Research article

Adsorption on activated carbon combined with ozonation for the removal of contaminants of emerging concern in drinking water

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ABSTRACT

The presence of Contaminants of Emerging Concern (CECs) in drinking water is raising concern for potential negative effects on human health. Ozonation and adsorption on activated carbon are the most suitable processes for CECs removal in drinking water treatment plants (DWTPs). This study aims at evaluating the performance of ozonation and adsorption as in-series processes compared to those of the stand-alone processes, focusing on 18 compounds representative of various CECs families. No CECs spike was performed to evaluate the effectiveness of these processes towards CECs at their environmental concentrations. Adsorption isotherms were performed on water samples collected before and after the full-scale ozonation in a DWTP, testing different combinations of ozone and activated carbon doses. Generally, the combination of the two processes was beneficial (83% average removal) compared to adsorption and ozonation alone (71% and 34% average removal respectively). The effect of ozonation on adsorption depends on CECs reactivity with ozone, since ozonation improves the adsorption performance of poorly-oxidizable CECs, but worsens that of well-oxidizable compounds. The removal of organic matter, investigated by absorbance at 254 nm and fluorescence, by ozonation reduces competition for the subsequent CECs removal by adsorption (up to 20% increase of total CECs adsorption). Finally, the removal of both absorbance and fluorescence seems to be a good proxy variables for total CECs adsorption, with different relationships depending on the presence of ozonation. Conversely, it is not effective for ozonation, since the relationship depends on the reactivity of the specific CEC with ozone.

1. Introduction

In the last decades, the presence of Contaminants of Emerging Concern (CECs) in the aquatic environment has become an environmental issue of growing global concern (Puri et al., 2023). CECs include more than 700 anthropogenic and natural compounds, as Pharmaceuticals and Personal Care Products (PPCPs), endocrine disrupting compounds, industrial chemicals and pesticides, commonly detected in the aquatic environment at trace concentrations, from ng/L to µg/L (Khan et al., 2020). CECs are accounted as pseudo-persistent, since they constantly enter the environment (Borrull et al., 2021), through different sources, mainly anthropogenic, being wastewater treatment plants (WWTPs) the most important one. WWTPs are not specifically designed to remove CECs (Luo et al., 2014; Margot et al., 2013), which are then discharged in natural environments, representing a threat for

the production of drinking water (Lladó et al., 2015; Vasilachi et al., 2021), since CECs produce adverse effects for human health (Fent et al., 2006). Hence, the removal of CECs during drinking water production is a current key issue. According to the precautionary principle, adequate removal processes should be adopted for the upgrade and/or retrofit of drinking water treatment plants (DWTPs), to maximize CECs removal and to comply with future standards on drinking water quality. Among the most effective processes available today for CECs removal and that are usually present in DWTPs, the most suitable are adsorption on activated carbon (Calisto et al., 2015) and advanced oxidation processes, being ozonation the most widely adopted (Guillossou et al., 2020). Compared to the numerous studies on the occurrence and removal of CECs in WWTPs, much less is known about their behavior in DWTPs (Borrull et al., 2021), especially when realistic conditions (e.g. wide range of CECs, CECs concentrations, presence of competing

compounds, process operating conditions) are considered. In fact, adsorption isotherms are mostly carried out on synthetic water matrices and/or with CECs spike, to greatly increase initial CECs concentrations with respect to those detected in water (Bachmann et al., 2021), due to analytical limitations (Egea-Corbacho et al., 2019). Similarly, studies on the removal of CECs in DWTPs by ozonation are still very limited for realistic conditions (Gorito et al., 2021).

While in WWTPs, ozonation and activated carbon adsorption are mainly used as stand-alone tertiary treatments, in DWTPs adsorption is usually preceded by ozonation (Xia et al., 2020). Nevertheless, the effect of ozonation on the subsequent adsorption has mainly been studied: (i) in synthetic water matrices (*inter alia*, Lee et al., 2013; Schoutteten et al., 2016), (ii) for wastewater tertiary treatment (*inter alia*, Zietzschmann et al., 2015; Guillossou et al., 2020; Sauter et al., 2021), or (iii) in drinking water spiked with one or multiple CECs at concentrations higher than the environmental ones (*inter alia*, Ahn et al., 2015). However, the performances of ozonation, adsorption and their combination are highly dependent on water quality, initial CECs concentrations, and concentration of competing compounds, as Dissolved Organic Matter (DOM), recognized as competitor for CECs removal during both ozonation (Rizzo et al., 2019) and adsorption (Guillossou et al., 2020). Therefore, results derived from synthetic water, wastewater or spiked drinking water do not provide reliable indications about the performance of ozonation and adsorption in real conditions, that conversely requires the investigation of real water matrices without CECs spike and where more than just one CEC is present together with DOM. Only Ulberg and co-authors (Ullberg et al., 2021) investigated the influence of ozonation on adsorption in a real drinking water with no CECs spike. However, the influence of ozonation on adsorption performance was only studied on the sum of the 15 target pharmaceuticals, without compound-specific indications on such effect.

Finally, limitations above reported are also due to the complexity and cost of CECs analysis, which restrict both the effective possibility to detect them and the affordable number of samples which can be analyzed. Absorbance at 254 nm and fluorescence excitation-emission spectroscopy, usually used to quantify and characterize DOM (Guillossou et al., 2021), have been proposed as surrogate parameters to monitor CECs removal, by-passing at least the restrictions about the number of analyzable samples. While some studies are available about the use of absorbance at 254 nm or fluorescence as proxy for CECs removal during adsorption (*inter alia*, Anumol et al., 2015; Cantoni et al., 2021), only very few and recent studies exist referred to ozonation (Deniere et al., 2021; Song et al., 2022). In addition, no study was conducted so far analyzing the effect of ozonation on the correlation between CECs removal and absorbance at 254 nm or fluorescence removal in the subsequent adsorption. Furthermore, it has to be mentioned that absorbance at 254 nm and fluorescence removal are mainly reported to be surrogates of the removal of a single compound (Guillossou et al., 2021; Park et al., 2019), and not of the overall removal of CECs present in water, that can be instead useful for full-scale process management.

In this framework, our study aims at providing new insights about the performance of the combination of ozonation (OX) and adsorption (ADS) on activated carbon for the removal of a wide range of CECs in drinking water. Compared to the current gaps on this topic, the study was designed with respect to the following aspects: (i) clarifying the influence of ozonation on the subsequent adsorption as a function of the investigated CECs, not from a mechanistic point of view, but focusing on the removal efficiency and the adsorption capacity; (ii) evaluating such performances in real environmental conditions, without spiking CECs in collected real water matrices; (iii) providing information on iodinated contrast agents, for which removals were not investigated in previous similar studies, although they are present at high concentrations in the water sources; (iv) investigating the possibility of using absorbance at 254 nm and fluorescence as surrogate parameters to monitor the total CECs removal for all the studied processes (OX, ADS, OX + ADS). In detail, the performances of the three processes (OX, ADS, OX + ADS)

were investigated, considering OX and ADS as benchmark for the assessment of the performance of the combined process OX + ADS. The fate of each CEC was monitored together with the fate of DOM, to account for its competitive effect on CECs adsorption. Besides, the feasibility to use absorbance at 254 nm and fluorescence as proxy for the total CECs removal was explored for the three processes. Real water matrices were collected at the inlet and outlet of the full-scale ozonation contactor of a DWTP in Italy and adsorption isotherms were determined for 18 CECs with no additional spike, to work at their environmental concentrations. The selected 18 CECs are representative of different affinity towards both ozonation and adsorption, including also iodinated contrast agents. Our results permit to derive general outcomes about the effectiveness of the combined process on CECs removal and absorbance at 254 nm and fluorescence as proxy variable for process control.

