Electrochemical treatment of pharmaceutical wastewater by combining anodic oxidation with ozonation

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Electrochemical treatment of pharmaceutical wastewater by combining anodic oxidation with ozonation

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Wastewater effluents from sewage treatment plants (STP) are important point sources for residues of pharmaceuticals and complexing agents in the aquatic environment. For this reason a research project, which started in December 2006, was established to eliminate pharmaceutical substances and complexing agents found in wastewater as micropollutants. For the treatment process a combination of anodic oxidation by boron-doped diamond (BDD) electrodes and ozonation is examined and presented. For the ozone production a non-conventional, separate reactor was used, in which ozone was generated by electrolysis with diamond electrodes For the determination of the achievable remediation rates four complexing agents (e.g., EDTA, NTA) and eight pharmaceutical substances (e.g., diazepam, carbamazepin) were analyzed in several test runs under different conditions (varied flux, varied current density for the diamond electrode and the ozone producing electrode of the ozone generator, different packing materials for the column in the ozone injection system). The flowrates of the treated water samples were varied from 3 L/h up to 26 L/h. For the anodic oxidation the influence of the current density was examined in the range between 22.7 and 45.5 mA/cm^2, for the ozone producing reactor two densities (1.8 a/cm^2 and 2.0 A/cm^2) were tested. Matrix effects were investigated by test runs with samples from the effluent of an STP and synthetic waste water. Therefore the impact of the organic material in the samples could be determined by the comparison of the redox potential and the achievable elimination rates of the investigated substances. Comparing both technologies anodic oxidation seems to be superior to ozonation in each investigated area. With the used technology of anodic oxidation elimination rates up to 99% were reached for the investigated pharmaceutical substances at a current density of 45.5 mA/cm^2 and a maximum sample flux of 26 L/h.

Keywords: Anodic oxidation, ozonation, pharmaceutical wastewater, endocrine substances, complexing agents, EDTA, diamond electrodes.

Introduction

In modern medicine pharmaceuticals play a decisive role. Because of an increased life expectancy and intensive care medicine an increasing amount of pharmaceuticals is produced. Thus these substances are consumed in a mass of tons per year in industrialized countries.[1] Pharmaceutical substances and complexing agents are introduced into wastewater to a high extent by households and special facilities (e.g., hospitals and chemical industry).[2] The occurrence of these substances, which are suspected to have an impact on humans and wildlife, has been reported in several studies. [3−6] The aim of the current project is to achieve the maximum elimination of the examined substances with the combination of electrochemical oxidation and ozonation. For the development of the treatment process a total running time of 2.5 years is scheduled.

Up to now, there are no existing threshold values for pharmaceutical substances in case of waste water treatment, but in future an adoption of such values appears to be likely. For complexing agents, there are still existing limit values in the european and national legal framework.[7−9] Although pharmaceuticals are absorbed by human and animal organisms after their intake, significant amounts of the active substances are excreted without alteration. Although these impurities are at very low concentrations (in the scale of ng/L up to μg/L), scientists have not yet been able to estimate all possible risks involved, their investigation will be intensified in the future. As an example, the release of pharmaceuticals into nature via wastewater could lead to an increased dissemination of antibiotic resistance. Endocrine substances like hormones are suspected to promote feminizing and masculinizing effects on organisms in ecosystems.[10−12]

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Table 1. Investigated substances.

Substance	CAS-number	Category
1.3-PDTA	1939-36-2	Complexing agent
DTPA	67-43-6	Complexing agent
EDTA	60-00-4	Complexing agent
NTA	139-13-9	Complexing agent
Carbamazepine	298-46-4	Anti-epileptic drug
Caffeine	58-08-2	Psychostimulant
Diazepam	439-14-5	Psychiatric drug
Erythromycin-H_2O	114-07-8	Antibiotic
Josamycine	16846-24-5	Antibiotic
Roxithromycin	80214-83-1	Antibiotic
Sulfamethoxazole	723-46-6	Antibiotic
Trimethoprim	738-70-05	Antibiotic

The complete treatment will be done in two steps. In the first one, the wastewater will be treated by electrochemical oxidation with diamond electrodes. After this step ozonation completes the process. Synthetic boron-doped diamond electrodes (BDD) are characterized by high anodic stability, a wide working potential window and low and stable voltammetric back-ground current in aqueous media. [13,14] Therefore, the electrochemical behaviour of BDD electrodes have been investigated with the goal of developing applications for wastewater treatment.[15–17]

In a further test runs next to the treatment with only one technology, i.e. anodic oxidation or ozonation, the influence of the sequence of the two treatment types in case of their combination was tested. The ozone will not be produced like in the conventional ozone producing systems, i.e. with coaxial dielectric-barrier-discharge in air. In this case ozone will be formed by electrolysis with diamond electrodes.

