

Electrochemical Approaches for Monitoring PFOA in Aqueous Environments

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Summary:

Perfluorooctanoic acid (PFOA) is commonly used as a marker of per- and polyfluoroalkyl substances (PFAS) contamination in aqueous environments due to its persistence and widespread occurrence. This work explores electrochemical approaches for PFOA monitoring, combining interfacial studies at electrode surfaces with the development of selective sensing materials. Molecularly imprinted polymers (MIPs) are investigated as recognition elements, while complementary electrochemical analyses are performed to identify suitable transduction mechanisms.

Keywords: PFAS, PFOA, electrochemical sensors, MIP, EIS

Background, Motivation and Objective

Per- and polyfluoroalkyl substances (PFAS) are persistent pollutants associated with adverse effects on human health and the environment. Their widespread use and resistance to degradation have led to increasing regulatory pressure to monitor and limit their presence in water systems. However, effective mitigation requires reliable detection: contaminants must first be identified and quantified before they can be controlled or eliminated.

In this context, PFOA is commonly used as a marker of PFAS contamination.[1] The objective of this work is to explore electrochemical strategies for its detection, aiming for selective response and low detection limits compatible with current and emerging regulatory requirements. Particular attention is given to interfacial phenomena and the development of selective recognition layers, such as molecularly imprinted polymers.

Description of the New Method or System

Due to the high chemical stability and low intrinsic electroactivity of PFOA, direct electrochemical detection is challenging. This work proposes a detection strategy based on interfacial phenomena. The approach exploits the adsorption properties of the carboxylic group of PFOA at electrode interfaces, either on platinum (Pt) surfaces or on electrodes modified with quaternary ammonium functional polymers. These interactions alter the structure of the electrochemical

double layer. The resulting changes in double-layer capacitance are measured and quantified using electrochemical impedance spectroscopy as a function of PFOA concentration.

In parallel, MIP nanoparticles are synthesized and deposited on electrode surfaces to introduce molecular selectivity. In this case, detection relies on an indirect (mediated) mechanism, where binding events within the imprinted sites modulate the electrochemical response of the interface. [2]

Results

The voltammetric behaviour of PFOA was first investigated at platinum (Pt) electrode surfaces using microfabricated silicon-based electrodes. Measurements were performed in both acidic (50 mM H₂SO₄) and carbonate (0.5 M K₂CO₃) electrolytes (Fig. 1).

Under these conditions, PFOA does not appear fully electrochemically inert. At higher concentrations (≈ 1 mM), an oxidation peak is observed starting at around 0.6 V vs. reference electrode. More notably, significant modifications are observed in the hydrogen underpotential deposition (HUPD) region, along with changes in the double-layer current. These features suggest specific adsorption of PFOA molecules at the Pt surface. The observed oxidation process at higher potentials may be associated with adsorbed species, although the mechanism is not yet fully understood and requires further investigation.

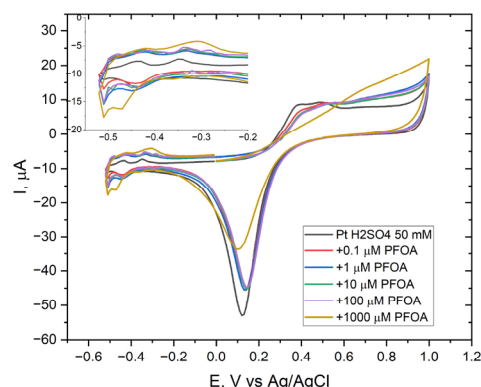


Fig. 1. Cyclic voltammograms of PFOA at a Pt electrode in 50 mM H_2SO_4 at varying concentrations (scan rate: 100 mV s^{-1}).

Based on these observations, changes in the electrochemical double-layer capacitance were quantified using electrochemical impedance spectroscopy. Measurements were performed at -0.2 V vs. reference electrode, and capacitance values were extracted at 100 Hz. A dependence of capacitance on PFOA concentration was observed, confirming that interfacial adsorption significantly influences the electrochemical response.

The obtained capacitance values are summarized in Fig. 2, comparing measurements in acidic and carbonate electrolytes, as well as results obtained with bare Pt electrodes and Pt electrodes modified with an anion exchange membrane (AEM, Fumatech®). The capacitance shows distinct trends depending on the electrolyte and surface modification. In acidic conditions (H_2SO_4), capacitance decreases with increasing PFOA concentration, consistent with surface adsorption and partial blocking of the electrode. In contrast, in carbonate electrolyte, a slight increase is observed, suggesting a different interfacial organization. The presence of the AEM layer leads to lower and more stable capacitance values, indicating a modified interaction mechanism. Overall, these results highlight the strong influence of both electrolyte composition

and surface functionalization on PFOA interfacial behavior.

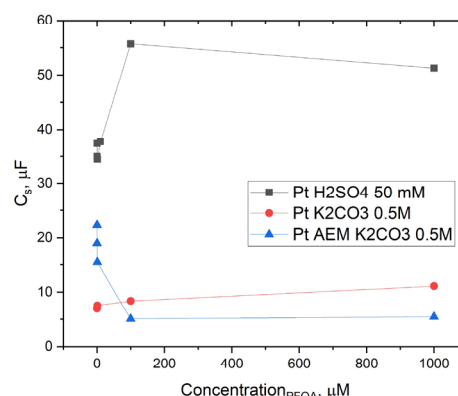


Fig. 2. Evolution of double-layer capacitance with PFOA concentration at Pt and AEM-modified Pt electrodes in different electrolytes, extracted from EIS measurements at 100 Hz.

Conclusions

This work demonstrates that PFOA, despite its low intrinsic electroactivity, can be detected through adsorption-induced modulation of interfacial electrochemical properties. The observed dependence of capacitance on electrolyte composition and surface modification highlights the complexity of the sensing mechanism, which requires further investigation. Nevertheless, these findings establish a foundation for adsorption-based electrochemical detection strategies. The integration of MIP modified electrodes, aimed at enhancing selectivity, will be discussed.

References

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