Fraunhofer FEP

Fraunhofer Institute for Electron Beam and Plasma Technology FEP

9th ITG International Vacuum Electronics Workshop 2024

Removal of Persistent Micropollutants From Wastewater By Hybrid Treatment With Low-Energy Electrons and Ozone

Lotte Ligaya Schaap, Tobias Teichmann, Andre Poremba, Gösta Mattausch, Simone Schopf, Elizabeth von Hauff

AGENDA

- Introduction
- Methodology
- Results
- Work in Progress
- Conclusion and Outlook

Introduction

Pharmaceuticals in the Aquatic Environment

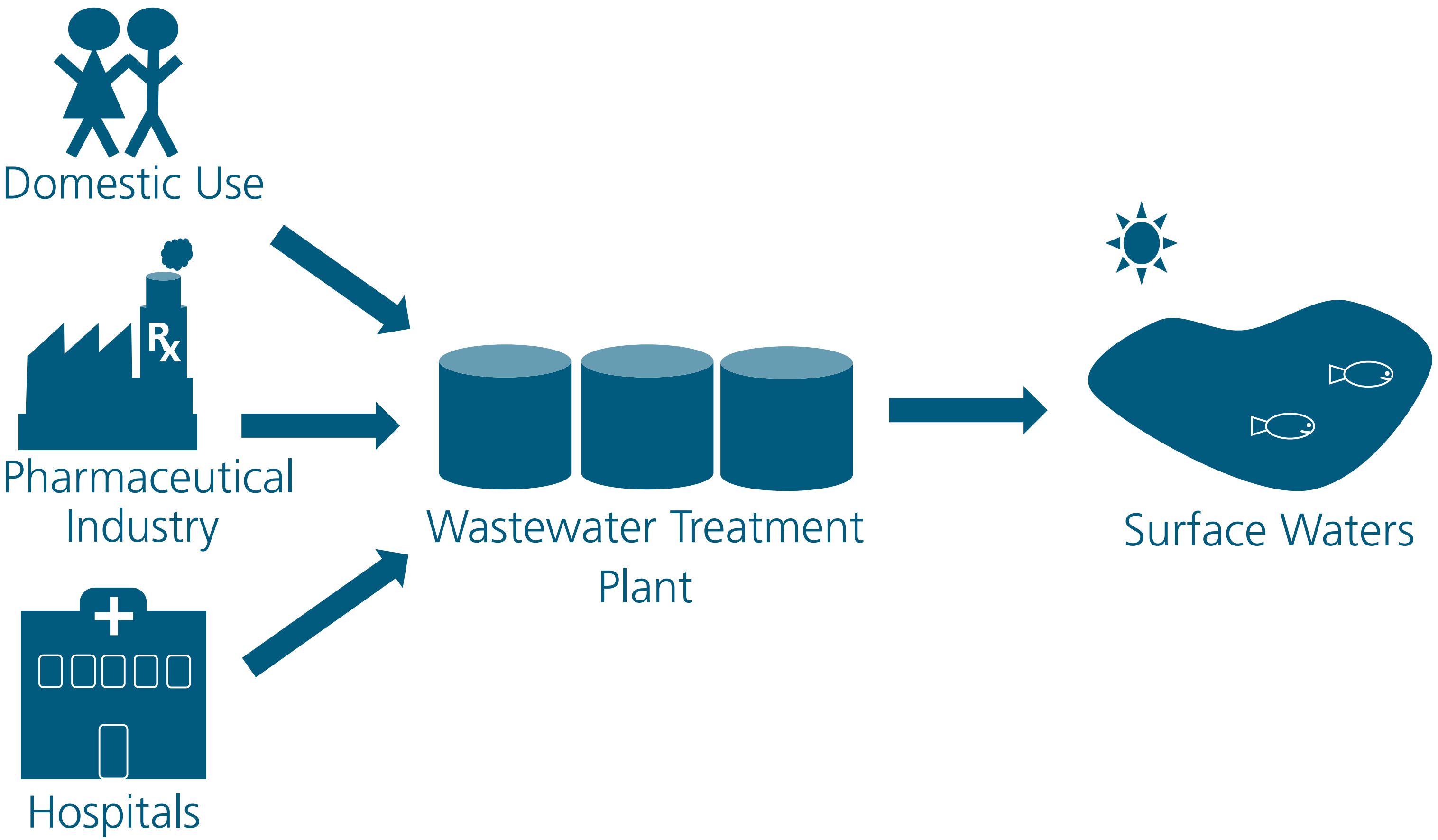


Figure 1. Main sources of pharmaceuticals in the aquatic environement.

- In Germany alone, **9,600 to 12,800 tons of unused pharmaceuticals** are disposed of or flushed down the toilet yearly [1]
- Their presence in effluents have been linked to **ecological toxicity** [2], **antimicrobial resistance** [3], **endocrine disruption**, and **gradual reduction of fertility** [4,5]

