Journal of Environmental Chemical Engineering 6 (2018) 7377–7385

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Combining ultrafiltration and non-thermal plasma for low energy degradation of pharmaceuticals from conventionally treated wastewater

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ARTICLE INFO

Keywords:
Fourth treatment step
Reactive oxygen species
Organic
Micropollutants
Non-thermal plasma
Ultrafiltration

ABSTRACT

Treatment with non-thermal plasma (NTP) is a promisingmethod to remove potentially harmful pharmaceuticals from wastewater treatment plant (WWTP) effluent. An application-oriented pilot-scale study was conducted to investigate the performance of an innovative process combining ultrafiltration (UF) and an NTP unit alternative to previously investigated thin-film designs. The studied NTP generator produces the plasma air separately and a specially designed turbine distributes the oxidizing species in the wastewater to be treated. The process was used for the treatment of effluents from a conventional activated sludge WWTP in Bad Reichenhall, Germany. Different set-ups in terms of hydraulic retention time and NTP composition (overall number of ions and ozone concentration) were tested to examine the removal efficiency of the target pharmaceuticals Diclofenac (DCF), Carbamazepine (CBM) and Sulfamethoxazole (SMX), as well as chemical and physical wastewater parameters. The reduction of DCF, CBM and SMX with optimal set-up was found to exceed 90% with initial concentrations in the WWTP effluent in the microgram per litre-range (0.80–15.15 $\mu g\,L^{-1}$). Traces of ozone in the range of 120/200 ppm within the NTP increased the overall performance of the process. Pre-treatment with UF removed fractions of pharmaceuticals and other oxidable substances, which led to a decrease in ozone demand and an enhancement of the overall removal efficiency of the process during varying influent loadings. Treatment via UF or NTP alone removed the pharmaceuticals by 46–67% and 54–71%, respectively, but did exceed the 90%-threshold. The studied NTP technology in combination with UF could be a viable as fourth treatment step, as it is highly energy-efficient, according to energy yield calculations, and larger amounts of wastewater can be treated.

1. Introduction

Anthropogenic micropollutants in natural water resources from human effluent have received increasing attention in both the public sphere and academia [1,2]. Pharmaceuticals represent a major part of these, which, after incomplete metabolisation of the human body, are usually transported to wastewater treatment plants (WWTP). There are seven main categories of organic micropollutants (OMPs): (i) anticonvulsants, (ii) antibiotics, (iii) anti-rheumatic agents, (iv) lipid lowering agents, (v) oestrogens, (vi) beta-blocker and (vii) diagnostics [3]. Many of these substances cannot be removed effectively with conventional activated sludge technology and are therefore still present in plant effluents [4,5].

Although most of these compounds only occur in a range between nano- and microgram per litre, they have caused adverse effects on the environment, and the possible consequences for humans being of constantly exposed to them through drinking water have provoked inconclusive discussions [6]. For instance, a recent study shows a list of pharmaceuticals which are potential risks to the aquatic environment, based on the predicted no-effect concentration (PNEC), and concludes that most substances in WWTP effluents in the UK exceed the respective estimated PNEC, which may serve as a guide to – so far absent in the UK

Abbreviations: AOP, advanced oxidation process; BOD, biochemical oxygen demand; CBM, Carbamazepine; CSTR, continuous stirred tank reactor; DCF, Diclofenac; COD, chemical oxygen demand; EEO, electrical energy per order; ELISA, enzyme-linked immunosorbent assays; GAC, granulated activated carbon; IC, inhibition concentration; LOQ, limit of quantification; MF, microfiltration; NF, nanofiltration; NPOC, non-purgeable organic carbon (also TOC – total organic carbon); NTP, non-thermal plasma; OMP, organic micropollutant; PAC, powdered activated carbon; PE, population equivalent; PNEC, predicted no-effect concentration; RO, reverse osmoses; SD, standard deviation; SMX, Sulfamethoxazole; UF, ultrafiltration; USEPA, United States Environmental Protection Agency; WWTP, wastewater treatment plant

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https://doi.org/10.1016/j.jece.2018.07.047
Received 29 May 2018; Received in revised form 2 July 2018; Accepted 27 July 2018
Available online 29 July 2018
2213-3437/

or EU – regulatory limits [7]. The overall load of these substances in the environment needs to be reduced either by lower consumption and/or prescription, or by a higher removal efficiency in WWTP. In the near term, the first option does not seem realistic as the consumption of medicine has been increasing for years [8]. The second possibility – increasing the removal efficiency in WWTP – could be more feasible and has already shown its first impact on governmental strategies: the number of recently implemented treatment systems for OMPs in WWTP effluent in Switzerland and some of Germany's federal states, e.g. North Rhine-Westphalia and Baden-Württemberg, has been considerably high [9].

As conventional WWTPs, including primary mechanical treatment and secondary activated sludge technology, retain only parts of the full spectrum of pharmaceuticals and other OMPs, a further treatment step after mechanical (primary), biological (secondary), and chemical or other advanced (tertiary) treatment – the so-called fourth treatment step – is necessary to achieve a removal of at least 70%, coming below the 0.1 $\mu g\,L^{-1}$ limit [10]. Membrane filtration (micro-, ultra- and nanofiltration, reverse osmosis), adsorption processes (activated carbon) and chemical oxidation (ozone, advanced oxidation) or combinations have been reported as fourth treatment process [11].

