Electrochemical Treatment of pharmaceutical and industrial wastewater by Anodic Oxidation

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Abstract

Scientific staff members of the Institute for Sustainable Waste Management and Technology (IAE) are currently working on applied research concerning an electrochemical treatment process for pharmaceuticals and chelating agents (for example EDTA and NTA) in municipal and sectoral (e.g. industrial and medical) waste water. Although these impurities have very low concentrations, scientists have not been able yet to estimate all possible risks for humans and animals. As an example the release of pharmaceuticals into surface waters may lead to an increased dissemination of antibiotic resistance. Endocrine substances like hormones are suspected to promote feminizing effects on organisms in ecosystems. Complexing agents like EDTA may cause a remobilization of sedimented heavy metals in surface waters. As these substances cannot be eliminated sufficiently using conventional waste water treatment procedures some new methods have to be investigated. This study is focused on two different topics – the anodic oxidation with boron doped diamonds and ozonation. During the first project phase, lab scale experiments were executed in the institutes' laboratory, to prove the operational reliability of both treatment methods was proven by eliminating even more then 90 % of the pollutants. In the second step a tech scale unit was constructed and installed

via a bypass system at the clean water outlet on the area of the local municipal waste water treatment plant. It consists of four parallel waste water flows, whereas three are equipped with electrochemical reactors of different electrode areas (3, 6 and 9 electrodes per reactor), and the fourth is taken as a reference value. Currently this tech scale unit is extended by an automatic sampler and an ozonation treatment.

Key Words: Anodic Oxidation; Ozonation; Pharmaceutical Wastewater; Endocrine Substances; Complexing Agents; EDTA; Diamond Electrodes

1. Introduction

Pharmaceuticals are discharged into the sewer system with human or animal excrements and finally end up in the municipal sewage plant. Because of their complex chemical structure some drugs (e.g. Carbamazepine) or chelating agents (for example EDTA and NTA) cannot be elimininated using conventional waste water treatment procedures, so they are inserted into the aquatic system (Ternes 1998, Hohenblum *et al.* 2004).

As an example the release of pharmaceuticals into surface waters may lead to an increased dissemination of antibiotic resistance (Balcioglu & Ötker 2003), endocrine substances like hormones are suspected to promote feminizing effects on organisms in ecosystems (Paumann *et al.* 2003). Complexing agents like EDTA may cause a remobilization of sedimented heavy metals in surface waters.

While there are already statutory thresholds for EDTA and NTA implemented in Austria (QZV Chemie OG 2006) according to the EU directive 2000/60/EC, the regulation setting of limits for pharmaceuticals is expected in the near future.

To be able to meet this requirements two innovative treatment procedures have been designed and are currently in testing state - one is the anodic oxidation with boron doped diamond electrodes and the other one the ozonation. For the second method a new sort of ozone generator is used and the ozone is contacted with the water flow in a venturi injector.

Analytics are carried out partly in the institutes own laboratory for environmental

analysis and partly at the 'Umweltbundesamt GmbH' (UBA), one of the project partners. The process design was developed in two steps. At first a small lab unit was constructed (flow rates ranged from 3-80 L/h). Treatment sources included synthetic waste water, cleaned waste water after the local municipal waste water treatment plant and a wide range of sectoral waste water. The technical results from this first phase were used for the design and construction of the tech scale unit.

2. Theoretical process background

The basic idea for the treatment of pharmaceuticals and industrial chemicals was to combine the anodic oxidation and the ozonation, as both process steps are able to provide the needed oxidants (O_3 and Hydroxyl radicals).
In fact these two processes are quite different, so both are described shortly.
When using boron doped diamonds electrodes, oxidants (O_3 and Hydroxyl radicals) are extracted directly from the waste water's organic matrix, which is done by applying direct current to the electrodes. These oxidants are able to eliminate the organic compounds thus no additional chemicals are needed.
Concerning ozonation, the oxidant (O_3) was generated by electrical production at the beginning and is meanwhile produced by a sort of dielectric barrier discharge.

3. Description of equipment

During the research project two technical plants were constructed and are being operated, a small plant in laboratory scale located at the institutes laboratory and a medium sized tech scale unit located at the local municipal waste water treatment plant.

3.1 Bench scale unit

The first lab scale unit (Fig. 1) was used in the first project step to determine the relevant process parameters for further process design and to get an idea about essential parts and sizes for constructing the tech scale unit. In the second step, the small plant is utilized for several test series treating different sources of sectoral waste water.

The plant follows a modular design concept und consists of two independent segments, one represents a flow reactor for the anodic oxidation, the other one a reaction well and the attached ozone generator. The named parts operate either separately or in combination. Hydraulic conveyance of the waste water to particular reaction circuit is provided by diaphragm pumps (Sera R203-2,4E 3 L/h) and flexible-tube pumps (Gardener, Watson-Marlow 323e max. 86 L/h).

