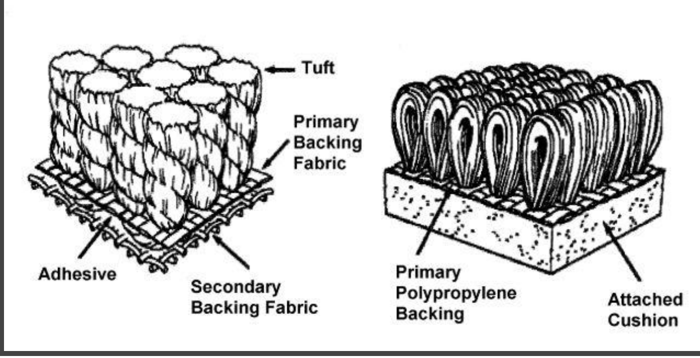
In collaboration with

DTSC
Department of Toxic Substances Control



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

Ned Antell, Andrew Cullen, & Michael Kado

Greener Solutions Course- Final Presentation
Thursday December 8th, 2020

https://www.recyclingproductnews.com/article/34775/californias-carpet-recycling-rate-soars-according-to-annual-report

Moody, V & Needles, HL. (2004) Tufted Carpet: Textiles, fibers, dyes, finishes, & processes. USA William Andrew Inc.

Who we are:

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Environmental Health Sciences

Overview of the Challenge

Berkeley School of Public Health

DTSC Department of Toxic Substances Control

Berkeley Center for Green Chemistry

The Challenge: **Investigate methods of removing PFASs from recycled carpet stock during carpet recycling**

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

<u>Final Product:</u> To create an opportunity map of the available options for PFAS removal during carpet recycling.

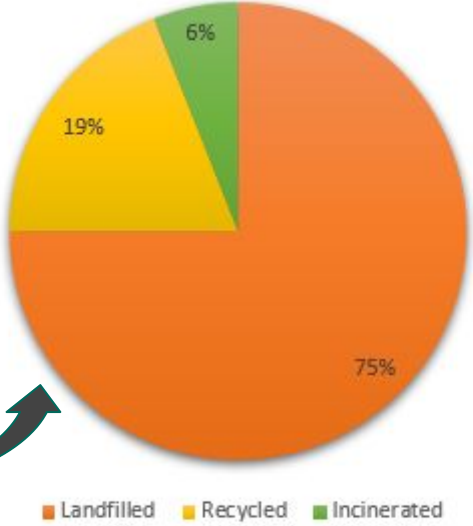
Carpets and rugs are a major waste stream

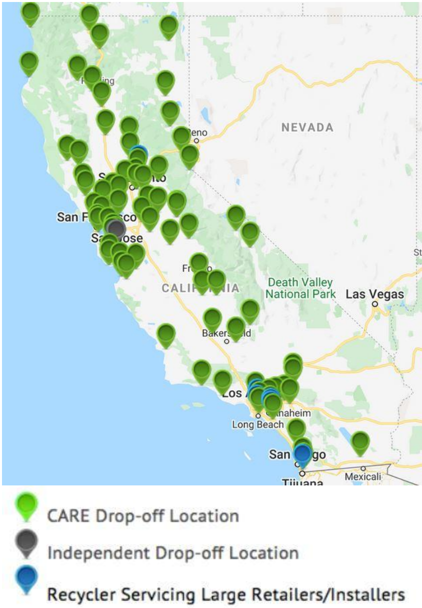
- Carpets make up over half of the flooring market and 3% of current landfill volume in the U.S.
- California passed AB 2398 and AB 1158 to increase carpet recycling to 24% by the end of 2020.
- In 2016, 343 million lbs were discarded in CA.

Circular Polymers™ re-made in the USA

LOS ANGELES FIBER

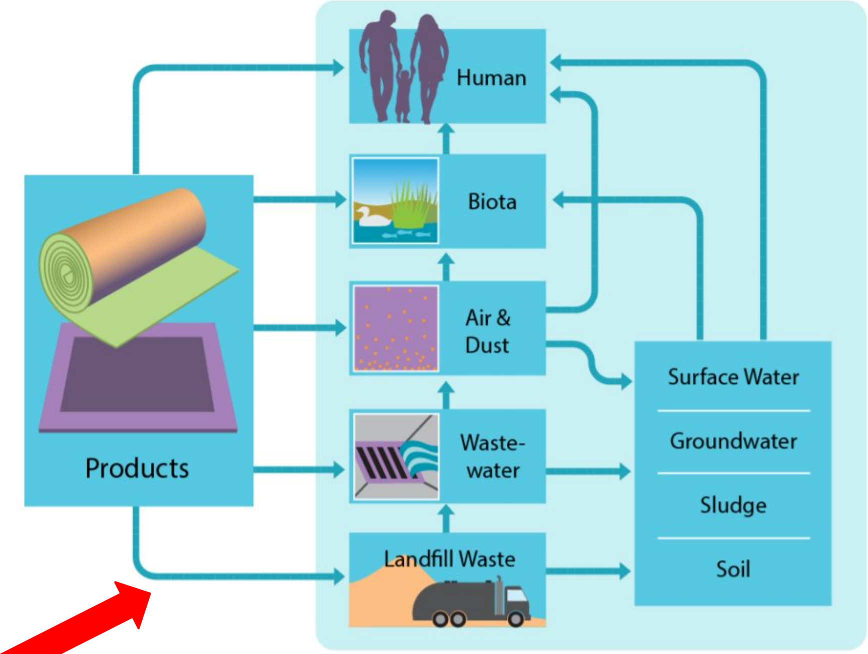
CARPET AMERICA RECOVERY EFFORT





Post-consumer carpets may contain PFAS for the next twenty years

- PFAS is added to the synthetic facefibers of carpets and rugs for stain, grease, and oil repellency.
- Phased out in 2019 from new carpets, but continues its presence in the disposal and recycling chain as a legacy chemical.



