



Polyfluorinated Organic Micropollutants Removal from Water by Ion Exchange and Adsorption

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Polyfluorinated organic micropollutants have been recently found in ground water in some industrialized areas of Veneto Region (north-east Italy). Very recent studies evidenced their presence also in River Lambro near Milan (Castiglioni et al, 2015). These compounds can be removed by adsorption on activated carbon with high efficiency, but frequent regeneration is requested especially because of polyfluorobutylic acid (PFBA) and polyfluorobutyl sulfonate (PFBS) that saturate activated carbon much more quickly than heavier molecules as polyfluoro-octanoic acid (PFOA) and polyfluorooctyl sulfonate (PFOS).

In this research work an alternative solution based on ion exchange resins and/or polystyrenic adsorbents was tested both in laboratory with batch tests and on pilot-scale with a continuously fed plant. Experimental work is still in progress and is focused on five different materials supplied by Purolite® Italia and called respectively A600E, PAD500, PAD428, A520E and MN102. Laboratory batch experiments were (and are) performed in order to study both sorption kinetics and spent resin regeneration; four materials have been tested until now: A600E, PAD500, A520E and MN102. Sorption isotherms showed a progressively decreasing adsorption capacity following the order PFOS>PFOA>PFBS> PFBA indicating a dependence of sorption phenomena both on the length of the perfluorinated tail and the pKa of the polyfluorinated acid. Further, batch experiments showed that for A600E the best regenerating solution was a 2 % NH₄Cl and 1 % NaCl aqueous solution. Pilot-scale experiments were (and are) conducted in cooperation with the water service company Centro Veneto Servizi of Monselice (PD, Italy) nearby a drinking water treatment plant. The pilot plant was and is made of four parallel columns filled with different materials, each one with a volume of 350 mL and fed with 35 mL/min (2.1 L/h) micro-filtered water; so residence time is 10 min and surface hydraulic load is 3.0 m³/m²h. Four materials have been tested until now: A600E, PAD500, PAD428 and MN102. Results of first 800 h working (that correspond to a total treated water volume which is ca. 4,500 times the volume of material in each column) were excellent for PFOA and PFOS removal, but a rapid decrease in PFBA and PFBS removal efficiency was encountered with PAD500 and PAD428. Further experiments are scheduled to test A520E on pilot-scale. Moreover, it would be interesting to test more hydrophobic resins which may display an increased affinity for super hydrophobic PFAS anions reducing competitive action of anions such as nitrates and sulfates.

1. Materials and Methods

Perfluorobutanoate (PFBA, sodium salt), perfluorobutanesulfonate (PFBS, potassium salt), Perfluorooctanoate (PFOA, sodium salt), perfluorooctanesulfonate (PFOS, potassium salt) used for laboratory batch tests were purchased from Sigma Aldrich. Resins and adsorbents Purolite® A600E, Purolite® A520E, PuroSorb® PAD 500, Macronet® MN102 were purchased from Purolite® Italia s.r.l.. Main characteristics of the five materials are listed in Tab. 1. Sample were taken in all experiments (PFAS solutions after sorption and after regeneration experiments for laboratory batch tests, untreated and treated water for pilot-scale tests) and filtered with a 0.2 µm cellulose acetate membrane; the concentration of PFAS was determined using a UPLC Waters® H Class TQD (LC-ESI/MS/MS). The separation column is a Waters C18 type, diameter: 2.1 mm –

length 150 mm. SPE cartridge uses a polystyrene-divinylbenzene WBA resin Phenomenex STRATA X-AW 200 mg/mL. The analytical method used is the EPA 537.

