Dr. Jochen Türk
Dipl.-Ing. H. Vitz, Dr. T.K. Kiffmeyer,
Dipl.-Ing. B. Becker, Dr.-Ing. S. Kabasci,
Prof. Dr. H.-M. Kuß

Institut für Energie- und Umwelttechnik e.V.

Removal of pharmaceuticals from the water cycle: efficiency, costs and benefits of different concepts and treatment technologies

AQUAbase Workshop on mitigation technologies
– eliminating trace organics during water treatment

Fraunhofer Institut Umwelt-, Sicherheits-, Energietechnik UMSICHT

Aachen, 27./28.11.2007

Ideen eine Zukunft geben

UNIVERSITÄT DUISBURG ESSEN

Overview

IUTA e.V

History

1989	founded as Institute for Environmental Technology and – Analytics
1991	Associated Institute of the University of Duisburg-Essen
1998	renamed in Institute of Energy and Environmental Technology

IUTA e.V.
Bliersheimer Str. 60
47229 Duisburg

Internet: www.iuta.de

Facts & Figures (2006):

Employees	139
Office/Laboratory	2400 m²
Technical Facilities	4000 m²
Turnover	ca. 5.7 Mio €

Introduction

- **Pharmaceuticals in the aquatic environment**
  - persistent,
  - toxic, mutagenic and/or endocrine effects,
  - antibiotic resistance promoter
- **hospital waste water = important input source**
  - especially potent and persistent agents
  - High concentrations at partial streams like toilet effluents
- **Industrial waste waters: special composition**
  - High COD, particles and highest compound concentrations
- **Development of suitable mitigation technologies for direct treatment and WWTPs necessary**

Possibilities for reduction of drug input

Occurrence of antineoplastic drugs

- Toilet effluents: 50 – 5.000 µg/L
- Hospital waste water: 1 – 50 µg/L

- STP inflow: max. 100 ng/L
- STP effluent: max. 80 ng/L
- Surface water: max. 180 ng/L

- Production waste water: up to 200.000 µg/L
  (special waste incineration or special treatment procedures like AOP; no disposal to surface water!)

Treatment of hospital waste waters

<u>*2002–2004*</u>*: Development in laboratory scale* → effectiveness

<u>*2005–2007*</u>*:* Up-Scaling, pilot plant → economic efficiency

→ test phase

<u>Partner</u>: Institute of Energy and Environmental Technology iuta

Fraunhofer Institut Umwelt-, Sicherheits-, Energietechnik UMSICHT

<u>Funding:</u> Federal Ministry of Economics and Technology through the German Federation of Industrial Cooperative Research Associations (AiF) in the program IGF

AiF Ideen eine Zukunft geben

Compounds and Conditions

- ***Antineoplastics*** toxic, mutagenic, carcinogenic, persistent
- ***Antibiotics*** *promotion of resistance, mutagenic* (some), persistent
- ***Steroids*** endocrine effects, persistent
- ***Contrast media*** persistent, accumulation

<u>Treatment of high loaded part streams</u>

- ***Toilets*** 1-10
- ***Volume*** 10-50 L/h; 100-500 L/d
- ***Concentrations*** 0.1 (cytotoxic drugs) – 1 mg/L (antibiotics)
- ***DOC*** 100 – 800 mg/L
- ***COD*** 300 – 1.000 mg/L

Advance Oxidation Processes (AOP)

Formation of hydroxyl-radicals by UV-light and oxidation agents

$$H_2O_2 \xrightarrow{h \cdot \nu \, (254\,nm)} 2 \cdot OH$$

$$R\text{-}H + \cdot OH \rightarrow R \cdot + H_2O$$

➔ **primary degradation and reduction of (eco-)toxicity**

➔ **better biodegradation**

(➔ complete degradation = mineralisation: too expensive !)

