Combination of ozone and activated carbon for Pharmaceuticals and Personal Care Products (PPCPs) removal in drinking water: influence of compounds characteristics and organic matter competition

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Abstract
The presence of Pharmaceuticals and Personal Care Products (PPCPs) in drinking water is raising concern for potential negative effects on human health. Ozonation and adsorption on activated carbon (AC) are the most promising processes for PPCPs removal among those usually present in drinking water treatment plants (DWTPs). To evaluate the performance of these processes, both individually and in combination, adsorption isotherms were determined on real matrices collected in a DWTP before and after ozonation, focusing on 10 PPCPs identified as the most critical for the analysed DWTP. AC showed higher PPCPs removals than ozonation, but the combination of the two processes was beneficial. However, the effect of ozone on adsorption depends on PPCPs reactivity with ozone. A competitive effect of organic matter on PPCPs adsorption was observed. Finally, the removal of absorbance at 254 nm is a good proxy variable for PPCPs removal.

Keywords
Activated carbon; Drinking water; Isotherms; Ozonation; Pharmaceuticals and Personal Care Products (PPCPs).

INTRODUCTION

The presence of Pharmaceuticals and Personal Care Products (PPCPs) 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 PPCPs 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). Lab-scale studies are mostly carried out on synthetic matrices and/or with spike of PPCPs, thus using initial concentrations much higher than those detected in the aquatic environment (Bachmann et al., 2021). In DWTPs, one of the typical configurations, in case of surface water as DW source, includes ozonation followed by granular AC filtration, 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 PPCPs removal, 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 fluorescence, indicators of the organic matter content, with PPCPs (Guillossou et al., 2021) and who have evaluated its removal by varying ozone (Jin et al., 2019) and PAC doses.

This study aims at evaluating the performance of ozonation and GAC filtration on PPCPs removal in DWTPs, not only as stand-alone processes, but also as combination of the two processes, considering also the effect of ozonation on the subsequent step of activated carbon adsorption and the competitive effect of organic matter for the removal of CECs in both processes.

MATERIALS AND METHODS

Isotherms experiments have been performed on four water matrices collected in a DWTP in northern Italy. Samples were collected at the inlet of the ozonation section ($PreO_3$) and at the outlet, at three different target ozone doses: low ozone dose ($PostO_3$-B: 0.5 mgO_3/L), medium ($PostO_3$-M: 1.0 mgO_3/L) and high ($PostO_3$-A: 1.5 mgO_3/L). No spike of PPCPs was done. The used 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, analysing 10 PPCPs (see Table 1) found to be the most critical for the DWTP where the water matrices were sampled. UVA_{254} and fluorescence were used to measure and characterize the organic matter in filtrated samples.

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

PPCP	Code	$logK_{OW}$	$logK_{O3}$	pKa	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	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

Experimental results were analysed looking firstly at PPCPs removal efficiencis achieved by each process (Figure 1).

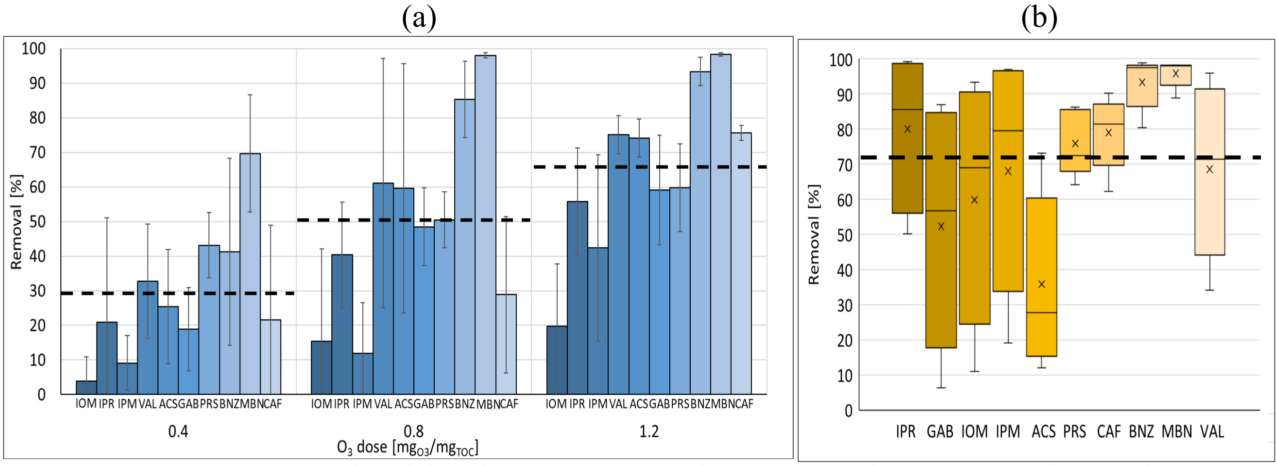
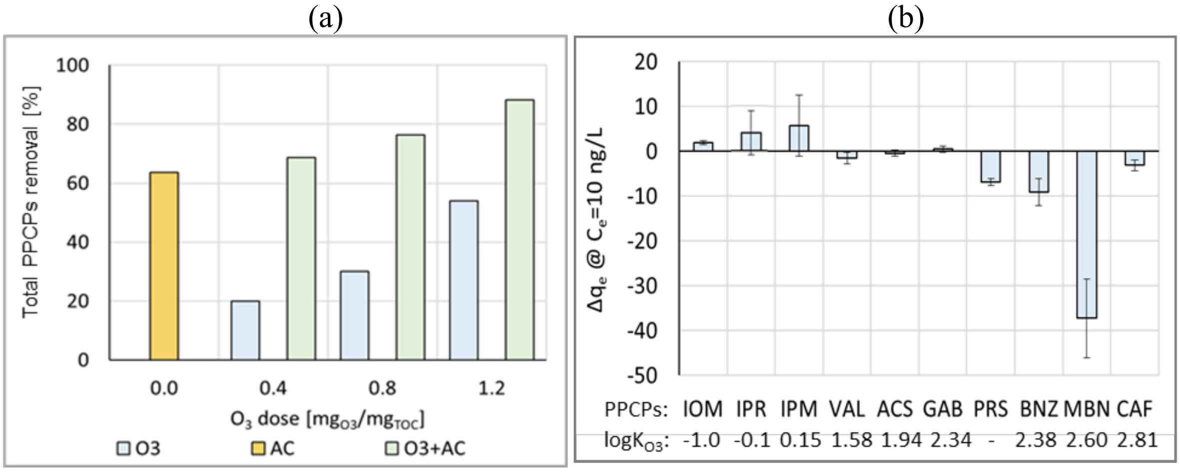


