Water and wastewater treatment – Homework 9 – Solutions

1. Oxidation of micropollutants

Ethinylestradiol (EE2) is the active ingredient of the contraceptive pill and can lead to feminization of fish in natural waters at concentrations below 1 ng/L. It reacts quickly with ozone with k_{app} (pH 7) = 2.8×10^{6} $M^{-1}s^{-1}$ and with OH radicals (k = 9.8×10^{9} $M^{-1}s^{-1}$).

1.1. If you assume an ozone concentration of 1 mg/L (2×10^{-5} M) and an OH radical concentration of 10^{-12} M, which one is the dominant reaction pathway at pH 7?
The fraction f_{O3} of EE2 reacting with ozone can be calculated as:

$$f_{O3} = \frac{k_{O3}[O_3]}{k_{O3}[O_3] + k_{OH}[OH]} = \frac{56}{56 + 9.8\times10^{-3}} = 99.98\%$$

With a f_{O3} of almost 100% the reaction occurs only with ozone directly.

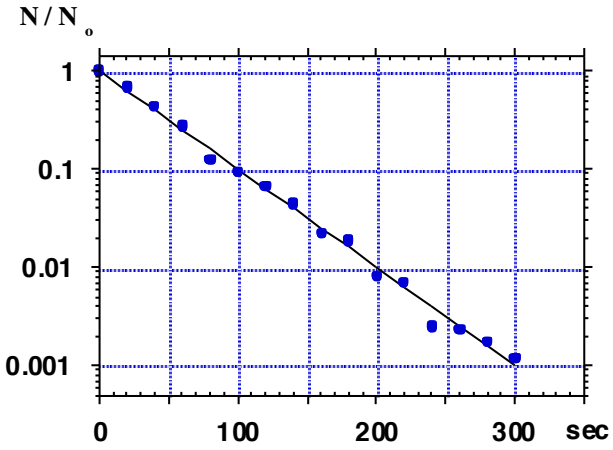
1.2. In a laboratory ozone dose experiment with a natural water, an ozone-dose based rate constant of 6 L/mg O_3 has been determined. What is the ozone dose required for 99% oxidation of EE2?

$$\ln\left(\frac{[EE2]}{[EE2]_o}\right) = -k \times O_3 - dose \Rightarrow O_3\text{-}dose = -\frac{\ln\left(\frac{[EE2]}{[EE2]_o}\right)}{k} = -\frac{\ln(0.01)}{6} = 0.77\ mg/L$$

The ozone dose for 99% degradation of EE2 is 0.77 mg/L.

2. Disinfection

The disinfection kinetics for inactivation of a microorganism with an oxidant in a batch system is shown in the figure below. The concentration of the disinfectant is kept constant during the whole process. The logarithm (log) of the germ count decreased linearly with time.



2.1. Determine the first-order rate constant for this inactivation process. You can do this graphically from the plot above.

$$\log\left(\frac{N}{N_0}\right) = \frac{1}{\ln(10)} \times \ln\left(\frac{N}{N_0}\right) = -\frac{1}{2.3} \times k \times t$$

$$\text{For } t = 200 \text{ s}: \quad \log(10^{-2}) = \; -2 \; = \; -\frac{1}{2.3} \times k \times 200$$

$$\Rightarrow \; k \; = \; \frac{2}{200} \times 2.3 \; = \; 0.023 \text{ s}^{-1}$$

2.2. What is the critical volume of a plug-flow reactor to achieve a 3-log inactivation (factor 1000)? Assumption: same oxidant concentration/UV dose as in the inactivation experiment and a flow rate of $1 m^3/s$.

$$\log\left(\frac{N}{N_0}\right) = -3 \; = \; -\frac{1}{2.3} \times 0.023 \times t$$

$$\Rightarrow t \; = \; 300 \text{ s} \; \Rightarrow \; V \; = \; 300 \text{ m}^3$$

2.3. What volume would be needed for a CSTR for a 3-log inactivation, if we assume the same concentration of the disinfectant?

