

#### Article

### **Evaluating the Performance of a Lab-Scale Water Treatment Plant Using Non-Thermal Plasma Technology**

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Received: 18 May 2020; Accepted: 3 July 2020; Published: 9 July 2020



Abstract: In this study, a lab-scale plant was designed to treat water in continuous flow condition using non-thermal plasma technology. The core was an electrode system with connected high-voltage (HV) pulse generator. Its potentials and limitations were investigated in different experimental series with regard to the high-voltage settings, additions of oxygen-based species, different volume flow rates, and various physical-chemical properties of the process water such as conductivity, pH value, and temperature. Indigo carmine, para-Chlorobenzoic acid, and phenol were chosen as reference substances. The best HV settings was found for the voltage amplitude  $\hat{U} = 30$  kV, the pulse repetition rate f = 0.4-0.6 kHz, and the pulse duration  $t_b = 500$  ns with an energy yield for 50% degradation  $G_{50}$ , which is of 41.8 g·kWh<sup>-1</sup> for indigo carmine, 0.32 g·kWh<sup>-1</sup> for para-Chlorobenzoic acid, and 1.04 g·kWh<sup>-1</sup> for phenol. By adding  $1 \times 10^{-3}$  mol·L<sup>-1</sup> of oxygen, a 50% increase in degradation was achieved for para-Chlorobenzoic acid. Conductivity is the key parameter for degradation efficiency with a negative exponential dependence. The most important species for degradation are hydroxyl radicals (c  $\approx 1.4 \times 10^{-8}$  mol·L<sup>-1</sup>) and solvated electrons (c  $\approx 1.4 \times 10^{-8}$  mol·L<sup>-1</sup>). The results show that the technology could be upgraded from the small-scale experiments described in the literature to a pilot plant level and has the potential to be used on a large scale for different applications.

**Keywords:** non-thermal plasma; continuous water treatment; AOP; G<sub>50</sub>; indigo carmine; para-Chlorobenzoic acid; phenol

#### 1. Introduction

In research and application, various approaches for the elimination of persistent substances in polluted water, such as biological, chemical and physical based or combined techniques were discussed. Over the past few years, the investigation on advanced oxidation processes (AOP) as a physical-chemical method has increased considerably. Water treatment using non-thermal plasma (NTP) technology is a relatively new technology within various types of AOP.

In related experimental set-ups, strongly oxidizing agents are produced within non-thermal plasma in ambient atmospheric pressure and brings them into contact with the water to be processed quasi simultaneously. A strong short-existing electric field is generated by high-voltage (HV) pulses with high repetition rates between HV electrode(s) and ground electrode(s) in the presence of dielectric(s). Electrons are accelerated due to the short-pulsed energy supply to the space located in the gap between the HV and ground electrodes. As a result, the high-energy electrons collide with molecules of the gas and/or water phase located in the inter-electrode space, which are excited and ionized [1,2]. During this process, e.g., more than 500 reactions are supposed to occur in a water-air atmosphere system in which at least 75 intermediate reactive, mostly very short-lived oxygen, hydrogen, and/or nitrogen based species are formed [3].

The experimental set-ups presented in the literature are designed differently. The types can be distinguished by the electrode geometry (foil, rod, mesh or plate), the electrode materials used (Al, Cu or stainless steel), the dielectric (epoxy resin, quartz glass or borosilicate glass), the site of electrical discharge (gas phase, gas-water phase or water phase), the process gas in the area of the electrode system (air, Ar, Ar/O<sub>2</sub>, He, O<sub>2</sub> or N<sub>2</sub>), and the size of the gas gap between the HV and ground electrode(s) (1 to 6 mm). Further differences are found in the HV parameters, such as the voltage amplitude  $\hat{U}$  (4.5 kV to 60 kV) and the pulse repetition rate *f* (0.02 kHz to 50 kHz), and finally also in the power consumption of the systems *P* (0.06 W to 200 W). Depending on the electrode configuration and HV conditions, different discharge forms are generated such as dielectric barrier discharge, corona discharge or gliding arc discharge. The volumes of the treated process water were rather small-scale (V = 0.003 L to 2 L). In the majority the experimental set-ups were operated in batch mode and less frequently in continuous flow mode with flow rates from Q = 0.04 L·h<sup>-1</sup> to 9.6 L·h<sup>-1</sup>. In some cases the water is treated without additives, in other examples certain substances (such as Fe(II) and/or H<sub>2</sub>O<sub>2</sub>) are used in order to force the formation of hydroxyl radicals (·OH) [4–25].

For water treatment, the formation of OH is of specific interest because of its very strong oxidative effect ( $E^0 = 2.8 \text{ eV}$  vs. SHE). Due to its life-time of only about 10  $\mu$ s [26] the steady-state ·OH concentrations in water matrix is less than  $10^{-12}$  mol·L<sup>-1</sup> [27]. OH have a low selectivity with regard to the oxidative attack to organic molecules. Therefore, it is able to oxidize a broad range of recalcitrant organic water pollutants. Due to the second order reaction rates k in the range of approx. 10<sup>9</sup> L·mol<sup>-1</sup>·s<sup>-1</sup> [26,28], a fast degradation is possible. Within various consecutive reactions, more long-lived but less strong oxidative species are formed like ozone ( $O_3$ ,  $E^0 = 2.07$  eV vs. SHE) and hydrogen peroxide ( $H_2O_2$ ,  $E^0 = 1.78$  eV vs. SHE). These oxidizing agents are known to react with organic substances much more selectively than OH, e.g., by Criegee mechanism of O<sub>3</sub> or electrophilic reactions at functional groups [29,30]. The kinetics of these reactions is usually lower by a factor of 10<sup>6</sup> to 10<sup>12</sup> in relation to the 2nd order reaction rate of •OH reactions [31,32]. But O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> themselves can also be the starting point for several consecutive radical forming chain reactions in water matrix e.g., depending on hydroxide ion (OH<sup>-</sup>) activity and co-solved contaminants [31,33–35] or in the presence of catalytic active materials (e.g., TiO<sub>2</sub>) [36]. Besides the mentioned species, the evidence of other oxidative agents is rare in respect to the lack of experimental techniques to intercept and detect radical species in aqueous plasmas and to the non-selectivity of the existing chemical probes [37].

In order to evaluate an AOP system under different modes of operation and/or different physical-chemical water properties, it is a feasible option to investigate the degradation behavior of various indicator substances such as indigo carmine, para-Chlorobenzoic acid, and phenol instead of determining the multitude of possible reactions.

The blue dye indigo carmine is suitable for determining the amount of produced  $O_3$  due to its high reaction rate of  $k_{indigo \ carmine/O_3} \ge 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  [38]. This detection method is described in the German standard DIN 38408-3:2011-04 [39]. In the presence of  $O_3$ , the molecule at the C=C bond between the heterocyclic nuclei is stoichiometrically fragmented leading to the formation of the colorless to pale yellow product isatin sulfonic acid [38,40,41]. Dissolved indigo carmine are also known to be decomposed by further oxygen-based reactants such as superoxide ( $O_2^-$ ) and singlet oxygen ( $^1O_2$ ) with the same effect of discoloration and with almost similar reaction rates compared to  $O_3$  [41–46]. The reaction rate with  $\cdot$ OH is three orders of magnitude higher [47].

The substance para-Chlorobenzoic acid (pCBA) is supposed to be applicable for the determination of radicals because of its negligible reactivity with O<sub>3</sub> ( $k_{pCBA/O_3} \le 0.15 \times 10^0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  [48]) and its high reaction rate with  $\cdot \text{OH}$  ( $k_{pCBA/\cdot OH} = 5 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  [49]) more or less at the same rate whether

as an acid or in the deprotonated form [48]. In the non-protonated form, hydrogen radical (·H)-based addition reactions at the benzene ring and also reactions with solvated electrons ( $e_{aq}^{-}$ ) with reaction rates of  $k_{pCBA/\cdot e_{aq}^{-}} = 3.6 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  to  $6.0 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  have also been identified [50]. The AOP study by Pi et al. [51] indicated that the degradation of para-Chlorobenzoic acid via free radical chain reactions indirectly promotes the O<sub>3</sub> decomposition via intermediately formed H<sub>2</sub>O<sub>2</sub> and its subsequent reactions.

