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Removal of micropollutants from water in a continuous-flow electrical discharge reactor

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Highlights

- Micropollutant removal is studied in a continuous-flow DBD reactor
- The influence of 4 operational parameters is studied
- Under optimal operational settings > 93 % of micropollutants are removed
- Energy efficiency is in the range 2.42 – 4.25 kWh/m³ for all micropollutants evaluated

Abstract

The emergence of micropollutants into our aquatic resources is regarded as an issue of increasing environmental concern. To protect the aquatic environment against further contamination with micropollutants, treatment with advanced oxidation processes (AOPs) is put forward as a promising technique. In this work, an innovative AOP based on electrical discharges in a continuous-flow pulsed dielectric barrier discharge (DBD) reactor with falling water film over activated carbon textile is examined for its potential application in water treatment. The effect of various operational parameters including feed gas type, gas flow rate, water flow rate and power on removal and energy efficiency has been studied. To this end, a synthetic micropollutant mixture containing five pesticides (atrazine, alachlor, diuron, dichlorvos and pentachlorophenol), two pharmaceuticals (carbamazepine and 1,7- α -

ethinylestradiol), and 1 plasticizer (*bisphenol A*) is used. While working under optimal conditions, energy consumption was situated in the range 2.42 – 4.25 kWh/m³, which is about two times lower than the economically viable energy cost of AOPs (5 kWh/m³). Hence, the application of non-thermal plasma could be regarded as a promising alternative AOP for (industrial) wastewater remediation.

Keywords: wastewater treatment; advanced oxidation process; non-thermal plasma; micropollutants; electrical energy per order

1. Introduction

Since 1970, a new class of organic contaminants, also referred to as “micropollutants” (MPs), has been systematically detected in several water bodies all around the world [1-3]. Secondary effluent, originating from municipal wastewater treatment plants (MWWTPs) has been identified as a major source of micropollutants into the environment [4]. Although they typically appear in very low concentrations ($\mu\text{g}\cdot\text{L}^{-1}$ – $\text{ng}\cdot\text{L}^{-1}$), this type of water pollutants is suspected to cause different adverse effect on both human and environment, and should therefore be properly removed. In this context, a viable solution could consist of upgrading MWWTPs with an additional tertiary treatment step [5]. Up till now, different physico-chemical water treatment methods including the coagulation-flocculation method, activated carbon adsorption and membrane filtration are under evaluation. Among them, advanced oxidation processes (AOPs) have been put forward as a promising technology. They constitute a wide group of oxidation processes, aiming for the generation of strong oxidizing species, predominantly hydroxyl radicals (HO^\bullet) [6].

Although AOPs have the potential to fully mineralize MPs into carbon dioxide and water, complete micropollutant destruction requires large dosage of chemicals, or high energy inputs [7]. Consequently, this has stimulated the development of novel, more efficient AOPs. In recent years, non-thermal plasma-based techniques have attracted significant attention. Non-thermal plasmas can be generated either in the gas phase or directly in the liquid, using various reactor geometries such as corona discharges, dielectric barrier discharges (DBD) and gliding arc discharges. Application of electrical discharges gives rise to the formation of various oxidative species such as hydroxyl radicals (HO^\bullet), singlet oxygen (O^\bullet), ozone (O_3), hydrogen peroxide (H_2O_2) and many others, that might diffuse into the liquid, eventually leading to micropollutant oxidation [8].

To date, non-thermal plasmas were found to be very effective in removing several classes of environmental pollutants, including textile dyes [9-12], pharmaceuticals [13-15] and pesticides [16-19]. Despite the promising obtained results, plasma-assisted decomposition of micropollutants has not reached the level of industrial application. Essentially, the lack of experimental studies evaluating the treatment capability and energy cost in continuous-flow reactor designs currently restricts the further development of plasma-based AOPs on the industrial level. Moreover, a comparative study, benchmarking the energy consumption for the removal of textile dyes in 27 frequently used plasma reactors revealed rather high energy inputs: on average, energy efficiencies calculated for 90% dye removal, were situated in the range 5 – 200 kWh/m³, with most values above 10 kWh/m³ [20]. Considering a current energy cost of approximately 0.12 €/kWh in Europe, this would correspond to an additional electrical cost of at least € 0.60 for the treatment of 1 m³ contaminated water. As this is still

too high for industrial application, optimization of operational settings or the combination of non-thermal plasma with catalysts fixed into the reactor has been proposed [21].

In this context a pulsed DBD reactor with falling water film over an activated carbon textile was previously developed and characterized in our research group [19]. In a subsequent study, the reactor revealed high efficiency for the removal of several pesticides in various single-compound tests [22]. From the viewpoint of real-life applications, however, it was reported that this type of reactor configuration is inappropriate to cope with large amounts of wastewater. Hence the reactor set-up was modified to allow operation in a continuous-flow (single-pass) mode.

As such, the present study aims to evaluate the efficiency of this reactor set-up operated in single-pass configuration. The effect of different operational parameters (feed gas composition, gas flow rate, water flow rate, applied power) is studied. A synthetic wastewater containing five pesticides (atrazine, alachlor, diuron, dichlorvos and pentachlorophenol), two pharmaceuticals (carbamazepine and 1,7- α -ethinylestradiol), and one plasticizer (bisphenol A) is used to evaluate the plasma treatment efficiency when applied to a wide group of structurally different organic pollutants. The results of this study allow to obtain a better understanding of the underlying plasma chemistry, to estimate the energy cost associated with micropollutant removal, and to provide a possible strategy for future reactor optimization.

