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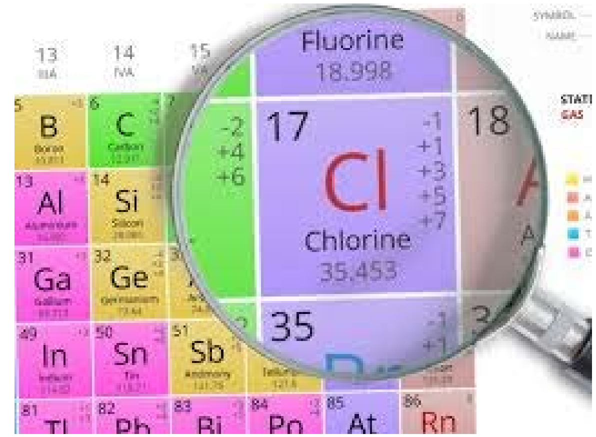
School of Engineering

Physical & chemical treatment processes of water and waste WAT - E2120

Chlorination, ozonation, UV and AOPs

Irina Levchuk, D.Sc (Tech)

Disinfection with chlorine



<u>Chlorine</u> is the one most commonly used disinfectant throughout the world.

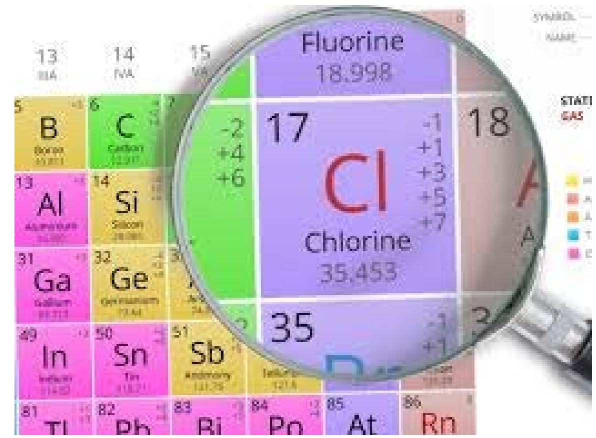
Chlorination is applied for

- drinking water disinfection
- disinfection of wastewater
- shock chlorination (private wells, storage tanks, etc.)
- swimming pools
- secondary disinfection of distribution networks

Disinfection with chlorine

Characteristics of chlorine compounds

- Chlorine (Cl_2)
- Sodium hypochlorite (NaOCl)
- Calcium hypochlorite ($Ca(OCl)_2$)
- Chlorine dioxide (ClO_2)



Disinfection with chlorine

Chlorine (Cl_2)

Chlorine can be present as gas or liquid. Chlorine gas is green-yellowish in color and about 2.48 times as heavy as air.

Liquid chlorine is amber colored and about 1.44 times as heavy as water. Unconfined liquid chlorine vaporizes rapidly to a gas at standard temperature and pressure with 1 liter of liquid yielding about 450 liters of gas.

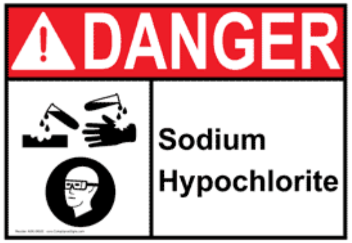
Disinfection with chlorine

Chlorine (Cl_2)

serious concerns:

- Chlorine is highly toxic substance that is transported by rail and truck, both of which are prone to accidents
- Chlorine poses health risks to treatment operators and the general public if released by accident
- Chlorine reacts with organic compounds in water to produce odorous compounds and carcinogenic and/or mutagenic byproducts
- Long-term effects of chloro-organic compounds formed after chlorination are not known
- Residual chlorine in treated wastewater may be toxic to aquatic life

Disinfection with chlorine

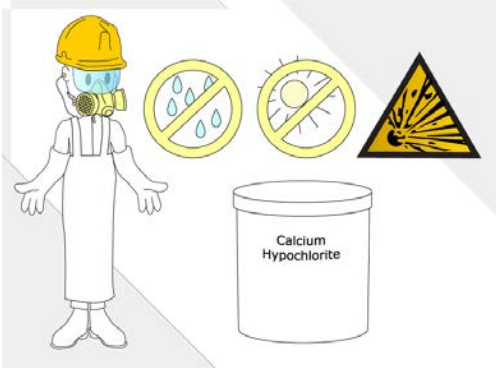


<u>Sodium hypochlorite</u>

Many of safety concerns related to transport, storage and feeding of liquid-gaseous chlorine are eliminated by the use of either sodium or calcium hypochlorite. Sodium hypochlorite (liquid bleach) is only available as liquid and contains **<u>12.5 to 17% available chlorine at time it is manufactured</u>**. The solution <u>*decomposes more rapidly at high concentrations*</u> and is affected by exposure to light and heat. For instance, a 16.7% solution stored at 26.7ºC will loose 10% of its strength in 10 days, 20% in 25 days and 30% in 43 days.

Another disadvantage of sodium hypochlorite is the cost. The purchase price may range from **<u>150 to 200% of the cost of liquid chlorine</u>**. The handling of sodium hypochlorite requires special design considerations because of its corrosiveness and the presence of chlorine fumes.

Disinfection with chlorine



<u>**Calcium hypochlorite**</u>

Calcium hypochlorite is available in either a dry (granules, compressed tablets or pellets) or a wet form. Granules are readily soluble in water, varying from about 21.5 g/100 mL at 0ºC to 23.4 g/100 mL at 40ºC.

Because of its oxidizing potential calcium hypochlorite should be stored in a cool, dry location away from other chemicals in corrosion-resistant containers. **Hypochlorite is more expensive than liquid chlorine**, **loses its available strength** on storage, and may be **difficult to handle**. It may clog pumps, piping and valves, because it tends to crystalize. It is most commonly used in small installations.

Disinfection with chlorine

Chlorine reactions in water

When chlorine in a form of Cl_2 gas is added to water, two reactions take place: *hydrolysis and ionization*

Hydrolysis reaction of chlorine – formation of hypochlorous acid (HOCl)

$$\underset{\text{Chlorine Gas}}{Cl_2 + H_2O} \leftrightarrow \underset{\text{Hypochlorous Acid}}{HOCl} + H^+ + Cl^-$$

Disinfection with chlorine

Chlorine reactions in water

When chlorine in a form of Cl_2 gas is added to water, two reactions take place: *hydrolysis and ionization*

Ionization – HOCl formed during the hydrolysis reaction ionizes to form the hypochlorite ion (OCl-).

$$\underset{\text{Hypochlorous Acid}}{HOCl} \leftrightarrow H^+ + \underset{\text{Hypochlorite Ion}}{OCl^-}$$