Introduction

Pharmaceuticals in the Aquatic Environment

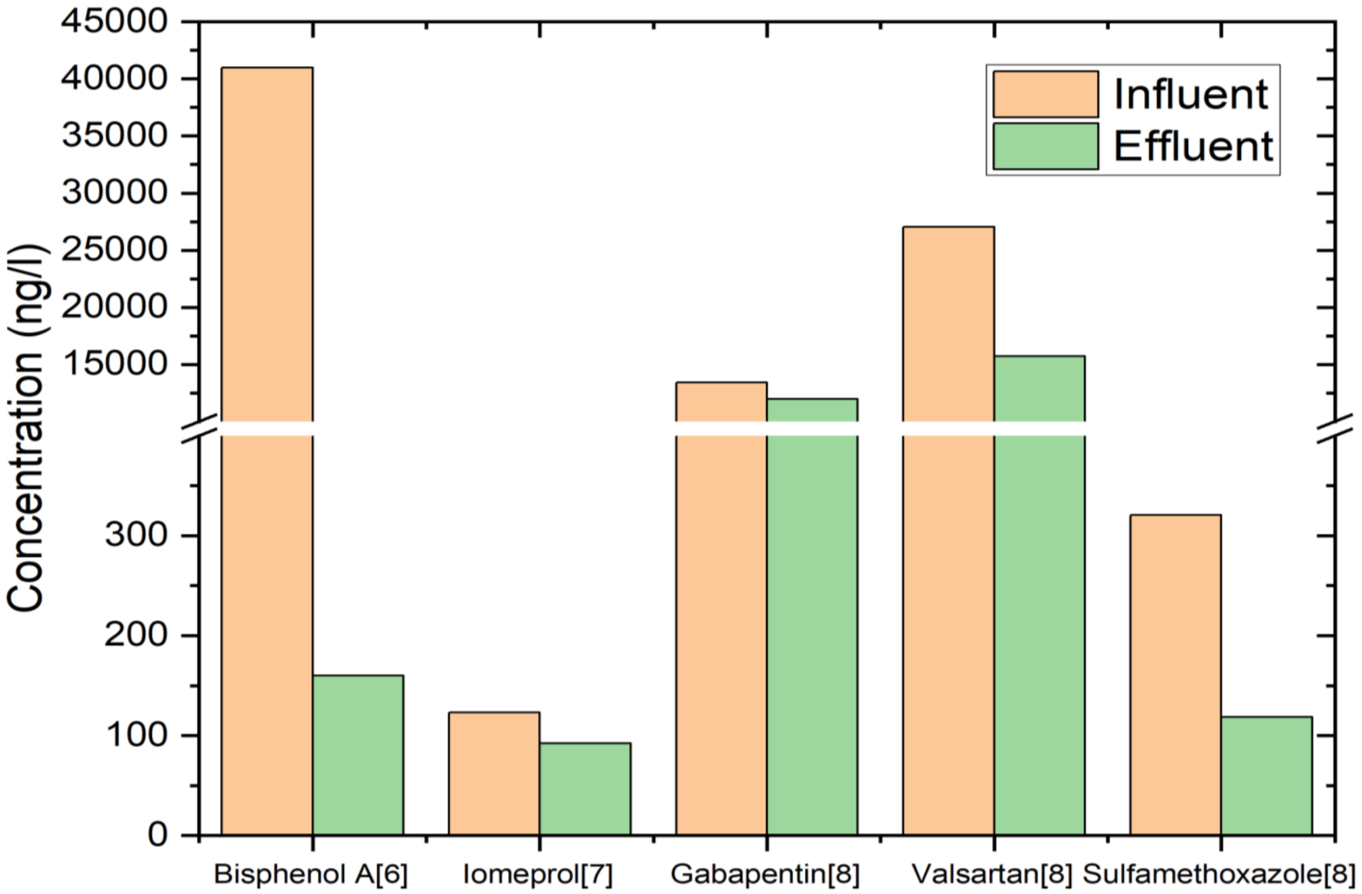
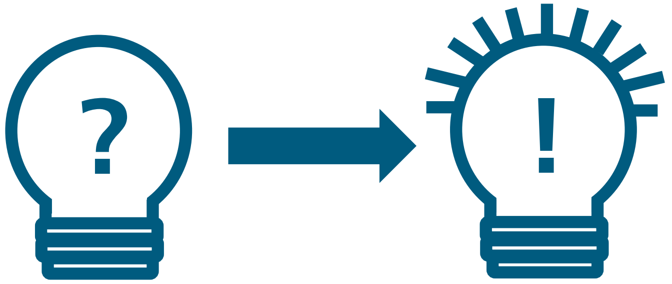


Figure 2. Concentration of micropollutants before and after conventional wastewater treatment.

