Modified Natural Zeolites for the Treatment of PFAS Contaminated water

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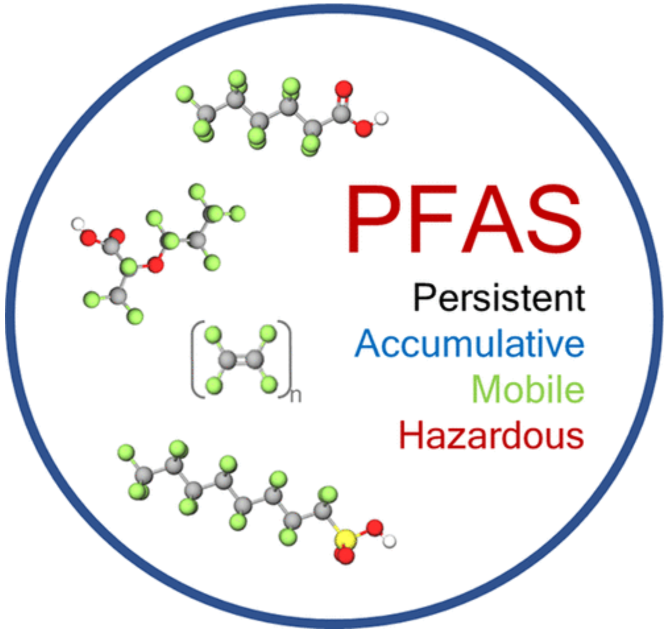
PFAS in water

The Problem

- Thousands of synthetic chemicals
- Persistent contaminants
- Dangerous to environment and human health



Current approaches

Adsorption
- Activated carbons
- Ion exchange resins

Separation
- Foam fractionation
- Nano-filtration

Destruction
- Incineration
- Supercritical water oxidation

Our Approach
Circularity principles

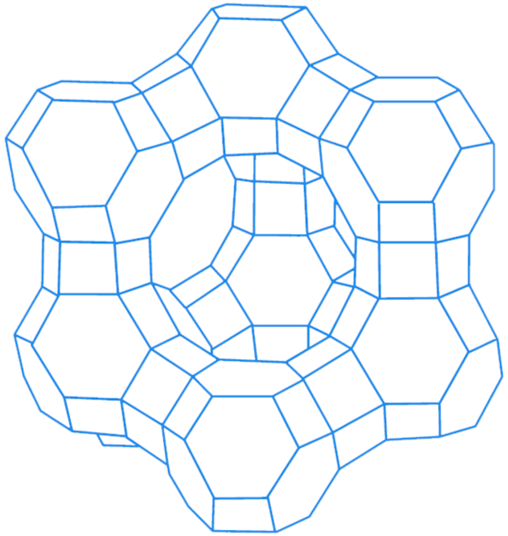
- Zeolite (natural or from upcycled waste streams)
- Regeneration potential
- Water reuse or recycle