2. Materials & Methods

2.1. Preparation of micropollutant solutions

In this study, the pesticides atrazine (ATZ), alachlor (ALA), dichlorvos (DVOS), diuron (DIU) and pentachlorophenol (PCP), the pharmaceuticals carbamazepine (CBZ) and 1,7- α -ethinylestradiol (EE2) and the plasticizer bisphenol A (BPA) have been chosen as representative target micropollutants. These micropollutants were selected, owing to their systematic detection in secondary effluent of MWWTPs, and their potential to cause different adverse effects on human health and aquatic ecosystems. An overview of physico-chemical constants, including Henry's law coefficient (H), water solubility (S), the octanol-water coefficient ($\log K_{OW}$) and the secondary reaction rate constants of target pollutants with hydroxyl radicals ($k_{HO\cdot/M}$) and ozone ($k_{O_3/M}$), is provided in Table S1 in the supplementary material.

Due to the limited solubility of most micropollutants, saturated solutions were prepared by dissolving an appropriate amount of each individual micropollutant in deionized water. The saturated solutions were filtrated and diluted to obtain individual working solutions with a concentration of 1 mg L⁻¹. Working solutions were mixed together and further diluted to the desired concentration (200 μ g L⁻¹) prior to the start of each experiment.

2.1. Experimental setup

All experiments were carried out in a lab-scale pulsed dielectric barrier discharge (DBD) reactor with falling water film over an activated carbon textile (Zorflex[®]), described in detail in our previous works [19],[22]. A schematic of the reactor is presented in Figure 1. The plasma chamber consisted of a quartz vessel with coaxial geometry. An outer mesh grid wrapped around the quartz tube served as a high voltage electrode, whereas a stainless steel tube placed inside the quartz tube functioned as grounded electrode. The ground electrode was covered with one layer of Zorflex[®] activated carbon. Plasma was generated in a discharge medium (air, argon or oxygen), which was continuously introduced into the reactor. Alternative voltage of 50 kHz frequency was applied to the reactor cell. The discharge was generated in a pulsed mode with a 15 % duty cycle in order to avoid extensive heating and to improve the discharge stability. Voltage and current waveforms were continuously monitored by a Tektronix[®] TD 1002 digital oscilloscope, using a Tektronix[®] P6015A HV probe and an IonPhysics[®] current probe, respectively.

2.2. Experimental procedure

In each experimental run, 2.5 l of synthetic water solution was fed to the reactor at a flow rate of 56.3 mL min⁻¹. The average residence time in the active plasma region was estimated to be 0.86 ± 0.02 s [19]. In order to estimate micropollutant removal by adsorption on Zorflex® a 60 mL sample was taken prior to plasma treatment. Then, the plasma was turned on and 60 mL samples were collected at regular time intervals (2.5, 5, 10, 15, 20, 25 and 30 min) after one pass through the reactor.

Residual micropollutant concentrations in the plasma treated samples were quantified using a validated gas chromatography – mass spectrometry (GC-MS) method. Details about the analytical procedure and method validation are provided in Text S1 in the supplementary material. Conductivity and pH changes after plasma exposure were monitored using a conductivity and pH meter (Metrohm®). Nitrite (NO₂⁻) and nitrate (NO₃⁻) were quantified with Quantofix® semi-quantitative teststrips (Mackerey-Nagel, Düren, Germany). The lower limit of detection was 1 mg L⁻¹ for nitrite and 10 mg L⁻¹ for nitrate.

3. Results and discussion

3.1 Differentiating between adsorption and (plasma) oxidation

Micropollutant removal in the plasma reactor was first assessed for the standard settings, highlighted in Table S2. These standard settings were tentatively chosen, in analogy with our previous work [19]. Normalized concentration versus time profiles obtained for the eight micropollutants studied are presented in Figure 2, whereas typical removal percentages, observed after one pass through the reactor, are summarized in Table S3. Considering the very short residence time in the plasma chamber (0.86 ± 0.02 s) for a water flow rate of 56.3 mL min⁻¹, micropollutants were already substantially removed, with overall removal efficiencies between 56.9 – 87.8 %. The pesticides ATZ, ALA, DIU, PCP and DVOS appeared to be the most persistent against plasma-assisted oxidation with 56.9 % removal for ATZ, 57.8 % for ALA, 62.4 % for DIU, 69.3 % for PCP and 70.2 % for DVOS. BPA and the pharmaceuticals CBZ and EE2 were found to be the most susceptible to plasma-oxidation while working at standard setting, with removal efficiencies of 76.7 %, 82.4 % and 87.8 % respectively.

In the absence of plasma, the individual micropollutant concentration was decreased by 33.2 – 58.9 % after 10 seconds of adsorption (see Table S3). However, it needs to be emphasized here that pollutant degradation does not occur in this step, since the target compounds are only physically transferred from the bulk liquid to the activated carbon surface. After plasma is switched on, final removal efficiencies between 56.9 – 87.8 % are reached under steady-state conditions. Taking into account the limited contact time between the solution under treatment and the plasma, adsorption equilibrium will certainly not be reached in the single-pass configuration. This can be concluded, for instance, from previous experiments carried out within the same reactor, but operated in a batch-recirculation mode. Here, micropollutant removal due to adsorption was found to be important, even after 30 minutes of experiment [19].

In heterogeneous plasma reactor systems that combine adsorption with plasma treatment, the chemical mechanisms leading to pollutant degradation may take place simultaneously on the activated carbon surface, and in the bulk liquid [19, 20]. Nonetheless, when the plasma is turned on, the individual contributions of adsorption and plasma treatment cannot be clearly distinguished in the single-pass configuration, as the removal of organic pollutants is a dynamical process.

