Assessing the potential of Activated Bauxite Residue (ABR) to remove PFAS in the water column

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Presentation Outline

(1) Introduction

- PFAS Overview
- Novel treatment methods to PFAS
- Fate of ABR

(2) Methodology

- Experimental design

(3) Result & Discussion

(4) Conclusion & Recommendations

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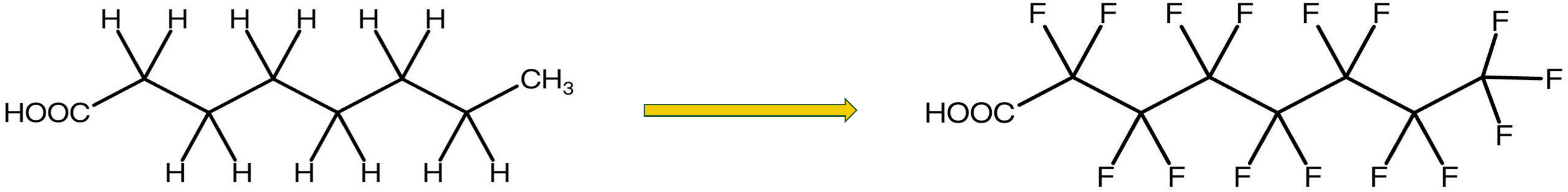
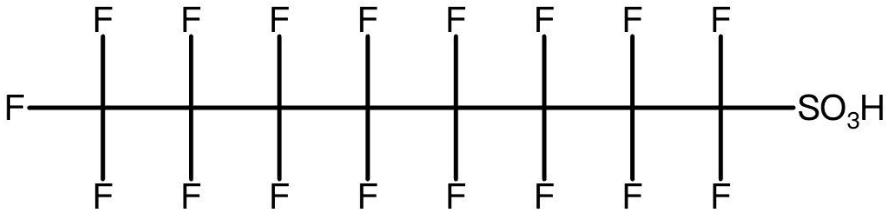
PFAS: perfluoroalkyl and polyfluoroalkyl substances



A group of synthetic organic compounds characterized by **at least one H substituted by F** and the presence of **other functional groups**.

PFSAs: perfluoroalkyl **sulfonic** acids

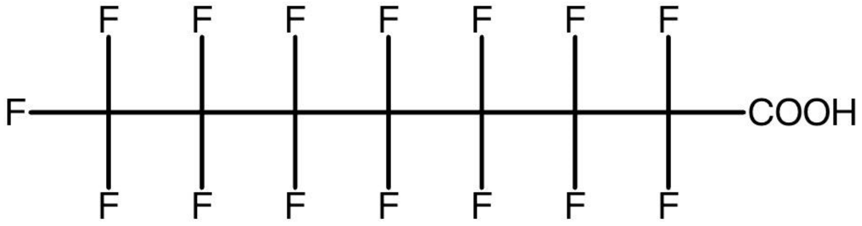
- long-chain PFSAs: **≥6** carbon



PFOS: $C_8F_{17}SO_3H$

PFCAs: perfluoroalkyl **carboxylic** acids

- long-chain PFCAs: **≥8** carbon



PFOA: $C_7F_{15}CO_2H$

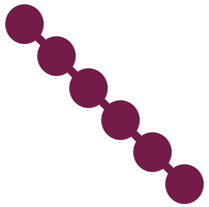
Background about PFAS

1 **Special properties**

2 Where does PFAS come from?

3 Detected everywhere

4 Potential risks



−COOH
$-SO_3H$
−O−
$-PO(OR)_2$
$-NH_2$

carbon chain

functional groups

Amphiphilicity

C−F	485 KJ/mol
C−O	358 KJ/mol
C−C	348 KJ/mol

Stability

Persistent, mobile, toxic substances (PMTs)

PFOS > 41 years

PFOA > 92 years

Long half-life

https://tipa-corp.com/blog/compostable-vs-biodegradable/

Poorly biodegradable

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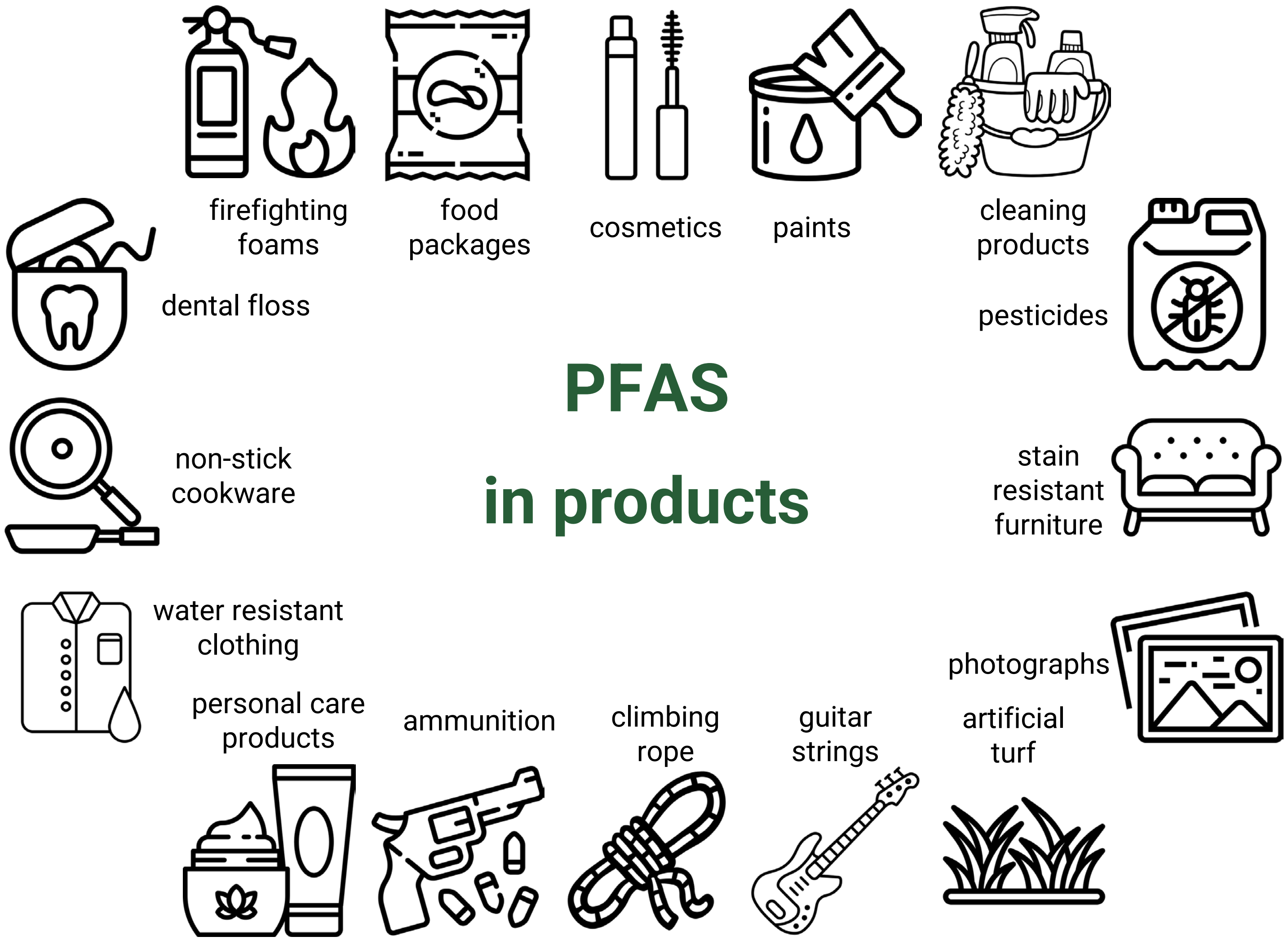

PFAS in products

firefighting foams

food packages

cosmetics

paints

cleaning products

dental floss

pesticides

non-stick cookware

stain resistant furniture

water resistant clothing

photographs

personal care products

ammunition

climbing rope

guitar strings

artificial turf

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https://www.pexels.com/photo/eye-level-photo-of-cultivated-land-1000057/

soil


https://www.pexels.com/photo/aerial-view-of-cloudscape-314726/

air

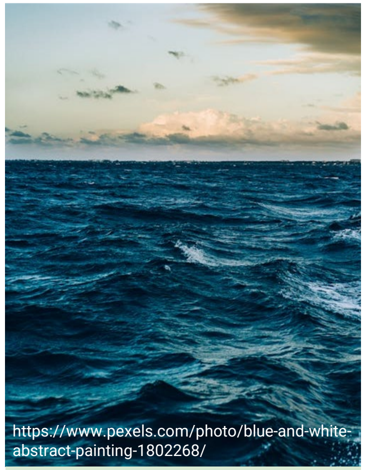

https://www.pexels.com/photo/lichen-and-green-sediment-on-the-rock-18771984/

sediments


https://www.pexels.com/photo/man-on-white-horse-next-to-dog-on-grassy-field-162520/

organisms

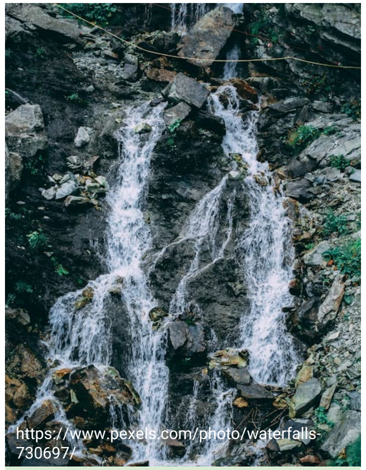
Particularly in various aquatic matrices


https://www.pexels.com/photo/blue-and-white-abstract-painting-1802268/

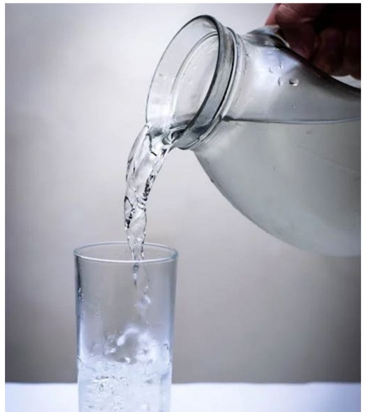
Ocean
0.195 – 4.925 ng/L


https://www.istockphoto.com/photo/mexican-cenote-sinkhole-gm178370792-20525069

Groundwater
5.3 – 615 ng/L


https://www.pexels.com/photo/waterfalls-730697/

Fresh water
0.4 – 207.59 ng/L


https://www.pexels.com/photo/clear-glass-pitcher-pouring-water-on-clear-drinking-glass-3500006/