2. Materials and methods

2.1. Water matrices

Pontelagoscuro DWTP (Ferrara, Italy) is located at the hydrological closure section of the Po River and is fed directly on Po River water. After pre-sedimentation, raw water flows in a storage basin (hydraulic retention time, HRT: 3 days), then to pre-oxidation with potassium permanganate, coagulation, flocculation and sedimentation, rapid sand filtration, ozonation, granular activated carbon adsorption and final disinfection by chlorine dioxide. The investigated water matrices were collected at the inlet and at the outlet of the full-scale ozonation contactor. Water matrix collected at the inlet of the ozonation will be referred as "PreO3" while water matrices collected at the outlet of the ozonation will be referred as "PostO3". During sampling, operating conditions were set to a specific flow rate (HRT: 18 min) and three target ozone doses: 0.5 mg_{O3}/L (PostO3-L, corresponding to 0.4 mg_{O3}/mg_{TOC}), 1.0 mg_{O3}/L (PostO3-M, 0.8 mg_{O3}/mg_{TOC}) and 1.5 mg_{O3}/L (PostO3-H, 1.2 mg_{O3}/mg_{TOC}); both HRT and ozone doses were set based on the DWTP operating data, as explained in Supplementary Materials (Section S1, Fig. S1). One HRT was waited between the samples collection of the PreO3 water matrix and the first PostO3 water matrix. After changing the ozone dose, two HRTs were waited before sampling the next PostO3 matrix, to achieve stable conditions in the ozonation contactor; sodium thiosulfate was immediately added in excess in the PostO3 samples, to quench residual ozone. All the water samples were maintained in dark conditions at 4 °C during transport to the laboratory. Three sampling campaigns were carried out between June and July 2021.

2.2. Activated carbon

Experiments were performed using the virgin microporous activated carbon (AC) derived from bituminous coal (Sicav, Italy) used in Pontelagoscuro DWTP. BET (Brunauer-Emmett-Teller) specific surface area, micropore volume fraction, iodine number and bulk density (as provided by the supplier) were >1000 m^2/g, >45%, >1000 mg/g and 480 g/L respectively; pH of point of zero charge (pH_{PZC}) was equal to 7.5. Activated carbon was milled and sieved (63–125 μm particle size) for isotherms batch experiments (ASTM International, 2004). An AC stock solution (5 g/L) was prepared in advance, for wetting purposes, using deionized water and stored in the dark at room temperature.

2.3. Selected CECs

18 CECs (Table 1) were selected among 114 CECs monitored in Pontelagoscuro DWTP, as the CECs mainly detected in concentrations much higher than the Limit of Quantification (LOQ) of the analytical methods. These 18 CECs differ for their main characteristics (Table 1), in detail: (i) the partition coefficient n-octanol-water ($logK_{OW}$), which indicates the hydrophobicity of a compound and therefore its affinity with AC; (ii) the kinetic constant of reaction with ozone ($logK_{O3}$), which

Table 1
List if the monitored CECs: abbreviation, main characteristics (logK$_{OW}$, logK$_{O3}$, pK$_a$), type of compound and limit of quantification (LOQ). The asterisk indicates compounds for which logK$_{O3}$ values are not available in literature; for OSS and PRS, they were estimated on the basis of their observed reactivity (see Fig. 3), as the mean value between ACS, BNZ, MBN for OSS, and the mean value between GAB, VAL for PRS.

CEC	Code	logK$_{OW}$	logK$_{O3}$	pK$_a$	Type	LOQ
		–	L/(s mol)	–		ng/L
Acesulfame	ACS	−0.55	1.94	2.0	Sweetener	1
Benzotriazole	BNZ	1.3	2.38	8.2	UV-filter	1
Caffeine	CAF	−0.07	2.81	10.4	Stimulant	10
Carbamazepine	CBZ	2.45	5.48	13.9	Antiepileptic	1
Diclofenac	DCF	4.51	6.20	4.2	Anti-inflammatory	1
Gabapentin	GAB	−1.51	1.18	3.7	Antiepileptic	1
Iomeprol	IOM	−1.45	< −1.00	11.7	Contrast agent	1
Iopamidol	IPM	−0.74	0.15	10.7	Contrast agent	10
Iopromide	IPR	−0.45	< −0.10	9.9	Contrast agent	1
Irbesartan	IRB	5.31	1.36	4.1	Antihypertensive	1
Metformin	MTF	−2.64	0.08	12.4	Diabetes drug	1
Methyl-benzotriazole	MBN	1.89	2.60	9.2	UV-filter	1
Oxypurinol*	OSS*	−1.67	2.3	6.3	Enzyme inhibitor	10
Paracetamol	PAR	0.46	3.15	9.5	Analgesic	1
Paraxanthine*	PRS*	−0.22	1.38	10.8	Stimulant	1
Saccharine*	SAC*	0.91	n.a.	1.9	Sweetener	1
Telmisartan	TLM	8.42	5.08	4.5	Antihypertensive	1
Valsartan	VAL	4.00	1.58	4.7	Antihypertensive	1

indicates the reactivity with ozone, (iii) the acid dissociation constant pK$_a$, which is an indicator of the charge of the compound. Higher logK$_{OW}$ and logK$_{O3}$ are, higher is the affinity of the compound towards AC and the reactivity with ozone. For OSS, SAC and PRS, the logK$_{O3}$ value was not found in literature.

2.4. Batch isotherm experiments

Isotherm experiments were performed on PreO$_3$ and PostO$_3$ matrices. AC doses (0, 2, 5, 10, 20 and 30 mg/L), typically applied in tests for AC performance evaluation towards CECs (Rout et al., 2021), were obtained adding the corresponding volumes of the AC stock solution (homogenized by stirring) into 2.5 L of each water matrix inside a glass beaker. Each beaker was then covered in the dark and mixed with a magnetic stirrer for 48 h at room temperature, whereupon AC was separated by filtration (0.7 μm pore size, glass microfiber, Whatman). The filtered water was analyzed for pH, alkalinity, TOC (Total Organic Carbon), absorbance at 254 nm (UVA$_{254}$), fluorescence and CECs. UV absorption spectra (190–800 nm) was also determined to correct fluorescence analyses.

CECs adsorption isotherms data were fitted by the Freundlich equation, assuming multiple adsorption sites working in parallel with different free energies (Schwarzenbach et al., 2003):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{1}$$

where q$_e$ [ng/mg] is the equilibrium concentration of the target compound on the solid phase, C$_e$ [ng/L] is the equilibrium concentration in solution, K$_F$ [(ng/mg)/(ng/L)$^{1/n}$] is the Freundlich adsorption coefficient and 1/n [-] is the Freundlich exponent which provides a measure for the adsorption intensity. The three isotherm replicates for each water matrix were used as a single data set, to which was applied a linear regression to estimate the parameters of the Freundlich isotherm model.

2.5. Process performance assessment

Removal efficiencies for the two stand-alone processes (OX, ADS) and the overall removal efficiency for their combination in series (OX + ADS) were calculated as follows:

$$OX\ removal[\%] = \frac{C_{PreO_3} - C_{PostO_3,i}}{C_{PreO_3}} \bullet 100 \tag{2}$$

$$ADS\ removal\ before\ OX[\%] = \frac{C_{PreO_3} - C_{PreO_3,j}}{C_{PreO_3}} \bullet 100 \tag{3}$$

$$ADS\ removal\ after\ OX[\%] = \frac{C_{PostO_3,i} - C_{PostO_3,i,j}}{C_{PostO_3,i}} \bullet 100 \tag{4}$$

$$OX + ADS\ removal[\%] = \frac{C_{PreO_3} - C_{PostO_3,i,j}}{C_{PreO_3}} \bullet 100 \tag{5}$$

where *i* is the ozone dose and *j* is the AC dose.

2.6. Analytical methods

The pH$_{PZC}$ was determined by the pH *drift method* (Lopez-Ramon et al., 1999). Water pH and temperature were measured with Hach Lange HQ40D equipped with a PHC101 probe. Alkalinity was determined through an autotitrator (MAN-TECH) by APAT-IRSA/CNR (2003) methods. TOC was measured according to the standard method ISO/DIS 20236. UV spectra and UVA$_{254}$ were measured with a quartz full transparent cuvette of 1 cm optical path using a *Hach Lange* UV-VIS Detector DR6000. Fluorescence analyses were performed using the same cuvette and setting the parameters as in Table S1 in an *Agilent Cary Eclipse* spectrofluorometer. Data were analyzed using MATLAB *drEEM-0.6.3* package, to correct Raman and Rayleigh scatters (Fig. S2a) through the absorbance spectrum determined on the respective sample. The total fluorescence (TF) was calculated as the integral of the fluorescence in the area inside the first order Raman and the second order Rayleigh (Fig. S2b).