Many studies of AOP systems used phenol as an indicator substance [11,23,52–58]. This aromatic substance can be degraded by both radical mechanisms and direct reaction with O<sub>3</sub> [54,55]. The degradation products are catechol and hydroquinone as primary intermediates and muconic acid, fumaric acid, maleic acid, oxalic acid, and formic acid as consecutive products [59]. The kinetics of the degradation is strongly pH-dependent due to the weak acid character of phenol ( $pK_a = 9.98$  [60]). The undissociated phenol has a considerably lower reactivity with O<sub>3</sub> compared to the acid residue phenolate ion ( $k_{phenol/O_3} = 1.3 \times 10^3$  L·mol<sup>-1</sup>·s<sup>-1</sup> vs.  $k_{phenolate ion/O_3} = 1.4 \times 10^9$  L·mol<sup>-1</sup>·s<sup>-1</sup>, [54]), so the degradation is enhanced in alkali milieu [61,62]. Furthermore, the phenol degradation is increased by forced ·OH formation by O<sub>3</sub> reaction with hydroxide ion [55] with a reaction rate of  $k_{phenol/·OH} = 1.4 \times 10^{10}$  L·<sup>-1</sup>·s<sup>-1</sup> [63].

Phenol was used to study the effect of discharge conditions in the electric field on the amount of degradation. The results of Tang et al. [56] and Zhang et al. [23] showed higher removal of phenol at rising voltage level due to the correlation of the input energy accelerating free electrons and the number of active species produced. Also secondary physical effects such as ultraviolet light (UV) emission and shock waves might be stronger during the discharge process at higher applied voltages, further enhancing radical formation [23]. Additionally, increasing repetition rates of the HV pulses seem to promote the degradation, which was attributed to rising energy input in the electrode system intensifying the electric field and the oxidizing agent formation [57]. Further studies characterized the electrical conductivity of the water to be important for degradation efficiency [18,58,64]. High water conductivity shortens the plasma channel lengths reducing the plasma-water boundary contact area and limits the formation of plasma channels and thus finally reduces the formation of  $\cdot$ OH and the oxidative phenol degradation [18].

The aim of the current study was to upscale the new innovative and versatile water treatment technology by NTP technology from small-scale experiments to a lab-scale water treatment plant. This plant was designed as a continuous flow system to verify that this technology can be used continuously in routine water treatment in principle. Research was focused on the degradation behavior of the reference substances indigo carmine as an indicator for the formation of ozone and other oxygen-based species, para-Chlorobenzoic acid as an indicator for  $\cdot$ OH formation, and phenol as one of the most important industrial precursor chemicals. The potential and limitation of this technology were investigated in different experimental series with regard to varying HV settings, additions of oxygen-based species H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> and air, different volume flow rates *Q*, and various physical-chemical properties of the process water such as conductivity  $\sigma$ , pH value, and temperature *T*.

#### 2. Materials and Methods

#### 2.1. Experimental Set-Up

The experiments were carried out in the specially developed lab-scale water treatment plant as shown in Figure 1. All components carrying  $O_3$  were installed in a fume cupboard with a footprint of 1.5 m × 0.6 m and a height of 1.4 m. The treatment plant was designed to allow its use as a mobile system.

The laboratory test facility had a 200 L water storage reservoir (FD-E 200, ARICON, Solingen, Germany) with attached stirrer. For the series of tests it was fully filled with distilled (DI) water (electric conductivity  $\sigma = 3 \pm 1 \ \mu\text{S}\cdot\text{cm}^{-1}$  at T = 293.15 K, pH 5.5). The DI water was doped with the reference

substances indigo carmine, para-Chlorobenzoic acid, or phenol and optionally with H<sub>2</sub>O<sub>2</sub>, phosphate buffer or sodium chloride.

The temperature of the process water could be set via an integrated cryostat bath with coupled thermocirculator (K31 TC250k, © GK Sondermaschinenbau, Arnsdorf, Germany).



Figure 1. Set-up of the lab-scale water treatment plant.

The process water was pumped with a gear pump (VGS260.07-SSET-2M 0,37/3000FU, Verder Liquids BV, Vleuten, The Netherlands) out of the water storage reservoir through a PTFE hose line with a flow rate between 40 L·h<sup>-1</sup> and 390 L·h<sup>-1</sup> monitored by Hall effect sensor flowmeter device (FCH-m-PVDF 0.07–7.5 LPM, BIO-TECH, Vilshofen, Germany). It was sprayed in the reaction chamber (stainless steel, 1.44, 55 L in volume) by an atomizer nozzle (90° spray angle, type 490.566, stainless steel, 1.44, Lechler, Metzingen, Germany). The pressure in the hose-line was monitored by a pressure sensor (A-10, WIKA, Klingenberg/Main, Germany). The generated spray was mixed with the ambient air in the upper zone of the reaction chamber under atmospheric pressure conditions. It was possible to purge the reactor chamber with compressed air during or after the experiment. The adjustable gas flow rate was from 0.3 Nm<sup>3</sup>·h<sup>-1</sup> to 8.0 Nm<sup>3</sup>·h<sup>-1</sup>. The exhaust gas was treated with a thermal ozone destructor (THERM 8, SEWEC OZON, Wehr, Germany).

The spray passed through the electrode system located about 0.06 m below the nozzle. The electrode configuration was a self-engineered system embedded in a plastic housing (PVC). It consisted of 13 rod-shaped HV electrodes (stainless steel, 1.43, each 0.25 m in length and 0.8 mm in diameter) in two superposed layers with an intermediate layer of 25 similar rod-shaped ground electrodes (tungsten 99.95%, each 0.25 m in length and 2 mm in diameter). The ground electrodes were enclosed by quartz glass dielectrics (inner diameter 2 mm, outer diameter 4 mm). Between HV and ground electrodes was a gas gap of 5 mm. The HV and ground electrodes were applied in electrical contact with the HV nanosecond pulse generator NSP-120-30-N-500 (Eagle Harbor Technologies, Seattle, USA). This device created negative rectangular impulses which were incrementally adjustable at voltage amplitudes between  $\hat{U} = 3$  kV and 30 kV with pulse repetition rates between f = 0.001 kHz and 10 kHz and pulse duration between  $t_b = 50$  ns and 500 ns. Its power consumption *P* was determined by energy logger 4000 (Voltcraft, Wollerau, Switzerland).

After the process water passed through the electrode system, the water was collected in a hydraulic sump of the reactor chamber. On its bottom two ports were installed. One was used as sampling port and the other for the transfer to the downstream water reservoir (stainless steel, 1.44, 26.67 L in volume). The downstream water reservoir was coupled with an ozone sensor system for the water phase (OZ7MA10 with measurement value recording system KM 3000, Meinsberg, Waldheim, Germany) which was calibrated by Diethyl-p-phenylenediamine/potassium iodate method according

to German standard method DIN 38408-3:2011-04 [39]. The process water was finally discharged into the drain via an activated carbon filter.

#### 2.2. Experimental Series

In the first series of experiments, the degradation of the reference substances indigo carmine, para-Chlorobenzoic acid, and phenol, and the power consumption *P* of the HV pulse generator were investigated by varying the settings of the HV generator (see Section 3.1). In 200 L of DI water,  $34.5 \pm 1.0$  g of indigo carmine ( $\geq$ 99%, Alfa Aesar, Kandel, Germany) or  $0.65 \pm 0.05$  g of para-Chlorobenzoic acid ( $\geq$ 98%, Alfa Aesar, Kandel, Germany) or  $0.83 \pm 0.04$  g of phenol ( $\geq$ 99%, VWR chemicals, Radnor, PA, USA) were added, resulting in initial concentrations of  $(3.7 \pm 0.1) \times 10^{-4}$  mol·L<sup>-1</sup> for indigo carmine,  $(2.1 \pm 0.2) \times 10^{-5}$  mol·L<sup>-1</sup> for para-Chlorobenzoic acid or  $(4.4 \pm 0.2) \times 10^{-5}$  mol·L<sup>-1</sup> for phenol. These concentration levels were applied in all test series. They were determined in preliminary tests. At least one third of the initially added amount of reference substances should not be degraded after the treatment step to detect the effects of the range of several parameters. The temperature of the process water was kept at *T* = 294 ± 2 K and the volume flow rate *Q* was set to 80 L ·h<sup>-1</sup>. At the HV generator, the voltage amplitude ( $\hat{U} = 21$  kV to 30 kV), the pulse repetition rate (*f* = 0.2 kHz to 1.0 kHz) and the pulse duration ( $t_b = 400$  ns to 500 ns) were changed.