Plasma-assisted decomposition of micropollutants is a very complex process, involving various oxidative species including hydroxyl radicals (HO[•]), atomic oxygen (O[•]), ozone (O₃), and hydrogen peroxide (H₂O₂). Among the considered different chemical species, ozone (O₃) and hydroxyl radicals (HO[•]) are often regarded as the major oxidants, responsible for micropollutant elimination. Panorel et al. [24] found an almost linear increase in ozone formation at increased oxygen concentration in a pulsed corona discharge reactor operated in air. However, the increase in pollutant removal efficiency was less pronounced: only 30 – 40 % higher efficiency was achieved, when initial oxygen concentration was increased fourfold [24]. In a subsequent study by Preis et al. [25] investigating the role of ozone in oxidation of a slow reacting (oxalic acid) and a fast reacting (phenol) compound with ozone, it was

shown that O₃ contributes for 20 % of the total removal efficiency of oxalic acid. Even for phenol, it was reported that ozone accounts for only 40 % of pollutant removal, suggesting the dominant role of HO[•] during pollutant abatement [24].

From an industrial point of view, the efficiency of pollutant degradation is preferably illustrated by means of its energy cost. The energy efficiency of micropollutant removal in plasma reactors is often evaluated according to the electrical energy per order (EE/O) figure-of-merit [25]. The EE/O value represents the electrical energy input (kWh) required to reduce the initial micropollutant concentration with 1 order of magnitude (90 %), in 1 m³ of contaminated water. For continuous-flow reactor systems, the EE/O value is calculated as follows [26]:

$$EE/O = \frac{P}{F \cdot \log\left(\frac{C_i}{C_f}\right)} \quad (1)$$

With EE/O the electrical energy per order in kWh/m³, P the total power dissipated in the reactor (kW), and F the water flow rate (m³ h⁻¹). C_i and C_f represent the initial and final micropollutant concentration in µg L⁻¹, respectively. The EE/O values for the plasma-assisted decomposition of micropollutants are shown in Figure 3. With the standard settings used, EE/O values were found to be in the range 13.2 kWh/m³ (EE2) – 33.2 kWh/m³ (ATZ). However, the aspired EE/O value required to remove micropollutants from industrial wastewater with AOPs at a reasonable cost should be between 2.5 - 5 kWh/m³ or lower [7, 27]. Improvement of the plasma-assisted removal can be achieved through optimization of the operational parameters. The effect of different operational parameters on the energy consumption of micropollutant removal will be further elaborated in the following sections.

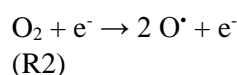
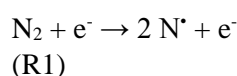
3.2 Influence of operational parameters

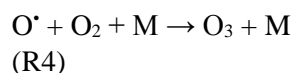
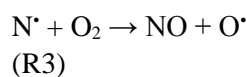
3.2.1 Influence of the feed gas composition

A one-parameter-at-a-time approach was employed to determine the effect of various operational parameters on the reactor performance. Optimization was performed starting from the standard operational settings enlisted in Table S2. First, the influence of the feed gas composition has been examined. In comparison to air plasma treatment, about 5 – 10 % higher removal efficiency was detected in argon plasma, and even 15 – 20 % higher removal was found when the discharge was operated in oxygen. For each compound, at least 90 % decomposition was observed in oxygen plasma (Table S4). Considering the energy efficiency, a similar behaviour is obtained (Figure 4), i.e. EE/O is found to decrease in the order:

EE/O oxygen plasma < EE/O argon plasma < EE/O air plasma

Apparently, switching the feed gas from air to oxygen offers an interesting way to enhance the efficiency of micropollutant removal in the reactor. The large difference in efficiency observed between plasmas sustained in air and oxygen implies that various chemical species might be generated in different proportions under air and oxygen atmosphere. The efficiency of ozone generation in different feed gases was extensively studied in Lukes et al. [28]. The authors reported that, by switching the feed gas from oxygen to air, the total amount of ozone generated in the discharge declined with approximately 25 %. This significantly lower ozone generation was ascribed to the presence of N₂ in the discharge medium, facilitating the formation of nitrogen oxide (NO), according to reactions (R1)-(R4) [29]:





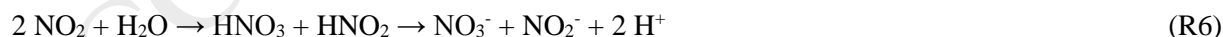
The formation of large amounts of NO is particularly undesirable as it leads to fast ozone quenching, yielding nitrogen dioxide (NO₂).



Consequently, it appears that the poor performance of air plasma as compared to oxygen plasma is likely the result of smaller active species production rates, especially HO[•] and O₃. Although literature suggests that the formation of O₃ is obviously promoted in the absence of N₂ in the carrier gas, an enhanced production of O₃ does not necessarily indicate that ozone participates to the direct oxidation of the micropollutants. In most DBDs ozone was found to be completely absent in the plasma-treated liquid [30], or was only present in very small concentrations [31]. Moreover, due to the presence of hydrogen peroxide (H₂O₂), commonly detected in plasma-treated liquids, ozone is rapidly converted in HO[•] radicals.

