Microalgal-based carbon encapsulated iron nanoparticles as novel adsorbents for PFAS removal: from dye proxies to target compounds

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ELSEVIER

Journal of Environmental Chemical Engineering

Volume 14, Issue 3, June 2026, 122508

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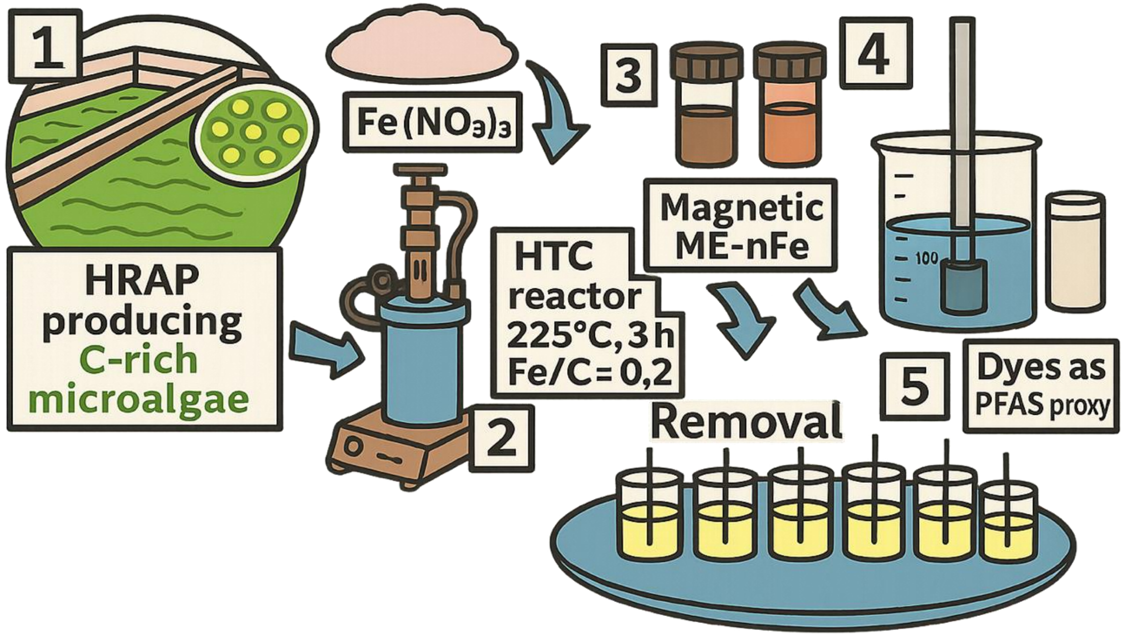
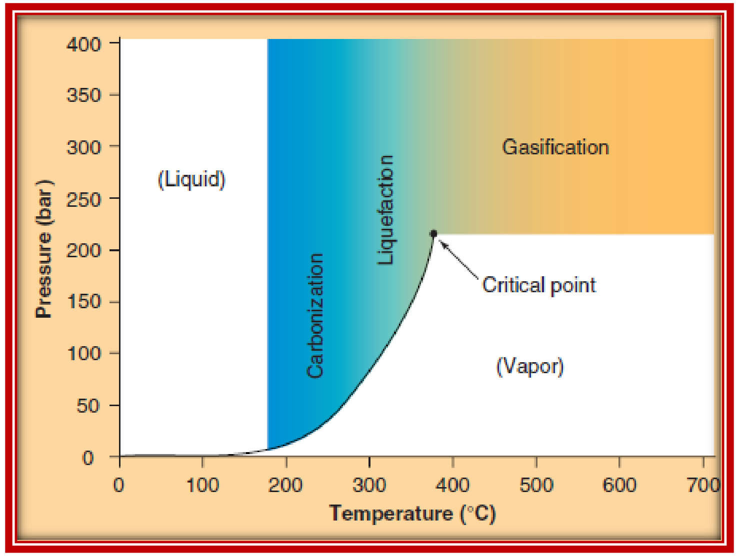
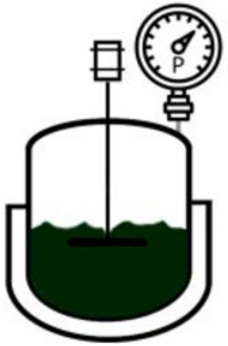