In the second experimental series, it was evaluated to what extent the degradation of the reference substances can be influenced by different oxygen-based additions (see Section 3.2). Using the examples of para-Chlorobenzoic acid and phenol, the degradation was investigated in the presence of  $H_2O_2$ . For this purpose 0.263 mL to 26.350 mL 30% (*w/w*) H<sub>2</sub>O<sub>2</sub> solution (EMSURE<sup>®</sup>, Supelco, Bellefonte, USA) was added to the process water in the water storage reservoir resulting in final H<sub>2</sub>O<sub>2</sub> concentrations of  $1.3 \times 10^{-5}$  mol·L<sup>-1</sup> to  $1.3 \times 10^{-3}$  mol·L<sup>-1</sup>. The influence of an oxygen (O<sub>2</sub>) supply was tested for the substances indigo carmine, para-Chlorobenzoic acid, and phenol. Technically it was achieved by mixing of 20 L·h<sup>-1</sup> pure O<sub>2</sub> (O<sub>2</sub> 5.0, Praxair, Danbury, CT, USA) into the water stream by a Venturi injector system (287-PVDF, Mazzei®, Bakersfield, CA, USA) controlled by a gas flowmeter (RAGL Rotameter, Yokogawa, Ratingen, Germany). Furthermore, it was examined whether a continuous air supply to the reactor chamber can influence the degradation of indigo carmine and para-Chlorobenzoic acid while the electrode system was operating. It was realized by supplying compressed air at the bottom of the reactor chamber (0.3  $\text{Nm}^3 \cdot h^{-1}$  to 2.2  $\text{Nm}^3 \cdot h^{-1}$ ) and simultaneously discharging the air at the top of the reactor chamber to the thermal ozone destructor. All experiments of this series were performed at the HV generator settings  $\hat{U} = 30$  kV, f = 0.6 kHz, and  $t_b = 500$  ns. The volume flow rate and the temperature of the process water were identical to the first experimental series.

In the third series of experiments, the degradation of the reference substances was investigated by varying the volume flow rate Q from 40 L·h<sup>-1</sup> to 390 L·h<sup>-1</sup> with the same physical-chemical water properties like in the first experiment series (see Section 3.3). The HV pulse generator was operated at  $\hat{U} = 30$  kV, f = 0.6 kHz, and  $t_b = 500$  ns.

In the fourth series of experiments the influence of the process water conductivity  $\sigma$ , the pH value, and the temperature *T* on the degradation of selected reference substances was investigated (see Section 3.4). The conductivity was investigated in a range of 143 µS·cm<sup>-1</sup> and 554 µS·cm<sup>-1</sup> by varying dosages of sodium chloride (NaCl, ≥99%, Alfa Aesar, Kandel, Germany) in the range of 13.8 g to 55.2 g  $(1.2 \times 10^{-3} \text{ mol·L}^{-1} \text{ to } 4.7 \times 10^{-3} \text{ mol·L}^{-1})$ . Due to the fact that the investigation of pH influence cannot be determined independently of conductivity, the phosphate buffers used to adjust the pH value was chosen as an alternative to NaCl. Therefore, different concentrated phosphate buffers were prepared based on K<sub>2</sub>HPO<sub>4</sub> (≥99%, Alfa Aesar, Kandel, Germany, m = 3.1 g to 60.6 g) and KH<sub>2</sub>PO<sub>4</sub> (≥99%, Alfa Aesar, Kandel, Germany, m = 3.1 g to 60.6 g) and KH<sub>2</sub>PO<sub>4</sub> (≥99%, Alfa Aesar, Kandel, Germany, m = 3.1 g to 60.6 g) and KH<sub>2</sub>PO<sub>4</sub> (≥99%, Alfa Aesar, Kandel, Germany, m = 3.1 g to 60.6 g) and KH<sub>2</sub>PO<sub>4</sub> (≥99%, Alfa Aesar, Kandel, Germany, m = 3.8 g to 75.1 g) resulting in ortho-phosphate concentrations of 2.3 × 10<sup>-4</sup> mol·L<sup>-1</sup> to 4.5 × 10<sup>-3</sup> mol·L<sup>-1</sup>, and conductivities from 40 µS·cm<sup>-1</sup> to 698 µS·cm<sup>-1</sup>, and a pH value of 7. Additionally, the pH dependence on degradation was investigated at pH values of 8 and 8.3 using 1 × 10<sup>-3</sup> mol·L<sup>-1</sup> phosphate buffers (30.1 g K<sub>2</sub>HPO<sub>4</sub> + 3.7 g KH<sub>2</sub>PO<sub>4</sub> for pH 8 or 32.3 g K<sub>2</sub>HPO<sub>4</sub> + 2.0 g KH<sub>2</sub>PO<sub>4</sub> for pH 8.3). The adjustment of the pH values was made with regard to an equidistant

setting for the hydroxide ions activity ( $a OH^- = 10^{-7} \text{ mol}\cdot\text{L}^{-1}$  at pH 7,  $a OH^- = 10^{-6} \text{ mol}\cdot\text{L}^{-1}$  at pH 8,  $a OH^- = 2 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$  at pH 8.3) because of the known reaction of O<sub>3</sub> with hydroxide ions to  $\cdot$ OH and other oxidative species [65,66]. Finally, the temperature influence on the degradation of the reference substances indigo carmine, para-Chlorobenzoic acid, and phenol at pH 7, 8 or 8.3 (adjusted with  $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  phosphate buffer) was also investigated. The temperature of the process water was set between T = 285 K and 296 K. The experiments of this series were performed at a volume flow rate of  $Q = 160 \text{ L}\cdot\text{h}^{-1}$ . The HV pulse generator was set to  $\hat{U} = 30$  kV, f = 0.6 kHz, and  $t_b = 500$  ns.

#### 2.3. Sampling Procedure

Sampling of the treated process water was routinely performed after t = 10 min after the HV generator was started. Preliminary tests had shown that after this time an approximately constant concentration level of the reference substances was achieved. The treated water was sampled in intervals of 5 min. The experiment was continued until at least three consecutive analyses of the samples were almost constant (maximum +/– 5% deviation). In order to determine the decrease of the reference substances ( $\Delta c$ /mol·L<sup>-1</sup>), the process water in the water storage reservoir was sampled at the beginning and the end of each experiment.

#### 2.4. Determination of Chemical Parameters

Indigo carmine was photometrically analyzed (DR 5000, Hach–Lange, Düsseldorf, Germany) measuring the extinction  $E(\lambda)$  at the wavelength of  $\lambda = 617$  nm. Its concentration was quantified by external calibration with a linear range between  $0.2 \times 10^{-5}$  mol·L<sup>-1</sup> and  $4.3 \times 10^{-5}$  mol·L<sup>-1</sup>. The samples with higher indigo carmine concentrations had to be diluted accordingly.

The concentration of para-Chlorobenzoic acid was determined in an analogous way measuring the extinction at the wavelength  $\lambda = 236$  nm with an external linear calibration with a range between  $0.1 \times 10^{-5}$  mol·L<sup>-1</sup> and  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup>. Additionally, the extinction of selected water samples was measured in a range between  $\lambda = 190$  nm and 390 nm (UV + visible range, VIS).

Phenol was quantified as phenol index as a quasi-sum parameter for phenolic substances using the phenol Spectroquant<sup>®</sup> kit (Hach-Lange, Düsseldorf, Germany). In the first preparation step, the samples were alkalified to convert phenol into phenolate ion. In the second step the diazotization followed. The resulting color change was analyzed photometrically according to German standard method DIN 38409-16:1984-06 [67] at  $\lambda = 460$  nm. The external calibration range was from  $2.1 \times 10^{-8}$  mol·L<sup>-1</sup> to  $5.3 \times 10^{-5}$  mol·L<sup>-1</sup>.

