ADVANCED WASTE GAS TREATMENT

PART II - Innovative air pollution abatement technologies

A. Advanced physical-chemical waste gas treatment

- Direct UV photolysis
- O_3/UV process
- Heterogeneous photocatalysis (TiO_2/UV)
- Advanced oxidative scrubbers (UV/H_2O_2, O_3/H_2O_2)
- Non-thermal plasmatechnologies

B. Advanced biotechnological waste gas treatment

- Membrane biofiltration
- Foamed emulsion bioreactor: an innovative bioreactor concept
- Microbial communities as indicator for bioreactor performance
- Biological waste gas treatment by fungi

C. CO_2-capture and sequestration

Physical-Chemical Waste Gas Treatment

Advanced Oxidation Technologies (AOP)

Traditional chemical oxidation

- Rate of oxidation with O_2 at ambient temperature and pressure is too slow to be economically feasible
- High temperatures are needed (thermal oxidation: 800-1100°C; catalytic oxidation: 300-400°C)
- Hazardous by-products can be formed (*e.g.* dioxines)

Advanced Oxidation Processes (AOP)

- Oxidation at ambient temperature and pressure
- High energy oxidants: O_3, H_2O_2, OH
- AOP in waste gas treatment:

  Direct UV photolysis, O_3/UV process, Heterogeneous photocatalysis (TiO_2/UV), Advanced oxidative scrubbers (UV/H_2O_2, O_3/H_2O_2), Non-thermal plasma technologies

Direct UV Photolysis - Principle

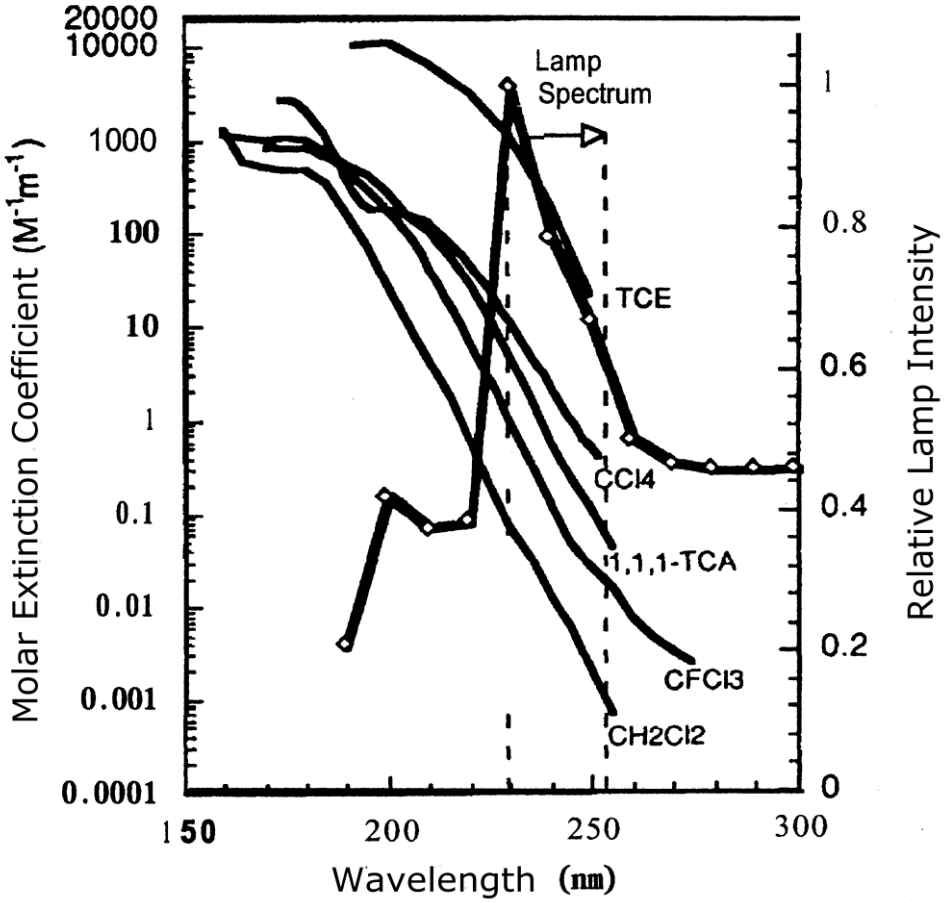
UV photons with energies from 4 eV to 7 eV (300 tot 175 nm, respectively) can break molecular bonds through photodissociation

By consequence, many organic compounds can undergo direct photolysis in the presence of UV radiation

The efficiency of direct photolysis depends on a number of factors:

- Molar absorptivity of the organic compounds at the used wavelength
- Quantum yield of the reaction
- Intensity of the UV-source

Direct UV Photolysis - Principle



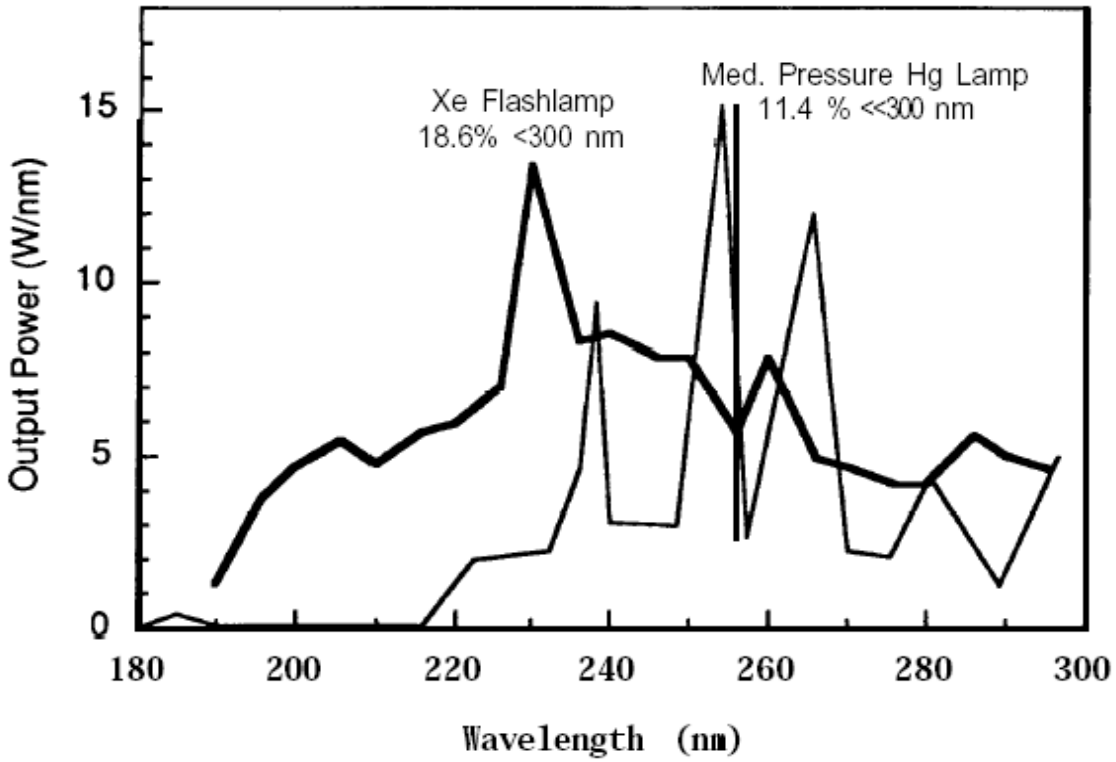
Direct UV Photolysis – UV sources

Low-pressure mercury lamps: monochromatic light at 254 nm (a second emission line at 185 nm is absorbed by the encasing). Effective for breaking hydrogen bonds, *e.g.* in DNA molecules (absorb light at 265 nm); commonly used for disinfection.

For the cleaving of intramolecular bonds, more energetic deep UV photons (< 250 nm) are more effective. Commercially available:

- Low-pressure mercury lamps with high purity silica encasing that does not absorb the emission line at 185 nm
- Medium- and high- pressure mercury lamps (second generation UV systems) with dopants to increase the number of UV lines in the deep UV region
- Xenon flashlamps (third generation UV systems) that are based on pulsed corona discharge technology and emit a broad band of deep UV radiation
- Xenon excimer lamps that emit monochromatic light at 172 nm (vacuum UV) that can dissociate water molecules

Direct UV Photolysis – UV sources



Direct UV Photolysis – Waste gas treatment

Most research in this field has focussed on chlorinated (volatile) organic compounds:

- These compounds pose major difficulties to traditional treatment technologies
- Low bonding energy of the C-Cl bond, compared to C-C and C-H bonds
- Cl radicals can initiate chain reactions resulting in high apparent quantum yields
- The formation of noxious photostable by-products (*e.g.* phosgene, DCAC) can make necessary further treatment

$$HClC{=}CCl_2 + h\nu \rightarrow HClC{=}CCl^{\cdot} + Cl^{\cdot}$$
$$Cl^{\cdot} + HClC{=}CCl_2 \rightarrow HCl_2C\text{-}CCl_2^{\cdot}$$
$$HCl_2C\text{-}CCl_2^{\cdot} + O_2 \rightarrow HCl_2C\text{-}CCl_2OO^{\cdot}$$
$$2\ HCl_2C\text{-}CCl_2OO^{\cdot} \rightarrow 2\ HCl_2C\text{-}CCl_2O^{\cdot} + O_2$$
$$HCl_2C\text{-}CCl_2O^{\cdot} \rightarrow HCl_2C\text{-}CClO\ (DCAC) + Cl^{\cdot} \rightarrow$$

Direct UV Photolysis – Waste gas treatment

Odour treatment: photolysis of sulphurous compounds is initiated by the photodissociation of the H-S bond:

$$H_2S + hu \rightarrow HS + H$$

$$RHS + hu \rightarrow RS + H$$

Radicals formed are effectively degraded further by reaction with oxygen to odourless compounds such as sulphates and sulphonates

Direct UV Photolysis – Waste gas treatment

Commercial VOC photooxidation system is marketed by AirQualityConcept (Belgium)

- Spray painting plant Copenhagen (Denmark)
- Flow: 36000 m^3/h ; Power : 30 kW
- Dimensions: 8.30 x 3.27 x 2.18 m (6 ducts)
- VOC abatement: 250 mg/Nm^3 → < 25 mg/Nm^3

O_3/UV process – *Principle*

Ozone (O_3) is fed into a UV photoreactor

In the presence of water vapour, UV sensitized ozone decomposition yields OH radicals that oxidize organic compounds

Since ozone exhibits an absorption maximum at 254 nm, traditional UV sources can be applied in the O_3/UV process

In the O_3/UV process, organic compounds are degraded via a combination of different reaction mechanisms :

- Direct UV photolysis
- Direct ozonation
- Indirect OH radical oxidation
- Cl chain reactions (if pollutants are chlorinated compounds)

Relative contribution of these mechanisms depends on UV radiation wavelength and intensity, ozone concentration, pollutant concentration and presence of moisture

O_3/UV process – *Principle*

Since low wavelength UV light generates ozone, it could be said that gas-phase direct UV photolysis processes are essentially UV/O_3 processes:

