associated with the steps in an aerobic digestion process.***

Process	Equation
Biomass Destruction in Aerobic Digestion	$C_5H_7NO_2 + 5O_2 = 4CO_2 + H_2O + NH_4HCO_3$
Nitrification	$NH_4 + 2O_2 = H_2O + 2H^+ + NO_3$
Biomass Destruction with Nitrification	$C_5H_7NO_2 + 7O_2 = 5CO_2 + 3H_2O + H^+ + NO_3$
Denitrification	$C_5H_7NO_2 + 4NO_3 + H_2O = +NH_{4+} 5HCO_3 + 2N_2$
Complete Nitrification-Denitrification	$C_5H_7NO_2 + 5.75O_2 = 5CO_2 + 3.5H_2O + 0.5N_2$

❖ There are ***five key optimization techniques*** that provide sludge stabilization sustainability of an aerobic digestion process and includes: *1) Tank Configuration*, *2) Thickening*, *3) Aerobic and Anoxic Control*, *4) Temperature Control*, *and 5) Operational Flexibility* (Water Environment Federation, 2007).

❖ There are several methods to ***define stabilized sludge*** such as ***specific volatile suspended solids (VSS) load***, ***types and concentration of vectors and pathogens occurred***.

- To meet the standard of stabilized sludge ***in pathogen elimination*** (Class A), the following criteria must be met: a fecal coliform density less than 1,000 most probable number (MPN) per gram of total dry solids or salmonella density less than 3 MPN per 4 grams of total dry solids (US EPA, 1993).
- In order to meet sludge stabilization where ***pathogens are significantly reduced but still present in large numbers*** (Class B), ***two criteria*** must be met as per the USEPA (1993).

  * ***The first criteria*** that must be met is Pathogen Reduction and this can be met by complying with one of these two requirements:

a) Pathogens in the sewage sludge containing less than 2,000,000 CFU per gram of total dry solids and

b) Meeting a time temperature requirement of 20 °C at 40 days SRT or 15°C at 60 days SRT.

* The **second criteria** is the **Vector Attraction** and can be met by meeting one of these two requirements:
  a) ***Volatile solids reduction of 38% or more or***
  b) ***Standard Oxygen Uptake Rate (SOUR)*** is the amount of oxygen used by microorganisms to burn volatile solids. 1.5 milligrams oxygen per hour per gram of dry solid (mg O2/g VSS/hr) or less (US EPA, 1993).

- For example, if a sludge sample has a SOUR of 1.49 mg O2/g VSS/hr and pathogens of 1,999,999 CFU per gram of total dry solids then it is in compliance with Class B stabilization requirements.

❖ The performance of an aerobic digestion system is also typically based on volatile solids destruction which is an indicator of sludge stabilization.

- However, volatile solids reduction may not be the best indicator of sludge stabilization or aerobic digestion performance.
- As noted above **SOUR** can also be used to meet the Vector Attraction Requirement of the US EPA.
- The **SOUR** is a good indicator of how much biodegradable organics are in the sludge hence indicating how stabilized sludge is.
  * A low SOUR means that there is not a lot of VS to burn in the solids.
  * *It is recommended to use the SOUR requirement for systems where the feed sludge being processed has low VS content.*

❖ ***What are the standard used in Ethiopia to dispose textile and leather industries sludge?***

- ❖ To determine volatile solids reduction, sludge with 85% VS processed to 75% VS content results in a volatile solids reduction of 47%. Compared to sludge with 70% VS content that is processed to 60% VS results in a volatile solids reduction of 35.7%.

  * As demonstrated reducing the volatile fraction of the solids 10% in both cases results in different volatile solids reduction. Going from 85% VS to 75% VS results in more volatile solids reduction than reducing from 70% to 60% which does not meet the Vector Attraction criteria for volatile solids reduction standards of the USEPA.
- ❖ However, sludge that is reduced to 60% has 50% less volatile solids content than sludge reduced down to 75%. This confirms that if sludge has higher volatile fraction it is much easier to achieve volatile solids reduction because of the presence of more readily biodegradable organics than one with lower volatile content.
- ❖ To conclude the SOUR is a better indicator of sludge stabilization than volatile solids reduction for a solids handling system including aerobic digestion.

- The SOUR is becoming a more common testing procedure for most operators instead of using the traditional volatile solids reduction (Water Environment Federation, 2007).
- **Equation: Van Kleeck Equation for Determining Volatile Solids Reduction**

$$Volatile\ Solids\ \mathrm{Re}duction\,(\%) = \left(\frac{VS_{IN} - VS_{OUT}}{VS_{IN} - (VS_{IN} x VS_{OUT})}\right) x100\%$$

- ❖ The **advantages** of aerobic digestion processes include low capital cost, low nitrogen and phosphorus in supernatant compared to anaerobic digestion processes, simple and robust operation, and ideal for treatment to Class B land application requirements.
- ❖ The **disadvantages** to this process is it has high energy costs associated with blowers used to provide air to the system, difficult to achieve Class A treatment since aerobic digestion requires a substantial quantity of microorganisms to stabilize the sludge, it is primarily used at small and medium facilities, and reduced efficiency during cold weather operations due to microbial activity being severely hindered.

▪ Aerobically digested sludge also has poor dewatering characteristics compared to anaerobically digested sludge since it contains less readily biodegradable organics.

* For example: The typical dewatered cake solids for aerobic digested PS plus WAS is typically between 16% and 25% with a centrifuge and 12% and 20% with a belt filter press. Compared to dewatered anaerobically digested PS plus WAS is between 22% to 32% with a centrifuge and 18% to 44% with a belt filter press (US EPA, 2000).

➢ Aerobic sludge treatment provided ***better organics removals*** compared to anaerobic sludge treatment for ***leather industry*** with a volatile suspended solids (VSS) removal of 38% and a Total/Dissolved Organic Carbon (TOC/DOC) removal of 65%.

➢ For textile industry, both aerobic and anaerobic treatment resulted in similar decreases in VSS (~50%) and TOC (~60%) concentrations.

▪ Although aerobic sludge stabilization was established after approximately 30 days for both leather and textile industries, as suggested by specific VSS loads, organic content of stabilized sludges did not decrease sufficiently to comply with the TOC/ DOC standards for landfill disposal and stabilized sludges are still classified as hazardous waste.