Oxidation technologies mainly use ozone (O_3) [12], which is injected into a reactor and degrades organic compounds directly or via generation of ·OH radicals. Advanced oxidation processes (AOP) rely on ozone, other oxidants (for instance hydrogen peroxide (H_2O_2) or UV light), or a combination of these, to generate hydroxyl and other radicals and boost the oxidation performance [13,14]. The main disadvantages of most AOP technologies are relatively high energy consumption, hazardous by-products, usage of oxidants and necessity of exhaust air ozone filters [15].

An alternative for radical generation in AOP is the utilisation of non-thermal plasma (NTP). Due to the non-selective oxidation of OMPs caused by formed oxygen ions, ozone and hydroxyl radicals from ambient air, the reaction mechanism is similar to the ozone and hydrogen peroxide reactions [16,17]. Several methods for the generation of these reactive species in the gas phase are known. Banaschik et al., Magureanu et al. and Aziz et al. recently summarised the degradation of pharmaceuticals and energy efficiency of NTP treatment compared to conventional AOP processes and, according to them, the main advantage is the reduced energy demand compared to ozone treatment [18–20]. For water treatment, the gas phase is often in contact with a thin layer of liquid, as described in Refs. [21–23], or a dielectric barrier discharge or corona discharge [24–27] is used.

The NTP technology used in this study is based on electrical glow discharge to form O_2^+, O_2^--clusters, O-radicals, OH-radicals and ozone [28]. In contrast to other NTP units (e.g. plasma gas in contact with a thin liquid film), the plasma is formed separately and brought into a water tank via a specially designed turbine. Hence, clogging is not an issue, as opposed to thin-film reactors, in which water passes fine perforations before entering the reactor [27]. Lee et al. used a similar method [29], but in the present study significantly higher gas flow rates and ion concentrations can be reached; thus, larger amounts of water can be treated. However, besides Gerrity et al. [26] and Ajo et al. [27], who both treated WWTP effluent in batch with a thin-film NTP unit, literature is lacking studies of NTP treatment at pilot-scale with real WWTP effluent, i.e. pharmaceutical levels in the low microgram per litre range [19].

The aim of the present study is the proof of principle and the parameter investigation of an innovative fourth treatment step of conventionally treated wastewater (after the final clarifier) in a continuous, application-oriented pilot-plant setup. It is noted that the effluent in this study met national and international regulatory standards, which do not encompass any of the studied pharmaceuticals so far; however, the PNEC for the substances given in Ref. [7] and other proposed limits [30,31] were frequently exceeded, hence a fourth treatment was required. The innovative NTP generation unit was coupled with UF to determine the influence on removal efficiency. Different set-ups were tested in order to investigate three main hypotheses: (I) moderate ozone concentrations within NTP act as enhancer for oxidation; (II) the proposed process set-up with retention times between 20 and 40 min is sufficient to remove Diclofenac (DCF), Carbamazepine (CBM) and Sulfamethoxazole (SMX) over 90%; and (III) hollow fibre UF for pre-treatment before NTP is suitable to increase the overall efficiency of the process. The continuous treatment of WWTP effluent and varying pharmaceutical concentrations made the data analysis challenging, but integrative loading calculations in $\mu g\,min^{-1}$ allowed for estimation of the removal efficiency and comparison of the applied methods.

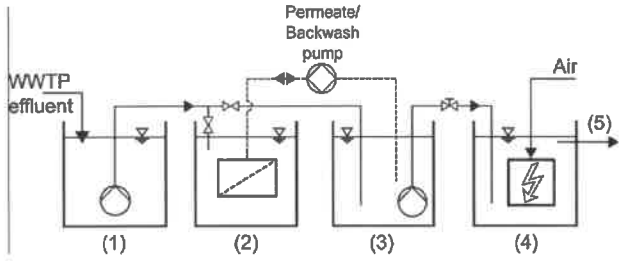

Fig. 1. Scheme of the used pilot plant in Bad Reichenhall, Germany; for detailed equipment list see Tables S1 and S2.

2. Materials and methods

2.1. Pilot plant set-up

The pilot plant with two independent treatment steps consisting of a submerged UF unit for pre-treatment and NTP as the main oxidation step was positioned at the outlet of the final clarifier of WWTP Bad Reichenhall (i.e. after tertiary-treated wastewater). A detailed flow scheme is shown in Fig. 1 and equipment specifications are given in Tables S1 and S2. WWTP effluent (1) between 10.3 and 20.5 $l\,min^{-1}$ was bypassed with a submerged pump into the filtration tank (2) equipped with the UF system (C-MEM, SFC Umwelttechnik GmbH, Austria). The UF system had an active filtration surface of 36 m^2 and was made of high density polyethylene hollow fibre membranes with an outer diameter of 0.4 mm and mean pore size distribution of 20 nm, operated in outside-in mode. The backwash tank (permeate tank) (3) was filled at a flux of 18.95 $L\,m^{-2}\,h^{-1}$ and a backwash ratio of 15%. Another submerged water pump installed in this tank (3) moved the water further to the downstream NTP tank (4). The desired flow rate was adjusted manually with a ball valve. The NTP tank with a net volume of 500 L and an operating volume of 410 L was equipped with an NTP unit (Fig. 2) and a submerged turbine (ionOXess GmbH, Austria) introducing plasma air at different flow rates and compositions. The NTP tank was operated as a continuously stirred tank reactor (CSTR) with bottom inlet and top outlet (5), which was returned to the WWTP feed. The used NTP unit operated at a fixed voltage of 16 kV and electrical pulses of 500 and 2000 Hz, respectively. In the present study, frequencies of 500 Hz at a current of 3 mA, and frequencies of 2000 Hz at a current of 6 mA were set. Hence, an electrical input power of 48 and 96 W was used for the plasma generation unit. Including the

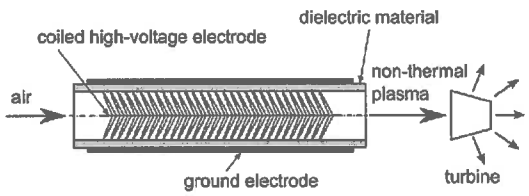

Fig. 2. Cross section of vertically aligned non-thermal plasma generation unit; turbine submerged at 1.7 m below water surface.

