

SWIM and Horizon 2020 Support Mechanism

Working for a Sustainable Mediterranean, Caring for our Future

Physical-Chemical Treatment

Presented by:

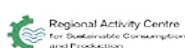
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Lecture
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Leachte Management Training Program

June 25th-29th, 2018, Beirut, Lebanon

This Project is funded by the European Union



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OUTLINE

- Introduction
- Selected physical/chemical treatment methods
 - Coagulation/flocculation methods
 - Precipitation method
 - Adsorption methods
 - Oxidation methods
- Physical-chemical unit operations in the pretreatment stage of a full treatment train

Physical Treatment Methods

- SEDIMENTATION
 - HOLDING POND
- EVAPORATION
 - SPRAYING
 - HEATING
- AIR STRIPPING
- FILTRATION
 - GRANULAR MEDIA
 - ULTRAFILTRATION
 - REVERSE OSMOSIS
- ADSORPTION
 - CARBON
 - ION EXCHANGE

Source: Shack, P.A, Leachate Treatment Technologies, Phoenix Env. Engineering,

Chemical Treatment Methods

- PH ADJUSTMENT
- SEPARATION TECHNOLOGIES
 - COAGULATION
 - METALS PRECIPITATION
 - HYDROXIDE
 - SULFIDE
 - AMMONIA STRIPPING
 - ELECTROCOAGULATION
- CHEMICAL OXIDATION TECHNOLOGIES
 - CHLORINATION
 - OZONE/UV
 - HYDROGEN PEROXIDE
 - PERMANGANATE
 - CHLORINE DIOXIDE

Source: Shack, P.A, Leachate Treatment Technologies, Phoenix Env. Engineering,

Selected Processes for the Presentation

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PROCESS	ADVANTAGES	DISADVANTAGES	SUB-PRODUCTS
Coagulation Flocculation	Adaptable flow of treatment Reduction of 40-50 % hard COD Agglomeration of suspended solids	Important production of sludge (20% the treated volume)	Sludge
Precipitation	Precipitation of metals Reduction in suspended solids Elimination of part of the carbonated and nitrified matter	Production of metallic hydroxide sludge	Sludge
Activated carbon	Elimination of residual COD. Reduction of the organohalogen compounds Reduction of colour	Renewal of absorbers	"Regeneration" by external suppliers
Ozone oxidation (+ H ₂ O ₂ and/or UV)	Elimination of the hard DCO. Decoloration Increase of the bio-degradable character	Sensitive to variations in loads; Energy consumption	Events with residual ozone (gaseous phase)

Adsorption

Oxidation

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Coagulation and Flocculation 1

Coagulation is the addition of chemicals that promote the aggregation of smaller, non-settleable particles and colloidal particles into larger, more settleable or floatable particles.

As a result of the common electrical charges on the surface of the small particles, the particles tend to repel each other. This is similar to magnets when similar poles are placed near each other. The repelling prevents the particles from clumping together, thereby enabling them to remain in suspension.

The coagulant chemical neutralizes the electrical charge on the surface of the small particles, resulting in the destabilization of the suspension.

Typical chemicals used in the coagulation process include hydroxides, such as lime (calcium hydroxide) and aluminum or magnesium hydroxide.

Flocculation is the process of forming larger particles from coagulated matter. It is typically accomplished by gentle mixing to promote additional inter-particle contact of the destabilized particles.

Typical chemicals used in the flocculation processes include synthetic organic polymers.