The whole process can be described as follows. Firstly, the wastewater under analysis will be taken from the effluent of a STP and will be treated in a lab scale unit (LSU). The needed amount of ozone will be produced in a non-conventional, separate generator. In this process the ozone will be produced directly from Sodiumhydrogensulfate ($NaHSO_4$) in a concentration of 1 mol/L by electrolysis with diamond electrodes. The injection of the ozonic concentrated water to the wastewater will be progressive. After ozone addition, a post mixing chamber will be used to install a sensor at this step. With the given ozone concentration, it will be possible to calculate an ozone balance of the reactor system. This balance combined with other parameters (e.g., Chemical Oxygen Demand, COD and Dissolved Organic Carbon, DOC) will result in conclusions about the ozone consumption of the substances existing in the sample, which depends on the existing organic matrix of the water samples (scavengers).

In the second treatment step, the wastewater will be delivered to an electrochemical reactor. Inside this component BDD electrodes are located to implement an anodic oxidation. In the process OH-radicals and other oxidants will be directly produced and used for the oxidation of the substances (pharmaceuticals and complexing agents).

Materials and methods

Sample preparation

For the experiments, wastewater from an effluent of a STP (90,000 population equivalents) in an Austrian city was used. The samples were gathered from the effluent tank by a tub, therefore mixing samples (20 L up to 40 L) were obtained for the experiments. Fixing agents were added to the drawn samples (2 L for the untreated sample, 3 L for the treated effluent). For stabilizing the pharmaceutical substances (Table 1) 100 mg of sodium azide (NaN_3) per L sample was used. To stabilize the complexing agents in the untreated and treated samples 10 mL formaldehyde (37%) per L sample were used. After fixing the substances, the samples were stored and transported in a cooling box to the Federal Environment Agency in Vienna.

Preliminary tests with EDTA remediation

In the first phase of the project, preliminary tests with EDTA-solutions (20 mg/L up to 80 mg/L) were performed on the built LSU. In this apparatus a central data logging system (Eurotherm 2500) is included (software Lookout v 4.0.1), the process data (pH, temperature, conductivity and redox potential) were online collected with sensors (EUtech Instruments). The flow rate (measured with an amperometric Honsberg Sensyflow sensor) of the treated water range of approx. 3 L/h was recorded and stored too. For the first tests a closed loop treatment process was realized. Therefore EDTA was diluted in distilled water and pumped (therefore a diaphragm pump with a maximum flow rate of 3.3 L/h from Sera was used) through the test installation with the reactor for the anodic oxidation (Fig. 1). The current density varies in this case from 25 to 37.5 mA/cm^2, while working at a voltage of about 80 V. For the treatment by ozonation—the O_3 is produced in an electrolytic process and afterwards injected in a water irrigated column (Fig. 2)—two current densities were tested (1.8 and 2 A/cm^2). At these values, the direct voltage was approx. 20 V. Sodium hydrogensulfate ($NaHSO_4$) in a concentration of 1 mol/L were added as electrolyte. To provide a greater reaction area between the produced ozone and the treated water, packing material (glass beads with a diameter of 2.1–3.3 and 6.6 mm) were filled in the column subsequent test runs. While in the tests with the anodic oxidation a water volume of 2 up to 6 L was treated, in the first ozone tests only volumes up to 800 mL were treated.

