Utilization of organic and inorganic waste products for removal of per- and polyfluoroalkyl substances in highly contaminated water

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1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic amphiphilic fluorinated organic compounds[1]. PFAS have been extensively used for commercial products and industrial applications for over 60 years[2]. Some general physiochemical traits of this large group with thousands of compounds are thermal- and chemical inertness, surface active properties and dirt repellency. These unique characteristics are the reason why PFAS have and still are being used in some extent for surface protection in textiles, car waxes, food packaging materials, fire-fighting foams, and electronics[2]. Perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) are the most studied subgroups in the PFAS family and are persistent due to the resilient C-F bonds. PFAS have high mobility and persistency and are ubiquitous in all environmental compartments. Partitioning between matrices is affected by the carbon chain length, degree of fluorination and functional group.

Recent identification of previously undiscovered PFAS using non-targeted analytical techniques, were a motivation for the Organization for Economic Co-operation and Development (OECD) to rework the previously definition of PFAS. This was made to include compounds that previously would not be classified as a PFAS[1,3]. Following the OECD definition a compound should now be categorized as PFAS if it consists of a perfluorinated methyl group (-CF_3) or a perfluorinated methylene group (-CF_2-) without any other halogens, including hydrogen attached to it[3].

Several techniques for PFAS remediation are available, and most methods use immobilization by adsorption to various solid materials such as resins, iron oxides and activated carbon, or destruction by oxidation[4,5]. Even though immobilization does not degrade PFAS, it prevents them from further transport[4]. Ab- and adsorption (sorption) to solid surfaces are the most used remediation techniques due to low operational costs and high removal efficiencies[5]. The specificity and surface area of the sorbent is dependent on the particle size[6]. The interactions between the sorbent and sorbate are influenced by the matrix. Ion exchange, electrostatic- and hydrophobic interactions are a few mechanisms between PFAS and surfaces[4]. Carbon-based materials consist of non-polar functional groups that interact with primarily long-chain PFAS (PFCA, $n \geq 7$ and PFSA, $n \geq 6$) by hydrophobic interactions[4]. Presence of other ions, natural organic matter, and pH are important factors affecting he sorption of PFAS[4,7]. Generally, PFAS have low pKa values, PFOS -3.27 and PFOA 2.5 and inhibits anionic properties in water[6].

The present study focuses on utilization of residual products available from industries, pine and spruce bark from the timber industry and steel slag from stainless steel manufacturing. The barks consist of wood fiber and chips ranging from fractions below 0.9 mm up to 2.2 mm. Argon oxygen decarburization (AOD) is a process for production of stainless steel, where the recovery of oxidized elements is done by reduction of either aluminum or silicon which produces a granular steel slag. In this study, in-column sorption tests were conducted to investigate and compare the efficiency of PFAS sorption to bark and steel slag. The objective was to compare the retention of PFAS in highly contaminated water, to these materials in single and multi-component columns. A selection of 11 different PFAS (PFAS-11) was used to evaluate the efficiency of these sustainable materials.

2 Materials and Methods

Native and isotope-labeled extraction and volumetric standard were purchased from Wellington Laboratories (Guelph, ON). The water sample originated from a waste management facility in Sweden, previously characterized for PFAS, having concentrations of PFAS in the µg/L range, with main proportion covered by 11 PFAS. In total, 8 L of water was sampled and stored in dark at 8°C until analysis. Aliquots were taken by shaking and sonicating the bottle for 10 minutes. Four materials, pine, and spruce bark along with aluminum and silicon reduced steel slag (Al-AOD and Si-AOD respectively) were used to prepare single-columns by packing the material between a thin layer of glass wool. The multi-component columns were made by placing two single-columns in series. Liquid to solid ratio (L/S) 20 was used for single-component and L/S 10 for multi-component experiments, the following solid-phase extraction (SPE) method was based on ISO 21675:2019 with minor modifications. For quality control of the method, powdered activated carbon (PAC) known to possess high sorption efficiency towards PFAS was used[5]. All samples were spiked with mass-labelled extraction standard prior SPE and two spiked quality control samples (2 ng of native PFAS) were included for each extraction batch.