Natural Zeolites

Microporous aluminosilicates

3D network structure

Tectosilicates

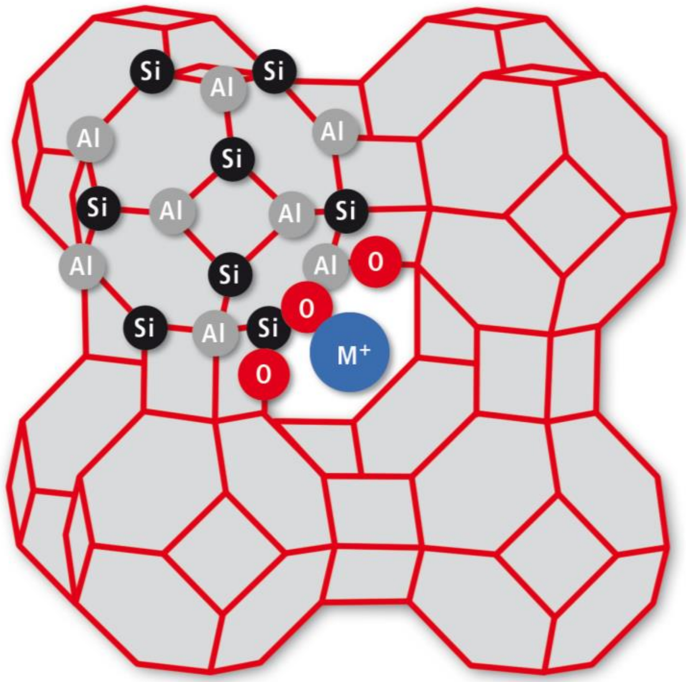


Crystalline

Pores
0.3 – 1.7 nm

> 40 natural
> 200 syntetic

Natural Zeolites - Properties

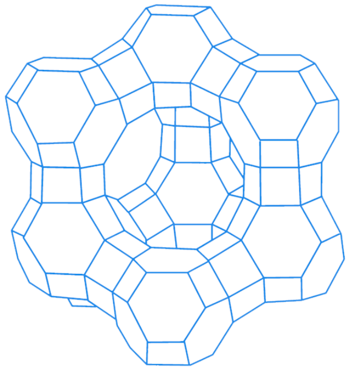


- **Composition** $M^{n+}_{d}[Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}] \cdot m\ H_2O$
- **Counterions** – e.g., Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} weakly bound, exchangeable!
- **Water absorption capacity**: up to 30% of their weight without structural changes
- High **specific surface area** – up to 1000 m^2/g
- Presence of **Si-OH reactive groups**
- **Carrier** for nutrients or microorganisms
- **Adsorption selectivity**: depending on the exchangeable cation

Natural Zeolites - Water filtration mechanisms

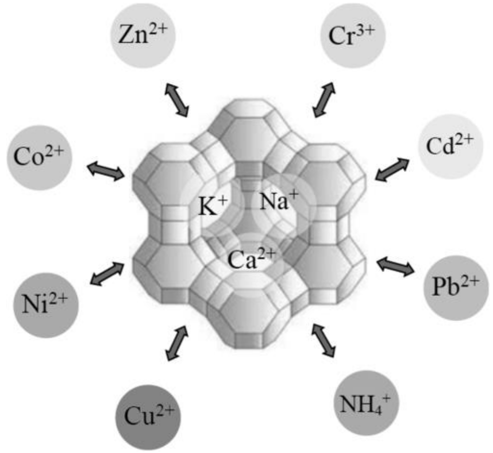
Physical barrier

It acts as a molecular sieve, trapping molecules and particles with diameters larger than the size of the zeolite channels.



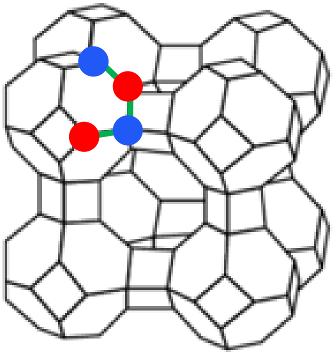
Cation exchanger

It releases sodium, calcium, magnesium, and potassium ions and captures cations present in water.



Chemical interaction

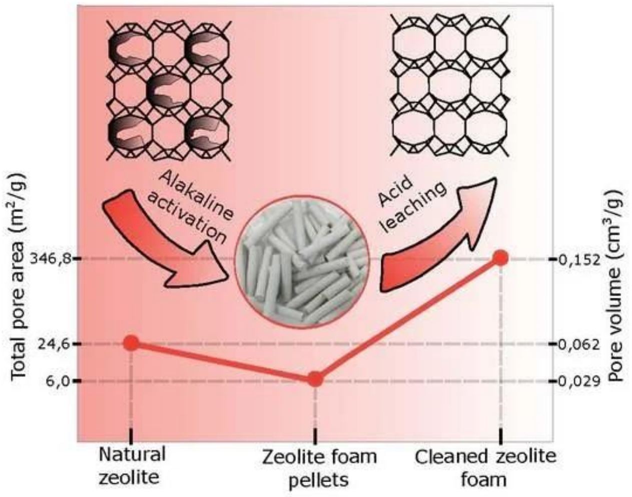
Contaminants are adsorbed on the mineral surface by weak chemical bonds.

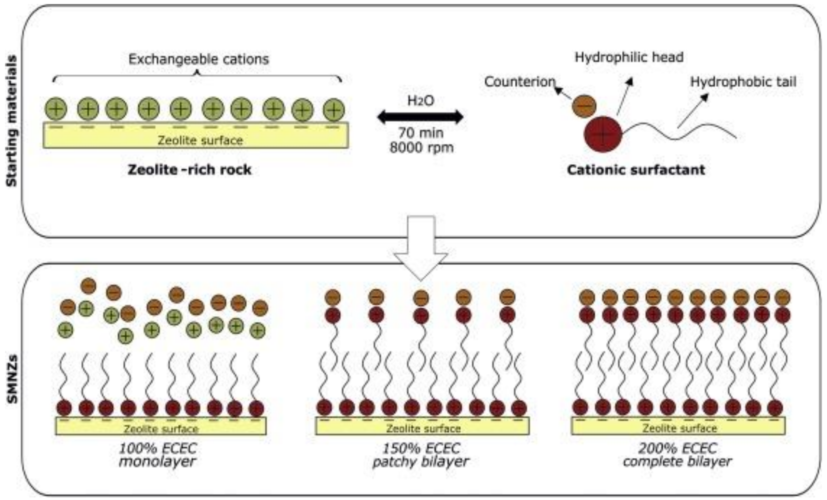


Natural zeolite modification

Targets of modification:

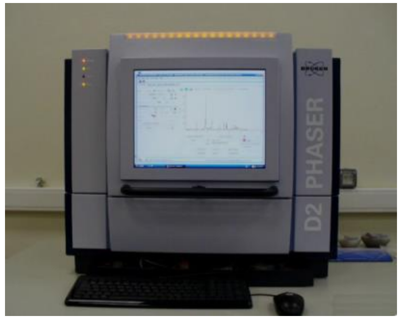
- Increasing the **specific surface area** (SSA)
- Increasing the **cation exchange capacity** (CEC)
- Changes in their **ionic affinity**
- Modify or enhance their **selectivity** towards contaminants
- Changing their **chemical behaviour** (inorganic to organic)
- Changing the number and type of **silanol groups**





Natural Zeolites Characterization

- X-Ray Powder Diffraction (XRD)
- Transmission electron microscopy (TEM)
- Scanning electron microscopy (SEM)
- Fourier transform infrared (FT-IR) microscopy
- Differential Scanning Calorimetry (DSC)
- Thermogravimetric analysis (TGA)



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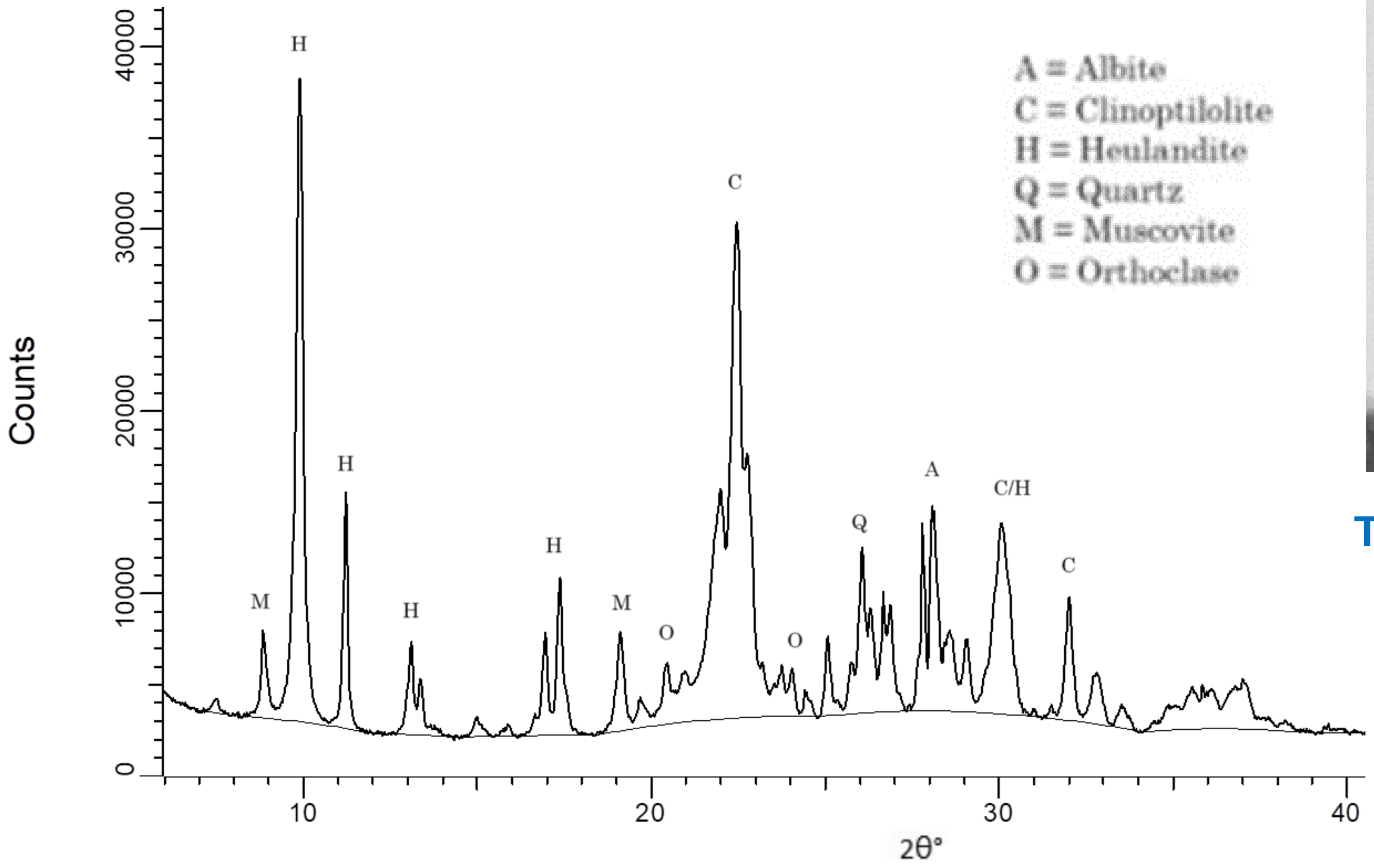
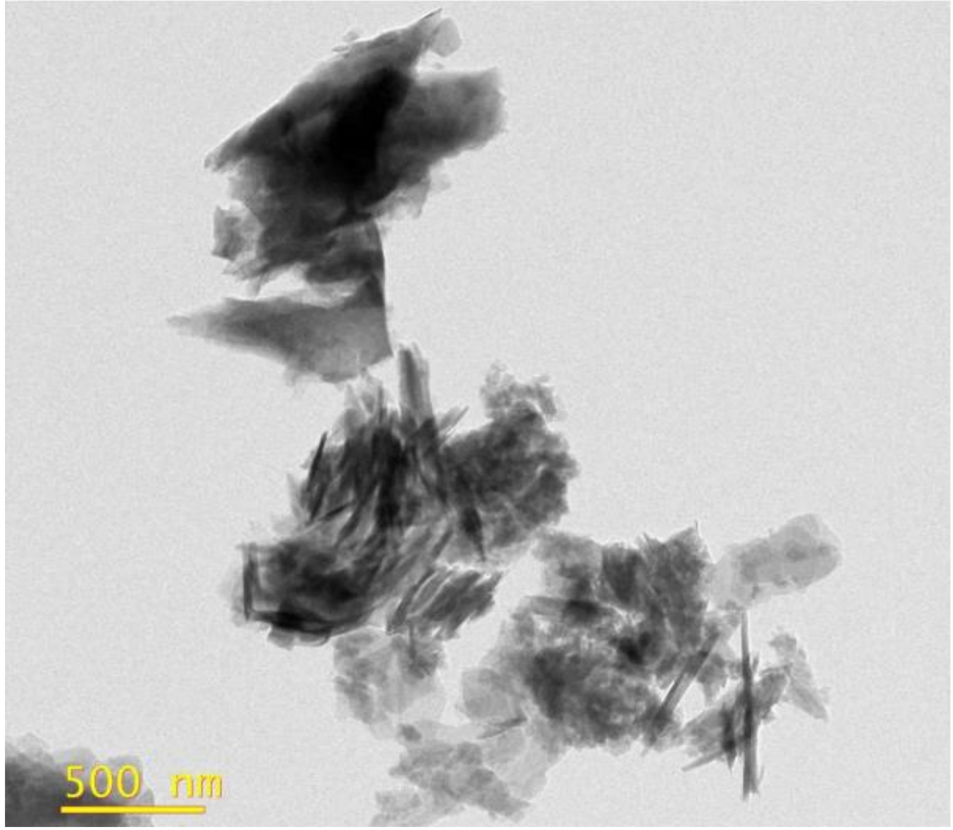
Natural Zeolites Characterization

Powder XRD – natural zeolite clinoptilolite





Transmission electron microscopy (TEM)