Degradation of pharmaceuticals and complexing agents

Since in the later tests the wastewater was although continuously pumped through the reactors, it was not recirculated in the system. Test runs with the BDD electrodes were executed, in which spiked synthetic and real wastewater (STP-effluent, wastewater from a hospital and an printed
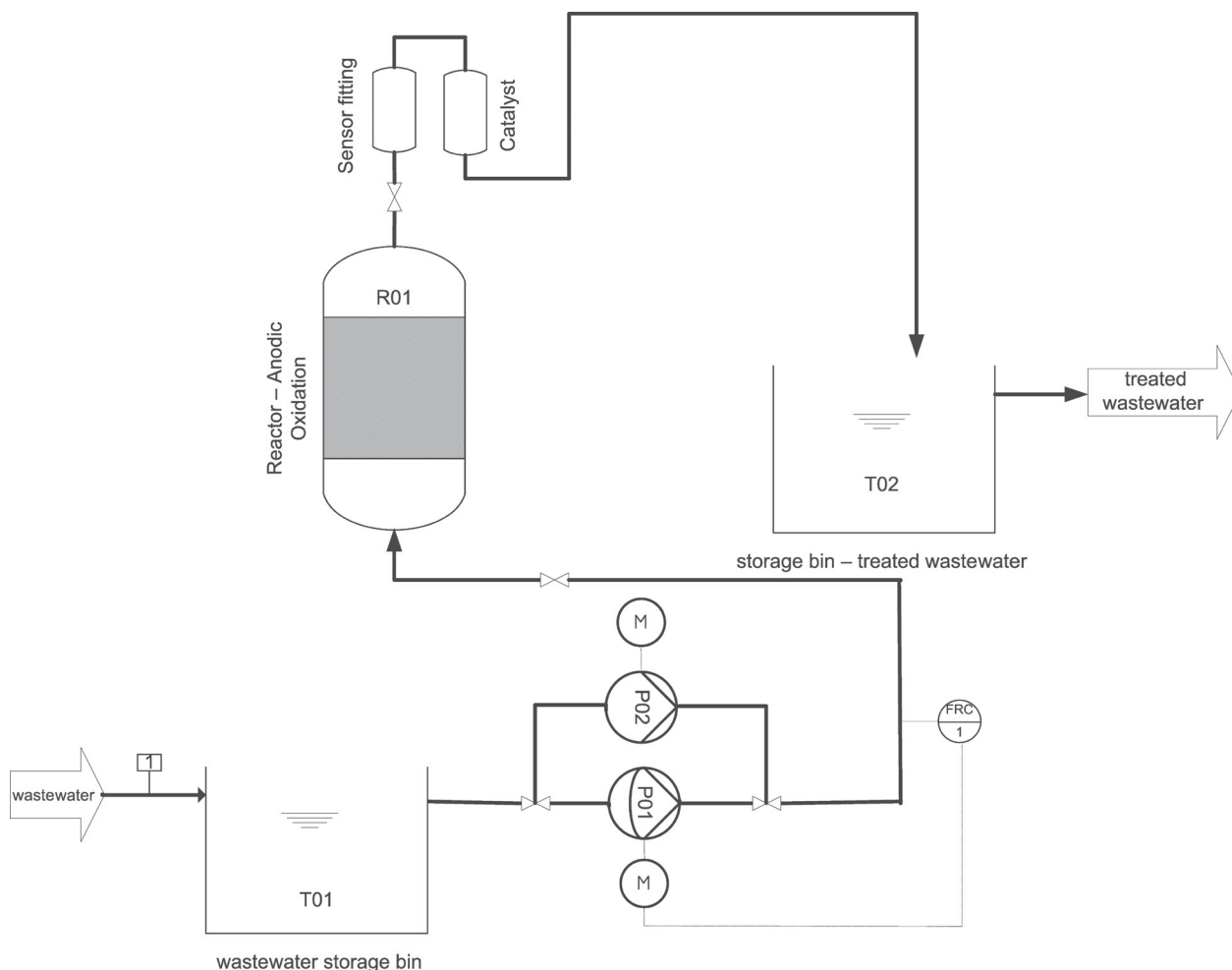
Fig. 1. Schema of the anodic oxdiation part of the lab scale unit.

circuit board producer) was generated. The synthetic one was made with a recipe out of the European directive of detergents.[18] To have a minimum concentration of the investigated substances, a concentrated solution including these substances was added to the untreated water samples to achieve concentrations of 50 μg/L and in consecutive tests 1 μg/L.

Analytical methods

As shown in Table 1, the samples taken after the treatment modules were analyzed for the parameters shown in Table 1, as well as DOC, COD, adsorbable organic halogen compounds (AOX), conductivity and redox potential. The pharmaceutical substances and also the complexing agents were analyzed by the Federal Environment Agency of Austria (this agency has been a project partner in different studies about pharmaceuticals in the ecosystem, as in the ARCEM project).[12] COD and DOC were analyzed by the laboratory of the Institute for Sustainable Waste Management

and Technology in Leoben, and the other parameters will be measured.