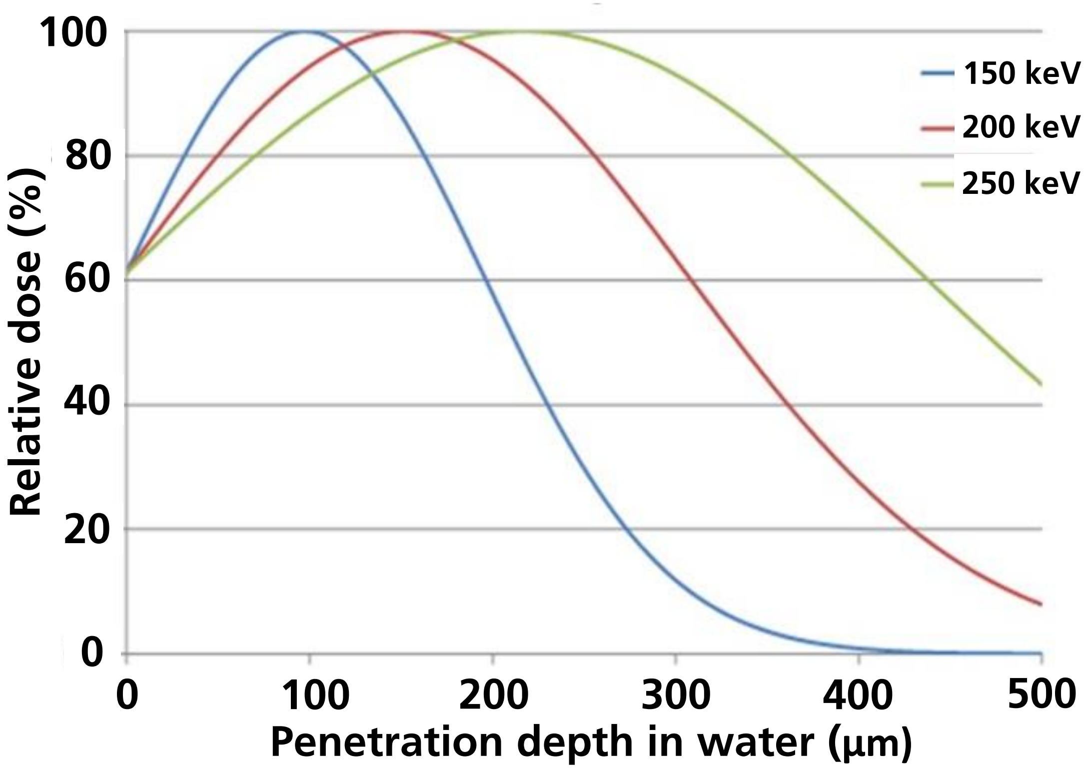


The Problem: Pollutants of low-level toxicy which cannot be degraded by traditional methods

The Solution: Low energy EB Treatment

Introduction

The Problem with Low-Energy Electrons



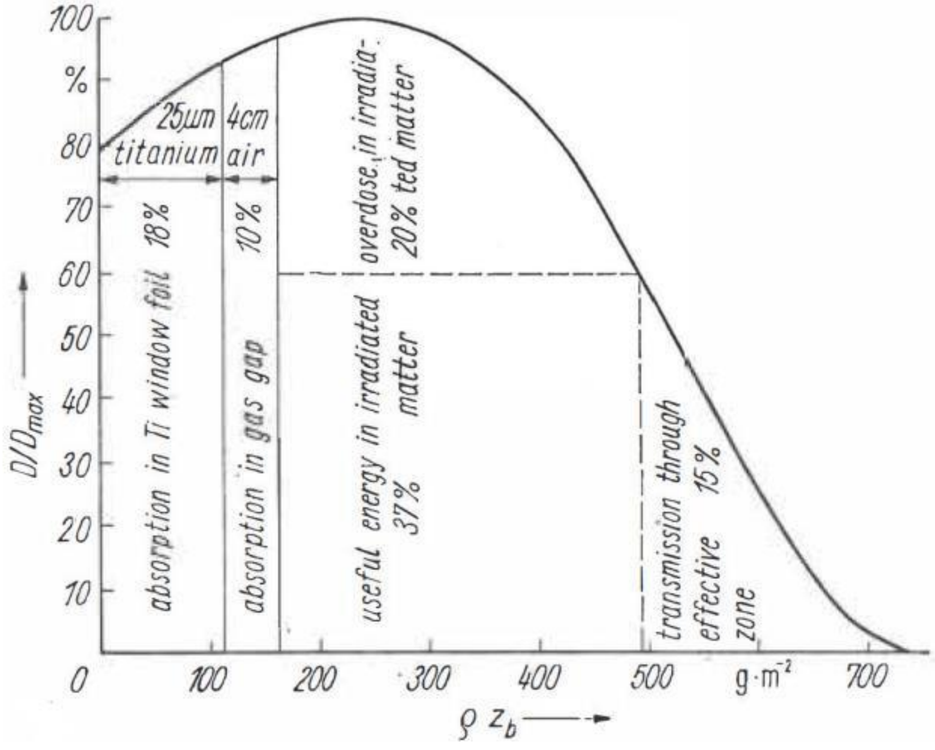


Figure 3. Penetration depth of accelerated electrons according to their energy and density of the absorber (left). Window foil and separating gap are sources of losses in low-energy EB processes (right) [9].

Introduction

Hybrid Wastewater Treatment

The irradiation of water produces several highly reactive, oxidizing and reducing radical species [10]:

$$H_2O \xrightarrow{EB} OH\cdot, e_{aq}{}^{-}, H\cdot, H_2, H_3O^{+}, H_2O_2 \qquad (1)$$

By combining low energy EB and ozone:

- The demands on radiation protection are kept to a minimum
- Low EB source dimensions and costs
- An economic, flexible and compact treatment module is realized