In addition, phenol and its primary intermediates catechol ( $\geq$ 99%, Sigma Aldrich), hydroquinone ( $\geq$ 99%, GPR RECTAPUR<sup>®</sup>, VWR chemicals, Radnor, PA, USA), and resorcine ( $\geq$ 99%, AnalaR NORMAPUR<sup>®</sup>, VWR chemicals, Radnor, PA, USA) were analyzed by high-performance liquid chromatography (HPLC) with photodiode array detection at  $\lambda = 220$  nm (UltiMate 3000 HPLC, DIONEX, Sunnyvale, USA) and quantified via external calibration ( $1.8 \times 10^{-7}$  mol·L<sup>-1</sup> to  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup>).

To investigate the total mineralization of phenol, the parameter DOC (dissolved organic carbon) was analyzed. The water samples were treated with nitrogen gas, filtered via 0.45  $\mu$ m syringe attachment filter, acidified with 35% (*w/w*) hydrochloric acid (p. A., VWR chemicals, Radnor, PA, USA) to pH < 2, and analyzed according to German standard method DIN EN 1484:2019-04 [68] using the TOC Analyzer 3000 (Shimadzu, Kyoto, Japan).

The parameters pH, conductivity, and temperature were measured for the process water in the water storage reservoir and for the samples of treated water using the portable measuring instrument Multi 3430 (Wissenschaftlich-Technische Werkstätten, Weilheim, Gemany) with connected pH electrode SenTix<sup>®</sup> 940 (Wissenschaftlich-Technische Werkstätten, Weilheim, Gemany) and the conductivity probe TetraCon<sup>®</sup> 925 (Wissenschaftlich-Technische Werkstätten, Weilheim, Gemany).

#### 3. Results and Discussion

## 3.1. Influence of the HV Pulse Generator Settings on the Degradation of the Reference Substances and on the Power Consumption

For each of the three reference substances indigo carmine, para-Chlorobenzoic acid, and phenol the influence of HV settings on the degradation was discussed. Further, it was calculated which oxidative species could be responsible for the degradation. Finally, the energy required for the degradation of the reference substances has been considered.

Indigo carmine: The decrease of indigo carmine concentration  $\Delta c$  as a function of HV conditions is shown in Figure 2 with the indication of the related power consumption *P*. With higher voltage amplitude  $\hat{U}$  a linear increase of the indigo carmine degradation can be observed (Figure 2a). The maximum degradation of  $\Delta c = (2.3 \pm 0.2) \times 10^{-4}$  mol L<sup>-1</sup> was achieved at the highest adjustable voltage amplitude of  $\hat{U} = 30$  kV at f = 0.6 kHz and  $t_b = 500$  ns (best case). With regard to the pulse repetition rate, the degradation of indigo carmine showed a strong improvement from f = 0.2 kHz to 0.6 kHz. Higher *f* led to slightly lower indigo carmine degradation (Figure 2b). Longer pulse duration resulted in higher indigo carmine degradation for all settings of  $\hat{U}$  (Figure 2c,d). The maximum of  $\Delta c$  was found at the highest possible setting of  $t_b = 500$  ns.



**Figure 2.** Decrease of indigo carmine concentration ( $\Delta c$ ) and related power consumption *P* of the high voltage (HV) generator as a function of (**a**) voltage amplitude  $\hat{U}$ , (**b**) pulse repetition rate *f*, and (**c**) and (**d**) pulse duration  $t_b$ .

The results can be used to calculate the total reaction rate of indigo carmine with all oxidizing agents  $k_{indigo \ carmine/oxidants}$  on the basis of a 2nd order kinetic analysis according to Equation (1) [69].

$$ln \frac{c_{indigo\ carmine,\ i}}{c_{indigo\ carmine,\ 0}} = -k_{indigo\ carmine/oxidants} \int_{t=0ms}^{t=4\pm 1ms} c_{oxidants} dt$$
(1)

In the best-case scenario, the concentration of indigo carmine after the treatment step was  $c_{indigo\ carmine,i} = (1.42 \pm 0.03) \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  at an initial indigo carmine concentration of  $c_{indigo\ carmine,0}$ =  $(3.70 \pm 0.02) \times 10^{-4}$  mol·L<sup>-1</sup>. The O<sub>3</sub> concentration determined with the ozone probe was  $c_{O_3}$ =  $(2.1 \pm 0.2) \times 10^{-5}$  mol·L<sup>-1</sup> without the presence of indigo carmine at the HV settings  $\hat{U} = 30$  kV, f = 0.6 kHz, and  $t_b = 500$  ns. Under the convention that the concentrations of all other oxidants are negligible compared to the  $O_3$  concentration  $c_{O_3}$ , this value can be equated to the total concentration of all oxidants *c*<sub>oxidants</sub>. The residence time of the process water in the zone of the electrode system is approx.  $t = 4 \pm 1$  ms. This value is based on the assumption of the vertical velocity of the water droplets of  $v = 2 \text{ m} \cdot \text{s}^{-1}$  up to  $3 \text{ m} \cdot \text{s}^{-1}$  at the position of the electrode system and the distance between the HV and ground electrodes of  $2 \times 5$  mm (corresponding to the gas gaps). The supposition of the vertical velocity of the droplets from the atomization results from the findings of Liu et al. [70], taking into account the nozzle pressure of  $p = 0.62 \pm 0.03$  bar measured in the experiment, the Sauter diameter of the droplets of  $d_{32} = 650$  nm specified by the manufacturer of the nozzle (Lechler, Metzingen, Germany), the dynamic viscosity of the process water of  $\eta = 1$  mPa·s at T = 298 K [71] and a spatial distance of the nozzle from the electrode system of 0.06 m. As a result of the analytical findings and assumptions made, the total reaction rate of indigo carmine with all oxidants k<sub>indigo carmine/oxidants</sub> is  $(1.2 \pm 0.5) \times 10^7$  mol·L<sup>-1</sup>·s<sup>-1</sup>. This value is similar to the value mentioned by Bader and Hoigné [38] for the reaction kinetics of indigo carmine in ozoniferous solutions.

The reaction rate of indigo carmine and O<sub>3</sub>, however, is three orders of magnitude lower, compared to the reaction rate with  $\cdot$ OH ( $k_{indigo\ carmine/\cdot OH} = 1.8 \times 10^{10}\ mol \cdot L^{-1} \cdot s^{-1}$  [47]). If the reaction with O<sub>3</sub> is assumed to be negligible, the  $\cdot$ OH concentration is calculated to  $c_{\cdot OH} = (1.4 \pm 0.3) \times 10^{-8}\ mol \cdot L^{-1}$ , analogous to Equation (1). This finding corresponds to a  $\cdot$ OH concentration 1000 times higher reached for the most other AOP systems [27].

The energy required for the degradation of indigo carmine was calculated as the quotient of indigo carmine degradation  $\Delta c$  and power consumption *P*. Within the investigated range, the  $\Delta c/P$  ratio was between  $0.4 \times 10^{-6}$  mol·L<sup>-1</sup>·W<sup>-1</sup> and  $1.2 \times 10^{-6}$  mol·L<sup>-1</sup>·W<sup>-1</sup>. The maximum indigo carmine degradation ( $\hat{U} = 30$  kV, f = 0.6 kHz and  $t_b = 500$  ns) resulted in a  $\Delta c/P$  ratio of  $1.1 \times 10^{-6}$  mol·L<sup>-1</sup>·W<sup>-1</sup>. The slightly higher maximum was achieved with the setting  $\hat{U} = 30$  kV, f = 0.4 kHz, and  $t_b = 500$  ns.

