

TOWARDS MORE EFFICIENT REMOVAL OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs) IN DRINKING WATER: CAN NANOFILTRATION COMBINED WITH ACTIVE CARBON OR ANION EXCHANGE DO THE TRICK?

Franke V¹, McCleaf P², Lindegren K¹, Ahrens L¹

¹Swedish University of Agricultural Sciences (SLU), Department of Aquatic Sciences and Assessment, Uppsala, SE-75007, vera.franke@slu.se; ²Uppsala Water and Waste AB, Uppsala, SE-75450

Introduction: The occurrence of per- and polyfluoroalkyl substances (PFASs) in drinking water is of global concern and contaminated raw water sources pose a great challenge for drinking water providers worldwide. Conventional drinking water treatment is not able to remove PFASs from water and concentrations in the finished drinking water are often similar to the concentrations found in source water¹⁻³. Certain filtration techniques, however, have been identified to remove PFASs in drinking water treatment: high-pressure membrane processes, such as nanofiltration, and adsorption to fresh granular activated carbon (GAC) or anion exchange resins (AIX)⁴. In case of source water contamination, it is usually recommended to apply GAC filters to treat water in drinking water treatment plants. This remains a costly interim solution for many drinking water providers, as filter beds need to be replaced or sent for regeneration by incineration several times a year, depending on PFAS concentration in the source water and treatment goals. Since nanofiltration can be used to remove PFASs and many other unwanted water constituents, even currently unknown pollutants. However, the water rejected by the membrane (retentate) might be laden with organic micropollutants such as PFASs and the treatment of the retentate remains a challenge. In this study we therefore investigate the combination of a full-scale nanofiltration unit and the adsorption materials GAC and AIX in column experiments. Both raw water and membrane reject water were treated with the adsorption techniques in order to draw conclusions on the influence of the feedwater's concentration factor to the material's PFAS removal efficiency.

Materials and Methods: Spiral wound nanofiltration membranes of the type NF270-400 (Dow Filmtech™ Membranes) with a nominal molecular weight cut-off of 270 Da were installed in one unit of a full-scale treatment system. A recovery rate of 78% was targeted with a feedwater flow-rate of 2.3 m³ h⁻¹. Prior the membrane, a 30 µm polypropylene patron filter was installed in order to remove larger particles from the membrane feedwater. Samples of the feedwater, membrane permeate and membrane retentate were taken over the course of nine months. Columns containing each GAC (Filtrisorb 400®, Calgon Carbon Cooperation, Feluy, Belgium) and AIX (Purolite A600®, Llantrisant, Wales) were connected to the treatment set-up to treat untreated membrane feedwater and membrane retentate, respectively (Figure 1). Column experiments were run over a period of three months with 250 mL samples taken every other week. Samples were analyzed by ALS Scandinavia located in Stockholm, Sweden, focusing on 15 PFASs including PFBA, PFPeA, PFHpA; PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFBS, PFHxS, PFOS, PFDS, FOSA, 6:2 FTSA.