- ***Bioremediation*** is the use of biological systems for the reduction of pollution from air or from aquatic or terrestrial systems.
  - It also involves extracting a microbe from the environment and exposing it to a target contaminant so as to lessen the toxic component.
- Thus, the goal of bioremediation for sludge treatment is the employment of biosystems such as microbes, higher organisms like plants (phytoremediation) and animals to reduce the potential toxicity of chemical contaminants in the environment by degrading, transforming, and immobilizing these undesirable compounds.
  - A complete biodegradation results in detoxification by mineralising pollutants to CO2, water and harmless inorganic salts.
  - Incomplete biodegradation (i.e., mineralization) will produce compounds that are usually simpler (e.g., cleared rings, removal of halogens), but with physical and chemical characteristics different from the parent compound.
  - In addition, side reactions can produce compounds with varying levels of toxicity and mobility in the environment.
- Therefore, appropriate parameters should be optimized during the aerobic sludge stablization.

Activated Sludge

- ***Activated sludge*** is a biological process that utilizes microorganisms to convert organic and certain inorganic matter from wastewater into ***cell mass***.
  - The activated sludge is then separated from the liquid by ***clarification***.
  - The settled sludge is either returned (recycled activated sludge (RAS)) or wasted (wasted activated sludge (WAS)).
- Thus, ***Activated sludge*** is commonly used as a wastewater treatment process because it is an effective and versatile treatment process and capable of a high degree of treatment.

❖ ***An activated sludge*** wastewater treatment system has at least ***four components***;

a) an aeration tank,

b) a settling tank (clarifier),

c) a return sludge pump and

d) a system of introducing oxygen into the aeration tank.

a) *Wastewater, either pretreated or not,* ***enters the aeration tank*** *and* ***is mixed with a suspension of microbes in the presence of oxygen***.

▪ This mixture is referred to as ***mixed liquor***.

▪ The microbes metabolize the organic pollutants in the wastewater (as shown in the figure presented on the next slide).

b) *After spending on average an amount of time equal to the hydraulic residence time in the aeration tank, the mixed liquor flows into the clarifier, where the solids (Mixed Liquor Suspended Solids- MLSS) separate from the bulk liquid by* ***settling*** *to the bottom*.

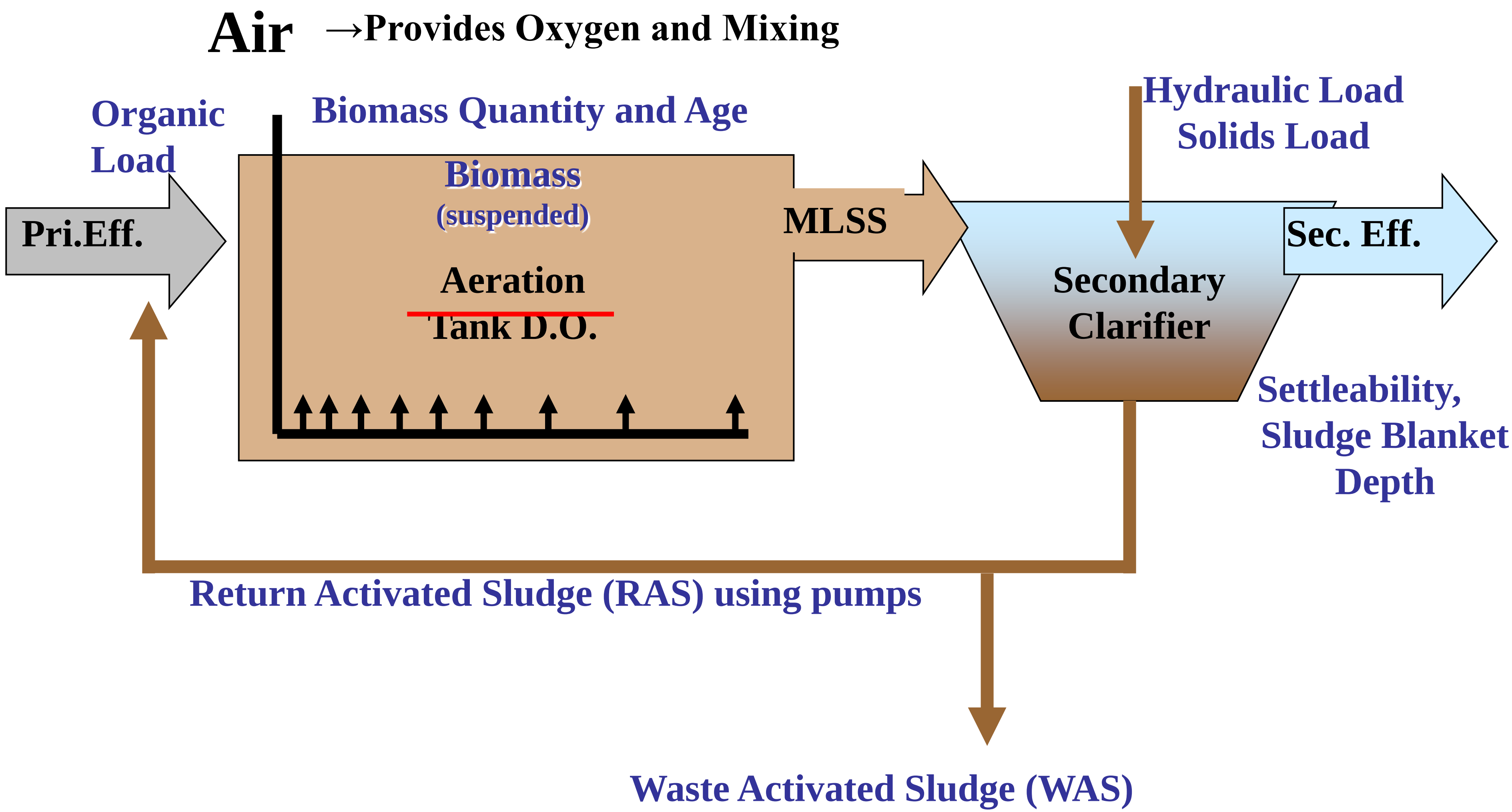
c) The clarified effluent then ***exits*** the system whereas the settled solids are harvested from the clarifier bottom and a fraction of the settled solids is ***recycled to the aeration tank*** whilst the remainder is discarded.

