Emerging contaminants in drinking water treatment plants: how ozonation affects activated carbon adsorption

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Summary

Contaminants of Emerging Concern (CECs) in drinking water are a growing concern for potential negative effects on human health. This study combines full-scale monitoring campaigns in a drinking water treatment plant (DWTP) and lab-scale experiments using real water matrices without CECs spike. Monitoring campaigns were performed over one year and over 116 monitored CECs, a maximum of 22 compounds have been detected at the DWTP inlet. The analyses show that ozonation and adsorption on activated carbon (AC) have the main impact in reducing a wide variety of CECs, with performances influenced by their characteristics. At lab-scale adsorption isotherms were performed on 4 different water matrices, before and after ozonation, the evaluate the effect of ozonation on the adsorption process. Ozonation is less effective than AC adsorption in CECs removal, but the combination of the two processes allows to reduce the variability of the removal efficiencies, providing a highest performance for the removal of all the investigated CECs.

Keywords: Contaminants of Emerging Concern; Ozonation; Adsorption

Introduction

The presence of Contaminants of Emerging Concern (CECs) in the natural sources used for drinking water (DW) production is of high interest since it may be associated with adverse effects for human health (Fent et al., 2006). Although most of these compounds are unregulated, considering the evolution of DW quality legislation, the removal of CECs during DW production is a key issue. According to the precautionary principle, adequate techniques must be adopted in DW treatment plants (DWTPs) to maximize the removal of micropollutants and to meet future directives and standards. The alternatives available today essentially consist in the use of advanced oxidation processes, where ozonation is the most widely used, and adsorption on activated carbon (AC) (Guillossou et al., 2021). In DWTPs, the most adopted process is granular AC (GAC) adsorption which is, in case of surface water, always preceded by ozonation. So, it is important to evaluate not only the performance of the stand-alone processes but also their combination and the effect of ozonation on the subsequent adsorption step. In fact, organic matter is a competitor for CECs adsorption, and ozonation could affect its characteristics and adsorption extent. To date, there are very few studies in literature that correlate the removal of absorbance at 254 nm (UVA_{254}) and total fluorescence (TF), indicators of the organic matter content, with CECs (Guillossou et al., 2021) and who use the two parameters as surrogate of CECs, also by varying ozone dose (Jin et al., 2019). Furthermore, lab-scale studies are mostly carried out on synthetic matrices and/or with spike of CECs, thus using initial concentrations much higher than those detected in the aquatic environment (Bachmann et al., 2021).
This study aims at evaluating the performance of ozonation on CECs removal in DWTPs, not only as stand-alone process, but also as combination with AC adsorption. The effect of ozonation on the subsequent step of adsorption was studied and also the possibility to use UVA_{254} and TF as surrogate of CECs removal by ozonation was investigated.

Materials and methods

The selected DWTP is located in Pontelagoscuro (Italy), that represents the closure section of the Po river basin, that is the largest Italian watershed with a surface of about 74,000 km^2. The Po river basin is a highly populated area (population density of 423 inhab/km^2), that is highly industrialized, intensely cultivated, and hosts vastly developed transport infrastructures.
Pontelagoscuro DWTP is located directly on Po river and withdraws raw waters directly from Po river and from groundwater (GW). Surface water is treated through a lagoon basin (Lag), a clariflocculation step followed by sand filtration and ozonation (O_3). Groundwater undergoes an

aeration step followed by sedimentation and sand filtration. The two streams are then merged and treated on GAC filters and disinfected by chlorine dioxide, before being distributed in the network.
Six monitoring campaigns have been performed at the DWTP from September 2020 to July 2021, collecting six samples in each campaign: the two raw waters, the water at the inlet and outlet of several treatment processes treating the surface water, and the water at the outlet of the GAC filters. The following parameters have been monitored: 116 CECs, pH, redox potential, conductivity, total dissolved solids (TDS), turbidity, absorbance at 254 nm and total organic carbon (TOC).
Isotherms experiments have been performed on four water matrices collected in the DWTP. Samples were collected in triplicate during three different days at the inlet of the ozonation section ($PreO_3$) and at the outlet ($PostO_3$), at different target ozone doses: low ozone dose ($PostO_3$-L: 0.5 mgO_3/L), medium ($PostO_3$-M: 1.0 mgO_3/L) and high ($PostO_3$-H: 1.5 mgO_3/L). No spike of CECs was done. The adsorbent was a bituminous-based microporous AC with a BET specific surface area >1000 m^2/g and pH of point of zero charge (pH_{PZC}) of 7.5. Adsorption isotherms were fitted testing six different doses of AC (0-30 mg_{AC}/L) into each of the four matrices, analyzing 10 CECs (Table 1), being the most critical for the investigated DWTP. UVA_{254} and total fluorescence were used to measure and characterize the organic matter in filtrated samples.

