Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents

Ronan Guillossou, Julien Le Roux, Stephan Brosillon, Romain Mailler, Emmanuelle Vulliet, Catherine Morlay, Fabrice Nauleau, Vincent Rocher, Johnny Gasperi

To cite this version:

Ronan Guillossou, Julien Le Roux, Stephan Brosillon, Romain Mailler, Emmanuelle Vulliet, et al.. Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents. Chemosphere, Elsevier, 2020, 245, pp.125530. 10.1016/j.chemosphere.2019.125530 . hal-02400040

HAL Id: hal-02400040

https://hal-enpc.archives-ouvertes.fr/hal-02400040

Submitted on 1 Jul 2020

Title

Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents.

Authors

Ronan Guillossou[1], Julien Le Roux[1*], Stéphan Brosillon[2], Romain Mailler[3], Emmanuelle Vulliet[4], Catherine Morlay[5], Fabrice Nauleau[6], Vincent Rocher[3], Johnny Gaspéri[1*]

[1] Ecole des Ponts ParisTech, Université Paris-Est Créteil, AgroParisTech, Laboratoire Eau Environnement et Systèmes Urbains, UMR-MA 102, Créteil, France

[2] Institut Européen des Membranes, IEM – UMR 5635, ENSCM, CNRS, CC047 Université de Montpellier, Montpellier, France

[3] Service public de l'assainissement francilien (SIAAP), Direction Innovation et Environnement, Colombes, France

[4] Université de Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences Analytiques, UMR 5280, Villeurbanne, France

[5] Université de Lyon, CNRS, Université Claude Bernard Lyon 1, INSA-Lyon, MATEIS, UMR 5510, Villeurbanne, France

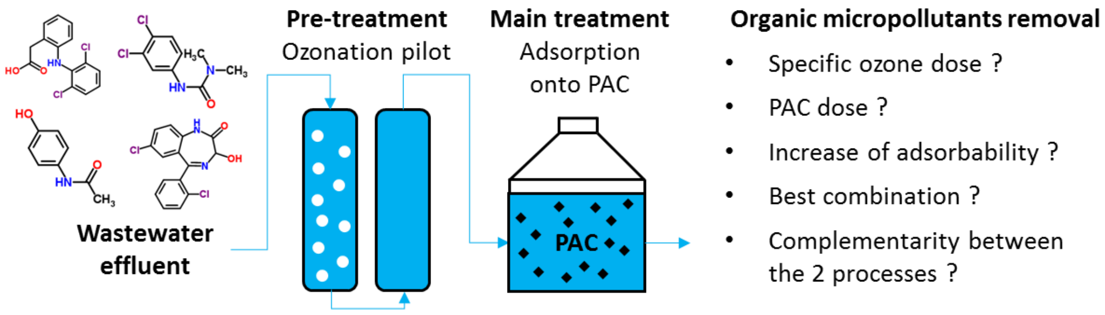
[6] Saur, Direction de la Recherche et du Développement, Maurepas, France

* Corresponding authors. gasperi@u-pec.fr ; julien.le-roux@u-pec.fr

Highlights

- OMPs adsorption increased after ozonation at high specific ozone doses only
- Ozonation performances were impacted by the presence of TSS
- Low specific ozone doses allowed the removal of OMPs refractory to adsorption
- Non-reactive OMPs toward ozone were well adsorbed onto PAC
- The best combination was 0.20-0.30 $gO_3/gDOC$ and 10 mg/L PAC

Graphical abstract



Abstract

Advanced processes for the removal of organic micropollutants (OMPs) from wastewater effluents include adsorption onto activated carbon, ozonation, or a combination of both processes. The removal of 28 OMPs present in a real wastewater effluent was studied by ozonation coupled to activated carbon adsorption and compared to a sole adsorption. The influence of the specific ozone dose (0.09-1.29 $gO_3/gDOC$) and the influence of the powdered activated carbon (PAC) dose (2, 5 and 10 mg/L) were first studied separately. OMPs removal increased with both the specific ozone dose (up to 80% for a dose higher than 0.60 $gO_3/gDOC$) and the PAC dose. Ozonation performances decreased in presence of suspended solids, which were converted to dissolved organic carbon. A correction of the specific ozone dose according to the suspended solids levels, in addition to nitrite, should be considered. The influence of ozonation (0.09, 0.22, 0.94 and 1.29 $gO_3/gDOC$) on OMPs adsorption was then assessed. OMPs adsorption didn’t change at low specific ozone doses but increased at higher specific ozone doses due to a decrease in DOM adsorption and competition with OMPs. At low ozone doses followed by adsorption (0.22 $gO_3/gDOC$ and 10 mg/L PAC), the two processes appeared complementary as OMPs with a low reactivity toward ozone were well absorbed onto PAC while most OMPs refractory to adsorption were well eliminated by ozone. Improved removals were obtained for all compounds with these selected doses, reaching more than 80% removal for most OMPs while limiting the formation of bromate ion.

Keywords

Wastewater advanced treatment; Organic micropollutants; Ozonation; Activated carbon adsorption.

1. Introduction

Activated carbon adsorption is widely used for drinking water production and is transferred to wastewater advanced treatment to remove organic micropollutants (OMPs) and particularly pharmaceuticals compounds that are refractory to biological treatments before reuse or discharge in aquatic ecosystems (Altmann et al., 2015b; Guillossou et al., 2019; Meinel et al., 2015; Ruel et al., 2011). Diverse types of activated carbon with different granulometries can be used, either powdered activated carbon (PAC) (Altmann et al., 2015a; Kårelid et al., 2017; Meinel et al., 2016), micro-grain activated carbon (µGAC) (Alves et al., 2018; Mailler et al., 2016a) or granular activated carbon (GAC) (Benstoem et al., 2017; Grover et al., 2011; Zietzschmann et al., 2016). The use of µGAC in fluidized bed was previously demonstrated to reach similar removals of OMPs to PAC (~80-90%) (Mailler et al., 2015, 2016a) with a simpler and easier operation. However, some pharmaceuticals such as diclofenac, erythromycin or sulfamethoxazole were poorly removed (< 50%) by fluidized-bed µGAC, due to specific physico-chemical properties decreasing their adsorption (e.g. size, charge, hydrophobicity). The presence of dissolved organic matter (DOM) in wastewater effluents also limits OMPs removal through competition for adsorption sites and pore blockage (Newcombe et al., 2002; Zietzschmann et al., 2014).

Ozonation is currently the most used oxidation process for OMPs removal in drinking water production and is also recently transferred to the advanced treatment of wastewater effluents (de Wilt et al., 2018; Hollender et al., 2009; Margot et al., 2013; Zimmermann et al., 2011). Bourgin et al. (2018) obtained removals higher than 80 % for the 12 OMPs used as indicator substances in the Swiss legislation (Office fédéral de l'environnement, Division Eaux, 2014) over a whole wastewater treatment plant upgraded with an ozonation step (0.55 $gO_3/gDOC$). Ozone is a powerful oxidant which reacts rapidly with electron-rich moieties such as alkenes, amines and aromatic rings (von Gunten, 2003a). The self-decomposition of ozone forms hydroxyl radicals ($^\bullet OH$) which can react with non-activated aromatic compounds, amides and alkanes. DOM and OMPs are usually not mineralized but rather transformed into smaller compounds called ozonation transformation products which are most of the time more biodegradable and less toxic (Hübner et al., 2015; Völker et al., 2019). Oxidation by-products such as bromate (BrO_3^-) and N-nitrosodimethylamine (NDMA), which are suspected to be human carcinogens, can however be formed depending on the ozone dose applied and on the presence of precursors. BrO_3^- can be produced from the reaction of ozone with bromide ion and NDMA from specific precursor compounds (e.g. anthropogenic organic compounds containing dimethylamine groups) (Sgroi et al., 2016; von Gunten, 2003b). An additional treatment step after ozonation such as sand filtration or activated carbon filters is therefore required to reduce transformation products and oxidation by-products.

In combination with activated carbon adsorption, ozonation appears as a complementary process to remove compounds that are refractory to adsorption, as well as to oxidize DOM in order to reduce the competition with OMPs onto activated carbon and then to limit the decrease of activated carbon adsorption capacity over time. Indeed, Muller et al. (1996) reported that the adsorption of the herbicide atrazine increased after pre-ozonation of DOM in river water. Matsui et al. (1999) studied the effect of ozonation on the adsorption of DOM from peat water and biological wastewater effluent and found a decreased in DOM adsorbability due to the formation of weakly adsorbing compounds after ozonation. Zietzschmann et al. (2015) observed a decrease in DOM adsorbability after the ozonation of a wastewater effluent due to a reduction of DOM aromaticity, molecular size and hydrophobicity. This decrease led to a reduced adsorption competition with OMPs and as a consequence improve the adsorption of OMPs on activated carbon over time.

The coupling of ozonation and activated carbon is well known and already in use at full scale in some wastewater treatment plants (WWTP) where ozonation is the main step for OMPs removal and adsorption (mostly GAC) is an additional step for post-treatment. However, a coupled process consisting of ozonation as a pre-treatment step (i.e. at lower doses than commonly employed) followed by activated carbon adsorption as the main treatment step has never been considered. The coupling could be an interesting option to increase the removal of OMPs refractory to adsorption and for disinfection purposes while limiting the production of oxidation by-products, but knowledge of its efficiency for real wastewater effluents, which are composed of a more complex matrix than surface water, is limited. Moreover, available studies only investigated a small number of OMPs spiked in wastewater effluents at relatively high concentrations (> 10 µg/L) (Zietzschmann et al., 2015). The aim of this study was to evaluate the removal of 28 OMPs present in wastewater effluents by ozonation coupled to adsorption onto activated carbon as the main treatment step, and to estimate the benefits provided by the coupling in comparison to activated carbon adsorption alone. The influence of various specific ozone doses on OMPs removal was first studied. The effect of the activated carbon dose was then evaluated with a preliminary ozonated effluent. DOM evolution during ozonation and adsorption were examined in parallel through UV_{254} and fluorescence excitation/emission analyses. Different combinations of specific ozone doses and activated carbon doses were tested to assess the potential beneficial effect of ozonation on OMPs adsorption through DOM oxidation, to evaluate the complementarity between both processes toward OMPs that are refractory to ozonation or adsorption and to find the most promising combination of specific ozone and PAC doses.