Table 1
Parameters of Pilot Testing Design.

Method	UF	Plasma air flow rate/L min^{-1}	Plasma frequency/ Hz	O_3 content in plasma air/ppm	Retention time/min	Plasma air to water volume ratio/(m^3 air/m^3 water)
1	yes	150	2000	120	20	7.3
					25	9.1
					30	11.0
					35	12.8
					40	14.6
2			500	20	20	7.3
					25	9.1
					30	11.0
					35	12.8
					40	14.6
3	no		2000	120	20	7.3
					30	11.0
					40	14.6
4			500	20	20	7.3
					30	11.0
					40	14.6
5	yes	70	2000	200	30	5.1
					40	6.8
6			500	50	40	6.8

electrical input of the submerged turbine system of 750 W, the overall power consumption was between 798 and 846 W.

2.2. Investigated process parameters

The selection and, where applicable, the range and/or exact values of the investigated process parameters, namely retention time, turbine frequency, NTP frequency and voltage, and UF-treated vs. non-UF-treated feed, was based on preliminary results [32]. Implications on the process and best operating conditions were subsequently derived from resulting pharmaceutical removal rates. All relevant design parameters are listed in Table 1.

2.2.1. Frequency of turbine and retention time of reactor: ratio of volume plasma air to WWTP effluent

The parameters retention time and turbine frequency influence the volumetric ratio of plasma air to WWTP effluent loaded with OMPs. While the air flow rate is influenced by the turbine frequency, the retention time is determined by the feed flow rate and the exchange rate of the reactor volume, correspondingly. The operating frequency of the frequency converter for the turbine was set to 25 Hz, which is equal to 660 rpm and an air flow rate of 150 L min^{-1}. To investigate the influence of plasma air to effluent volume ratio, the turbine frequency was reduced to 15 Hz (400 rpm, 70 L min^{-1}). According to preliminary tests retention times of 40 min achieved the best elimination results in a first-generation NTP unit [32]. As investment costs and space requirements for basin construction – decisively determined by the retention time – should be as low as possible in large scale plants, retention times between 20 and 40 min were selected, which allows for calculation of the plasma air to water volume ratio (Table 1).

2.2.2. Frequency and voltage of NTP unit: ozone level and ion number

Frequency and voltage of the NTP unit determine the number and proportion of the positively and negatively charged oxygen ions and of the ozone produced. In order to assess the influence of the ozone content on the elimination of pharmaceuticals, the two following adjustments were examined: one with a relatively high (120 or 200 ppm) and one with a relatively low ozone level (20 or 50 ppm) with plasma unit frequency settings of 2000 Hz, and 500 Hz, respectively, both at a voltage of 16 kV. The ozone level of the plasma air was measured with an ozone monitor (Model 106-M, ENVILYSE GmbH, Essen, Germany).

In terms of oxygen ions, the number of negative ions reaches a maximum value at 500 Hz (3.5 M ions cm^{-3} at 16 kV), whereas positive ions reach a maximum value at 2000 Hz (4.2 M ions cm^{-3} at 16 kV). The concentration of the ions in the plasma air was determined with an ion-counter (Ionometer IM806, Umweltanalytik Holbach GmbH, Wadern, Germany)

2.2.3. Pre-treatment of NTP feed with UF

Conventional final clarifiers do not provide a complete separation of particulate substances, causing residual particulate and oxidable substances to be present in the WWTP effluent and possibly impeding the performance of OMP elimination. Consequently, in order to remove particulate matter, experiments with a volume flow of 150 L min^{-1} were carried out twice – once with UF-treated feed and once without UF pre-treatment.

2.3. Analytics

The concentrations of the selected target pharmaceuticals (DCF, CBM, SMX) were measured before ((3) in Fig. 1) and after the NTP reactor ((5) in Fig. 1) via Indirect-Competitive Enzyme-Linked Immunosorbent Assays (ELISA) at the Technical University of Munich, according to [33] and [34] for CBM [35], for DCF and [36] for SMX. The advantage of this method is the absence of sample pre-treatment via solid-phase extraction, which would be required for most chromatographic procedures, and validation with LC/MS-MS revealed highly satisfactory measurement performance [34]. The target pharmaceuticals were selected based on anticipation of pharmaceutical occurrence due to hospital (SMX), retirement home (CBM), and rehabilitation centre (DCF) effluents in the sewage system. The selection is in accordance with target substance suggestions based on reviewed literature on OMP occurrence in WWTP effluent [37]. The intervals between the grab samples were 5–95 min before the NTP reactor and 5 min after the NTP reactor. The experiments were carried out on 7 days between July 29 2016 and August 8 2016, sparing out intermittent days with strong rainfalls and ensuring similar sewage flow data. The limits of quantification (LOQ) of each pharmaceutical are given in Table 2. In addition, other relevant wastewater parameters were tested. A summary of analytical methods is listed in Table 3.