<u>direct photolysis</u>

pollutant + hυ → …

<u>oxidation</u>

3 O_2 + hυ (185 nm) → 2 O_3

O_3 + hυ (254 nm) → O_2 + $O(^1D)$

$O(^1D)$ + H_2O → 2 OH

pollutant + OH → …

O_3/UV process – *Waste gas treatment*

Most of research in this field has focussed on chlorinated (volatile) organic compounds:

e.g.: chloroform, tetrachloromethane, trichloroethene, tetrachloroethene, 1,1,2- trichloroethane

- Direct ozonation contributed to the oxidation of chloroethenes
- OH reactions contributed to the oxidation of chloroform, 1,1,2-trichloroethane and to a lesser extent trichloroethene
- Neither ozone nor OH significantly enhanced the oxidation of tetrachloromethane

UV/O_3 process faces similar obstacles as direct photolysis:

- Although ozone promotes further decomposition, complete mineralisation remains difficult
- Additional treatment remains necessary
- Furthermore, ozone needs to be removed from the gas stream before discharge

Heterogeneous Photocatalysis – Definition

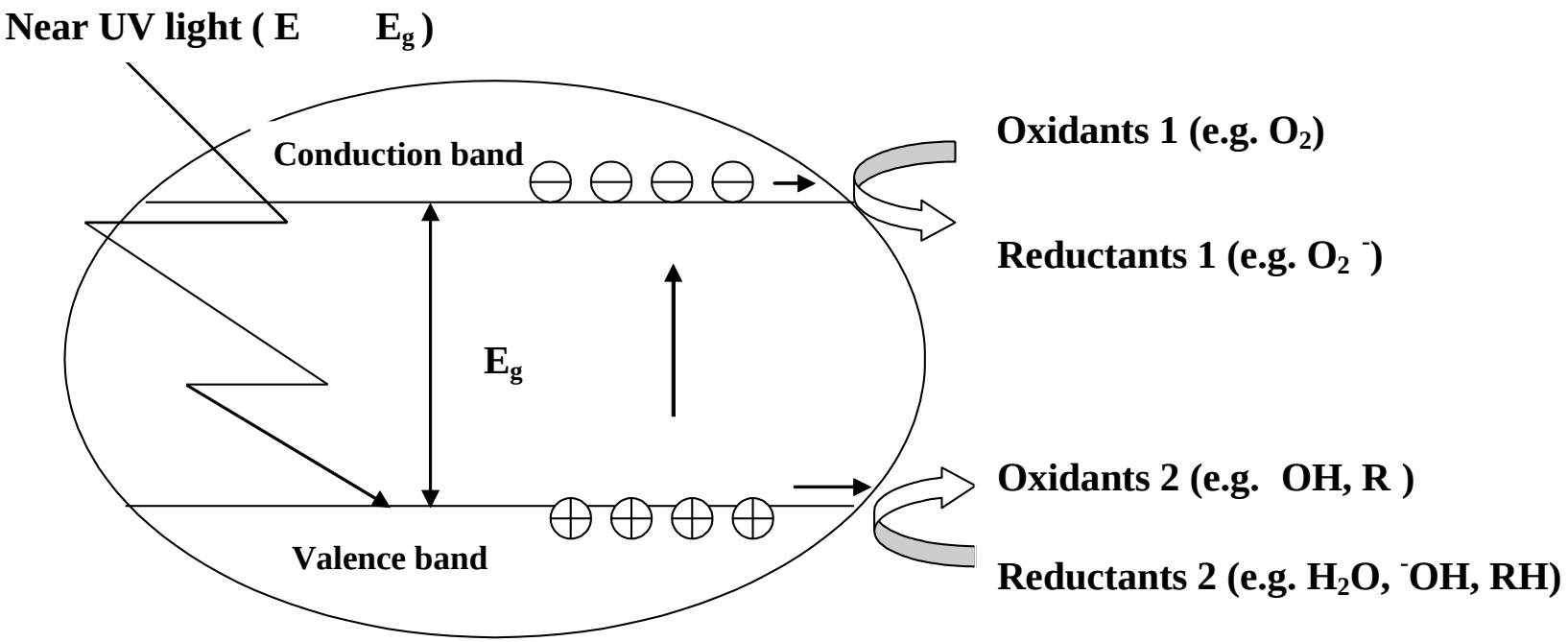
Heterogeneous Photocatalysis

=

"a catalytic process during which one or more reaction steps occur by means of electron-hole pairs photogenerated on the surface of semiconductor materials illuminated by light of suitable energy"

(Palmisano & Sclafini, 1997)

Heterogeneous Photocatalysis – Principle



Heterogeneous Photocatalysis – Principle

A photocatalytic reaction proceeds on the surface of semiconductors via several steps:

(1) Production of electron-hole pairs by irradiating the semiconductor with light having an energy higher than the band-gap energy of the semiconductor

(2) Separation of the photogenerated electrons and holes due to trapping by species that are adsorbed on the semiconductor

(3) Redox reactions between the trapped electrons and holes and the adsorbates present on the surface

(4) Desorption of the products and reconstruction of the surface

Heterogeneous Photocatalysis

Choice of photocatalyst

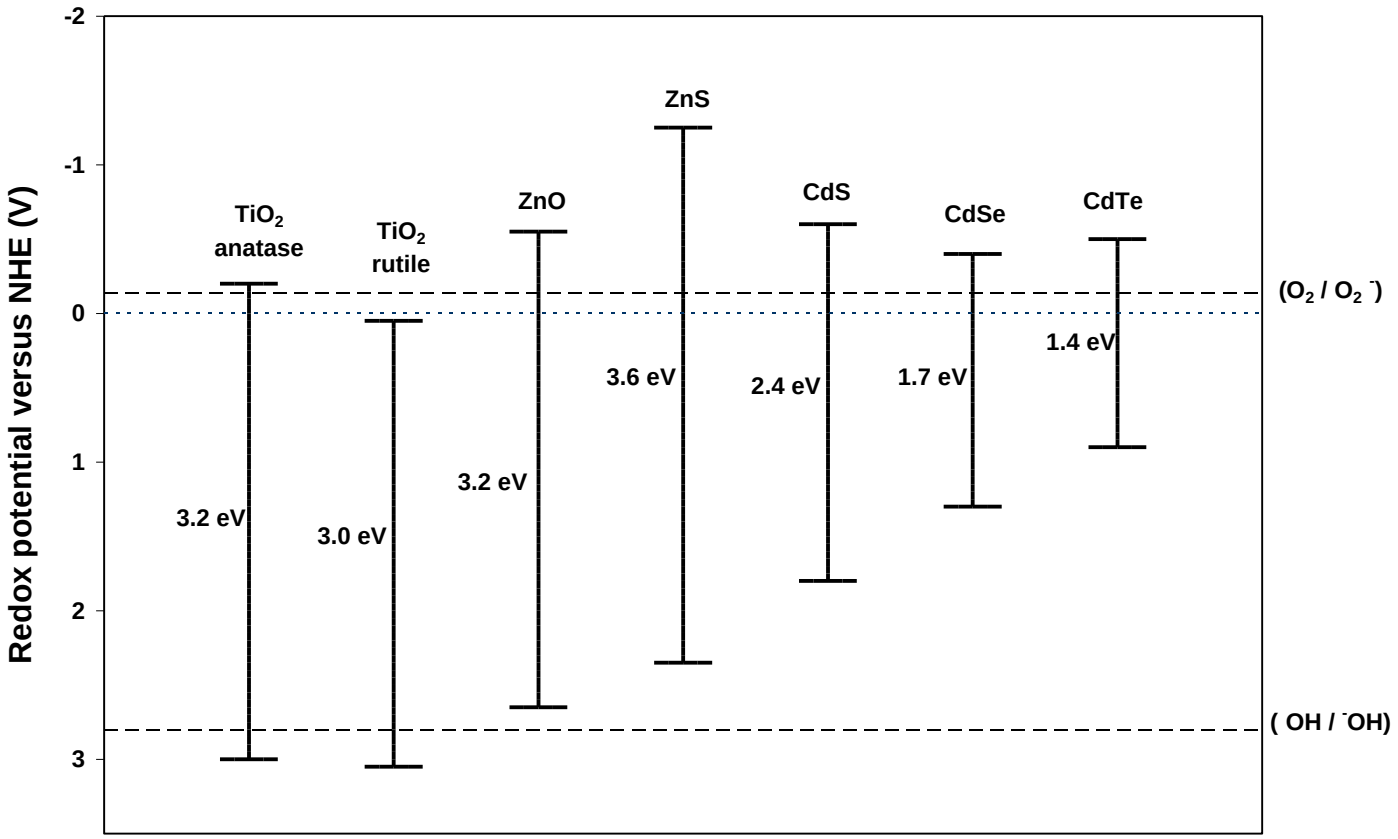
Semiconductor photocatalysts: TiO_2, ZnO, WO_3, CdS, ZnS, CdSe, CdTe

Research standard photocatalyst: ***TiO_2 (Degussa P25)***

- It has high absorptivities for UV radiation. Band-gap energy : 3.0 eV (rutile) - 3.2 eV (anatase), corresponding with near-UV radiation (388 nm for anatase; 413 nm for rutile), produced by UV black light lamps
- It exhibits good adsorption characteristics for many contaminants
- The redox potential of its valence and conduction band edges are suitable for oxidizing organic contaminants
- It displays high photocatalytic activity while being highly resistant to photocorrosion
- It is inexpensive and non-toxic

Heterogeneous Photocatalysis

Choice of photocatalyst



Heterogeneous Photocatalysis

Mechanistic considerations

Initiating reaction step

$TiO_2 + h \quad TiO_2 (e^- + h^+)$ with 388 nm

Reaction with holes

$TiO_2 (h^+) + H_2O_{ads} \quad TiO_2 + H_2O_{ads}^{\cdot +} \quad TiO_2 + \cdot OH_{ads} + H^+$

$TiO_2 (h^+) + {}^-OH_{ads} \quad TiO_2 + \cdot OH_{ads}$

$TiO_2 (h^+) + RH_{ads} \quad TiO_2 + RH^{\cdot +}_{ads} \quad TiO_2 + R^{\cdot}_{ads} + H^+$

Heterogeneous Photocatalysis

Mechanistic considerations

Reaction with electrons

$TiO_2\ (e^-) + O_2 \quad TiO_2 + O_2^{\cdot -}$

$O_2^{\cdot -} + H^+ \quad HOO^{\cdot}$

$2\ HOO^{\cdot} \quad H_2O_2 + O_2$

$H_2O_2 + O_2^{\cdot -} \quad HO^{\cdot} + O_2 + OH^-$

$H_2O_2 + h \quad 2\ HO^{\cdot}$

$TiO_2\ (e^-) + H_2O_2 \quad TiO_2 + {}^{-}OH + {}^{\cdot}OH$

$TiO_2\ (e^-) + RX_{ads} \quad TiO_2 + RX_{ads}^{\cdot -} \quad TiO_2 + R_{ads}^{\cdot} + X^-$

Heterogeneous Photocatalysis

Waste gas treatment

Ambient temperature and pressure conditions

Large volumes of slightly contaminated air (pollutant concentration < 500 ppmv)

Wide range of organic and inorganic pollutants:

- Alkanes and alkenes
- Alcohols and ketones
- Aromatic compounds
- Organic acids
- Heteroatom containing organic compounds (*e.g.* odorous compounds)
- Halogenated compounds (TCE: research standard)
- NH_3, H_2S,…