Malik [72] described the efficiency of different non-thermal plasma reactor types by the energy yield term  $G_{50}$ . This value represents the reciprocal relationship of the energy input required for the degradation of the half of the mass of a substance. Equation (2) shows this mathematical approach adapted to the example of indigo carmine.

$$G_{50}[g \cdot kWh^{-1}] = \frac{c_{indigo\ carmine,\ 0}[mol \cdot L^{-1}] \cdot M_{indigo\ carmine}[g \cdot mol^{-1}]}{2} \cdot \frac{Q[L \cdot h^{-1}]}{P_{50}[kW]}$$
(2)

The initial mass of indigo carmine is the product of the molar concentration of  $3.7 \times 10^{-4}$  mol·L<sup>-1</sup> set in the water storage reservoir multiplied with the molar mass  $M_{indigo\ carmine} = 466.36$  g·mol<sup>-1</sup> and the water volume of 80 L which has been treated per hour.  $P_{50}$  is the value which represents the power consumption at which half of the indigo carmine was degraded. According to the findings shown in Figure 2a,  $P_{50}$  is 0.165 kW. As a result  $G_{50}$  is 41.8 g·kWh<sup>-1</sup>. According to Malik's study this value is in between the energy yields of different non-thermal plasma experimental set-ups with  $G_{50} = 0.149$  g·kWh<sup>-1</sup> up to 622 g·kWh<sup>-1</sup> for indigo carmine [72].

*para-Chlorobenzoic acid:* In comparison to indigo carmine degradation, the removal of para-Chlorobenzoic acid was two orders of magnitude lower (Figure 3). The maximum reduction in concentration was about  $(7.5 \pm 0.3) \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  for the setting  $\hat{U} = 30 \text{ kV}$ , f = 0.4 kHz, and  $t_b = 500 \text{ ns}$ . As likewise proposed for indigo carmine, there is a linear correlation between voltage amplitude  $\hat{U}$  and para-Chlorobenzoic acid degradation  $\Delta c$  (Figure 3a). With regard to the pulse repetition rate, the degradation of para-Chlorobenzoic acid was already in maximum at f = 0.4 kHz and it decreased with higher f more pronounced compared to the findings for indigo carmine (Figure 3b). Again a higher degradation was measured for  $t_b = 500 \text{ ns}$  (Figure 3c,d). The relatively weak dependence from the voltage amplitude  $\hat{U}$  on the decay of para-Chlorobenzoic acid at  $t_b = 500 \text{ ns}$  is noticeable, but difficult to deduce.

Analogous to Equation (1), the concentrations of the reactive species could be calculated. The concentrations of para-Chlorobenzoic acid were  $c_{pCBA, 0} = (1.95 \pm 0.05) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  in the water storage reservoir and  $c_{pCBA, i} = (1.20 \pm 0.01) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  after the treatment step. The direct reaction with O<sub>3</sub> is negligible [48], but ·OH and e<sub>aq</sub><sup>-</sup> are known to react with para-Chlorobenzoic acid with a 2nd order reaction rate of  $k_{pCBA/\cdot OH} \approx k_{pCBA/e_{aq}^-} \approx 5 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  [49,50]. Hence, formal average concentrations of  $c_{\cdot OH} \approx c_{e_{aq}^-} = (1.3 \pm 0.2) \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$  were obtained. The calculated findings on ·OH concentration correspond approximately to the findings of the experiments with indigo carmine.



**Figure 3.** Decrease of para-Chlorobenzoic acid concentration ( $\Delta c$ ) and related power consumption *P* of the HV generator as a function of (**a**) voltage amplitude  $\hat{U}$ , (**b**) pulse repetition rate *f*, and (**c**) and (**d**) pulse duration  $t_b$ .

Besides the degradation of para-Chlorobenzoic acid via  $\cdot$ OH and  $e_{aq}^{-}$ , there are also indications of degradation via  $\cdot$ H radicals. The analysis of the UV/VIS spectrum from samples before and after the electrode system passage revealed a slight increase in absorbance in the range of  $\lambda = 290$  nm to 340 nm (Figure 4). According to Zona et al. [50] it can be attributed to a hydrogen addition reaction at the benzene ring of the para-Chlorobenzoic acid molecule. These findings suggest that the reaction of  $e_{aq}^{-}$  with water molecules forming  $\cdot$ OH and  $\cdot$ H radicals may play an important role.



**Figure 4.** (a) Ultraviolet (UV)/visible range (VIS) spectrum of para-Chlorobenzoic acid in a sample from the water storage reservoir and in a sample after the treatment in the reaction chamber, (b) is the enlarged section of (a).

The ratio between para-Chlorobenzoic acid degradation  $\Delta c$  and power consumption P was between  $1.6 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}\cdot\text{W}^{-1}$  and  $6.4 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}\cdot\text{W}^{-1}$ . It means the energy required for the degradation of para-Chlorobenzoic acid is about 20 times higher than for indigo carmine. The optimum was at the setting  $\hat{U} = 21 \text{ kV}$ , f = 1 kHz, and  $t_b = 500 \text{ ns}$  with a degradation of para-Chlorobenzoic acid of  $\Delta c = (6.7 \pm 0.8) \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ . For the determined maximum of para-Chlorobenzoic acid degradation the  $\Delta c/P$  ratio was about  $5.1 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}\cdot\text{W}^{-1}$ . The  $G_{50}$  value is  $0.32 \text{ g}\cdot\text{kWh}^{-1}$  in accordance to the Equation (2) with  $P_{50} = 0.376 \text{ kW}$  (cf. Figure 3a). This is 130 times lower compared to the results for indigo carmine.

*Phenol:* Phenol degradation was measured in a range between  $(1.7 \pm 0.2) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  and  $(2.3 \pm 0.3) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  based on the findings for phenol index (Figure 5). Thus, it is two up to three times higher than para-Chlorobenzoic acid degradation with a maximum of  $(7.5 \pm 0.3) \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ , but a magnitude lower than indigo carmine degradation with a maximum of  $(2.3 \pm 0.2) \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ . The influence of voltage amplitude, pulse repetition rate, and pulse duration on phenol degradation is analogous to the findings for indigo carmine. The highest value for  $\Delta c$  was found at  $\hat{U} = 30 \text{ kV}$ , f = 0.6 kHz, and  $t_b = 500 \text{ ns}$ .

The variation of the HV parameters presented in Figure 5 had no significant effects on the relative distribution of the phenol degradation products determined by HPLC and DOC analysis. Half of the added phenol (47% of  $c = (4.4 \pm 0.2) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ) remained in the process water. The other part was mainly degraded to different intermediate products. About one quarter of the degraded phenol was stoichiometrically converted to the primary aromatic intermediates catechol ( $c = (0.29 \pm 0.13) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ) and hydroquinone ( $c = (0.23 \pm 0.16) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ), but not resorcine ( $c < 0.02 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ). Most of the degraded phenol, approx. 67% or  $\Delta c = (1.6 \pm 0.3) \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , was further converted, most likely into less toxic [73] carboxylic acids and aldehydes (cf. "other reaction products" in Figure 5d). According to the findings of the *DOC* parameter, between 5 and 10%

of the decrease in phenol concentration ( $\Delta c = (0.18 \pm 0.02) \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) can be attributed to the total degradation to CO<sub>2</sub> and H<sub>2</sub>O.

Similar to the degradation of indigo carmine and para-Chlorobenzoic acid, the direct reaction of O<sub>3</sub> with phenol at the given pH value of the process water of 5.5 is negligible compared to the reaction of phenol with ·OH [53,62]. Based on the findings of the best-case experiment with  $c_{phenol index, 0} = (4.4 \pm 0.2) \times 10^{-5} \text{ mol·L}^{-1}$  in the water storage tank and  $c_{phenol index, i} = (2.1 \pm 0.1) \times 10^{-5} \text{ mol·L}^{-1}$  after the water treatment step and considering the 2nd order reaction rate of  $1.4 \times 10^{10} \text{ mol·L}^{-1} \cdot \text{s}^{-1}$  [63], an ·OH concentration of  $c_{.OH} = (1.4 \pm 0.3) \times 10^{-8} \text{ mol·L}^{-1}$  is calculated in analogy to Equation (1). This result is in agreement with the calculations for indigo carmine ( $c_{.OH} = (1.4 \pm 0.3) \times 10^{-8} \text{ mol·L}^{-1}$ ).



**Figure 5.** Decrease of phenol index concentration ( $\Delta c$ ) and related power consumption *P* of the HV generator as a function of (**a**) voltage amplitude  $\hat{U}$ , (**b**) pulse repetition rate *f*, and (**c**) pulse duration  $t_b$  and (**d**) relative stoichiometric composition of the quasi-sum parameter phenol index after water treatment.

