

# MULTISORB: A LOW-COST APPROACH TO REMOVE MULTIPLE METALS AND ORGANICS FROM LEACHATE

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# Professional Background

2024 - Scientific Apparatus Engineering Technician

2024 – Founder, CrossFit Green Leaf

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2022 – Intern Conifer Systems – Archaea Energy (RNG)

2016 – 2022 – GTA - Environmental Science & Geology

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2009 - 2016 – High School Science teacher (CISD & AISD)

Jan – Jun 2008 –Intern at St. Gobain Vetrotex Wichita Falls, Texas

2005 – 2006 – Technician: Envi. Testing Unit – St. George’s University

1999 – 2005 – QA/QC Laboratory Technician

# Introduction

A challenge for landfills today is removal of heavy metals and recalcitrant organics from leachate.

Leachate is a complex mixture of heavy metals, organics, pesticides, pharmaceuticals, etc. that ends up in water resource recovery facilities (**WRRFs**) for treatment.

The total amount of leachate generated by solid waste sanitary landfills has reached **30 million tons per year** (Wang et al., 2018).

# Why is Leachate Treatment Is Important?

- Pre-treatment removal of **heavy metals and organics** from leachate is needed to:
  - Avoid inhibition of **WRRF biological processes**
  - Avoid accumulation in **sludge** (preventing use as compost or fertilizer) (Zhao *et al.*, 2013; Bilardi *et al.*, 2018)
  - Remove Natural Organic Matter (NOM) that can pass through to the **WRRF disinfection system**, reducing its efficiency by absorbing UV light (Deng *et al.* 2018).
  - Reduce Per- and poly-fluoroalkyl substances (PFAS) and Pharmaceuticals and Personal care products (PPCPs) that can still reach receiving waters by **staying in treated wastewater**, as WRRFs may be unable to remove them completely (Shon *et al.* 2006; Wang and Wang, 2016).

# Which pollutants in treated wastewater are of concern?

Per- and poly-fluoroalkyl substances (PFAS) and Pharmaceuticals and Personal care products (PPCPs) can **remain in treated wastewater**, as WRRFs are unable to remove them (Shon *et al.* 2006; Wang and Wang, 2016).

General Category	Sub-Category	Compound	Use/Significance	Health/Environmental Concerns
NOM	N/A	Humic acid	Primary NOM constituent	Blocks pores, reduces adsorption of PFAS, Aquatic life gets affected if excess
PFAS	Long chain	PFOA (perfluorooctanoic acid)	One of the original widely used PFAS. No longer manufactured in US but can be imported in carpet, textiles, paper, packaging, coatings.	May lower infant birth weights, increase cholesterol levels, affect the immune system, and increase cancer risk
	Short chain	PFBA (perfluorobutyrate)	Product of breakdown of other PFAS; has been detected in drinking water supplies.	In animal studies, exposure to high levels affected thyroid and liver, delayed development, decreased red blood cells/hemoglobin.
PPCPs	Acidic	Naproxen	Anti-inflammatory drug used to treat pain	Bioaccumulation from soil causes toxicity to organisms and adds potential threat to humans.
	Weakly Acidic	Triclosan	Antimicrobial used in soaps and body washes, toothpastes, and cosmetics	Alters hormone regulation in animals; might be harmful to the immune system
	Neutral	N, N-diethylmeta-toluamide (DEET)	Insect repellent	Eye and skin irritation
	Basic	Atenolol	Beta-blocker	Creates ecotoxicity for fresh and saltwater biota

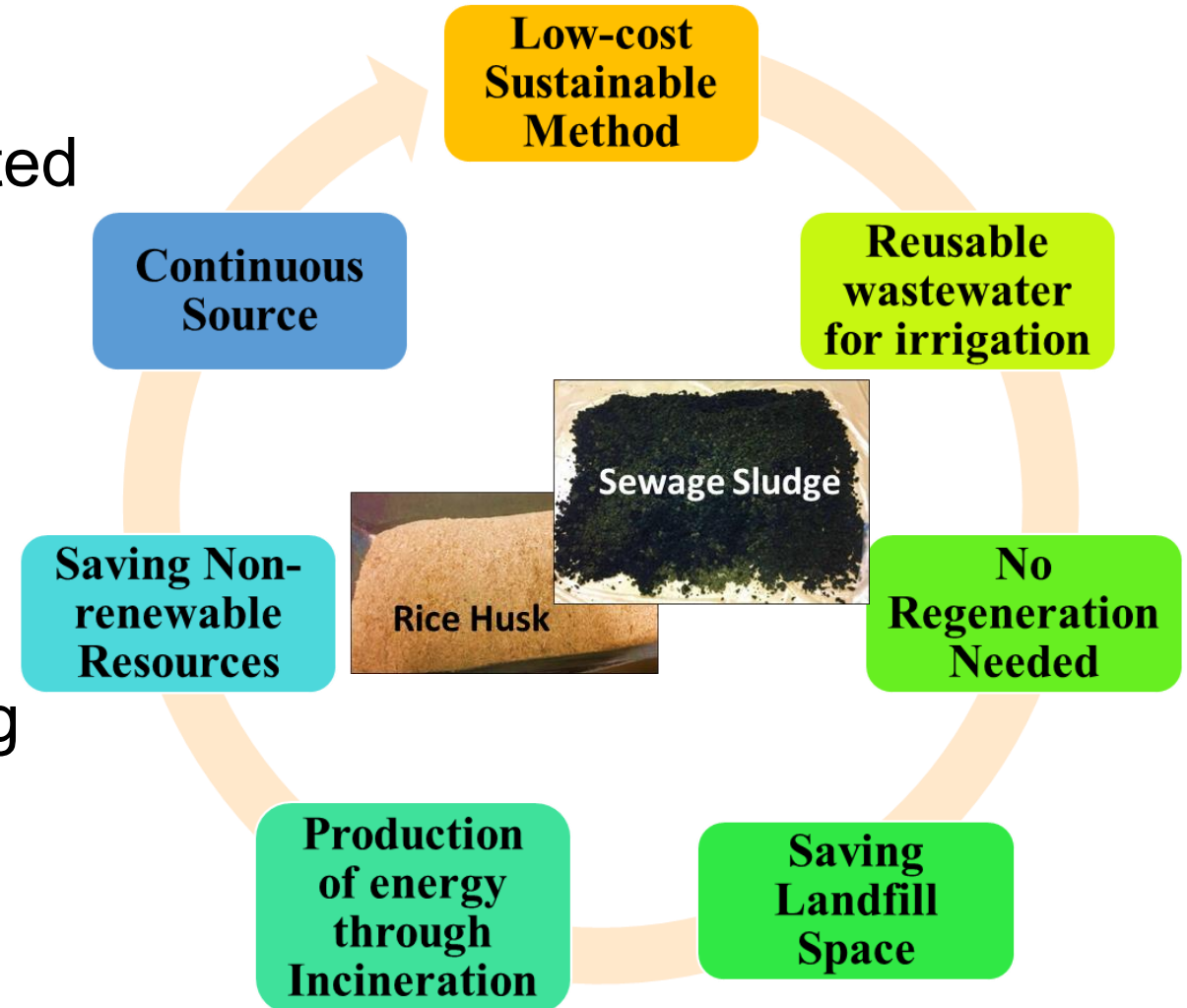
# Common Methods of Leachate Treatment

Methods (Physical and/or Chemical)	Advantages	Disadvantages
<b>Oxidation</b>	Rapid process for toxic pollutants removal	High energy costs and formation of byproduct
<b>Ion Exchange</b>	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
<b>Membrane Filtration Technologies</b>	Good removal of heavy metals	Concentrated sludge production, expensive
<b>Coagulation/Flocculation</b>	Economically feasible	High sludge production and formation of large particles
<b>Electrochemical Treatment</b>	Rapid process and effective for certain metal ions	High energy costs and formation of byproduct
<b>Ozonation</b>	Applied in gaseous state: alteration of volume	Short half-life
<b>Photochemical</b>	No sludge production	Formation of byproduct
<b>Irradiation</b>	Effective at lab scale	Requires a lot of dissolved O <sub>2</sub>
<b>Electro-kinetic Coagulation</b>	Economically feasible	High sludge production
<b>Fenton's Reagents</b>	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
<b>Biological Treatment</b>	Feasible in removing some metals	Technology yet to be established and commercialized
<b>Adsorption</b>	<b>Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants</b>	<b>Adsorbents requires regeneration</b>