Intervention

Product – Chemical Profile for Carpets and Rugs Containing Perfluoroalkyl or Polyfluoroalkyl Substances, DTSC, 2019

Existing approaches to recycle or dispose of carpet do not remove or treat PFASs

Landfilling

Contaminates ground/surface waters and wastewater effluents with PFAS

Incineration

Releases short-chain PFAS, CFCs, and greenhouse gases

Recycling

Reintroduces PFAS into new consumer products that are not controlled

https://citytile.net/going-green-recycling-reusing-rethinking-old-rugs/

https://www.waste360.com/landfill/worlds-trash-increasingly-ending-incinerators

https://www.pca.state.mn.us/waste/construction-and-demolition-landfills-groundwater

PFAS exposures from carpets and rugs are significant

- Recent intake study estimates up to 1.9 ng PFAS/kg body weight per day from carpets in use at CA childcare facilities.
- EPA established an individual chronic reference dose for PFOA and PFOS of 0.02 ng/kg body weight per day.

https://www.woolino.com/products/sheepskin-rug-for-baby-natural-shorn-lambskin-2x3-ivory

Constituent	Median Concentration* (ng/g)
6:2 FTOH	69
8:2 FTOH	18.8
PFHxA	10
PFBA	8.09
PFOA	6.13
PFPeA	4.62
PFNA	2.7
PFOS	2.32
PFHxS	1.31
PFTeDA	0.97
8:2 FTSA	0.78
PFTrDA	0.57
PFBS	0.53

*Found in >90% of all child daycare carpets sampled by Wu et al. (2020)

The hazards of not intervening

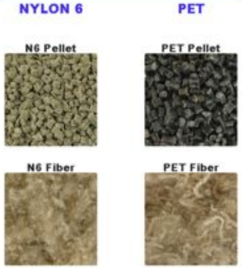
Human Endpoints							Environmental	
Constituent	C/M	D/R	Endocrine	Systematic	Neurotoxicity	Irritation	Aquatic	Bioaccumulative
6:2 FTOH			M	M		H	H	H
8:2 FTOH			M	M		H	H	VH
PFHxA		M	M	M		VH	M	M
PFBA				H		H	H	L
PFOA	M	H	H	H	H	VH	M	H
PFPeA		M	M	M		VH	M	L
PFNA	M	VH	M	M		VH	H	VH
PFOS	M	H	M	H	H	M	M	H
PFHxS		H	H	M		H	M	L
PFTeDA						VH		VH
8:2 FTSA				M		M	H	VH
PFTrDA			M	M				VH
PFBS			H	M		VH	M	L

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

Approach

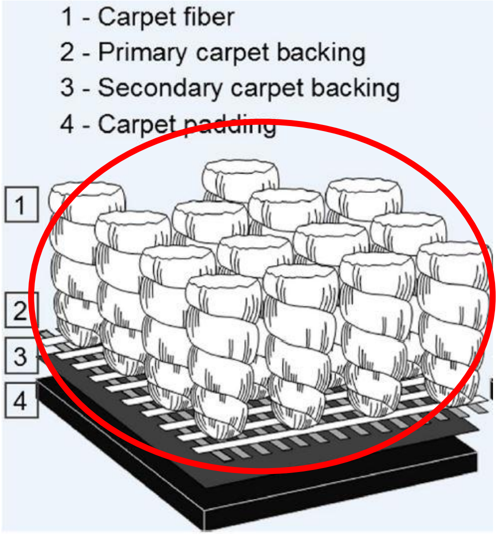
General carpet recycling processes allow for multiple points of intervention

Carpet Removal & collection → Sorting, Baling, and Storing → Separating Carpet Face Fiber → Sorting the Face Fiber → Cleaning &/or Extrusion *



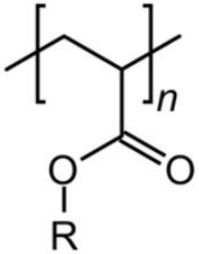
*These represent general processes and vary based upon recycling center and final products.

Boundary Conditions - focus on Nylon 6 and 6,6 carpet face fiber fluff and side-chain fluorinated polymers

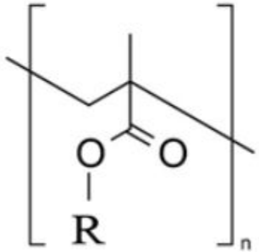


Haines, S. R., Adams, R. I., Boor, B. E., Bruton, T. A., Downey, J., Ferro, A. R., … Dannemiller, K. C. (2020). Ten questions concerning the implications of carpet on indoor chemistry and microbiology. *Building and Environment*, *170*, 106589. https://doi.org/10.1016/j.buildenv.2019.106589

Acrylate Linkage



Methacrylate Linkage



Where R = PFAS,
n = # of monomers in the polymer

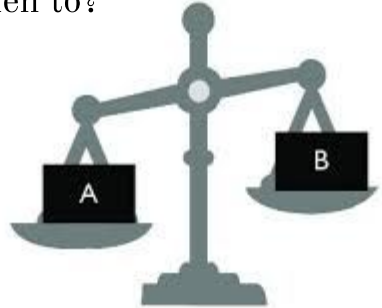
Image Sources: Polysciences.com and Wikipedia.com

Criteria for Success: Health & Environmental Hazards

Workplace/community exposure?

New waste streams from reagents?

Who are we shifting the hazard burden to?



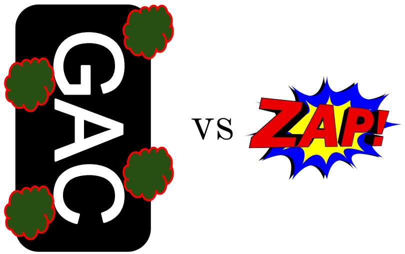
Human Endpoints							Environmental	
Constituent	C/M	D/R	Endocrine	Systematic	Neurotoxicity	Irritation	Aquatic	Bioaccumulative
PFOA	M	H	H	H	H	VH	M	H

https://sphweb.bumc.bu.edu/otlt/mph-modules/exposureassessment/exposureassessment3.html

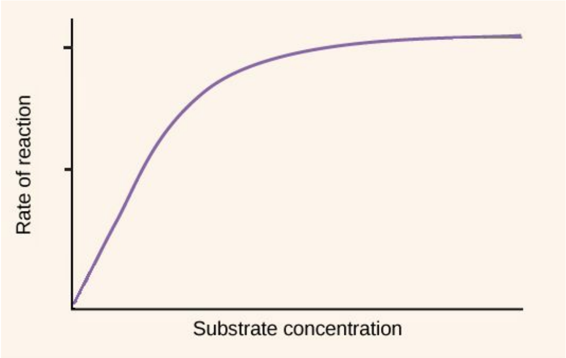
L: Low	M:Moderate	H: High	VH: Very High	Probable	Data Gap