❖ ***Activated sludge processes*** are ***designed*** based on the ***mixed liquor suspended solids (MLSS)*** and ***the organic loading*** of the wastewater, as represented by the ***BOD or COD***.

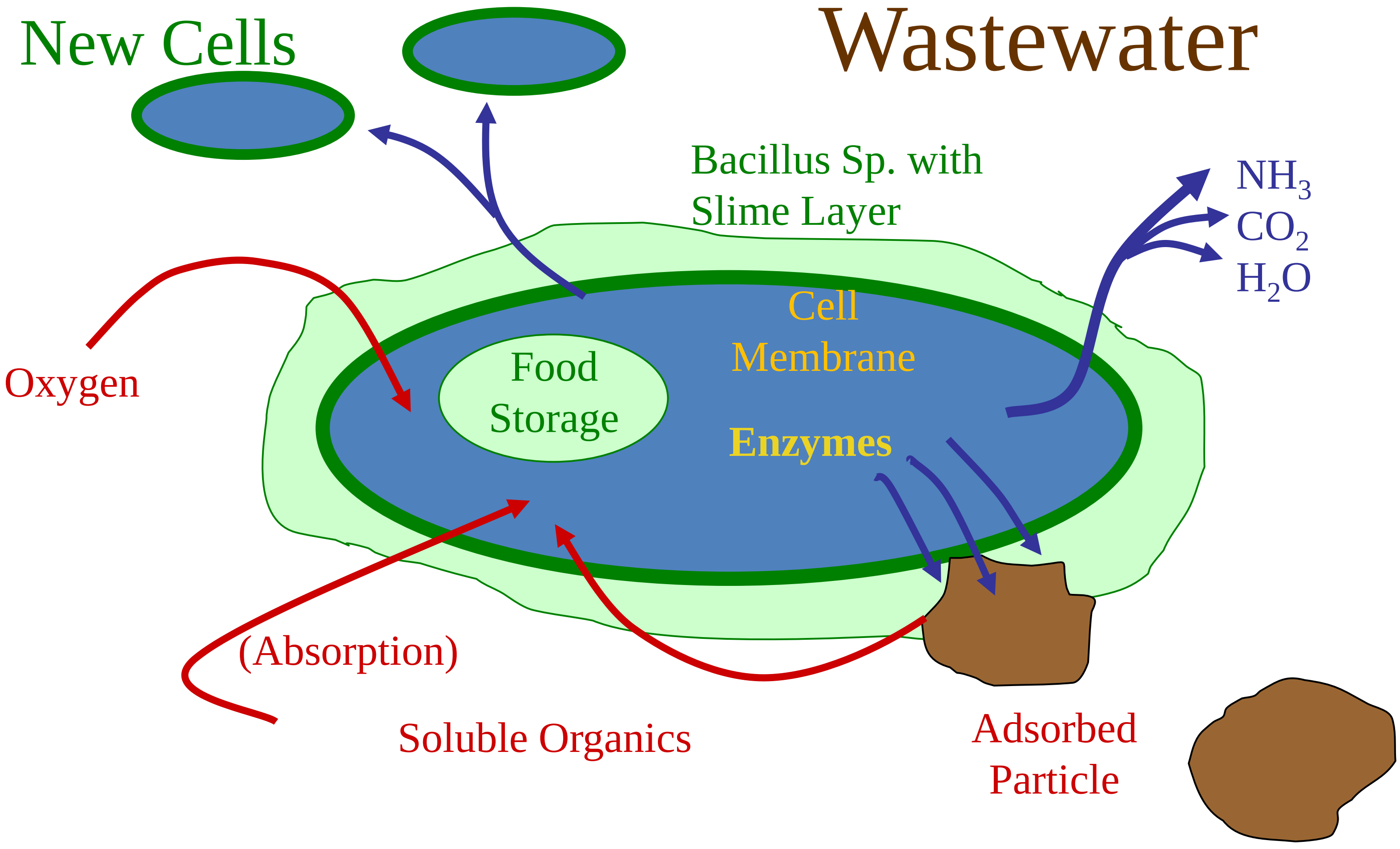
▪ The *MLSS represents the quantity of microorganisms* involved in the treatment of the organic materials in the aeration basin.

▪ The ***organic loading*** determines the requirements for the design of the aeration system.

- The result is the ability to control the average time microorganisms will remain in the reactor, called the ***sludge age (SRT)*** or ***mean cell retention time (MCRT).***
- Over time as wastewater moves through the aeration basin, *food (BOD) decreases with a resultant increase in cell mass (mixed liquor suspended solids (MLSS) concentration).*
- *Since MOs use oxygen to break down organic matter (food) for their growth and survival.*
- Those ***Mixed Liquor Volatile Suspended Solids (MLVSS)*** that are returned to the aeration tank are microbes in a starved condition, having been separated from untreated wastewater for an extended period and are thus referred to as **activated**.
- The main role of microorganisms in the activated sludge process is to ***convert dissolved*** and ***particulate organic matter***, measured as biochemical oxygen demand (BOD), into cell mass.
- This process of returning microbes from the clarifier to the aeration tank enables buildup of their concentrations to high levels (1,800 to 10,000 mg/L) and that, indeed, characterizes the activated sludge process itself (Woodard, 2001).
- The solids in the sludge contain nutrients of high value to plants, as well as humus like material which improves the capacity of poor soils to hold water and air.
- Unfortunately, industrial sources, household wastes and urban runoff, introduce quantities of toxic materials into municipal sludge.
- Human waste also contains harmful organisms such as disease-causing bacteria, viruses and parasites.
- The generated sludge usually is in the form of a liquid or semisolid, ***containing 0.25 to 12 % solids by weight***, depending upon the treatment operations and processes used.



- ❖ Need favorable conditions for growth and for separation from the water.
- ❖ Growth rate produces about 0.31751 kg (0.7lbs) of biological solids per 0.45359 kg (1lb) BOD removed.