CECs analyses were performed using Ultra Performance Liquid Chromatography with a triple quadrupole mass detector (Agilent UPLC-QqQ: 1290 UPLC-system with ECLIPSE Plus C18 150 mm × 2.1 μm x 3.0 mm column and 6470 QqQ) and evaluated by linear calibration with nine to twelve calibration points in the range of 0.001–1.0 μg/L and correlation coefficients for all the analytes greater than 0.99. Details are reported in Supplementary Materials (Section 2). LOQ values were verified prior to the analysis by multiple measurement of spiked water samples at the concentration levels of LOQ according to ISO/TS 13530 Annex A. The analytical method LOQs for each CECs are reported in Table 1.

3. Results and discussion

First, we characterize the water matrices in terms of DOM, which is considered the main competitors for CECs adsorption. About CECs removal processes, ozonation and adsorption are often adopted as in series processes in DWTPs, instead of as stand-alone processes, as main barrier for anthropic micropollutants spread (De Ridder et al., 2011; Guillossou et al., 2020). The performance of each stand-alone process represents the benchmark for evaluating the performance of the combined process OX + ADS, having in mind that knowledge on the performances of those processes are still very limited for the 18 target CECs, especially at environmental concentrations in DWTPs (Borrull et al., 2021; Gorito et al., 2021). For this reason, we firstly evaluated the efficiency of the OX and ADS as stand-alone processes at doses typically adopted in DWTPs, and then we compared their performances with the one of the combined process OX + ADS to investigate its potential in effectively remove a wide range of CECs. Finally, we report the assessment of absorbance at 254 nm and fluorescence as proxy variables of CECs removal. In fact, absorbance at 254 nm and fluorescence measurements are usually less demanding both in terms of time and costs with respect to CECs analysis. Therefore, it is important to evaluate whether it is possible to use them to monitor CECs removal by OX and ADS, before drinking water entering the distribution network.

3.1. Organic matter in not-oxidized and oxidized water matrices

The main characteristics of the $PreO_3$ and $PostO_3$ matrices collected at the full-scale DWTP are summarized in Table 2. In accordance with previous studies (Jin et al., 2019; Rizzo et al., 2019), no significant TOC differences were observed between the oxidized ($PostO_3$) and not-oxidized matrices ($PreO_3$), stressing how TOC is not enough sensitive to monitor organic matter variations during ozonation, especially at low TOC concentrations as in this case study. Instead, when absorbance at 254 nm or fluorescence are adopted, a decrease of these parameters is observed while increasing the ozone dose in $PostO_3$ matrices compared to $PreO_3$ matrix, confirming their sensitivity in describing changes in organic matter, as highlighted also by Guillossou et al. (2020).

Both absorbance at 254 nm and total fluorescence decrease with increasing ozone and activated carbon doses, as shown in Fig. 1a and b, confirming results by Huang et al. (2017). Ozonation is quoted for the reduction of molecules size transforming them into simpler ones (Jin et al., 2019). This leads to a lower occupation rate of adsorption active sites, a smaller probability of pore blocking and less competition for the same active sites promoting the adsorption of organic matter, but also of other compounds (Kennedy and Summers, 2015). The behavior of absorbance at 254 nm and total fluorescence can be well described by an exponential decay ($R^2 = 0.92$–0.98), so a double exponential decay has been selected to describe removals as a function of both ozone and activated carbon doses ($R^2 = 0.82$-0.81). Equations are reported in Table S3, while fitted curves are shown in Fig. 1c and d. In the investigated conditions, the removal of absorbance at 254 nm and total fluorescence is more strongly affected by ADS instead of OX, as confirmed by the Spearman correlation coefficients greater for the activated carbon dose (0.739 for UVA_{254} and 0.777 for TF) than for the ozone dose (0.490 for UVA_{254} and 0.499 for TF). As shown in Fig. 1c and 1d, a higher removal of absorbance at 254 nm and total fluorescence can be obtained by ADS as stand-alone process (maximum removal, to be read on the x-axis where ozone dose is 0 mg/L, equal to 65% and 85% respectively) than by OX alone (maximum removal, to be read on the y-axis where AC dose is 0 mg/L, equal 50% and 76% respectively). However, the combination of the two processes OX + ADS, that can be observed in the area of the graphs according to the color scale, allows to achieve the highest removal (77% and 92% respectively).

Fluorescence analyses, compared to aborbance at 254 nm, allowed to

Table 2

Main characteristics (mean ± standard deviation of the 3 sampling campaigns) of the $PreO_3$ and $PostO_3$ matrices: pH, alkalinity, organic matter content (TOC, UVA_{254} and TF) and concentration of CECs (listed by increasing $logK_{OW}$). The percentage of CECs concentration values below LOQ, among all the 18 samples before and after adsorption tests, is also reported for each matrix. CECs neglected in data analyses are highlighted in grey.

| Matrix	$PreO_3$		$PostO_3$-L		$PostO_3$-M		$PostO_3$-H	
Specific O_3 dose mg_{O3}/mg_{TOC}	–		0.4		0.8		1.2	
pH	8.3 ± 0.10		8.2 ± 0.12		8.2 ± 0.10		8.2 ± 0.11	
Alkalinity mg/L	180 ± 1.5		178 ± 1.5		178 ± 1.5		178 ± 1.5	
TOC mg/L	1.3 ± 0.12		1.6 ± 0.59		1.1 ± 0.14		1.4 ± 0.38	
UVA_{254} 1/m	2.6 ± 0.55		1.7 ± 0.35		1.6 ± 0.76		1.3 ± 0.20	
TF a.u.	294 ± 40.8		131 ± 28.8		99 ± 32.6		70 ± 12.9	
CECs	C_o ng/L	<LOQ %	C_o ng/L	<LOQ %	C_o ng/L	<LOQ %	C_o ng/L	<LOQ %
MTF	179 ± 79	0	195 ± 85	0	179 ± 88	0	158 ± 90	0
OSS	1094 ± 1059	37	272 ± 118	30	92 ± 84	53	101 ± 51	61
GAB	16 ± 2	11	13 ± 3	0	8 ± 2	0	7 ± 3	0
IOM	241 ± 57	11	265 ± 88	10	208 ± 93	16	207 ± 103	22
IPM	1612 ± 690	11	1542 ± 650	15	1566 ± 784	11	1039 ± 754	28
ACS	182 ± 82	0	132 ± 47	0	78 ± 54	0	53 ± 46	0
IPR	157 ± 32	21	126 ± 62	30	94 ± 31	21	71 ± 37	50
PRS	27 ± 11	5	18 ± 11	0	11 ± 3	0	14 ± 11	0
CAF	62 ± 38	5	74 ± 42	0	62 ± 28	0	43 ± 42	0
SAC	3 ± 1	42	3 ± 1	40	3 ± 1	37	3 ± 1	56
PAR	2 ± 1	58	2 ± 1	30	2 ± 1	37	1 ± 0	78
BNZ	213 ± 41	0	122 ± 56	0	30 ± 23	0	14 ± 8	6
MBN	388 ± 84	5	118 ± 76	0	7 ± 3	0	6 ± 2	0
CBZ	28 ± 5	79	2 ± 0	90	1 ± 0	89	<1	100
VAL	29 ± 14	21	21 ± 14	25	22 ± 13	47	7 ± 4	39
DCF	2 ± 1	47	1 ± 0	60	1 ± 0	63	1 ± 0	44
IRB	524 ± 363	26	255 ± 240	50	112 ± 114	47	95 ± 118	61
TLM	449 ± 286	46	127 ± 163	50	34 ± 44	37	18 ± 15	72

(a)

(b)

(c)

