TREATMENT OF EMERGING CONTAMINANTS FOR NON-POTABLE WASTEWATER REUSE – AN EVALUATION OF A NOVEL COMBINATION OF MEMBRANE ULTRAFILTRATION AND A NON-THERMAL PLASMA BASED OXIDATION PROCESS

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Abstract

Currently, water scarcity is a worldwide problem with growing severity. Wastewater reuse has been promoted to overcome potential water limitations for non-potable applications - a strategy that needs to be backed with a WWTP treatment upgrade to improve effluent quality for reuse, especially for the removal of emerging contaminants. This communication presents the results of a pilot study performed at a municipal WWTP for the treatment of pharmaceutical present in the final effluent, performed with an advanced oxidation process by non-thermal plasma (NTP) - an emerging technology in the field of water treatment, also applied in combination with membrane ultrafiltration. This NTP has potential to form a wide spectrum of physical and chemical phenomena that, without the usage of chemical reagents, allows for a more diversified and effective action on the various contaminants to be treated. Initial results here presented demonstrate the potential of this NTP technology for the pharmaceutical removal in wastewaters. UF pre-treatment is advantageous for the reduction of organic matter and solids prior to the NTP, and also contributes to the pharmaceutical removal.

Keywords

Advanced oxidation; emerging contaminants; membrane technology; non-thermal plasma; pharmaceuticals; ultrafiltration; wastewater reuse; wastewater treatment;

Introduction

The growing presence of emerging pollutants in surface waters poses a new threat to water quality worldwide, due to the adverse or persistent effects they can have on human health and ecosystems. The European network for monitoring NORMAN emerging pollutants already has more than 700 emerging substances registered as being present in the European aquatic environment (Geissen *et al.* 2015). Pharmaceuticals have stood out in the last decade as one of the most widespread classes of contaminants in surface waters worldwide, with more than 203 pharmaceuticals being detected in surface waters among 41 countries, which demonstrates the extent and transversality of this environmental problem (Hughes *at al.*, 2012). Conventional Wastewater Treatment Plants (WWTP) are not equipped to efficiently eradicate these micro-pollutants and can therefore be a source of surface water pollution with these emerging pollutants.

Currently, there is no European legislation applicable to the discharge of these emerging pollutants into waterways, however a European Watchlist was instituted in 2015 for monitoring in surface water that includes substances, or groups, for which water monitoring data are being collected, and will serve as a basis for risk assessments to support the definition of future legislation on these substances (EC, 2015). It is therefore expected that these substances will be included in future legislation and their monitoring will be mandatory. The Swiss Confederation has already imposed in its Water Protection Act a removal efficiency target for WWTP of 80% of a group of 12 selected emerging pollutants, including carbamazepine, diclofenac, venlafaxine, citalopram, and clarithromycin (Swiss Confederation, 2021).

Recently, there has been a major focus on the research of advanced oxidation processes (AOP), as an additional treatment of wastewater treated in conventional WWTP to remove emerging pollutants such as pharmaceuticals (Poyatos *et al.* 2010). The AOP produce highly reactive oxidizing species that attack and degrade organic pollutants, even the most recalcitrant ones that have low biodegradability. Among these processes, the application of atmospheric non-thermal plasma (NTP) has gained visibility due to its potential to form a broad spectrum of oxidizing species physical and chemical phenomena: formation of oxidizing species, such as radicals ($H^\bullet$; $O^\bullet$; $OH^\bullet$) and others oxidizing species (H_2O_2, O_3, etc.), shock waves, ultraviolet radiation and electro-hydraulic cavitation, all without the use of chemical reagents (Hijosa-Valsero *et al*. 2014; Jiang *et al.* 2014). This NTP mechanism allows for a more diversified and effective action on the various organic pollutants to be treated (Vanraes *et al.* 2016). Despite these advantages, the applications of this technology in a real environment context for water treatment are still very limited, although it has been shown to have great potential for the treatment of emerging pollutants in WWTPs in a competitive way (Magureanu *et al.* 2015). The combination of AOP with membrane separation has also been shown to be advantageous for the removal of emerging pollutants (Liu *et al.*, 2014; Back *et al*., 2018).

In this work, the potential application of a non-thermal atmospheric plasma oxidation-based process was investigated as a tertiary treatment in the treatment of pharmaceutical compounds present in treated wastewaters, and also in combination with pre-treatment stage using membrane ultrafiltration.

Materials and methods

This study was carried out in a municipal WWTP dimensioned for a population of 300,000 inhabitants, with an average effluent treatment flow of ca. 70,000 m^3/day. The WWTP has a sewage treatment process with the following stages: preliminary treatment by sieving, primary settling with sand and grease removal and secondary treatment with activated sludge followed by secondary settling.