$$N_0 = N_1 + k \times N_1 \times t$$

$$\frac{N_0}{N_1} = 1000 \; = \; 1 \; + \; kt$$

$$\frac{999}{k} \; = \; t \; = \; 43'434 \text{ s} \; \Rightarrow \; V \; = \; 43'435 \text{ m}^3$$

2.4. What is the reactor volume needed if the reactor in 2.3 is divided into two compartments?

(1) First CSTR: $N_0 = N_1 + k \times N_1 \times t$

(2) Second CSTR: $N_1 = N_2 + k \times N_2 \times t$

$$\frac{N_2}{N_0} = \frac{1}{1000}$$

For the sequence of the two CSTRs we can write
(substituion of N1 in equation by N1 from equation 2):

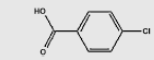
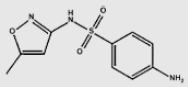
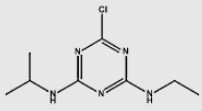
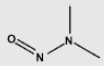
$$N_0 = N_2 + 2k \times N_2 \times t + k^2 \times N_2 \times t^2 = N_2\left(1 + 2kt + k^2t^2\right) = N_2\left(1 + kt\right)^2$$

$$\sqrt{\frac{N_0}{N_2}} = 1 + kt \Rightarrow t = \frac{\sqrt{\frac{N_0}{N_2}} - 1}{k} = \frac{\sqrt{1000} - 1}{k} = \frac{31.6 - 1}{0.023} = 1331 \text{ sec}$$

$\Rightarrow$ Two reactors of 1331 m^3 each are required, yielding a total reactor volume of 2662 m^3

3. Energy requirements for various advanced oxidation processes

The degradation of various micropollutants (see Table below) has been investigated for ozone, ozone/hydrogen peroxide and UV/hydrogen peroxide. The rate constants for the reactions of the compounds with ozone (k_{O3}) and OH radicals (k_{OH}) are given in the table as well as the quantum yield (ϕ) and the fluence based rate constant (k_{Eo}= $2.3 \times \varepsilon \times \phi$). Note that k_{OH} is typically > 10^9 $M^{-1}s^{-1}$.

Target compound	Structure	k_{O3}/M^{-1} s^{-1}	k_{OH}/M^{-1} s^{-1}	Direct phototransformation(λ = 254 nm)	
				φ [a]/mol einstein^{-1}	k_{Eo}^{o} [b]/m^2 einstein^{-1}
p–chlorobenzoic acid (pCBA)		<0.1 [c]	5×10^9 [c]	0.013 [d]–0.026 [e]	n. a.
Sulfamethoxazole (SMX)		2.5×10^6 [f] (at pH 7)	5.5×10^9 [f]	0.046 [g]	176 [g]
Atrazine (ATR)		6 [h]	3×10^9 [h]	0.046 [i]	40.9 [j]
N-Nitrosodimethylamine (NDMA)		0.052 [k]	4.5×10^8 [k]	0.3 [l]	≈ 104 [m]

a Quantum yield.
b Photon fluence-based rate constant (see Canonica et al., 2008).

3.1. Discuss the main mechanism of oxidation in relative terms, based on the kinetic information shown in the Table above (Which compounds are preferentially oxidized directly by ozone, by OH radicals or photolyzed)?

pCBA: low rate constant for reaction with ozone, high rate constant for reaction with OH radicals, quantum yield low. It is expected that pCBA is mainly transformed by OH radicals.

SMX: high rate constant for the reaction with ozone, high rate constant for the reaction with OH radicals, high photon fluence based rate constant.
All mechanisms are efficient to transform SMX.
ATR: low rate constant for the reaction with ozone, intermediate rate constant for the reaction with OH radicals, intermediate fluence-based rate constant. Mainly oxidized by OH radicals.
NDMA: low rate constant for the reactions with ozone and OH radicals. The compound can be well photolyzed. Direct photolysis is the main process for its transformation.