For the first preliminary tests of the two applied technologies an analysis of the EDTA elimination was made. Therefore a complexometric titration according to the DIN methods for determination of calcium and magnesium ions in water by EDTA was used.[14] Titrating with a calcium solution of determined concentration the amount of EDTA in the treated solution could be calculated. Thereby 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 was added. The sample was then titrated with a calcium chloride solution (CaCl$_2$, 50 mg/L) till a color 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.[19]

For the analysis of pharmaceutical compounds, 500 mL of the samples were acidified, spiked with a isotopically marked surrogate standard mixture and subsequently enriched by means of solid phase extraction. Analytes were
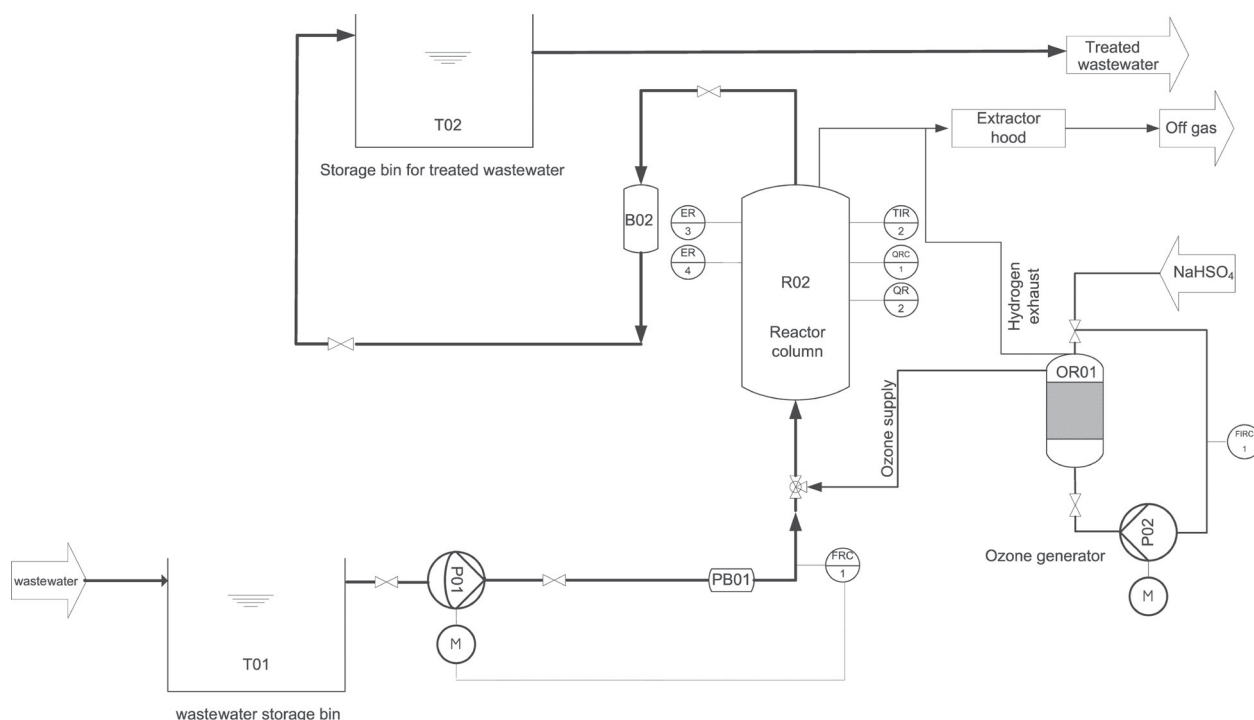
Fig. 2. Schema of the ozonation part of the lab scale unit.

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 and analyzed by means of liquid chromatography-electrospray ionization-tandem mass spectrometry. The achievable limits of quantifications (LOQ) as well as the limits of detections (LOD) are listed in Table 2.

For the 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 concentrated hydrochloric acid. After evaporation of the acid the residues were esterified with a mixture of n-butanol and acetylchloride. The resulting esters were resolved in n-hexane, the extracts were washed with a sodium hydroxide solution and dried over sodium sulphate, and finally analyzed by means of gas chromatography-mass spectrometry. In Table 2 are the achievable values for LOQ and LOL listed.

