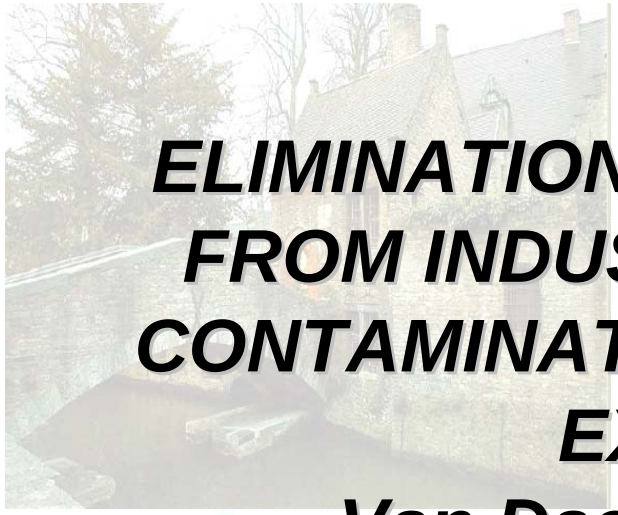

ELIMINATION OF PERSISTENT ORGANICS FROM INDUSTRIAL WASTE WATER AND CONTAMINATED GROUND WATER ON THE EXAMPLE OF EDTA

Van Daele D.[1], Sörensen M.[2] and Weckenmann J.[2]

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[2] a.c.k. aqua concept GmbH, CEO's, engineering, design and production of UV disinfection and oxidation processes, Wikingerstrasse 9A, 76189 Karlsruhe, Germany.

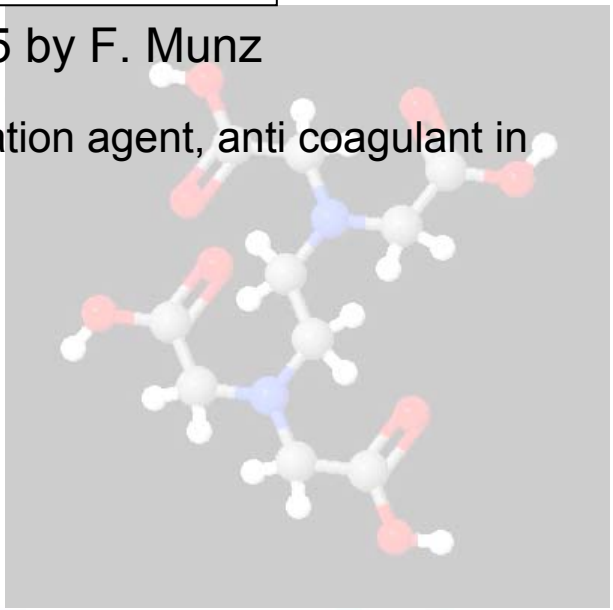
Problem definition

- Protection Ground water layers (EU)
  - ✓Dehydration due to intensive pumping
  - ✓Degradation of the water quality
- Industry is looking for alternatives for their water supply
  - ✓Surface water
  - ✓Reuse process water, waste water
  - ✓Rainwater
- Clean up of contaminated soil and related ground water

Chelators, organic micro pollution, persistent components are the cause and the effect of the problem

Example EDTA

Pateted in Germany 1935 by F. Munz

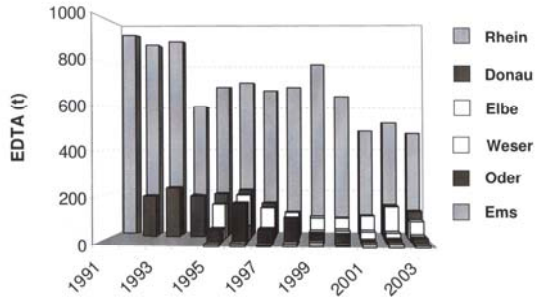


- Widely USED as complexation agent, anti coagulant in
  - ✓Personal care products
  - ✓Pharmacy
  - ✓Surface treatment
  - ✓Food
  - ✓Paper industry etc.
- Properties
  - ✓Strong chelating properties
  - ✓Non toxic (overall), other chelators are toxic (cyanide, polyamines a.o.)
  - ✓Persistent

Environmental behavior

- ✓Slow removal under many environmental conditions, accumulation
- ✓The most abundant anthropogenic compound in surface water
- ✓Low concentration can either stimulate or decrease plankton and algea growth.
- ✓In elevated concentrations toxic to bacteria and mammals (high concentrations)

Langjährige Entwicklung EDTA



- Komplexbildner-Fachgespräch 18.11. 2004 -

M. Lehmann
November 2004

Conventional treatment Physical separation

EDTA is not degraded or removed in conventional waste water treatment

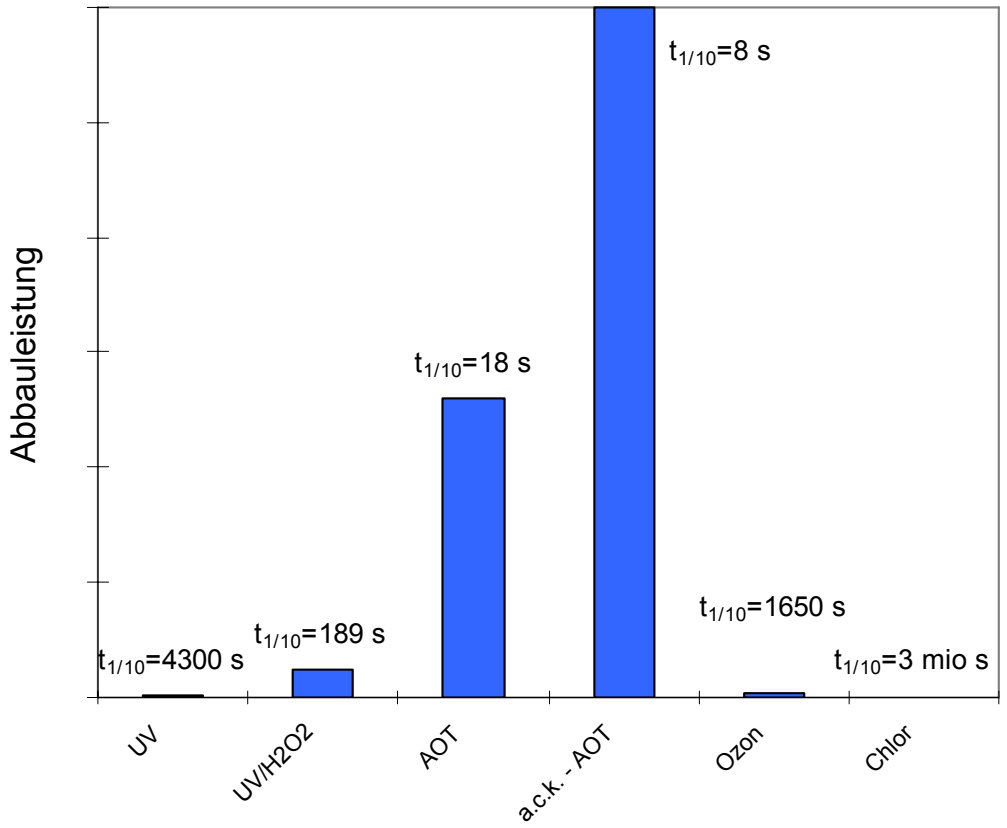
- Precipitation
  - ✓Not possible, strong chelating properties, used as anti-coagulant
  - ✓Metals are remobilized from the sludge
  - ✓Bad performance, effluent specifications not kept
- Filtration, Ion-exchange
  - ✓Concentrated waste stream, can not be discharged without treatment.
- Recovery
  - ✓High costs, bad quality after recuperation
  - ✓High emissions, safety precautions necessary
- Activated carbon
  - ✓Production of AC is energy consuming
  - ✓Not reliable due to competitive components
  - ✓Waste stream (burning or regeneration necessary)
  - ✓For EDTA AC is useless due to its hydrophylic character