# Adsorption and Waste-made Adsorbents

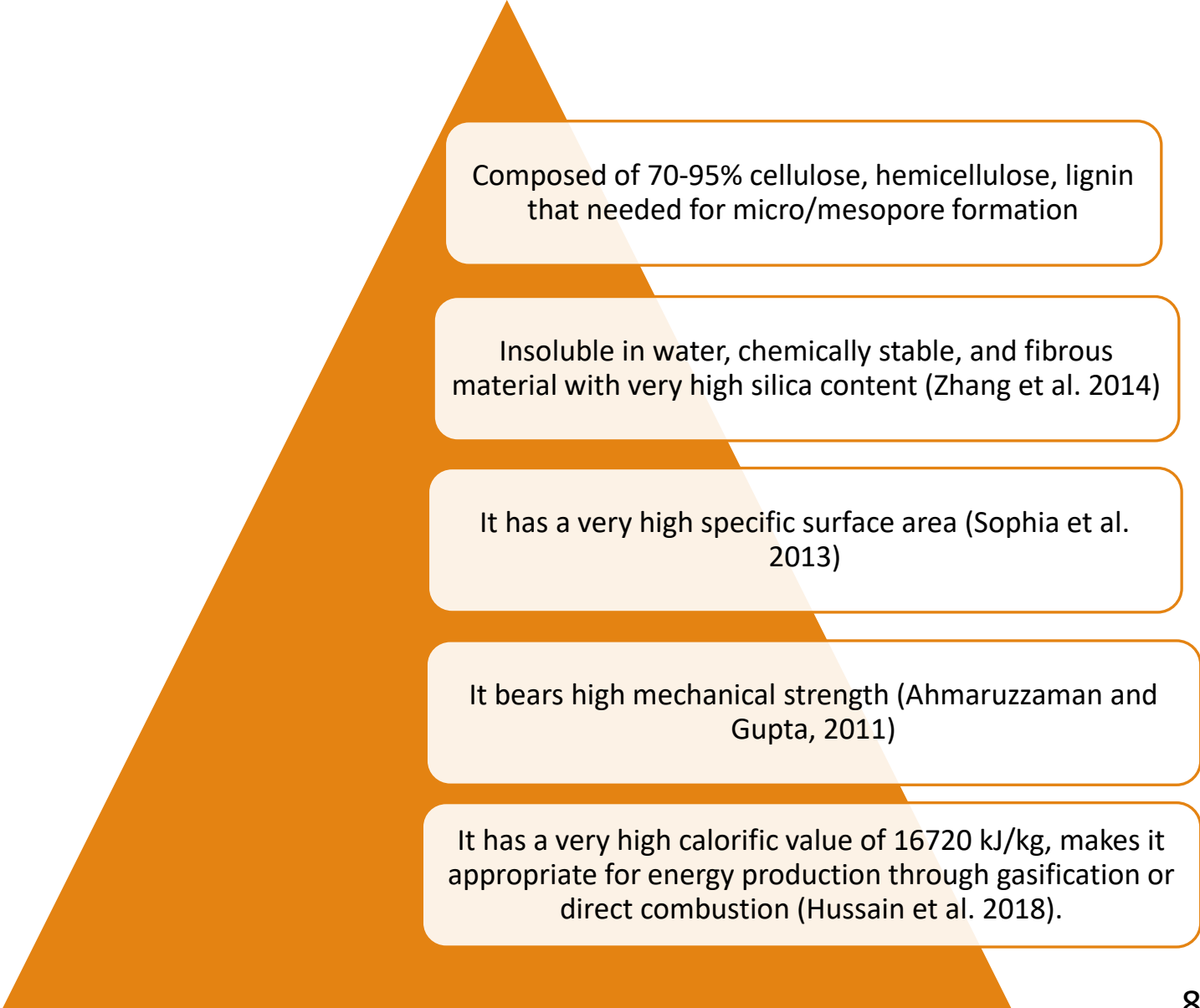
## Waste-Made Adsorbents

- Adsorbents have been demonstrated to:
  - **Effectively remove** heavy metals and organics from leachate (Deng *et al.*, 2018)
  - **Need less chemicals and energy** than many competing techniques (e.g. advanced oxidation processes) (Biliardi *et al.*, 2018)



# Why Rice Husk?

- Rice is the staple food of many countries and one of the most cultivated crops all over the world.
- Around 1.8 million tons of rice husk waste were produced in the US in 2017 (USDA 2020; Baniya et al, 2020)
- The general practice is feeding the cattle, burning to produce energy for cooking, or simply dumping them as waste.



Composed of 70-95% cellulose, hemicellulose, lignin that needed for micro/mesopore formation

Insoluble in water, chemically stable, and fibrous material with very high silica content (Zhang et al. 2014)

It has a very high specific surface area (Sophia et al. 2013)

It bears high mechanical strength (Ahmaruzzaman and Gupta, 2011)

It has a very high calorific value of 16720 kJ/kg, makes it appropriate for energy production through gasification or direct combustion (Hussain et al. 2018).

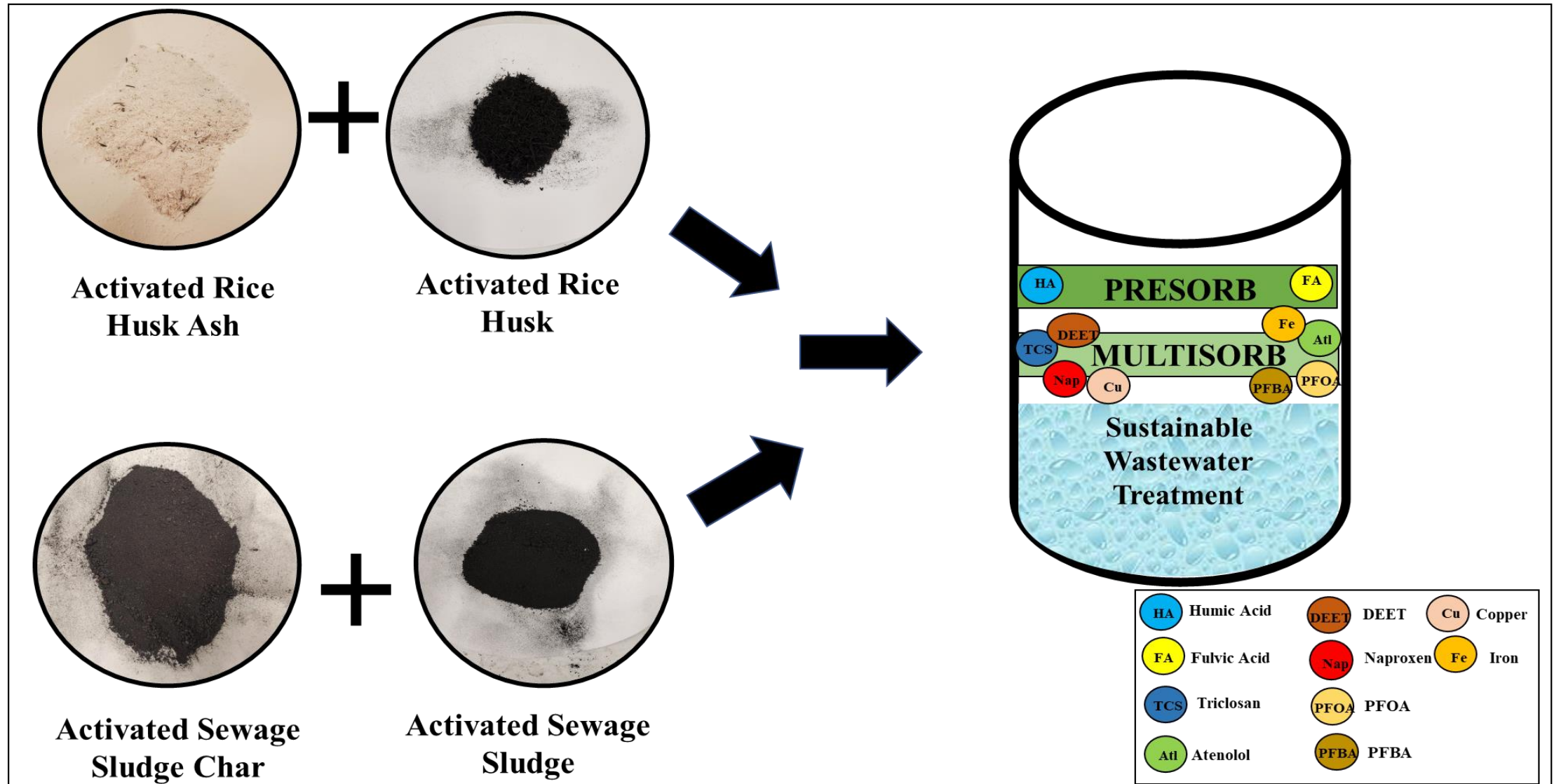
# Research Goal and Objectives

The **principal goal** was to develop a multiple sorbent mixture “MultiSorb” from readily-available waste materials, to cost-effectively remove heavy metals and organics from leachate/treated wastewater.