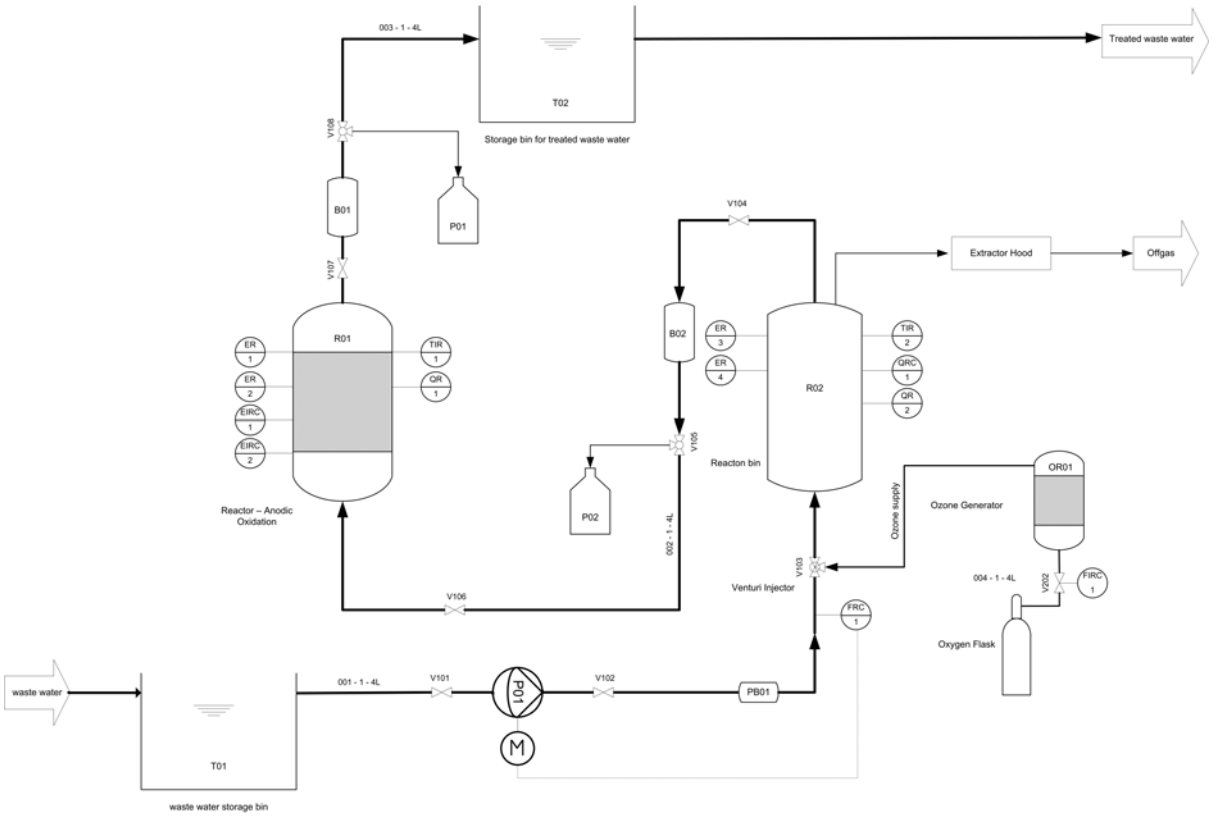

Fig. 1: Sketch of the of the lab scale unit - a combination of anodic oxidation and ozonisation

3.1.1 Anodic Oxidation

The treatment unit for the anodic oxidation in the lab scale consists of a flow reactor, which is equipped with eight parallel plate electrodes (total area 352 cm²). The treated medium is seeping through this reactor, process parameters are detected by downstream sensors. As experiences gained in the preliminary tests pointed out an improvement treatment when using a downstream catalyst based on metal oxide, so this type of catalyst was used for a after- reaction for the follow up test series.

Voltage supply for the electrodes is provided by an EA-HV 9000-600-2000 power supply (I = 0 ~ 3 A), whereas the current density is kept at a constant level.

3.1.2 Ozonisation

The ozonisation process consists of two steps, the production of O_3 and the treatment reactor for contacting the oxidant with the waste water. This gives the advantage of two ways to optimize the treatment plant. In lab scale different sorts of production and insertion have been investigated. At the beginning diamond electrodes located on titan-oxide-plates where used, but as these caused technical problems (electrodes lifetime, operating stability) finally the process was substituted throw an advanced corona-discharge generator for the ozone.
Reduction tests were carried out in counter current flow at the beginning, in further project steps a venturi injector has been used to mix waste water and ozone. Similar to the anodic oxidation, interconnection of sensors is possible.

