

Proof of Principle of Wastewater Treatment using Plasma Discharge to Reduce the Amount of Methylparaben

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Synthetic substances like many pharmaceuticals, preservatives or other chemical compounds are actually very difficult to handle in sewage treatment. These compounds are very stable in aqueous solution and their degradation reactions are insufficient. Therefore, to eliminate these substances from wastewater additional effort is necessary. Extreme conditions like pH value, redox potential, chemical or physical energy need to be present. With our study we try to show that the use of plasma discharge could be a solution to this problem. Using the example of methylparaben, a preservative, we could show, that the physical energy of plasma discharge is able to initialize the degradation reaction in aqueous environment. The concentration was reduced by up to 70 percent in our setting depending on the treatment duration. Overall, the system showed potential to optimize wastewater treatment. Further examinations are necessary for example regarding undesirable by-products.

Keywords: wastewater treatment, plasma discharge, high voltage, degradation

Introduction

Wastewater treatment generally takes place in three stages. The first treatment stage is the mechanical treatment, which consists of pre-treatment and primary treatment (Sonune and Ghate 2004). The second stage of treatment is the biological treatment, for which there are three common processes: the activated sludge process, the biofilm process, and the near-natural process (Resch and Schatz 2020). The standard is the activated sludge method with a total of around 99% of the wastewater connected to the system throughout Germany being treated using biological methods (Umwelt Bundesamt 2021). Chemical purification serves as the third purification stage, whereby precipitants and flocculants can be used to remove phosphorus, for example.

In 2016, approximately 9.6 billion cubic meters of wastewater were treated in 9105 public wastewater treatment plants across Germany (Statistisches Bundesamt

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- Destatis 2018). Here, 97% of the German population is connected to the public sewage system [Statistisches Bundesamt - Destatis (2018)]. Especially biological and chemical contamination and pollution have increased in the last 30 years and represent a major environmental problem (Crini and Lichtfouse 2018).

It has been clear for some time that trace substances often cannot be completely removed from wastewater if the wastewater treatment plant only has a mechanical and biological treatment stage (Clara et al. 2002). The term "trace substances" refers to all substances foreign to nature that occur in wastewater in millionths or billionths of a gram per liter (Metzger et al. 2012), and this can be numerous, as more than 100,000 products foreign to nature are distributed throughout Europe (as of 2018) (Eberlein et al. 2018). These products sooner or later enter the environment and accumulate in the water (Eberlein et al. 2018). To minimize the discharge of trace substances into water bodies and the environment, wastewater treatment plants, which represent the main input pathway for organic, anthropogenic trace substances (Benstom 2017), are to be retrofitted with a fourth treatment step. At present, this mostly consists of adsorption on activated carbon or ozonation since both the cleaning performance and the economic efficiency are achieved with these methods (Metzger et al. 2019). The general cost of wastewater treatment by ozonation ranges from 0.03-0.12 €/m³ and that of wastewater treatment with powdered activated carbon from 0.05-0.10 €/m³ (Resch and Schatz 2020).

The use of plasma in water treatment is not completely unknown, though still in the early stages of development (Cui et al. 2018). Plasma is referred to as a fourth state of matter. It is defined as matter with a sufficiently high proportion of ions and electrons and is created when gas is ionized by an energy input, although the definition does not exclude liquids as well (Stroth 2018). Plasma is considered to be an advanced oxidant, and when reacting with water, hydrogen radicals are formed, which are considered to be highly reactive. Ozone is also formed, which again leads to radical formation and further oxidation reactions. In addition, the formation of hydrogen peroxide can occur, as well as further radical formation through the so-called silent electrical discharge of the plasma. This makes the entire system highly reactive (Cui et al. 2018).

