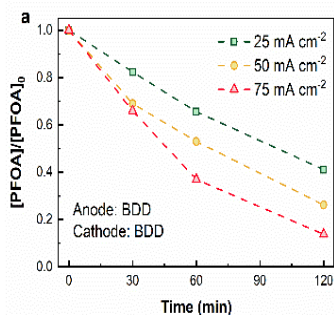# Electrochemical Elimination of Perfluoroalkyl Substances (PFAS): Understanding the Role of Cathode Materials

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Poly- and perfluoroalkyl substances (PFAS) represent a significant public health concern in water contamination. Various treatment methods have been explored, including adsorption, thermolysis, plasma, and biological treatment. However, addressing PFAS contamination is complicated by their low concentrations and the high energy demands of conventional treatment approaches. Among advanced oxidation processes, electrochemical oxidation has emerged as a promising method for PFAS removal, initially thought to be solely dependent on the anode. However, recent studies have highlighted the role of the cathode in the defluorination process. This study investigates the influence of cathode materials on removing perfluorooctanoic acid (PFOA) at low concentrations. The use of BDD, Pt, graphite, stainless steel, and Ti as cathodes was evaluated in single and divided cell configurations. Pt cathode demonstrated higher participation in the PFOA removal than other materials with high PFOA reduction rates. The findings provide insights into system optimization, emphasizing the importance of selecting suitable materials for both the cathode and the anode in the electrochemical treatment of PFAS.

Introduction

Poly- and perfluoroalkyl substances (PFAS) represent a diverse group of compounds utilized as surfactant additives, characterized by a hydrophobic fluorinated carbon chain and a polar group. Over the last decade, these chemicals have undergone rigorous toxicity evaluations, revealing their extreme danger to public health. Among PFAS compounds, perfluorooctanoic acid (PFOA) is particularly concerning, with an ultra-low maximum contaminant level of 4 ng L^{-1}. Consequently, numerous studies have focused on developing methods for eliminating PFOA and related compounds. Various approaches have been evaluated, including adsorption, biological treatment, plasma, thermolysis, and advanced oxidation processes (AOPs) [1]. However, these methods have highlighted the recalcitrant nature of PFAS compounds, with their low concentrations posing a significant challenge during treatment.

In the AOPs frame, electrochemical oxidation has been investigated for PFOA removal, with the assumption that removal primarily occurs at the anode. Nevertheless, recent studies suggest that the defluorination process also takes place at the cathode, indicating its crucial role in PFOA elimination [2]. Therefore, understanding the contribution of the cathode in this process is an essential yet unexplored parameter that requires attention.

In this study, we evaluate for the first time the performance of boron-doped diamond (BDD) anodes and various cathode materials, such as graphite carbon (GC), stainless steel (SS), platinum (Pt), and titanium (Ti). We assess environmentally relevant concentrations of PFAS and utilize higher concentrations for analytical measurements to identify degradation products and fluoride release. Through this investigation, we aim to elucidate the role of cathode materials in electrochemical setup for PFAS elimination.

Material and Methods

The evaluation of electrodes was conducted using both H-type and single-chamber cells. A BDD electrode was used as a anode, and different materials as cathode. A synthetic solution containing PFOA at a concentration of 100 $\mu g\ L^{-1}$ was utilized to simulate environmental conditions. For analytical measurements, a PFOA concentration of 1 mg L^{-1} was employed to assess total organic carbon and fluoride release.

Using a both cell configurations, different current densities, ranging from 5 to 75 mA cm^{-2}, were applied during 2 h. Samples were withdrawn for PFOA determination using ultra-high pressure liquid-chromatography coupled to tandem mass spectroscopy (UHPLC-MS/MS). Total organic carbon was determined using a Shimadzu TOC analyzer, while fluoride concentration was measured using Shimadzu Ion chromatography.

