



Application of advanced oxidation process (AOP) for degradation of hazardous pharmaceuticals in hospital waste water

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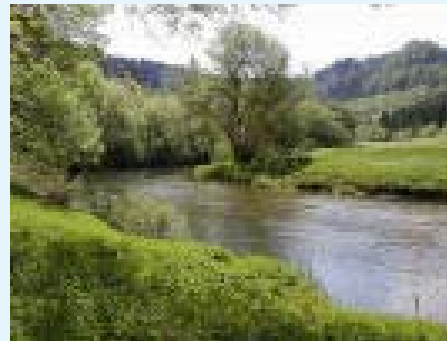
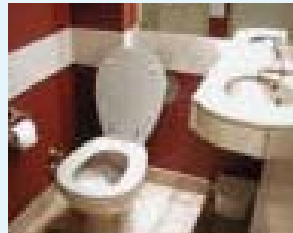
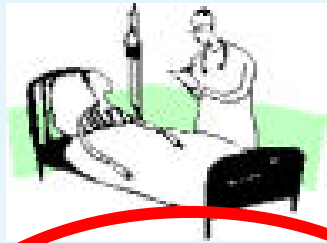
OVERVIEW

- **Introduction**
- **Present results**
 - Development and Validation of compound analysis
 - Advanced oxidation process (AOP)
 - UV source (emitter)
 - Oxidation agents
 - Different matrices
 - Influence of temperature
 - Toxicity and mutagenicity
- **Further experiments**
- **Outlook (technical realisation) and discussion**

Introduction

- Pharmaceuticals in the environment
 - persistence,
 - Toxic and mutagenic effects,
 - antibiotic resistance promoter,
 - endocrine effects
- hospital waste water = important input source
- Development of a procedure for reduction of the drug contaminations using AOP

Possibilities for reduction of drug input



Work Program

1st Stage: April 2002 – March 2004

- Development of procedure (laboratory scale)
- Optimization (effectiveness, costs)
- Modelling of pilot plant

2nd Stage: April 2004 – March 2006

- Construction of pilot plant
- Optimization (effectiveness, costs)
- Test phase in a hospital

Conditions for treatment of toilet effluent

- Toilets: 1-10 (oncology ward)
- Volume: 10-50 L/h; 100-500 L/d
- Concentr: up to 0.1(anticancer) - 1mg/L (antibiotic)
- TOC: 100 - 400mg/L (liquid phase)
- COD: 300 - 1000mg/L (liquid phase)

Selected marker substances

➤ *Anticancer drugs*

- Chlorambucil
- Cyclophosphamide
- Cytarabine
- Etoposide
- 5-Fluorouracil
- Ifosfamide
- Methotrexate