3.2. Tech scale unit

The tech scale unit (TSU) consists of four parallel waste water flows, whereas three are equipped with electrochemical reactors, manufactured by "pro aqua Diamantelektroden GmbH", of different electrode areas (3, 6 and 9 electrodes per reactor). This plant design (Fig. 2) permits a reference value on the fourth water flow on the one side, and the possibility to take three samples at the same time for comparison. Furthermore the unit is equipped with an automatic polarity changer to avoid lime scale on the electrodes. In the next stage of expansion, an automatic sample collector and a fluid level indicator for the waste water source will be connected to the plant, so further automation can be achieved.

Fig. 2: Tech scale unit; left side: controlling station, right side: reactor unit

4. Test series

During January to September 2007 miscellaneous test series have been carried out using the lab scale unit (LSU) on the Institute for Sustainable Waste Management and Technology (IAE) to examine the single procedure steps and combinations of the reactors used in waste water treatment process. To gain knowledge about the interaction of the different chemicals in the matrix and to optimize the treatment the fluid flow rate and the current density were varied. Based on these experiences test series on the tech scale unit and series with sectoral waste water were started in the second project phase (Tab. 1)

Tab. 1 – Overview of the test series

Project-phase	Experiment parameter	Aggregate		
		Lab scale unit		Tech scale unit
		Anodic Oxidation	Ozoni-sation	
I	Synthetic waste water with EDTA	x	x	
	Degradability experiments with pharmaceutics endowment	x	x	
	Real waste water without additional endowment	x	x	
	Variation of current densities and flow rates	x	x	
	Different contact methods		x	
	Treatment combinations	x	x	
II	Experiments with industrial waste water	x	x	
	Variation of current densities and flow rates	x	x	x
	Serial connections of the reactors			x
	Venturi injector for the ozone contact		x	
	Ozonization as reference method			x

4.1 Sample preparation

For determination of so called principal parameters fixing agents have to be added shortly after sample drawing. This way further degradation of the ingredients need to be analyzed is prevented. To prevent disassembling of pharmaceuticals 100 mg NaN_3/L sample is added, for fixating chelating agents Formaldehyde (w = 37 %, 10 mL/L) provides the needed capabilities. Afterwards the samples were sent to the UBA in cooling boxes.

4.2 Analytics

The process parameters temperature, pH-value and redox potential were directly monitored by sensors, in case of the anodic oxidation current and voltage were recorded. The analytic of pharmaceuticals and chelating agents (Tab. 2) were carried out by the 'Umweltbundesamt' (UBA), where similar

projects were accomplished before (Scharf *et al.* 2002, Paumann *et al.* 2003).

Tab. 2: Analytic program

Substance groups	Experiment parameter	IAE	UBA	LOQ ng/L	LOD ng/L
Sum parameter	DOC	x		10	---
	Redox potential, pH-value,	x		---	---
	COD, mg/L	x		15	---
Pharma-ceutical	Carbamazepine		x	2.0	1,0
	Caffeine		x	20	10
	Roxithromycine		x	20	10
	Erythromycine-H_2O		x	20	10
	Josamycine		x	20	10
	Diazepame		x	2.0	1.0
	Trimethoprime		x	20	10
	Sulfamethoxazole		x	20	10
Complexing agent	EDTA, µg/L		x	1	1
	NTA, µg/L		x	1	1
	DTPA, µg/L		x	2.5	5
	1,3-PDTA, µg/L		x	1	1

LOQ Limits of Quantification, LOD Limits of Detection

During the first preliminary tests of the two applied technologies on the LSU an analysis of the EDTA elimination was made. Therefore complexometric titration according to DIN method DIN 38406-3 for determination of calcium and magnesium ions in water by EDTA was used. Titrating with a calcium solution of defined concentration gives the possibility to calculate the amount of EDTA in the treated solution. Therefore EDTA was added to the untreated water sample. After treatment 50 mL samples were taken and sodium hydroxide (NaOH, 2 mol/L) as well as an indicator salt were added. The sample was then titrated with a calcium chloride solution ($CaCl_2$, 50 mg/L) till a colour change from blue to purple was achieved. The concentration of EDTA in the titrated sample was then calculated according to the DIN standard DIN 38406-3.

4.2.1 Pharmaceuticals

For analysis of pharmaceutical compounds 500 mL of the samples were acidified, spiked with an isotopically marked surrogate standard mixture and subsequently enriched by means of solid phase extraction. Analytes were eluted using dichlormethane, ethylacetate and methanol. The resulting extract was concentrated under a gentle stream of nitrogen and solvents were changed to acetonitrile and water. The final extract was spiked with an internal standard to follow instrument stability and compensate for matrix effects. Samples were analyzed by means of liquid chromatography-electrospray ionization-tandem mass spectrometry. Quantification was performed by external standard method.

