Investigating PFAS Removal Strategies During Carpet Recycling: A Greener Solutions Approach

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1. Executive Summary:

Per- and Polyfluoroalkyl substances (PFAS) have been used for decades to increase the stain, grease, and oil repellency of carpets and rugs. These chemicals possess unique physicochemical properties based on the presence of an alkyl carbon-fluorine tail that does not break down in the environment. Many studies have demonstrated that PFASs pose numerous health and environmental hazards ranging from suppressed immune systems in children to bioaccumulative effects in the environment. When carpets and rugs are recycled, PFAS is not intentionally removed and is in turn reintroduced into the environment. In this work, we evaluated points to intervene in current carpet recycling practices and the available technologies to remove and potentially mineralize PFAS to avoid reintroduction of harmful chemicals to the environment.

We focused our PFAS removal and treatment strategies on the face fiber of carpets and rugs because of its high PFAS content and its current economic value as a recycled output. In addition, implementation of a removal or treatment for the face fiber is the most practical given that face fibers are typically washed in an aqueous solution during the recycling process and most PFAS removal or mineralization technologies take place in an aqueous media. Based on this intervention point in the carpet and rug recycling process, we identified four strategies to address the PFAS on face fiber in the near term and long term. We found that the most feasible and readily available technology can potentially remove and concentrate the PFAS from carpets and rugs, but will require future treatment strategies to mineralize the PFAS. Looking further out, we also identified one near term and one long term strategy that can mineralize PFAS.

In the immediate, we propose implementation of a PFAS removal strategy that utilizes a strong base to break the linkages between the face fiber treatment polymer and PFAS to release the PFAS into solution. Once in solution, the released PFAS would be adsorbed onto a solid material such as granular activated carbon (GAC). GAC is the most common type of adsorbent used for PFAS treatments currently because of its high adsorption capacity, wide availability, and proven performance in complex matrices. We also identified an emergent technology for PFAS treatments that utilizes plasma to fully mineralize PFAS as a substitute for adsorbing PFAS onto GAC. Both of these strategies exhibit high technical performance and significantly decrease the health hazards to the community and the environment.

Looking into the future, we identified two strategies that utilize enzymes to perform part or all of the removal and mineralization. As a substitute for the strong base required to remove the PFAS from the face fiber, we propose development of an esterase treatment which is capable of carrying out the same reaction. An enzyme treatment has the advantages of being less hazardous to human health, less energy intensive for the plasma strategy, and less likely to damage the face fibers. Finally, we identified laccase as a long term strategy based on its demonstrated ability to selectively mineralize PFAS in a single step. While the currently identified laccase lacks the necessary environmental and technical performance at present, we see opportunities for advancement of green chemistry and engineering in the solution.

This report was prepared for our partner organization, the California Department of Toxic Substances Control (DTSC) within the California Environmental Protection Agency in response to its recent listing of carpets and rugs as priority products under the Safer Consumer Product Regulations. Our report is designed to assist DTSC with the development of regulatory responses to address the potential exposure to PFAS and widespread adverse impacts from PFAS in carpets and rugs. In addition to the development of an end of life management plan and the advancement of green chemistry, we identified additional policy

levers for DTSC to pursue with the United States Environmental Protection Agency (EPA) and recycling stakeholders in California.

2. Challenge Statement and Background:

2.1 Challenge Statement

With the environmental health concerns over PFASs in recycled carpet stock, DTSC partnered with the Berkeley Center for Green Chemistry to enlist graduate students of Public Health 271H: Greener Solutions to investigate methods of removing PFASs from recycled carpet stock during carpet recycling.The objectives of this project are outlined below.

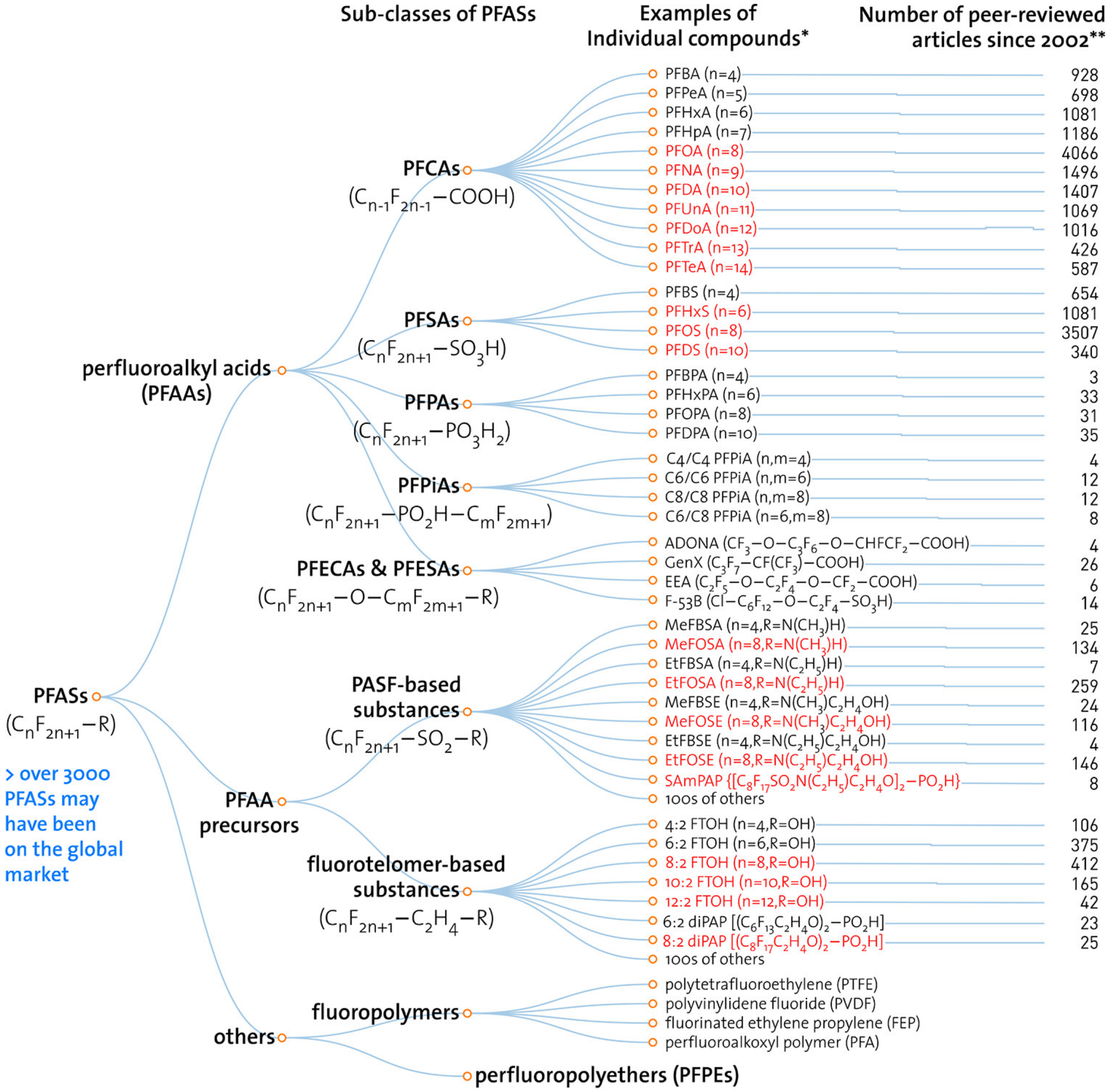
1. Identify carpet recycling processes and intervention points where PFAS removal methods can be implemented
2. Review current PFAS treatment options
3. Conduct a comparative chemical hazard assessment on the treatments proposed
4. Present the hazards, efficacy and feasibility of each approach

The final product was to create an opportunity map of the available options for PFAS removal during carpet recycling.

2.2 PFAS Physicochemical Properties

Polyfluoroalkyl substances (PFAS) are a diverse family of more than 3000 xenobiotic chemicals that have been in production since the 1940s (KEMI, 2015). PFAS possess unique physicochemical characteristics that include the ability to withstand extreme temperatures, resist staining, and avoid corrosion (Buck, 2011). PFAS derive their stability and persistence from the strength of covalent carbon-fluorine bonds, which do not break down under normal environmental conditions (HBN, 2017). PFAS can vary in the number of carbon atoms that make up the backbone, from two carbons to large molecular-weight polymers. PFAS are broadly subdivided into polymers and non-polymers. Polymers can be further divided into fluoropolymers, side-chain fluorinated polymers and perfluoropolyethers. Within the non-polymers, there are two primary categories: perfluoroalkyl acids (PFAAs) and PFAA precursors. Figure 1 gives a more detailed overview of the types of PFAS. While PFAAs make up less than 1% of PFAS on the market, they are the terminal degradation products of many other PFASs.

PFAS are extremely persistent in the environment and are capable of long-range transport by air or water. Once released into the environment, PFAS has been shown to be present in indoor and outdoor environments where it accumulates in terrestrial and aquatic organisms. PFAS has been detected in surface waters, groundwater sources, wastewater treatment plant effluent, landfill leachate, soils, and biological organisms around the globe (Wang, 2016). Short chain PFAS, defined by 4-7 carbon backbone, are more mobile in the environment due to their greater water solubility.



* PFASs in **RED** are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 1: Family tree of PFASs and their citations in peer-reviewed articles since 2002 (Wang, 2017)

2.3 Health Effects of PFAS

PFAS are known to cause negative health effects in humans and wildlife. Based on human biomonitoring data, all humans sampled show evidence of exposure to PFAS despite limitations in the types detectable PFAS (Calafat, 2007). The Centers for Disease Control and Prevention's National Health and Nutrition Examination Survey has found PFAS in every person tested with average concentrations between 1.3-6.3 ug/L (ATSDR, 2017). For human health endpoints, a systematic review of 64 epidemiological studies found positive correlations between children's PFAS exposure and suppressed immune system response, dyslipidemia, impaired kidney function and delayed menstruation (Rappazzo, 2017). Perfluorooctanoic acid has also been associated with low birth weight in humans (Malits, 2017).

In addition to reproductive and developmental toxicity, PFAS is known to bioaccumulate, with increasing accumulative effects with increasing perfluoroalkyl chain length. The half-life of PFAS in humans has been shown to range from days for short-chain PFAS (Nilsson, 2010) to years for long-chain PFAS (Seals, 2011). Similarly, biomagnification has been observed for PFAS in freshwater and marine organisms (Houde, 2006). Biomagnification factors (BMFs) and bioaccumulation factors (BAFs) values greater than 1,000 or BMF greater than 1 meet the bioaccumulation hazard trait criteria outlined in the California Code of Regulations, Title 22, Division 4.5, Chapter 54, Article 5. The BMFs and BAFs some PFAS are close to 1,000, and exceed it for a few PFAS, such as perfluorooctanesulfonic acid (PFOS) and perfluorohexadecianoic acid (PFHxA). The European Food Safety Authority (EFSA) estimated that “fish and other seafood” account for up to 86% of dietary PFAS exposure in adults (Sunderland 2019). The human health effects studied have primarily focused on long-chain PFAS due to the questionable assumption that short-chain PFAS are less toxic because of their shorter half-life in organisms. However, there are notable studies that have shown reproductive and developmental toxicity, hepatotoxicity, and neurotoxicity in rodents from exposure to perfluorobutanesulfonic acid (PFBS), a short-chain PFAS (DTSC, 2019). Despite their reduced biological half-life, short-chain PFAS appear to retain their toxicity. Furthermore, they are just as persistent and more mobile in the environment than their longer-chain congeners.

To address the potential health effects from cumulative exposures to PFAS, exposure limits and testing methods are in their early stages of development and implementation in the U.S.. The U.S. Environmental Protection Agency (EPA) established an individual chronic reference dose for both PFOA and PFOS of 0.02 ng/kg body weight/day (U.S. EPA 2016) and a lifetime drinking water health advisory level for combined PFOS and perfluorooctanoic acid (PFOA) of 70 ng/L in 2016. In 2018, the Agency for Toxic Substances and Disease Registry (ATSDR) in the United States established Minimum Risk Levels (MRLs) at 11 ng/L for PFOA and 7 ng/L for PFOS. Although these are low exposure limits which suggest higher health risks, these limits are neither enforceable nor legally binding under the current regulatory framework. The average PFOA in one public water supply in Ohio, the Little Hocking water system, was 3,550 ng/L (range 1,500 ng/L to 7,200 ng/L) between 2002 and 2005 (Sunderland, 2019).