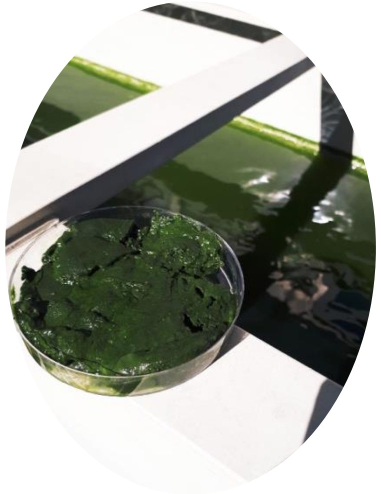
Microalgal-based carbon encapsulated iron nanoparticles (ME-nFe)



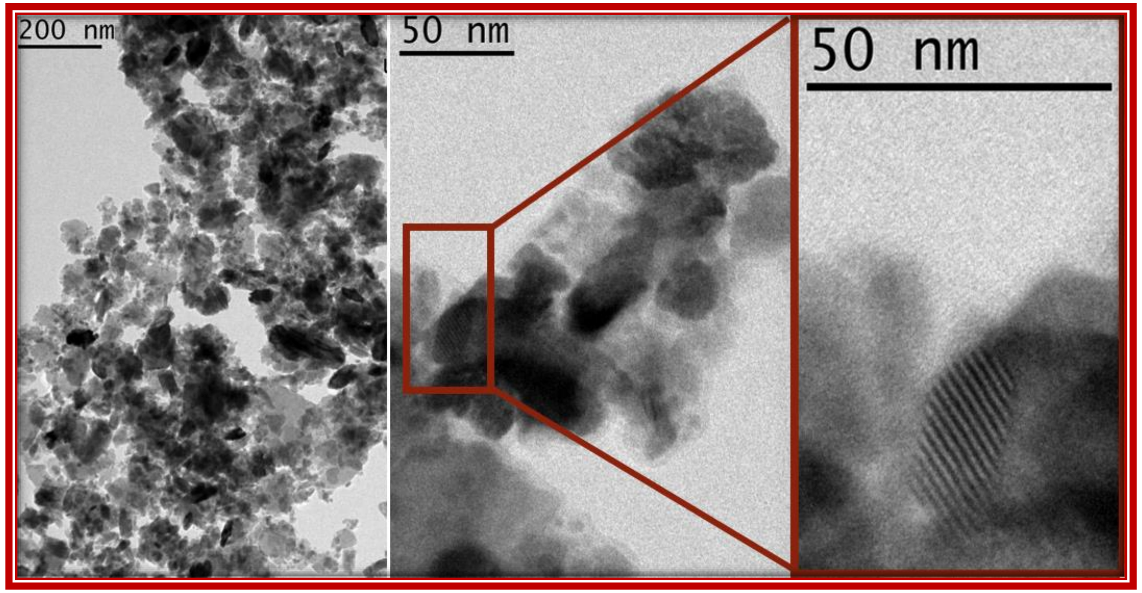
Hydrothermal processing conditions in the water phase
(Patrick Biller & Andrew B Ross (2012))

Hydrothermal carbonization (HTC)





- **Microalgae** biomass is mixed with **iron nitrate** in a proper ratio and the mixture undergoes **Hydrothermal Carbonization** (225°C, 30 bar, 3h)
- Water in the biomass lowers the activation energy of many chain reactions
- The biomass is de-structured, iron nanoparticles are formed and incapsulation in the algal biomass carbon matrix



