Water Harmony
Erasmus+

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Industrial wastewater

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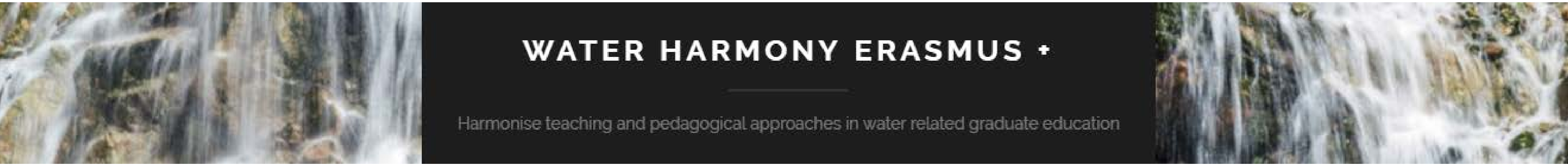


Outline

– Wastewater generated in industries
– Treatment concepts – general remarks
– Overview of treatment processes
– Solid-liquid separation
– Removal of dissolved inorganic substances
– Removal of dissolved organic substances
– Final remarks

Wastewater generated in industries

Important types of industrial wastewater:

- Process water
- Water from rinsing and cleaning processes
- Scrubber and vacuum pump water
- Water from hydraulic transport processes
- Blow-down water from cooling systems
- Concentrates from water treatment processes
- Sanitary water
- Polluted rain water

Treatment concepts – general remarks

Development

In the past: Treatment in a central mechanical-biological plant on-site or together with domestic wastewater (end-of-pipe)

Now: Decentralized (pre-)treatment of separate wastewater streams (point-of-source), followed by a central plant if needed

Challenges with separate wastewater streams

1. small volumetric flow rates
2. high concentrations of pollutants
3. often discontinuous flow

Treatment concepts – general remarks

Conclusions

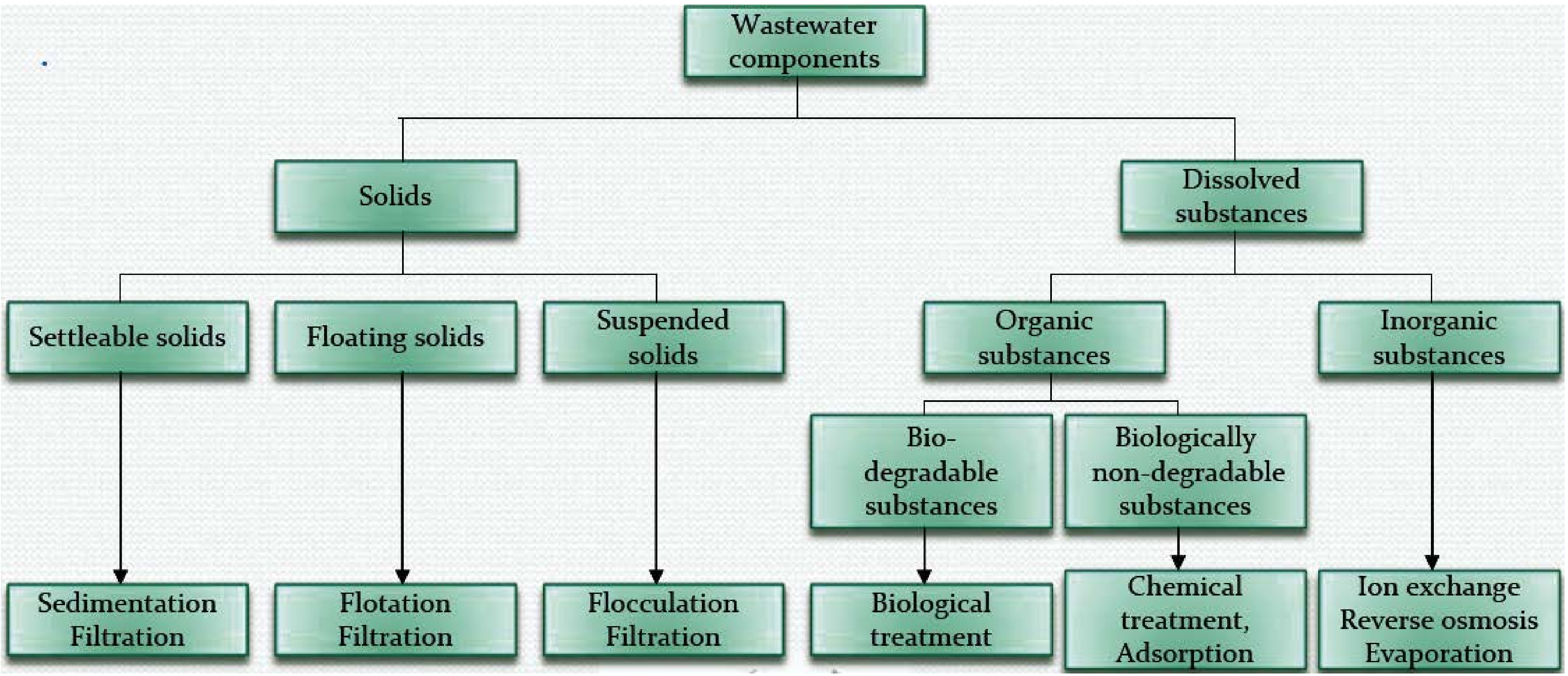
For pre-treatment purposes, biological processes are suited if

