NASF/AESF Foundation Research Reports

Project R-120 (Q8)

Electrochemical Destruction of Perfluorooctanesulfonate in Electroplating Wastewaters

Eighth Quarterly Report
January – March 2022
AESF Research Project #R-120

by
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Summary

This quarter, a wastewater sample was procured from an electroplating facility, and experiments were conducted to investigate PFAS oxidation in both the wastewater sample and in synthetic solutions. Analysis of the sample determined that 6:2 FTS was the primary PFAS detected at a concentration of 220 µg/L (~0.5 µM). The ionic content was mainly comprised of NaCl and Na_2SO_4 salts, and the chemical oxygen demand (COD) of the sample was ~ 50 mg/L, which was attributed to other organic compounds besides PFAS.

The wastewater sample was treated with the Ti_4O_7 reactive electrochemical membrane (REM), with a residence time of ~11 sec. Results for 6:2 FTS oxidation are still pending LC-MS analysis. However, the COD removal at potentials of 2.2, 2.9, and 3.6 V_{SHE} was 10, 24, 83%, respectively. A synthetic solution with a similar ionic content to the real wastewater was prepared and spiked with 0.5 µM of 6:2 FTS. Once again, PFAS analysis is still pending, but fluoride production in permeate samples increased as a function of potential and reached as high as 4.9 µM (*i.e.*, 75% defluorination) at a potential of 3.6 V_{SHE}. In addition, a synthetic sample with a similar ionic strength to the wastewater was prepared but with an elevated 6:2 FTS concentration (40 µM). This sample was used to represent a PFAS concentrate from electroplating wastewater that could result from nanofiltration or foam fractionation. Results showed 66, 78, and 83% oxidation of 6:2 FTS at potentials of 2.2, 2.9, and 3.6 V_{SHE}, respectively. Product analysis indicated the formation of short chain PFAS (*i.e.*, PFHpA, PFHxA, PFPeA, and PFBA) at concentrations less than 1.35 µM. These results indicate that concentrating PFAS in wastewater may be a more efficient treatment strategy and that the residence time in the REM needs to be increased to prevent the accumulation of short chain PFAS byproducts.

Table 1 - General water quality parameters for electroplating wastewater sample.

Constituents	Conc. (mM)
Calcium	0.594
Sodium	61.5
Magnesium	0.650
Ammonium	1.57
Chloride	24.7
Fluoride	0.90
Nitrate	0.81
Sulfate	13.9
Bicarbonate	6.12
pH	7.35
COD	50 mg/L
Conductivity	6.3 mS/cm

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Results

The electroplating wastewater was analyzed for PFAS and general water quality parameters. The total PFAS concentration was 228 µg/L, which consisted of 220 µg/L 6:2 FTS and low concentrations of 4:2 FTS (0.81 µg/L), PFHpA (0.38 µg/L), PFHxA (1.4 µg/L), and PFOS (2.2 µg/L). The general water quality parameters are listed in Table 1. Results indicate that the ionic content consists primarily of NaCl and Na_2SO_4 salts, the solution pH = 7.35, and COD = 50 mg/L.

Electrochemical oxidation of the wastewater sample was tested in the REM system. The flux was held constant at 240 L/m^2/hr, which corresponded to ~11 sec residence time in the reactor. Applied potentials of 2.2, 2.9, and 3.6 V_{SHE} were tested, and PFAS removal is still pending LC-MS analysis. The COD analysis of the wastewater is shown in Figure 1, and results indicated it decreased by 10%, 24%, and 83% at potentials of 2.2, 2.9, and 3.6 V_{SHE}, respectively. Indicating the REM was effective for bulk oxidation of the organics present in the wastewater.

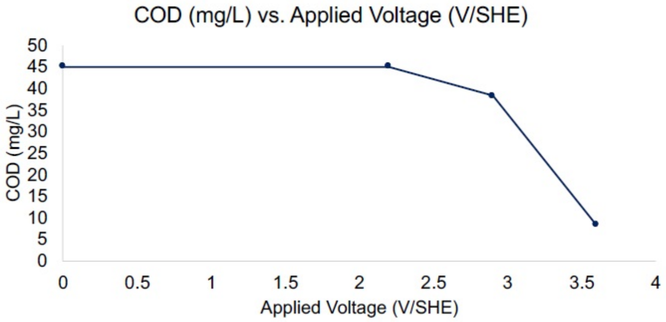

Figure 1 - Chemical oxygen demand (COD) of wastewater as a function of potential in the REM system. Residence time ~ 11 sec.