UV treatment plants

Laboratory scale (Heraeus)

Semi technical scale (UMEX/IBL)

Optimised parameter

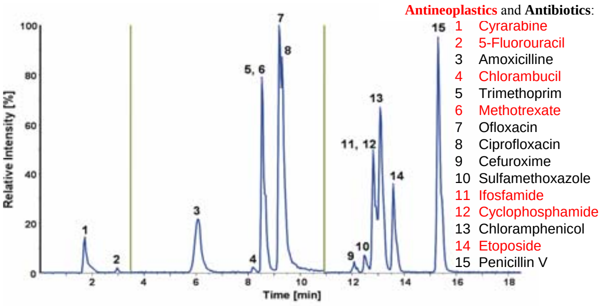
- ***Separation***: **sedimentation >** filtration
- ***UV-sources***: Hg-low pressure or Hg-medium pressure lamp
- ***Oxidants***: $\mathbf{H_2O_2 > O_3 >}$ H_2O_2/O_3
- ***Concentrations***: 0.1 - 7.5 g/L H_2O_2; 25 - 80 mg O_3 min^{-1} L^{-1}
- ***Temperature***: 20 - 40°C
- ***Treatment time***: 30 - 120 min

Analysis

1. *Compound specific analysis* (LC-MS/MS und LC-MS^n)
   ➔ primary degradation, detection of degradation products
2. *Sum parameters*: DOC, $BOD_{5\,(28)}$/COD
3. *Toxicity*: Luminescent Bacteria
4. *Mutagenicity*: umu & ames - Test
5. *Microbiological:* Determination of CFU
6. (*Biological degradation:* *laboratory WWTP)*

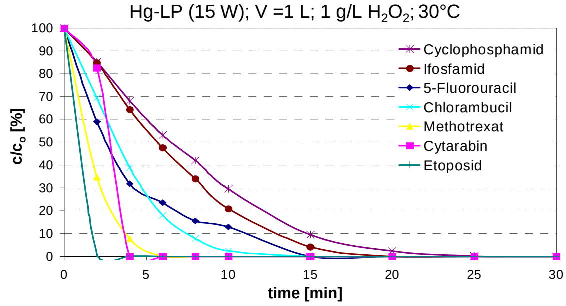
LC-MS/MS – Chromatogram (TIC)

of a spiked toilet effluent (100 µg/L)



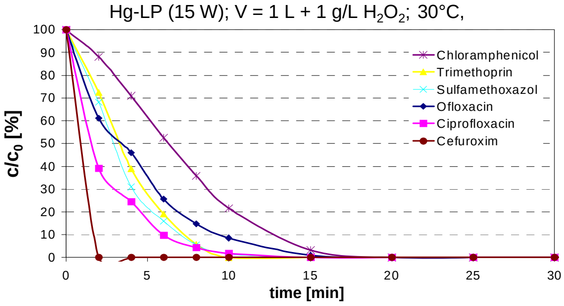
Results: Degradation of Antineoplastics

spiked toilet effluent (100 µg/L); 24 h sedimentation;
Hg-LP (15 W); V =1 L; 1 g/L H_2O_2; 30°C



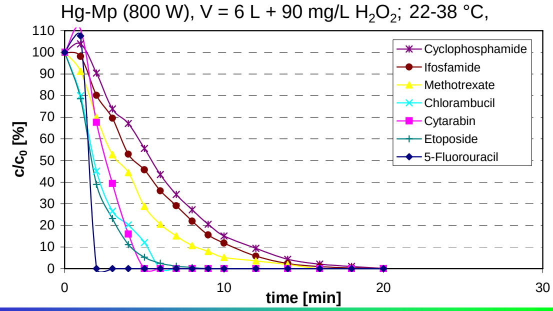
Results: Degradation of Antibiotics

spiked toilet effluent (1000 µg/L); 24 h sedimentation;
Hg-LP (15 W); V = 1 L + 1 g/L H_2O_2; 30°C,