The ionization constant for the reaction: $K_a = \frac{[H^+][OCl^-]}{[HOCl]}$

Disinfection with chlorine

Free available chlorine

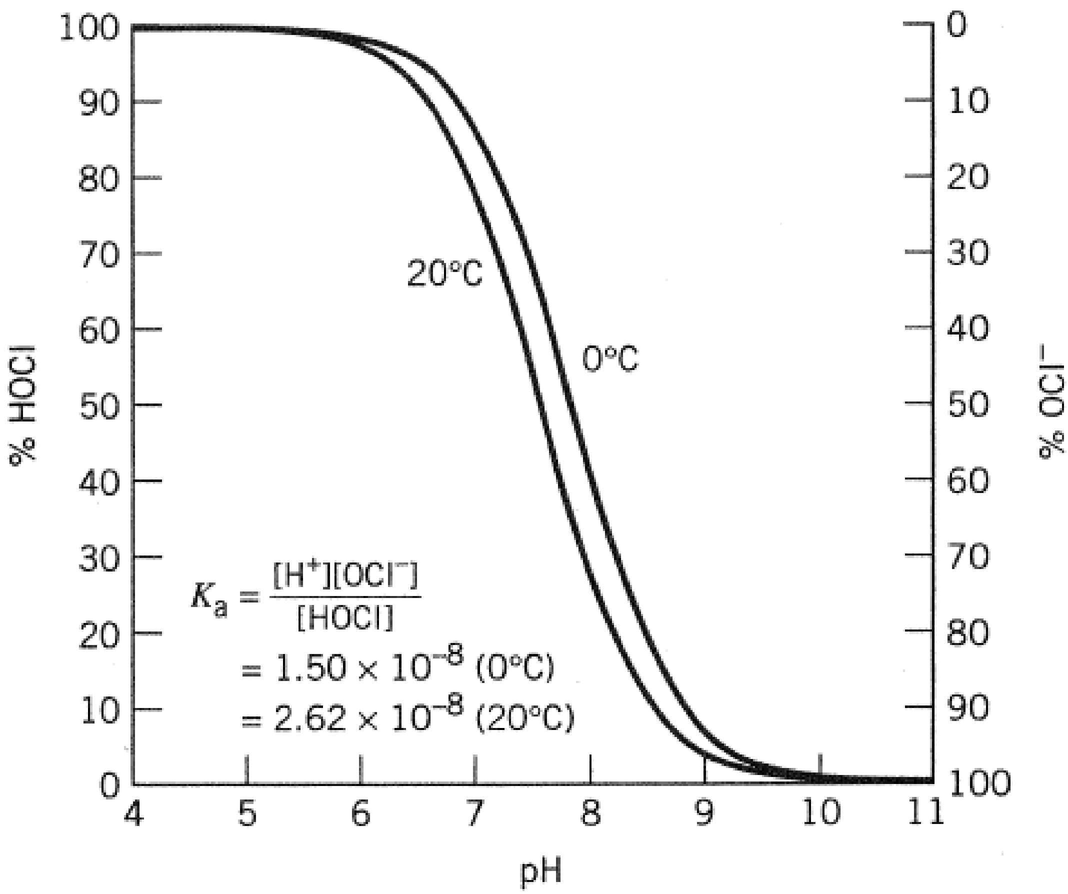
$$[HOCl] + [OCl^-]$$

Hypochlorous acid *Hypochlorite ion*

- The most stable oxidation state for Cl in water is −1 (Cl^-)
- Both HOCl and OCl^- are in the +1 oxidation state, so they "want" to become more stable (oxidize something and acquire electrons)
- The killing efficiency of HOCl is about 40-80 times that of OCl^-

Disinfection with chlorine

Ionization of hypochlorous acid (HOCl) at different pH values



- At a pH of 7.0, 76 percent of the chlorine is in its active, killing form (HOCl). The rest has ionized into the inactive form (OCl-).
- At a pH of 7.8, only 33 percent of the chlorine is in HOCl form.

Disinfection with chlorine

Hypochlorite reactions in water

Free available chlorine can also be added to water in form of hypochlorite salts. Both calcium and sodium hypochlorite hydrolize to form hypochlorous acid (HOCl) as follows:

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2$$

$$NaOCl + 2H_2O \rightarrow HOCl + NaOH$$

Disinfection with chlorine

Reactions with ammonia

If water contains nitrogen in the form of ammonia (for example effluent from wastewater treatment plants) hypochlorous acid will react readily with ammonia in water to form three types of chloramines:

$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$	Monochloramine
$HOCl + NH_2Cl \leftrightarrow NHCl_2 + H_2O$	Dichloramine
$HOCl + NHCl_2 \leftrightarrow NCl_3$	Trichloramine

These reactions are dependent on pH, temperature, and contact time and on the ratio of chlorine and ammonia. Usually monochloramine and dichloramine are predominating species.

Disinfection with chlorine

Reactions with ammonia

Combined available chlorine – chlorine present in chloramines

Chloramines also serve as disinfectants, although they are very slow-reacting.

Chlorine Demand (amount of chlorine that must be added to reach desired level of residual)

Organic N and ammonia exert a chlorine demand

- Wastewater (40-60 mg/L)
- Potable water (2 -5 mg/L)

Once demand is met additional Cl_2 added reacts to form free available chlorine which is more effective for disinfection

Disinfection with chlorine

Breakpoint chlorination

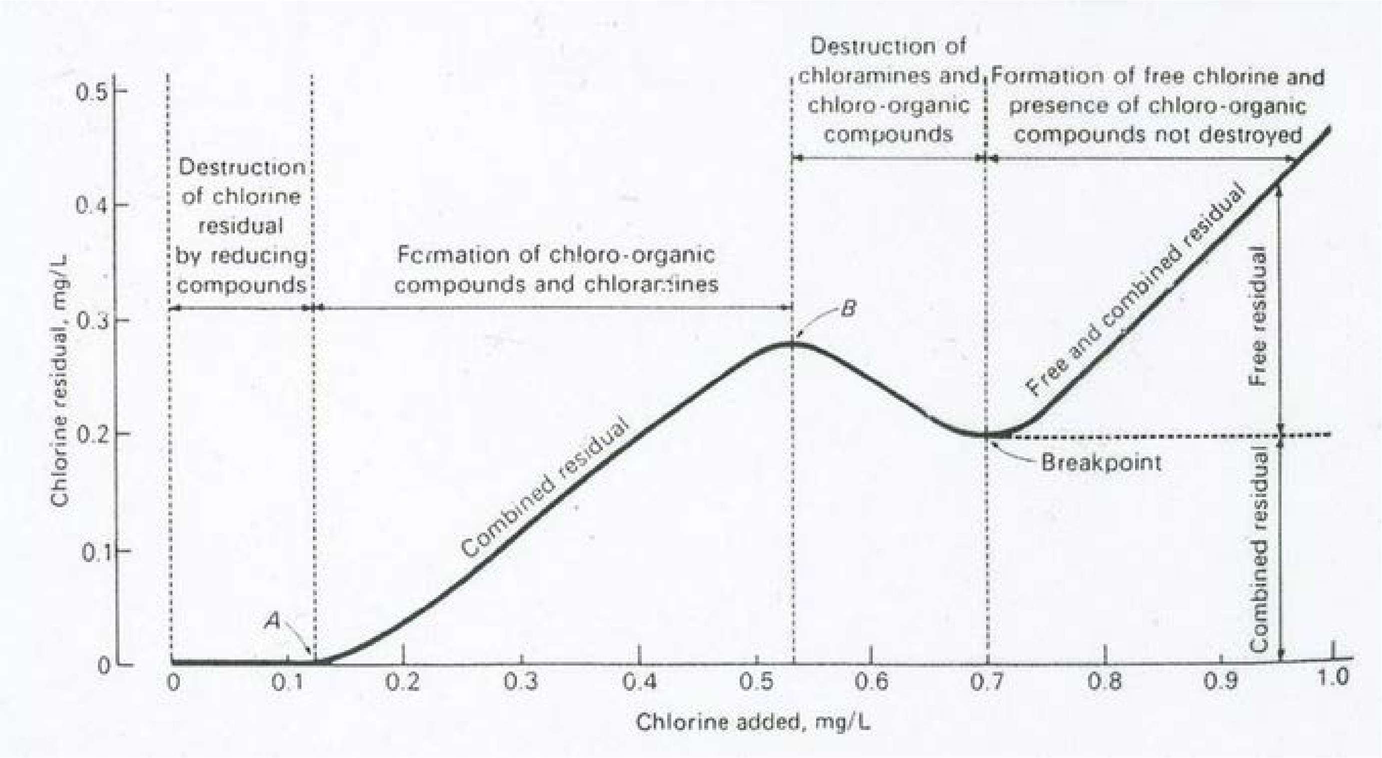
The term *breakpoint chlorination* is the term applied to the process whereby enough chlorine is added to react with all oxidizable substances such that if additional chlorine is added it will remain as free chlorine.