Methodology

Experimental Device

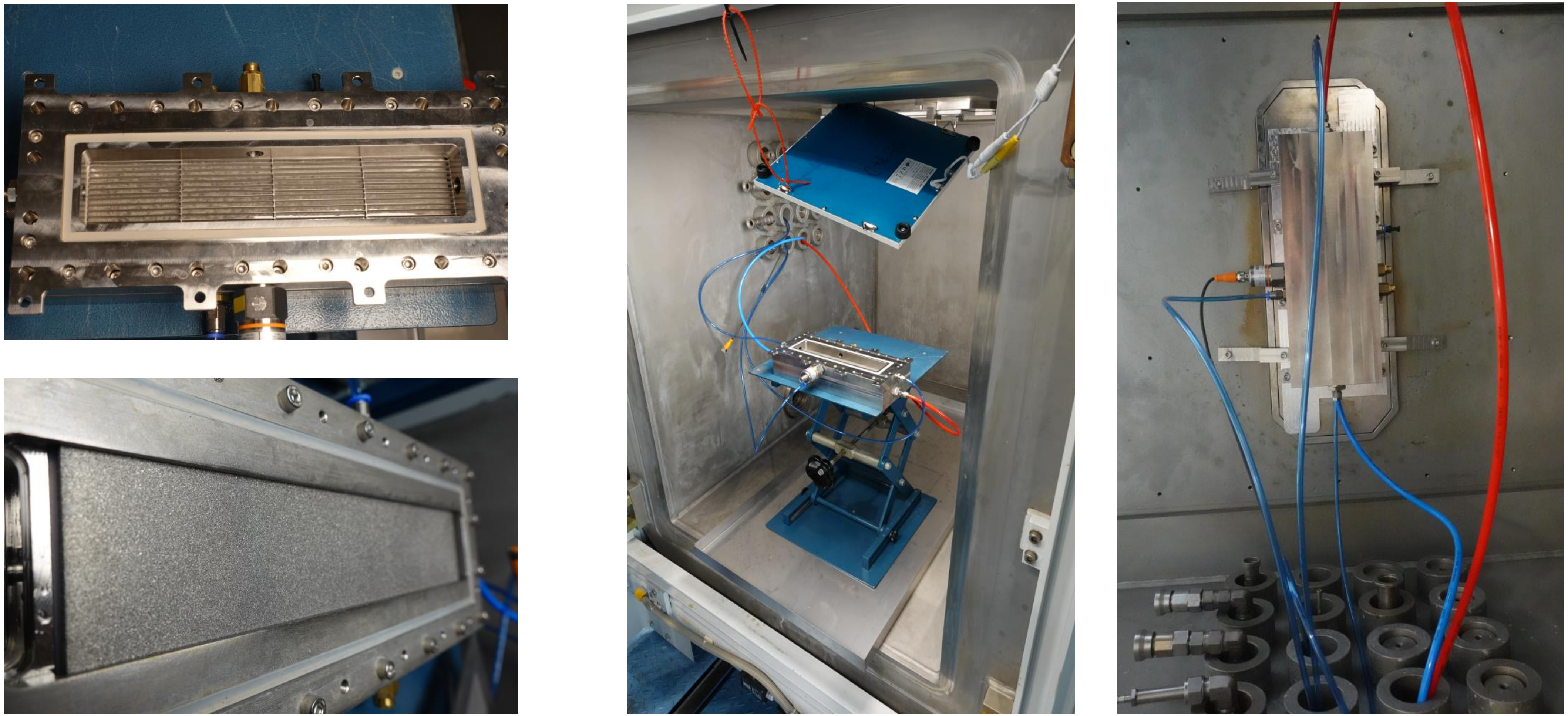
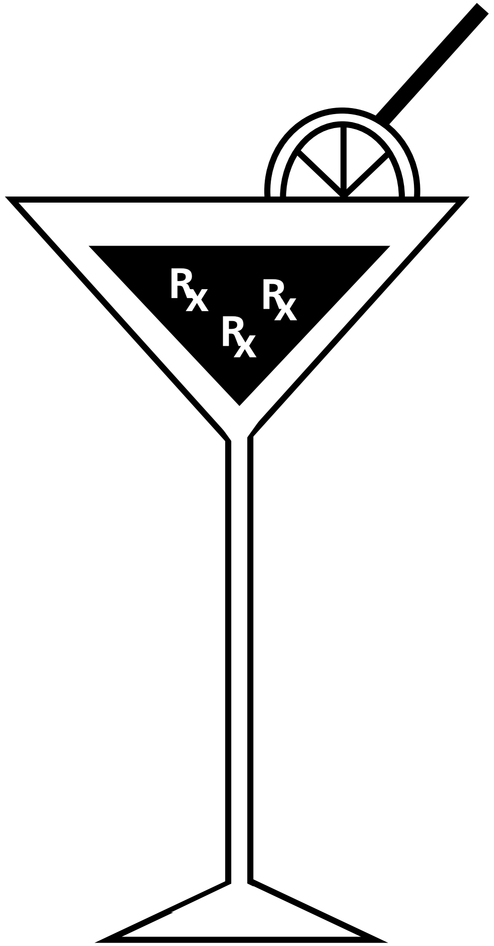


Figure 4. Treatment module (left) and treatment module inside REAMODE (right).

Methodology

Substance Irradiation



Pharmaceutical "cocktail" of five select substances in *deionized (DI) water* and *synthetic wastewater* were mixed

↓

Cocktail was treated using treatment module

↓

Concentration of substances before and after treatment determined using high-performance liquid chromatography

Methodology
Substance Irradiation

Figure 5. EB Facility REAMODE.