Figure 1. PPCPs removal efficiencies for (a) ozonation as a function of ozone dose and PPCPs, displayed in ascending order of $logK_{O3}$, and (b) adsorption on AC considering all AC doses tested in the $PreO_3$ matrix, and PPCPs displayed in ascending order of $logK_{OW}$.
The black hatching lines indicate the average PPCPs removal in each matrix.

As for the ozone, it is noted that, as the ozone dose increases, there is an increase in the average removal of the analysed PPCPs (29% for $PostO_3$-B, 50% for $PostO_3$-M and 65% for $PostO_3$-A). Furthermore, at the same ozone dose, this removal seems to be correlated with the constant of reactivity with ozone ($logK_{O3}$) of the individual PPCPs. The average PPCPs removal efficiencies achieved at the tested doses of AC (72%) is greater than those achieved by ozonation. It can be seen that AC removals are influenced by PPCPs hydrophobicity: hydrophobic PPCPs (with high $logK_{OW}$) are characterised both by a narrower distribution of removal values and higher removal efficiencies compared to hydrophilic compounds (low $logK_{OW}$), whose removal is highly variable within the range of tested AC doses. Lower efficiencies compared to this trend were observed for ACS and VAL, that are the only negatively charged PPCPs at the tested pH (8-8.5). Since the pH_{PZC} of the AC is equal to 7.5, lower than the water pH, the AC is negatively charged, establishing a repulsive charge with ACS and VAL, explaining their lower affinity towards the AC.

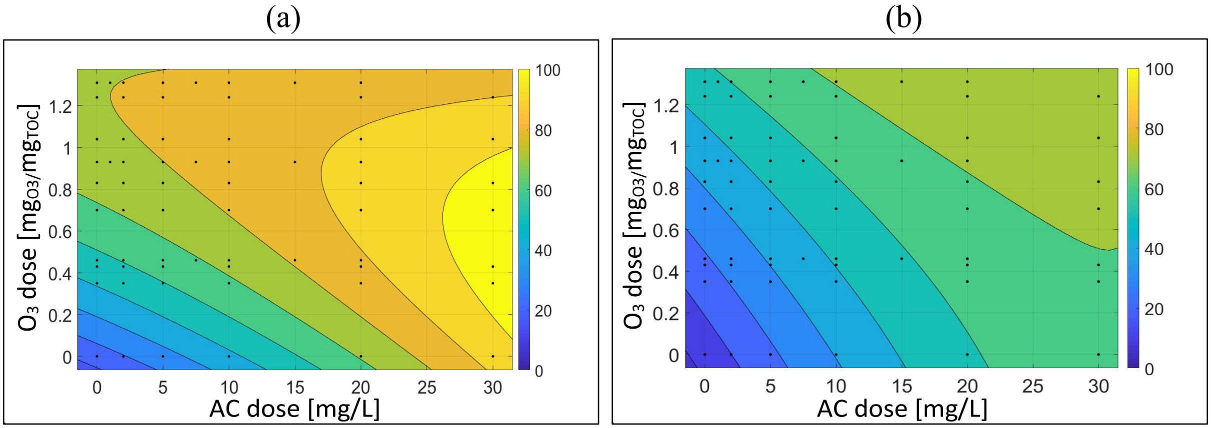
Looking at the combination of ozonation and AC adsorption (Figure 2), the mean total PPCPs removal efficiency of the treatments' combination is improved compared to single treatments, even if the overall effect is less than additive. However, looking at the individual PPCPs, the improvement extent depends on the PPCPs' characteristics: for PPCPs with low reactivity with ozone ($\log K_{O3}<1$ L/(s mol)) there is a significant improvement in efficiencies, while for highly reactive PPCPs, removals achieved with the combination of the two treatments is similar or lower than the one achieved by single treatments. This is confirmed by the lower adsorption capacity (q_e) reached in ozonated matrices compared to the non-ozonated one for highly reactive PPCPs (Figure 2.b). This suggests, therefore, that ozone acts on hydrophobic and highly reactive PPCPs, making them more hydrophilic and therefore less adsorbable (Guillosou et al., 2020).


