

Midterm exam

- 3. December: 8.15-9.45
- Material of introduction, particles, oxidation 1: exercises 1-3
- Handouts and notes, calculator, no computer, no exercise solutions
- 2 Rooms
 - GC 3 31: Last names A-G
 - CE 1 100: Last names H-Z
- Detailed information on moodle
- Lecture: 10.15-12.00

Oxidation and Disinfection Processes in Water Treatment

2. Advanced oxidation

3. Disinfection

4. Disinfection by-products

Urs von Gunten

Advanced oxidation processes

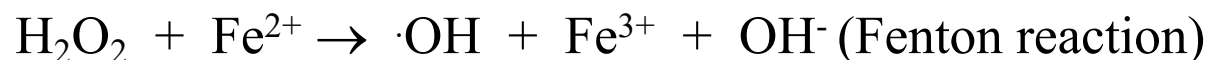
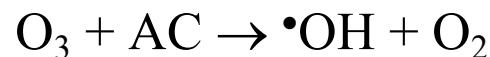
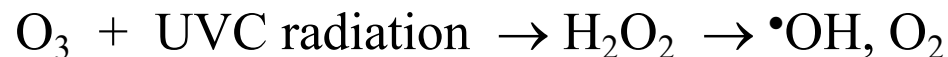
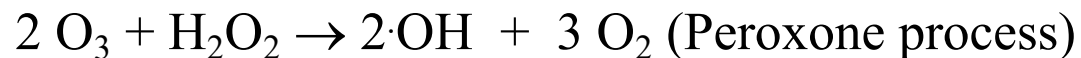
- Processes based on $\cdot\text{OH}$ radicals
- “Broadband” solution: $\cdot\text{OH}$ radicals react diffusion controlled with most inorganic and organic compounds
- Mostly consumed by water matrix (DOM, carbonate/bicarbonate)
- Very short lifetimes in μs -range
- Very low steady-state concentrations ($< 10^{-12}$ M)
- Efficiency quite low

$$\ln\left(\frac{[\text{P}]}{[\text{P}]_0}\right) = k[\cdot\text{OH}]t$$

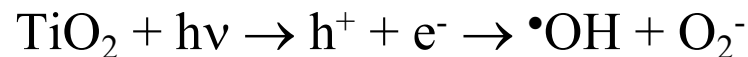
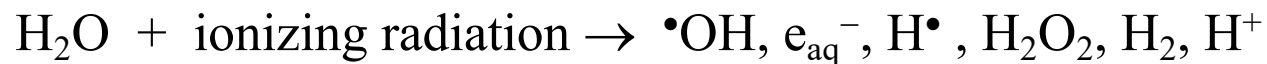
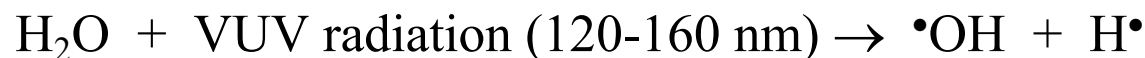
Efficiency depends on k and $[\cdot\text{OH}]$

Production of OH radicals – AOPs

Addition of chemicals



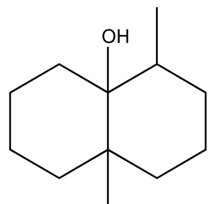
No dissolved
chemicals



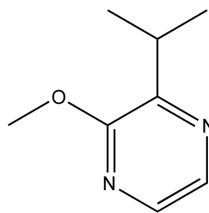
Oxidation kinetics during ozonation, ozone and OH radicals have to be considered: rate law and rate constants

$$\frac{d[P]}{dt} = -k_{O_3}[O_3][P] - k_{OH}[OH][P]$$

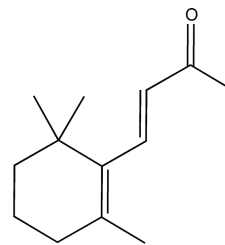
Taste and odor compounds



geosmin



IPMP



β -Ionone

k : second-order rate constants ($M^{-1}s^{-1}$)

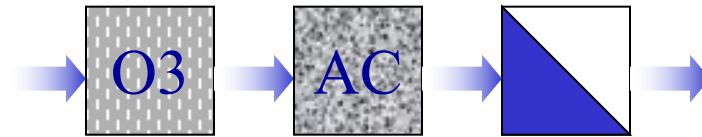
Ozone ($\approx 10^{-5}M$)	0.1	50	1.6×10^5
$\cdot OH$ ($\approx 10^{-12}M$)	7.8×10^9	4.9×10^9	7.8×10^9
$t_{1/2}$ (s) 1 mg/L O_3	3.5×10^5	700	0.2

Oxidation mostly by OH

Oxidation by ozone

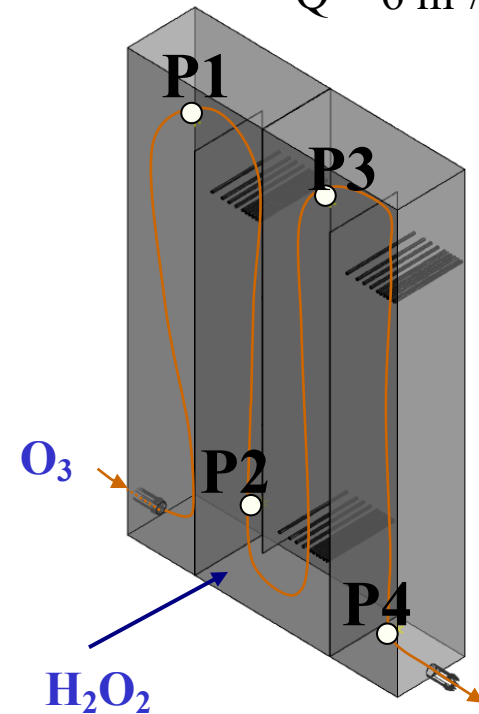
Advanced oxidation in a pilot plant: Lake Zurich