Drinking water
average of 6.4 ng/L

Removal efficiency of PFAS in WWTPs

PFAS are **highly recalcitrant** to conventional wastewater treatment processes.

PFAS compounds	Influent conc (ng/L)	Effluent conc (ng/L)	Removal efficiency (%)	Country	Reference
∑13 PFAS	125.69	174.11	−39	Canada	(Guerra et al., 2014)
∑9 PFAS	55	94	−71	Australia	(Gallen et al., 2018)
∑12 PFAS	20.14	23.15	−15	Sweden	(Filipovic et al., 2015)
∑16 PFAS	57.95	57.93	0	China	(Zhang et al., 2013)
∑12 PFAS	4410	6640	−51	USA	(Houtz et al., 2018)
∑10 PFAS	760.2	943.45	−24	Thailand	(Kunacheva et al., 2011)
∑20 PFAS	10−15	14−24	−60~−40	Jordan	(Shigei et al., 2020)
∑21 PFAS	49.8	214.2	−330	Spain	(Lorenzo et al., 2019)
∑18	121.95	116.79	4	Greece	(Arvaniti et al., 2012)

Existing wastewater treatment processes are insufficient in removing PFAS and may even introduce more PFAS into the water.

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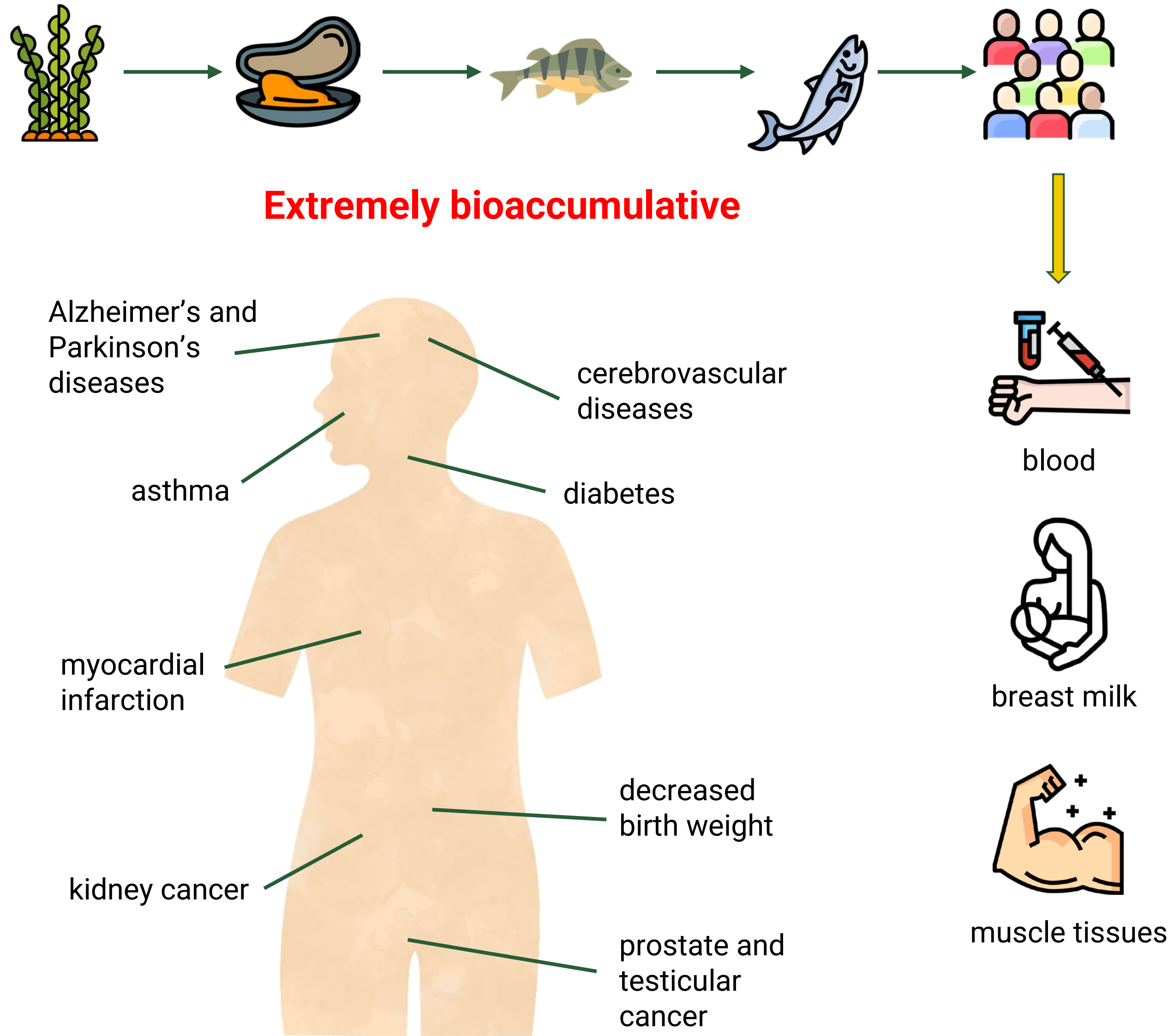


Extremely bioaccumulative

Alzheimer's and Parkinson's diseases

cerebrovascular diseases

asthma

diabetes

myocardial infarction

decreased birth weight

kidney cancer

prostate and testicular cancer

blood

breast milk

muscle tissues

Regulations on PFAS in drinking water

- 1987, the **Montreal Protocol** defined essential uses of fluorine, related to health, safety and the functioning of our society..
- 2019, the **Stockholm Convention** on Persistent Organic Pollutants added **PFOA and PFOS** to the limited/forbidden list.

Health-based guidance for PFAS concentrations in drinking water in Canada

PFAS	Abbreviation	Screen value (ng/L)
Perfluorobutanoate	PFBA	30
Perfluorobutane sulfonate	PFBS	15
Perfluorohexanesulfonate	PFHxS	0.6
Perfluoropentanoate	PFPeA	0.2
Perfluorohexanoate	PFHxA	0.2
Perfluoroheptanoate	PFHpA	0.2
Perfluorononanoate	PFNA	0.02
Fluorotelomer sulfonate	6:2 FTS	0.2
Fluorotelomer sulfonate	8:2 FTS	0.2

Europe: 4.4 ng/kg weekly dose of ∑PFOA, PFOS, PFNA, PFHxS, 2020, EFSA

Germany: 3 g/L for lifelong PFOA and PFOS exposure

300 ng/L for PFOA and PFOS in drinking water

Italy: PFOS ≤30 ng/L, PFOA ≤500 ng/L, and other PFAS ≤500 ng/L in drinking water

Australia:

the highest daily intake of 20 ng/person for ∑PFOS and PFHxS

160 ng/person for PFOA

70 ng/L for ∑PFOS, PFHxS and

650 ng/L for PFOA in drinking water

Guideline	Advisory Level (ng/L)		Reference Dose (ng/kg-day)	
	PFOA	PFOS	PFOA	PFOS
USEPA, 2016	70	70	20	20

Issues associated with short-chain compounds

In Canada, short-chain PFAS are the most prevalent species.

In source and drinking water, PFBA showed the highest concentration, 2.64 ng/L and 2.59 ng/L.