Criteria for Success: Strategy Effectiveness

Adsorption or Destruction

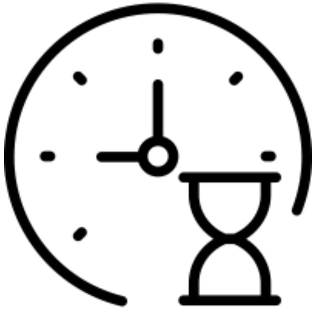


Reaction Kinetics



Capital/Running costs

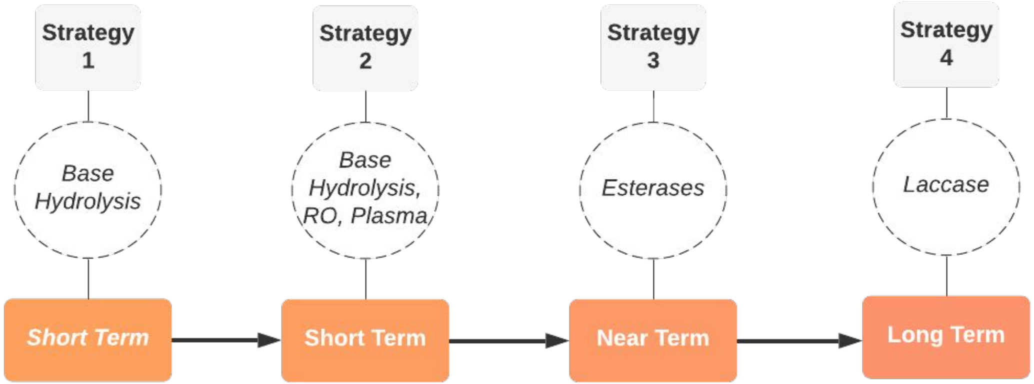
Time to implement



Approach	Removal or Destruction	Time to Implement	Reaction speed	Energy Input	Feasibility
Example Strategy 1	Removal	Immediately	Minutes to Hours	Low	Easy

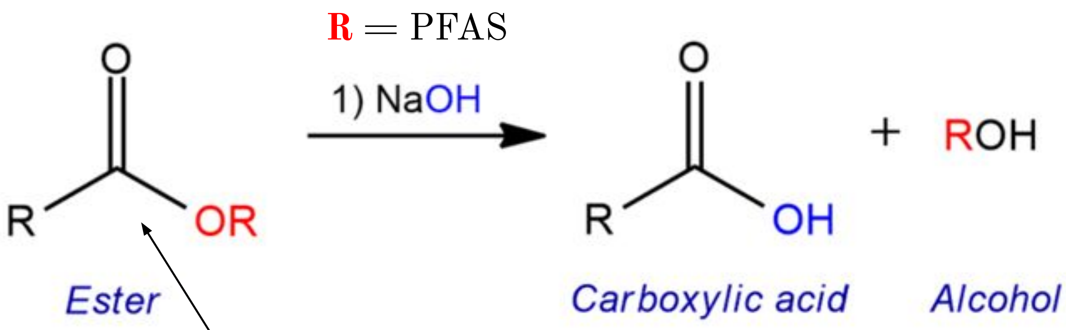
Overview of Proposed Strategies

1. Base Hydrolysis + Granular Activated Carbon (GAC) Adsorption
2. Base Hydrolysis + Reverse Osmosis (RO) + Plasma Treatment
3. Esterase substitute for Base Hydrolysis
4. Enzymatic Laccase

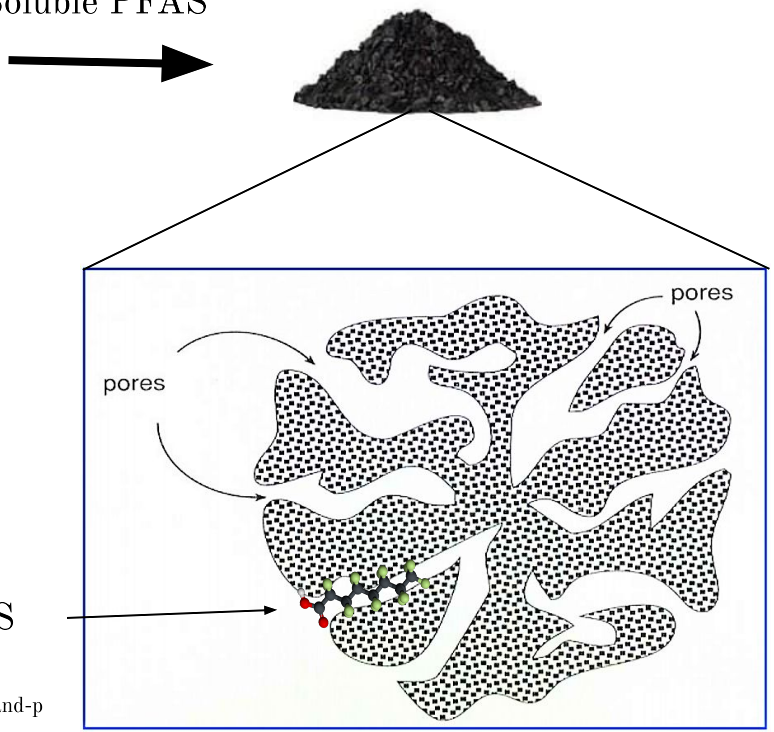


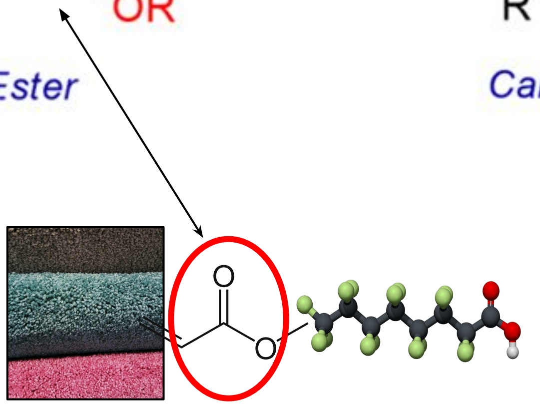
Proposed Solution #1- Base Hydrolysis + Granular Activated Carbon

Base Hydrolysis + Granular Activated Carbon (GAC)