Table 1: Features of the five resins/adsorbents tested.

| Resins | Matrix | Porosity | Functional group | Exchange capacity (meq/L) |
|-----------------|--------------------------|-------------|-------------------------------------|---------------------------|
| Purosorb PAD428 | Brominated Polystyrenic | Macroporous | Nonionic | N.A. |
| Purosorb PAD500 | Polystyrenic | Macroporous | Nonionic | N.A. |
| Macronet MN102 | Polystyrenic crosslinked | Macroporous | Tertiary amine | 0.2 |
| Purolite A600E | Polystyrenic | Gelular | Quat. ammonium with trimethyl group | 1.4 |
| Purolite A520E | Polystyrenic | Macroporous | Quat. ammonium with triethyl group | 0.9 |

2. Batch Sorption Experiments

Batch sorption experiments were carried out with 5 g resin in flasks containing 250 mL of different solutions of a specific PFAS (perfluorobutanoate, perfluorobutansulfonate, perfluorooctanoate, perfluorooctansulfonate); they were continuously mixed with magnetic stirrer at 250 rpm kept at 20 °C in a thermostatic oven for 80 h. Solution pH was adjusted to 7.5 using diluted ammonium hydroxide. The initial concentration of PFAS solution were 0.5 mmol/L and it was measured regularly during each experiment. The amount of PFAS adsorbed was calculated according to the difference of initial and equilibrium PFAS concentration. The different capacity of different resins and polymers in removing micropollutants depends mainly on three parameters including polymer matrix, porosity and functional groups. It is noteworthy that these three parameters affect both sorption capacity and sorption kinetics (Deng et al., 2010). So four different types of anion exchange resins, adsorbent polymers and hybrid polymers were tested in batch sorption experiments in order to determine the kinetic profiles of removal processes for four specific PFAS (PFBA, PFBS, PFOA, PFOS) investigating the effect of resin and polymer properties on sorption capacity and sorption kinetics. In the literature, there are several examples of application of anion exchange resins for the removal of PFAS but there are no references for the use of adsorbent polymers and hybrid polymers (Yu et al., 2009).

Fig. 1 shows the sorption kinetics for PFBA, PFBS, PFOA and PFOS on the four resins and adsorbent tested. The kinetic profiles were characterized by two parameters: the initial sorption rate (v_0) which represents the sorption rate when the concentration gradient is maximum ($\mu\text{mol/g}\cdot\text{h}$) and sorption capacity at equilibrium (q_e) which represents the adsorbed quantity at equilibrium ($\mu\text{mol/g}$). Strong base anion exchange resins display the highest values for both v_0 and q_e . The pure adsorbent Purosorb® PAD 500 is practically ineffective in removing both PFBA and PFBS whereas the weak base hybrid polymer Macronet® MN102 shows only a weak affinity for short chain PFAS. Although the two strong base anion resins (Purolite® A600E and A520E) displayed a similar shape in the kinetic profile reaching the equilibrium after 40 h their values for v_0 and q_e are significantly different (see Table 2). Both resins have the same polystyrene matrix crosslinked with divinylbenzene but the A600E has a gelular structure with more hydrophilic trimethyl functional groups whereas A520E has a macroporous structure with more hydrophobic triethyl functional groups. The sorption of all PFAS onto the macroporous resin A520E is faster than onto the gelular A600E indicating that the diffusion through the resin gel structure is the kinetic limiting factor of the sorption process. These data are in good agreement with those reported in literature (Li et al, 2000). Beside the faster kinetics, A520E displayed also a much higher sorption capacity than A600E (almost 5 times higher than the q_e for A520E) notwithstanding its lower exchange capacity (1.4 eq/L for A600E and 0.9 eq/L for A520E). The higher hydrophobicity of the functional groups of A520E (triethyl) compared to the more hydrophilic trimethyl of A600E may explain the higher affinity of active sites for highly hydrophobic perfluorinated anions. In contrast with data reported by Deng et al. (2010) both A600E and A520E, which have a polystyrene matrix, displayed an higher affinity for long chain PFAS than for shorter ones indicating that size exclusion effects are probably negligible. It is noteworthy that both A600E and A520E are characterized by slower sorption kinetics for short chain PFBA and PFBS than for long chain PFOA and PFOS indicating the need of longer residence times in order to obtain a quantitative removal and decreasing thus the risk of fast breakthrough. These data were also confirmed by the continuous test performed on A600E resin in which the breakthrough of the short PFBA took place long before the breakthrough of PFOA.