2. Material and methods

2.1. Ozonation pilot

The ozonation experiments were conducted on a pilot comprising a cylindrical stainless-steel transfer column (height = 100 cm, diameter = 25 cm, volume = 56 L) and a contact column of similar dimensions (Figure S1). The ozone gas was produced in a corona-discharge tube from an oxygen-enriched gas stream (90% O_2) produced by an oxygen concentrator (OnyxUltra, CAIRE Inc.). The gas was sent to the transfer column from a porous diffuser at the bottom at counter-current flow in the transfer column. The concentration of the ozone inlet and outlet gas of the transfer column was measured by an ozone gas analyser (BMT 964, BMT Messtchnik GMBH). The ozone gas flow was maintained at a constant value (2 NL/min) and the concentration of ozone ranged from 8 to 45 g/Nm^3. The ozonated water was sampled after the contact column for each specific ozone dose in 20-L cleaned glass bottles. The water flow was maintained constant (10 L/min) and measured by a flowmeter. The hydraulic retention time in each column was about 5 min. The water pH (7.0-7.4) and temperature (20-25°C) were monitored by probes (Endress+Hauser, Germany).

The pilot was fed continuously by nitrified water directly pumped from the second biofiltration stage from the Seine-Centre WWTP (Colombes, France). The plant is operated by the Paris public sanitation service (SIAAP) and treats wastewater for 800 000 inhabitants with a flow of 240 000 m^3/day. The treatment is composed of a pre-treatment step (screening, grit and oil removal) followed by the primary treatment (physico-chemical lamellar settling for the removal of suspended particles, colloids and phosphorus) and the biological treatment (3 stages of biofiltration for the removal of carbon and nitrogen). After treatment, the effluent is discharged in the Seine River. The ozone dose transferred in the liquid phase was normalized by the dissolved organic carbon concentration (DOC) after subtraction of the ozone consumption by nitrite ion (NO_2^-) (Naumov et al., 2010) to obtain the value of the parameter "specific ozone doses" used all along the article.

$$Specific\ O_3\ dose = \frac{Transferred\ O_3\ dose - 1.04 * \ [NO_2^-]_{consumption}}{[DOC]}$$

With the specific O_3 dose in $gO_3/gDOC$, the transferred O_3 dose in $gO_3/L_{wastewater}$, $[NO_2^-]$ consumption in gNO_2^-/L and [DOC] before ozonation in g/L.

An instantaneous ozone demand (IOD) of the nitrified water in nominal conditions was evaluated at 3.8 ± 0.5 mgO_3/L (DOC = 6 mgC/L, TSS < 2 mg/L, NO_2^- < 0.06 mg/L) following the method developed by Roustan et al. (1998). The IOD was satisfied for specific ozone dose up to 0.7 $gO_3/gDOC$.

Apart from the water quality, the operating conditions did not change during the experiments except the concentration of the ozone gas sent to the transfer column. An equilibration time of 15 min was allowed between the application of each specific ozone dose.

2.2. Experimental plan

The removal performances of 28 OMPs (19 pharmaceuticals, 6 pesticides, 2 hormones and 1 perfluorosulfonic acid – Table 1) were studied. A set of 5 experiments was conducted at various specific ozone doses (ranging from 0.09 to 1.29 $gO_3/gDOC$) (Table 2). Nitrified water from the Seine Centre WWTP was sampled on 2018-05-02, 2018-05-23, 2018-07-06, 2019-04-09 and 2019-08-07 (experiments 1 to 5, respectively). The quality of the wastewater effluent is generally similar over this period of the year (Rocher et al., 2012). Experiment 1 and 2 were conducted to study the influence of the specific ozone dose. Experiment 3, 4 and 5 were performed to study the influence of the activated carbon dose, the performances of the coupled processes and the influence of ozonation on adsorption performances, respectively. For experiments involving PAC adsorption (experiments 3, 4 and 5), a µGAC (CycleCarb 305, Chemviron Carbon) was crushed and sieved to keep only particles between 50 and 63 µm to guarantee a fast adsorption. This activated carbon was chosen due to its previous use in a fluidized-bed industrial pilot (CarboPlus®, Saur) (Mailler et al., 2016a) and the chemical, physical and textural properties of this activated carbon (Table S1) were determined in a previous study (Guillossou et al., 2020). An average OMPs removal of 70% in this pilot was equivalent to 30% in batch with a similar PAC dose (10 mg/L) (Mailler et al., 2016b, 2015). Each desired PAC dose (2, 5 or 10 mg/L) was added to 10 L of nitrified or ozonated water in 20 L flasks then adsorption tests were performed under fast stirring for 30 min using a stainless-steel blades stirrer. The range of PAC doses was chosen from a previous work which reported that the removal gain obtained when increasing the PAC dose from 5 mg/L to 10 mg/L was more important than when increasing from 10 mg/L to 20 mg/L (Mailler et al., 2016b). Prior to adsorption in experiment 5, the 28 studied OMPs were spiked at a concentration of 100 ng/L to ensure their presence in the effluent after ozonation (high specific ozone doses).

Table 1. List of the 28 analysed OMPs, their reaction rate constant with ozone (k_{O3}), molecular weight (M_w), hydrophobicity (log D) and charge at 20-25°C and pH = 7.0, and their limits of quantification (LOQ). The M_w, log D and charge were calculated using MarvinSketch (ChemAxon).

Compound	Use	k_{O3} (L.mol^{-1}.s^{-1})	Reference for k_{O3}	M_w (g/mol)	Log D	Charge	LOQ (ng/L)
Acetaminophen	Analgesic	2.6x10^{6}	Hamdi El Najjar et al., 2014	151.2	0.91	0	0.5
Acetamiprid	Insecticide	0.25	Cruz-Alcalde et al., 2017	222.7	1.11	0	1
Atenolol	Betablocker	2.1x10^{3}	Mathon et al., 2017	266.3	-2.24	+1	1
Carbamazepine	Anticonvulsive	3.0x10^{5}	Huber et al., 2003	236.3	2.77	0	1
Ciprofloxacin	Antibiotic	1.9x10^{4}	Dodd et al., 2006	331.3	-1.47	0	35
Clothianidin	Insecticide	-	-	249.7	-4.53	0	3
Diclofenac	Analgesic	1.0x10^{6}	Huber et al., 2003	296.2	1.26	-1	0.5
Diuron	Pesticide	1.5x10^{1}	Mathon et al., 2017	233.1	2.53	0	1
Erythromycin	Antibiotic	7.0x10^{4}	Mathon et al., 2017	734.0	1.20	+1	4
Estradiol	Hormone	3.0.x10^{6}	Huber et al., 2003	272.4	3.75	0	7
Estrone	Hormone	1.5x10^{5}	Deborde et al., 2005	270.4	4.31	0	2.5
Ibuprofen	Analgesic	9.6	Huber et al., 2003	206.8	1.69	-1	6
Imidacloprid	Insecticide	-	-	255.7	-1.95	0	2
Ketoprofen	Analgesic	0.4	Real et al., 2009	254.3	0.49	-1	1
Lorazepam	Anxiolytic	-	-	321.2	3.53	0	1.5
Naproxen	Analgesic	2.0x10^{5}	Huber et al., 2005	230.3	0.18	-1	2
Norfloxacin	Antibiotic	4.5x10^{5}	Ling et al., 2018	319.3	-1.57	0	5
Ofloxacin	Antibiotic	2.0x10^{6}	Márquez et al., 2013	361.4	-0.05	-1	1
Oxazepam	Anxiolytic	1.0	Lee et al., 2014	286.7	2.92	0	2
PFOS	Additive	1.0	Arias Espana et al., 2015	500.1	-4.89	-1	0.5
Propranolol	Betablocker	1.0x10^{5}	Mathon et al., 2017	259.3	-0.09	+1	1.5
Roxithromycin	Antibiotic	7.0x10^{4}	Huber et al., 2003	837.1	0.92	+1	0.5
Sulfadiazine	Antibiotic	1.0x10^{5}	Garoma et al., 2010	250.3	0.08	-1	1
Sulfamethoxazole	Antibiotic	2.5x10^{6}	Huber et al., 2003	253.3	-0.11	-1	1
Tetracycline	Antibiotic	1.9x10^{6}	Dodd et al., 2006	444.4	-0.57	0	22
Thiaclopride	Insecticide	-	-	254.7	2.06	0	2.5
Thiamethoxam	Insecticide	-	-	291.7	1.29	0	0.5
Trimethoprim	Antibiotic	3.0x10^{5}	Dodd et al., 2006	290.3	0.89	+1	2

2.3. Analytical procedures

For each experiment, the concentrations of the 28 studied OMPs were analysed within 48 h (Institut des Sciences Analytiques – Villeurbanne, France) by liquid chromatography coupled to tandem mass spectroscopy. These micropollutants were chosen because of their frequency of detection in the effluents of wastewater treatment plants in the Paris conurbation (Mailler et al., 2015, 2014) or because they were molecules of recent interest (e.g. the 5 insecticides). Prior to analysis, all samples were homogenized and filtered on 0.7 µm GF/F glass filters (Whatman). Details of the analytical methods are described in supplementary information (Text S1) (Vulliet et al., 2011). OMPs removal was calculated following the approach of Choubert et al. (2017), which stated that the uncertainty of OMPs concentrations in wastewater generally ranges between 30% and 100% when the measured value is lower than 2.5 to 10 times the limit of quantification (LOQ) of the compound. Therefore, when a compound was quantified at levels above 5 times the LOQ in the nitrified water and above the LOQ after treatment, the removal was conventionally calculated. When a compound concentration was above 5 times the LOQ in the nitrified water but below the LOQ after treatment, the removal was estimated using LOQ/2. Removals were not calculated when concentrations in the nitrified water and after treatment ranged between the LOQ and 5 times the LOQ.

Conventional wastewater quality parameters were analyzed by the certified SIAAP laboratory: total organic carbon (TOC), dissolved organic carbon (DOC), NH_4^+, NO_2^-, NO_3^- and total suspended solids (TSS) (Table S2). Bromide (LOQ = 50 µg/L) and bromate (LOQ = 5 µg/L) concentrations were measured for the first experiment after filtration on 0.7 µm GF/F glass filters (Whatman) by ion chromatography (CARSO laboratory, Vénissieux, France).

