Does ozonation enhance activated carbon adsorption of PFAS in textile wastewater?

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Summary

Per- and polyfluoroalkyl substances (PFAS) are used in numerous industrial applications, such as in textile manufacturing, because of their special chemical properties. To avoid PFAS spread in the environment, removal strategies need to be implemented at the wastewater treatment plants (WWTP) to reduce their environmental risk on receiving water bodies. The fate of 14 PFAS in a full-scale WWTP treating textile and civil wastewater (WW) was investigated. The addition of an adsorption step before or after the ozonation process was studied through adsorption isotherms tested on the WW collected before and after the full-scale ozonation step. Ozonation is not aimed at PFAS removing, but it lowers organic matter competition towards long-chain PFAS in the following adsorption step. The removal of UVA_{254} seems to be a good proxy variable for PFAS adsorption, with relationships not dependent on the presence of ozonation step.

Keywords: Adsorption, Ozonation, PFAS removal, Textile wastewater

Introduction

Per- and poly-fluoroalkyl substances (PFAS) are a class of contaminants of emerging concern (CECs) characterized by aliphatic chains in which hydrogen atoms are either partially or fully substituted by fluorine atoms. Due to their hydrophobic and lipophobic characteristics, PFAS have been widely applied in industry as surfactants and in the manufacturing of textiles (Renner, 2001). Release of untreated PFAS into the environment is becoming a source of concern due to widespread environmental presence, bioaccumulation, persistence, and their (eco-)toxicological effects (McDonough et al., 2021).

The major point sources of PFAS release into the environment are industrial and civil wastewater treatment plants (WWTPs). Advanced processes usually employed for the removal of organic micropollutants from wastewater effluents include ozonation, adsorption onto activated carbon, or a combination of both processes. However, the presence of a strong C-F bond in PFAS structures makes these compounds generally resistant to oxidation, even by molecular ozone and hydroxyl radical (Flores et al., 2013; Thompson et al., 2011).

However, the effect of ozonation on the adsorption performance towards PFAS is still not fully evaluated, in terms of reduction of organic matter competition towards long- and short-chain PFAS (Gao et al., 2020). Finally, to date, there are very few studies that correlate PFAS removal with the removal of absorbance at 254 nm (UVA_{254}) and total fluorescence (TF), indicators of the organic matter content (Cantoni et al., 2021), to be adopted for a real-time control of process performance.

This study aims at evaluating the effect of ozonation on the enhancement of the subsequent PFAS adsorption, especially in case of short-chain PFAS, which are more subjected to competition, and also the possibility to use UVA_{254} and TF as surrogate of PFAS removal for real-time monitoring.

Materials and methods

The selected WWTP is located in Northern Italy and collects wastewater from both a textile industry district (between 2 and 20% of the inlet flowrate) and from civil origin. The wastewater is treated through a pre-denitrification activated sludge biological treatment, a coagulation-flocculation step followed by a lamella clarifier step and final ozonation (O_3).

Six monitoring campaigns have been performed at the WWTP from April to July 2021, collecting two samples in each campaign: at the inlet of the ozonation step (IN-O_3) and at the WWTP outlet (OUT-O_3), with the ozonation process operating at 6-10 mgO_3/L, with an average residual ozone of 1 mgO_3/L.

Table 1. PFAS abbreviations and main characteristics: molecular weight (MW), octanol-water partition coefficient at pH 7.0 (log Dow), chain length, number of fluorinated carbons, functional groups and acid dissociation constant (pKa).

PFAS	MW [g/mol]	Log Dow at pH=7	Chain length	Number of fluorinated carbons	Carboxylate group (c), sulfonate group (s)	pKa
PFBA	214	-1,22	4	3	c	1.07
PFHxA	314	0,18	6	5	c	-0.78
PFBS	300	0,25	4	4	s	-3.31
GENX	347	0,47	6	6	c	-
PFPeA	264	0,52	5	4	c	0.20
PFHpA	364	0,88	7	6	c	-1.36
PFOA	414	1,58	8	7	c	-4.20
PFHxS	400	1,65	6	6	s	-3.32
PFNA	464	2,46	9	8	c	-0,17
PFDA	514	2,98	10	9	c	-
PFOS	500	3,05	8	8	s	-3.32
PFUnA	564	3,37	11	10	c	-
PFDoA	614	4,39	12	11	c	-
PFOSA	499	4,97	8	7	c	-

