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

Aachen, 27./28.11.2007
Overview

1. IUTA e.V.
2. Introduction
3. Development of an AOP for hospital waste waters
   • Laboratory and semi technical experiments
   • Scale up to a pilot plant
   • Costs and comparison to WWTP
4. Treatment of special pharmaceutical waste waters
5. Comparison of different concepts and technologies
   • Collection - Direct treatment – WWTP – DW
   • Incineration – MBR/NF/RO – AC/PAC – AOP/Ozone
6. Summary and Outlook
7. Acknowledgement
IUTA e.V.

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Internet: www.iuta.de

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


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

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet effluents</td>
<td>50 – 5,000 µg/L</td>
</tr>
<tr>
<td>Hospital waste water</td>
<td>1 – 50 µg/L</td>
</tr>
<tr>
<td>STP inflow</td>
<td>max. 100 ng/L</td>
</tr>
<tr>
<td>STP effluent</td>
<td>max. 80 ng/L</td>
</tr>
<tr>
<td>Surface water</td>
<td>max. 180 ng/L</td>
</tr>
<tr>
<td>Production waste water</td>
<td>up to 200,000 µg/L</td>
</tr>
</tbody>
</table>

- Special waste incineration or special treatment procedures like AOP; no disposal to surface water!
Treatment of hospital waste waters

**2002–2004:** Development in laboratory scale ➔ effectiveness

**2005–2007:** Up-Scaling, pilot plant ➔ economic efficiency ➔ test phase

**Partner:** Institute of Energy and Environmental Technology

**Funding:** Federal Ministry of Economics and Technology through the German Federation of Industrial Cooperative Research Associations (AiF) in the program IGF
## Compounds and Conditions

- **Antineoplastics**
  - toxic, mutagenic, carcinogenic, persistent

- **Antibiotics**
  - *promotion of resistance, mutagenic* (some), persistent

- **Steroids**
  - endocrine effects, persistent

- **Contrast media**
  - persistent, accumulation

## Treatment of high loaded part streams

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Toilets</strong></td>
<td>1-10</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>10-50 L/h; 100-500 L/d</td>
</tr>
<tr>
<td><strong>Concentrations</strong></td>
<td>0.1 (cytotoxic drugs) – 1 mg/L (antibiotics)</td>
</tr>
<tr>
<td><strong>DOC</strong></td>
<td>100 – 800 mg/L</td>
</tr>
<tr>
<td><strong>COD</strong></td>
<td>300 – 1.000 mg/L</td>
</tr>
</tbody>
</table>
Advance Oxidation Processes (AOP)

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

\[ \text{H}_2\text{O}_2 \xrightarrow{h \cdot \nu (254 \text{ nm})} 2 \cdot \text{OH} \]

\[ \text{R} - \text{H} + \cdot \text{OH} \rightarrow \text{R} \cdot + \text{H}_2\text{O} \]

- primary degradation and reduction of (eco-)toxicity
- better biodegradation

(\(\Rightarrow\) 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:** \( \text{H}_2\text{O}_2 > \text{O}_3 > \text{H}_2\text{O}_2 / \text{O}_3 \)
- **Concentrations:**
  - \( 0.1 - 7.5 \text{ g/L H}_2\text{O}_2 \)
  - \( 25 - 80 \text{ mg O}_3 \text{ min}^{-1} \text{ L}^{-1} \)
- **Temperature:** 20 - 40°C
- **Treatment time:** 30 - 120 min
Analysis

1. **Compound specific analysis** (LC-MS/MS und LC-MS\textsuperscript{n})
   → primary degradation, detection of degradation products

2. **Sum parameters**: DOC, BOD\textsubscript{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)

Antineoplastics and Antibiotics:
1. Cyrrabine
2. 5-Fluorouracil
3. Amoxicilline
4. Chlorambucil
5. Trimethoprim
6. Methotrexate
7. Ofloxacin
8. Ciprofloxacin
9. Cefuroxime
10. Sulfamethoxazole
11. Ifosfamide
12. Cyclophosphamide
13. Chloramphenicol
14. Etoposide
15. Penicillin V

Relative Intensity [%]

Time [min]
Results: Degradation of Antineoplastics

spiked toilet effluent (100 µg/L); 24 h sedimentation; Hg-LP (15 W); V =1 L; 1 g/L H₂O₂; 30°C