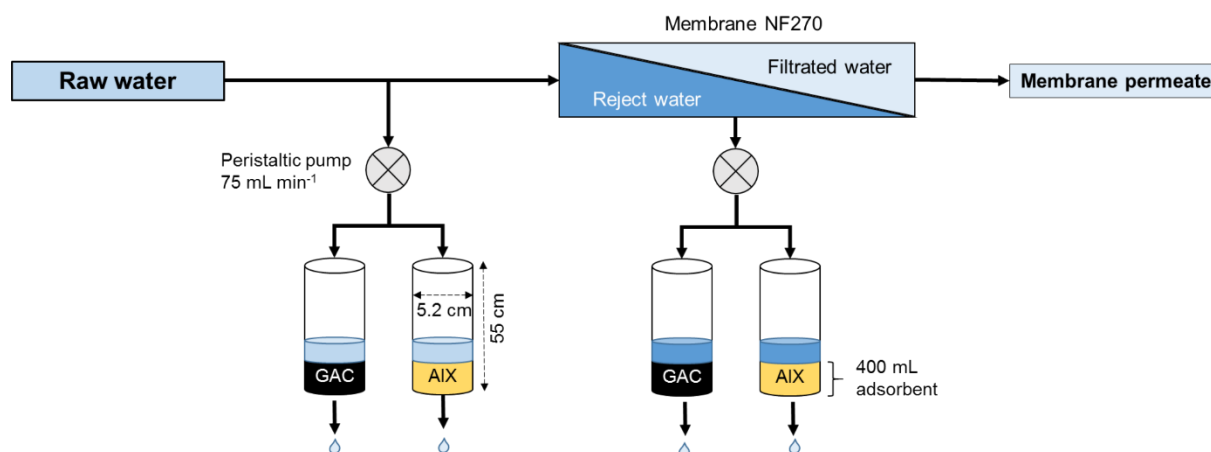


Figure 1. Experimental set-up; raw water was treated by a full-scale nanofiltration membrane unit, resulting in membrane permeate and membrane retentate (reject water). Columns with each granular activated carbon (GAC) and anion exchange (AIX) material were connected to treat the untreated membrane feedwater and membrane retentate, respectively.

Results and Discussion: The nanofiltration process removed PFASs on average to > 98% during the course of the 9 month experiment (Table 1). On average, concentrations found in the water permeating the membrane were below quantification limits. In single occasions, PFHxS and PFOS were detected above the limit of quantification in the membrane permeate due to pre-filter clogging. Removal efficiencies were, however, found to be > 95% at all times. Interestingly, even PFASs with a molecular weight lower than the nominal molecular weight cut-off of 270 Da were found to be concentrated in the membrane retentate. These results suggest rejection mechanisms other than size exclusion might be responsible for the rejection of PFASs by the membrane. Examples could be electrostatic repulsion or diffusion of PFASs into the polymeric phase of the membrane⁵⁻⁷. The removal efficiency of the adsorbents GAC and AIX treating the different water types is shown in Figure 2. Both materials removed longer chain PFAS homologues more efficiently than shorter chain PFASs where perfluoroalkyl sulfonates (PFASs) generally were retained better than perfluoroalkyl carboxylates (PFCAs). This was in line with earlier research⁸. Desorption processes (removal efficiencies < 0%) were observed for both materials over time which can most likely be explained by displacement of adsorbed PFASs by organic matter, other contaminants and longer chain PFASs^{3,8,9}. Slopes describing the decrease of removal efficiency generally were less steep for the GAC material than for the AIX. The AIX material showed a rapid decrease for the frequently detected PFCAs (PFHxA, PFHpA and PFOA) in the column treating the membrane retentate once compounds started breaking through. In contrast, the GAC material consistently showed removal efficiencies of ca. 20% for those compounds. Even though initial concentrations of PFOA, PFBS, PFHxS and PFOS were by factors of > 4, 5, 4, and 5 greater in the membrane retentate than in the raw water, half-times of saturation were found to only be enhanced by a factor of approximately two for the GAC material for the treatment of raw water compared to retentate. Initial PFAS concentrations were therefore found to have a complex influence on GAC adsorption performance and breakthrough curves do not superimpose each other when expressed on a concentration normalized basis. GAC can therefore be described as being more efficient in removing PFASs from the more concentrated membrane retentate than from the dilute membrane feedwater. Total PFAS adsorption was evaluated for GAC and AIX on a material volume basis at the end of the experiment. It was observed that GAC overall removed 2.6 as much PFAS mass per material volume from the membrane retentate compared to the raw water (10 vs. 4.1 mg total PFAS L⁻¹ material), while the AIX material even showed an increase of 4.1 times larger PFAS adsorption (19 vs. 4.5 mg total PFAS L⁻¹ material). Performance differences between the two materials appeared more clearly for the columns treating membrane retentate than the columns treating membrane feedwater. In terms of total PFAS loading per material volume, AIX outperformed GAC by a factor of 1.8 when treating membrane retentate, while the total adsorption merely was 1.1 times greater for AIX compared to GAC, when treating dilute membrane feedwater. It is reported in the literature, that GAC adsorption of PFASs and other organic micropollutants, in contrast to that of AIX, is highly influenced by the presence of organic matter in the column feedwater, indicating that organic matter competes for potential sorption sites^{1,2,3}. The AIX's lower capacity for organic carbon, might therefore explain the performance differences between the two materials¹⁰. On the other hand, AIX adsorption would be expected to be adversely affected by the presence of other water constituents, such as sulfate and bicarbonates, however our results suggest, that PFAS adsorption to AIX is influenced by the water quality to only a limited extent.