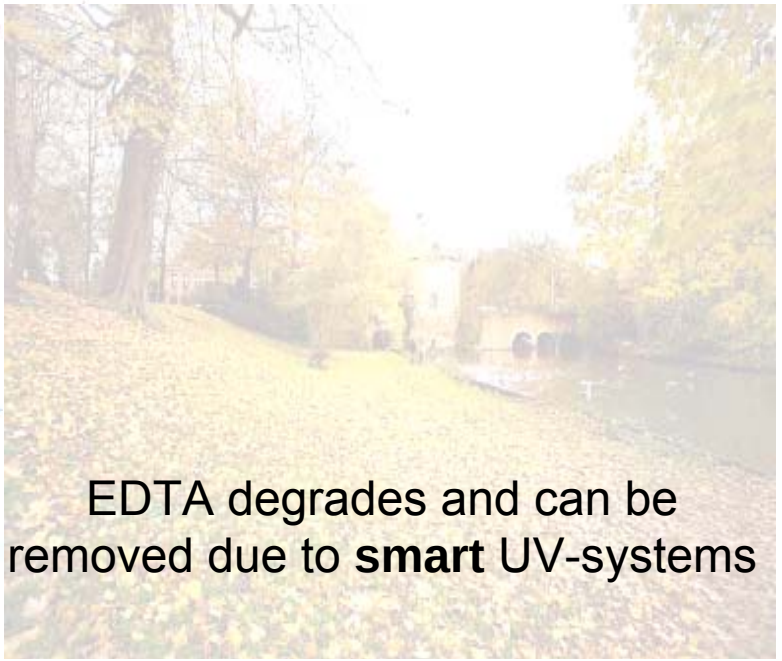
Conventional treatment Oxidation processes

EDTA is not degraded or removed in conventional waste water treatment

- Biology
  - ✓Recalcitrant, due to strong metal chelating properties. Other chelates toxic.
- Electrolyses (AOP)
  - ✓Recuperation of metals OK
  - ✓Chelate changes into other forms (EDTA → EDDA-N,N, EDMA, IMDA) with same properties
  - ✓Energy consuming
  - ✓High investment costs
  - ✓Creation of high sludge amounts
  - ✓Corrosion problems
- Chlorination
  - ✓Formation of persistent by-products (AOX)
- Ozon
  - ✓Is dangerous product, must be destroyed by UV
  - ✓Ozon doesn't or slowly reacts with amines, in the case of EDTA, destruction of Ozon
  - ✓Formation of by-products (e.g. Formaldehyde)