The main reason for adding enough chlorine to obtain a free chlorine residual is that effective disinfection can usually be assured.

Specific levels of free chlorine residual must be maintained (0.5-1 mg/L) in the water supply to ensure effective disinfection treatment

Disinfection with chlorine

Breakpoint chlorination



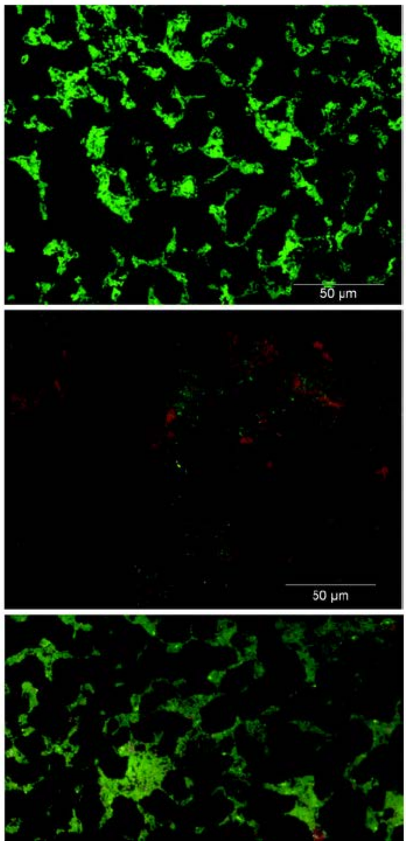
https://www.youtube.com/watch?v=3rXZg6VDVRQ

Bacteria regrowth

a

b

c

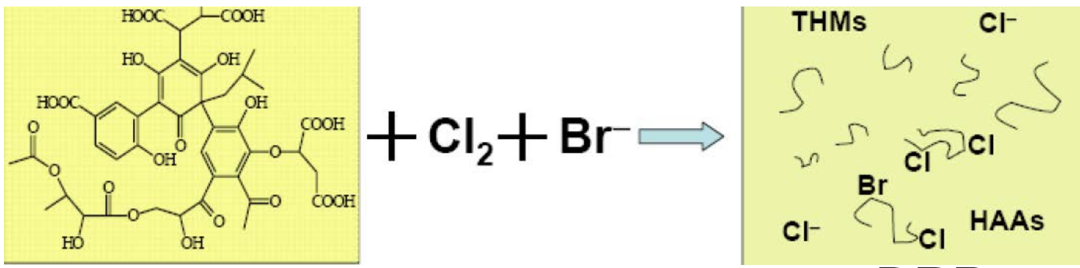


Effects of chlorine disinfectionon the viability of drinking water multispecies biofilms and their ability to recover after treatment

- The epifluorescence photomicrograph show the biofilms (a) before treatment with10 mg l^{-1}sodium hypochlorite; (b) immediatelyafterand (c) 24 h later Magnification, ×400; bar= 50 µm
- Viable cells are green and non-viable cells are red

Disinfection with chlorine

Formation of disinfection byproducts (DBPs)



NOM DBPs

Halogenated organic byproducts are formed when natural organic matter (NOM) reacts with free chlorine or free bromine. Free chlorine can be introduced to water directly as a primary or secondary disinfectant, with chlorine dioxide, or with chloramines. Free bromine results from the oxidation of the bromide ion in source water.

Disinfection with chlorine

Formation of disinfection byproducts (DBPs)

Formation of DBPs is of great concern because of the potential impact of these compounds on public health and the environment.

Many of DBPs have been classified as probable **human carcinogens**. Many unknown and potential public health and environmental risks are associated with DBPs.

Disinfection with chlorine

<u>Formation of DBPs due to addition of chlorine for disinfection</u>

Trihalomethanes (THMs) and other DBPs are formed as a result of series of complex reactions between free chlorine and humic acids. The reactions lead to formation of single carbon molecules that are often designates as

$$HCX_3$$

Where X is chlorine (Cl) or bromine atom

For example, chemical formula of chloroform (well-known animal carcinogen) is $HCCl_3$

Disinfection with chlorine

Formation of DBPs due to addition of chlorine for disinfection

The rate of DBPs formation depends on number of factors:

- ❑ Presence of organic precursors
- ❑ Free chlorine concentration
- ❑ Bromide concentration
- ❑ pH
- ❑ Temperature

Disinfection with chlorine

<u>Approaches to remove DBPs from water</u>

- ❑ Use a disinfectant that is less likely to form DBPs or forms less problematic ones
- ❑ Remove or alter the NOM so it does not react with the free chlorine
- ❑ Remove DBPs after they form

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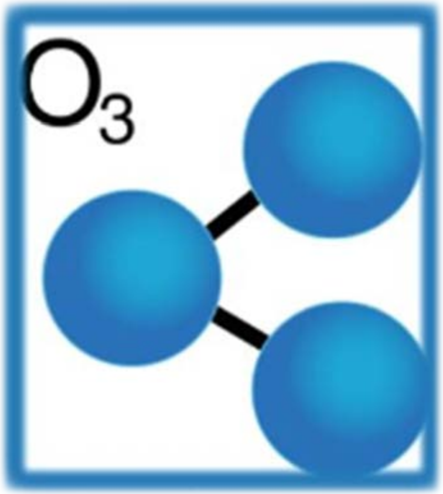
Ozonation

Ozonation

Ozone was first used to disinfect water supplies in France in early 1900s. Its use increased and spread into several western European countries and to North America.



Ozonation

Properties of ozone

- Ozone is unstable gas produced when oxygen molecules dissociate into atomic oxygen

- Ozone is a blue gas at normal room temperatures and has distinct odor

- Liquid ozone is dark blue (-112ºC)

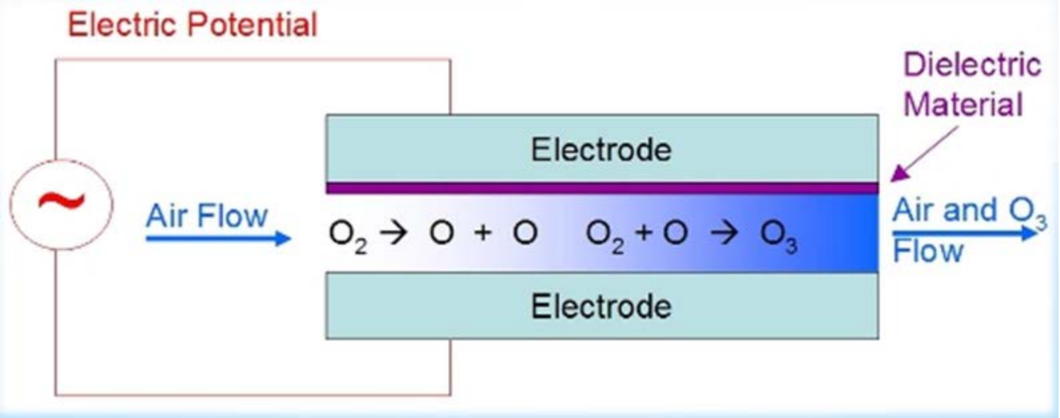
- Stability of ozone in air is greater than in water (order of minutes)

- Gaseous ozone is explosive when concentration reaches about 240 g/cm^3

Ozonation

Ozone generation

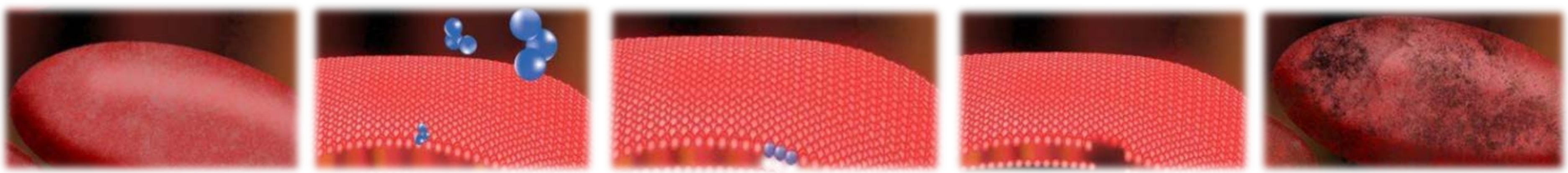
Because of its instability, ozone should be generated onsite. Ozone can be generated from oxygen present in air or high purity oxygen. Very often ozone is generated by electrical discharge. Ozone generation consumes power at a rate of 8 to 7 kWh/kg O_3. On-site generation saves a lot of storage space.



