Advanced Treatment by Oxidation/Disinfection

A part of NTNU/XUAT postgraduate course

Wastewater as a resource

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Presented at Xi'an University of Architecture and Technology

Main topics

- Waterborne diseases and organic pollutants
- Water quality requirement
- Oxidation and disinfection technologies
- Chlorination
- Ozonation
- Ultraviolet irradiation
- Membrane filtration (disinfection)
- Advanced oxidation processes
- Conclusions

Waterborne diseases and related microorganisms

- Waterborne diseases are the most important concern about the quality of water.
- Waterborne diseases are typically caused by enteric pathogens belonging to the group of organisms transmitted by faecal-oral route.
- Important waterborne pathogens transmitted by the faecal-oral route are normally classified into Bacteria, Viruses and Protozoa.
- Other microorganisms repsonsible for diseases include Helminths (parasites), Opportunistic pathogens (skin and mucous membranes of eyes, ears, noses, and throat), Toxin from cyanobacteria (blue-green algae), and Nuisance orgainsms.
- Water quality monitoring is carried out by regulating indicator microorgainsms (E. Coli, total coliforms, fecal coliform, total microbial count, enterococci, etc) instead of pathogens for many reasons.

Indicator microbials in drinking water
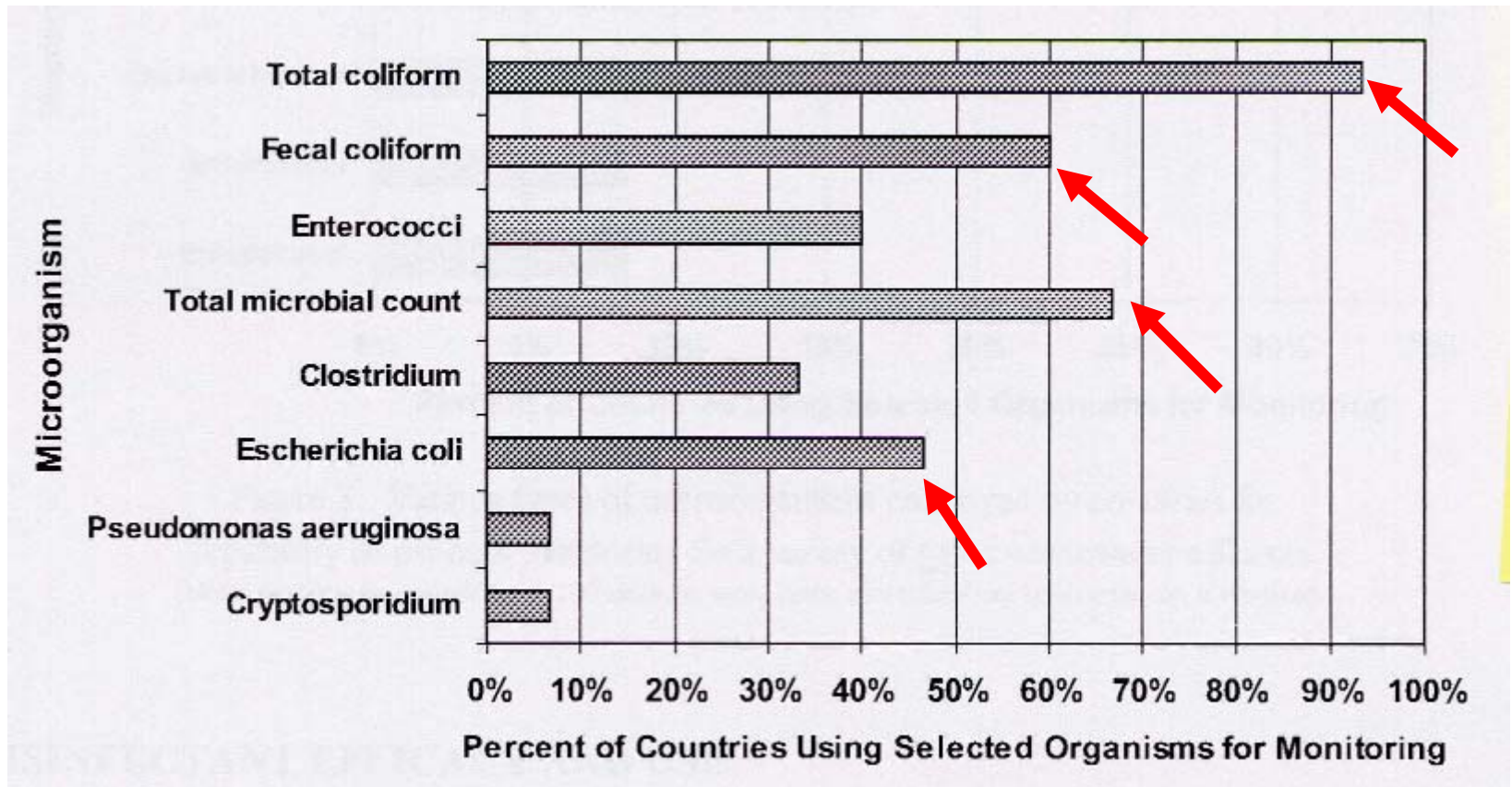
Indicator microbials in wastewater
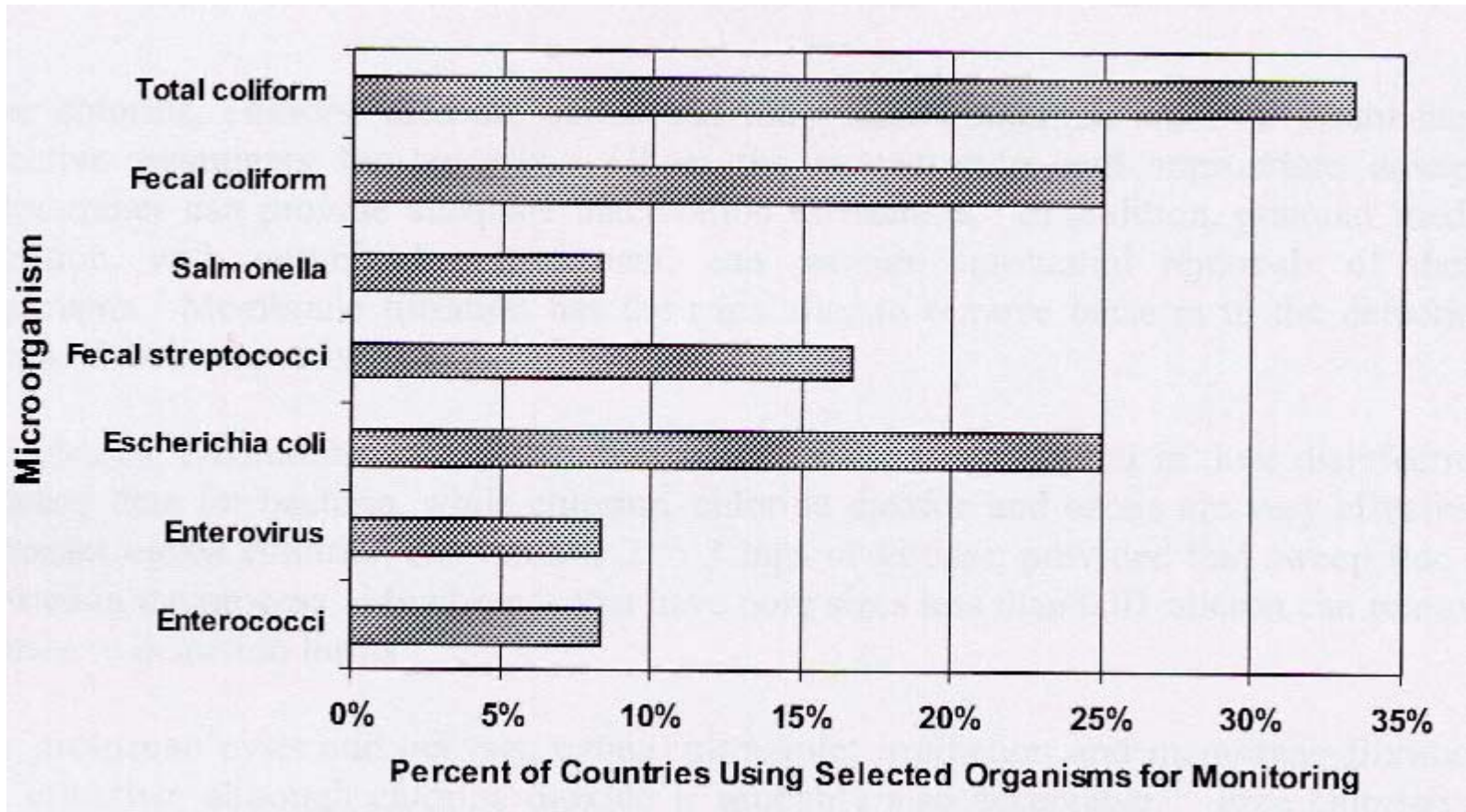
Microbial quality of drinking water

- WHO Guideline (2001): All water intended for drinking—E. Coli or thermotolerant coliform non detectable in 100 ml sample, treated water entering distribution system—E. Coli, termotolerant coliform, and total coliform non detectable in 100 ml sample, Treated water in distribution system—E.coli and termotolerant coliform non detectable in 100 ml sample and total coliform non detectable in 100 ml sample or not presenting in 95% samples through 12-month period.

- USEPA(National Primary Drinking Water Regulations) (as of 01.01.2002): *Cryptosporidium, Giardia lamblia (Legionella), Viruses (enteric)*—99% removal/inactivation, Heterotrophic plate count—500 /100 ml, totoal coliform (incl. Faecal coliform) 5% occurrence, turbidity—never over 1 NTU and 95% less than 0.3 NTU.

Water purification and disinfection on public health—Typhoid fever in Philadephia
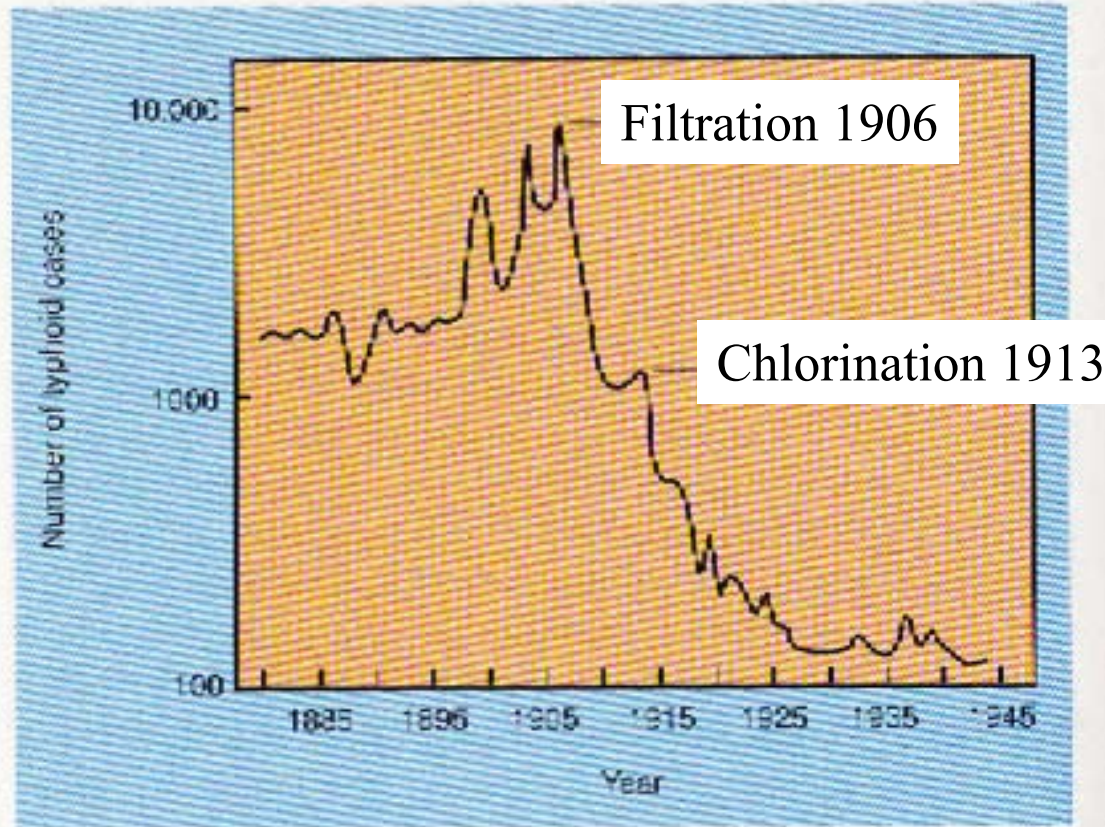

Filtration 1906

Chlorination 1913

Figure 23.55 The dramatic effect of water purification on the incidence of waterborne disease. The graph shows the incidence of typhoid fever in Philadelphia during the early part of the twentieth century. Note the marked reduction in incidence of the disease after the introduction of filtration and chlorination.