Results and discussion

Preliminary tests with EDTA in a lab-scale unit

Figure 3 shows the degradation of the diluted EDTA in the water samples. A direct relation between the treatment by anodic oxidation and ozonation is feasible. Equation 1 indicates the number of recirculations of the samples (n). With the number of recirculations a better comparability of different sample volumes (V_{water}) is given at a determined flux of the untreated samples through the reactor and treatment time $t_{treatment}$.

$$n = V_{water}[L] / (Flux\ [L\ /\ h] \times t_{treatment}t\ [h]) \qquad (1)$$

The application of anodic oxidation (EDTA dissolved in distilled water) shows comparable results to operation with ozonation. Treating synthetic wastewater with anodic oxidation the concentration of EDTA diminishes significantly more rapidly than by ozonation treatment. Including a catalyst at the end of the treatment chain, the results could be further enhanced.

Figure 4 clearly demonstrates that the EDTA degradation by anodic oxidation depends on the matrix of the water sample. In this case the oxidants will be produced directly from the substances in the water and therefore can be used for the oxidation of the investigated substances. The redox potential of a test run with real wastewater and synthetic wastewater shows the more oxidative environment in the real wastewater (Fig. 4). The higher the redox potential value for a given solution, the stronger the oxidation effect. A redox potential of approx. 800 mV was obtained with real wastewater whereas only approx. 220 mV could be reached with synthetic wastewater.

Degradation tests of the investigated substances with anodic oxidation and ozonation

Table 2 shows the degradation rates for the samples of the STP effluent. A solution with concentrated substances

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Table 2. Degradation rates by anodic oxidation treatment (37.5 mA/cm^2) and ozonation (1.8 A/cm^2).

Substance	LOQ*	LOD**	Anodic oxidation			Ozonation		
			Treated (mg L^{-1})	Untreated (mg/L)	Degradation (%)	Treated (mg L^{-1})	Untreated (mg L^{-1})	Degradation (%)
1.3-PDTA	0.2	0.1	n.d.	n.d.	—	<0.2	<0.2	—
DTPA	1	0.5	n.d.	5.3	—	3.9	3.9	0.00
EDTA	0.2	0.1	28.5	97	70.83	74	70	1.43
NTA	0.2	0.1	36	58.5	38.16	55	55	3.64
Carbamazepine	0.02	0.01	<0.002	43.5	100.00	41.5	41	—
Caffeine	0.02	0.01	0.1125	49	99.77	34	32	—
Diazepam	0.02	0.01	0.0053	42	99.99	41	46	10.87
Erythromycin-H$_2$O	0.02	0.01	<0.02	46.5	99.96	47.5	48	4.17
Josamycine	0.02	0.01	n.d.	77.5	—	73	92	20.65
Roxithromycin	0.02	0.01	<0.02	47.5	99.96	64	67	4.48
Sulfamethoxazole	0.002	0.001	n.d.	n.d.	—	40.5	45	10.00
Trimethoprim	0.02	0.01	n.d.	41	—	53.5	53	0.00

*LOQ Limits of Quantification, **LOD Limits of Detection, n.d. not detectable.

(10 mg/L) was added to the real wastewater. An inlet concentration of 50 μg/L was provided. With a current density of 37.5 mA/cm^2 an almost complete degradation of the pharmaceutical substances was achieved. For the complexing agents an elimination of about 71% (EDTA) was achievable. In a subsequent test run the inlet concentration was decreased to 1 μg/L which corresponds to realistic values in Austrian STPs.[5,6] The spiked wastewater was treated by three different current densities (22.7, 37.5 and 45.5 mA/cm^2). Preliminary analyses show a complete degradation at 37.5 mA/cm^2. For the treatment of the pharmaceuticals and complexing agents (inlet concentration 50 μg/L) with ozonation a maximum degradation of approx. 21% (Josamycine) was obtained.

Figure 5 shows the achievable elimination rates by anodic oxidation (STP-effluent) at different current densities. It can be seen that the elimination efficiency varies according to the type of pharmaceutical substance (e.g., carbamazepin, coffein). Complexing agents are more difficult to eliminate which can be seen in the application of higher current densities.