<table>
<thead>
<tr>
<th>Substance</th>
<th>C/c₀ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclophosphamid</td>
<td></td>
</tr>
<tr>
<td>Ifosfamid</td>
<td></td>
</tr>
<tr>
<td>5-Fluorouracil</td>
<td></td>
</tr>
<tr>
<td>Chlorambucil</td>
<td></td>
</tr>
<tr>
<td>Methotrexat</td>
<td></td>
</tr>
<tr>
<td>Cytarabin</td>
<td></td>
</tr>
<tr>
<td>Etoposid</td>
<td></td>
</tr>
</tbody>
</table>

C/c₀ [%] vs. time [min]
Results: Degradation of Antibiotics

spiked toilet effluent (1000 µg/L); 24 h sedimentation; Hg-LP (15 W); V = 1 L + 1 g/L H2O2; 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 \( \text{H}_2\text{O}_2 \); 22-38 °C,
Ozonisation

spiked toilet effluent (100 µg/L); 24 h sedimentation;
O₃ bubble column (WEDECO) cₒ₃ = 25 mg/min L⁻¹; V = 4 L; 20°C,
## Results: sum parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>untreated</th>
<th>treated</th>
<th>reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7,5 - 8,5</td>
<td>6,8 - 8,2</td>
<td>-</td>
</tr>
<tr>
<td>DOC [mg/L]</td>
<td>200 - 800</td>
<td>200 - 700</td>
<td>10 - 30 %</td>
</tr>
<tr>
<td>COD [mg O₂/L]</td>
<td>200 - 600</td>
<td>80 - 200</td>
<td>30 - 60 %</td>
</tr>
<tr>
<td>BOD-values</td>
<td>not clear</td>
<td>→ interferences of peroxides</td>
<td></td>
</tr>
<tr>
<td>Lum. bact. [GL]</td>
<td>32 - 200</td>
<td>2 - 12</td>
<td>50 - 90 %</td>
</tr>
<tr>
<td>umu-Test [Gₑᵤ]</td>
<td>384 - 1536</td>
<td>1,5 - 12</td>
<td>90 - 99 %</td>
</tr>
<tr>
<td>Bioburden</td>
<td>no CFU detectable after AOP</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
AOP – Pilot plant

- Toilet effluent
- Fresh water
- Overflow
- Sedimentation tank
- Filter
- Primary substances
- Ozone injection system
- Heat exchanger
- H₂O₂
- Reaction container (150-480 litres)
- UV-mp-lamp
- UV-lp-lamp
- Flow measurement
- Exhaust
- Sewerage
Experimental design

- Waste water of 14 toilets (urine, faces, rinsing water, hand basin)
- Collection and sedimentation in the first tank (1 m³)
- Pump of the supernatant to the reaction tank (standard experiment: 230 L)
- Spiking with the investigated compounds (e.g. Cyclophosphamide, Chloramphenicol, Ciprofloxacin, 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\textsubscript{254}, TOC, DOC, CSB, BSB\textsubscript{5}, [AOX, c(H\textsubscript{2}O\textsubscript{2}), c(O\textsubscript{3})]
  → no trends detectable
- CO\textsubscript{3}\textsuperscript{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 H₂O₂, 20°C

- Cylophosphamide (CP)
- Chloramphenicol (CAP)
- Caramazepine (CBZ)
- Sulfamethoxazole (SMX)
- Ciprofloxain (Cipro)
Pilot plant results: Hg-MP (2.200 W)

spiked toilet effluent (100 µg/L); 24 h sedimentation;  
V = 230 L, 1 g/L H₂O₂, 20°C

- Cyclophosphamide
- Chloramphenicol
- Carbamazepin
- Sulfamethoxazole
- Ciprofloxacin
Pilot plant results: Ozone

spiked toilet water (100 µg/L); 24 h sedimentation; 47 g O₃/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 H₂O₂; 20°C
Iodated Contrast media

spiked toilet water (100 µg/L); 24 h sedimentation; Hg-MP; V = 230 L; 32 g/h H₂O₂; 20°C
Efficiency increase from 1 L laboratory scale to a 500 L pilot plant

![Graph showing half time (t) values for Hg-LP, Hg-MP, and Ozone in laboratory scale, technical, and pilot plant configurations.](image)