Microbial quality of wastewater reuse

(US EPA suggested Guidelines)

Reuse	NTU/SS	Fecal coli/100ml	Cl2 residual	Treatment
Urban	*2NTU	N. D.	/1 mg/l	S+F+D
Irrigation	*30 mg/l SS	*200	*1 mg/l	S+D
Agr. Foodcrop not processed	*2NTU	N.D.	/1 mg/l	S+F+D
Agr. Foodcrop processed	*30 mg/l SS	*200	/1 mg/l	S+D
Agr. nonfood	*30 mg/l SS	*200	/1 mg/l	S+D
Recreational	*2NTU	N.D.	/1 mg/l	S+F+D
Landscape	*30 mg/l SS	*200	/1 mg/l	S+D
Construction	*30 mg/l SS	*200	/1 mg/l	S+D
Industrial (once-trough cooling)	*30 mg/l SS	*200	/1 mg/l	S+D
Environmental	*30 mg/l	*200		S+D
Groundwater recharge	Site specific	Site specific	Site specific	Site specific
Indirect potable (drinking water)	*2NTU	N.D.	/1 mg/l	S+F+A
S: secondary treatment, F: filtration, D: disinfection, A: advanced treatment, N.D.: non detectable				

Organic pollutants related to water quality

- Halogenated aliphatic (chain) hydrocarbons: Trihalomethanes (THMs) may be formed during disinfection of drinking-water; other compounds used as solvents for decaffeinating coffee, general solvents and in products such as propellant, degreasers, spot removers and dyes

- Aromatic (ring) hydrocarbons: Many products derived from fossil fuels, also as additives in petrol, moth balls, adhesives and cigarette smoke

- Chloro- and nitro-aromatic hydrocarbons: Fungicides and explosives

- Phthalates: Phthalates are added to plastic to make them flexible; found in rain wear, footwear, shower curtains, childrens toys

- Halogenated ethers: Halogenated ethers are used in production of plastics and resins and in research laboratories

- Phenols: Fungicide; wood preservative; Chloro-dichloro-, trichloro-phenols are by-products in the production of pentachlorophenol

- Organochlorines: DDT, lindane, aldrin and chlorodane are examples of the extremely persistent organochlorine pesticides widely used in the 1950s and 1960s.

- A total of 30 organic substances reviewed in WHO Guidelines, including: Chlorinated alkanes (5 substances), Chlorinated ethenes (5 substances), Aromatic hydrocarbons (6 substances), Chlorinated benzenes (5 substances), Miscellaneous organic constituents (9 substances). A total of 54 organic subatances are regulated in US EPA National Standard.

Disinfection, general concepts

- Disinfection—the destruction of pathogenic microorganisms in water and wastwater.
- The characteristics of a good disinfectants: effective kill of pathogenic microorganisms, nontoxic to humans and domestic animals, nontoxic to fish and other aquatic species, easy and safe to store transport and dispense, low cost, easy and reliable analysis in water, provides residual protection in drinking water.
- Disinfection approaches: Chemical oxidation (by strong oxidants e.g. Halogens, Ozone, OH• radical systems), irridation (UV, γ, laser, electron beam), thermal treatment (heating/boiling, freezing), electrochemical treatment, and (membrane) filtration (deep bed filters, MF, UF, and NF).
- Commonly used disinfectants: Chlorine series, ozone, UV, (+filtration)

Oxidation, general concepts

- Oxidation—A process in which an oxidant receives electrons to cause the reductant to donor electrons. The oxidant causes the oxidation to occur while being reduced itself. The oxidant lowers its oxidation number by accepting electrons while the reductant increases its oxidation number by donoring electrons.
- Oxidants used in water and wastewater treatment—Chlorine, ozone, OH• radicals (induced from H_2O_2 hydrogen peroxide), and the combinations (e.g. Fenton reagent, UV/ H_2O_2, H_2O_2 /O_3, UV/ O_3 , UV/ H_2O_2 /O_3, and modifications)

$$\text{Oxidants}(Cl_2, O_3, OH\bullet) + \text{Reductants(e.g. C in organics or microorganisms)}$$

$$\xrightarrow[\text{Inactivation}]{\text{Removal}} \text{Redox products}$$

Disinfection, kinetics

- Chick-Watson model—based on Chick's first-order law of dieoff (1908) and Watson's relationship of disinfectant concentration.
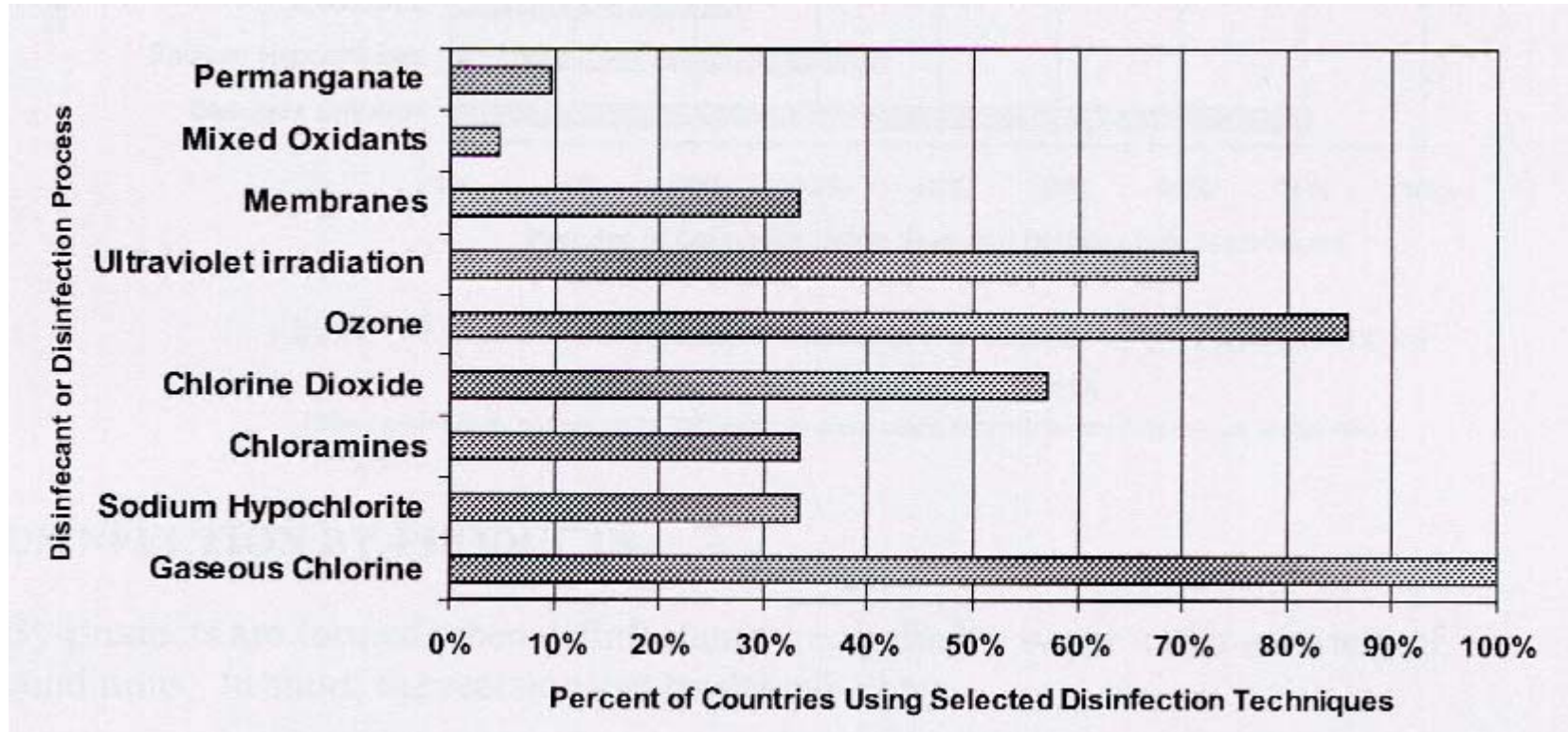
$$\ln(\frac{N}{N_0}) = -\alpha C^n t$$

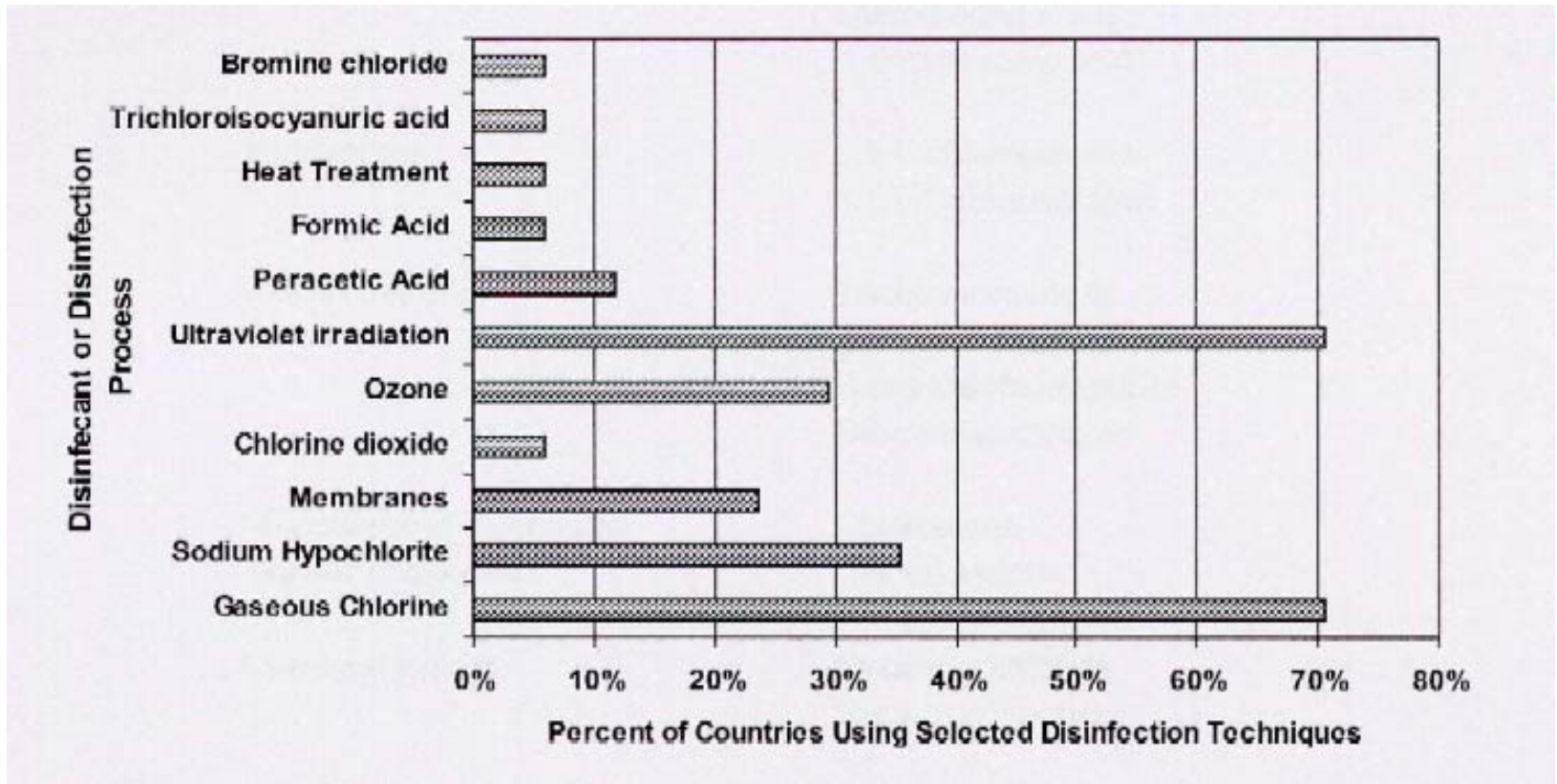N and N_0: number at contact time t and initial number of microorganism