Magnetic properties: recovery and reusability

Specific surface area 120 $m^2 \cdot g^{-1}$

ME-nFe

Porosity: macro, meso and micropores

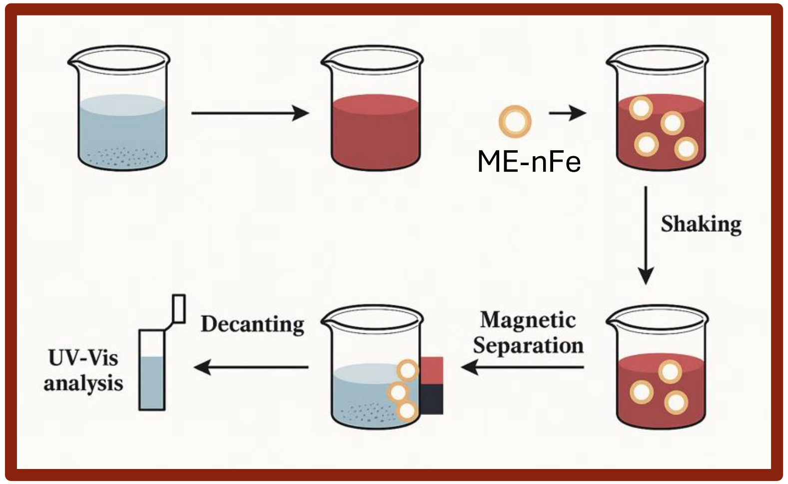
Fast sorption capacity: mesopouros

Morphology: carbon shell envelopes iron oxides (30% wt.) and metallic iron (8% wt.)

High reactivity

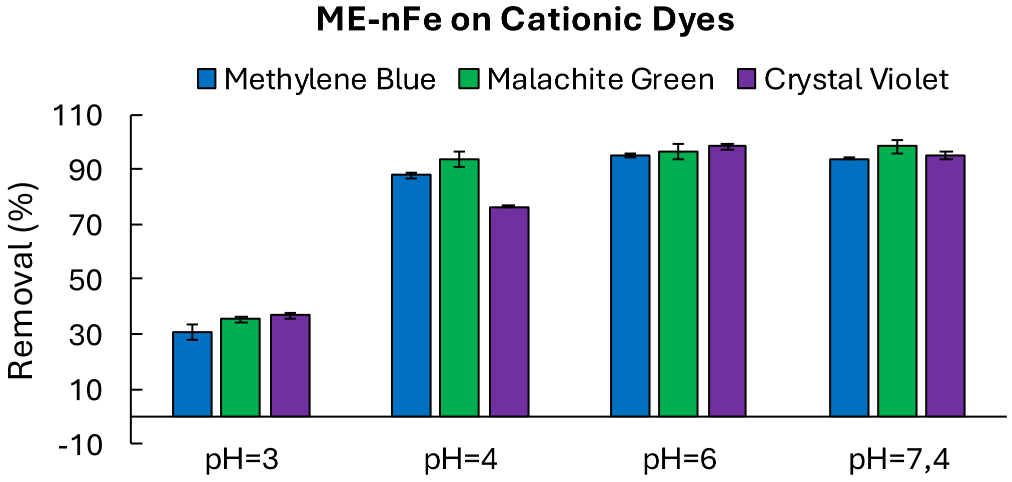
Can we use Dye Adsorption Experiments to predict PFAS removal?

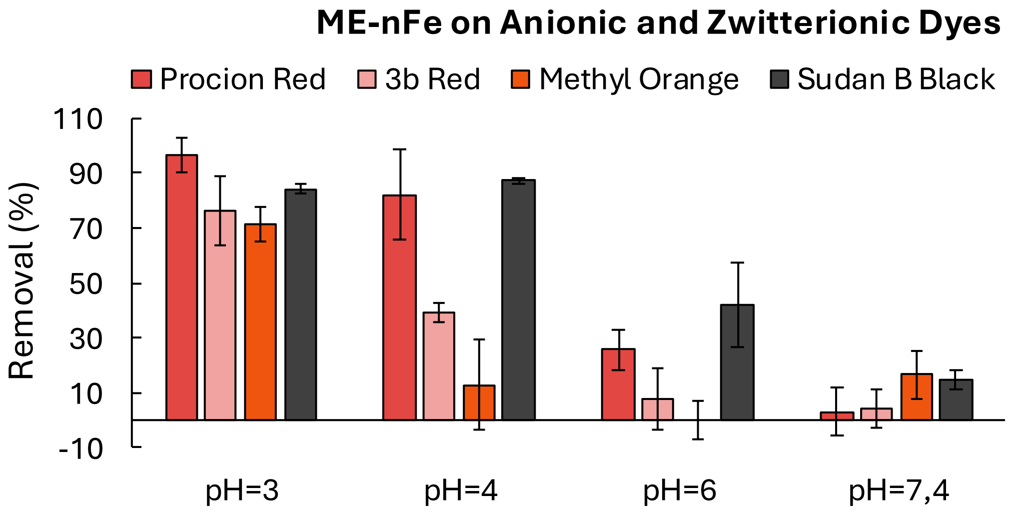
Equilibrium test:
ME-nFe: 1 g/L
30 minutes contact time
C_0: 1mg/L-2.5 mg/L of selected dyes in MilliQ water
pH: 3,4,6 and 7.4