Testing steps

- Zeolite functionalization

- Selection of best formulations

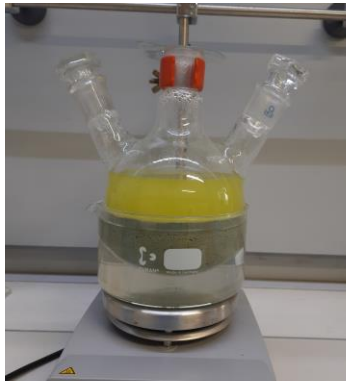
- Lab testing: Adsorption

Adsorption isotherms
Breakthrough curves

- Lab testing: Regeneration

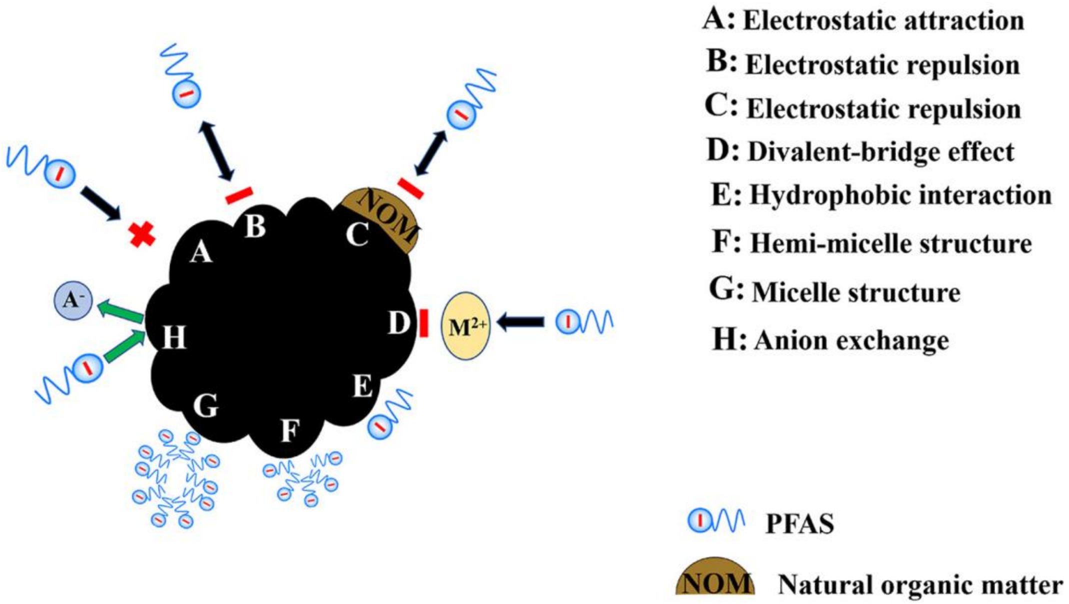
Electro-chemical processes

- Scale up and pilot testing



About the project

PFAS sorption mechanisms



Our objective

Develop a new **natural modified zeolite** to effectively remove PFAS from water

Targets

- Increase electrostatic and hydrophobic sites that are highly specific for PFAS
- Increase Si/Al ratio to enhance hydrophobicity of zeolite
- Make the zeolite an anion exchanger