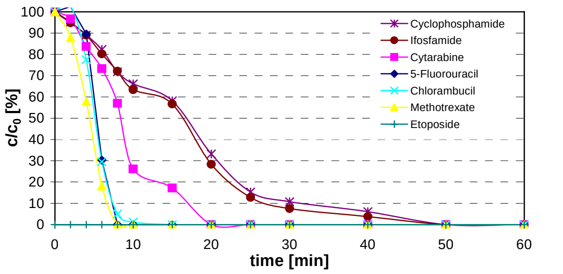
Hg-Medium Pressure Lamp

spiked toilet effluent (100 µg/L); 24 h sedimentation;
Hg-Mp (800 W), V = 6 L + 90 mg/L H_2O_2; 22-38 °C,



Ozonisation

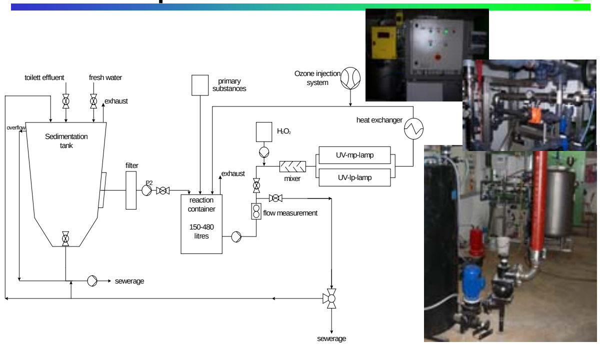
spiked toilet effluent (100 µg/L); 24 h sedimentation;
O_3 bubble column (WEDECO) c_{O_3} = 25 mg/min L^{-1}; V = 4 L; 20°C,



Results: sum parameters

	untreated	*treated*	*reduction*
pH	7,5 - 8,5	6,8 - 8,2	-
DOC [mg/L]	200 - 800	200 - 700	10 - 30 %
COD [mg O_2/L]	200 - 600	80 - 200	30 - 60 %
BOD-values	not clear → interferences of peroxides		
Lum. bact. [GL]	32 - 200	2 - 12	50 - **90 %**
umu-Test [G_{EU}]	384 - 1536	1,5 - 12	90 - **99 %**
Bioburden	no CFU detectable after AOP		

AOP – Pilot plant



Experimental design

- Waste water of 14 toilets (urine, faces, rinsing water, hand basin)
- Collection and sedimentation in the first tank (1 m^3)
- Pump of the supernatant to the reaction tank
  (standard experiment: 230 L)
- Spking with the investigated compounds
  (e.g. Cyclophosphamide, Chloramphenicol, Ciprofloxacine, Sulfamethoxazole, Carbamazepin)
- Batch - treatment using the different oxidation processes
- Release of the clean water after control analysis and of the sediments to the sewer

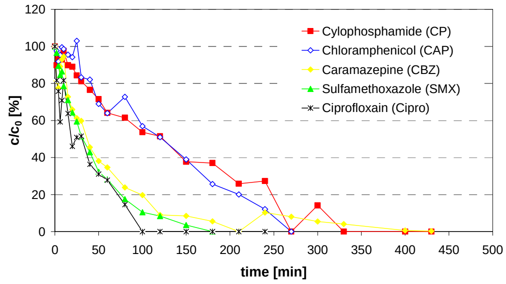
Analysis

Compounds: **antibiotics, cytostatic drugs,** Carbamazepine, Diclofenac, ICM, psychiatric drugs

- LC-MS/MS: compound specific
- pH, SAK_{254}, TOC, DOC, CSB, BSB_5, [AOX, $c(H_2O_2)$, $c(O_3)$]
  → **no trends detectable**
- CO_3^{2-}, Ca, Mg, Fe, Mn
  → **no scaling on the UV lamps observed**
- Lum. bact., umu- and ames-test
  → **no toxicity after UV-oxidiation and Ozonisation!**