Comparison in EDTA degradation speed with different techniques





a.c.k. AOT = Enviolet® systems

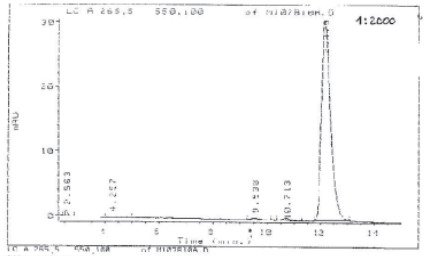
New treatment ENVIOLET®-systems

EDTA degrades and can be removed due to **smart** UV-systems

0 h Enviolet®

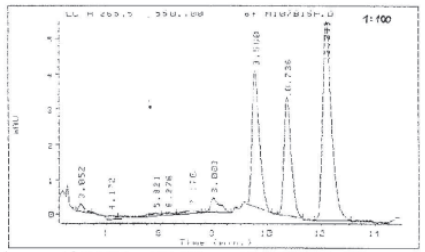
Highly diluted sample

EDTA – metal bath



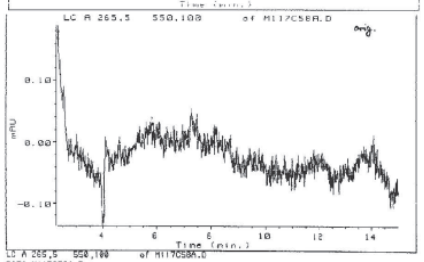
2 h Enviolet®

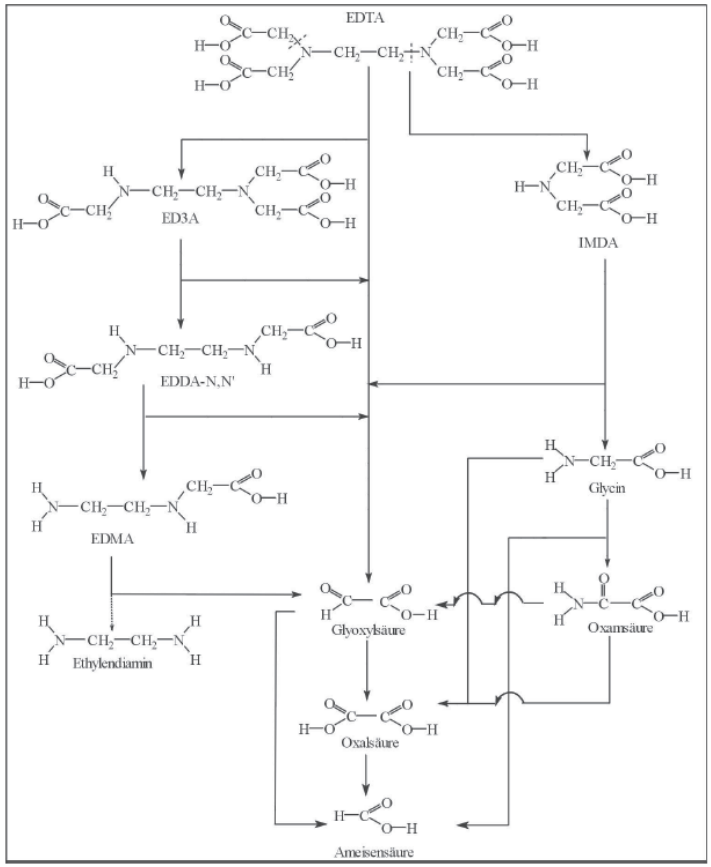
Diluted



4 h Enviolet®

Undiluted





EDTA

NH_4

NO_3

CO_2

SMART ENVIOLET®-systems

- Enviolet® UV oxidation process → Cold combustion in the water phase. Chelates (EDTA tartrate, citrate etc.) → CO_2
- Enviolet® basic equipment:
  - Batch tank
  - Enviolet® UV-reactor(s)
  - Dosing station(s)
  - Control panel

A combination of High performance Enviolet® UV reactors and fully automated intelligent designed process control, results in an innovative UV technology.

SMART ENVIOLET®-systems

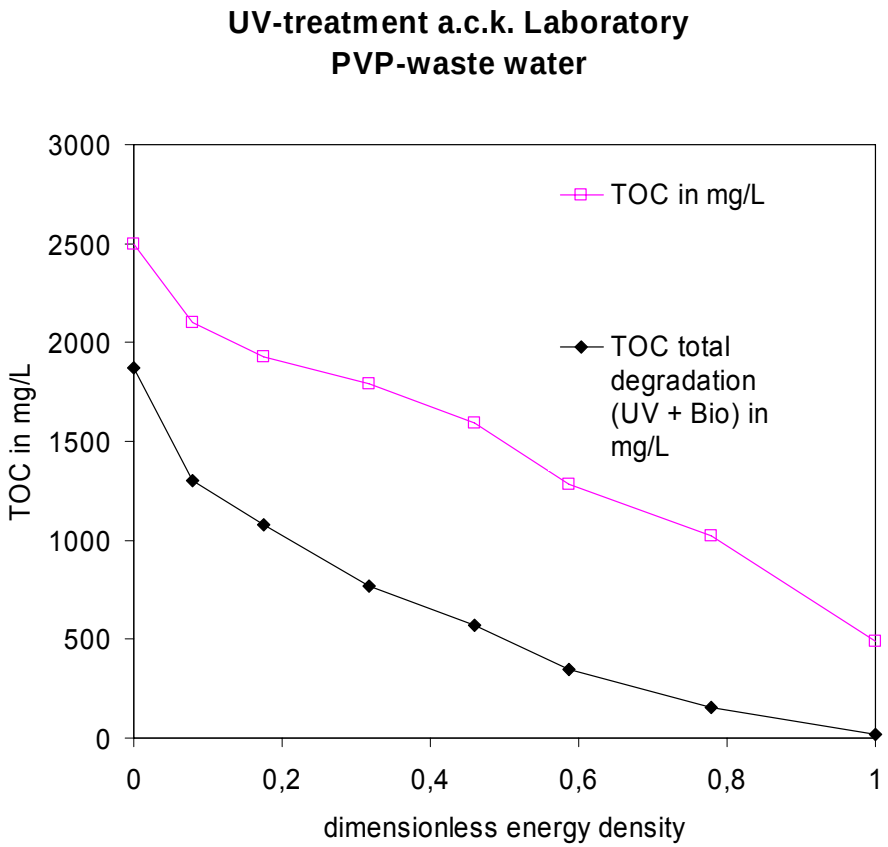
- The abrasive rotational flow in the reactor
- A very good material transfer, guaranteed by the induced high turbulence, even in very dirty and turbid media (optimisation of the process)
- The high quality of the chosen components

Application examples ENVIOLET®-systems

- Flexible and compact
- Applicable:
  - ✓ for small and big flows.
  - ✓ for liquids with low UV transmission and high concentrations of suspended solids (e.g. sludge)
  - ✓ for corrosive streams
  - ✓ for different waste streams in combination or in successive batch treatment
- Energy and water recuperation possible
- Improvement of product quality and at the same time prevention of waste water.