➢**The mechanism of biological Sludge treatment follow three steps:**

a) Transfer of Food from Wastewater to Cell: use adequate mixing and enough detention time.

b) Conversion of Food to New Cells and Byproducts.

c) Flocculation and Solids Removal: proper mixing, proper growth environment, secondary clarification

Anaerobic Sludge Stabilization

- ❖ Anaerobic digestion (AD) is a bacterial decomposition process that stabilizes organic wastes and produces a mixture of ***methane and carbon dioxide gas***.
- ❖ The *calorific value of methane is the same as natural petroleum gas*, and *biogas is valuable as an energy source*.
- ❖ Anaerobic digestion is typically carried out in a specially built digester, where the content is mixed and the digester maintained at **35°C to 40°C** by combusting the biogas produced.
- ▪ After digestion, Biogas is collected from the digester, and the sludge is passed to a sedimentation tank where the sludge is thickened.
- ▪ The thickened sludge requires further treatment earlier to reuse or disposal.
- ➢ Anaerobic digestion treatment of sludge will ***decrease the volatile organics by 40 to 50%*** and ***reduce the numbers of pathogenic organics in sludge***.
- ▪ Traditional methods are accomplished by holding the sludge in closed tanks for periods of ***up to 90 days*** due to used unheated, unmixed tanks, results in very long detention time.
- ▪ ***However more recent processes involve complete mixing and heating to temperatures of 35 to 40 °C, reducing detention time up to 10 to 20 days.***
- ➢ The main features of **AD process** are ***mass reduction, biogas production and improved dewatering properties of the treated sludge.***
- ❑ ***The advantages*** of anaerobic digestion include the *production of usable energy in the form of methane gas, low solid production and very low energy input*.
- ▪ ***Disadvantage*** includes very high capital costs, susceptibility to upsets from shock loads or toxics, and complex operation requiring skilled operators.

Biogas Production Process

➢ *The anaerobic digestion process is characterized by a series of* ***four biochemical transformations processes*** *occur* ***simultaneously using different consortia of bacteria.***

❖ **These process includes:**

* ***hydrolysis, acidification, acetogenesis and methanogenesis.***

▪ ***These four processes are categorized into two: fermentation and methanogenic processes.***

a) Hydrolysis process: macro molecules like proteins, polysaccharides such as cellulose, hemicellulose, lignin and fats that compose the cellular mass of the excess sludge are converted into molecules with a smaller atomic mass that are soluble in water.

* The hydrolysis or solubilisation process is carried out by extracellular enzymes excreted by fermentative bacteria.

* *The rate of hydrolysis depends on the pH, temperature, composition and concentration of intermediate compounds.*

* The products are peptides, amino acids, fatty acids and simple sugar.

b) Acidification/Acidogenesis Process: a process that results in the conversion of the hydrolysed products into simple molecules with a low molecular weight, like ***volatile fatty acids*** (e.g. acetic-, propionic- and butyric acid), ***alcohols***, ***aldehydes*** and ***gases*** like H_2, CO_2 and NH_3.

▪ Acidification is effected by a very diverse group of bacteria, the majority of which are ***strictly anaerobic***, i.e. ***the presence of oxidants like oxygen or nitrate is toxic.***

▪ The acidogenic bacteria are able to metabolize organic material down to a ***very low pH*** of ***around 4***.

c) Acetogenesis Process: the products of the acidification are converted into ***acetic acids***, ***hydrogen***, and ***carbon dioxide*** by acetogenic bacteria.

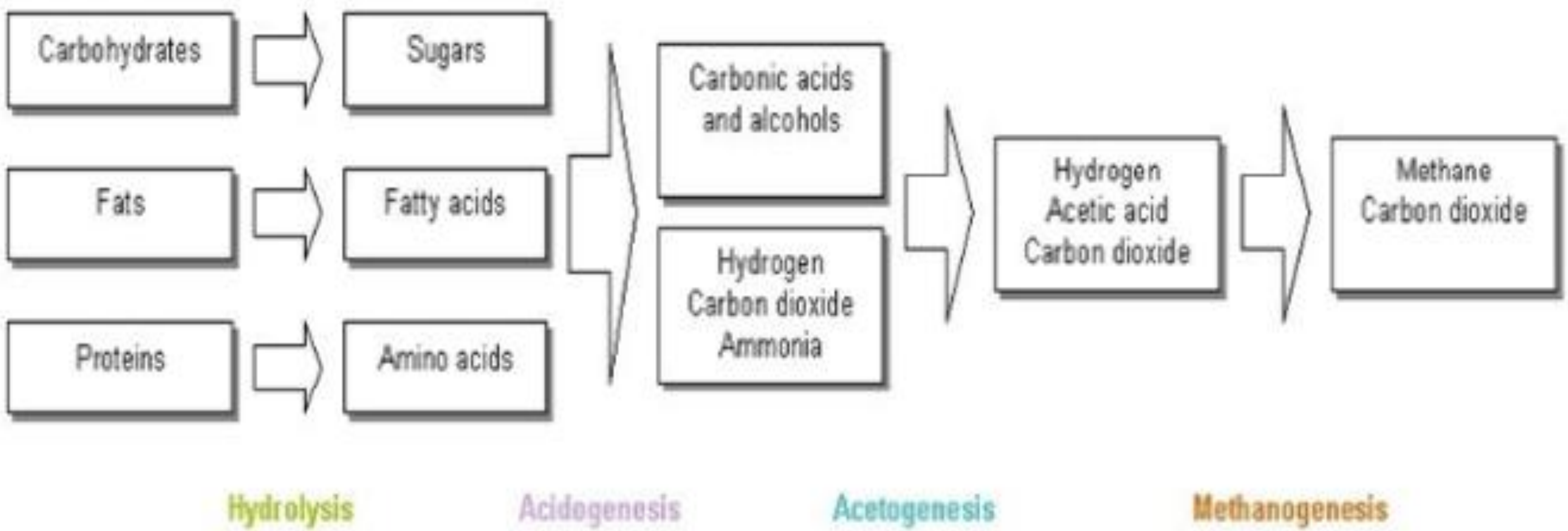
- ***The first three steps of anaerobic digestion are often grouped together as acid fermentation.***
- It is important to note that in the acid fermentation, no organic material is removed from the liquid phase: it is transformed into a form suitable as substrate for the subsequent process of methanogenesis.

d) Methanogenesis Process: the products of the acid fermentation (mainly acetic acid) are converted into CO_2 and CH_4, and organic material will be removed, as the produced methane gas will largely desorbs from the liquid phase. ***S***trictly anaerobic methane forming bacteria like Methanobacterium, Methanococcus, *Methano sarcina*, etc are involved.