Quantitative analysis of PFAS-11, see Table 1 (PFCA, n = 7, PFSA, n = 3 and FTSA, n = 1) was performed using ultra-performance liquid chromatography electrospray ionization tandem mass spectrometry (UPLC-ESI-MS/MS from Waters Co, Milford, US) in negative mode. The separation was performed with a reversed-phase C18 BEH column (2.1 x 100 mm, 1.7 μm) set to 50°C, with a gradient flow of 30:70 mixture of methanol/water and 100% methanol both consisting of 2 mM ammonium acetate. Quantification was made using a single point quantification standard, verified to be within ± 20% against an internal calibration curve. The linear range for PFCA and PFSA were up to 30 ng, and for FTSA and PFOS-isomers up to 10 ng. Initial concentrations (Table 1) were all within the linear range. Acceptable recoveries were within the range of 50-120% and the ratio between two transitions were monitored, with exception of PFBA and PFPeA that only produces one stable transition.

3 Results

The initial concentrations of PFAS-11 are displayed in Table 1, the sum of short-chain PFAS was 587 ng/L (31%) and long-chain 802 ng/L (43%). Lowest concentrations were measured for PFDA and PFNA with ≤15 ng/L and the highest concentration for an individual compound was 6:2 FTSA comprising 489 ng/L (26%).

Table 1. Initial concentrations of PFAS in the ingoing contaminated water used for sorption tests using various residual materials. Definition of subgroups and chain lengths from Buck et al.[1] short-chain[a], long-chain[b] PFAS.

Subgroup	Carbon chain-length	Name	Abbreviation	Concentration (ng/L)
PFCA	4[a]	Perfluorobutanoic acid	PFBA	58
PFCA	5[a]	Perfluoropentanoic acid	PFPeA	195
PFCA	6[a]	Perfluorohexanoic acid	PFHxA	160
PFCA	7[b]	Perfluoroheptanoic acid	PFHpA	106
PFCA	8[b]	Perfluorooctanoic acid	PFOA	51
PFCA	9[b]	Perfluorononanoic acid	PFNA	15
PFCA	10[b]	Perfluorodecanoic acid	PFDA	7
PFSA	4[a]	Perfluorobutanoic acid	PFBS	174
PFSA	6[b]	Perfluorohexanesulfonic acid	PFHxS	86
PFSA	8[b]	Linear-Perfluorooctanesulfonic acid	L-PFOS	327
PFSA	8[b]	Branched-Perfluorooctanesulfonic acid (Dimethyl, 6/2 and 3/4/5)	Br-PFOS	210
FTSA	8	6:2 Fluorotelomer sulfonic acid	6:2 FTSA	489
Sum PFAS-11				1878