(d)
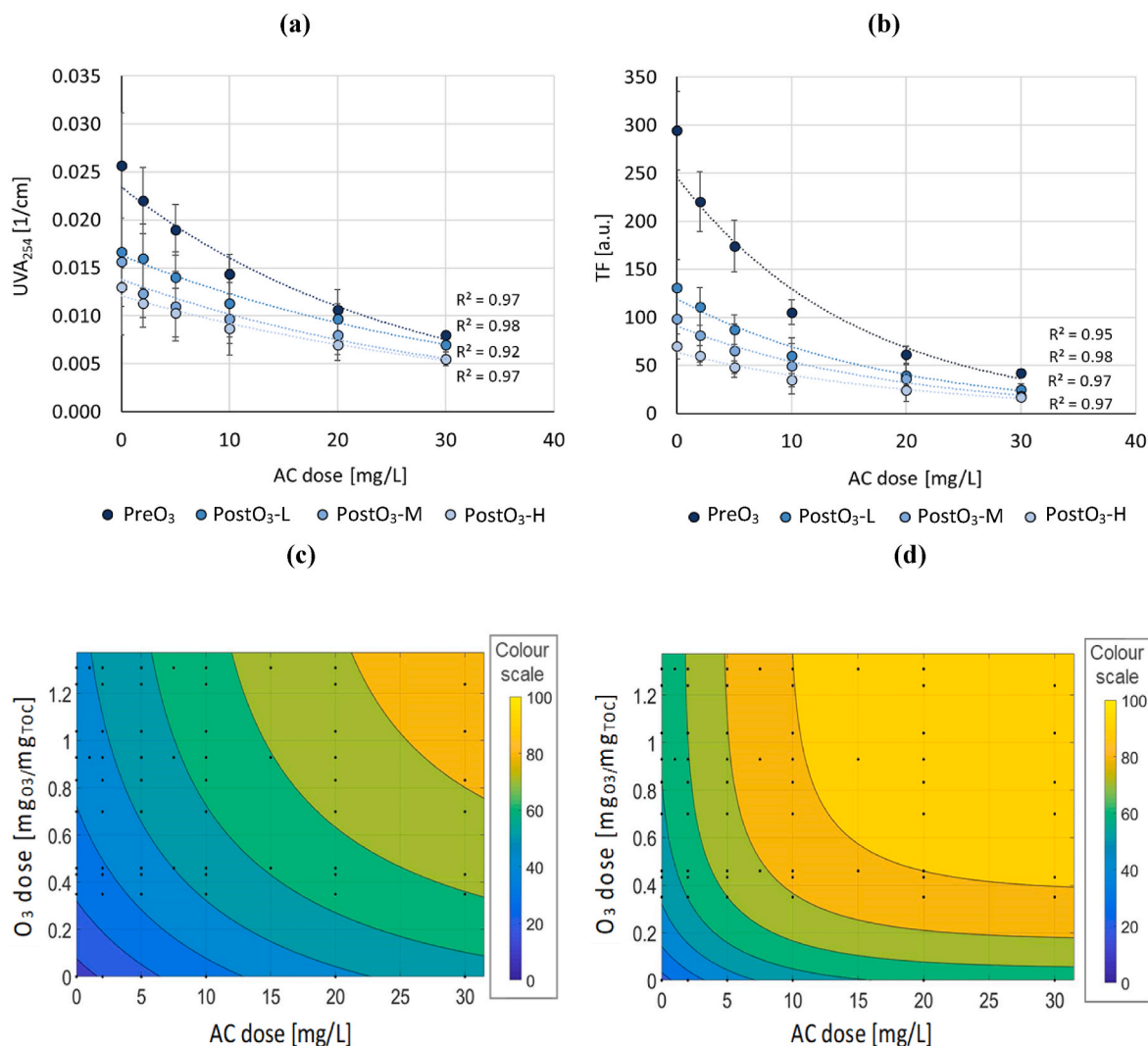
Fig. 1. Mean values ± standard deviation (3 replicates) of (a) UVA_{254} and (b) TF, as a function of AC dose in $PreO_3$ and $PostO_3$ matrices. The exponential fitting curves are shown and respective R^2 values are reported. Removal of (c) UVA_{254} and (d) TF as a function of the specific ozone dose and AC dose.

observe variations in the composition of organic matter due to OX and ADS. In agreement with Jin et al. (2019) and Park et al. (2019), a relevant decrease in total fluorescence with increasing ozone and activated carbon doses was observed, evident also by a visual inspection of the excitation-emission matrices of the various samples. As example, the excitation-emission matrices of one replicate of $PreO_3$, $PostO_3$-L, $PostO_3$-M and $PostO_3$-H matrices are shown in Fig. S3 while all water matrices treated with 2, 10, 30 mg_{AC}/L are shown in Fig. S4. On average, total fluorescence decreased of 55% by OX and of 65% by ADS.

3.2. CECs occurrence in not-oxidized and oxidized water matrices

As for CECs concentrations in $PreO_3$ and $PostO_3$ matrices (Table 2), high variability can be observed among different CECs and, for the same CECs, among the four water matrices.

Moreover, high variability exists also in the percentages of data below the LOQ, among all the samples before and after ADS. These variabilities can be ascribed to the wide range of both reactivity with ozone ($logK_{O3}$ between −1 and 6) and affinity with activated carbon ($logK_{OW}$ between −3 and 8.5) covered by the 18 CECs, as represented in the treatment suitability map in Fig. 2. In this map, CECs are displayed as a function of their $logK_{OW}$ and $logK_{O3}$, providing a readily available preliminary indication about the possibility to remove them by OX and/ or ADS. In previous studies the investigated CECs were represented as a

function of $logK_{O3}$ (Guillossou et al., 2020; Kovalova et al., 2013) for ozonation removal efficiency, or as a function of $logK_{OW}$ for adsorption removal efficiency (Campinas et al., 2021; Kovalova et al., 2013; Viegas et al., 2020), but no studies could be found proposing the joint visualization of these information as support to the selection of the most appropriate process for CECs removal.

Among the 18 analyzed CECs, 8 CECs were discarded (in grey in Table 2) for further extensive analyses, due to: (i) percentage of values below LOQ higher than 45% for at least 3 out of 4 types of water matrices (CBZ, DCF, IRB, TLM); (ii) initial concentration (C_0) values very close to LOQ (C_0 - LOQ <2 ng/L) indicating a negligible presence of these compounds in the analyzed water matrices (PAR, SAC, DCF); (iii) variability of ADS removal in the same order of magnitude of the uncertainty of the analytical method (MTF, OSS). The CECs discarded due to the high percentage of values below LOQ are medium- (IRB) or well-oxidizable (high $logK_{O3}$>5) and the most hydrophobic (high $logK_{OW}$) among the 18 CECs. Thus, it can be assumed that they can be well removed by OX and/or ADS, leading to high removal efficiencies and hence a high number of concentration values below LOQ. This is in agreement with previous studies reporting the high removals of CECs with $logK_{O3}$ higher than 5 (Lee et al., 2013; Guillossou et al., 2020). DCF concentrations was already very close (C_0 - LOQ <2 ng/L) or equal to LOQ, indicating its negligible presence in the analyzed water matrices. CBZ is removed both by ozone and activated carbon between 93% and
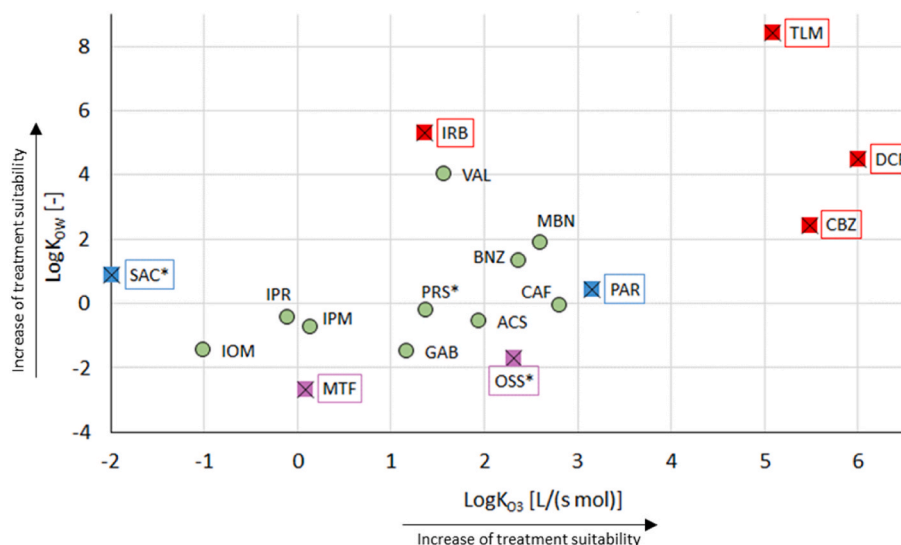
Fig. 2. Treatment suitability map, where CECs are displayed as a function of $logK_{O3}$ and $logK_{ow}$. In green the CECs selected for data analysis, in red the CECs discarded due to the high number of values lower than the LOQ, in blue the CECs discarded due to the proximity of average initial concentration to LOQ, in purple the CECs whose concentration after adsorption is in the same order of magnitude as the uncertainty of the analytical method. The asterisk indicates estimated $logK_{O3}$ values. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