The  $\Delta c/P$  ratio was between  $0.8 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{W}^{-1}$  and  $1.9 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{W}^{-1}$ . Thus, the energetic efficiency of phenol degradation is about 4 times higher compared to the findings for para-Chlorobenzoic acid, but about 6 times lower compared to indigo carmine degradation. The optimum occurred at  $\hat{U} = 30 \text{ kV}$ , f = 0.2 kHz and  $t_b = 500 \text{ ns}$  in contrast to the results for indigo carmine and para-Chlorobenzoic acid. At the maximum of phenol index degradation, the  $\Delta c/P$  ratio was  $1.1 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{W}^{-1}$  and thus significantly below the energetic optimum. It is noticeable that the parameter phenol index also

covers the aromatic intermediate products. Therefore, the results are only partly transferable to the substance phenol. With regard to the calculation method according to Equation (2), the  $G_{50}$  value of 1.04 g·kWh<sup>-1</sup> is obtained considering a  $P_{50}$  value of 0.16 kW (cf. Figure 5b). This determined  $G_{50}$  value, for example, is about 1.5 to 3 times greater compared to the findings of Bosi et al. [9].

#### 3.2. Influence of Different Oxygen-Based Additions on the Degradation of the Reference Substances

The addition of three oxygen-based species was investigated to evaluate a possible increase in degradation. Therefore,  $H_2O_2$  was added to the process water,  $O_2$  was mixed into the process water by Venturi injection, and compressed air was supplied to the reaction chamber.

Addition of  $H_2O_2$ : The reaction of  $H_2O_2$  with  $O_3$  produces  $\cdot OH$  and other intermediate oxidizing agents and it is known as the peroxone process [74]. A simplified formal reaction scheme is

$$H_2O_2 + 2O_3 \rightarrow 2 \cdot OH + 3O_2 \tag{3}$$

Using phenol and para-Chlorobenzoic acid as reference substances, it was investigated to what extent different additions of  $H_2O_2$  can lead to an increased degradation due to the much faster reaction with  $\cdot$ OH compared to the direct reaction with  $O_3$ . Indigo carmine was not used due to its degradability by  $O_3$  and  $\cdot$ OH. For the investigation of phenol degradation, the  $H_2O_2$  dosages were chosen in a stoichiometric  $H_2O_2$ : $O_3$  ratio of 1:2, 2:1, 3:1, 6:1 and 60:1 mol:mol in the water phase. In the experiments with para-Chlorobenzoic acid,  $H_2O_2$  was added in such a quantity that  $H_2O_2$ : $O_3$  ratios of about 1.5:1, 3:1 and 5:1 mol:mol resulted.

The experimental data, in Figure 6, show for para-Chlorobenzoic acid and phenol a slight increase in degradation from >0% to a maximum of 19%. It was achieved at  $H_2O_2:O_3$  ratios of 1:2 up to 5:1 or 6:1 mol:mol (or  $c H_2O_2 = 1.3 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  up to  $1.3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ) compared to the analogous findings without  $H_2O_2$  addition. At a stoichiometric  $H_2O_2:O_3$  ratio of 60:1 mol:mol (or  $c H_2O_2 =$  $1.3 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ) no increase in degradation could be observed. When  $H_2O_2$  is added in excess,  $H_2O_2$  possibly acts as a scavenger in the complex radical forming process at the electrode system as has been proposed by De Witte et al. [75].



**Figure 6.** Decrease of (**a**) para-Chlorobenzoic acid and (**b**) phenol index concentration ( $\Delta c$ ) depending on H<sub>2</sub>O<sub>2</sub> concentration in the process water.

Addition of  $O_2$ : The process water was enriched by adding 20 L·h<sup>-1</sup> pure  $O_2$  at Q = 80 L·h<sup>-1</sup> through Venturi injection in excess with regard to its gas solubility ( $c O_2 = 1 \times 10^{-2} \text{ mol·L}^{-1}$ ) before passing through the electrode system. This measure enhances the formation of  ${}^{1}O_2$  and  $O_3$  in low-temperature plasma, in whose subsequent reactions numerous other radical oxygen-based species are formed [76]. As a result of the additional  $O_2$  supply, indigo carmine degradation increased by approx. 22% compared to the results under identical HV conditions without  $O_2$  addition (Figure 7a). The  $O_2$  addition even resulted in an increase of more than 50% in the degradation of para-Chlorobenzoic acid (Figure 7b). In contrast to that, the phenol degradation could not be significantly enhanced (Figure 7c). These three different results indicate that the main effect of this supplementation was due to a higher  $O_3$  concentration. This is supported by the fact that indigo carmine is selectively oxidized by  $O_3$  [38,40,41]. The better degradation of para-Chlorobenzoic acid may be consistent with the theory formulated by Pi et al. [51]. According to their findings para-Chlorobenzoic acid is degraded via indirect radical chain reactions triggered by the surplus of  $O_3$ , despite the direct  $O_3$  based reaction is in fact negligible [48]. The degradation of phenol is not significantly affected by an increase of  $O_3$  concentration, because its reaction rate with  $O_3$  is relatively low and its degradation by  $\cdot OH$  is more considerable [54,55]. In conclusion, it can be stated that an enhanced degradation by adding  $O_2$  is appropriate for those substances that react directly with  $O_3$  or are degraded by ozone-promoted radical chain reactions (e.g., dyestuffs [77]).



**Figure 7.** Decrease of (**a**) indigo carmine, (**b**) para-Chlorobenzoic acid, and (**c**) phenol index concentration ( $\Delta c$ ) without and with the addition of  $1 \times 10^{-2}$  mol·L<sup>-1</sup> of oxygen in the process water.

*Compressed air supply:* The ventilation of the reactor chamber with compressed air was intended to ensure an  $O_2$  supply for the treatment of oxygen-poor process water and/or at highly oxygen species consuming processes at the electrode system. Using indigo carmine and para-Chlorobenzoic acid as references, the influence of a continuous ventilation of the reactor chamber during electrode system operation on the degradation of the substances was examined. The lowest possible ventilation of 0.3 Nm<sup>3</sup>·h<sup>-1</sup> corresponds to an air exchange of one reactor volume per 600 s. Related to the gas volume of the electrode system this means an air volume exchange every 4 s. The maximum ventilation level was  $8.0 \text{ Nm}^3 \cdot h^{-1}$ . The upper limit was based on the maximum permissible air flow of the thermal ozone destructor coupled to the reactor chamber. As can be seen in Figure 8, even the smallest adjustment of the air ventilation significantly reduced the degradation of indigo carmine and para-Chlorobenzoic acid compared to the findings without ventilation. The degradation of para-Chlorobenzoic acid was reduced by half. With a further increase of the ventilation to 0.7 Nm<sup>3</sup>·h<sup>-1</sup> the effect was similar. For indigo carmine the degradation decreased by approx. 9% at 0.3  $Mm^3 \cdot h^{-1}$  and about 33% at 2.2  $\text{Nm}^3 \cdot h^{-1}$ . The ventilation changed the  $O_2/O_3$  ratio at the electrode system, which must be of decisive importance for the formation of reactive oxygen-based species. This can be deduced from the findings of para-Chlorobenzoic acid degradation. This substance is not affected directly by O<sub>3</sub>, but mathematically half of it is attacked by  $e_{aq}^{-}$  and  $\cdot OH$  [48–50]. The degradation by  $e_{aq}^{-}$  was presumably not significantly influenced by ventilation, since their formation should depend on the HV

conditions at the electrode system. Consequently, the formation of  $\cdot$ OH must have been reduced as a result of the ventilation to such an extent that only the degradation of para-Chlorobenzoic acid by  $e_{aq}^{-}$  occurred, thus halving the degradation of para-Chlorobenzoic acid. Since the half-life of  $\cdot$ OH is about 10 µs [26], ventilation should not be directly responsible for their reduction, but rather for that of the more long-lived species O<sub>3</sub>. Due to the fact that O<sub>3</sub> itself rarely reacts with para-Chlorobenzoic acid [48], it is assumed that O<sub>3</sub> plays an important role in radical formation.