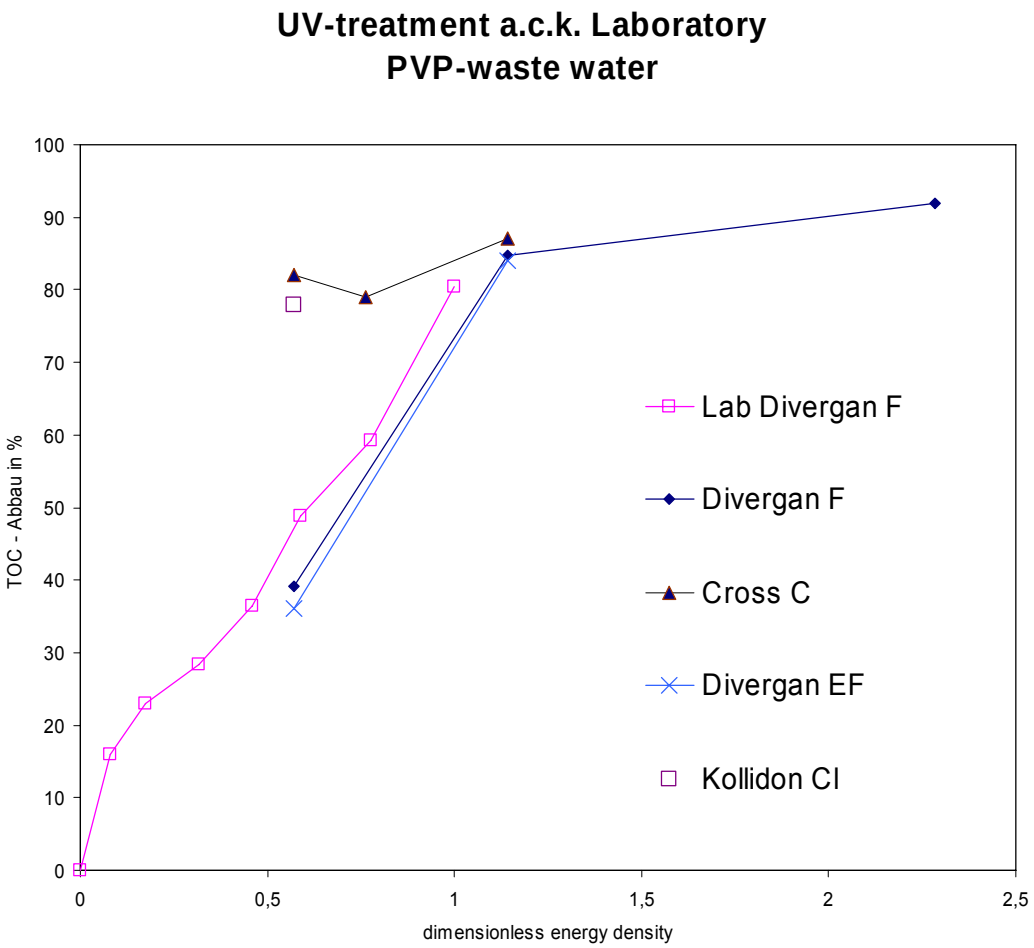
Testing

The way from lab-test work to full-scale UV-applications



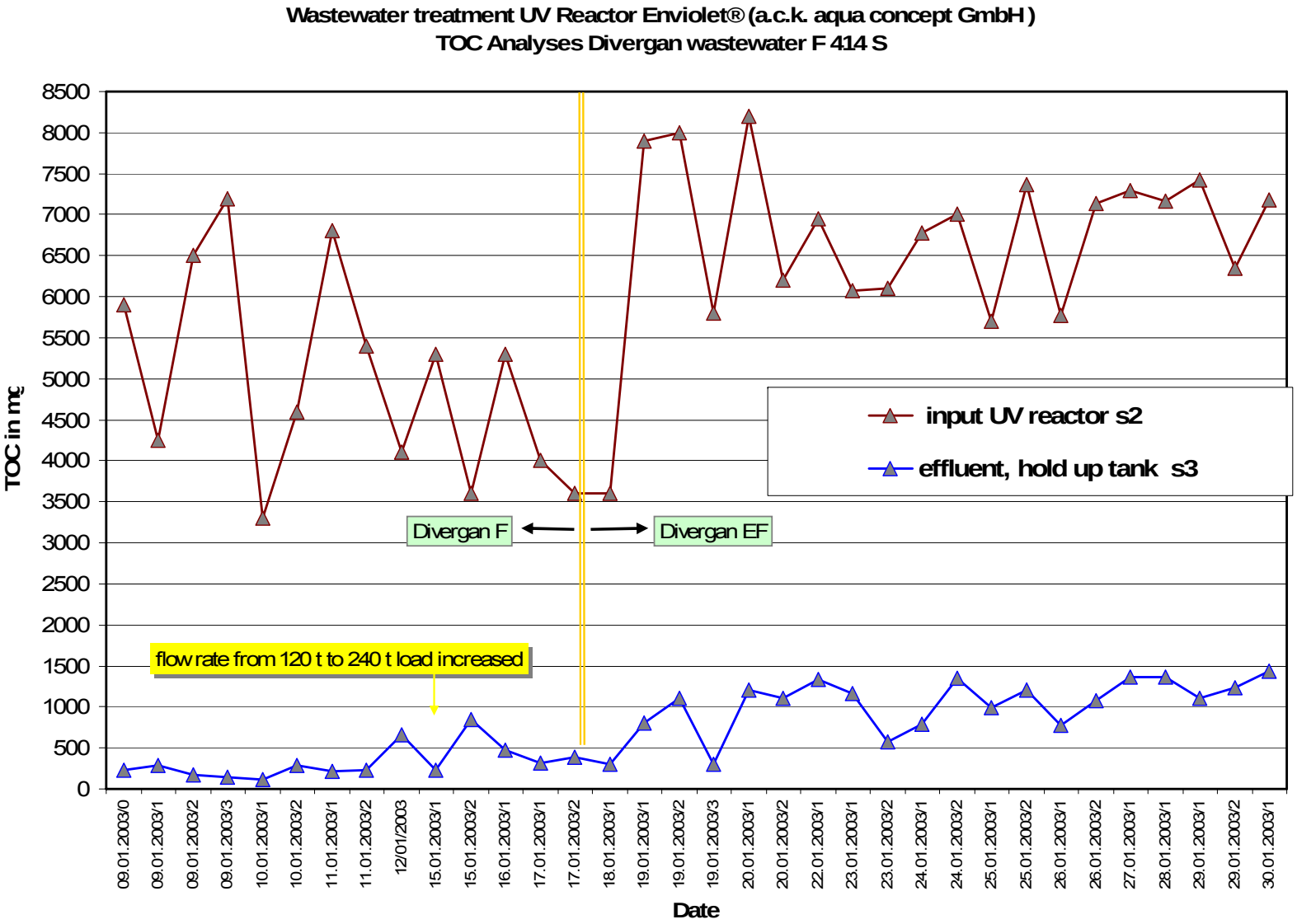
•Diagram 1: Laboratory treatment. TOC-degradation by UV-oxidation and subsequent biological elimination (Z/W-Test after 2 d)

The way from lab-test work to full-scale UV-applications



•Diagram 2: Pilot-operation by the client (a.c.k. pilot plant). Comparison of the degradation by the laboratory scaled facility and the pilot plant