In Figure 6 a comparison between the two technologies is displayed. Therefore, elimination rates were studied for each treatment method. Furthermore, the test runs indicated if
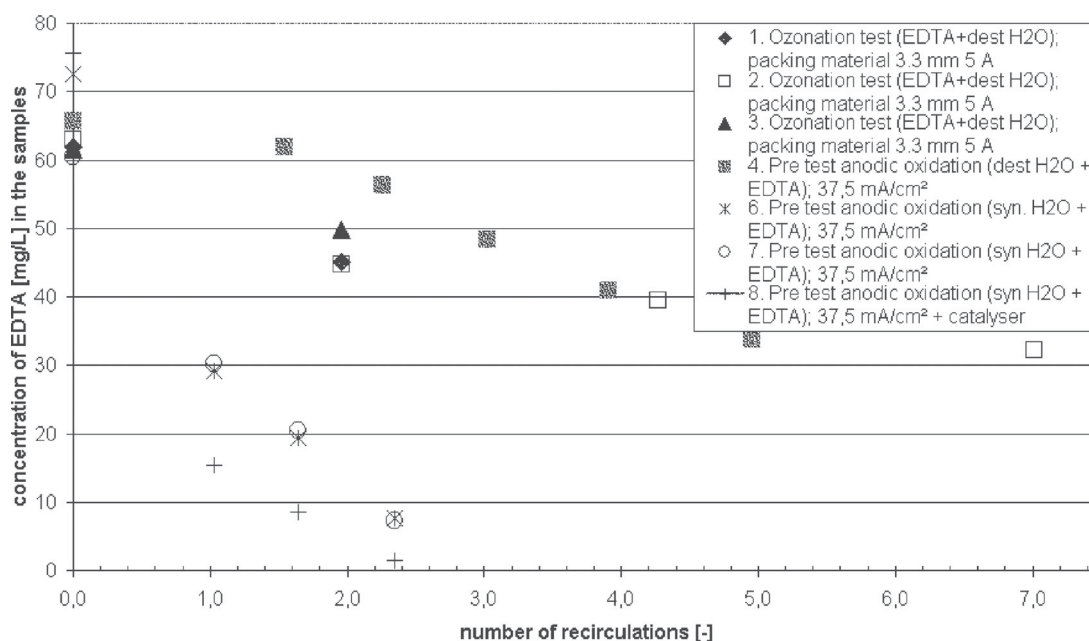