Table 1: Average concentrations [ng L⁻¹] found in membrane feedwater (raw water), membrane permeate and membrane retentate for each of the frequently detected PFASs. Values below the respective quantification limit are denoted with "<". For comparison to the nominal molecular weight cut-off of the nanofiltration membrane of 270 Da, molecular weights (MW) are listed for each compound. C_{ret}/C_{raw} describes the concentration factor reached for compounds in the membrane retentate compared to the membrane feedwater

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFOS
MW [g mol ⁻¹]	213.03	263.04	313.04	363.05	413.06	299.09	399.10	499.12
Raw water	< 6	< 7	14	< 8	< 10	11	107	39
Permeate	< 6	< 5	< 5	< 5	< 5	< 5	< 10	< 7
Retentate	12	23	65	15	35	47	471	194
C _{ret} /C _{raw}	> 2	> 1.5	5	> 1.5	> 3.5	4	4	5

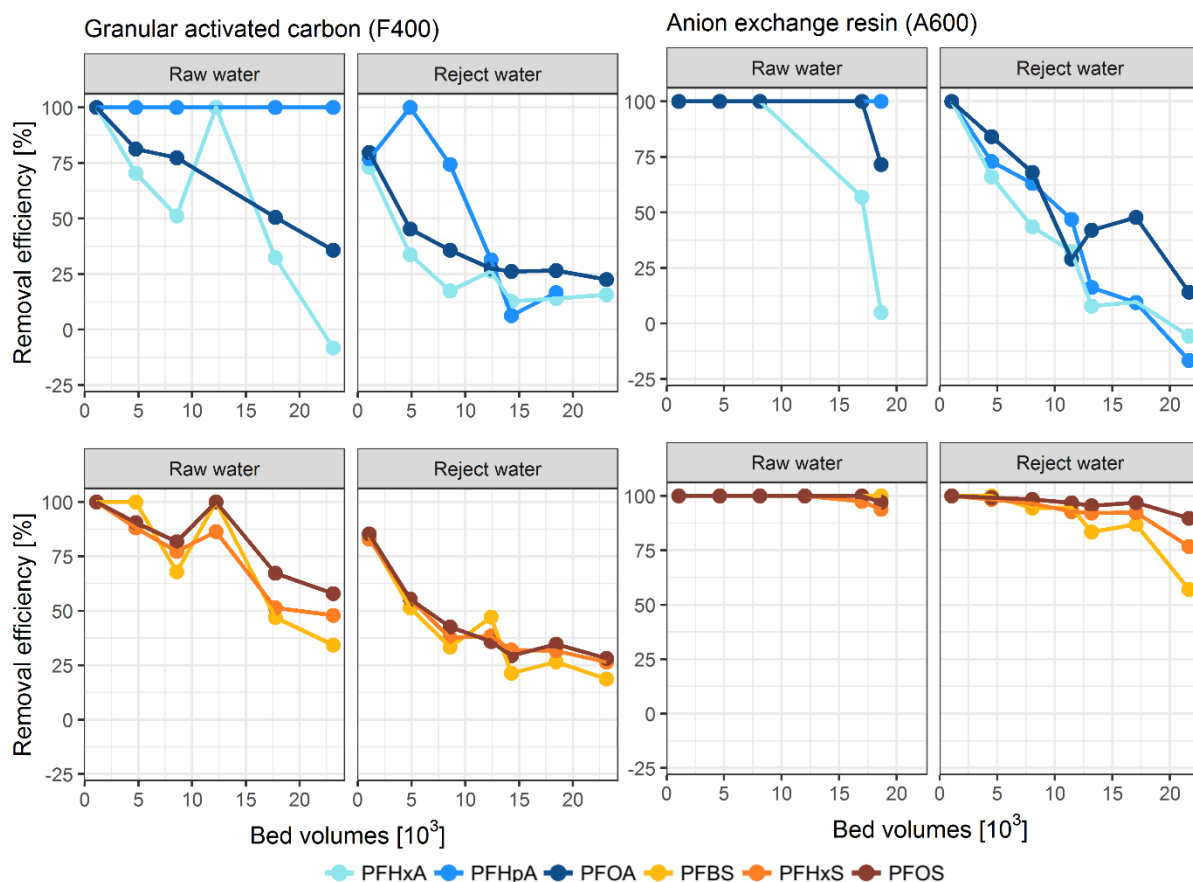


Figure 2. Removal efficiency of the adsorbents for frequently detected PFCAs (top row) and PFSA (bottom row) during the course of the three-month column experiment. The experiment compared the treatment of dilute membrane feedwater (raw water) and membrane retentate (reject water).