Soluble PFAS





Methacrylate
linkage

Soluble PFAS

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

Drop-in treatment during fluff washing followed by adsorption

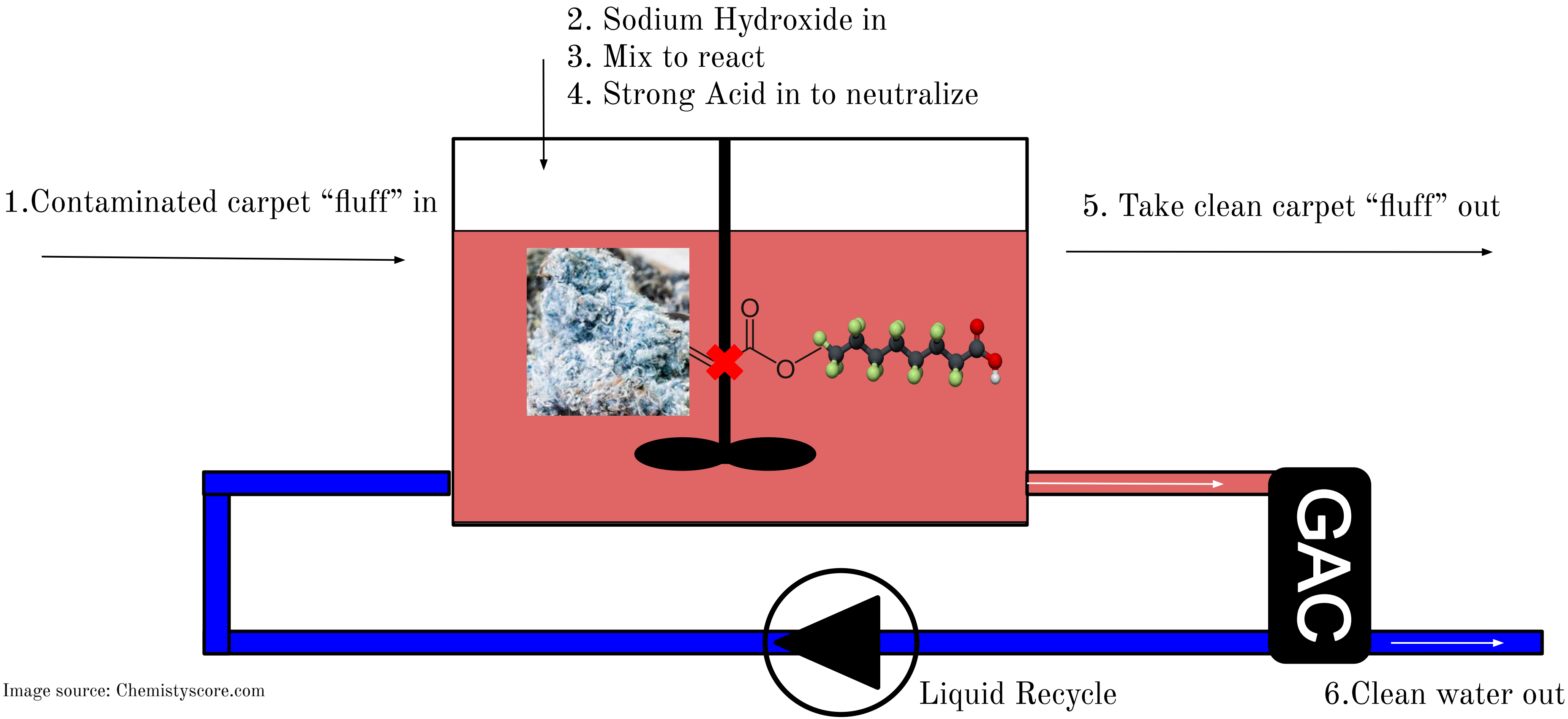
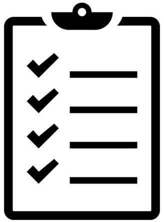


Image source: Chemistyscore.com

Technical Performance of Base Hydrolysis + GAC

	Removal or Destruction	Time to Implement	Reaction speed	Energy Input	Feasibility
Base Hydrolysis + GAC	Removal	Immediately	Minutes to Hours	Low	Easy

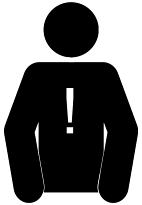
https://icon-library.com/icon/checklist-icon-free-7.html



Base hydrolysis doesn't introduce significant health or environmental hazards

Human Endpoints							Environmental	
Constituent	**C/M**	**D/R**	**Endocrine**	**Systematic**	**Neurotoxicity**	**Irritation**	**Aquatic**	**Bioaccumulative**
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**



https://sphweb.bumc.bu.edu/otlt/mph-modules/exposureassessment/exposureassessment3.html

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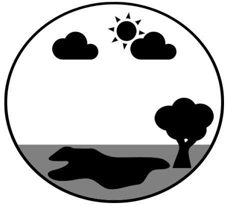


This approach shows effective PFAS removal and fast implementation, but could degrade the nylon & shifts the PFAS burden from carpet to GAC.

PROS:

- Effective method to remove the fluorinated side chains from the carpet fluff.
- Easiest and cheapest solution to implement right now.

CONS:

- Potential degradation of nylon fibers from a strong base/acid treatment.
- Doesn't mineralize the PFASs, but transfers the burden of PFASs to a different medium.
- Introduces new potential occupational exposures to strong bases and acids.