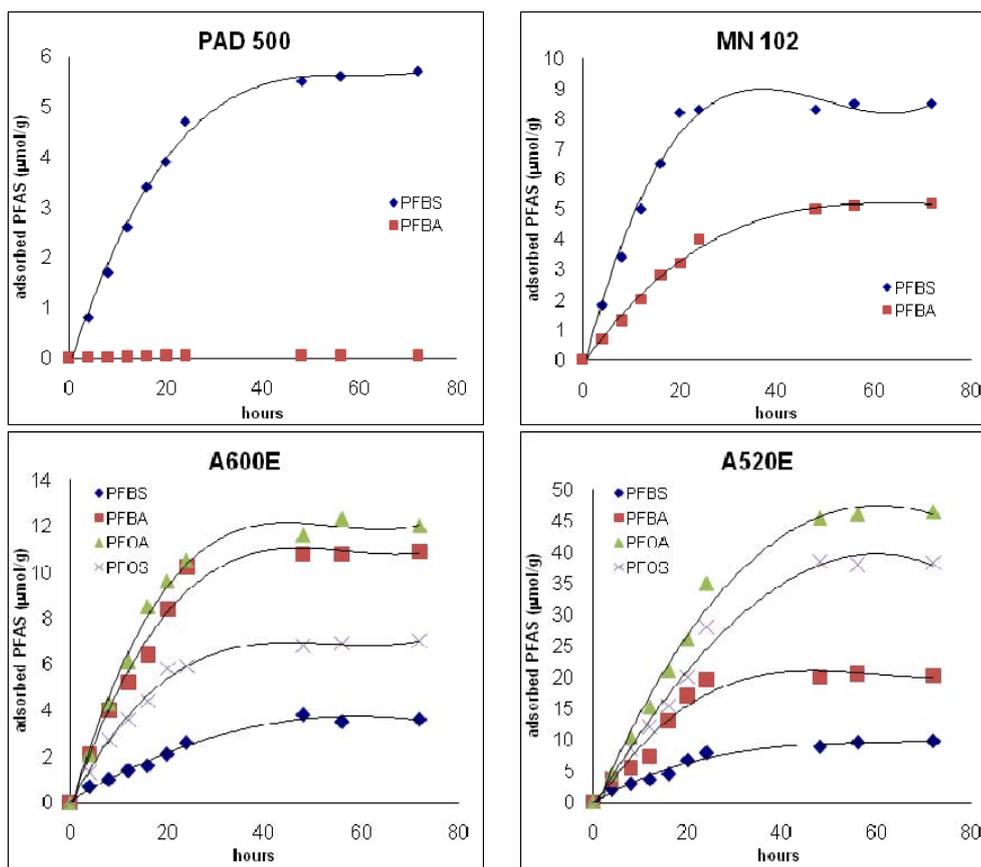


Figure 1: Sorption kinetics of PFBA, PFBS, PFOA and PFOS on adsorbent polymer Purosorb® PAD500, weak base hybrid polymer Macronet® MN102, strong base gelular resin Purolite® A600E and strong base macroporous resin Purolite® A520E.

Table 2: Kinetic parameters for PFBS sorption with the 4 resins.

| Resins | v_0 (mmol/g·h) | q_e (mmol/g) |
|-----------------|------------------|----------------|
| Purosorb PAD500 | 0 | 0 |
| Macronet MN102 | 0 | 0 |
| Purolite A600E | 2.1 | 10.9 |
| Purolite A520E | 3.6 | 20.2 |

3. Batch Regeneration Study

Studying the process of spent resins regeneration is a crucial issue. The main advantage of application of ion exchange resins with respect to activated carbon is the possibility to regenerate them in situ in a simple way. Various solutions have been tested for regeneration depending on the mechanism of removal of PFAS (adsorption or ion exchange). Regeneration agents include aqueous solution of diluted NH_4Cl , NH_4OH , methanol and mixtures thereof. In order to enhance effectiveness of regeneration process, NH_4Cl and NH_4OH were used in place of the typical NaCl and NaOH because of the higher water solubility of PFAS ammonium salts compared to sodium salts. Regeneration of adsorbent polymers and hybrid polymers is historically performed with solutions of solvents such as methanol and soda. The use of large amounts of solvents is required to promote desorption of adsorbates from the polymer matrix.