Heterogeneous Photocatalysis

Important process parameters

- Relative humidity: competitive adsorption versus OH-radicals
- Temperature: adsorption-desorption equilibrium, reaction kinetics,…
- Irradiation conditions: wavelength, light intensity,…
- Oxygen concentration: threshold concentration
- Pollutant concentration
- Photocatalyst properties: e.g. specific surface area, UV-VIS absorbance
- Desactivation of the photocatalyst during reaction?
- Reactor-related parameters: residence time, flow regime, mass transfer,…

Advanced Oxidative Scrubbers – Principle

Scrubbers : mass transfer from gas to liquid phase

Reactive scrubbers (alkaline, acid or oxidative scrubbers) : reagents are added to the scrubbing liquid → contaminants react upon absorption → driving force is maintained

Advanced oxidative scrubber : OH-radicals generated via an advanced oxidation process are used as oxidants instead of traditional oxidants (O_3, H_2O_2, NaOCl)

- Due to high reactivity of OH, advanced oxidative scrubbers can also be used for less reactive compounds
- Since the life time of OH is very short, OH should not be dosed in the scrubbing liquid storage tank (as in traditional oxidative scrubbers), but initiation of the oxidation process should take place in the scrubber reactor itself
- Two advanced oxidation processes haven been applied in advanced oxidative scrubbers : UV/H_2O_2 and peroxone process (O_3/H_2O_2)

Advanced Oxidative Scrubbers – UV/H_2O_2

Waste gas stream is contacted with a scrubbing liquid, *e.g.* in a bubble column

Pollutants are present in gas stream; H_2O_2 is dosed via the scrubbing liquid

System is irradiated by photons of 254 nm

$H_2O_2 + hu \rightarrow 2\ OH$

$OH + RH \rightarrow R + H_2O$ (hydrogen abstraction: alkanes)

$OH + R_2C{=}CR_2 \rightarrow R_2C(OH)\text{-}C\ R_2$ (electrophylic addition: alkenes, aromatics)

$OH + RX \rightarrow RX^+ + {}^-OH$ (electron transfer)

$OH + OH \rightarrow H_2O_2$ (radical-radical recombination)

Advanced Oxidative Scrubbers – UV/H_2O_2

If an excess of H_2O_2 is used, OH radicals will produce hydroperoxyl radicals (OOH), which are much less reactive

Scavenging of OH radicals by HCO_3^- and CO_3^{2-} :

$$OH + HCO_3^- \rightarrow H_2O + CO_3^-$$

$$OH + CO_3^{2-} \rightarrow HO^- + CO_3^-$$

Advantages of H_2O_2 as an oxidant:

- readily commercial available
- Thermal stability and storage on-site
- Infinite solubility in water
- Costs are less sensitive to scale of operation than for ozone

Advanced Oxidative Scrubbers

O_3 / H_2O_2 : peroxone process

Hydroxyl radicals are produced by combination of H_2O_2 and O_3

Gas phase: pollutant, ozone (O_3)

Liquid phase: hydrogen peroxide (H_2O_2)

Both phases are contacted with each other in a scrubber (e.g. bubble column)

$H_2O_2 \leftrightarrows HO_2^- + H^+$ $\quad pK_a = 11.7$

$HO_2^- + O_3 \rightarrow HO_2 + O_3^-$

$HO_2 \leftrightarrows O_2^- + H^+$ $\quad pK_a = 4.8$

$O_2^- + O_3 \rightarrow O_2 + O_3^-$

$O_3^- + H^+ \leftrightarrows HO_3$ $\quad pK_a = 6.15$

$HO_3 \rightarrow O_2 + OH$

Overall reaction: $H_2O_2 + 2\ O_3 \rightarrow 3\ O_2 + 2\ OH$

Non-thermal plasmatechnology – Definitions

Plasma: partial ionized gas containing neutral atoms and molecules and a quasi equal concentrations of positive and negative charged particles (electrons, ions) (plasma = quasi neutral).

> In an electric field, charged particles accelerate and collisions with other gas constituents occur, resulting into the formation of new charged particles. Charge losses result finally into a stable plasma.

Non-thermal plasma (non-equilibrium plasma): due to large difference in mass, electrons (m_e = 9.02.10^{-31} kg) in the plasma have a higher mean energy (T_e >> 1 eV) than the other constituents of the gas (ions (m_{ion} = 5000-50000 m_e), atoms and molecules, T_g < 0.1 eV)

Thermal plasma (equilibrium plasma): the constituents of the gas are in thermal equilibrium (at higher pressure, the frequency of collisions is higher, resulting into a higher energy transfer to the background gas)

Non-thermal plasmatechnology – Principle

The essential of a non-thermal plasma technique is that the available energy is is added selectively to the plasma electrons (no energy loss by heating the background gas)

Through electron-impact dissociation and ionisation of the background gas molecules, the energetic electrons produce free radicals (oxygen and hydroxyl radicals) and additional electrons which, in turn, oxidize or decompose organic molecules

Electrons may also react directly with the pollutants, which allows the treatment of perhalogenated saturated compounds (*e.g.* freons)

Non-thermal plasmatechnology – Plasma sources

Electron beam irradiation:

- High energy electrons are generated outside the reactor chamber under high vacuum in an electron accelerator
- The electron beam generated is injected into the reaction chamber through a thin foil titanium window

Electrical discharge process:

- High energy electrons are produced by an electric field generated between two high voltage electrodes within the reactor chamber
- Plasma is generated by accelerating electrons in the field
- Under atmospheric conditions, collisions with other gas constituents will transfer energy from the electrons to the rest of the gas. Local heating of the gas will result in a spark discharge in which the plasma is confined to a small filament

Non-thermal plasmatechnology – Plasma sources

Electrical discharge process (2):

- However, different reactor configurations have been developed that extend non-thermal discharge plasma processing to atmospheric pressure conditions
  - Dielectric barrier discharges:

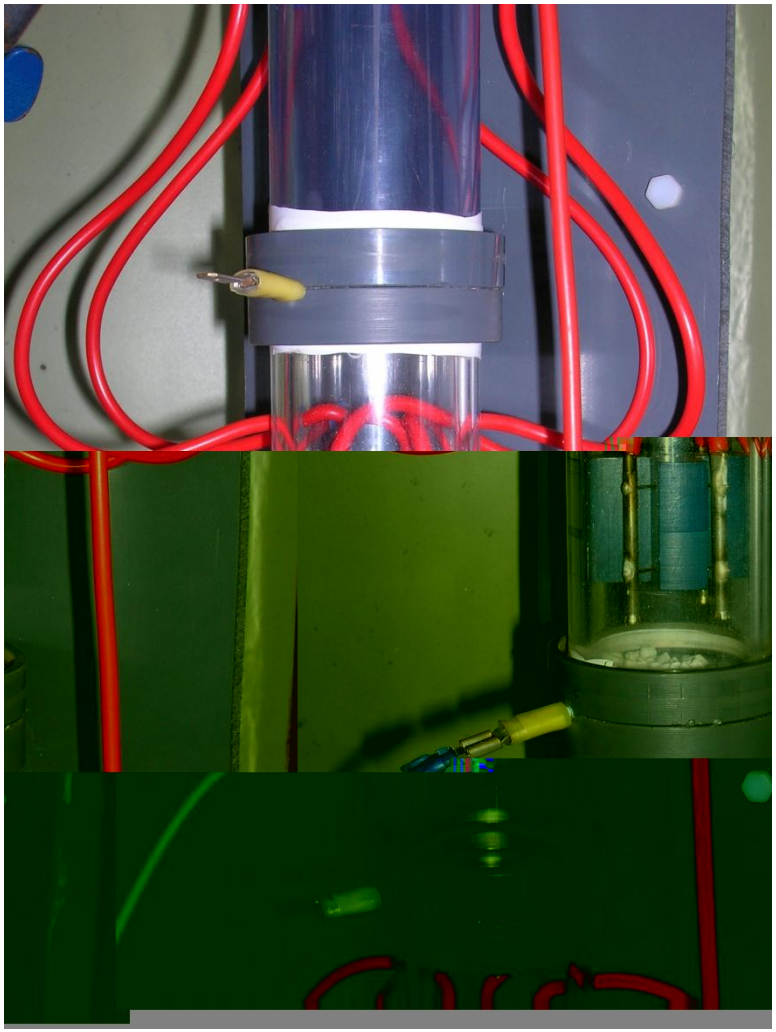
    sparks are prevented by a dielectric barrier between the metal electrodes
  - Pulsed corona discharges:

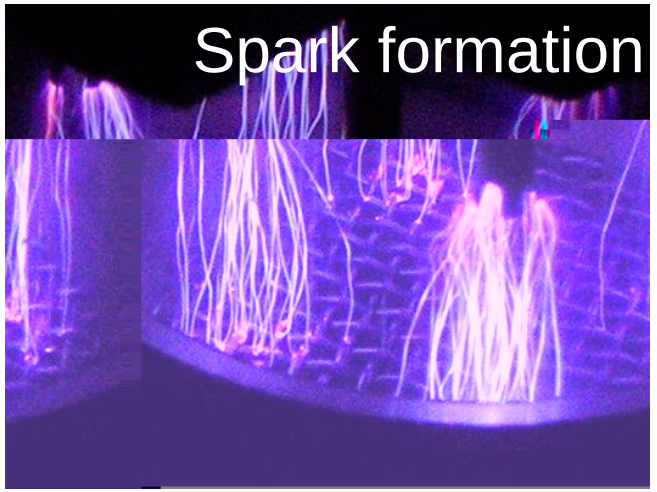
    the applied voltage time during pulses is too short to generate spark discharges
  - Flow stabilized discharges:

    a fast gas flow cools the electrodes, preventing spark discharges

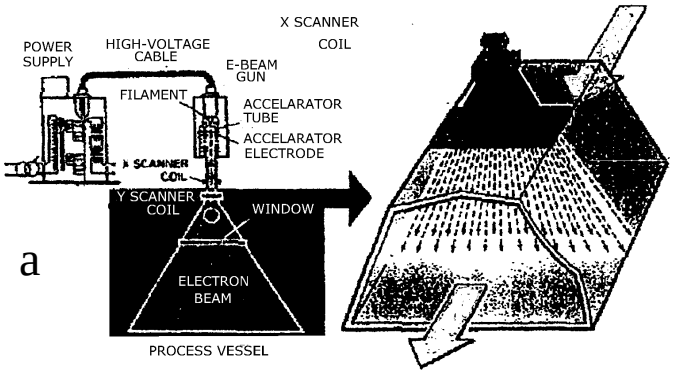
Plasma	Voltage (V)	Current (A)	Efficiency (%)	Pressure drop	Flow (m^3/h)
Electron beam	10^5-2.10^8	10^{-3}-10 (dc)	80-95	small	10^3-10^5
Barrier discharge	5.10^3-2.10^4	10^{-3}-10	30-80	large	10^{-2}-1
Pulsed corona	3.10^4-2.10^5	10^{-2}-1	20-70	middle	1-10^2
Flow stabilised	10^4-10^5	10^{-5}-10^{-1}	90-95	middle	1-10^2