greater than 98% considering all the tested doses. This is in agreement with previous studies reporting removals for CBZ and DCF above 92% at low ozone doses (<1 mg_{O3}/mg_{DOC}) (Bourgin et al., 2018; Kovalova et al., 2013; Mousel et al., 2021; Reungoat et al., 2010; Sun et al., 2018) and greater than 96% for doses equal to 8 mg_{AC}/L (Kovalova et al., 2013). A smaller number of studies are conducted on IRB and TLM. For TLM a removal of 96% is obtained already at the medium ozone dose (0.8 mg_{O3}/mg_{TOC}), while IRB can be removed at 81% at the medium ozone dose and 85% at the highest ozone dose (1.2 mg_{O3}/mg_{TOC}) in line with its $logK_{O3}$ value. This is also in agreement with Bourgin et al. (2018) that found removals equal to 89% for IRB and $>94\%$ for TLM, at a 0.97 mg_{O3}/mg_{DOC} in a full-scale WWTP. Their $logK_{OW}$ value is greater than those of CBZ and DCF, so they are expected to be well removed also by adsorption on activated carbon. In this study we found that 10 mg_{AC}/L can remove more than 99% of both these compounds in all the tested water matrices, that is comparable to Margot et al. (2013), who found 98% removal of IRB with 12 mg_{AC}/L in a WWTP. No evidence about TLM removal by adsorption on activated carbon was found in literature. As for MTF, whose removal variability by ADS is comparable with the uncertainty of the analytical method, it is clear from the treatment suitability map that it has low chances to be well removed by ADS, being the most hydrophilic (low $logK_{OW}$) among the 18 investigated CECs, and by OX (low $logK_{O3}$), considering that it has also the lowest $logK_{O3}$ value with respect to the other low oxidizable CECs (Rizzo et al., 2019). In fact, even with 30 mg_{AC}/L only 26% MTF removal was observed and it was also poorly removed by OX (negligible removal at the lowest ozone dose and 13% at the highest dose), in agreement with Sauter et al. (2021), who found null removal at 0.65 mg_{O3}/mg_{DOC}. About CECs whose removal variability by ADS is comparable with the uncertainty of the analytical method, they are the most hydrophilic (low $logK_{OW}$) and have the lowest $logK_{O3}$ value with respect to the other low-oxidizable CECs, as shown in the treatment suitability map in Fig. 2. Hence, those CECs display low chances to be well removed by ADS or OX, leading to highly variable removal efficiencies as a function of the specific water matrix characteristics. The only exception is related to OSS removal by ADS: OSS $logK_{OW}$ suggests a hydrophilic behavior which is not in agreement with what was found in the present study. Actually, in line with our study, Sperlich et al. (2017) found that OSS was readily adsorbable at extents roughly comparable to the ones for CBZ. This finding could be of practical importance since

mass-spectrometric monitoring of CBZ is much less laborious than the one for OSS (Sperlich et al., 2017), thus CBZ behavior could be studied in order to give indications also on OSS removal efficiencies. About OSS reactivity with ozone, its $logK_{O3}$ value was not found in literature; nevertheless, OSS could be removed at 53%, 74%, 96% respectively in PostO3-L, PostO3-M and PostO3-H matrices, which is in line with Sauter et al. (2021), that found 45% removal at 0.65 mg_{O3}/mg_{DOC}.

Summarizing, the use of the treatment suitability map may help in giving preliminary indications for predicting CECs behavior during ozonation and/or activated carbon adsorption. Due to the large variety of CECs present in the environment and the frequently adopted high LOQs compared to the environmental concentrations, it is well known that the fate of some CECs cannot be analyzed in detail, so an approach using the proposed treatment suitability map could be useful for the design and management of the removal processes. For this reason, the map is derived by basic compound characteristics usually available, such as $logK_{OW}$ and $logK_{O3}$, being a supporting decision tool, not a tool to explain detailed reaction mechanisms.

3.3. Performances of ozonation and adsorption as stand-alone processes

The removal efficiency of OX and ADS, calculated with Eq. (2) and Eq. (3), are reported in Fig. 3 for each CEC, ozone dose and for all tested activated carbon doses. Removal efficiencies are summarized in Table S4.

CBZ is removed both by OX and ADS between 93% and greater than 98% considering all the tested doses, in agreement with previous studies with comparable operating conditions (Bourgin et al., 2018; Kovalova et al., 2013; Mousel et al., 2021; Reungoat et al., 2010; Sun et al., 2018; Kovalova et al., 2013, 2013). A smaller number of studies are available on IRB and TLM. For TLM a removal of 96% was obtained in PostO3-M matrix, while IRB was removed at 81% in PostO3-M matrix and 85% in PostO3-H matrix, in agreement with Bourgin et al. (2018). Good adsorption removals of both these compounds were observed in all the tested water matrices, that is comparable to Margot et al. (2013) as for IRB, while no evidence about TLM removal by ADS was found in literature. As for MTF, low removal efficiencies were obtained both by OX (13% in PostO3-H matrix and 26% with 30 mg_{AC}/L), in agreement with Sauter et al. (2021). These results can be explained analyzing the treatment suitability map: MTF has low chances to be well removed by
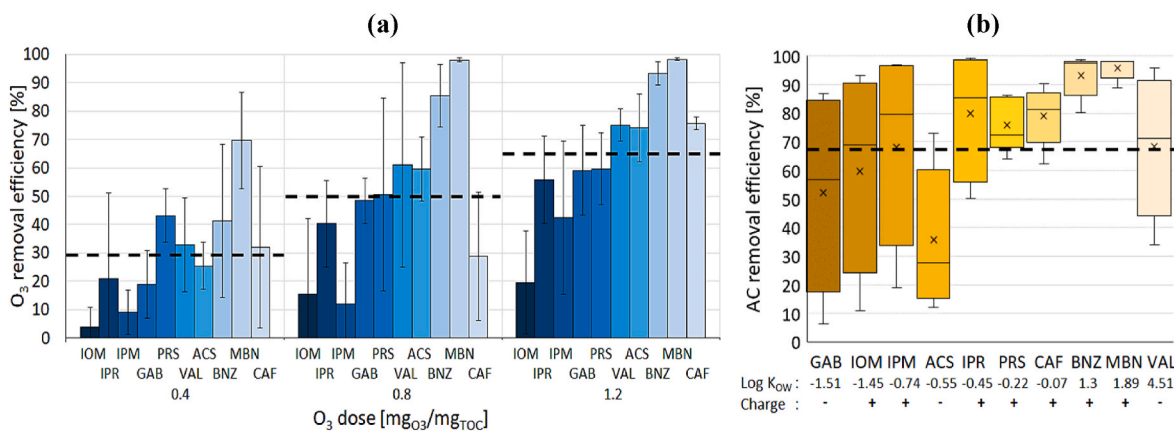
Fig. 3. CECs removals (mean ± standard deviation) by (a) OX and (b) ADS (considering all AC doses in PreO$_3$ matrix), calculated using Eqs. (2) and (3). CECs are listed by increasing logK$_{O3}$ (a) and logK$_{ow}$ (b). The black hatching lines indicate the average CECs removals.

