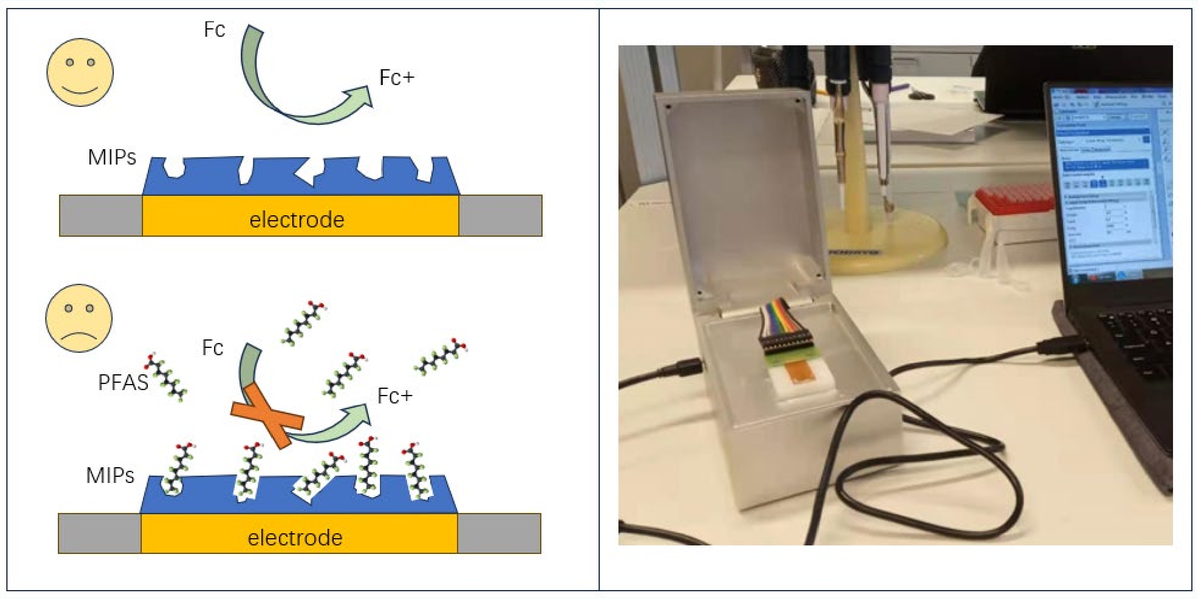
MIP ENABLED PFAS SENSOR

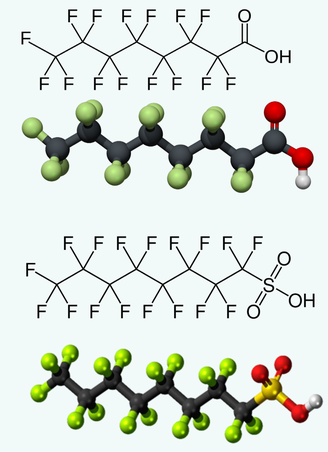
Xiaojun Yang, Tijs Bitter, Bert Swennenhuis, Martin Bennink

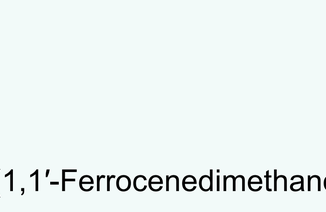
Applied Nanotechnology Research Group, Saxion University of Applied Sciences, Enschede/Deventer, The Netherlands

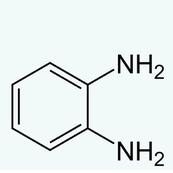
Introduction



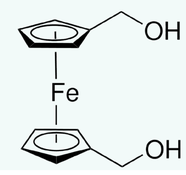
- PFAS (Per- and polyfluoroalkyl substances) are persistent contaminants with background levels of 1.4 µg/kg **PFOS** (Perfluorooctanesulfonic acid) and 1.9 µg/kg **PFOA** (Perfluorooctanoic acid) in Dutch soil [1].
- Current lab methods (e.g., chromatography coupled with mass spectroscopy) are expensive and slow (~200 pM detection limit) [2-3].
- Goal: Develop a portable MIP-based (Molecularly Imprinted Polymer) electrochemical PFAS sensor for on-site detection.
- Method: MIP sensing uses electro-polymerized o-PD (o-phenylenediamine) to create selective cavities for PFAS, reducing redox mediator (Fc, 1,1′-Ferrocenedimethanol) current upon rebinding.