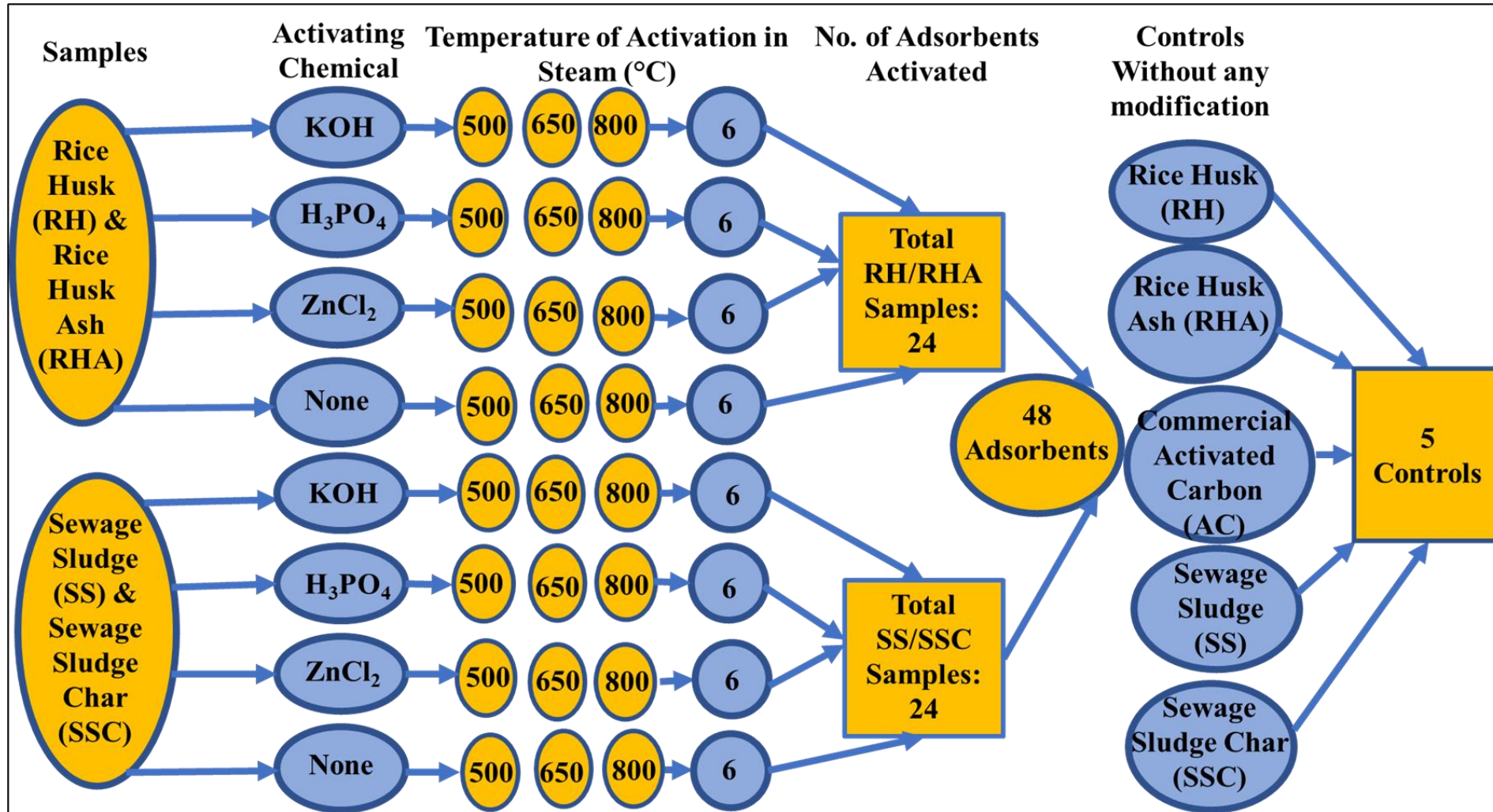
**The Specific objectives were to:**

1. Prepare and characterize waste-made adsorbents
2. Develop and test Presorb to assess NOM adsorption.
3. Develop and test MultiSorb to assess Heavy Metal, PFAS and PPCPs adsorption.

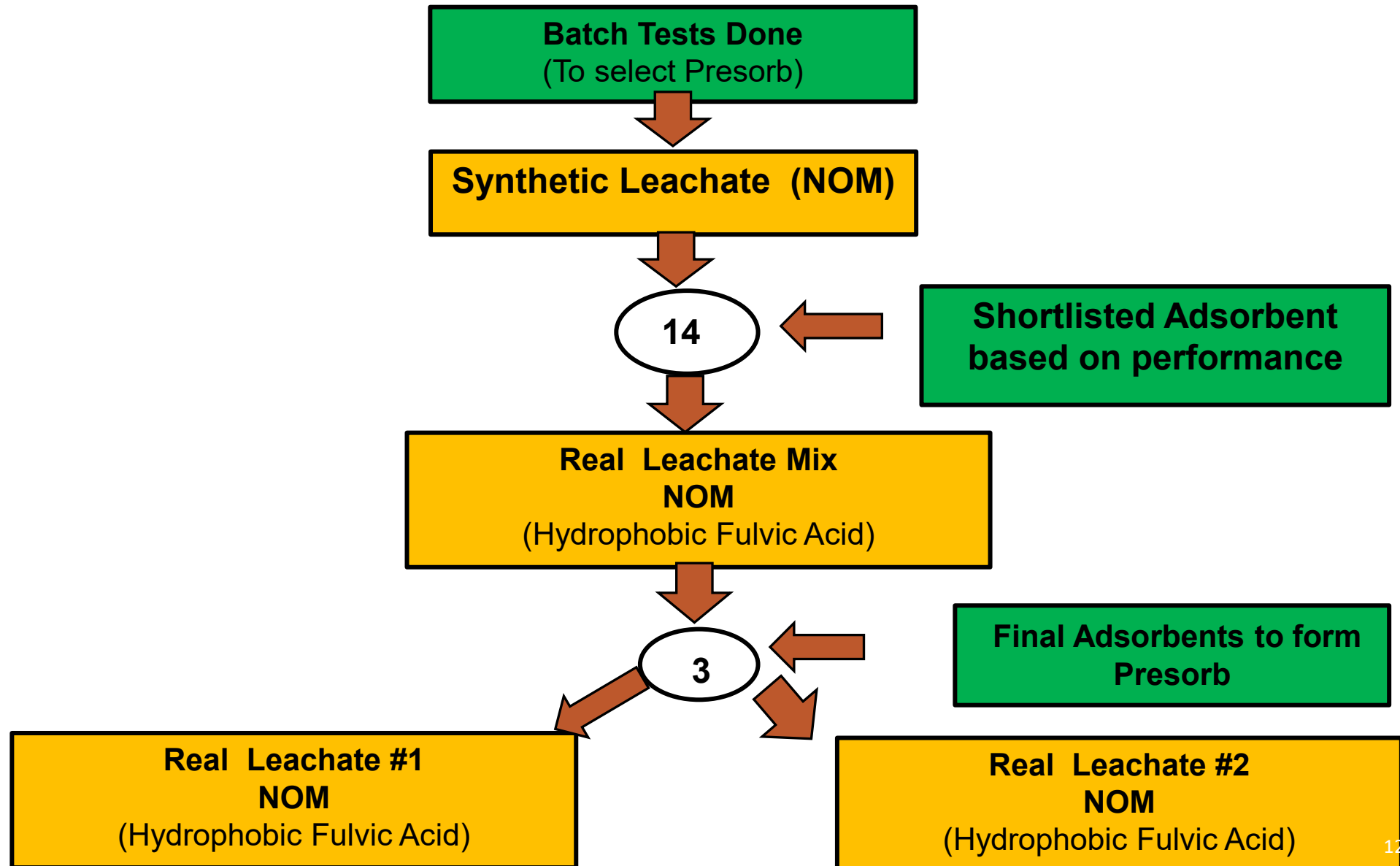
# Research Summary



# Types of Adsorbents Prepared



# Batch Tests to select Presorb



# Selection of Presorb Candidates

Table: Performance of Presorb Candidates compared to commercial activated carbon (CAC)