Although the EPA has not established an enforceable limit, often referred to as the Maximum Contaminant Limit (MCL), several states have set lower health advisories. California has established a recommended interim notification level of 14ng/L for PFOA and 13 ng/L for PFOS in drinking water based on the Office of Environmental Health Hazard Assessment’s evaluation of the scientific evidence (OEHHA, 2018). The evidence of toxicity is limited to a few PFAS and many of the fluorinated polymers and intermediate degradation products are poorly understood.

2.4 PFAS in Carpets and Rugs

Carpet is made of four main layers: the face fiber, primary backing, secondary backing, and carpet padding (Figure 2). Since carpet face fiber is made from synthetic materials such as nylon, polypropylene, acrylic, and polyester which can absorb water and oil-based compounds, PFAS treatments have been used by the carpet industry since the 1980s to impart stain repellency (EPA, 2012, Hilton 2017). As a result, most commercial and residential carpets and rugs in the United States have been treated with PFAS. It is estimated that during the early 2000s, about fifty percent of fluorotelomers and associated side-chain fluorinated polymers in production were used for textiles and clothing, including carpets and rugs (EPA, 2009). Starting with an initiative by the San Francisco Department of the Environment to only purchase carpets without PFAS intentionally added, major carpet and rug manufacturers in the United States have since then voluntarily phased out PFASs from their products without sacrificing performance. It is unclear what chemicals were used to replace the PFAS.

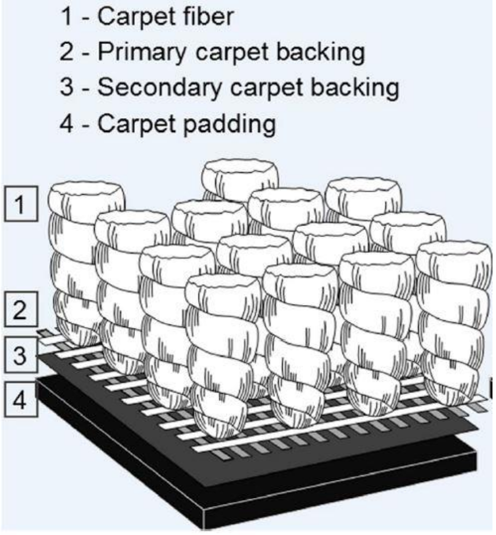


Figure 2: Anatomy of tufted carpet (source Haines et al. 2020).

There are different estimates of the quantity of PFAS remaining in carpets and rugs. The European Commission estimates that old carpets contain 75 parts per million of PFAS and that carpets in use worldwide contain approximately 1.64 million kg of PFAS (European Commission, 2011). A recent study estimated that there are ~800 kg of PFAS emissions attibutatble to in-use carpets in California as of 2020 (Chen, 2020). Connecting those emissions to exposures, another study measured child intake of PFAS from carpets in 18 California childcare facilities to range between 0.023 to 1.9 ng/kg body weight/day. These exposure estimates are all above the EPA's individual chronic reference dose for both PFOA and PFOS of 0.02 ng/kg body weight/day which highlights the need to address the remaining PFAS in carpets and rugs (Wu, 2020). While this health advisory is not an enforceable exposure limit for the community, this study suggests that human contact with carpets alone can exceed a safe threshold for exposure to PFASs by up to two orders of magnitude. This is cause for alarm as there are other sources of PFAS in the environment such as drinking water that can lead to even greater cumulative exposures. Although there is extensive evidence of widespread environmental contamination of PFAS from use in carpets and rugs, studies of aggregate exposures are lacking.

2.5 Difficulties of Measuring PFAS

In order to determine how much PFAS is removed from carpet and how much remains on the carpet, the initial concentration of PFAS on the carpet must first be determined. The most common method used for analyzing PFAS content in solid matrices is particle-induced gamma ray emission (PIGE) spectroscopy. This method is not capable of speciating PFAS, but rather gives the total elemental fluorine content on a two dimensional surface (nmoles F/cm^2). Included in this would be any fluorinated polymers such as PTFE, which could mask effective removal of fluorinated side chains if PTFE is abundant. PIGE is also not currently commercially available, though research on this front is actively being funded by the Department of Defense (Peaslee, DoD Award). A similar, technically simpler method is total organofluorine combustion ion chromatography (TOF-CIC) and has been commonly used to quantify unknown PFAS (McDonough et al. 2019), though the method suffers from similar problems as PIGE by not speciating PFAS. It is also in the process of being optimized for rapid field testing (Hanigan, DoD Award). Alternatively, targeted liquid chromatography tandem mass spectrometry (LC-MS/MS) and gas chromatography mass spectrometry (GC-MS) can quantify specific PFAS compounds, but the analyte list is limited to about 40 compounds in most commercial labs (Eurofins USA, 2020), which likely doesn't encompass the sum of all PFAS present in the carpet (Robel et al. 2017), and would require extraction from carpet. If the extraction is incomplete, this will not provide an accurate assessment of the initial PFAS concentration on the carpet.

Another potential option would be to use PIGE or TOF-CIC and develop an empirical understanding of how much fluorine is typically bound up in fluoropolymers, which are likely to be less bioavailable, and subtract that mass from what is measured by PIGE or TOF-CIC. There will certainly be variability from carpet to carpet, but this would hopefully give an approximate measure of how much monomeric PFAS can be removed. With all that in mind, we are hesitant to recommend a target removal efficiency because there are so many unknowns around analyzing any potential results. Additionally, to the best of our knowledge, no one has ever tried to remove PFAS from carpet so we don't have a baseline expectation for what is reasonable. All of that said, one log removal may be a reasonable target. Ideally, this reaction would be completed in a matter of hours rather than days since this could pose a significant bottleneck in recycling.

2.6 Carpet Recycling Processes

In 2016, 343 million pounds of postconsumer carpet was discarded in California, of which 257 million pounds were landfilled, 65 million pounds were recycled, and 21 million pounds were incinerated (CARE, 2016). Although carpets are highly recyclable, they continue to be a substantial contribution to landfill mass, accounting for 3% of all landfill mass in the U.S. (HBN, 2017). In 2015 and 2017, California established a carpet stewardship program through California Assembly Bills (AB) 2398 and 1158 to establish a non-governmental organization to coordinate statewide carpet recycling to increase carpet recycling to 24% by the end of 2020 (CARE, 2018). While this initiative in California has the potential to divert substantial mass away from landfills or incineration, it may reintroduce PFAS into the environment and into consumer products from the recycled carpet fibers contaminated with PFAS and further perpetuate exposures (Figure 3). To add to this, PFAS is not removed, treated, or monitored by any regulatory requirement. Despite the voluntary removal of PFAS from new carpets, PFAS will remain a legacy chemical issue because of the ten to twenty year lifetime of carpets. Furthermore, current aftermarket treatments for stain, soil, and grease repellency still contain PFAS (HBN, 2017). As a result, it is precautionary to assume that all carpets in the waste or recycling pipeline are contaminated with PFAS until a strategy to identify and treat PFAS is implemented. The number of carpet and rug recyclers in the U.S. is limited and subsidized from proceeds collected at the point of sale of new carpets and rugs (Figure 4).

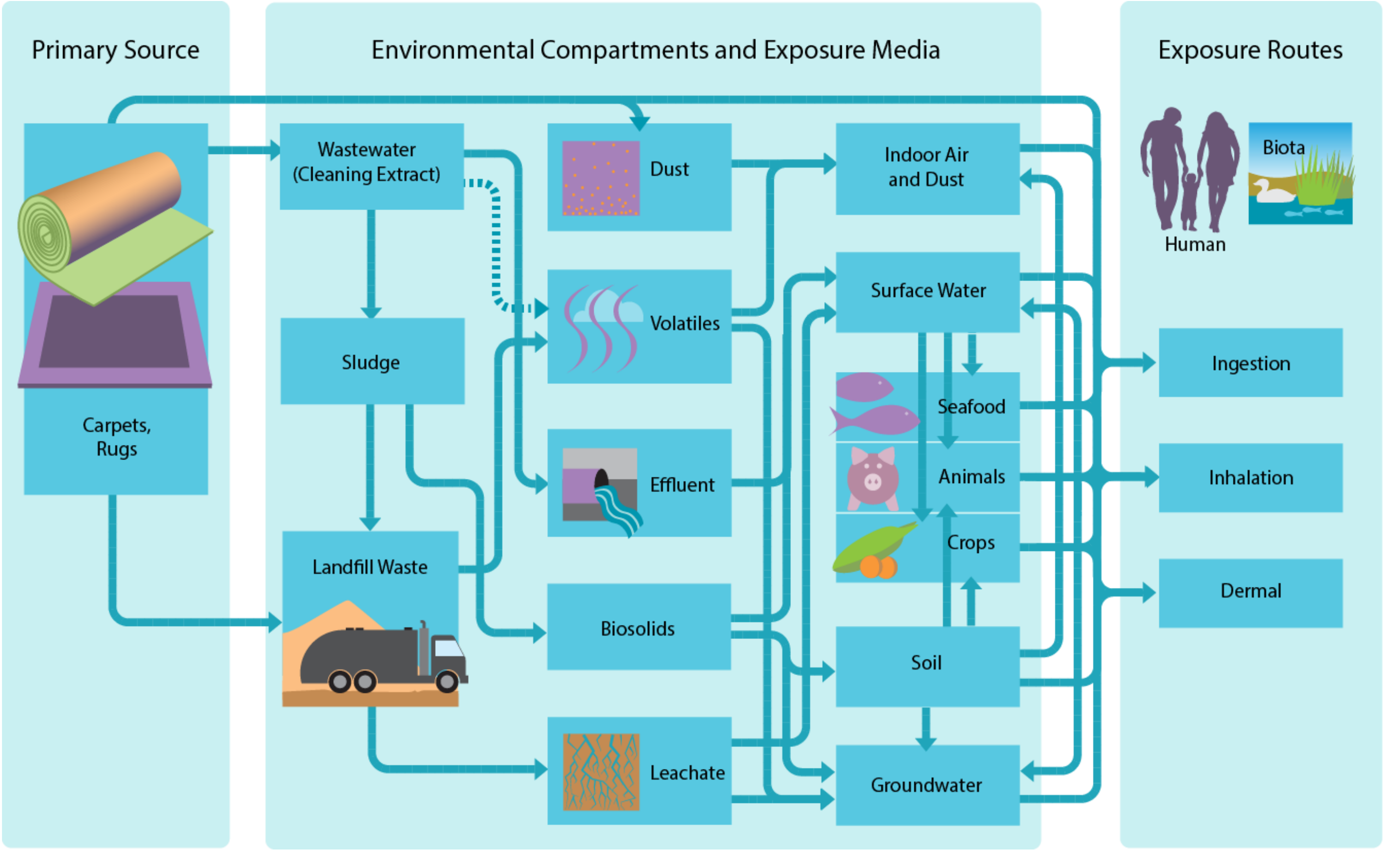
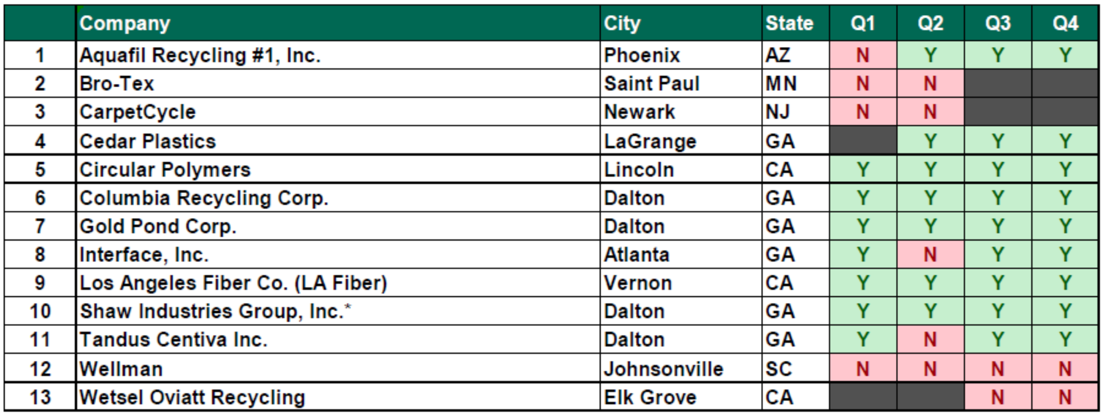