Ozonation

Inactivation efficiency

Ozone is one of the most potent and effective germicide used in water treatment. It is effective against bacteria, viruses, and protozoa. It is generally considered that bacteria kill through ozonation occurs directly because of cell wall disintegration. Inactivation efficiency for bacteria and viruses is not affected by pH; at pH levels between 6 and 9.



Not damaged cell **damaged cell**

Ozonation

Advantages

- Ozone is more effective than chlorine, chloramines, and chlorine dioxide for inactivation of viruses, Cryptosporidium, and Giardia
- Ozone oxidizes iron, manganese, and sulfides.
- Ozonation is useful for micropollutant removal
- It can sometimes enhance the clarification process and turbidity removal
- Ozone controls color, taste, and odors
- It requires a very short contact time
- In the absence of bromide, halogen-substitutes DBPs are not formed
- Upon decomposition, the only residual is dissolved oxygen
- Biocidal activity is not influenced by pH

Ozonation

Disadvantages

- DBPs are formed, particularly by bromate
- The initial cost of ozonation equipment is high
- The generation of ozone requires high energy and should be generated on-site
- Ozone is highly corrosive and toxic
- Ozone decays rapidly at high pH and warm temperatures
- Ozone provides no residual
- Ozone requires higher level of maintenance and operator skill

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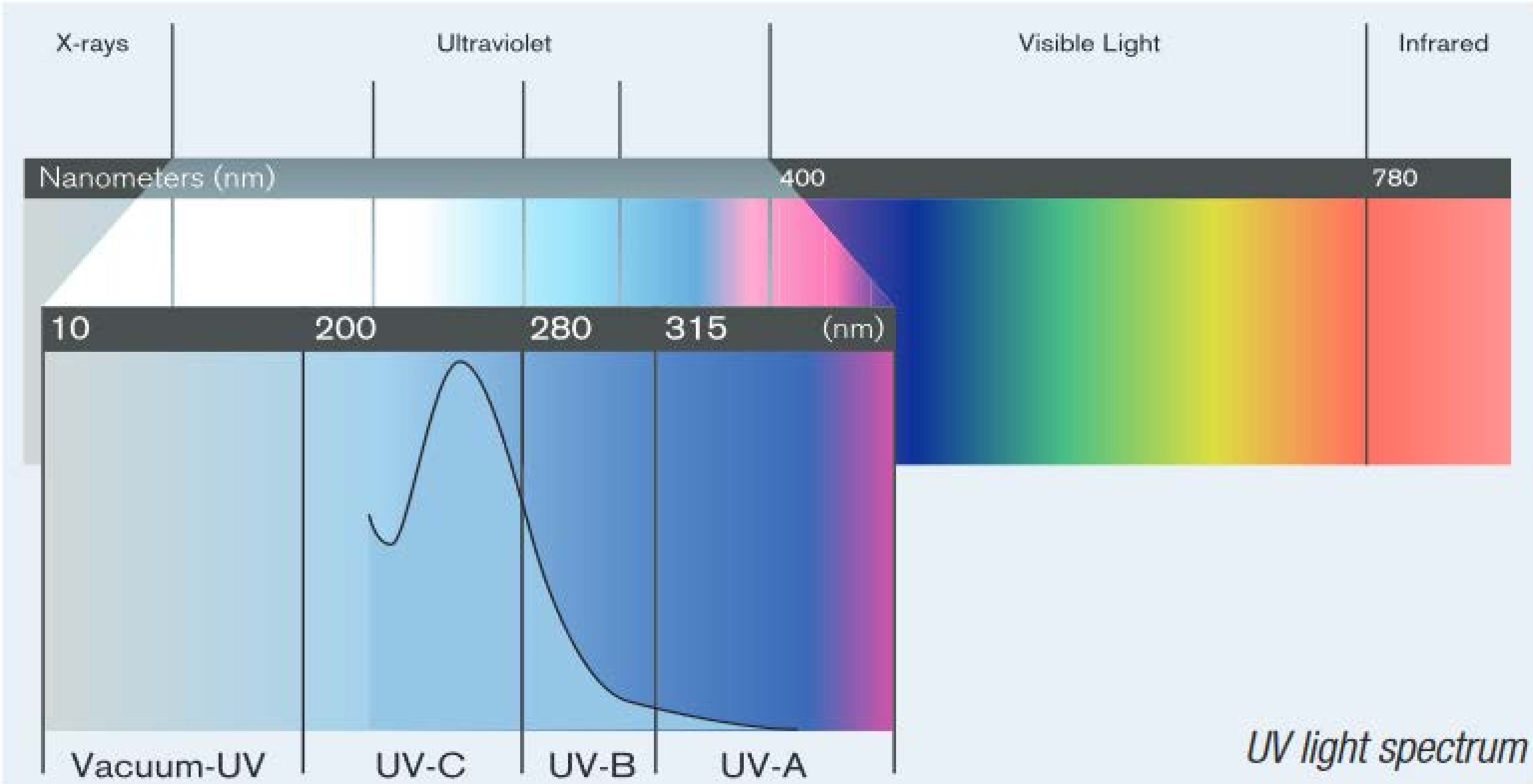
Ultraviolet radiation

UV



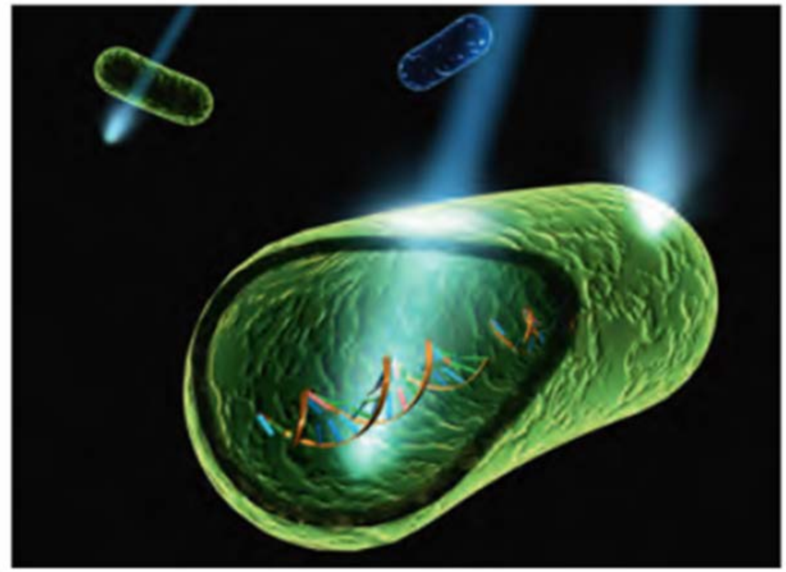
The germicidal portion of UV radiation – 220-320 nm

UV

Germicidal effectiveness of UV radiation

UV light is physical agent. UV penetrates the cell wall of microorganism and absorbed. This can cause death of the cell or prevent its replication.
The effectiveness of UV disinfection depends on number of variables:

- characteristics of UV system
- the presence of particles
- the characteristics of microorganisms
- characteristics of water



DNA effected by UV light

UV

Definition of UV dose

The effectiveness of UV disinfection depends on the UV dose to which microorganisms are exposed.