- the substances to be removed are degradable,
- the process is not affected by other toxic substances, and
- adequate adaptability to the fluctuating conditions is possible.

Therefore, physical-chemical or chemical processes must often be applied for the (pre-)treatment of separate streams.

These processes are also important as process-related measures for emission reduction.

Overview of treatment processes



Solid-liquid separation

Sedimentation in inclined-plate settlers

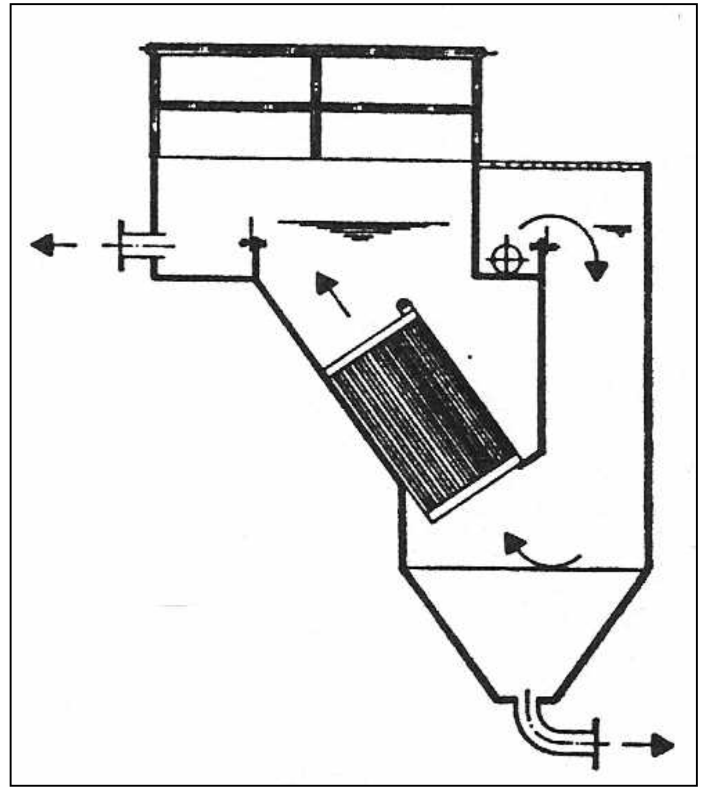
Idea: Enlargement of the effective settling area

Important aspect: Up-flow operation

Typical design parameters:

- distance between plates: 20 -100 mm
- angle of inclination: 55 - 60°

Manufactured sizes: Q = 1 - 300 m^3/h



Inclined-plate settler
(Courtesy Vereinigte Kesselwerke)

Solid-liquid separation

Oil removal by coalescence separators

Operating principle:

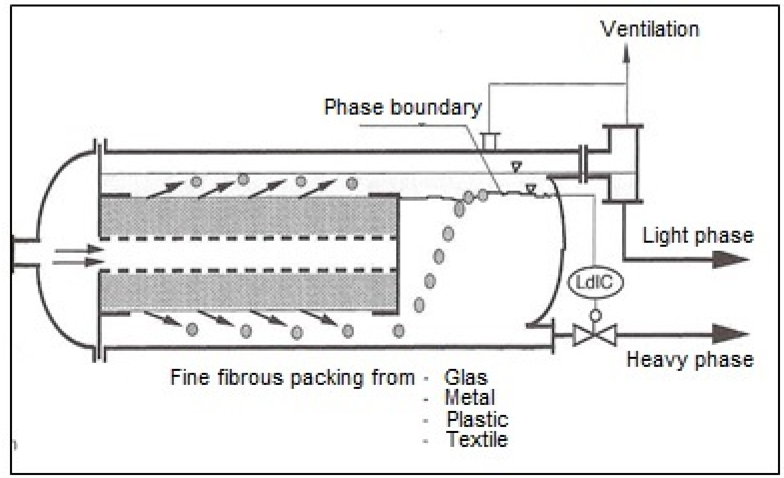
Formation of larger oil drops from fine oil droplets (5 - 20 µm) by hydrodynamic effects

General requirements in Germany:

Effluent concentrations < 5 mg/L HC when tested with a water/oil mixture according to DIN 1999

Limitation of mechanical oil separation:

Removal of stable emulsified oil droplets



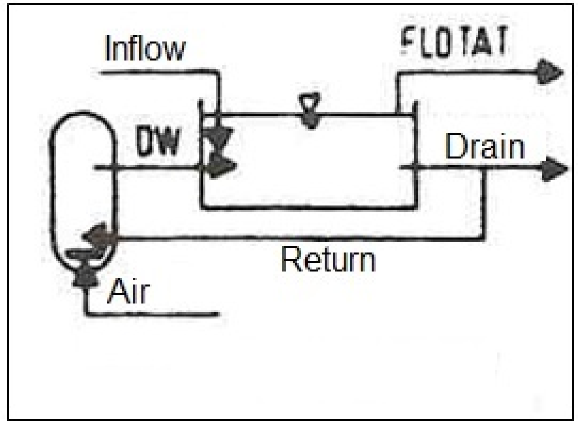
Coalescence separator

Solid-liquid separation

Dissolved air flotation (DAF)

Operating principle:

- saturation of recycled effluent with pressurized air
- formation of air bubbles in the flotation basin
- attachment of particles on air bubbles
- floating of the air-solid aggregates to the surface



Principle of DAF

Typical design parameters:

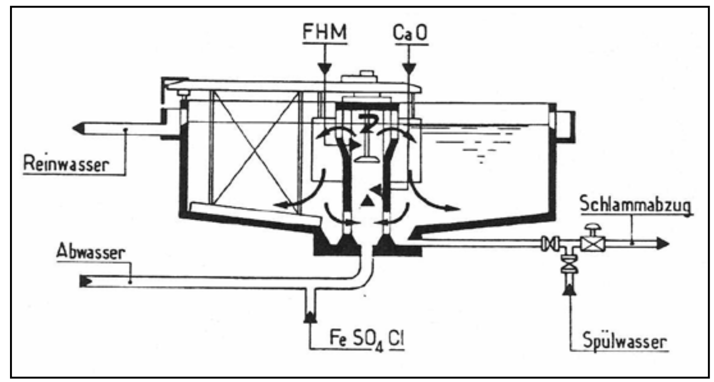
- hydraulic surface loading: 2 - 15 $m^3/(m^2 * h)$
- operating pressure: 2 - 6 bar
- recycle ratio: 0.1 - 0.5 (except sludge thickening)
- air : solids ratio: 3 - 100 L_N / kg TSS

Solid-liquid separation

Flocculation in circular reactors

Principle:

- dosing of metal coagulants (iron or aluminium salts) into the inflow
- floc formation in the central part of the reactor, supported by polymer addition
- floc separation by settling in the outer volume of the reactor



Turbo-Circulator (Courtesy Ph. Müller)

Operating parameters:

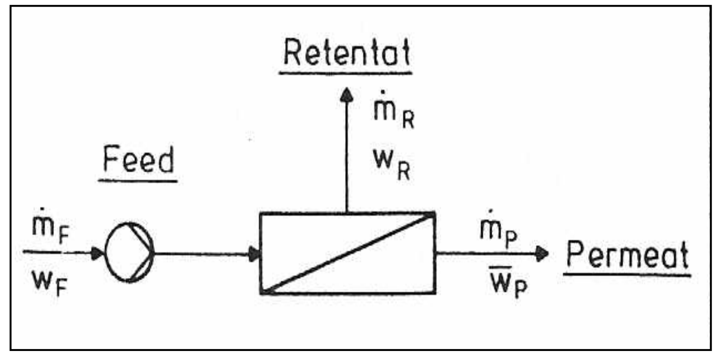
- hydraulic surface loading: 2 - 6 $m^3/(m^2 * h)$
- coagulant dosages: 5 - 50 mg/L Me
- pH adjustment: pH = 5.5 - 7.5