ADS, being the most hydrophilic among the 18 investigated CECs, and by OX, considering that it has also the lowest logK$_{O3}$.

As for OX performance, the average CECs removal (29% in PostO$_3$-L, 50% in PostO$_3$-M and 65% in PostO$_3$-H), as well as the removal of each CEC, increases as the ozone dose increases. As expected, at the same ozone dose, the removal extent is related to the logK$_{O3}$ of each CEC, being higher for more oxidizable compounds (having higher logK$_{O3}$), as also observed by Kovalova et al. (2013). This suggests that the logK$_{O3}$ is a good parameter for the description of the suitability of ozonation to remove CECs in the DWTP, and no significant errors result from neglecting information on CEC logK$_{OH}$, that represents CECs reactivity constant with hydroxyl radicals (•OH) generated during ozonation. This could be due to the fact that ozone exhibits reaction rate constants (logK$_{O3}$) over several orders of magnitude in the range from 0 to 7 L/(mol s) (von Sonntag and von Gunten, 2012). Most of the analyzed CECs display logK$_{O3}$ values falling in this range, permitting to appreciate different behaviors towards ozone. In addition, the main source for the generation of •OH is organic matter at basic pH. Thus, it is possible to speculate that oxidation through hydroxyl radicals, even if it occurs, provides a minority contribution in the studied DWTP, where ozonation is located almost at the end of the treatment train and water has stably low TOC values (see Table 2). Thus, it is possible to identify three groups of compounds related to three classes of removal efficiencies: (i) removals below average for slowly reactive compounds (logK$_{O3}$<1: IOM, IPR, IPM); (ii) removals similar to average for medium reactive compounds (1<logK$_{O3}$<2: GAB, PRS, VAL, ACS); (iii) removals above average for very reactive compounds (logK$_{O3}$>2: BNZ, MBN). One exception is observed for CAF, whose logK$_{O3}$ is the highest, but the removal is affected by high variability, especially at the lower and medium ozone doses. However, it is important to report that this classification is based on the observed removals by ozonation for this case study and it is slightly different from other classifications found in the literature, mainly due to differences in the analyzed water matrices and target CECs (Lee et al., 2013; Kovalova et al., 2013; Guillossou et al., 2020; Sauter et al., 2021). In detail, in other studies, wastewater is used, characterized by a higher organic matter content, raising the importance of considering also hydroxyl radicals in CECs removal. Then, other studies classified CECs having logK$_{O3}$ between 1 and 7, setting a threshold equal to 5, while in our case, monitored CECs had logK$_{O3}$ between −1 and 3; thus the two ranges overlap only partially. For this reason, the classifications proposed in literature were modified to fit the conditions of the investigated case study, specifically: (i) neglecting the reactivity towards hydroxyl radicals relying only on the reactivity towards ozone, and (ii) setting two values of logK$_{O3}$ matching the monitored group of CECs.

Average ADS performance (69%) is better than the one of OX, not only for organic matter removal, but also for CECs removal.

Hydrophobic compounds (having higher logK$_{OW}$) exhibit higher and less variable removal efficiencies, with respect to hydrophilic compounds. However, there are two exceptions: ACS and VAL, which display a worse removal compared to compounds with similar logK$_{OW}$. ACS and VAL are both characterized by a negative charge, having pK$_a$ equal to 2 and 4.73, respectively. Since the pH$_{PZC}$ of the used activated carbon is equal to 7.5 and the average pH of the PreO$_3$ and PostO$_3$ water matrices is in the range 8–8.5, the activated carbon is negatively charged, therefore, a repulsive force is established between activated carbon and negatively charged compounds. The lower affinity of ACS and VAL with activated carbon can be, therefore, ascribed to their charge. This evidence highlights that logK$_{OW}$ influences the adsorption, but it is not an all-encompassing predictor of adsorption performance, and also the surface charge is fundamental when selecting the proper activated carbon to remove target CECs, in accordance with previous findings (Cantoni et al., 2021; Mailler et al., 2015).

3.4. Performance of ozonation and adsorption as in-series processes

The performance of OX + ADS process was assessed with reference to both total CECs removal (considering the sum of the concentrations of the 10 target CECs) and to each CEC, to understand the influence of the properties of each compound. ADS removal was calculated with Eq. (3) considering all activated carbon doses in the PreO$_3$ matrix only, to neglect the effect of ozonation on adsorption performance. Instead, the OX and OX + ADS removals were calculated with Eqs. (2) and (5), respectively, considering all activated carbon doses for OX + ADS. Obtained removal efficiencies are shown in Fig. 4 and summarized in Table S4, with values in agreement with previous studies that are summarized in Table S5 as a function of the analyzed CEC, the water matrix, the treatment train and some operating conditions (Reungoat et al., 2010; Kovalova et al., 2013; Margot et al., 2013; Bourgin et al., 2018; Sun et al., 2018; Mousel et al., 2021; Sauter et al., 2021).

As it can be observed in Fig. 4a, the combined process OX + ADS results in median removal efficiencies not very different from the median removal obtained by ADS alone (13% improvement at the highest ozone dose), but higher compared to the ones achieved by OX alone (increase from 16% to 87% at the lowest ozone dose and from 47% to 92% at the highest ozone dose). Anyway, the overall effect of OX + ADS is less than additive. However, the combined process displays a reduced performance variability with respect to ADS or OX alone: the removal achieved by ADS or OX alone ranged in 13%–98% and 9%–75% respectively, while OX + ADS combination at the highest ozone dose guarantees removals above 80% even at lowest activated carbon dose (5 mg$_{AC}$/L).

The removals of individual CECs by the different processes are reported in the bubble plot in Fig. 4b, which is built based on the same
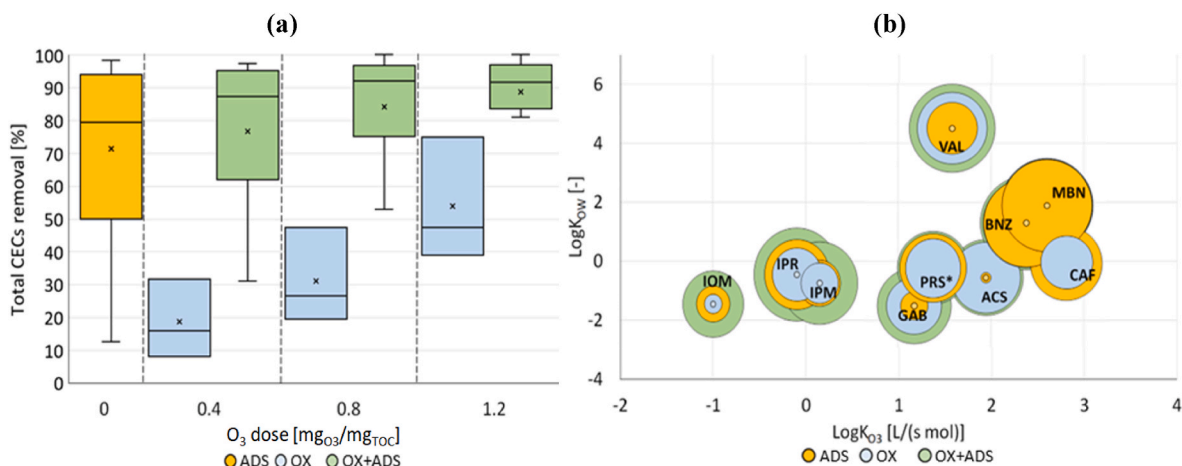
Fig. 4. (a) Total CECs removal for each process and water matrix, referring to all the tested AC doses for both ADS and OX + ADS. (b) Treatment suitability map as bubble chart: bubbles' centers are located according to CEC reactivity with ozone ($logK_{O3}$) and hydrophobicity ($logK_{OW}$), while bubble diameters are proportional to the average CEC removal for each process (AC dose of 5 mg_{AC}/L and 1.2 mg_{O3}/mg_{TOC}).