Spectroscopic measurements were performed at room temperature directly after sampling and filtration on 0.45 µm polyvinylidene fluoride filters (Milex®, Merck). UV_{254} was measured in a 1 cm quartz cuvette using a spectrophotometer (Genesys 10S UV-Vis, Thermo Scientific).

Fluorescence emission/excitation matrices (EEMs) were obtained using a spectrofluorometer (FP-8300, 150-W Xenon lamp, Jasco) with excitation wavelengths ranging from 240 nm to 450 nm at an interval of 5 nm and emission wavelengths from 250 nm to 600 nm at an interval of 2 nm. The samples were diluted with ultrapure water if the UV_{254} was higher than 0.080 1/cm to avoid inner filter effects due to adsorbing species present in the wastewater (Alberts and Takács, 2004). EEMs of ultrapure water were subtracted from the sample EEMs, which were also normalized by the Raman peak of ultrapure water (excitation wavelength of 350 nm), to obtain fluorescence data in Raman units (Lawaetz and Stedmon, 2009). A modified peak-picking approach based on a set of six fluorescence indexes (excitation/emission wavelengths) was applied on the corrected EEMs. These fluorescence indexes are based on maximum localization of 6 specific PARAFAC components (C1-C6), similarly to the studies of Murphy et al. (2011) and Sgroi et al. (2017), that were previously obtained from wastewater samples of the Seine Centre WWTP (Goffin et al. 2018). The C1 index (275/304 nm) is related to tyrosine-like compounds, C2 (285/344 nm) to tyrosine/tryptophan-like compounds, C3 (275/378 nm) to tryptophan-like compounds, C4 (295/404 nm) to humic-like compounds from a recent biological activity and C5 (360/434 nm) and C6 (275/464 nm) to humic-like compounds.

3. Results and discussion

3.1. Influence of the specific ozone dose

3.1.1. DOM removal

DOC removal globally increased with an increase of the specific ozone dose when TSS concentration was below LOQ (experiment 1): < 5, 5, 14 and 17% at 0.18, 0.32, 0.67 and 0.97 $gO_3/gDOC$, respectively. When TSS were detected (2-7 mg/L), DOC removal was negligible (i.e. < 5%) at 0.94 and 1.29 $gO_3/gDOC$ (experiment 5), and was even negative during experiment 2 with removals about -10, -25, and -14% for doses of 0.24, 0.60 and 0.90 $gO_3/gDOC$, respectively

(Table 2). The reaction of suspended solids (7 mg/L) with ozone during experiment 2 likely converted particulate organic matter contained in TSS to DOC, as suggested by the decrease in TSS concentration (from 7 to 3 mg/L) while TOC remained stable (~ 7 mgC/L). The effect of TSS was also clearly observed during experiment 5 (TSS = 4 mg/L), exhibiting almost no removal of DOC (< 5%) at 0.94 and 1.29 $gO_3/gDOC$, respectively, while TOC and TSS concentrations decreased from 6 to ~ 4.5 mgC/L and 4 to 2 mg/L, respectively. Similar effects of suspended solids on DOC removal by ozonation were observed in other studies (Jekel, 1994; Zhang et al., 2018).

Unlike DOC, the effective destruction of the unsaturated structures during ozonation, caused by the electrophilic addition of ozone, lead to a regular UV_{254} decrease with the specific ozone dose (~ 10 to ~ 50%), but no effect of the TSS concentration was noted (Table 2). The absence of plateau at high ozone doses was attributed to aromatic molecules (i.e. absorbing at 254 nm) present in important quantity in the nitrified water. All WWTP-specific fluorescence indexes strongly reacted with ozone, exhibiting a regular loss of intensity in all regions of EEMs (Figure S2) at increasing ozone doses (Table 2). The loss of intensity was > 70% for specific ozone doses from 0.32 $gO_3/gDOC$ and higher. At low specific ozone doses (0.18 and 0.24 $gO_3/gDOC$), tyrosine-like organic compounds (C1 index) were less removed than other fluorescing DOM components, while humic-like compounds (C5 index) were better removed at a dose of 0.18 $gO_3/gDOC$ than other components. The high reactivity of humic-like substances would be due to their high aromaticity, conferring a high electron donating capacity and hence a high extent of the ozone-reactive sites. Those results suggest a different reactivity of the various DOM components at low ozone doses but a high removal of all fluorescing compounds at higher doses. Fluorescing moieties can therefore be considered more reactive toward ozone than the DOM moieties absorbing at 254 nm.

Table 2. DOC, TSS and NO_2^- levels in the nitrified water before ozonation and removal of DOC, UV_{254} and 6 fluorescence WWTP-specific indexes (C1-C6) obtained from PARAFAC analysis (Goffin et al. 2018) for different specific ozone doses.

Specific ozone dose ($gO_3/gDOC$)	Experiment	Nitrified water global parameters				Removal (%)							
		TSS (mg/L)	TOC (mgC/L)	DOC (mgC/L)	NO_2^- (mg/L)	DOC	UV_{254}	C1	C2	C3	C4	C5	C6
0.18	1	< 2	6	5.9	< 0.06	< 5	3	25	32	33	35	43	27
0.32						5	18	79	79	79	80	82	73
0.67						14	37	91	91	90	91	90	83
0.97						17	49	98	96	95	95	94	90
0.24	2	7	7.2	5.9	0.49	-10	15	25	42	45	41	43	35
0.60						-25	36	64	77	75	73	73	62
0.90						-14	49	91	91	89	87	85	77
0.24	3	< 2	5.1	4.8	< 0.06	< 5	15	34	39	37	36	44	28
0.09	4	< 2	4.6	4.5	0.26	< 5	12	-66	9	9	20	29	13
0.22						< 5	19	24	42	44	41	45	30
0.94	5	4	6.1	4.5	< 0.06	< 5	46	90	91	89	86	84	81
1.29						< 5	54	94	95	93	91	89	87

3.1.2. Bromate formation

The concentration of bromide ion in the nitrified water was 90 µg/L and did not vary significantly after ozonation at all specific ozone doses used in experiment 1 (0.18-0.97 $gO_3/gDOC$). No bromate ion was detected at any specific ozone doses (i.e. < 5 µg/L) despite bromide levels in the range 50-100 µg/L where bromate formation may become a problem (von Gunten, 2003b). The absence of bromate formation can be explained by the low reaction rate constant of bromide ion with ozone (160 $L.mol^{-1}.s^{-1}$, von Gunten, 2003b) in comparison to more reactive compounds such as DOM and OMPs. Zimmermann et al. (2011) observed bromate formation only at specific ozone doses higher than 0.90 $gO_3/gDOC$. The authors also observed NDMA formation at a specific ozone dose of 1.24 $gO_3/gDOC$ and no N-nitrosomorpholine (NMOR). Contrary to bromate for which formation is mostly related to the specific ozone dose, NDMA formation rather depends on the concentrations and the conversion rate of precursors as well as matrix composition (Hollender et al., 2009). N-nitrosamines were not monitored in the study but future work will investigate their occurrence in similar conditions.

3.1.3. OMPs removal

Among the 28 analysed compounds, 7 OMPs were never quantified in the nitrified water (clothianidin, estradiol, estrone, ibuprofen, imidacloprid, thiaclopride and thiamethoxam), 11 OMPs were occasionally detected (acetaminophen, acetamiprid, ciprofloxacin, diuron, ketoprofen, norfloxacin, PFOS, roxithromycin, sulfadiazine, tetracycline and trimethoprim) and 10 OMPs were always present (atenolol, carbamazepine, diclofenac, erythromycin, lorazepam, naproxen, ofloxacin, oxazepam, propranolol and sulfamethoxazole) for each experiment (Table S3). Removals of the quantified OMPs were calculated at each specific ozone dose employed (Figure 1). Negative removals were obtained for diuron and PFOS at low specific ozone doses (< 0.30 gO_3/gDOC). They were attributed to matrix effects during analyses or to the formation of these molecules after ozonation of metabolites/parent molecules. However, these negative removals were low (-10 to 0%) and were not subsequently considered.As proposed by Margot et al. (2013), OMPs were categorized in 3 groups depending on their expected reactivity and observed removals (Table S4). Group A contained 11 OMPs (acetaminophen, carbamazepine, diclofenac, naproxen, norfloxacin, ofloxacin, propranolol, sulfadiazine, sulfamethoxazole, tetracycline and trimethoprim) exhibiting removals higher than 80% at specific ozone doses higher than 0.30 gO_3/gDOC (Figure 1.A). These results were in agreement with reaction rate constants from the literature, compounds from group A being rapidly oxidized by ozone ($k_{O3} > 1x10^5$ $L.mol^{-1}.s^{-1}$).

4 OMPs (atenolol, ciprofloxacin, erythromycin and roxithromycin, listed as group B) were supposed to react moderately with ozone ($1x10^3$ $L.mol^{-1}.s^{-1} < k_{O3} < 1x10^5$ $L.mol^{-1}.s^{-1}$). Atenolol and ciprofloxacin did react poorly with ozone at specific doses lower than 0.50 gO_3/gDOC (removals < 40%) while high removals (> 80 %) were achieved for erythromycin and roxithromycin for a dose of 0.32 gO_3/gDOC, similarly to group A (Figure 1.B). Erythromycin and roxithromycin have a higher ozonation constant rate ($7x10^4$ $L.mol^{-1}.s^{-1}$) than atenolol and

ciprofloxacin ($2x10^3$ L.mol^{-1}.s^{-1} and $2x10^4$ L.mol^{-1}.s^{-1}, respectively). A higher reactivity of erythromycin and roxithromycin with hydroxyl radicals may also explain their higher removal. DOM is rich in humic substances that can act either as radical scavenger or help in the formation of hydroxyl radicals (Lee at al., 2013).The removal of atenolol and ciprofloxacin only reached 90% at specific ozone doses higher than 0.80 gO_3/gDOC.