C and t : concentration of disinfectant and contact time

Increasing resistence to disinfection for Various microorganisms

Decreasing disinfection by various disinfectants
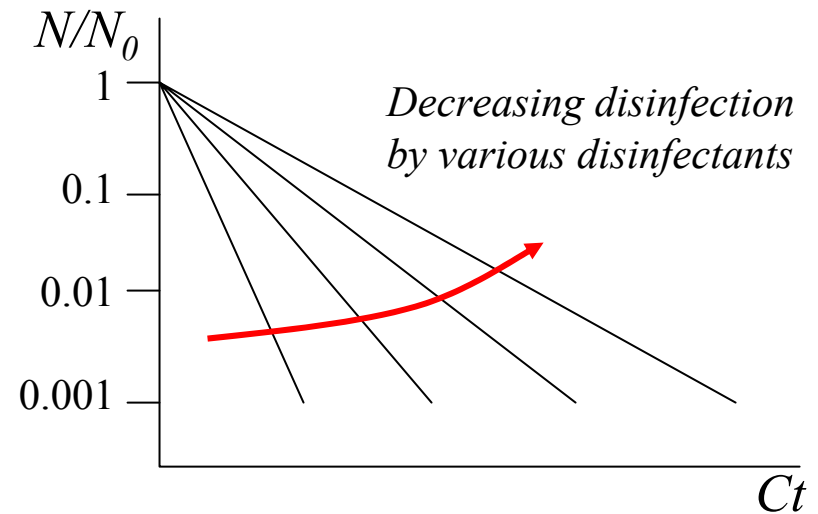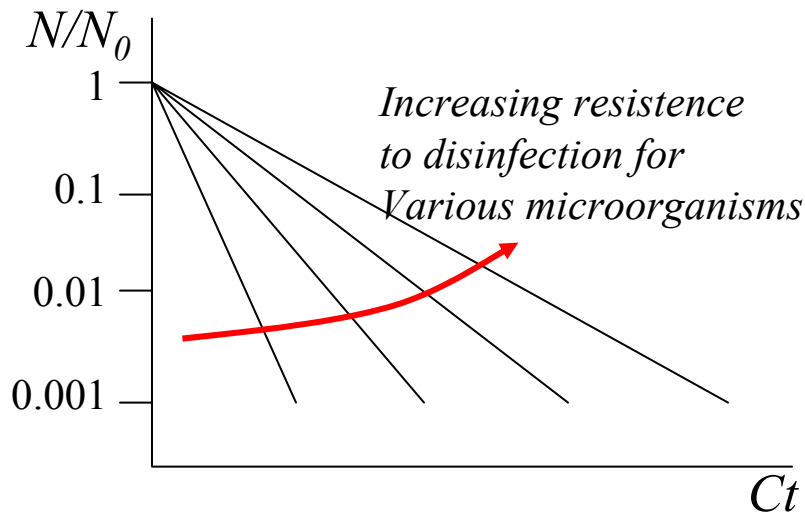
Disinfection technologies in drinking water

Disinfection technologies in wastewater

Comparison of disinfection effect of several disinfectants

Summary of C.t values (mg/L.min) for 99% inactivation at 5 degree
(Clark et al, 1993)

| Organisms	Disinfectants			
	Free chlorine pH 6-7	Pre-formed chloramine pH 8-9	Chlorine dioxide pH 6-7	Ozone pH 6-7
E. coli	0,034-0,05	95-180	0,4-0,75	0,02
Polio virus 1	1,1-2,5	768-3740	0,2-6,7	0,1-0,2
Rotavirus	0,01-0,05	3806-6476	0,2-2,1	0,006-0,06
Bacteriophages f2	0,08-0,18	-	-	-
G. lamblia cysts	47-150	-	-	0,5-0,6
G. muris cysts	30-630	-	7,2-18,5	1,8-2,0a
C. Parvum	7200b	7200c	78b	5-10c
(a—99.9% at pH6-9; b—99% pH7 and 25 degree; c—90% pH7 and 25 degree				

Chlorination—chemistry

- Chlorine: a gas, easily dissolved in water and hydrolyzed as hypochlorous acid HOCl.

$$HOCl \leftrightarrow H^+ + OCl^-$$

- Free available chlorine is in the forms of Cl_2, HOCl, and OCl^-

- Dissociation of HOCl is pH and temperature dependent.

  At pH 5 and lower, HOCl; at pH10 and higher, OCl^-

- HOCl is a very strong disinfectnat, 200-800 times as strong as OCl^-
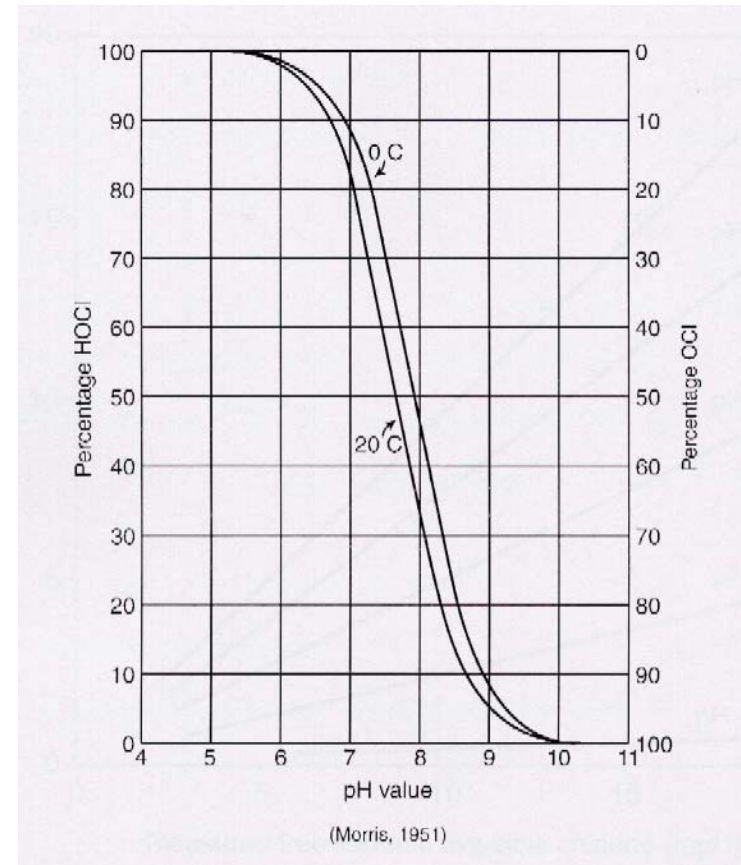
Chlorination--mechanisms

- HOCl reacts with the enzymes essential to the metabolic processes of living cells.
- Chlorine reacts with reducing agents such as S^{2-}, Fe^{2+}, Mn^{2+}, and NO_2^-
- Chlorine reacts with functional groups and other reactionsites on orgainc molecules.
- HOCl reacts with ammonia to produce (mono-, di- and tri-) chloramines (breakpoint chlorination increases chlorine demand)

Figure 16.2 Chlorine demand curve.
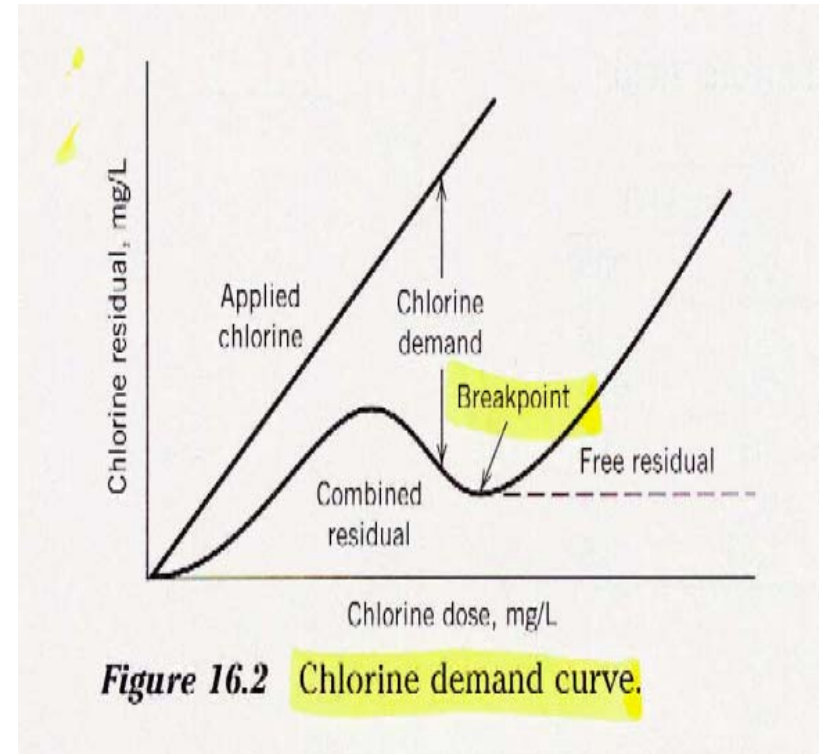
Chlorination—water treatment

- Effective chlorination is based on Ct concept. Ct value for e.g. 99.9% reduction of *Giardia lamblia* is pH and temperature dependent together with concentration of free chlorine.

- At 2mg/l free chlorine and 99.9% reduction, the Ct(mg/l.min) values in table.

pH	Temperature, ^{o}C			
	1	5	15	25
6	165	116	58	29
7	236	165	83	41
8	346	243	122	61
9	500	353	177	88

- Total chlorine dosages vary from 0.2 to 40 mg/l (rarely exceeding 15 mg/l) depending on water quality (especially ammonia) (White 1992)

- Free chlorine residual of around 1 mg/l retards the growth and regrowth of heterotrophic bacteria in distribution system.

- Concern over disinfection byproducts manily THMs requires dosages as low as possible.

- Potential of THM formation increases with chlorine dose and organic matters in water.

- Measurements to decrease THMs include other disinfectant-oxidants, using chloramines, using activated carbon, etc.

Chlorination—wastewater treatment

- Wastewater effluent needs to be disinfected before dischage or reuse to meet microbial standard.

- Chlorination of raw sewage: odour and slime and corrosion control.

- Chlorination in biological processes: curative measure for poor settling, foaming, and nuisance larve. Amonia removal and grease removal.

- Much higher concentrations and variations of organic matters in wastewater increase the chlorine demands and the complexity.

- Potential of formation of THMs and other byprodcuts is much higher.

- Dosages:

  Prechlorination—10-12 mg/l in fresh domestic sewage, 30-40 mg/l in septic sewage.