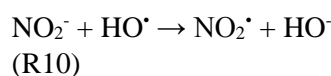
Furthermore, it should be stressed that gas phase chemical species will dissolve into the plasma-treated liquid, giving rise to the generation of secondary oxidants in the liquids. The formation of secondary oxidants potentially affects the physico-chemical characteristics such as pH and conductivity of the solution under treatment. In order to study these effects, pH and conductivity changes in deionized water were evaluated after one pass through the reactor for plasma discharges sustained in different gaseous atmospheres (air, argon and oxygen). Each experiment was performed at standard settings, highlighted in Table S2. It is clear that strongest acidification is recorded for deionized water treated in air plasma, with a decrease from pH = 7.78 ± 0.08 to pH = 3.17 ± 0.03 after one pass through the reactor. For discharges operated in oxygen the final pH value was 4.48 ± 0.06. On the contrary, the observed pH drop was much less pronounced in argon plasma, with a value around 5.78 ± 0.03. In all investigated gaseous environments, the decrease in pH was accompanied with a conductivity rise. Deionized water conductivity increased from 11 ± 8 μS/cm to the highest value of 424 ± 12 μS/cm when treated by air plasma. The conductivity changes were rather limited for treatment in oxygen (107 ± 5 μS/cm) and argon (53 ± 8 μS/cm) plasmas.

The acidification of plasma-treated liquids has been related to the accumulation of hydrogen cations (H⁺) in solution. In air plasmas, several studies have evidenced the presence of nitric (HNO₃) and nitrous (HNO₂) acid in solution [8, 32-34]. The formation mechanisms of these acids have been thoroughly discussed in Lukes et al. [8], and are ascribed to the production of nitrogen oxides in the plasma which may subsequently dissolve into the liquid, forming nitrite (NO₂⁻), nitrate (NO₃⁻) and hydrogen (H⁺) ions (R6)- (R7):



To confirm that nitrogen containing species contributed to acidification of deionized water after plasma exposure, nitrite and nitrate concentrations were determined in the plasma-treated samples. High concentrations of nitrate, up to 100 mg L⁻¹ could be detected in air plasma-treated liquids. Conversely, only a small amount of nitrite was measured (1 mg L⁻¹). For the other feed gases, nitrite and nitrate were not detected in the plasma-treated liquid.

It is interesting to note that the residual nitrite concentration in the liquid is very small in comparison with nitrate. This can be attributed to the oxidation of nitrite by multiple active species i.e. through the reactions (R8)-(R10):



Consequently, the low performance of air plasma is likely the result of both O_3 quenching by NO in the gas phase (R5), as well as nitrite conversion in the liquid (R8)-(R10). The latter process is promoted by multiple oxidants, and yields nitrate as one of the major by-products. The presence of nitrate at such a high level in air plasma-treated water poses an additional challenge for application on industrial scale. Given a maximal allowable concentration of 50 mg L^{-1} in surface and groundwater by the EU Nitrates Directive (91/676/EEC), this indicates that additional treatment costs are potentially required in order to remove nitrate before effluent discharge in the receiving water.

3.2.2 Influence of the gas flow rate

Due to higher efficiency of micropollutant removal for plasma discharges sustained in O_2 gas, the influence of three different oxygen flow rates on the reactor performance is further evaluated. By decreasing the oxygen flow rate from 1.0 SLM to 0.1 SLM, degradation efficiency of all micropollutants is increased by 5 – 10 % (Table S5). At a flow rate of 0.1 SLM, ATZ is degraded for 94.9 %, whereas at least 96.6 % degradation was observed for DVOS, BPA, CBZ and EE2. Along with an increase in removal efficiency, EE/O declines with decreasing gas flow rate giving EE/O values between 9.4 kWh/m^3 (ATZ) and 6.8 kWh/m^3 (EE2), as presented in Figure 5. The positive effect of enhanced micropollutant removal and higher energy efficiency while working under lower flow rates is obviously due to a higher residence time of the oxygen gas in the discharge zone. Consequently a larger amount of active species is likely to be formed [35-36].

3.2.3. Influence of the water flow rate

The energy efficiency generally rises upon increasing water flow rate. For the lower flow regimes ($25.8 - 56.3 \text{ mL min}^{-1}$), EE/O abruptly drops with 50 - 60 %, followed by a rather slow increase of only 5 – 10 % at flow rates between $73.6 - 120 \text{ mL min}^{-1}$. According to the data presented in Table S6, an increase in removal efficiency is generally observed at flow rates between 25.8 and 56.3 mL min^{-1} , whereas a decrease in efficiency is found for flow rates above 73.6 mL min^{-1} (Table S6).

Some authors found a decrease in efficiency when decreasing the water flow rate [37,38], whereas others reported the opposite effect [39,40]. The experimental results observed throughout this work are very similar to the ones obtained in a planar DBD reactor, equipped with activated carbon fibres [40]. Apparently, the obvious discrepancy in between the published studies, suggests that the influence on the removal efficiency is rather complex, and likely depends on the reactor configuration and the experimental conditions applied. In this study, the observed increase in removal efficiency at low flow rates might be attributed to a better cooling of the reactor, which promotes the formation of thermolabile compounds, such as O_3 and H_2O_2 , and hence their transport to the liquid. Moreover, increasing the water flowrate will leads to a more turbulent behaviour in the liquid film, which allows for a better mixing of the target compounds with the plasma-generated oxidants. However, when the water flow rate is further increased above a certain value ($> 73.6 \text{ mL min}^{-1}$), the positive effect of reactor cooling on the removal efficiency starts to be compensated by the negative effect of a shorter residence time in the discharge zone. Thus, a maximum in removal efficiency could be expected, in agreement with our experimental observations.