Finally, group C comprised 4 OMPs (diuron, ketoprofen, oxazepam and PFOS) that were demonstrated to be recalcitrant to ozone ($k_{O3} < 1x10^3$ L.mol^{-1}.s^{-1}) and 2 OMPs (acetamiprid and lorazepam) which ozone rate constants were not found in the literature but exhibited low removals (< 50% at doses < 0.5 gO3/gDOC). High specific ozone doses (> 0.90 gO_3/gDOC) allowed to achieve high removals (> 80%) for most OMPs of group C, but low removals were still obtained for acetamiprid and PFOS (48% and 52% at 0.97 gO_3/gDOC, respectively).

The average removal at each specific ozone dose was determined based on the removals of the 10 OMPs systematically quantified in each experiment (Figure 1.D). The average removal was low (< 40%) at the lowest specific ozone doses and increased up to 90% with the higher specific dose. The removal of many OMPs from groups A and B (i.e. 13 compounds) reached a plateau above 0.30 gO3/gDOC (> 80%). Going further this specific ozone dose only provided major gains of removal for the remaining 8 OMPs (atenolol and ciprofloxacin and group C). A high variability was observed at a specific ozone dose of 0.24 gO_3/gDOC showing average removals of 47 and 69 % in the presence and absence of TSS, respectively. This difference can be explained by the TSS levels during experiment 2. As proposed above, ozone probably reacted with the TSS which decreased the quantity of ozone available to react with OMPs. The degradation of all OMPs was affected at this specific ozone doses by TSS, especially naproxen (-39%), sulfadiazine (-93%), sulfamethoxazole (-40%) and trimethoprim (-38%). Such a negative effect of suspended solids on OMP removal from wastewater effluents by ozonation was also reported elsewhere (Zucker et al., 2015), but the reason why some molecules are more impacted than others is not yet known.

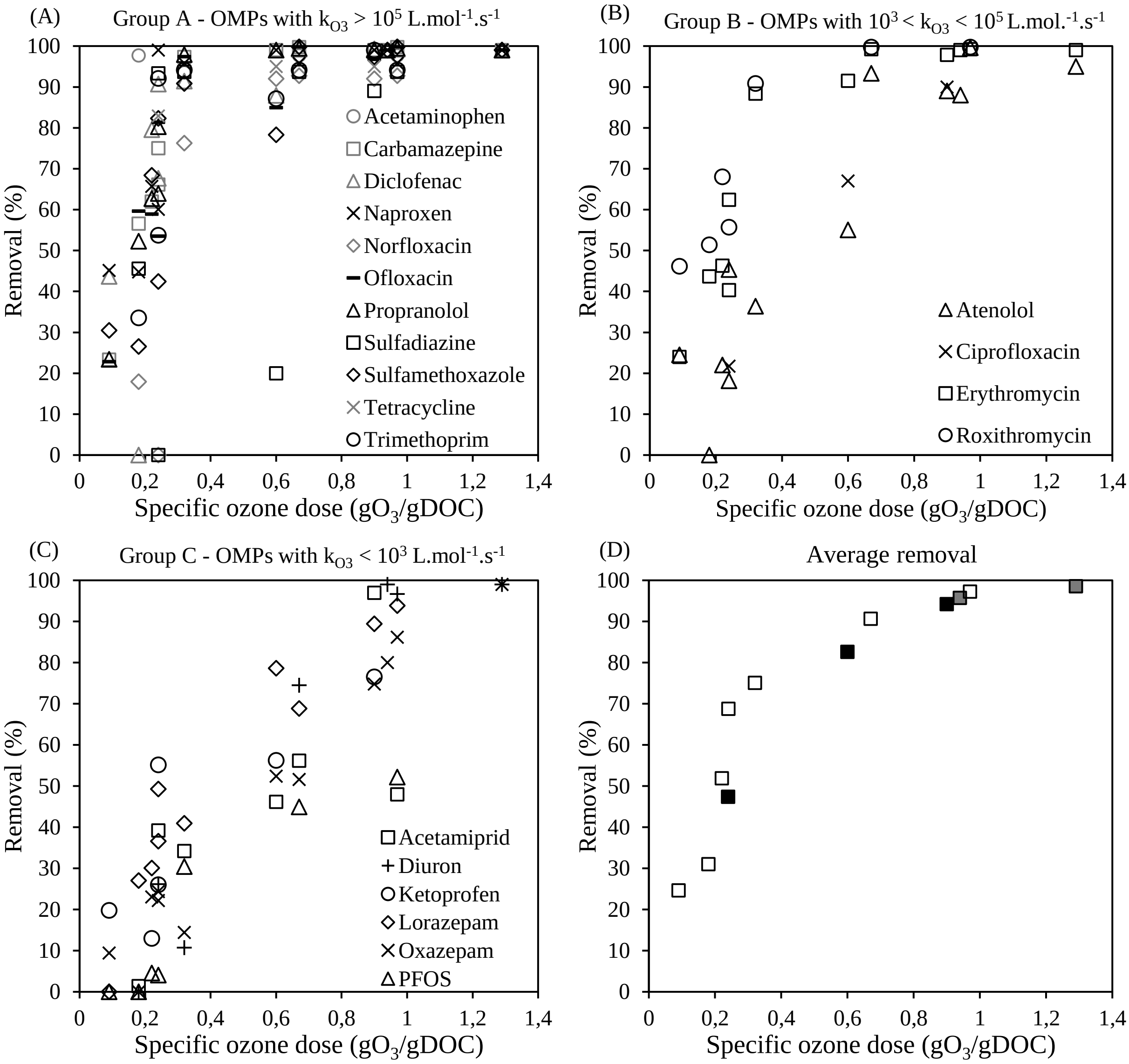


Figure 1. Removals of the quantified OMPs (A, B and C) and average removal (D) at different specific ozone doses (white squares TSS = 2 mg/L, grey squares TSS = 4 mg/L, black squares TSS = 7 mg/L). The average removal was calculated from the removals of 10 OMPs that were systematically detected in each experiment. A table with detailed results for OMPs removal is presented in supplementary information (Table S4).

3.2. Influence of the activated carbon dose

3.2.1. DOM removal

Before adsorption, the nitrified water was ozonated at a dose of 0.24 gO_3/gDOC (experiment 3). The removal of DOC, UV_{254} and fluorescence WWTP-specific indexes increased with the PAC dose (Table S5). At the lowest PAC dose of 2 mg/L, all removals were low and similar (0-6 %), the highest removal being attained for the C2 index related to tyrosine and tryptophan-like compounds. At a PAC dose of 5 mg/L, the C2 index exhibited again the highest removal (20%)

and other removals ranged between 1 and 11%. A low removal was observed for UV_{254} with a PAC dose of 10 mg/L, while the best removals were obtained for indexes C1, C2, C3 and C4 (18-23%). These 4 indexes are related to small DOM fractions (aromatic proteins-like, tyrosine-like, tryptophan-like and humic-like from a recent biological activity) which had probably a better access to the PAC porosity in 30 min. Sgroi et al. (2018) observed a better removal of humic-like fractions than tyrosine and tryptophan-like, but it is well known that that the distribution of activated carbon porosity between macro-, meso- and micropores has an influence on DOM adsorption (Guillossou et al., 2020; Li et al., 2003). As a result, the different type of activated carbon used in this study led to a different behavior toward the adsorption of various DOM fractions.

3.2.2. OMPs removal

Among the 28 compounds analyzed, 10 OMPs (acetaminophen, acetamiprid, clothianidin, estradiol, ibuprofen, imidacloprid, norfloxacine, tetracycline, thiacloprid and thiamethoxam) were not quantified in the ozonated water (0.24 gO_3/gDOC, experiment 3). 8 compounds (ciprofloxacin, estrone, ketoprofen, lorazepam, naproxen, sulfadiazine, sulfamethoxazole and trimethoprim) were quantified at concentrations close to their LOQ so their removal was not calculated. Removals of the 10 remaining OMPs at the 3 different PAC doses (2, 5 and 10 mg/L) are presented in Figure 2.

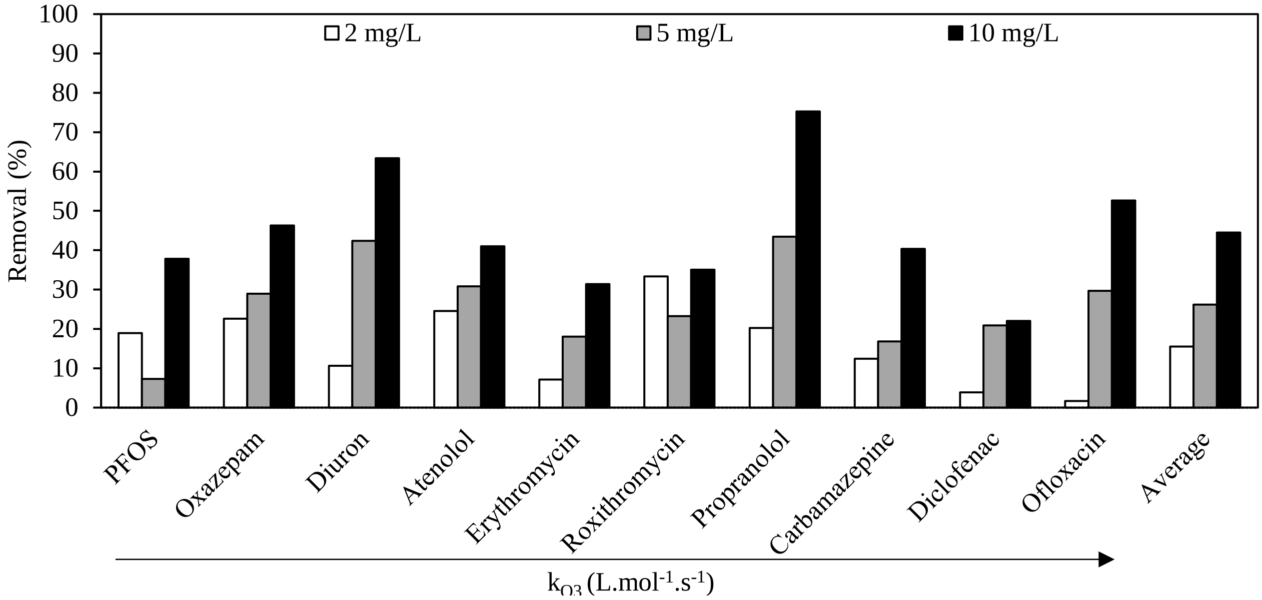


Figure 2. Removals of the 10 OMPs quantified in the ozonated effluent (0.24 gO_3/gDOC) and the average removal at 3 different PAC doses (2, 5 and 10 mg/L) after 30 min of contact time (experiment 3). OMPs are ranked with respect to their k_{O3} value (increasing from left to right).