- **Hg-LP**
  - Laboratory scale: 0.5
  - Technical: 3.8
  - Pilot plant: 3.9

- **Hg-MP**
  - Laboratory scale: 0.1
  - Technical: 0.4
  - Pilot plant: 2.6

- **Ozone**
  - Laboratory scale: 0.04
  - Technical: 26
  - Pilot plant: >100

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28.11.2007  
Efficiency of Pharmaceutical removal
**Case study I: Industrial Waste Water**

\[ V = 20 \text{ L}, \ 2 \text{ g/L H}_2\text{O}_2, \ 30^\circ\text{C}, \]

- **MTX (spiked toilet effluent, Hg-Lp)**  \( c_0 = 100 \mu\text{g/L} \)
- **MTX (pharmaceutical waste water, Hg-Lp)**  \( c_0 = 5200 \mu\text{g/L} \)
- **MTX (pharmaceutical waste water, Hg-Mp)**

\[
\begin{align*}
\text{time [min]} & \quad 0 & 10 & 20 & 30 & 40 & 50 & 60 \\
\text{c/c}_0 [%] & \quad 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0
\end{align*}
\]
Pharmaceutical waste water II

$V = 200 \text{ L, } c_0 = 200.000 \mu g/l, O_3: 110 \text{ g/Nm}^3, \text{ gasflow: } 0.5 \text{ Nm}^3/h, 15^\circ C$

$\frac{c}{c_0} (\text{Capecitabin}) [%]$

Zeit [min]

Off-Gaskonzentration von Ozon [g/Nm$^3$]

[Capecitabin - Ozon-Konzentration im Off-Gas]

## Treatment costs with the AOP pilot plant

<table>
<thead>
<tr>
<th></th>
<th>Hg-Nd</th>
<th>Hg-Md</th>
<th>Ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invest</td>
<td>23,600 €</td>
<td>28,100 €</td>
<td>41,000 €</td>
</tr>
<tr>
<td>Annuity (12 years operation, 6 % interest)</td>
<td>2,815 €/a</td>
<td>3,352 €/a</td>
<td>4,902 €/a</td>
</tr>
<tr>
<td>treatment duration for 230 L toilet waste water</td>
<td>342 min</td>
<td>106 min</td>
<td>94 min</td>
</tr>
<tr>
<td>Electric energy costs (0.10 €/kWh)</td>
<td>781 €/a</td>
<td>2,398 €/a</td>
<td>648 €/a</td>
</tr>
<tr>
<td>Operation facilities (0.45 €/kg H₂O₂)</td>
<td>160 €/a</td>
<td>515 €/a</td>
<td>--</td>
</tr>
<tr>
<td>Maintenance costs (3 % of Invest)</td>
<td>708 €/a</td>
<td>843 €/a</td>
<td>1233 €/a</td>
</tr>
<tr>
<td>Personnel (0.5 resp. 0.2 h/week, 40 €/h)</td>
<td>1040 €/a</td>
<td>1040 €/a</td>
<td>416 €/a</td>
</tr>
<tr>
<td>Max. treatment volume per day [m³/d]</td>
<td>1.0</td>
<td>3.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Yearly costs for treatment of max. volume [€/a]</td>
<td>5,504</td>
<td>8,148</td>
<td>7,200</td>
</tr>
</tbody>
</table>
Treatment costs with the AOP pilot plant

- **Hg-LP**
  - Total costs per year: 6000 €/a
  - Total costs per m³: 4 €/m³

- **Hg-MP**
  - Total costs per year: 8000 €/a
  - Total costs per m³: 6 €/m³

- **Ozone**
  - Total costs per year: 5000 €/a
  - Total costs per m³: 10 €/m³
Specific treatment costs

![Graph showing the relationship between waste water volume and specific treatment costs for different methods: Hg-MD, Ozon, and Hg-ND. The graph illustrates the decrease in costs as the waste water volume increases.]
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)

![Diagram showing freight calculations for Hg-ND, Hg-MD, and Ozon with respective efficiencies: 5.3, 4.8, and 4.6]
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 €/m³
  - 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 € /m³
  - 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 of WWTPs
  - Control of effluents, surface and drinking waters

- $\text{O}_3$ and PAC are effective and also economic efficient
  - Additionally costs: approx. 0.05 – 0.20 €/m$^3$

- Further research on oxidation products and ecotoxicity tests

- Consideration of the state of the art for updated water protective regulations is needed!
Acknowledgments

We gratefully acknowledge the BMWi for founding the IGF projects Nr. 13147 + 14396 through the AiF and especially the support of VEU and the companies:
Thank you for your attention!

Any Questions?