3.2.4. Influence of power

For pulsed power plasma reactor systems, total input power delivered to the reactor is determined by multiplying the power during one period of voltage with duty cycle:

$$P = P_0 \cdot DC$$

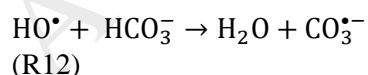
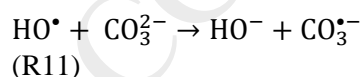
(2)

With P the total input power (W), P_0 the power per pulse (W), and DC the applied duty cycle (%). Duty cycle is expressed as the plasma 'on' time (T_{on}) relative to the period of the pulse ($T_{on} + T_{off}$). In the present work, the total power dissipated in the reactor is adjusted by changing the amplitude of the voltage pulse. Micropollutant removal efficiency was tested for five different power settings (40 W, 52.5 W, 65 W, 77.5 W and 90 W) at a constant 15 % duty cycle. In order to maintain the duty cycle at 15 %, T_{on} was set at 4.5 ms, and T_{off} was 25.5 ms, which gives a total pulse duration of 30 ms.

It is found that total degradation efficiency of micropollutants varied between 90.0 – 95.8 % for a power of 40 W and further increased to 96.5 - 99.5 % at 65 W, as presented in Table S7 in the supplementary material. For higher power settings (77.5 and 90 W), all micropollutants were completely eliminated. Specifically, as power increases, electrons generated in the plasma discharges will gain more electrical energy from the electric field. Higher micropollutant removal efficiency at elevated power is likely the result of enhanced hydroxyl radical production. This is in agreement with the study in [41], where HO^\bullet generation almost increased linearly with discharge power in pulsed corona, as measured with laser-induced fluorescence (LIF) spectroscopy. Regardless of enhanced micropollutant removal efficiency at higher power settings, however, it was observed that energy efficiency of slightly increased with 10 – 15 % for ATZ, ALA, DIU, PCP, DVOS and BPA by increasing power in the range 40 W - 65 W, whereas a small decrease was found for CBZ and EE2 (Figure 7). Hence it could be concluded that the contribution of power to the energy efficiency is probably compound-specific, and its influence seems to be limited within the tested power range.

According to the results presented in sections 3.2.1 – 3.2.4, optimal reactor efficiency in terms of energy costs is achieved i) while working under oxygen atmosphere ii) with gas and liquid flow rates of 0.1 SLM and 120 mL min⁻¹ and a power input of 40 W. In a final experiment, conducted with optimal parameters settings more than 93 % of micropollutants are removed from the water solution, whereas energy efficiency is found to be between 2.42 kWh/m³ and 4.25 kWh/m³ (Table 1).

It must be noted that the optimal EE/O values presented in Table 1 have been measured in deionized water, spiked with micropollutants. In real wastewaters, however, the presence of matrix constituents will influence the efficiency of advanced oxidation processes, likely increasing the total energy consumption. Although the chemical composition depends on the type of the wastewater considered, it is characterized by the presence of natural organic matter (NOM), trace organic pollutants and various inorganic ions. NOM is generally present in most ground, surface and wastewaters. It is a complex mixture that usually consists of hydrophilic and hydrophobic substances. It has been found these high molecular weight organic molecules, predominantly humic and fulvic acids, will compete with MPs for hydroxyl radicals, and hence a substantial reduction in micropollutant decomposition at a constant energy-input is expected [42]. Besides, it has been reported that the presence of some inorganic ions influence the aqueous oxidation chemistry. Among them, bicarbonate and carbonate are usually considered to be the most important ones. The reaction of HO^\bullet with HCO_3^- and CO_3^{2-} yields the carbonate radical ($CO_3^{\bullet-}$) which is a rather mild oxidant (R11 - 12) [43].



For instance, the secondary order reaction rate constant between $CO_3^{\bullet-}$ and atrazine is $6.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, [37], which is about 3 orders of magnitude lower as the secondary rate constant of HO^\bullet with atrazine ($3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [44].

In summary, this suggests that the abatement of micropollutants from real water matrices by plasma technology is very complex process, where the overall process performance is affected by multiple factors, including i) the type of the plasma reactor considered, ii) the type of wastewater being treated,

iii) the process conditions applied, and iv) the presence of matrix constituents. A thorough examination, of all these aspects, however, falls beyond the scope of this work and will be further addressed in detail in our future publications.

4. Conclusion

In the present work, a pulsed dielectric barrier discharge reactor with falling water film, operating in a continuous mode was evaluated in view of future application for water treatment. The experimental study is performed in a synthetic water mixture, containing eight micropollutants (alachlor, atrazine, diuron, pentachlorophenol, bisphenol A, carbamazepine and 1,7- α -ethinylestradiol) with initial concentration set on 200 $\mu\text{g L}^{-1}$.

Due to the presence of an activated carbon textile in the plasma reactor, fast micropollutant removal is observed while working under standard settings, with overall removal efficiencies between 56.4 – 87.8 %, after one pass through the reactor. Higher removal and energy efficiencies are achieved when the plasma discharge is sustained in oxygen gas. In particular, it is shown that the presence of N_2 in the discharge medium is unfavourable and leads to very low reactor performance, both in terms of removal and energy efficiency. Poor removal while working under air atmosphere is explained by the formation of different nitrogen containing species, which act as O_3 and HO^\bullet scavengers.