The general removal efficiencies for single-component columns were between 40% and 70% of PFAS-11 (Figure 1). Long-chain PFAS were removed by all materials. Steel slags were the only material demonstrating a reduction of PFHxS and Al-AOD additionally removed short-chain PFAS with more than 20%. Pine bark was generally the most effective sorbent, removing over 60% of PFNA, PFDA and all PFOS-isomers. Spruce bark was notably less effective as compared to pine with highest sorption of L-PFOS with 40%. The method was verified by PAC which reduced all PFAS with over 95%.
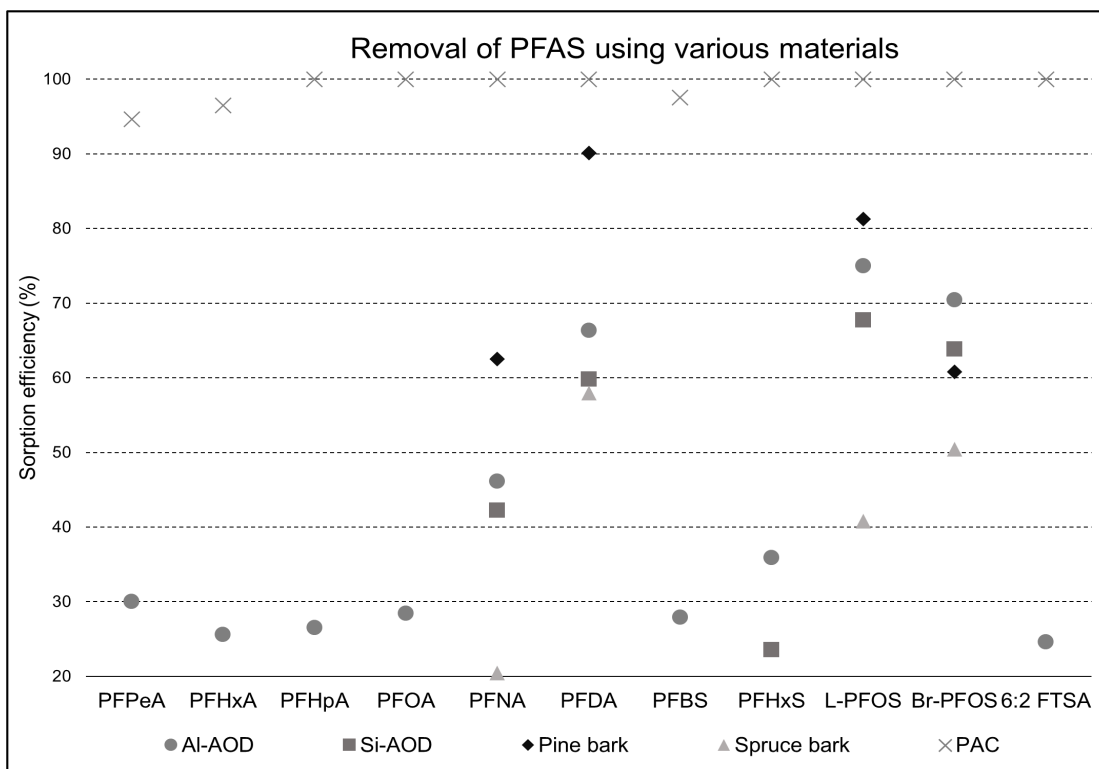
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Figure 1. Comparison in reduction of PFAS from a high contaminated water by aluminum reduced steel (Al-AOD), silicone reduced steel (Si-AOD), pine bark, spruce bark, and powdered activated carbon (PAC). Sorption conditions: PFAS-11 1.9 µg/L, 5 g sorbent, 10 mL water, pH 8, and flow rate of 0.06 mL/min. Efficiency limit were set to minimum of 20% and reduction below was seen unsatisfactory.