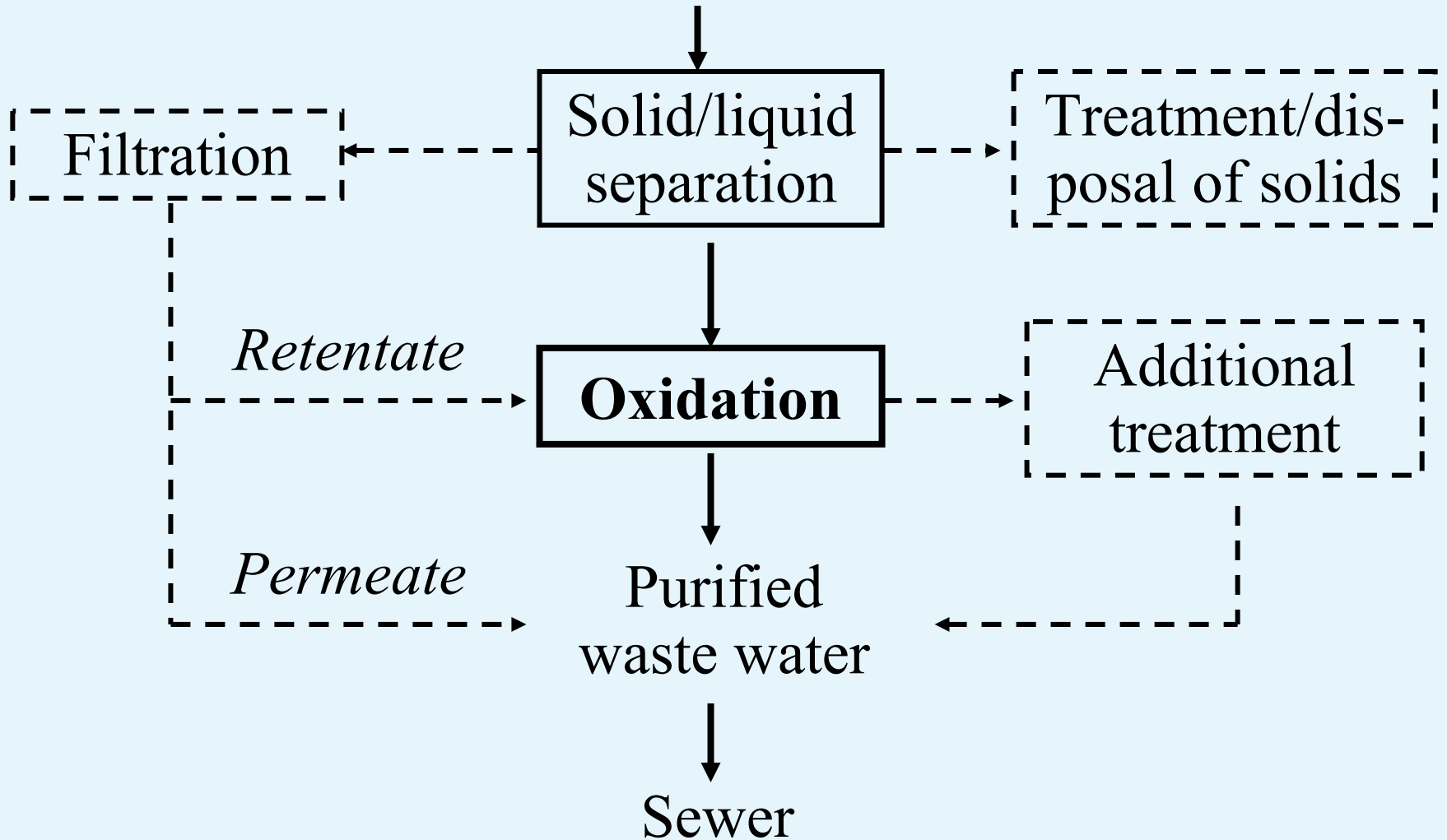
→ 100 µg/L each

➤ *Antibiotic drugs*

- Cefuroxime
- Chloramphenicol
- Ciprofloxacin
- Ofloxacin
- Sulfamethoxazole
- Trimethoprim

→ 1000 µg/L each

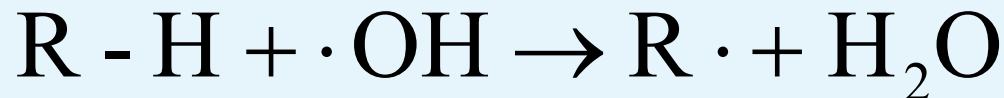
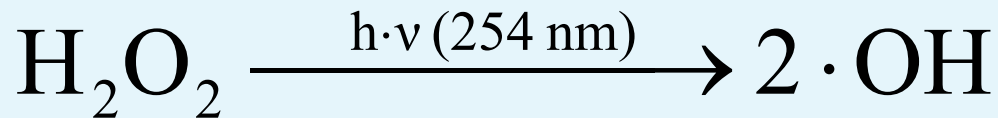
Contaminated
toilet effluent



Advanced Oxidation Process (AOP)

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

➤ H_2O_2 , $\text{H}_2\text{O}_2/\text{O}_3$ and O_3 , (TiO_2)



Oxidans	$E_{\text{H}}^0 [\text{V}]$
F_2	2,87
$\cdot \text{OH}$	2,81
O_3	2,07
H_2O_2	1,76
MnO_4^-	1,70
Cl_2	1,36
O_2	1,23

Laboratory scale treatment plant



Hg-low pressure + Ozone



Hg-low pressure + H₂O₂ (thermostated)