An additional experiment was also conducted with a synthetic wastewater with 0.5 µM 6:2 FTS and a similar ionic content as Table 1, but without the bulk organics. The PFAS analyses is once again pending LC-MS analysis. However, fluoride analysis is shown in Figure 2. Results indicate that fluoride increases as a function of potential and reached a concentration of 4.9 mM, which corresponds to 75% defluorination of 6:2 FTS. This calculation was based on the fact that 1 mole of 6:2 FTS contains 13 moles of fluorine. Chlorate and perchlorate were also monitored, as they can form from chloride oxidation and have undesirable health risks. Perchlorate was below the detection limit (~1 µg/L) and chlorate was detected at concentrations of 1.2, 23, and 95 mg/L at potentials of 2.2, 2.9, and 3.6 V_{SHE}, respectively. Chlorate is not currently regulated, but the EPA has set a health reference level (HRL) at 210 µg/L. Since the chlorate concentrations are much higher than the HRL, the water may need further treatment depending on discharge permitting.

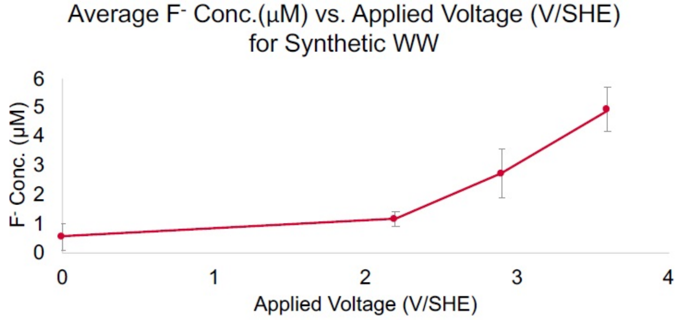

Figure 2 - Fluoride analysis for 0.5 µM 6:2 FTS oxidation in synthetic wastewater sample as a function of potential. Residence time ~ 11 sec.

An additional synthetic sample was prepared with a similar ionic strength as the real wastewater, but with an elevated 6:2 FTS concentration (*i.e.*, 40 µM). This sample was used to represent a concentrated PFAS sample that may be generated during nanofiltration, foam fractionization, or another separation method. Oxidation experiments indicated that 66%, 78%, and 83% removal of 6:2 FTS at potentials of 2.2, 2.9, and 3.6 V_{SHE}, respectively (Figure 3a). Product analysis indicated the formation of short chain PFAS (Figure 3b). For example, the highest concentrations of PFHpA, PFHxA, PFPeA, and PFBA formed at a potential of 2.9 V_{SHE}, with concentrations of 1.4, 1.0, 0.7, 0.06 µM, respectively. The concentrations of all of these PFAS decreased at 3.6 V_{SHE} to concentrations less than 0.5 µM. These results indicate that concentrating PFAS in wastewater may be a viable and efficient treatment strategy and that the residence time in the REM needs to be increased to prevent the accumulation of short chain PFAS byproducts.

Previous reports

1. Quarters 1-5 (April 2019-June 2021): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, 86 (1), 19 (October 2021); Full paper (With Project Introduction): http://short.pfonline.com/NASF21Oct1.
2. Quarter 6 (July-September 2021): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, 86 (4), 19 (January 2022); Full paper: http://short.pfonline.com/NASF22Jan2.

About the author

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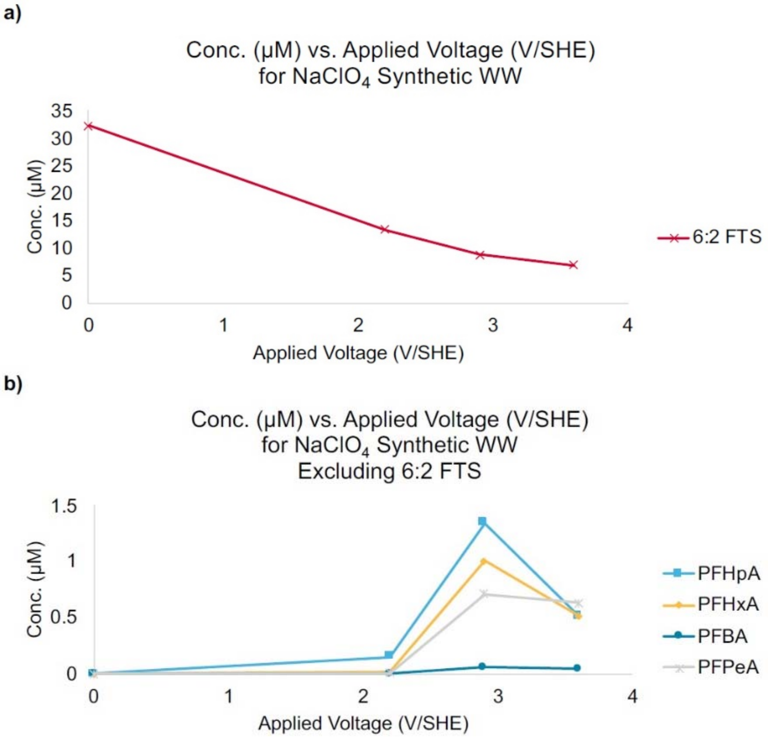

Figure 3 - (a) Concentration of 6:2 FTS as a function of the applied potential. Initial concentration of 6:2 FTS = 40 μM; (b) products from 6:2 FTS as a function of the applied potential. Residence time is ~11 sec.