**Figure 8.** Decrease of (a) indigo carmine and (b) para-Chlorobenzoic acid concentration ( $\Delta c$ ) without or with different compressed air supply to the reaction chamber.

#### 3.3. Degradation of Indigo Carmine, Para-Chlorobenzoic Acid, and Phenol Depending on Volume Flow Rate

The variation of *Q* is an additional variable that changes the properties of the spray with which the electrode system was moistened. It has effects on the generated water-air contact surface corresponding to the statistical droplet size proportion and distribution and the water mass input into the electrode system, the residence time of the individual droplets and also on the electric discharge and thus on the intensity of the ionization in the electric field.

All three variables are interdependent and, according to the findings shown in Figure 9 regarding the degradation of the reference substances, they obviously do not act in the same direction. Especially with regard to indigo carmine degradation, this can be deduced from the analytical findings at Q = 40, 60, 80, 120, and 160 L·h<sup>-1</sup> with identical settings of the HV pulse generator. The decrease in molar concentration  $\Delta c$  is not progressively related to the volume flow rate Q, but has a maximum which is between 60 L·h<sup>-1</sup> and ≈80 L·h<sup>-1</sup> at  $\Delta c = (2.3 \pm 0.2) \times 10^{-4}$  mol·L<sup>-1</sup> (Figure 9a). At lower and higher volume flow rates  $\Delta c$  is considerably less (e.g., -30% at Q = 160 L·h<sup>-1</sup>).

In the case of para-Chlorobenzoic acid (Figure 9b) and phenol degradation (Figure 9c), on the contrary, between  $Q = 80 \text{ L}\cdot\text{h}^{-1}$  and  $Q = 160 \text{ L}\cdot\text{h}^{-1}$  there were no significant differences at all on concentration reduction. The example of phenol shows that at even higher volume flow rates a significant reduction of the decrease in concentration  $\Delta c$  occurs. From  $Q = 160 \text{ L}\cdot\text{h}^{-1}$  to  $Q = 390 \text{ L}\cdot\text{h}^{-1}$  it has approximately halved. Considering the degraded molar amount per hour as the product of  $\Delta c$  and Q, a more or less constant level can be determined for all three reference substances for  $Q \ge 160 \text{ L}\cdot\text{h}^{-1}$  (Figure 9d). As a result, this finding means that with the selected system configuration a maximum of about  $2.1 \times 10^{-2} \text{ mol}\cdot\text{h}^{-1}$  (9.79 g·h<sup>-1</sup>) of indigo carmine,  $1.3 \times 10^{-3} \text{ mol}\cdot\text{h}^{-1}$  (0.20 g·h<sup>-1</sup>) of para-Chlorobenzoic acid, and  $3.6 \times 10^{-3} \text{ mol}\cdot\text{h}^{-1}$  (0.34 g·h<sup>-1</sup>) of phenol can be degraded.



**Figure 9.** Decrease of (**a**) indigo carmine, (**b**) para-Chlorobenzoic acid, and (**c**) phenol index concentration  $(\Delta c)$  depending on the volume flow rate Q, and (**d**) the molar degradation of the substances per hour depending on the volume flow rate Q.

#### 3.4. Degradation of the Refernce Substances Depending on Physical-Chemical Water Properties

The three water properties—conductivity, pH value, and temperature—were investigated in different test series. All three parameters are interdependent and had to be discussed in relation to each other.

*Conductivity:* Using the example of phenol degradation, the influence of the conductivity of process water on the degradation of the substance was investigated. The conductivities were varied by different additions of phosphate buffer or sodium chloride in DI water. The concentration of the phosphate buffer ranged from  $2.3 \times 10^{-4}$  mol·L<sup>-1</sup> to  $4.5 \times 10^{-3}$  mol·L<sup>-1</sup>, resulting in conductivities of 40 µS·cm<sup>-1</sup> to 698 µS·cm<sup>-1</sup>. According to Bezbarua et al. [78] only a slight ·OH scavenging effect of the phosphate buffer occurs at this concentration level. The selected range of sodium chloride concentrations was from  $1.2 \times 10^{-3}$  mol·L<sup>-1</sup> to  $4.7 \times 10^{-3}$  mol·L<sup>-1</sup> with conductivities from 143 µS·cm<sup>-1</sup> to 554 µS·cm<sup>-1</sup>. Within this range, the scavenger effect of Cl<sup>-</sup> with respect to ·OH is likewise negligible based on the findings of Gultekin and Ince [79].

According to the findings in Figure 10a, there is a clear negative exponential correlation between conductivity and phenol degradation in both test variants. The stronger the conductivity, the lower is the phenol degradation. This can be explained by the fact that the ions dissolved in the water droplets, when passing through the electrode system, dissipate the electrical charges between the HV

and ground electrodes. Therefore, this is weakening the electrical field and the ionization potential resulting in lower amounts of oxidizing agents. This effect varies considerably due to the dependence of conductivity for different ions and its concentration levels according to Kohlrausch's law. If the findings of phenol degradation instead of electrical conductivity are compared with the ionic strength *I*, the results are in the same range of an exponential correlation (Figure 10b). The decline of phenol degradation must therefore correlate more significantly with the current that was discharged via water droplets. The current is proportional to the density of the volume charge, i.e., it depends on the number of charge carriers and their charge number, which ultimately represent the ionic strength *I*. The determined empirical correlation, shown in Figure 10b, is:



$$\Delta c \ phenol \ index \left[ mol \cdot L^{-1} \right] = (2.5 \pm 0.1) \cdot 10^{-5} \left[ mol \cdot L^{-1} \right] \cdot e^{(119 \pm 3)[L \cdot mol^{-1}] \cdot I[mol \cdot L^{-1}]}$$
(4)

**Figure 10.** Decrease of phenol index concentration ( $\Delta c$ ) (**a**) in relation to electric conductivity  $\sigma$  of the process water referenced to *T* = 293.15 K or (**b**) in relation to the ionic strength *I*.

*pH value:* Within the experiments shown in Figure 11, the degradation of phenol was investigated at pH 7, pH 8 and pH 8.3 based on varying compositions of the phosphate buffers. The results for the degradation of phenol at pH 7 are identical to those shown in Figure 10a. The experiments for phenol degradation at pH 8 and pH 8.3 were prepared with a phosphate buffer concentration of  $c = 1 \times 10^{-3}$  mol·L<sup>-1</sup>. Two experiments each for pH 8 and pH 8.3 were performed. The results are plotted against the water conductivity  $\sigma$  in Figure 11, since the procedure means that the pH value set in each case cannot be independent of conductivity.

As a result of raising the pH value to >7, a 9% to 40% higher molar conversion of the phenol with respect to the conductivity could be observed, but there is not a linear correlation. Several effects are presumably overlapping behind this finding. Firstly, according to Gurol and Singer [80] and Beltrán [81] it can be assumed that changing  $H_3O^+/OH^-$  equilibrium to increasing amount of  $OH^-$ , the  $O_3$  decomposition yield via several intermediate states to unselective and strong oxidizing  $\cdot OH$  species would be enhanced. This finding is supported by the fact that, with regard to the intermediates distribution when the pH was raised from pH 7 to pH 8, the proportion of intermediates has shifted slightly from the initial intermediates catechol and hydroquinone towards the consecutive formed non-aromatic products (referred as "other reaction products" in Figure 11b). Further, a part of the non-aromatic intermediates were then processed to total degradation at pH 8.3. Secondly, the shift in the molar phenol/phenolate ion equilibrium from approx. 99.9%/0.1% at pH 7 to 97.8%/2.2% at pH 8.3 may also have played a minor role, since according to Hoigné and Bader [61] a significantly higher reaction rate with  $O_3$  is attributed to phenolate ion. The positive effects of an increasing pH value on

the degradation of phenol are then in turn compensated to a certain extent by the weakening of the electric field strength caused by the accompanying increase in the conductivity of the water.



**Figure 11.** (a) Decrease of phenol index concentration ( $\Delta c$ ) to electric conductivity  $\sigma$  in phosphate buffer matrix at pH 7, pH 8, and pH 8.3 and (b) relative stoichiometric composition of  $\Delta c$  phenol index after treatment determined by high-performance liquid chromatography (HPLC) and dissolved organic carbon (DOC) analysis.