Proposed Solution #2- Base Hydrolysis + Reverse Osmosis + Plasma Treatment

Base Hydrolysis + Reverse Osmosis (RO) + Plasma treatment

RO concentrate treated by plasma

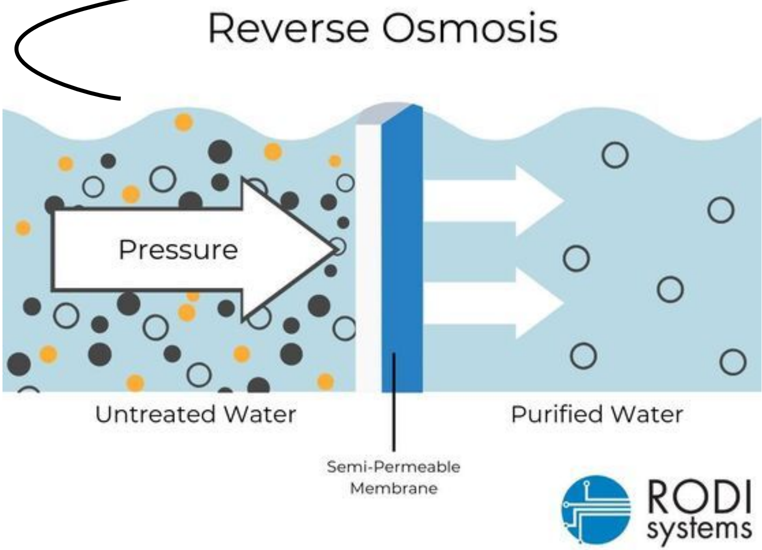


Image Source: https://www.rodisystems.com/how-does-reverse-osmosis-work.html

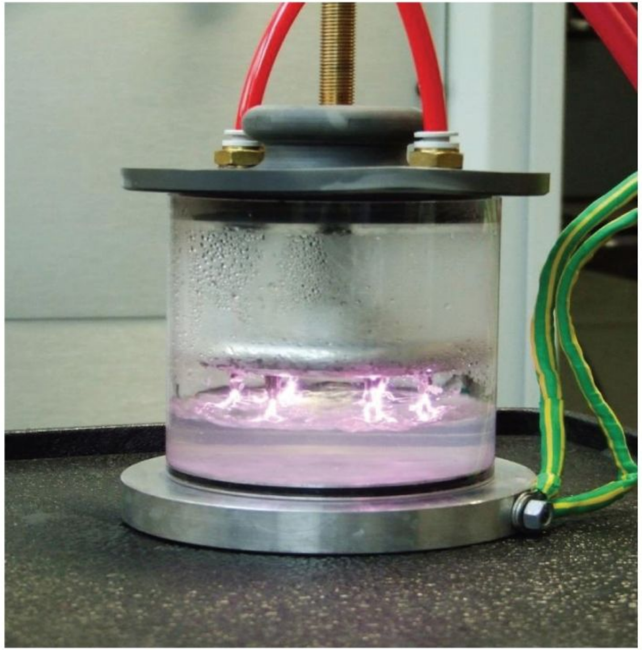
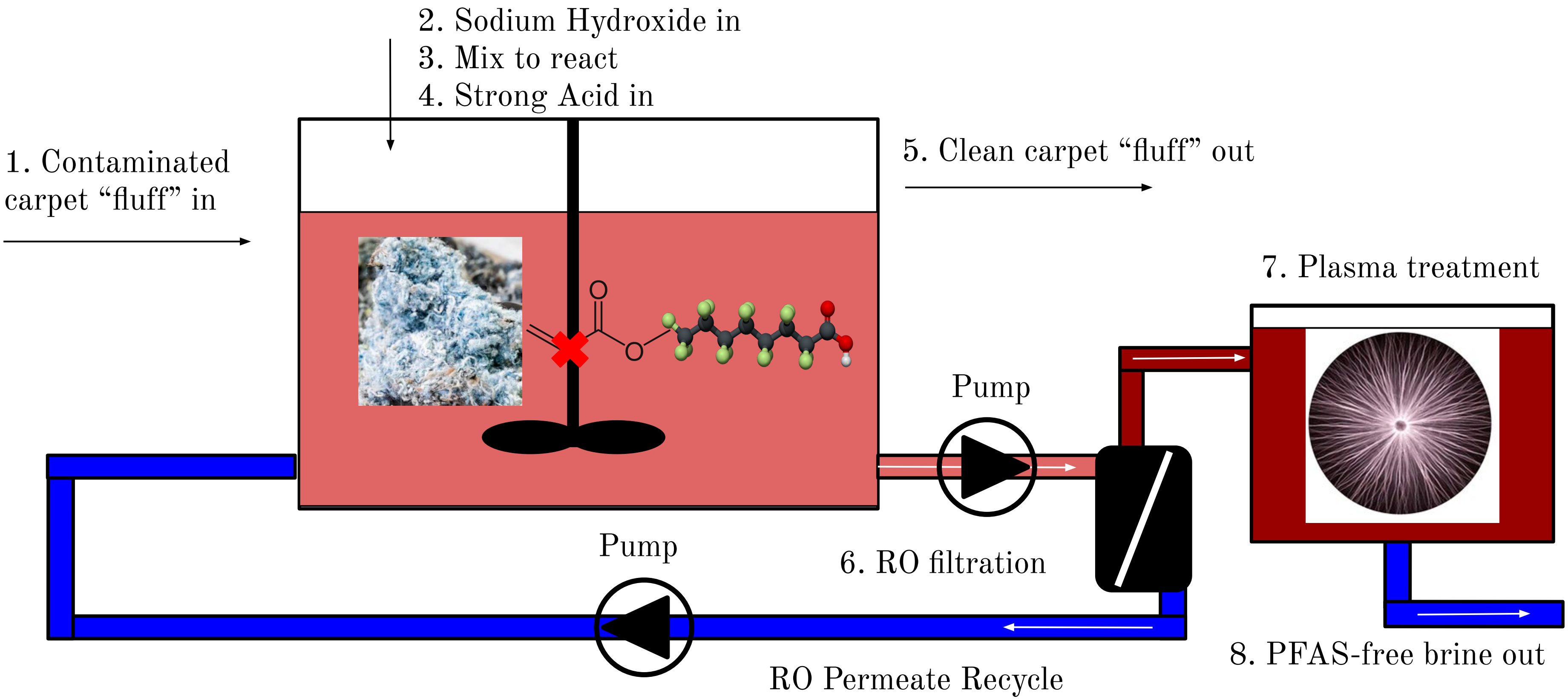


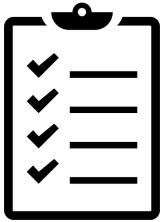
Image source: https://www.hindawi.com/journals/ijmicro/2011/462832/

A bit more complicated…



Technical Performance of Base Hydrolysis + RO + Plasma treatment

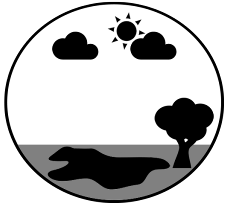
	Removal or Destruction	Time to Implement	Reaction speed	Energy Input	Feasibility
Base Hydrolysis + RO + Plasma	Destruction	Months to Years	Minutes to Hours	High	Moderate-Easy

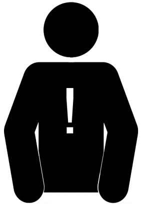


Any destructive treatment adds the potential for HF generation

Human Endpoints							Environmental	
Constituent	**C/M**	**D/R**	**Endocrine**	**Systematic**	**Neurotoxicity**	**Irritation**	**Aquatic**	**Bioaccumulative**
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**





Pros/Cons of this approach

PROS:

- Plasma-based pilot scale operations are underway
- Requires no additional chemicals
- Fast reaction times (minutes to hours)
- Mineralizes a significant fraction of PFAS

CONS:

- Three discrete steps
- RO + Plasma is much more expensive to build and operate than GAC
- Hazards associated with high voltage

Proposed Solution #3- Esterase

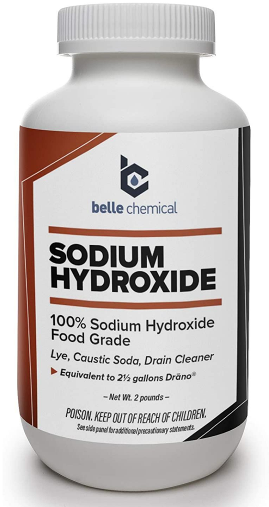
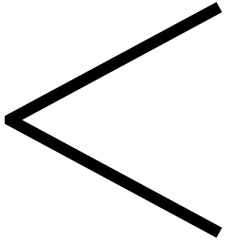


Image Source: https://www.amazon.com/Sodium-Hydroxide-Grade-Caustic-Pound/dp/B07KNR9SVF



Esterase Enzyme

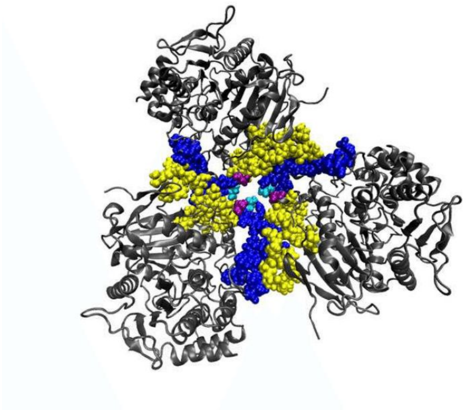
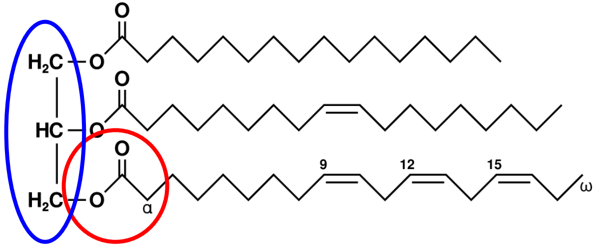