Multibarrier treatment



$$V = 2.2 \text{ m}^3$$

$$Q = 6 \text{ m}^3/\text{h}$$

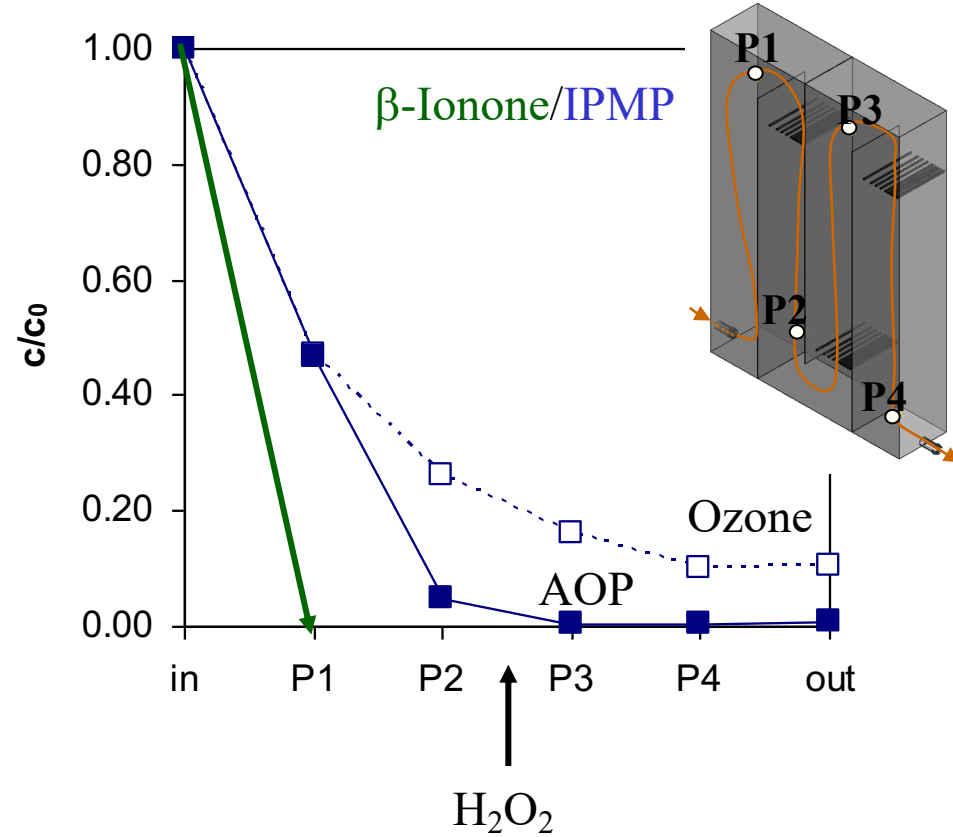
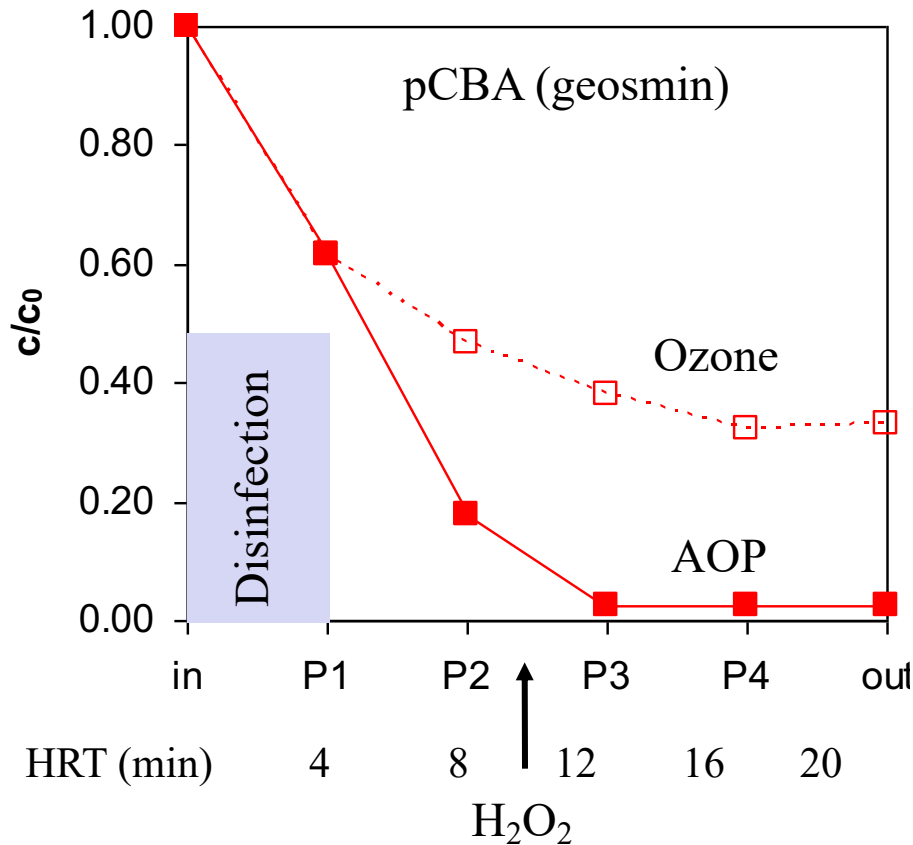


Oxidation of T&O compounds during pilot-plant ozonation: Peroxone process (AOP)

Ozone dose: 2.5 mg/L

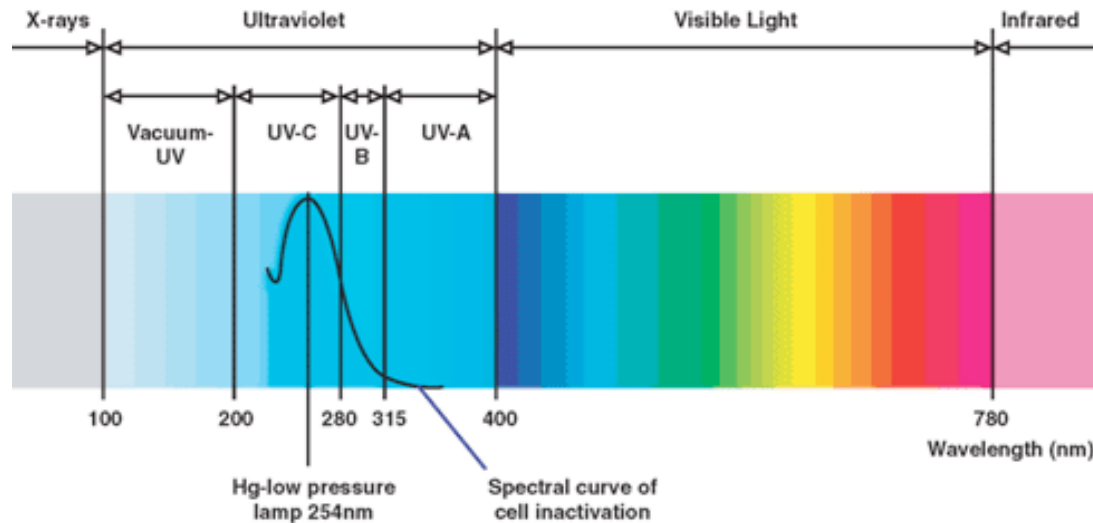
Hydrogen peroxide dose: 0.85 mg/L

pCBA, β -Ionone, IPMP



Hydrogen peroxide addition is a flexible option for seasonally occurring T&O episodes or accidental spills

UV-based processes



$$H = I \times t_R$$

H: Fluence ($\text{J/m}^2 = 0.1 \text{ mJ/cm}^2$) or “Dose”

I: Fluence Rate (W/m^2) or “Intensity”, depends on lamp and water quality

t_R : Duration of exposure (s) “Residence time”

Advanced Oxidation Process UV/H₂O₂



Oxidation of micropollutants by **direct photolysis** and **OH radicals**

Rate law for oxidation of P:

$$-\frac{d[\text{P}]}{dt} = k_{\text{abs}}\phi[\text{P}] + k_{\text{OH}}[\cdot\text{OH}][\text{P}]$$

