Practical Course "Drinking water treatment"

UV-degradation and UV based advanced oxidation processes (AOPs) – Decolouration of a Rhodamine B solution

1. Introduction

The following experiment will give you first impressions about the use of UV-radiation for the removal of organic water pollutants.

UV-radiation is a part of electromagnetic radiation between visible light and X-rays. In general it is the range of wave lengths between 100 nm < λ < 400 nm and energies from 3 eV to 124 eV.



Fig. 1: Range of electromagnetic radiation, especially UV

The energy-rich electrons of the valence shells are lifted up by absorption of the UV-energy. In these excited states reactions will be possible which are impossible under normal conditions. The transformation of a compound depends on the wavelength λ respectively on the frequency following the Planck-Einstein equation:

$$E = h \cdot v$$
 $v = \frac{c}{h}$ $E - energy, v - frequency, \lambda - wavelength, c - speed of light$

Photons are acting like reactants. In consideration of the quantization behaviour of electromagnetic radiation the yield of such reactions is called quantum yield σ .

$$\sigma = \frac{\text{transformed molecules of the absorbing compound}}{\text{absorbed quantums}}$$

The excitation of a molecule depends on the wavelength λ . These wavelengths have to be absorbed by the reacting molecule. Therefore the specific absorption spectrum of a compound has to be known. The best results of a photochemical transformation take place by using the shortwave absorption maximum of the compound. Beer-Lambert Law describes this effect:

$$\mathsf{E} = \log \frac{\mathsf{I}}{\mathsf{I}_0 = \varepsilon \cdot \mathbf{c} \cdot \mathsf{d}}$$

E - extinction, c - concentration, I_0 - intensity of the incoming light, I - intensity of the outcoming light after the absorption, ϵ - extinction coefficient

Photolysis is the complete degradation of organic chemicals to small inorganic molecules, like CO_2 , H_2O , HCl, by interaction with light. Persistent organic pollutants (POPs) like halogenated aromatic hydrocarbons, pesticides and other not readily biodegradable substances can be degraded by UV-radiation.

If a compound is not degraded by direct photolysis, advanced oxidation processes could be applied. The main characteristic of an **advanced oxidation process (AOP)** is the formation of highly reactive hydroxyl radicals (OH•) which degrade the micropollutants. This process is called photoinitiated oxidation. The rate constants for the reaction of hydroxyl radicals with organic compounds are in the range of 10^8 - 10^{10} mol/(L·s). Hydroxyl radicals show the highest redox potential of nearly 2.8 V. Hydroxyl radicals are highly reactive but not selective in the mineralisation of organic substances. Important AOP are the Peroxone-Process (combination of ozone (O₃) and hydrogenperoxide (H₂O₂)), the application of Fenton's reagent (Fe(II)/H₂O₂/H⁺) and the application of special UV-treatment (VUV) and combined UV-procedures (UV/O₃, UV/H₂O₂). Under advanced oxidation conditions micropollutants are degraded in the reaction with OH•.

The addition of H_2O_2 creates advanced oxidation conditions, H_2O_2 absorbs the UV radiation and dissociates into OH•.

$$H_2O_2 \xrightarrow{h_{\upsilon}} H_2O_2^* \rightarrow 2OH \bullet$$

High pressure and low pressure mercury lamps are radiation sources with a high intensity in the UV-C range ($\lambda = 200 - 280$ nm). Mercury emits at 253.7 nm, a wavelength that is absorbed by many organic compounds. If the lamp is covered by a special quartz glass envelope it emits additionally at 185 nm (vacuum-UV range, VUV).

The application of VUV is a further possibility to create OH• is the photolysis of water under radiation below 200 nm:

$$H_2O \xrightarrow{h_0(VUV)} H_2O^* \rightarrow H \bullet + OH \bullet + e^{-}_{aq}$$

Advantages of the application of UV light for water treatment:

- no residuals \rightarrow no dumping; no accumulation of pollutants,
- no addition of chemicals \rightarrow no input of chemicals to the environment,
- broad field of application, especially point-of-use systems on household scale or application in health risk zones (hospitals),
- disinfection of water (inactivation of bacteria and viruses),
- easy to upgrade in an existing treatment plant,
- easy to supervise and high reliability

Disadvantages are:

- high investment and energy costs due to limited lifetime of lamps and electrodes,
- undesired by-products (nitrite, bromate)

The efficiency of an AOP depends highly on the water matrix. The reaction of the hydroxyl radicals is non-selective and fast with nearly all water constituents. When the hydroxyl radicals react with the natural organic matter (NOM) in the water they are no longer available for the oxidation of micropollutants. Such scavengers are humic substances, carbonate and hydrogen carbonate. Therefore, the efficiency of an AOP decreases in well-buffered natural waters.