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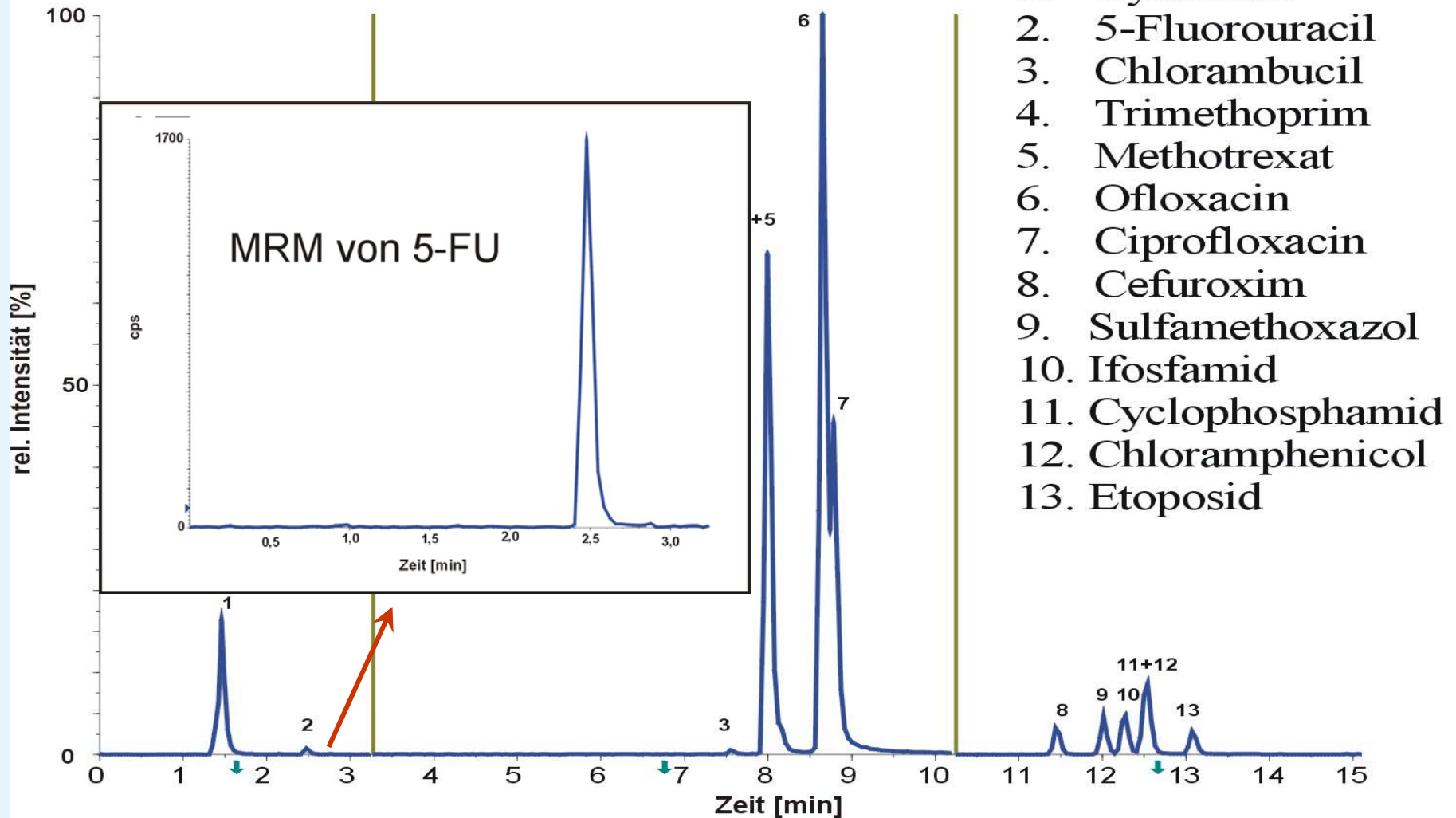
Quantitation of pharmaceuticals



LC-MS/MS

- **Excellent limits of detection (0.1 - 3 $\mu\text{g/L}$)**
- **Reduction of matrix effects by matrix calibration**
- **Identification of metabolites**

