Electrochemical Approaches to Treatment of PFAS in Plating Wastewater

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Editor's Note: *The NASF-AESF Foundation Research Board selected a project addressing the problem of PFAS and related chemicals in plating wastewater streams. This report covers the eleventh quarter of work (July-September 2023). A printable PDF version of this report is available by clicking **HERE**.*

1. Introduction

This project started in January 2021 with the goal of developing applicable electrochemical approaches to remove per- and polyfluoroalkyl substances (PFASs) present in plating wastewaters, including electrooxidation (EO) and electrocoagulation (EC). This project includes three research tasks that are designed to investigate EC, EO and EC-EO treatment train, respectively, designed to probe three hypotheses specified follows:

    1) EC generates amorphous metal hydroxide flocs that can effectively adsorb PFASs in plating wastewater, which, through an appropriate treatment, can release PFASs into a concentrated solution.

    2) EO enabled by a Magnéli phase Ti_4O_7 anode can be used to effectively destruct PFASs in plating wastewater.

    3) The electrochemical treatment train comprised of EC and EO by Ti_4O_7 anode can remove and degrade PFASs in plating wastewater more efficiently than either process operated individually.

In our last report, we described the performance and effect of surface fluorinated Ti_4O_7 anodes on PFAS degradation in a batch reactor operation mode. We discovered that surface fluorination of Ti_4O_7 anodes slightly inhibited PFAS degradation, while it significantly suppressed the formation of chlorate and perchlorate formation during EO treatment of PFOA, PFOS and 6:2 FTS, three representative PFASs. In this report, we will discuss the effect of surface fluorinated Ti_4O_7 anodes on PFAS degradation in a reactive electrochemical membrane (REM) operation mode.

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2. Experiments

Electrooxidation (EO) experiments were performed in a reactive electrochemical membrane (REM) operation mode. The porous Ti_4O_7 plate was used in the REM reactor simultaneously as the anode and a membrane through which the feed solution was filtered in crossflow mode (Figure 1). Both the pristine and F-18.6 Ti_4O_7 anodes were tested for comparison, and two current densities, 10 mA/cm^2 and 40 mA/cm^2, were applied, corresponding respectively to 2.79 V and 4.05 V_{SHE} anodic potentials. The feed solution contained PFOA, PFOS and 6:2 FTS (2.0 µM each), 100 mM Na_2SO_4, and 1 mM Cl$^-$.
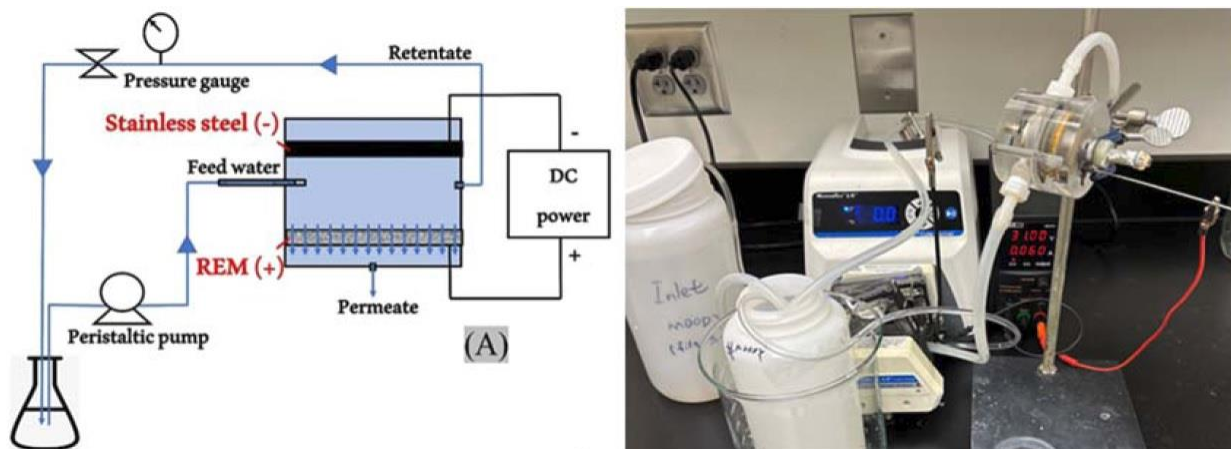

Figure 1 – (Left) A schematic diagram of the REM reactor with the Ti_4O_7 anode in cross-flow filtration operation and (Right) a photo of the actual operation system.