Solid-liquid separation

Micro- and Ultrafiltration

Operating principle:

Separation of an inflow (feed) stream into a filtrate (permeate) stream and a concentrate (retentate) stream by organic or inorganic membranes with well-defined pore sizes



Principle of membrane filtration

Differentiation:

Microfiltration → separation size 50 - 10,000 nm
operating pressure 0.5 - 5 bar

Ultrafiltration → separation size 5 - 50 nm
operating pressure 1 - 10 bar

Solid-liquid separation

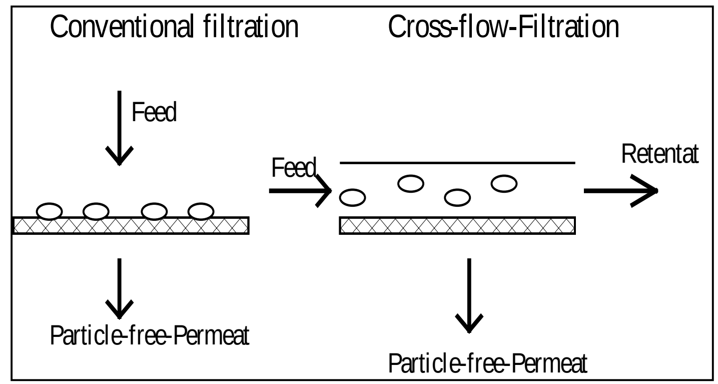
Micro- and Ultrafiltration

Design selection criteria:

- TSS feed concentration
- recovery
- operating mode
- energy demand
- residuals and their disposal
- fouling potential of the membrane
- rinsing and cleaning procedures

Operating mode:

→ cross-flow (applied in wastewater treatment)
→ dead-end (used for process water treatment)



Operating modes of membrane filtration

Solid-liquid separation

Typical applications in industries

Inclined-plate settlers:	Removal of particles and chemical flocs, e.g. after precipitation of heavy metals from metal-plating wastewater streams
Coalescence separators:	Pre-treatment of wastewater containing oil droplets, e.g. effluents from machine shops
Dissolved air flotation:	Removal of hydrophobic solids with low density, e.g. from wastewater streams generated in food industries and slaughterhouses
Compact flocculation:	Coagulation of fine particle and colloids, e.g. for producing process water from river water

Solid-liquid separation

Typical applications in industries

Microfiltration: Removal of fine particles and oil droplets from all kinds of small wastewater streams

Ultrafiltration: Separation of emulsions (e.g. drilling oils, compressor condensates) with cross-flow inorganic membranes

Separation of proteins from whey, soya extracts etc.

Recovery of dyes and sizing agents from dying of textiles

Recovery of water-based paints from electrocoating processes

Separation of activated sludge flocs from effluents in membrane bio-reactors

Removal of dissolved inorganic substances

Ion exchange

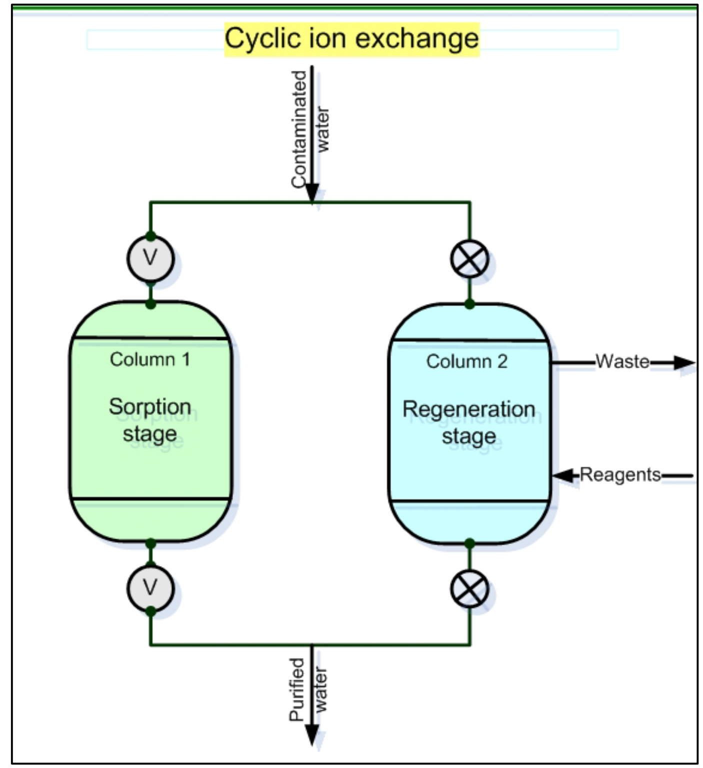
Operating principle:

Uptake of cations or anions from wastewater by porous resin beads that release a stoichiometric amount of ions (of the same charge) originally bound to the resin (sorption stage)

Desorption of these ions from the resin by applying a concentrated solution of the ions initially present on the resin (regeneration stage)

Operating mode:

→ co-current (for high ion concentrations)
→ counter-current (for high effluent qualities)



Source: http://www.ion-exchange.com.aa

Removal of dissolved inorganic substances

Precipitation of heavy metals

Principle of precipitation processes:

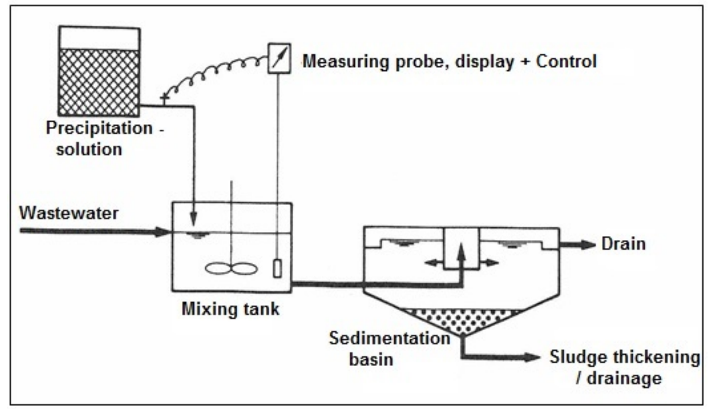
Transformation of dissolved substances by chemical reactions in components with low solubility

→ Hydroxide precipitation: Precipitation of metal ions as hydroxides or basic salts

Solubility product $L = a(Me^{z+}) \cdot a(OH^{-})^{z} << 1$

→ Sulphide precipitation: Precipitation of divalent metal ions as sulfides

Solubility product $L = a(Me^{2+}) \cdot a(S^{2-}) << 1$



Precipitation stage

Removal of dissolved inorganic substances

Oxidation

Principle of oxidation processes:

Release of electrons by a substance, increase of its oxidation state

Oxidizing agents in industrial wastewater treatment, applied for instance for the detoxification of cyanide:

- Hydrogen peroxide H_2O_2

$$CN^- + H_2O_2 + H_2O + H^+ \Leftrightarrow NH_4^+ + HCO_3^-$$

- Ozone O_3

$$CN^- + O_3 + 2\,H_2O + H^+ \Leftrightarrow NH_4^+ + O_2 + HCO_3^-$$

- Sodium hypochlorite NaOCl

$$2\,CN^- + 5\,OCl^- + H_2O \Leftrightarrow N_2 + 5\,Cl^- + 2\,HCO_3^-$$

Removal of dissolved inorganic substances

Reduction

<u>Principle of reduction processes</u>:

Uptake of electrons by a substance, decrease of its oxidation state

<u>Reducing agents in industrial water and wastewater treatment</u>, applied for instance for the detoxification of chromate:

- Sodium hydrogen sulfite $NaHSO_3$

$$Na_2Cr_2O_7 + 3\ NaHSO_3 + 4\ H_2SO_4 \Leftrightarrow Cr_2(SO_4)_3 + 3\ NaHSO_4 + Na_2SO_4 + 4\ H_2O$$

  followed by hydroxide precipitation of $Cr(OH)_3$

- Fe(II) salts, e.g. $FeSO_4$

$$Na_2CrO_4 + 3\ FeSO_4 + 4\ NaOH + 4\ H_2O \Leftrightarrow Cr(OH)_3 + 3\ Fe(OH)_3 + 3\ Na_2SO_4$$