Image Source: https://www.researchgate.net/publication/46404626_Simulation_on_the_structure_of_pig_liver_esterase

Esterases typically hydrolyze triglycerides



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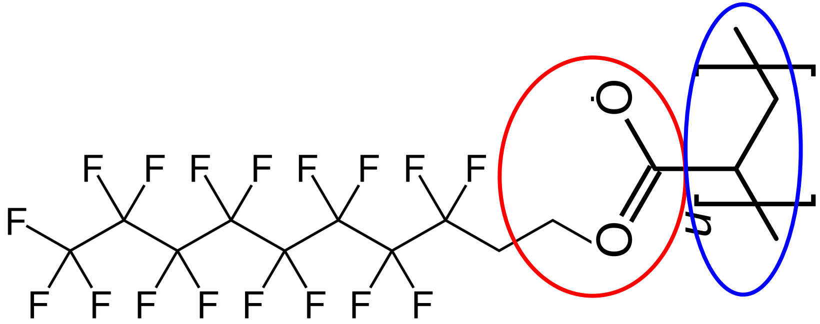

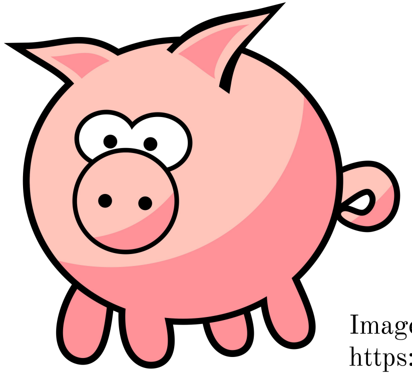

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Image Source:
https://creazilla.com/nodes/16939-funny-pig-clipart

Pig Liver Esterase has no known hazards!

Human Endpoints							Environmental	
Constituent	**C/M**	**D/R**	**Endocrine**	**Systematic**	**Neurotoxicity**	**Irritation**	**Aquatic**	**Bioaccumulative**
Pig Liver Esterase	**DG**	**DG**	**DG**	**DG**	**DG**	**DG**	**DG**	**DG**

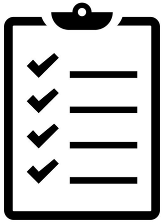
L: Low	M:Moderate	H: High	VH: Very High	Probable	Data Gap

Image Source: https://www.pngegg.com/en/png-ddmjv

Image Source: https://www.dreamstime.com/cute-smart-pig-sitting-floor-anf-reading-book-funny-cartoon-animal-vector-illustration-cute-smart-pig-sitting-floor-image101298624

Technical Performance of esterase treatments

	Removal or Destruction	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



Pros/Cons of this approach

PROS:

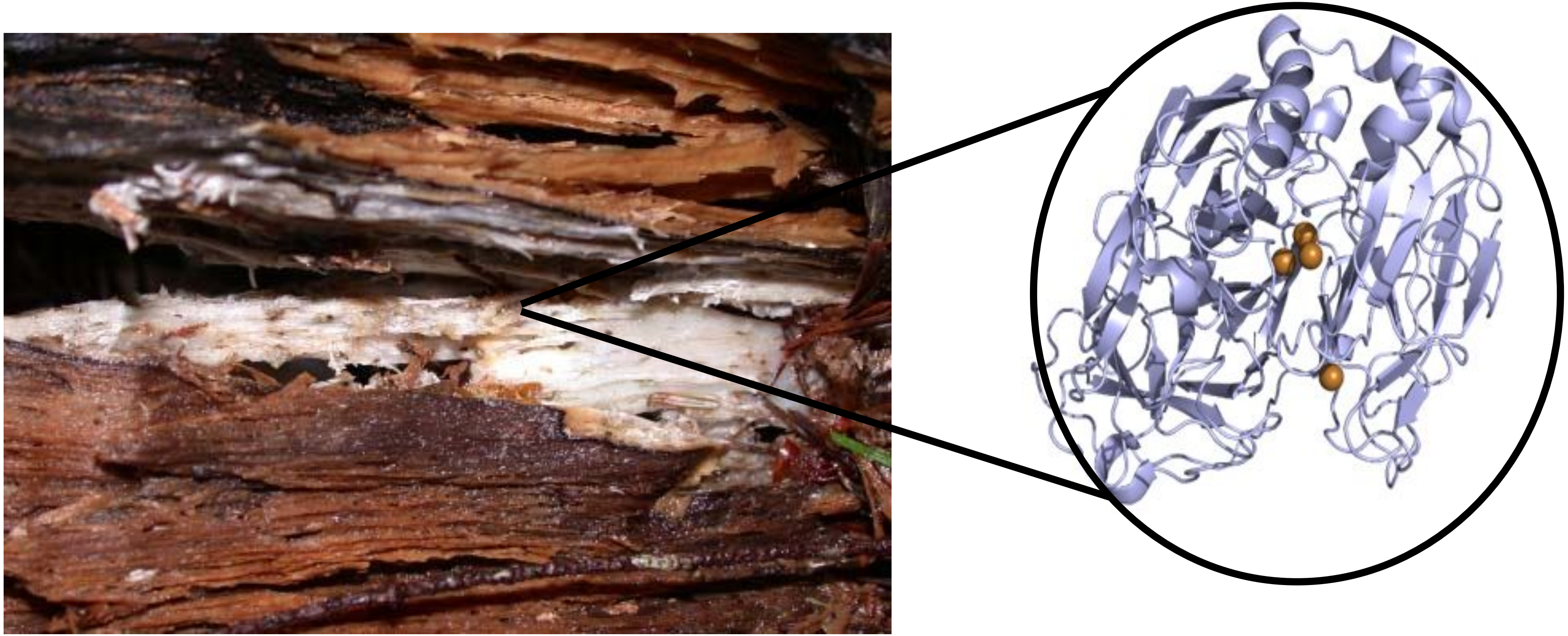
- Enzyme requires no cofactors or mediators
- No known hazard
- Cheap and widely available

CONS:

- **Does it work in our system?**
- If Pig Liver Enzyme doesn't work, finding a suitable enzyme would take time.
- Enzymatic reactions are typically slower than chemical