Natural modified zeolites – first formulations

PFAS TYPE	Cationic	Anionic	Non-ionic
ZEOCEL ZEOLITES			

Case 1: water sample from soil washing

Tested zeolites

- Natural zeolite ZN
- Modified zeolite ZNS

Water initial concentration

PFOS [ng/L]	PFOA [ng/L]	PFBA [ng/L]	PFAS [ng/L]
410	60	34	680

Batch Tests

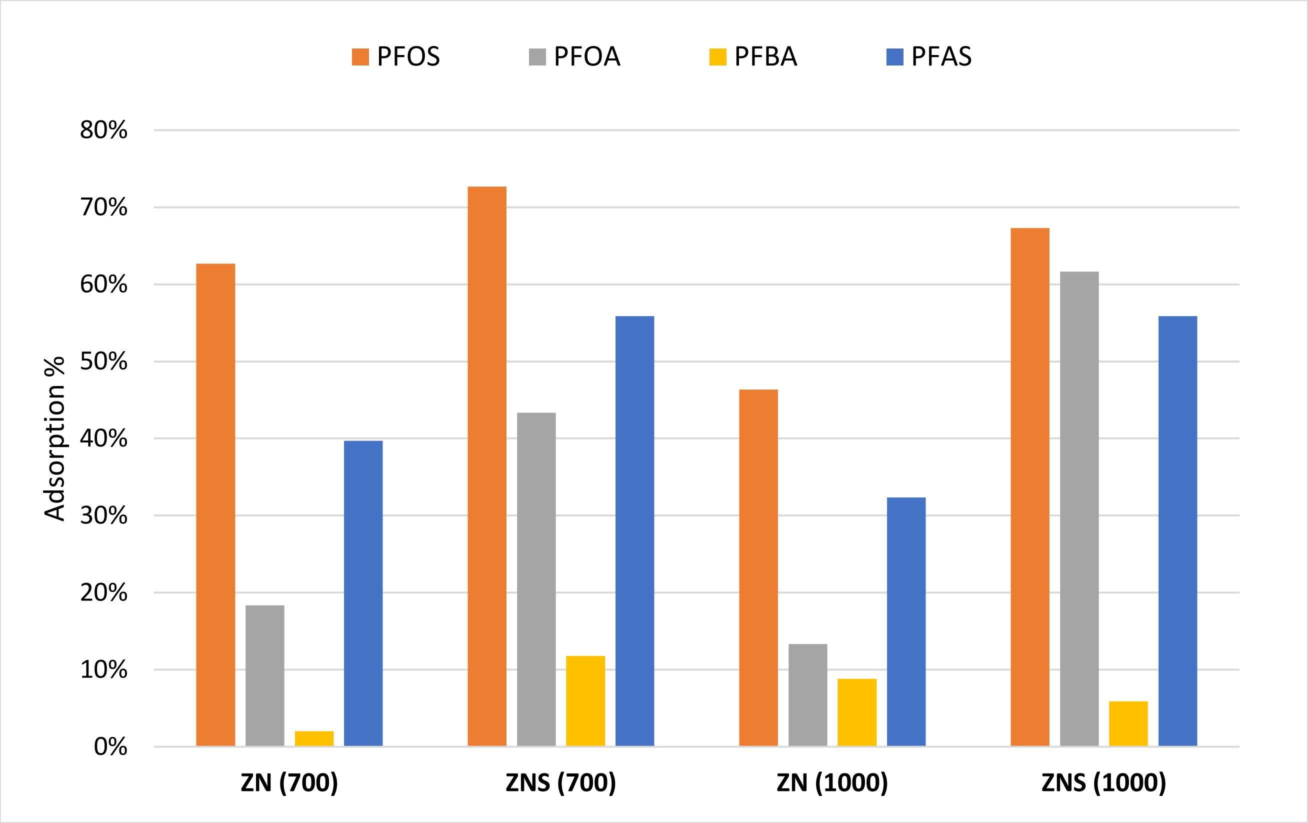
- 200 ml of contaminated water
- Different amounts of zeolites (700 mg/L and 1000 mg/L)
- Mixing for 24 hours

Case 1: water sample from soil washing

Water initial concentration

PFOS [ng/L]	PFOA [ng/L]	PFBA [ng/L]	PFAS [ng/L]