The UV-vis determination allows for a **fast screening of many adsorption conditions** (contact time, dosage, concentrations, pH, matrix effects, type of adsorbent…)

The most promising condition can be selected **and applied for testing PFAS removal**





PFAS Adsorption experiments

Based on dyes removal, pH 3 and pH 6 were chosen for testing the ME-nFe on a water solution containing 10 PFAS

PFAS in the treated solution (≈ 15 µg/L PFAS):

Short chain (3 < C < 8) ⟶ PFBS, PFPeA, PFHxA, PFHpA

Long chain (8 ≤ C < 12) ⟶ PFOA, PFOS, PFNA, PFDA, PFUnDA, PFDoDA

Equilibrium test:

1-2 g/L ME-nFe

200 minutes contact time

UPLC-MS analysis

Main results:

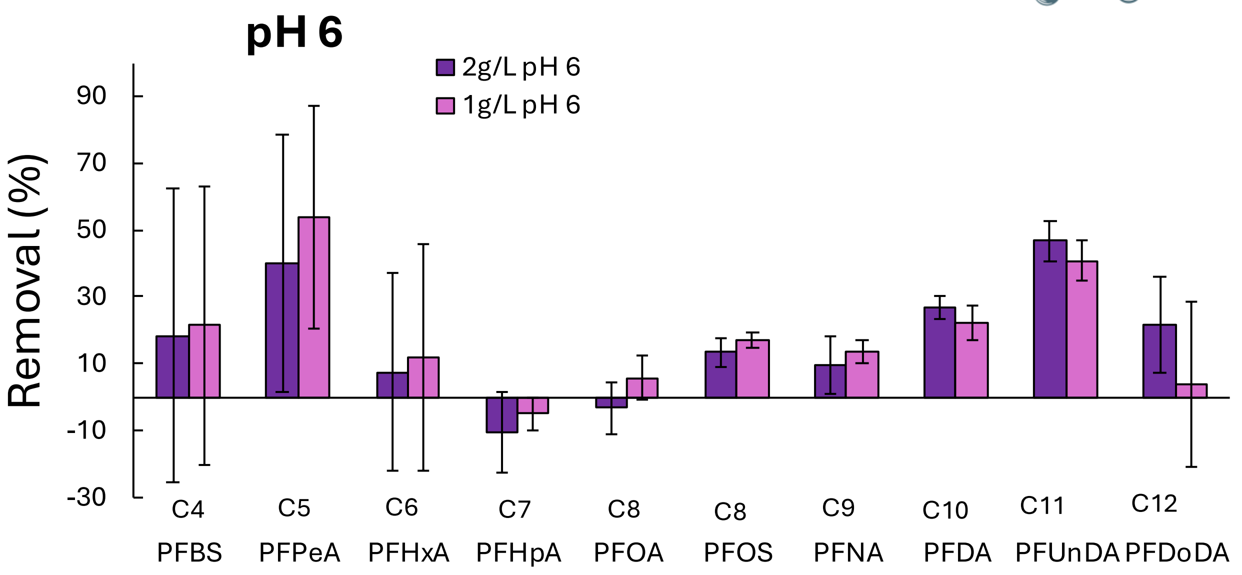
Low removal at **pH 6** for all the compounds