criteria used for the treatment suitability map in Fig. 2. Hence, the centers of the bubbles are located as a function of CECs affinity with ozone and hydrophobicity, while bubbles diameters are proportional to the removal efficiency of each CEC at the highest ozone dose and at 5 mg_{AC}/L. These doses were selected since they provide comparable total CECs removals (about 60%) in ADS and OX adopted as stand-alone processes (Fig. S5), but similar conclusions could be found considering also the low and medium ozone doses, as shown in Table S6 and Fig. S6. It can be noted that the improvement extent achieved by OX + ADS, compared to ADS and OX alone, depends on the CECs' characteristics. In detail, the combination of the two processes plays a fundamental role for: (i) low oxidizable and hydrophilic CECs like the iodinated contrast agents (IOM, IPR, IPM), which are not investigated in previous similar studies, but were found at high concentrations in the water sources, and (ii) for compounds that establish a repulsive force with the surface of activated carbon (VAL, ACS, GAB): this kind of compounds are removed better from the combination of the two processes with respect to the stand-alone ones. Medium-highly oxidizable and hydrophobic compounds (PRS, BNZ, MBN, CAF) are removed by OX + ADS in the same way as the stand-alone processes.

It is important to understand better the role of ozonation in affecting adsorption: besides removal efficiency, also activated carbon lifetime could be affected. In fact, ozonation has multiple effects on the water matrix: besides the reduction of the target CEC, by-products could form competing for adsorption active sites and organic matter content also changes displaying a different competition effect with respect to not-oxidized organic matter (Kennedy and Summers, 2015). However, since adsorption performance depends strongly by the activated carbon dose adopted, we also evaluated the role of ozonation in affecting adsorption, and therefore the potential of OX + ADS combination, in terms of adsorption capacity variations towards target CECs in ADS compared to OX + ADS. Data from adsorption isotherms were fitted with Eq. (1) for each CEC in PreO$_3$ and PostO$_3$ matrices. The estimated parameters and the main descriptive statistics are summarized in Table S5 for each CEC in each water matrix, while experimental data and interpolating curves are shown in Fig. S6. Based on these estimates, the effect of OX on ADS was quantified as the difference in adsorption capacity (Δq_e) between tests performed in PostO$_3$-H and PreO$_3$ matrices. Δq_e was calculated at the median equilibrium concentration (C_e) of the two matrices for each CEC (see Table S6). The Δq_e values are shown in Fig. 5 as a function of ozonation efficiency for each CEC. A negative value of Δq_e suggests a worsening of adsorption performance due to ozonation. For well-oxidizable CECs (high $logK_{O3}$), ozonation negatively affects adsorption, resulting in lower adsorption capacity in the PostO$_3$-H
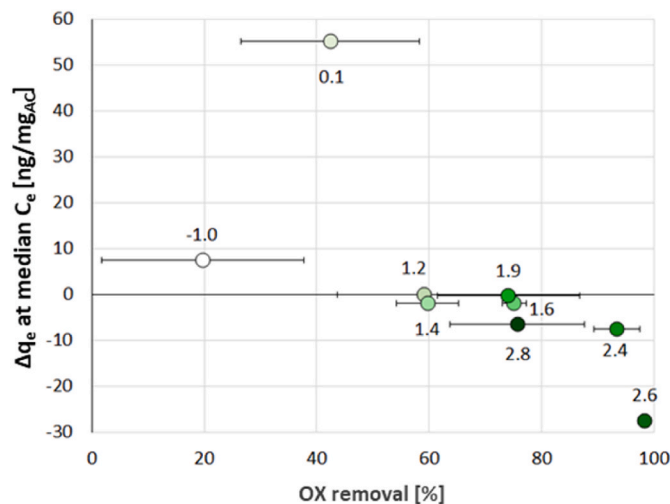

Fig. 5. Change in adsorption capacity Δq_e for each CEC in PostO$_3$-H matrix with respect to PreO$_3$ matrix, calculated at median equilibrium concentration (C_e) achieved in the two water matrices, as a function of OX mean removal efficiency in the PostO$_3$-H matrix. The $logK_{O3}$ value for each CEC is also reported.

compared to PreO$_3$. This reduction depends on OX removal efficiency of the target CEC: the lower is the CEC concentration in the oxidized matrix compared to the not-oxidized matrix, the lower is the adsorption performance. This evidence highlights the role of the bulk CEC concentration in controlling the adsorption extent. In fact, being the difference in solute concentration between the liquid and solid phases the driving force for solute diffusion up to adsorption sites, lower initial bulk concentration results in lower adsorption capacities (Yu et al., 2009). On the other hand, the adsorption of poorly oxidizable compounds in PostO$_3$-H is higher than those obtained in PreO$_3$. The extent of the improvement is greater for IPM, which has the highest bulk concentration (i.e. initial concentration, C_0), indicating that in the not-oxidized matrix competition is the limiting factor for its adsorption. Actually, the better adsorption performance after ozonation is due to the lower competition performed by oxidizable CECs and organic matter, as discussed in Section 3.4. Thus, using ozonation prior to adsorption, well oxidizable CECs can be removed by ozonation but they will be less adsorbed, while poorly oxidizable CECs cannot be well removed by ozonation, but they will be favored in the subsequent adsorption step.

To sum up, the effect of ozone on a subsequent adsorption step depends on the characteristics of the target CECs. The treatment suitability map can provide some preliminary indications on the treatment train to be applied as a function of the target CECs characteristics, since those compounds closer to the origin (low $logK_{OW}$ and $logK_{O3}$) are better removed by the combination of the two processes: for example, even if MTF is hard to be removed when OX or ADS are considered as stand-alone processes, a 50% removal can be obtained when combining OX and ADS both at the highest tested doses. Anyway, considering the high number of CECs present in the water to be treated, a precautionary multibarrier approach considering the combined process OX + ADS should be preferred also to reduce the potential oxidation by-products produced by OX that could increase the final toxicity.

3.5. Organic matter as a proxy for CECs removal

We assessed the correlation between the removal of the sum of CECs (total CECs) by ADS and the removal of the surrogate parameters of the organic matter (absorbance at 254 nm and total fluorescence) in PreO$_3$ and PostO$_3$ matrices, to take into account the role of ozonation in modifying the adsorption extent of both CECs and organic matter.

Removals were calculated with Eq. (4), and data and fitting curves are shown in Fig. 6; fitting equations are reported in Table S3. Adsorption related to the PostO$_3$ matrices have been grouped together, since at a management level it is more useful to distinguish only between not-oxidized and oxidized water, regardless the applied ozone dose.