The comparability of the different treatment methods was ensured by loading calculations with the assumption that the concentration of the pharmaceuticals was constant during each measurement interval. The pharmaceutical loading in µg min^{-1} was calculated as a product of the volumetric flow rate of the influent/effluent water in L min^{-1}, and the individual pharmaceutical concentration in µg L^{-1}. As, due to the application-oriented experimental design, the influent and effluent concentrations vary considerably, this integrative measure for the pharmaceutical loading in µg min^{-1} will provide a better comparability between the applied treatment methods than the pharmaceutical concentration alone. An example is given in Fig. 3, where the influent (solid) and effluent loading (dashed) for DCF at a hydraulic retention time of 20 min were determined. The removal was calculated from the average effluent and influent loading (dotted).

Table 2
Quantitative data of used ELISA method; LOQ...limit of quantification; IC... inhibition concentration (50% or 80% inhibition).

Substance	LOQ/µg L^{-1}	IC50/µg L^{-1}	IC80/µg L^{-1}
DCF	0.028 ± 0.004	0.10 ± 0.01	0.40 ± 0.09
SMX	0.49 ± 0.13	1.95 ± 0.45	7.81 ± 1.70
CBM	0.15 ± 0.02	0.61 ± 0.13	2.53 ± 0.85

Table 3
Used analytical methods for the determination of the selected parameters.

Device/Institution	Description	Parameter
Turbidimeter	Hach 2100P ISO Turbidimeter	Turbidity in NTU
Colorimeter	Hach DR/890 Colorimeter	Colour of filtrate in Co/Pt equivalent units
Multiparameter Meter	Hach Sension 156	Conductivity in $\mu S\,cm^{-1}$, pH value, temperature, O_2 in $mg\,L^{-1}$
Photospectrometer	Hach DR 3900	BOD_5, COD, TP, TN in mg/L^{-1}
Ozone monitor	Model 106-M; Germany	O_3 in ppm
TOC Analyzer	Shimadzu TOC-V series	TOC as NPOC in $mg\,L^{-1}$
Ioncounter	Ionometer IM806	Number of ions in Ions cm^{-3}
TU München	Indirect-competitive enzyme-linked immunosorbent assays (ELISA)	Diclofenac (DCF) in $\mu g\,L^{-1}$
TU München	ELISA	Carbamazepine (CBM) in $\mu g\,L^{-1}$
TU München	ELISA	Sulfamethoxazole (SMX) in $\mu g\,L^{-1}$

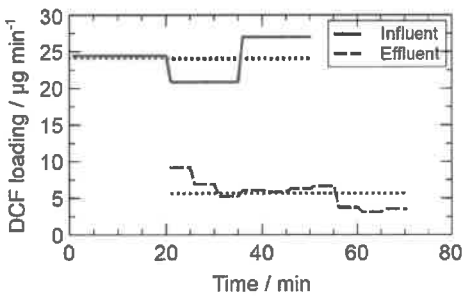

Fig. 3. Selected example (DCF, Method 1) for calculation of influent and effluent loadings at a retention time of 20 min; Dotted lines represent mean; Removal is 76%.

3. Results and discussion

A pilot-plant study was conducted at the WWTP Bad Reichenhall, Germany, to investigate if the process combination of UF and NTP is suitable to remove DCF, CBM, and SMX as target pharmaceuticals from the investigated wastewater.

3.1. Chemical and physical parameters of feed and treated water

Several chemical and physical parameters were tested so that the pharmaceutical removal, apart from different UF-NTP process parameters, can also be related to the overall pollution of the WWTP effluent (Tables 4 and 5). The WWTP Bad Reichenhall was operated at around 30,000 population equivalents (PE) at the time of carrying out the experiments, but was designed for 55,000 PE. As a result, the high sludge age and low hydraulic loading of the final clarifier led to relatively low effluent values in terms of carbon, nitrogen and phosphorous content. German national regulatory standards for WWTP effluent quality [38] as well as guidelines from the United States Environmental Protection Agency (USEPA) [39], which both do not encompass OMP limits, are met by the effluent. When membrane filtration is applied, particularly the colour and turbidity can be further reduced – up to 77 % and 96%, respectively. The phosphorus content was also reduced in membrane filtration experiments, which indicates that particulate phosphorous was retained by the UF membranes. The COD reduction is in a similar range – of 6–9 % – with or without membrane filtration, indicating a high soluble organic content and very little mineralization via NTP, which is consistent with reviewed literature [19]. Interestingly, BOD_5 values increase after treatment methods without membrane filtration by 27%. Possibly, parts of the remaining particulate COD were converted to biodegradable fractions through NTP, which has also been observed before [19]. Total nitrogen concentration varies and ranges from a slight increase of 4 % with membrane filtration to reduction of 11% without pre-filtration. This only minor increase and, most notably, the reduction without UF treatment preclude that nitrogen from ambient air used for NTP production is transferred into the water by generated NO_x compounds. Regardless of the used treatment method, there is also a slight increase of pH which is ascribed to the degradation of acidic organic compounds and the by-products of the reactive oxygen species after treatment.

3.2. Removal of pharmaceuticals (Testing of hypotheses I, II, and III)

The results from the different experiments were tested for three hypotheses, namely: (I) moderate ozone concentrations within NTP act as enhancer for oxidation; (II) the proposed process set-up with retention times between 20 and 40 min is sufficient to remove DCF, CBM and SMX over 90%; and (III) hollow fibre UF as pre-treatment before NTP is suitable to increase the overall efficiency of the process.