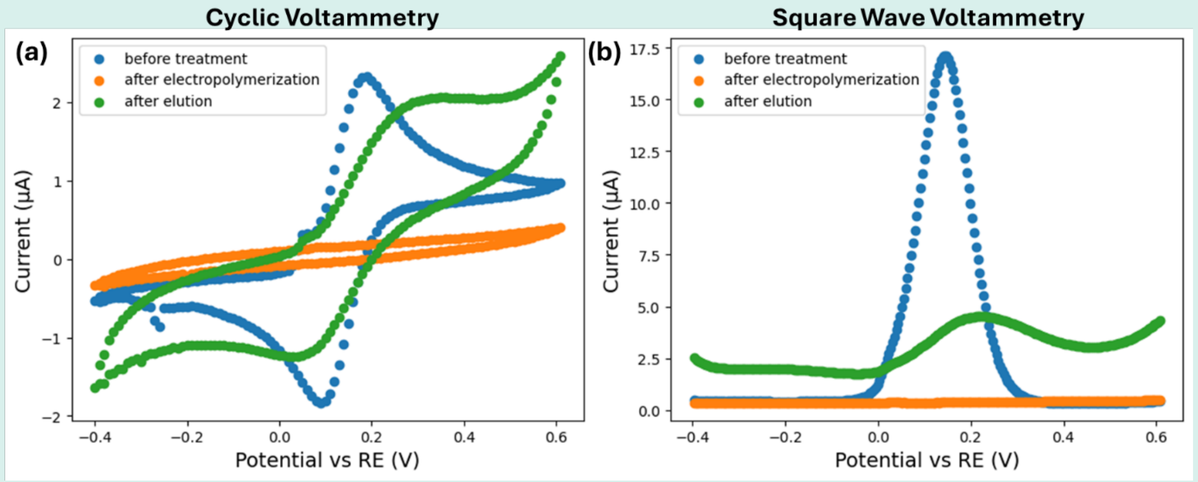


o-PD (o-phenylenediamine)



Fc (1,1′-Ferrocenedimethanol)

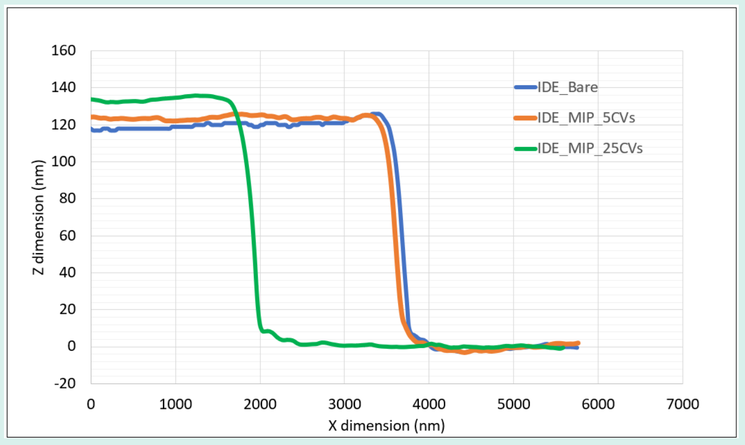
MIP Electro-Polymerization



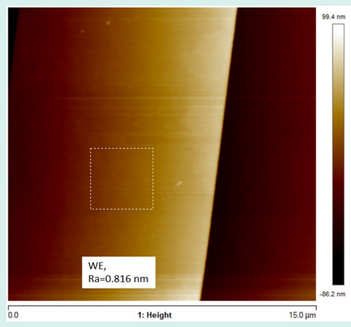
CV (left, cyclic voltammetry) and SWV (right, square wave voltammetry) measurements of the MIP formation on a CSPE (carbon screen printed electrode), performed in 2 mM Fc with 10 mM ammonia buffer pH 8.4.

- MIP layers successfully formed on CSPE (carbon screen printed electrode), glassy carbon macroelectrode, and gold microelectrodes via o-PD electropolymerization.
- Electropolymerization creates a polymer layer with PFAS trapped inside → Fc can not reach the electrode surface → current drops to near zero.
- Elution with methanol: water (1:1) for 15 min removes PFAS, creating cavities → current increases .
- adding 30% methanol during electropolymerization enhances layer stability.

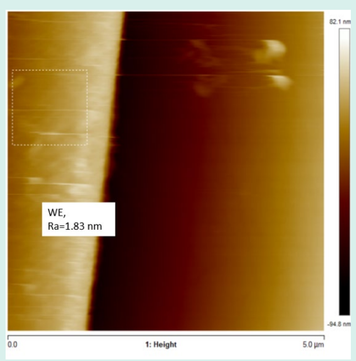
AFM (Atomic Force Microscopy)



AFM measurements on a bare IDE , IDEs with 5 and 25 cycles of electropolymerization.