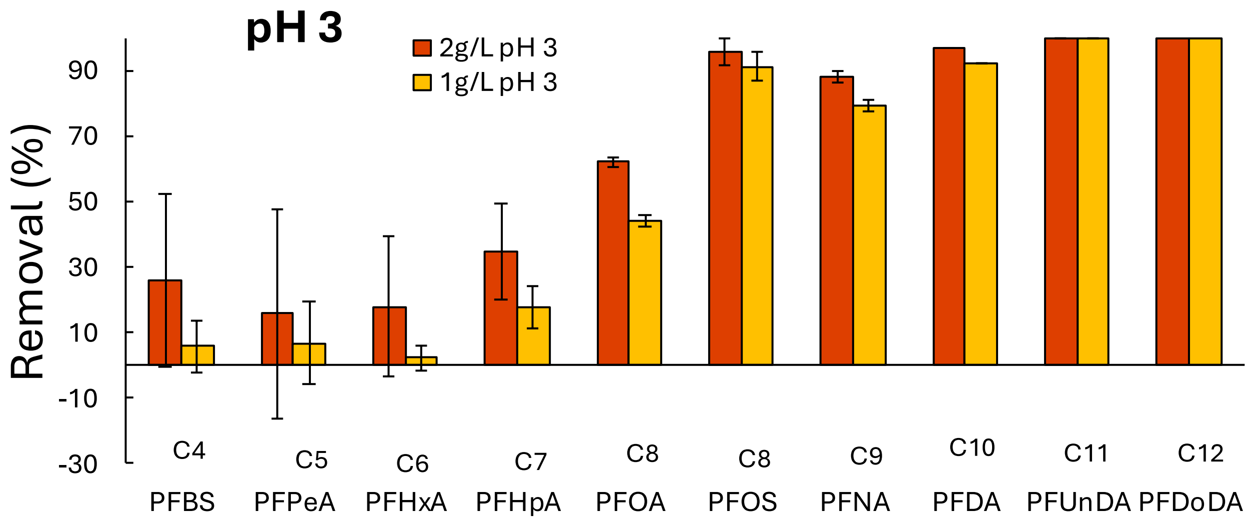
54% for PFPeA (C=5)