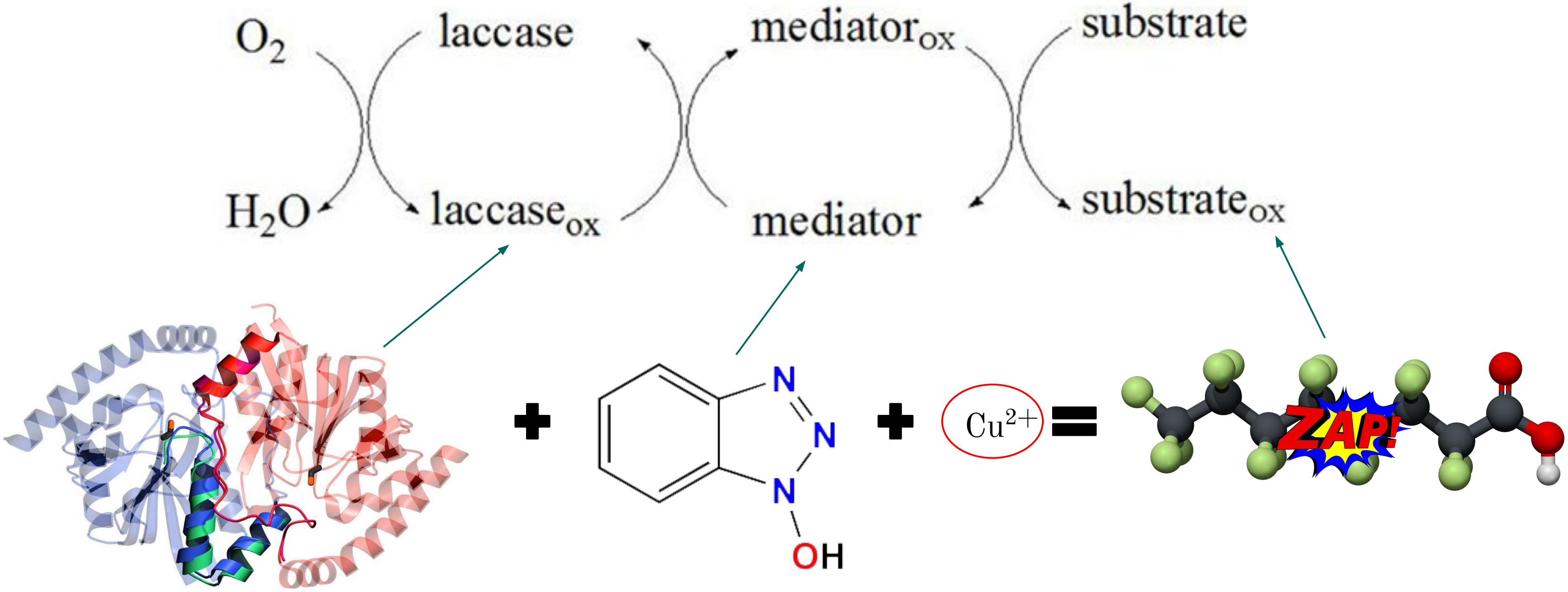
Proposed Solution #4- Laccase

Laccase mediator systems



https://www.creative-enzymes.com/similar/laccase_388.html

PFAS Removal Strategies- Laccase Mediator



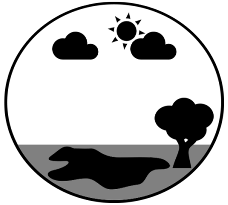
https://news.unl.edu/newsrooms/today/article/enzymes-and-x-rays-study-reveals-hidden-acrobatics-of-cellular-catalysts/

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

Hazard Information of Laccase Treatment

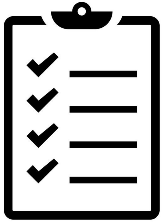
Human Endpoints							Environmental	
Constituent	C/M	D/R	Endocrine	Systematic	Neurotoxicity	Irritation	Aquatic	Bioaccumulative
Copper(II) sulfate	DG	M	M	M	VH	VH	VH	VH
1-hydroxybenzotriazole (HBT)	DG	DG	DG	L	DG	H	M	DG
Laccase	DG	DG	DG	DG	DG	H	DG	DG
Hydrofluoric Acid	L	M	M	H	H	VH	M	L

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



Technical Performance of Laccase Treatment

	Removal or Destruction	Time to Implement	Reaction speed	Energy Input	Feasibility
Laccase + (GAC)	Destruction	Long	Unknown	Low	Difficult



Pros/Cons of this approach

PROS:

- Single reaction step
- Enzymatic process with potential to eliminate need for hazardous chemicals
- Has potential to mineralize PFAS
- Very low energy input

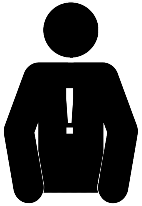
CONS:

- Currently requires hazardous HBT and Cu(II)
- Currently results in numerous high fluorinated transformation products
- Slow reaction times (days to months)
- **Years away from being commercially viable,might miss the window of PFAS contaminated carpets and rugs**
- Any defluorination process runs the risk of generating HF

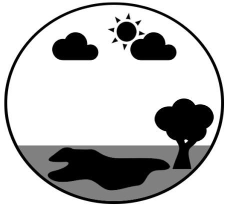
Conclusions and Remaining Questions

Hazard Score Summaries for All 4 Methods

Human Endpoints							Environmental	
Strategy	**C/M**	**D/R**	**Endocrine**	**Systematic**	**Neurotoxicity**	**Irritation**	**Aquatic**	**Bioaccumulative**
Baseline	**M**	**VH**	**H**	**H**	**H**	**VH**	**H**	**VH**
Base Hydrolysis	**L**	**L**	**DG**	**H**	**DG**	**VH**	**M**	**DG**
Base Hydrolysis + Plasma	**L**	**L**	**DG**	**H**	**DG**	**VH**	**M**	**DG**
Esterases	**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**



Technical Performance Summary

	Removal or Destruction	Time to Implement	Reaction speed	Energy Input	Feasibility
Base Hydrolysis + GAC	Removal	Immediately	Minutes to Hours	Low	Easy
Base Hydrolysis + RO + Plasma	Destruction	Short	Minutes to Hours	High	Moderate-Easy
Esterase + GAC	Removal	Medium	Unknown	Low	Moderate
Esterase + RO + Plasma	Destruction	Medium	Unknown	Medium	Moderate
Laccase + (GAC)	Destruction	Long	Unknown	Low	Difficult

Regulatory responses are needed at the state and federal level

Regulatory Response by DTSC (CA):

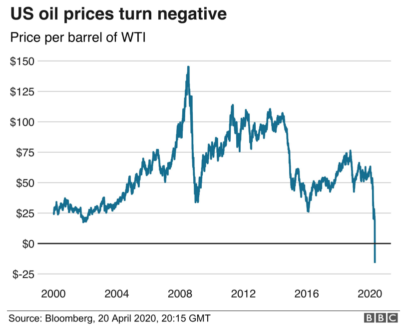
1. End-of-life product management program
2. Advancement of green chemistry or green engineering