3. Results and discussion

The concentrations of PFOA, PFOS and 6:2 FTS in the permeate dropped immediately and were maintained at low level when the electric current was applied (Figure 2). The PFAS removal was greater at the higher current density, while it was slightly lower on the F-18.6 anode than on the pristine one. At 40 mA/cm^2, the removal of PFOA, PFOS and 6:2 FTS reached 70.5%, 88.3% and 58.9% on a pristine Ti_4O_7 anode, and 68.6%, 86.7% and 56.3% on the F-18.6 anode, respectively.

The concentrations of chlorate and perchlorate in the permeate flow during REM treatment were measured, and the results for the treatment at 10 mA/cm^2 with 1 mM Cl$^-$ in the feed solution are presented in Figure 3(A) and that with 10 mM Cl$^-$ in Figure 3(B). Both chlorate and perchlorate were detected when a pristine anode was used. The concentrations of chlorate and perchlorate were 95.3 µM and 48.0 µM, respectively with 10 mM Cl$^-$ in the feed solution, 2.1-3.5 times greater than those with 1 mM Cl$^-$. Interestingly, chlorate and perchlorate were below detection limits when the F-18.6 anode was used at 10 mA/cm^2 with either initial Cl$^-$ concentration, indicating effective inhibition of chlorate and perchlorate formation in REM treatment at a practical current density. This observation has profound implications, as the formation of chlorinated byproducts is a major hurdle to overcome for water/wastewater treatment technologies involving EO and other advanced oxidation processes.[1,2]
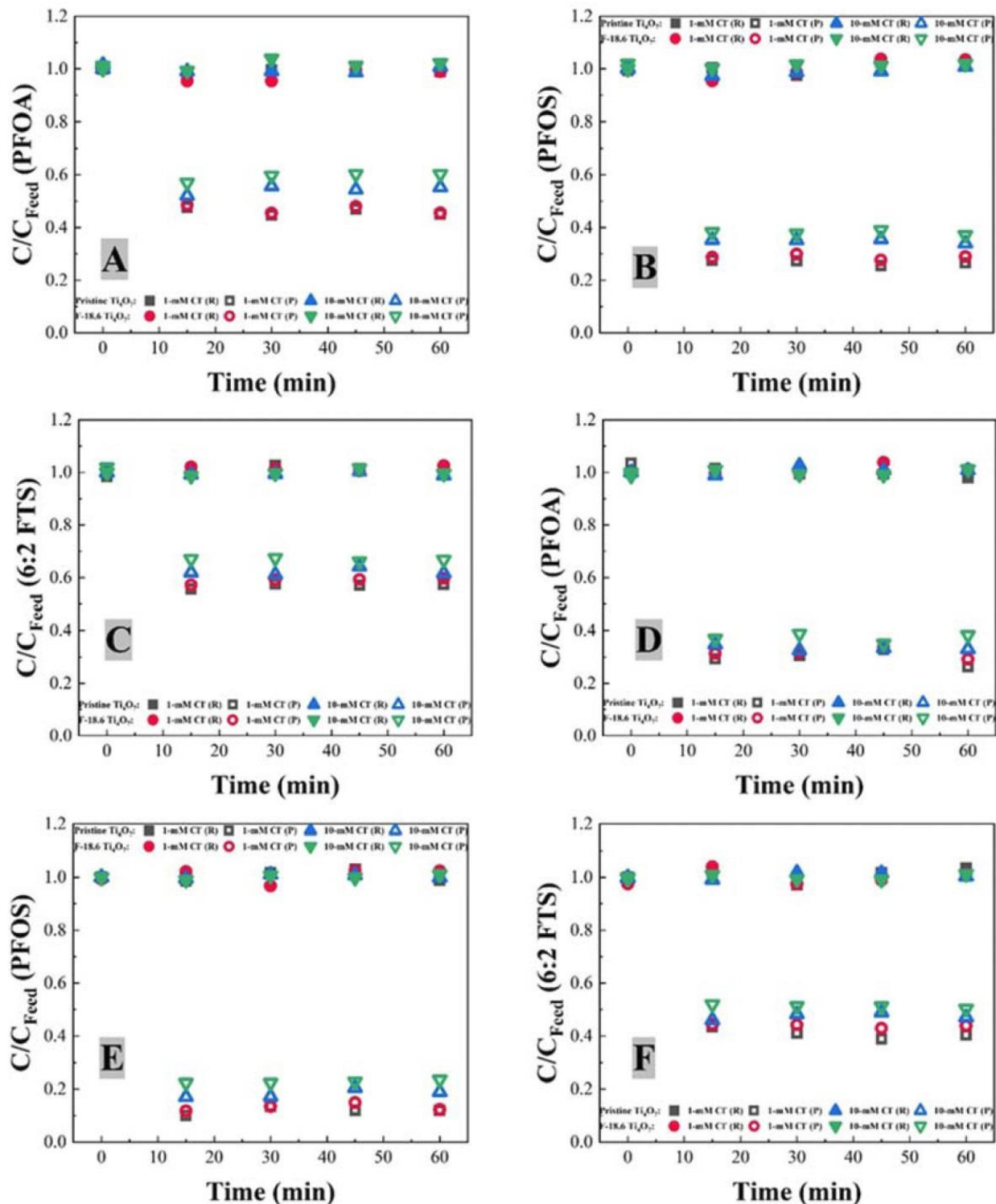