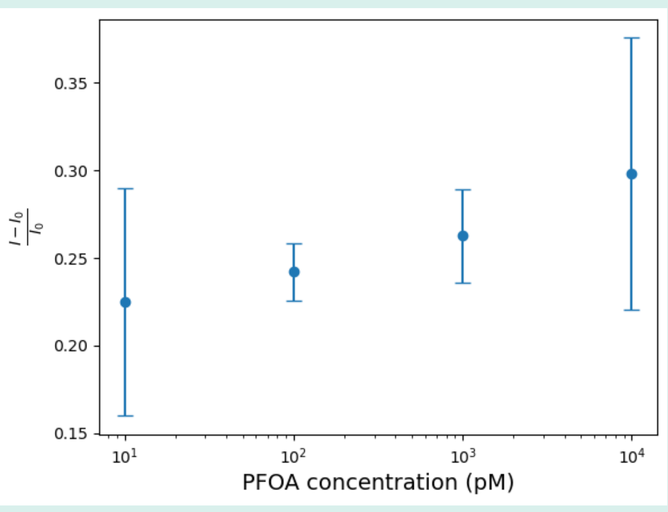
Bare working electrode



MIP coated working electrode.

- AFM assessed MIP thickness on IDE (interdigitated electrodes), at 4-20 nm.
- Thickness correlates with electro-polymerization voltammetry cycles , 5 and 25 cycles (a cycle process lasts 40 seconds).
- Roughness of MIP coating is significantly higher than bare electrode.

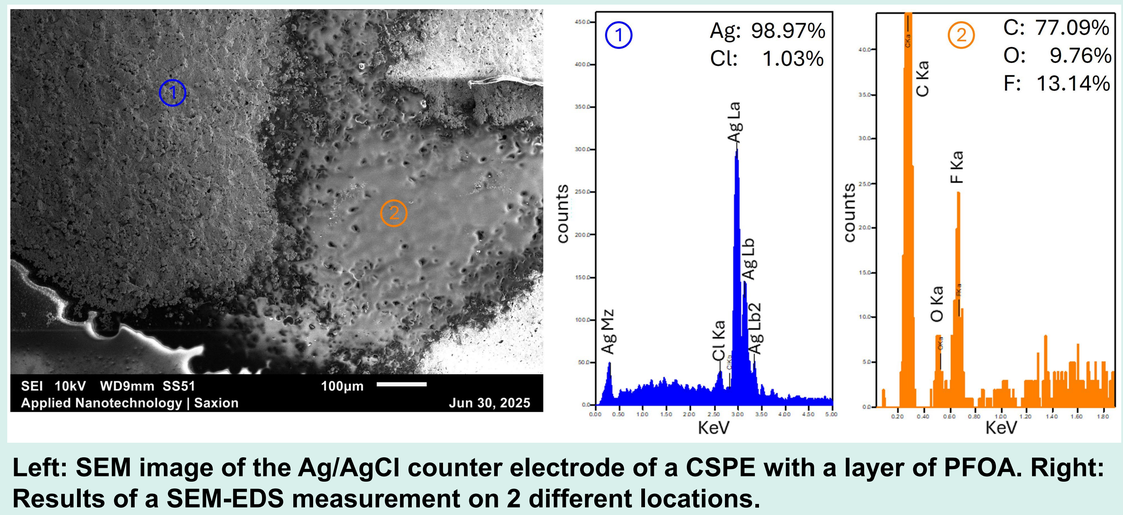
PFOA Rebinding Test



Normalized peak current changes from SWV (square wave voltammetry) measurements vs. PFOA concentrations, performed in 2 mM Fc and 10 mM ammonia buffer pH 8.4 spiked with various PFOA concentrations with an incubation time of 30 minutes .

- The peak current does not decrease after increasing the PFOA concentration; however, it increases.
- This counterintuitive response, seen in both MIP and bare electrodes, points to non-specific PFOA effects overriding MIP binding.
- Potentially due to adsorption or mediator interactions, undermining the expected correlation with concentration.

SEM-EDS (Scanning Electron Microscopy with Energy Dispersive X-ray)



Left: SEM image of the Ag/AgCl counter electrode of a CSPE with a layer of PFOA. Right: Results of a SEM-EDS measurement on 2 different locations.

- SEM-EDS can be used to measure thick PFOA layer.
- The MIP layer is too thin to be analyzed, as the SEM-EDS has a measuring depth of around 500 - 3000 nm.

Conclusions

- MIP layers were prepared on various electrodes with stable electrochemical signals.
- Varying the electropolymerization time gives control over the thickness of the MIP layer.
- Challenges: Unexpected signal upon sensing PFOA, and SEM-EDS limitations.

Future Work

- Experiments: Test PFOS with adjusted concentrations.
- Techniques: Use EIS and SEM-EDS for better characterization.
- Adjustments: Explore other PFAS and MIP agents.

Acknowledgment

Mandy ten Bloemendal (Saxion researcher)
Femke van Ederen (Saxion student)
Yoran Raben (Saxion student)