410	60	34	680

PFAS Removal rate (%)



Results

- Modified zeolite **ZNS** > Natural zeolite **ZN**
- Higher affinity for **PFOS**
- Lower efficiency for **short-chain PFBA**

Case 2: water sample from soil washing

Tested zeolites

3 modified zeolites (granulometry 0.5-1 mm)

- **ZNS**
- **ZH**
- **ZI**

Batch Tests

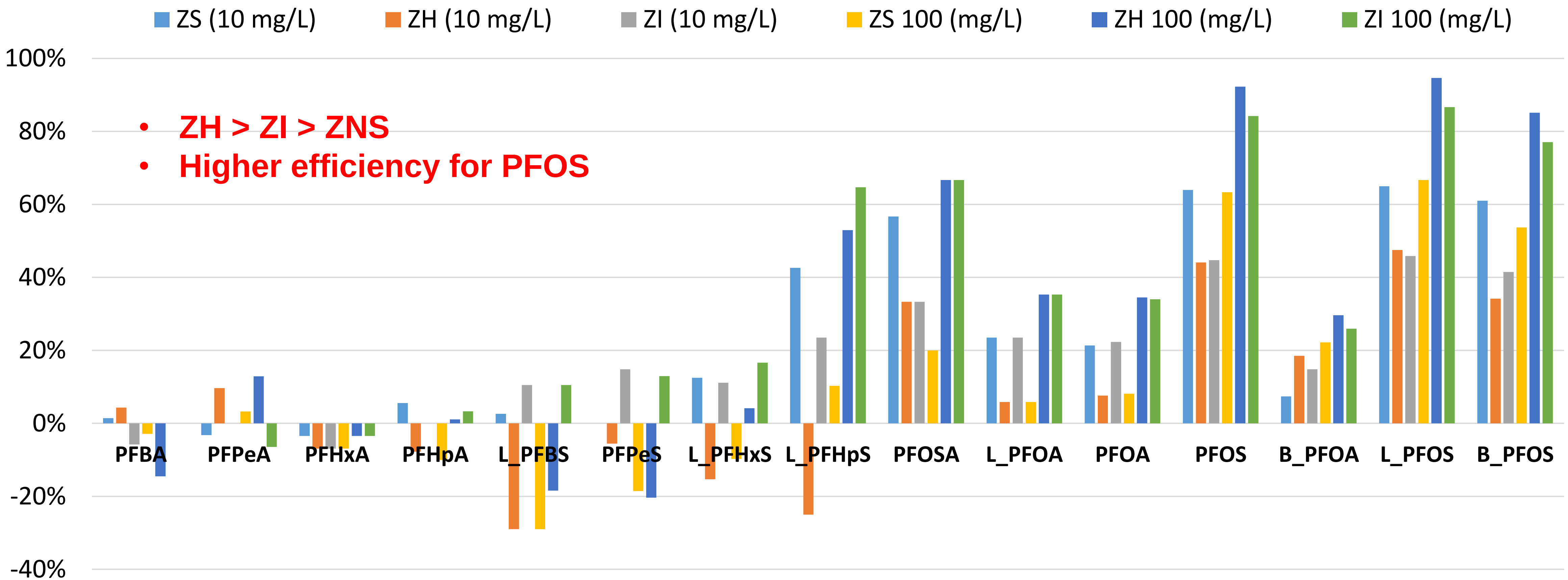
- All zeolites were washed and dried
- 10 grams of zeolite grinded to 150 µm
- 1 Control (no zeolite), 3 zeolites at 10 mg/L and at 100 mg/L
- X mg/L of zeolite into 1L of PFAS water in a PE bottle, shaking for 1 night