LC-MS/MS – Chromatogram

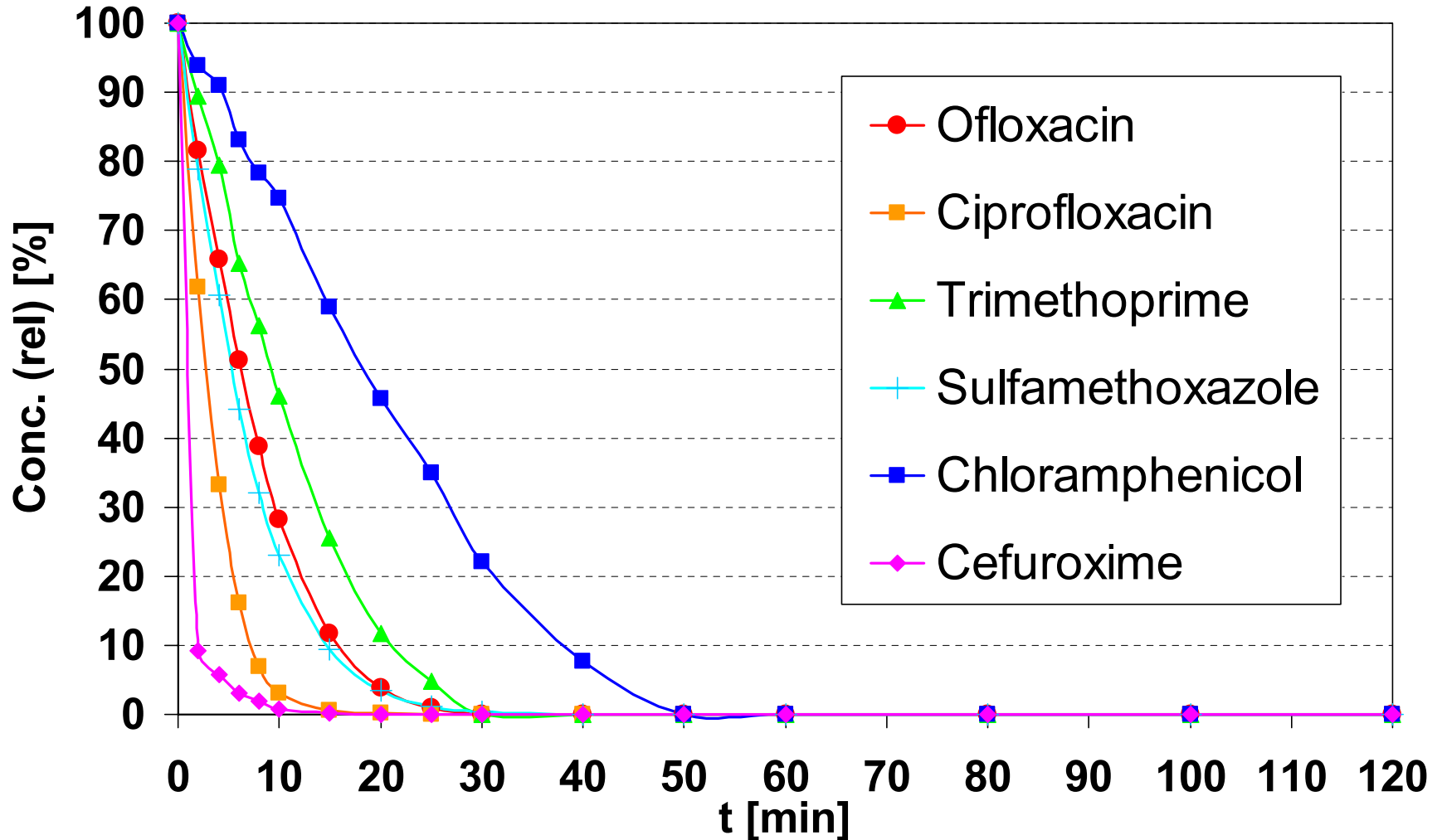


Optimized parameters

- ***Matrix:*** water > synth. waste water \approx toilet effluents
- ***Solide/liquid separation:*** Sedimentation > Filtration
- ***UV-Source:*** Hg-low pressure > Hg-medium pressure
- ***Oxidating agent:*** H_2O_2 > $\text{H}_2\text{O}_2/\text{O}_3$ > O_3 (> TiO_2)
- ***Concentration:*** H_2O_2 : 0.5 - 7.5 g/L; O_3 : 0.3 - 0.6 g/m³
- ***Duration of treatment:*** 30 - 120min
- ***Temperature:*** 20 - 40°C