  Secondary effluent—10 mg/l

  Control of activated sludge bulking—5 mg/l
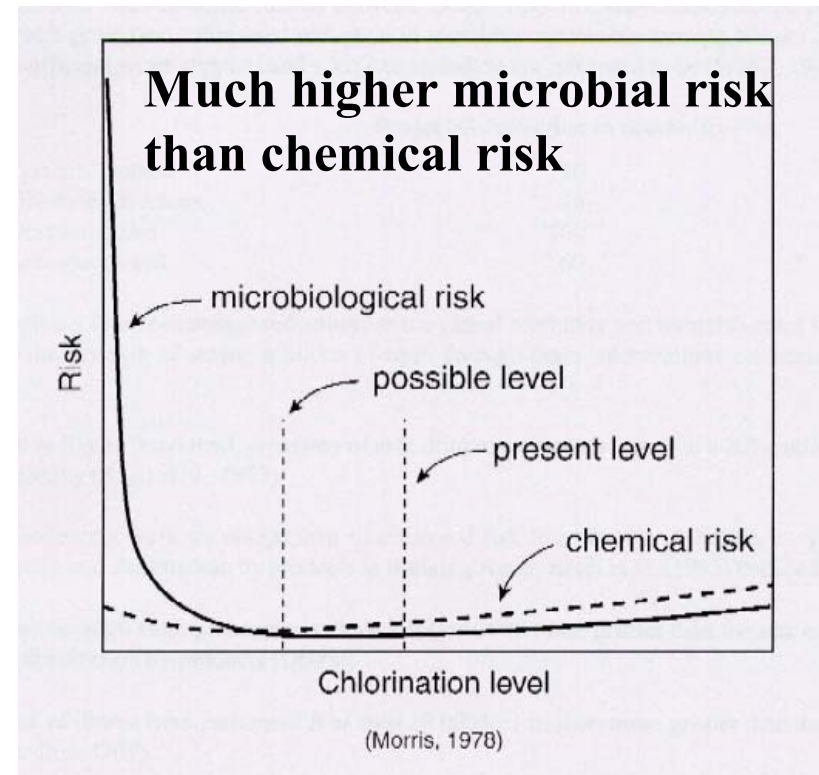
  Sludge thickener—50 mg/l.

Chlorination—chlorine dioxide, an alternative to chlorine

- ClO_2—unstable gas, explosive, site generation.
- Strong oxidant: 2.5 times as strong as chlorine, E_0 1.15 V as gas (25 °C), 0.95 V as aqueous solution, decreases linearly by –0.062 V with increase in pH, dependent on temperature.
- Bactericidal and virucidal action of chlorine dioxide is **not lowered** by increasing pH from 4-8.
- Mode of action with microbials: Chlorine dioxide free-radical gas easily access to vital molecules (amino acids) in cells especially in an alkaline medium.

- Reaction with organic compounds:

  Practically **no THMs** are formed.

  Phenolic compunds undergo ring-opening reactions.

  Humic acids are decomposed as carboxylic acids, aldehydes, and glyoxal.

  Aliphatic hydrocarbons do not react significantly with ClO2.

  Aromatic hydrocarbons react fast with ClO2.

- Inorganic reaction prodcuts:

  Chlorite ClO_2^- is the principal product. Others are chlorate and chloride.

  Removal of iron and manganese.

Chlorination—balancing chemical and microbial risks

- DBPs:

  Chlorine—free chlorine, THMs, Chlorinated acetic acids, Halogenated acetonitriles, Trichloroacetaldehyde, Chlorophenols, MX.

  Chlorine dioxide—do not form significant THMs with humics, main byproducts are chlorite, chlorate and chloride.
- Chlorine is more effective on E.coli and rotaviruses while chlorine dioxide is more effective on Giardia cysts.


Much higher microbial risk than chemical risk

microbiological risk

possible level

present level

chemical risk

Risk

Chlorination level

(Morris, 1978)

Ozonation—general aspects

- Ozone—O_3, very unstable gas, a very strong oxidant (**E° = 2,07 V**), produced by lightning or circulating dried air or oxygen on dielectric elements applied to a high-voltage (5-20 KV) althernating current (mostly low 50-60 Hz, or medium 600-1000Hz) called corona discharge. *(''Whatever new problems have arisen, ozone has always been part of the solution'')*

- Ozonation—a process using ozone to treat water and wastewater, used for—*Disinfection; oxidation of organic substances (taste and odour, toxic subtances, pesticides and herbicides, etc); oxidation of inorganic substances (e.g. Fe^{2+} and Mn^{2+}); colour (humus) removal; THM control; turbidity removal and microflocculation; promotion of biodegradability.*

Ozonation— mechanism for disinfection

- Mechanism—
  -Direct attacking
  pollutants (right)
  -Indirect attacking
  by OH• radical formed to oxidate microorganisms.

OXYGEN (O₂) ▶ HIGH VOLTAGE ▶ O₃ ▶ ATTACKING POLLUTANTS ▶ OXYGEN, H & CO₂
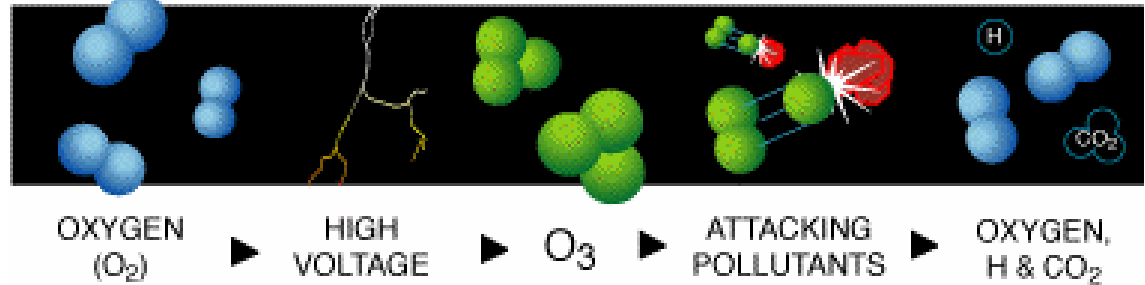
- Effective disinfectant—most effective disinfectant for all mcrobials.

  -for inactivation of *E. Coli*, enterococci, fecal streptococci, 0.05 mg O3/l contact time 10 min (compare 0.05 mg Cl2/l 30 min);

  -for inactivation of *Giardia lamblia* cyst, Ct of 0.48 (mg/L.min) at 90%, 0.95 at 99% and 1.43 at 99.9% (compare to chlorine dioxide at Ct of 7.7, 15, and 23 for 90%, 99%, and 99.9%);

  -for inactivation of viruses, Ct of 0.5, 0.8, and 1.0 for 99%, 99.9% and 99.99% removal (compare chlorine 3, 4, 6 for same inactivation)
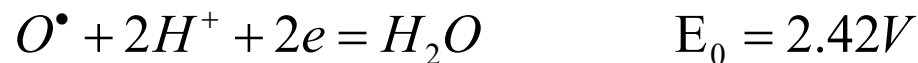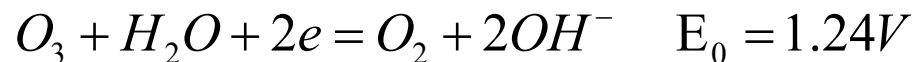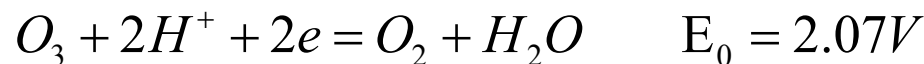
Ozonation—oxidation of inorganic substances

- Iron : $\qquad Fe^{2+} + O_3 + H_2O = Fe^{3+} + O_2 + 2OH^-$

$\qquad\qquad Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$

- Manganese: $\qquad Mn^{2+} + O_3 + H_2O = Mn^{4+} + O_2 + 2OH^-$

$\qquad\qquad Mn^{4+} + 4OH^- = MnO_2 + 2\,H_2O$

- Ammonium: $\qquad 4\,O_3 + NH_3 = NO_3^- + 4\,O_2 + H^+ + H_2O$

- Nitrite: $\qquad NO_2^- + 3\,O_3 = NO_3^- + O_2$

- Chlorite: $\qquad ClO_2^- + O_3 = ClO_3^- + O_2$

The reaction rate is evaluated by kinetic constants.

Ozonation—oxidation of organic substances

- Electronic structure of ozone is dipolar with both a positive and a negative center.
- Ozone can be both an electrophilic and nucleophilic reagent.
- The electrophilic reaction predominates in direct ozone reaction.
- The decomposition of ozone into OH• radicals determines the indirect reaction with organic matters.
- Standard oxidation reduction potentials are:

$$O_3 + 2H^+ + 2e = O_2 + H_2O \qquad E_0 = 2.07V$$

$$O_3 + H_2O + 2e = O_2 + 2OH^- \qquad E_0 = 1.24V$$

$$O^\bullet + 2H^+ + 2e = H_2O \qquad E_0 = 2.42V$$

$$OH^\bullet + 1e = OH^- \qquad E_0 = 2.80V$$

Ozonation—oxidation of organic matter

- General concepts associated with direct reaction of ozone include:

  -Saturated alkyl groups react very little, most chlorinated hydrocarbons do not react directly with ozone and need indirect oxidation by OH radical, benzene reacts very slowly, polycyclic hydrocarbons react more rapidly.

  -Phenolic compounds react within seconds.

  -Carboxylic acids, keto acids are stable end products.

  -Amines reacts very slowly.

  -Alcohols can react with ozone with intermediate formation of hydroperoxides. Carbonhydrates reacts hardly at all with ozone.

  -Mercaptans are transfered into sulfonic acids, disulfides and sulfones are intermediates, sulfur-containing amino acids react similarly and fast.

  -Amino acids react through the electrophilic mechanisms.

Ozonation—colour removal

Model for colour removal

$$C/C_0 = \frac{1}{1 \ + \ 20 \ D/C_0}$$

C = initial colour
C_0 = final colour
D = dosage in mg O_3/mg Pt

Rules of thumb:
- 0,15 mg O_3/mg Pt
- 1,0-1,5 mg O_3/mg TOC

Ozonation—colour removal: dissolved matters

•The conjuncated double bonds in humus molecules are broken down with colour removal.

• Part of difficultly biodegradable organic matters are decomposed into easily biodegradable ones

• Easily biodegradable matters:
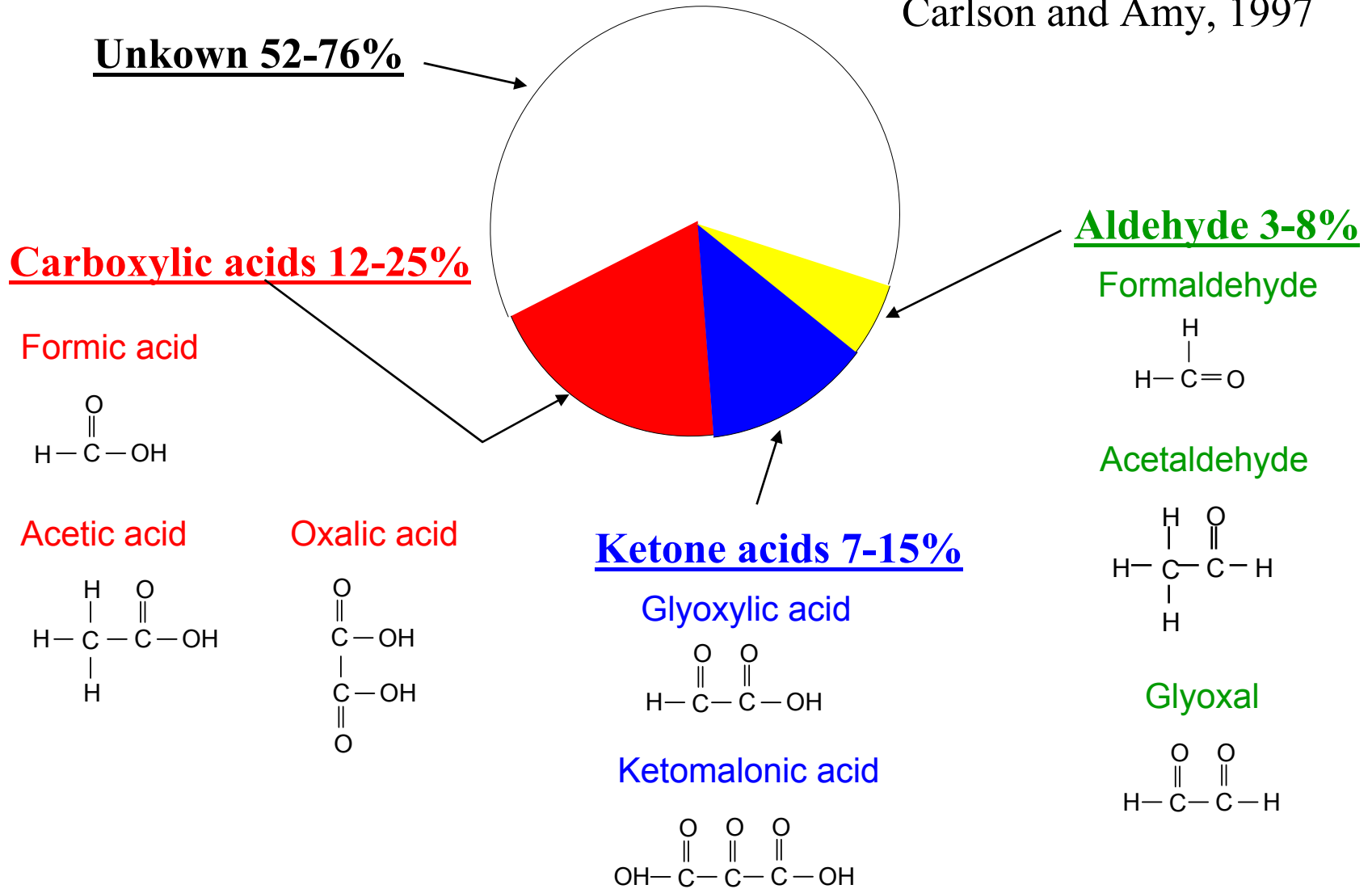 - Carbonxylic acids
  - Ketone acids
  - Aldehyde