P: micropollutant

$k_{\text{abs}}(\lambda) = I(\lambda) \times \varepsilon(\lambda)$; specific rate of light absorbance by P

I: Fluence rate (intensity), ε : molar extinction coefficient

ϕ : Quantum yield $\left(\frac{\text{moles of products formed}}{\text{moles of photons absorbed at } \lambda} \right)$

k_{OH} : Second order rate constant for the reaction of P with OH

Note: direct photolysis depends on product of ϕ and ε

Typically > 10 times higher UV doses required than for UV disinfection

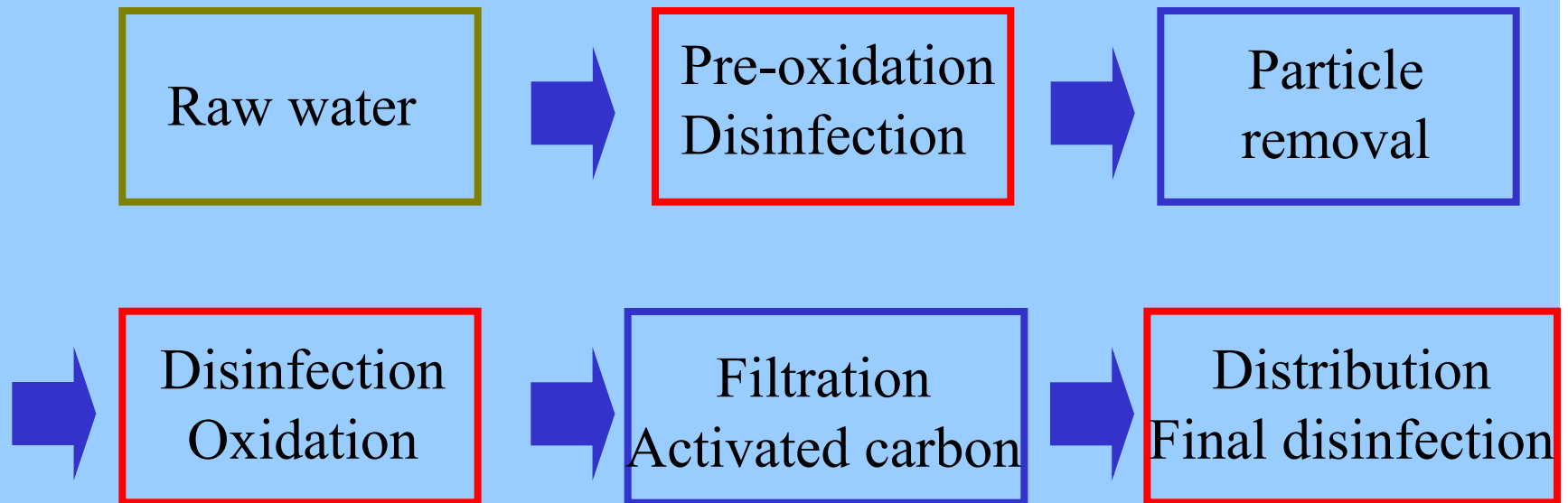
Energy requirements for UV/H₂O₂ typically 5-20 higher than for O₃-based processes



Disinfection

Treatment schemes for disinfection

Surface water



Groundwater



C*T (oxidant exposure) (mgL⁻¹min) values for 99% inactivation of microorganisms at 5 °C

	Disinfectant			
Microorganism	free chlorine pH 6 - 7	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 1	1.1 - 2.5	770 - 3740	0.2 - 6.7	0.1 - 0.2
Rotavirus	0.01 - 0.05	3810 - 6480	0.2 - 2.1	0.006 - 0.06
Giardia lamblia	47 - > 150	--	--	0.5 - 0.6
Giardia muris	30 - 630	1400	7.2 - 18.5	1.8 - 2.0
Cryptosporidium	7200	--	> 78	~20

CT: product of oxidant concentration and contact time

Kinetics of disinfection: Chick and Watson (1908)

$$-\frac{dN}{dt} = kC^n N$$

C = concentration of disinfectant

N = number of pathogens or germs

N₀ = number of pathogens or germs at time t = 0

t = time

k = specific lethality or inactivation coefficient

n = dilution coefficient



C = constant

N = N₀ at time t = 0

n = 1

Batch reactor



$$\frac{N}{N_0} = e^{-k \cdot C \cdot t}$$

$$\ln\left(\frac{N}{N_0}\right) = -k \cdot C \cdot t$$

Inactivation of *B. subtilis* spores by ozone at pH 7

Temperature dependence

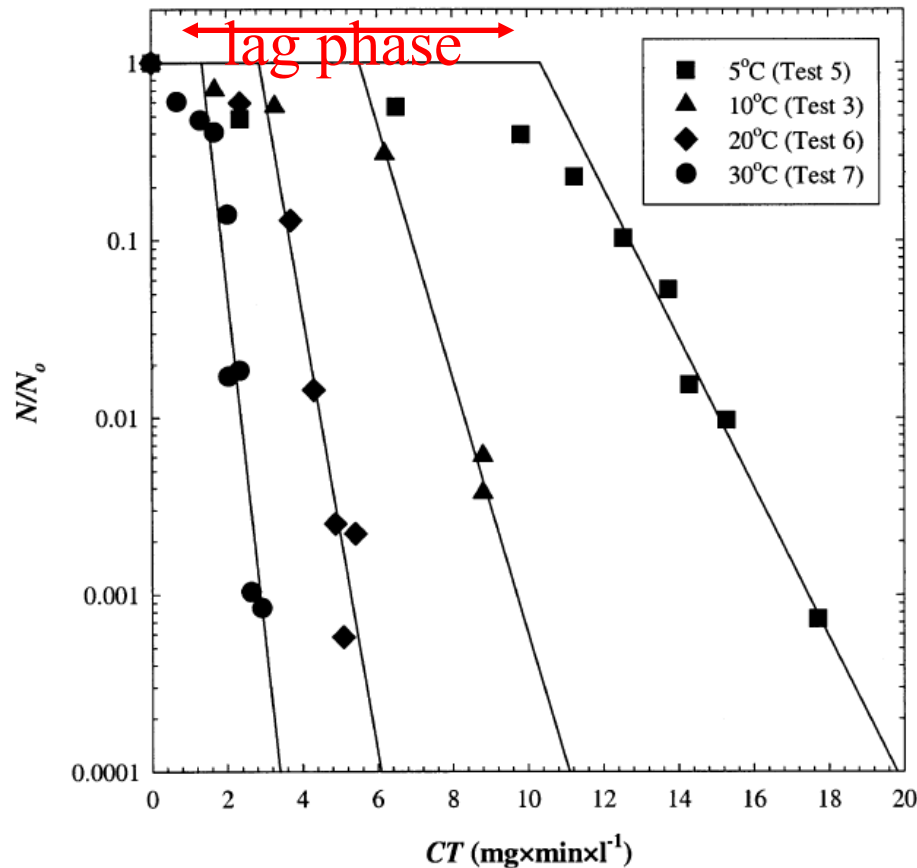


Fig. 3. *B. subtilis* inactivation at pH 7.0 as a function of temperature.

