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

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ABSTRACT

Natural clean and save water sources are becoming rare and therefore a lot is going on to find sustainable alternatives for it, such as reuse of water in industry and re-establish ground water aquifers for later usage as drinking water. Persistent components (e.g. PHA, Phenols, Pesticides, …) in waste water, surface water, filtration concentrates etc. are often making reuse complicated or even impossible, while common treatment of contaminated ground water in sanitation projects needs to be reviewed.
EDTA is also an example of a persistent compound used in a lot of industrial processes, e.g. metal finishing, pharmacy and personal care etc., is difficult to be replaced by other substances due to the extraordinary properties of EDTA and its non-toxic behaviour. There are also several other chelators used for other applications, but they often show additionally a significant toxicity: Cyanides, polyamines and other strong chelators.
Using the chelators in industry leads to good results in the production processes, but the substances are not allowed to be discharged into the environment, because they accumulate due to their persistent character.
Enviolet® systems an advanced oxidation process and sustainable technology, is capable to treat these chelators, so that they loose their chelating capacity and become bio available. This processes showed to be superior in comparison with other AOP's.

Keywords: Enviolet®, chelates, persistent, increasing bio available character.

INTRODUCTION

The advantages of EDTA towards the better quality of industrial formulas and processes, as formation of strong chelates and their superior electrochemical properties are the disadvantages in water treatment and in the environment. Especially when heavy metals are in the environment. [1]
Traditional treatment methods, as Physical-Chemical treatment are not always adequate, because EDTA complexes are very strong and prefer to stay in solution
Recuperation of the EDTA, has several disadvantages, such as high costs, high emissions, extra safety precautions necessary for production people.
Electrolyses, is often used in metal industry, to recuperate the metals, in that case most of the complexes will be kept or converted, the problem is not solved.
Activated carbon and other filtration techniques, often used in remediation projects, but also in industry, are just physical techniques, with at the end a contaminated stream, which has to be destroyed by burning or further treatment, with a lot of extra costs (see fig..) Only to produce AC one need a lot of energy
Chlorination technique is an AOP with a lot of persistent side effects, e.g. formation of AOX. Ozone also used in AOP, is a very dangerous product for the environment and for the people who have to work in the production area. Ozone can be produced and can be destroyed by UV-licht, in nature and in industrial processes, so UV light is more powerful then Ozone, which was proved in different applications, when the technologies were compared. (Examples are EDTA-treatment, Cyanide treatment)

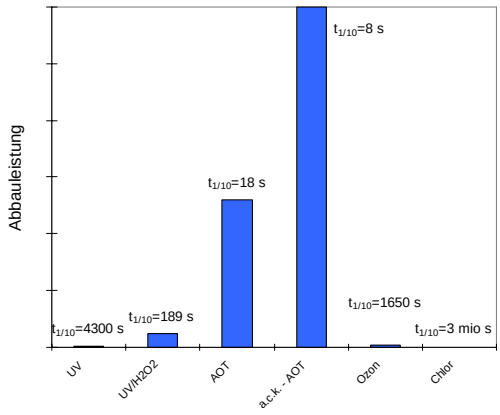

Fig. 1: *Comparison of the degradation capacity of different oxidation processes (UV, UV/H_2O_2, AOT, a.c.k.-AOT=Enviolet®, Ozon and Chloor) for the elimination of the organic complex (EDTA) and the reaction time needed to eliminate 90 % of the organic complex ($t_{1/10}$)*

Enviolet® UV-oxidation treatment breaks down all strong chelates and cyanide, oxidises inorganic phosphoric substances (hypophosphite and phosphate) to phosphate etc. [2-5]
Enviolet® UV-oxidation is a selective process precisely cut for an application, or a wide range of applications. In every case the application will be fit to the task. It can be used for water streams and gas streams (contaminated air streams), even in combination in certain cases.