❖ ***Methanogenesis produces methane by two groups of methanogenic bacteria:***

a) the first group splits acetate into methane and carbon dioxide and

b) the second group uses hydrogen as electron donor and carbon dioxide as acceptor to produce methane.



Sludge from Municipal Wastewater Treatment Plant

- Sludge generated from municipal wastewater treatment plants are mainly primary sludge and activated sludge.
- The end-product after handling the two types of sludge through *anaerobic or aerobic digestion* is *digested sludge*.

Primary sludge

- Primary is also called raw sludge which comes from the bottom of the primary clarifier.
- Primary sludge is easily biodegradable since it consists of more easily digestible carbohydrates and fats, compared to activated sludge which consists of complex carbohydrates, proteins and long chain hydrocarbons. *So biogas is more easily produced from primary sludge.*

Activated sludge

- Activated sludge is also called excess sludge or waste activated sludge which comes from the secondary treatment, and is more difficult to digest than primary sludge.
- It‘s a result of overproduction of microorganisms in the activated sludge process.

Digested sludge

- After anaerobic digestion of primary and activated sludge the residual product is digested sludge.
- The digested sludge is reduced in mass, less odorous, safer in the aspect of pathogens and more easily dewatered than the primary and activated sludge (Anders, 2005).

Sludge Pre-treatment for Increased Biogas Production

- ❖ Anaerobic digestion has a great future amongst the biological technologies of sludge treatment in view of *biogas generation as well as reducing solids mass*.
- ***However, the low overall biodegradation efficiency of the sludge solids and long retention times (20-30 days)*** **result in only moderate efficiencies.**
- Thus, ***Biogas production can be improved by several pretreatments*** in order *to lyse sludge cells further to facilitate hydrolysis*, since the biogas production mainly depends on the biodegradability and hydrolysis rate.
- Thermal, chemical, biological and mechanical processes, as well as combinations of these, can be possible pre-treatments *cause the lysis of or disintegration of sludge cells permitting* the release of intracellular matter that becomes more accessible to anaerobic microorganisms.
- *This fact* ***improves the overall digestion process velocity*** and the ***degree of sludge degradation***, *thus* ***reducing anaerobic digester retention time and increasing methane production rates***.

Thermal pre-treatment

- ➢ While the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected from the enzymatic hydrolysis by the cell wall.
- ➢ Heat applied during thermal treatment destroyed the chemical bonds of the cell wall and membrane, thus makes the proteins accessible for biological degradation.
- ➢ *In practice, the optimum temperature is in range of 160-180ºC and treatment times from 30 to 60 min, pressure associated to these temperatures may vary from 600 to 2500 kPa.*
- Gavala et al. (2008) has concluded that temperature and duration of the optimum pretreatment depend on the ***nature of the sludge***:
  - * the greater the proportion of difficult hydrolyzing biological sludge substrates, higher the intensity of pretreatments needed.

Chemical pre-treatment

❑ An efficient and cost-effective method to hydrolyze the cell wall and membrane and thus increase solubility of the organic matter contained within the cells.

▪ According to different studies, chemical methods can be divided to acid and alkaline hydrolysis and oxidation.

❑ The most frequent studied oxidative methods are ozonation and peroxidation.

▪ Acid and alkaline hydrolysis will be introduced in the thermo-chemical pretreatment part.

Biological pre-treatment

❖ The use of microbial enzymes for the enhancement of degradation of waste activated sludge called the *Enzymatic Hydrolysis (EH)* process was proposed by Mayhew *et al. (2002).*

❖ EH process was first used to kill pathogens, however, an enhancement of biogas production was observed during anaerobic digestion.

❖ Mayhew et al. (2003) kept the waste activated sludge at 42 ºC using a holding chamber, with 2 days' retention time of EH stage in lab scale, they found a 10% improvement in biogas production.

❖ Miah et al. (2004) measured a 210% enhanced biogas production during thermophilic digestion (at 65 ºC) caused by the protease activity of the Geobacillus sp. Strain AT1.

Mechanical pre-treatment

➢ Mechanical pretreatment plays an important role because it ***favors solubilization*** of particulate matters in liquid phase.

➢ This method is increase the degradability of organic matters by disrupting the flocs and/or lysing the bacterial cells.

➢ The most often used techniques in mechanical pretreatment are ***ultrasonication, grinding and high pressure homogenization.***

Ozonation

- **Ozone** is a strong cell-lytic agent, which can kill the microorganisms in activated sludge and further oxidize the organic substances released from the cells.
- The sludge biodegradation is affected by ozone dose.
- *Following ozonation, the characteristics of the sludge are greatly changes.*

a) The flocs are broken down into fine, dispersed particles.