Non-thermal plasmatechnology – Plasma sources

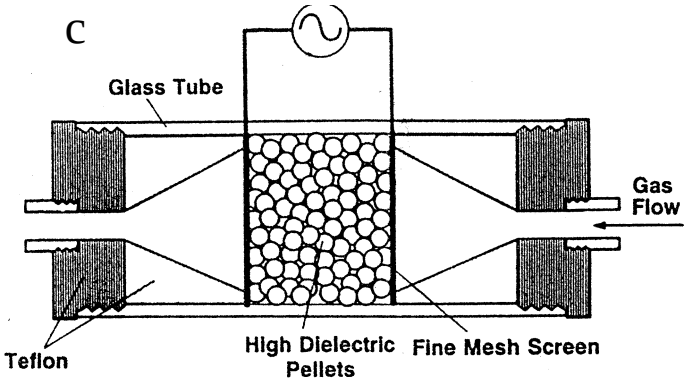




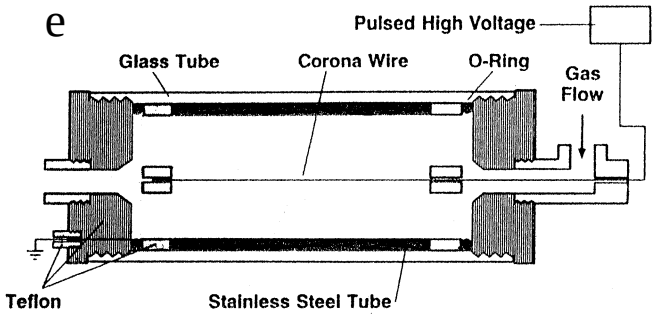
Non-thermal plasmatechnology – Plasma sources



Electron beam



Dielectric packed bed



Pulsed corona

Non-thermal plasmatechnology

Waste gas treatment

DeNO$_x$:

- NO_X : acid rain, photochemical smog
- Oxidation of NO_x by means of O_3, O, OH
- Reduction of NO_x to N_2 by means of NH_3, ureum

DeSO$_x$:

- SO_X : acid rain, photochemical smog
- Oxidation : $SO \rightarrow SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$
- Synergetic effect between SO_2 and NO_x

DeCO$_x$:

- CO : toxic ; CO_2 : greenhouse gas
- $CO_2 + e \rightarrow CO + O + e$
- $CO_2 + e \rightarrow C + O_2 + e$

Non-thermal plasmatechnology

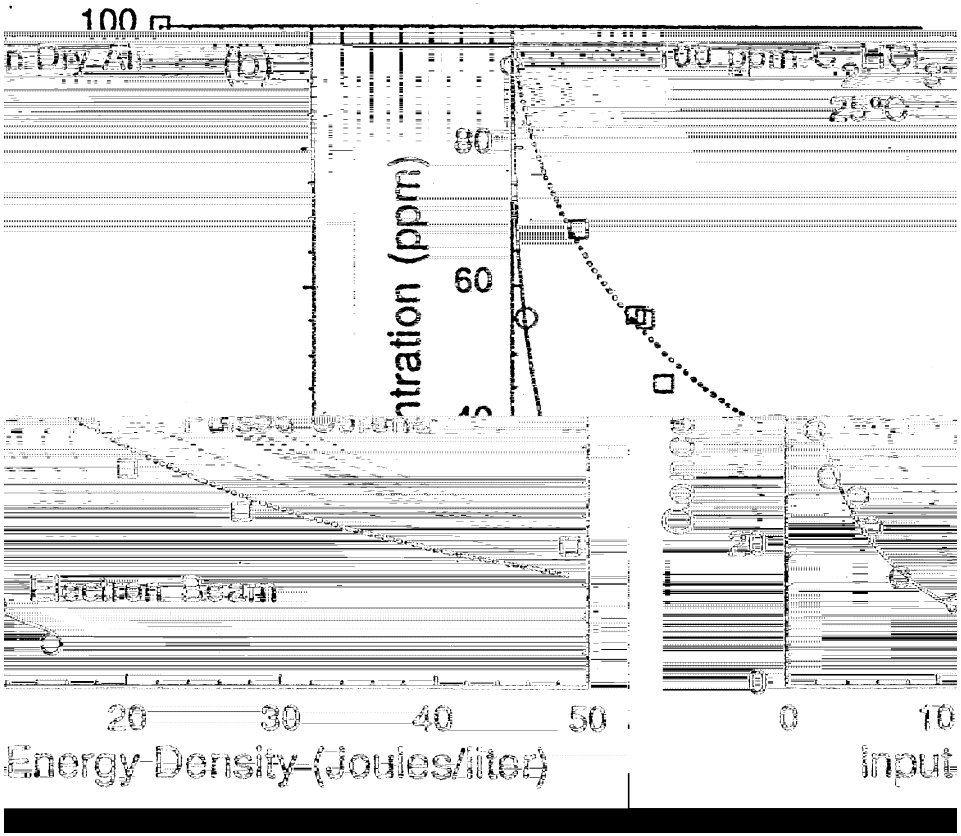
Waste gas treatment

DeVOC:

- **Target compounds** : ethane, propane, butane, pentane, vinyl chloride, ethyl chloride, chloromethane, bromomethane, dichloromethane, 1,1,1-trichloroethane, trichlorofluoroethane, tetrafluoromethane, tetrachloromethane, trichloroethene, formaldehyde, methanol, aceton, methyl ethyl ketone, benzene, toluene, styrene,…
- **Reactor configurations** : pulsed corona discharge, dielectric packed bed, silent discharge, electron beam, surface discharge
- **Hybrid systems** : combination of non-thermal plasma and adsorbents or (photo)-catalysts
- **Commercial plasmatechnologies** : Applied Plasma Physics ASA (Norway, www.app.no)
- Large variety on experimental conditions and reactor configurations makes it difficult to compare results

Non-thermal plasmatechnology

Waste gas treatment



Non-thermal plasmatechnology

Waste gas treatment

Deodorization:

- **Target compounds**: acetaldehyde, NH_3, sulphurous compounds (H_2S, SF_6, CH_3SH, $(CH_3)_2S$, CS_2, COS, SO_2)

- **Illustration**: non-thermal plasma discharge reactor operating at an animal house

Biological Waste Gas Treatment

New tendencies

Traditional biological waste gas treatment techniques

- Biofilter
- Biotrickling filter
- Bioscrubber

New tendencies

- Membrane biofiltration
- Foamed emulsion bioreactor: an innovative bioreactor concept
- Study of microbial communities as indicator for bioreactor performance
- Biological waste gas treatment by fungi

Membrane Biofiltration – Principle

Traditional biological techniques:

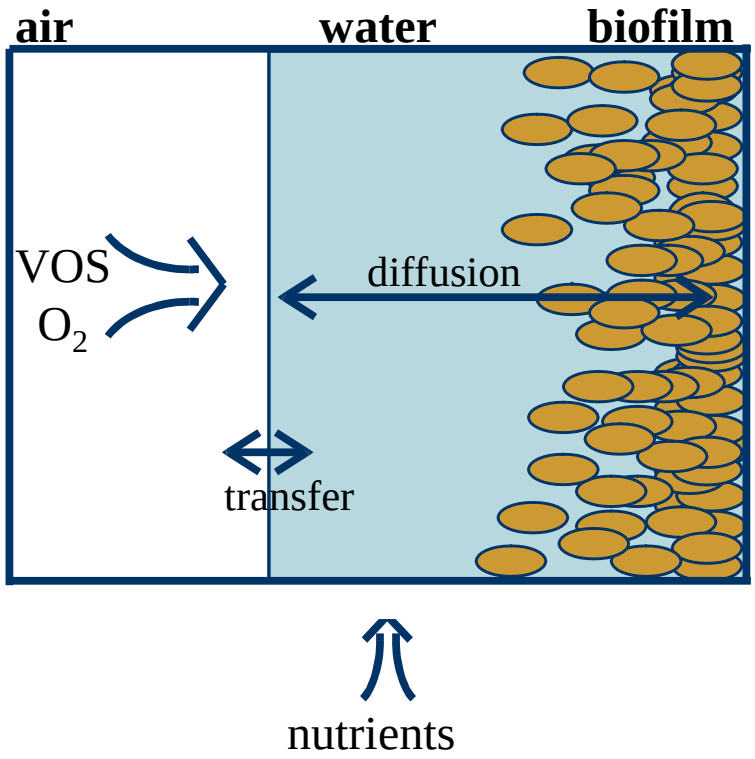
- Biofilter, biotrickling filter, bioscrubber
- Biofilm is covered by a water layer, forming a barrier between the micro-organisms and hydrophobic compounds in the air phase

Membrane bioreactor:

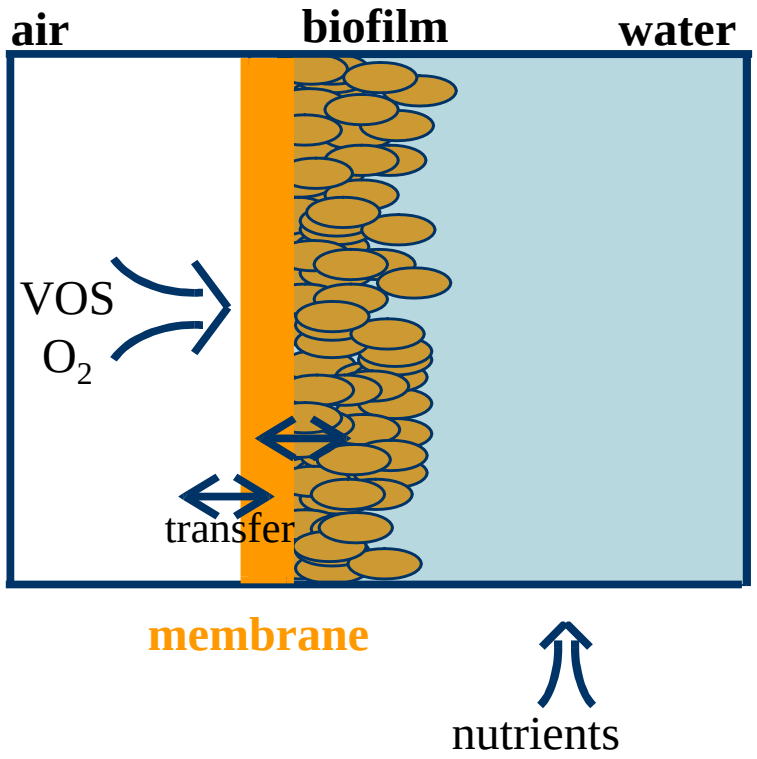
- Liquid and air phase are separated by a membrane
- Pollutants diffuse through the membrane and are subsequently degraded by the micro-organisms in the biofilm
- Because of the separation of the liquid and air phase, waste air containing hydrophobic compounds can be treated effectively
- Oxygen is supplied from the air phase, while nutrients are present in the liquid phase
- Since the liquid phase is continuously recirculated, the pH can easily be corrected and toxic degradation products can be removed

Membrane Biofiltration – Principle

Traditional bioreactors



Membrane bioreactor



Membrane Biofiltration – Membrane types

Porous membranes:

- Advantage: low mass transfer resistence
- Disadvantage: biofouling

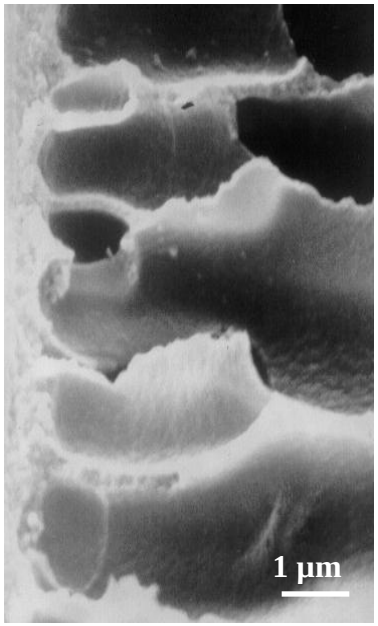
Dense membranes:

- Advantage: less chance on biofouling
- Disadvantage: higher mass transfer resistence

Composite membranes:

- Porous support layer (*e.g.* PVDF), dense top layer (*e.g.* PDMS)
- Combines the advantages of both types of membranes

Membrane Biofiltration – Membrane types

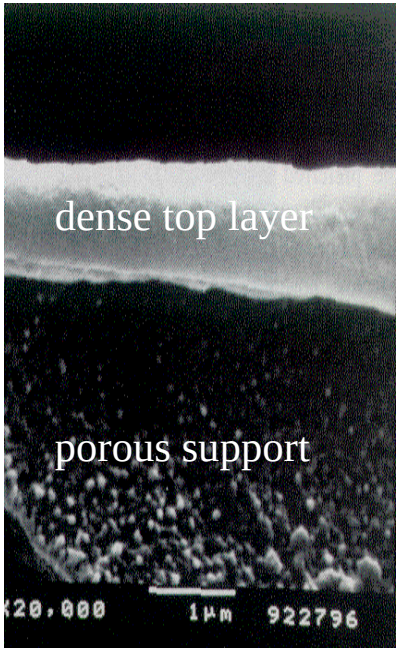


Porous membrane

e.g. PVDF
(polyvinilydene fluoride)

Dense membrane

e.g. PDMS
(polydimethylsiloxane)



Composite membrane

Membrane Biofiltration – Reactor configurations

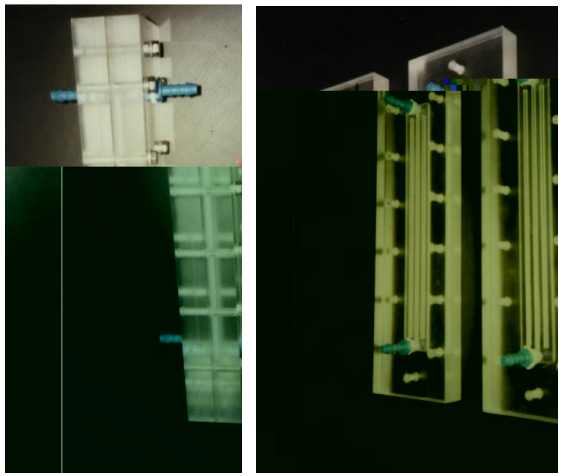
Hollow fibres membrane bioreactor:

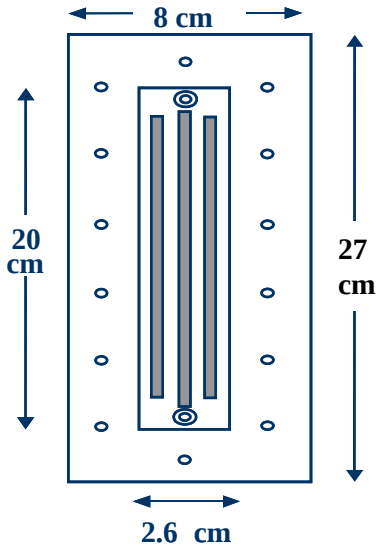
- Internal diameter < 0.5 mm
- Very large specific membrane-gas contact area

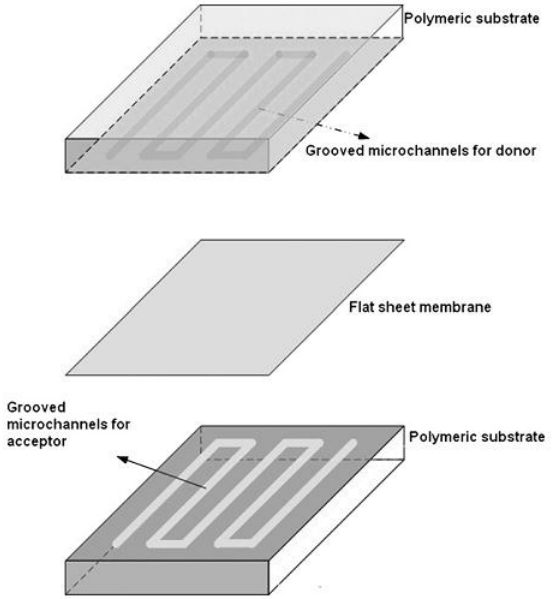
Capillar membrane bioreactor:

- 0.5 mm < internal diameter < 10 mm

Flat membrane bioreactor:







Membrane Biofiltration – Mechanistic aspects

Mass transfer and microbial kinetics of a gaseous pollutant within a membrane bioreactor module can be described as a sequence of events:

- Bulk mixing of the contaminant in the air entering the bioreactor
- Boundary layer transport
- Transport through membrane
- Exit from the membrane and dissolution and diffusion into the biofilm
- Diffusion through and degradation within the biofilm
- Boundary layer transport through the liquid phase
- Subsequent mixing and degradation within the cell suspension

Flux over the membrane: $J = K_{ov} A (C_{gas} - H C_{liquid})$ $[g.s^{-1}]$

- K_{ov} : overall mass transfer coefficient ($m.s^{-1}$)
- A : membrane surface area (m^2)
- C_{gas}, C_{liquid} : concentration is gas, liquid phase ($g.m^{-3}$)
- H : dimensionless Henry-constant

Membrane Biofiltration – Waste gas treatment

Target compounds:

- hexane, propylene
- methanol, 1-butanol,
- dichloromethane, 1,2-dichloroethane, trichloroethylene
- benzene, toluene, ethylbenzene, xylene
- ammonia, dimethyl sulphide, nitric oxide

⇨ Compounds with a broad range of air-water partitioning coefficients (five orders of magnitude)

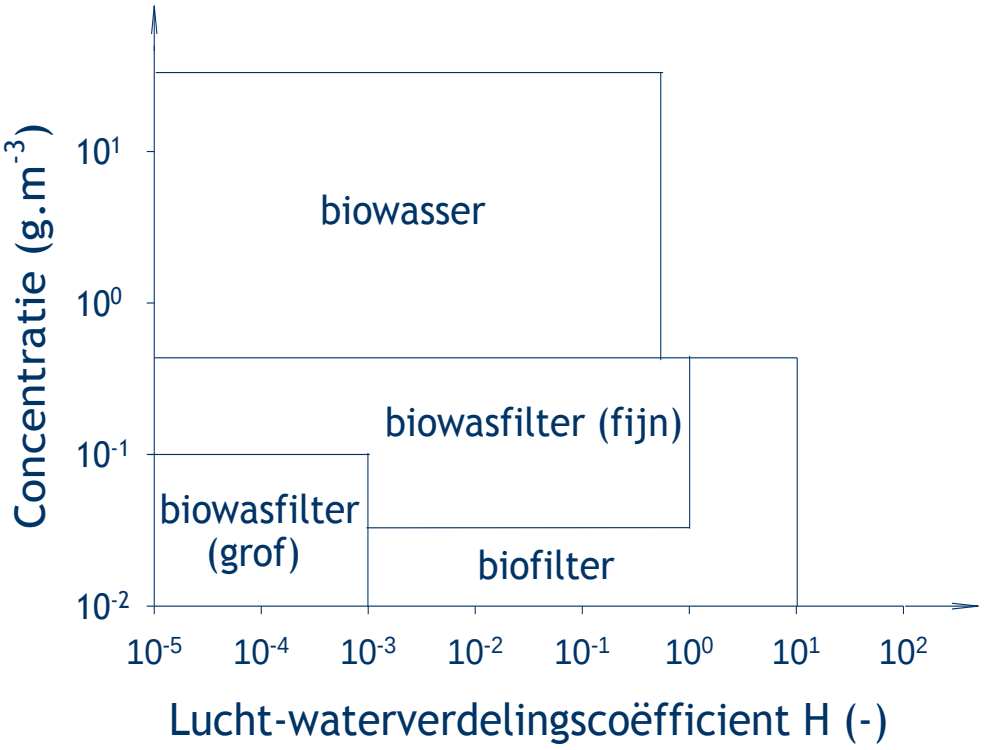
⇨ Both inorganic and organic compounds

⇨ Most research on single compounds degradation, less research on the degradation of mixtures of compounds

⇨ Lab-scale experiments

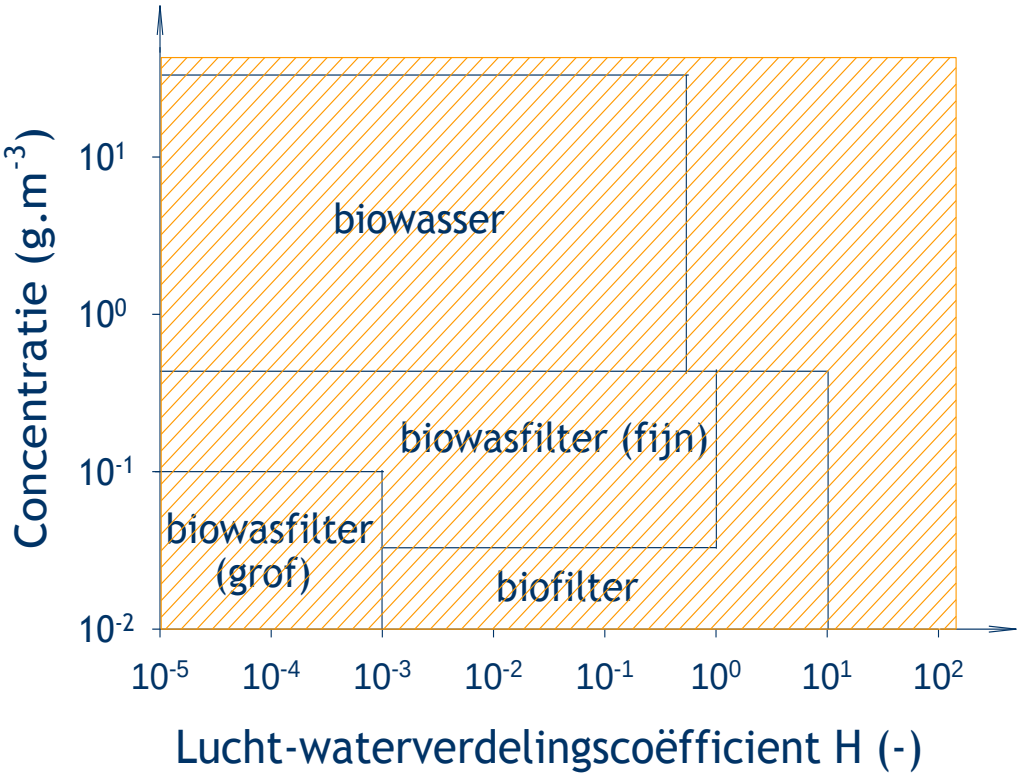
Membrane Biofiltration – Waste gas treatment