Table 1. CECs' abbreviation codes and main characteristics: $logK_{OW}$, $logK_{O3}$, pKa, type, LOQ.

CEC	Code	$logK_{OW}$ -	$logK_{O3}$ L/(s mol)	pKa -	Type	LOQ 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	Stimolant	10
Gabapentin	GAB	-1.51	2.34	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	-2.05	-0.10	9.9	Contrast agent	1
Methyl-benzotriazole	MBN	1.89	2.60	9.2	UV-filter	1
Paraxanthine	PRS	-0.22	ND	10.8	Stimolant	1
Valsartan	VAL	4.00	1.58	4.7	Antihypertensive	1

Results and discussion

In the Po river surface water a maximum number of 22 CECs was detected (concentration higher than LOQ) compared to the 116 analyzed (19%), while only 7 (6%) were detected in wells water. For this reason, the sampling points were mainly concentrated on the treatment train of Po river surface water. Figure 1 shows the sum of the CECs concentrations detected at the various sampling points during the 6 campaigns.

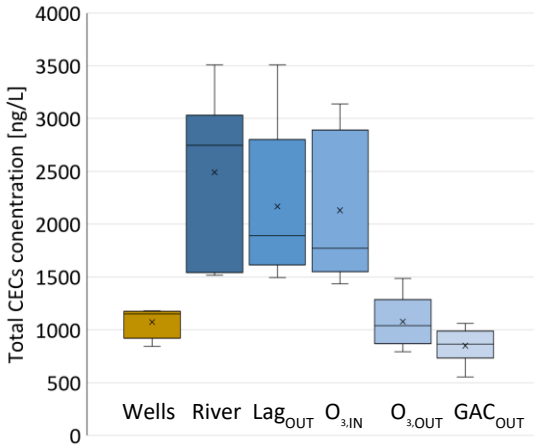

Figure 1. Boxplot of the sum of CECs concentrations in each sampling point, considering all 6 monitoring campaigns.

Besides the number of CECs detected, CECs concentrations in Po raw water and those in wells water also differ greatly, probably due to the action displayed by bank filtration. A clear variability in CECs concentration can be observed in Po raw water among the various campaigns, which is

possibly due to a multiplicity of affecting factors: (i) seasonality in drugs used, (ii) variability of hydrological conditions of the Po river, (iii) uncertainty of the analytical methods, (iv) restrictions due to the SARS-CoV-2 pandemic before and during the sampling campaigns.
As regards the treatment performance related to Po raw water, a wide variability and a high concentration can be observed also at the post-lagoon and at the inlet of ozonation monitoring points, confirming that there is no significant reduction in CECs concentrations in the clariflocculation and sand filtration sections, as expected by literature studies. Finally, a significantly great decrease in CECs concentration is operated by ozonation and adsorption on activated carbon, also in terms of number of CECs detected (5 and 3 out of 22 at the outlet of ozonation and GAC adsorption respectively) and reduction in concentration variability.
As shown in Figure 2, as the ozone dose increases, there is an increase in the average removal of the analyzed CECs (29% for $PostO_3$-L, 50% for $PostO_3$-M and 65% for $PostO_3$-H). Furthermore, at the same ozone dose, the removal seems to be correlated with the constant of reactivity with ozone ($logK_{O3}$) of the individual CECs.

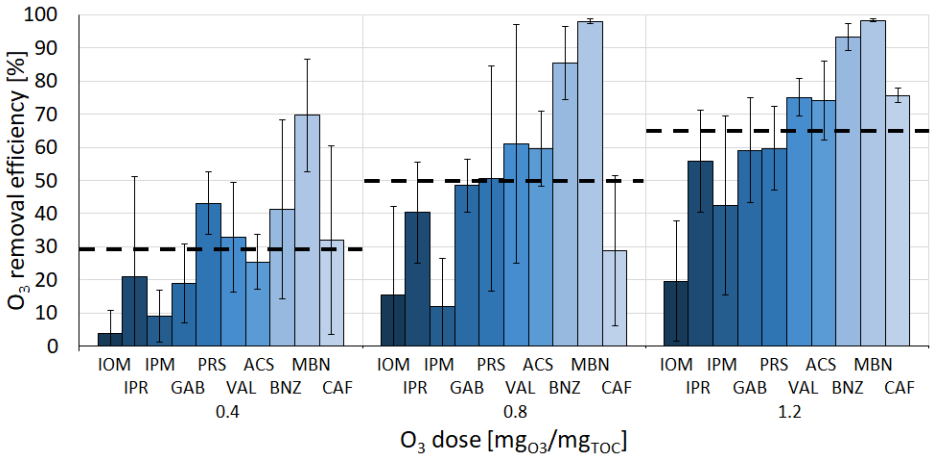

Figure 2. CECs removal efficiencies for ozonation as a function of ozone dose and CECs, displayed in ascending order of $logK_{O3}$. The black hatching lines indicate the average CECs removal in each matrix.