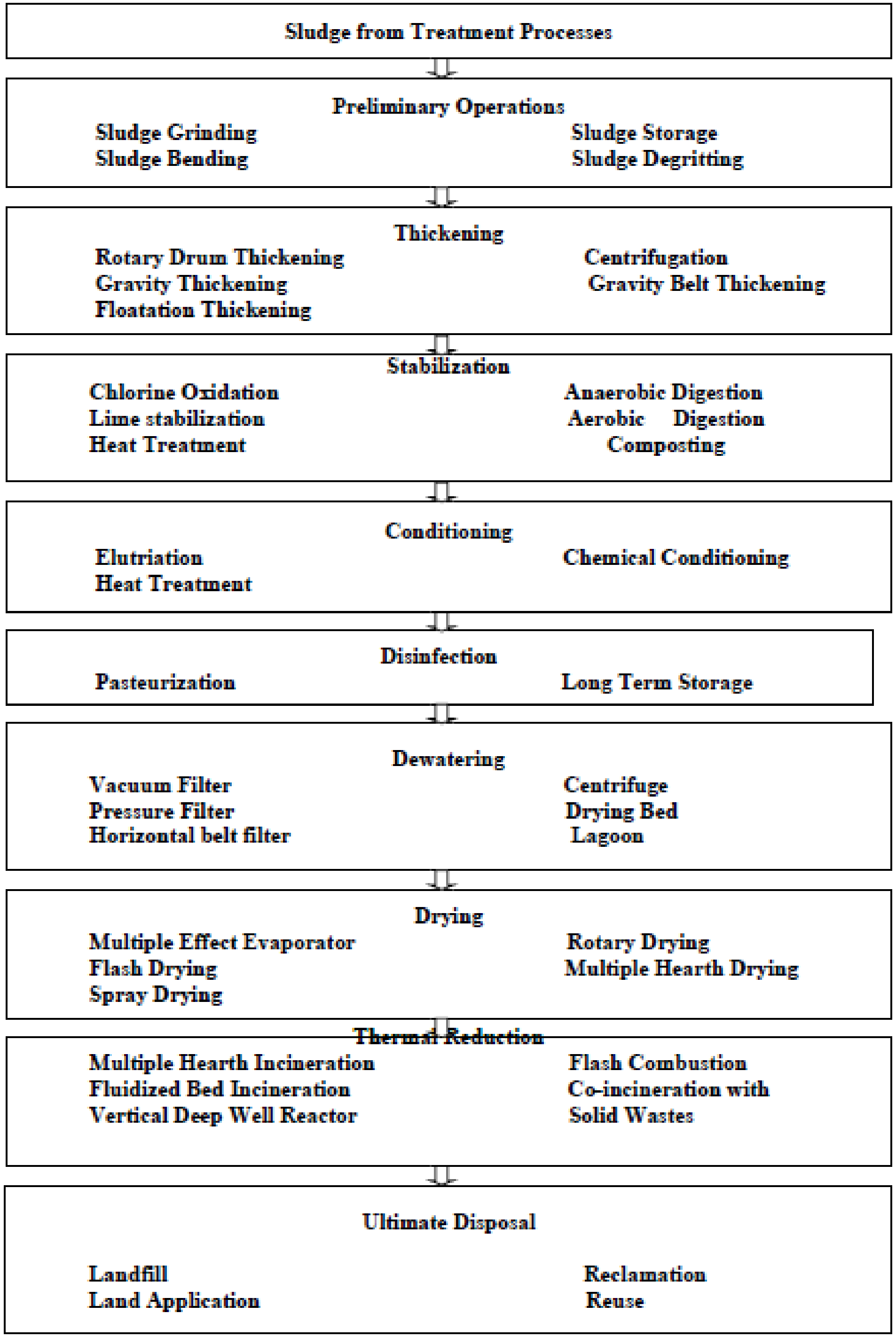
b) Floc integration and solubilization generates a large number of micro-particles dispersed in the supernatant in addition to soluble organic substances.

- *Ozonation treatment has two counteracting effects:*

a) degradation of molecules and cell structures that are undegradable for methanogenic bacteria will increase biogas production;

b) <u>oxidation of organic molecules that are degradable for methanogenic bacteria will decrease biogas production</u>.

- Yeom et al. (2002) showed that when the ozone dose was 0.1 g O3/g TSS, the biodegradation was about 2-3 times greater compared with raw sludge in both aerobic and anaerobic conditions for 5 days.



- ❖ Sludge is treated by various processes that can be used in various combinations.
- ❖ The chart flow in the left shows the different process of sludge treatment.

STABILIZATION

- ➢ Sludge is stabilized to reduce their pathogen content, eliminate offensive odors, heavy metals and reduce or eliminate the potential for putrefaction.
- ➢ Technologies used for stabilization include lime stabilization, heat treatment, aerobic digestion, anaerobic digestion and composting.

Heavy Metal Bioleaching from Sludges

- During the treatment of sewage, a huge volume of sludge is generated, which is disposed of on land as soil fertilizer/conditioner due to the presence of nitrogen, phosphorus, potassium and other nutrients (copper, zinc, molybdenum, boron, iron, magnesium and calcium) and organic matter which are beneficial to forestry, vegetation production and landscaping.
- The ***enhanced biomass yield*** have an increase in organic matter content (2.38%), nitrogen content (0.20%), moisture content (5%), porosity (11%) and water retention capacity in soil.
- ***The increased microbial activity, respiration and enzymatic activities were reported in the soil amended with sludge.***
- ***However, the presence of toxic heavy metals and other toxic compounds in the sludge restricts its use as a biofertilizer for all wastes.***
- The concentration of heavy metals in the sludge is found to be nearly **0.5–2% on dry weight** basis, which may go up to as **high as 6%** in some cases.
- ***Contamination of soil, ground and surface water by the metals leached from the sludge is a serious environmental issue.***
- Further, ***the excess nutrients such as nitrogen and phosphorus present in the sludge*** may ***leach to the ground water***, ***if not consumed by the vegetation.***
- A variety of ***toxic organic pollutants such as PAHs, PCDD/Fs*** and ***pathogenic bacteria*** present in the sewage sludge are also a cause of serious environmental concern.
- ***Therefore, decontamination of the sewage sludge prior to its disposal assumes great importance in land application.***

- Use of various chemicals such as ***$Fe_2(SO_4)_3$ and $FeCl_3$***, ***chelating agents*** such as ***Ethylene Di- amine Tetraacetic Acid (EDTA)*** and ***Nitrilotriacetic acid (NTA)*** and ***organic and inorganic acids*** have been reported for extraction of metals from sludge.

❖ *However, the practical application of the chemical processes is still limited due to the requirement of large amount of chemicals, the high operating cost, the operational difficulties and the secondary pollution problems associated with them* (Blais et al., 2005).

➢ **Therefore, the research interest towards *bioleaching process* that has been reported to be an efficient and economical method for removal of heavy metals from the sludge.**

- **Hence, Biotechnological bioleaching should be developed as an environmentally friendly and cost effective technology for the removal of heavy metals from the sludge.**

❖ During sewage treatment, about ***50–80% of the total quantity of heavy metals*** present in sewage gets ***fixed into the sludge by various physicochemical and biological interactions***.

- ***The mobility, bioavailability and eco-toxicity of the metals*** depend on the ***specific chemical forms or bindings in which the metals exist in the sludge***.

❖ ***Bioleaching*** *is defined as the solubilization of metals from solid substrates either* ***directly by the metabolism of leaching bacteria*** *or* ***indirectly by the products of microbial metabolism***.