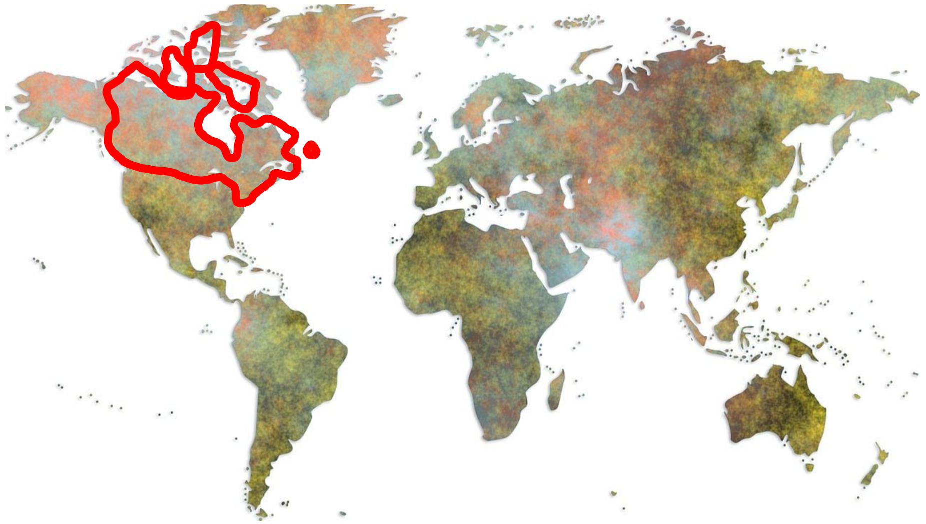
In WWTPs, short-chain PFAS are up to 73% of ∑42PFAS in both influent and effluent.

Persistence (P)	**Similar persistence** to the long-chain ones.
Bioaccumulation potential (B)	**Less bioaccumulative** than long-chain ones in animals and humans, but **higher uptake** into the leaves, stems, and fruit of plants
(eco)toxicity (T)	**A less toxic trend** except for PFHxA (a higher ecotoxicity than PFOA to aquatic species)
Long-range transport potential (LRTP)	**More mobile** due to their higher solubility in water and weaker sorption to solids

Regulations on PFAS in drinking water

Health-based guidance for PFAS concentrations in drinking water in Canada

	PFAS	Abbreviation	Screen value (ng/L)
3C	Perfluorobutanoate	PFBA	30
4C	Perfluorobutane sulfonate	PFBS	15
6C	Perfluorohexanesulfonate	PFHxS	0.6
4C	Perfluoropentanoate	PFPeA	0.2
5C	Perfluorohexanoate	PFHxA	0.2
6C	Perfluoroheptanoate	PFHpA	0.2
8C	Perfluorononanoate	PFNA	0.02
8C	Fluorotelomer sulfonate	6:2 FTS	0.2
10C	Fluorotelomer sulfonate	8:2 FTS	0.2



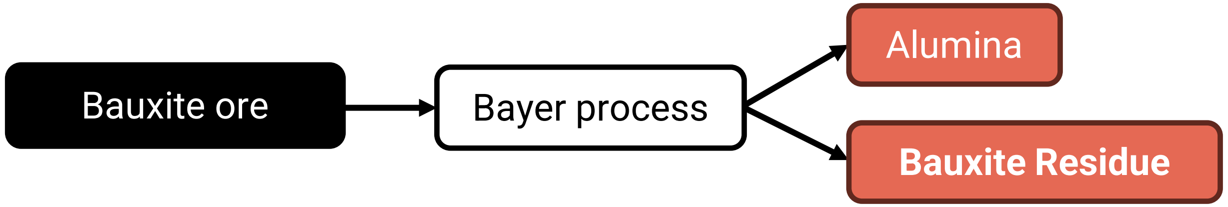
Adsorption as a treatment option

Adsorption

- Flexible, highly efficient, easy to operate, stable to noxious substances, environment sustainable, low cost;
- Can be derived from different sources;
- Produce no secondary pollution;
- Increase recovery and reuse.

Activated carbon	Inefficient for short-chain PFAS
Metal-organic frame	high cost of production and regeneration
Biochar	high time-consuming
Ion exchange resin	frequent replacement

What is bauxite residue?


Bauxite ore

Bayer process

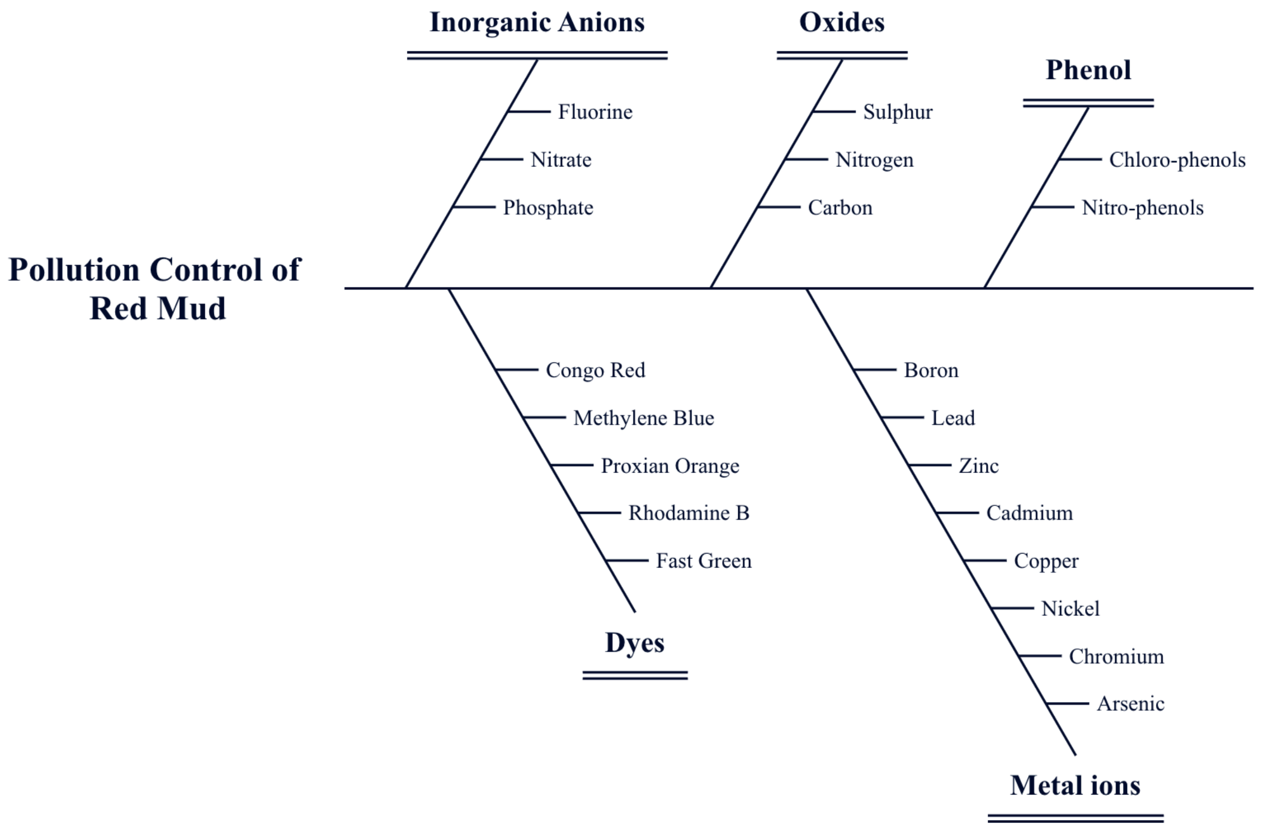
Alumina

Bauxite Residue

Composition	Weight%
Fe_2O_3	30–62
Al_2O_3	10–23
SiO_2	3–50
TiO_2	Trace–25
Na_2O	2–10
CaO	0.5–8

- High alkalinity
- Substantial generation and storage
- Leaching and contamination risks