The way from lab-test work to full-scale UV-applications



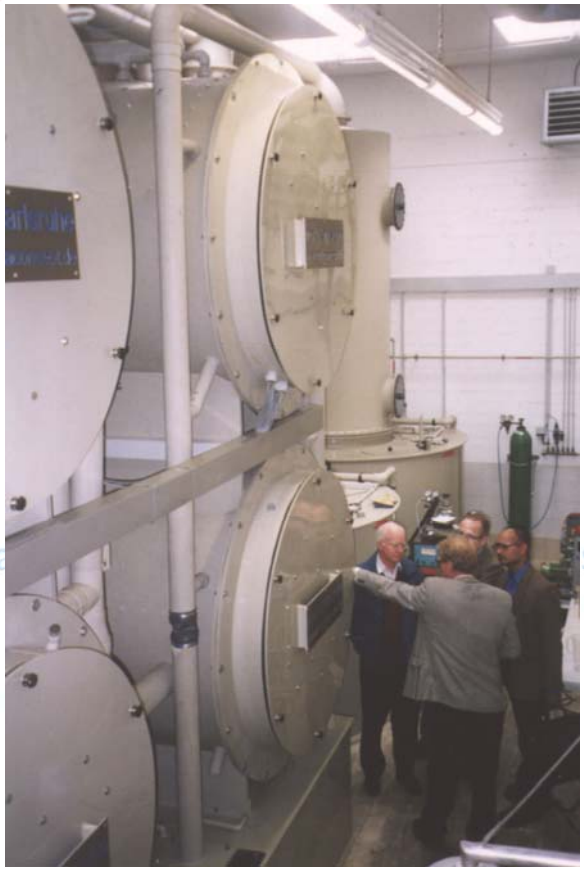
Application examples ENVIOLET®-systems

Enviolet®– UV – Reactors

Upgrading without additional space

- Flexible and compact

Application examples ENVIOLET®-systems



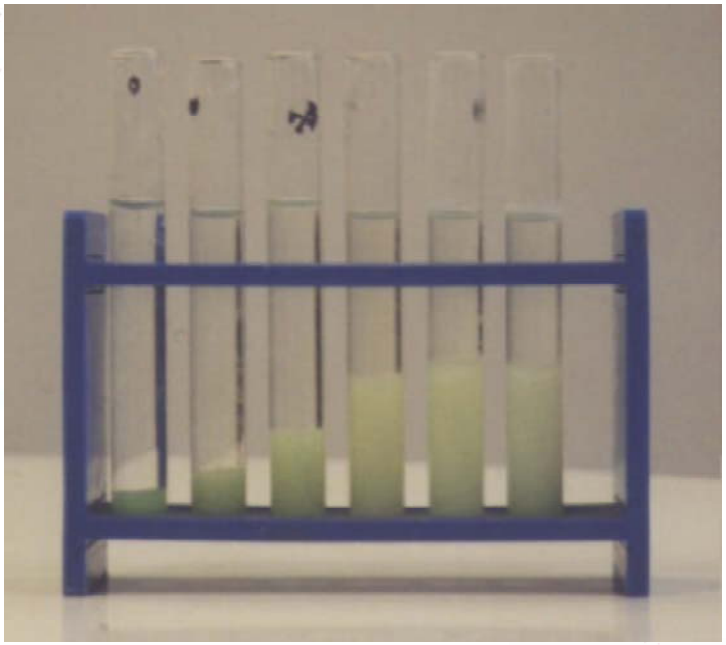
• for small and big flows

Application examples ENVIOLET®-systems

precipitation after Enviolet® treatment,

samples shown are without addition of coagulant

Formation of a very dense, compact sludge



Application examples ENVIOLET®-systems Surface finishing

***Table I**: Chemical composition of the waste streams of treatment processes in surface finishing*

Process	Chelators	Classical treatments	Modern Enviolet® method
Electroless Nickel	*Organic carbonates, ammonia*	*Rinse waters only*	*Rinses & concentrates e.g. Enviolet®*
Electroless Copper A	*Organic carbonates (tartrate, citrate)*	*Rinse waters only*	*Rinses & concentrates e.g. Enviolet®*
Electroless Copper B	*Polyaminocarboxylate(EDTA & other complexes)*	*Already difficult for rinse waters*	*Rinses & concentrates e.g. Enviolet®*
Zinc-Nickel	*Polyamines (EDTA, cyanide & other complexes*	*Already difficult for rinse waters -*	*Rinses & semi concentrates e.g. Cyanomat®*
Cyanide	*Cyanide*	*Good to satisfactory*	*Rinses & concentrates e.g. Cyanomat®*

Application examples ENVIOLET®-systems Surface Finishing

Table II. *Gives an Overview of the described case study plants and waste water produced.*

User	*Waste water source*	*Method of treatment*
Multilayer Technologies (PCB – manufacturer)	*Electroless copper rinses & concentrates*	*Batch*
FUBAG (GMF)	*Cyanide baths & waste water Electroless nickel*	*Sequential*
Thoma Metallveredelung (metal finishing)	*Electroless Nickel & Zinc/Nickel*	*Alternating*

Application examples ENVIOLET®-systems Surface Finishing

Table III. *Contents of the electroless CuEDTA bath and levels at Multek after treatment with the a.c.k. UV-process.*

	Concentration in the bath in mg/dm³	*Concentration after alkaline precipitation*
Copper	*5,000 – 6,000*	*0.2 – 0.5 mg/dm³*
Na-EDTA	*25,000 – 35,000*	*< 10 µg/dm³*
Formaldehyde	*6,000*	*n.n.*
COD	*43,000 – 60,000*	*Approx. 1,000 mg/dm³*
TOC	*14,000 – 20,000*	

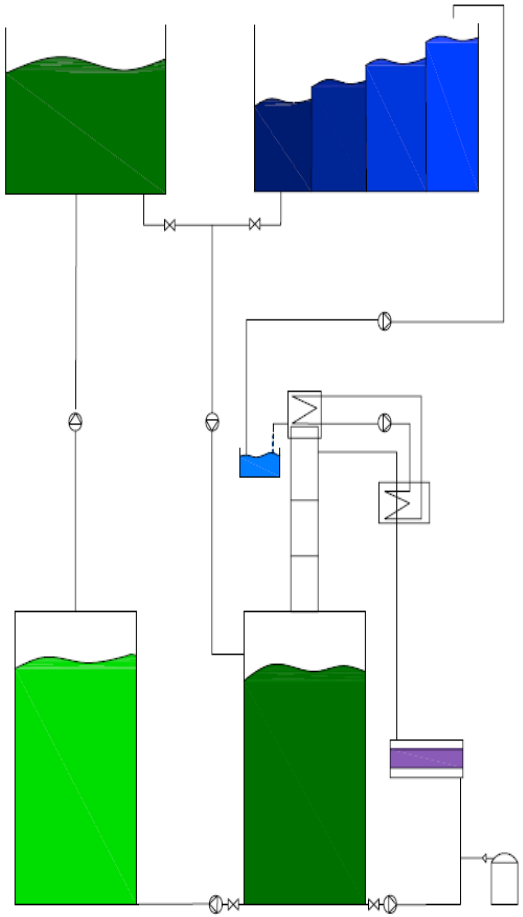
Table IV: *Waste water configuration at FUBAG, metal plating AG (CH)*

