Electrochemical Destruction of Perfluorooctanesulfonate
in Electroplating Wastewaters

Sixth Quarterly Report
July-September 2021
AESF Research Project #R-120

by
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Summary

Work this past quarter focused on the electrochemical oxidation of poly- and perfluoroalkyl substances (PFAS) using a tubular Magnéli phase titanium sub-oxide (Ti_4O_7) reactive electrochemical membrane (REM). The oxidation experiments were performed in synthetic solutions, using a crossflow setup in full recycle mode. The synthetic solutions were prepared by spiking perfluorooctane sulfonate (PFOS) to a background electrolyte with an ionic strength that was representative of industrial electroplating wastewaters (*i.e.*, 240 mM $NaClO_4$). The solution was subjected to electrochemical oxidation at a constant potential of 3.0 V_{SHE} and as a function of the permeate flux. Results indicated that negligible removal was accomplished at a low permeate flux, but approximately 60% PFOS removal could be accomplished with less than a 2 min electrolysis time under high flux conditions. A mathematical reactive transport model was used to investigate the effect of flux as a function of REM reactivity at a given electrode to solution volume ratio. It was found that higher flux always outperformed lower flux conditions with regard to PFOS removal. Simulations also indicated that further improvements in reaction kinetics for PFOS destruction would have minimal impacts on removal under low flux conditions, but significant increases in overall removal at high flux conditions. Therefore, future work is focused on improving electrocatalytic activity for PFOS and other PFAS.

Electrochemical oxidation experiments

The operating conditions for the electrochemical oxidation experiments are shown in Table 1 and results are shown in Figure 1. PFOS oxidation experiments were conducted with 100% recycle of both the permeate and feed solutions. The applied anodic potential was 3.0 V_{SHE} and permeate fluxes (J) of 60 and 1800 L m^{-2} hr^{-1} (LMH) were tested. Results show that negligible PFOS was removed at 60 LMH, while approximately 60% was removed at 1800 LMH. These results were attributed to the small amount of solution volume that was processed at the low flux conditions relative to the high flux conditions.

To further explore the effect of J on PFOS removal, a mathematical reactive transport model was used to estimate PFOS removal under different reactivity conditions at J = 60 and 800 LMH (Fig. 2). Results indicated that simulations at J = 800 LMH always resulted in more total PFOS removal than simulations at J = 60 LMH, even though single pass removals under J = 60

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LMH were always higher (*e.g.*, >90%). Results also indicated that increasing the PFOS oxidation rate constant from 0.3 to 5.0 min⁻¹ did not significantly increase total PFOS removal in the recirculating feed tank at J = 60 LMH, due to the fact that conversion was already high under all conditions tested. However, at J = 1800 LMH total PFOS removal increased significantly, as single pass removals increased from 16% to 95% with increasing rate constant of 0.3 to 5.0 min⁻¹, respectively. Future work will thus focus on evaluating REM properties to enhance PFAS reaction rates.

Parameter	Value
[PFOS]	10 µM
Electrolyte	240 mM $NaClO_4$
pH	6.8
Conductivity (mS/cm)	22
Flowrate (LMH)	60 and 1800
Anode Potential (V/SHE)	3.0
Mode	100% recycle

Table 1 - Operating parameters of PFAS oxidation experiments.
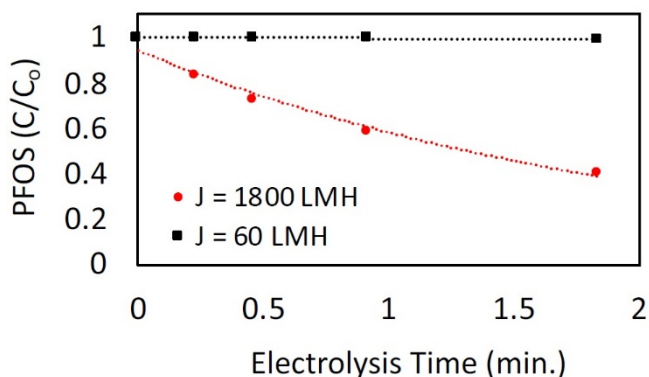
Figure 1 - PFOS oxidation results at 3.0 V_{SHE} for permeate fluxes (J) of 60 and 1800 L m⁻² hr⁻¹ (LMH).
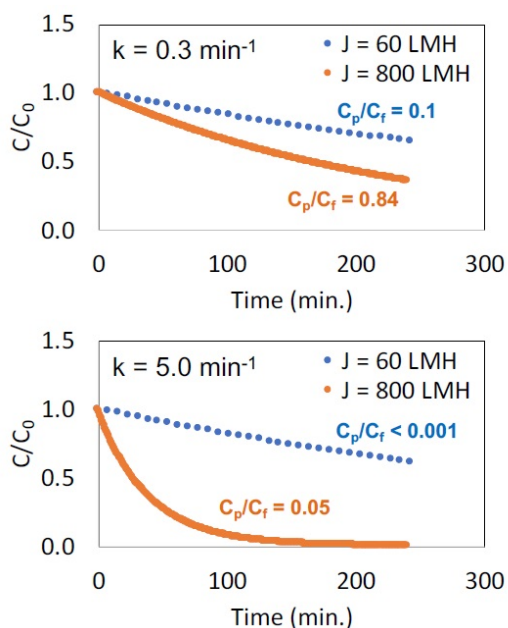
- Kinetic modeling in recycle-mode
- REM loading of 10 m²/m³ water
- Changed reactivity of PFOS (k = 0.3, 1.0, 5.0 min⁻¹)
- As rate constant increased, higher J values performed better

Figure 2 - Reactive transport modeling for PFOS oxidation as a function of J and reaction rate constant (k).

About the author

Dr. Brian P. Chaplin is Associate Professor in the Department of Chemical Engineering, at the University of Illinois at Chicago. He holds a B. Civil Engineering (1999) and an M.S. (2003) in Civil Engineering from the University of Minnesota and a Ph.D. in Environmental Engineering (2007) from the University of Illinois at Urbana-Champaign.