Tests	Unit	Analysis Method	LOQ	Control
PFBA	ng/l	NEN-ISO 21675	10	69
PFPeA	ng/l	NEN-ISO 21675	10	310
PFHxA	ng/l	NEN-ISO 21675	10	290
PFHpA	ng/l	NEN-ISO 21675	10	90
L_PFBS	ng/l	NEN-ISO 21675	10	38
PFPeS	ng/l	NEN-ISO 21675	10	54
L_PFHxS	ng/l	NEN-ISO 21675	10	720
L_PFHpS	ng/l	NEN-ISO 21675	10	68
PFOSA	ng/l	NEN-ISO 21675	10	30
L_PFOA	ng/l	NEN-ISO 21675	10	170
PFOA	ng/l	NEN-ISO 21675	-	197
PFOS	ng/l	NEN-ISO 21675	-	16100
B_PFOA	ng/l	NEN-ISO 21675	10	27
L_PFOS	ng/l	NEN-ISO 21675	10	12000
B_PFOS	ng/l	NEN-ISO 21675	10	4100

Case 2: water sample from soil washing

PFAS Removal rate (%) after treatment with modified natural zeolites

PFOS
16100 ng/L



Natural modified zeolites – new formulations

ZeoCu – Saline exchange

ZIB – Metal surface modification

ZNAVS – Organic functionalization

Case 3: PFAS adsorption in groundwater

Tested zeolites

3 natural zeolites (ZN, ZNC, ZNAV)
8 modified zeolites (ZNS, ZNAVS, ZH, ZIB, ZIT, ZF, ZZ, ZeoCu)

