UNESCO-IWRA ONLINE CONFERENCE

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Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Evaluation of Sustainable materials to boost Emerging pollutants sorption during Soil Aquifer Treatment for Water Reuse

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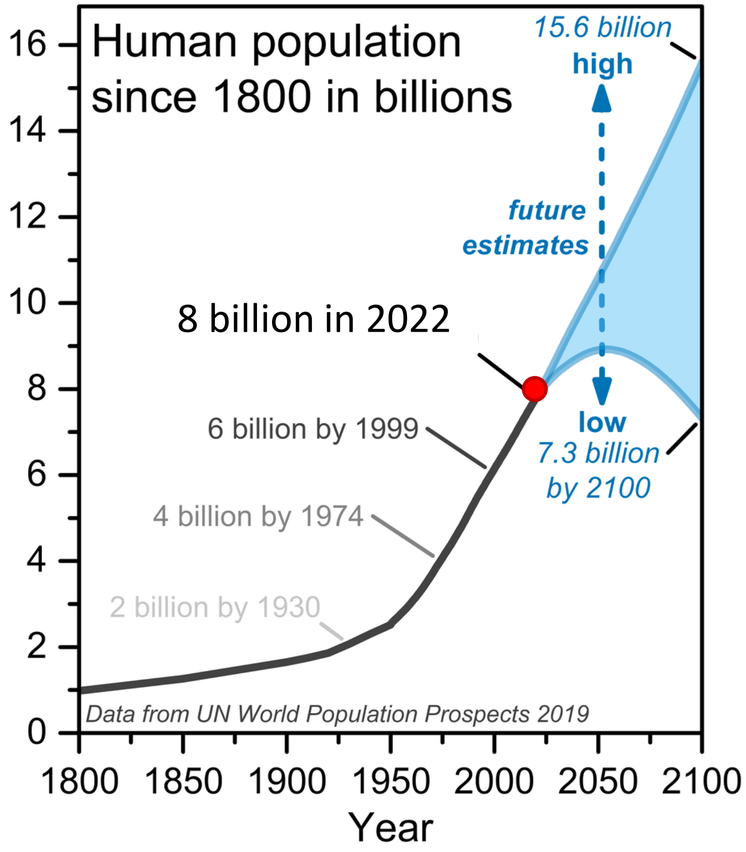
Programme hydrologique intergouvernemental

IWRA International Water Resources Association

Soil Aquifer Treatment (SAT) as a powerful technology for WATER REUSE

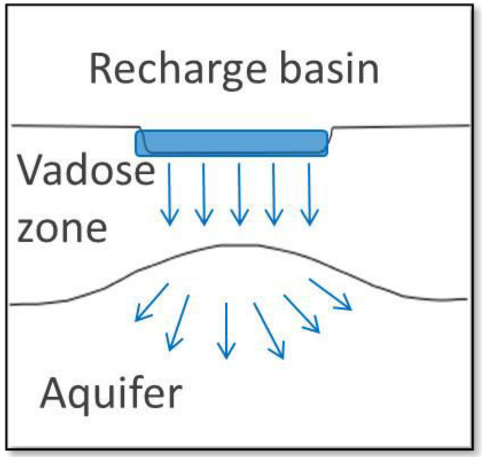


Water Reuse is a MUST!

Wastewater TPs effluents

Effluents alternative discharge →

Soil Aquifer Treatment



SAT technologies →

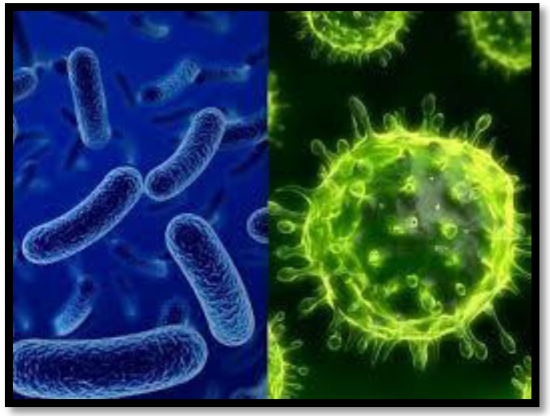
- **Increase** groundwater **resources**
- **Improve** recharged **water quality**
- **Reduces** WWTP effluents **discharge**