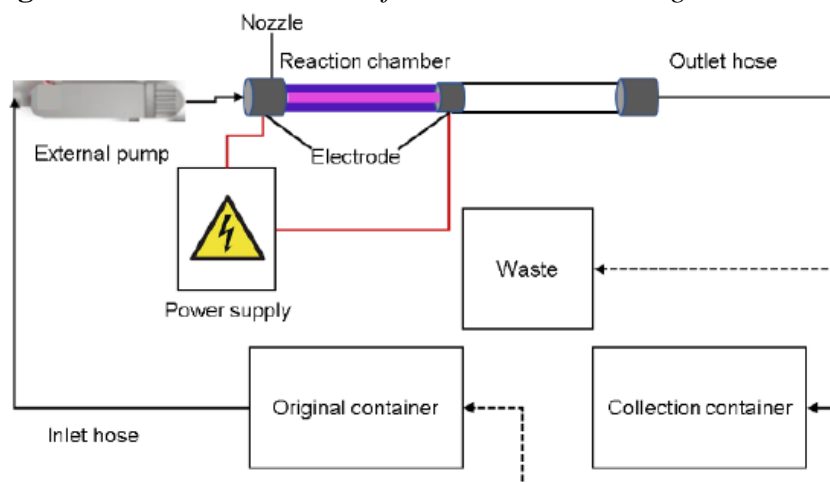
In the plant used, a similarly reactive environment is created by the interaction of cavitation, plasma with radical formation, UV radiation, shock waves, and charged particles, which has already been successfully tested in a previous pilot plant (Abramov et al. 2021).

The research objective of the work was to investigate whether this plant is able to break down chemical compounds in water. This is a conceptual proof, for which methylparaben was chosen as a model molecule. Methylparaben finds its application as a preservative in shampoos and other cosmetics, as well as in liquid pharmaceuticals and in research in bacterial agar plates to prevent fungal infestation (Fiedler and Haufe 2010). It was to be determined to what extent the methylparaben can be disintegrated by the plant, whether undesirable by-products occur, and how economical the plant is at this point in time.

Experimental

Figure 1 shows a scheme of the plant used. The plant used for the tests is larger than the first pilot plant that was developed (Abramov et al. 2021), but has less measuring equipment and a copper electrode instead of a silver electrode. The connected external pump can bring the liquid to a maximum pressure of 250 bar. From there, the sample passes through a nozzle into the reaction chamber, where it meets the plasma. The device has a power supply that is connected to an external transformer. The resulting high voltage can be regulated in a range from 10 to 24 kV alternating current. The frequency can be varied between 30 and 45 kHz. The transformer is attached to the two copper electrodes, at the two ends of the reaction chamber. Frequency and voltage can be adjusted by rotary controls. When the ratio, which can vary depending on the experimental condition such as temperature of the sample, is correct, the plasma ignites. At a pressure of 80 bar, which was used during the experiments, up to 960 L/h can be passed over the plasma once with the aid of the application.

Figure 1. Schematic Structure of the Plasma Generating Plant



For the methylparaben treatment, 20 L of a 1000 mg/L methylparaben demineralized water solution was prepared. This solution was circulated through the system three times, with sampling after each run. The 20 L batch of sample was then cycled through the system continuously for 5 minutes and finally for an additional 5 minutes, resulting in a maximum treatment time of 3 cycles + 10 minutes. A pressure of 80 bar was used and both voltage and frequency had to be constantly readjusted, so that no clear parameters could be established. However, since this is a prototype and the initial aim is to provide conceptual proof of the functionality, the determination of specific parameters was not the goal of the experiment for the time being.

During the plasma treatment of the samples, the light spectrum generated by the plasma was measured with the aid of a spectrometer (Ocean Optics Inc., Spectrometer USB2000+).

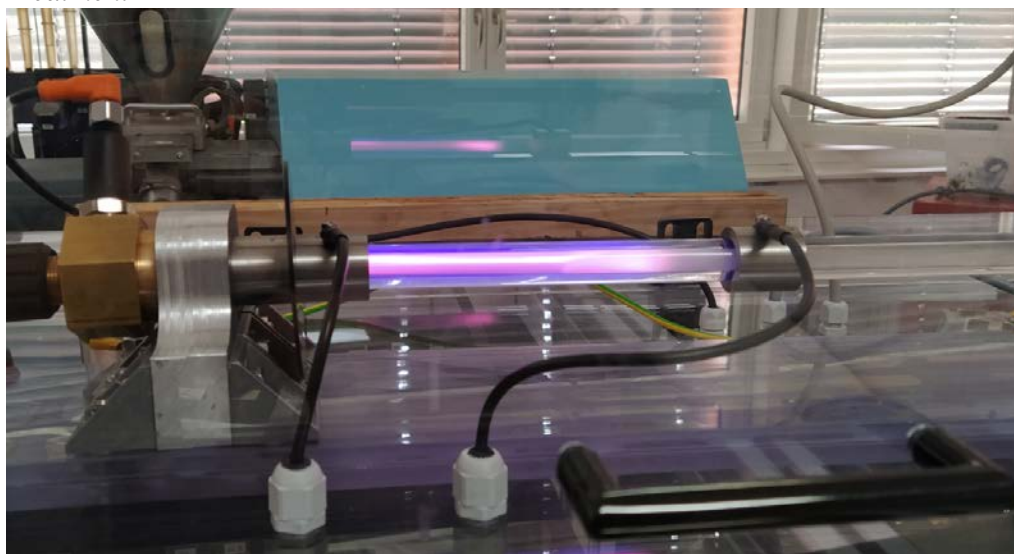
For HPLC analysis, 2 mL of sample was filtered (0.2 μm Phenomenex Inc.) and placed in HPLC sample vials. The tubes were then placed in the system (capillary LC system series 1100; column: ZORBAX Eclipse Plus C18 4.6 x 100; 3.5 mm). A flow rate of 1.2 mL/min and a temperature of 40 °C were used. A methanol-water mixture (composition 1:1) served as the mobile phase, detection was performed by a UV/VIS detector at 254 nm, and 5 μL of sample was injected in each case.