Coagulation and Flocculation 2

Removal of colloids:

- The individual colloids must aggregate and grow in size
- Coagulation & flocculation are used to agglomerate colloids prior to separation of solids

Coagulation: the addition and rapid mixing of coagulant

- for destabilization of particles
- for initial aggregation of the destabilized particles

Flocculation: the slow stirring or gentle agitation

- to aggregated stabilized particles
- to form rapidly settling flocs

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Coagulation



Jar Testing

Jar Testing is a laboratory procedure that simulates coagulation, flocculation, and precipitation results with differing chemical dosages

- The single most valuable tool in operating and controlling a chemical treatment process is the variable speed, multiple station Jar Test Apparatus.
- Various chemicals and/or dosages can be tested simultaneously and the results compared side-by-side.
- Tests are good indications of dosage and concentrations of treatment chemicals required, but should be followed by full-scale laboratory testing.
- Tests will only have meaning if the tested water exactly resembles the flow stream that will ultimately be treated. A single batch of grab sample tests will rarely provide reliable information



Precipitation

Precipitation is the chemical conversion of soluble substances (including metals) into insoluble particles.

Coagulation and flocculation cause a chemical reaction that promotes the formation and agglomeration, or clumping of these particles to facilitate settling.

The amount or dosage of a precipitant, coagulant, or flocculant needed to precipitate and remove substances in water solutions is dependent on many factors. These include:

- Concentration of substance in solution
- Solution pH
- Chemical used to adjust the pH
- Different types (and concentrations) of substances present
- Amount and types of complexing agents present
- Amount of residual oxidizers present
- Coagulants and flocculants used
- Sequence in which chemicals are added

Coagulation/Flocculation Treatment

- Use mostly of iron or aluminum salts for coagulation/precipitation and polymers for flocculation
- Frequent testing for dose control and type of products are absolutely essential for a good performance
- The process is efficient in reducing suspended solids, colloidal particles and heavy metals
- Separation of chemical sludge with contaminants for subsequent treatment and disposal

Advantages:

- Low investment cost

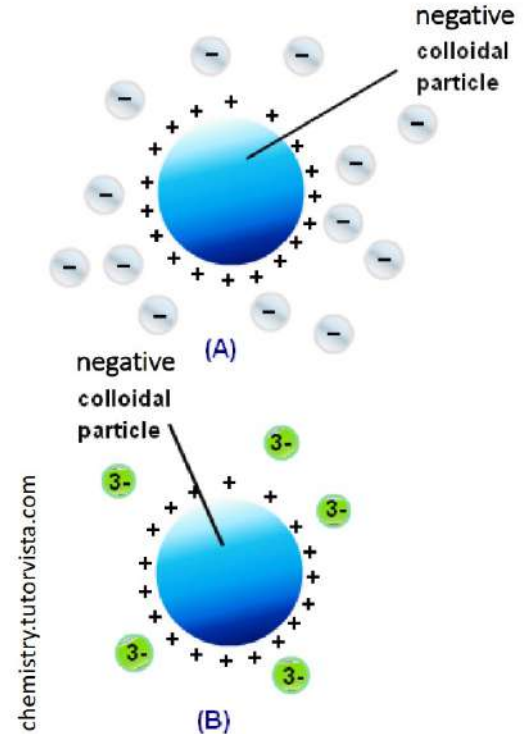
Disadvantages:

- High demand operation (analysis and tests)
- High operation cost
- High production of chemical sludge

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Coagulation basics

- Colloidal particles size ranging 1 nm-1 μ m Cause turbidity color in raw surface water
- It is difficult to separate colloids from water. Colloids do not settle by gravity. They pass through the pores of most common filter media
- Colloidal particles adsorb water molecules and oppositely charged ions from bulk water on their surface gaining repulsion from each other and stability in solution