$$D_t = I \cdot t$$

Where D=UV dose (mW·s/cm^2 or mJ/cm^2)
I = UV intensity, mW/cm^2
t = exposure time, s

UV

Definition of UV dose

$$I_i = I_0 \cdot T^d$$

Where

I_i UV intensity received at certain point inside the reactor, mW/cm^2

I_0 UV intensity of the lamp, mW/cm^2

T Transmittance of water at 254 nm

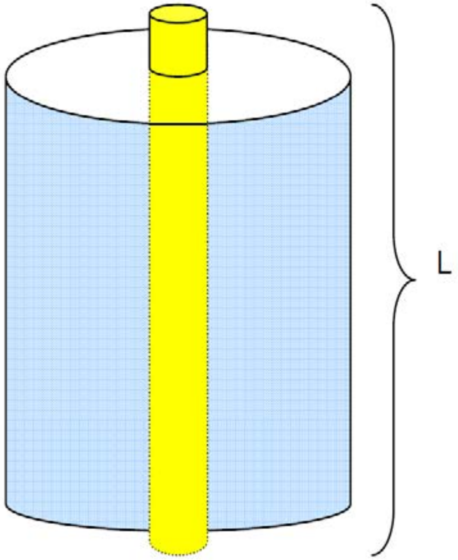
d distance from the surface of the lamp to desired point in the reactor, cm

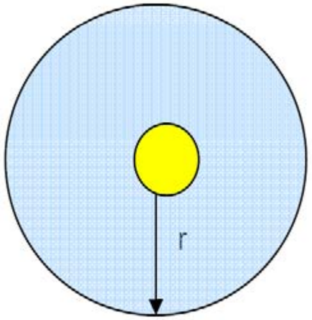
UV

Definition of UV dose

How we determine I_0?

$$I_0 = \frac{P}{2 \cdot \pi \cdot r_i \cdot L}$$





Where
P is power of the lamp, W
L is length of the lamp, cm
r_i is radius of the lamp, cm

UV

Definition of UV dose

Determine Dose recieved at red point $(\mathrm{mW.s/cm^2})$

Where

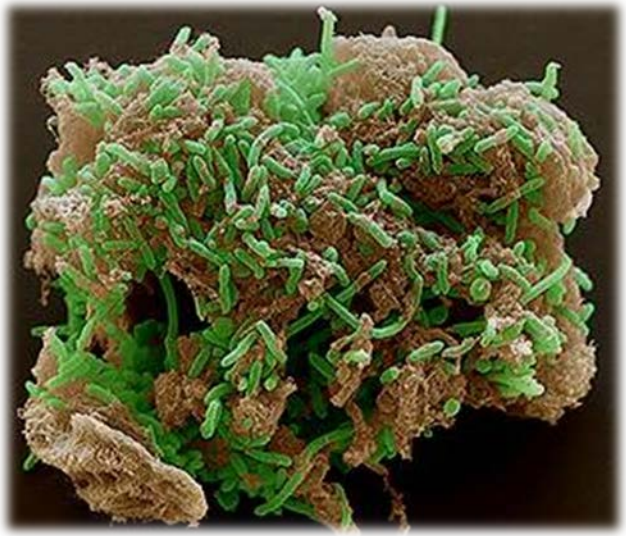
P (UVC) = 4 W
Diameter of the lamp = 2 cm
Length of the lamp = 30 cm
d (distance from lamp to desired point in reactor) = 3 cm
T = 85 %
t = 0,5 min

I_0= 21,23 mW/cm^2

I_1= 13,04 mW/cm^2

D_t ≈ 391 mW s/cm^2

UV



Impact of particles

- Many microorganisms in water occur in disperse state and particle-associated state (bound to other objects, such as particles).
- Disperse microorganisms are readily inactivated because they are fully exposed to UV. Microorganisms can associate with particles to such degree that they are completely shielded from UV light.

UV

Characteristics of microorganisms

Select Disease-causing Microbes Found in Water

Pathogen	Average UV Dose (mJ/cm²) Needed to Inactivate*
E. Coli 0157:H7	5.6
Giardia lamblia	<10
Crypto. parvum	10
Salmonella typhi	7.1-8.2
Legionella pneumonophila	9.4
Vibrio chloerae	2.9
Hepatitis A virus	16-30

*4-log reduction
Data summarized from USEPA Workshop on UV Disinfection of Drinking Water April, 1999

UV

Effect of water chemical constituents

Dissolved compounds affect UV disinfection in following ways:

- ❑ Directly via absorbance impacts
- ❑ Via fouling UV lamps such that reduced intensity is applied

Constituent	Effect
Iron	Strong absorber of UV, can precipitate on quartz tubes
Humic substances	Strong absorbers of UV
Nitrate	No or minor effect

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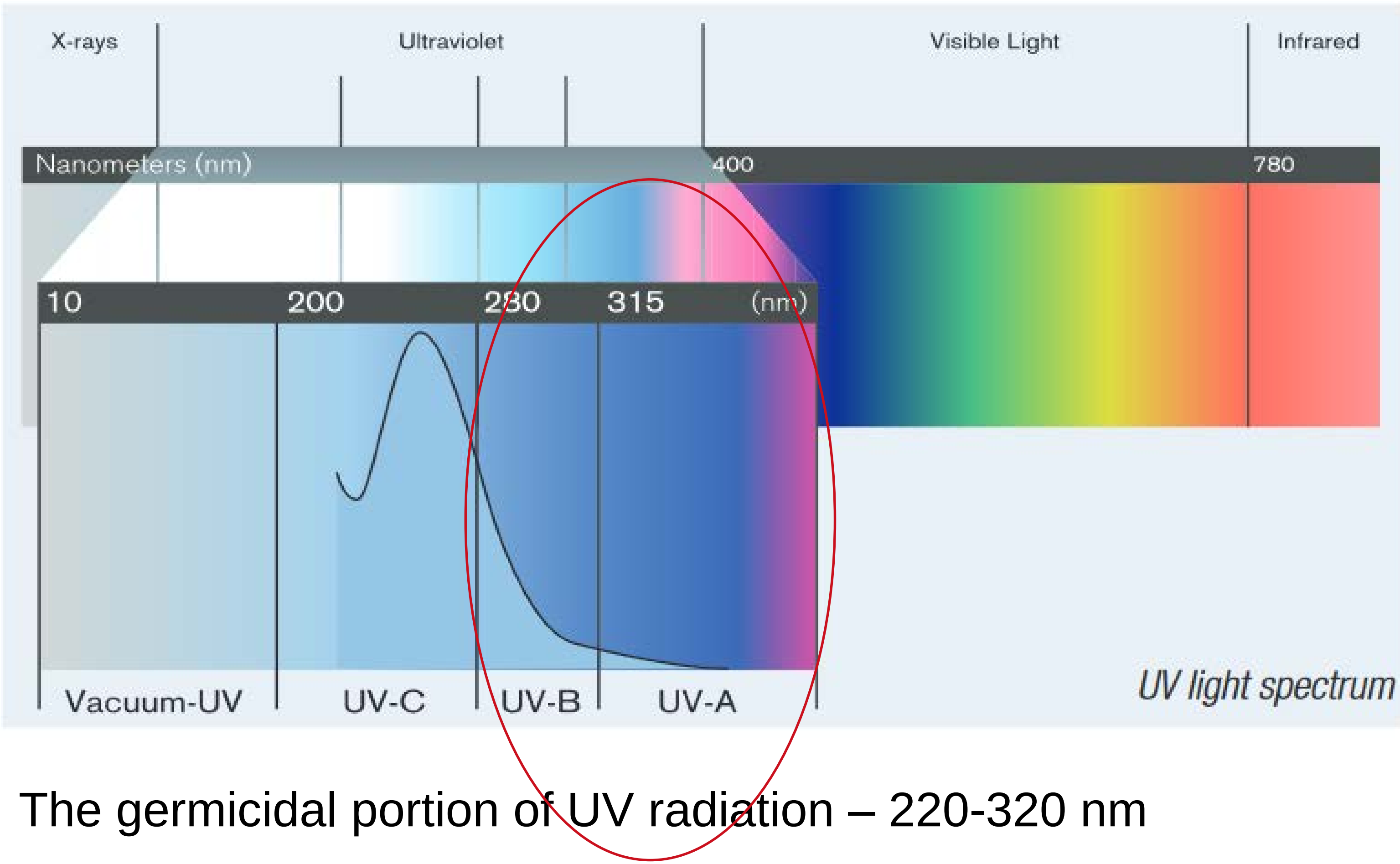
SODIS
Safe drinking water for all.