T (°C)	k (l mg ⁻¹ min ⁻¹)	k (M ⁻¹ s ⁻¹)	CT_{lag} (mg min l ⁻¹)
5	0.97	7.8×10^2	10
10	1.6	1.3×10^3	6.1
20	2.9	2.3×10^3	2.9
30	4.5	3.6×10^3	1.4

Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

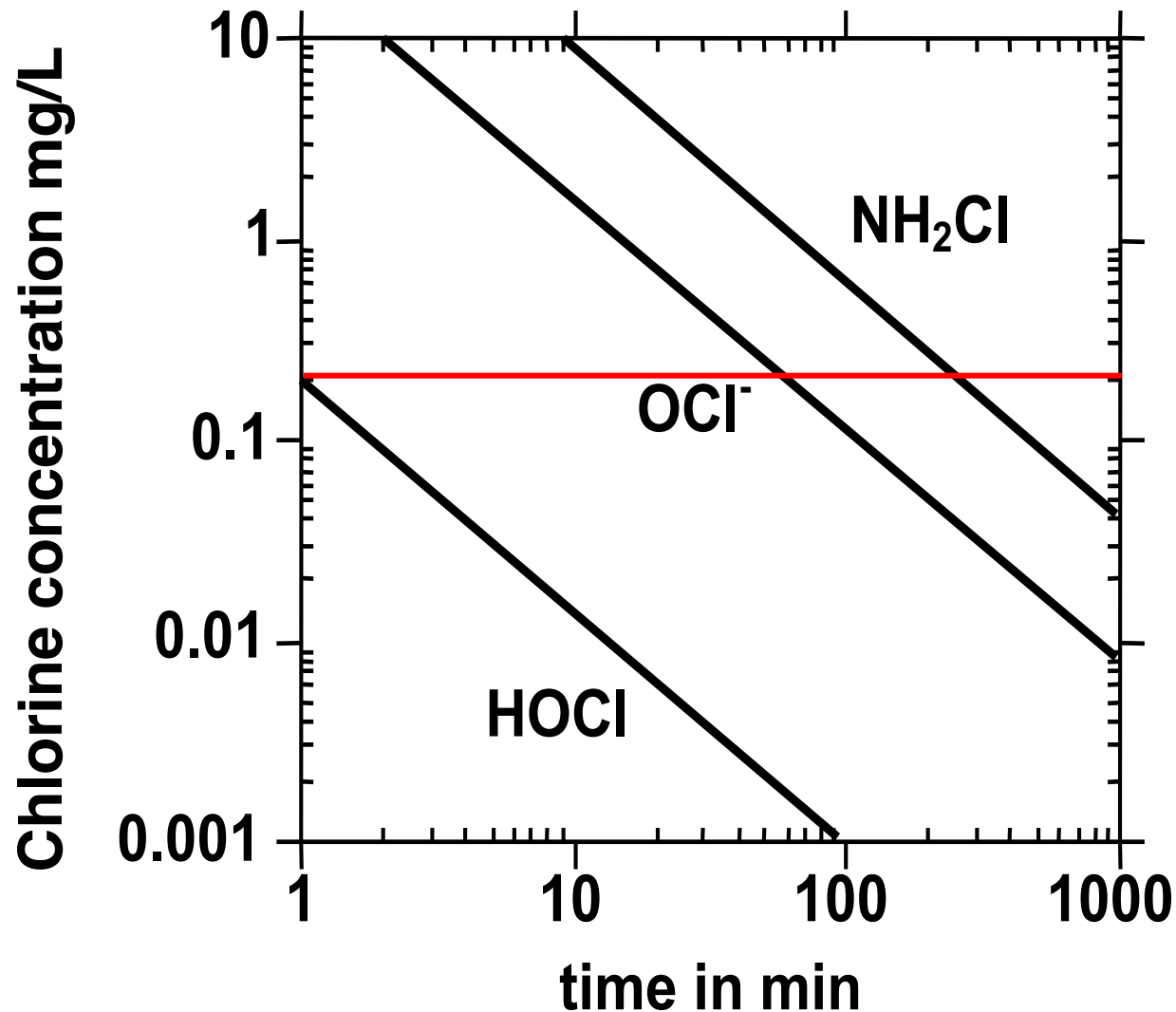
$$\log(k) = \log(A) - \frac{E_a}{2.303 \times RT}$$

A: collision frequency parameter

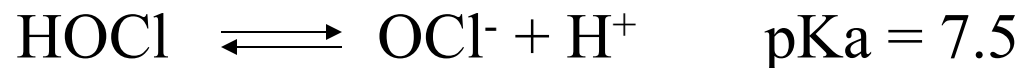
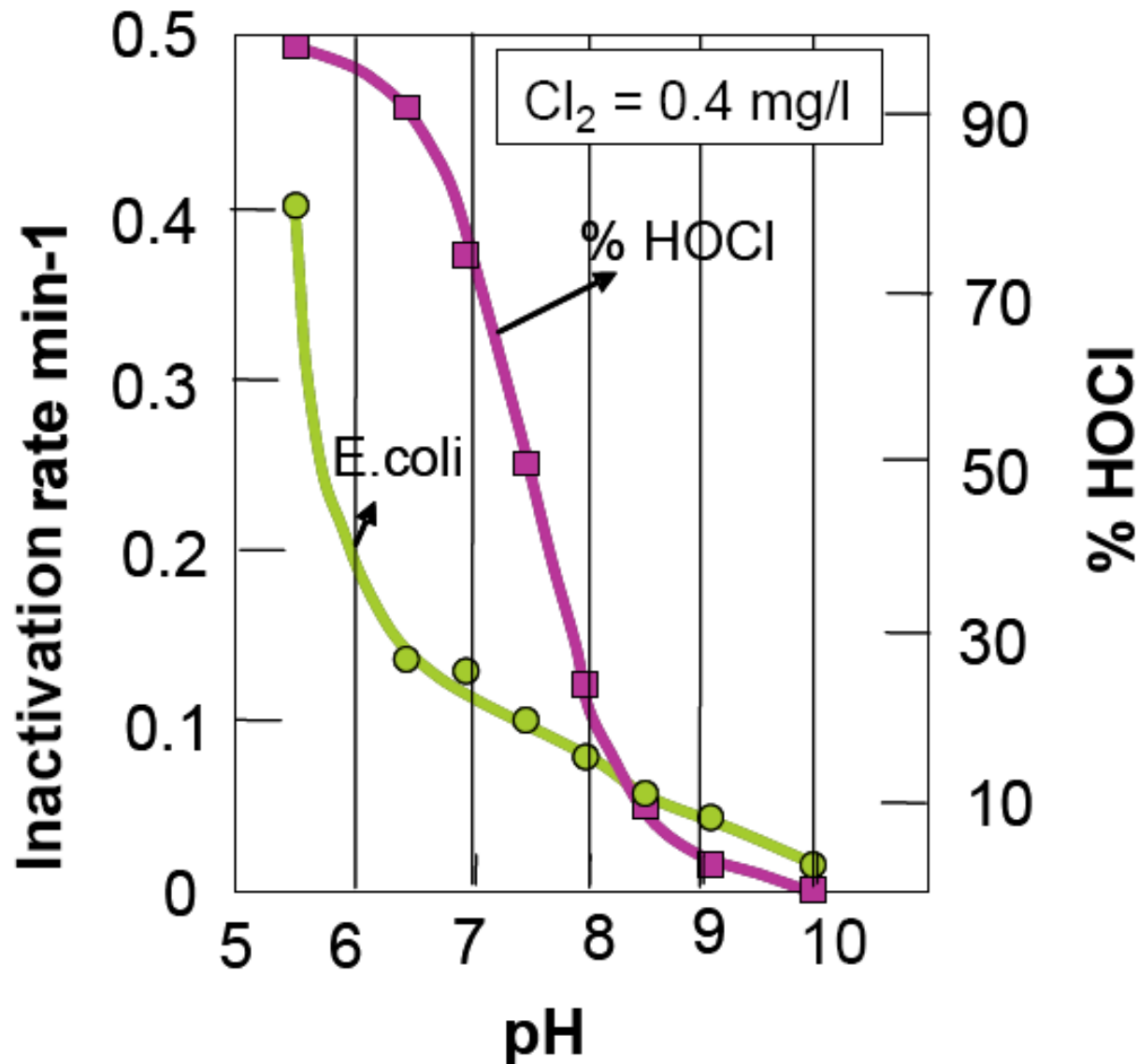
E_a : activation energy from
plot of $\log(k)$ vs $1/T$