Results and Discussion

The H-cell configuration utilized a Nafion membrane to separate the anolyte and catholyte compartments. Blank experiments were conducted to ensure there was no diffusion, adsorption, or accumulation of PFOA within the system. Subsequently, the cathode role evaluation was performed in a divided H-cell with identical initial PFOA concentrations to detect the decay in both chambers during electrolysis at fixed current densities (25, 50, and 75 mA cm^{-2}).

Moreover, under identical conditions for high concentration PFOA evaluations, TOC and fluorine mass balance were assessed in both the anolyte and catholyte compartments. TOC analysis was employed to evaluate the PFOA degradation, and the results were compared to those obtained using UHPLC-MS/MS. Fluoride release was identified and correlated with the fluorine mass balance in the each chamber.

In the divided cell setup, the cathode role was investigated to understand PFOA interactions with different cathode materials. These findings were then extrapolated to elucidate any synergistic effects using each configuration in an undivided cell. Figures 1a and b depict the effects in an undivided cell , showcasing the configurations with BDD as both anode and cathode, and BDD as the anode and SS as the cathode, respectively.

The BDD-BDD system demonstrates removal performances of 59, 74, and 86 % at current densities of 25, 50, and 75 mA cm^{-2}, respectively. In contrast, the system BDD-SS achieves PFOA removal performances of 66, 75, and 78 % at 25, 50, and 75 mA cm^{-2}, respectively. The slight differences between the two systems can be attributed to the performance of the cathode as evaluated in the H-type cell. Depending on the cathode material, PFOA may undergo defluorination, leading to a reduction in PFOA concentration.

The kinetics observed during the electrochemical elimination of PFOA using the BDD-BDD system were determined to be 8.4 x 10^{-3}, 11.1 x 10^{-3}, and 16.4 x 10^{-3} min^{-1} using 25, 50, and 75 mA cm^{-2}, respectively. In comparison, the kinetics for the BDD-SS system were calculated to be 5.1 x 10^{-3}, 11.3 x 10^{-3}, and 12.9 x 10^{-3} min^{-1} at the same current densities. Consequently, in terms of kinetics, using both electrodes BDD results in higher kinetics rates compared to using SS as the cathode. This finding is supported by the cathode evaluation, which demonstrated that the BDD cathode attained higher PFOA removal compared to the SS cathode.
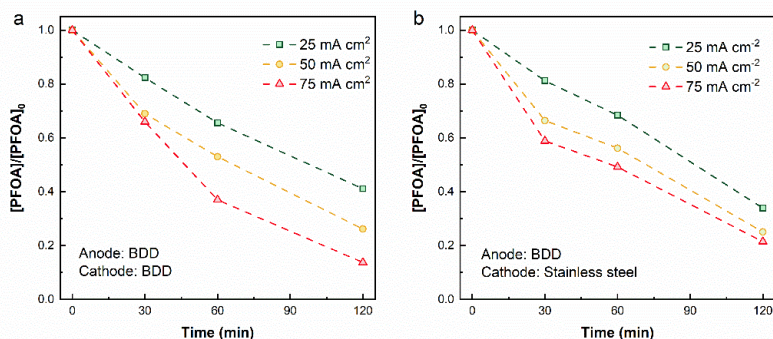
Figure 1. Time-course PFOA concentration during electrolysis at different current densities (25, 50, and 75 mA cm^{-2}) using BDD anode and cathode material: (a) BDD, and (b) Stainless steel. Initial PFOA concentration of 100 µg L^{-1} and 50 mM Na$_2$SO$_4$.

Conclusions

The electrochemical oxidation of PFOA may involve reduction processes depending on the cathode material, which boosts the overall elimination of PFOA. Using both H-cell type and undivided cell setups, the evaluation of each cathode underscores its contribution to the overall PFOA removal processes. Pt cathode demonstrated a high contribution during the removal of PFOA compared to other materials evaluated. These findings offer a new framework for the rational design of cathodes to enhance the removal of PFAS compounds.

References

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