OMPs removals were all lower than 30% at a PAC dose of 2 mg/L. At 5 mg/L of PAC, removals remained between 10 and 30% except for diuron (42%) and propranolol (43%). Those 2 compounds showed a better adsorption than other OMPs in other studies (Margot et al., 2013; Ruel et al., 2011). In a previous study using PAC, their removal was higher than 60% at a dose of 10 mg/L while those of other OMPs remained between 20 and 60% (Mailler et al., 2015). More information on the effect of the physico-chemical properties of OMPs on their adsorption can be found in a previous study (Guillossou et al., 2020). The average removal increased regularly with the dose (14, 25 and 42%). A PAC dose of 10 mg/L provided the highest removals after ozonation and was thus selected for the subsequent experiments. Notably, substantial removals (> 30%) were obtained for compounds presenting a low k_{O3} (e.g. PFOS, oxazepam, diuron) which would guarantee their removal during a coupled ozonation/adsorption process.

3.3. Influence of ozonation on adsorption performances

3.3.1. Influence of ozonation on DOM adsorption

DOC and UV removals by adsorption after ozonation at low specific doses (0.09 and 0.22 gO_3/gDOC, experiment 4) remained low (< 12%) and were not significantly different from nitrified water, while a slight increase was observed for fluorescence indexes (Table S6). However, the removal of DOC, UV_{254} and all fluorescence indexes by adsorption after ozonation at 0.94 and 1.29 gO_3/gDOC (experiment 5) decreased, which suggests that DOM adsorbability decreased at high specific ozone doses. These results are in accordance with the observations of Zietzschmann et al. (2015) who found a decrease in DOM adsorbability at high specific ozone consumptions (0.65 and 1.64 gO_3/gDOC) due to a reduction of DOM aromaticity, molecular size and hydrophobicity.

3.3.2. Influence of ozonation on OMPs adsorption

Removals by adsorption onto PAC (10 mg/L) after ozonation at 4 different specific ozone doses were obtained for the 13 OMPs quantified before adsorption (Figure 3). The average removal after adsorption was similar between the nitrified water (31-36%) and the ozonated water at low specific ozone doses (33 and 36% at 0.09 and 0.22 gO_3/gDOC, respectively, experiment 4) suggesting no effect of pre-ozonation on OMP adsorption at these specific doses.

OMPs adsorption increased at higher specific ozone doses (experiment 5) with an average removal of 52% for a dose of 0.94 gO_3/gDOC and 61% for a dose of 1.29 gO_3/gDOC, confirming the positive effect of high ozone doses (> 0.50 gO_3/gDOC) on the subsequent adsorption, as previously suggested by Zietzschmann et al. (2015). The decrease in DOM adsorbability (also observed in the study, see part 3.3.1) probably involves a reduction of the competitive adsorption with OMPs. Individual removals of atenolol, carbamazepine, ketoprofen, lorazepam, ofloxacin, oxazepam and propranolol (Figure 3.A) followed a similar behavior to the average removal (Figure 3.D). For some OMPs (diclofenac, PFOS and sulfamethoxazole), the increase of their removal was only observed at the highest specific ozone dose (1.29 gO_3/gDOC), while ozonation at any dose had no effect on the adsorption of erythromycin, naproxen and roxithromycin. The adsorption of erythromycin and roxithromycin was previously demonstrated to be impacted by steric hindrance because of their high molecular weight, and thus are not subject to competition with DOM (Guillossou et al., 2020).

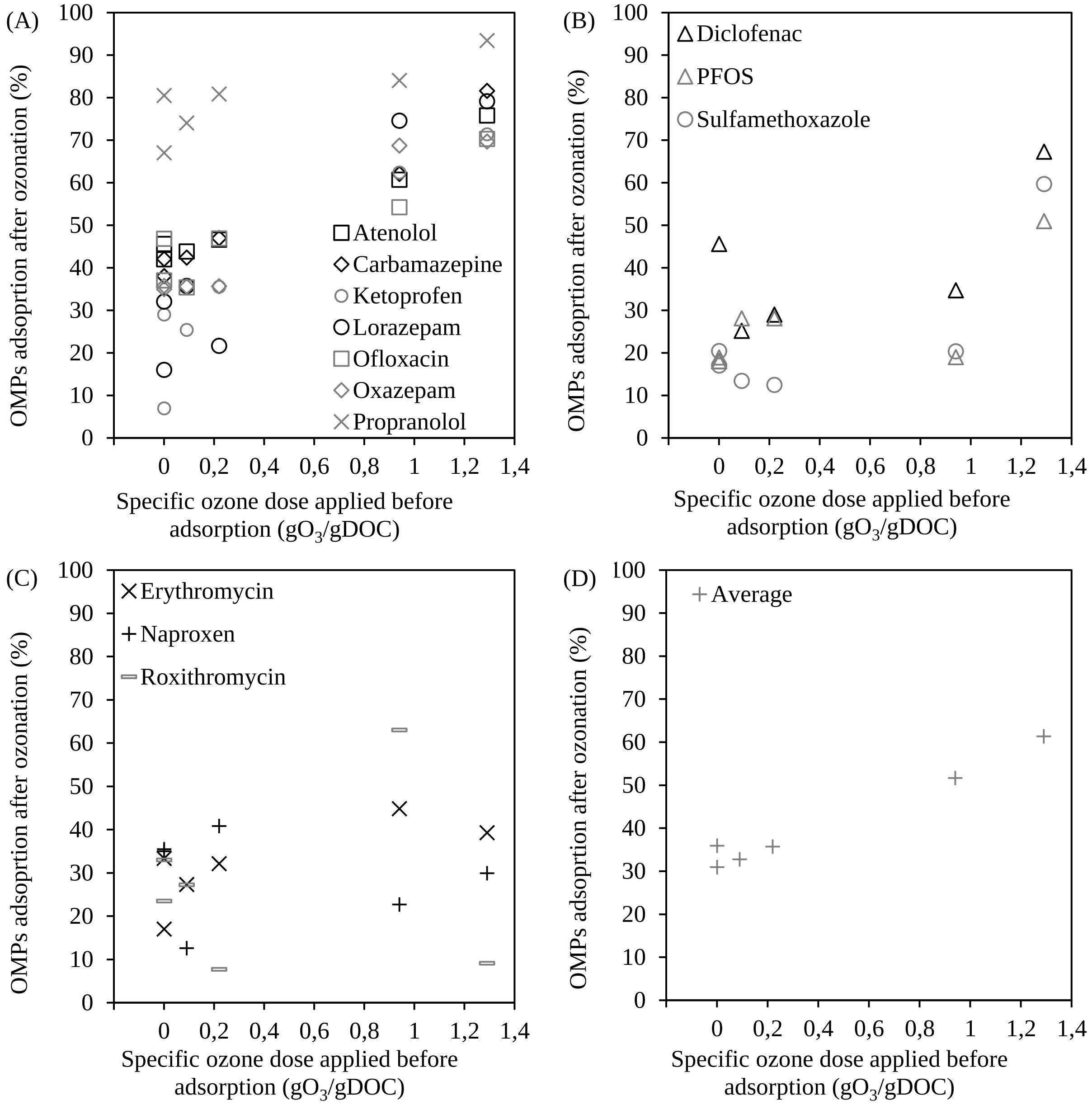


Figure 3. OMPs removal by adsorption onto PAC (10 mg/L) after ozonation of the nitrified water at various specific ozone doses.

3.4. Comparison of coupled ozonation/adsorption with adsorption alone

3.4.1. OMPs removal

Among the 28 analyzed compounds, 7 OMPs (acetamiprid, clothianidin, estradiol, estrone, imidacloprid, thiacloprid and thiamethoxam) were not quantified in the nitrified water during experiment 4 (Table S3). In addition, the removal of 8 OMPs (acetaminophen, ciprofloxacin, diuron, estrone, ibuprofen, norfloxacine, sulfadiazine and trimethoprim) was not calculated because their concentrations in the nitrified water were close to their respective LOQ. As expected, higher overall removals were obtained with ozonation coupled to adsorption (average removal of 49 and 66% with 0.09 and 0.22 $gO_3/gDOC$ + 10 mg/L of PAC, respectively) than the sole adsorption (average removal of 31% with a PAC dose of 10 mg/L) (Figure 4). The highest removals were achieved when combining 0.22 $gO_3/gDOC$ and 10 mg/L of PAC, reaching more than 80% for 4 OMPs (carbamazepine, diclofenac, naproxen and propranolol). 5 OMPs exhibited moderate removals ranging from 58 to 72% (atenolol, erythromycin, ofloxacin, roxithromycine and sulfamethoxazole) and 4 OMPs were less removed than the average with removals ranging from 31 to 50% (ketoprofen, lorazepam, oxazepam and PFOS). At higher ozone doses (0.94 and 1.29 $gO_3/gDOC$, experiment 5), all OMPs reached removals > 99%, except atenolol and oxazepam with 88 and 80% removal at 0.94 gO3/gDOC (data not shown on Figure 4).