High removal at pH 3 for all C ≥ 8

>92% for PFOS, PFDA, PFUnDA, PFDoDA and >62% for PFOA

C < 8 ⟶ low removal



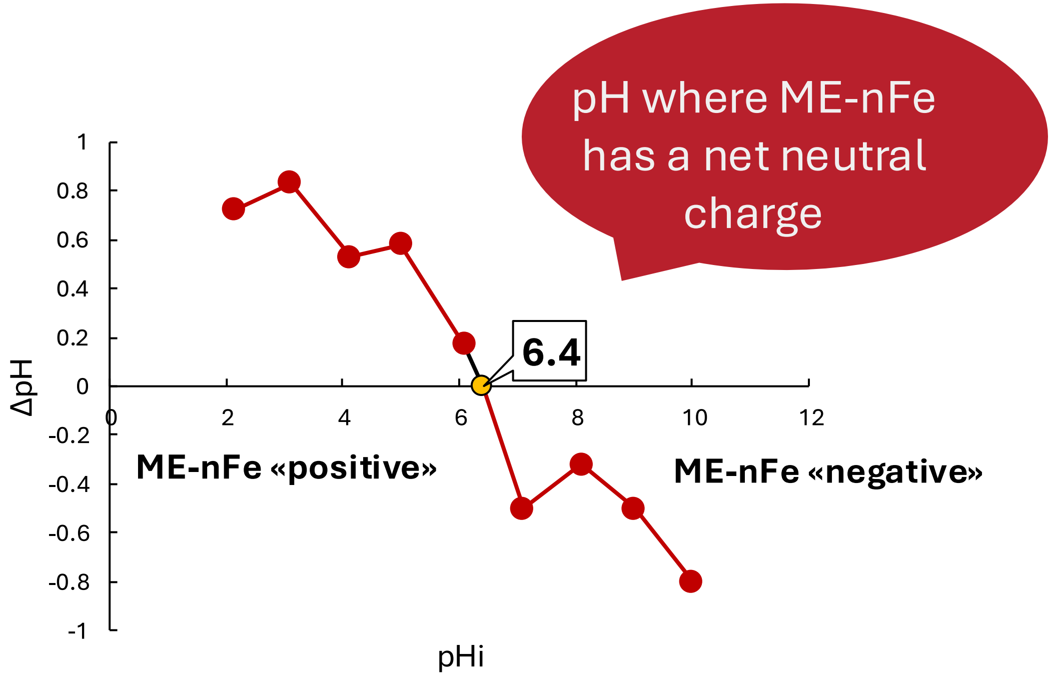


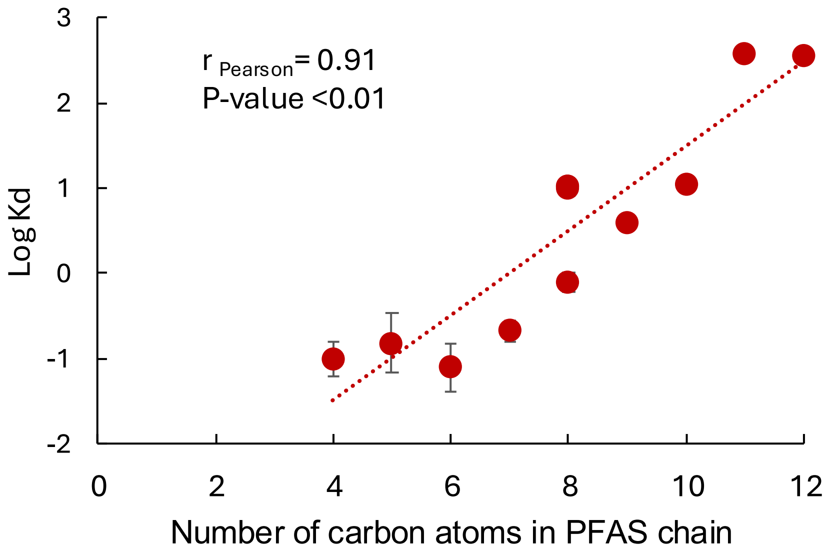
Interpretation of the results:

Affinity between PFAS, dyes and ME-nFe depends on:
PZC of ME-nFe, solution pH, pollutant pKa and PFAS chain length

pH < pH_PZC ⟶ ME-nFe have a **net positive charge**: **electrostatic attraction** with medium/long-chain **PFAS** and **anionic dyes**; **electrostatic repulsion** with **cationic dyes**

pH > pH_PZC ⟶ ME-nFe have a **net negative charge**: **electrostatic attraction** with **cationic dyes**;
repulsion for PFAS





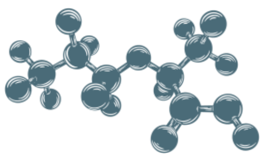
Dye–PFAS correlation: can these dyes be used as proxies?

The **affinity** of each **dye** and **PFAS** for **ME-nFe** was deduced by calculating their experimental **Distribution Coefficient** (Kd) at the same treatment condition (pH and ME-nFe dosage)

$$Log\ K_d = \text{Log}\ \frac{C_{sorbent}}{C_{water}}$$

Each dye and **PFAS** was coupled to evaluate the relation:

Δ Log Kd= Log Kd $_{PFAS}$- Log Kd $_{Dye}$



pH 3

Δ Log Kd Table	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFOS
Methyl orange	-1.21	-1.50	-1.07	-0.50	0.19	0.66	2.18	2.15	-1.41	0.62
Methylene blue	-0.45	-0.74	-0.32	0.26	0.95	1.42	2.94	2.91	-0.65	1.38
Malachite Green	-0.53	-0.82	-0.39	0.18	0.87	1.34	2.86	2.83	-0.73	1.30
Procion Red	-1.88	-2.17	-1.74	-1.17	-0.48	-0.01	1.51	1.48	-2.08	-0.05
Crystal Violet	-1.14	-1.43	-1.00	-0.43	0.26	0.73	2.25	2.22	-1.34	0.69
3b Red	-1.41	-1.71	-1.28	-0.70	-0.01	0.46	1.98	1.95	-1.62	0.41
Sudan B Black	-1.34	-1.63	-1.20	-0.63	0.06	0.53	2.05	2.02	-1.54	0.49

pH 6

Δ Log Kd Table	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFOS
Methyl orange	1.09	0.09	-0.36	-0.16	0.04	0.30	0.69	-0.03	-0.07	0.20
Methylene blue	-0.88	-1.88	-2.33	-2.13	-1.93	-1.67	-1.28	-2.00	-2.03	-1.77
Malachite Green	-0.93	-1.93	-2.38	-2.18	-1.98	-1.72	-1.33	-2.05	-2.09	-1.82
Procion Red	0.64	-0.36	-0.81	-0.61	-0.41	-0.15	0.24	-0.48	-0.51	-0.25
Crystal Violet	-0.62	-1.62	-2.07	-1.88	-1.67	-1.41	-1.03	-1.74	-1.78	-1.51
3b Red	0.99	-0.01	-0.47	-0.27	-0.07	0.19	0.58	-0.14	-0.17	0.10
Sudan B Black	0.44	-0.56	-1.02	-0.82	-0.62	-0.36	0.03	-0.69	-0.72	-0.45