ABR in wastewater treatment



Pollution Control of Red Mud

Inorganic Anions
- Fluorine
- Nitrate
- Phosphate

Oxides
- Sulphur
- Nitrogen
- Carbon

Phenol
- Chloro-phenols
- Nitro-phenols

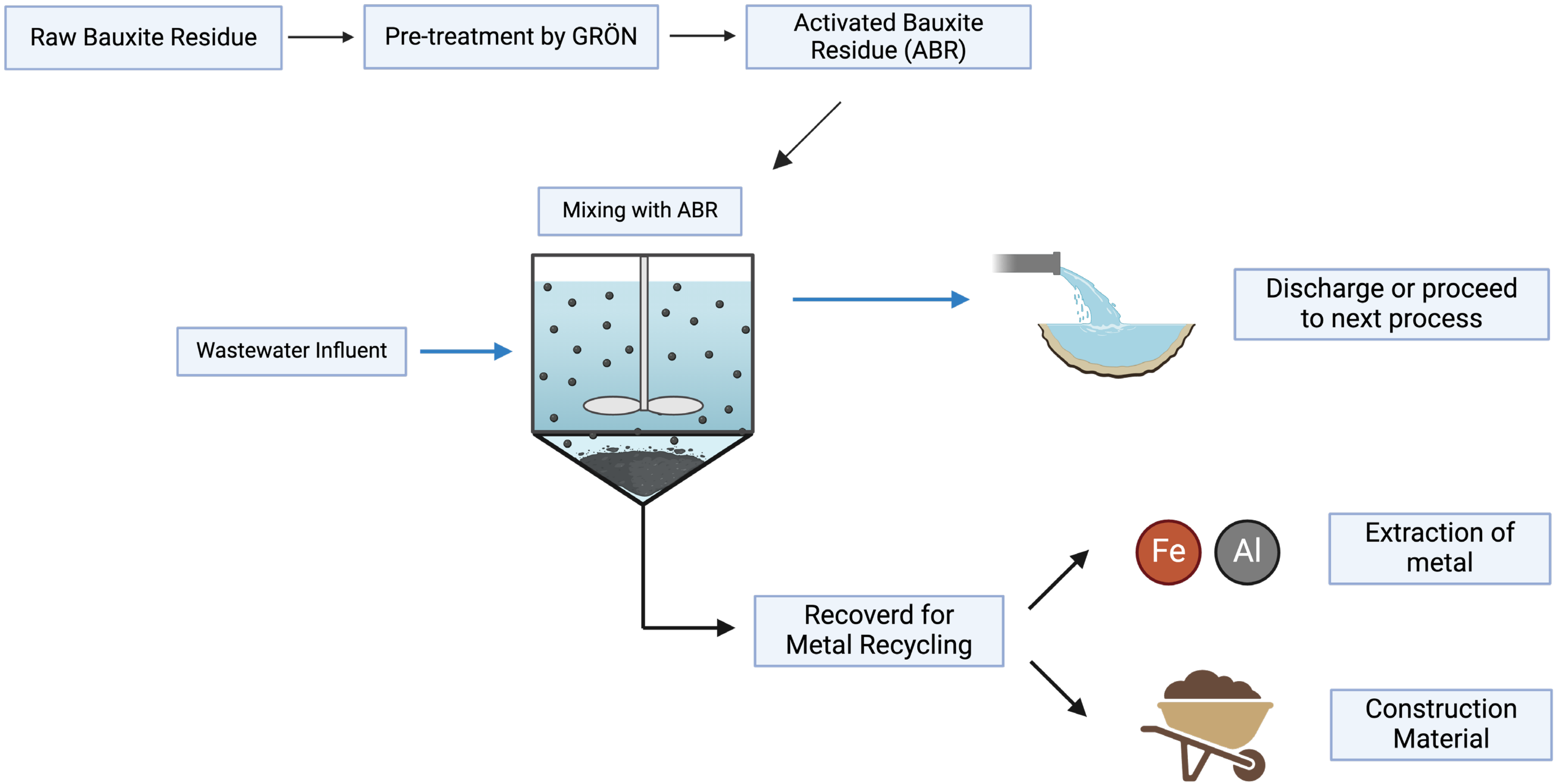
Dyes
- Congo Red
- Methylene Blue
- Proxian Orange
- Rhodamine B
- Fast Green

Metal ions
- Boron
- Lead
- Zinc
- Cadmium
- Copper
- Nickel
- Chromium
- Arsenic

Raw bauxite residue

Activated bauxite residue

ABR residual management



Raw Bauxite Residue

Pre-treatment by GRÖN

Activated Bauxite Residue (ABR)

Mixing with ABR

Wastewater Influent

Discharge or proceed to next process

Recoverd for Metal Recycling

Extraction of metal

Construction Material

Research Objectives

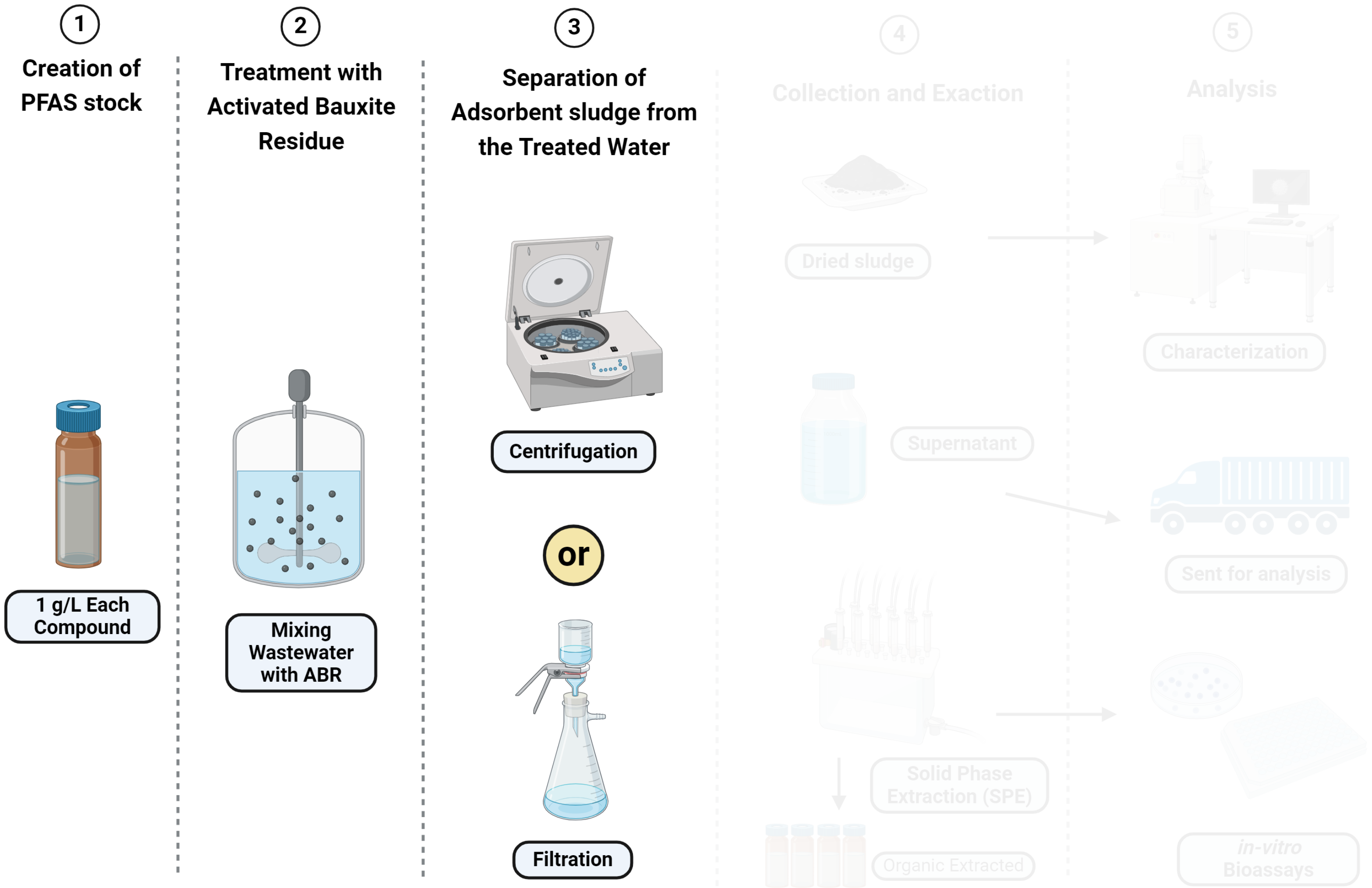
Evaluate the potential of the **activated bauxite residue (ABR) as an adsorbent material** for removing PFAS from the water column.

1. **Characterize "virgin" and "spent" ABR (i.e., before and after applications)**

2. **Determine adsorption kinetics and isotherm** for the removal of different PFAS substances

3. **Assess the removal efficiency** of PFAS through adsorption by ABR and **compare** with powdered activated carbon (PAC).

General experimental design



① Creation of PFAS stock

1 g/L Each Compound

② Treatment with Activated Bauxite Residue

Mixing Wastewater with ABR

③ Separation of Adsorbent sludge from the Treated Water

Centrifugation

or

Filtration

④ Collection and Exaction

Dried sludge

Supernatant

Solid Phase Extraction (SPE)