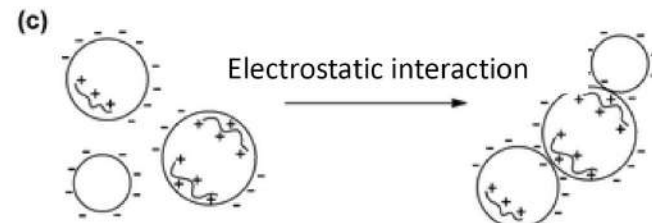
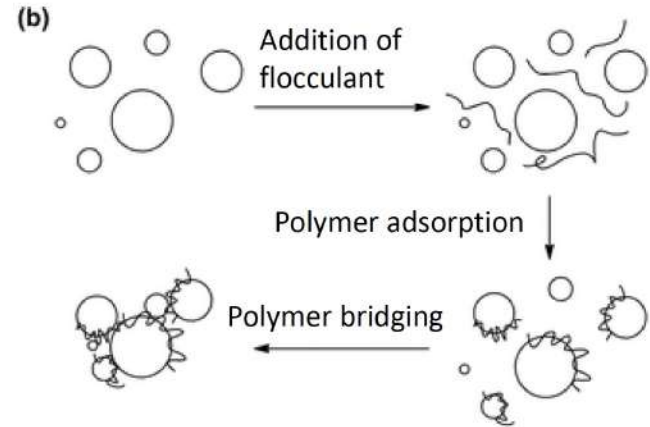
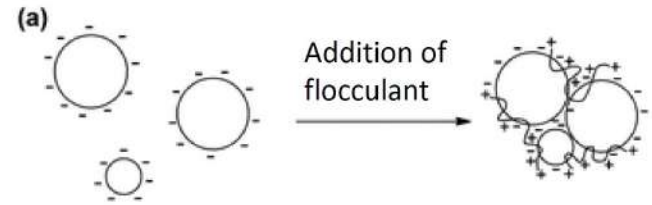
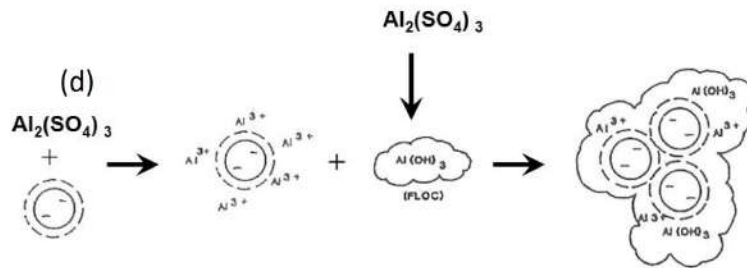


Source: Aalto University, course notes on physical and chemical treatment of water and wastewater, lecture on “precipitation, coagulation and flocculation”.

Flocculation mechanisms

Schematic representation of colloidal suspension flocculation by:

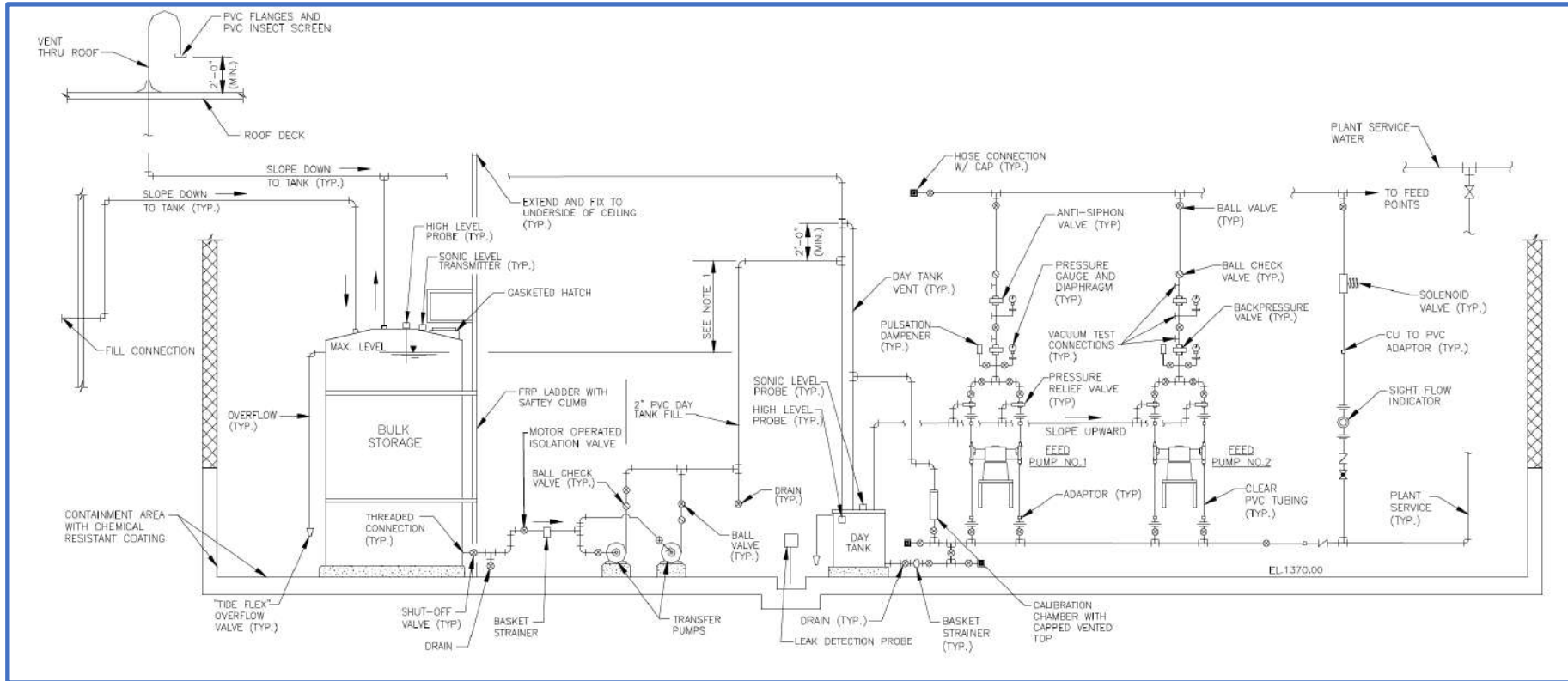
- (a) Charge neutralization
- (b) Polymer adsorption and bridging
- (c) Electrostatic patch
- (d) Enmeshment (trapping) in the precipitate or sweep flocculation (with metal cations)



