

# Adsorption on activated carbon for PFAS removal: should we act at the source or before the discharge into the environment?

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## Abstract

Per- and polyfluoroalkyl substances (PFAS), used in several industrial applications, such as textile production, are gaining increasing concern due to their spread in the environment, their stability and eco-toxicity. To avoid PFAS spread in the environment, removal strategies need to be implemented at both industrial and municipal wastewater treatment plants (WWTP). This study presents a case study in a textile district in northern Italy where PFAS removal in wastewater (WW) through adsorption on activated carbon was tested at lab and pilot-scale at different points of the system (textile companies and municipal WW treatment plant). This lab-testing was proved to be useful to identify where to apply such process in the system and to optimize process configuration and operating conditions.

## Keywords (maximum 6 in alphabetical order)

Adsorption; Isotherms; Ozonation; PFAS; Rapid Small-scale Column tests; Textile wastewaters

## INTRODUCTION

In the last decades, the presence of per- and polyfluoroalkyl substances (PFAS) in the aquatic environment has become an issue of growing global concern (Griffin et al., 2022). PFAS are ubiquitous and persistent, since they constantly enter the environment through different sources, being the most important the wastewater treatment plants (WWTPs), especially those collecting industrial wastewaters (WW). Worldwide always more stringent limits are posed for PFAS concentration in WW (e.g., the proposed European Directive on Environment Quality Standards (EQS) (European Parliament, 2022)). Thus, to avoid PFAS spread in the environment, treatments need to be implemented at both the industry discharge and municipal WWTPs. As for the industrial discharge, some studies characterized PFAS occurrence in textile industries showing their constant presence at concentrations in the order of  $\mu\text{g/L}$ . However, very few studies studied treatment technologies for PFAS removal in these concentrated streams. One of the most successful well-established processes to remove PFAS from water and WW is adsorption onto activated carbon (AC), particularly for long-chain PFAS (Appleman et al., 2014). The majority of the available studies focused on PFOA and PFOS adsorption through lab-scale isotherm tests, and only recently few studies were performed to assess PFAS breakthrough in drinking water through rapid small-scale column tests (RSSCTs) (Cantoni et al., 2021). Finally, activated carbon adsorption directly after ozonation is a process combination extensively applied in drinking water treatment, and less applied for wastewater. Such process combination has been mainly investigated in municipal WW for Pharmaceuticals and Personal Care Products (PPCPs) and in textile WW for dyes, and very few studies analysed the performance of such treatment train towards PFAS. The objective of this study is to assess adsorption performance at the source and at the final WWTP stage through lab- and pilot-scale tests to evaluate where to apply such treatment in a textile district in northern Italy.

## MATERIALS AND METHODS

The case study is focused on a textile district composed by 42 textile industries whose WW is discharged in a sewer system together with WW from civil origin. The sewer system conveys WW to a WWTP (20-35% of the inlet flowrate from industrial origin), composed by pre-treatments, activated sludge biological treatment (pre-denitrification, nitrification/oxidation), coagulation-flocculation followed by a lamella clarifier and ozonation.

### Lab-scale batch experiments

To assess adsorption performance of different ACs towards PFAS, also considering the interfering action of organic matter, batch isotherm experiments were performed on three water matrices (Table 1): a mix in equal parts of four textile WWs (TWW), treated WW collected at the WWTP before (IN-O3) and after (OUT-O3) the full-scale ozonation unit. The TWW samples, with mean PFAS concentration equal to 4 µg/L, were not spiked. IN-O3 and OUT-O3 samples were spiked with 15 PFAS (from C4 to C12) (PFBA, PFHxA, PFBS, GENX, PFPeA, PFHpA, PFOA, PFOS, PFHxS, PFNA, PFDA, PFUnA, PFDoA, PFOSA, C6O4) to achieve initial concentration of 4 µg/L per single PFAS.

**Table 1.** Main characteristics (mean value ± standard deviation) of the aqueous matrices used in the experimental tests. UVA<sub>254</sub> represents the absorbance at 254 nm (1 cm optical path).