Figure 3: Possible pathways of exposure to PFAS from the life cycle of carpets and rugs (DTSC, 2019)

Carpet face fiber is typically constructed from nylon 6, nylon 6,6, polyethylene terephthalate (PET), polypropylene or wool. According to CARE's 2016 national survey, nylon 6 constituted 46% of the material sorted out of the carpet waste stream (CARE, 2016). The primary and secondary backings are made from recycled polypropylene and sandwich a fly ash or calcium carbonate filler. The face fiber and backing are the most recycled components of carpets, making up 98% of the recycled output in California (CARE, 2018). The remaining components are less valuable and must be separated out prior to recycling the fiber or backing. The current practices of carpet recycling to accomplish this involves five main steps; 1) removing carpet and collection, 2) sorting and baling the carpet based upon face fiber type, 3) separating the face fiber from backing using a mechanical process of shearing, shredding, hammer milling, or rotary impact separation, 4) sorting the face fiber from backing, and 5) cleaning and/or extruding the face fiber (CARE 2012) (Figure 5). Mechanical recycling is less expensive than chemical recycling. Chemical recycling breaks down the face fibers into their original chemical components and toxic chemicals are easier to separate. So far, only nylon 6 chemical recycling has been commercialized and mechanical recycling is likely to dominate the carpet and rug recycling industry for a long time (HBN, 2017).



	Company	City	State	Q1	Q2	Q3	Q4
1	Aquafil Recycling #1, Inc.	Phoenix	AZ	N	Y	Y	Y
2	Bro-Tex	Saint Paul	MN	N	N	■	■
3	CarpetCycle	Newark	NJ	N	N	■	■
4	Cedar Plastics	LaGrange	GA	■	Y	Y	Y
5	Circular Polymers	Lincoln	CA	Y	Y	Y	Y
6	Columbia Recycling Corp.	Dalton	GA	Y	Y	Y	Y
7	Gold Pond Corp.	Dalton	GA	Y	Y	Y	Y
8	Interface, Inc.	Atlanta	GA	Y	N	Y	Y
9	Los Angeles Fiber Co. (LA Fiber)	Vernon	CA	Y	Y	Y	Y
10	Shaw Industries Group, Inc.*	Dalton	GA	Y	Y	Y	Y
11	Tandus Centiva Inc.	Dalton	GA	Y	N	Y	Y
12	Wellman	Johnsonville	SC	N	N	N	N
13	Wetsel Oviatt Recycling	Elk Grove	CA	■	■	N	N

**Discontinued processing operations in late 2016 but continues to report processed output from inventory*

■ Not active participant in AB 2398 program during this time

Figure 4: List of recyclers (Tier-1 processors) that received funding from CARE in 2018 (CARE, 2018).

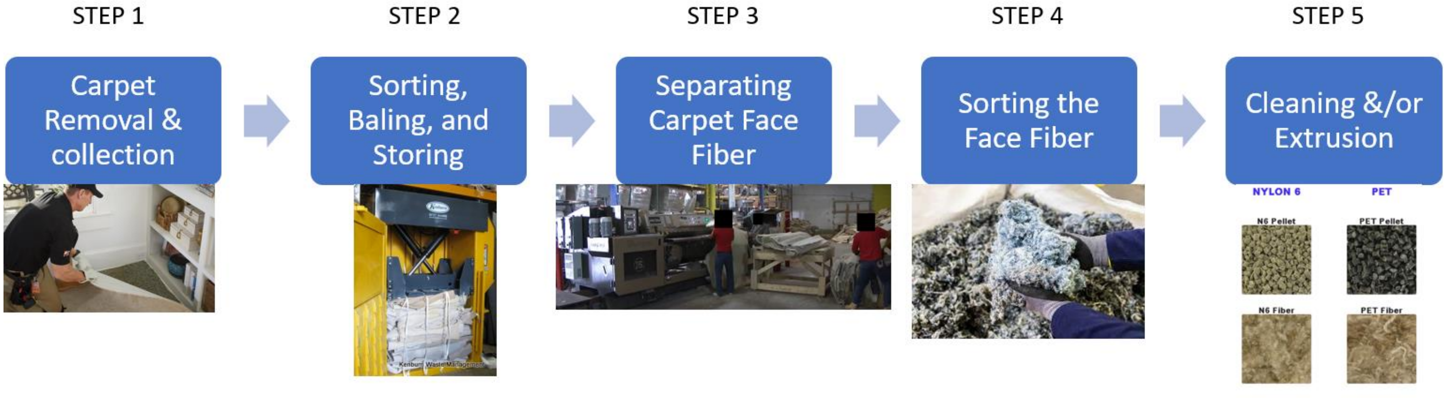


Figure 5: A general overview of the carpet recycling process. These processes vary by recycling center and final products. (Image Sources in order: 1) https://www.homedepot.com/c/ah/how-to-remove-carpet/9ba683603be9fa5395fab90eb8b5a1b, 2)https://www.kenburn.co.uk/flooring-company-make-great-savings-recycling-carpets-bramidan-baler-kenburn/, 3) www.youtube.com 4)https://www.healthyseas.org/2020/04/21/tarkett-closes-the-loop/, 5) https://circularpolymers.com/products/.

2.7 Safer Consumer Product Regulations

In 2008, California signed into law two of six California Green Chemistry Initiatives, AB 1879 and SB 507, to improve the environment and health performance of chemicals by providing DTSC the authority to regulate chemicals in consumer products. These statutes authorized and required DTSC to adopt regulations that identify and prioritize chemicals in consumer products. To do this, DTSC implemented new regulations in 2013 called the Safer Consumer Product (SCP) Program that utilizes a four-step, science-based, ongoing process to identify alternatives. In the first step, DTSC maintains a Candidate Chemical list that is based on authoritative lists and a given chemical's hazard trait to cause harm to people or the environment. In the second step, DTSC identifies Priority Products based on the potential exposure to a Candidate Chemical and the potential for widespread adverse impacts. DTSC starts this step by proposing a Priority Product on its Initial Priority Products List and then undergoes an extensive rulemaking process to finalize it into regulation, known as "adoption." To date, three have been adopted and seven have been proposed.Unlike the Toxic Substances Control Act, the next step places the burden of determining risk on industry instead of the regulator. Once adopted into regulation, the SCP regulations require manufacturers, importers, assemblers, and retailers (known as "responsible entities") to notify DTSC that their product is a priority product in regulation. It is then on the responsible entities to conduct an alternatives analysis on their use of the Candidate Chemical to determine how to limit exposure or reduce harm. In the fourth step, DTSC reviews the alternatives analysis submitted by responsible entities and generates a regulatory response. The regulation gives DTSC latitude to require further analysis or revisions to the alternatives analysis, restrict its use or sale, implement engineering or administrative controls, develop an end-of-life management program and advance green chemistry.

In 2018, DTSC determined that carpets and rugs containing PFAS met the department's criteria and prioritization as a Priority Product and placed them on its Initial Priority Product List. DTSC has spent 2020 working through the rulemaking process to finalize carpets and rugs as Priority Products. As stated in section 2.4, the responsible entities for carpets and rugs voluntarily phased out PFAS from carpets and rugs, likely in response to the listing on the Initial Priority Product List. This will make it challenging for DTSC to have the industry generate an alternatives analysis and to review the data behind their substitution decisions under the current regulatory framework. Regardless, this report is intended to provide DTSC with the best available science to aid its decision making on generating a regulatory response. Although there are short-comings in holding industry responsible within the current CSP regulations, DTSC is actively revising the regulations and this work may assist with restructuring the regulations given the wide scope and authority of the original statutes.

3. Approach:

3.1 Boundary Conditions:

All of our strategies are bounded by three conditions. The first limits what part of the carpet our solutions will target. Face fiber will be the only material that is treated, rather than the entire carpet. Face fiber was targeted because it is the most recyclable and most valuable component of the carpet (CARE 2019). It is also where the majority of PFAS is applied on a carpet (Hilton 2017, DTSC 2018, EPA 2009, EPA 2012). Furthermore, by removing the other components of the carpet, we minimize the production of unwanted, potentially hazardous byproducts during treatment. In addition, by targeting only the face fiber, the efficiency of any suggested treatment may be increased by eliminating physical barriers and chemicals that may interfere with the desired reaction. Treatment of carpet fluff also provides us with a drop-in intervention point because carpet fluff is sometimes washed before being processed. However, this boundary condition does have a significant drawback. When face fiber is separated from the carpet backing, a large amount of dust is released into the air, which may well contain PFAS and be inhaled by carpet recycling workers (CCSP, 2018). Nevertheless, treating the pure fluff remains the most practical option for the reasons outlined above. To minimize worker exposure to this potential hazard, engineering controls should be considered during face fiber removal.

The second condition limits the type of face fibers that will be treated with our interventions. We will focus solely on the nylon 6 and nylon 6,6. Nylon has been shown to have PFASs added to the face fibers as it can readily absorb water or oil based compounds into the fibers (Hilton 2017). According to industry experts, more PFASs are added to nylon fibers versus PET fibers, likely due to the inherent olio- and hydrophobicity of PET (though this has been disputed by other industry experts during personal communication). Additionally, nylon face fiber is more recyclable and valuable than other common fiber types, which make it more desirable to reclaim (CARE 2019). Table 1 shows that nylon is the preferred choice, constituting over 70% of all recycled carpet in California in 2019. However it is important to note that PET increased in the Q4 of 2019, suggesting a potential avenue for future research. In talking with industry experts, carpet recycling companies are targeting nylon face fiber due to its high value in the secondary market. However, the demand in the secondary market is highly dependent upon the economy and the price of oil (CARE 2019). For example, in 2019, the demand for nylon 6 decreased slightly as the demand by the automotive industry decreased, as seen in Table 1 (CARE 2019). By narrowing the scope of this report to nylon-type face fibers, we are able to target our intervention point and start to assess the effect of treatments on face fiber quality.

Table 1: face fiber breakdown that was shipped and sold in 2019 (CARE 2019).

Face Fiber Breakdown - Shipped and Sold				
	Q1 2019	**Q2 2019**	**Q3 2019**	**Q4 2019**
Nylon 6	58%	53%	50%	39%
Nylon 6,6	28%	32%	24%	25%
Modular Carpet Tile	3%	2%	5%	4%
Polypropylene	2%	2%	3%	2%
PET	8%	11%	17%	29%

The third and final boundary condition limits the scope of PFAS that our solutions will treat. While we realize that fluoropolymers and perfluoropolyethers share many characteristics with other fluorinated compounds that make them concerning, we have chosen to omit them from serious consideration for two main reasons: (1) Literature on treatment of these compounds is nearly non-existent, save for incineration; (2) Multiple experts have said that side-chain fluorinated polymers make up the majority of PFAS used in carpet treatment. Critical to evaluating treatment of side-chain fluorinated polymers is their chemical structure. The polymeric backbone is often made up of acrylate or methacrylate groups (Figure 6), where R is a PFAS. Carpets may also contain PFAAs, but since these are monomeric impurities not bound to any polymer backbone, any washing step will likely remove these compounds simply by dissolution into the aqueous phase.

Figure 6. Depictions of acrylate (left) and methacrylate (right) linkages. n is the number of monomeric repeats in the polymer. R in this case in a PFAS species. Image sources: Polysciences.com and Wikipedia.com.

4. Criteria For Success:

4.1 Health and Environmental Performance

The health and environmental performance will be based on understanding: (1) who is potentially exposed and the route or likelihood of exposure; and (2) the chemical hazards associated with the process. We are focusing on comparing the hazards presented by PFASs in the baseline with the chemicals used in our interventions. We acknowledge that our treatment strategies won't remove 100% of PFAS in carpet, but we are assuming that the hazards posed by PFAS after the removal process will be significantly reduced.