Dosing systems for flocculants

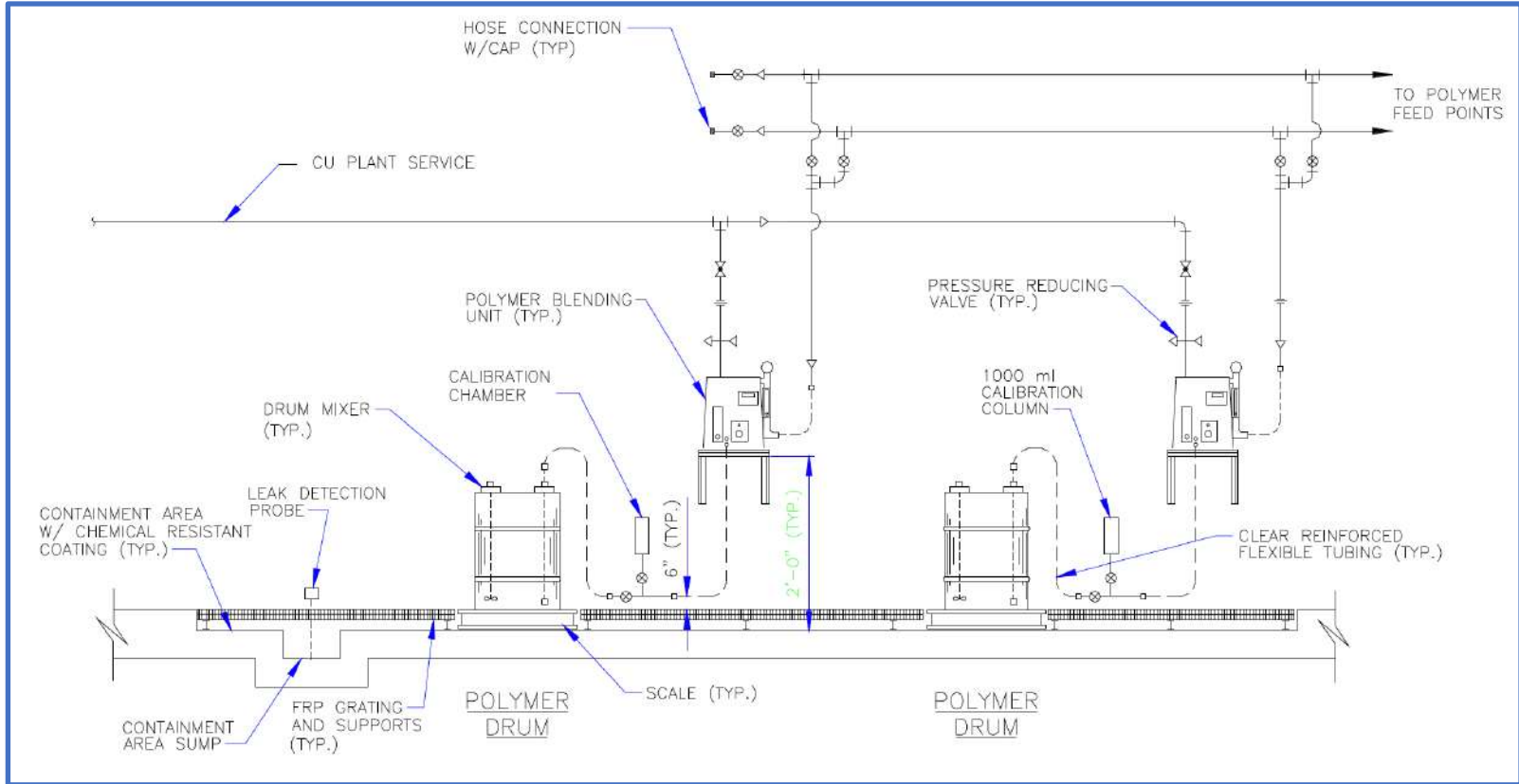
- Industrial scale dissolution of flocculants requires a procedure which has to be adapted to the flocculant specifications
 - solutions are very viscous
 - high shear should be avoided during mixing
 - flocculant particles if not properly dispersed tend to agglomerate lumps of flocculant do not dissolve easily
- A dissolution plant has the following components
 - a disperser system to ensure a proper wetting of the powder without agglomeration
 - a dissolving tank
 - a transfer pump
 - a stock tank
 - a metering pump and dilution system

Liquid Chemical Feed System



Source: Pennsylvania Department of Env. Protection, WWTP operator certification program, Module 7, Basics of Chemical Feed Systems