Fig. 3. Elimination of EDTA versus number of recirculations (comparison of anodic oxidation and ozonation).
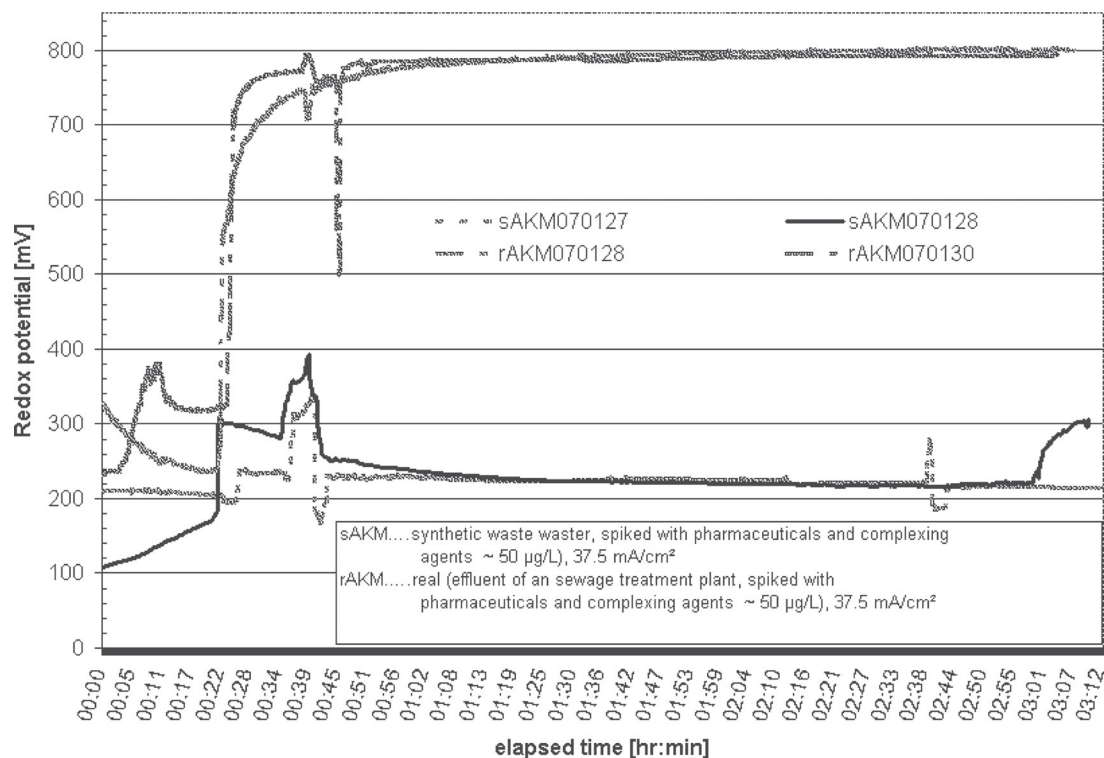
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Fig. 4. Comparison of the redox potential—synthetic wastewater vs. real waste water sample form an STP effluent (flow rate 3 L/h).
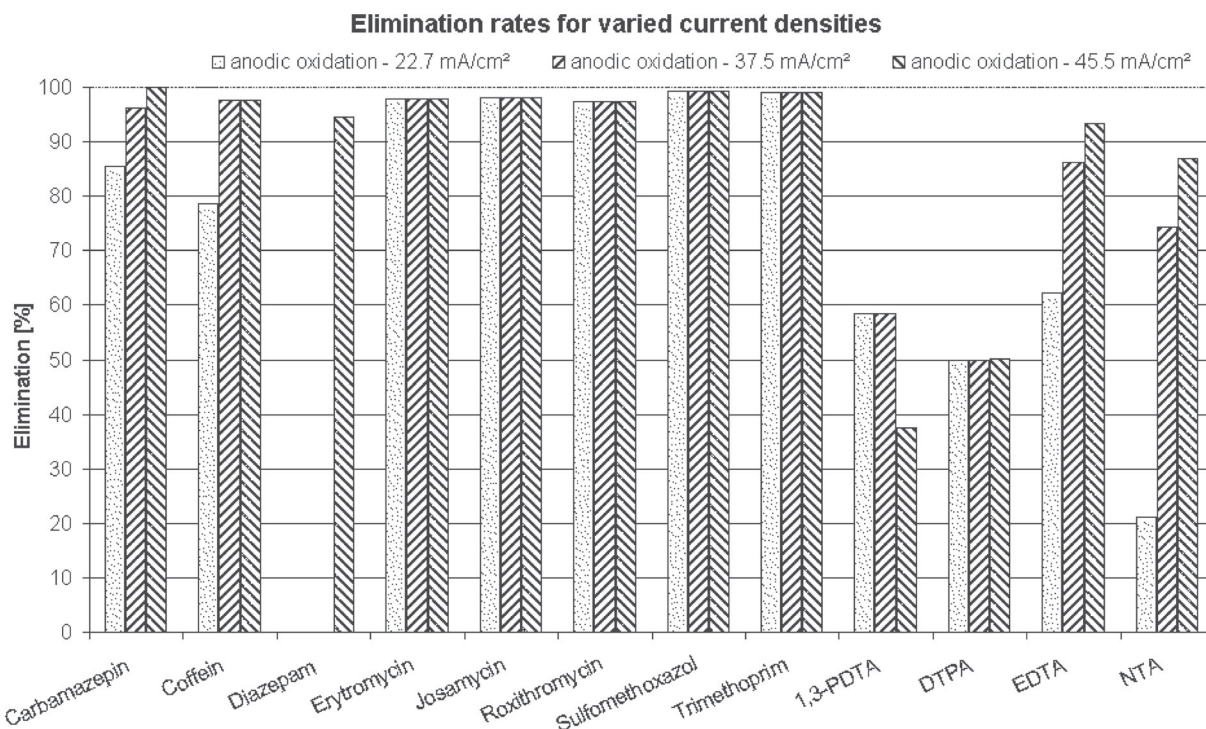