The concentration in the WWTP effluent (measured at (3), Fig. 1, when no UF was used) ranged from 0.80 to 4.07 $\mu g\,L^{-1}$ for DCF, from 0.97 to 2.71 $\mu g\,L^{-1}$ for CBM, and from 2.45 to 15.15 $\mu g\,L^{-1}$ for SMX, respectively. These levels partially exceed PNEC estimated by Comber et al. [7] (DCF: 0.05 $\mu g\,L^{-1}$, CBM: 2.5 $\mu g\,L^{-1}$) and proposed guidelines for Switzerland [30,31] (DCF: 0.05 $\mu g\,L^{-1}$, CBM: 2.5 $\mu g\,L^{-1}$, SMX:

Table 4
Chemical and physical parameters after WWTP (influent, (3) in Fig. 1) and after treatment process (effluent, (5) in Fig. 1) for methods with UF and NTP treatment (methods 1, 2, 5 and 6).

Parameter	Unit	Influent (n = 13)		Effluent (n = 26)		Removal (positive indicates decrease, negative indicates increase)
		mean	SD	mean	SD	
Temperature	°C	22.4	0.6	25.7	1.0	
Conductivity	$\mu S\,cm^{-1}$	1,014	117.0	1,050	207.3	−4 %
COD	$mg\,L^{-1}$	10.5	0.8	9.6	1.0	9 %
NPOC	$mg\,L^{-1}$	6.3	0.9	6.1	0.4	3 %
BOD_5	$mg\,L^{-1}$	0.8	0.2	0.6	0.2	25 %
total Nitrogen	$mg\,L^{-1}$	5.3	0.7	5.5	0.9	−4 %
total Phosphorus	$mg\,L^{-1}$	0.7	0.0	0.6	0.0	14 %
pH	pH	6.9	0.0	7.8	0.1	
Turbidity	NTU	1.3	0.2	0.3	0.4	77 %
Colour	Pt/Co	31.3	6.6	1.1	1.1	96 %

Table 5
Chemical and physical parameters after WWTP (influent, (3) in Fig. 1) and after treatment process (effluent, (5) in Fig. 1) for methods with NTP and without UF treatment (methods 3 and 4).

Parameter	Unit	Influent (n = 6)		Effluent (n = 12)		Removal (positive indicates decrease, negative indicates increase)
		mean	SD	mean	SD	
Temperature	°C	22.3	0.9	25.5	0.9	
Conductivity	$\mu S\,cm^{-1}$	1617	42.2	1,609	46.4	1 %
COD	$mg\,L^{-1}$	13.4	1.2	12.6	1.2	6 %
NPOC	$mg\,L^{-1}$	8.2	0.5			
BOD_5	$mg\,L^{-1}$	1.1	0.1	1.4	0.6	−27 %
total Nitrogen	$mg\,L^{-1}$	8.5	0.3	7.6	3.2	11 %
total Phosphorus	$mg\,L^{-1}$	0.6	0.1	0.6	0.1	0 %
pH	pH	6.9	0.1	7.8	0.1	
Turbidity	NTU	1.1	0.3	1.0	0.1	9 %
Colour	Pt/Co	40.2	17.5	21.8	11.1	46 %

$0.6\,\mu g\,L^{-1}$), and hence the necessity for a fourth treatment step is assumed. The considerable amounts measured in the WWTP effluent most likely originate from the hospital, the rehabilitation centre, and the retirement home in Bad Reichenhall, which are connected to the WWTP's sewer. The pharmaceutical loadings for each compound in the influent to the pilot plant were calculated with the volumetric flow rate as shown in Fig. 3.

As implied in hypothesis II, the hydraulic retention time in the NTP unit theoretically influences the removal of pharmaceuticals. With an increase in hydraulic retention time, higher degradation rates would be expected at constant concentration of the pharmaceuticals and other oxidable substances due to pseudo first-order degradation with the NTP [26]. However, removal rates calculated from the pharmaceutical loading for only the NTP unit in Figs. 4 and 6 indicate no clear trend for removal with higher retention times. It is noted that in the present study the influent concentration varied considerably, as the experiments were performed in an application-oriented setup with continuous WWTP effluent treatment at different times of the day. This seems reasonable, as a peak in pharmaceuticals intake and toilet flushing takes place in the morning hours of each day. Thus, loading calculations provided for a better estimate of the individual method efficiency, although normalization to the retention time only allowed for comparison of the method efficiencies, and no influence of the retention time was observed. Consequently, in order to compare the efficiency of the NTP unit for each method, the removal rates for only the NTP step averaged over all retention times are tabulated in Table 6.

The comparison between method pairs 1&2, 3&4, and 5&6 indicates that best removal rates were achieved by using plasma air with moderate O_3-concentrations of 120/200 ppm (methods 1, 3, 5) compared to plasma treatment with lower O_3-concentrations of 20/50 ppm (methods 2, 4, 6). These findings confirm the assumption that adjusting the NTP unit towards moderate ozone production is favourable for OMP removal, because ozone acts as promoter for the oxidation process as stated in hypothesis I. The simultaneous formation of peroxides and ozone is assumed to react to form hydroxyl radicals with a higher oxidation strength compared to pure ozone. However, the exact reaction and degradation mechanisms remain unclear. The similar removal ranges for the pharmaceuticals in each method (61–75% for M1, 24–44% for M2, ...) confirm that NTP is a non-selective treatment method, as opposed to, for instance, activated carbon adsorption [40].