Removal of dissolved inorganic substances

Reverse Osmosis

Operating principle:

similar to Micro- and Ultrafiltration

Characteristic differences:

- separation size 1 - 2 nm (dense membranes)
- operating pressure 10 - 200 bar
- very good removal of ions and large organic molecules
- limited rejection of dissolved gases and small uncharged molecules, e.g. silicic acid

Source:
http://www.ameriwater.com/products

Removal of dissolved inorganic substances

Evaporation

<u>Operating principle</u>:

Separation of wastewater and both dissolved and suspended substances by applying energy in order to transform the water into vapor

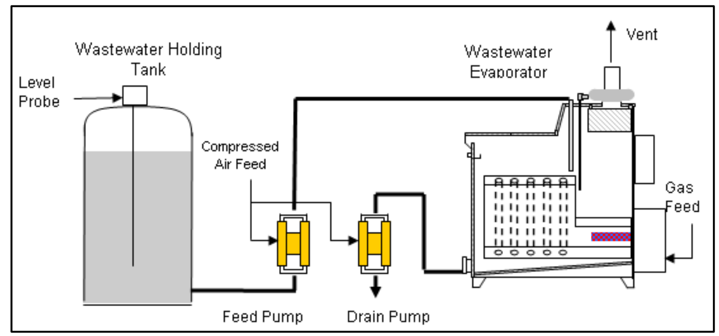
<u>Boundary conditions</u>:

→ high energy demand (ca. 800 kWh/m^3) for single-stage evaporation

→ precipitation of salts, formation of deposits

→ pollution of condensate by volatile compounds

→ corrosion and foam generation



Source: http://www.wastewaterevaporators.com

Removal of dissolved inorganic substances

Typical applications in industries

Ion exchange: Regeneration of process solutions in metal-plating companies

Recovery of noble metals and non-ferrous metals from metal-plating rinsing waters

Removal of residual heavy metals from wastewater streams after a precipitation stage

Precipitation: Removal of heavy metals in wastewater from metal-plating industries and from flue gas washing processes

Removal of fluoride (as CaF_2), sulfate (as $CaSO_4$ or as ettringite), phosphate (as $MePO_4$ with iron and aluminium salts, or as hydroxyl apatite with calcium hydroxide), and ammonium (as struvite) in wastewaters of different origin

Removal of dissolved inorganic substances

Typical applications in industries

Oxidation:	Detoxification of cyanide and nitrite in wastewater streams from metal-plating industries
Reduction:	Detoxification of chromate and nitrite in effluents from metal-plating processes
Reverse Osmosis:	Concentration of wastewater streams from chemical industries, electroplating, and landfills (in Germany)
	Recovery of process water in the semiconductor industry and other sectors
Evaporation:	Recovery of resources from wastewater streams
	Pre-treatment prior to combustion, e.g. in pulp production

Removal of dissolved organic substances

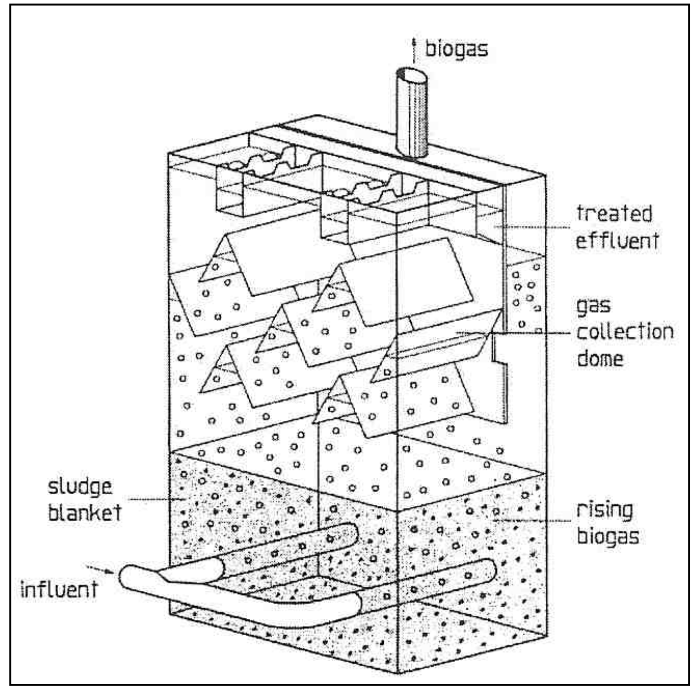
Anaerobic biological treatment

<u>Principle</u>:

- conversion of organic matter to biogas (CH_4, CO_2) that can be utilized
  → gain instead of consumption of energy
- two-stage process:
  1. pre-acidification, 2. methane production
- production of surplus sludge quite small

<u>Operating parameters</u>:

- hydraulic loading: 2 - 30 kg COD / ($m^3 * d$)
- temperature: 30 - 40°C (mesophilic conditions, preferred operating mode)



Scheme of an UASB-reactor
(Lettinga und Hulshoff Pol, 1991)

Removal of dissolved organic substances

Aerobic biological treatment

Principle:

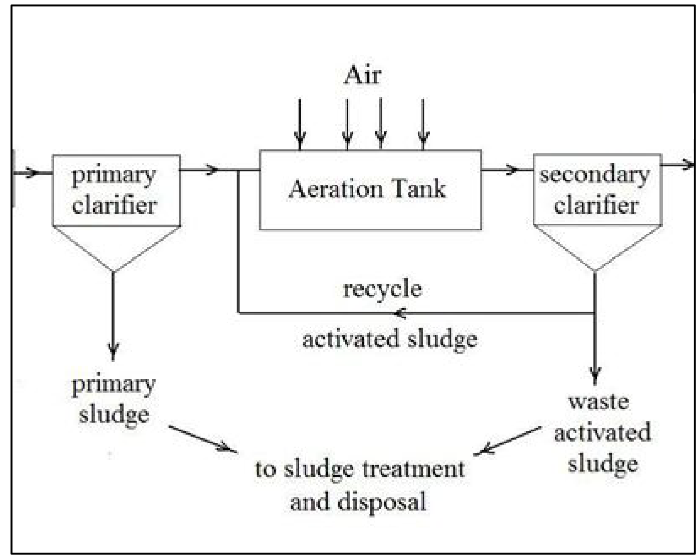
- conversion of organic matter to CO_2, H_2O and biomass; yield up to 50 %
- removal of nitrogen (nitrification/denitrification)

Process realisation:

- (multi-stage) activated sludge systems
- biofilm reactors

Operating parameters:

- sludge loading: < 0.1 - 0.5 kg BOD / (kg MLSS * d)
- hydraulic retention time: 6 - > 24 h



Flow diagram of the activated sludge process

Removal of dissolved organic substances

Application of biological processes in industries

Anaerobic treatment:	Pre-treatment of wastewater with high concentrations of biodegradable organic matter (COD = 1.5 - 40 g/L), e.g. wastewater from food industries, breweries and pulp and paper production
Aerobic treatment:	Removal of biodegradable organic matter from waste-water generated by all kind of industries, in particular by food companies, petrochemical plants, chemical industries, tanneries, textile companies, and paper mills
	Post-treatment of anaerobically treated wastewater in order to remove residual BOD and nutrients (nitrogen, phosphorous)

Removal of dissolved organic substances

Adsorption

<u>Principle</u>:

Accumulation of organic substances at the inner surface of a porous solid (adsorbent), most often activated carbon

<u>Process configurations</u>:

- application of powdered material in a three-step batch process that includes a) dosing, b) reaction and c) separation of the adsorbent
- use of granular adsorbent as a filter material in a continuously operated adsorption column

Source: http://generalcarbon.com

Removal of dissolved organic substances

Oxidation at low temperatures

... with hydrogen peroxide H_2O_2:

Activation by UV-irradiation or addition of Fe(II)-salts (Fenton's reagent) in order to generate OH radicals

$$H_2O_2 + Fe^{2+} \Leftrightarrow {}^{\bullet}OH + OH^{-} + Fe^{3+}$$

If iron salts are used, they will precipitate as hydroxides, i.e. management of residuals will be required.