4.2 Exposure Implications:

At a typical carpet recycling facility, there are five main processing steps (Figure 5). Some of these processes can vary depending on the facility and what product is produced, but these five steps are sufficient for an initial assessment of occupational hazard. There is a paucity of data on the amount of PFAS that is in post-consumer carpet, nor are there any data for how much is released during the carpet recycling processes. In addition, it is hypothesized that numerous other constituents of the carpet are released into the air when the carpet is processed (DTSC 2018 & HBN 2017). Currently, no literature exists on quantifying these exposures. However, we can hypothesize which processes might (1) expose workers through dust inhalation; or (2) inadvertently remove PFASs from the carpet and potentially lead to environmental contamination. As mentioned previously, it is likely that the face fiber contains the majority of the PFASs added in carpet. Thus, we hypothesize steps 3 and 4 (shearing and sorting the carpet face fiber) will lead to the highest workplace exposures while step 5 (cleaning and extruding) could lead to highest environmental contamination. Routes of dust exposure could be through inhalation, ingestion, or dermal routes (Figure 7). In addition to workers, the nearby community may be exposed, though there are no studies that measure volatile PFAS, PM or effluent from these facilities.

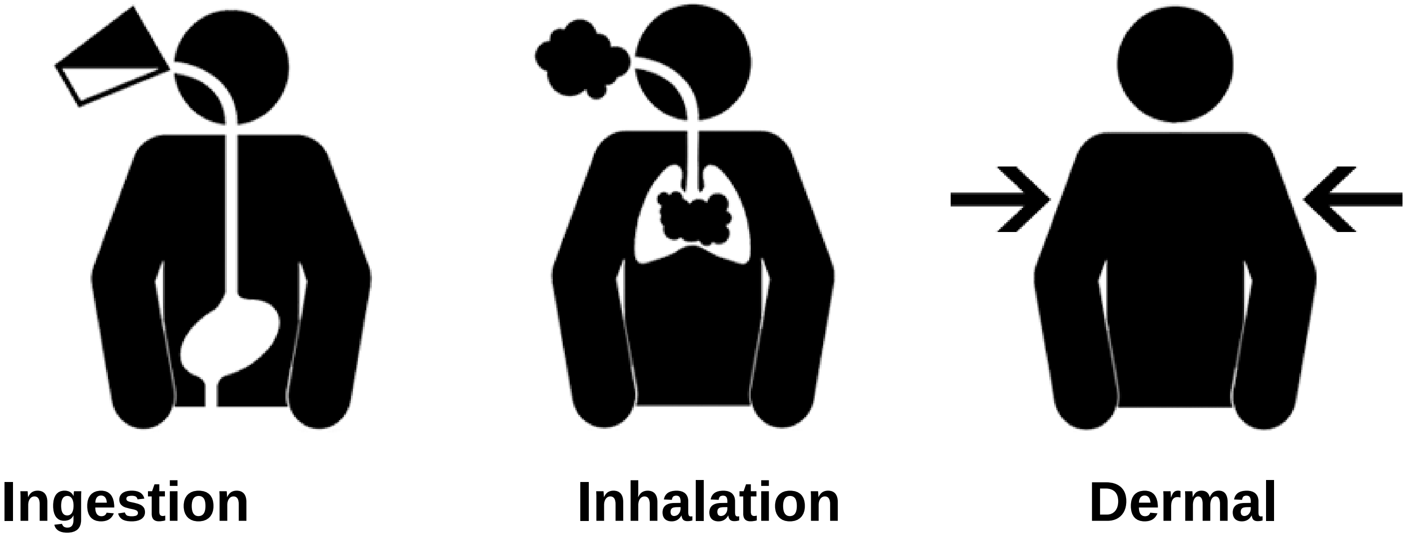


Figure 7: The three most common exposure routes related to carpet recycling. https://sphweb.bumc.bu.edu/otlt/mph-modules/exposureassessment/exposureassessment3.html

4.3 Chemical Hazard Tables:

As part of evaluating each of our strategies, the chemical hazards associated with each approach are considered. All chemicals involved in the reactions are included. PFASs are not included in our strategy hazard tables since we are assuming that the strategy will remove PFASs from the carpet. We gathered all chemical hazard data from Globally Harmonized System (GHS) criteria and guidance, authoritative chemical hazard sources (IARC, Proposition 65), and peer-reviewed literature to survey the human (carcinogenicity, mutagenicity, developmental/reproductive toxicity, endocrine disruption, systemic toxicity, neurotoxicity, and irritation) and environmental (aquatic toxicity and bioaccumulation) endpoints (Table 2). Each hazard was assessed and classified by hazard using a color rating based on the GreenScreen Hazard Assessment Guidance (Greenscreen 2018). Our hazard assessment did not complete the entire GreenScreen method, such as applying benchmarks, to keep the scope within the time limits of a single semester project. An example is provided in Table 3 with PFOA, which exhibits moderate to very high human and environmental endpoints, suggesting it is a high hazard chemical. These tables provide a clear and concise visual of the health and environmental endpoints of the proposed strategies.

Table 2: Hazard table abbreviation key

Abbreviation	Meaning
C/M	Carcinogenicity & Mutagenicity
D/R	Developmental & Reproductive Toxicity
Endocrine	Endocrine Activity
Systematic	Systemic Toxicity & Organ Effects
Neurotox.	Neurotoxicity
Irritation	Eye & Skin Irritation
Aquatic	Acute Aquatic Toxicity
Bioaccum.	Bioaccumulation

Table 3: Example of PFOA human and health hazards with qualitative rating color.

Constituent	Human Endpoints						Environmental Endpoints	
	C/M	**D/R**	**Endocrine**	**Systematic**	**Neurotox.**	**Irritation**	**Aquatic**	**Bioaccum.**
PFOA	**M**	**H**	**H**	**H**	**H**	**VH**	**M**	**H**

L: Low	**M:Moderate**	**H: High**	**VH: Very High**	**Probable**	**Data Gap**

4.4 Technical Performance and Design Constraints

Our strategies will be evaluated against the following primary technical performance criteria: (1) Does the strategy remove or destroy PFAS? (2) How fast can the strategy be implemented into the current carpet recycling processes? (3) How long do the reaction(s) take? (4) How much energy is required? and (5) How difficult will it be to implement at scale? Each of these technical criteria are graded using a qualitative color ranking (Table 4), with green being the most ideal outcome, red the least desirable and orange as an intermediate. Table 5 shows an example strategy that exhibits removal of PFAS, immediate implementation speed, fast reaction speed, low energy input, and a feasible implementation, suggesting a strong candidate to implement.

The quality of the fiber after treatment is also an important consideration. If the fiber quality has deteriorated during a treatment strategy, this will limit or eliminate its value. This was a particular concern with our first proposed strategy which involves the use of a strong base. In some recycling processes, the fiber is melted and extruded into crumb, in which case the tactile quality of the fiber might be less important. Nevertheless, determining the effect on fiber quality is still important, though difficult to predict. Evaluating any strategy in the lab was beyond the scope of this report. Therefore, the effect on fiber quality was not listed as one of the performance criteria. Instead, we do provide some literature-based inferences, but this would need to be confirmed with empirical studies.

Table 4: Criteria key for technical performance

Criteria	**Ranking**
Destruction, Removal, or Nothing	Destruction
	Removal
	Nothing
Time to Implement	Immediately
	Months to Years
	Years
Reaction Speed	Minutes to Hours
	Days to Weeks
	Months
Energy Input	Low
	Medium
	High
Feasibility	Easy
	Moderate
	Hard

Table 5: Example table for technical performance

Approach	Destruction, Removal or Nothing?	Time to Implement	Reaction speed	Energy Input	Feasibility
Example Strategy 1	Removal	Immediately	Minutes to Hours	Low	Easy

4.5 Baselines of Comparison

We have three baseline bad actors to which we compare our strategies: (1) Landfilling; (2) Incineration; and (3) Allowing PFAS contaminated carpets to be recycled as is. Each of these bad actors vary in the types and quantity of PFAS and other chemicals that are released, the routes of exposure and who or what is exposed. For the scope of this assignment, we will focus only on option 3 as our primary baseline.

4.5a Bad Actor 1: Landfilling Carpets

PFAS from discarded carpets and rugs can be mobilized once it enters landfill leachate. To demonstrate the significance of this effect, a recent study found that old carpets release considerable amounts of short-chain PFAS into leachate after 100 days in landfill conditions (Lang, 2016). Once in the leachate, PFAS is able to enter the environment if the liners that separate the landfill's leachate from the outside environment are absent or compromised. Once through the cracks or tears in the liners, PFAS can then contaminate ground and surface waters. Similarly, when leachate is collected and sent to a wastewater treatment plant, the PFAS in the contaminated leachate is typically not intentionally treated because of the costs to treat PFAS and the lack of discharge regulations for PFAS. Landfills that collect carpets and rugs are typically municipal solid waste landfills (MSWLF). The liners and groundwater monitoring programs at MSWLFs are not designed or intended to prevent an environmental release of PFAS or other hazardous chemicals. PFAS compounds are not listed as hazardous waste under the Resource Conservation and Recovery Act (RCRA), California's Environmental Health Standards for the Management of Hazardous Waste, or as hazardous air pollutants under the Clean Air Act. Because of this, there are no land disposal or air emission restrictions for waste contaminated with PFAS in California or across the U.S. As a result, end users of PFAS contaminated carpets and rugs have no reason to dispose at hazardous waste facilities, since it is considerably more expensive than disposal at MSWLFs.

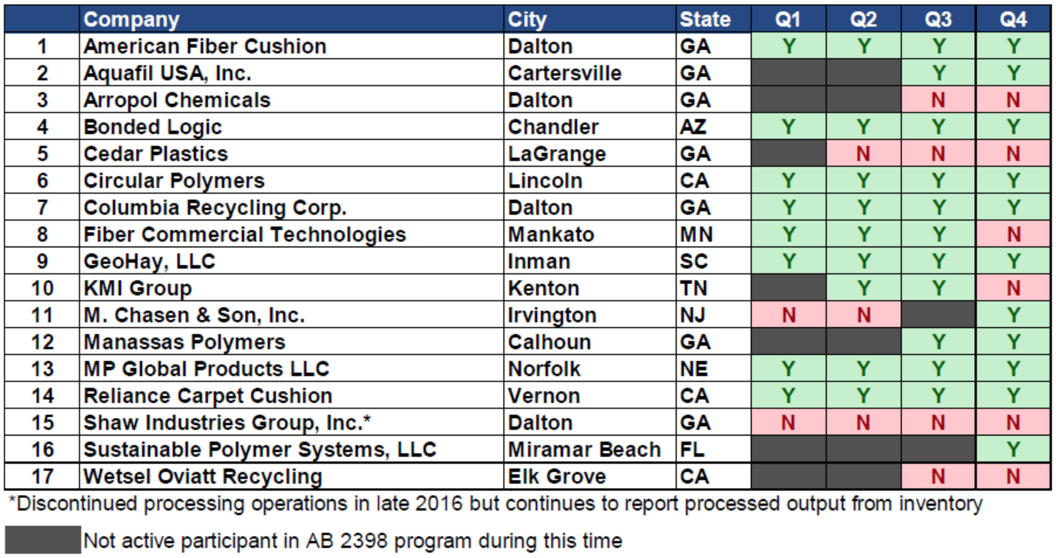
4.5b Bad Actor 2: Incinerating Carpets

PFAS in treated carpets and rugs can be broken down through high temperatures during incineration. Mechanistically, incineration of halogenated organic compounds occurs via unimolecular decomposition and radical reactions. The stability of perfluorinated radicals can sometimes lead to a build up in their concentrations and their ability to recombine, creating larger molecules that are distinctive from the original PFAS (EPA, 2020).

Like other carbon-halogen chemicals such as PCBs, halogens can be captured and recovered from the flue gas as an alkali-halogen. However, there are concerns about the products of incomplete combustion (PIC) from ineffective incineration of PFAS due to insufficient temperatures, residence time, and mixing. Incomplete combustion can result in the formation and emission of small-chain PFAS, ozone depleting CFCs, and greenhouse gases from the incinerator stacks to the environment (Huber, 2009).