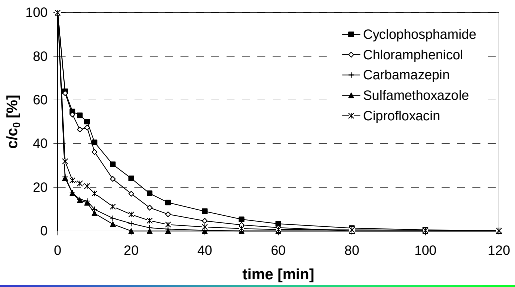
Pilot plant results: Hg-LP (80 W)

spiked toilet effluent (100 µg/L); 24 h sedimentation;
V = 230 L, 1 g/L H_2O_2, 20°C



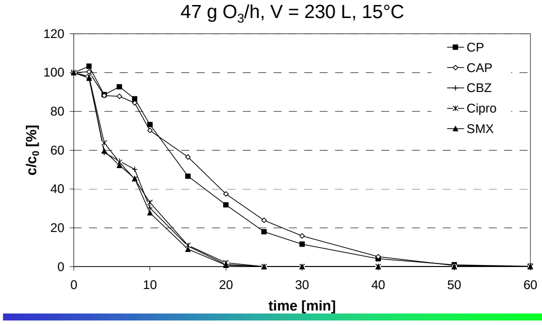
Pilot plant results: Hg-MP (2.200 W)

spiked toilet effluent (100 µg/L); 24 h sedimentation;
V = 230 L, 1 g/L H_2O_2, 20°C



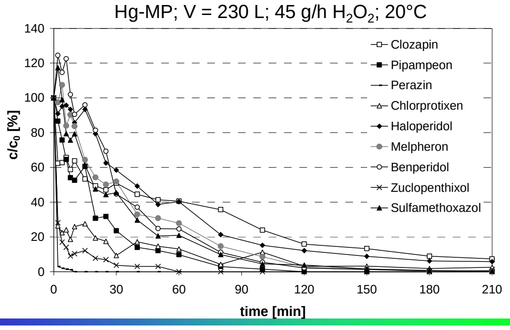
Pilot plant results: Ozone

spiked toilet water (100 µg/L); 24 h sedimentation;
47 g O_3/h, V = 230 L, 15°C



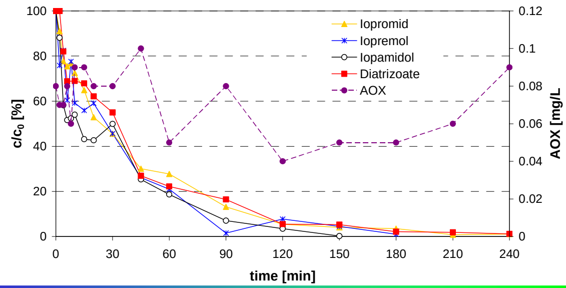
Psychiatric drugs

spiked toilet water(100 µg/L); 24 h sedimentation;
Hg-MP; V = 230 L; 45 g/h H_2O_2; 20°C

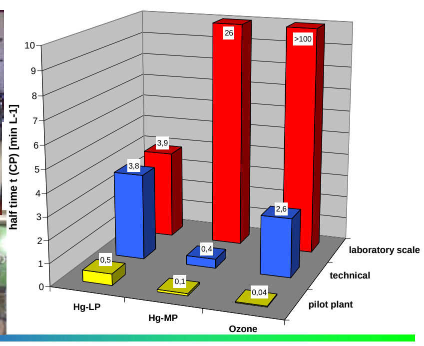


Iodated Contrast media

spiked toilet water(100 µg/L); 24 h sedimentation;
Hg-MP; V = 230 L; 32 g/h H_2O_2; 20°C