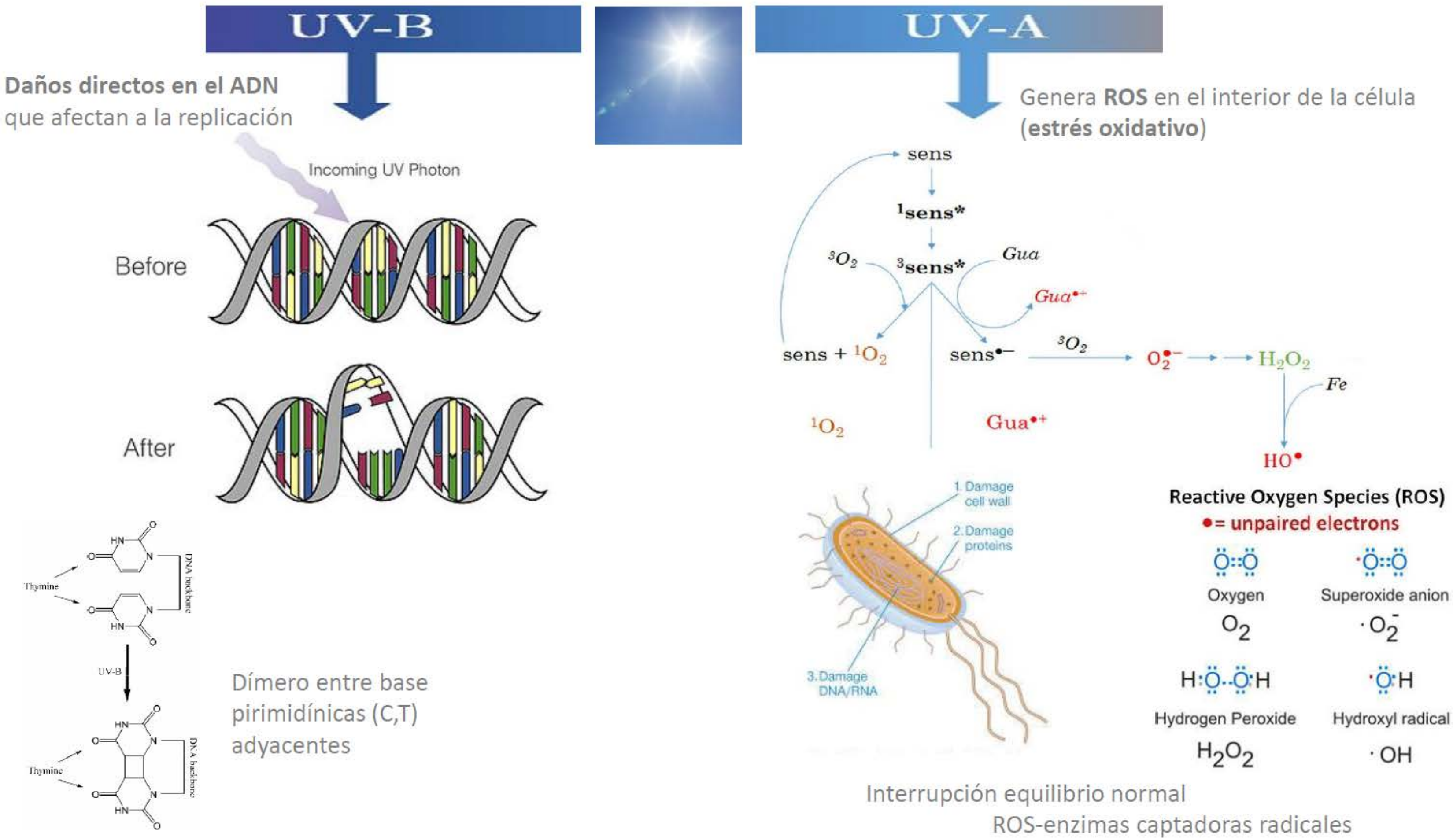
Solar disinfection

Solar light



The germicidal portion of UV radiation – 220-320 nm

Solar disinfection



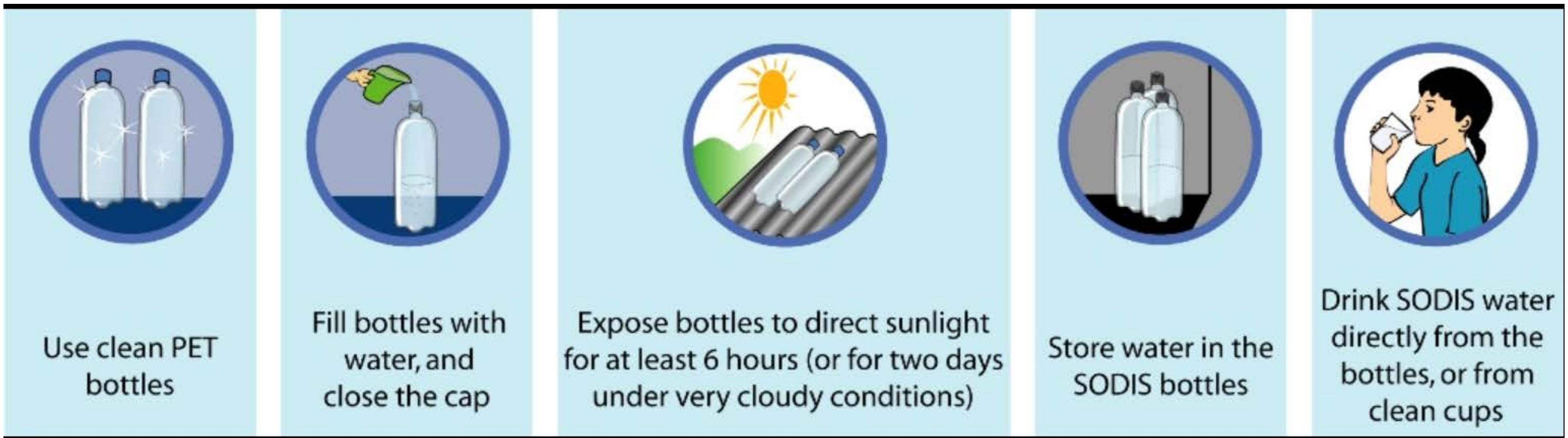
Solar disinfection

Solar disinfection of potable water

Tubular reactors

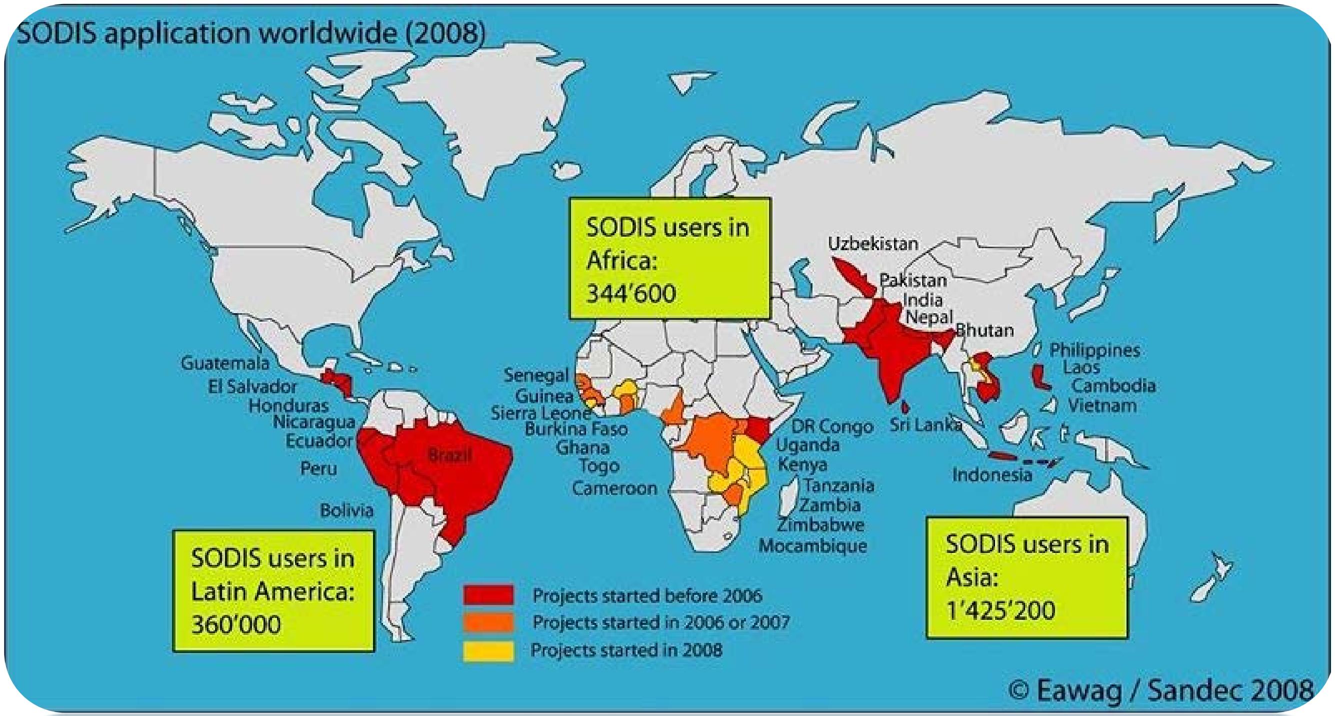
Solar disinfection