4.5c Bad Actor 3: Recycling Carpets without Removal or Treatment

PFAS is not intentionally removed from carpet face fiber during current carpet recycling practices. Recycled carpet and rug outputs can feed into new carpets, insulation, mattresses, pillows and automotive parts (Figure 8), but there is very little publicly available data on quantities of these secondary products. Furthermore, there is no public analysis of PFAS content in these new products. As a conservative estimate, we assume that any PFAS in the carpet prior to recycling will still remain in the material after recycling. Therefore, we use data on PFAS content in virgin carpet as our baseline.



	Company	City	State	Q1	Q2	Q3	Q4
1	American Fiber Cushion	Dalton	GA	Y	Y	Y	Y
2	Aquafil USA, Inc.	Cartersville	GA	■	■	Y	Y
3	Arropol Chemicals	Dalton	GA	■	■	N	N
4	Bonded Logic	Chandler	AZ	Y	Y	Y	Y
5	Cedar Plastics	LaGrange	GA	■	N	N	N
6	Circular Polymers	Lincoln	CA	Y	Y	Y	Y
7	Columbia Recycling Corp.	Dalton	GA	Y	Y	Y	Y
8	Fiber Commercial Technologies	Mankato	MN	Y	Y	Y	N
9	GeoHay, LLC	Inman	SC	Y	Y	Y	Y
10	KMI Group	Kenton	TN	■	Y	Y	N
11	M. Chasen & Son, Inc.	Irvington	NJ	N	N	■	Y
12	Manassas Polymers	Calhoun	GA	■	■	Y	Y
13	MP Global Products LLC	Norfolk	NE	Y	Y	Y	Y
14	Reliance Carpet Cushion	Vernon	CA	Y	Y	Y	Y
15	Shaw Industries Group, Inc.*	Dalton	GA	N	N	N	N
16	Sustainable Polymer Systems, LLC	Miramar Beach	FL	■	■	■	Y
17	Wetsel Oviatt Recycling	Elk Grove	CA	■	■	N	N

*Discontinued processing operations in late 2016 but continues to report processed output from inventory

■ Not active participant in AB 2398 program during this time

Figure 8: List of manufacturers (Tier-2 manufactures) that used down-cycled carpets and rugs that received funding from CARE in 2018 (CARE, 2018).

4.6 Bad Actor Health and Environmental Performance

There are many chemical hazards associated with the baseline recycling method of not removing PFAS. The chemical hazards associated with the baseline method are carcinogenicity/mutagenicity, developmental/reproductive toxicity, endocrine activity, systemic toxicity, and irritation (Table 6).

Table 6. Summary of health hazards of PFAS in carpet. Data is taken from Wu et al. (2020) which analyzed PFAS content in carpet from child daycare facilities. We included PFAS species that were present in greater than 90% of the facilities analyzed.

Constituent	**Median [PFAS] (ng/g)**	**Human Endpoints**						**Environmental Endpoints**	
		C/M	**D/R**	**Endocrine**	**Systematic**	**Neurotox.**	**Irritation**	**Aquatic**	**Bioaccum.**
6:2 FTOH	69	🟪	🟪	M	M	DG	H	H	H
8:2 FTOH	18.8	DG	DG	M	M	DG	H	H	VH
PFHxA	10	DG	M	M	M	DG	VH	M	M
PFBA	8.09	DG	DG	DG	H	DG	H	H	L
PFOA	6.13	M	H	H	H	H	VH	M	H
PFPeA	4.62	▨	M	M	M	DG	VH	M	L
PFNA	2.7	M	VH	M	M	DG	VH	H	VH
PFOS	2.32	M	H	M	H	H	M	M	H
PFHxS	1.31	🟪	H	H	M	DG	H	M	L
PFTeDA	0.97	🟪	DG	DG	DG	DG	VH	DG	VH
8:2 FTSA	0.78	DG	DG	DG	M	DG	M	H	VH
PFTrDA	0.57	🟪	DG	M	M	DG	🟪	DG	VH
PFBS	0.53	DG	DG	H	M	DG	VH	M	L

L: Low	**M:Moderate**	**H: High**	**VH: Very High**	**Probable**	**Data Gap**

4.7 Overview of Our Proposed Strategies

We have four proposed strategies (Figure 9). The first and second strategies attempt to treat the fluff through a base hydrolysis reaction, which has been shown to release PFAS from polymeric backbones under ideal conditions (Peaslee 2020), followed by adsorption or destruction. The second two strategies use enzymes to either replace the base hydrolysis step or directly mineralize the PFAS. The strategies are presented in order of implementation time.

1. Base Hydrolysis + Granular Activated Carbon (GAC) Adsorption
2. Base Hydrolysis + Reverse Osmosis (RO) + Plasma
3. Esterase replacement of base hydrolysis
4. Laccases

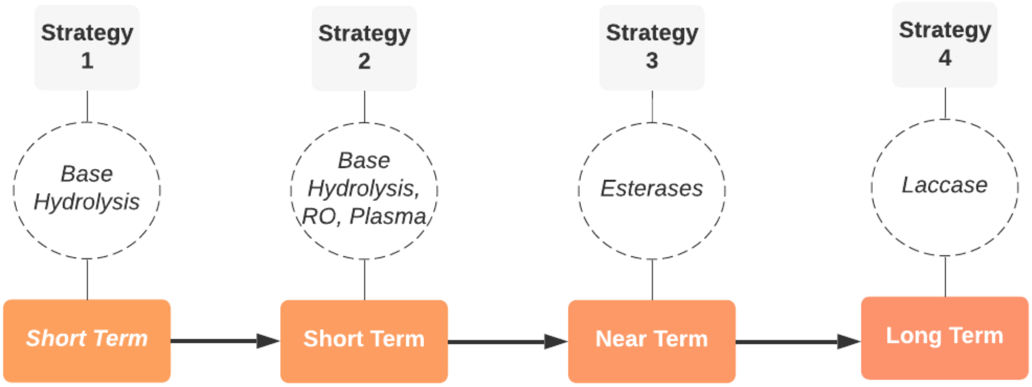


Figure 9: Overview of the proposed 4 strategies in order of implementation time.

5. Strategy Approaches

Strategy Approach #1: Base Hydrolysis + Granular Activated Carbon (GAC) Adsorption

We propose using a strong base, such as sodium hydroxide or potassium hydroxide, to break the (meth)acrylate linkages to release the fluorinated side-chains from carpet treatment polymers into solution. The released PFAS would then be adsorbed onto a solid material such as granular activated carbon (GAC). This design was inspired by a recent article from Peaslee et al. (2020), which used a 2M NaOH solution to extract PFAS from firefighting textiles. The mechanism behind the strategy is base hydrolysis of the ester group found in the (meth)acrylate linkage. The carbonyl carbon is prone to nucleophilic attack by hydroxide resulting in a carboxylic acid group on the polymer and an alcohol leaving group (Figure 10). By increasing the pH, we increase the concentration of hydroxide ions which are responsible for initiating this reaction and therefore increase the overall rate of reaction. Furthermore, there is also evidence that fluorine substitutions can greatly increase the rate of hydrolysis of ester bonds. For example, Uchimaru et al. (2013) found that the ester bond in ethyl trifluoroacetate hydrolyzed at a rate seven orders of magnitude greater than the non-fluorine-substituted ethyl acetate. After successful hydrolysis, the PFAS solution would then need to be neutralized with a strong acid before passing through GAC.

Neutralizing the solution is an essential step because GAC performs better when the point of zero charge (p_{zc}) is greater than the solution pH, which facilitates electrostatic interactions. For example, PFOA is negatively charged at all environmentally relevant pHs (pKa << 0). If a GAC's p_{zc} is circumneutral and the solution pH is 14 (as might be the case in our treatment), the GAC functional groups would deprotonate and become negatively charged, repelling the negatively charged PFAS. GAC's hydrophobic effects also contribute to adsorption and are independent of pH, but overall adsorption efficiency would still decline (Ahmadi et al. 2018). After adsorption, the solution could be reused for further base hydrolysis. A simple schematic of the design can be seen in Figure 11.

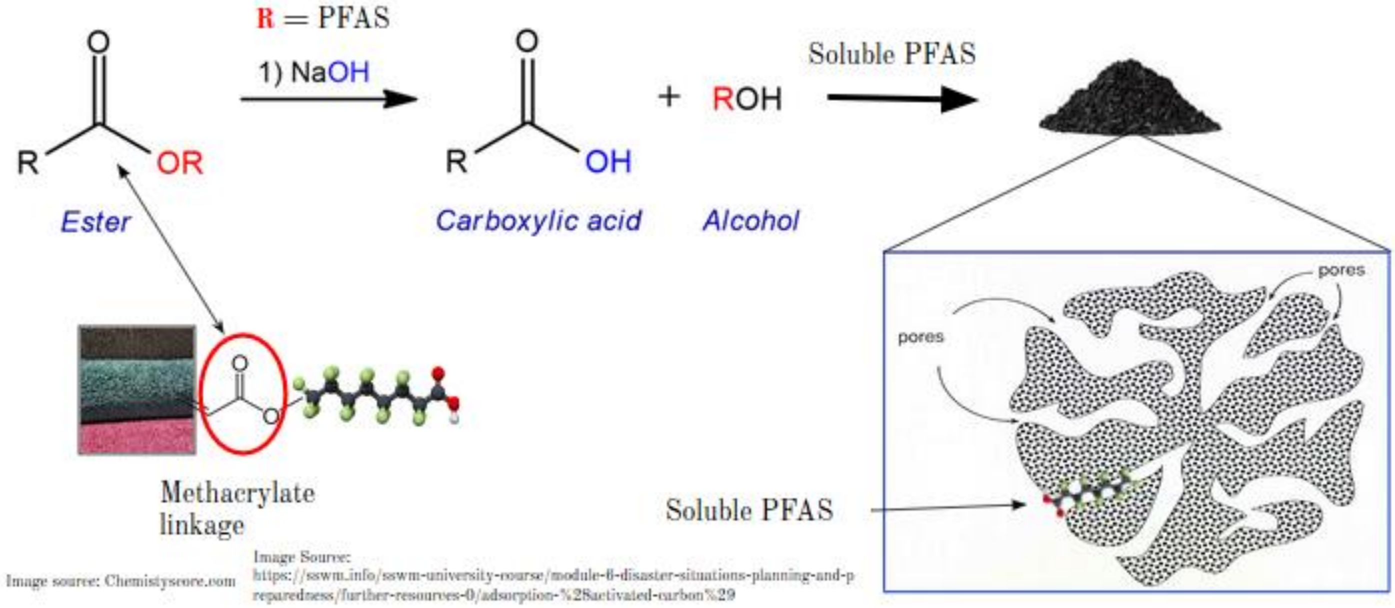


Image source: Chemistyscore.com

Image Source: https://sswm.info/sswm-university-course/module-6-disaster-situations-planning-and-preparedness/further-resources-0/adsorption-%28activated-carbon%29

Figure 10. Chemical mechanism for ester hydrolysis. Image source: Chemistyscore.com