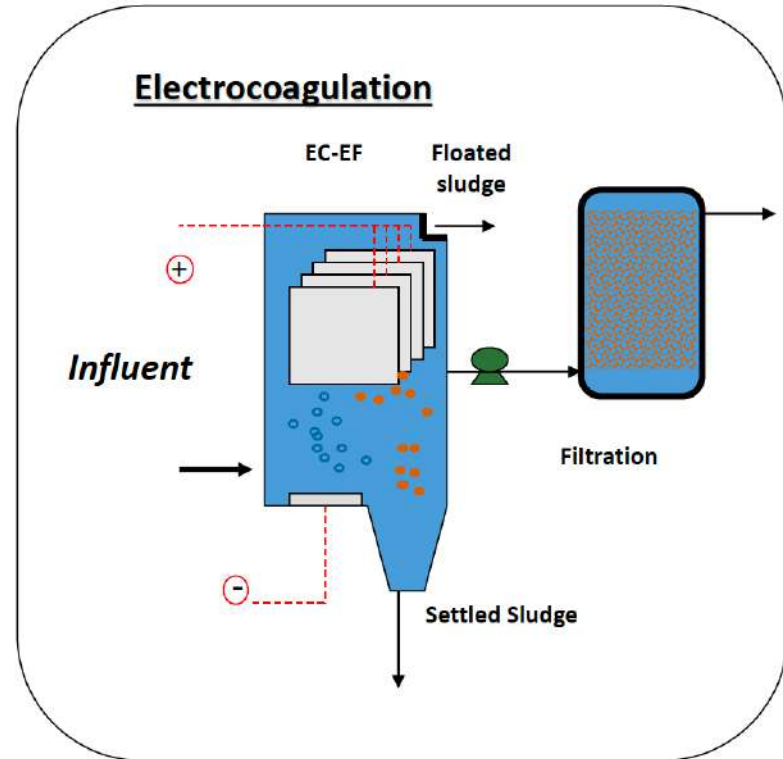
Liquid Polymer Feed System



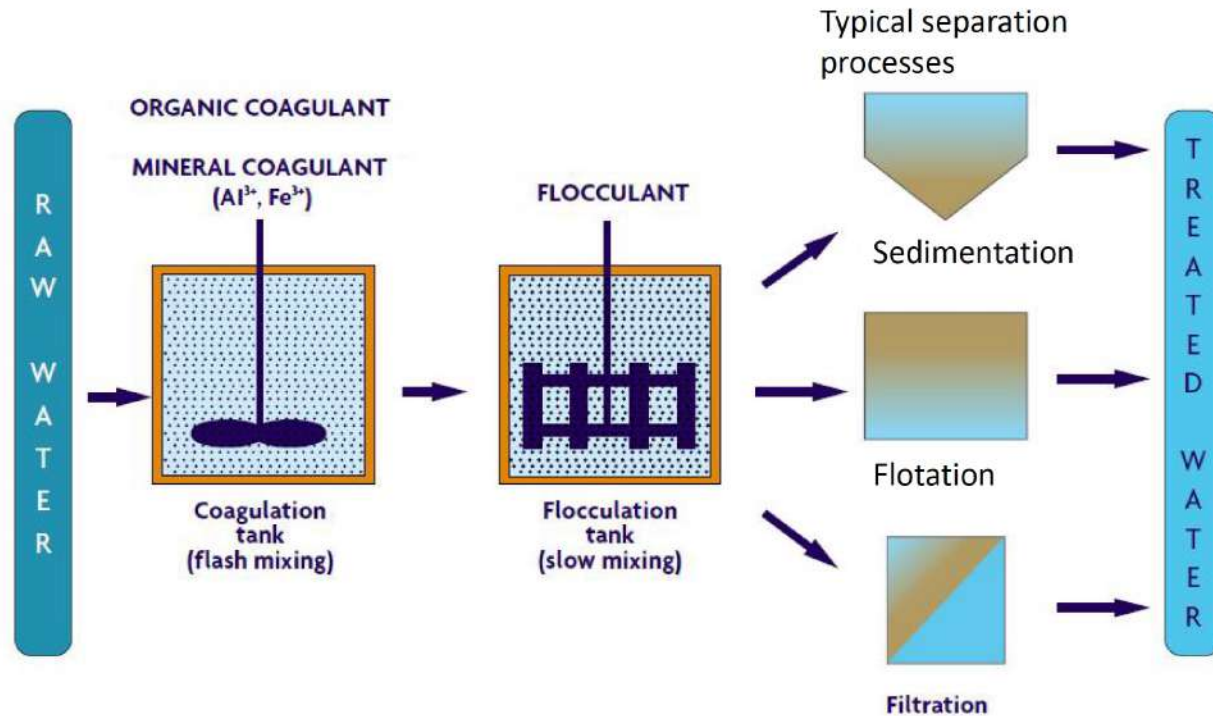
Electro-coagulation

Electrocoagulation

An alternative to the direct use of a solution containing the coagulant salts, is the in situ generation of coagulants by electrolytic oxidation of an appropriate anode material (e.g. iron or aluminium). This process is called electrocoagulation or electrochemically assisted coagulation.