But careful!
There are some contaminants frequently present in WWTPs effluents

Contaminants of emerging concern (CECs) are commonly present in WWTP effluents:
- Trace organic Contaminants (Pharmaceuticals, Personal Care products) which are not remove in WWTP
- Virus and bacteria: not completely removed in WWTP and related with antibiotic resistance
- Micro- and nano-plastics: highly persistent and involved in the transport of other contaminants

Trace Organic Contaminants

Virus and bacteria

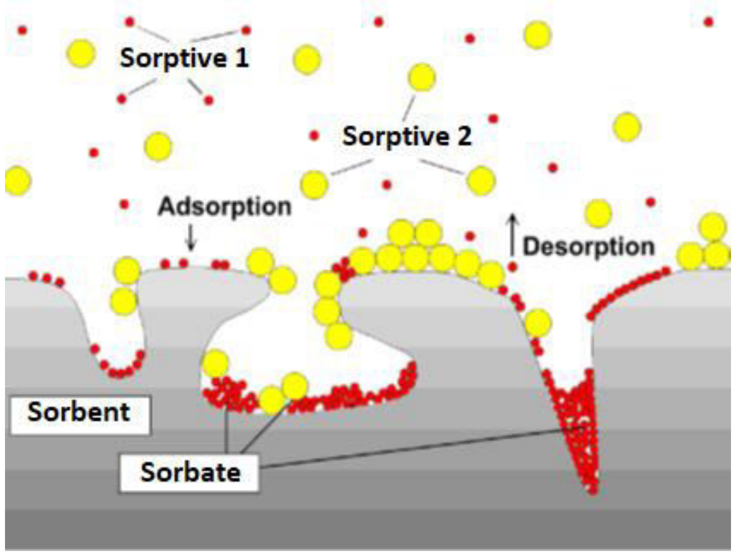


Microplastics

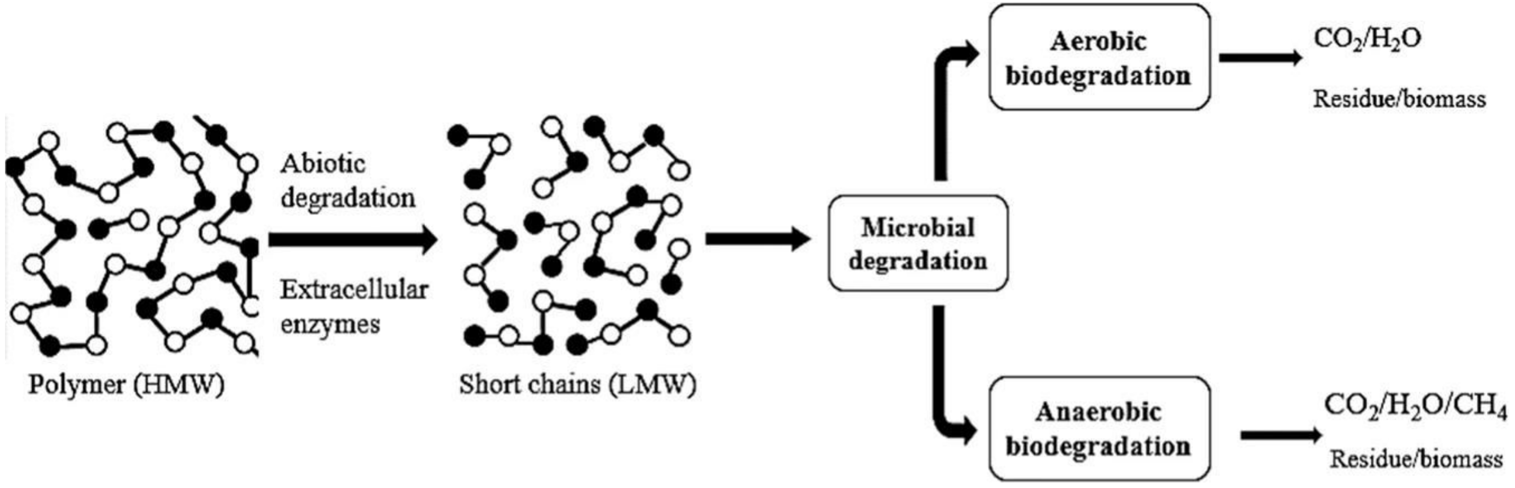
Sorption and biodegradation are the main processes involved in water quality improvement during SAT

Main processes involved in the removal of CECs during SAT:

- **Sorption**: attachment of molecules of the liquid phase onto a solid surface
  (molecule ionization, molecule Log KOW, solid reactive area, dissolution Ionic strength, solid components, …)
- **Biodegradation**: Degradation mediated by microorganisms highly dependent on the redox conditions



https://www.rubolab.de/sorption-measurement

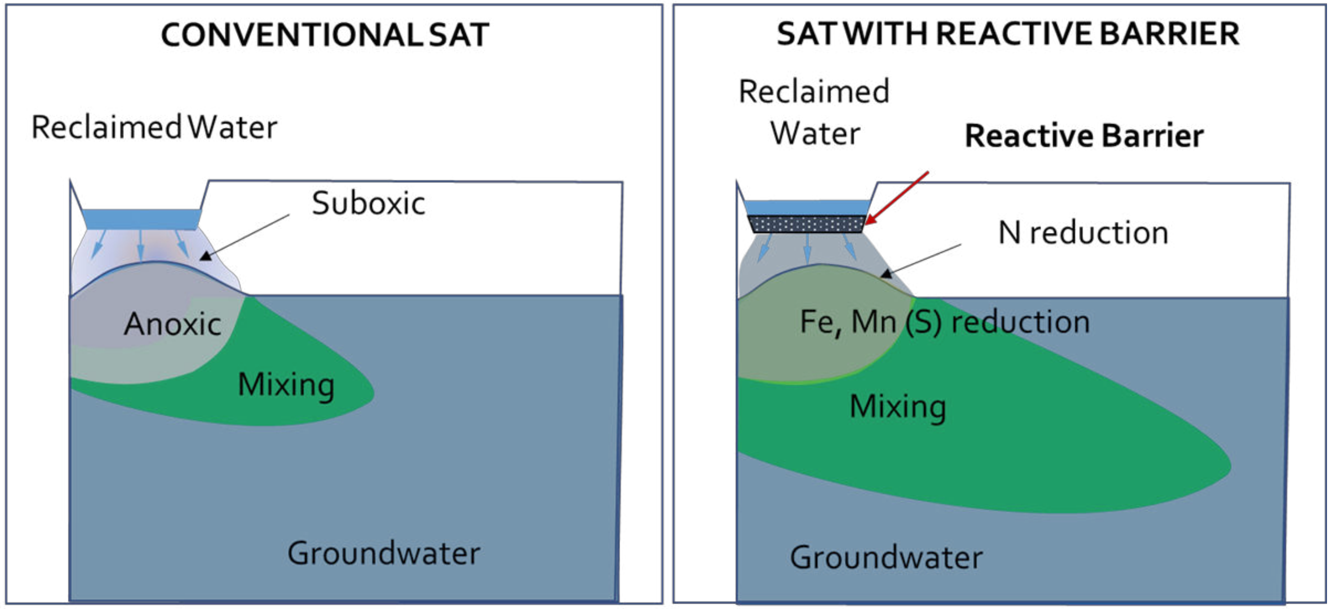


Samir et al., 2022 (https://doi.org/10.1038/s41529-022-00277-7)

The installation of REACTIVE BARRIERS in SAT systems promotes the improvement of water quality

We can promote sorption and biodegradation by installing reactive barriers based on sustainable materials:

- **To increase Sorption**: We can add materials with high reactive areas, cation exchange capacity, and charges.
- **To increase biodegradation**: We can add materials that release dissolved organic carbon (DOC) to favor diverse redox environment and microbial community development



Valhondo et al., 2020 (https://doi.org/10.3390/w12041012)

Objective

The objective of this study was to determine the sorption capacity of 5 sustainable materials and evaluate their suitability to be include in reactive barrier for SAT.

We did it through batch experiments.

Sustainable materials selected based on their properties

- Sand ➔ is our reference material
- Compost
- Woodchips
- Biochar
- Clay
- Zeolite

