Water and wastewater treatment – Homework 9

1. Oxidation of micropollutants

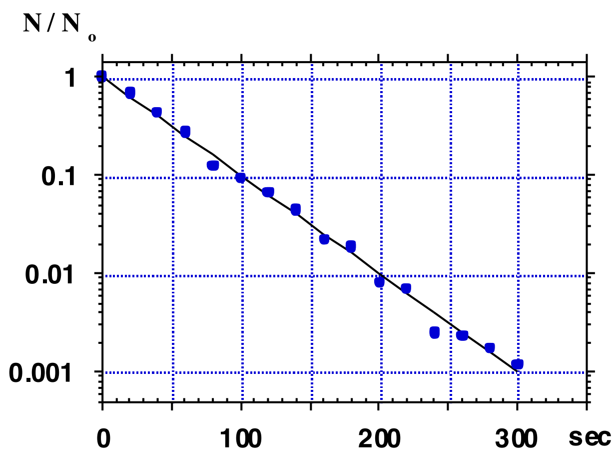
Ethinylestradiol (EE2) is the active ingredient of the contraceptive pill and can lead to feminization of fish in natural waters at concentrations below 1 ng/L. It reacts quickly with ozone with k_{app} (pH 7) = $2.8\times10^{6}\ M^{-1}s^{-1}$ and with OH radicals ($k = 9.8\times10^{9}\ M^{-1}s^{-1}$).

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?

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?

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.

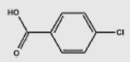
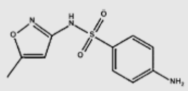
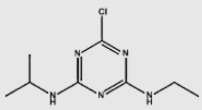
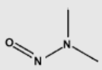
2.2. What is the critical volume of a plug-flow reactor to achieve a 3-log inactivation (factor 1000)? Assumption: same oxidant concentration/UV dose as in the inactivation experiment and a flow rate of $1 m^3/s$.

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

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

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}	$k_{E_p^0}$ [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)?

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.

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