The NTP tank with an operating volume of 6 m^3 was equipped with an NTP unit and a submerged turbine (ionOXess GmbH, Austria) introducing plasma air. The NTP tank was operated in batch, and an electrical input power of 90W was used for the plasma generation unit.

The submerged ultrafiltration unit was equipped with two UF modules (C-MEM, SFC Umwelttechnik GmbH, Austria). The UF system had an active filtration surface of 768 m^2 and was made of high-density polyethylene hollow fibre membranes with an outer diameter of 0.4mm and mean pore size distribution of 20 nm, operated in outside-in mode. The average permeate flux was 6 m^3/h.

The WWTP effluent used in the tests was collected after secondary settling, in the effluent discharge point. Grab samples were collected from WWTP effluent and from the outlet of the technologies tested. Chemical and physical analytical analysis of the inlet and treated effluent samples were performed by a certified laboratory using the Standard Methods' methodologies. Pharmaceutical compounds were analysed by chromatographic analysis were performed on a Shimadzu Nexera UHPLC system (Shimadzu Corporation, Kyoto, Japan) equipped with two solvent delivery pumps (LC-30 AD), a column oven (CTO-20 AC), an auto-sampler (SIL-30 AC), a degasser (DGU-20A 5R), and a system controller module (CBM-20A) coupled to a triple-quadrupole mass spectrometer (Ultra-Fast Mass Spectrometry series LCMS-8030, Shimadzu Corporation, Kyoto, Japan) operated in the electrospray ionization (ESI) mode. Lab Solutions software (Shimadzu Corporation, Kyoto, Japan) was used for control and data processing. Pharmaceuticals were analysed by UHPLC-MS/MS as described by Paíga *et al. (*2019*)*.

Results

The pilot study was conducted at a municipal WWTP to investigate the potential of the non-thermal atmospheric plasma oxidation-based technology for the removal of pharmaceuticals from treated wastewaters. Two tests were performed in batch with the NTP pilot unit: Test 1) test with effluent from the WWTP; Test 2) test with WWTP effluent pre-treated with UF (UF permeate was treated in the NTP).

Chemical and physical characterization of feed and treated effluents

The WWTP where the study was carried out was operating in normal conditions and complied with the local environmental regulations. The chemical and physical characterization of the effluent was evaluated before and after the tests were carried out, and the results are shown in Tables 1 and 2, for Tests 1 and 2 respectively.

During the NTP an increase in the pH was observed, which could be due to the degradation of organic acids or oxidation by-products formed during treatment *(*Back *et al.*, 2018*)*. A pronounced reduction of the BOD_5 and COD was achieved with the UF pre-treatment, with 91,6% and 46,9% removal respectively. With the NTP there was a slight reduction in the Total Organic Carbon (TOC) in both tests, which indicates a modest mineralization of the organic content in the effluent. In Test 2 an increase in CBO_5 was observed, which could suggest that more biodegradable fractions of the organic matter were formed during the NTP treatment. The absorbance at 254 nm is also considered an indirect indicator of the organic matter oxidation, and a reduction of about 10% was achieved during the NTP treatment in both tests, and also 32,2% removal with the UF pre-treatment *(*Wert *et al.* 2008*)*. Additionally, in the conditions tested, the UF pre-treatment also contributed to a 4-log reduction in *E. coli* in the treated effluent. Comparing both tests is clear that the UF pre-treatment could present an advantage in the reduction of the organic matter and solids prior to the NTP treatment.

Table 1: Chemical and physical characterization – Test 1: NTP

Parameter	WWTP Effluent	NTP - 21h	Removal NTP - 21h (%)
pH	7,26	8,91	---
BOD_5 (mgO_2/L)	21,2	21,1	0,47
COD (mgO_2/L)	36,8	<35	ND
TOC (mg/L)	20,2	17,6	12,9
TSS (mg/L)	16	18	-12,5
Absorbance @ 254nm	0,253	0,227	10,3

Table 2: Chemical and physical characterization – Test 2: UF+NTP

Parameter	WWTP Effluent	UF Permeate	NTP - 21h	Removal UF (%)	Removal NTP - 21h (%)
pH	7,34	7,46	8,53	---	---
BOD_5 (mgO_2/L)	49	4,1	14,6	91,6	-250
COD (mgO_2/L)	64	34	32	46,9	5,9
TOC (mg/L)	---	15,1	14,6	---	3,3
TSS (mg/L)	29,5	16,5	<5	44,1	>70
Absorbance @ 254nm	0,319	0,215	0,194	32,8	9,8

Removal of pharmaceuticals during NTP treatment

The UHPLC-MS/MS analysis was used to search over 30 pharmaceuticals and conjugates/metabolites in the effluent samples. Analysis performed to the WWTP inlet raw sewage and outlet effluent, showed that the overall pharmaceutical removal in the conventional WWTP treatment was on average above 95%. Still, the concentrations of some pharmaceuticals in the WWTP effluent were still significant, with detection of 20 substances with concentrations above 100 ng/L, and some maximum values exceeding 1000 ng/L *(*Figure 1*)*. Also, the removal of harder to degrade compounds included in the EU Watchlist and Swiss regulations, were much lower than the overall removal, with individual removal efficiencies lower than 30% for diclofenac, venlafaxine, carbamazepine and citalopram. Thus, further treatment for pharmaceuticals removal is advised.