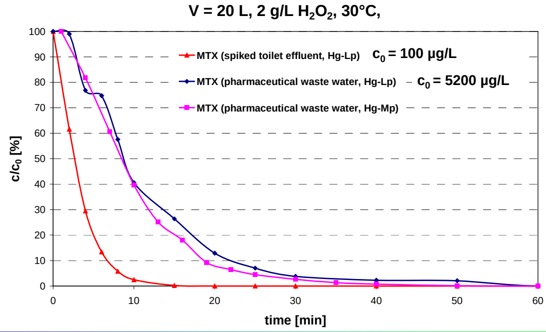


Efficiency increase from 1 L laboratory scale to a 500 L pilot plant



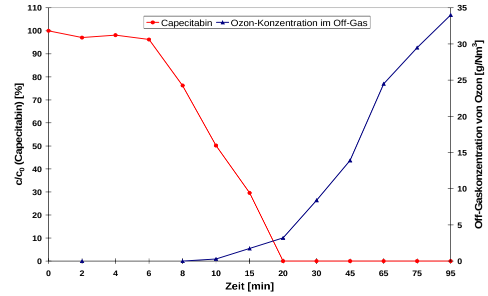
Case study I: Industrial Waste Water

V = 20 L, 2 g/L H_2O_2, 30°C,



Pharmaceutical waste water II

V = 200 L, c_0 = 200.000 µg/l, O_3: 110 g/Nm³, gasflow: 0.5 Nm³/h, 15°C

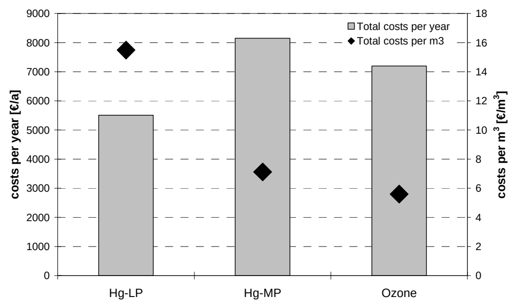


[E. Billenkamp, J. Straub, M. Studer, J. Türk. *Pharm. Ind.* 2007, 69 (10): 1211-1213]

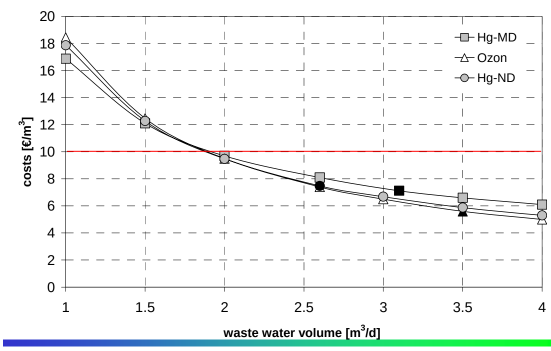
Treatment costs with the AOP pilot plant

	Hg-Nd	Hg-Md	Ozone
Invest	**23,600 €**	**28,100 €**	**41,000 €**
Annuity (12 years operation, 6 % interest)	2,815 €/a	3,352 €/a	4,902 €/a
treatment duration for 230 L toilet waste water	342 min	106 min	94 min
Electric energy costs (0.10 €/kWh)	781 €/a	2,398 €/a	648 €/a
Operation facilities (0.45 €/kg H_2O_2)	160 €/a	515 €/a	--
Maintenance costs (3 % of Invest)	708 €/a	843 €/a	1233 €/a
Personnel (0.5 resp. 0.2 h/week, 40 €/h)	1040 €/a	1040 €/a	416 €/a
Max. treatment volume per day [m³/d]	**1.0**	**3.1**	**3.5**
Yearly costs for treatment of max. volume [€/a]	**5,504**	**8,148**	**7,200**