Irradiation done at Fraunhofer FEP's electron beam facility REAMODE with the following parameters:

- Maximum electron energy 200 keV
- Irradiation current 0.1-4 mA and 2 mA (multiple passes)
- Volume flow 4 l/min
- Gas flow 2 l/min

Results
Substance Irradiation

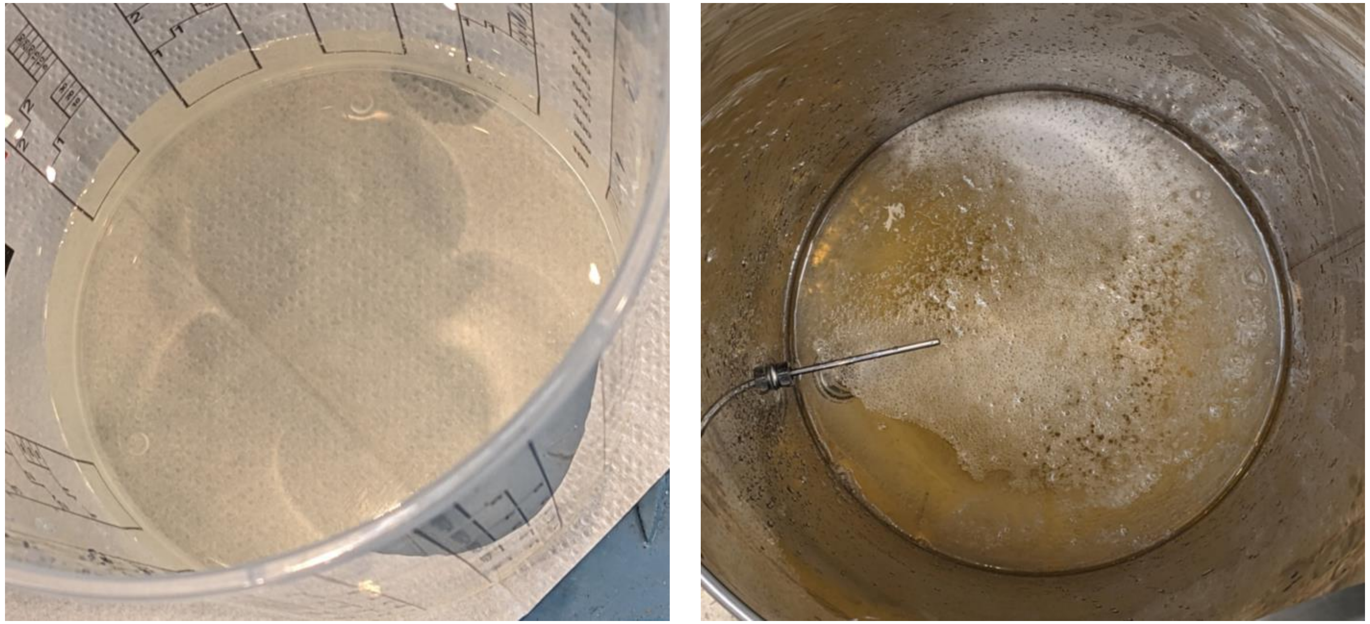


Figure 6. Pharmaceutical cocktail after irradiation.

Results

Substance Irradiation

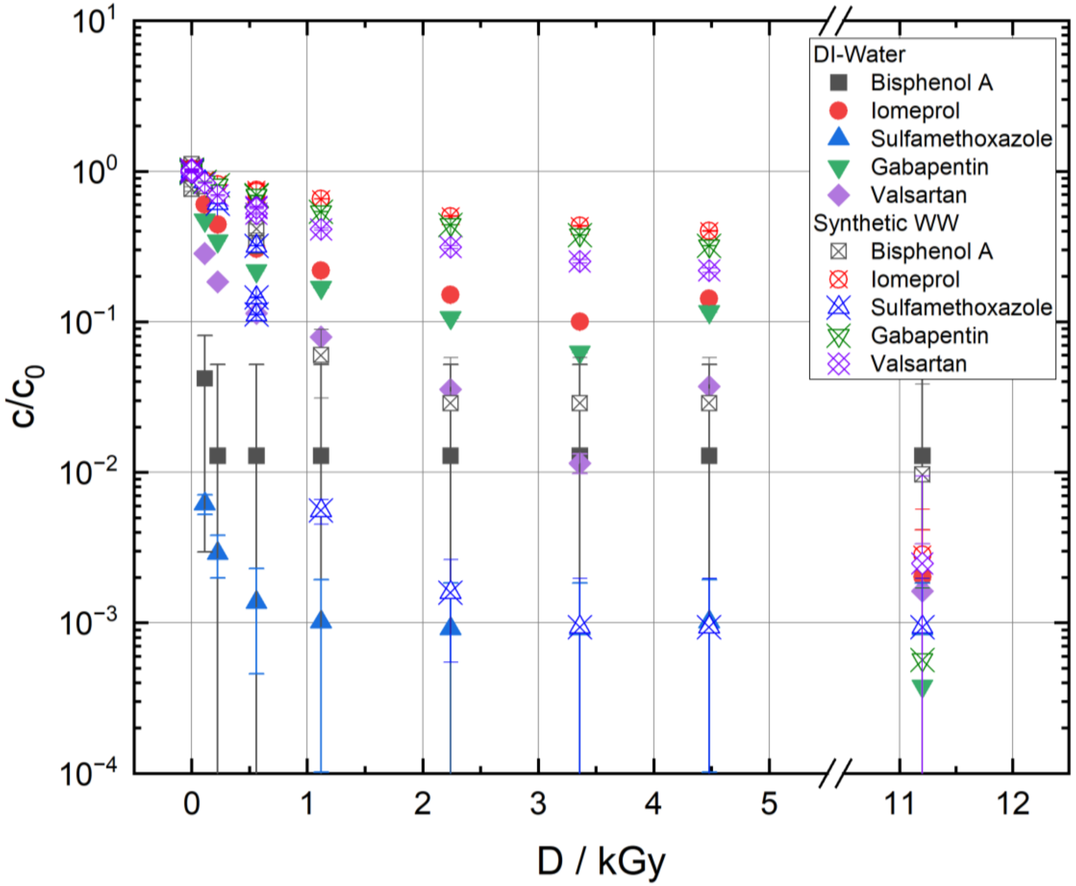


Figure 7. Relative concentration vs dose for five substances in DI-water and synthetic wastewater.