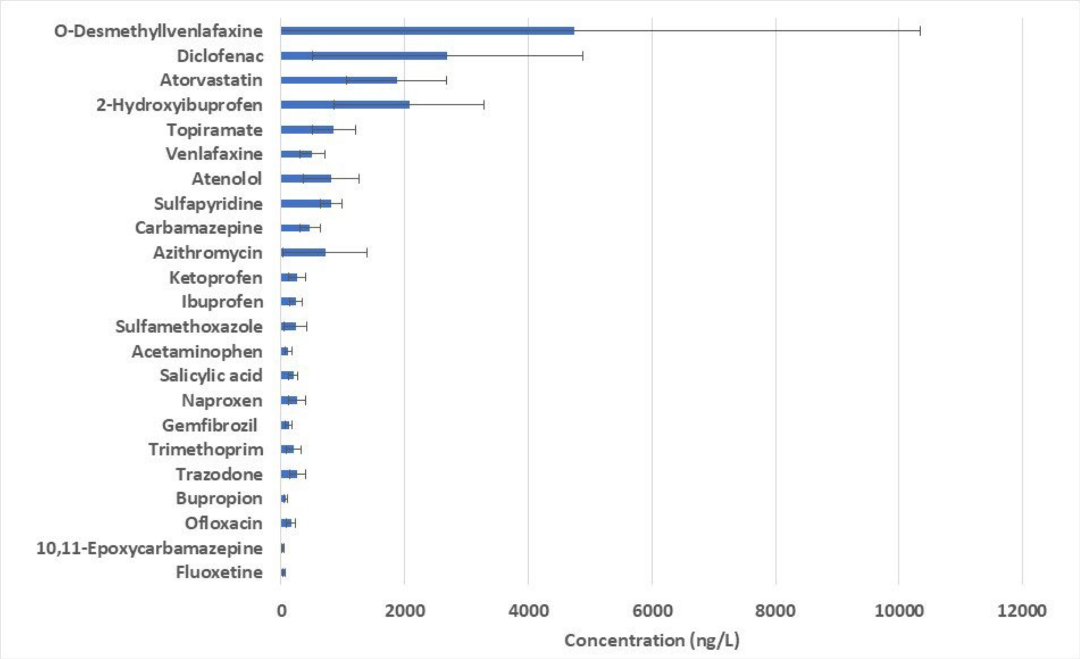

Figure 1: Average concentrations of pharmaceuticals in the WWTP effluent after secondary settling (n=7 and error bars with standard deviation).

The results for the pharmaceutical removal in both Tests, for a total of 23 substances, are presented in Table 3. During the NTP batch tests, samples were collected after 2, 6 and 21h of treatment.

A wide range of removal efficiencies (RE) was recorded for the detected pharmaceuticals during the NTP treatment in both tests, demonstrating that different pharmaceuticals may respond differently to NTP treatment.

For Test 1, with NTP only, the highest RE values, considered here as greater than 90% after 6h, were obtained for the following pharmaceuticals: O-desmethylvenlafaxine, atorvastatin, venlafazine, trimethoprim, trazodone, bupropriom, azithromycin, ofloxacin and fluoxetine. The lowest RE values, considered to be less than 25% after 6h, were obtained for the following pharmaceuticals: diclofenac, 2-Hydroxyibuprofen, topiramate, carbamazepine, ketoprofen, ibuprofen, sulfamethoxazole, salicylic acid, naproxen and 10,11-Epoxy carbamazepine. This last group includes pharmaceuticals that have practically not been removed. After 21 h, there was a considerable increase in RE for some pharmaceuticals included in this last group, such as diclofenac, atenolol and sulfapyridine.

For Test 2, with UF pre-treatment and PNT, it was observed that the UF had a contribution in the removal of some pharmaceuticals, especially in the removal over 90% of citalopram, trazadone, ciprofloxacin, trimethoprim and fluoxetine, removing overall abort 30% of the total pharmaceuticals. Comparing the results of the NTP treatment in the two Tests, with and without pre-treatment, it can be observed that after 21h of treatment the RE achieved were similar for most pharmaceuticals, with a few exceptions. A higher RE was recorded in the PNT test with UF pre-treatment for 2-Hydroxyibuprofen, carbamazepine, sulfamethoxazole, naproxen. It should be noted that carbamazepine and sulfamethoxazole are two of the most complex pharmaceuticals, so the UF pre-treatment may be advantageous in the NTP treatment.