The multi-component columns (Figure 2) with pine-spruce bark had the greatest removal of PFDA, and all PFOS-isomers over 80%. The Al-AOD and spruce bark column successfully decreased PFCA (C5 and C8) concentrations. Overall, an increased retention of PFOS was seen in the multi-component columns compared to the single-component columns.
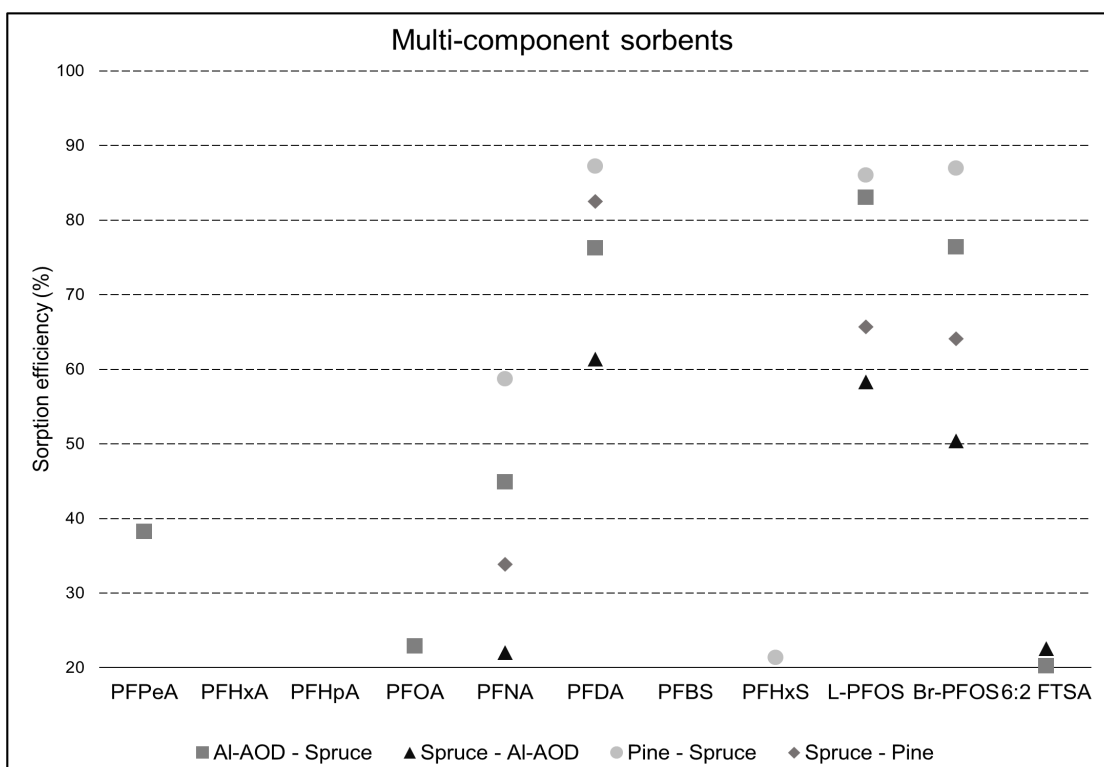

Figure 2. Impact on sorption of PFAS from high contaminated water using combination of two materials, spruce in combination with aluminum reduced steel slag (Al-AOD) and pine. Sorption conditions: PFAS-11 1.9 µg/L, 1 g sorbent, 10 mL water, pH 8, and flow rate of 0.06 mL/min.

4 Discussions

The presence of PFAS in landfills depends on what the waste consists of, age of the landfill and how the waste is stored. PFAS with chain-lengths up to nine carbons, can be produced *in situ* with presence of precursors. Oxidation and biodegradation by microbes can breakdown polyfluorinated structures to stable perfluorinated compounds. For example, oxidation of 6:2 FTSA produces PFCA with lengths of C4-C7[8]. It is therefore difficult to determine whether all PFAS originates from the waste itself or degradation from precursors. Quantification of short-chain PFAS such as PFBA and PFPeA, which only produce one stable transition during tandem mass spectrometry analysis possess a larger risk for interfering co-eluting compounds. Release of compounds could occur during the sorption experiments, and organic material consists of compounds which are structurally like PFAS. Co-eluting interferences were observed for PFBA and was therefore excluded from this study. Single-component columns have some efficiency on short-chain PFAS, while this reduction is decreased for multi-component columns. One explanation could be due to release of compounds in the first material which are interfering with the interactions between PFAS and the second sorbent. The two experiments had different L/S and if this has any effects on the results requires further investigation. More hydrophobic interactions to the organic materials, could explain the larger reduction of long-chain compared to short-chain PFAS. Steel slag contains exchangeable hydroxides, which could explain why these materials retain short-chain PFAS better compared than the tree barks. The results in Figure 2 shows that the order is of importance when combining two materials, bigger removal efficiencies are shown when pine bark is placed before spruce bark than the reverse order. The method was verified by almost complete removal of targeted PFAS by PAC.

5 Conclusion

The four residual materials show capability of removing long-chain PFAS, while the short-chain PFAS was notably less retained. Consideration is required when placing two materials in series. Pine bark was the material showing most promising results for a potential pretreatment method for removing PFAS in highly contaminated water. Additional field studies are necessary to evaluate the maximum capacity of these materials and how different physiochemical properties affect the immobilization of PFAS to these potential sorbent materials. One potential benefit of utilizing residual products as sorbent materials, could be an extended lifetime for other sorbent materials used for PFAS remediation

6 Acknowledgments

7 References

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