Treatment costs with the AOP pilot plant

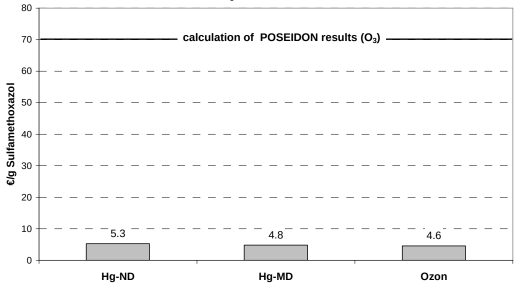


Specific treatment costs



Freight calculations

Degradation of 1 g sulfamethoxazole in hospital waste water (c_0 = 1000 µg/L) and WWTP with ozone (c_0 = 0,6 µg/L, EU Project POSEIDON)



Direct Treatment

- Collection of urine

  + Elimination of ICM from the water cycle
  - Adsorption — not possible
  - Oxidation — not possible
  - Reduction with Fe^0 — possible, but under investigation (TU Berlin) — costs ?
  - Incineration: **expensive** → not suitable
  - Rotary kiln with I_2 recovery - Bayer Schering Pharma produced 2006 283 t I_2 from solid and liquid wastes
    → possible **costs/profits ?**

  - Elimination of other pharmaceuticals not suitable

Hospital waste water

- **Ozone/AOP of high loaded part streams**
  (pilot stage - IUTA)
  - + Effective, but installation is only in new buildings suitable
  - + Early elimination of high potent agents like antineoplastics or psychiatric drugs
  - + approx. 5,000 – 8,000 €/a
  - – Further treatment for the reduction of other compounds necessary
- **Treatment of the hole hospital effluent**
  (full scale – Waldbröl [Pöyry/RWTH Aachen])
  - + MBR + tertiary treatment (AOP, PAC ?)
  - – Costs ?
  - – Only 20 – 30 % of the total load!

Centralized treatment in WWTPs

- **CAS + MBR comparable worse efficient!**
- **NF/RO**
  (full scale plants available)
  - – Effective, but expensive 0.20 – 0.50 €/m^3
  - – Further treatment of retentate necessary
- **PAC**
  (pilot plant WWTP Steinhäule, Ulm, Germany)
  - + Effective adsorption (> 90 %) with 10 to 20 mg/L (diatrizoate only 44 %)
  - + Costs: 0.10 – 0.20 € /m^3
  - - PAC recycling/incineration

Centralized treatment in WWTP

- **UV/H2O2**
  - Effective, but too expensive 0.60 – 0.90 €/m³
- **Ozonisation**
  - \+ Effective (> 99 %)
  - – Not suitable for ICM
  - – Formation of oxidation products and bromate
    → Sandfiltration/biofilter
    → further ecotoxicity tests/investigations necessary
  - **+ "Cheap"**, but costs differ between pilot and full scale estimations:
    - pilot: 0.02 – 0.05 €/m³ (POSEIDON, Berlin, Dortmund)
    - Full scale: 0.07 - 0.14 €/m³ (ARA Wüeri Regensdorf/EAWAG)

Summary

- **Successful development of AOPs from laboratory scale to a 500 L pilot plant**
- **Effective treatment of high loaded toilet waste waters is possible with all three investigated procedures**
- **AOPs are also the suitability for treatment of production waste water from the pharmaceutical industry** (8-12 €/m³)
- **AOPs could not eliminate ICM**
- **Sustainable protection of the water cycle needed**
  → source control
  → extension of WWTPs

Summary and Outlook

- **Elimination is economically possible**
  - Separation of urine
  - Treatment of hot spots
  - Treatment of hospital waste waters
  - Extension o WWTPs
  - Control of effluents, surface and drinking waters
- **O_3 and PAC are effective and also economic efficient**
  - Additionally costs: approx. 0.05 – 0.20 €/m³
- **Further research on oxidation products and ecotoxcicity tests**
- **consideration of the state of the art for updated water protective regulations is needed!**

Acknowledgments

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Thank you for your attention!

Any Questions?

tuerk@iuta.de 28.11.2007 Efficiency of Pharmaceutical removal 41