Matrix	pH	Conductivity	COD	UVA <sub>254</sub>
	[–]	[µS/cm]	[mg/L]	[m <sup>-1</sup> ]
TWW	4.4	1589	23900	-
IN-O3	7.7 ± 0.09	1332 ± 4.7	36 ± 1.2	20.5 ± 0.42
OUT-O3	7.8 ± 0.07	1401 ± 3.9	30 ± 1.4	16.0 ± 0.73

Four activated carbons (Table 2) were tested, having different origin, porosity pH of Point of Zero Charge (pH<sub>PZC</sub>) and applicability (as granules, GAC, and/or powder, PAC, based on their availability on the market), at doses from 3 to 150 mg/L, with 48 h contact time. Only BP2 and G9 were tested for TWWs.

**Table 2.** Tested adsorbents' main characteristics: origin, iodine number, porosity, pH<sub>PZC</sub>, applicability (characteristics provided by the AC supplier, Jacobi, except for pH<sub>PZC</sub> which was determined).

Adsorbent	Origin	Iodine number (mg/g)	Main porosity	pH <sub>PZC</sub>	Applicability
CP1	Coconut	1,000	Micro	8.0	PAC/GAC
BP2	Bituminous-coal	850	Meso	9.2	PAC/GAC
MP25	Bituminous-coal	1,000	Meso-macro/Macro	9.1	PAC/GAC
G9	Wood	950	Meso-macro/Macro	9.2	PAC

Processed water samples were analysed for PFAS, COD, pH, conductivity, absorbance spectrum, and fluorescence.

### Pilot-scale column experiments

Rapid Small Scale Column Tests (RSSCT) and Field Adsorption Pilot Plant (FAPP) tests have been performed at the centralized WWTP on IN-O3 and OUT-O3 matrices. For RSSCT, water matrices were spiked with 15 PFAS at 4 µg/L per single PFAS, while for FAPP tests, no PFAS spike was performed, being the initial concentration of PFAS sum varying from 0.05 to 1.4 µg/L.

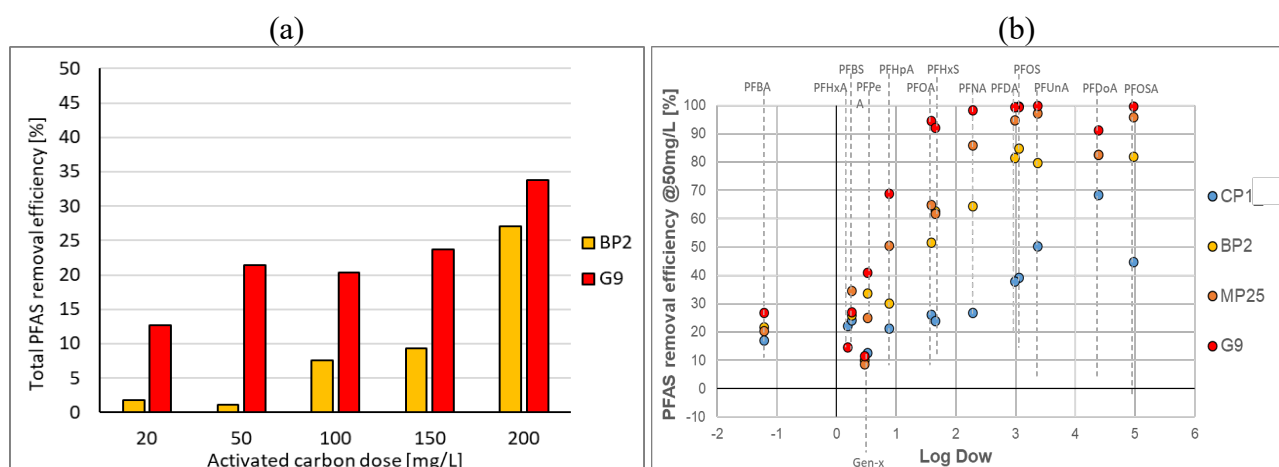
In the RSSCT and FAPP, respectively, three ACs (CP1, BP2 and MP25) and two ACs (CP1, BP2) were tested in single column configuration. In addition, RSSCT were carried out in lead-lag configuration: MP25 was selected as “lead”, to reduce organic matter and hydrophobic PFAS, while both CP1 and BP2 were tested as “lag”, to evaluate the improvement of their performance, especially on hydrophilic PFAS. In these tests, samples were taken at the Lead column inlet, at the Lead column outlet and at the Lag column outlet, to apportion each column contribution to the overall PFAS breakthrough.