Photo 1**:** *Left side is a Pharmaceutical application (Antibiotics and X-ray waste)*
Middle is in metal industry (cyanide detoxification, Phosphite –Ortho Phosphate oxidation and oil emulsions sequential treatment)
Right side: combination of gas washing and UV treatment, without residue

PROCESS

The Enviolet® UV-oxidation process can be compared with a “cold” combustion in the water phase. The chelates (EDTA, tartrate, citrate, etc.) are oxidised by means of UV-oxidation, under standard reaction conditions to inorganic carbon dioxide.
The treatment plants consists basically out of a batch-tank with one or more Enviolet®-UV-reactors and chemical dosing stations and a control panel. The combination of the High performance Enviolet® UV-reactors, an intelligent developed automated and controlled process, lead to an innovation in UV-technology, which proved itself in a big range of applications in different industries all over the world.
UV-technology, often described as a good technology for clear streams, without suspended solids and low volumes, is a superseded view, thanks to the Enviolet®-Technology.
The process is capable to treat rinse waters, concentrated streams and baths, even sludge that you can find in electrolytes an such.
The Enviolet® UV-reactors are placed under extreme performance requirements, when treating e.g. concentrates. The requirements can optimally be achieved by the Enviolet® series, because of:

- 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

- The never ending search of the inventors of the technology to improve even the smallest detail, which can make the technology even better.