Significant degradation (>80%) achieved already at 2.2 kGy for all substances in deionized water and synthetic wastewater.

Fraunhofer FEP

Results

Substance Irradiation

Table 1. Doses at which significant degradation (>80%) is achieved for five select substances in deionised water (DI) and synthetic wastewater (SW).

Substance	Deionised Water	Synthetic Wastewater
Bisphenol A	0.1 kGy	0.6 kGy
Sulfamethoxazole	0.1 kGy	0.6 kGy
Valsartan	0.2 kGy	1.1 kGy
Gabapentin	1.1 kGy	1.1 kGy
Iomeprol	2.2 kGy	2.2 kGy

Results

Comparing Wastewater Treatment Methods

Energy Demands of Different Wastewater Treatment Methods

Powdered Organic Carbon (PAC)

10-40 mg/l

- 0.020-0.035 kWh/m^3 for adsorption step [11]
- 0.45 kWh/m^3 for whole process [12]

Ultraviolet (UV) Treatment

7200 J/m^2

- 0.026 kWh/m^3 for irradiation step [13]
- 0.5-1 kWh/m^3 for whole process [12]

EB + Ozone

2.2 kGy

- 0.003 kWh/m^3 for irradiation step

Results

Comparing Wastewater Treatment Methods

Table 2. Measured removal efficiencies with EB and ozone for 5 select substances in synthetic wastewater compared to traditional methods: powdered organic carbon (PAC) and ultra-violet (UV).

Substance	EB + O_3 (2.2 kGy)	EB + O_3 (11 kGy)	PAC [14]	UV [14]
Bisphenol A	97.1%	> 99.0%	5.3%	67.0%
Iomeprol	49.7%	> 99.7%	65.0%	65.0%
Sulfamethoxazole	99.8%	> 99.9%	31.0%	81.0%
Gabapentin	56.0%	> 99.9%	41.0%	2.0%
Valsartan	68.6%	> 99.8%	99.0%	5.0%

Work in Progress

Testing Biodegradability

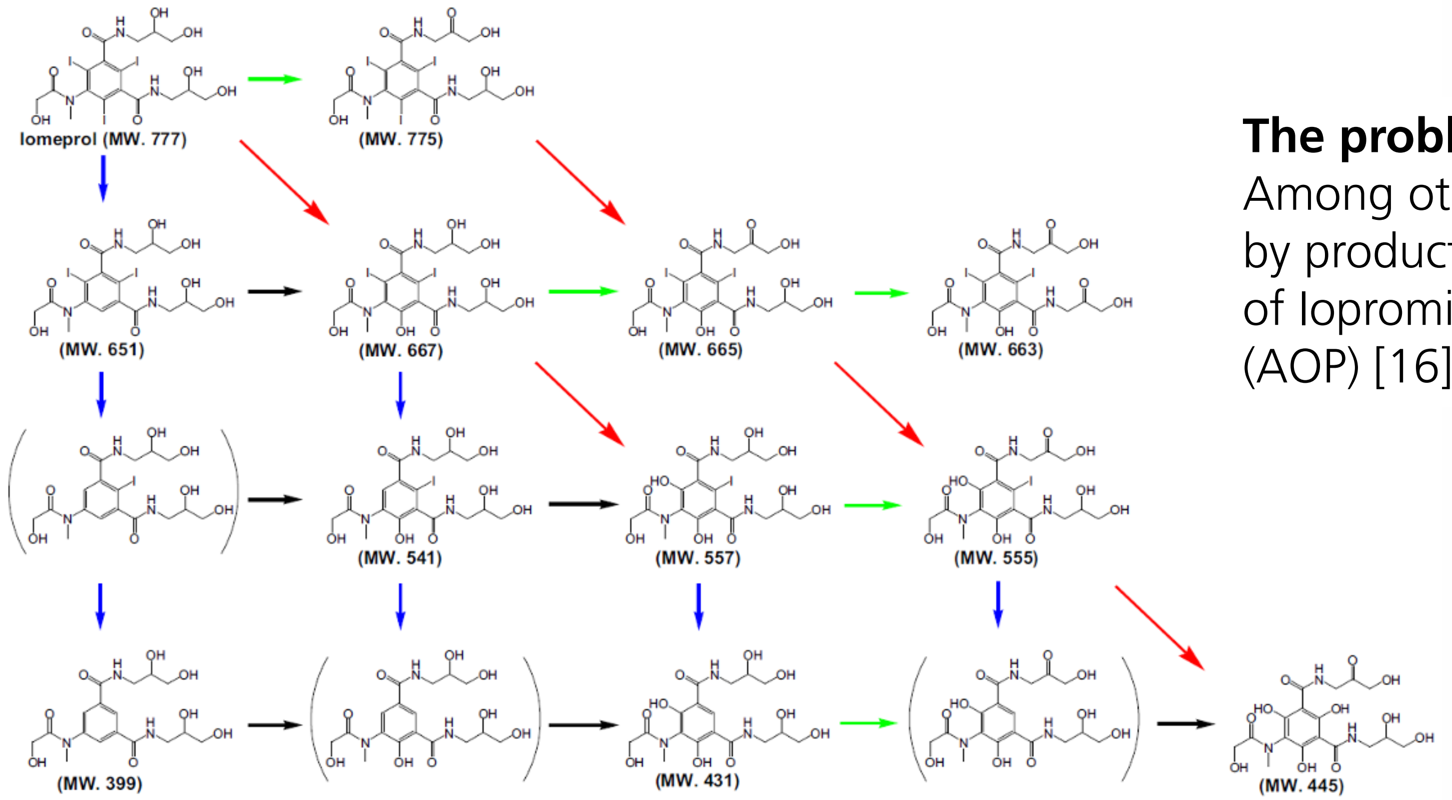


Figure 8. Degradation pathway of Iopromide. Taken from Jeong et al. [15].