4.2.2 Complexing agents

For analysis of complexing agents isotopically marked surrogates and an internal standard were added to the samples. Samples were concentrated to dryness on a sand bath at 120°C, and the residue was resolved in 1M hydrochloric acid. After evaporation of the acid the residues were esterified with a mixture of n-butanol and acetylchloride. After the rection was stoppen by addition of sodium hydroxide solution, the resulting esters were extracted with n-hexane and dried over sodium sulphate and finally analyzed with gas chromatography-mass spectrometry in Single Ion Recording (SIR) mode. Quantification was performed with internal standard method by means of isotope dilution.

5. Analysis

During the experiments (Fig.3) we observed a strong dependency of the treatment success on the applied current density, the reactor surface and the time of contact could be observed. The results also showed a different degradability of the individual substances as Carbamazepin showed a better degradability than Diazepam. The degradability of Complexing agents showed a deterioration of the degrading performance at a low concentration range (µg/L-Area).

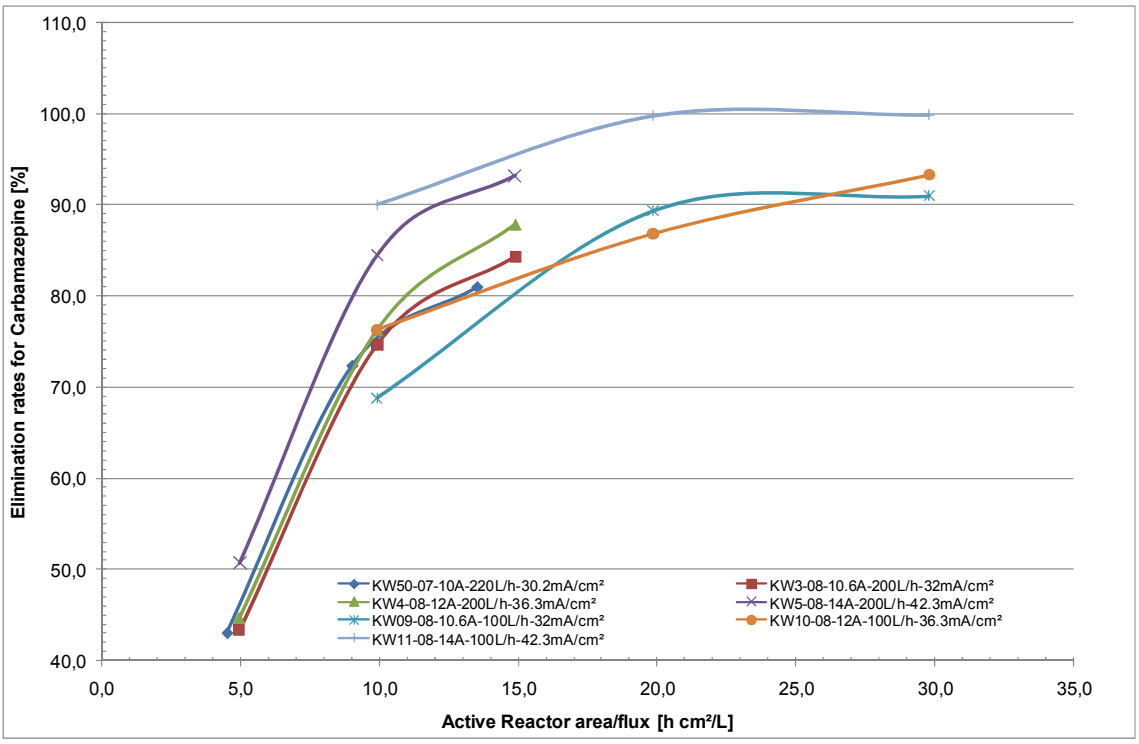

Fig. 3: Actual rates of elimination for the Anti-epileptic drug Carbamazepin, TSU – different current densities and flow rates

6. Summary

With the meanwhile accomplished experiments the applicability of the used treatments for a continuing waste water treatment was proven (Menapace *et al.* 2008). Furthermore the experiments on the TSU were performed under the most possible realistic terms, to get data material for the optimization (e.g. reactor dimension to increase the contact time).

Based on a comparison of the particular treatment successes of the municipal and industrial waste water, a statement concerning the applicability for central and decentral waste water treatment should be made. Beside the treatment success the costs of investment and the costs of treatment should be considered. Based on 0,07 €/kWh and after a first estimation for the flow rate with 200 L/h the costs for the treated waste water depending on current densities from 30,2-42,3 mA/cm² will range between 0,16-0,60 €/m³.

7. Acknowledgment

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