Disinfection with chlorine and monochloramine

2-log Inactivation of *E. coli* by chlorine at 2-6 °C

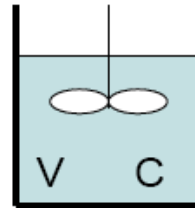


Inactivation of *E. coli* by chlorine: Role of HOCl

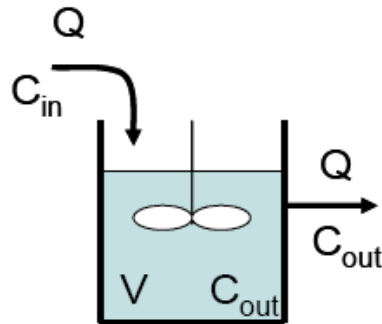
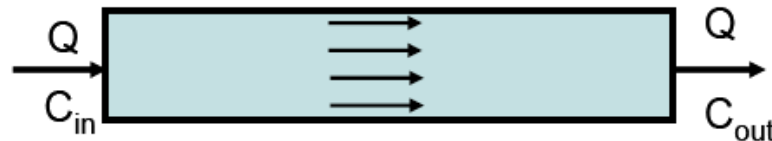


Disinfection: Role of hydraulics

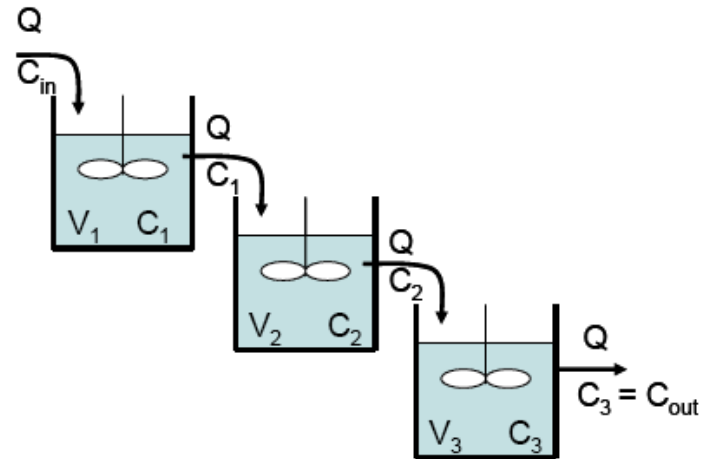
Batch-reactor



Plug flow reactor (PF)



Completely mixed tank reactor
(CSTR)



Cascade of CSTRs

Elimination of microorganisms in ideal reactors I

$$\frac{dN}{dt} = -kc_{ox}N$$

c_{ox} constant :

$$\ln\left(\frac{N}{N_0}\right) = -kc_{ox}t \quad \Rightarrow \quad \frac{N}{N_0} = e^{-kct_{ox}}$$

Plug flow

c_{ox} variable :

$$c_{ox} = c_{ox,o} \times e^{-k_{ox}t}$$

$$\frac{dN}{dt} = -kc_{ox,o}e^{-k_{ox}t}N$$

$$\ln\left(\frac{N}{N_o}\right) = -\frac{kc_{ox,o}}{k_{ox}}(1 - e^{-k_{ox}t})$$

Elimination of microorganisms in ideal reactors II

input = output + disappearance by reaction:

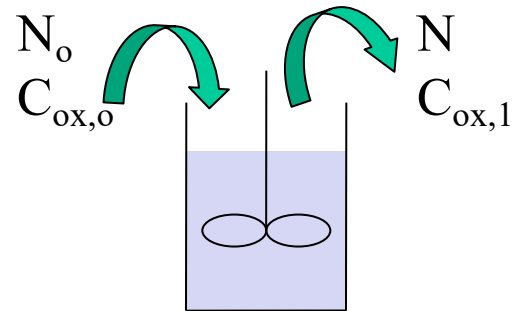
$$QN_0 = QN + kc_{ox}NQ t$$

CSTR

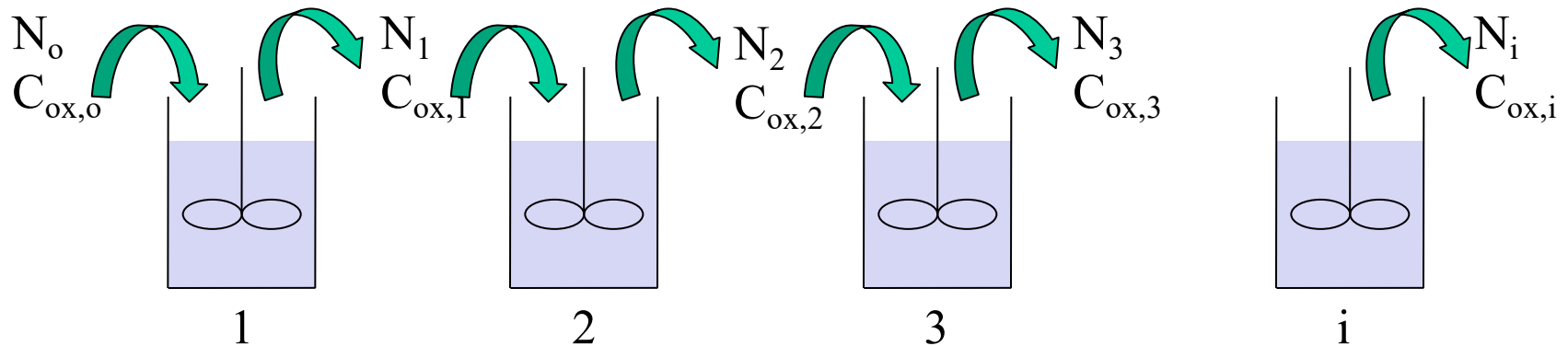
$QN = (\text{mass, number, mole})/\text{time unit}$