Isotherms experiments have been then performed on the two water matrices, spiking the samples with 14 PFAS to achieve an initial concentration of 4 µg/L per single PFAS. Five activated carbons (AC), as in Table 2, were tested, having different origin, porosity (nano, micro, meso or macro-porosity), pH of Point of Zero Charge (pH_{PZC}) and applicability (as granular material, GAC, and/or powder, PAC). Adsorption isotherms were fitted testing six different doses of adsorbent (0-200 mg/L) into both the matrices. The following parameters have been monitored: 14 PFAS (LOD=0.01 µg/L), whose main characteristics are reported in Table 1, pH, conductivity, total suspended solids (TSS), total nitrogen, total phosphorous and chemical oxygen demand (COD), UVA_{254} and fluorescence.

Table 2. Tested adsorbents' main characteristics: origin, iodine number, porosity, pH_{PZC}, applicability.

Adsorbent	Origin	Iodine number (mg/g)	Main porosity	pH_{PZC}	Applicability
CP1	Coconut	1000	Micro	8,0	PAC/GAC
BP2	Bituminous-coal	850	Meso	9,2	PAC/GAC
MP25	Bituminous-coal	1000	Meso-macro / Macro	9,1	PAC/GAC
G9	Wood	950	Meso-macro / Macro	9,2	PAC

Results and discussion

As shown in Figure 1, displaying the boxplot of single PFAS concentrations at the different sampling points, four short-chain PFAS (PFBA, PFPeA, PFHxA and PFHpA) were detected, with maximum single PFAS concentration of 0.27 µg/L. Among long-chain PFAS, only PFOA and PFOS were detected at maximum concentration of 0.05 and 0.04 µg/L, respectively. As expected, the ozonation process showed a negligible removal (on average 5%) for all the monitored PFAS.

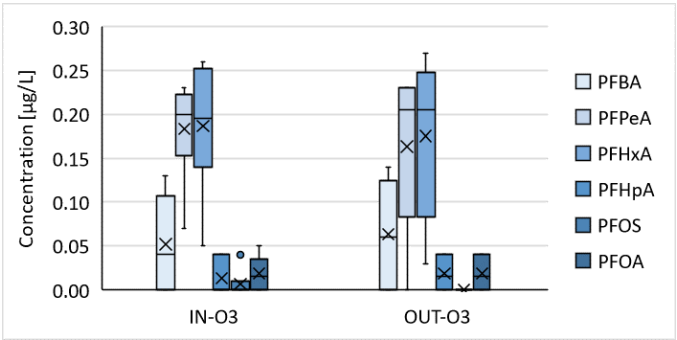

Figure 1. Boxplot of single PFAS concentrations in each sampling point, considering all 6 monitoring campaigns. Non-displayed PFAS were not detected (concentration lower than the LOD) in any sampling point in any campaign.

To evaluate a potential upgrade of the WWTP for PFAS removal before discharge into the receiving water body, an adsorption process was tested through isotherms on the non-ozonated (IN-O_3) and ozonated (OUT-O_3) water matrices, to understand the best positioning in the treatment train. The removal efficiency achieved by different adsorbents for all the PFAS at 50 mg/L adsorbent dose in both the matrices is shown in Figure 2.