Solar disinfection of potable water



Solar disinfection

More than 5 million people use SODIS
Still there is almost **1 billion people without access to safe drinking water**



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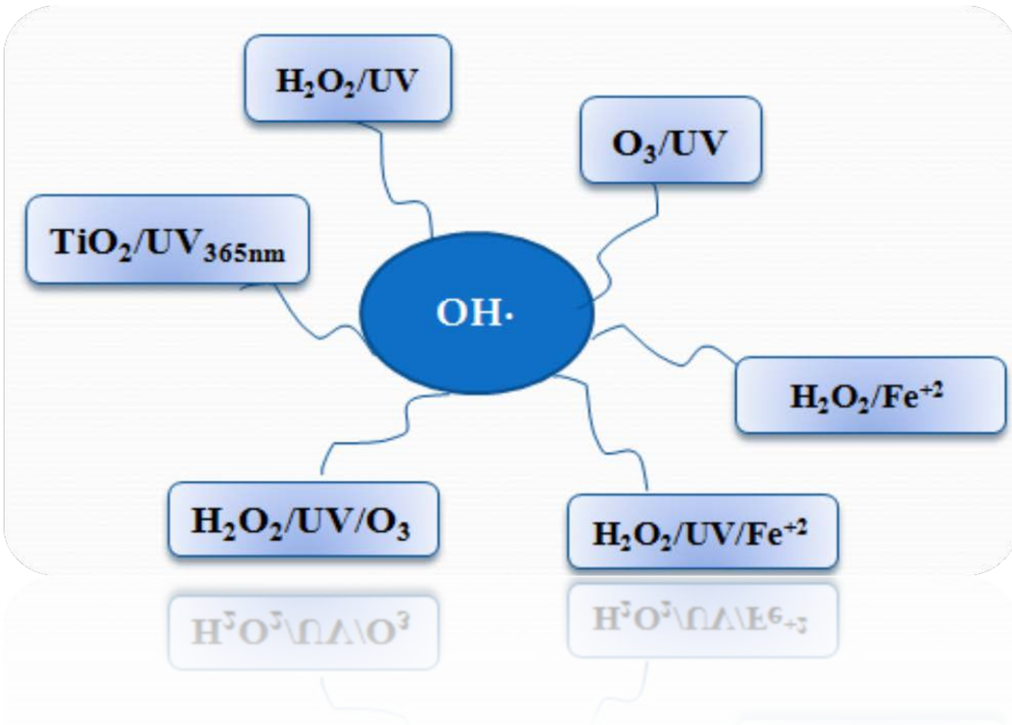
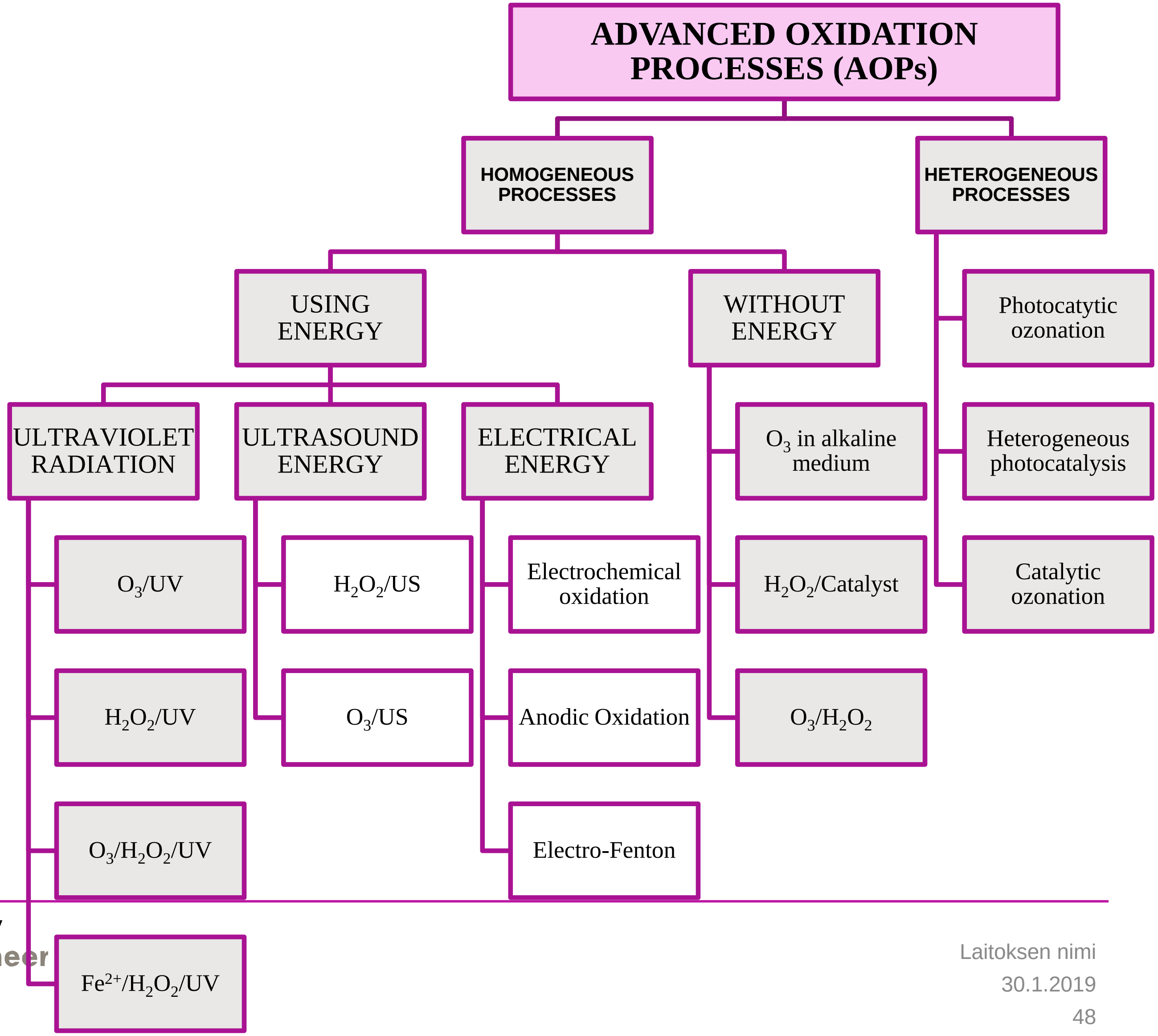
Advanced Oxidation Processes