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics include investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

The concentration vs. time graph of the experiment can be described by the first order rate law:

$$c(t) = c_0 \cdot e^{-(kt)}$$

c(t) – concentration at time t, c_0 – initial concentration, k – reaction rate constant

The specific reaction rate k is independent of the initial concentration of the degraded component. The specific reaction rate can be simply calculated by linearization:

$$lnc(t) = lnc_0 \cdot \frac{1}{k \cdot t}$$
 $ln\frac{c_0}{c(t)} = k \cdot t$

By drawing the experimental data $ln(c_0/c)$ vs. time in an EXCEL-diagram, you can calculate the specific reaction rate k by calculating the slope of the fitted linear trend line function. Statements for the efficiency of the UV-degradation under different conditions can be made by comparison of the calculated specific reaction velocities k and the half-life time $t_{1/2}$.

$$ln \frac{c_0}{0.5 \cdot c} = k \cdot t_{1/2}$$
 $t_{1/2} = \frac{ln^2}{k}$

2. <u>Tasks and objectives</u>

The degradation of micropollutants in the AOPs UV/ H_2O_2 and H_2O/VUV is investigated with a model substance. First, the effect of UV radiation, VUV radiation and H_2O_2 is investigated separately. Afterwards the combined application of UV and H_2O_2 is carried out. For each experiment a degradation curve is measured and the degradation rate constant is determined. An additional experiment shall investigate the influence of natural organic matter (NOM) on the degradation.

3. <u>Materials</u>

3.1 Model substance Rhodamine B

The intensive red xanthen dye Rhodamin B is used as colourant for lasers and is stable under UV and visible light. The colour of this compound is based on light adsorption of the expanded delocalized π electron system.



3.2 Chemicals

- Pure water
- Stock solution Rhodamine B (2 g/L)
- stock solution: Rhodamine B (10 mg/L)
- Wash bottle with ultrapure water
- Graduated flasks, pipettes for calibration
- Beakers for samples
- Cuvette for photometer (1 cm)
- Stock solution for DOC: Potassium hydrogen phthalate (1 g/L)

3.3 UV lamp

Type:	low-pressure mercury lamp
λ Emission:	254 nm (UV-lamp), 254 + 185 nm (UV/VUV-lamp)
Power:	11 Watt

4. Experimental procedure

5.1 Photometric measurements - calibration

You have to prepare 7 calibration solutions (see Table 1) use the following equations to calculate the volumes of the stock solution necessary to prepare the solutions.

Tab. 1:Pr	reparation	of	calibration	solutions
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	concentration	V [mL] Stock	volume [mL]	extinction	
	[mg/L]	solution	volumetric flask		
1	0.1		50		
2	0.2		50		
3	0.5		50		
4	1.0		50		
5	1.5		50		
6	2.0		50		
7	2.5		50		

stock solution:
$$c = 10 \text{ ma/L}$$

$$c_{s tandard} [mg / L] = \frac{x[mL] \cdot c_{stock solution} [mg / L]}{50 mL}$$

$$x[mL] = \frac{c_{Standard}[mg/L] \cdot 50mL}{c_{stocksolution}[mg/L]}$$

First the absorption maximum of Rhodamine B is determined.

Afterwards the calibration curve of Rhodamine B is measured at the highest absorption wavelength.

5.2 Preparation of solutions

2 L of Rhodamine B solution are prepared for each experiment from the stock solution to an initial concentration of 2 mg/L.

5.3 Photochemical treatment of Rhodamine B

2 L Rhodamine B solution (2.0 mg/L) are filled in the recirculation batch reactor. The chemicals are added and the UV lamp is installed according to the protocol. After complete mixing of the solution the first sample (t = 0) is taken. Afterwards the UV lamp is switched on and the timer s started. The sampling follows the instructions of the protocol.

5. Data analysis and discussion

- Evaluate the results of the calibration of Rhodamine B
- Analyse the data of the UV experiments: Plot c/c₀ versus t
- Calculate the rate constant k and the half-life time t_{1/2} for each experiment
- Discussion of results:

Which influence does the hydrogen peroxide dose show on the degradation process? How does the natural organic matter (NOM) influence the degradation? On which reaction is the observed degradation based? Which other treatment process could be used to degrade the model compound?

Protocol

Experiment 1 UV-irradiation

Experiment 2 VUV-irradiation

 H_2O_2 addition (1 mL, 30%) Experiment 3

Experiment 4 UV + H₂O₂ (0.2 mL, 30%)

Experiment 5

UV + H_2O_2 (1 mL, 30%) VUV-irradiation, DOC: 5 mg/L (add 10 mL DOC stock solution (1 g/L) to 2 L) Experiment 6

t [min]	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Experiment 6
0						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						