Total CECs removal increases as the removal of absorbance at 254 nm and total fluorescence increases, showing a saturation trend according to a logarithmic regression ($R^2 = 0.81–0.96$). Therefore, the removal of absorbance at 254 nm and total fluorescence can be considered useful surrogate parameters for overall CECs removal, with an important practical implication for the monitoring of activated carbon adsorbers. For example, absorbance on-line monitoring data can be easily obtained in a full-scale DWTP, and this allows to promptly identify possible system failures, which may result in human health risk, and to apply rapidly mitigation measures. Also Cantoni et al. (2021), even dealing with perfluorinated compounds (PFAS) spiked in tap water, found a logarithmic relationship when interpolating PFAS removal and UVA_{254} removal. However, Anumol et al. (2015) found a linear relationship between PPCPs removal, absorbance at 254 nm and total fluorescence removal, as observed also by Guillossou et al. (2021). This discrepancy may be due to the type of water matrix (WWTP effluent)
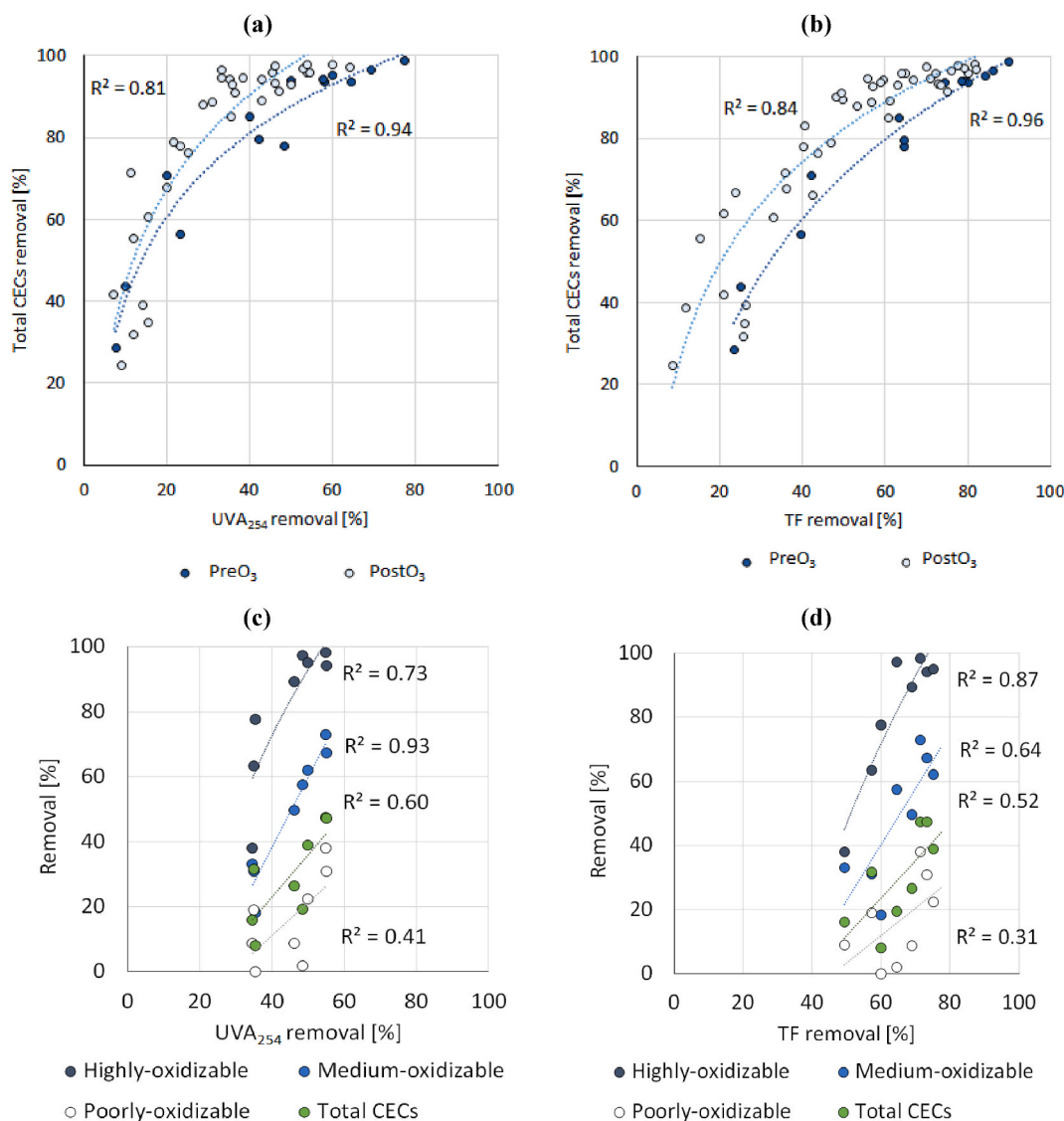

Fig. 6. Correlations between CECs removal and UVA_{254} (a, c) and TF (b, d) by ADS (a, b) and OX (c, d). For graphs (a) and (b), a subdivision into two water matrices was done, where the PostO$_3$ matrix groups the data related to PostO$_3$-L, PostO$_3$-M and PostO$_3$-H. The R^2 values for the fitted correlations are reported, while equations are summarized in Table S3.

used by Anumol et al. (2015) and Guillossou et al. (2021).

It is interesting to note that, for both absorbance at 254 nm and total fluorescence, the correlations curves are shifted on the left for the PostO$_3$ matrix compared to PreO$_3$ matrix. This implies that, fixing the removal of absorbance at 254 nm and total fluorescence, the expected CECs adsorption is higher in the PostO$_3$ matrix with respect to the PreO$_3$ matrix, with an improvement in adsorption up to 20%. The increase of total CECs removal in PostO$_3$ matrix is likely due to the reduced competition for adsorption, to be attributed to the action of the preliminary oxidation.

While the use of absorbance at 254 nm and total fluorescence as proxy variables has been widely studied to monitor adsorption performance, very few and only very recent studies are present in literature that uses absorbance at 254 nm and total fluorescence as proxy parameters during ozonation (Deniere et al., 2021; Song et al., 2022). Compared to the correlations found for adsorption, different behavior is observed when considering absorbance at 254 nm and total fluorescence as proxy parameters for total CECs removal by ozonation. In fact, as shown in Fig. 6, no good linear correlation can be found between the removal of the two proxy parameters and the removal of total CECs (R^2 = 0.60, 0.52 respectively for UVA$_{254}$ and TF), but the correlation improves when selecting only specific groups of CECs, e.g. considering only highly-oxidizable CECs (R^2 = 0.73, 0.87 respectively for UVA$_{254}$ and TF), or only medium-oxidizable CECs (R^2 = 0.93, 0.64 respectively for UVA$_{254}$ and TF). However, the results worsen in the case of poorly-oxidizable CECs (R^2 = 0.41, 0.31 respectively for UVA$_{254}$ and TF). Our result is in agreement with findings by Wang et al. (2021), reporting different relationships between the removal of the phenolic compounds and absorbance at 254 nm, depending on compound molecular weight.

4. Conclusions

This study analyzed the combination of the two best available technologies, namely ozonation and activated carbon adsorption, typically present in DWTPs, for the removal of a wide range of CECs at environmental concentrations, including some compounds, as iodinated contrast agents, that are present at high concentration in water sources but were not studied in previous literature studies.

When looking at the sum of the analyzed CECs, the removals obtained through the combination of the two processes are greater than the ones obtained using ozonation and adsorption as stand-alone processes, but the effect is less than additive. However, this study highlighted that the extent of the benefits of such combination depends on the characteristics of the individual CEC and the treatment suitability map is a useful tool to provide indications on the process to be preferred (OX, ADS or OX + ADS) based on the characteristics of the target compounds. In fact, the lowest removal was observed for compounds refractory to ozonation (low logK$_{O3}$) and/or adsorption (low logK$_{OW}$ and presence of repulsive force with activated carbon), such as MTF, IOM, ACS. Furthermore, in oxidized matrices very reactive CECs with ozone (logK$_{O3}$>2) result to be poorly adsorbed (MBN), possibly due to a very low water concentration reflecting in a low adsorption driving force, while for low reactive CECs adsorption is improved (IPM), possibly due to a reduced competition by other CECs and organic matter. Considering the different reactivity with ozone and hydrophobicity among the CECs mix present in the aquatic environment, the combination of the two processes should be preferred assuring a higher safety extent of treated water, especially if intended for potable use.

UVA254 and TF are good proxies for online monitoring of CECs removal by adsorption, but the type of water matrix should be considered, since different relations were found in not-oxidized and oxidized water matrices. Finally, the two parameters cannot be easily used as proxy of CECs removal by ozonation, since no good relations can be found, unless a selection of CECs is done, resulting in the two parameters used as proxy only of a specific mixture of CECs.

Notes

All authors confirm the absence of any financial and personal relationships with other people or organizations that could inappropriately influence (bias) their work.

CRediT authorship contribution statement

Beatrice Cantoni: Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Jessica Ianes:** Formal analysis, Investigation, Visualization, Writing – original draft. **Beatrice Bertolo:** Writing – review & editing, Funding acquisition. **Selena Ziccardi:** Writing – review & editing, Funding acquisition. **Francesco Maffini:** Validation, Resources, Writing – review & editing. **Manuela Antonelli:** Supervision, Conceptualization, Methodology, Writing – original draft, Writing – review & editing.

Declaration of competing interest

All authors confirm the absence of any financial and personal relationships with other people or organizations that could inappropriately influence (bias) their work.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.119537.

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