Both RSSCT and FAPP, were sized through the constant-diffusivity down-scaling equation (Crittenden et al., 1987) simulating the performance of full-scale GAC filters with 20 minutes of Empty Bed Contact Time (EBCT) and 1.7 mm of AC granules diameter. Thus, RSSCT and FAPP

were characterized respectively by: EBCT of 0.2 min and 3.4 min, AC volume of 0.45 mL and 1.6 L, AC granules diameter of 0.16 mm and 0.5 mm. Based on this design, 100,000 bed volumes (BV) of operation correspond to 7 and 60 days.

## RESULTS AND DISCUSSION

Looking at the PFAS removals (Figure 1) achieved by the two ACs for TWW, removal efficiencies are influenced by the type of AC, its dose and the target PFAS. In detail, mesoporous AC (BP2) showed worse adsorption (2-25% on the sum of PFAS) compared to meso/macro-porous AC (G9) (12-34%), due to decreased competition of organic matter. As for municipal WW (Figure 1.b), PFAS hydrophobicity and adsorbent type (porosity, origin) have great influence on the adsorption capacity. In detail, as PFAS hydrophobicity increases (greater  $\text{Log } D_{ow}$ ), the removal increases. For long-chain hydrophobic PFAS ( $\text{Log } D_{ow} > 1$ ), efficiencies are higher compared to short-chain PFAS and significantly influenced by the ACs type. The efficiency, in fact, increases with the pore size.

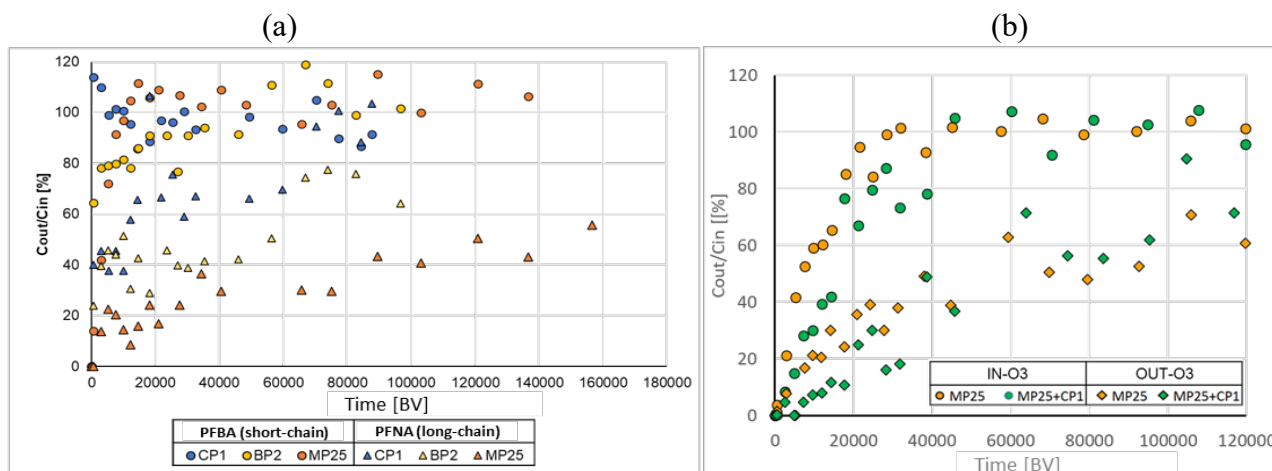


**Figure 1.** PFAS removal efficiencies for: (a) PFAS sum in TWW as a function of AC type and dose; (b) in IN-O3 at 50 mg/L of different ACs as a function of PFAS hydrophobicity ( $\text{Log } D_{ow}$ ).