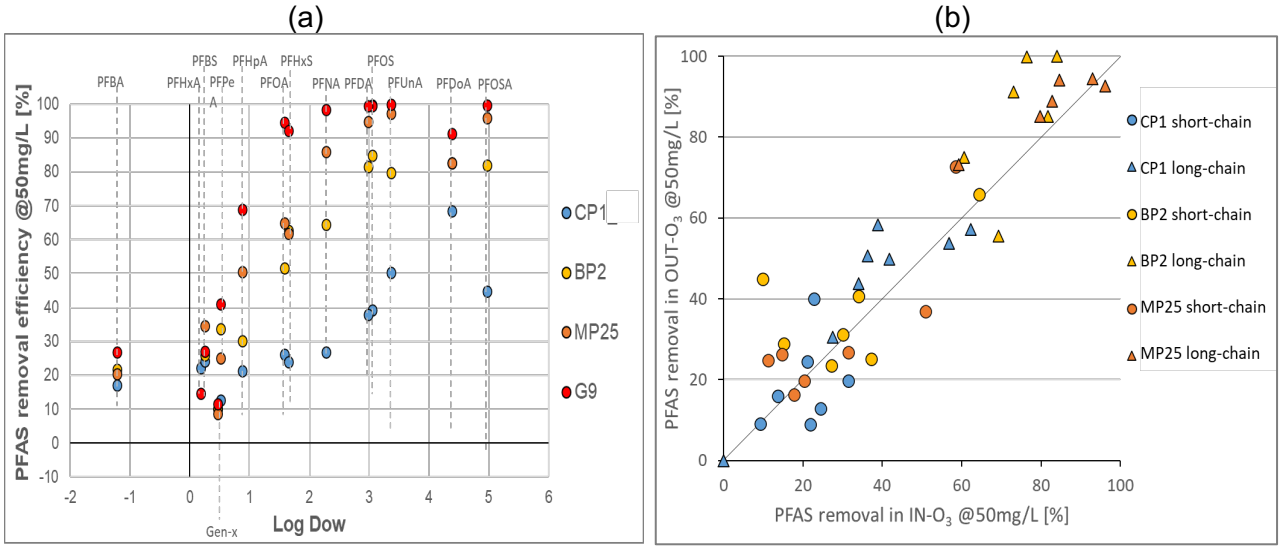

Figure 2. PFAS removal efficiencies by adsorption at 50 mg/L of different adsorbents: (a) in IN-O3 matrix as a function of PFAS hydrophobicity (Log Dow) and (b) comparison of removal efficiencies for IN-O_3 and OUT-O_3 matrices as a function of PFAS length.

PFAS hydrophobicity and the adsorbent type have greater influence on the adsorption capacity compared to the presence of ozonation step. In detail, as PFAS hydrophobicity increases (for greater Log D_{OW}), the removal increases. In fact, short-chain PFAS, that are hydrophilic and marginally hydrophobic (Log D_{OW}<1), are removed with efficiencies between 8% and 50%, with no significant differences between the ACs. For long-chain hydrophobic PFAS (Log D_{OW}>1), the efficiencies are higher and significantly influenced by the type of ACs. The efficiency in fact increases with the pore size: the microporous AC (CP1) has efficiencies between 25% and 70%, followed by the mesoporous AC (BP2) (50%-85%), then by the meso/macroporous bituminous AC (MP25) (60%-95%) and finally by meso/macroporous wood-based AC (G9), which for all long-chain PFAS showed efficiencies higher than 90%. On the other hand, the influence of the aqueous matrix seems less relevant than PFAS hydrophobicity adsorbent surface charge and porosity. In fact, looking at Figure 2.b, the removal efficiencies are similar for the two matrices, as the data do not differ significantly from the bisector. However, it can be noted that short-chain PFAS have removal efficiencies across the bisector; instead, long-chain PFAS tend to have higher efficiencies in the ozonated matrix than in the non-ozonated matrix. This result highlights how long-chain PFAS suffer more competition from organic matter, while the lack of improvement in the removal of the ozonated matrix for short-chain PFAS highlights how they undergo competition in adsorption by long-chain PFAS.