For gas chromatography, the sample was also filtered (0.2 μm Phenomenex Inc.), placed in the proper slots, and the gas chromatography (GCMS-QP2010 SE) was started. 6 μL of sample were injected and heated to 250 °C. A split ratio of 1:10 was used and helium served as the mobile phase. Detection and identification were performed using the mass-specific detector, which was coupled to the "NIST" database.

Results

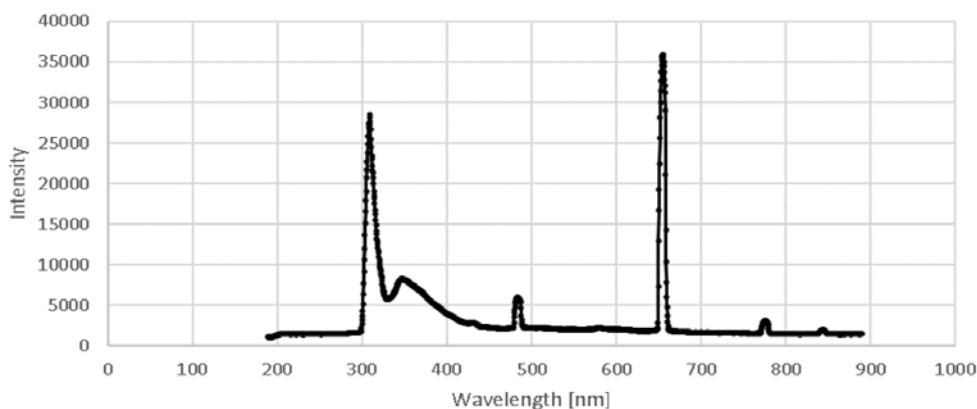
Figure 2 shows the plasma generated during the experiment, which was characterized by a pinkish-purple color. During the experiment, there were temporary dropouts of the plasma which required a readjustment of the voltage and frequency. The light emission from the plasma was measured spectroscopically and shown in Figure 3, where several peaks were observed.

Figure 2. Section of the System with the Plasma Generated during Sample Treatment



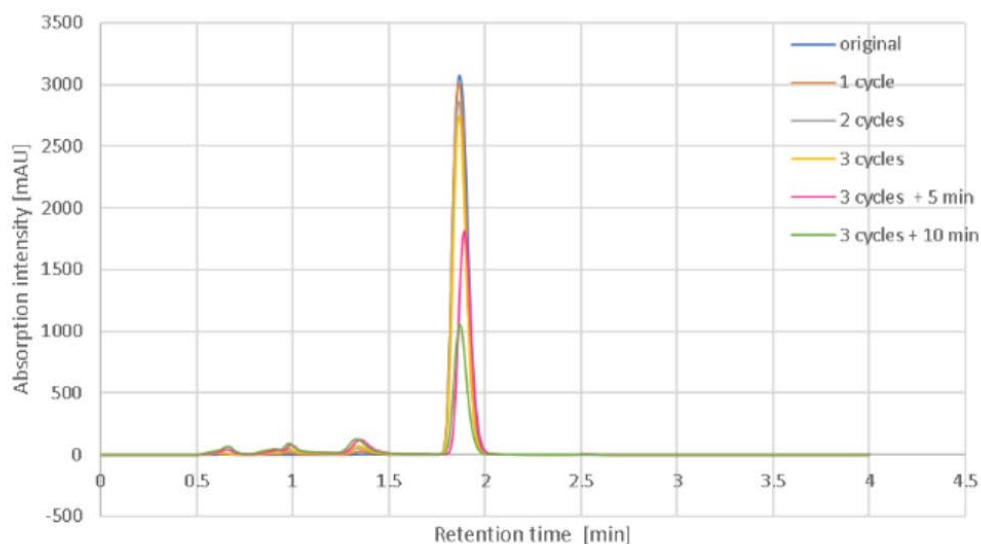
During treatment, discoloration of the samples to a brownish color occurred. This discoloration intensified with increasing treatment time.