Regulatory Response by EPA (US):

1. List PFAS as a hazardous waste constituent under RCRA
2. Establish enforceable community exposure limits for PFAS

Support by CalRecycle and CARE:

1. Continue and expand subsidies for carpet recyclers
2. Use proceeds from Greenhouse Gas Reduction Fund



https://www.bbc.com/news/business-52350082

DTSC Department of Toxic Substances Control

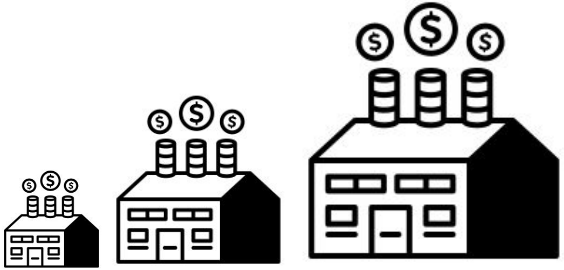
EPA

Background | Approach | Strategy 1 | Strategy 2 | Strategy 3 | Strategy 4 | Performances | Recommendations

Remaining Questions

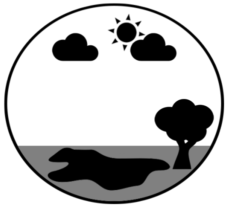
SCALING UP

- What are the costs of these operations at a larger scale?
- Who would fund the PFAS removal efforts?
- How can these operations be scaled up?



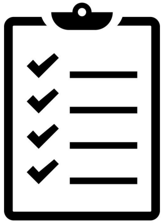
HEALTH AND ENVIRONMENT

- What are the occupational exposures?
- What is the fate of the adsorbed PFAS?
- Is simply removing the PFASs enough right now?
- Does GAC remove acrylate and methacrylate waste in the treatment water?



TECHNICAL

- Does base hydrolysis degrade the fiber?
- Can these enzymes be optimized such that they are competitive with chemical options?
- How much PFAS will the destructive technologies destroy?



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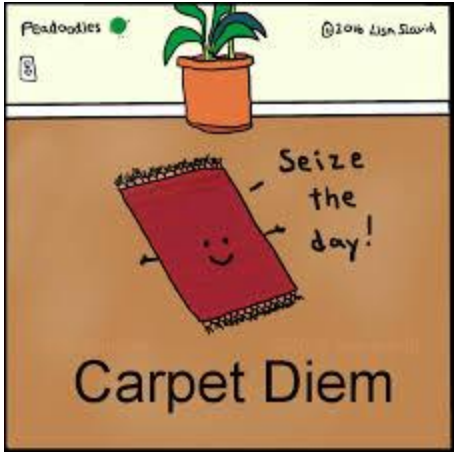
Questions?



http://peadoodles.blogspot.com/2016/02/carpet-diem.html

Supplementary Slides

Nylon face fiber and pH

ELSEVIER

Journal of Molecular Structure (Theochem) 635 (2003) 83–89

THEO CHEM

www.elsevier.com/locate/theochem

Effect of fluorine substitution on the rate for ester hydrolysis: estimation of the hydrolysis rate of perfluoroalkyl esters

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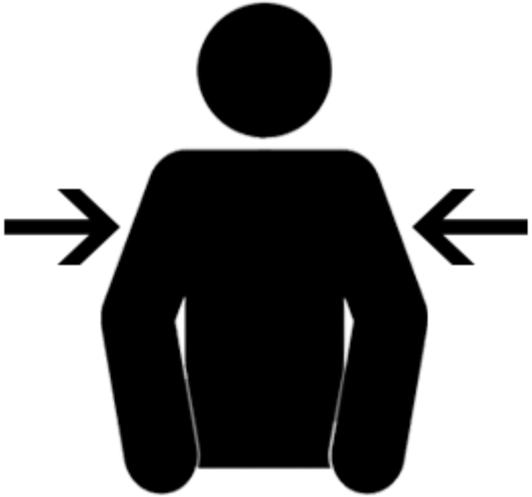
Routes of Exposure

Ingestion

Inhalation

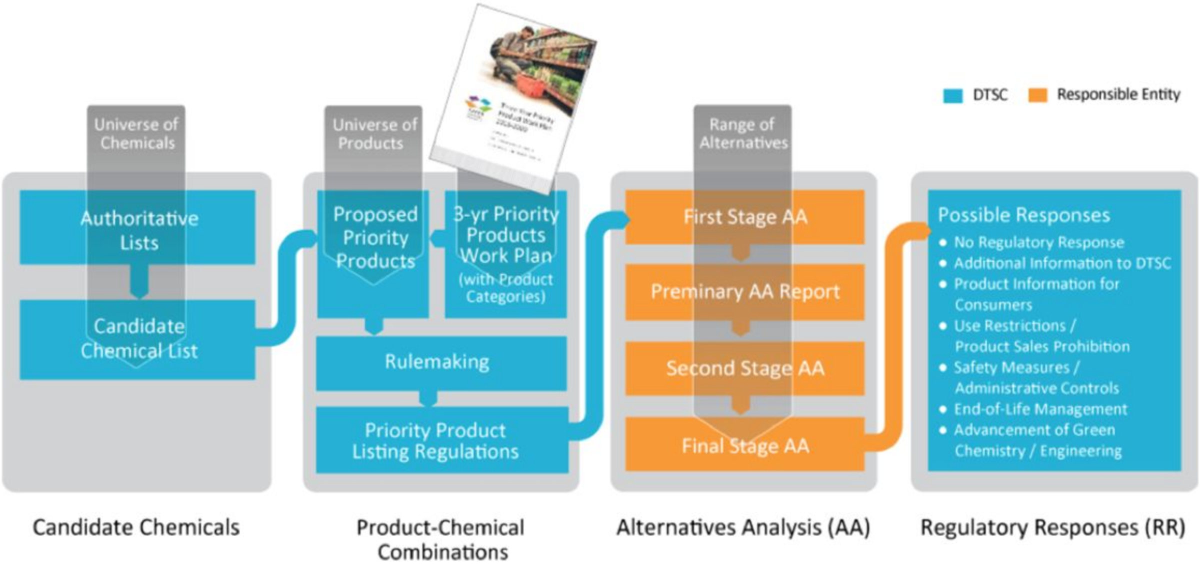


Dermal

https://sphweb.bumc.bu.edu/otlt/mph-modules/exposureassessment/exposureassessment3.html

How to intervene in CA: Safer Consumer Product Regulations
(SB 509 & AB 1879)

- Carpets and rugs were listed by DTSC as a proposed priority product in 2018
  - Potential **exposure** to a Candidate Chemical
  - One or more exposures leads to **significant or widespread adverse impacts**



https://dtsc.ca.gov/scp/

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