Parameters	*Waste water*	*After treatment*
Waste water in m3/d	*5*	*5*
Cyanide in mg/L	*6.500 – 10.000*	*< 0,2*
Copper in mg/L	*approx. 5.000*	*< 0,3*
Nickel in mg/L	*10.000 – 15.000*	*<0,25*
Zinc in mg/L	*approx. 1.000*	*< 0,4*
Silver in mg/L	*approx. 10*	*< 0,1*
Gold in mg/L	*traces*	*n.d.*
Treatment time	*4,5 h*	
Color	*brown-green*	*clear*

Table V. Effluent streams and the important chemical components at Thoma Metallveredelung

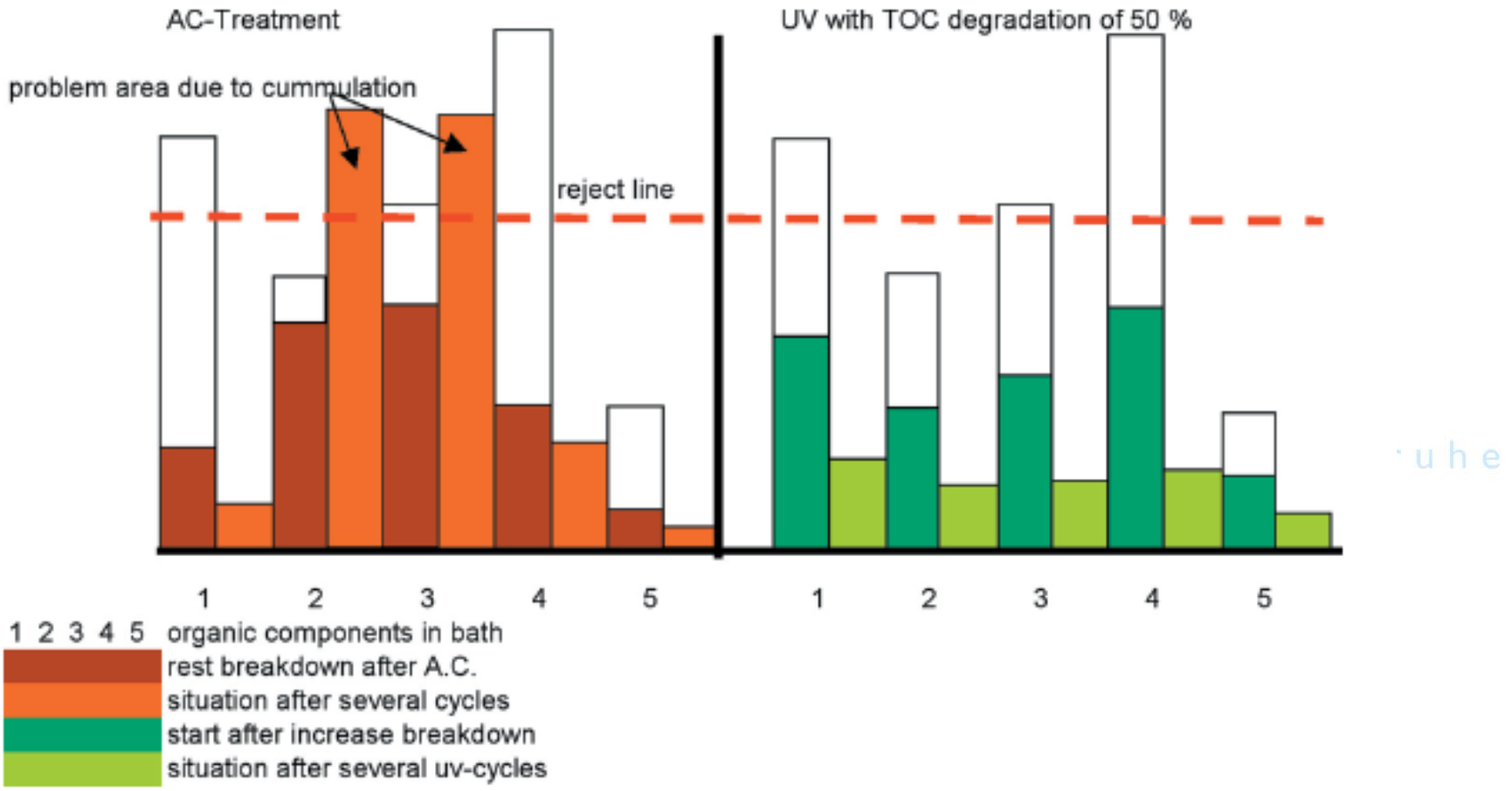
Total volume of the batch:12 m³	*Proportion in batch in m³*	*Chelates in effluent*	*Concentration chelates in mg/dm³*
Electroless nickel	*4– 5*	*Carboxylates, Gluconates*	*1,000 – 4,000*
Zinc pickling	*2*	*Aromatic Carboxylates*	*1,000 – 2,000*
Acid pickle (HNO3)	*2*	*Ammonium, carboxylates*	*max. 500*
Ammoniumbifluoride	*2*	*Ammonium*	*2,000 – 3,000*
Zinc – nickel	*9*	*Aminocarboxylates, Cyanides*	*Approx. 8,000*