Figure 2 - PFAS concentration in retentate and permeate flow during REM treatment on the pristine and F-18.6 Ti$_4$O$_7$ anodes at 10 mA/cm^2: (A) PFOA, (B) PFOS, (C) 6:2 FTS and at 40 mA/cm^2: (D) PFOA, (E) PFOS, (F) 6:2 FTS with 1-mM or 10-mM Cl$^-$ in the feed solution. Initial PFAS concentration: 2.0 µM, supporting electrolyte: 100-mM Na$_2$SO$_4$
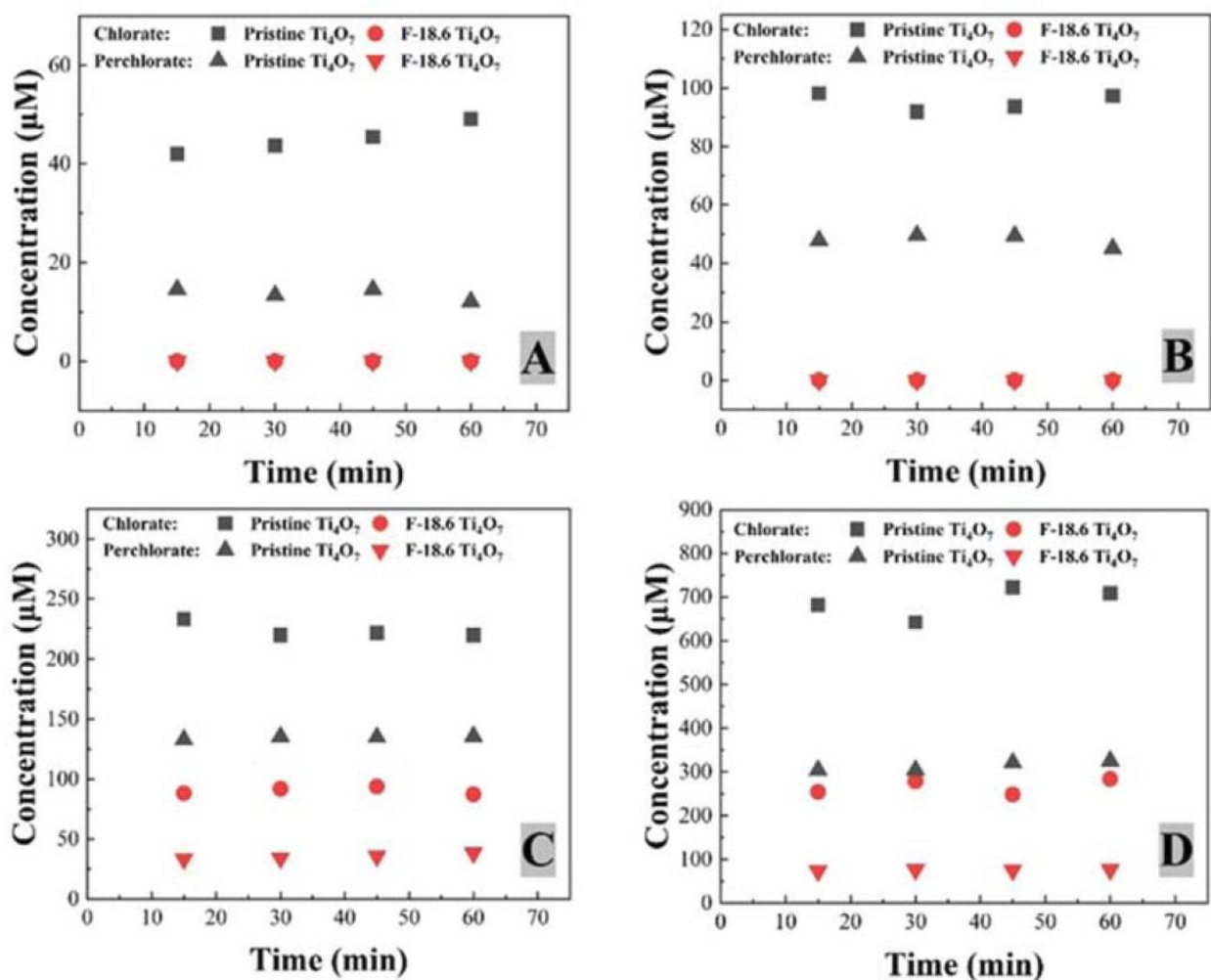
Figure 3 - Chlorate and perchlorate generation in permeate flow during REM treatment on the pristine Ti_4O_7 and F-18.6 Ti_4O_7 anodes at 10 mA/cm^2: (A) 1-mM Cl$^-$, (B) 10-mM Cl$^-$ and at 40 mA/cm^2: (C) 1-mM Cl$^-$, (D) 10-mM Cl$^-$ with 1-mM or 10-mM Cl$^-$ in the reaction solution. Initial PFAS concentration: 2.0 µM, supporting electrolyte: 100-mM Na_2SO_4.