No similarity	Δ Log Kd < –0.3 The dye was removed more than the PFAS
High similarity	Δ Log Kd≤ **0.1** Dye and PFAS have the same affinity for ME-nFe.
Moderate similarity	**0.1 ≤ Δ Log Kd ≤ 0.2 Dye and PFAS have similar affinity for ME-nFe.**
Low similarity	0.2 ≤ Δ Log Kd ≤ 0.3 Dye and PFAS **have low affinity** for ME-nFe.
No similarity	Δ Log Kd > 0.3 The PFAS was removed more than dye

Dye–PFAS correlation: Which dye can be used as proxy?

$$Log\ K_d = \text{Log}\ \frac{C_{sorbent}}{C_{water}}$$

At pH 3 the best correlation were:

Procion Red MX-5B ⟶ PFOS and PFDA;

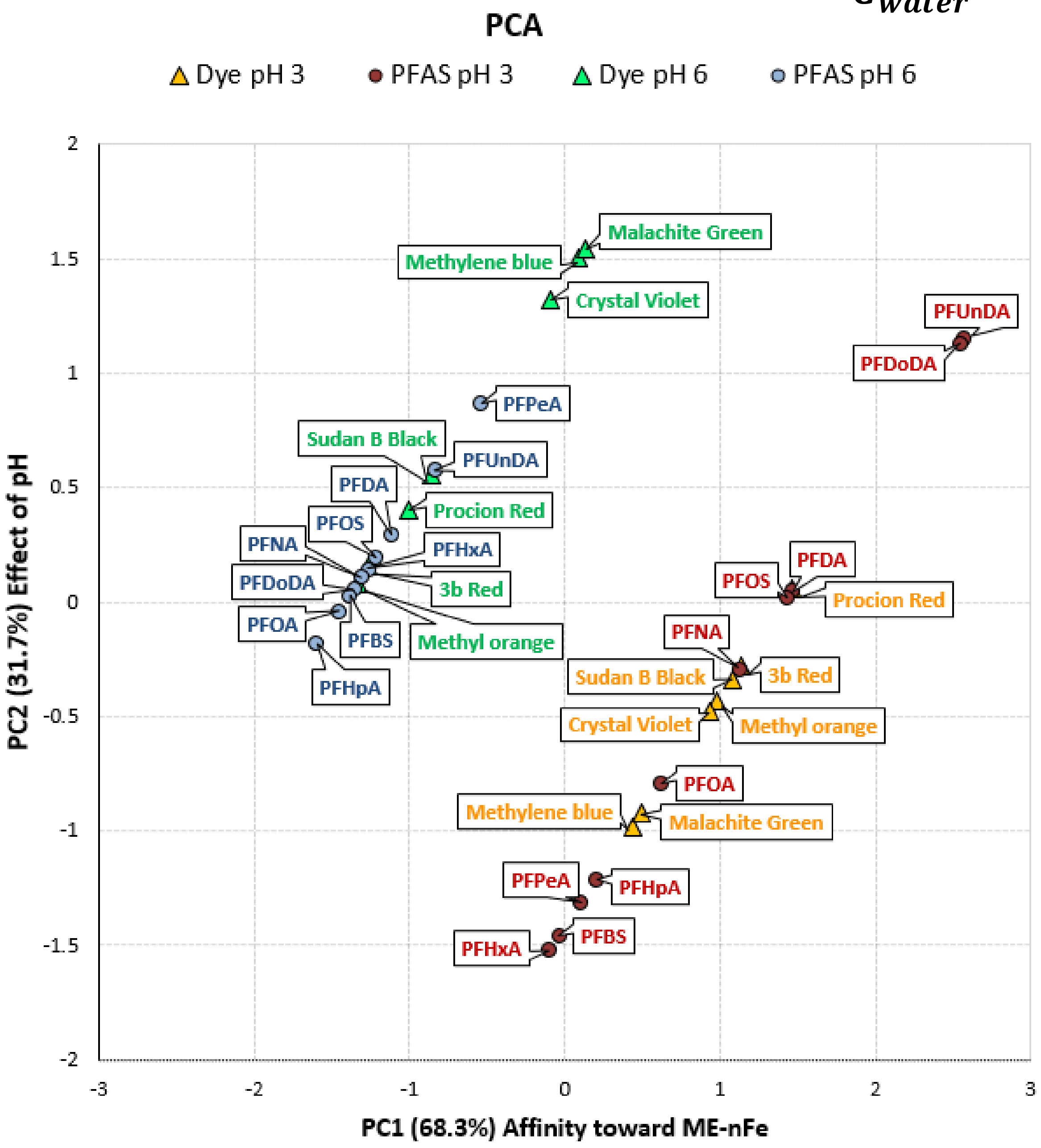
Cibacron Brilliant Red 3B-A, **Sudan Black B**, **(Methyl Orange)** } PFNA