Improvement in efficiency of the reactor system is obtained through optimization of the operational parameter settings. To this end, the effect of oxygen gas flow rate, water flow rate and applied power has been studied. In general, it is found that removal efficiency is enhanced with i) decreasing gas flow rate, ii) increasing water flow rate, and iii) increasing power, whereas energy efficiency is improved by i) decreasing gas flow rate, ii) increasing water flow rate and iii) decreasing applied power. The application of optimal operational settings obtained throughout this work resulted in overall removal efficiencies > 93.8 % for all micropollutants investigated, and energy efficiencies varying between 2.42 – 4.25 kWh/m^3 . Since, these values are within the range or even lower than the aspired EE/O values for water treatment in an economical feasible way (EE/O: 2.5 - 5 kWh/m^3), non-thermal plasma technology is a promising technology for industrial water treatment.

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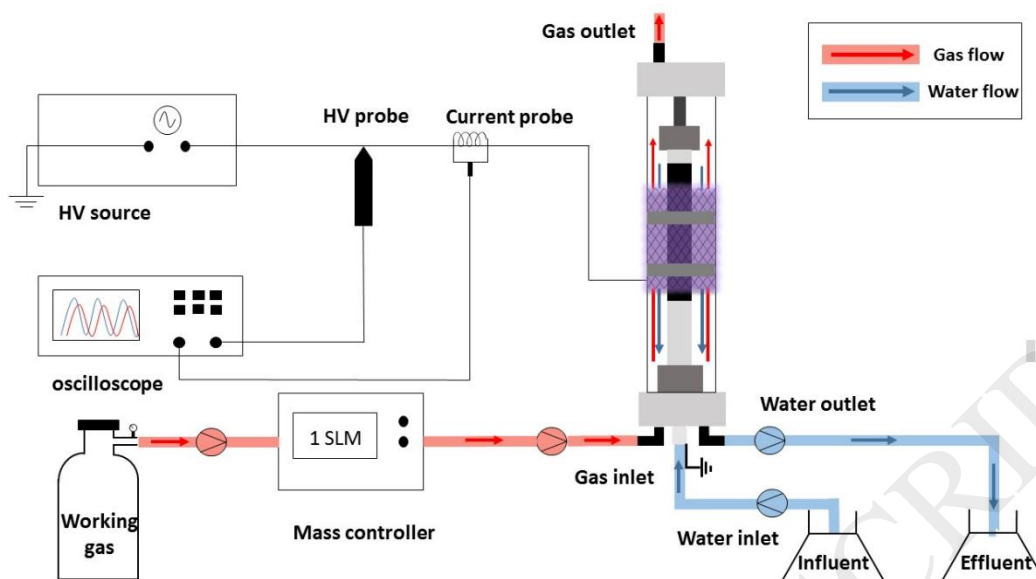


Figure 1. Schematics of the pulsed DBD reactor system, operated in single pass mode.

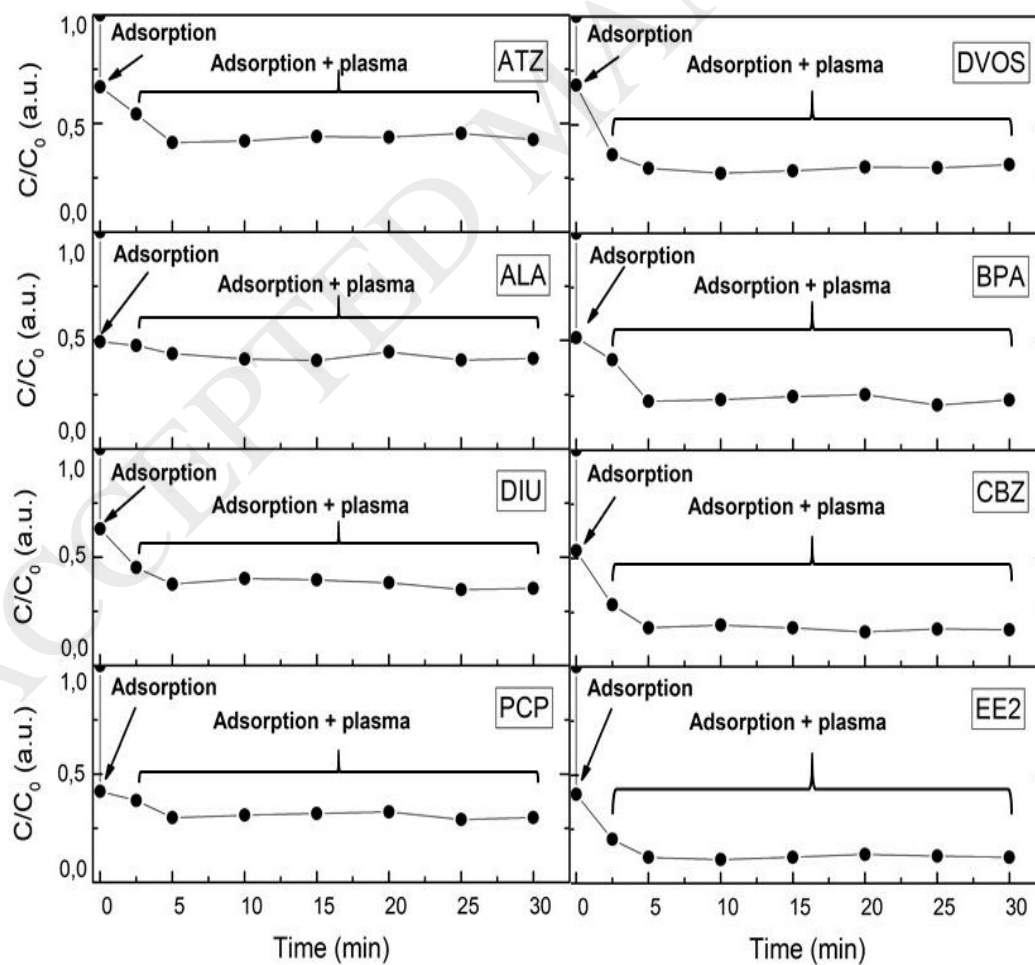


Figure 2. Concentration versus time profiles recorded during micropollutant removal in the plasma reactor (operational settings: feed gas, air; gas flow rate, 1.0 SLM; water flow rate, 56.3 mL min⁻¹; initial micropollutant concentration, 200 µg L⁻¹; duty cycle, 0.15; power, 40 W).