The problem with degradation by-products:
Among other examples, 30 different degradation by products are formed from the transformation of Iopromide by advanced oxidation processes (AOP) [16].

Work in Progress

Testing Biodegradability

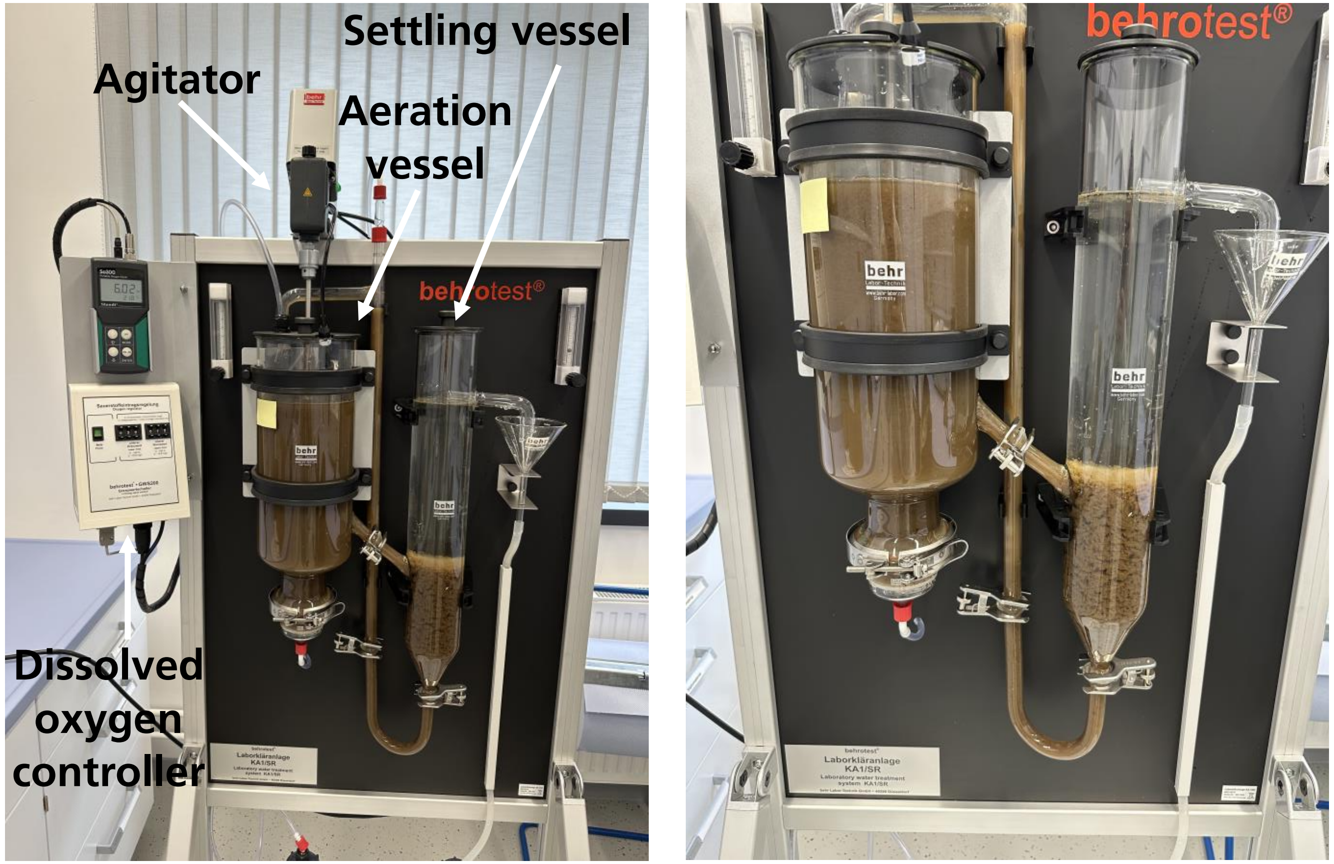


Figure 9. Laboratory scale wastewater treatment plant.

Meet Daisy, FEP's Laborkläranlage!

- The presence of numerous degradation by-products highlights the need for a biodegradability test
- Degradability is measured by taking chemical oxygen demand (COD) measurements
- 70% degradation = inherent ultimate biodegradability

Conclusion and Outlook

The hybrid treatment of EB + Ozone successfully degraded five select pharmaceuticals in DI water and synthetic wastewater

Analysis of degradation byproducts and their fate in further wastewater treatment and the environment is needed

An upscaling of the concept and expansion of its field of application must be developed

Thank you for your attention !