Figure 3. Recorded Light Spectrum of the Plasma. The Spectrum was recorded Several Times during the On-Phase of the Plasma



In the HPLC analysis of the plasma-treated methylparaben samples, a major peak was detected in each sample. As can be seen in Figure 4, this peak, which was between a retention time of 1.8 min and 2 min, declined with increasing treatment time. In addition, other small peaks between 0.5 min and 1.5 min retention time could be detected in the treated samples, which were not present in the untreated sample. At the highest treatment duration, the total area reduction was over 70%.

Figure 4. HPLC Chromatograms of the Methylparaben Samples. The Absorbance Intensity was plotted against the Retention Time of Each Sample in Single Determination

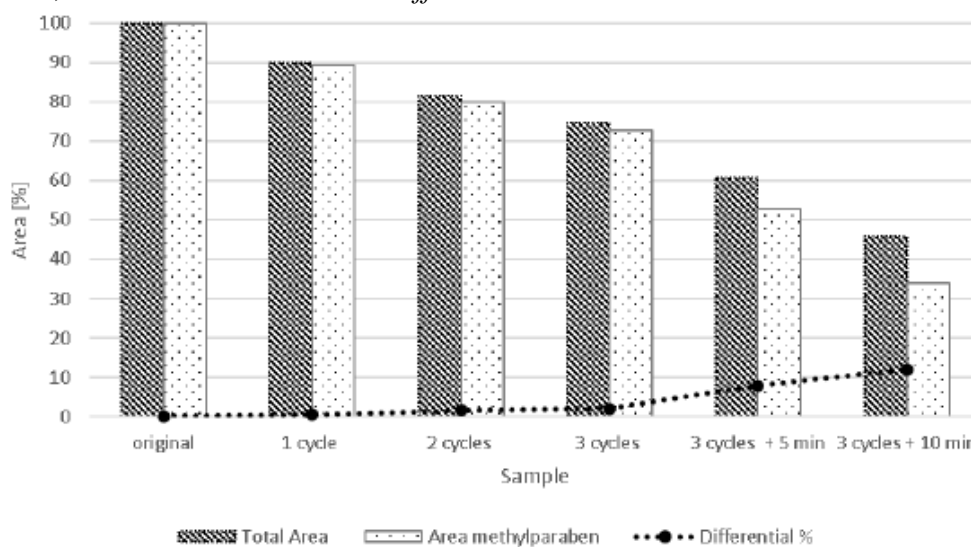


GC-MS of all methylparaben samples detected one large peak each and identified it as methylparaben. This peak was declining with rising treatment time, which can be seen in Figure 5. Additional peaks were only visible when the baseline was examined more closely. Not all peaks could be identified. Among the top emerging compounds that could be allocated were guaiacol and methyl

protocatechuate. The highest number of newly formed peaks was found in the sample with the longest treatment time and amounted to 26 new detected peaks of which 19 could be identified.

Despite the appearance of new peaks, the total area of all peaks combined dropped significantly, reaching an overall reduction of over 50% at the highest treatment duration, which was only 12% less than the change in the methylparaben peak. It can be concluded that methylparaben was not completely converted to by-products. Total peak decrease and methylparaben peak decrease are shown in Figure 6.