After batch sorption experiments the spent resin (5 g) was filtered out, recovered and rinsed twice with 50 mL deionized water and added into 250 mL regeneration solution. Regeneration experiments were performed with a magnetic stirrer at 250 rpm at 20 °C in a thermostatic oven for 80 h. The concentration of specific PFAS in regeneration solution was measured for the whole experiment duration and regeneration percentage was

then calculated. Figure 2 shows results obtained for regeneration of polymers and resins exhausted with PFOA using different regeneration solutions: 5 % NH_4Cl solutions, 5 % NH_4OH and diluted methanolic solutions are completely ineffective in regenerating Purosorb® PAD 500 and Macronet® MN 102. When the concentrated mixture methanol and NH_4OH was used, it was found that regeneration rate of Macronet® MN 102 increased from almost 0 of diluted methanolic solution to 94.5 %. In contrast to the adsorbent Purosorb® PAD 500 and the hybrid polymer Macronet® MN102 regeneration of strong base anion resins Purolite® A600E and A520E is easily accomplished with diluted solutions of 3 % NH_4OH and 3 % NH_4Cl . These results emphasize that the effectiveness of desorption of PFOA from spent polymers/resins strongly depends on the sorbent-sorbate interactions and water solubility; the use of regeneration agents which maximize water solubility of PFAS-cation couples is thus of crucial importance.

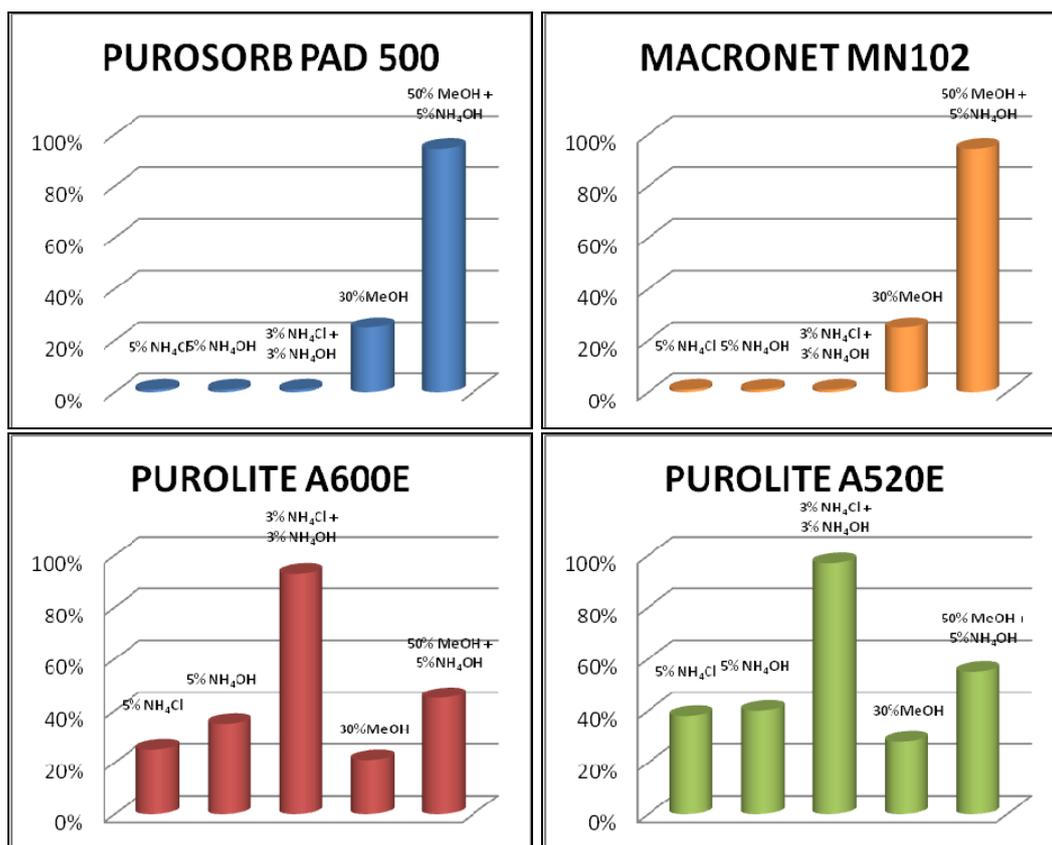


Figure 2: Regeneration results of spent polymers saturated with PFOA and resins Purosorb® PAD500, Macronet® MN102, Purolite® A600E and Purolite® A520E with different regeneration solutions.