Separation after precipitation and coagulation-flocculation



Solid Separation

Solid Separation Unit Operations:

- Sedimentation
- Flotation
- Filtration
- Centrifugation

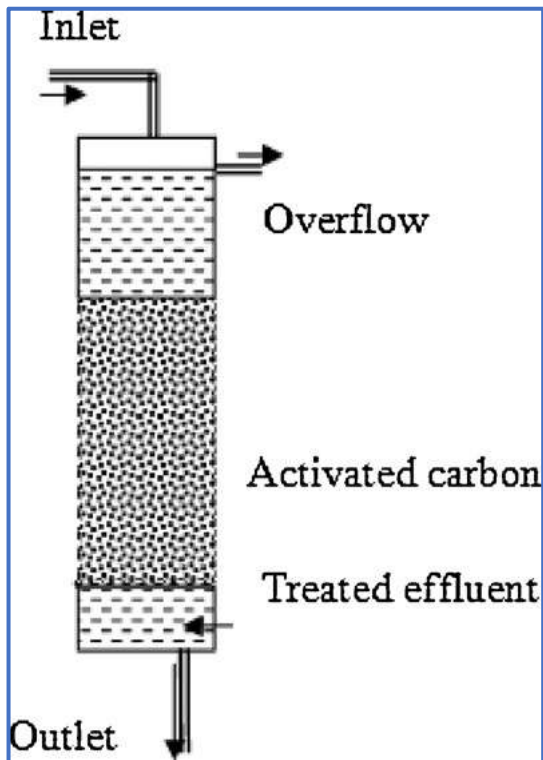
Source: ISWA¹⁵ World Congress
Antwerp, Leachte Management
Presentation, September 2015



Adsorption Methods

- Granular activated carbon (GAC) in combination with biological pretreatment is the leading technology for the treatment of landfill leachate for the removal of COD, adsorbable organic halogens (AOX) and other toxic substances.
- Adsorption is the process by which molecules with particular characteristics of size and polarity are attracted and held to the adsorbing surface. More than 130 different types of organics have been identified on spent carbon from leachate treatment plants.
- GAC is used to remove AOX and COD, both of which are not the primary focus of biological treatment systems.
- With particularly dilute leachate, it may be operated with a plate separator or pressurized sand filter to remove suspended solids from the flow to ensure that they do not block the carbon filter. It is necessary to ensure that no substances are present in the leachate that would damage the carbon prior to selecting a system.
- Activated carbon has been used as a final polishing step after biological treatment, ultra-violet (UV)-oxidation, sedimentation and other physico-chemical treatment methods.

Adsorbent Types and Applications



Adsorbent	Technology	Application
Granular Activated Carbon (GAC)	Fixed bed, e.g. filter	Organics removal (bulk and micropollutant)
Biological Activated Carbon (BAC)	Fixed bed, e.g. filter	Organics removal (bulk and micropollutant), often after oxidation process to remove biodegradable matter
Powdered Activated Carbon (PAC)	Dosed in suspension, needs removal, often applied temporarily as emergency response to contamination	Organics removal (bulk and micropollutant), often to combat seasonal taste & odour problems in WTP
Zeolites	Both, suspended and fixed bed	Ion exchange, softening, heavy metals
Ion exchange resins	Suspended, need regeneration	Ion Exchange, softening, natural organic matter removal
Novel materials: carbón nanotubes, graphene oxide, etc	Diversity of tailored surfaces, adsorbents, applications,	

Leachate Adsorption Units



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Chemical Oxidation Methods

Oxidant	Oxidizing Potential (V)
Fluorine (F)	3.03
Hydroxyl radical (OH \cdot)	2.80
Oxygen atom (O)	2.42
Ozone (O $_3$)	2.07
Hydrogen peroxide (H $_2$ O $_2$)	1.76
Permanganate ion (MnO $_4^-$)	1.67
Chlorine dioxide (ClO $_2$)	1.15
Chlorine (Cl $_2$)	1.36

- COMMON OXIDANTS
 - BLEACH
 - HYDROGEN PEROXIDE
 - FENTONS REAGENT
 - OZONE
 - CHLORINE DIOXIDE



Conventional and Applied Oxidation Processes

HOCl: chiefly employed as disinfectant, inconvenience of generating halogenated disinfection byproducts (DBPs)

NH₂Cl: disinfectant for distribution, fewer DBPs, but e.g. NDMA formation.