Organic Extracted

⑤ Analysis

Characterization

Sent for analysis

in-vitro Bioassays

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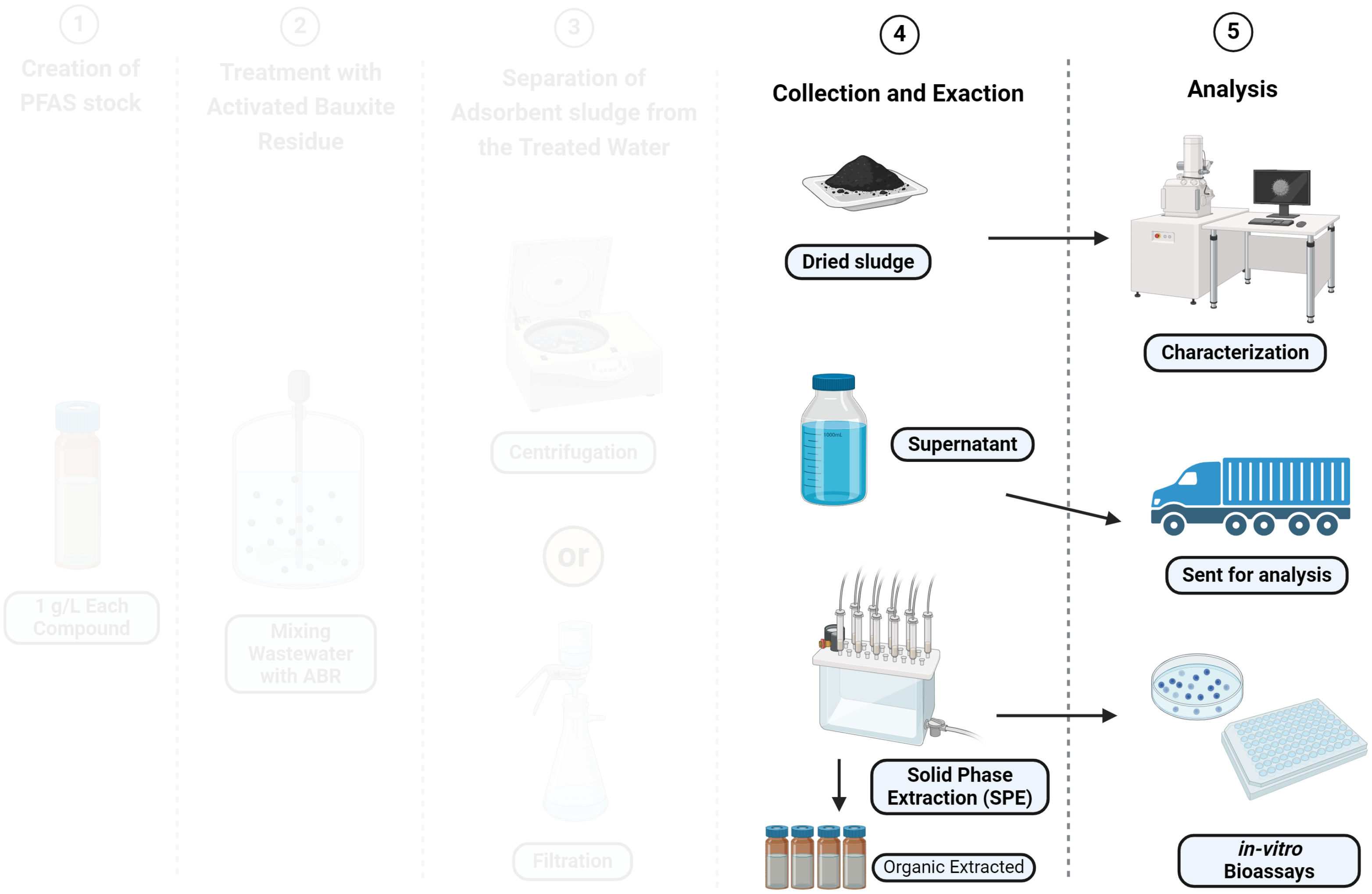
General experimental design



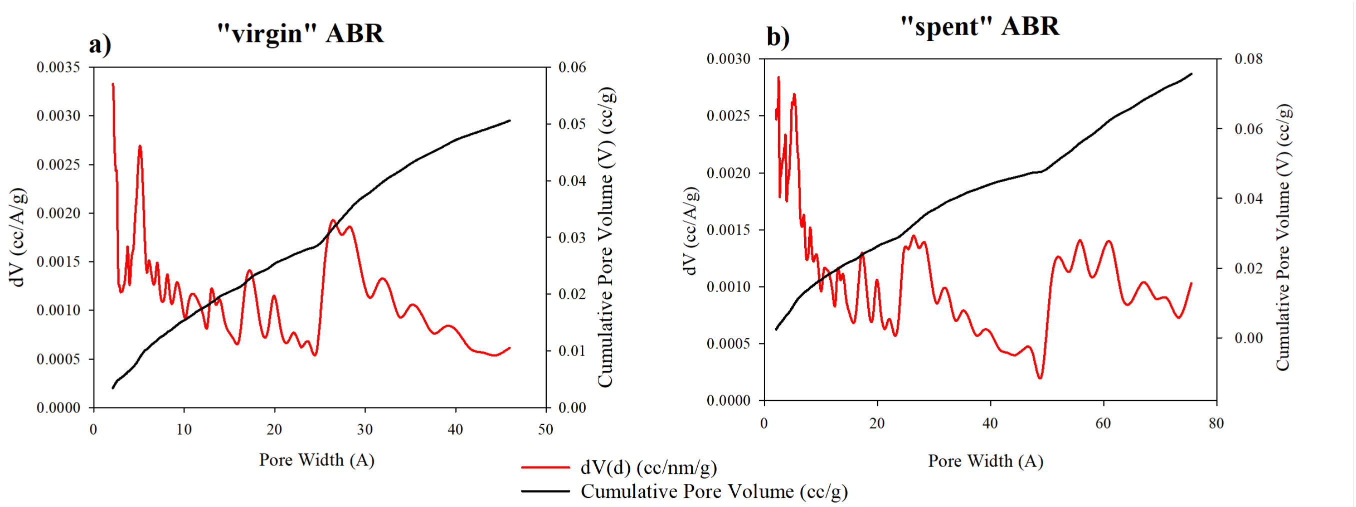
PFAS substances used

	Full name – Short (s) or Long chain (L)	Abb	Chemical Formula	MW (g/mol)
PFCA	Perfluorobutanoic – S	PFBA	$C_4HF_7O_2$	214.04
	Perfluoropentanoic – S	PFPeA	$C_5HF_9O_2$	264.05
	Perfluorohexanoic – S	PFHxA	C6HF11O2	314.05
	Perfluoroheptanoic – S	PFHpA	$C_7HF_{13}O_2$	364.06
	Perfluorooctanoic – L	PFOA	$C_8HF_{15}O_2$	414.07
	Perfluorononanoic – L	PFNA	$C_9HF_{17}O_2$	464.08
	Perfluorodecanoic – L	PFDA	$C_{10}HF_{19}O_2$	514.08
	Perfluoroundecanoic – L	PFUnA	$C_{11}HF_{21}O_2$	564.09
	Perfluorotetradecanoic – L	PFTEDA	$C_{14}HF_{27}O_2$	714.11
PFSA	Perfluorobutanesulfonic – S	PFBS	$C_4HF_9O_3S$	300.1
	6:2 Fluorotelomer Sulfonic – L	6:2 FTSA	$C_8H_5F_{13}O_3S$	428.16

Results — Surface area analysis

Sample	Surface area (m^2/g)	Total pore volume (mL/g)	Pore size diameter (nm)
”virgin” ABR	25.3	0.137	2–46
“spent” ABR	25.1	0.116	2–76

- Surface area and total pore volume did not change substantially.
- Pore sizes are heterogenous.
- **Mesopores dominated (2–50 nm).**



Mesopores can promote the adsorption capacity and removal efficiency of PFAS

- ✓ Access to adsorption sites is easier for long-chain PFAS.
- ✓ Larger PFAS molecules can easily get in and aggregate.

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Results — Surface area analysis

Type	Adsorbent	Surface area (m^2/g)	Total pore volume (mL/g)	Reference
Bauxite Residue	**ABR**	**25.3**	**0.137**	**This study**
	Bauxite residue A	7.96	0.0317	(Qi et al., 2018)
	Bauxite residue B	6.31	0.0318	
	10% Bauxite Residue + 10% Clinoptilolite or 10 wt% Bentonite	61.35–77.94	0.0388–0.0729	(Mohamed et al., 2021)
	Raw bauxite Residue	20	ND	(Mangrulkar et al., 2010)
Activated Carbon	GAC	975	0.52	(Stebel et al., 2019)
	PAC from GAC of Singi Chemical	1014	ND	(Son et al., 2022)
	4 types of activated carbons	444–985	0.2435–0.5066	(Mailler et al., 2016)
	GAC	895.5	ND	(Huggins et al., 2016)
	Raw Activated carbon	912	1.02	(Cheng et al., 2018)
	4 bituminous coal-based activated carbons	755–788	0.31–0.41	(Park et al., 2020)
Biochar	Granular biochar	152.3	ND	(Huggins et al., 2016)
	Maize Tassel	2.52	ND	(Omo-Okoro et al., 2020)
Metal-organic frame	Fe-BTC	1051	ND	(Yang et al., 2020)
	MIL-100-Fe	1237		
	MIL-101-Fe	1811		
	ZIF-7	14	ND	(Chen et al., 2016)
	ZIF-8	1291		
	Uio-66-10/25/50/DF	687–1423	0.32–0.72	(Clark et al., 2019)
	Three MIL-101-(Cr)	433.16–6955	0.62–3.44	(Pala et al., 2023)

<100 m^2/g

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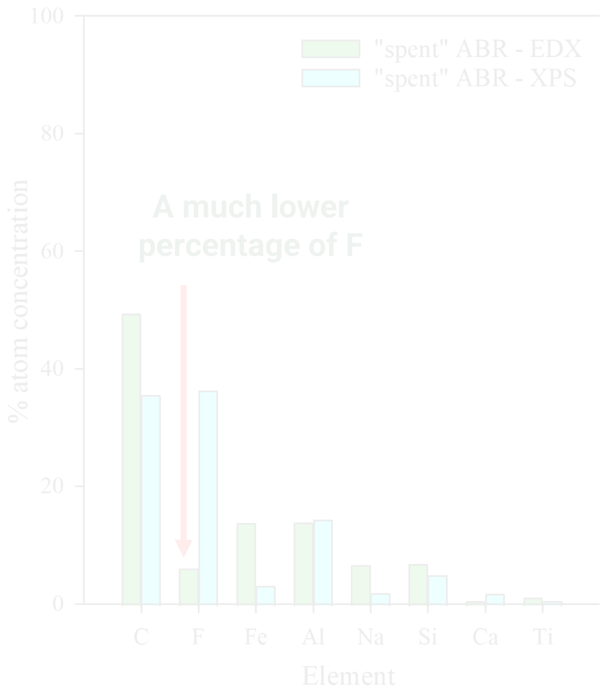
Surface element concentration

Element concentrations on the surface of ABR via XPS

Relative % atom concentration					
PFAS Conc	**0.1 mg/L**				**100 mg/L**
ABR Dose	**2 g/L**	**6 g/L**	**10 g/L**	**0 g/L**	**3 g/L**
F	**4.60**	**2.00**	**2.07**	**1.37**	**57.69**
Na	20.54	20.63	21.45	22.17	2.97
Fe	18.05	17.78	19.09	19.65	4.88
Ti	2.13	2.17	2.21	2.31	1.11
Ca	4.42	5.10	5.31	4.73	3.01
Si	15.41	16.86	15.50	16.18	7.88
Al	34.86	35.46	34.36	33.60	22.46

- PFAS: 0.1 mg/L → 100 mg/L, %atom: 4.60% → 57.69%

EDX vs **XPS scan depth**
1–5 μm vs **0.1–3μm**



A much lower percentage of F

- Supporting that PFAS adsorbed on the surface of ABR.