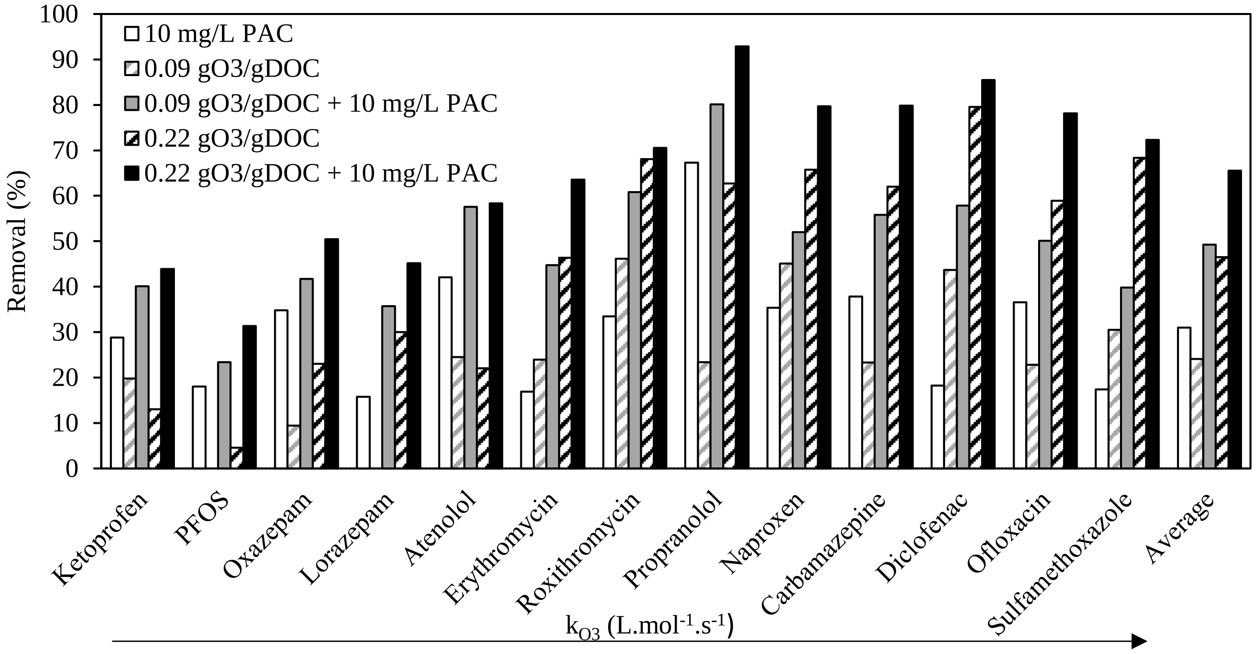


Figure 4. Removals of the 13 quantified OMPs and the average removal at different ozone and PAC doses (experiment 4). OMPs are ranked with respect to their k_{O3} value (increasing from left to right).

3.4.2. Complementarity of the two processes

As illustrated in Figure 5, a general increase in removals was provided by the coupling of ozonation with adsorption, especially for molecules that were not well removed by ozonation alone. After ozonation at 0.22 gO_3/gDOC (experiment 4), PAC adsorption improved the removal of OMPs with low k_{O3} values (e.g. ketoprofen, oxazepam, PFOS, $k_{O3} < 10^4$ $L.mol^{-1}.s^{-1}$) with an addition removal of 25% in average. OMPs with high k_{O3} values (e.g. diclofenac, naproxen, ofloxacin, $k_{O3} > 10^4$ $L.mol^{-1}.s^{-1}$) exhibited an additional removal by adsorption of only 12% in average. At the lower ozone dose of 0.09 gO_3/gDOC (experiment 4), overall removals of compounds reacting slowly with ozone were also higher (additional removal by PAC of 28% in average) as compared to the ozone-reactive OMPs (additional removal by PAC of 22% in average) (Figure S3). At higher ozone doses (0.94 and 1.29 gO_3/gDOC, experiment 5), the removal of OMPs by ozone was largely predominant (> 99% for almost all molecules), so the gain provided by the adsorption was insignificant (data not shown).

Conversely, ozonation coupled to activated carbon adsorption was also interesting for OMPs exhibiting a low affinity with PAC such as diclofenac, erythromycin, lorazepam, PFOS and sulfamethoxazole (Figure 6 and Figure S4). The addition of an ozonation step before adsorption provided an additional removal, for OMPs refractory to adsorption (i.e. removal < 30% for the sole adsorption), of 21 and 38% in average for specific ozone doses of 0.09 and 0.22 gO_3/gDOC, respectively. For compounds that were better adsorbed such as atenolol, carbamazepine, ketoprofen, naproxen, ofloxacin, oxazepam, propranolol and roxithromycin (removals > 30% by PAC), the additional removal provided by ozonation was lower but still significant (16 and 32% in average at 0.09 and 0.22 gO3/gDOC, respectively). The removal of all the quantified OMPs was higher than 30% after ozonation and adsorption. These results are particularly interesting because they highlight a possible optimum in the operating conditions when ozonation is combined with activated carbon adsorption to treat OMPs in real wastewater effluents. In addition, the use of activated carbon should allow the adsorption of ozonation byproducts formed during ozonation (e.g. hydroxylated products or N-oxides) (Merel et al., 2017). Additional studies should be conducted (e.g. by using non-targeted analyses, Schollée et al. (2018)) to study if such transformation products can be effectively adsorbed on activated carbon.

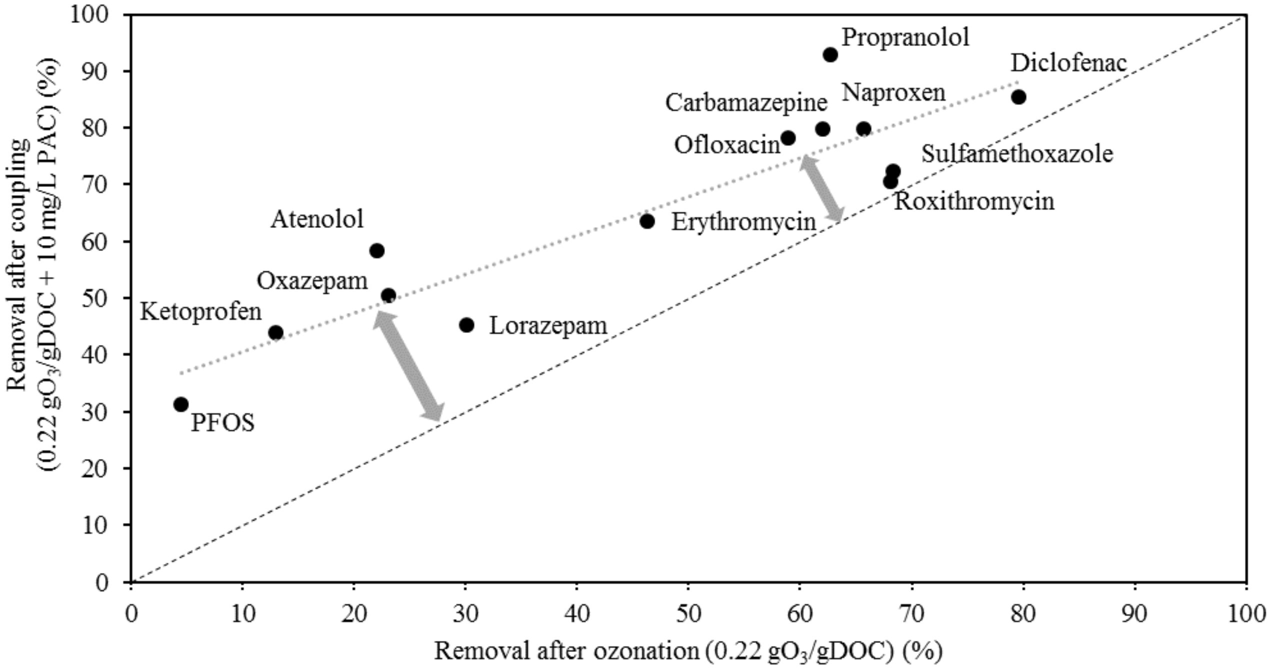


Figure 5. OMPs removal after coupling (0.22 gO_3/gDOC + 10 mg/L PAC) compared to ozonation alone (0.22 gO_3/gDOC).

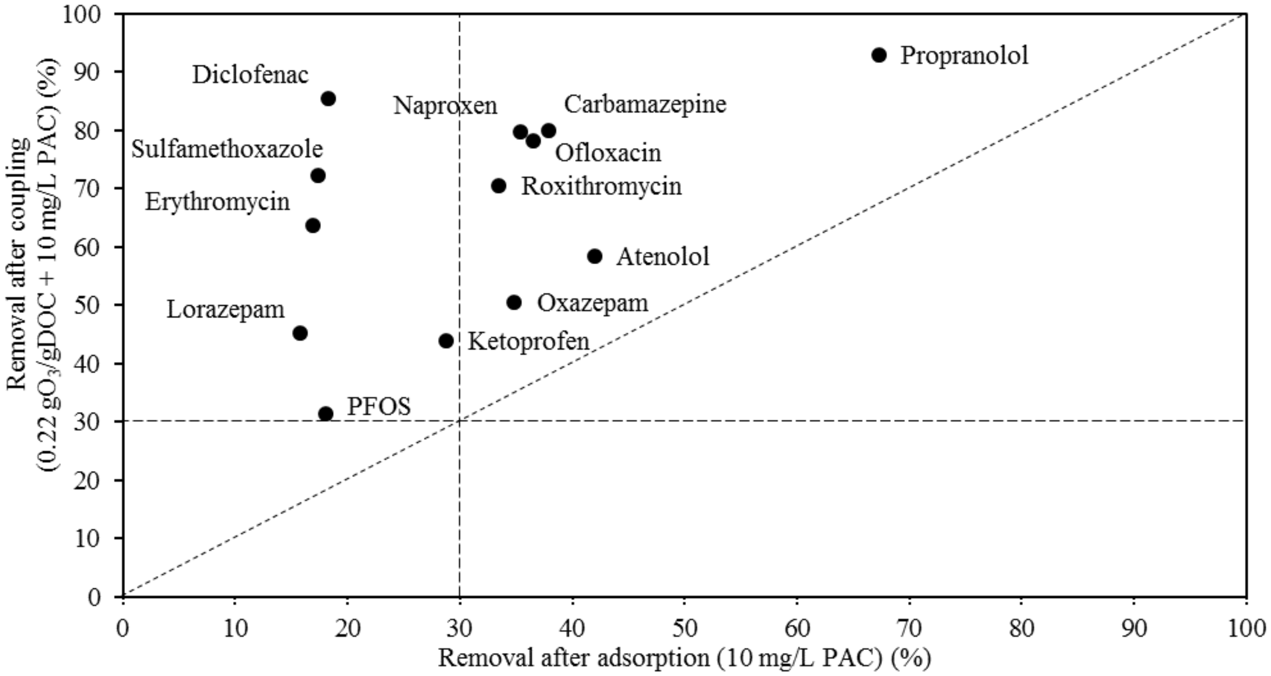


Figure 6. OMPs removal after coupling (0.22 gO_3/gDOC + 10 mg/L PAC) compared to adsorption alone (10 mg/L).