Fractionation of dissolved organic matters in ozonated humus water
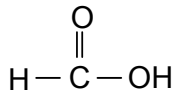
NBDOC

DOC

SBDOC

BDOC

RBDOC

AOC
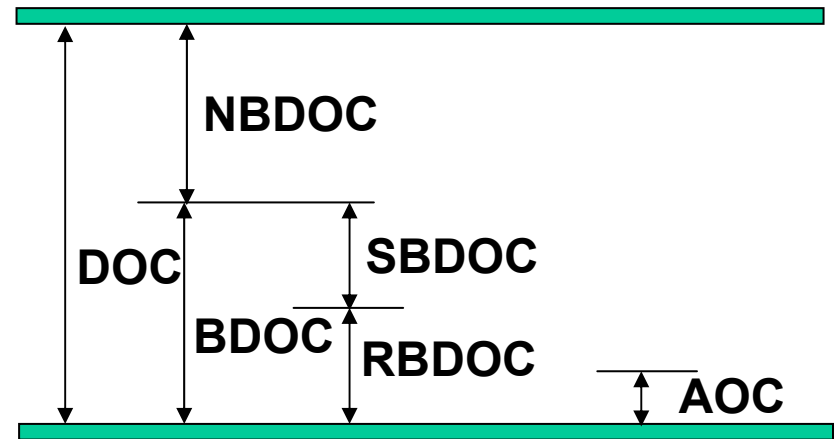
It is difficult to determine contents of BDOC and AOC if the concentration is so low. GC is used to directly measure the residual matters.
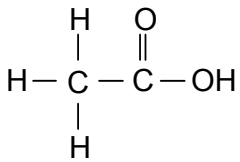
Ozonation—colour removal: BDOC
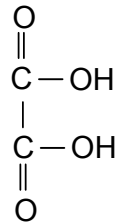
Carlson and Amy, 1997

Unkown 52-76%

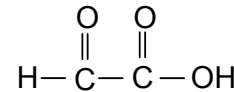**Carboxylic acids 12-25%**

Formic acid

$$H-\underset{\underset{}{}}{\overset{\overset{O}{\|}}{C}}-OH$$

Acetic acid

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$$

Oxalic acid

$$\overset{\overset{O}{\|}}{C}-OH$$
$$\underset{\underset{O}{\|}}{C}-OH$$

Ketone acids 7-15%

Glyoxylic acid

$$H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

Ketomalonic acid

$$OH-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$
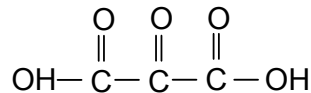
Aldehyde 3-8%

Formaldehyde

$$H-\underset{}{\overset{\overset{H}{|}}{C}}=O$$

Acetaldehyde

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-H$$

Glyoxal

$$H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H$$
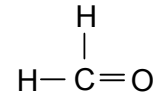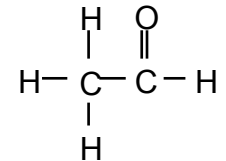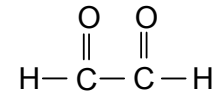
Ultraviolet irradiation—general aspects

- The elctromagnetic spectrum for ultroviolet irradiation is divided into vacuum UV, UV-C, UV-B, and UV-A. The UV part of sunlight reaching the earth is merely high than 290 nm.
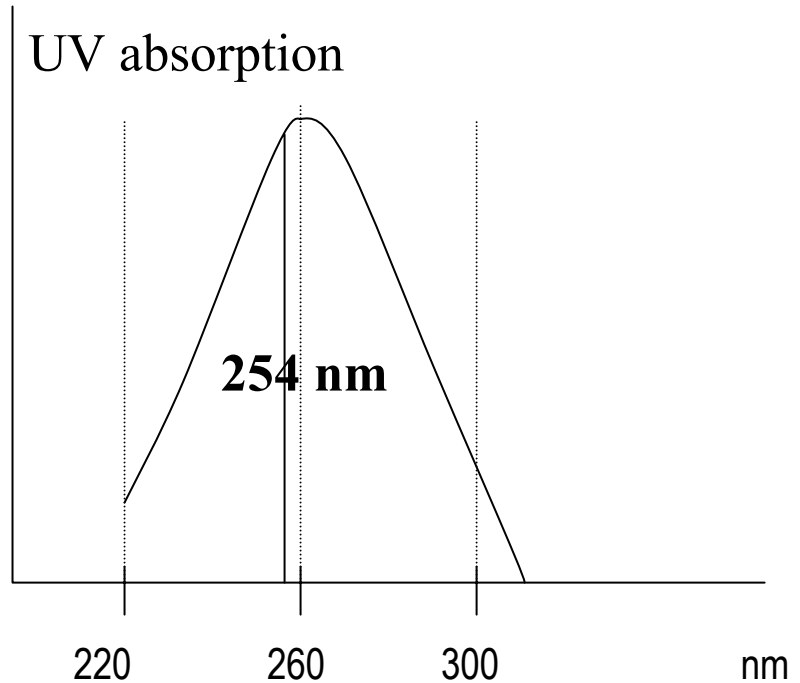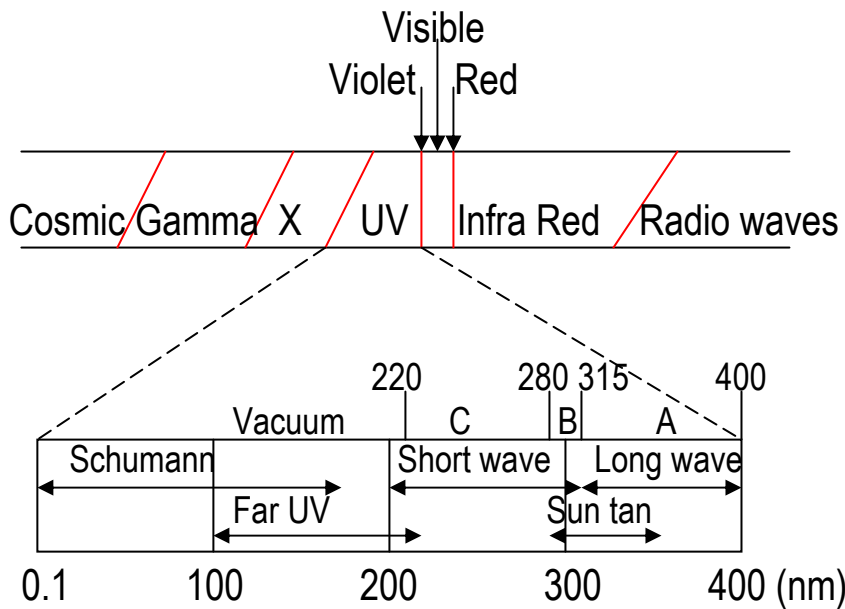
- The UV absorption spectrum of bacteria is reaching a peak at 254 nm-260 nm. The practical UV lamp prduces UV light of wavelength at 254 nm.

Visible

Violet | Red

Cosmic / Gamma / X / UV | Infra Red / Radio waves

| 220 | | 280 | 315 | | 400 |

Vacuum | C | B | A

Schumann

Short wave | Long wave

Far UV

Sun tan

0.1   100   200   300   400 (nm)

UV absorption

254 nm

220   260   300   nm

Ultraviolet irradiation—mechanism of disinfection

- Damage to the cell wall—cell lysis and death.
- Alteration of cell permeability—vital nutrients (N and P) escape.
- Alteration of the colloidal nature of protoplasm—coagulate the cell protein and denature protein with lethal effect.
- Inhibition of enzyme activity—delay formation of cell structure.
- Damage to the DNA and RNA in cell—unable to reproduce

UV   Repair

(photo/enzyme)
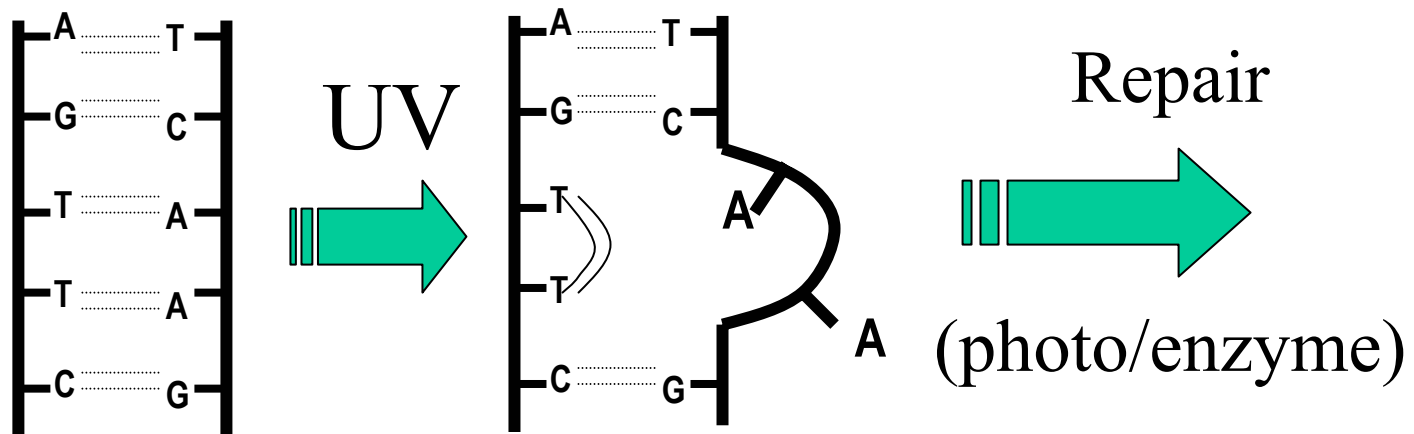
Ultraviolet irradiation—dose (I•t) and effectiveness

- UV is effective for inactivation of bacterial and viral pathogens at 5-25 mW.s/cm² for 2-log removal and 90-140 mW.s/cm² for 4-log removal.

- UV is not effective for inactivation of Cryptosporidium and Giardia (100-8000 mW.s/cm² for 2-log removal).

- Effect of water quality (TSS, humic, hardness, and iron) has adverse impact on UV trnasmittance and inactivation effectiveness.