$$\Rightarrow N_0 = N + kc_{ox}Nt$$

$$\Rightarrow \frac{N}{N_0} = \frac{1}{1 + kc_{ox}t}$$



Cascade of CSTRs



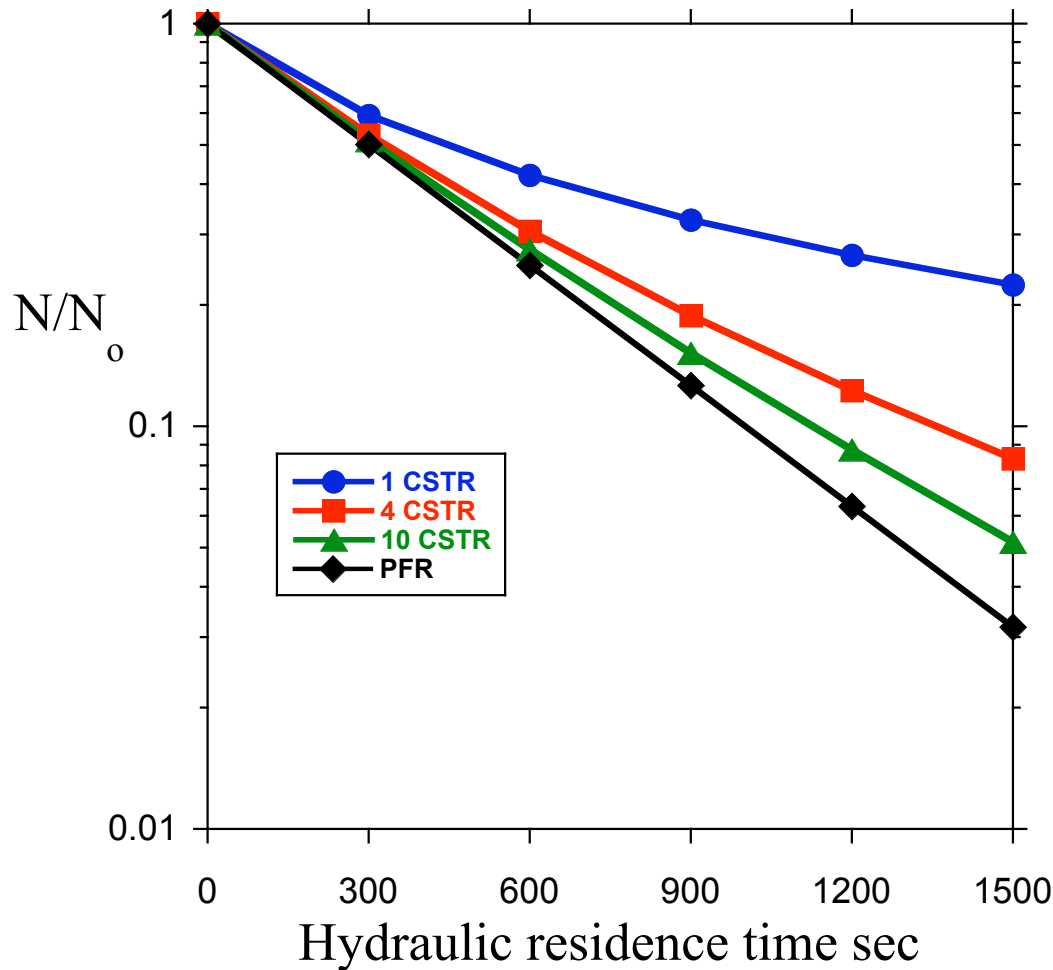
$$\frac{N_i}{N_0} = \prod_i^m \left(\frac{1}{1 + \frac{t}{m} k_{N,ox} C_{ox,o} \left(\frac{1}{1 + k_{ox} \frac{t}{m}} \right)^i} \right)$$

$k_{N,ox}$: second order rate constant for inactivation of microorganisms

k_{ox} : first order rate constant for oxidant decrease

t : total residence time; m : number of reactors

Comparison of disinfection efficiency in various reactors: constant oxidant concentration