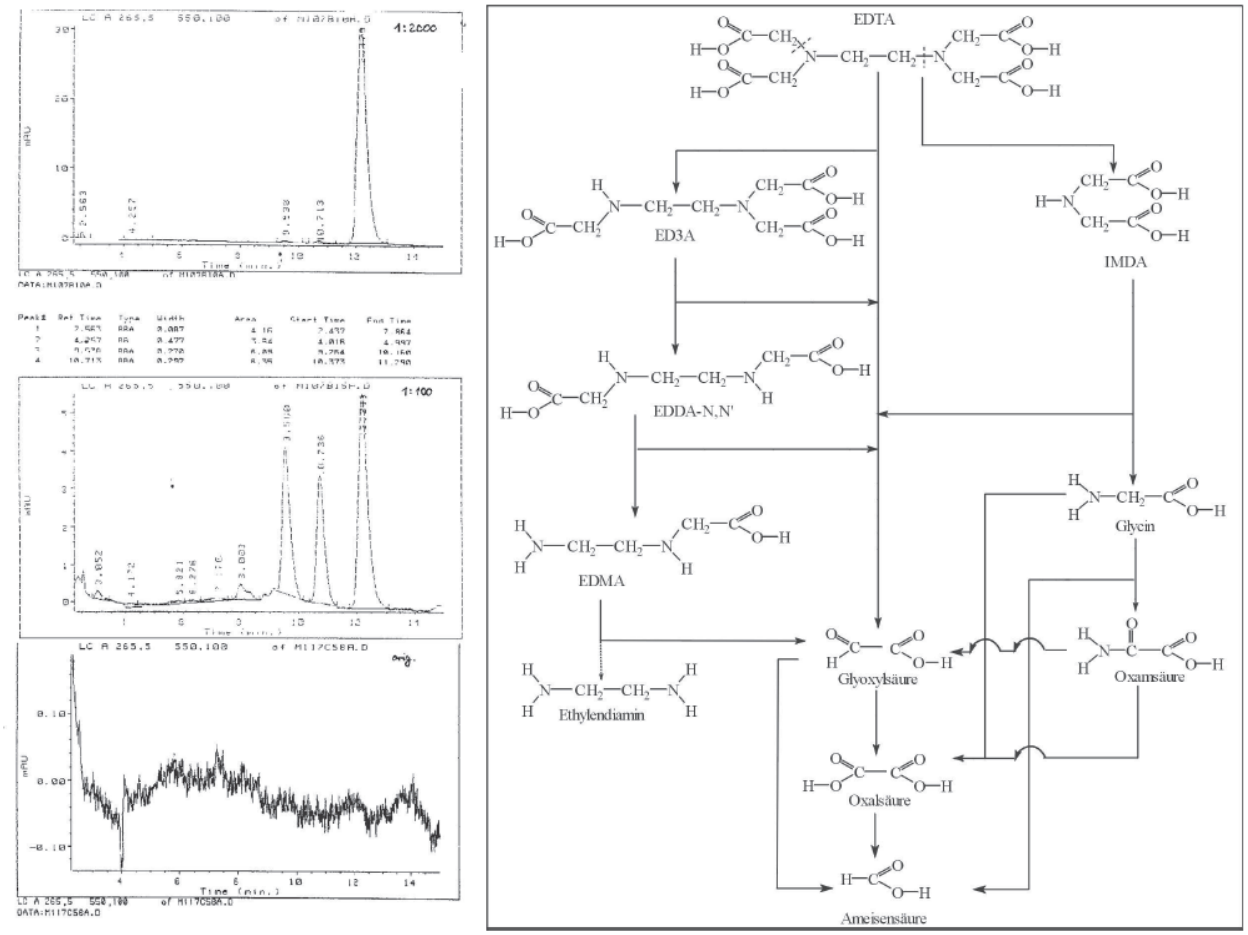

Fig. 2: *On the left: For analytical reasons, highly diluted sample of the original metal EDTA bath (top graph), diluted sample after 2 h of Enviolet®-treatment (middle graph) and undiluted sample after 4 h of treatment (bottom graph). On the Right: Breakdown of EDTA by means of Enviolet® -UV-oxidation. At the end of the reaction Nitrate, Ammonium and carbon dioxide is remaining [6]*

Last but not least, the process can be optimised with additional innovation processes as heat recovery. This heat can be used in the same process or in other processes (see industrial applications)

INDUSTRIAL APPLICATIONS AND RELATED RESULTS

Surface technology industry

Because of the increasingly higher specification requirements in surface finishing, chelates based on polyamines are being introduced more extensively, and chelates such as EDTA that were largely replaced earlier, have found their way back into surface finishing technology. In table 1, an overview of the finishing processes.


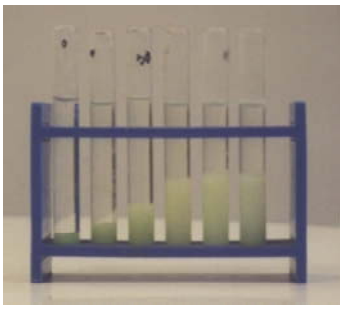

Photo 2:left *the treatment plant for the detoxification of Cu EDTA at Multek, completely delivered and installed by a.c.k. aqua concept, the inventor of the Enviolet®-technology*
Photo 3 *right: precipitation after Enviolet® treatment, (samples shown are without addition of coagulant) a very dense, compact sludge is formed, which can be easily filtrated, due to the low salt level associated with the Enviolet®-UV-process*

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®*

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*

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*	

Next to the elimination of the metals and the chelators, a significant COD reduction can be achieved.

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*

For the Enviolet®-treatment, some of the old chemicals (e.g. old acids) are used, so that the chelates in this old chemicals are eliminated also. This double (treatment and process adjustment) function of the old chemicals, saves a lot of cost (disposal costs and purchase costs)

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*

The next example is a proof that the Enviolet® is also capable to prevent waste streams and in the mean time improve the process quality in surface finishing.[7][8]

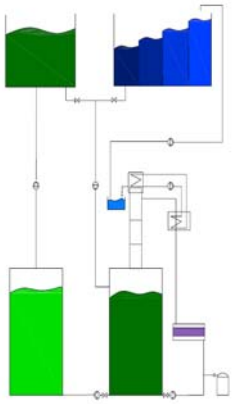

Fig. 3*:patented cleaning process scheme of electrolytic plating bath, without waste streams en with heat recovery*

The costs to process nickel electroplating, nearly doubled since 2006. The Enviolet®-UV-Oxidation unit gives an integral process solution for reduction of costs, improvement of quality and for environmental protection, while operating nickel electroplating lines.