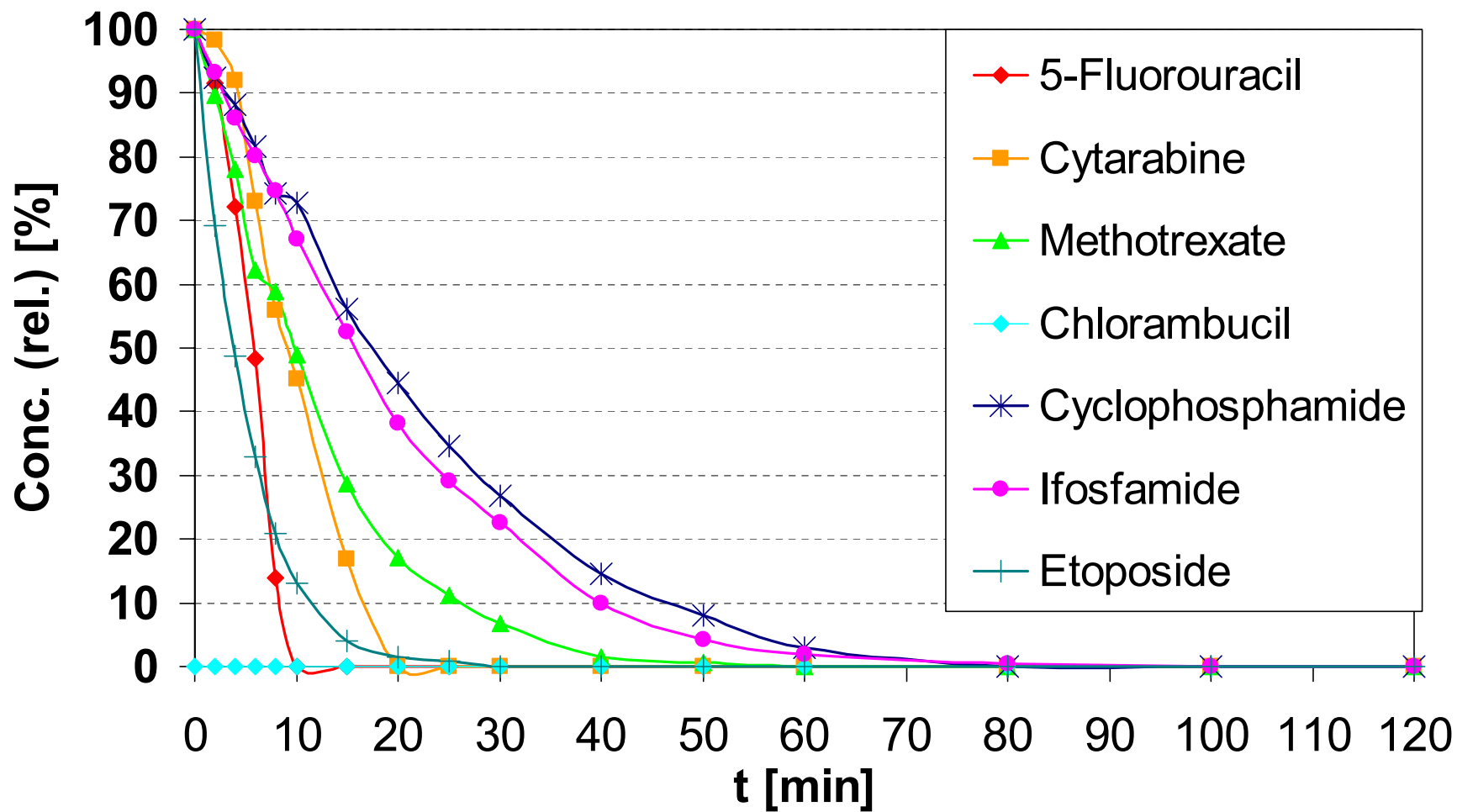
Results: Antibiotics

spiked toilet effluent, 24 h sediment.; UV-LP; 2.5 g/L H₂O₂; 20°C

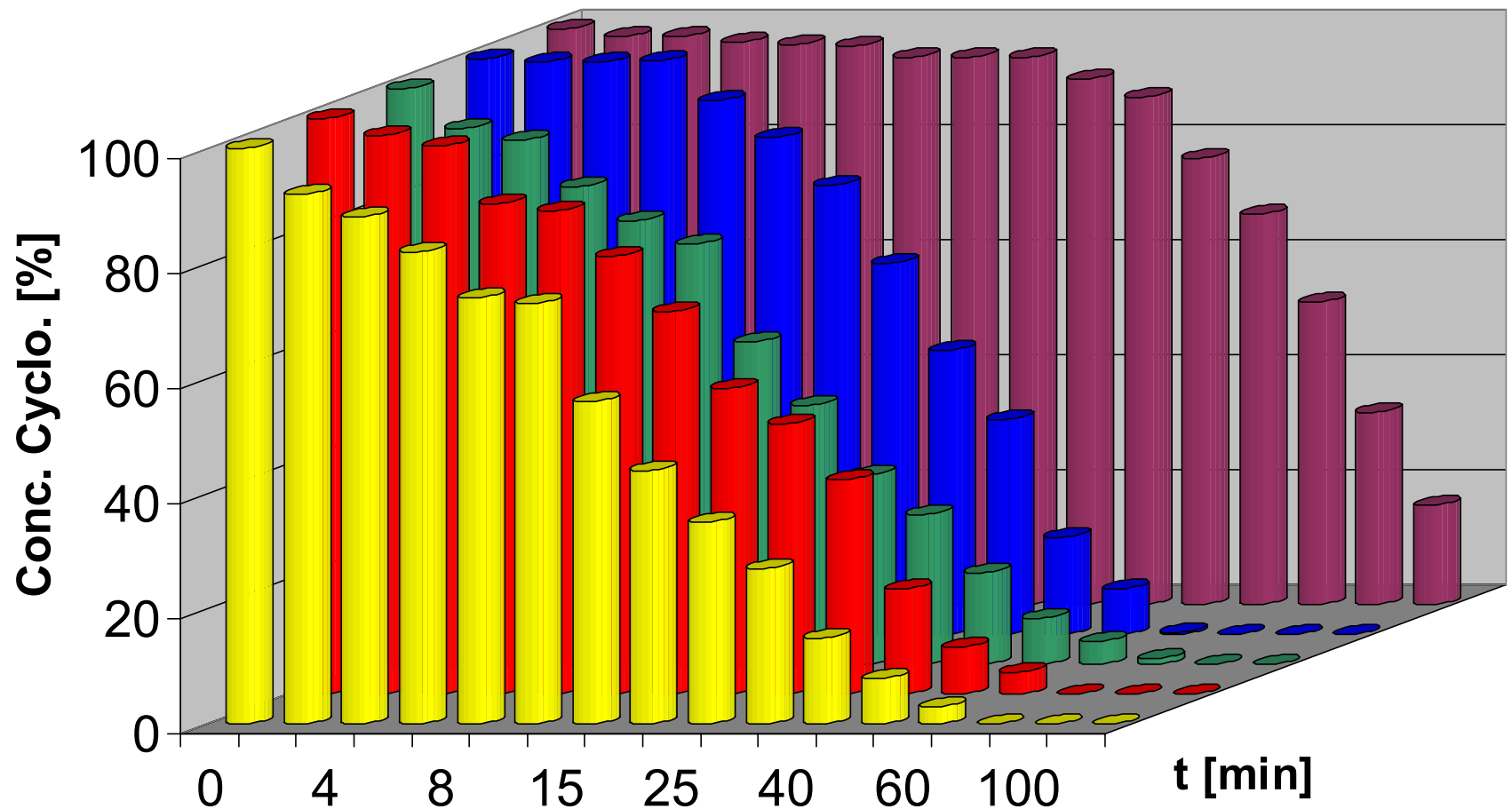


Results: Cytostatics

spiked toilet effluent; 24 h sediment.; UV-LP; 2.5 g/L H₂O₂; 20°C