The effect of ozonation on the subsequent AC adsorption step was evaluated comparing the adsorption capacity of each CEC in $PreO_3$ and $PostO_3$ water matrices. The comparison was based on adsorption isotherms determined for the two water matrices ($PreO_3$ and $PostO_3$), considering the three replicates for each water matrix as a single data set, to which a linear regression was applied to estimate the parameters of the Freundlich isotherm model (1/n and K). The difference in adsorption capacity (Δq_e) between tests performed in $PostO_3$-H and $PreO_3$ water matrices is calculated at the median equilibrium concentration (C_e) of the two matrices for each CEC. A negative value of Δq_e suggests a worsening of the AC adsorption performance due to ozonation. For well-oxidizable CECs (high $logK_{O3}$), ozonation negatively affects AC adsorption, resulting in lower adsorption capacity in the $PostO_3$-H compared to $PreO_3$. This reduction depends on the O_3 removal efficiency of the target CEC: the lower is the CEC concentration in the oxidized matrix compared to the non-oxidized matrix, the lower is the adsorption performance. On the other hand, the adsorption of poorly oxidizable compounds in $PostO_3$ water matrices is higher than those obtained in $PreO_3$ water matrix. Actually, the better adsorption after ozonation is due to the lower competition performed by oxidizable CECs and organic matter. Thus, using ozonation prior to adsorption, well oxidizable CECs can be removed by ozonation, but they will be less adsorbed on AC, while poorly oxidizable CECs cannot be well removed by ozonation, but they will be favored in the subsequent adsorption.

UVA_{254} 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 and predict CECs removal. Thus, in $PreO_3$ and $PostO_3$ water matrix, the correlation between the removal of the sum of CECs (Total CECs) by ozone and the removal of the surrogate parameters of the organic matter (UVA_{254} and TF) was assessed. Usually for CECs removal by AC adsorption, a good relationship can be found (Cantoni et al., 2021) while, in case of ozonation, no good linear correlation can be found between the removal of the two proxy parameters and the

removal of total CECs (Figure 3, R^2=0.61-0.77). Anyway, the correlation improves when selecting only specific groups of CECs, e.g. discarding poorly oxidizable CECs. Very few and only very recent studies are present in literature that uses UVA_{254} and TF as proxy parameters during ozonation. Our results are in agreement with findings by Wang et al. (2021), reporting different relationships between the removal of the phenolic content and UVA_{254}, depending on the molecular weight of the compounds.

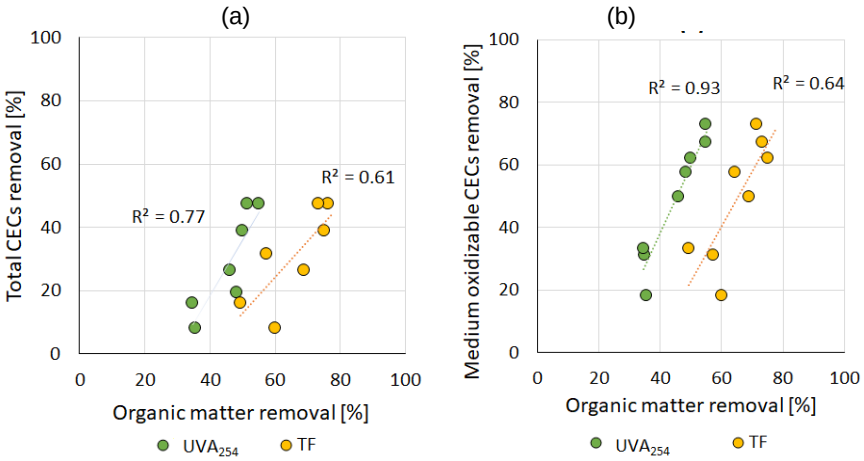

Figure 3: Correlations between removal by O_3 of UVA_{254}, TF and (a) total CECs removal; (b) medium oxidizable CECs removal. The R^2 values for the fitted linear regression are reported in the graphs.

Conclusions

In conclusion, the monitoring campaigns indicates that in a DWTP the processes that are more effective in removing CECs from water are ozonation and AC adsorption. AC adsorption performed better than ozonation for CECs removal, but the use of ozone prior to adsorption guarantees very high removals even at low AC doses, mainly thanks to the reduced competition of organic matter operated by ozone before AC adsorption, demonstrated by the increase of adsorption capacity for poorly oxidizable CECs.

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