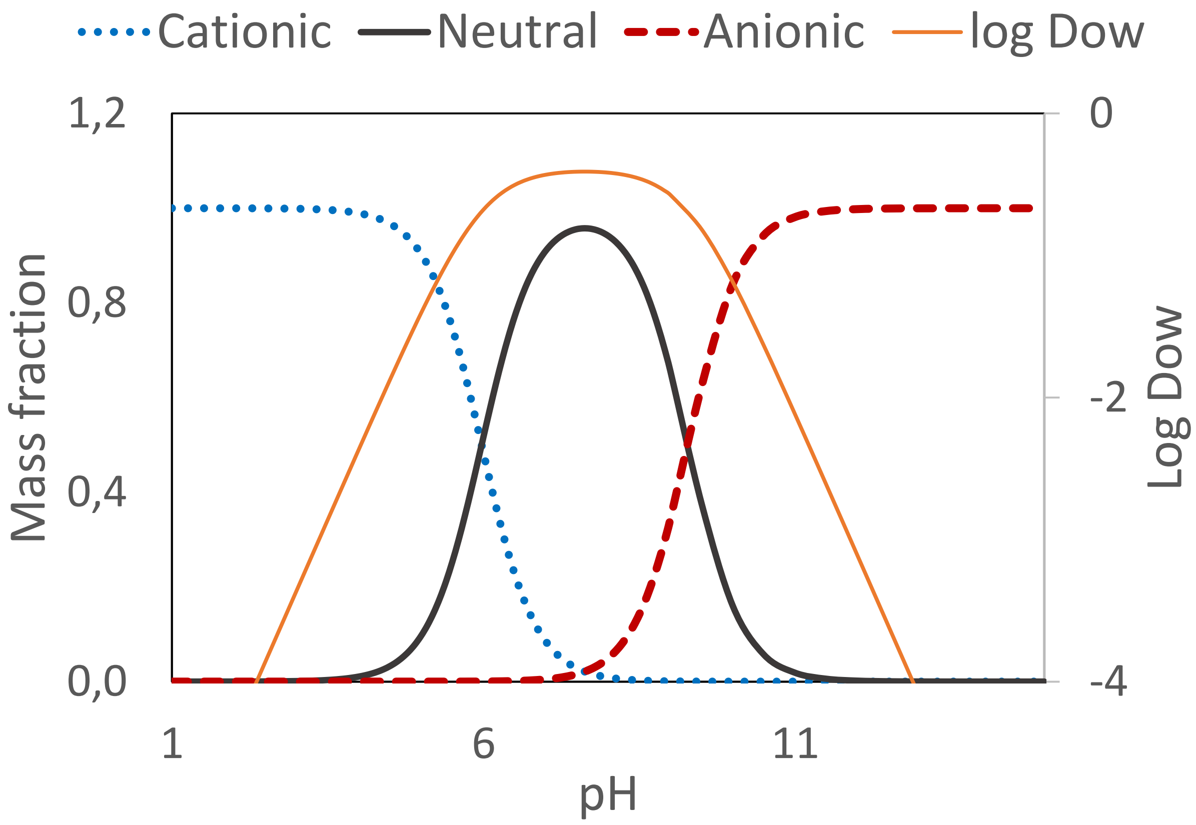
Compost, Woodchips, Biochar: **DOC release** and **sorption** site for neutral compounds

Biochar, Clay, Zeolite: **sorption** sites

Material	pH	CE µS/cm	Surface BET (m^2/g)	COT % (480ºC)	Si mg/Kg	Fe mg/Kg
Sand	8.5	32.8	1.6	0.7	58.2	20.97
Compost	7.8	192.2	4	21.0	77.0	12.37
Clay	8.7	62.7	23	3.1	67.6	4.67
Zeolite	6.3	6.1	33	3.7	114.2	6.72
Woodchips (pine)	5.3	69.1	0	94.83	17.11	2.60

Selection of organic molecules with a wide range of Pka and Kow values

	pKa		log Kow
acetominofen	-4,4	9,38	0,46
Carbamazepine	-3,8	13,9	2,45
Oxazepam	1,55	10,9	2,24
Sulfamethoxazole	1,6	5,7	0,89
Fenofibric acid	3,1		4,45
Diazepam	3.4		2,82
Diclofenac	4.15		4,51
Ketoprofen	4,45		3,12
Ibuprofen	4,9		3,97
Ofloxacin	5,97	9,28	-0,39
Benzophenone-1	7.1		3,18
Benzophenone-3	7,1		3,79
Benzotriazole	8,37		1,44
Propanolol	9,42		3,48
Atenolol	9,6		0,16
Venlafaxine	10,1		3,2



We determined the sorption capacity of the 5 materials through Batch experiments (in triplicates) and we compared them to Sand capacity (reference)