$$k_{N,O_3} = 2.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

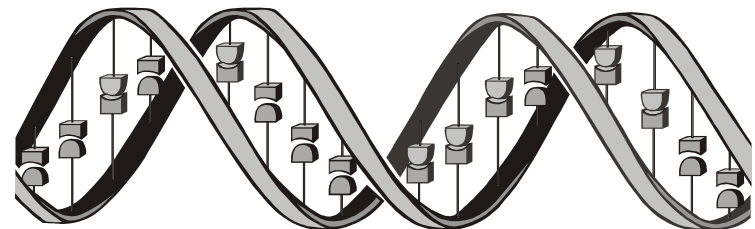
$$O_{3,o} = 0.05 \text{ mg/L}$$

$$= 10^{-6} \text{ M}$$

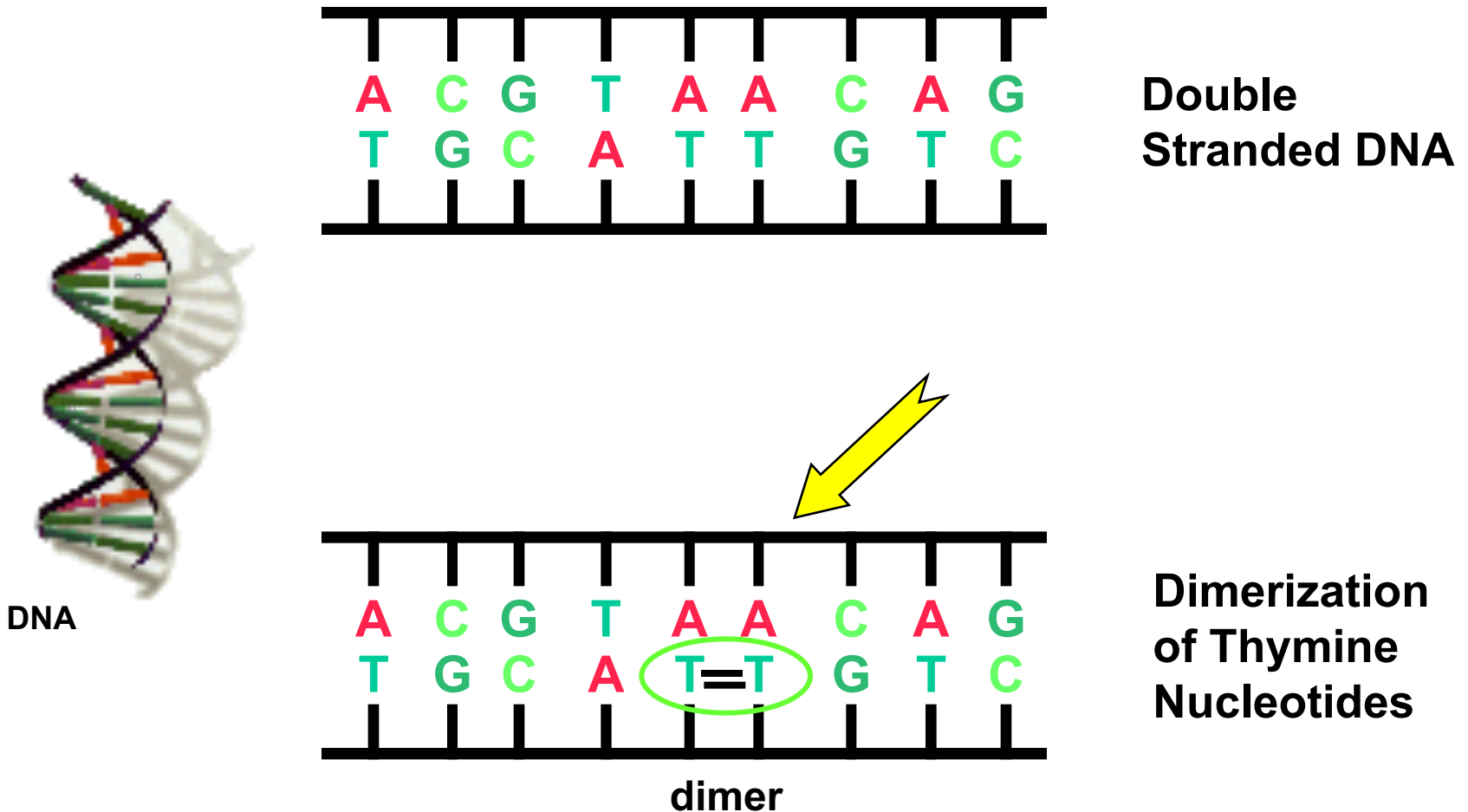
An increasing number of CSTRs approaches a plug-flow reactor

UV disinfection: germicidal action of UV light

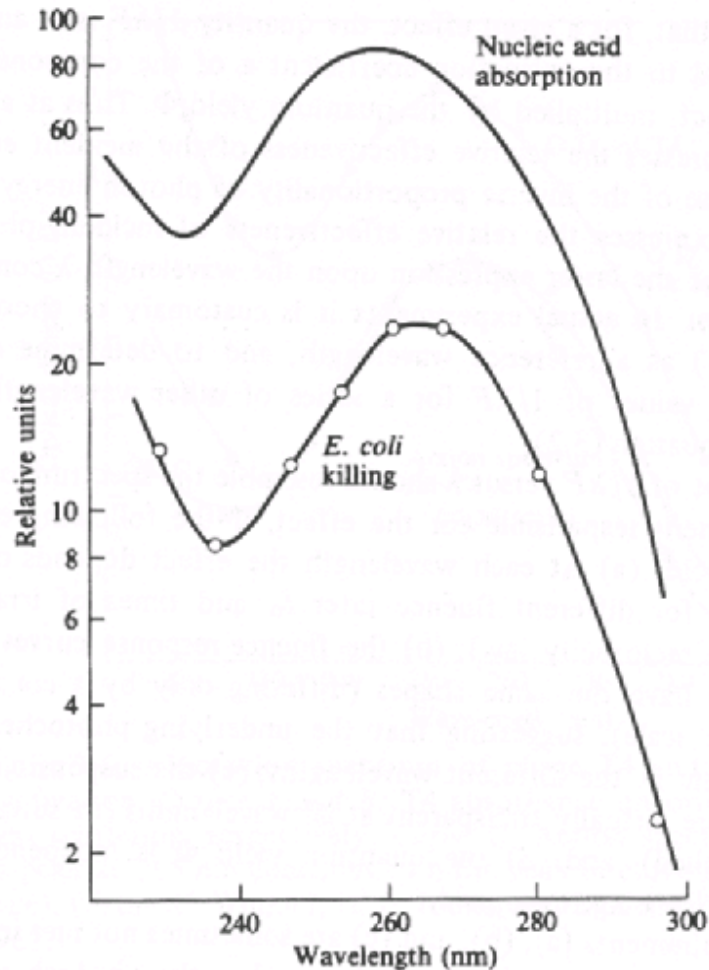
- UV light energy is absorbed by microbial nucleic acid.
- The amount of damage depends on the UV dose absorbed.
- Damage to nucleic acid prevents reproduction.



Example of UV damage to DNA



DNA vs *E.coli* action spectrum



Low pressure UV lamps
Emission at 254 nm

Figure 3.5. Similarity of the action spectrum for inactivation of *E. coli* cells, determined by F. L. Gates, to the absorption spectrum of nucleic acids. (Redrawn from C. S. Rupert, in: *Comparative Effects of Radiation*, M. Burton, J. S. Kirby-Smith, and J. L. Magee, eds., Wiley, New York, 1960, pp. 49-61.)