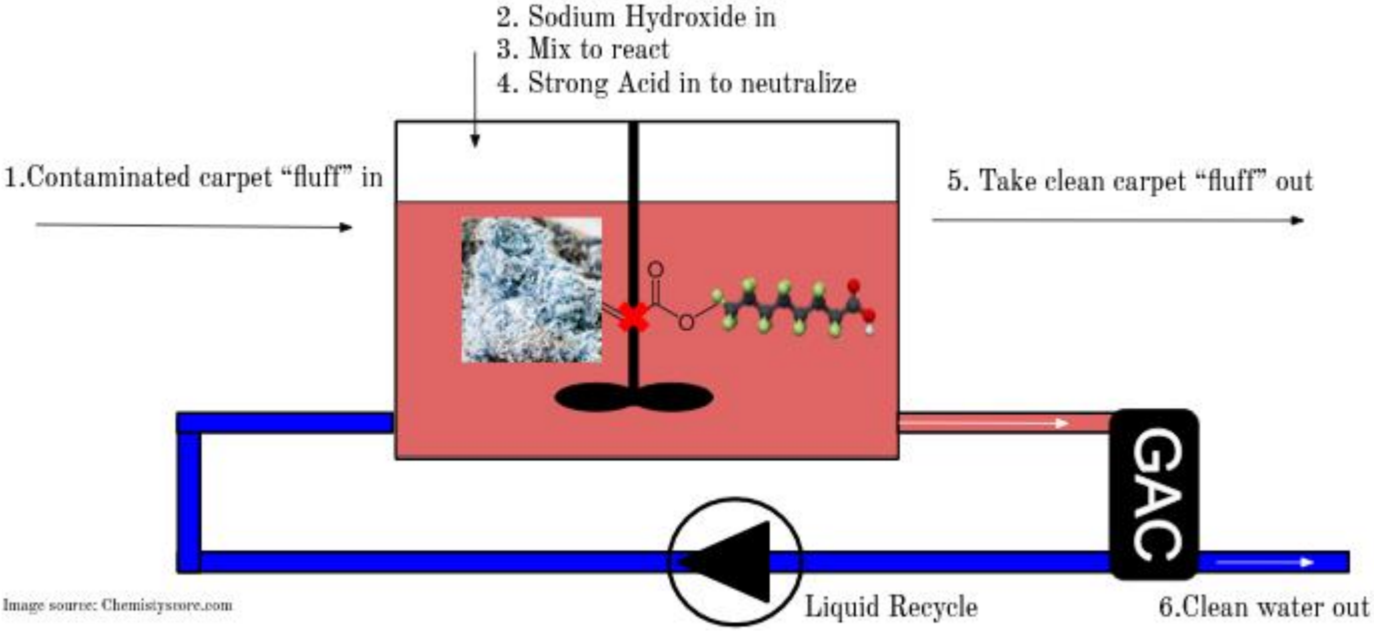


Image source: Chemistyscore.com

Figure 11: Simple diagram of proposed base hydrolysis strategy.

Technical Performance:

As stated, base hydrolysis requires adsorption to capture the released PFAS. This is not our ideal outcome because it merely moves the problem to a different media, albeit in a much more concentrated and containable form. Thermal regeneration of GAC (700°C under N_2 atmosphere) can potentially enable reuse of GAC, while also mineralizing the sorbed PFAS (Watanabe et al. 2018), but this type of regeneration is likely to draw skepticism due to the high energy input and potential to release PFAS into air. Alternatively, saturated GAC can be stored until a better alternative is developed.

We chose GAC because it is the most common type of adsorbent used for PFAS treatment, owing to its high adsorption capacity and wide availability (Yao et al. 2014). It has also been demonstrated at full-scale under complex matrices (Boone et al. 2019) and is effective due to a combination of electrostatic and hydrophobic interactions with PFAS (Zhao et al. 2014). Anion exchange resins are also a possible choice of adsorbent because of their high removal capacity, especially with short chain PFAS, where GAC can sometimes underperform (McCleaf et al. 2017). However, these resins specifically target anionic PFAS, but not neutral or cationic PFAS. According to a recent study from Wu et al. (2020), neutral PFAS such as fluorotelomer alcohols make up a significant fraction of PFAS found in carpet, which would not be captured by anion exchange resins. Minerals, biomaterials and polymers have also been studied for the removal of PFAS, and while there are many characteristics that make these materials desirable (lower cost, highly selective, carbon-neutral sourcing), these processes have not been demonstrated outside of the lab and will not be ready for full-scale application for several years (Vu et al. 2020). For these reasons, using GAC would be a conservative and predictable strategy, though ensuring that the GAC is replaced before breakthrough of short chain PFAS is critical to proper performance.

The cost and time to be implemented for this strategy should be relatively low in this solution. If the recycling facility already has a unit to wash the fiber, then very little capital investment will be needed. Sodium hydroxide and GAC is also relatively cheap, though a more in-depth cost analysis is still needed. Similarly, this process's simplicity also makes it easy to implement. All the technologies used are well established and low risk making it a potentially cheap, fast and reliable way to remove PFAS from carpet.

Concerns about fiber quality after the base hydrolysis treatment do exist. The question can be preliminarily addressed by the literature on the depolymerization process of nylon carpet fibers, which involves high temperatures (300□C) and above standard atmospheric pressures, along with a base/acid catalyst (CARE Carpet 101 and Mihut 2001). This suggests that in the absence of high temperature and pressure, depolymerization will not take place. Nevertheless, there are effects outside of depolymerization that could reduce fiber quality. Empirical tests would most likely be required to make any strong conclusions about the effect of an alkaline solution on fiber quality.

Table 7: Technical performance summary for the base hydrolysis + GAC strategy.

Approach	Destruction, Removal or Nothing?	Time to Implement	Reaction speed	Energy Input	Feasibility
Base Hydrolysis + GAC	Removal	Immediately	Minutes to Hours	Low	Easy

Health and Environmental Performance

There are relatively few chemicals involved in the base hydrolysis method, though using a strong base (and a strong acid to neutralize the base) introduces new hazards and potential exposures for workers (Table 8). Sodium hydroxide exhibits moderate systemic toxicity and very high irritation to mucous membranes. Hydrochloric acid exhibits low carcinogenicity/mutagenicity, developmental/reproductive, systemic, neurotoxic endpoints, but very high irritation to mucous membranes. Potential exposures to these two compounds could be reduced through automation in a closed system and proper training.

By removing the PFAS within carpet recycling in a controlled manner, we are able to capture much of the PFAS that would otherwise persist in the lived environment. However, what to do with PFAS saturated

GAC is an open question. Additionally, if the strong base is effective at removing the fluorinated side chains, there is potential for acrylate and methacrylate contamination in the wastewater as well. Acrylates and methacrylates have potentially high aquatic toxicity (Staples 2000). Future tests in a controlled laboratory environment should confirm how much acrylate/methacrylate is produced and if GAC can capture it.

Table 8: The health and environmental hazards of chemicals involved with the base hydrolysis removal approach.

Constituent	**Human Endpoints**						**Environmental Endpoints**	
	C/M	**D/R**	**Endocrine**	**Systematic**	**Neurotox.**	**Irritation**	**Aquatic**	**Bioaccum.**
Sodium Hydroxide	**DG**	**DG**	**DG**	**M**	**DG**	**VH**	**DG**	**DG**
Hydrochloric Acid	**L**	**L**	**DG**	**L**	**L**	**VH**	**L**	**L**

L: Low	**M:Moderate**	**H: High**	**VH: Very High**	**Probable**	**Data Gap**

Strategy Approach #2: Base Hydrolysis + Reverse Osmosis (RO) + Plasma Treatment

In this strategy, PFAS are again released into solution by base hydrolysis, which is neutralized after the reaction. The PFAS solution is then passed through an RO membrane to concentrate the PFAS. The RO permeate can be recycled back to the reactor, while the concentrate is pumped to a plasma reactor for PFAS destruction. The steps in this treatment are outlined in detail below and in Figure 12.

RO is a simple process where water is pushed through pores to exclude charged and large MW compounds to generate nearly pure water in the permeate and a concentrated PFAS solution in the rejected water. In order to push water through the membrane, pumps must generate a substantial amount of pressure to overcome the osmotic pressure generated by the solution. For example, seawater has an osmotic pressure of about 400 psi. An RO facility treating that water must generate substantially more pressure than that in order to force the seawater through the pores. By adding a strong base such as sodium hydroxide, we would be greatly increasing the osmotic pressure of the solution and therefore the pumping costs. Further increasing this cost, neutralization with a strong acid like hydrochloric acid prior to RO is also necessary to prevent scaling on or damaging the RO membrane (Richards et al. 2010). Future research could determine the minimum alkalinity needed to hydrolyze the ester bonds to reduce hazard as well as pumping costs. While cost is a drawback to this part of the strategy, RO is a well established and effective method of removing PFAS from water (Tang et al. 2006).

In an engineered setting, plasma is created when an extremely high electric potential is generated between two electrodes until an arc is formed. Numerous plasma reactor designs have been put forward in the literature, but the most effective design for PFAS treatment uses a negative electrode in a gas headspace and a positive electrode at the bottom of the bulk liquid (Singh et al. 2019a). When the plasma is formed, it arcs from the negative electrode through an argon headspace to the liquid surface where it creates a variety of oxidizing and reducing radicals including hydrated electrons, which are thought to be responsible for most of the reactions with PFAS. Meanwhile, a gas diffuser at the bottom of the liquid bubbles argon to concentrate the PFAS, which like to partition at air-water interfaces, at the liquid surface where the short lived hydrated electrons are most concentrated. Multiple pilot scale demonstrations prove that this is an effective and scalable technology (Singh et al. 2019b), but it is not currently commercially available. A collaboration with Clarkson University, where this technology is being spearheaded, or a similarly equipped lab, would likely be necessary.

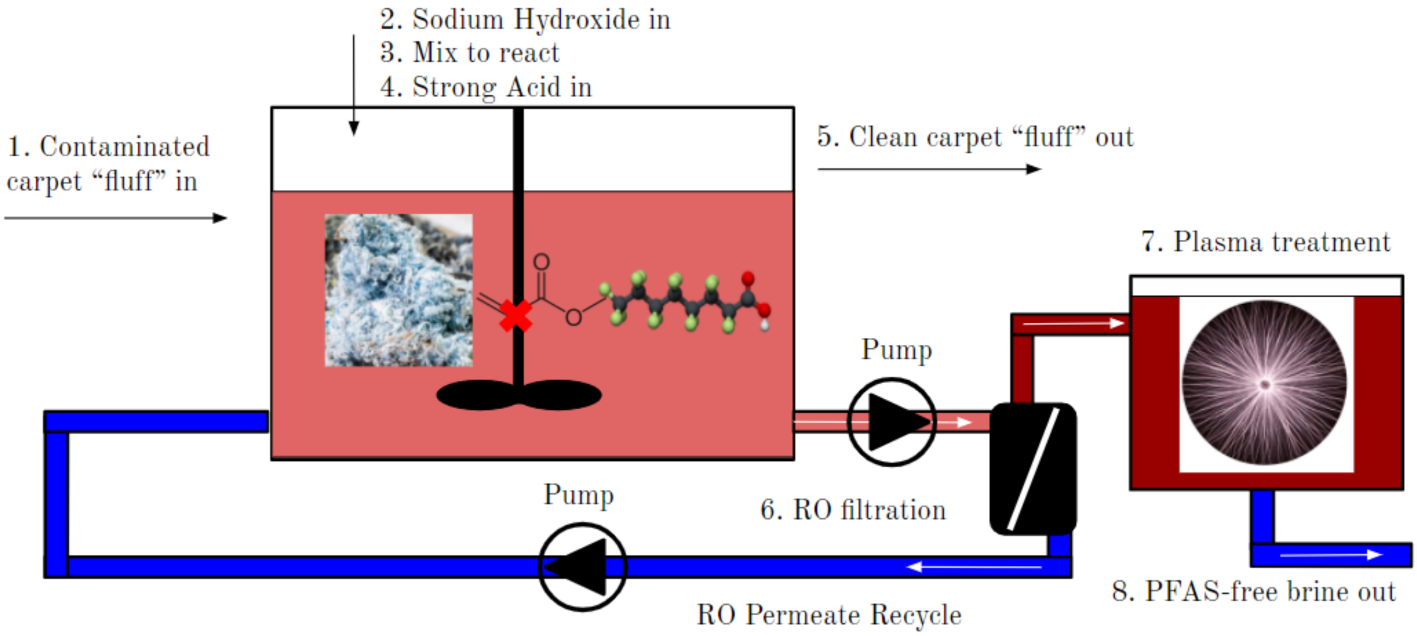


Figure 12. Simple schematic of the base hydrolysis, RO, plasma strategy.