Individual Adsorbent	Fulvic Acid Adsorption (ppm)
	Real Leachate
RH-500	N/A
RH-650	N/A
RH-800	N/A
RH-500-Zn	3900
RH-650-Zn	N/A
RH-500-P	N/A
RH-800-P	N/A
<b>RHA-800</b>	<b>7000</b>
RHA-650-Zn	5300
RHA-800-Zn	6100
SS-650	6000
SS-500-Zn	4800
<b>SS-650-Zn</b>	<b>7200</b>
SS-800-Zn	5900
SS-500-P	N/A
SSC-500	6700
SSC-500-P	N/A
SSC-800-P	N/A
<b>Cont.: 2-RHA</b>	<b>7200</b>
Cont.: 3- SS	N/A
Cont.: 4-SSC	6000
Cont.: 5-CAC	7000
Cont.: 6-CAC (2)	4800
<b>Average CAC</b>	<b>5900</b>

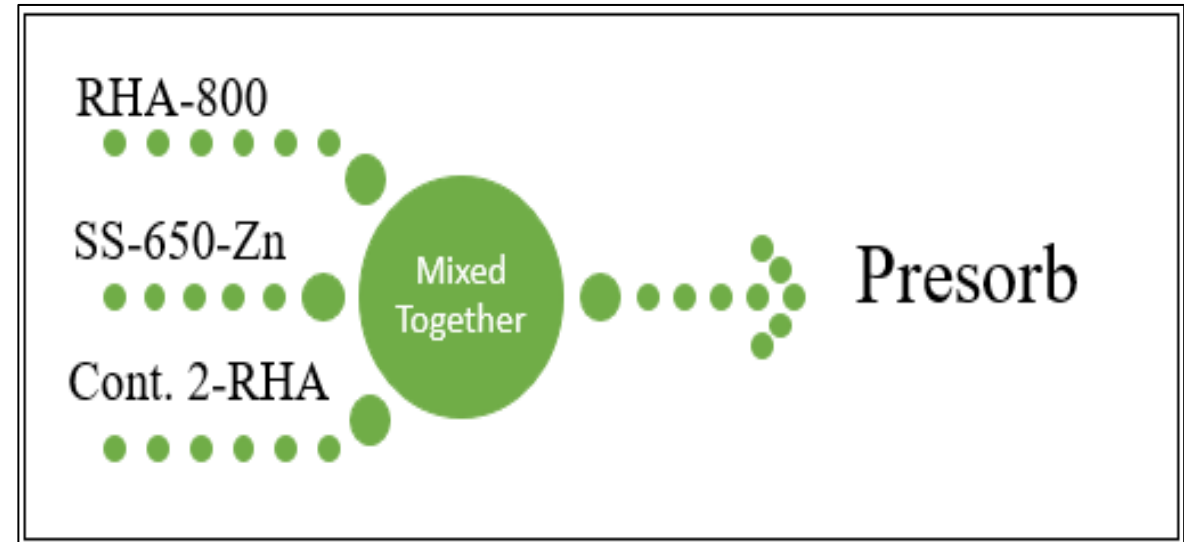


Figure: Shortlisted Presorb Candidates

# Adsorption by selected Presorb

Table: Presorb's Performance in adsorbing NOM

<b>Real Leachate Test</b>		
<b>Landfill Leachate #1</b>		
<b>Adsorbent</b>	<b>Adsorbed Hydrophobic Fulvic Acid (ppm)</b>	<b>Presorb &gt; CAC</b>
Presorb (avg.)	8900	
Commercial (avg.)	-4850	
<b>Landfill Leachate #2</b>		
Presorb (avg.)	200	<b>Equal</b>
Commercial (avg.)	200	

# Morphology of Presorb Candidates

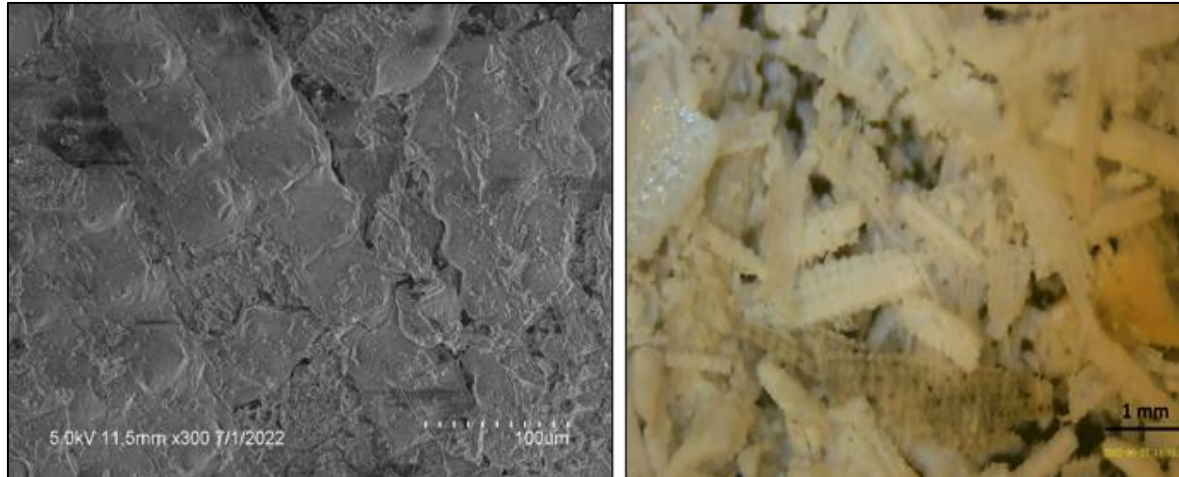


Figure: FESEM and Optical Microscopy of RHA-800

- ✓ Highly porous with rough surface
- ✓ RHA-800, RHA are rod shaped and SS-650-Zn is spherical
- ✓ Surface area ranges from 25.7 to 187.8 m<sup>2</sup>/g
- ✓ Mainly Mesoporous (>2 nm to <50 nm)
- ✓ Dominated by C, N, O, Si, Zn, P, S