Conclusions: The present study evaluated full-scale nanofiltration treatment in combination with adsorption to GAC and AIX in pilot-scale column tests for the removal of PFASs from contaminated water. Nanofiltration was shown to remove PFASs to > 98%, with average concentrations in the membrane permeate being lower than the limit of quantification and thus below the Swedish drinking water guideline value of 90 ng L⁻¹ for the Σ_{11} PFASs (i.e. PFBA, PFPeA, PFHpA; PFHxA, PFOA, PFNA, PFDA PFBS, PFHxS, PFOS, 6:2 FTSA). Rejection mechanisms other than size-exclusion seemed to be responsible for the rejection of PFASs by the membrane, as even PFASs with molecular weights lower than the molecular weight cut-off of 270 Da were found to be concentrated in the membrane retentate. In column tests it was shown that both GAC and AIX were more efficient in removing PFASs from the concentrated membrane reject water compared to the more dilute membrane feedwater. As nanofiltration is a versatile treatment method removing unwanted water constituents mainly by size-exclusion, it represents a save and reliable process, that ensures the removal of PFASs and other, today potentially unknown, micropollutants. Accepted concentrations of PFASs and other micropollutants in finished drinking water are lower than ever before, posing a great challenge for drinking water providers. The combination of nanofiltration with regenerable adsorption materials like GAC and AIX gives the benefit of effective treatment of the nanofiltration waste stream, where this study showed AIX to clearly outperform GAC. Future studies should address cost-benefit calculations and the possibility to regenerate the adsorption materials in order to provide a cost-efficient method for the removal of PFASs in drinking water production and to reduce PFAS release into the environment. Furthermore, the influence of organic matter and other water constituents for the removal efficiency of the adsorption materials should be investigated in the future. Our results suggest, that running nanofiltration processes with even larger recoveries (e.g. 90 - 95%) and thus higher PFAS concentration in the membrane retentate (concentration factor > 10) might make the combination with GAC or AIX treatment even more efficient.

Alternatively, nanofiltration could also be combined with destructive treatment methods such as electrochemical or sonochemical techniques or coagulation/filtration processes with subsequent incineration of the filter residuals.

Acknowledgements:

This work was partly funded by the Swedish Research Council Formas (PFAS-FREE, contract no 942-2015-1554). The authors would also like to thank Uppsala Water and Waste AB for the provided support.

References

1. Appleman T D , Higgins C P, Quiñones O, et.al. (2014) *Water Res.*, 51: 246–255.
2. Rahman M F, Peldszus S, Anderson W B (2014) *Water Res.* 50: 318-340.
3. Eschauzier C, Beerendonk E, Scholte-Veenendal P, et.al. (2012) *Environ. Sci. & Technol.*, 46:1708-1715.
4. Merino N, Qu Y, Deeb R A, Hawley E L, et. al. (2016) *Environ. Eng. Sci.*, 33(9):615–649.
5. Steinle-Darling E and Reinhard M (2008) *Environ. Sci. Technol.* 42:5292–5297.
6. Bellona C and Drewes J E (2007), *Water Res.*, 41:3948–3958.
7. Nghiem L D, Schäfer A I and Elimelech M (2004) *Environ. Sci. Technol.*, 38:1888–1896.
8. McCleaf P, Englund S, Östlund A, et. al. (2017) *Water Res.*, 120:77–87.
9. Zaggia A, Conte L, Falletti L, et. al. (2016) *Water Res.*, 91:137–146.
10. M. Jiang M, Yang W, Zhang Z, et. al. (2015) *J. Environ. Sci.*, 31:226 – 234..