Technical Performance

The technical performance for this strategy is summarized in Table 9. A substantial benefit of this strategy is that it breaks down PFAS rather than adsorbs it to GAC. Plasma, like most other destructive technologies though, is slower to treat short-chain PFAS like PFBA or PFBS, compared to long chain PFAS like PFOA and PFOS. This is likely due to the reduced hydrophobicity of shorter chains which prevents strong air-water interface partitioning. This can be improved with addition of a non-fluorinated, cationic surfactant such as cetrimonium bromide (CTAB), which can "pick up" the shorter chain PFAS as it migrates to the surface. CTAB, a quaternary amine, is potentially toxic, but is readily broken down in the plasma reactor (Singh et al. 2020). Nevertheless, the method should be thoroughly validated to prevent any inadvertent release of short-chain PFAS or quaternary amines into the environment. Unlike other treatment scenarios where the groundwater is already contaminated and any treatment is better than none, this challenge has the potential to contaminate pristine water if not carried out carefully.

By PFAS destruction technology standards, this technology is relatively mature. It also could be relatively quick to implement, assuming that the proper expertise is garnered. It may be slightly slower than the previous strategy because of the additional steps. For example, a weaker base solution might be used to reduce the osmotic pressure of the solution, which may then require a longer hydrolysis reaction time. After RO, plasma treatment takes an addition one to two hours (Singh et al. 2020). The entire process is also much more energy intensive than the previous strategy. Both RO and plasma require electricity. While the authors of the previously cited papers claim that a bench-scale plasma reactor runs on the same electricity as a hair dryer, the same cannot be said of RO. Due to the pumping requirements, RO is notoriously energy intensive.

Table 9. Summary of performance criteria for Base Hydrolysis + RO + Plasma.

Approach	Destruction, Removal or Nothing?	Time to Implement	Reaction speed	Energy Input	Feasibility
Base Hydrolysis + RO + Plasma	Destruction	Months to Years	Minutes to Hours	High	Moderate

Health and Environmental Performance

RO and plasma are physical processes and therefore require no additional chemicals. A cationic surfactant may aid in the plasma process but this was excluded from our analysis since this process was described for the first time within the last month so we were unable to conduct a hazard assessment for this chemical. Therefore, the hazard table for this strategy includes a strong base and acid similar to the first strategy, but we also included hydrofluoric acid (HF) since any PFAS destruction technology runs the risk of producing it (Table 10). In the event that HF is produced, it would likely quickly dissociate to fluoride. Nevertheless, it is prudent to include it in the hazard table because it carries such a strong potential hazard.

While plasma may not introduce chemical hazards, it does have significant physical hazard. These reactors operate at a peak amperage of about 100 amps, which is lethal. Strict engineered controls would need to be in place to operate a plasma reactor safely.

Table 10. Summary of health and environmental hazards for Base Hydrolysis + RO + Plasma.

Constituent	Human Endpoints						Environmental Endpoints	
	C/M	D/R	Endocrine	Systematic	Neurotox.	Irritation	Aquatic	Bioaccum.
Sodium Hydroxide	DG	DG	DG	M	DG	VH	DG	DG
Hydrochloric Acid	L	L	DG	L	L	VH	L	L
Hydrofluoric Acid	L	M	M	H	H	VH	M	VH

L: Low	M:Moderate	H: High	VH: Very High	Probable	Data Gap

Strategy #3: Esterase Hydrolysis

Using a strong base and strong acid as outlined in strategies 1 and 2 has several drawbacks: (1) It is hazardous; (2) It could damage the fiber or equipment; and (3) It would make running an RO system far more expensive. As an alternative to base hydrolysis, we also explored esterase enzymes, which are similarly capable of hydrolyzing the ester bonds found in (meth)acrylate linkages. We present this strategy as a greener replacement for base hydrolysis in the first two strategies.

Researchers have documented esterase hydrolysis of monomeric and polymeric (meth)acrylate linkages for many decades as a result of research on materials used in dentistry (e.g. Bean et al, 1994). Porcine Liver Enzyme (PLE) is a particularly versatile esterase frequently cited in the literature due to its relatively non-selective hydrolysis of ester bonds. This is appealing given the diversity of PFAS compounds that could be linked to the (meth)acrylates. Nevertheless, it is unclear if PLE will be able to hydrolyze ester bonds when the (meth)acrylate is attached to large compounds like long-chain PFAS. The bulky electron cloud associated with a carbon-fluorine tail could conceivably prevent an enzyme from accessing the ester bond. While this shielding could occur, the evidence cited in the first strategy suggesting that fluorine substitutions increase the rate of ester hydrolysis give us reason to be optimistic. If PLE can physically access the bond, the reaction will readily occur. A simple lab experiment could determine if PFAS is released from side-chain fluorinated polymers when exposed to PLE.

Technical Performance

Using an esterase instead of a strong base would increase the time needed to implement the technology. As stated above, a simple lab test could determine if such a reaction would take place, but determining the optimum conditions for the reaction would take time. Similarly, if the reaction was too slow to be commercially viable, or failed to release some species of PFAS, identifying a replacement enzyme would be time consuming. Another significant unknown is the reaction speed and would need to be empirically determined in the lab.

A substantial draw of the esterase replacement is its impact on energy usage in the RO + plasma strategy. By eliminating the need for a strong base and strong acid, the osmotic pressure of the reaction solution is minimized, which reduces the pressure necessary to push the solution through the RO membrane. A summary of the technical performance can be found in Table 11.

Table 11. Summary of technical performance for esterase replacement of base hydrolysis

Approach	Destruction, Removal or Nothing?	Time to Implement	Reaction speed	Energy Input	Feasibility
Esterase + GAC	Removal	Months to Years	Unknown	Low	Moderate
Esterase + RO + Plasma	Destruction	Months to Years	Unknown	Medium	Moderate

Health and Environmental Performance

Perhaps the most significant draw of this strategy is its health and environmental performance (Table 12). Across multiple databases, we could not identify any indication that PLE poses any health or environmental hazard. Compared to the base hydrolysis strategy, this is a substantial improvement.

Table 12. Summary of the health and environmental performance for esterase replacement of base hydrolysis

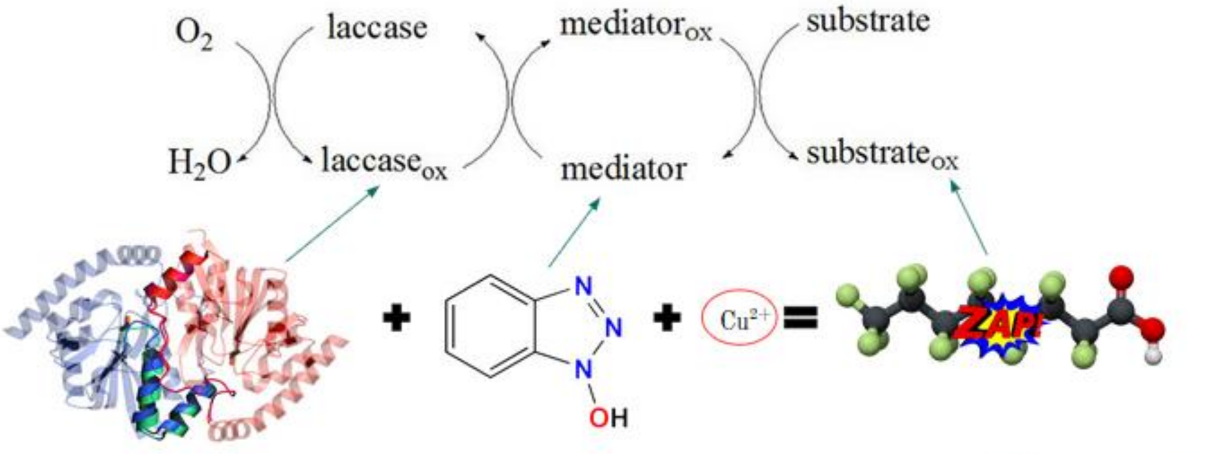
Constituent	Human Endpoints						Environmental Endpoints	
	C/M	D/R	Endocrine	Systematic	Neurotox.	Irritation	Aquatic	Bioaccum.
Pig Liver Esterase	DG	DG	DG	DG	DG	DG	DG	DG

L: Low	**M:Moderate**	**H: High**	**VH: Very High**	**Probable**	**Data Gap**

Strategy Approach #4: Laccase Treatment

Laccases are multi-copper enzymes that catalyze the reduction of molecular oxygen to water by one-electron oxidation of substrates such as substituted phenolic compounds (Yang et al., 2017). They are broadly found in plants, fungi, insects, and bacteria and are capable of oxidizing many aromatic and non-aromatic compounds directly (Mate and Alcalde, 2017). Laccases can also indirectly oxidize chemicals with bulky structures or high redox potentials with the aid of mediators (Guan et al., 2018). Mediators are low-molecular-weight laccase substrates, which can be easily oxidized by laccases to form free radicals. These radicals can subsequently react with target compounds that cannot directly react with the enzymes (Figure 13). This laccase mediator system approach has recently been shown to transform perfluorooctane sulfonic acid (PFOS) (Luo et al. 2018), which was thought to be recalcitrant to biological degradation. This process was shown to only work in the presence of a divalent cation such as Cu^{2+}, which is thought to aid in a conformational change in PFOS by interacting with the negatively charged sulfonate head group.

This strategy would operate in a single step where laccase and a chemical mediator are added directly to face fiber fluff suspended in water. The ideal result from this reaction would be complete mineralization of PFAS, but the technology is years away from being capable of this. In its current state, laccase oxidation of PFAS is extremely slow. In the experiments conducted by Luo and colleagues, 60% of the PFOS was transformed after 150 days. Furthermore, most of the PFOS was transformed into non-quantifiable transformation products rather than mineralized to fluoride and carbon dioxide, and likely still retained some of the toxicological characteristics associated with the parent compound. Nevertheless, with the proper investment in research and green chemistry to further develop this strategy, we believe that a laccase mediator system has the potential to have the least hazard while still mineralizing PFAS.



https://news.unl.edu/newsrooms/today/article/enzymes-and-x-rays-study-reveals-hidden-aerobatics-of-cellular-catalysts/

https://www.frontiersin.org/files/Articles/86385/fenrg-02-00012-HTML-r1/image_m/fenrg-02-00012-g004.jpg

Figure 13. Theoretic illustration of a laccase mediator system

Technical Performance

The laccase mediator system, in its current form, is able to partially oxidize PFOS and PFOA, though it is extremely slow. Furthermore, there have been no studies on shorter chain PFAAs or fluorotelomers, which is a substantial gap. Finally, the system would need to be optimized to not just transform PFAS, but completely mineralize the compounds. This scale of research and development may put this solution ten or more years away from being commercially viable. However, optimization and scale-up of enzymes and biocatalysts for industrial use is a burgeoning field of biotechnology. Techniques like high throughput screening and enzyme engineering could produce an enzyme that is commercially viable for this purpose. A summary can be found in Table 13.

Assuming that such an enzyme is discovered or developed, there are numerous technical benefits to this strategy. It is a single reaction, meaning a simplified reactor configuration that is simple to operate, and smaller footprint which would reduce the capital costs. It would also be very energy efficient since the reaction requires no energy input. Finally, it would actually break down the PFAS, a benefit which can't be overstated.

Table 13: Laccase technical performance

Approach	Destruction, Removal or Nothing?	Time to Implement	Reaction speed	Energy Input	Feasibility
Laccase	Destruction	Years	Unknown	Low	Hard

Health and Environmental Performance

In its current form, the laccase mediator system performs relatively poorly from a health and environmental perspective. This is primarily due to the use of copper(II) sulfate and the mediator, 1-Hydroxybenzotriazole (HBT). Copper(II) is particularly hazardous across multiple endpoints whereas HBT, while relatively hazardous, is also very explosive, a fact which isn't included in our hazard table (Table 14). HF was also included in the table as a precaution, but as stated earlier, the likelihood of contact with HF before it dissociates seems low. Nevertheless, this should still be a consideration when testing this technology. Finally, laccase itself is relatively non-hazardous. The only endpoint where data was available was for skin irritation.