Advanced Oxidation Processes



Advanced Oxidation Processes



Advanced Oxidation Processes

non-biodegradable industrial wastewater
(source: google maps)

- Textile industry;
- Petrochemical industry;
- Olive oil mill;
- Pharmaceutical wastewater;

→ **AOPs** → Biological treatment →

effluent for discharge or reuse

Possible risks for subsequent biological treatment:

- Excessive use of H_2O_2 and/or catalyst during AOPs can possibly produce toxic effect for microorganisms;
- Possible formation of compounds with lower biodegradability than parental molecules;
- Decomposition of non-biodegradable pollutants can not be guaranteed due to non-selective nature of AOPs, etc.

(source: Oller, I., Malato, S., & Sánchez-Pérez, J. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. *Science of the total environment*, *409*(20), 4141-4166)

urban or industrial wastewater
(source: google maps)

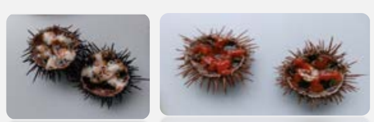
→ Biological treatment → **AOPs** →

Possible presence of by-products

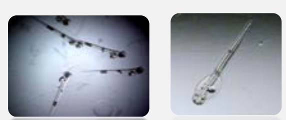
Possible presence of residual H_2O_2

effluent for discharge or reuse

Possible risk of toxicity for aquatic organisms



Sea urchin



Sparus aurata larvae

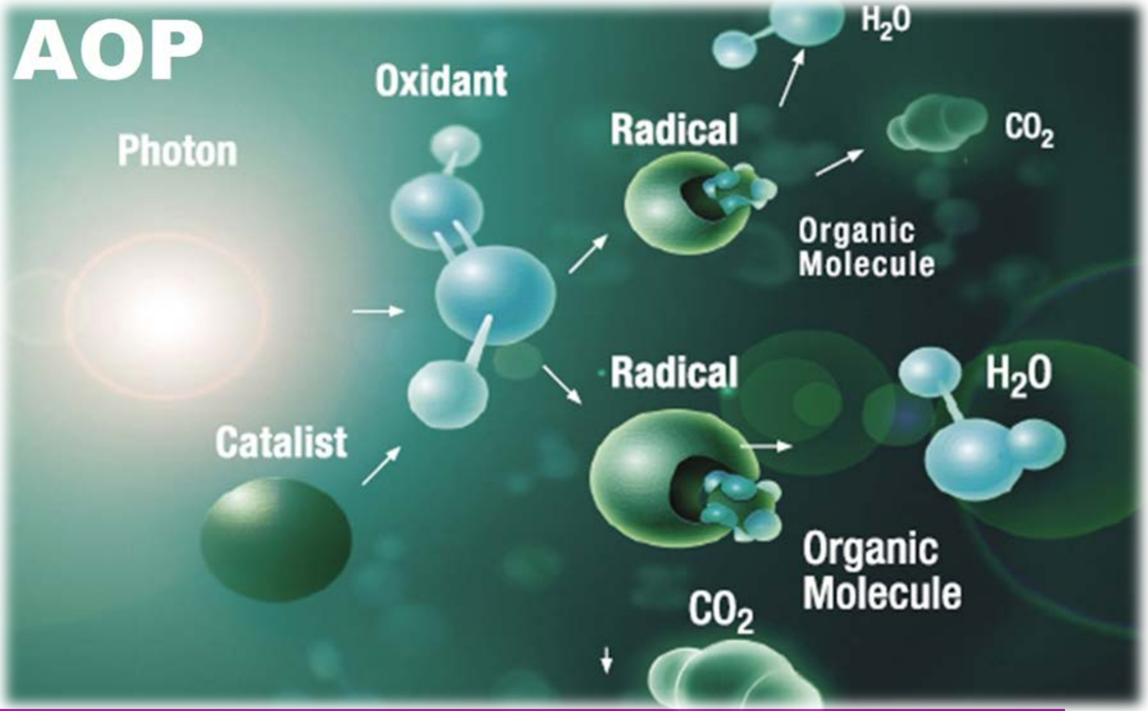
Advanced Oxidation Processes

Oxidizing species	Relative oxidation power
Chlorine	1.00
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	**2.05**

Advanced Oxidation Processes

Main advantages of AOPs

- non-selectivity
- complete mineralization of organic pollutants
- lack of solid wastes
- Fast disinfection



Advanced Oxidation Processes

Wastewater effluents

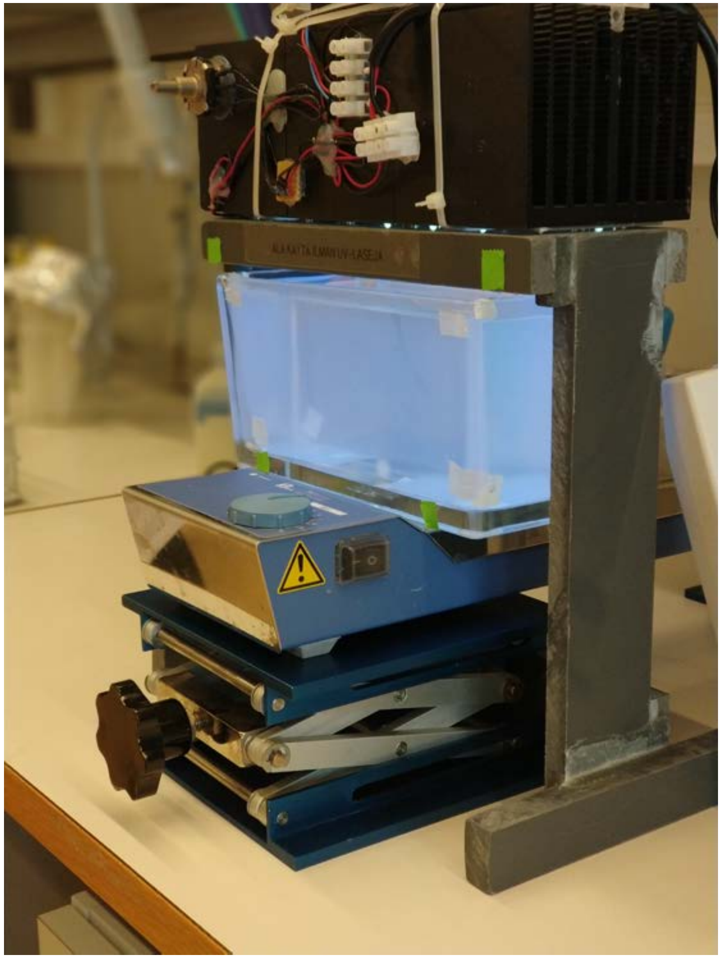
Potable water

Advanced Oxidation Processes

the gold standard for advanced recycled water

https://www.youtube.com/watch?v=192HM0pzJWU

Research in our lab



- **Drinking water disinfection;**
- **Urban wastewater disinfection;**
- **Aquaculture effluents (marine water).**