Table 3: **Pharmaceutical removal results in the tests performed**

Pharmaceutical	TEST 1: NTP				TEST 2: UF + NTP				
	WWTP Effluent (ng/L)	RE 2h (%)	RE 6h (%)	RE 21h (%)	WWTP Effluent (ng/L)	RE UF (%)	RE 2h (%)	RE 6h (%)	RE 21h (%)
O-Desmethylvenlafaxine	15697,3	69,6	99,6	100	10951,4	40,3	-0,2	81,0	100
Diclofenac	4502,3	-19,2	4,3	87,5	6293,5	8,4	-3,0	15,5	89,7
Atorvastatin	1994,4	100	100	100	3238,9	29,1	100	100	100
2-Hydroxyibuprofen	1867,5	5,1	20,0	26,6	2695,2	31,7	7,0	15,6	46,5
Topiramate	1271,4	-5,2	-2,7	-4,5	1399,6	7,1	-1,4	5,2	10,0
Sulfapyridine	634,8	41,7	41,9	81,7	980,9	33,6	30,7	57,6	74,5
Venlafaxine	864,8	70,9	100	100	692,5	60,4	-30,0	78,6	100
Carbamazepine	566,7	5,9	8,1	30,9	587,9	-2,6	2,1	1,5	58,6
Trazodone	85,8	100	99,0	99	496,2	100	---	---	---
Sulfamethoxazole	340,6	24,8	20,8	39,1	484,9	46,9	29,9	68,7	67,8
Ketoprofen	428,6	-1,2	-13,5	28,1	470,4	7,2	-10,7	-16,0	10,5
Azithromycin	72,3	100	92,0	92	400,6	100	---	---	---
Ibuprofen	384,1	5,1	13,9	13,2	362,3	-7,8	1,5	10,1	16,1
Atenolol	636,6	29,4	42,7	99,6	264,2	12,6	-4,9	7,7	100
Ciprofloxacin	ND	ND	ND	ND	235,8	100	---	---	---
Citalopram	ND	ND	ND	ND	223,0	100	---	---	---
Naproxen	159,6	-11,1	-1,5	31,3	213,7	17,8	-5,4	-5,7	58,3
Trimethoprim	86,5	97,9	97,9	100	191,2	99,1	100	100	100
Salicylic acid	177,2	-2,6	-5,2	-9,9	170,4	2,6	-1,7	-3,2	22,6
Gemfibrozil	119,4	14,6	32,1	31,4	132,0	4,2	10,9	16,0	34,1
Acetaminophen	214,7	2,9	30,4	32,4	99,4	2,0	-8,3	15,5	29,7
Bupropion	84,9	99,3	99,3	99,3	97,7	67,5	-5,0	73,9	64,2
Fluoxetine	22,2	98,7	98,7	98,7	55,1	99,5	100	100	100

RE – Removal Efficiency; ND – Not Detected

The majority of NTP published papers on pharmaceuticals removal are studies performed at laboratory scale, with synthetic or spiked waters, which are conducted under very controlled conditions and thus promote higher oxidation rates of the few selected compounds. There are also very different reactor configurations that hinder direct comparison with this study. Few studies have yet been performed at pilot scale using real wastewaters. One of these studies, carried out by Back et al. (2018) with a similar reactor configuration, has reported similar to higher RE for carbamazepine, diclofenac and sulfamethoxazole, but for continuous NTP tests with hydraulic retention times up to 40 minutes. The difference in this performance can be in part attributed to the effluent quality after the WWTP conventional treatment used in these tests, which had much higher organic and solids content. It has been shown that the NTP efficiency declines when the wastewater contains high concentration of organic matter and mineral salts, which can compete for or inhibit the effect of the plasma-generated oxidant species (Hijosa-Valsero *et al*. 2014). Further optimizations of the NTP configuration are under study, including the optimization of the plasma to liquid ratio, in order to improve the NTP performance.

Despite the variations in the individual RE observed during NTP tests, a considerable overall removal of pharmaceuticals was achieved. The cumulative global RE in Test 1 with only NTP, considering the sum of the concentration of quantified pharmaceuticals, shows that after 2h there was a removal of 45% of the pharmaceuticals, and in the following samples at 6h and 21h, global RE of 66% and 83%, respectively. These initial results show the potential of this technology for the pharmaceutical removal.

Conclusions

This case study has showed the potential of the atmospheric non-thermal plasma technology for the treatment of pharmaceutical compounds present in treated wastewaters. The combination with UF improved further the overall quality of the wastewater effluent.

There are still challenges in the application of this NTP technology to real effluents, due to variable composition and complexity of this matrix. This research and treatment optimization will be continued in order to improve the performance of NTP under these real application conditions and achieve higher removal efficiencies for pharmaceuticals.

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