PFAS in textile wastewater: an integrated approach to reduce the environmental risk for their mixture

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Abstract
Per- and polyfluoroalkyl substances (PFAS), used in several industrial applications, are gaining increasing concern due to their spread in the environment, their stability and eco-toxicity. To avoid PFAS spread in the environment, reducing the environmental risk on receiving water bodies, 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 monitoring campaigns were combined with testing at lab and pilot-scale of two promising removal processes (membrane separation, adsorption on activated carbon) and data used for environmental risk assessment. This combination was proved to be useful to support the identification of the optimal combination of prevention and treatment interventions to be applied at different system points to reduce the environmental risk.

Keywords (maximum 6 in alphabetical order)
Adsorption; Environmental risk assessment; Membrane separation; PFAS; Scenarios analysis; Textile Wastewater

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are used in numerous industrial applications, such as in textile manufacturing, for their unique chemical properties. The widespread use of PFAS and their persistence make them ubiquitous compounds of increasing concern due to their eco-toxicity (Lewis et al., 2022). To avoid PFAS spread, both prevention and removal strategies should be implemented at both industrial and municipal wastewater treatment plants (WWTP).

As for the prevention strategies, some studies evaluated the substitution of long-chain PFAS with short-chain ones or with non-fluorinated compounds. As for the treatment of textile industry wastewaters (WW), numerous articles investigated decolorization by several technologies, assessing the removal of dyes or COD from target WW (inter alia, Chollom et al., 2015). However, very few studies can be found on the use of such technologies in removal PFAS in these concentrated streams. Moreover, there are no literature studies comparing PFAS reduction strategies at the sources (i.e. textile industries) and at the centralized municipal WWTP.

Thus, the objective of this study is to combine field monitoring, lab- and pilot-scale experiments, and environmental risk assessment to evaluate the current risk for the receiving water body in a textile district in northern Italy and compare prevention and removal strategies for risk minimization.

MATERIALS AND METHODS

The case study is focused on a WWTP collecting WW from textile industries (25-40% of the inlet COD load) and civil origin. The WWTP comprises pre-treatments, activated sludge biological treatment (pre-denitrification, nitrification/oxidation), tertiary coagulation-flocculation followed by a lamella clarifier and ozonation.

Monitoring campaigns

Three monitoring campaigns have been performed in four textile industries: 1 textile printing, 1 fabric dyeing and 2 yarn dyeing companies. Concerning the WWTP, 11 campaigns have been performed, collecting four samples in each campaign: the WWTP inlet, the biological treatment outlet, the ozonation inlet and the WWTP effluent. Monitored parameters were: 14 PFAS (PFBA, PFHxA, PFBS, GENX, PFPeA, PFHpA, PFOA, PFOS, PFHxS, PFNA, PFDA, PFUnA, PFDoA, PFOSA), pH, conductivity, TSS and COD.

Lab- and pilot-scale experiments

As for textile WW, pressure-driven membrane separation has been tested, assessing both microfiltration (MF) and nanofiltration (NF) and their combination. A SEPA CF Cell cross-flow filtration unit was used in "feed and bleed" mode, under pressure and filtration rate conditions comparable to full-scale ones. Three tests were carried out on a mixture of textile WWs collected from the monitored industries with no PFAS spike. The water matrix was characterized by 23.9 g/L COD, 1440 µS/cm conductivity, pH of 4.5, sum of PFAS equal to 9.5 µg/L.

In the centralized WWTP, adsorption on activated carbon (AC) was tested at lab and pilot-scale. Rapid Small Sale Column Tests (RSSCT) and Field Adsorption Pilot Plant (FAPP) tests have been performed on two water matrices, collected before (IN-O3) and after (OUT-O3) the full-scale ozonation, spiking the samples with 14 PFAS to achieve a concentration of 4 µg/L per single PFAS. The water matrices IN-O3 and OUT-O3 were characterized respectively by: COD of 36 mg/L and 30 mg/L, pH of 7.7 and conductivity around 1350 µS/cm. 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). 3 ACs were tested, differing for the porous structure and volume.

Scenarios analysis

To estimate PFAS mass balance throughout the system, the average measured values of flowrate (Q) and PFAS concentrations (C_{PFAS}) (Q_{CIV}=14,240 m^3/d; Q_{TEX}=6,765 m^3/d, $C_{PFAS,CIV}$=0.5 µg/L; $C_{PFAS,TEX}$=0,31 µg/L), and removal efficiencies observed at the lab- pilot-scale were used. The percentage of the total PFAS load leaving the plant through the dewatered sludge, according to the monitoring data, was 0.8%. In scenarios without additional treatments in the WWTP, PFAS concentrations were assumed stable along the treatment train, according to the monitoring data.