Conclusion

- Ozonation is an efficient process for OMPs elimination from wastewater effluents, with average removals higher than 80% for specific ozone doses higher than 0.60 $gO_3/gDOC$. An increase in the average removal was observed with the increase of the specific ozone dose and the removals of 13 reactive compounds reached a plateau above 0.30 $gO_3/gDOC$. Higher doses (> 0.80 $gO_3/gDOC$) were necessary for less reactive compounds.
- The ozonation performances for OMPs removal thus seemed to be dependent of the wastewater quality, especially for low specific ozone doses where a higher competition between OMPs and the matrix for ozone can be expected. Online monitoring of the quality of the matrix (DOC, TSS, NO_2^-) therefore seems interesting to achieve stable ozonation performances. Further study is needed to better understand the negative influence of TSS on ozonation performances and the conversion of TSS to DOC. A correction of the specific ozone dose according to the TSS concentration, as for nitrites, could then be considered. No bromate was detected at any specific ozone doses in this study.
- The influence of ozonation on adsorption performances was not significant at low specific ozone doses (0.09 and 0.22 $gO_3/gDOC$) but an increase in OMPs adsorption was observed at higher doses (0.94 and 1.29 $gO_3/gDOC$). This increase was attributed to the decrease in DOM adsorbability which led to a reduced adsorption competition with OMPs. Further experiments are needed to determine precisely the specific ozone dose at which the adsorbability of DOM decreases and to identify which DOM fractions are responsible for this decrease after oxidation.
- A better adsorption of OMPs that were poorly reactive toward ozone was observed as compared to the adsorption of highly ozone-reactive OMPs. Conversely, OMPs refractory to adsorption were well removed by ozonation. As a result, the removal of all OMPs were substantially improved with the addition of ozonation prior to adsorption. Even if low

specific ozone doses did not improve OMPs adsorption in comparison to higher doses, low ozone doses coupled to activated carbon adsorption appear as complementary and an adequate process for the removal of various micropollutants in wastewater effluents. The formation and adsorption of ozonation transformation products should also be carried out to better evaluate the complementarity of the two processes. A life cycle analysis is needed to estimate the benefit of reducing ozone doses in terms of energy consumption while using a subsequent adsorption onto activated carbon as compared to a single ozonation step at higher doses coupled to adsorption or sand filtration.

- Based on the quality of the wastewater studied, a specific ozone dose of 0.20-0.30 $gO_3/gDOC$ and a PAC dose of 10 mg/L is recommended to achieve satisfactory performances for a wide range of OMPs (e.g. a removal higher than 80% for carbamazepine and diclofenac which are used as indicator substances in the Swiss regulation).

Acknowledgments

This study was performed within the framework of the OPUR research program. The authors would like to thank the SIAAP laboratory, Céline Briand, Kheira Dahou and Perrine Meche (SIAAP), Martin Maréchal, Angélique Goffin and Gilles Varrault (LEESU) and Barbara Giroud (ISA) for the analyses and their help in the laboratory.

References

Alberts, J.J., Takács, M., 2004. Comparison of the natural fluorescence distribution among size fractions of terrestrial fulvic and humic acids and aquatic natural organic matter. Org. Geochem. 35, 1141–1149. https://doi.org/10.1016/j.orggeochem.2004.06.010

Altmann, J., Ruhl, A.S., Sauter, D., Pohl, J., Jekel, M., 2015a. How to dose powdered activated carbon in deep bed filtration for efficient micropollutant removal. Water Res. 78, 9–17. https://doi.org/10.1016/j.watres.2015.03.031

Altmann, J., Sperlich, A., Jekel, M., 2015b. Integrating organic micropollutant removal into tertiary filtration: Combining PAC adsorption with advanced phosphorus removal. Water Res. 84, 58–65. https://doi.org/10.1016/j.watres.2015.07.023

Alves, T.C., Cabrera-Codony, A., Barceló, D., Rodriguez-Mozaz, S., Pinheiro, A., Gonzalez-Olmos, R., 2018. Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon. Water Res. https://doi.org/10.1016/j.watres.2018.07.037

Arias Espana, V.A., Mallavarapu, M., Naidu, R., 2015. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing. Environ. Technol. Innov. 4, 168–181. https://doi.org/10.1016/j.eti.2015.06.001

Benstoem, F., Nahrstedt, A., Boehler, M., Knopp, G., Montag, D., Siegrist, H., Pinnekamp, J., 2017. Performance of granular activated carbon to remove micropollutants from municipal wastewater—A meta-analysis of pilot- and large-scale studies. Chemosphere 185, 105–118. https://doi.org/10.1016/j.chemosphere.2017.06.118

Bourgin, M., Beck, B., Boehler, M., Borowska, E., Fleiner, J., Salhi, E., Teichler, R., von Gunten, U., Siegrist, H., McArdell, C.S., 2018. Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products. Water Res. 129, 486–498. https://doi.org/10.1016/j.watres.2017.10.036

Choubert, J.-M., Martin Ruel, S., Miege, C., Coquery, M., 2017. Rethinking micropollutant removal assessment methods for wastewater treatment plants – how to get more robust data? Water Sci. Technol. 75, 2964–2972. https://doi.org/10.2166/wst.2017.181

Cruz-Alcalde, A., Sans, C., Esplugas, S., 2017. Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation. Sci. Total Environ. 599–600, 1454–1461. https://doi.org/10.1016/j.scitotenv.2017.05.065

de Wilt, A., van Gijn, K., Verhoek, T., Vergnes, A., Hoek, M., Rijnaarts, H., Langenhoff, A., 2018. Enhanced pharmaceutical removal from water in a three step bio-ozone-bio process. Water Res. 138, 97–105. https://doi.org/10.1016/j.watres.2018.03.028

Deborde, M., Rabouan, S., Duguet, J.-P., Legube, B., 2005. Kinetics of Aqueous Ozone-Induced Oxidation of Some Endocrine Disruptors. Environ. Sci. Technol. 39, 6086–6092. https://doi.org/10.1021/es0501619

Dodd, M.C., Buffle, M.-O., von Gunten, U., 2006. Oxidation of Antibacterial Molecules by Aqueous Ozone: Moiety-Specific Reaction Kinetics and Application to Ozone-Based Wastewater Treatment. Environ. Sci. Technol. 40, 1969–1977. https://doi.org/10.1021/es051369x

Garoma, T., Umamaheshwar, S.K., Mumper, A., 2010. Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. Chemosphere 79, 814–820. https://doi.org/10.1016/j.chemosphere.2010.02.060

Goffin, A., Guérin, S., Rocher, V., Varrault, G., 2018. Towards a better control of the wastewater treatment process: excitation-emission matrix fluorescence spectroscopy of dissolved organic matter as a predictive tool of soluble BOD5 in influents of six Parisian wastewater treatment plants. Environ. Sci. Pollut. Res. https://doi.org/10.1007/s11356-018-1205-1

Grover, D.P., Zhou, J.L., Frickers, P.E., Readman, J.W., 2011. Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: Impact on receiving river water. J. Hazard. Mater. 185, 1005–1011. https://doi.org/10.1016/j.jhazmat.2010.10.005

Guillossou, R., Le Roux, J., Mailler, R., Morlay, C., Vulliet, E., Nauleau, F., Rocher, V., Gasperi, J., 2020. Influence of the properties of 7 micro-grain activated carbons on organic micropollutants removal from wastewater effluent. Chemosphere 243, 125306. https://doi.org/10.1016/j.chemosphere.2019.125306

Guillossou, R., Le Roux, J., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Gasperi, J., Rocher, V., 2019. Organic micropollutants in a large wastewater treatment plant: What are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment? Chemosphere 218, 1050–1060. https://doi.org/10.1016/j.chemosphere.2018.11.182

Hamdi El Najjar, N., Touffet, A., Deborde, M., Journel, R., Karpel Vel Leitner, N., 2014. Kinetics of paracetamol oxidation by ozone and hydroxyl radicals, formation of transformation products and toxicity. Sep. Purif. Technol. 136, 137–143. https://doi.org/10.1016/j.seppur.2014.09.004

Hollender, J., Zimmermann, S.G., Koepke, S., Krauss, M., McArdell, C.S., Ort, C., Singer, H., von Gunten, U., Siegrist, H., 2009. Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration. Environ. Sci. Technol. 43, 7862–7869. https://doi.org/10.1021/es9014629

Huber, M.M., Canonica, S., Park, G.-Y., von Gunten, U., 2003. Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. Environ. Sci. Technol. 37, 1016–1024. https://doi.org/10.1021/es025896h

Huber, M.M., GÖbel, A., Joss, A., Hermann, N., LÖffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A., von Gunten, U., 2005. Oxidation of Pharmaceuticals during Ozonation of Municipal Wastewater Effluents: A Pilot Study. Environ. Sci. Technol. 39, 4290–4299. https://doi.org/10.1021/es048396s

Hübner, U., von Gunten, U., Jekel, M., 2015. Evaluation of the persistence of transformation products from ozonation of trace organic compounds – A critical review. Water Res. 68, 150–170. https://doi.org/10.1016/j.watres.2014.09.051

Jekel, M.R., 1994. Flocculation Effects of Ozone. Ozone Sci. Eng. 16, 55–66. https://doi.org/10.1080/01919519408552380

Kårelid, V., Larsson, G., Björlenius, B., 2017. Effects of recirculation in a three-tank pilot-scale system for pharmaceutical removal with powdered activated carbon. J. Environ. Manage. 193, 163–171. https://doi.org/10.1016/j.jenvman.2017.01.078

Lawaetz, A.J., Stedmon, C.A., 2009. Fluorescence Intensity Calibration Using the Raman Scatter Peak of Water. Appl. Spectrosc. 63, 936–940.