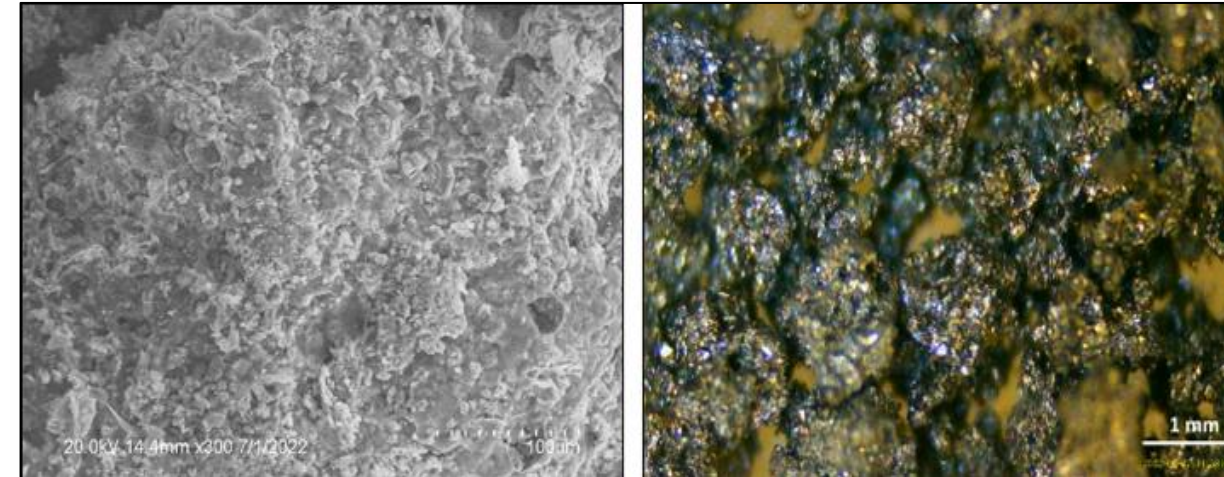


Figure: FESEM and Optical Microscopy of SS-650-Zn

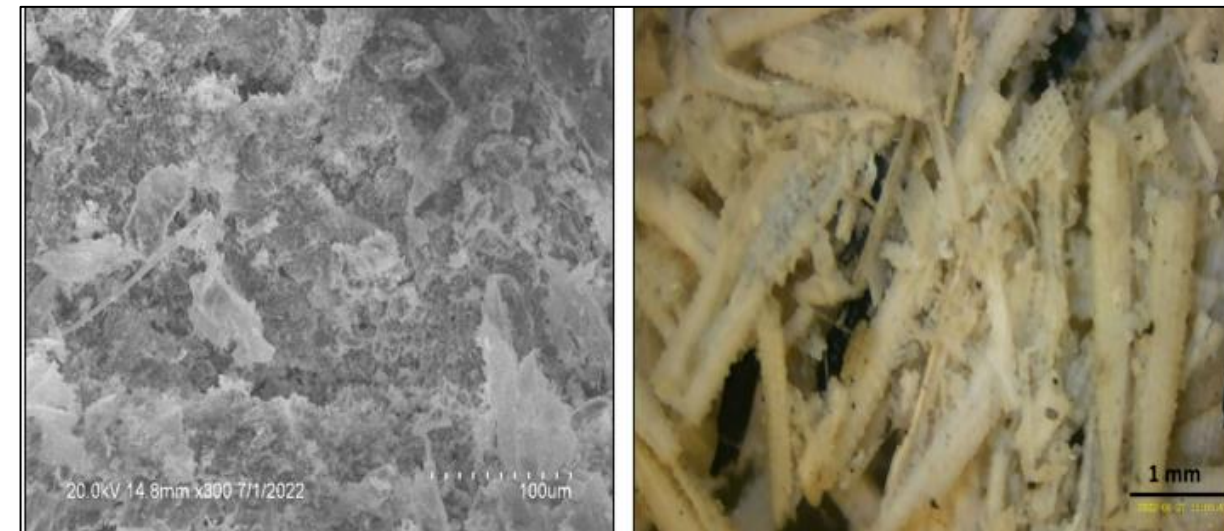
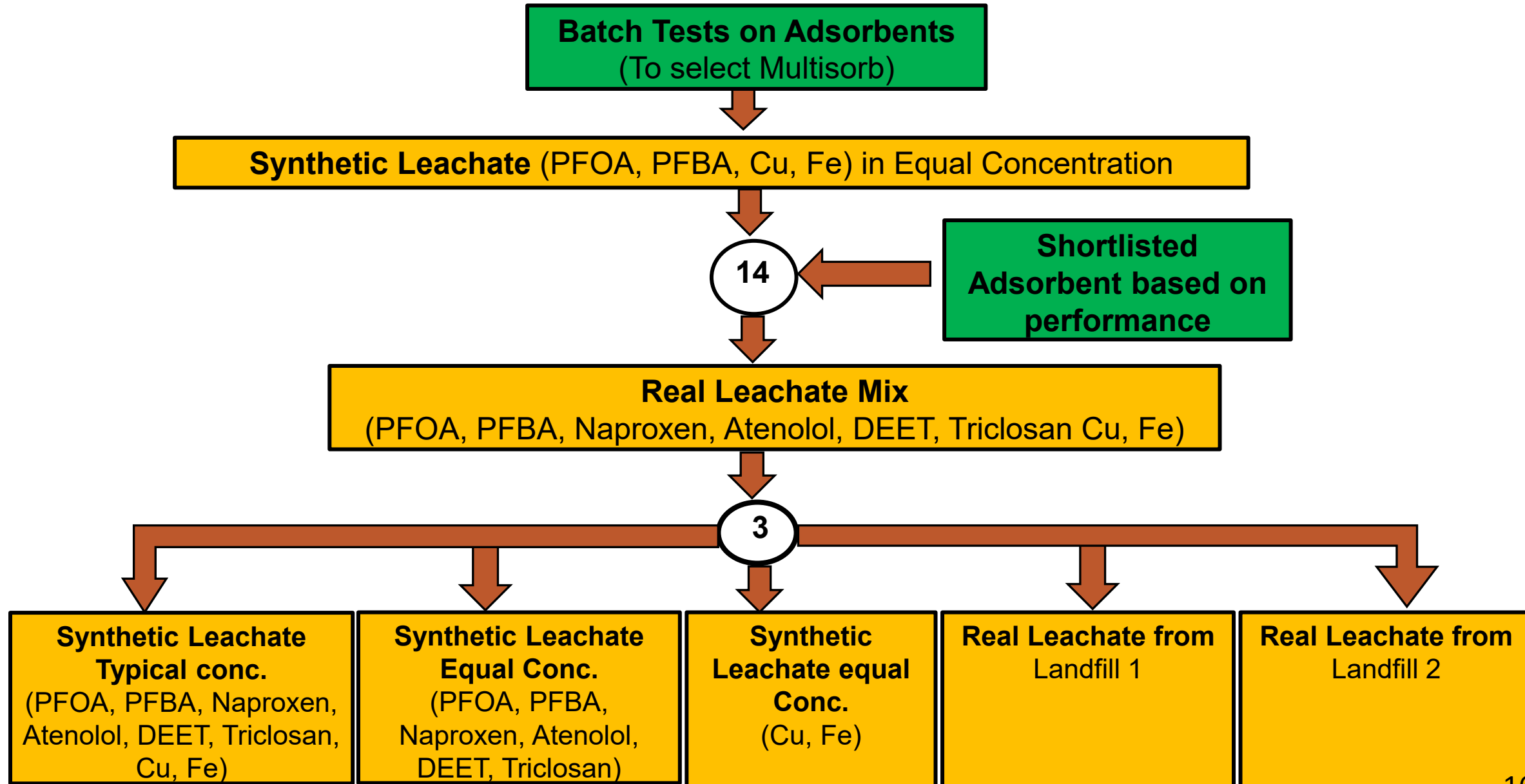


Figure: FESEM and Optical Microscopy of Cont. 2: RHA

# Batch Tests to select Multisorb



# Development of Multisorb from Synthetic Leachate

Table: Shortlisting adsorbent candidate for Multisorb from Synthetic Leachate

Adsorbent Sample	PFAS+Heavy Metal Batch (Synthetic: Same above maximum conc.) Adsorbed Conc. (ppb)			
	Cu	Fe	PFBA	PFOA
Rice Husk (RH)-500-Zn	316	-210	24,748	2853
Rice Husk (RH)-800-Zn	225	-519	23,763	3144
Rice Husk Ash (RHA)-650	416	154	2541	231
Rice Husk Ash (RHA)-800	306	153	1903	117
Rice Husk Ash (RHA)-650-Zn	462	155	3071	148
Rice Husk Ash (RHA)-800-Zn	308	154	6338	585
Sewage Sludge (SS)-650	675	160	1158	215
Sewage Sludge (SS)-500-Zn	657	149	21,047	1772
Sewage Sludge (SS)-650-Zn	671	154	23,028	1413
Sewage Sludge (SS)-800-Zn	561	108	25,531	2488
Sewage Sludge Char (SSC)-500	627	149	109	353
Sewage Sludge Char (SSC)-650	674	150	-339	444
Control: 2: RHA	421	149	1479	655
Control: 4: SSC	679	160	696	457
Control_4_SSC_(R)	672	134	-3912	-794
Control: 5: CAC	704	159	25,199	2104
Control_5_CAC_(R)	631	129	26,502	1417
<b>Avg. of commercial activated carbons</b>	<b>667</b>	<b>144</b>	<b>25,850</b>	<b>1760</b>
<b>Total Adsorbents &gt;CAC</b>	<b>For Heavy Metal and PFAS from Leachate</b>			

# Development of Multisorb from Real Leachate

Table: Adsorption of compounds from real leachate

Adsorbent Sample	Pollutant Adsorbed amount (ppb)		
	DEET	PFOA	Fe
RH-500-Zn	5.69	0.13	179
RH-800-Zn	3.95	0.01	-267
RHA-650	-0.98	0.03	-636
RHA-800	-2.73	0.05	-558
RHA-650-Zn	-4.33	0.06	449
RHA-800-Zn	-5.35	0.05	-433
SS-650	-7.37	-0.06	-3338
SS-500-Zn	-4.57	0.11	767
SS-650-Zn	-2.26	0.13	572
SS-800-Zn	-5.94	0.00	-523
SSC-500	9.03	-0.04	598
SSC-650	9.03	-0.06	-47
Cont: 2- RHA	3.55	-0.05	-454
Cont: 4-SSC	9.03	-0.10	328
Cont: 5-CAC-L	9.03	0.14	493
Cont:6-CAC (2)-L	7.13	0.10	235
<b>Average of CAC</b>	<b>8.08</b>	<b>0.12</b>	<b>364</b>