Application area of traditional biological waste gas treatment techniques

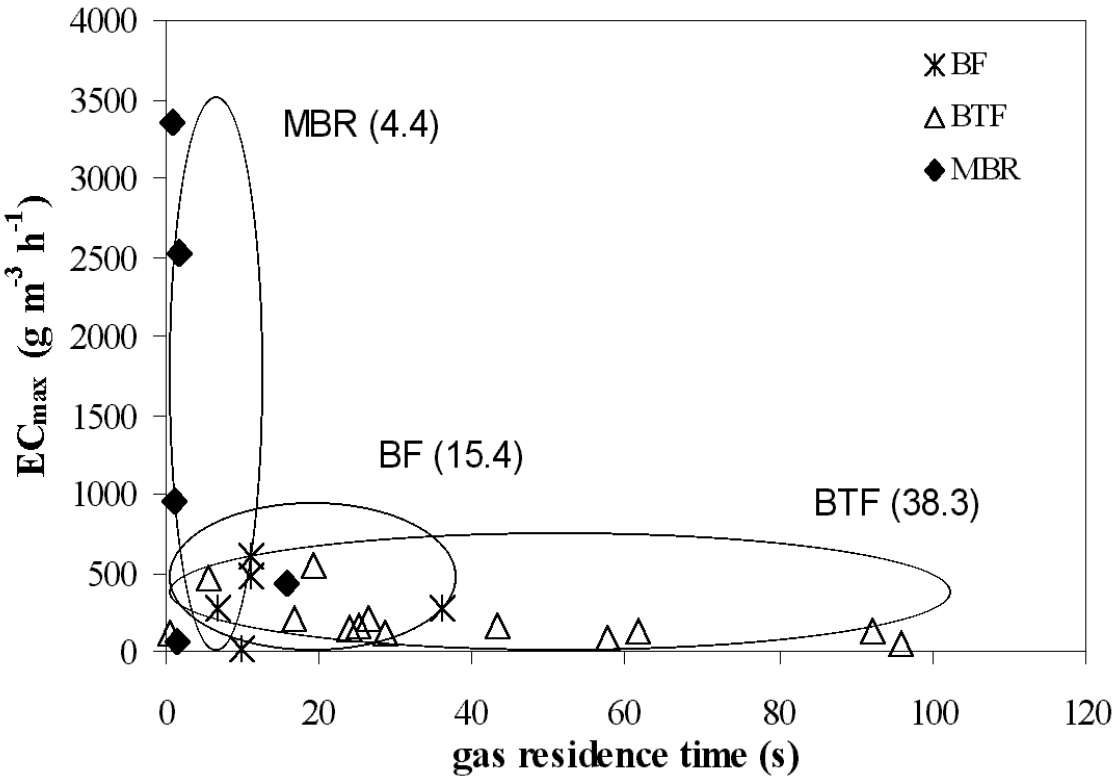


Membrane Biofiltration – Waste gas treatment

Application area of membrane biofiltration



Membrane Biofiltration – Waste gas treatment



Comparison of maximum volumetric toluene elimination capacities (ECmax) using a biofilter (BF), a biotrickling filter (BTF) and a membrane bioreactor (MBR) as a function of the gas residence time

Membrane Biofiltration – Advantages

- Incorporation of mass transfer of gaseous pollutants across a media with high specific surface area and low diffusion length
- Presence of high biomass concentrations
- Ability to continuously remove biomass to prevent clogging at high loading rates
- Ability to remove by-products and add pH buffers, nutrients, co-metabolites
- Ability to treat low solubility compounds (e.g. hexane, ethene)
- Ability to treat gas streams at elevated temperatures
- Ability to inoculate bioreactor with specific cultures for poorly biodegradable compounds
- Separation of the microbial process from the gas being treated
- Operation at lower pressure drop than in biofilters
- Gas and liquid flow rates can be varied independently without flooding or foaming
- Modular design and so easy to scale-up by adding more membrane
- No gas channeling

Membrane Biofiltration – Challenges

- High investment costs
- The technology has not been demonstrated at full-scale
- Removal declines over time as the biofilm ages resulting in decreased biomass activity and the biofilm thickness increases
- Hollow fibre bundles tend to clump when biofilm growth is high, resulting in fibre tangling and thus reduction of available membrane surface area
- Biomass grows in porous membranes, resulting in declining reactor performance;
  there is no good method available for cleaning the porous membrane bioreactor systems

Foamed emulsion bioreactor

An innovative bioreactor concept

Principle:

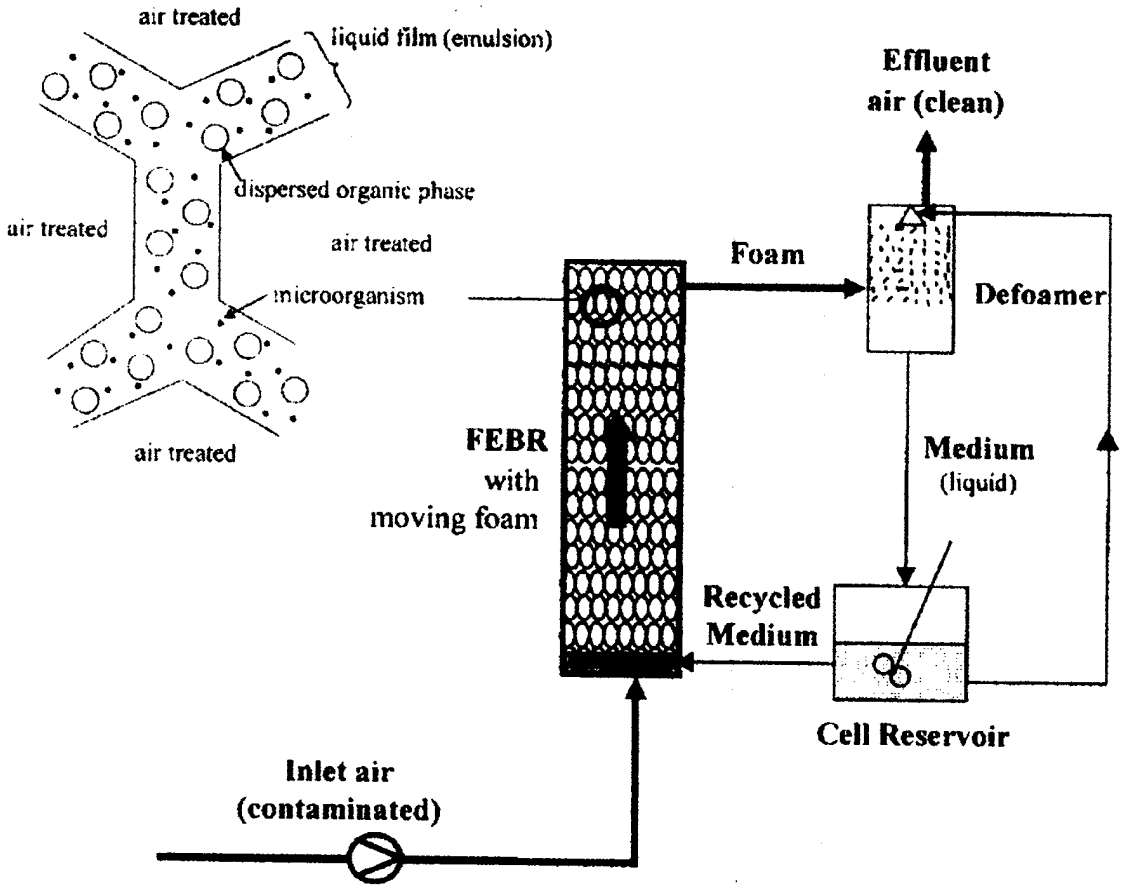
- Foamed emulsion bioreactor (FEBR) = emulsion of
  1. highly active pollutant-degrading microorganisms
  2. a water-immiscible organic phase
- The emulsion is converted into a foam (by addition of a surfactant) during waste air treatment

Advantages:

- Increased gas/liquid interfacial area provided by the fine foams
- Increased driving-force for mass transfer resulting from the presence of a water-immiscible organic phase (Henry coefficient partition coefficient between gas and organic phase)
- Since no packing material is present in the FEBR, bed clogging and associated pressure drop problems are avoided
- High-density culture of actively growing organisms is present, resulting in high volumetric pollutant removal rates

Foamed emulsion bioreactor

An innovative bioreactor concept



Foamed emulsion bioreactor

An innovative bioreactor concept

- Contaminated air stream is introduced into the foam column through a gas sparger
- Emulsion consisting of mineral medium, active culture, organic phase (oleyl alcohol) and surfactant (DC-100 silicone) are introduced at the bottom of the reactor
- The foam leaving the reactor at the top is defoamed in a defoamer by continuously spraying the foam with the emulsion from the cell reservoir
- Liquid is returned to the cell reservoir prior to being recycled to the foam column

Example : toluene degradation (Kan and Deshusses, 2003)

- Elimination capacities up to 285 g TOL/$m^3_{reactor}$.h in air
- Removal efficiencies of 95% at a = 15 s and TOL inlet concentrations of 1.0-1.3 g/m^3
- The FEBR performance far exceeds that of currently used bioreactors for TOL pollution control

Challenges for near future

- Foam stability at high air velocity
- Supply enough oxygen to the cell culture

Microbial communities

Indicators for bioreactor performance

Biofilters are nowadays used in industry for treating odorous airstreams or airstreams containing low pollutant concentrations.

However, little information is available about the composition and the dynamics of the complex microbial communities present in the biofilter material, and about their relationship with *e.g.* pollutant removal and resistance towards stress conditions.

Recent research aims at finding a relationship between parameters obtained from microbial community fingerprinting and pollutant removal efficiencies in compost biofilters.