Surface element concentration

Element concentrations on the surface of ABR via XPS

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Ca	4.42	5.10	5.31	4.73	3.01
Si	15.41	16.86	15.50	16.18	7.88
Al	34.86	35.46	34.36	33.60	22.46

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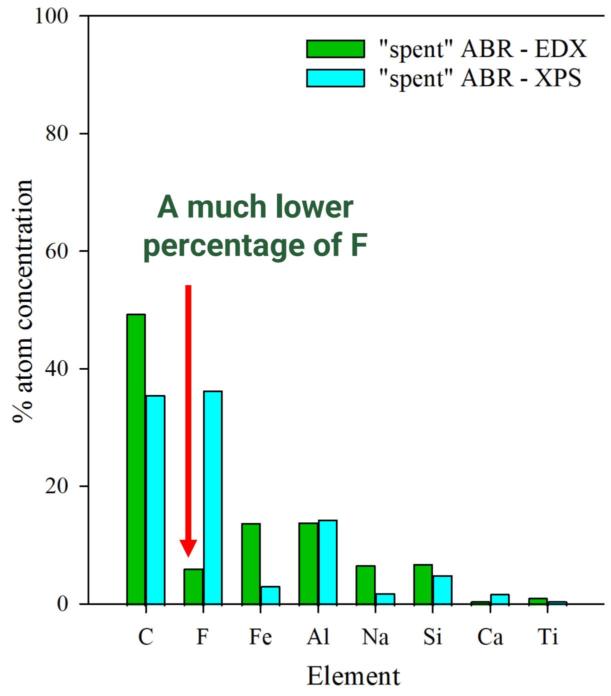

A much lower percentage of F

- Supporting that PFAS adsorbed on the surface of ABR.

Bond types on the surface of ABR

How did F interact with ABR?

F-bond types can be qualitatively analyzed using the **XPS spectra**.

ABR dosage (g/L)	PFAS concentration (mg/L)	F bond energy position (eV)	Bond Type
0	0	ND	ND
100	0.1	685.0 685.5	Metal bond Carbon bond
	0.1_post_baking	685.5	Metal bond
3	100	688.93	Carbon bond

F mainly comes from PFAS.

- Thermal treatment can beak C-F bond.
- F might still present

F might be interacting with other metallic elements on the surface

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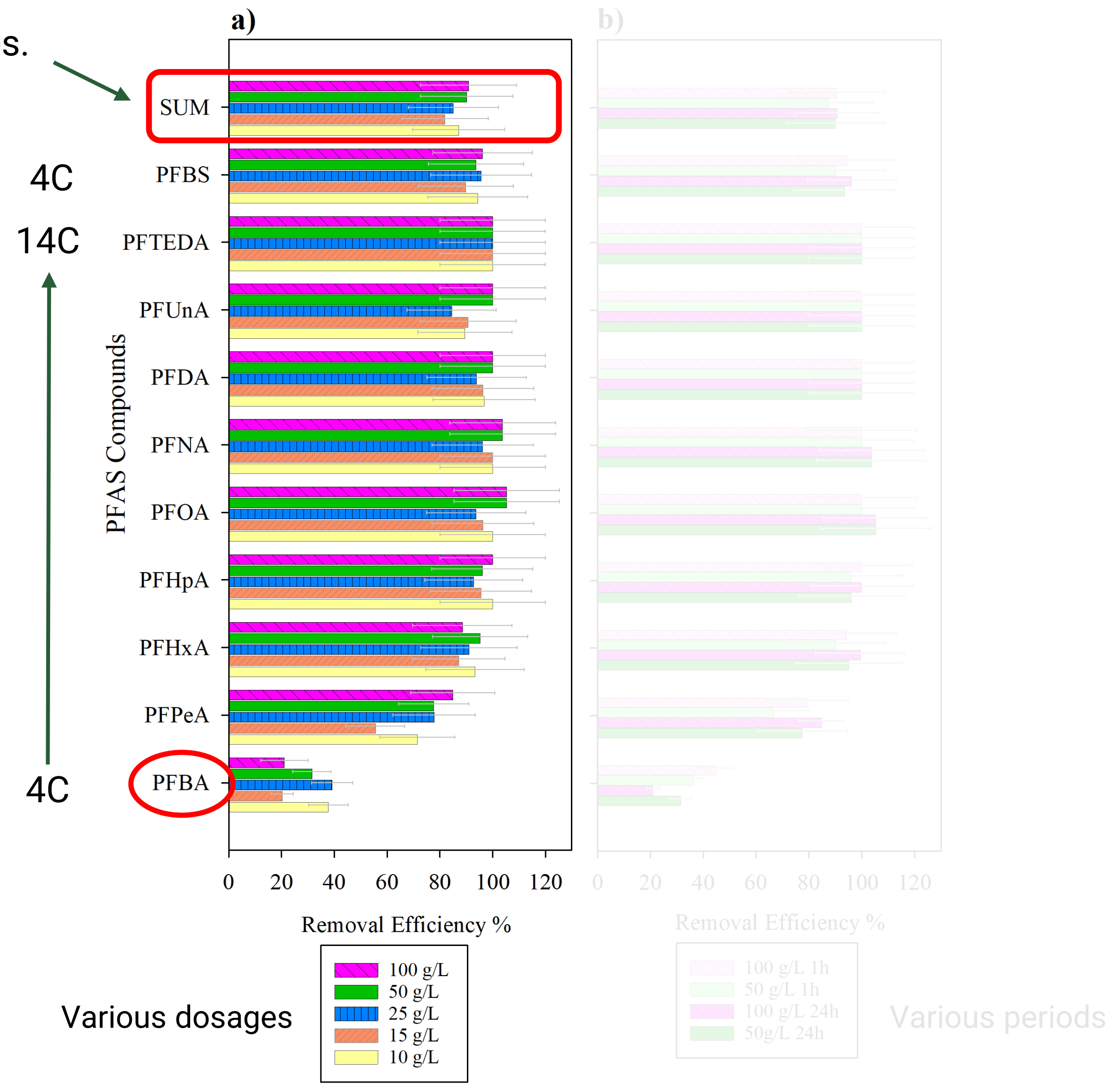
Preliminary investigation on dosage and period

C$_0$ = 600 ng/L

- Very similar at all dosages.



- The removal% of PFBA did not show any trend with dosages.
- Below 10 g/L may be appropriate for ∑PFAS removal.

Preliminary investigation on dosage and period

C_0 = 600 ng/L

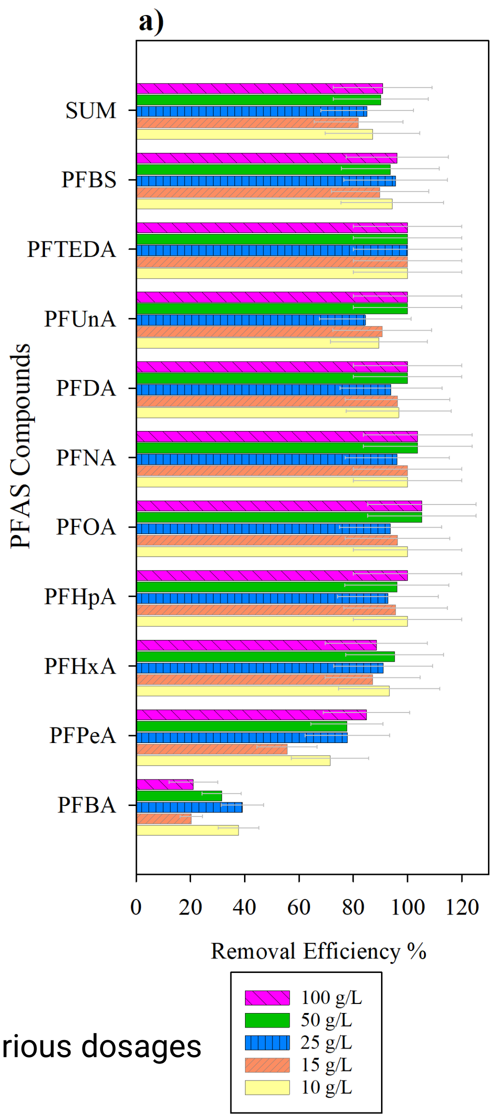
Long-chain PFAS compounds achieved nearly 100% removal.