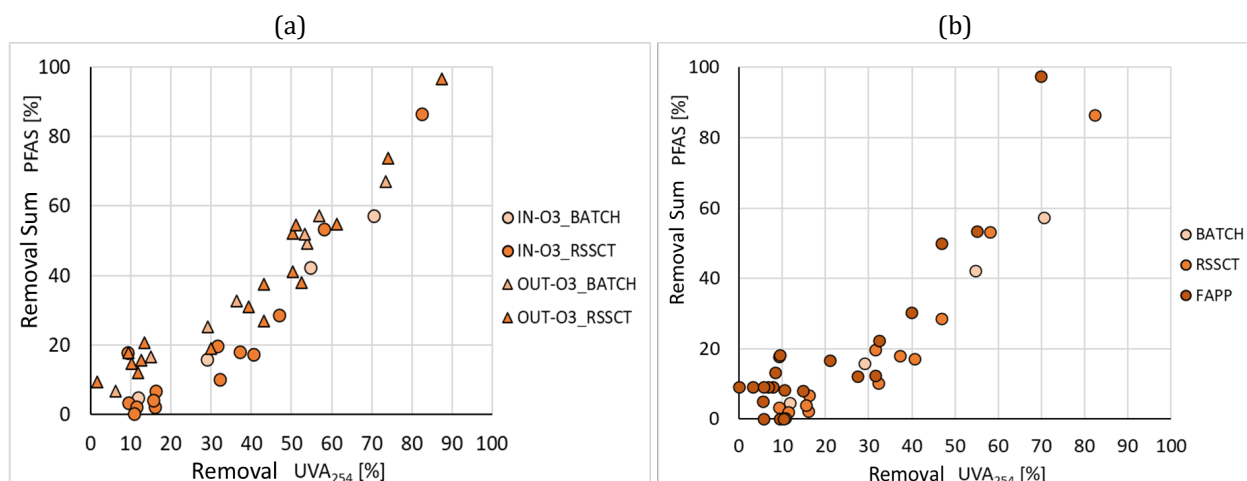
Similar results were found with column tests: the breakthrough in RSSCT slows down with the PFAS hydrophobicity (Figure 2). The different porosity of the ACs significantly influences the results: a slower breakthrough of long-chain PFAS is observed as the porosity of the AC increases. For short-chain PFAS, on the other hand, the breakthrough is very rapid, and no significant differences were found between the 3 tested ACs. The competition between PFAS and organic matter for adsorption active sites plays a key role, especially in the case under examination where a real WW is used. Thus, in Figure 2.b it is assessed the effect of both ozonation, comparing IN-O3 and OUT-O3, and lead-lag configuration, comparing MP25 and MP25+CP1, on the adsorption performance. The influence of ozonation is greater than that of the lead-lag configuration in improving adsorption performance. In fact, the AC life (calculated at 100% breakthrough) increases in the OUT-O3 matrix with respect to the IN-O3 matrix by a range between 50,000 BV and more than 100,000 BV, depending on the tested PFAS. Instead, comparing the breakthrough of the single MP25 column with the lead-lag configuration, the AC life increases less significantly, in the range 10,000-25,000 BV, depending on the tested PFAS.

Finally, the correlations between organic matter (as  $\text{UVA}_{254}$ ) removal and PFAS removal, obtained at the three testing scales for the MP25 AC in both tested water matrices, were compared (Figure 3). Despite a certain variability for removal of organic matter and PFAS lower than 30%, the relationships found at the three different scales of tests (batch, RSSCT and FAPP) follow the same trend. This is useful because this relationship can be estimated for the AC to be used at full scale through batch tests, which are faster and simpler to prepare; then, it can be adopted in column operations at different scales, simply monitoring organic matter through absorption measurement

(faster and cheaper) to estimate the overall removal of PFAS in real time, useful as an early-warning system.



**Figure 2.** Breakthrough curves in RSSCTs for: (a) PFBA (short-chain) and PFNA (long-chain) with 3 ACs in IN-O3 matrix; (b) for PFNA with MP25 and MP25+CP1 in IN-O3 and OUT-O3 matrices.



**Figure 3.** Proxy correlation between removal of UVA<sub>254</sub> and the sum of PFAS for MP25: (a) in the two matrices for batch tests and RSSCT; (b) in the IN-O3 matrix for batch tests, RSSCT, FAPP.

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