... with ozone O_3:

Combination with UV-irradiation for an increased generation of hydroxyl radicals is advantageous

$$O_3 + H_2O \overset{h*\nu}{\Leftrightarrow} 2\,{}^{\bullet}OH + O_2$$

Removal of dissolved organic substances

Oxidation at high temperatures

Operating principle of “wet oxidation”:

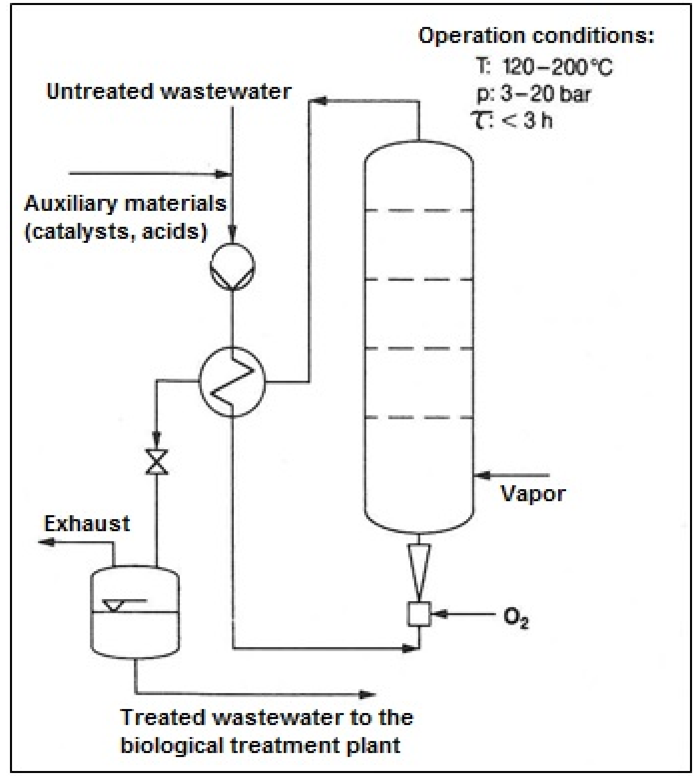
Conversion and partial mineralization of refractory organic substances with air or oxygen

Process schemes:

→ low-pressure oxidation (p = 6 - 10 bar, T = 140 - 180 °C)

→ high-pressure process (p = 20 - 200 bar, T = 250 - 330 °C)

→ oxidation in super-critical water (still under development)



Scheme of the wet oxidation process

Removal of dissolved organic substances

Combustion

<u>Principle</u>:

Evaporation of water and oxidation of organic substances in a gas burner

<u>Pre-condition</u>:

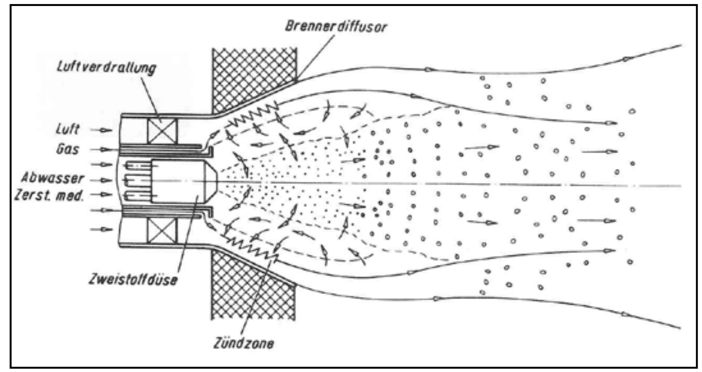
High concentration of organic material (> 10 % by mass, or COD > 100 g/L)

<u>Estimate of the net calorific value</u>:

$$H_U \text{ [kJ/kg]} = 13 * \text{COD [g/kg]})$$

<u>Operational challenge</u>:

Handling of slag from salts in the wastewater



Gas burner for wastewater combustion (System BASF)

Removal of dissolved organic substances

Application of physico-chemical processes in industries

Adsorption:	Removal of specific components or total COD, e.g. in chemical or metal-processing industries
Low-temperature oxidation:	Pre-treatment of wastewater with refractory matter (COD concentrations of 0.5 - 5 g/L)
	Removal of chelating agents in wastewater from metal-plating industries
High-temperature oxidation:	Pre-treatment of chemical wastewater with refractory matter (COD content of 5 - 100 g/L)
Combustion:	Disposal of wastewater with very high organic content, e.g. in chemical industries and refineries

Final remarks

- Industrial wastewater treatment can be based on a central biological plant, but it often requires the application of physical-chemical or chemical processes for the (pre-)treatment of separate streams.
- These processes must be selected and designed by taking all of the specific boundary conditions into account.
- Therefore standard solutions are not the best option but individual process configurations have to be developed in order to obtain optimal removal efficiencies at reasonable costs.