3.2. The Table below shows the dose-based (O_3) and fluence-based rate constants for the transformation of the selected compounds. Calculate the energy requirement in kWh/m^3 for a 90% conversion of these compounds by ozone and UV/H_2O_2 (UV process 1cm path length) in ZH-water (Lake Zurich water, S_λ=0.95). In the case of UV/H_2O_2, the H_2O_2 concentration was 0.2 mM. Energy requirements: ozone production: 15 kWh/kg; H_2O_2: 10 kWh/kg.

Table 3 – Ozone dose-based and fluence-based rate constants for the transformation of micropollutants during conventional ozonation in ZH- and DW-waters and by LP-UV/H_2O_2 in ZH-water respectively[a].

Target compound	O_3 dose-based rate constants in ZH-water (L mgO_3^{-1})	O_3 dose-based rate constants in DW-water (L mgO_3^{-1})	Fluence-based rate constant in ZH-water (m^2 J^{-1})
SMX	22.3	0.74	6.7×10^{-4}
pCBA	1.00	0.17	3.3×10^{-4}
ATR	0.67	0.11	2.46×10^{-4}
NDMA	0.067	0.038	1.43×10^{-4}

a Experimental conditions: Target compound concentration = 0.5 μM, pH = 8, T = 20 °C.

Ozonation:
The elimination of a compound C as a function of the ozone-based rate constant is expressed as:

$$\ln\left(\frac{[C]}{[C]_0}\right) = -k \times (O_3 - \text{dose})$$

90% conversion:

$$\ln(0.1) = -k \times (O_3 - \text{dose})$$

$$O_3 - \text{dose (90\%)} = -\frac{\ln(0.1)}{k} = \frac{2.3}{k}$$

$$\text{Energy requirement: } (O_3 - \text{dose } (\text{kg}/\text{m}^3)) \times (15\text{kWh}/\text{kg})$$

compound	Ozone energy requirement kWh/m^3
SMX	0.0015
pCBA	0.035

ATR	0.05
NDMA	0.5

UV/H_2O_2:

$$\ln\left(\frac{[C]}{[C]_0}\right) = -k \times \text{Fluence}$$

90% conversion:

$$\ln(0.1) = -k \times \text{Fluence}$$

$$\text{Fluence (90\%)} = -\frac{\ln(0.1)}{k} = \frac{2.3}{k}$$

Energy requirement for SMX:

$$H'_\lambda = H'^{avg}_\lambda / S_\lambda$$

H'^{avg} corresponds to fluence(90%) = 3433 J/m^2

➔ $H'_\lambda = H'^{avg}_\lambda / S_\lambda = 3614$ J/m^2

$$E_{lamp} = \frac{H'_\lambda(x\%)}{I^{avg} \times \eta_{UV}} \times \frac{\text{kWh}}{3.6\times10^6\,\text{J}} = \frac{3614}{0.01\times0.3\times3.6\times10^6}\frac{\text{kWh}}{\text{m}^3} = 0.33 \text{ kWh/m}^3$$

Energy for H_2O_2: 0.2mM = 0.2 mol/m^3 = 0.2 x 34 g/m^3 => 0.068 kWh/m^3

Total energy: 0.33 + 0.068 = 0.398 kWh/m^3

compound	UV/H_2O_2 energy requirement kWh/m^3
SMX	0.40
pCBA	0.75
ATR	0.98
NDMA	1.64

3.3. What can be concluded from these energy calculations in relation to the efficiency of these processes?

Ozonation is generally much more energy efficient. Exception: Compounds such as NDMA, which are non-reactive with ozone and OH radicals, but are relatively well photolyzed. Note that for NDMA the energy requirement is only three times higher for UV/H_2O_2 than for O_3, whereas for atrazine the UV-based process requires 20 times more energy than ozone. If we assume a deeper penetration of UV in the water (10 cm), the energy consumption for NDMA degradation would be lower for the UV-based process than for O_3.