Table 14: Laccase treatment health and environmental hazards

Constituent	Human Endpoints						Environmental Endpoints	
	C/M	D/R	Endocrine	Systematic	Neurotox.	Irritation	Aquatic	Bioaccum.
Copper(II) sulfate	DG	M	M	M	VH	VH	VH	VH
1-Hydroxybenzotriazole	DG	DG	DG	L	DG	H	M	DG
Laccase	DG	DG	DG	DG	DG	H	DG	DG
Hydrofluoric Acid	L	M	M	H	H	VH	M	VH

L: Low	M:Moderate	H: High	VH: Very High	Probable	Data Gap

6. Conclusions, Recommendations, and Remaining Questions:

Overall, our four approaches are an improvement on the current health and environmental performance of leaving PFASs in the carpet recycling stream. All four approaches remove highly persistent and toxic PFASs from recycled carpets and other down-cycled products.

The summary below shows the health hazards for our baseline and four PFAS removal/destruction strategies (Table 15). The results clearly show that even a simple removal strategy like base hydrolysis with GAC is much better than doing nothing. All four strategies remove the PFAS from the post-consumer carpet fluff, and therefore from the consumer lifecycle, reducing exposure for numerous populations. In strategies that involve base hydrolysis, the hazards stem from the use of a strong base and acid, which can be easily mitigated with engineered controls. While engineered controls should be treated as the last line of defense in protecting human and environmental health, controlling exposure to these specific chemicals in this specific situation is extremely practical. On the other hand, substituting esterases for base hydrolysis would make for a very safe process. If these enzymes can be optimized such that they can compete with the reaction time and cost of the chemical option, this strategy is clearly the better option. It is unfortunate that the benefit of reduced cost might outweigh health risk, but that is our current reality. In talking with a carpet recycler, they were dismissive of any enzymatic treatment in favor of a chemical treatment for what we can only assume is this exact reason.

Looking at laccase, we see that it has “Very High” scores across multiple endpoints in its current level of development, despite being an enzymatic process. This is not due to the enzyme itself, but rather the mediator and copper cation that were used in the publications on this strategy. We are optimistic that research on optimizing this technology would identify less hazardous mediators and divalent cations. Given the technology’s relative infancy, it would be premature to dismiss this strategy because of its current hazard assessment.

Table 15. Summary hazard table for our baseline and strategies. If strategies had multiple chemicals, the most hazardous chemical for each endpoint was chosen for the summary.

Strategy	**Human Endpoints**						**Environmental Endpoints**	
	C/M	**D/R**	**Endocrine**	**Systematic**	**Neurotox.**	**Irritation**	**Aquatic**	**Bioaccum.**
Baseline	**M**	**VH**	**H**	**H**	**H**	**VH**	**H**	**VH**
Base Hydrolysis + GAC	**L**	**L**	**DG**	**H**	**DG**	**VH**	**M**	**DG**
Base Hydrolysis + RO + Plasma	**L**	**L**	**DG**	**H**	**DG**	**VH**	**M**	**DG**
Esterase	**DG**	**DG**	**DG**	**DG**	**DG**	**DG**	**DG**	**DG**
Laccase	**DG**	**M**	**M**	**M**	**VH**	**VH**	**VH**	**VH**

L: Low	**M:Moderate**	**H: High**	**VH: Very High**	**Probable**	**Data Gap**

When considering the technical performance of all of our strategies, there are a number of good options. Choosing a single strategy will depend on the priorities of the recycling facility and what support they receive from the state and federal government. Any destruction-based strategy may only be practical if the cost is subsidized by a government grant that specifically targets PFAS destruction. On the other hand, if getting a process running quickly and cheaply is the priority, then base hydrolysis with GAC is probably the best solution. It is a simple and reliable solution, but doesn't address the root problem of PFAS contamination. The base hydrolysis followed by RO followed by plasma treatment solution may be the most practical and reliable destructive technology that we have presented. All of the technology involved is relatively mature, though implementing plasma treatment would require considerable expertise. It would also be important to verify that short chain PFAAs are not present in the effluent, which could be prevented with the addition of CTAB or longer reaction times. A summary can be found in Table 16.

When considering the strategies that involve an enzyme, we can assume that the reaction rates will be slower than if using a chemical or physical strategy. For example, we assume that an esterase enzyme will hydrolyze ester bonds more slowly than an alkaline solution. Similarly, we assume that laccase will degrade PFAS more slowly than plasma. However, reaction speed is not the only metric of performance. Enzymatic processes are extremely energy efficient. By replacing base hydrolysis with esterase, an RO treatment would be far less energy intensive and produce less brine, which is costly to dispose of. A laccase system would similarly use less energy than a plasma system. So while reaction rates may be slower, this trade off could be worthwhile.

Table 16. Technical performance summary of all strategies

Approach	Destruction, Removal or Nothing?	Time to Implement	Reaction speed	Energy Input	Feasibility
Base Hydrolysis + GAC	Removal	Immediately	Minutes to Hours	Low	Easy
Base Hydrolysis + RO + Plasma	Destruction	Months to Years	Minutes to Hours	High	Moderate
Esterase + GAC	Removal	Months to Years	Unknown	Low	Moderate
Esterase + RO + Plasma	Destruction	Months to Years	Unknown	Medium	Moderate
Laccase	Destruction	Years	Unknown	Low	Hard

Below is a summary of the pros and cons of each approach.

Strategy #1: Base Hydrolysis + Granular Activated Carbon

Pros	Cons
Effective removal of fluorinated side chains from carpet	Introduces new occupational exposures to strong acids/bases and PFAS contaminated GAC
Easiest solution to implement right now	Doesn't destroy the PFAS, but transfers it to a new medium
Cheapest solution to implement right now	Potential degradation of nylon carpet face fibers

Strategy #2: Base Hydrolysis + Reverse Osmosis + Plasma

Pros	Cons
Requires no additional chemicals	Three steps to remove the PFAS
Fast reaction times	Reverse osmosis and plasma are much more expensive to operate than GAC
Mineralizes the PFAS	Introduces occupational hazards to high voltage

Strategy #3: Esterase

Pros	Cons
Enzymes require no co-factors of mediators	Further tests are needed to confirm their effectiveness on carpet face fibers
No known hazards with these enzymes	Slower reaction times than base hydrolysis
Very cheap to purchase	
Easy to implement	

Strategy #4: Laccase

Pros	Cons
Single step reaction	Hazardous copper and HBT mediators/co-factors
Lower hazard enzymatic approach	Unknown, highly fluorinated transformation products
Potential to mineralize PFAS	Slow reaction times
Very low energy input	Years away from implementation

Environmental Policy Directions:

In the SCP regulations, DTSC prefers a regulatory response that provides the greatest level of inherent protection. That protection is defined in the California Code of Regulations, Title 22, as the avoidance or reduction of adverse impacts, exposures, and/or adverse waste by changing a product or process rather than controlling exposures in any of their regulatory responses. To do this, we recommend that DTSC establish an end of life product management program by requiring carpet and rug manufacturers to develop a comprehensive product stewardship plan that addresses the legacy of PFASs. In addition, we recommend that DTSC advance green chemistry behind PFAS mineralization methods, such as the enzymatic esterase and laccase strategies as long term regulatory responses. The advancement of greener solutions will benefit other consumer products and environmental media contaminated with PFAS into the future. The scope of the PFAS issue is only starting to be realized by regulators and industry.

In addition to regulatory responses, hazardous waste is a challenge to control at the state level alone. Unlike new chemical products sold in California where many industries are incentivized to comply with more protective environmental health regulations set by the California Environmental Protection Agency to sell their products to the sixth largest economy in the world, waste is often sent to another state or country with less restrictive regulations for much less financially. We recommend that DTSC use its political capital with an incoming new presidential administration to have the EPA regulate at least PFOA and PFOS as a Resource, Conservation, and Recovery Act listed toxic wasted (federally regulations for hazardous waste) and to set enforceable community exposure limits for safe drinking water and wastewater discharge. Joseph Biden has stated and published his support for regulating PFOA and PFOS in his policy agenda to reduce environmental injustices as the incoming President of the United States. Important to carpets and rugs, if PFOS and PFOA are regulated, we believe that the carpet and rug recycling industry will assume that all incoming carpets are contaminated with PFAS based on the challenges of detecting the range of PFASs with existing analytical technologies.

Even with these proposed regulatory responses, we see a defined role for CalRecycle and CARE in the solution to remove PFAS in carpets and rugs through improving the economic feasibility for the carpet and rug recyclers. Regulations can be adopted, but for them to be effective, there has to be the public policy and investment that supports the implementation and attainment of them, especially at the beginning when the startup costs are at their highest. In order to remove PFAS from carpets and rugs, all of these strategies require new expensive technologies and processes to implement. In addition, given the already narrow margins for recycled outputs from falling oil prices, additional subsidies for carpet and rug recyclers will be critical. We recommend that CalRecycle utilize its Greenhouse Gas Reduction Fund from Cap and trade proceeds for carpet and rug recyclers to supplement existing or future subsidies from CARE. In 2019 alone, California saved over 200,000 metric tons of carbon dioxide from entering the atmosphere by recycling carpets and rugs (CARE, 2019).

Strengths and Limitations of the Report:

Overall the report outlines potential PFAS removal strategies from carpet. There are some strengths, but there are some limitations to this preliminary report.

Strengths:

1. First report to investigate potential avenues of applying PFAS removal technologies during carpet recycling.
2. Balances not only technical feasibility, but also human and environmental health for the approaches.
3. Offers a variety of solutions to suit different needs of carpet recyclers.

Limitations:

1. These proposed approaches are all based upon literature and industry expert advice. No laboratory tests were conducted and further tests are warranted to test the effectiveness of each strategy.
2. For the purposes of this report, which was a 3 month timeline, we narrowed our scope to only nylon type face fibers. However, there are 3-4 types of face fibers which were not included in this report.
3. In our hazard assessment for each strategy, we assumed that PFAS is removed to an extent where it is no longer considered a hazard. However, this is unlikely true and further laboratory testing should be conducted to determine what percent of PFAS is removed during these treatment options.
4. Carpet is a highly variable medium depending on age, material, other treatment chemicals, and use.
5. We did not consider the other chemicals that are in carpet and how they might affect or react during our treatments. Some might produce unwanted transformation products while others might scavenge the reactive species meant to mineralize PFAS.

Remaining Questions:

After all our research, there are still looming questions regarding scaling up these approaches, health and environmental impacts, and technical considerations.

Scaling Up:

1. Can the science be transferred from bench to full scale?
2. What costs will be incurred by scaling up these operations?
3. Who will fund these PFAS removal efforts?

Health and Environmental Impacts:

1. What are the occupational exposures involved with introducing these new approaches?
2. What are the unintended consequences of these processes that might affect local communities?

3. What is done with the adsorbed GAC and waste water?
4. Is removing the PFAS enough for now?
5. Does GAC remove acrylate and methacrylate waste in the treatment water?
6. What other contaminants might be produced or released as a result of these treatments?

Technical Considerations:

1. What the effect of these treatment strategies would have on other types of carpet face fiber?
2. How much PFAS is removed from the carpet face fiber? How much is left on the carpet? Are those PFASs less likely to be released from the fiber during future use?
3. Can the enzymes be optimized to compete with these harsh chemicals?
4. How do recyclers monitor the performance of these strategies to make sure they aren't accidentally releasing PFAS into the environment, given the cost and time associated with PFAS quantification?

7. Biosketches:

Ned Antell is a 3rd year PhD student in Civil and Environmental Engineering. His research focuses on PFAS remediation from water using combinations of biological and chemical techniques. He is also interested in developing forensic tools to determine possible sources of PFAS contamination by leveraging large datasets to "fingerprint" these sources. He has an undergraduate degree in Ecology and worked for six years as a field and lab technician in several research groups prior to graduate school.

Andrew Cullen is an interdisciplinary MPH student whose interests focus on reducing environmental and occupational exposures to hazardous materials. At Lawrence Berkeley National Laboratory (LBNL), he works full-time as an emergency management specialist that analyzes natural, technological, and man-made hazards to prepare the laboratory for hazardous material releases. He has an undergraduate degree in chemistry from UC Berkeley combined with several years of research in chemical biology prior to switching to an operational support role at LBNL.

Michael Kado is a 3rd year PhD student in the School of Public Health, Division of Environmental Health Sciences. His interests are in environmental health as it relates to vulnerable populations. He has an undergraduate degree in Physiology and has years of experience in public health at the county, state, and academic levels.

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