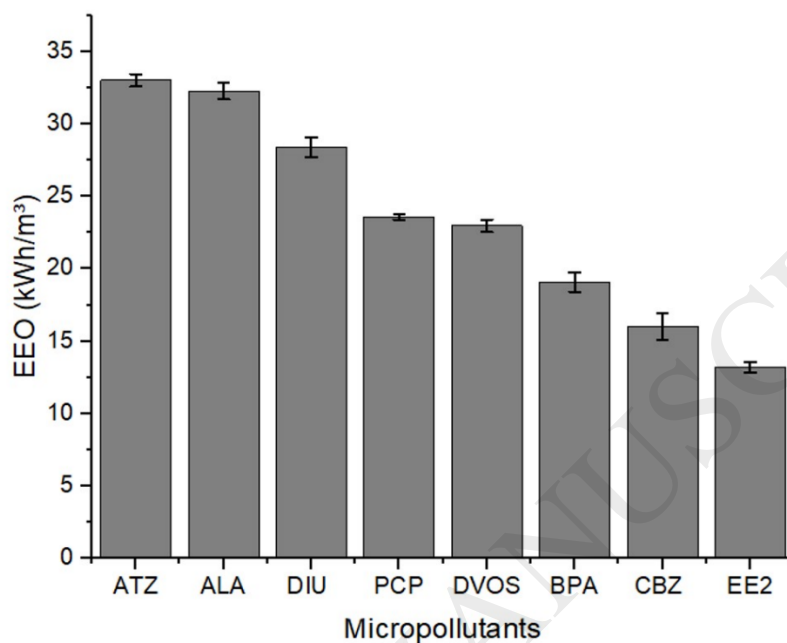


Figure 3. EE/O values for micropollutant removal in the plasma reactor for standard settings (feed gas, air; gas flow rate, 1.0 SLM; water flow rate, 56.3 mL min⁻¹; initial micropollutant concentration, 200 µg L⁻¹; duty cycle, 0.15; power, 40 W).

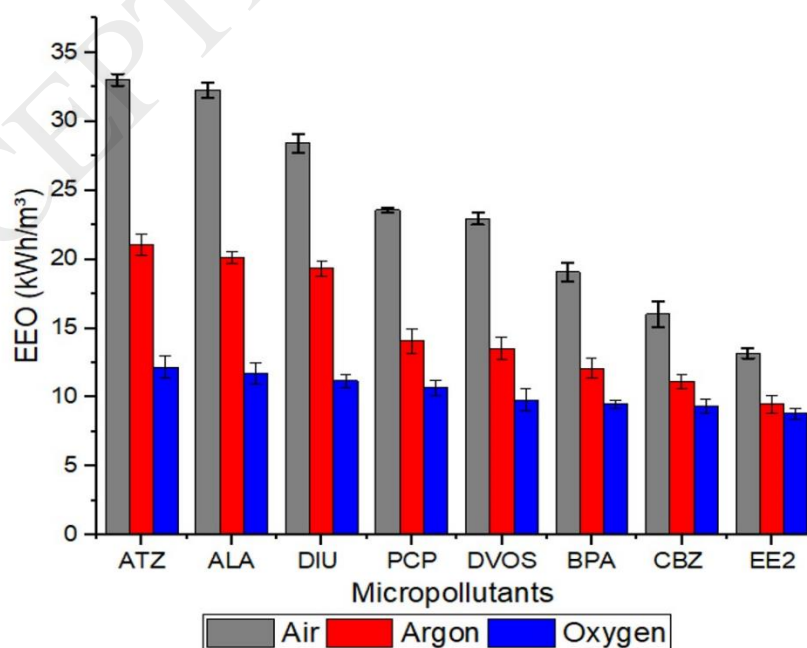


Figure 4. Influence of various feed gases on the energy efficiency of micropollutant removal (Operational settings: gas flow rate, 1.0 SLM; water flow rate, 56.3 mL min⁻¹; micropollutant concentration, 200 µg L⁻¹; power, 40 W).

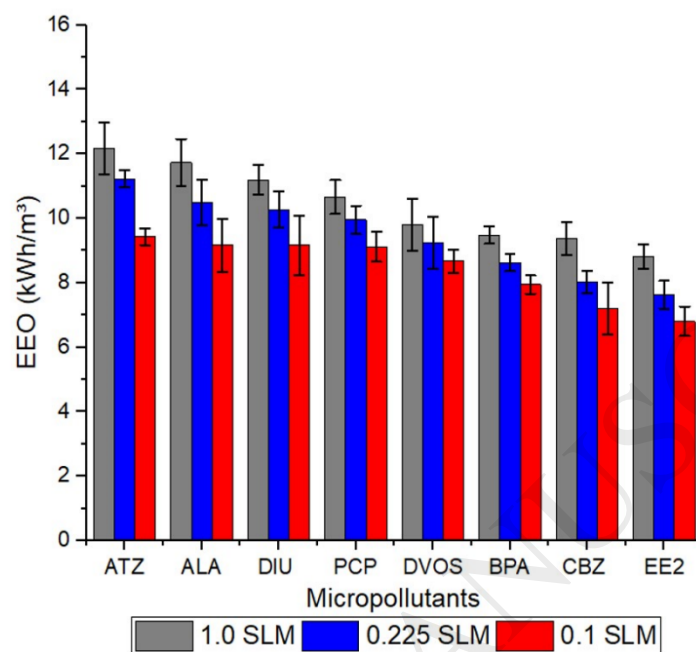


Figure 5. Influence of various oxygen flow rates on the energy efficiency of micropollutant removal. (Operational settings: feed gas, oxygen; water flow rate, 56.3 mL min⁻¹; micropollutant concentration, 200 µg L⁻¹; duty cycle, 0.15; power, 40 W).