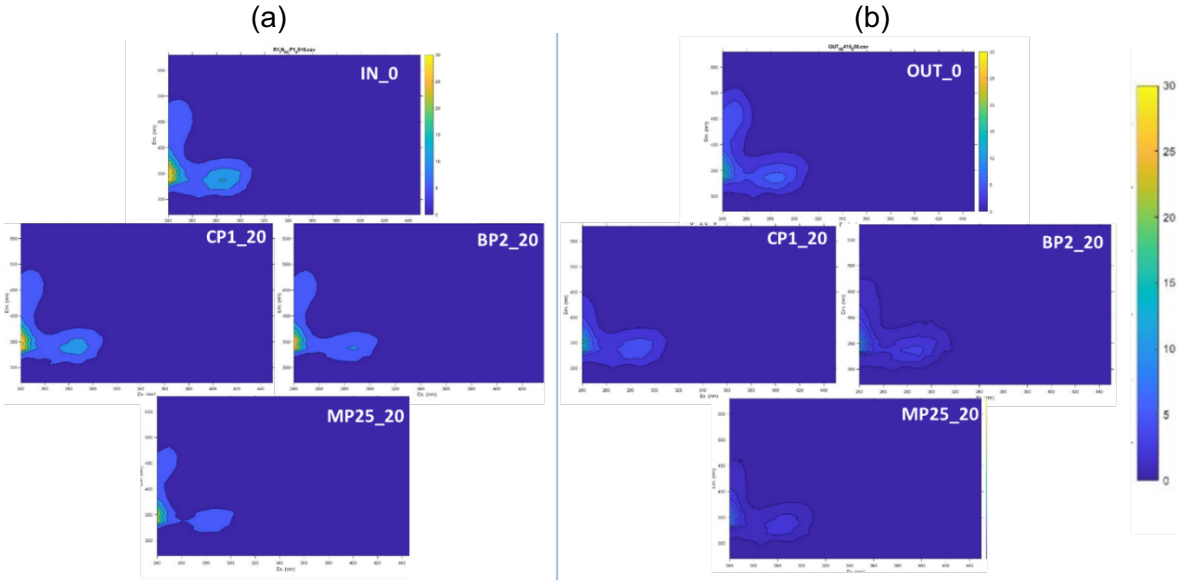

Figure 3. EEMs characterizing the organic matter in raw water matrices and after contact with 20 mg/L of different adsorbents for (a) IN-O_3 and (b) OUT-O_3.

The effect of ozonation on adsorption has been investigated characterizing organic matter, through fluorescence measurements. From the excitation-emission matrices (EEMs), showed in Figure 3 for IN-O_3 and OUT-O_3 samples, ozonation lowers organic matter content (with total fluorescence reduction around 55%), especially peaks T and N, related to proteins, and peaks M and A, related to terrestrial humic substance.
UVA_{254} and fluorescence measurements are less time and costs demanding compared to PFAS analyses. Thus, it is interesting to evaluate whether it is possible to use them as proxy variables to monitor and predict PFAS removal in real time. Figure 4 shows the relationships between the organic matter removal efficiency (as total fluorescence) and the removal of the sum of PFAS. The correlation between organic matter and PFAS removal for different ACs and matrices depends on the AC type; however, for a selected AC, the correlation is independent of the water matrix, confirming the limited effect of ozonation on PFAS adsorption.

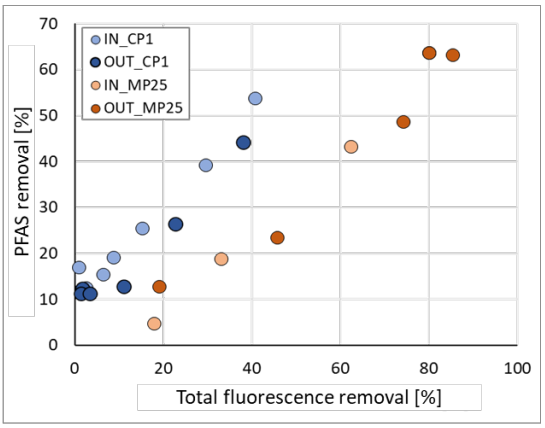

Figure 4. Proxy correlations between removal of the organic matter and removal of the sum of the PFAS for CP1 and MP25 in the two water matrices with the measured organic matter as total fluorescence.

Conclusions

In conclusion, the monitoring campaigns indicates that the current WWTP is not effective in reducing PFAS concentration. Lab scale AC adsorption performed on two water matrices collected before and after ozonation showed that short-chain PFAS, whose use and concentrations are expected to increase in the future, suffer the competition from both organic matter and long-chain PFAS, while long-chain PFAS removal is improved after ozonation, thanks to the reduction of organic matter competition. Finally, UVA_{254} and fluorescence proved to be good proxy variables (faster and cheaper) to estimate the overall removal of PFAS in real time, also useful as an early-warning system.

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