Lee, Y., Kovalova, L., McArdell, C.S., von Gunten, U., 2014. Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent. Water Res. 64, 134–148. https://doi.org/10.1016/j.watres.2014.06.027

Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos, C., 2003. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. Water Res. 37, 4863–4872. https://doi.org/10.1016/j.watres.2003.08.018

Ling, W., Ben, W., Xu, K., Zhang, Y., Yang, M., Qiang, Z., 2018. Ozonation of norfloxacin and levofloxacin in water: Specific reaction rate constants and defluorination reaction. Chemosphere 195, 252–259. https://doi.org/10.1016/j.chemosphere.2017.12.079

Mailler, R., Gasperi, J., Coquet, Y., Buleté, A., Vulliet, E., Deshayes, S., Zedek, S., Mirande-Bret, C., Eudes, V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G., Rocher, V., 2016a. Removal of a wide range of emerging pollutants from wastewater treatment plant discharges by micro-grain activated carbon in fluidized bed as tertiary treatment at large pilot scale. Sci. Total Environ. 542, Part A, 983–996. http://dx.doi.org/10.1016/j.scitotenv.2015.10.153

Mailler, R., Gasperi, J., Coquet, Y., Derome, C., Buleté, A., Vulliet, E., Bressy, A., Varrault, G., Chebbo, G., Rocher, V., 2016b. Removal of emerging micropollutants from wastewater by activated carbon adsorption: Experimental study of different activated carbons and factors influencing the adsorption of micropollutants in wastewater. J. Environ. Chem. Eng. 4, 1102–1109. https://doi.org/10.1016/j.jece.2016.01.018

Mailler, R., Gasperi, J., Coquet, Y., Deshayes, S., Zedek, S., Cren-Olivé, C., Cartiser, N., Eudes, V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G., Rocher, V., 2015. Study of a large scale powdered activated carbon pilot: Removals of a wide range of emerging and priority micropollutants from wastewater treatment plant effluents. Water Res. 72, 315–330. https://doi.org/10.1016/j.watres.2014.10.047

Mailler, R., Gasperi, J., Rocher, V., Gilbert-Pawlik, S., Geara-Matta, D., Moilleron, R., Chebbo, G., 2014. Biofiltration vs conventional activated sludge plants: what about priority and emerging pollutants removal? Environ. Sci. Pollut. Res. 21, 5379–5390. https://doi.org/10.1007/s11356-013-2388-0

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M., Barry, D.A., 2013. Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Sci. Total Environ. 461–462, 480–498. https://doi.org/10.1016/j.scitotenv.2013.05.034

Márquez, G., Rodríguez, E.M., Beltrán, F.J., Álvarez, P.M., 2013. Determination of Rate Constants for Ozonation of Ofloxacin in Aqueous Solution. Ozone Sci. Eng. 35, 186–195. https://doi.org/10.1080/01919512.2013.771530

Mathon, B., Coquery, M., Miege, C., Penru, Y., Choubert, J.-M., 2017. Removal efficiencies and kinetic rate constants of xenobiotics by ozonation in tertiary treatment. Water Sci. Technol. 75, 2737–2746. https://doi.org/10.2166/wst.2017.114

Matsui, Y., Yuasa, A., Li, F.-S., 1999. Pretreatment effects on activated carbon adsorption of humic substances: Distributed fictive component analysis. Water Sci. Technol. 40, 223–230. https://doi.org/10.1016/S0273-1223(99)00660-5

Meinel, F., Ruhl, A.S., Sperlich, A., Zietzschmann, F., Jekel, M., 2015. Pilot-Scale Investigation of Micropollutant Removal with Granular and Powdered Activated Carbon. Water. Air. Soil Pollut. 226. https://doi.org/10.1007/s11270-014-2260-y

Meinel, F., Zietzschmann, F., Ruhl, A.S., Sperlich, A., Jekel, M., 2016. The benefits of powdered activated carbon recirculation for micropollutant removal in advanced wastewater treatment. Water Res. 91, 97–103. https://doi.org/10.1016/j.watres.2016.01.009

Merel, S., Lege, S., Yanez Heras, J.E., Zwiener, C., 2017. Assessment of N-Oxide Formation during Wastewater Ozonation. Environ. Sci. Technol. 51, 410–417. https://doi.org/10.1021/acs.est.6b02373

Muller, U., Hess, F., Worch, E., 1996. Impact of organic matter adsorbability on micropollutant removal by activated carbon. J. WATER SUPPLY Res. Technol.-AQUA 45, 273–280.

Murphy, K.R., Hambly, A., Singh, S., Henderson, R.K., Baker, A., Stuetz, R., Khan, S.J., 2011. Organic Matter Fluorescence in Municipal Water Recycling Schemes: Toward a Unified PARAFAC Model. Environ. Sci. Technol. 45, 2909–2916. https://doi.org/10.1021/es103015e

Naumov, S., Mark, G., Jarocki, A., von Sonntag, C., 2010. The Reactions of Nitrite Ion with Ozone in Aqueous Solution - New Experimental Data and Quantum-Chemical Considerations. OZONE-Sci. Eng. 32, 430–434. https://doi.org/10.1080/01919512.2010.522960

Newcombe, G., Morrison, J., Hepplewhite, C., Knappe, D.R.U., 2002. Simultaneous adsorption of MIB and NOM onto activated carbon II. Competitive effects. Carbon 40, 2147–2156.

Office fédéral de l’environnement, Division Eaux, 2014. Rapport explificatif concernant la modification de l’ordonnance sur la protection des eaux.

Real, F.J., Benitez, F.J., Acero, J.L., Sagasti, J.J.P., Casas, F., 2009. Kinetics of the Chemical Oxidation of the Pharmaceuticals Primidone, Ketoprofen, and Diatrizoate in Ultrapure and Natural Waters. Ind. Eng. Chem. Res. 48, 3380–3388. https://doi.org/10.1021/ie801762p

Rocher, V., Paffoni, C., Gonçalves, A., Guérin, S., Azimi, S., Gasperi, J., Moilleron, R., Pauss, A., 2012. Municipal wastewater treatment by biofiltration: comparisons of various treatment layouts. Part 1: assessment of carbon and nitrogen removal. Water Sci. Technol. 65, 1705. https://doi.org/10.2166/wst.2012.105

Roustan, M., Debellefontaine, H., Do-Quang, Z., Duguet, J.-P., 1998. Development of a Method for the Determination of Ozone Demand of a Water. Ozone Sci. Eng. 20, 513–520. https://doi.org/10.1080/01919519809480338

Ruel, S.M., Choubert, J.M., Esperanza, M., Miège, C., Madrigal, P.N., Budzinski, H., Le Ménach, K., Lazarova, V., Coquery, M., 2011. On-site evaluation of the removal of 100 micro-pollutants through advanced wastewater treatment processes for reuse applications. Water Sci. Technol. 63, 2486. https://doi.org/10.2166/wst.2011.470

Schollée, J.E., Bourgin, M., von Gunten, U., McArdell, C.S., Hollender, J., 2018. Non-target screening to trace ozonation transformation products in a wastewater treatment train including different post-treatments. Water Res. 142, 267–278. https://doi.org/10.1016/j.watres.2018.05.045

Sgroi, M., Anumol, T., Roccaro, P., Vagliasindi, F.G.A., Snyder, S.A., 2018. Modeling emerging contaminants breakthrough in packed bed adsorption columns by UV absorbance and fluorescing components of dissolved organic matter. Water Res. https://doi.org/10.1016/j.watres.2018.09.018

Sgroi, M., Roccaro, P., Korshin, G.V., Vagliasindi, F.G.A., 2017. Monitoring the Behavior of Emerging Contaminants in Wastewater-Impacted Rivers Based on the Use of Fluorescence Excitation Emission Matrixes (EEM). Environ. Sci. Technol. 51, 4306–4316. https://doi.org/10.1021/acs.est.6b05785

Sgroi, M., Roccaro, P., Oelker, G., Snyder, S.A., 2016. N-nitrosodimethylamine (NDMA) formation during ozonation of wastewater and water treatment polymers. Chemosphere 144, 1618–1623. https://doi.org/10.1016/j.chemosphere.2015.10.023

Völker, J., Stapf, M., Miehe, U., Wagner, M., 2019. Systematic Review of Toxicity Removal by Advanced Wastewater Treatment Technologies via Ozonation and Activated Carbon. Environ. Sci. Technol. 53, 7215–7233. https://doi.org/10.1021/acs.est.9b00570

von Gunten, U., 2003a. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res. 37, 1443–1467. https://doi.org/10.1016/S0043-1354(02)00457-8

von Gunten, U., 2003b. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Res. 37, 1469–1487. https://doi.org/10.1016/S0043-1354(02)00458-X

Vulliet, E., Cren-Olivé, C., Grenier-Loustalot, M.-F., 2011. Occurrence of pharmaceuticals and hormones in drinking water treated from surface waters. Environ. Chem. Lett. 9, 103–114. https://doi.org/10.1007/s10311-009-0253-7

Zhang, S., Wu, C., Zhou, Y., Wang, Y., He, X., 2018. Effect of wastewater particles on catalytic ozonation in the advanced treatment of petrochemical secondary effluent. Chem. Eng. J. 345, 280–289. https://doi.org/10.1016/j.cej.2018.03.184

Zietzschmann, F., Mitchell, R.-L., Jekel, M., 2015. Impacts of ozonation on the competition between organic micro-pollutants and effluent organic matter in powdered activated carbon adsorption. Water Res. 84, 153–160. https://doi.org/10.1016/j.watres.2015.07.031

Zietzschmann, F., Stützer, C., Jekel, M., 2016. Granular activated carbon adsorption of organic micro-pollutants in drinking water and treated wastewater – Aligning breakthrough curves and capacities. Water Res. 92, 180–187. https://doi.org/10.1016/j.watres.2016.01.056

Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A.S., Sperlich, A., Meinel, F., Jekel, M., 2014. Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater. Water Res. 65, 297–306. https://doi.org/10.1016/j.watres.2014.07.043

Zimmermann, S.G., Wittenwiler, M., Hollender, J., Krauss, M., Ort, C., Siegrist, H., von Gunten, U., 2011. Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection. Water Res. 45, 605–617. https://doi.org/10.1016/j.watres.2010.07.080

Zucker, I., Lester, Y., Avisar, D., Hübner, U., Jekel, M., Weinberger, Y., Mamane, H., 2015. Influence of Wastewater Particles on Ozone Degradation of Trace Organic Contaminants. Environ. Sci. Technol. 49, 301–308. https://doi.org/10.1021/es504314t