$Log(N/N_0)$ vs UV dose (mW.s/cm²); features labeled *Shoulder*, *Slope k*, and *Tailing due to shielding by particulates*.
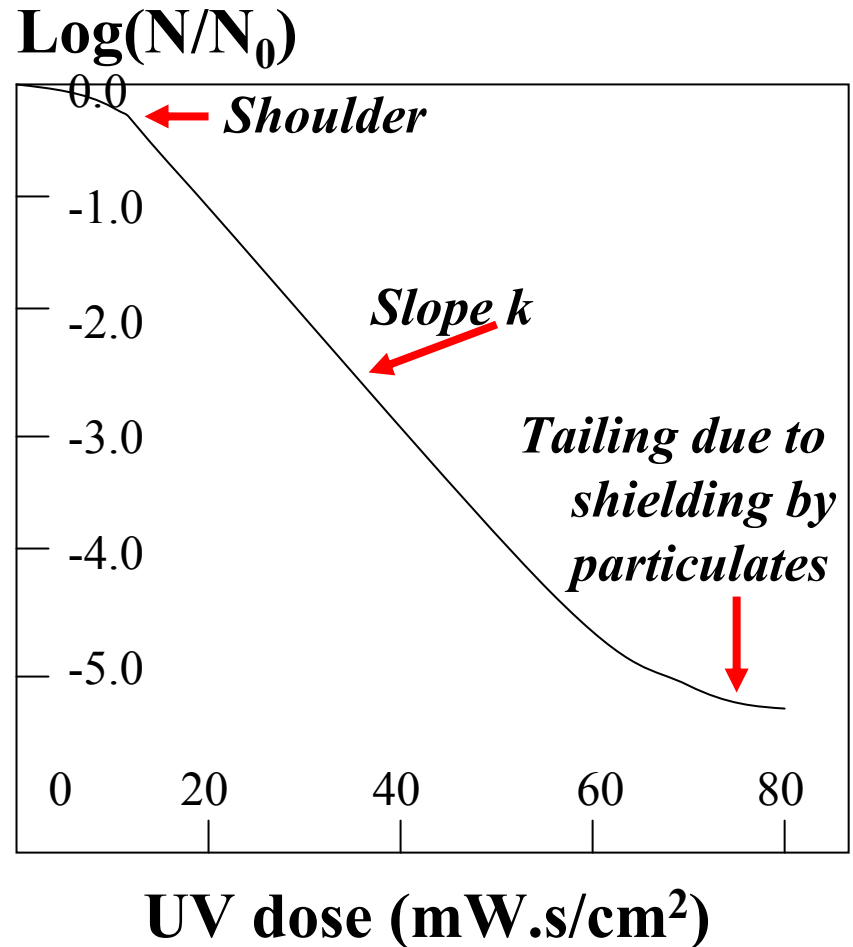
Ultraviolet irradiation—various lamp systems

- Low pressure low intensity UV lamp—slimline design, wall temperature 40 °C, internal fill pressure 7×10^{-3} torr, 88% output at 253.7 nm.

- Low intensity G64T5L lamp parameters—60 years history, length 64 in., arc length 58 in., 65 Watts, input current 0.425 A, UV output at 253.7 nm 26.7 W, lamp life 8760 hrs.

- Medium pressure high intensity UV lamp—wall remperature 600-900 °C, internal fill pressure 10^2-10^4 torr, 27-44% output at 253.7 nm, much higher UV output per lamp.

- Parameters—length 64 in., arc length 58 in., wattage 1000-3000 W, input current 3-11 A, germicidal output per lamp 10-30 W/in., lamp life 3000-5000 hrs.

Higher output is advantageous in poor quality effluent applications (primary secondary or CSOs)

Ultraviolet irradiation—design considerations and operation

- **Design considerations**
1. Selection of an optimal system configuration—after determination of
2. Hydraulic design—including approach channel, headloss along
3. Reliability design—Backup power, Electrical safety design, (seismic
- **Operation**
1. Monitoring and alarming—continuous monitoring of dose, water
2. Cleaning of UV lamps—on-line cleaning integral
3. Lamp aging

Membrane filtration for disinfection

An emerging technology that becomes more and more economically

- Proper selection of membrane depends on the sizes of microbial
- Classification of membrane is based on the nominal pore sizes of
- Low TMP membrane with pore size of 0.01 μm (or 10 nm) is able to
- Virus particles are often associated with other particles through

Comparing selected disinfection

Microbial inactivation or removal efficacy

Approaches	Bacteria	Viruses	Protozoa	Overall
Free chlorine	E	E	F/P	G
Chloramines (in situ)	F	P	P+	P
Chlorine dioxide	G/E	G/E	F	G
Ozone	E	E	G/E	**G/E**
Ultraviolet irradiation	G/E	F	G	G
Granular media filtration (w/coagulation+settling)	G	F	G	G
Low-TMP membrane filtration (0.01 μm nominal pore size)	E	E	E	**E**
E: excellent, F: fair, G: good, P: poor				

Advanced oxidation processes (AOPs)

- Advanced oxidation processes AOPs are based on the strong oxidation capacity of OH• radical (E^0 2.8V) on most of organic substances, a non selective processes with simple end products.

- H_2O_2 (hydrogen peroxide) is a strong oxidant (E^0 1.77V), it is also safe to use and easily available. By using some catalysts (e.g. Fe^{2+}, UV) or other oxidant such O_3, the OH• radical is produced and the oxidation is greatly enhanced.

- Often used AOPs systems inlcude:

    Fenton reagent (Fe^{2+}/H_2O_2)

    UV/ H_2O_2

    UV/ O_3

    H_2O_2 /O_3

    UV/ H_2O_2/ O_3

    Photocatalytical (TiO_2) reactors

AOPs—OH radical reactions

- OH radicals can oxide dissolved inorganic and organic compounds by different reactions.

- In natural water, OH radicals are consumed with rate constant of 10^5 s^{-1}. Or the mean lifetime of 10 microseconds.

- Organic radicals are formed and then add a dissolved oxygen to form peroxyl-type intermediates.

- The peroxyl intermediates further form hydroperoxyl radicals, hydrogen peroxide ans series of different peroxides, aldehydes, acids, ets.

- Final oxidation products depends on many different parameters.
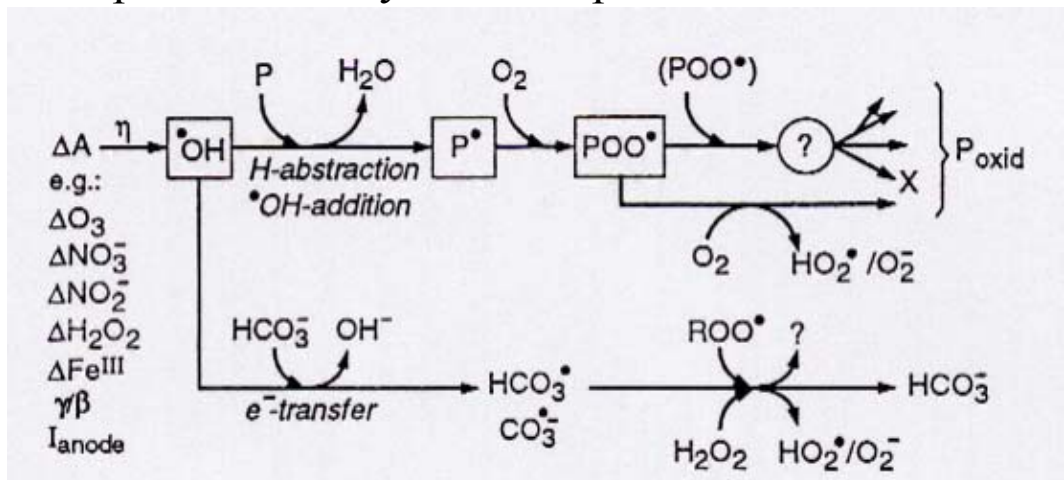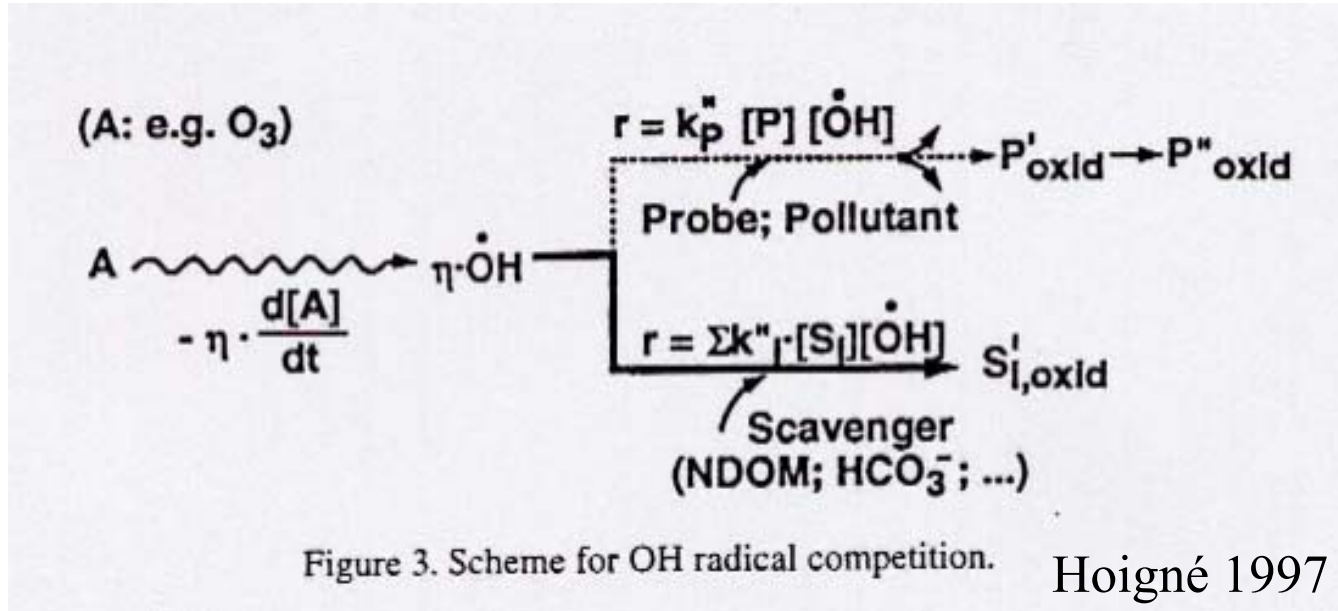
From Hoigné 1997

Figure 2. OH radical initiated chains of reactions.

AOPs—OH radical competition

Figure 3. Scheme for OH radical competition.