Comparison of oxidants



2,5 g/L H₂O₂

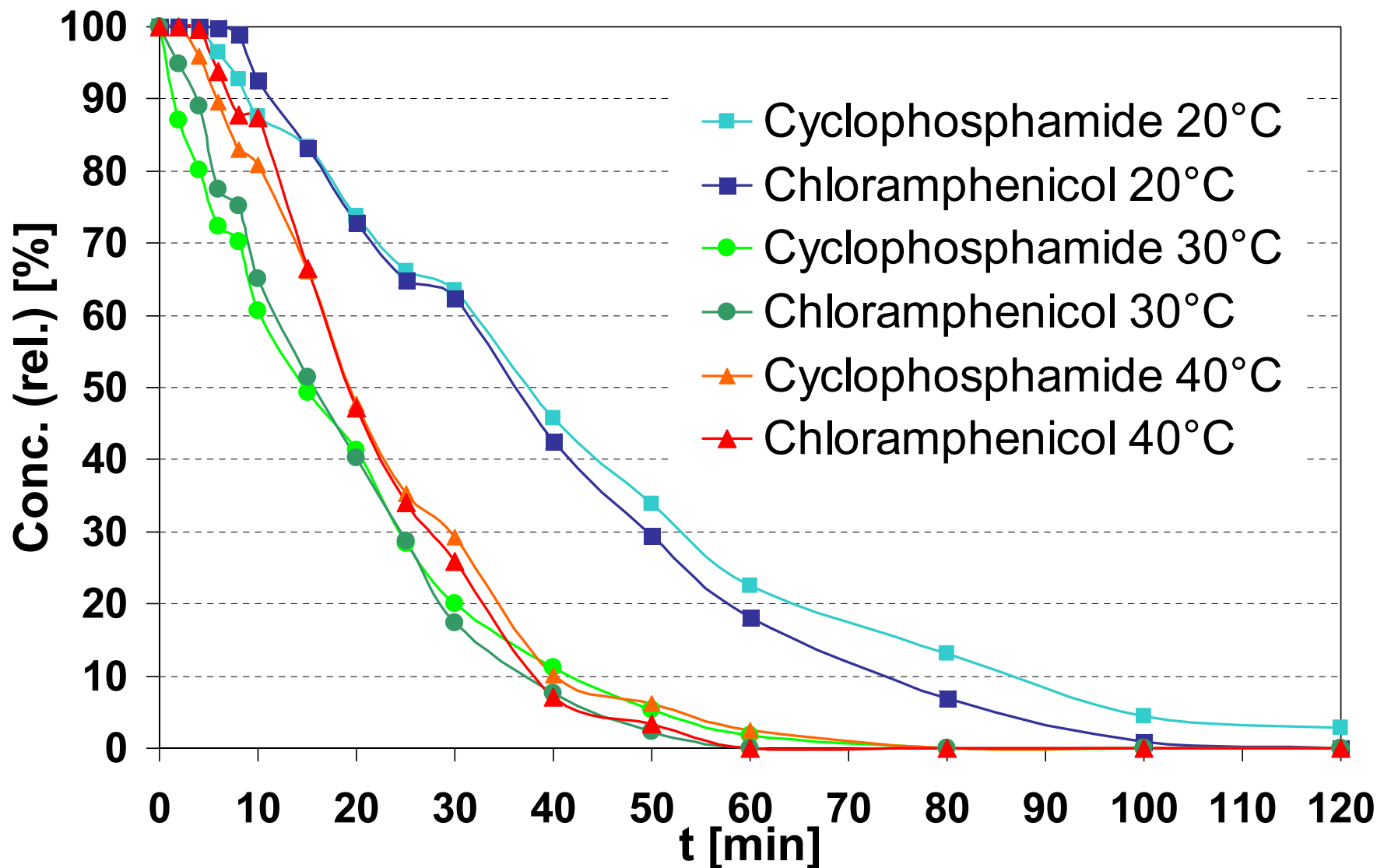
5 g/L H₂O₂

7,5 g/L H₂O₂

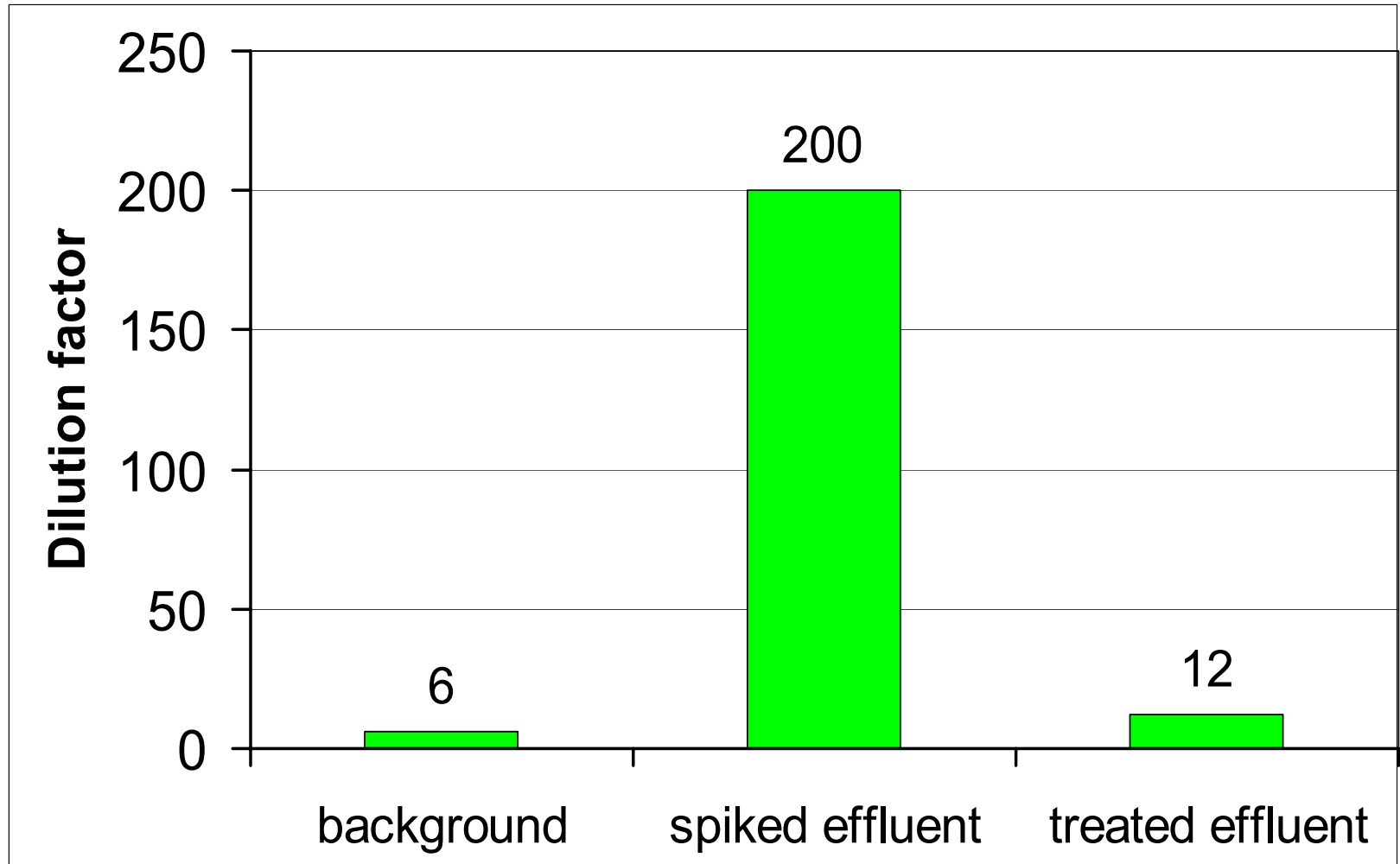
5 g/L H₂O₂ + O₃

0,5 g/L H₂O₂ + O₃

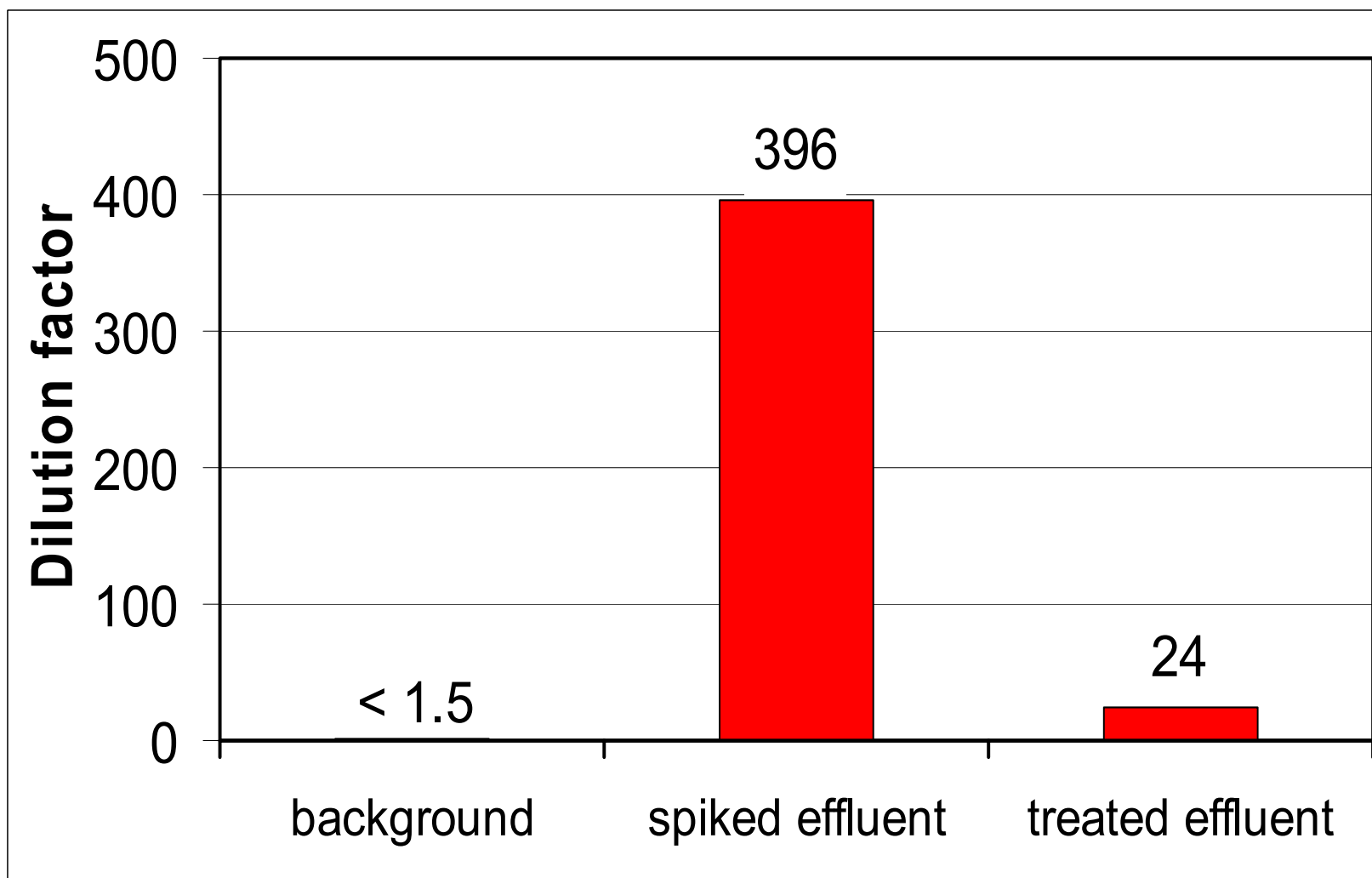
Influence of temperature



Reduction of toxicity: Luminescent Bacteria



Reduction of mutagenicity: UMU test



Summary

- Relative simple and sufficient procedure
- Duration of treatment: **1 hour**
- ➔ Degradation of substances > 95%
- ➔ Reduction of toxicity > 90%
- ➔ Reduction of mutagenicity > 90%

Remaining work

- Investigation on metabolites
- Quantification of drugs absorbed on solid material; treatment of sludge
- Further substances (drugs, x-ray contrast media, disinfectants, ...)
- Experiments with real effluents
- Scale up

Acknowledgments

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