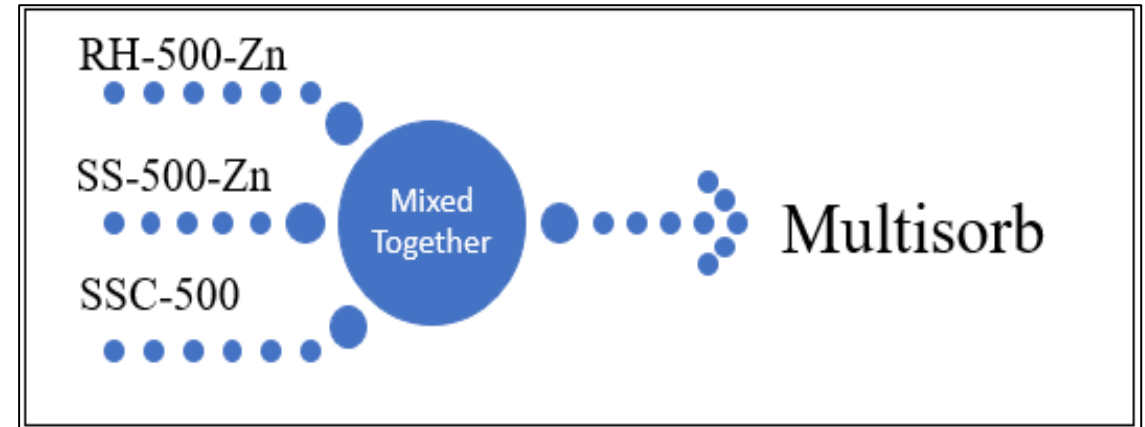


Figure: Multisorb Candidates

# Adsorption by Selected Multisorb

Table: Adsorption of PFAS, PPCP and Heavy Metal from Real Leachate by Multisorb

Real Leachate samples								
Detail	PFAS Adsorbed conc. (ppb)		PPCP Adsorbed conc. (ppb)				Heavy Metals (ppb)	
	PFOA	PFBA	Naproxen	Atenolol	DEET	Triclosan	Cu	Fe
<b>Leachate #1</b>								
Multisorb Avg.	0.155	NA	NA	NA	2.45	NA	1.9	375
Commercial Avg.	0.205	NA	NA	NA	10.75	NA	10.2	-145
Ratio of Multisorb Avg. to CAC Avg.	76%				23%		19%	>100% <sup>+</sup> +
Mass of Multisorb needed to adsorb = to CAC	1.3xCAC				4.3xCAC		5.3xCAC	>CAC
<b>Leachate #2</b>								
Multisorb Avg.	0.09	NA	NA	NA	NA	NA	4.5	>39 <sup>+</sup>
Commercial Avg.	0.335	NA	NA	NA	NA	NA	5.54	-3.5
Ratio of Multisorb Avg. to CAC Avg.	27%						81%	>122% <sup>+</sup> +
Mass of Multisorb needed to adsorb = to CAC	3.7xCAC						1.2xCAC	>CAC

# Morphology of Multisorb Candidates

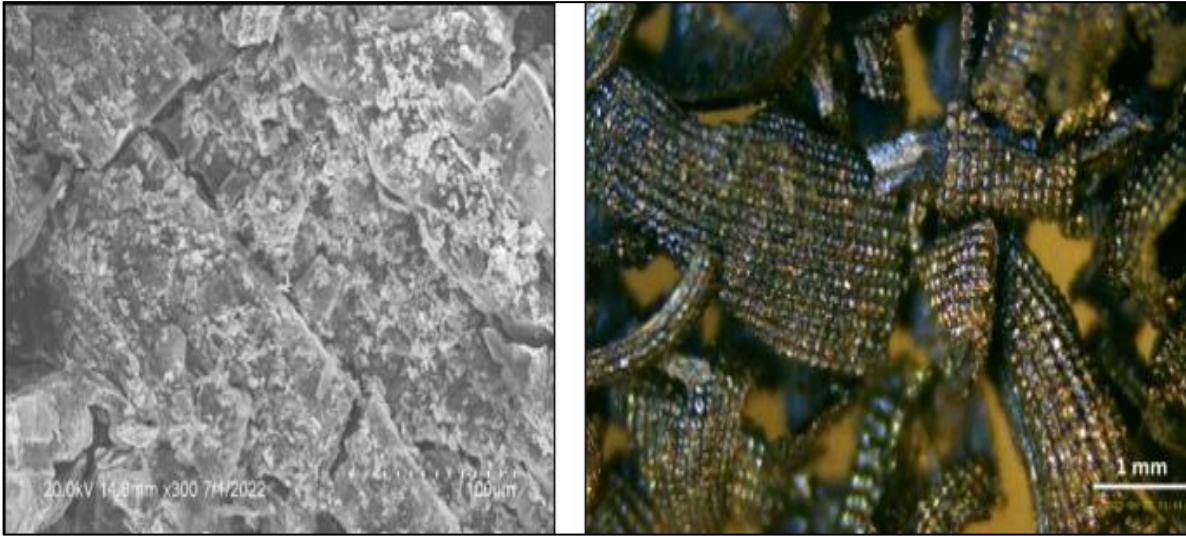


Figure: FESEM and Optical Microscopy of RH-500-Zn

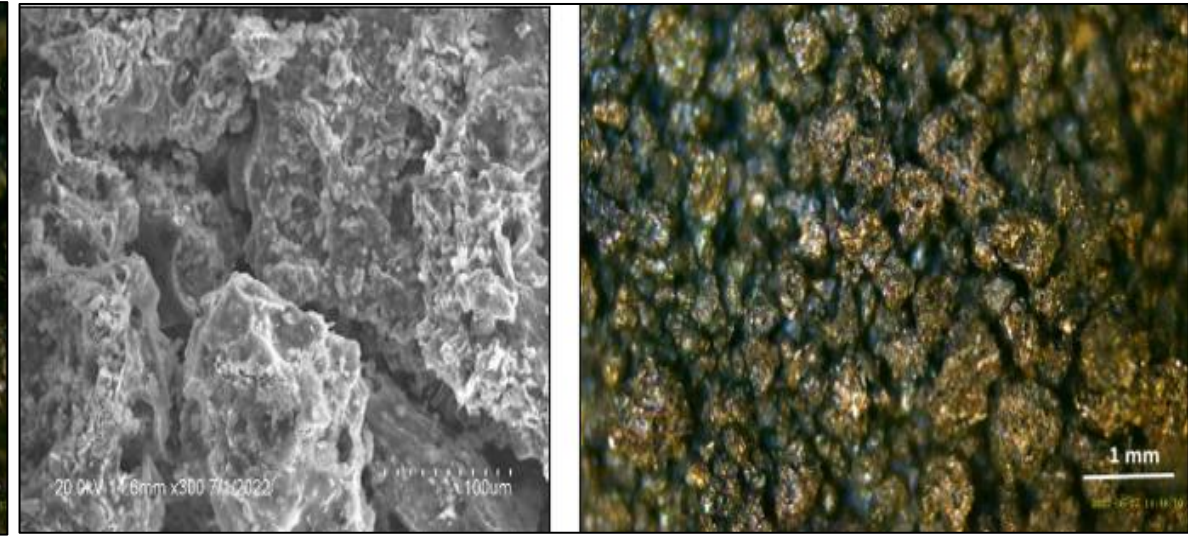


Figure: FESEM and Optical Microscopy of SS-500-Zn

- ✓ RH-500-Zn is rod shaped, whereas SS-500-Zn and SSC-500 are spherical
- ✓ Highly porous and Rough surface
- ✓ Surface area ranges from 31.9 to 634.29 m<sup>2</sup>/g
- ✓ Mainly Mesoporous (>2 nm to <50 nm)
- ✓ Dominated by C, N, O, Si, Zn, P, S, Mg, Cl