Hoigné 1997

$$-\ln([P]_t/[P]_0) = \eta(\Delta A)\,k_{OH,P}\,/\left(\sum(k_{OH,S}[S_i])\right)$$

P: micropollutant

A: precusor to OH radical (e.g. O_3)
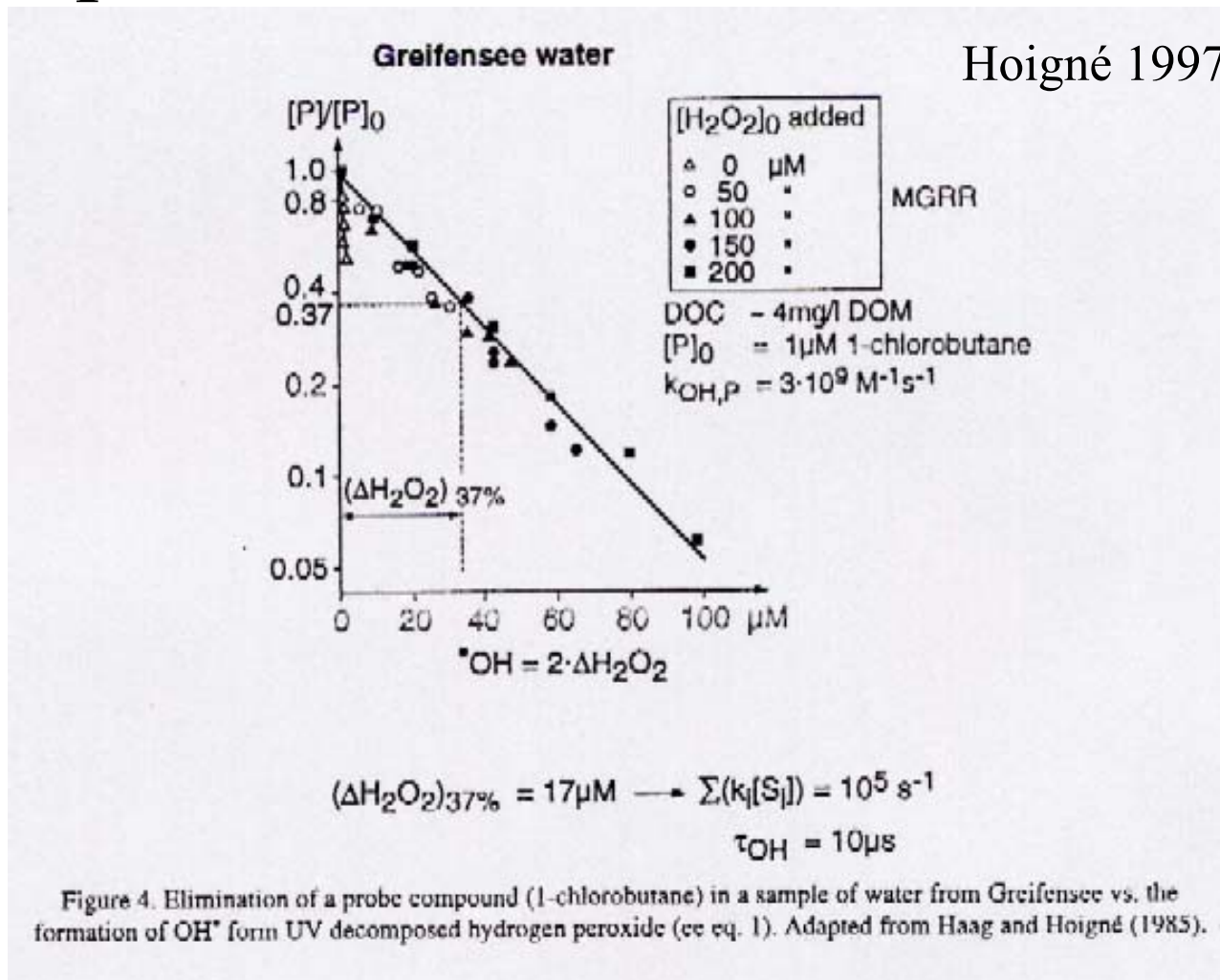
η: yield factor

S: OH scavenger

$k_{OH,P}$: rate constant of reaction (P+OH)

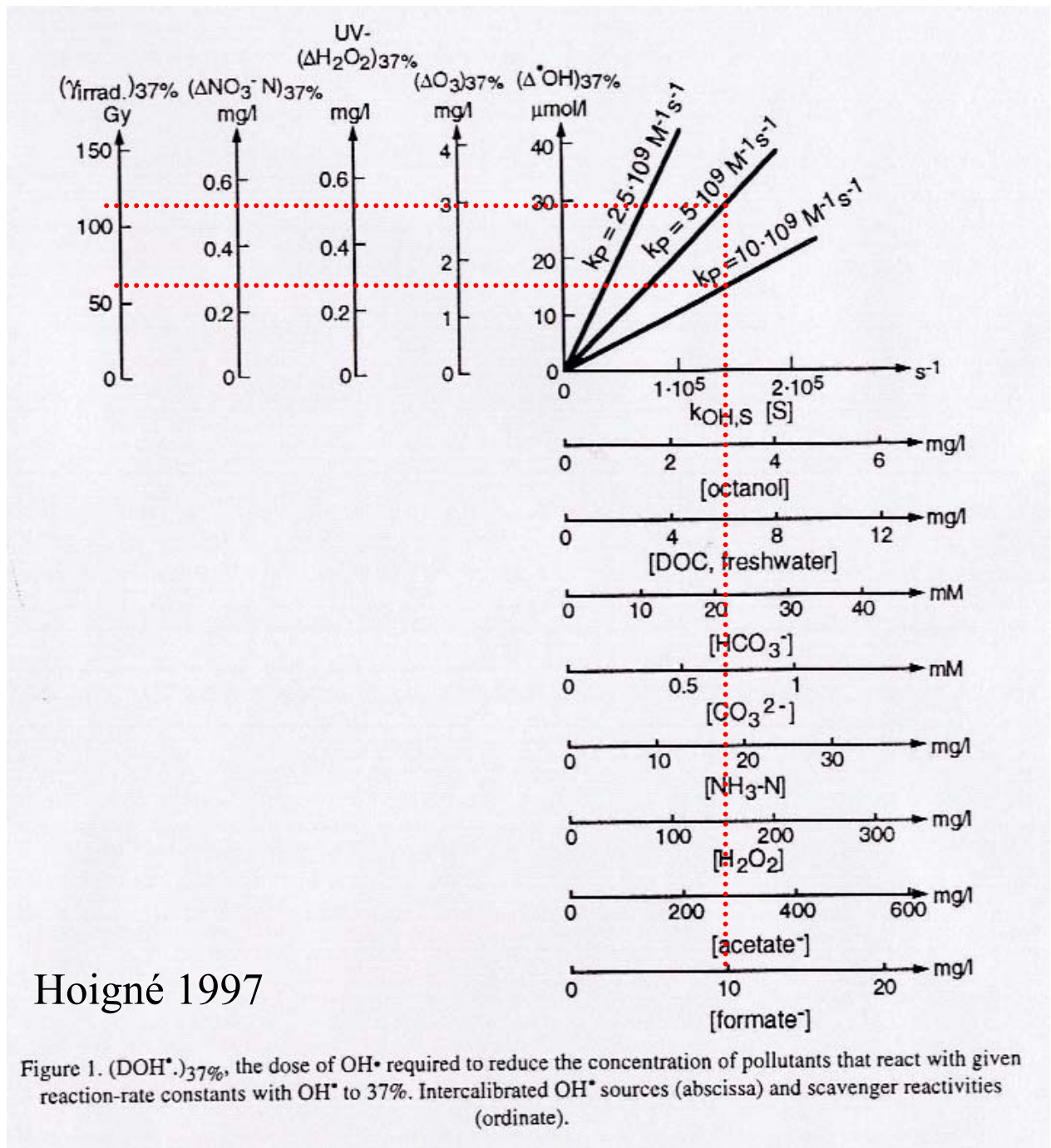$k_{OH,S}$: rate constant of reaction (S+OH)

AOPs—fate of peroxyl radicals in aqueous solution

- OH radicals are first produced.
- OH radicals react with organic matters.
- With oxygen, carbon-centered radicals (with O) produce peroxyl radicals ($O_2\bullet$).
- Formation and decay of peroxyl radicals contribute decisively to the oxidation of DOC.
- It must be ensured that the oxygen is not depleted in the course of reaction.
- In most cases, the formation of peroxyl radicals is irreversible.
- Unimolecular decay and bimolecular decay are followed for different sources of peroxyl radicals.
- When OH radicals are produced by O_3/H_2O_2 or UV/O_3 systems, the $HO_2\bullet/O_2\bullet^-$ generate further OH radicals by rapid reaction of $O_2\bullet^-$ with O_3.

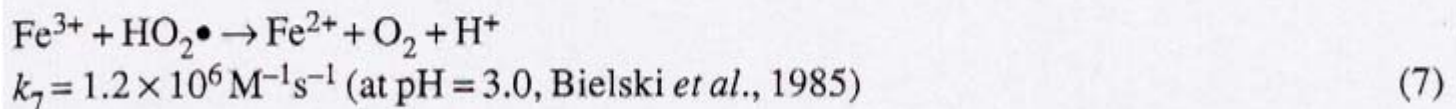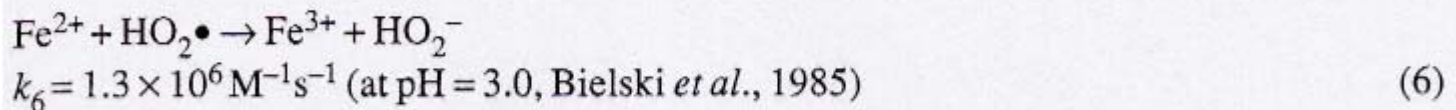# AOPs—Elimination of pollutants, example

Hoigné 1997

Figure 4. Elimination of a probe compound (1-chlorobutane) in a sample of water from Greifensee vs. the formation of OH° form UV decomposed hydrogen peroxide (ce eq. 1). Adapted from Haag and Hoigné (1985).

AOPs— Dose of OH radical for reduction of pollutants at given rate constant

Hoigné 1997

Figure 1. (DOH·)$_{37\%}$, the dose of OH· required to reduce the concentration of pollutants that react with given reaction-rate constants with OH· to 37%. Intercalibrated OH· sources (abscissa) and scavenger reactivities (ordinate).

AOPs—Fenton system reactions

Yoon et al 2001

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$$
$$k_1 \approx 70 \text{ M}^{-1}\text{s}^{-1} \text{ (Rigg } et\ al., 1954)$$
\hfill (1)

$$Fe^{3+} + H_2O_2 \Leftrightarrow [FeOOH^{2+}] + H^+ \rightarrow Fe^{2+} + HO_2\bullet$$
$$k_2 = 0.001\text{–}0.01 \text{ M}^{-1}\text{s}^{-1} \text{ (Walling and Goosen, 1973)}$$
\hfill (2)

$$OH\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^-$$
$$k_3 = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \text{ (Buxton } et\ al., 1988)$$
\hfill (3)

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$$
$$k_4 = 3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \text{ (Buxton } et\ al., 1988)$$
\hfill (4)

$$OH\bullet + (CH_3)_3COH \rightarrow \bullet CH_2(CH_3)_2COH\ (R_{tB}\bullet) + H_2O$$
$$k_5 = 5.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \text{ (von Piechowski } et\ al., 1992)$$
\hfill (5)

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^-$$
$$k_6 = 1.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \text{ (at pH} = 3.0, \text{Bielski } et\ al., 1985)$$
\hfill (6)

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+$$
$$k_7 = 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \text{ (at pH} = 3.0, \text{Bielski } et\ al., 1985)$$
\hfill (7)

$$OH\bullet + CH_3OH \rightarrow \bullet CH_2OH + H_2O$$
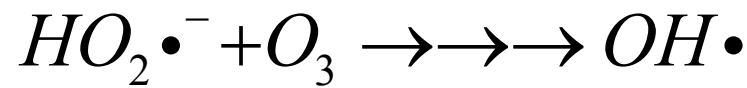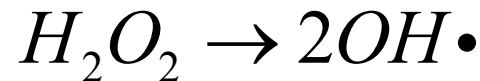$$k_8 \approx 10^8 \text{ (Walling } et\ al., 1974)$$
\hfill (8)

AOPs—Fenton system conditions

- High $[Fe^{2+}]_0$: produce sufficient OH radicals in very short time.

  Scavenging of OH radical by ferrous ion Fe^{2+} becomes important at high $[Fe^{2+}]_0/[H_2O_2]_0$.

  Coagulation effect of ferric ion and disposal of ferric sludge must be considered.

  Large production of OH radicals consumes dissolved oxygen instantaneously. Oxygen deficient state has a great impact on the process of mineralisation of orgaincs.

- **Low $[Fe^{2+}]_0$ (less than 1mM): effectively utilize the iron redox cycle for oxidation of orgainc substances.**

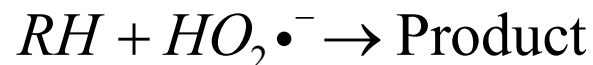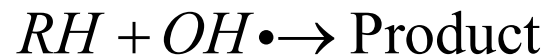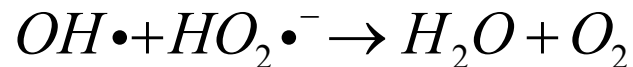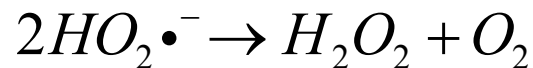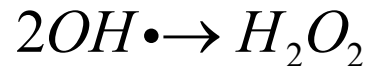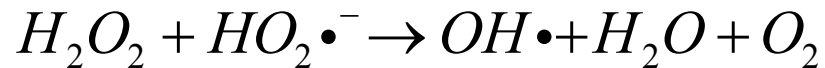# AOPs—Ozone/UV system reactions

- The existance of UV light enhances the production of OH radicals even though ozone alone can also produce this radicals.