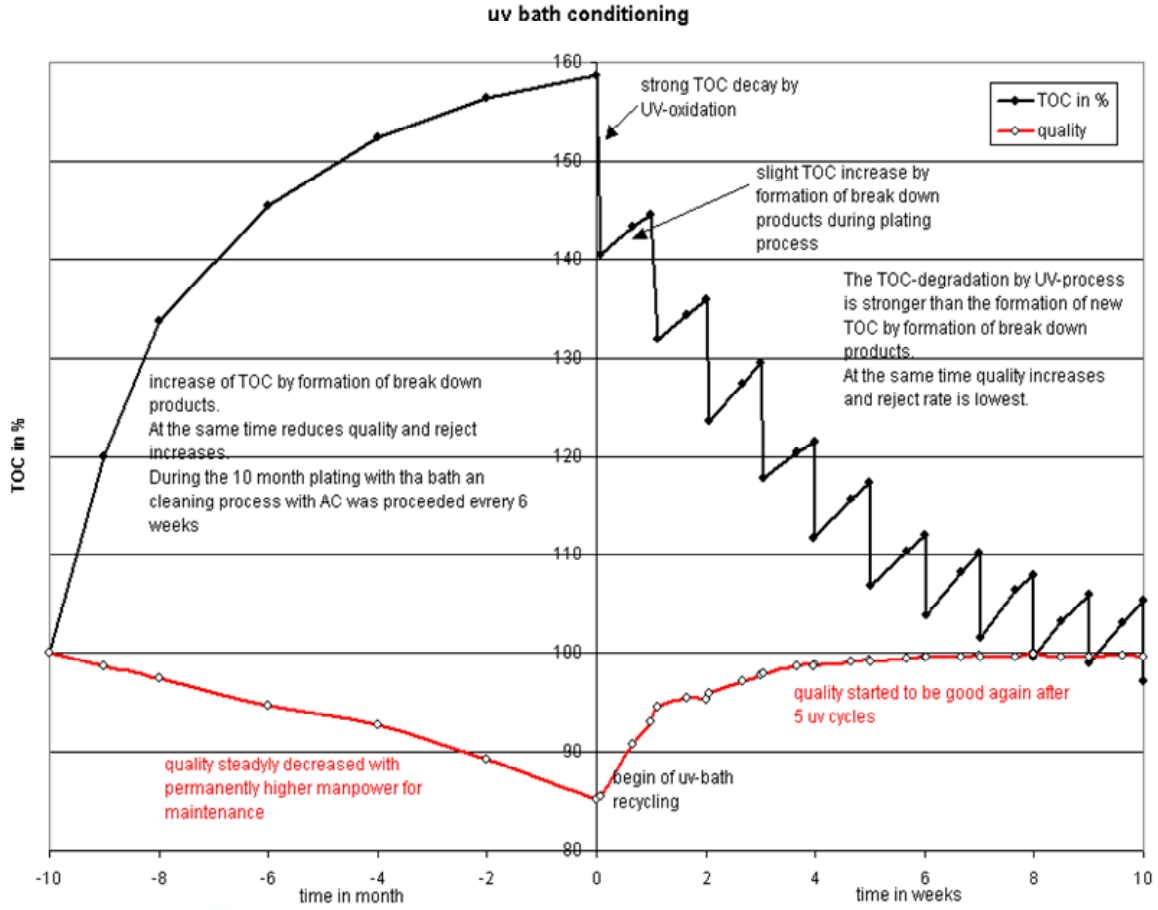
Ni or Cu plating process by means of electrolyses

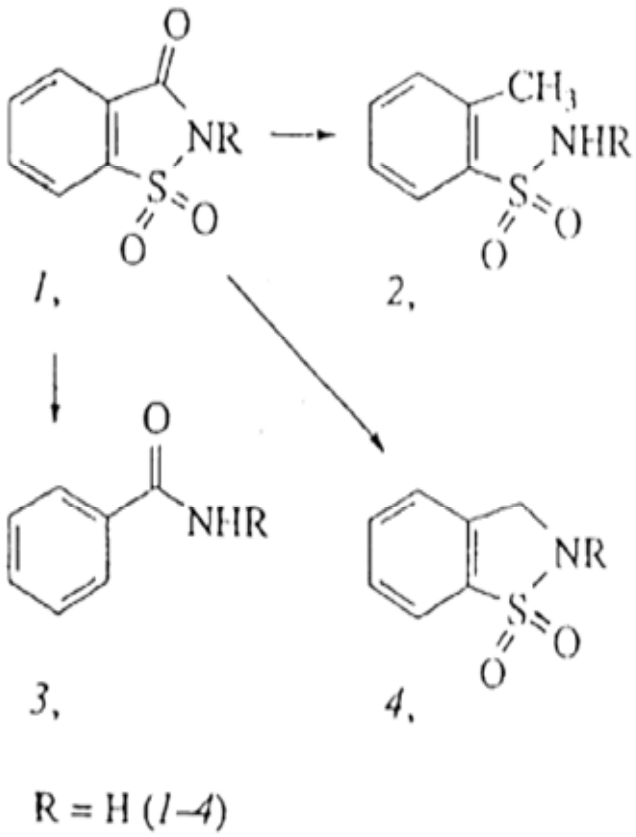


- Energy and water recuperation possible
- Improvement of product quality and at the same time prevention of waste water.

Improvement of product quality
Recuperation of metal and water
Prevention of waste water







Comparison between old AC technology and new Enviolet® technology

Application examples ENVIOLET®-systems

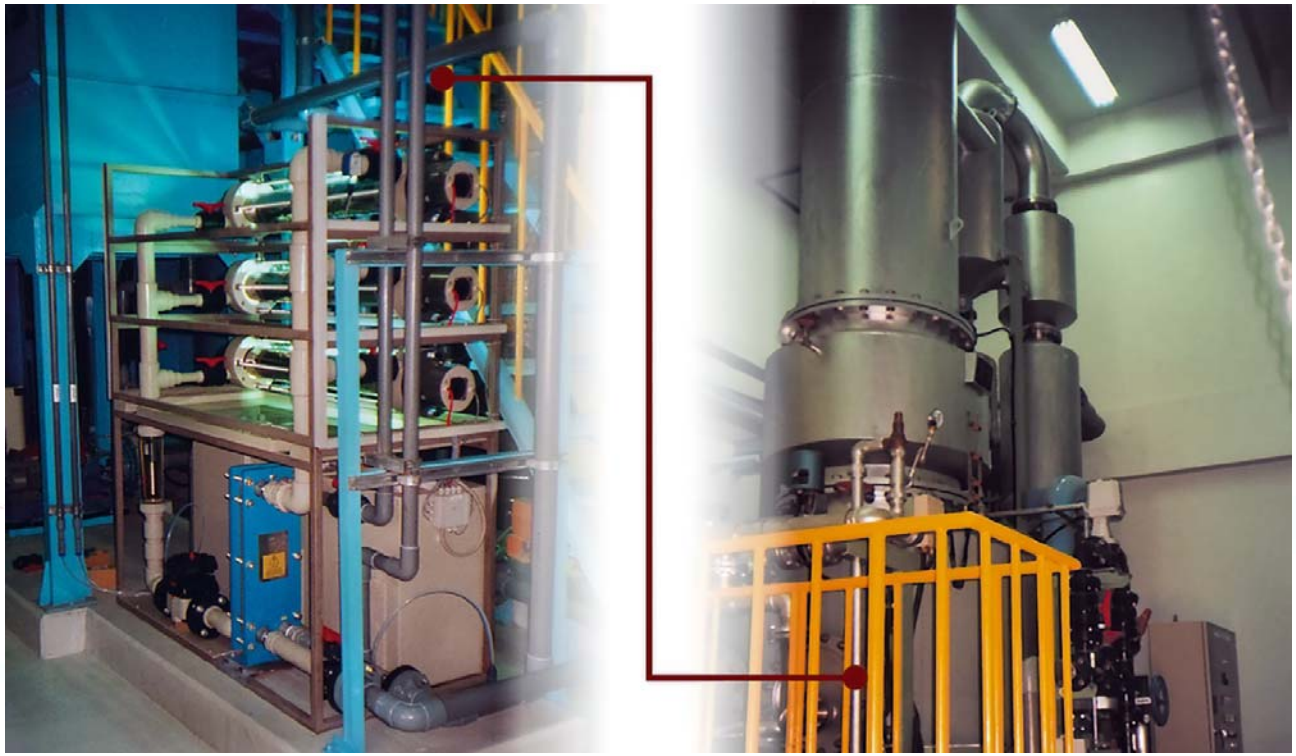
- for different waste streams in combination
  - ✓ Antibiotics and X-ray waste