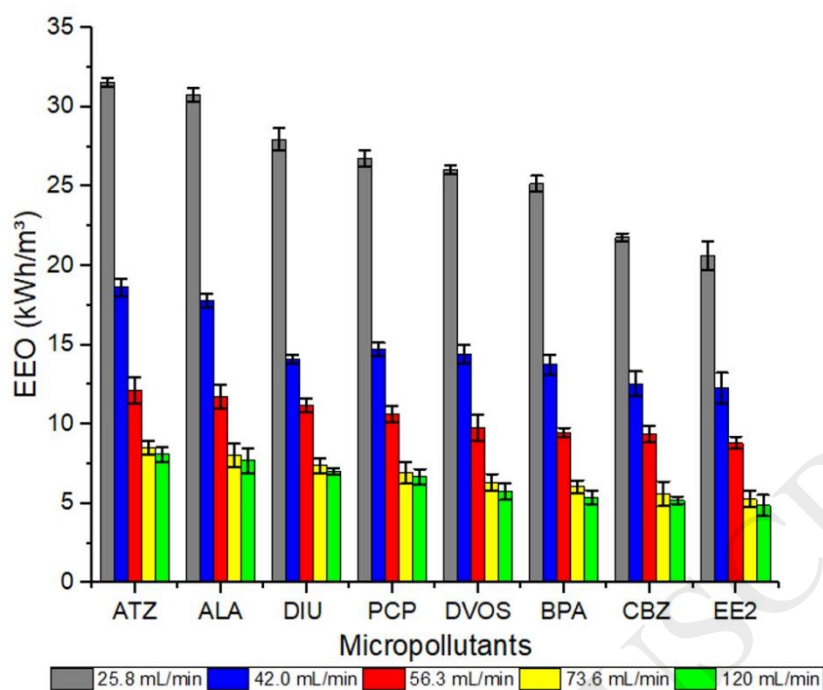


Figure 6. Influence of various water flow rates on the energy efficiency of micropollutant removal. (Operational parameter settings: feed gas, oxygen; gas flow rate, 1.0 SLM; micropollutant concentration, $200 \mu\text{g L}^{-1}$; duty cycle, 0.15; power, 40 W).

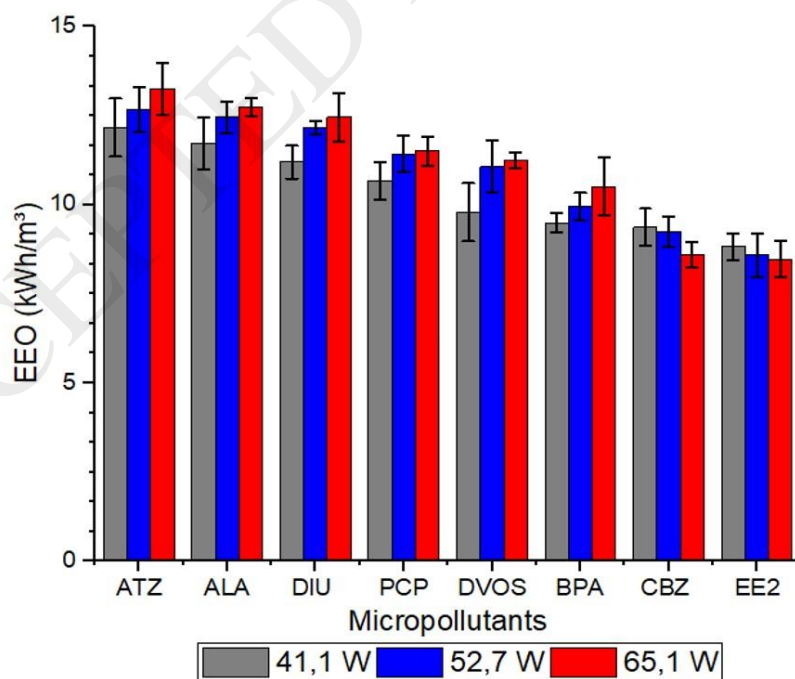


Figure 7. Influence of various power settings on the energy efficiency of micropollutant removal. (Operational settings: feed gas; oxygen, gas flow rate, 0.1 SLM; water flow rate, 56.3 mL min^{-1} ; micropollutant concentration, $200 \mu\text{g L}^{-1}$; duty cycle, 0.15).

Table 1: Overview of reactor parameter settings for optimal removal of micropollutants using an initial micropollutant concentration: 200 $\mu\text{g L}^{-1}$, feed gas: oxygen, gas flow rate: 0.1 SLM, water flow rate: 120 mL min^{-1} , power: 40 W

Compound	% Removal	EE/O (kWh/m^3)
ATZ	93.9	4.25
ALA	96.1	4.08
DIU	97.4	3.63
PCP	97.9	3.51
DVOS	98.4	3.19
BPA	98.8	2.96
CBZ	99.3	2.69
EE2	99.6	2.42