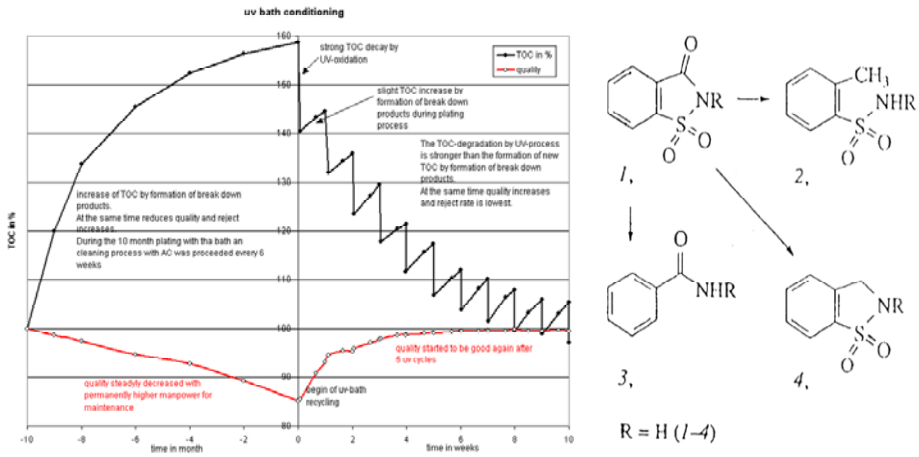

***Fig. 4*:** *left side graph, increase TOC and decrease quality during plating.. Right side graph Oscillating TOC decrease due to off-line UV treatment cycles. The noticeable TOC increases result from the plating process, whereas the decreases are the result from the UV purification process. Right, reaction products of saccharine during plating, mainly on the cathode*

Table VI: Economic data from US motorcycle manufacture (chromium plating)

Electrolyte:	Semi-Bright nickel	V=38m³
Electrolyte:	Bright-Nickel	V=38m³
Electrolyte:	Micro-Porous-Nickel	V=9,5m³
Investment:		ca. 250.000 €
Saved costs:		ca. 375.000 $/year

This gives a return on investment between 9-12 months, no waste water is coming from the plating line, no loss of expensive metal and a better quality of the plated parts.

The Enviolet®-UV-treatment is in comparison with the old method, namely AC treatment, more effective (see fig.5). With AC treatment you need to renew [9] the bath from time to time, that means a loss of high concentrations of expensive metals

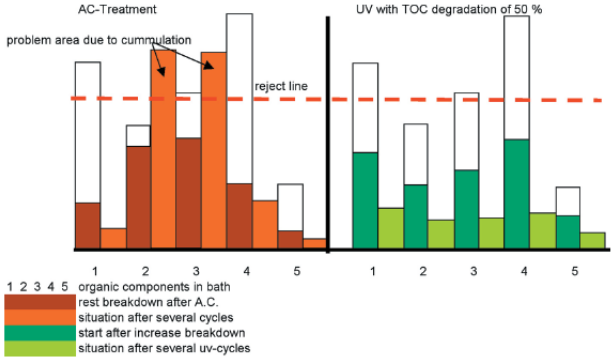

Fig. 5*: Chart shows precise comparison between activated carbon (AC) and UV-treatment over a prolonged,time period. With AC-treatment the poorly adsorbed organic compounds keep accumulating, while* they are reduced to a controlled level below the "product reject line" with UV-treatment

Chemical industry

BASF Ludwigshafen as producer of EDTA committed itself to reduce the EDTA-load discharged to the waste water by 50%. To come to this reduction, BASF compared different technologies as sorption, oxidation methods as Ozon and UV (see fig.1). The technology requirements: a simple process, selective (to keep the operational costs low) and the formed by-products must be bio-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*

The Enviolet®-UV-treatment fulfilled the requirements [10]. It is a completely automatic installation, which adapts itself to the incoming flow, towards energy and chemical demand. It results in minimal operation costs and a maximum of bio-availability.

Ground water and remediation applications

Also in this field Enviolet®-UV-technology showed its advantage, as well in-situ (funnel and gate) as with pump and treat (last is more economical feasible), it is a powerful instrument for elimination of PAH, VOCl, cyanide etc.[11 to13]

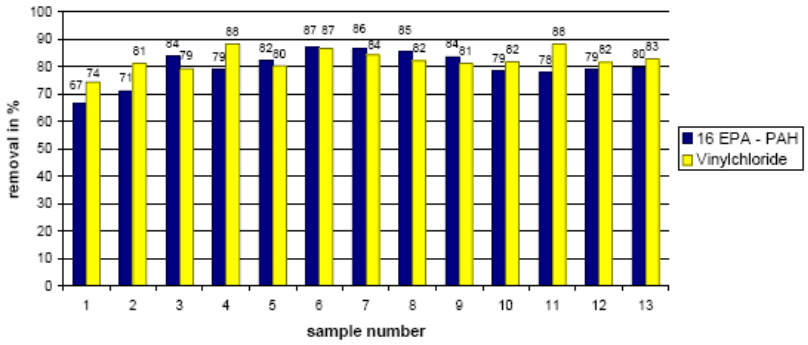

Fig. 3: Removal of PAH and Vinyl-chloride with UV-oxidation, results from the in situ pilot in old gas factory Karlsruhe

CONCLUSIONS

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.

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