Microbial communities – Analytical techniques

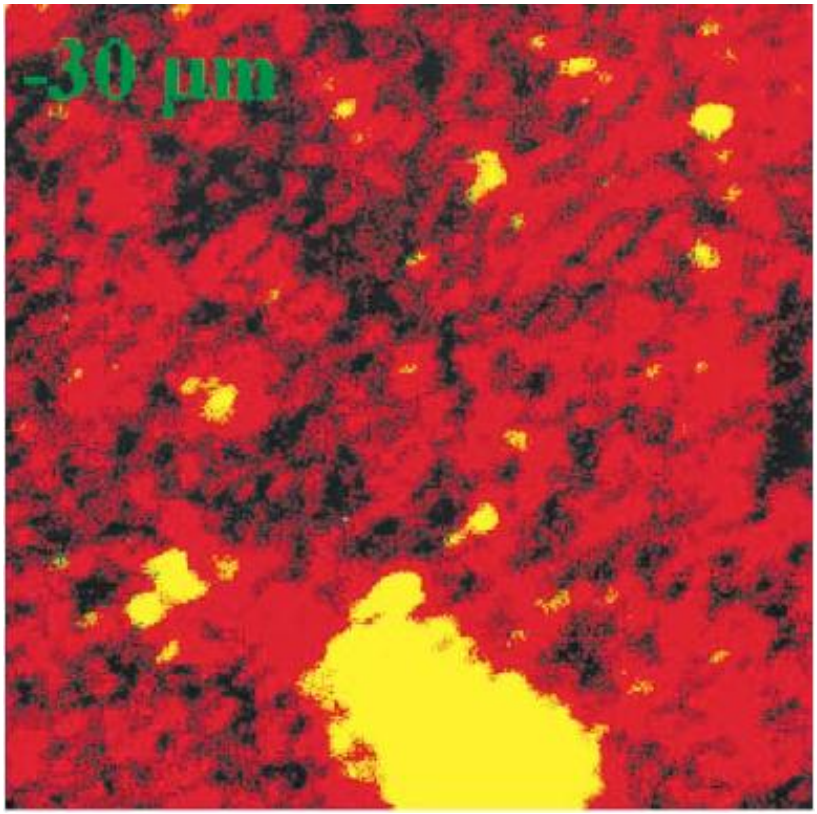
Traditional techniques

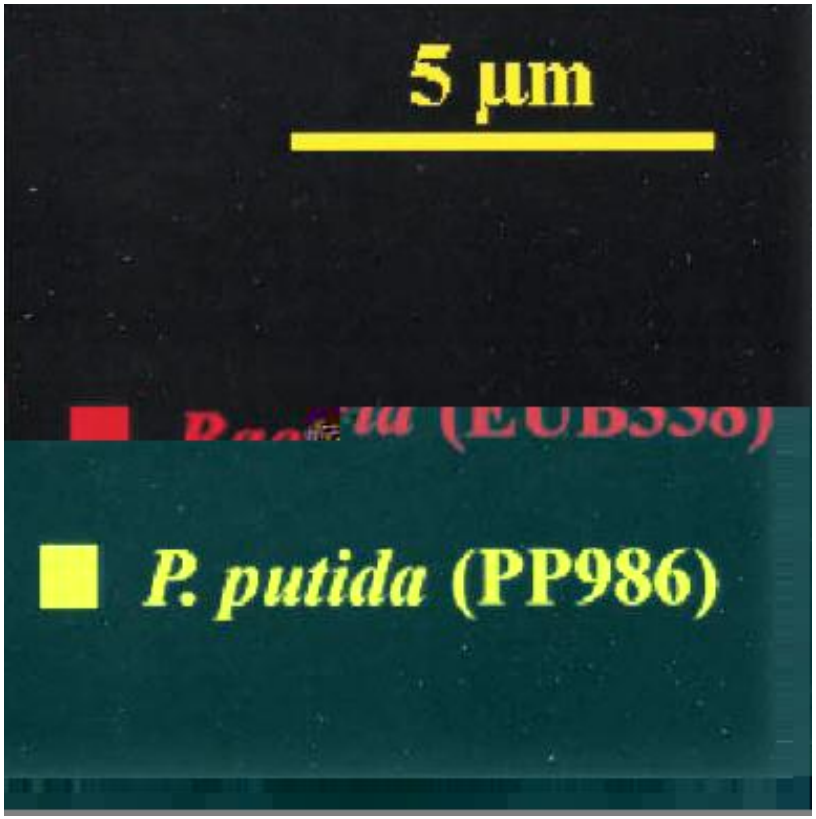
- Microscopic analysis
  - unstable morphology of microorganisms
  - small differences between bacteria
- Plating bacteria
  - Choice of nutrient medium : selectivity !
  - Counting number of bacteria and/or isolation of one group of bacteria
  - Only applicable to 0.1 to 10% of bacteria
- PLFA (polyfosfolipid fatty acid) analysis
  - Polyfosfolipid fatty acids are characteristic components of cel membrane
  - Extraction of PLFA + GCMS

Molecular techniques

- Analysis of nucleic acids (DNA, RNA)
- PCR (polymerase chain reaction), DGGE (denaturating gradient gel electrophoresis), FISH (Fluoresence In Situ Hybridization)

Microbial communities – Analytical techniques



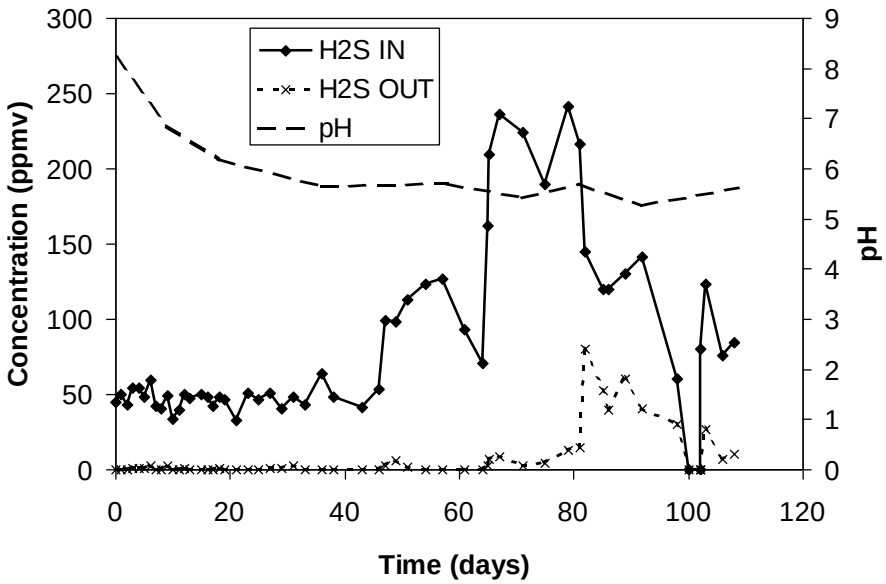


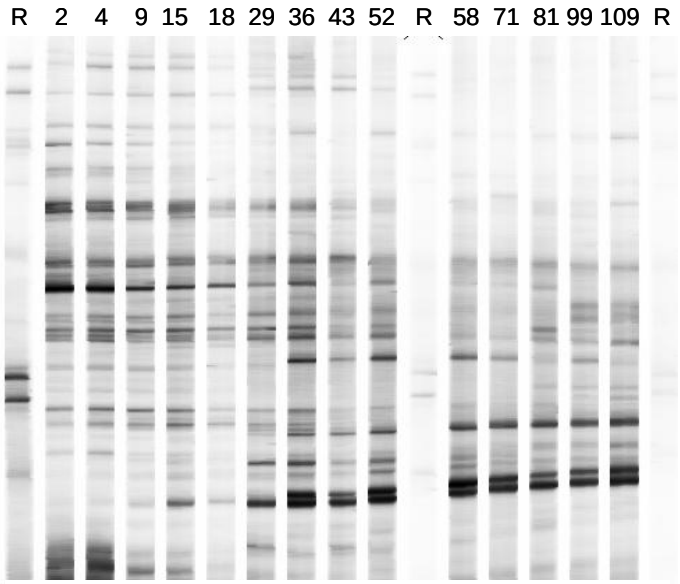
FISH – Toluene degrading BTF

Microbial communities – Evaluation tools

(1) Presence of microbial species

- DGGE profiles for different subgroups (*e.g.* eubacteria, ammonium oxidizing bacteria,…) of bacteria are analysed
- Each 'band' represents a species
- Appearance or disappearance of species can be followed as a function of time, operational parameters,…





DGGE profile of Eubacteria

Microbial communities – Evaluation tools

(2) Community diversity

From DGGE-profiles: diversity indices

- Number of species (S) = number of bands
- Shannon diversity index

$H = - \quad P_i \log P_i$

$Pi : n_i/N$ $\qquad$ n_i : intensity of one band

$N = \quad n_i$: total intensity

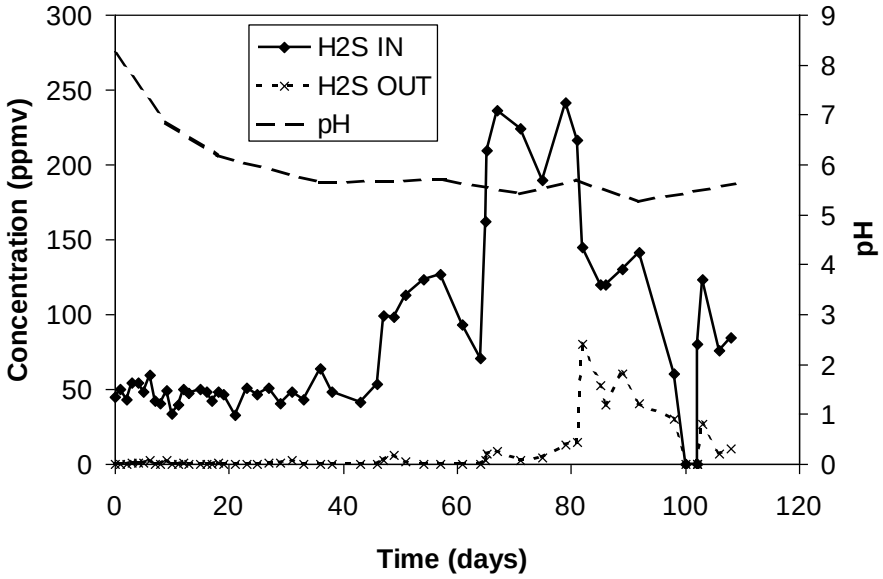
(3) Community dynamics

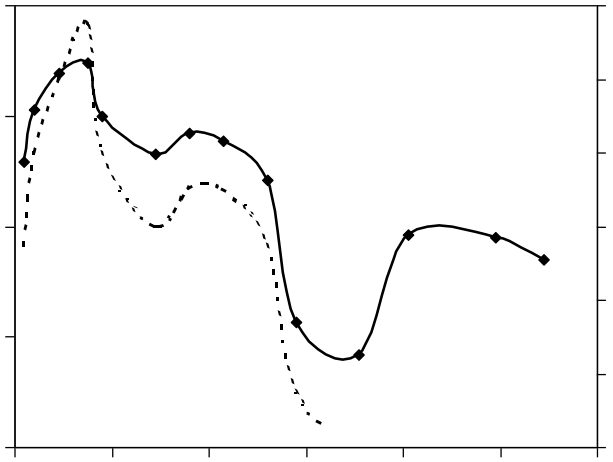
Community dynamics (CD) = 100 – R

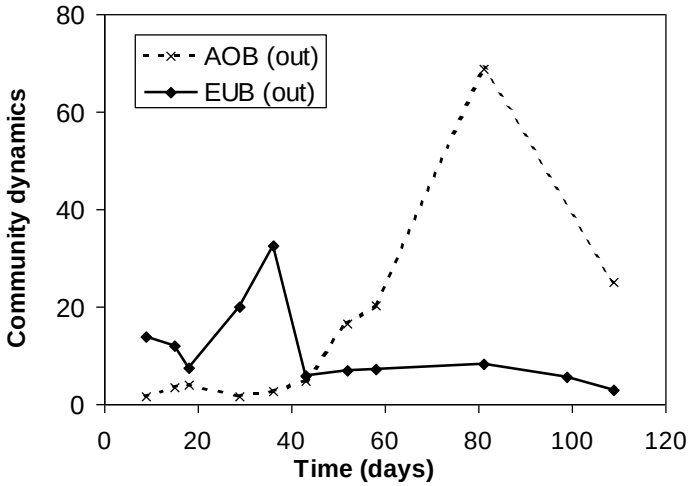
R = mean Pearson correlation (%) of samples during time interval of 15 days

(measure for similarity between two different lanes of bands)