Fig. 5. Elimination rates for varied current densities (anodic oxidation, STP-effluent, flow rate 3 L/h).
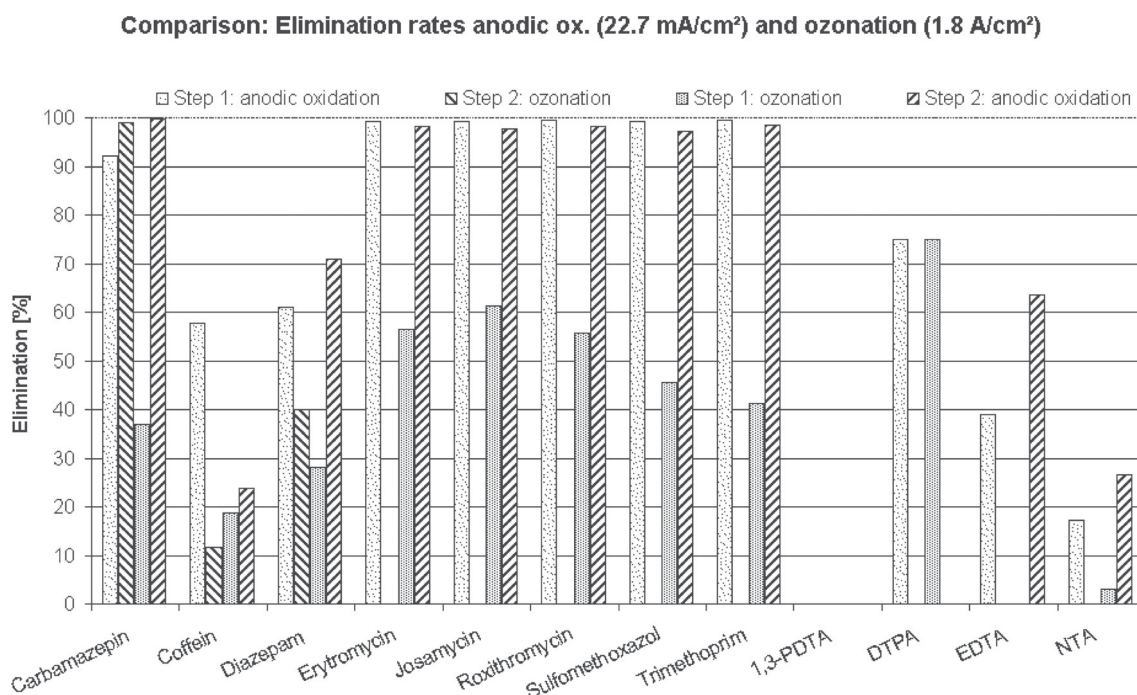
Fig. 6. Comparison of achievable elimination rates by usage of a combination of the investigated techniques (varied treatment order of the two reactors, STP-effluent, flow rate 3 L/h).

the sequence of treatment facilities matters in case of a combined application. For the calculation of the elimination rates the concentration of the treated substances was determined before treatment, after the first treatment step and after the second one. The elimination rate always refers to the anterior treatment step. Generally, the assays showed that much higher elimination is achieved by anodic oxidation than with ozonation. However, comparing the two treatment facilities applied as first treatment process shows that ozonation can be enhanced and yield better elimination results (e.g., Josamycin 21% non-optimized, approx. 60% optimized).

Conclusion

The evidence of the possible degradation of the analyzed micropollutants in municipal wastewater could be provided by treatment with BDD electrodes. In the anodic oxidation process the added pharmaceutical substances can be completely degraded. For the test runs with anodic oxidation the dependence of the performance on the applied current density could be shown clearly. Furthermore, the treatment efficiency depends on the organic matrix of the effluent in the treatment solution. This can be explained by the fact that oxidizing agents can be generated directly from the substances present in the waste water. In the also investigated treatment by ozone a maximum elimination rate of 21% was achieved in the first test run. After a first enhance-

ment of the ozone generator (flow, increase of residence time in the reaction column) elimination rates of up to 60% could be achieved.

Further optimizations of reactive contact area and injection system will be enforced in the incoming experiments. For this case the generated amount of ozone will be determined in order to submit a balance of the oxidizing agent. In the first phase of this study, the main focus was put on the general feasibility of the application of these two treatment technologies for waste water rich in pharmaceutical substances. Comparing both technologies anodic oxidation seems to be superior to ozonation in each investigated area. This can partly be explained by the simpler set up of the reactor for anodic oxidation. While for an ozonation treatment the ozone needs to be generated in a separate reactor and then be administered to the reaction column in order to react with the contaminant the generation of the oxidant and the chemical reaction in case of anodic oxidation take place at the same time in the same reactor. Therefore an ozonation process would be imply a more complex set-up and is thus more difficult to optimize.

Acknowledgments

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