*Temperature:* The process water temperature was varied in a range of 285 K and 296 K. As a result, a negative gradient of  $-2.5 \pm 0.7\%/K$  with regard to the change in molar concentration of indigo carmine, para-Chlorobenzoic acid, and phenol could be determined for all reference substances at pH 7, 8 or 8.3 without distinction (Figure 12). The antagonistic effects of the decreasing gas solubility in water with increasing temperature according to Henry's law and the usually increasing reaction kinetics by elevating temperature according to Arrhenius equation might be partly responsible. The positive temperature dependence of the permittivity of the quartz glass dielectric and the dielectric strength of the air according to Paschen's law is also involved but to a lesser extent. However, the main effect is probably due to the positive temperature dependence of conductivity. In drinking water applications, this parameter is usually referenced with an average temperature coefficient of  $\approx 2\%/K$  to T = 293.15 K or 298.15 K [82]. As already recognized, the electric field strength and the correlating oxidant generation are indirectly proportional to the conductivity. In view of the obvious similarities to the experimentally determined temperature-dependent gradient of the reference substance degradation, it can therefore be assumed that the results shown in Figure 12 are essentially related to the weakening of the electric field strength based on the conductivity which increases with temperature.



**Figure 12.** Decrease of (**a**) indigo carmine, (**b**) para-Chlorobenzoic acid, and (**c**) phenol index concentration ( $\Delta c$ ) in phosphate buffer matrix at pH 7, 8, and 8.3 depending on process water temperature *T* and (**d**) percentage temperature-dependent gradients of the decrease in concentration of the reference substances  $\Delta c \cdot \Delta T^{-1}$ .

#### 4. Conclusions

A lab-scale water treatment plant based on non-thermal plasma technology was designed and constructed to process 40 L·h<sup>-1</sup> up to 390 L·h<sup>-1</sup> in continuous flow condition. The essential part was the reactor chamber with an embedded electrode system connected with a high-voltage pulse generator (voltage amplitudes between  $\hat{U} = 3$  kV and 30 kV, pulse repetition rates between f = 0.001 kHz and 10 kHz and pulse duration between  $t_b = 50$  ns and 500 ns.) The performance of this set-up was investigated in different experimental series with regard to the HV settings, additions of oxygen-based species (H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, and air), different volume flow rates Q, and various physical-chemical properties of the process water such as conductivity, pH value, and temperature. The evaluation based on the analytically determined degradation behavior of the reference substance indigo carmine as an indicator for the formation of ozone and other oxygen-based species, that of para-Chlorobenzoic acid as a special indicator for hydroxyl radical formation and that of phenol as one of the most important industrial precursor chemicals. The best HV settings was found for  $\hat{U} = 30$  kV, f = 0.4 kHz to 0.6 kHz, and  $t_b = 500$  ns with a degradation of indigo carmine of (2.3 ± 0.2) × 10<sup>-4</sup> mol·L<sup>-1</sup>, (7.5 ± 0.3) × 10<sup>-6</sup> mol·L<sup>-1</sup> of para-Chlorobenzoic acid, and (2.3 ± 0.3) × 10<sup>-5</sup> mol·L<sup>-1</sup> of phenol at a volume flow rate Q of

80 L·h<sup>-1</sup>. It could be mathematically proven that the degradation is mainly due to hydroxyl radicals  $(1.4 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1})$ , solvated electrons  $(1.4 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1})$ , ozone  $(2.1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})$ , and hydrogen radicals (unknown concentration). The energy yield  $G_{50}$  which represents the energy required for 50% degradation of the amount of reference substances is 41.8 g·kWh<sup>-1</sup> for indigo carmine, 0.32 g·kWh<sup>-1</sup> for para-Chlorobenzoic acid, and 1.04 g·kWh<sup>-1</sup> for phenol.

The degradation could be increased of about 10% by the addition of H<sub>2</sub>O<sub>2</sub>, if the stoichiometric ratio of H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> in the water phase did not exceed a level of 6:1 mol:mol. The oxygen supply to the process water led to an enhanced degradation of indigo carmine (+22%) and para-Chlorobenzoic acid (+59%), but barely in the case of phenol (+3%). This is due to the different direct or indirect reaction behavior of the substances with ozone. The continuous air supply to the reactor chamber is contra-productive in terms of degradation performance, even at minimum gas volume flow, because O<sub>3</sub> was faster removed from the system than it was produced. The results of the experiments under variation of the volume flow rates showed that there are different optima for each reference substance. For indigo carmine it was in a range of 60 L·h<sup>-1</sup> and 80 L·h<sup>-1</sup>, for para-Chlorobenzoic acid between 80 L·h<sup>-1</sup> and 160 L·h<sup>-1</sup>, and for phenol between 80 L·h<sup>-1</sup> and 120 L·h<sup>-1</sup>. The degraded amount per hour reached a maximum for all reference substances at higher volume flow rates ( $Q \ge 160$  L·h<sup>-1</sup>), e.g.,  $2.1 \times 10^{-2}$  mol·h<sup>-1</sup> (9.79 g·h<sup>-1</sup>) for indigo carmine,  $1.3 \times 10^{-3}$  mol·h<sup>-1</sup> (0.20 g·h<sup>-1</sup>) for para-Chlorobenzoic acid, and  $3.6 \times 10^{-3}$  mol·h<sup>-1</sup> (0.34 g·h<sup>-1</sup>) for phenol.

Water conductivity is one of the most critical parameter for the process, since the degradation of the reference substances decreases exponentially with increasing conductivity. A comparison between these tests showed that the ionic strength of the process water is the decisive parameter. The effect of the pH value was investigated at pH 7, pH 8 and pH 8.3 based on varying compositions of the phosphate buffers. A higher degradation of 9% to 40% occurs in an alkaline milieu, but there is not a linear correlation. If the pH was raised from pH 7 to pH 8, the proportion of intermediates has shifted slightly from the initial intermediates catechol and hydroquinone towards the consecutive formed non-aromatic product. Further, a part of the non-aromatic intermediates were processed to total degradation at pH 8.3. The positive effects of an increasing pH value on the degradation of phenol are compensated to a certain extent by the weakening of the electric field strength caused by the accompanying increase in the conductivity by the used phosphate buffers in the test series. Finally, the temperature influence on the degradation of indigo carmine, para-Chlorobenzoic acid, and phenol was investigated in water matrices with pH values of 7, 8, and 8.3. For a process water temperature between T = 285 K and 296 K the degradation of all three reference substances decreased by 2% to 3% per Kelvin with increasing temperature. The magnitude of the gradient corresponds approximately to that of the dependence of conductivity on temperature.

In summary of the research, it could be shown the water treatment process using low-temperature plasma technology can be upgraded from a small-scale laboratory experiment to the level of a pilot plant. In principle, the process can be scaled for an industrial application.

#### 5. Patents

The plant for the oxidative treatment of drinking, industrial and waste water presented in this study was applied for a patent under the file number DE 10 2018 121 551 A1.

**Author Contributions:** Conceptualization, S.S., S.U., A.W., A.L. and C.P.; methodology, S.S. and S.U.; validation, S.S., S.U. and A.W.; formal analysis, S.S., K.W. and R.P.; investigation, S.S., K.W. and R.P.; resources, K.B.; data curation, K.W. and A.W.; writing—original draft preparation, S.S.; writing—review and editing, A.W., K.B., S.U., A.L.; visualization, S.S., K.B.; supervision, A.L.; project administration, C.P. and A.L.; funding acquisition, C.P, S.U., S.S., A.W., A.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the operational program of the Free State of Saxony for the European Regional Development Fund (ERDF) via SAB Sächsische AufbauBank, grant number 100240893 and 100240188. The APC was funded by Technische Universität Dresden.

Acknowledgments: We would like to thank T. Schulz and J. Kolb from the Leibniz Institute for Plasma Science and Technology (INP Greifswald) for their technical support in design, assembly, and testing of the electrode system.

Furthermore we would like to thank H. Brückner, U. Gebauer, and S. Heidt from the Technische Universität Dresden, Institute of Urban and Industrial Water Management, for their support and sample analysis.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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