For estimation of the overall process efficiency of the UF-NTP combination, the average WWTP effluent loading was calculated from the loadings in (3), Fig. 1, when no UF pre-treatment was applied, i.e. method 3 and 4 (on average $44.82\,\mu g\,min^{-1}$ for DCF, $33.73\,\mu g\,min^{-1}$ for CBM, $182.29\,\mu g\,min^{-1}$ for SMX). These two methods were sampled on two different experiment days (August 2 2016 and August 3 2016) and the deviation from the mean loading was less than 15%. Although the actual WWTP effluent loading might have deviated during the remaining experiment days, this is the best estimate for the mean WWTP effluent loading, as in the experimental design it was not sampled for

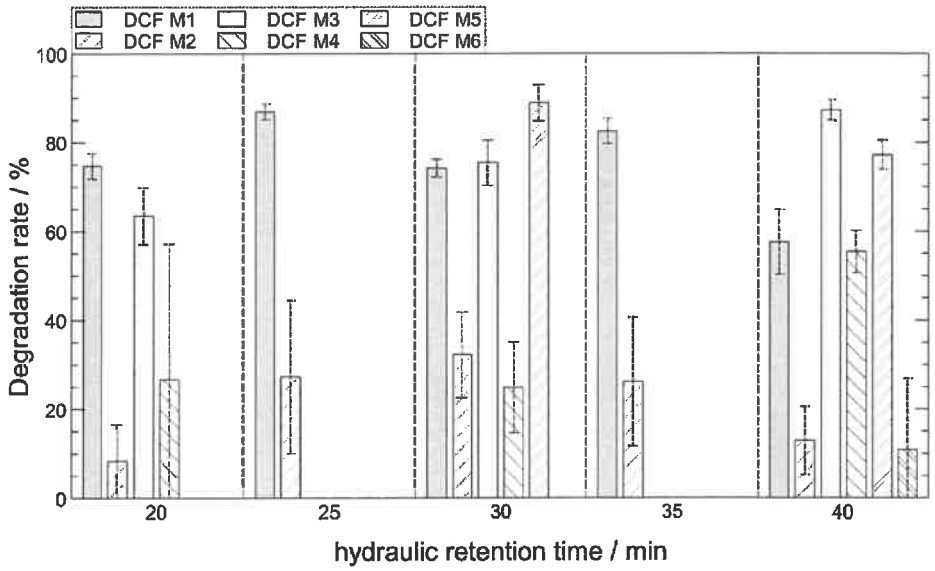

Fig. 4. Rate of degradation of Diclofenac in NTP unit under various conditions (Method 1–6); error bars represents variation over the sampling time (compare Fig. 3).

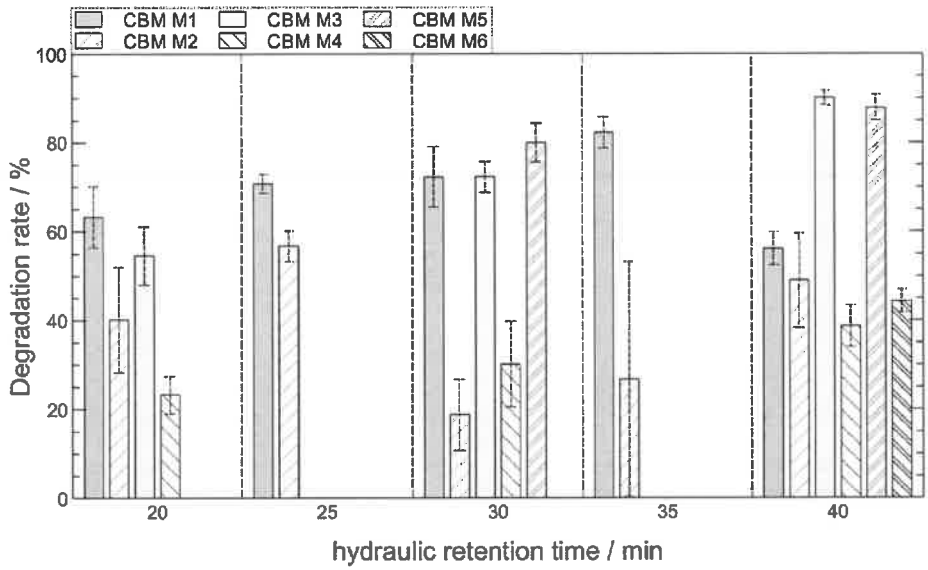

Fig. 5. Rate of degradation of Carbamazepine in NTP unit under various conditions (Method 1–6).

the remaining methods 1, 2, 5 and 6. Subsequently, from the mean influent loading for the latter methods, the removal efficiency of only the UF treatment can be assessed (on average 57% removal for DCF, 46% for CBM, and 67% for SMX, respectively, see Fig. 7). Albeit comparison to OMP removal by UF in other studies [27] indicates that these assumptions may overestimate the UF removal efficiency, in this study the large reduction of physiochemical parameters (Tables 4 and 5) also implies that UF does remove a significant fraction of, particularly suspended, organics in the WWTP effluent. Hence, the removed fraction may be ascribed to pharmaceuticals adsorbed on sludge and other particles during UF. CBM removal via UF is the lowest of the tested compounds in this study, which is consistent with observations that CBM is eliminated rather poorly via conventional wastewater treatment due to insufficient attachment onto sludge [41].

Returning to the overall process efficiency shown in Fig. 7, the loading for the combination of UF and NTP is given in the effluent of method 1, 2, 5, and 6. Here, pharmaceuticals bound in sludge particles were removed by UF, the loading of other oxidable substances was also reduced by UF, and NTP degraded remaining dissolved pharmaceuticals not removed by UF, leading to the lowest achievable loading in the given process setup. The highest possible overall removal via the UF/NTP combination was achieved with method 5, i.e. 95% for DCF, 94% for CBM, and 90% for SMX, respectively, if constant WWTP effluent loading is assumed as described above. Method 1 represented the next best removal with 92%, 83%, and 85% for DCF, CBM, and SMX, respectively. This enhanced behaviour shown by method 5 can be explained, on the one hand, by a reduced plasma air to water volume ratio (Table 1) which leads to an assumed finer air bubble distribution in the reactor. This enhanced the reactive surface in the NTP unit and also the contact time between plasma air bubbles and water. On the other hand, the highest ozone concentration in method 5 (200 ppm), compared to the remaining methods, is also assumed to have increased the degradation. The pharmaceutical degradation with only NTP ranged from 54% to 71% for method 3 (see also Table 6). The sum of these findings confirms both hypotheses 2 and 3. The process combination of UF and NTP is sufficient to remove the tested pharmaceuticals over 90%,