Batch experiments (20 mL)
CECs concentration: 10 µg/L

Centrifugation
4000 rpm – 5 min

1 mL of extract

With **12 deuterated internal standards**

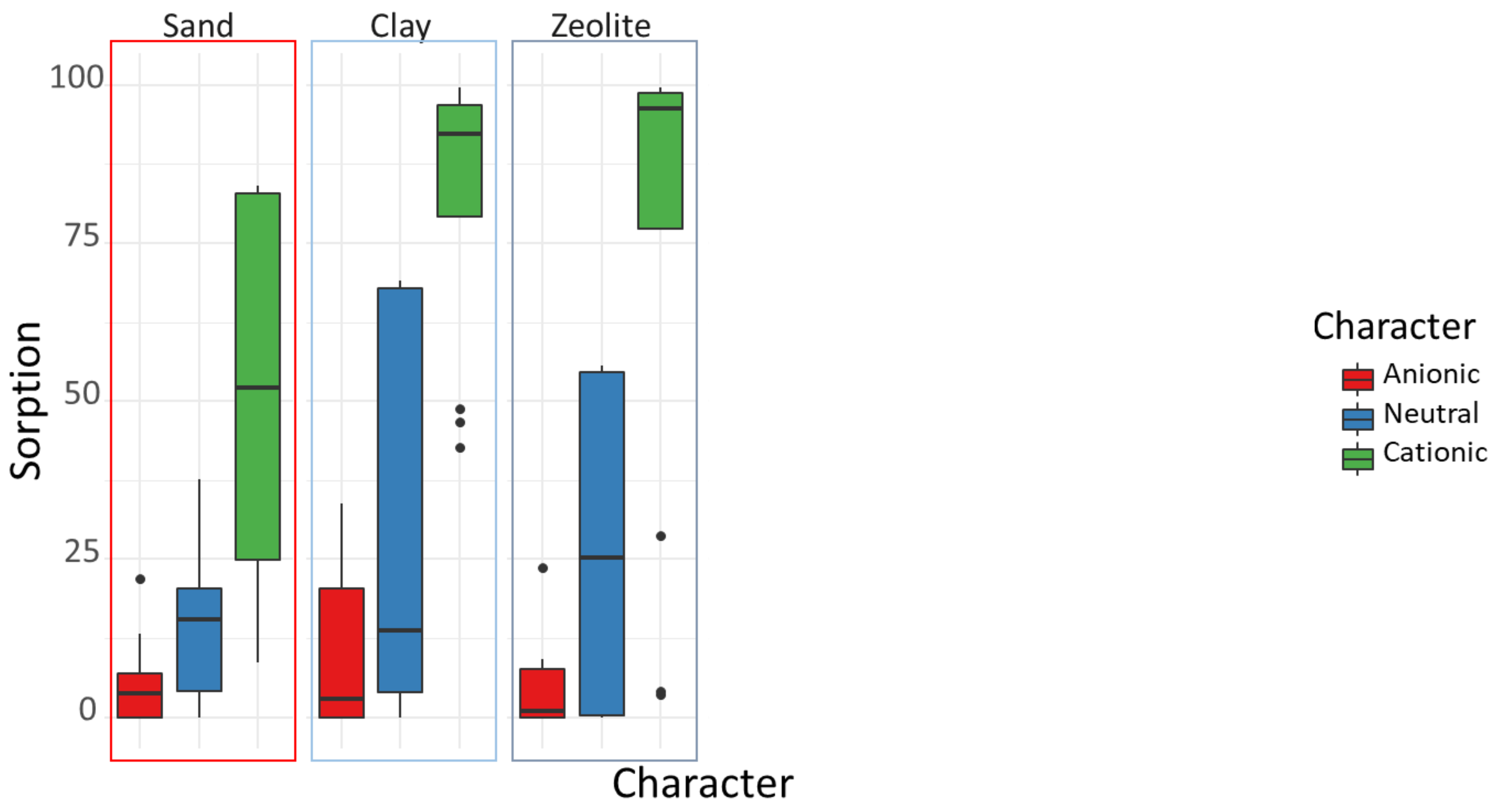
Filtration
Syringe filter PTFE 0,2 µm

HPLC-HRMS
Positive and negative mode

- **pH measurements** in water solution after batch experiments
- **Desorption tests** without CECs (blank experiments)
- **Batchs without materials** (Reference experiments in triplicate for all experiment series)

Limit of quantification:
Pharmaceutical compounds: 0.1-4 ng/L
UV-filters: 7-100 ng/L
No reconcentration

All five tested materials display higher sorption capacity than Sand



- Clay and zeolite display similar capacity to sorbed the tested molecules, coherent with their similar reactive area and organic carbon contain.