The following scenarios have been simulated:

- Scenario 0: Scenario in the current situation (Business As Usual, BAU).
- Scenario 1a: Scenario on voluntary action to reduce total PFAS in textile processes by 35%.
- Scenario 1b: Scenario on voluntary action to replace long-chain PFAS with short-chain PFAS in textile production processes, considering that on average twice the amount of short-chain PFAS is needed to produce fabrics with same performance of long-chain PFAS.
- Scenario 2: Scenario of treatment of textile WW by membrane separation: MF+NF.
- Scenarios 3a and 3b: Scenarios combining scenarios 1a and 2 (3a) and 1b and 2 (3b).
- Scenario 4: Scenario of treatment in the centralised WWTP through adsorption on AC after ozonation, operated for 100,000 bed volumes (BV) (equal to one year operation).
- Scenarios 5a and 5b: Scenarios combining scenarios 1a and 4 (5a) and 1b and 4 (5b).
- Scenarios 6a and 6b: Scenarios combining scenarios 1a, 2 and 4 (6a) and 1b, 2 and 4 (6b).

Environmental risk assessment for PFAS mixture

The environmental risk due to the concentration of the individual PFAS in the effluent of the treatment plant was calculated according to the methodology proposed in the new European Directive proposal for the Environmental Quality Standards (EQS) (European Parliament, 2022).

The concentration of each *i-th* PFAS was multiplied by its relative potency factor (RPF_i) to convert it into equivalent concentration of PFOA. The overall concentration of PFAS was calculated as:

$$C_{PFAS,TOT}\ [\mu g/L\ di\ PFOA\text{-}eq] = \sum_{i=1}^{15} C_{PFAS,i} \times RPF_i$$

The risk of the PFAS mixture was calculated through the risk quotient (RQ), that is the ratio between PFAS concentration, as PFOA equivalent, expected in the river (assuming a dilution factor DF of the discharge equal to 0.1, the default value of the risk assessment), and the EQS for surface water reported by the proposed Directive (0.0044 µg/L of PFOA-eq), with the following formula:

$$RQ_{PFAS,TOT} = \frac{C_{PFAS,TOT}\ x\ DF}{EQS}$$

RESULTS AND DISCUSSION

The monitoring campaign was useful to evaluate which PFAS are effectively present and their fate in the WWTP. The textile WW are mainly characterized by short-chain PFAS (91.7% of the total PFAS). In the raw WW a maximum of 7 PFAS was detected over the 14 monitored ones (Figure 1). In the WWTP, the biological treatment increases short-chain PFAS concentration. At the outlet of the final ozonation an average 5% concentration decrease was observed for PFPeA, PFHxA and PFOS, while no effects were observed for PFBA, PFHpA and PFOA. Overall, PFAS sum was not changed throughout the WWTP treatment train.

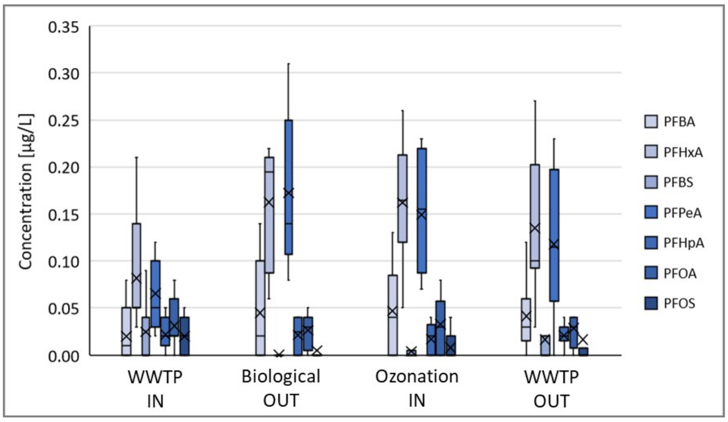

Figure 1. Boxplot of detected PFAS concentrations at each sampling point within the WWTP, for the 11 campaigns carried out.

As for tests on MF and NF on textile WW (Figure 2.a), PFAS rejections by MF were variable; the rejections by NF, fed with the permeate of the MF, were around 80%. Overall, the rejection obtained with the MF+NF sequence was between 88% and 93% and equal to 90% for PFAS sum.
In the centralized WWTP, ozonation showed to reduce organic content and improve PFAS removal in the subsequent adsorption step. The breakthrough curves (Figure 2.b) show that AC adsorption improves with PFAS chain length and within 100,000 BV, the average removal for short- and long-chain PFAS is 11% and 56%, respectively.