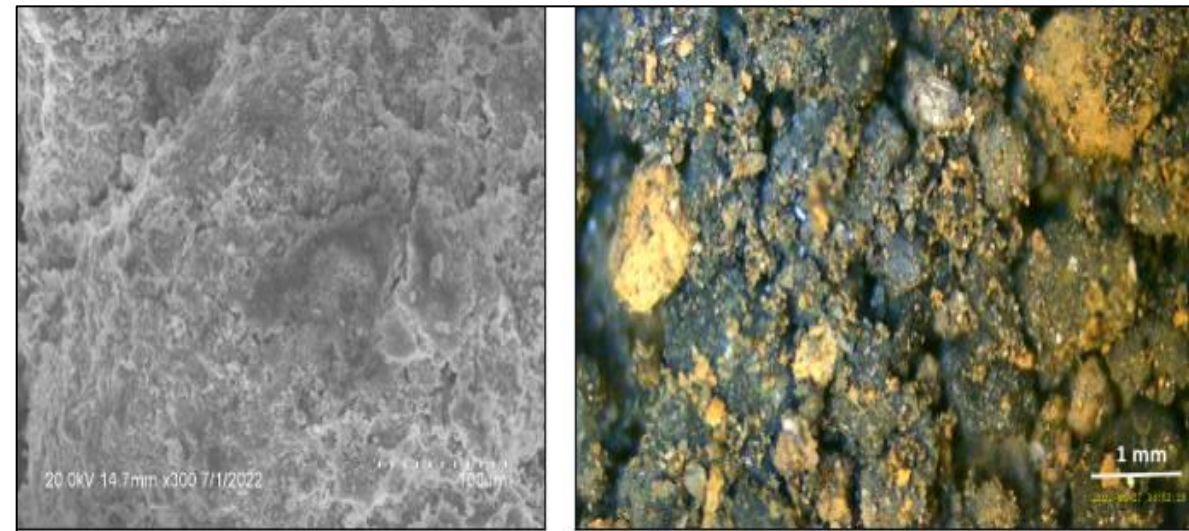


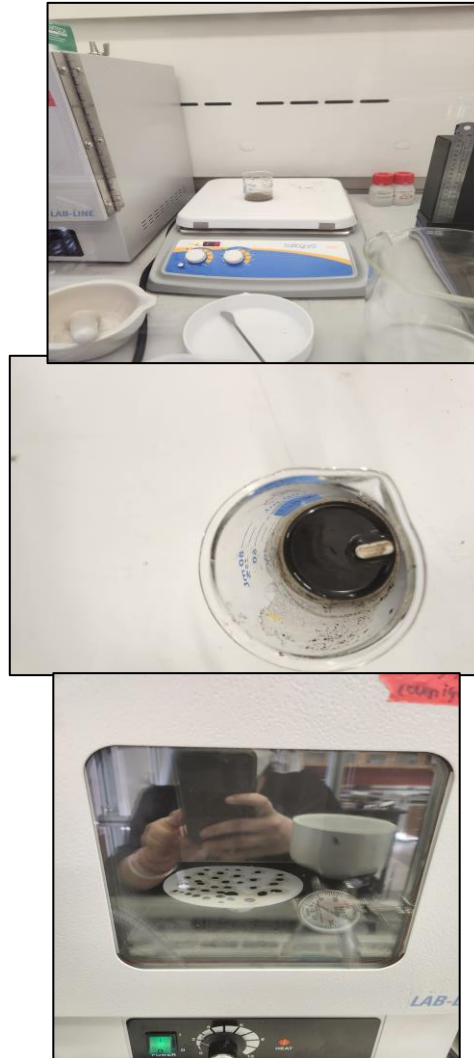
Figure: FESEM and Optical Microscopy of SSC-500

# Granular Activated Carbon Formation

Trial 1 (Binder+Molasses)



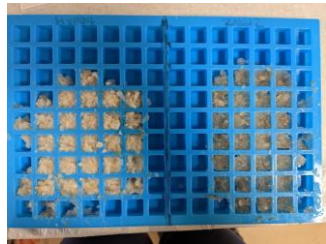
Trial 2 (Binder only following literature of Saeidi and Lotfollahi, 2015)



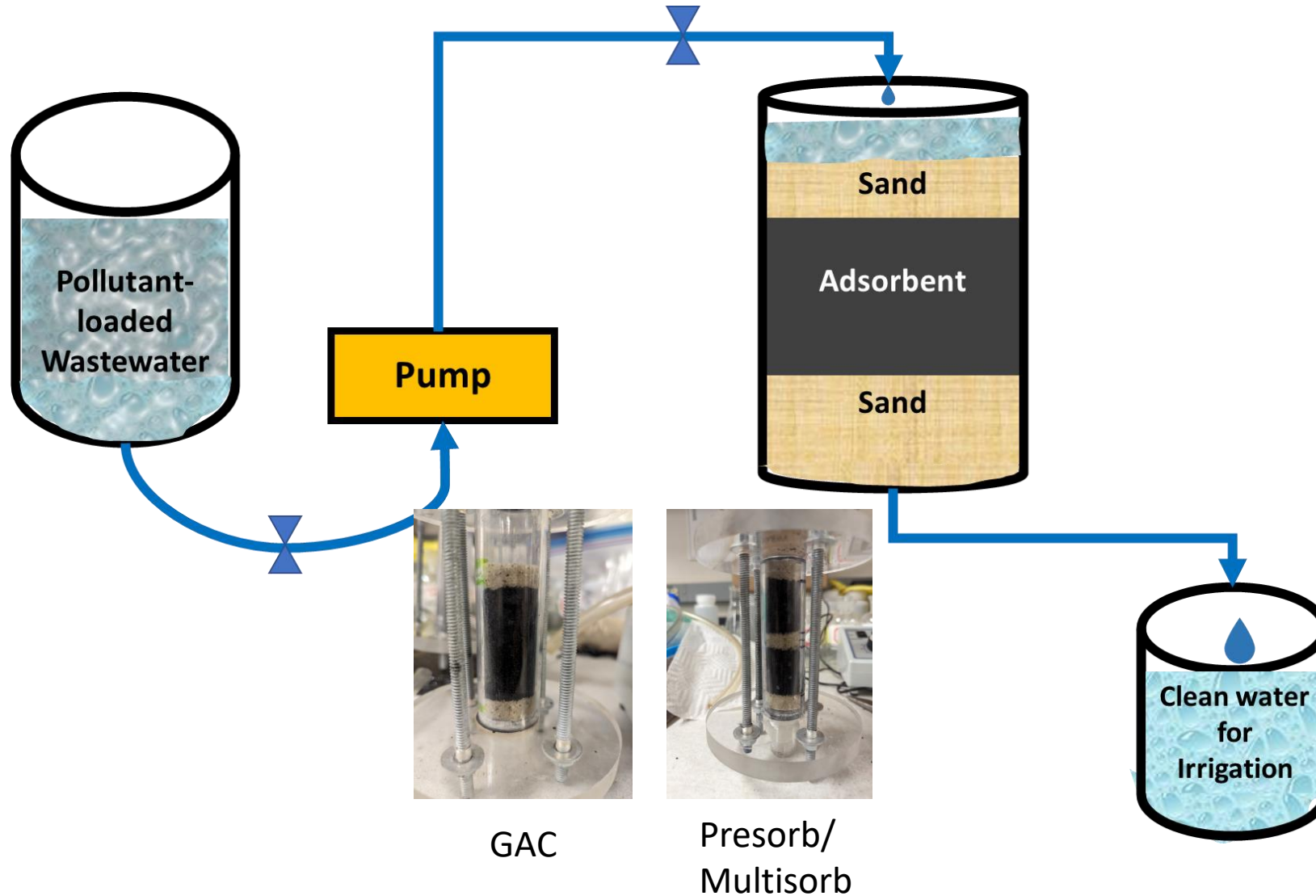
Trial 3 (Binder+Molasses)