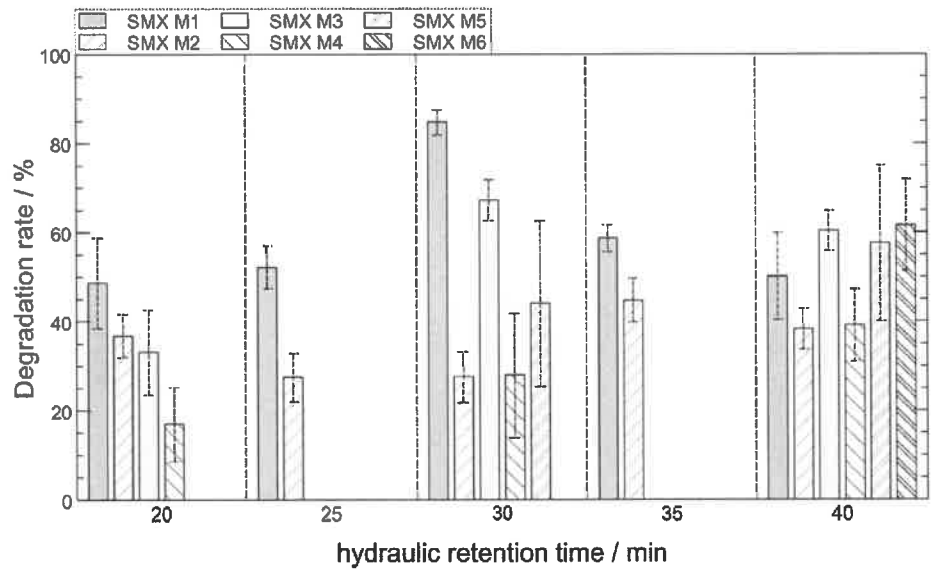

Fig. 6. Rate of degradation of Sulfamethoxazole in NTP unit under various conditions (Method 1–6).

Table 6
Wastewater loading of selected drugs before ((3) in Fig. 1) and after NTP treatment ((5) in Fig. 1); mean values over all retention times for each applied method; Ozone to NPOC ratio.

Method	Compound	Mean before NTP/μg min^{-1}	Mean after NTP/μg min^{-1}	Mean removal by NTP/ %	Ozone to NPOC ratio/ (g O_3/ g NPOC)
1 (UF)	DCF	14.90	3.69	75	0.25–0.65
	CBM	18.85	5.81	69	
	SMX	71.39	27.95	61	
2 (UF)	DCF	31.92	24.30	24	0.04–0.07
	CBM	24.29	13.81	43	
	SMX	95.25	63.74	33	
3 (no UF)	DCF	49.76	14.24	71	0.21–0.49
	CBM	36.07	11.84	67	
	SMX	182.99	82.87	54	
4 (no UF)	DCF	39.87	26.26	34	0.04–0.07
	CBM	31.39	22.26	29	
	SMX	181.59	136.38	25	
5 (UF)	DCF	16.13	2.27	86	0.33–0.44
	CBM	13.00	2.10	84	
	SMX	35.89	17.68	51	
6 (UF)	DCF	14.45	12.88	11	0.11
	CBM	16.71	9.31	44	
	SMX	39.26	15.06	62	

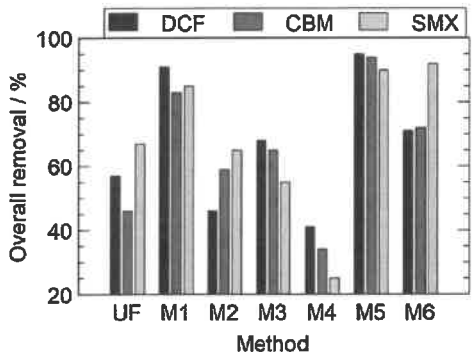

Fig. 7. Overall removal efficiency of different treatment methods assuming constant influent loading; M1, M2, M5, M6 with UF pre-treatment; M3, M4 without UF pre-treatment; for method details see Table 1.

although, due to considerable WWTP effluent loading variation, removal values are to be taken as estimates of the overall process efficiency. Filtration with UF prior to NTP treatment is suitable to increase the overall efficiency of the process, as oxidable substances and adsorbed pharmaceuticals are removed with UF, leading to better efficiency of the subsequent NTP step.

3.3. Ozone to NPOC ratio

In order to relate the studied technology to other AOPs, the results are compared to a previous study by Schaar and Kreuzinger [42], who investigated the influence of the O_3 to NPOC ratio as well as the reaction time on the removal of pharmaceuticals from municipal wastewater via conventional O_3 treatment without UF pre-treatment. According to them, when using pure O_3, a minimum ratio of 0.4 g O_3 per g NPOC should be applied to reduce ozone-affine compounds such as DCF and CBM. However, a ratio of 0.7 is recommended to also degrade only moderately ozone-affine compounds by 60% and more. For more stable compounds such as Benzotriazole, a minimum ratio of 0.9 is necessary. Moreover, a reaction time of 10 min is (usually) enough for sufficient degradation [42].