- Bioleaching process uses the ***catalytic*** effect produced by the metabolic activities of microbes such as iron-oxidizing and sulfur-oxidizing microorganisms resulting in an acceleration of the chemical degradation of the sulfides.

- It is a low cost, environment friendly technique which is ***80% cheaper*** in terms of chemical consumption compared to the traditional chemical methods employed for metals leaching from the sludge and recovery of metals from the leachate.

Microorganisms

- Different types of microorganisms play an important role in the bioleaching process.
- The microorganisms intensively used in bioleaching process belong to the genus of *Thiobacillus (Acidithiobacillus).*
- ***Eg.:*** *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*
- ***The maximum leaching occurs when conditions are optimum for bacterial growth and metal solubilization.***

➢ ***Bioleaching*** process using acidophilic iron and sulfur oxidizing bacteria (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thioosidans)* and neutrophilic microorganisms (*Aspergillus niger)* has been intensively investigated for successful removal of metals from sediment, municipal solid and sludge.

➢ Sulfur oxidizing bacteria oxidizes and produces acid for solubilization of heavy metals by obtaining power supplied from the utilization of elemental sulfur and thiosulfate in bioleaching process.

- The method for elimination of toxic metal contaminated soil and water by application of the sulfur bio cycle.
- Bio-oxidation reactions on the principle of direct or indirect oxidation often participate in the bioleaching process in parallel.
- *Thiobacillus ferooxidants and T. thiooxidants* are responsible for the bacterial leaching process, which is carried out in acidic environment where the pH value remain at ***1.5-3*** and other metal compounds remain in solution. At lower pH acidophilic *Thiobacillus ferooxidants and T. thiooxidants* can grow.
- Other *thiobacilli* are capable to oxidize sulfur and sulfide to sulfate at higher pH in which condition other metal ions do not remain in solution.

- ***The microorganisms exploited for bioleaching of metals can be classified broadly as mesophiles and thermophiles*** on the basis of the ***temperature range for their growth***.
- The most dominant mesophiles used in bioleaching of metals from sludge are *sulfur-oxidizing bacteria (At. thiooxidans) and iron-oxidizing bacteria (At. ferrooxidans).*
- ***These are chemolithotrophic bacteria which get their energy by oxidation of ferrous iron or reduced sulfur compounds.***
- The optimum temperature for growth of *thiobacillus spp* is around **33 °C**, although it can grow at any temperature in the range **20–40 °C**.
- The growth occurs at a **pH** in the range **1.0–4.5** with an optimum value between **2.0 and 2.3**.
- *Acidithiobacillus caldus* was reported to be the key bacteria in bioleaching at **pH <2** instead of *At. thiooxidans* which was earlier reported to be the dominant acidophile in bioleaching of sludge.

Mechanisms of Metal Bioleaching

- The most widely used microorganisms in metal bioleaching are At. thiooxidans and At. ferrooxidans because of their unique property to ***survive in acidic environment*** and ***to carry out oxidation of insoluble iron and sulfur compounds***.
- In particular, since these acidophilic, chemoautotrophic bacterium requires atmospheric CO2 as a carbon source and derives energy to support growth and maintenance, from such inorganic substances as ***reduced iron/sulfur***, these microbes obviates the need to provide additional exogenous carbon sources and electron donors.
- In addition, no rigorous sterilization is required during practical operation because, at the low pH values preferred by this acidophile, other potential biocontaminants cannot metabolize actively and are unable to compete with *At ferrooxidans* and *At thiooxidans*.
- ***Two mechanisms of bacterial metal leaching have been proposed.***

A) In ***sulfur based bioleaching process***, the dissolution of metal sulfides takes place by *direct and indirect mechanisms.*

1) In direct bacterial leaching, the bacteria are in direct contact with the metallic sulfide in the sludge.

* *Metal sulfide is directly oxidized by the At. thiooxidans into soluble metal sulfate according to the following reaction:*

$$\mathbf{MeS + 2O2 \xrightarrow{At.\ thiooxidans} MeSO4} \qquad (1)$$

where MeS is the insoluble metal sulfide; MeSO4 is *soluble metal sulfate*

* Thus, the metallic sulfides such as NiS, CuS, ZnS etc. present in the sewage sludge can be solubilized by the above mechanism.

2) In indirect bacterial leaching, the elemental sulfur or reduced sulfur compounds in the sludge are oxidized by sulfur-oxidizing bacteria into ***sulfuric acid*** which reduces the pH of the sludge medium, thereby enhancing the solubilization of the metal.

$$\mathbf{S° + H2O + 1{:}5O2 \xrightarrow{At.\ thiooxidans} H2SO4} \qquad (2)$$

$$\mathbf{H2SO4 + sludge – Me \longrightarrow sludge - 2H + MeSO4} \qquad (3)$$

* Where **S°** is elemental or reduced sulfur; Me is a bivalent metal.

* In reaction (2) Acidithiobacillus take active part, whereas reaction (3) takes place chemically without any involvement of bacteria.

* In indirect leaching, bacteria accelerate the oxidation of elemental sulfur, which otherwise takes place very slowly in the absence of bacteria.

B) ***In Iron based bioleaching process***, the oxidation of reduced iron and sulfur compounds takes place by direct and indirect mechanisms.

1) ***In the direct bacterial leaching***, non-ferrous metallic sulfide is directly oxidized by At. ferrooxidans into soluble metal sulfate according to following reaction:

$$\mathbf{MeS + 2O_2 \xrightarrow{\text{At. ferroxidans}} MeSO_4} \quad (4)$$

2) ***In the indirect mechanism***, the bacteria *oxidize Fe+2 to Fe+3 in the liquid phase* and the Fe+3 in turn leaches through a chemical reaction.

$$\mathbf{2FeSO_4 + 0{:}5O_2 + H_2SO_4 \xrightarrow{\text{At. ferroxidans}} Fe_2(SO_4)_3 + H_2O} \quad (5)$$

$$\mathbf{4Fe_2(SO_4)_3 + 2MeS + 4H_2O + 2O_2 \longrightarrow 2Me^{2+} + 2SO_4^{-2} + 8FeSO_4 + 4H_2SO_4} \quad (6)$$

* where **MeS** is the metal sulfide and **Me2+** is soluble metallic ion.