# Granular Activated Carbon Formation



# Column Set-up

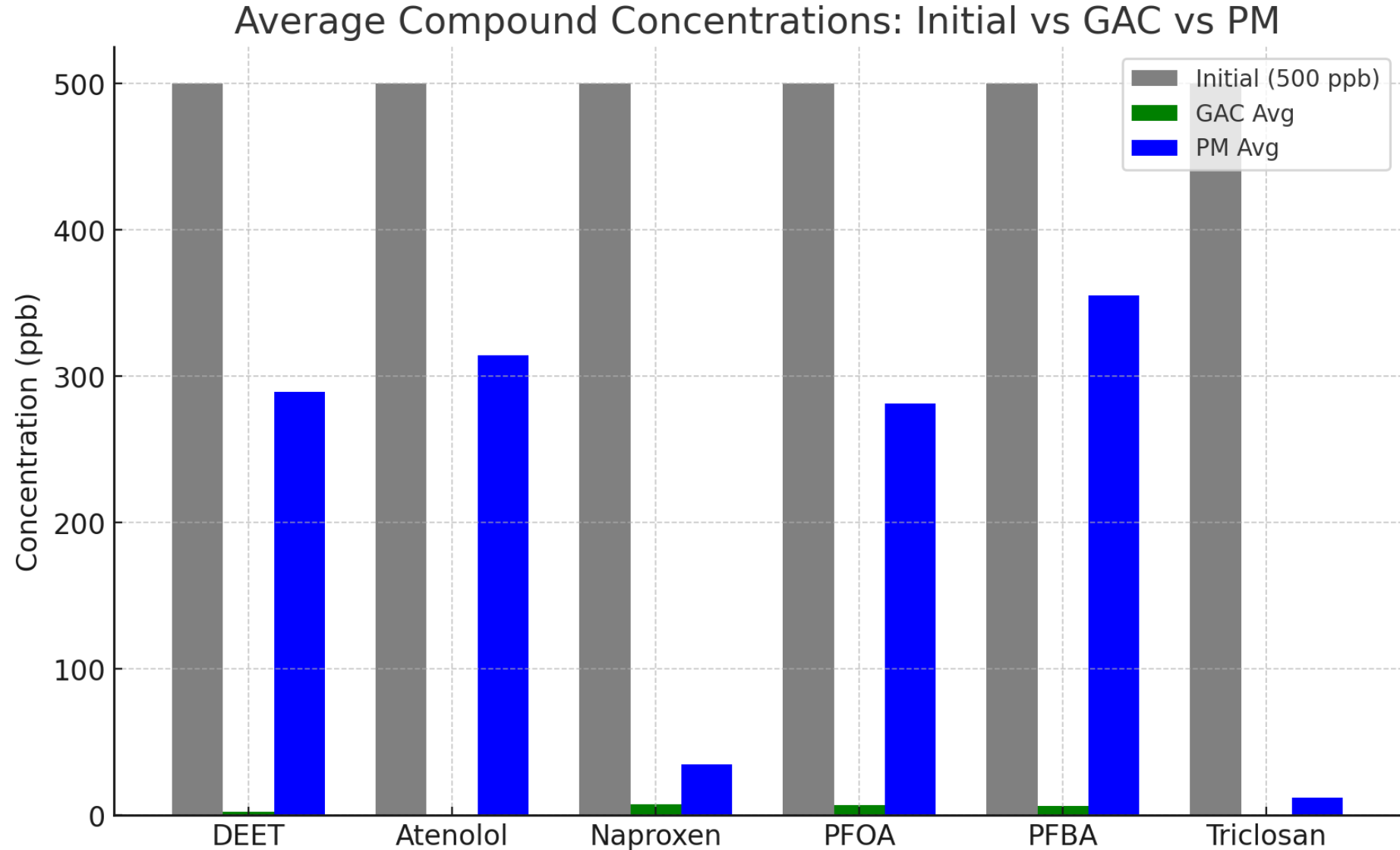


# Wastewater result

		Compound Concentration (ppb)					
	Sample	DEET	Atenolol	Naproxen	PFOA	PFBA	Triclosan
	GAC1	6.022	4.416	7.618	9.371	8.983	-80.925
	GAC2	1.406	-1.593	7.402	7.933	8.378	-74.569
	GAC3	3.693	-2.077	7.454	7.785	7.169	-99.244
	GAC4	1.203	-3.369	7.293	6.096	5.288	-54.36
	GAC5	1.062	-3.434	7.278	6.082	4.941	-88.627
	GAC6	0.923	-3.622	7.273	5.934	4.268	-108.511
	PM1	287.556	317.578	36.178	308.343	375.99	-4.508
	PM2	277.347	313.124	33.02	272.688	347.662	-40.321
	PM3	299.715	320.719	34.432	281.118	358.636	60.024
	PM4	300.279	311.501	34.632	277.8	347.447	2.064
	PM5	273.019	309.727	35.842	269.385	346.815	15.73
	PM6	296.818	312.531	35.579	280.518	353.776	39.457
	<b>Detection Limit</b>	<b>17.049</b>	<b>13.772</b>	<b>18.454</b>	<b>16.233</b>	<b>16.595</b>	<b>61.753</b>
	<b>Initial Concentration</b>	<b>500 ppb</b>					
	*GAC	Granulated Activated Carbon					
	*PM	PreSorb/Multisorb					

# Granular Activated Carbon (GAC) vs PreSorb/Multisorb (PM) treatment performance

## Treatment Performance Summary



# Cost Comparison with Commercial Activated Carbon

- A detailed cost comparison was done for waste-made adsorbents to compare with the commercial activated carbons cost.
- All the stages like raw material acquisition, manufacturing, use-reuse-maintenance, and end of life were considered.
- Neither type of adsorbent is assumed to be regenerated; regeneration would lower costs per lb of pollutant removed.

# Cost Comparison with Commercial Activated Carbon

Table: Costs for processing waste-made and commercial activated carbons

Item		Cost
<b>Processing of Rice Husk</b>		
Rice husk collection		\$14,930/year
Muffle furnace	Annualized capital cost	\$1,613/year
	Electricity*	\$2,393/year
Two tube furnaces	Annualized capital cost	\$7,106/year
	Electricity	\$6,790/year
<b>Processing of Sewage Sludge</b>		
Sewage sludge collection		\$0.00/year
Muffle furnace	Annualized capital cost	\$1,613/year
	Electricity	\$2,393/year
Five tube furnaces	Annualized capital cost	\$17,764/year
	Electricity	\$33,952/year
Disposal for rice husk and sewage sludge		\$478
Incineration of both rice husk and sewage sludge		\$53
Total for Waste-made Activated Carbon (14,346 lbs/year)		<b>\$443,327/year</b>
Total for Waste-made Activated Carbon		<b>\$21/lb</b>
<b>For Commercial Activated Carbon</b>		
The same amount of rice husk and sewage sludge processing cost		\$1,341,085
Average Disposal Cost		\$478
Average Incineration Cost		\$53
Total for Commercial Activated Carbon (14,346 lbs/year)		<b>\$1,341,616/year</b>
Total for Commercial Activated Carbon		<b>\$63/lb</b>

# Cost Comparison with Commercial Activated Carbon

- Multisorb costs about 33% of CAC, which is near the higher end for the typical range for waste-made sorbents (5-16% of commercial AC, Devi and Saroha, 2017, Ahmad *et al.* 2012).
  - Use of Presorb prior to Multisorb would double this cost to 66%.

# Conclusions

## Findings Related to Presorb

- The best performer chosen for Presorb were:

**Rice Husk- chemically activated with  $\text{H}_3\text{PO}_4$  at  $800^\circ\text{C}$**

- **BET** (Brunauer-Emmett-Teller) surface area analysis showed Presorb adsorbents dominated by **mesopores**, which was expected in terms of the size of NOM.
- In real wastewater, adsorption of NOM (represented by fulvic acid) by waste-made Presorb equaled or exceeded that of CAC.

## Findings Related to Multisorb

- The best performers to form Multisorb were:

**Rice Husk-chemically activated with  $\text{ZnCl}_2$  at  $800^\circ\text{C}$**

- Highly effective in adsorbing **PFAS/PPCP**

# Conclusions

## Findings Related to Multisorb

- BET surface area analysis showed Multisorb adsorbents dominated by **mesopores**, which was expected in terms of the size of long-chain PFAS. Surface functional groups, as well as micropores, likely aided in adsorption of short-chain PFAS.
- Tests of Multisorb with real wastewater showed that it adsorbed like CAC. Adding a larger amount of Multisorb could make its performance equal to CAC. It would still be cost-effective because its cost is only 33% that of CAC.

# Conclusions

## General Findings

- ✓  $\text{ZnCl}_2$  proved to be a better activating agent than  $\text{KOH}$  and  $\text{H}_3\text{PO}_4$ , in terms of creating adsorbents with high potential for removal of NOM, PFAS, PPCP, and heavy metals.
- ✓ Waste-made adsorbents cost is 33% that of commercial activated carbon (assuming neither is regenerated).
- ✓ Treated wastewater effluents did not contain any of the PFAS or PPCP target chemicals.

# Conclusions

## General Findings

- ✓ **GAC consistently outperforms PM**, achieving ~98–100% removal across all compounds.
- ✓ **PM is effective mainly for Naproxen and Triclosan** but underperforms for PFAS (PFOA, PFBA), DEET, and Atenolol.
- ✓ GAC is the superior treatment medium for emerging contaminants and PFAS. PM may only be suitable as a pre-treatment step, not a standalone solution.

# Recommendation for Future Research

## Recommendations for future work include:

1. Measure micropore volume and diameter to assess their role in adsorption.
2. Consider how PFAS issues can be dealt with if pollutant-loaded adsorbents are burned in an incinerator instead of direct disposal in a hazardous waste landfill.
3. Conduct life cycle environmental impact assessment of waste-made adsorbents vs. traditional

# Acknowledgment

This work is funded by a grant from the US Dept. of Agriculture National Institute of Food and Agriculture.



## Granular Activated Carbon (GAC) vs PreSorb/Multisorb (PM) treatment performance Treatment Performance Summary

Treatment Performance Summary					
Compound	Initial (ppb)	GAC Final (ppb)	% Removal (GAC)	PM Final (ppb)	% Removal (PM)
DEET	500	0.9–6.0	~99%	273–300	~40–45%
Atenolol	500	~0	~100%	309–320	~38–40%
Naproxen	500	~7.3	~98.5%	33–36	~93%
PFOA	500	6–9	~98%	269–308	~40–45%
PFBA	500	4–9	~98%	346–376	~25–30%
Triclosan	500	Negative values	~100%	~0–60	~90–100%