or in successive batch treatment:

- ✓ Cyanide detoxification
- ✓ Ni phosphite
- ✓ Oil emulsions

- At the same time flexible and compact

Application examples ENVIOLET®-systems



• for different waste streams such as waste gas (e.g. VOX, NOx removal)

EDTA removal at producer

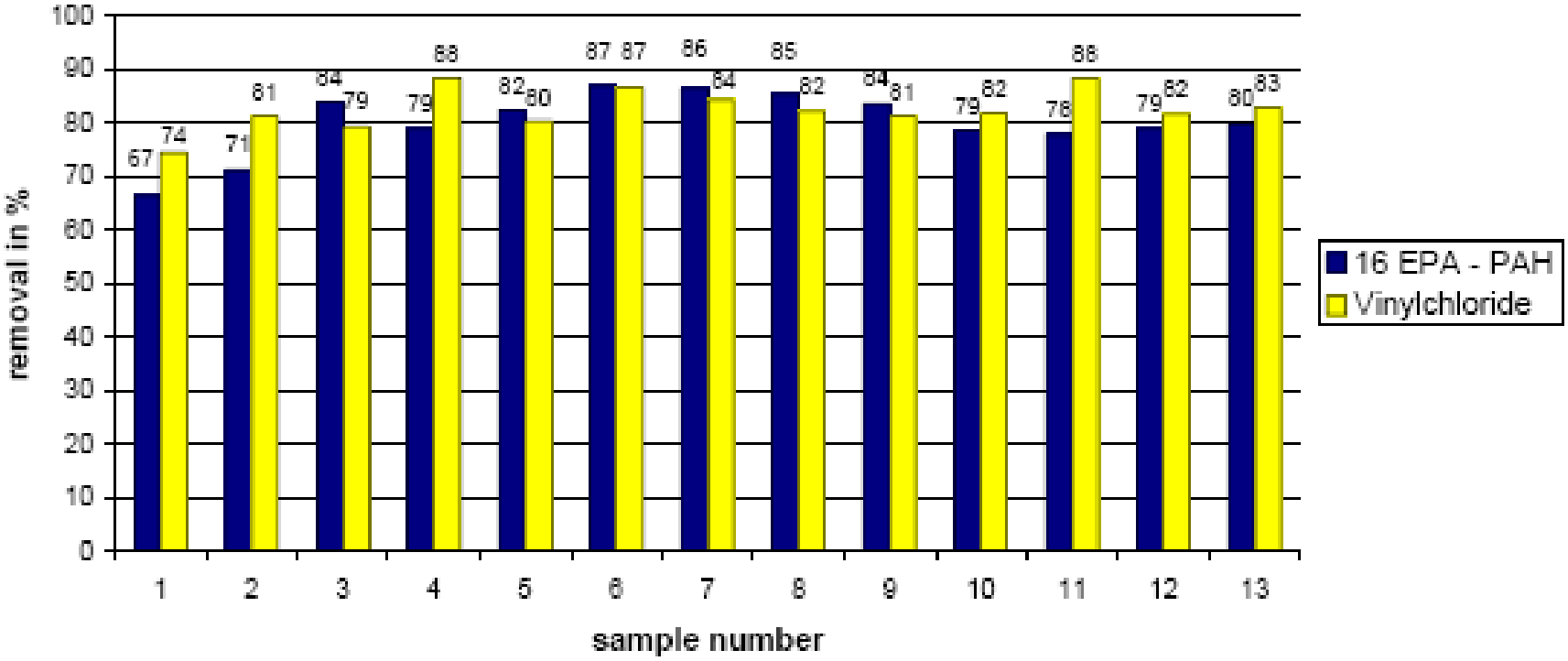
The producer of EDTA compared different technologies, The focus was:

- simple process
- Selective to keep the operational costs low.
- By-products are biological available

Table VII: *Resume of the assignment and waste water specifications*

Parameters	
Flow in m3/h	*8 - 12 m3*
EDTA–Konzentration	*400 - 500 mg/l*
Other components	*org. by-products ca. 0,3%*
	Na_2SO_4 ca. 18,5 %
	COD ca. 2000 – 3000 mg/l
	Chloride im ppm-range
Waste water temperature	*30 - 40 °C*
Degradation rate EDTA	*> 50 %*
Costs in Euro/m3	*< 0,5*
pH-Value	*1,5 - 2*

Groundwater and remediation applications



Enviolet® is a powerful instrument for elimination of PAH, VOCl, cyanide etc.

Conclusion

• Enviolet®-UV-technology is an effective technology in a wide range of small and large applications in different industries.

• It is economical feasible, were other cheaper methods fail or were other methods need to be helped to come to the final results.

• The Enviolet®-systems are well engineered compact, flexible systems, which can be used for several problems as stand alone or combined with other technologies as there is:

- ✓ energy recuperation,
- ✓ water recuperation,
- ✓product recuperation and or product quality improvement.

With thanks to the owners of the Enviolet® technology
Dr. Ing. Martin Sörensen
Dipl. Ing. Jürgen Weckenmann