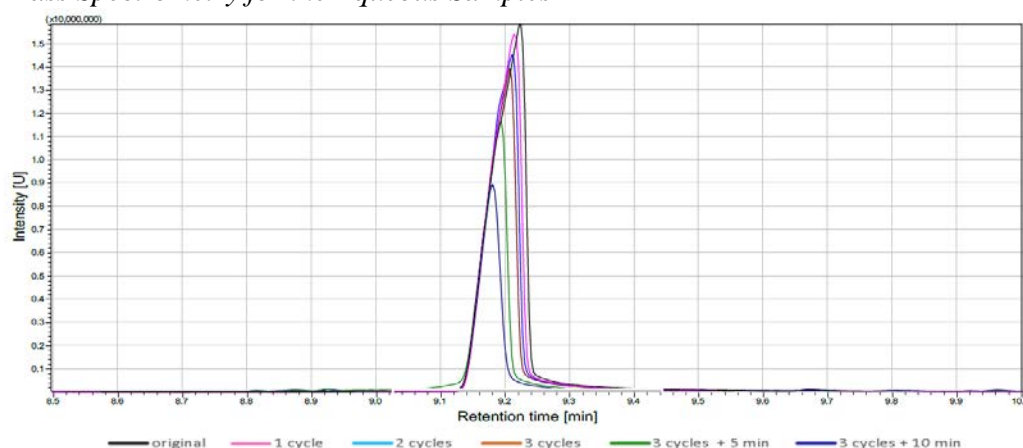
Figure 5. During GC-MS of Methylparaben Determined Areas of Methylparaben Peaks, Total Peak Areas and the Differential



Discussion

Both the HPLC and GC-MS results demonstrated that degradation of methylparaben occurred, although by-products were formed in the process. The GS-MS results indicated that the methylparaben was completely decomposed to a certain extent, with carbon dioxide and water as the presumed end products. The decomposition presumably takes place here due to the highly reactive environment and the strong radical formation (Cui et al. 2018, Abramov et al. 2021, Bang et al. 2019). However, even with the longest treatment period, elimination was not even close to 100%. The reduction was nevertheless in the competitive range for ozonation. Depending on the pH value and the intensity of ozonation, reductions of 34% to 90% can be achieved with a 10-minute treatment period (Dona et al. 2019).

Figure 6. Comparison of the Peaks after Gas Chromatography with Coupled Mass Spectrometry for the Aqueous Samples



Unwanted by-products could be detected and should be avoided. For example, the identified guaiacol can react in wastewater with nitrogen dioxide present to form nitroguaiacol and 2-methoxybenzene-1,4-diol, which have a higher toxicity than guaiacol itself (An et al. 2019). However, guaiacol is also not without hazard and exhibits acute toxicity to mice (Martinez et al. 2009). Methyl protocatechuate, on the other hand, shows no significant toxic properties, showing evidence of prolonging the life of the nematode *Caenorhabditis elegans* (Zhang et al. 2014) and exhibits neuroprotective effects in the disease retinitis pigmentosa in mice (Zhang et al. 2017). Hydroquinone was also detected in lower amounts but kept increasing with the duration of treatment. Hydroquinone exhibits elevated levels of toxicity to microorganisms in the soil (Chen et al. 2009). Accordingly, the input into ecological systems should be avoided.

The prototype shows potential for further development and possible improvements. Particular attention should be paid to the efficiency of the application, an extension of the instrumentation, and an automated control of the system. These requirements were concluded for the following reasons. In terms of efficiency, the plant cannot compete at present with the already established methods like ozonation and adsorption on activated carbon (Metzger et al. 2012). Especially in terms of energy efficiency, there is a big potential for improvement. With a total energy consumption by the prototype of approx. 13.3 kWh, the price of a single cycle treatment would be over 1 €/m³ (Considering the average electricity price of 0.3263 €/kWh in Germany in 2021 (Umwelt Bundesamt 2021)), however, parts of the consumption are also due to external pumps and here lies a potential for cost savings. The use of oxidizing agents, such as hydrogen peroxide, would also be conceivable (Bang et al. 2019), to heighten the efficiency and reduce the number of cycles needed. An extension of the monitoring equipment for an actual industrial plant would also make sense in order to be able to ensure a constant plasma intensity. In this process, a possible automation of the plant is also recommended to reduce manual readjustments and therefore reduce staff deployment. The occurrence of the undesirable by-products should be kept as low as possible. However, this problem is not a new one in wastewater treatment

and also occurs with ozonation (Statistisches Bundesamt - Destatis 2018). Here, a post-treatment, for example in the form of rapid filtration, may be selected in order to remove the unwanted components (Crini and Lichtfouse 2018). Overall, the pilot plant displayed potential to be further developed into an industrial plant.

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