In the present study, the use of UF in combination with NTP resulted in O_3 to NPOC ratios between 0.03 and 0.65, depending on the method and the retention times (see Table 6). Methods with low O_3-concentrations (2, 4, and 6) represented the lowest ratios, but also the lowest removal. This once more supports hypothesis I, as the combination of O_3 with oxygen-ions produced in the NTP unit acts as an enhancer for the degradation. Comparing method 1 and 3 indicates that the NPOC level was reduced by UF, leading to higher a higher O_3 to NPOC ratio, which, in turn, leads to an enhanced degradation rate, supporting hypothesis III. Method 5 achieved an overall pharmaceutical removal (Fig. 7) over 90% with relatively low O_3 to NPOC ratios (0.33–0.44). However, as no clear trend for the removal with higher retention time was observed (Figs. 4–6), no suggestion for a specific retention time in the NTP reactor can be derived from the results.

3.4. Energy consumption

According to Magureanu et al. [19], the energy yield for each compound based on the plasma generation energy consumption was calculated by the following equation:

$$Y = \frac{c_0 \cdot V \cdot R}{P \cdot t} \cdot \frac{1}{100}$$

where Y is the energy yield (in mg/kWh), c_0 is the initial concentration (in mg/L), V is the solution volume (in L), R is the removal rate through the NTP unit (in %), P is the discharge power of the plasma unit (in kWh) and t is the treatment time (in h). Compared to the review by Magureanu et al. [19], who calculated the energy yield from previous studies [21,22,24], an enhanced energy yield for CBM of 81.4 to 470 mg/kWh compared to 18.5 to 44.4 was determined, whereas for DCF the yield is in the same range or lower (see Table 7).

The values for the electrical energy per order (EEO) of magnitude degradation were calculated as described by Gerrity et al. [26], who based their work on a first order degradation [43]. They reported that in the described single-pass experiment on tertiary-treated wastewater, which is comparable to the present methods, the median EEO value of CBM is 1.8 kW h/m^3, whereas in the present study the values, depending on the utilised method, range from 0.081 to 0.74 kW h/m^3 (see Table 8). These comparisons indicate that the studied process is highly energy-efficient. However, it is noted that both the energy yield and the EEO calculations in this and other studies were based on only the NTP generation. For a holistic evaluation, the skid energy (e.g. 3 kW in Ref. [26], 750 W turbine power in this study) should also be included.

4. Conclusion

The successful application-oriented pilot-scale study clearly indicates that the combination of an innovative non-thermal plasma technology with membrane processes leads to a significant reduction of measured pharmaceuticals in a conventionally treated WWTP effluent. The studied NTP generator could be a viable alternative to other (e.g. thin-film) designs, as it produces the plasma air separately and a specially designed turbine distributes the oxidizing species in the wastewater to be treated. A lack of studies treating WWTP effluent with pharmaceuticals at ambient concentrations via NTP in continuous pilot-scale setup also motivated the present work. NTP Pharmaceutical loading calculations allowed for evaluation of the removal efficiency, even though the influent and effluent concentrations varied

Table 7
Comparison of the energy yields of CBM and DCF.

Pharmaceutical Compound	Energy yield / mg/kWh (data from Ref. [19])	Energy yields/mg/kWh (present study)
CBM	18.5 [21], 44.4 [22]	81.4–469.7
DCF	760 [24]	20–715
SMX	N/A	134–1720

Table 8
Mean NTP-specific EEO values in kWh/m³-log.

Pharmaceutical Compound	EEO According to Ref. [26]	M1	M2	M3	M4	M5	M6
CBM	1.8	0.29	0.38	0.081	0.74	0.17	0.31
DCF	N/A	0.29	0.67	0.089	0.51	0.20	1.55
SMX	N/A	0.35	0.36	0.17	0.73	0.43	0.19

considerably throughout the experiments. The treated effluent met national and international regulatory standards, which do not encompass any of the studied pharmaceuticals so far, but predicted no-effect concentrations for the substances proposed limits were partially exceeded. The proposed treatment combination of UF and NTP showed over 90% removal for DCF, CBM and SMX with retention times of between 20 and 40 min by in WWTP effluent (hypothesis II), whilst increasing biodegradability of the treated wastewater. Moderate ozone concentrations of up to 200 ppm generated within the NTP unit increased the performance significantly by acting as an enhancer for oxidation process (hypothesis I). Pre-filtration with UF increased the overall removal efficiency of the process by eliminating pharmaceuticals attached onto sludge particles and other oxidable substances and lowered the demand of ozone as enhancer; also, UF improved the chemical and physical effluent quality (hypothesis III). As a remarkably smaller amount of ozone was injected than in conventional ozone treatment facilities, it is assumed that exhaust air treatment is not necessary. Further research in terms of stability of the process, investigation of degradability of other pharmaceuticals, the degradation mechanism, and the number of hazardous by-products are ongoing. In addition, compared to conventional methods like ozone and comparable pilot-scale NTP degradation, the present study indicates a very low energy consumption at comparable or higher degradation rates, while larger amounts of wastewater can be treated. After careful review and analysis of the data collected from this study, the authors conclude that this innovative treatment method could be a feasible technology for removal of pharmaceuticals from WWTP and other industrial wastewater effluents.

Declaration of conflicts of interest

Hereby we declare no conflicts of interest.

Acknowledgments

The authors thank the Technical University of Munich for ELISA-testing, the wastewater treatment plant Bad Reichenhall for pilot testing and assistance, the funding agency ITG Salzburg for assistance during the funding application, and the Government of Tirol (Project number WA-540-02-00312/01-0021) and Salzburg (20102-P1600928-KOP01-2016) for funding.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jece.2018.07.047.

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