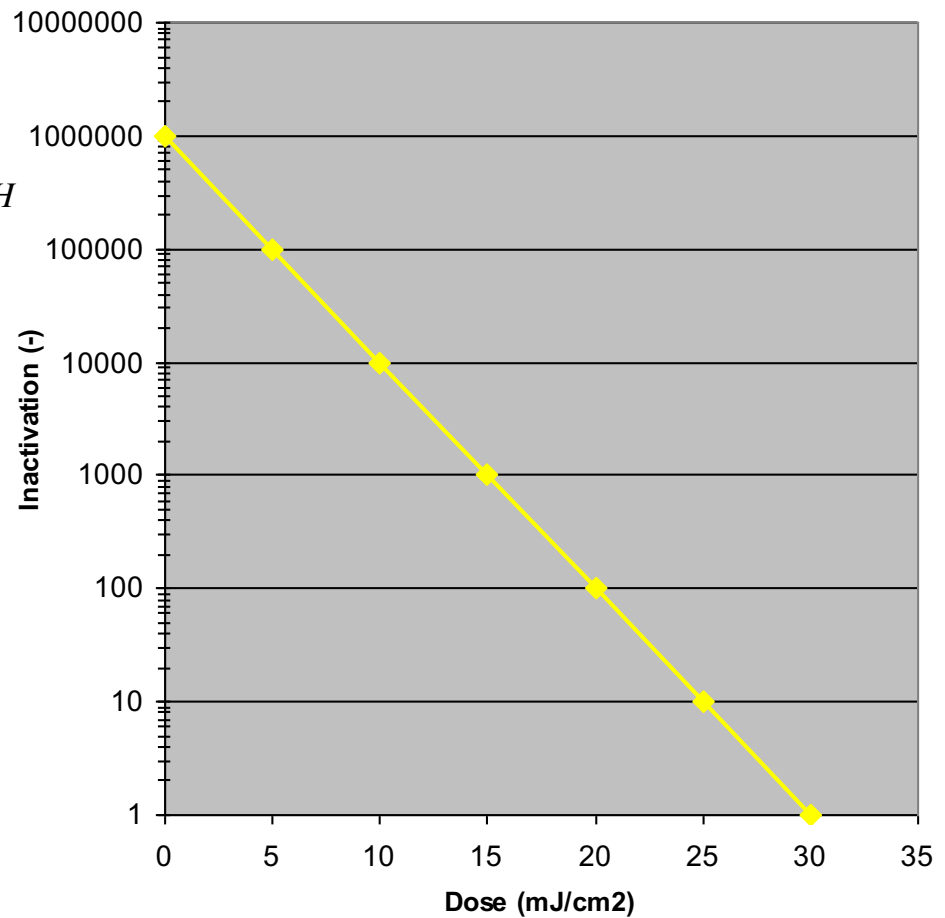
UV inactivation kinetics

$$\frac{dN}{dt} = -kIN \rightarrow \frac{N}{N_0} = e^{-k I t} = e^{-k H}$$

In drinking water mostly
first-order kinetics

Recommended dose 400J/m²

= 40 mJ/cm²



UV dose for a 2-log reduction

Bacteria	Dose to achieve 99% Inactivation
<i>Shigella dysenteriae</i>	42 J/m ²
<i>E.coli</i>	66 J/m ²
Fecal coliforms	68 J/m ²
<i>Salmonella enteritidis</i>	76 J/m ²
<i>Pseudomonas Aeruginosa</i>	105 J/m ²
<i>Clostridium tetani</i> spores	220 J/m ²
<i>Bacillus subtilis</i> spores	220 J/m ²

Required dose for drinking water: 400 J/m²

UV dose for a 2-log reduction

Difficult to inactivate by chemical disinfectants

Virus	Dose to achieve 99% Inactivation
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Influenza	66 J/m ²
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Polio	140 J/m ²
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Rotavirus	150-190 J/m ²
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Protozoa	
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Giardia Lamblia	50 J/m ²
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Cryptosporidium parvum oocysts	49 J/m ²
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Required dose for drinking water: 400 J/m²

Oxidation/Disinfection by-products

Reaction of oxidants with water
matrix components

The Chlorine Dilemma

David L. Sedlak¹ and Urs von Gunten^{2,3}

Chlorine disinfection has been instrumental in the provision of safe drinking water, but the use of chlorine has a dark side: In addition to inactivating waterborne pathogens, chlorine reacts with natural organic matter to produce a variety of toxic disinfection by-products (DBPs). Regulatory guidelines were established in the United States for DBPs, such as chloroform, shortly after they were discovered in chlorinated drinking water in the mid-1970s, and the discovery of a potential link between DBPs and

increased rates of miscarriages and bladder cancer led to more stringent regulations and substantial changes in the operation of water treatment systems during the past decade (1). These concerns and the risks associated with storing chlorine gas have recently led many drinking-water and wastewater treatment plants to discontinue the use of chlorine disinfection (see the figure). A series of recent studies suggest that some of these changes have had unintended consequences that pose risks to public health and the environment.

Chlorine DBPs can be controlled in drinking-water systems by more effective removal of natural organic matter—the main precursors of DBPs—through physical-chemical treatment processes such as enhanced coagulation and activated carbon filtration. Although these approaches are

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WATER INFRASTRUCTURE

How do you like your tap water?

Safe drinking water may not need to contain a residual disinfectant

By Fernando Rosario-Ortiz,^{1,2} Joan Rose,³ Vanessa Speight,⁴ Urs von Gunten,^{2,5} Jerald Schnoor^{2,6}

The expectation that tap water is safe has been sorely tested by the recent events in Flint, Michigan, where lead contamination has caused a public health emergency (1). Apart from contamination with heavy metals and other harmful substances, a key concern is the control of microbial contamination. To prevent microbial growth and protect con-

sumers from pathogens from other sources, some countries, such as the United States, require the presence of residual disinfectant in drinking water. However, the presence of a disinfectant can lead to the formation of potentially carcinogenic disinfection by-products, issues with corrosion, and complaints based on the fact that people dislike the taste of disinfectants in their water (2). The experience of several European countries shows that such residual disinfectants are not necessary as long as other appropriate safeguards are in place.

From the early 1900s, the control of microbial waterborne pathogens, including *Salmonella typhi* and *Vibrio cholera*, led to a major reduction of waterborne diseases in the industrialized world. Filtration and chlorine disinfection reduced mortality in the United States substantially. But in 1974, chloroform, a probable human carcinogen formed by the reaction of chlorine with naturally occurring organic matter, was discovered in chlorinated drinking water. This discovery led to a debate about microbiological safety versus exposure to harm-

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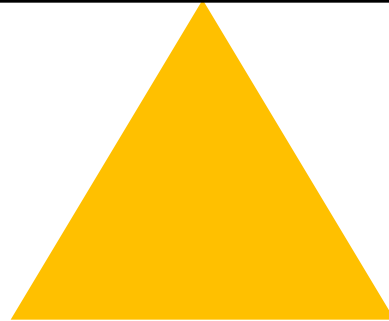
Disinfection vs By-product formation

Disinfection

Disinfection By-products

*Acute Toxicity
from pathogenic
microorganisms*

Chronic Toxicity



- Concept for overall risk assessment
- Danger of export to developing countries (Peru)
 - No chlorination in small water supplies (USEPA study DBPs)
 - Cholera epidemic 1991: 300' 000 cases (> 3000 †)

- Non-halogenated organic compounds
 - Aldehydes, Ketones, Hydroxy-ketones, Keto-acids, Carboxylic acids → assimilable organic carbon (AOC)
 - Nitrosamines (e.g. NDMA)
- Halogenated organic compounds
 - Chlorinated, brominated, iodinated products
- Inorganic compounds
 - Bromate, iodate, chlorite, chlorate

Desinfection by-products:

Trihalomethanes (THM)

- THMs: CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3
- Formation during Chlorination of drinking waters
- Discovery by J. Rook 1974
- 1976, USEPA study: THM's are always formed during chlorination of drinking water
- 1976, National Cancer Institute: Chloroform leads to cancer in rats
- 1998 (Swan and Waller): Significantly higher risk for spontaneous abortion for consumption of drinking water with high THM's (**Showers!**)
- Today the issue of spontaneous abortions is controversial

Conclusions

- Ozonation and AOPs are useful processes for micropollutant degradation
 - Direct reaction with ozone, reaction with OH radicals, direct photolysis
- Ozone-based AOPs are typically more energy efficient than UV/H₂O₂
- Chemical disinfection
 - Kinetics (pH, T, lag phase)
 - Inactivation of protozoa may be problematic (-> UV)
 - Reactor hydraulics play an important role (several log inactivation)
- Disinfection by-products
 - Always formed during chemical disinfection
 - pH, T, DOC, bromide