4. Pilot Plant Experiments

A pilot plant was arranged in cooperation with the water service company Centro Veneto Servizi of Monselice (PD, Italy) nearby a drinking water treatment plant. The pilot plant was and is made of four parallel columns filled with different materials, each one with a length of 50 cm (0.5 m), diameter 3 cm (0.03 m), volume 350 ml and fed with 35 mL/min (2.1 L/h) micro-filtered water; so residence time is 10 min and surface hydraulic load is 3.0 $\text{m}^3/\text{m}^2\text{h}$. Filling materials tested were respectively A600E, PAD500, PAD428 and MN102. Samples of untreated water and treated water were (and are) taken every 8 h and analyzed by liquid LC-MS as described before to determine polyfluorinated organic compounds with particular attention to PFBA, PFBS, PFOA and PFOS. Particle diameters are respectively 300-1200 μm for A600E, 300-500 μm for PAD500, 350-1200 μm for PAD428 and 450-620 μm for MN102.

All the four resins had very high removal efficiency for PFOA and PFOS, but they showed very different behavior towards PFBA and PFBS. Results are reported in figure 3 for the resin PAD500, in Figure 4 for the resin MN102 and in Figure 5 for the resin A600E. Since Italian limits in drinking water are stated as maximum concentration of PFOS (30 ng/L) and as maximum sum of all the other PFAS (500 ng/L), experimental results are represented in these terms, and continuous lines represents limits in all the three graphs.

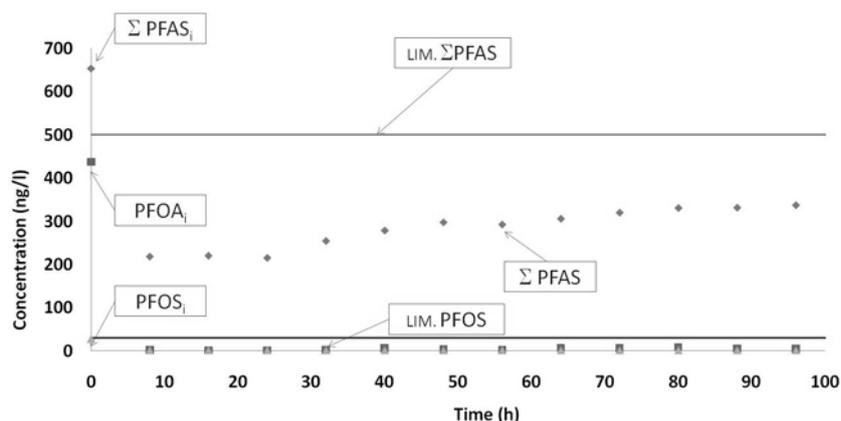


Figure 3: Concentration of PFOS and Σ PFAS in treated water with resin PAD500.

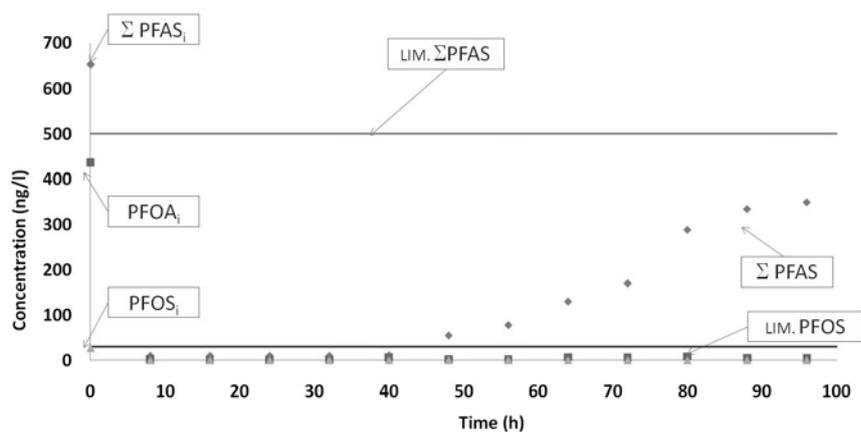


Figure 4: Concentration of PFOS and Σ PFAS in treated water with resin MN102.