Malachite Green, **Methylene Blue** } PFOA

At pH 6 the best correlation were:

Sudan Black B ⟶ PFUnDA

Cibacron Brilliant Red 3B-A, **Methyl Orange** } PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFBS



Conclusion:

ME-nFe nanoparticles **remove PFAS from water** at concentrations comparable to industrial wastewaters (µg/L), **but are effective mainly at acidic pH**

Selected **dyes can be used as PFAS proxies**, especially anionic dyes (Procion Red MX-5B; Cibacron Brilliant Red 3B-A; Sudan Black B and Methyl Orange)

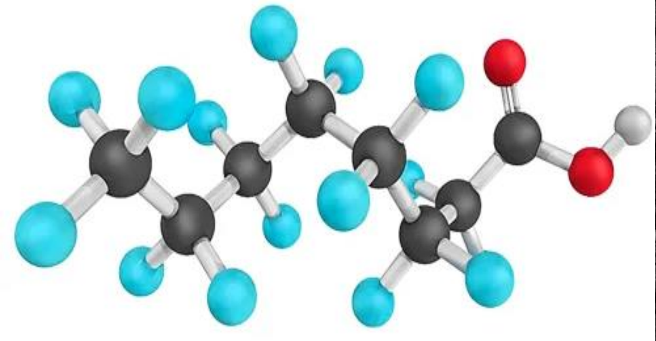
Testing these dyes **first** can be useful to avoid many costly HPLC analysis, **identifying the most promising conditions for removing PFAS**

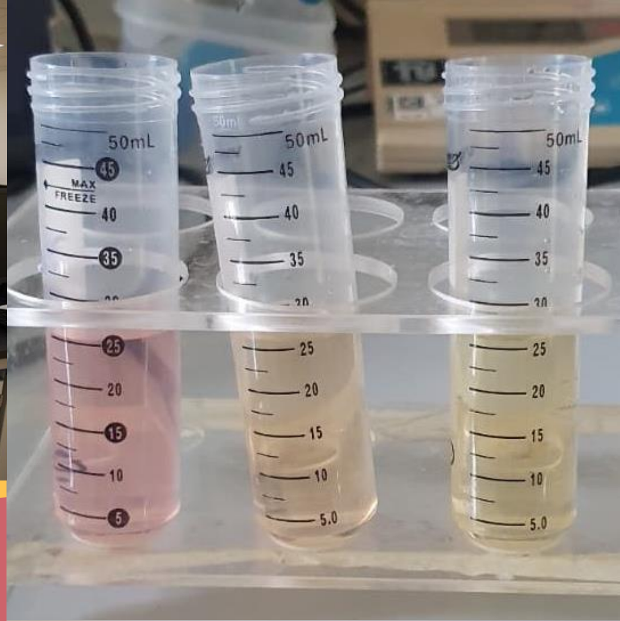
Microalgal biomass is an effective, sustainable matrix for HTC iron nanoparticles production. It can be obtained by alternative biological treatment processes performed to remove nutrients and other pollutants from wastewaters or digestates

⟶ lower costs, lower environmental impact

Work in progress:

Making **ME-nFe effective at neutral pH** by post modifications to improve their application even in more complex matrices (urban wastewaters and groundwater). The **new Adsorbents can be tested first on proxy dyes**, saving time and effort and later used on **PFAS**.





THANK YOU
FOR YOUR ATTENTION!

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