Microbial communities – Evaluation tools







CO_2-capture and sequestration

Greenhouse gases: H_2O, CO_2, O_3, CH_4, N_2O, CFK (chlorofluorohydrocarbons)

- Transmission of solar irradiation
- Absorption of IR irradiation → earth's temperature 15°C instead of -18°C

Heating up of the earth surface:

- 0.6 – 1.0°C during the last 150 years
- Prediction : further increase of average year temperature of 1.4°C – 5.8°C (1990-2100)
- Big climatological and ecological problems (*e.g.* floods, disappearance of plant and/or animal species,…) can be expected

Increase of CO_2 concentration from 280 ppmv (1750) to 388 ppmv (2010), caused by anthropogenic emission:

- Combustion of fossil fuels (70-90%): domestic, traffic, industrial activities
- Reduction of forest areas

CO_2-emission for 2/3 responsible for global warming effect

CO_2-capture and sequestration
International legislation

1991 : first meeting of Intergovernmental Negotiation Committee (INC)

1992 : United Nations Framework Convention on Climate Change (UNFCCC)

1992 : United Nations Conference on Environment and Development (UNCED)

→ 'Earth Summit' declaration (implementation in 1994)

1997: Kyoto-protocol

- Industrial countries: emission reduction of greenhouse gases of 5% in 2008-2012 compared with that in 1990
- European Union: emission reduction of 8%

2009: United Nations Climate Change Conference in Copenhagen

- Non-binding agreements

CO_2-capture and sequestration
Emission reduction strategies

Preventive strategies

- Decreased use of fossil fuels (currently 85% of energy supply)
- Use of alternative energy sources
  - Nuclear energy
  - Renewables : solar and wind energy

CO_2-fixation in biomass (forests, wetlands, agriculture areas, humus,…)

End-of-Pipe strategies

- Separation and capture of CO_2 from waste gases
  - Chemical / Physical absorption
  - Adsorption
  - Cryogenic methods
  - Gas separation membranes
  - Gas absorption membranes
- Once the CO_2 is captured, it needs to be securely stored (sequestered)

CO_2-capture and sequestration
End-of-Pipe technologies

Chemical absorption

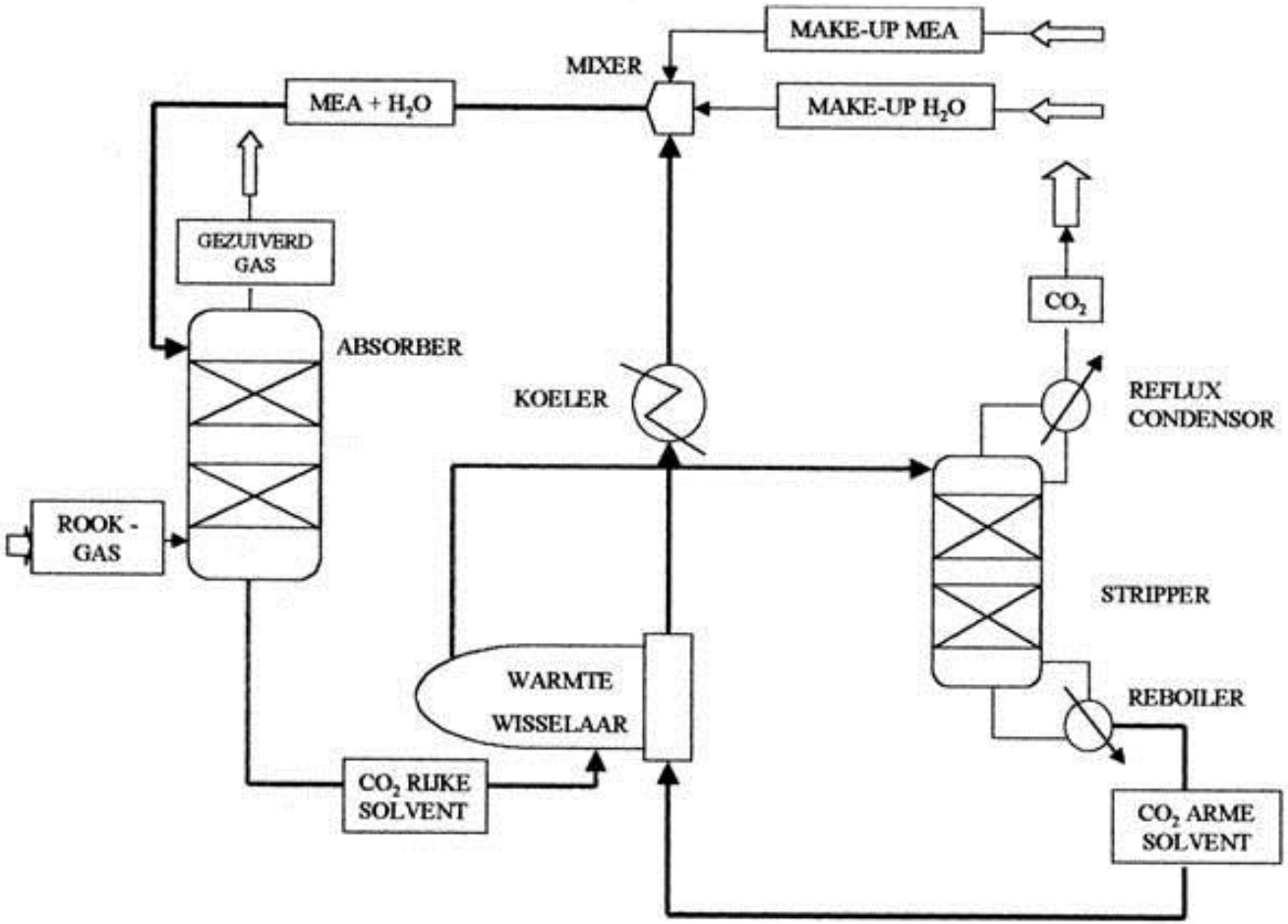
- CO_2 containing gas stream in contact with solvent
- Reaction between solvent and CO_2 → intermediate
- Solvent regeneration by heating
- Mostly applied when CO_2-concentration is low
- Most applied solvent : monoethanolamine (MEA – $HOCH_2CH_2NH_2$): high affinity for CO_2

Physical absorption

- Absorption according to Henry's law
- Solvent regeneration by decreasing pressure
- Mostly applied for gas mixtures with high partial pressures of acid gases (high CO_2 concentrations)

CO_2-capture and sequestration

End-of-Pipe technologies



CO_2-capture and sequestration
End-of-Pipe technologies

Chemical absorption unit: absorber, heat exchanger, stripper

Absorption:

- Mass transfer from gas to liquid phase
- Due to reaction of CO_2 with solvent : mass transfer rate is increased

Heat exchanger:

- CO_2-rich solvent is preheated by the CO_2-lean solvent coming from the stripper

Stripper:

- Preheated CO_2-rich solvent is stripped by steam
- CO_2 is released at the top of the stripper
- CO_2-lean solvent is cooled in the heat exchanger and cooler and returns to the absorption unit

Continuous regeneration of the solvent

CO_2-capture and sequestration
End-of-Pipe technologies

Adsorption

- Physical attraction between CO_2 and active sites of solid
- Adsorbents : aluminium, molecular sieves, active coal
- Limitations : low selectivity and capacity of adsorbents

Cryogenic methods

- CO_2 physically separated from other gases by condensation of CO_2 at cryogenic temperature
- Low temperatures and high pressures

CO_2-capture and sequestration
End-of-Pipe technologies

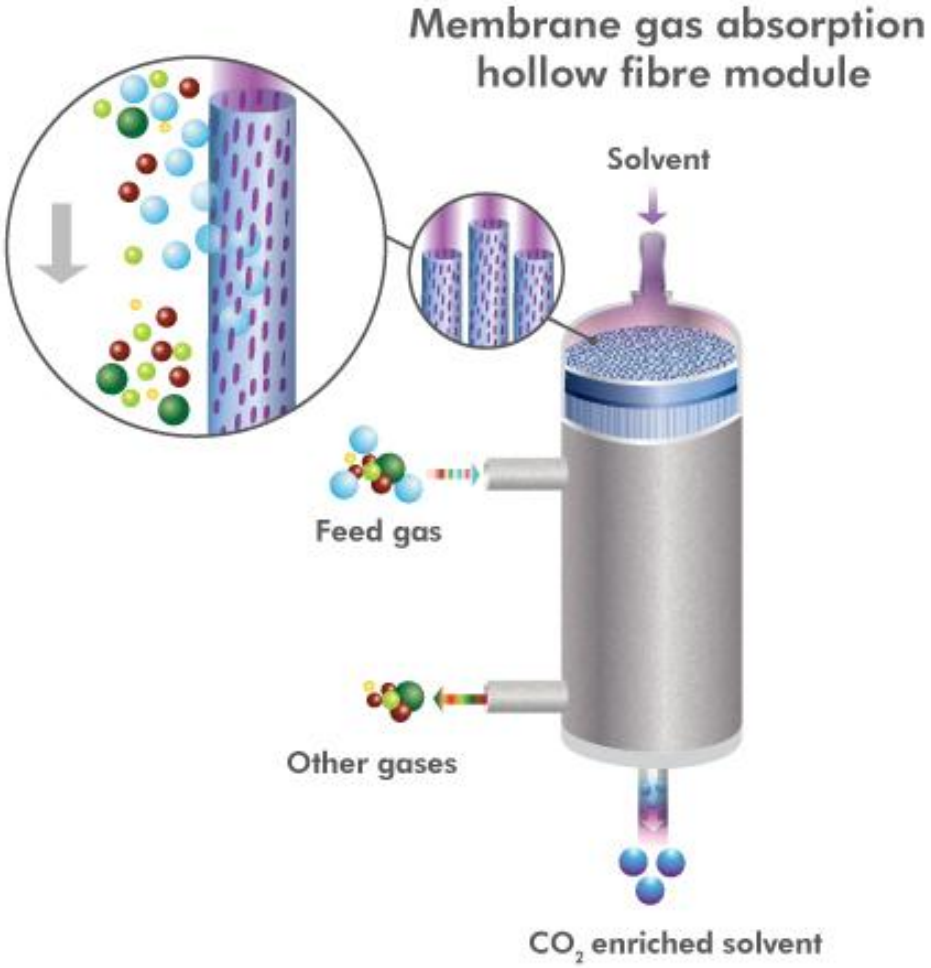
Gas separation membranes

- Due to different physical-chemical properties, some compounds of the gas stream diffuse faster through membrane than others do
- Multi-step systems are necessary due to low membrane selectivity
- By increasing pressure → increased driving force

Gas absorption membranes

- Gas and liquid (solvent) stream are separated by membrane
- Choice of a selective absorption liquid (solvent, e.g. MEA)

CO_2-capture and sequestration
End-of-Pipe technologies



CO_2-capture and sequestration
End-of-Pipe technologies

Utilization of captured CO_2:

- Production of ureum and dry ice
- Food and beverage industry
- Enhanced oil recovery (EOR) : increased mobility of oil by injecting CO_2 in existing oil field → increased efficiency

Sequestration of CO_2 (= safe storage):

- Geologic formations: deep saline reservoirs, depleted oil and gas wells, unmineable coal seams
- Oceans:
  - Very high CO_2 capacity
  - CO_2 injection below thermocline (100-1000 m below sea level): very slow mixture with surface water

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