- Stronger electrostatic interactions
- Stronger hydrophobic interactions
- Higher molecular weight (MW)
- Preference to form molecular/colloidal aggregates

4C

14C

4C



Various dosages

Various periods

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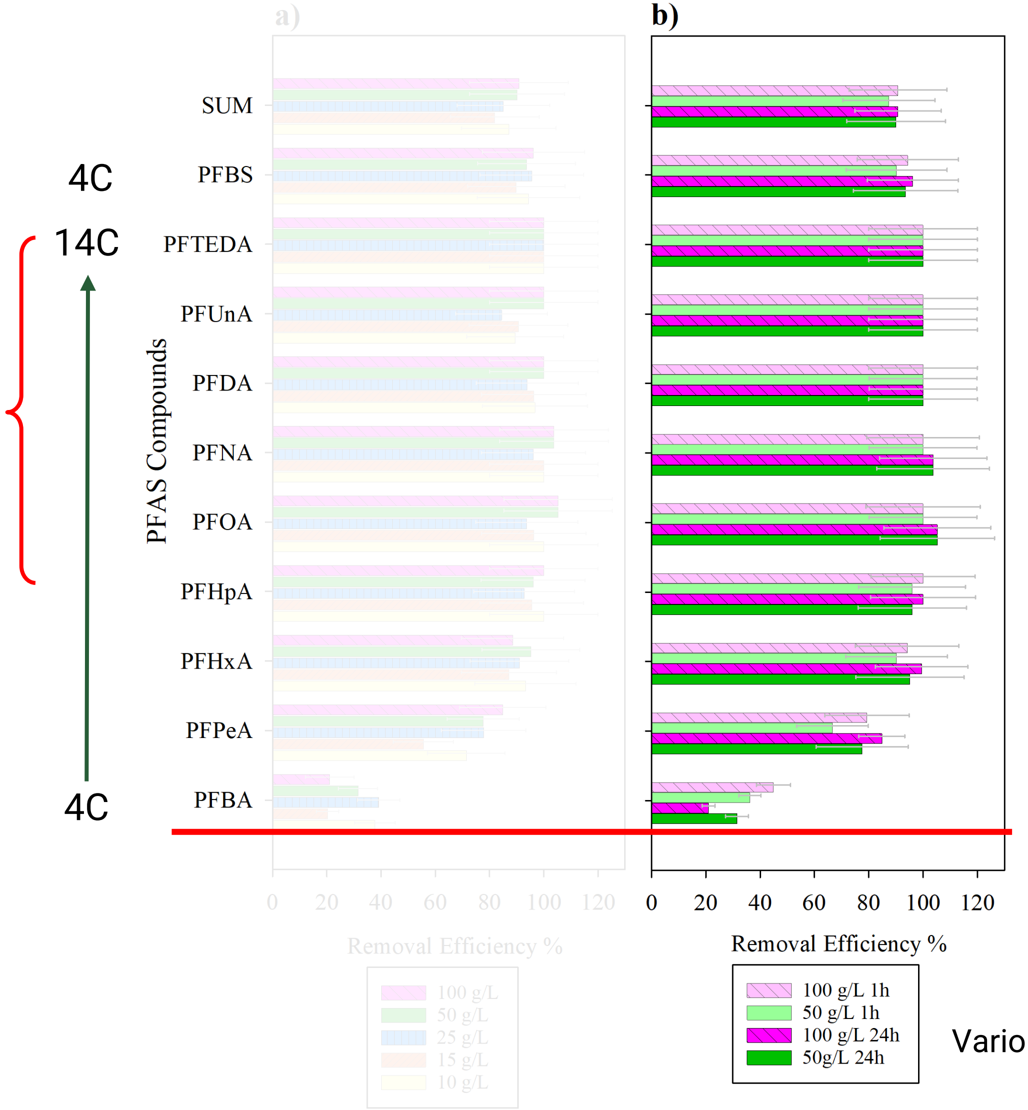
Preliminary investigation on dosage and period

C_0 = 600 ng/L



All were between 80 and 90%.

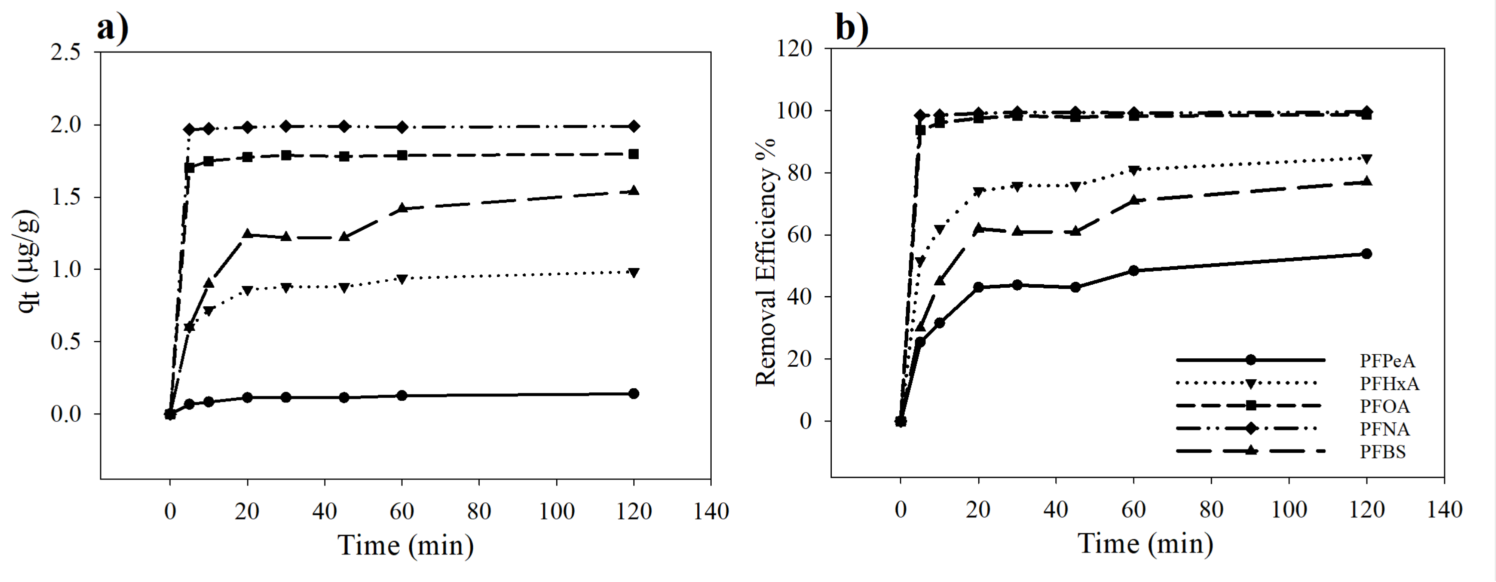
Either short- (1h) or long-term (24h) was suitable for long-chain PFAS.

PFBA may desorb from ABR as time went by.

Various periods

PFAS adsorption kinetics with ABR

PFAS
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnA
PFTEDA
PFBS



- The adsorption equilibrium could be reached between 5 and 60 min.
- The adsorption capacity ranged from 0.1 to 2 µg/L.

PFAS adsorption kinetics with ABR

PFAS compound	**Pseudo First Order**			**Pseudo Second Order**		
	K_1 (/min)	q_e (μg/g)	**R^2**	K_2 (μg/g/min)	q_e (μg/g)	**R^2**
PFPeA	5.484	0.136	**0.965**	0.807	1.147	**0.995**
PFHxA	3.239	0.979	**0.983**	0.228	1.012	**0.999**
PFOA	0.28	1.800	**0.984**	1.747	1.802	**1**
PFNA	0.063	1.990	**0.838**	5.691	1.992	**1**
PFBS	8.171	1.599	**0.981**	0.065	1.638	**0.995**

- The rate-limiting step is chemisorption.
- Specific bond formation likely happened.

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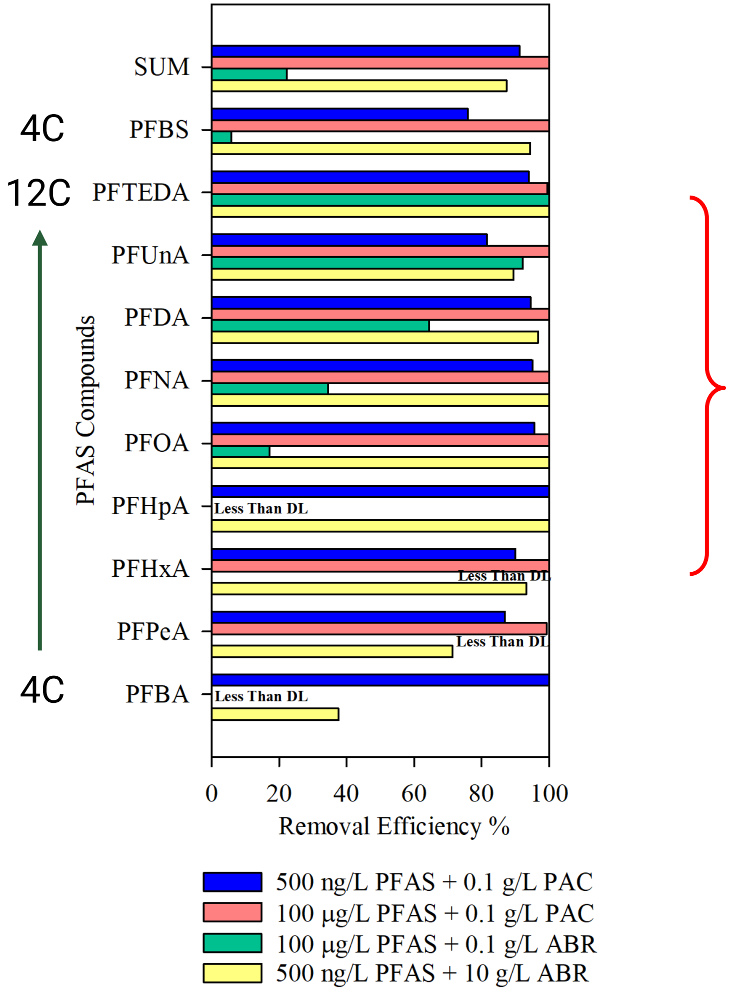
Comparison with commercially available PAC



- 10 g/L ABR was comparable to 0.1 g/L PAC.
- ABR worked better for PFAS with ≥6 carbons.
- ABR has the potential to exhibit higher adsorption capacity when containing higher concentration PFAS in the mixture.