All five tested materials display higher sorption capacity than Sand

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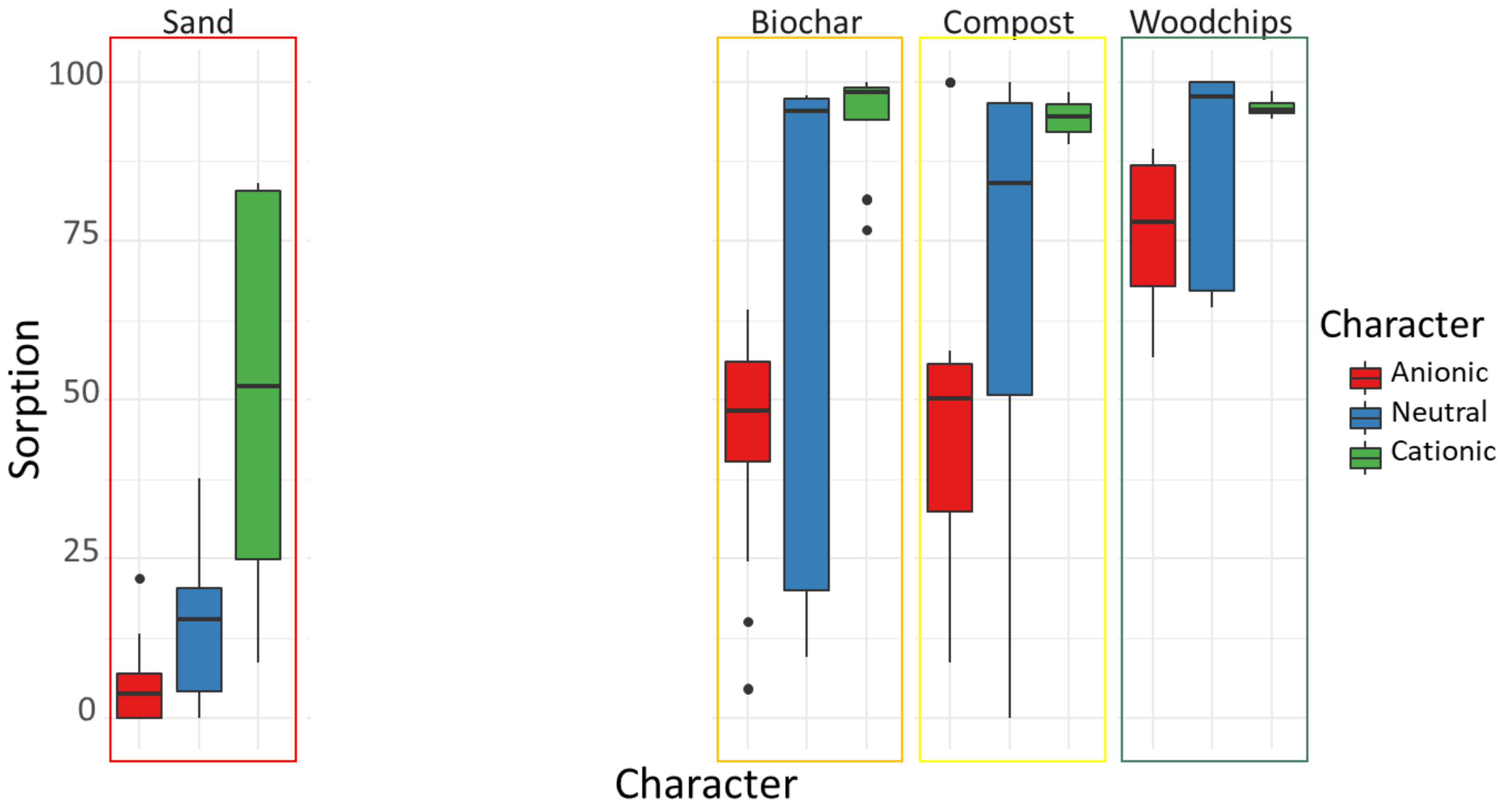

- Clay and zeolite display similar capacity to sorbed the tested molecules, coherent with their similar reactive area and organic carbon contain.
- Highly organic carbon contain materials displayed highly sorption capacity, especially Woodchips (is the material with lower pH)