Fraunhofer FEP

Fraunhofer Institute for Electron Beam and Plasma Technology FEP

9th ITG International Vacuum Electronics Workshop 2024

Removal of Persistent Micropollutants From Wastewater By Hybrid Treatment With Low-Energy Electrons and Ozone

Lotte Ligaya Schaap, Tobias Teichmann, Andre Poremba, Gösta Mattausch, Simone Schopf, Elizabeth von Hauff

Contact

Lotte Ligaya Schaap
Department
“Customized Electron Beam Systems and Technologies”
Fraunhofer Institute for
Electron Beam and Plasma Technology FEP
Tel. +49 351 2586 375
Lotte.Ligaya.Schaap@fep.fraunhofer.de

Acknowledgements

This research was performed in a joint project with CREAVAC GmbH and co-funded by the European Union

creavac

Co-funded by the European Union

Freistaat Sachsen

This project is co-financed from tax revenues on the basis of the budget adopted by the Saxon State Parliament.

Appendix

Table 3. Removal efficiencies for 5 select substances in deionised water (DI) and synthetic wastewater (SW).

Substance	Medium	RE (2,2 kGy)	RE (11 kGy)
Bisphenol A	DI	> 98,7%	> 98,7%
	SW	97,1%	> 99,0%
Iomeprol	DI	84,8%	> 99,8%
	SW	49,7%	> 99,7%
Sulfamethoxazole	DI	> 99,9%	> 99,9%
	SW	99,8%	> 99,9%
Gabapentin	DI	89,3%	> 99,9%
	SW	56,0%	> 99,9%
Valsartan	DI	96,4%	> 99,8%
	SW	68,6%	> 99,8%

References

[1] T. J. Scheytt, P. Mersmann, and T. Heberer, “Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments,” *Journal of contaminant hydrology*, **83**, 1-2 (2006); doi: 10.1016/j.jconhyd.2005.11.002.

[2] L. Szabó *et al.,* “Electron beam treatment for tackling the escalating problems of antibiotic resistance: Eliminating the antimicrobial activity of wastewater matrices originating from erythromycin,” *Chemical Engineering Journal*, **321** (2017); doi: 10.1016/j.cej.2017.03.114.

[3] A. Capodaglio, “Contaminants of Emerging Concern Removal by High-Energy Oxidation-Reduction Processes: State of the Art,” *Applied Sciences*, **9**, 21 (2019); doi: 10.3390/app9214562.

[4] H. M. Coleman, M. I. Abdullah, B. R. Eggins, and F. L. Palmer, “Photocatalytic degradation of 17β-oestradiol, oestriol and 17α-ethynyloestradiol in water monitored using fluorescence spectroscopy,” *Applied Catalysis B: Environmental*, **55**, 1 (2005); doi: 10.1016/j.apcatb.2004.07.004.

[5] A. Kimura, M. Taguchi, Y. Ohtani, Y. Shimada, H. Hiratsuka, and T. Kojima, “Treatment of wastewater having estrogen activity by ionizing radiation,” *Radiation Physics and Chemistry*, **76**, 4 (2007); doi: 10.1016/j.radphyschem.2006.04.005.

[6] Tappert, L., Bunge, M., Hoehne, D., Dlugi, I., Fetters, K., Fischer, B., ... & Gestermann, S. (2024). Bisphenol A in surface waters in Germany: Part I. Reassessment of sources and emissions pathways for FlowEQ modeling. *Integrated Environmental Assessment and Management*, *20*(1), 211-225.

[7] Kormos, J. L., Schulz, M., & Ternes, T. A. (2011). Occurrence of iodinated X-ray contrast media and their biotransformation products in the urban water cycle. *Environmental science & technology*, *45*(20), 8723-8732.

References

[8] Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman Jr, C. U., & Mohan, D. (2019). Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods. *Chemical reviews*, *119*(6), 3510-3673.

[9] S. Schiller et al., Electron Beam Technology, 477 (1982).

[10] H. Bluhm, B. Han, A. G. Chmielewski *et al.*, "Electron beam devices for materials processing and analysis," in *Vacuum Electronics – Components and Devices*, J. A. Eichmeier and M. Thumm, Eds., Springer Science & Business Media, Berlin, Heidelberg, New York (2008).

[11] Mousel, D., Krebber, K., Palmowski, L., Lyko, S., Thöle, D., & Pinnekamp, J. (2015). Energy demand for micropollutant removal in municipal wastewater treatment plants. IWA YWP Advanced wastewater treatment and water reuse–the future is now.

[12] Adamczak, K., Lyko, S., Nafo, I., Evenblij, H., Cornelissen, A., Igos, E., ... & Stalder, T. (2012). Pharmaceutical residues in the aquatic system–a challenge for the future.

[13] Bailey, J. R., Ahmad, S., & Batista, J. R. (2020). The impact of advanced treatment technologies on the energy use in satellite water reuse plants. *Water*, *12*(2), 366.

[14] Verlicchi Aukidy , M.; , P.; Al and treatment of hospital effluent? 514, pp. 467 Zambello , E. (2015): What have we learned from worldwide experiences on the management an overview and a discussion on perspectives. In The Science of the total environment 491. DOI: 10.1016/j.scitotenv.2015.02.020.

References

[15] Jeong, J., Jung, J., Cooper, W. J., & Song, W. (2010). Degradation mechanisms and kinetic studies for the treatment of X ray contrast media compounds by advanced oxidation/reduction processes. Water Research, 44(15), 4391

[16] Nowak, A., Pacek , G., & Mrozik 4398. , A. (2020). Transformation and ecotoxicological effects of iodinated X-- ray contrast media. Reviews in Environmental Science and Bio/Technology, 19(2), 337 354