(a)

(b)

Figure 2. (a) Mean total PPCPs removal for each treatment train and matrix. (b) Change in adsorption capacity ($q_e(PostO_3) – q_e(PreO_3)$) calculated at C_e=10 ng/L for each PPCP, reported in ascending order of $\log K_{O3}$.

To evaluate the competition of organic matter on PPCPs adsorption, the removal of UVA_{254} and total fluorescence in the different water matrices was studied; results are displayed Figure 3.


(a)

(b)

Figure 3. Removal efficiencies of organic matter evaluated as (a) UVA_{254} and (b) total fluorescence, compared to $PreO_3$ water matrix, as a function of the specific ozone and AC dosage.

It is observed that a high organic matter removal is obtained already at the lowest dose of ozone and AC, indicating that a low dose of ozone is enough to remove 40% when evaluated as UVA_{254} and 65% when evaluated as fluorescence. While, at a low dose of ozone, 30 mg/L of AC is needed to obtain a further 30% removal of organic matter. Furthermore, the dependence of organic matter adsorption on the AC dose is greater compared to ozone dose.

Finally, it was evaluated whether the removal of UVA_{254} and fluorescence can be used as proxy variable for the removal of the overall PPCPs, that is useful in order to facilitate the prediction of PPCPs removal by monitoring these parameters that are easily monitored with online sensors. The overall PPCPs removal increases with organic matter removal according to a logarithmic regression (R^2=0.82÷0.94). Moreover, it can be noted that, at equal organic matter removal, PPCPs removals are lower in the matrix not treated with ozone ($PreO_3$). This is due to the greater quantity of organic matter adsorbed in the AC active sites in $PreO_3$ resulting in a greater competition against PPCPs that are worse removed.

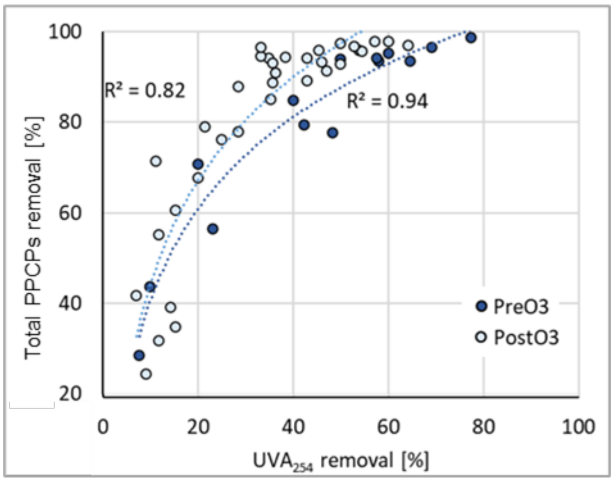


Figure 4. Correlations between removals of UVA_{254} and total PPCPs removal as a function of the water matrix.

In conclusion, the removal obtained through the combination of the two treatments is greater than that which would be obtained using only one of the two treatments, mainly thanks to the reduced competition of organic matter operated by ozone before AC adsorption. However, the benefits of the combination depend on the mix of PPCPs present in the analysed water matrix.

REFERENCES

Bachmann, S.A.L., Calvete, T., Féris, L.A., 2021. Caffeine removal from aqueous media by adsorption: An overview of adsorbents evolution and the kinetic, equilibrium and thermodynamic studies. Science of the Total Environment **767**, 144229.

Fent, K., Weston, A.A., Caminada, D., 2006. Ecotoxicology of human pharmaceuticals. Aquatic Toxicology **76**(2), 122-159.

Guillossou, R., Le Roux, J., Brosillon, S., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Rocher, V., Gaspéri, J., 2020. Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents. Chemosphere **245**, 125530.

Guillossou, R., Le Roux, J., Goffin, A., Mailler, R., Varrault, G., Vulliet, E., Morlay, C., Nauleau, F., Guérin, S., Rocher, V., Gaspéri, J., 2021. Fluorescence excitation/emission matrices as a tool to monitor the removal of organic micropollutants from wastewater effluents by adsorption onto activated carbon. Water Research **190**, 116749.

Jin, X., Zhang, W., Hou, R., Jin, P., Song, J., Wang, X.C., 2019. Tracking the reactivity of ozonation towards effluent organic matters from WWTP using two-dimensional correlation spectra. Journal of Environmental Science (China) **76**, 289–298.