- In reaction (5) At. ferrooxidans take active part, whereas reaction (6) takes place chemically without any involvement of bacteria.
- ***A cyclic process between these two reactions leads to more and more metal solubilization*.**
- ***The production of sulfuric acid further enhances the overall efficiency of the process.***

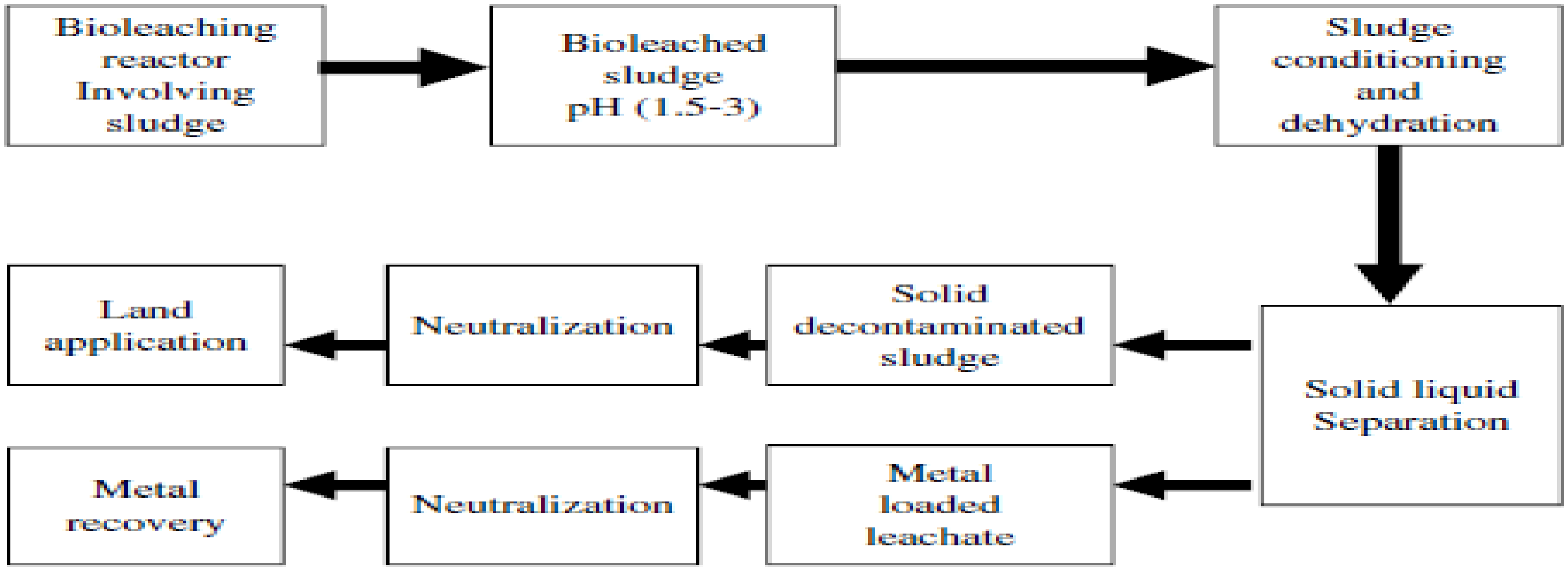
➢ Studies reported batch bioleaching with anaerobic digested sludge using *At. ferrooxidans* and *FeSO4 as an energy source*.

- The sludge was pre-acidified to ***pH 4*** and the effect of ***aeration rate, pH and temperature*** on the ***efficiency of metal removal was kept to the optimum***.
- They reported solubilization of **65% Cu**, **78% Ni**, **87% Zn**, **86% Cd** and **0% Pb** in **8 days** of batch experiments.

➢Bioleaching was also found efficient in removal of ***90% of the heterotrophic microorganisms without affecting the sludge nutrients and conditioning properties.***

- For metal solubilization, the optimum initial pH was found to be 4 and the optimum range of temperature was between 25 and 30 °C.

➢***A schematic diagram of the overall bioleaching process is shown in the following figure.***



Factors affecting the process of bioleaching:

- ***Physicochemical as well as microbiological*** factors of the leaching environment are affecting rates and efficiencies.

* Particularly, properties of the solids to be leached, pulp density, pH, particle size, activities of the bacteria itself, cell adaptation, initial concentration of bacteria, source energy and inorganic nutrients, mineralogical composition and concentration, temperature, oxygen and surfactants and organic compounds were identified as major factors.

❖ ***Table shows the factors and parameters influencing bacterial mineral oxidation and metal mobilization***

Factor	Parameter
Physicochemical parameters of a bioleaching environment	temperature pH redox potential water potential oxygen content and availability carbon dioxide content mass transfer nutrient availability iron(III) concentration light pressure surface tension presence of inhibitors
Microbiological parameters of a bioleaching environment	microbial diversity population density microbial activities spatial distribution of microorganisms metal tolerance adaptation abilities of microorganisms
Properties of the minerals to be leached	mineral type mineral composition mineral dissemination grain size surface area porosity hydrophobicity galvanic interactions formation of secondary minerals
Processing	leaching mode (*in situ*, heap, dump, or tank leaching) pulp density stirring rate (in case of tank leaching operations) heap geometry (in case of heap leaching)

Metal recovery and economy of the process

- One of the advantages of bioleaching process is that it can be integrated with various physical and hydrometallurgical techniques to recover all the precious metals in various forms.
- The integrated process for the removal of heavy metals from the sludge and recovery of the metals from the metal rich leachate is a key consideration for efficient performance and cost effectiveness of the bioleaching process.
- Various methods such as precipitation, adsorption, biosorption, ion-exchange, solvent extraction and electrochemical technology can be used to recover the metals from the leachate.
- ***Generally, soluble metals in the leachate are converted into insoluble metallic forms by chemical precipitation and is the most simple and widely used method.***
- For recovery of the metals from the leachate, the solution pH has to be increased up to 7 or more so that the metals can be precipitated from the solution.
- ***However, recovery of the metals from the leachate requires following considerations:***

i. use of controlled quantity of precipitating reagents to avoid undesirable concentration in treated effluent;
ii. efficiency of the technique for separation of metal from the leachate;
iii. safe disposal of metal rich chemical sludge generated in the metal precipitation process;
iv. the type of reagent affecting the process cost.