- Experiments demonstrated the effectiveness of Ozone/UV on decomposition of nitrobenzene (only reacts with OH radicals, essentially nonreactive to ozone and hydrogen peroxide)

$$O_3 + H_2O \xrightarrow{\quad UV \quad} H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2OH\bullet$$

$$H_2O_2 \leftrightarrow HO_2\bullet^- + H^+$$

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

AOPs—UV/H_2O_2 system reactions

- The existance of UV light enhances the formation of OH radicals from hydrogen peroxide. Reactions are summarised as follows

$$H_2O_2 + hv \rightarrow 2OH\bullet$$

$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet^- + H_2O$$

$$H_2O_2 + HO_2\bullet^- \rightarrow OH\bullet + H_2O + O_2$$

$$2OH\bullet \rightarrow H_2O_2$$

$$2HO_2\bullet^- \rightarrow H_2O_2 + O_2$$

$$OH\bullet + HO_2\bullet^- \rightarrow H_2O + O_2$$

$$RH + OH\bullet \rightarrow \text{Product}$$

$$RH + HO_2\bullet^- \rightarrow \text{Product}$$
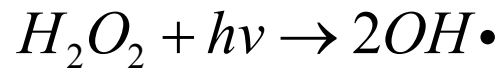
AOPs—comparison of three systems: UV/ozone, UV/H_2O_2, and Ozone/H_2O_2

- Műller and Jekel (2001) compared three systems by a non-specific figure-of-merit consisting the electrical energy per order of magnitude in oxidation per m^3, EE/O.

$$EE/O = \frac{P_{el}}{V_l' \log(c_0/c)} \quad \text{Flow-through operations}$$

$$EE/O = \frac{P_{el}t \cdot 1000}{V_l' \log(c_0/c)} \quad \text{Batch operations}$$
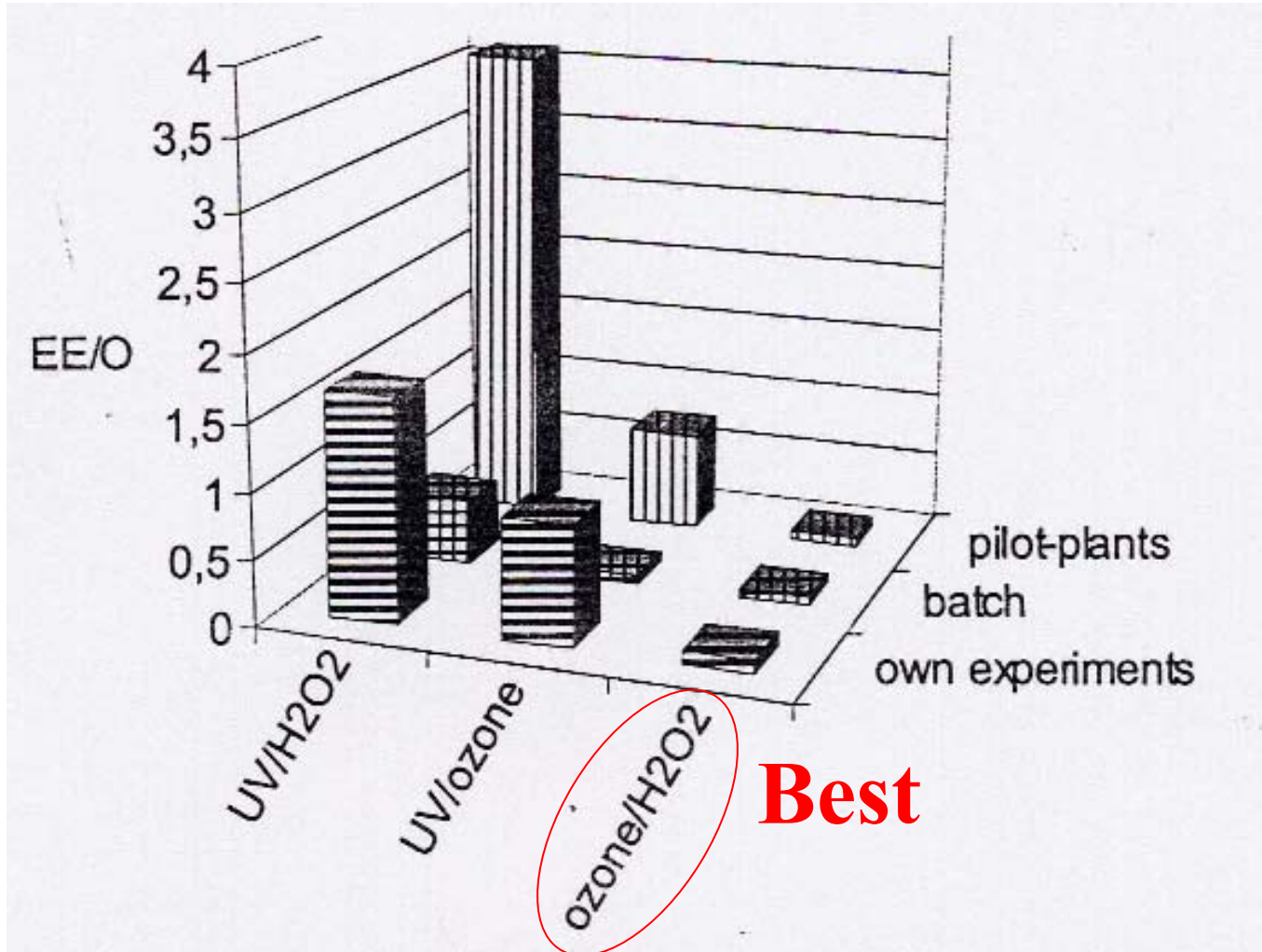
P_{el} is power as kW

V_l' is reactor volume as m^3

c_0 and c are pollutant concentration

before and after treatment

AOPs—comparison results

Table 1 EE/O-values from the AOPs UV/H_2O_2, UV/O_3 and O_3/H_2O_2 in Berlin tap water, 90% degradation of atrazine (extrapolated)

process	UV [kWh/m³] consumption	E_{O3} [g/m³] transferred	C_{H2O2} [g/m³]	EE/O [kWh/m³]
UV (135 W)				
48 1/h; 1-stage	2.81	–	–	2.81
UV/ozone (60 W)				
48 1/h; 1-stage	1,25	6.0	–	1.34
UV/ozone (135 W)				
48 1/h; 1-stage	2.81	7.6	–	2.92
UV/ozone (135 W)				
120 1/h; 2-stages	1.13	6.0	–	1.22
140 1/h; 2-stages	0.96	8.0	–	1.08
170 1/h; 2-stages	0.79	7.5	–	0.90
UV/H_2O_2 (135 W)				
60 1/h	2.25	–	2.0	2.27
90 1/h	1.50	–	17.0	1.67
H_2O_2/ozone				
100 1/h; V'_g/V'_1 = 1.1	–	7.7	2.3	0.135
100 1/h; V'_g/V'_1 = 0.4	–	6.7	2.0	0.120
100 1/h; V'_g/V'_1 = 0.2	–	5.5	1.7	0.102

AOPs—comparison results

AOPs—
photocatalytical
TiO_2 system in
sunrich areas:
Thin Film Fixed
Bed Reactor
(TFFBR) and
Parabolic
Trough Reactor
(PTR)
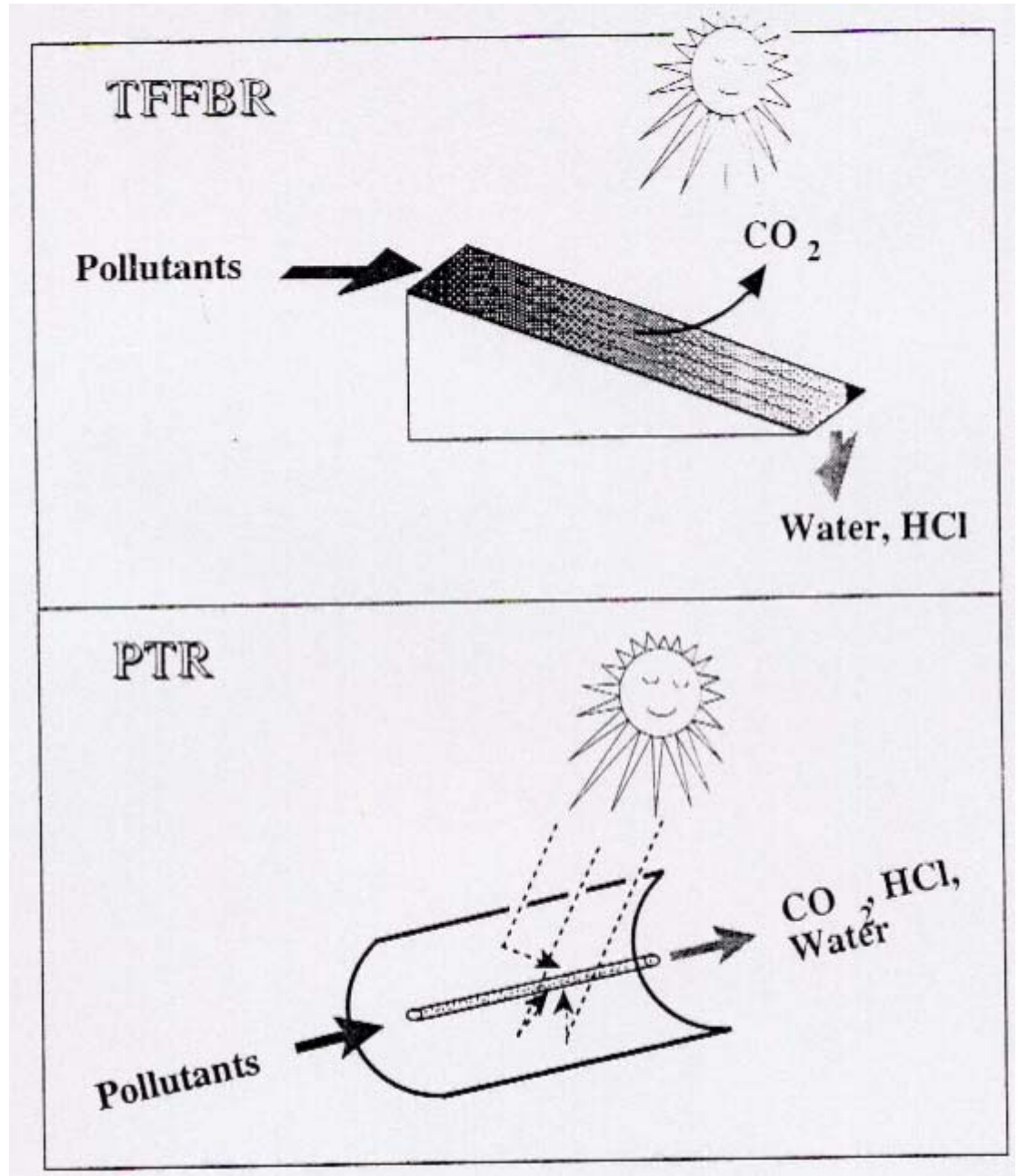
Conclusions

- Disinfection is the final hygiene barrier for safe water and wastewater effluent quality. Selection of various technologies is site-specific, depending on technological, financial, water quality-related, and management aspects.

- Oxidation is very effective removing difficultly biodegradable pollutants, yet expensive. Oxidation is considered as a barrier to chemical pollution.

- Combination of disinfection and oxidation seems to be a trend in water treatment especially when the water sources have been contaminated by various harmful and toxic organic matters. It is also a trend in wastewater reclamation and reuse especially for indirect or direct potable water.