PFAS adsorption isotherm with ABR

PFAS	Langmuir			Freundlich			Sips			
	K_L (L/μg)	Q_m (μg/g)	R^2	K_F	1/n	R^2	K_S	b	Q_m (μg/g)	R^2
PFHxA	0	4.11×10^{11}	0.515	0.009	2.050	**0.966**	-			
PFHpA	-			1.523	1.416	**0.998**	-			
PFOA	0.029	188.679	0.963	5.958	0.834	**0.950**	0.001	2.433	198.793	**0.982**
PFNA	0.005	3333.333	**0.977**	20.469	0.791	0.881	-			
PFDA	0	5.380×10^{9}	0.523	60.632	0.693	0.641	-			
PFBS	0	2.288×10^{12}	0.802	0.009	1.887	0.915	1.24×10^{-12}	6.123	106.729	**0.973**

- The surface of the adsorbent is homogeneous.
- The adsorption is reversible.

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- Nonideal, multilayer, and irreversible adsorption at a heterogeneous surface.

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- The surface of the adsorbent is homogeneous.
- The adsorption is reversible.

- Nonideal, multilayer, and reversible adsorption at a heterogeneous surface.

- A hybrid of Langmuir and Freundlich
- Can represent adsorption equilibrium in a wide range of adsorbate concentrations.

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PFAS adsorption isotherm with ABR

Calculation of Dosage: (PFHpA as an example)

Apply usage rate for PAC:

(Freundlich isotherm)

$$D_{PAC} = \frac{C_{inf} - C_{eff}}{q_e|C_{eff}}$$

$$q_e|C_{eff} = KC_{eff}^{\frac{1}{n}}$$

Initial Concentration ($C_{influent}$) (100μg/L)	Removal Efficiency (treatment goal)	$C_{effluent}$ (μg/L)	q_e (μg/g)	D (g/L)
100	99%	1	1.52	64.99
	95%	5	14.88	**6.39**
	90%	10	39.69	2.27
	50%	50	387.59	0.13
	30%	70	624.13	0.05
	10%	90	890.87	0.01

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Removal efficiency of short-chain PFAS

PFAS	Adsorbent	Concentration (PFAS)	Dosage (g/L)	Removal efficiency	Reference
PFBA, PFPeA, PFHxA, PFHpA, PFBS	ABR	500 ng/L	10	38%, 71%, 93%, 100%, 94%	This study
		100 µg/L	50	31%, 77%, 95%, 96%, 94%	
PFHxA, PFHpA	BAC	30 mg/L	0.2	<10%, 10–30%	(Du et al., 2015)
PFBA, PFHxA, PFBS	GAC	1 and 100 µg/L	0.2	50% (10%), 68% (30%), 70% (40%)	(Liu et al., 2021)
PFPeA, PFHxA, PFHpA, PFBS	GAC, PAC	100 ng/L	0.01 and 0.05	(GAC) 20%, 30%, 50%, 45%, (PAC) 10% for all	(Son et al., 2020)
PFBA, PFHxA, PFBS	IRA910 (ion-exchange resin)	30 mg/L	0.05	<10%, <10%, 15%	(Maimaiti et al., 2018)
PFBA, PFPeA, PFHxA, PFHpA, PFBS	PEI-F-CMC (Poly ethylenimine -functionalized cellulose microcrystals)	1 µg/L	0.025	2%, 2%, 12%, 37%, 5%	(Umeh et al., 2024)

Conclusions

1. The activation process of ABR can enhance the adsorption capacity.
2. The adsorption of FPAS on ABR occurred on the surface.
3. F might be interacting with metallic elements and dominated by chemisorption.
4. < 10 g/L ABR may be appropriate for ∑PFAS removal, where the removal efficiency is maximized.
5. The use of ABR to remove PFAS substances offers sustainable potential and environmental and economic benefits.

Recommendations

1 Characterize ABR saturated with a wider range of PFAS and organic compounds.

2 Assess ABR treatment performance for real-life wastewater scenarios.

3 Assess the regeneration capability.

4 Explore pilot-scale options.

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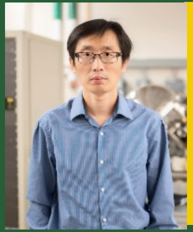

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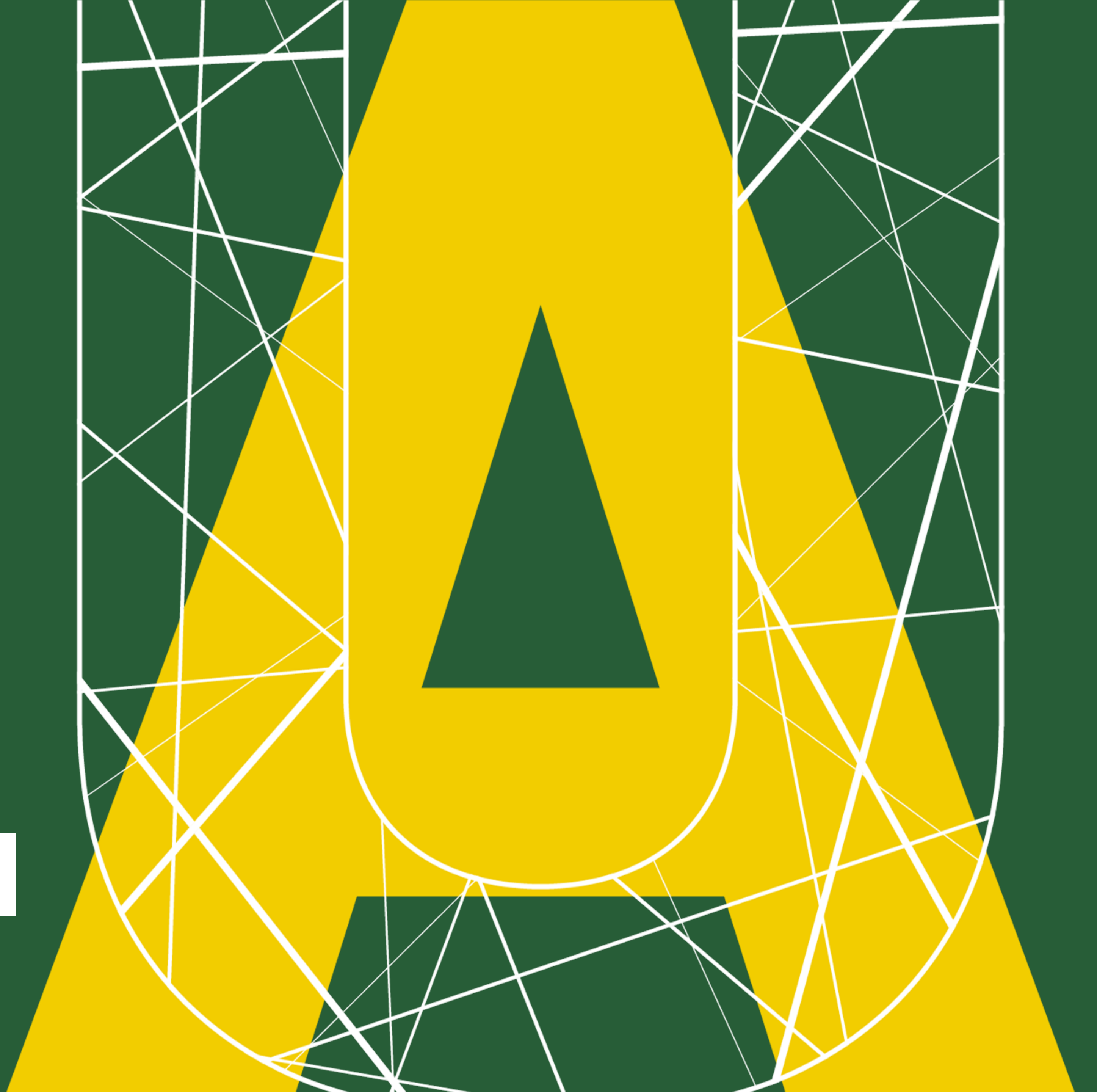
Thank you for your attention!



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