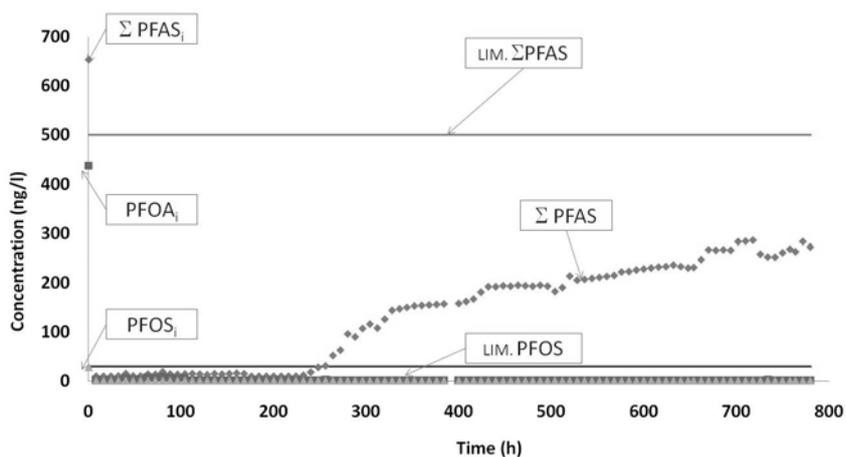


Figure 5: Concentration of PFOS and Σ PFAS in treated water with resin A600E.

Resin PAD500 (figure 3) removed almost 100 % of PFOA and PFOS, but it showed no efficiency for PFBA since the beginning of experiments, so the sum of PFAS (in which the most important component was PFBA in this water) was relatively high since the beginning of the test. Moreover, laboratory batch experiments evidenced difficulties in regeneration of PAD500, so experiments with this material were interrupted. Results encountered with PAD428 were very similar to the ones obtained with PAD500, so they are not represented in

a graph. Resin MN102 (figure 4) removed almost 100 % of PFOA, PFOS and PFBS without significant variations, but PFBA removal efficiency decreased rapidly after 48 h working (that correspond to a total treated water volume which is 288 times the volume of resin) and PFBS removal efficiency decreased after 100 h working; moreover, hydraulic problems were encountered for clogging and rise of head losses, so experiments were interrupted also with this material. Resin A600E (Figure 5) removed and still removes almost 100 % of PFOA and PFOS after 800 h working (that correspond to a total treated water volume which is ca. 4,500 times the volume of material), and removal efficiency for PFBA was high for ca. 250 h working (800 times, so this was the best resin in pilot-scale tests. Moreover, batch tests evidenced facility in regeneration of this resin, so pilot-scale experiments are now carried on until saturation of this resin.

5. Conclusions and suggestions for further work

Batch sorption experiments showed that adsorbents and hybrid polymers did not show any appreciable ability in removing PFAS. In contrast anion exchange resins are very effective in removing PFAS because of both fast kinetics and high equilibrium capacities. In particular the more hydrophobic macroporous resin Purolite® A520E showed both faster kinetics and greater equilibrium capacities indicating that its porous structure speeds up the mass transfer phenomena and its more hydrophobic active sites preferentially interact with strongly hydrophobic PFAS. Further, batch regeneration experiments showed that the exchange process is reversible and easy to perform requiring dilute and non-dangerous solutions of dilute NH_4Cl and NH_4OH . Pilot-scale experiments showed that all tested materials removed PFOA and PFOS with almost 100 % efficiency for long time, but they evidenced significant differences in PFBA removal. PAD500 and PAD428 did not remove PFBA at all, while MN102 had a very limited removal efficiency for PFOA; the resin A600E had good removal efficiency also for PFBA. Further experiments are scheduled to test A520E on pilot-scale. On the basis of the experimental data obtained from batch tests it would be interesting to test more hydrophobic resins which may display an increased affinity for super hydrophobic PFAS anions reducing thus the competitive action of anions such as nitrates and sulfates.

Acknowledgments

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