Molecules ionization highly affect their sorption behavior

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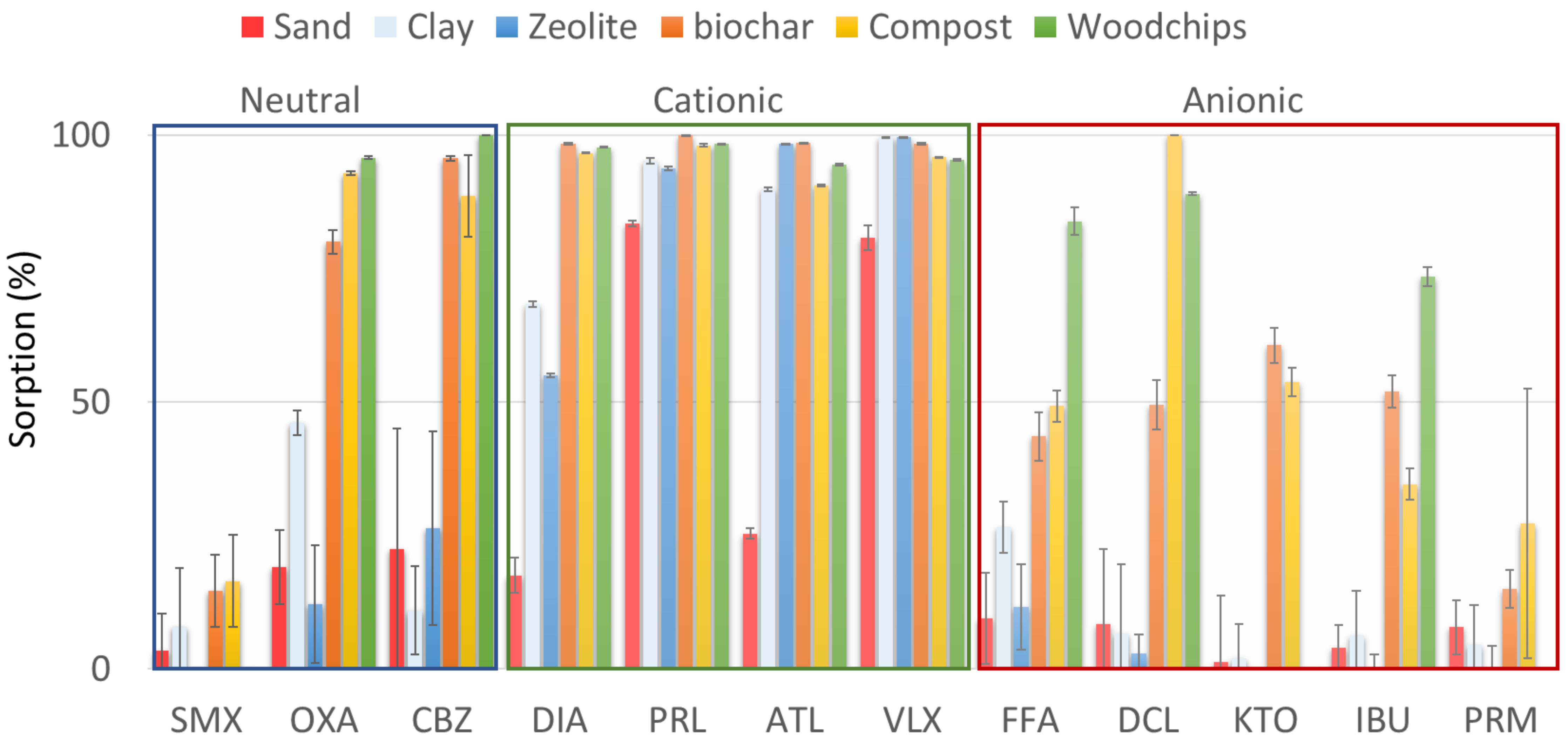

CONCLUSSIONS

- We have studied the sorption capacity of several sustainable materials to design a reactive barrier capable of reducing the concentration of organic molecules in the recharged water during SAT operations.

- The physicochemical properties of molecules and materials play a role in the sorption of contaminants, especially the molecules ionization and the organic carbon contain of the material.

- A mixture of different materials with different properties will be desirable to adsorb molecules exhibiting a wide range of pKa and log Dow.

Questions and/or Comments?

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