ClO₂: disinfectant or pre-oxidation before HOCl to reduce DBP formation, but forms chlorite.

O₃: cheap, energy efficient, good removal for many electron rich contaminants, generates bromate in bromide rich waters

UV/H₂O₂: more expensive, higher cost/energy compared to O₃, no byproduct/ bromate formation

All oxidation processes generally only transform molecules but don't mineralize! Even if a process is capable of mineralizing, doing so would be uneconomical in most situations.

Advanced Oxidation Processes

- **Major mechanism**
 - Direct or indirect production of radicals OH^\cdot
- **Typical processes**
 - Fenton ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$)
 - Ozonation (O_3)
 - Radiation UV (+ H_2O_2)
- **Advantages:**
 - Partial destruction and size reduction of molecules – degradability improvement of “hard” COD.
 - Increase of biological processes performance.
 - Partial conversion of organic contaminants in CO_2 and N_2 .
- **Disadvantages:**
 - Subsequent production of sludge and treatment.
 - Due to presence of chlorine compounds in leachate, potential formation of toxic products (e.g. trihalomethane).
 - High demand of electrical energy for devices (e.g. ozonisers, UV lamps ultrasounds), which results in rather high treatment costs.
 - For complete degradation (mineralization) of the pollutants to occur, high quantities of oxidants are required



Source: ISWA¹⁵ World Congress Antwerp, Leachate Management Presentation, September 2015

Advanced Oxidation Processes

UV-C/H₂O₂: mostly $\cdot\text{OH}$ reaction pathways

O₃: mix of ozone and $\cdot\text{OH}$ reaction pathways, addition of H₂O₂ and/or UV-C and/or raising pH can promote $\cdot\text{OH}$ generation.

Fenton & photo-Fenton (with UV or solar): wide variety of conditions, typically pH=3, sludge generation. Mix of reactions, e.g. also photolysis of iron-organic complexes

Semiconductor photocatalysis (UV-A or solar): suspension or immobilised – both with respective trade-offs. A lot of materials research on photocatalyst development, TiO₂ remains the standard. Inherently low quantum efficiency due to prevalent electron – hole recombination. Much research (>40'000 papers) – Little application.

Electrochemical oxidation: Existing applications rely on mediated oxidation (e.g. generate HOCl from Cl⁻ in situ), sulfate as mediator “hot topic”, electrode and reactor development required. Also direct oxidation.

Sonolysis & Hydrodynamic cavitation: generate bubbles that collapse generating high temperature & pressure in minute space. Complex chemistry (e.g. water splitting). Energy intensive.

Advanced Oxidation Processes

- A lot of (advanced) oxidation processes, but only few are really applied broadly. Others only applied in research or niche applications.
- Many processes generate a mix of reactive species.
- Water chemistry (matrix) and treatment objective will define the fit-for-purpose application.
- Homogeneous versus heterogeneous reaction systems taking into account oxidant lifetime and mass transfer.
- (Electrical) energy per order of contaminant transformation typical figure-of-merit.
- Oxidation rather transforms organic contaminants instead of mineralizing them.
- Most organic contaminants can be treated by AOPs (fewer by conventional oxidation) – the questions is which is the process least costly, energy intensive, does not generate undesired secondary contamination, by-products, most safe, resilient etc.
- Some exceptions exist, e.g. polyfluorinated compounds, but most react simply more or less rapidly, i.e. treatment becomes more or less effective.

Physical-chemical unit operations in the pretreatment stage of a full treatment train