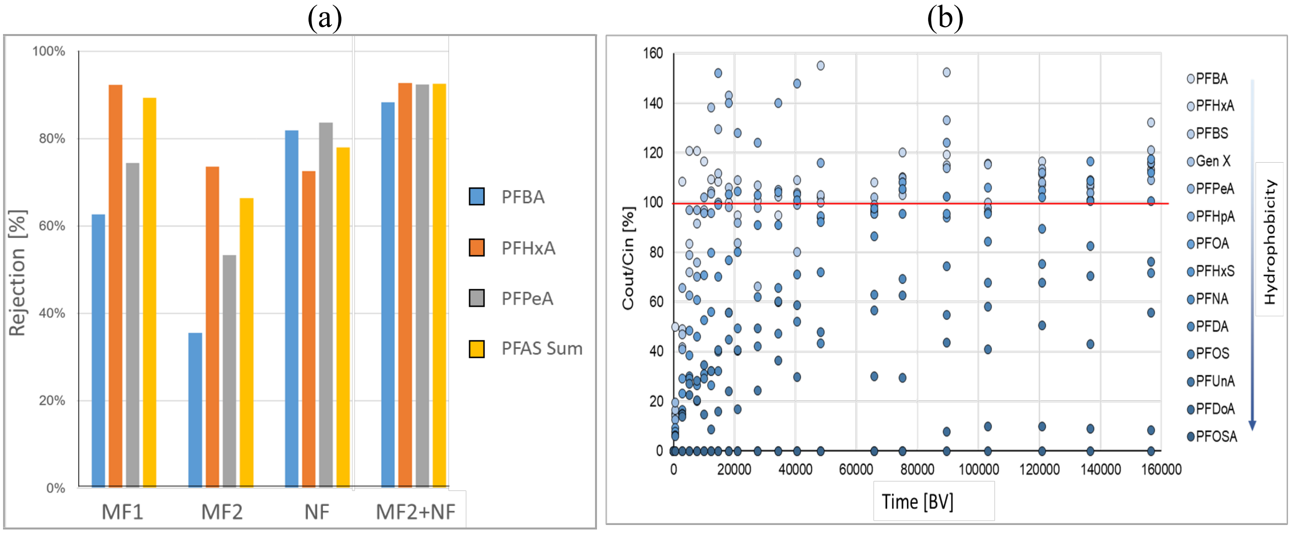
(a) (b)

Figure 2. Results of the tests on: (a) PFAS rejections by MF and NF membranes; (b) PFAS breakthrough curves for AC RSSCT tests in OUT-O3.

The overall environmental risk due to the concentrations of each PFAS in the WWTP effluent and the contribution of each PFAS to the risk is depicted in Figure 3.

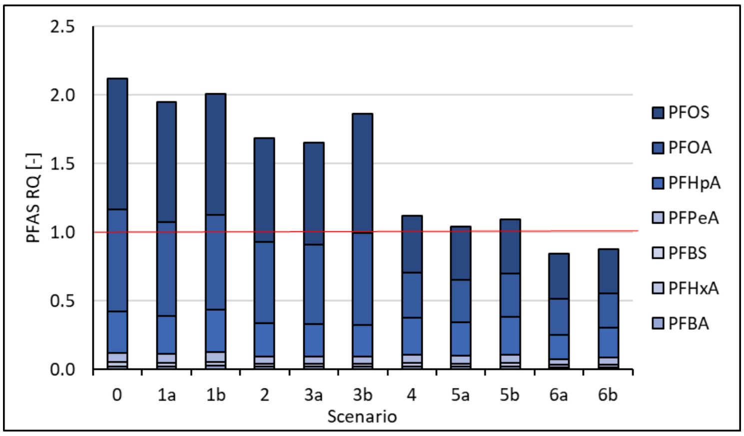

Figure 3. Overall environmental risk due to PFAS mixture for different intervention scenarios (the red line represents the risk threshold RQ=1).

CONCLUSIONS

The mass balance and environmental risk outlined the following evidences:

- Textile WW contribution to the PFAS load entering the WWTP is lower than the civil one.
- In the current scenario (Scenario 0), there is an environmental risk (RQ>1), mainly due to PFOS and PFOA, followed by PFHpA.
- The reduction of 35% of the total PFAS in textile production (Scenario 1a) leads to 8% reduction of the environmental risk, not enough to lower under RQ=1.
- Replacing long-chain with short-chain PFAS in production processes (Scenario 1b) leads to a deterioration in the final effluent quality, due to the higher quantities used.
- The treatment of textile WW through membrane separation (MF+NF) (Scenario 2) reduces by 20% the overall PFAS discharge and environmental risk compared to Scenario 0.
- Combining the reduction or replacement of PFAS in textile production and the treatment via MF+NF (Scenarios 3a and 3b) do not lead to a significant benefit compared to Scenario 2.
- The addition of activated carbon adsorption downstream ozonation in the centralized WWTP (Scenario 4) reduces the discharged PFAS mass by 20% compared to Scenario 0, and the risk by 50%. Moreover, it is interesting to notice that, although AC filter removal efficiency (11%-56%) is lower than membrane separation one (90%), the overall PFAS risk reduction is higher in Scenario 4 than in Scenario 2 because membrane separation is performed only on the industrial WW that contain mainly short-chain PFAS, while AC in the WWTP treats both industrial and municipal WW containing also long-chain PFAS, whose eco-toxicity is more critical.
- Combining prevention, treatment at source and treatment at WWTP) interventions (Scenarios 6a and 6b), an acceptable environmental risk is reached (RQ<1), even if it needs attention (RQ>0.1).

Finally, to have a more comprehensive assessment and prioritization of the proposed interventions, the proposed environmental risk analysis should be combined with an economic evaluation.

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