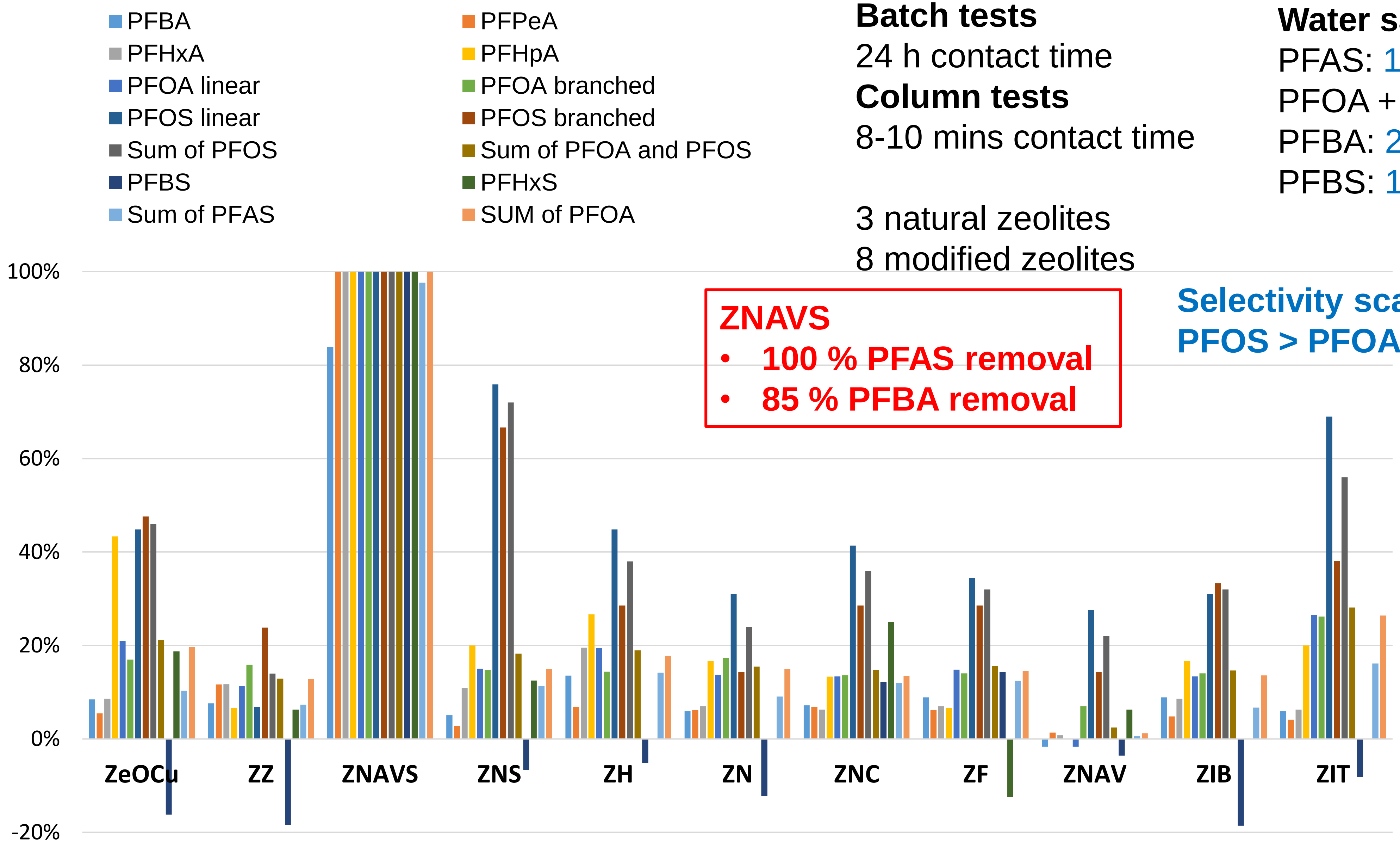
granulometry 0.5-1 mm

Batch Tests

- All zeolites were washed and dried
- 10% w/w zeolite in PFAS contaminated water
- 1 Control (no zeolite)
- Contact for 24 hours on orbital shaker

Tests	Unit	Analysis Method	LOQ	Control
PFBA	ng/l	PFAS LC-MS	5	236
PFPeA	ng/l	PFAS LC-MS	5	146
PFHxA	ng/l	PFAS LC-MS	5	128
PFHpA	ng/l	PFAS LC-MS	5	30
PFOA linear	ng/l	PFAS LC-MS	5	539
PFOA branched	ng/l	PFAS LC-MS	5	271
PFOS linear	ng/l	PFAS LC-MS	5	29
PFOS branched	ng/l	PFAS LC-MS	5	21
PFOS Sum	ng/l	PFAS LC-MS	5	50
Sum of PFOA and PFOS	ng/l	PFAS LC-MS	5	860
PFBS	ng/l	PFAS LC-MS	5	196
PFHxS	ng/l	PFAS LC-MS	5	16
Sum of PFAS	ng/l	PFAS LC-MS	5	1612
PFOA Sum	ng/l	PFAS LC-MS	5	810

Case 3: PFAS adsorption in groundwater



Batch tests
24 h contact time
Column tests
8-10 mins contact time

3 natural zeolites
8 modified zeolites

Water sample
PFAS: 1612 ng/L
PFOA + PFOS: 860 ng/L
PFBA: 236 ng/L
PFBS: 198 ng/L

ZNAVS
- **100 % PFAS removal**
- **85 % PFBA removal**

Selectivity scale:
PFOS > PFOA > PFBS > PFBA

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Conclusions & Next Steps

Conclusions

First adsorption testing with natural modified zeolites

- Sulfonic acids are removed more efficiently than carboxylic acids
- Longer chains are removed more efficiently than shorter chains
- New zeolite formulation for PFAS adsorption

Effective to long and short-chain PFAS molecules

Next steps

Evaluation of ZNAVS maximum adsorption capacity for PFAS

- Batch tests for adsorption isotherm build-up and “Dynamic” batch tests
- Testing combination of multiple adsorption media

Evaluation of ZNAVS filter performance

- Column test for breakthrough curve build-up

Regeneration tests

- Evaluation of different chemical regeneration processes

Modified Natural Zeolites for the Treatment of PFAS Contaminated water

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