The concentrations of chlorate and perchlorate in the permeate flow during REM treatment at 40 mA/cm^2 with 1 mM Cl$^-$ and 10 mM Cl$^-$ in feed solution are shown in Figure 3(C) and 3(D), respectively. With 1-mM Cl$^-$ in the feed solution, 223 µM chlorate and 134 µM perchlorate were formed for the REM with a pristine Ti_4O_7 anode, while their formation dropped to 90.3 µM and 35.4 µM on the F-18.6 anode. With 10-mM Cl$^-$ in the feed solution, the formation of chlorate and perchlorate on a pristine anode was 688 µM and 314 µM, respectively, while those on the F-18.6 anode were significantly reduced to 266 µM and 75.4 µM. It should be noted that the background Cl$^-$ is 12 – 46 mg/L in groundwater,[3] close to 1 mM. Thus, REM tests were performed with 1-mM Cl$^-$ in the feed solution at 15 mA/cm^2 (2.99 V), 20 mA/cm^2 (3.28 V), 25 mA/cm^2 (3.59 V), 30 mA/cm^2 (3.77 V) and 35 mA/cm^2 (3.98 V), in addition to 10 mA/cm^2 (2.86 V) and 40 mA/cm^2 (4.19 V) described above, and the concentrations of chlorate and perchlorate in the permeate flow are compared in Figure 4. The results in Figure 4 suggests that the formation of chlorate and perchlorate in REM can be avoided by using fluorinated Ti_4O_7 anode under a proper anodic potential range (< 3.0 V_{SHE}).
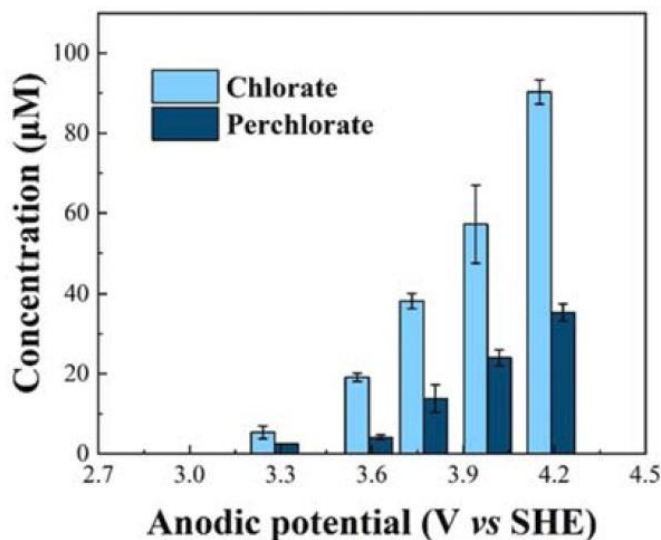
Figure 4 - The concentrations of chlorate and perchlorate in the permeate during REM with the F-18.6 anode at different anodic potentials, including 2.86 V (10 mA/cm^2), 2.99 V (15 mA/cm^2), 3.28 V (20 mA/cm^2), 3.59 V (25 mA/cm^2), 3.77 V (30 mA/cm^2), 3.98 V (35 mA/cm^2) and 4.19 V (40 mA/cm^2). Initial PFAS concentration: 2.0 μM, supporting electrolyte: 100-mM Na$_2$SO$_4$ + 1-mM NaCl.

4. References

1. J. Radjenovic, N. Duinslaeger, S.S. Avval and B.P. Chaplin, "Facing the Challenge of Poly- and Perfluoroalkyl Substances in Water: Is Electrochemical Oxidation the Answer?" *Environmental Science & Technology*, **54** (23), 14815-14829 (2020); https://doi.org/10.1021/acs.est.0c06212 .
2. J. Radjenovic, and D.L. Sedlak, "Challenges and Opportunities for Electrochemical Processes as Next-Generation Technologies for the Treatment of Contaminated Water," *Environmental Science & Technology*, **49** (19), 11292-11302 (2015); https://doi.org/10.1021/acs.est.5b02414.
3. J.R. Mullaney, D.L. Lorenz and A.D. Arntson, "Chloride in Groundwater and Surface Water in Areas Underlain by the Glacial Aquifer System, Northern United States," *Scientific Investigations Report 2009-5086*, United States Geological Survey, Connecticut Water Science Center, East Hartford, CT (2009); https://pubs.usgs.gov/sir/2009/5086/.

5. Past project reports

1. Introduction to Project R-122: Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **85** (6), 13 (March 2021); Full paper: http://short.pfonline.com/NASF21Mar1.
2. Quarter 1 (January-March 2021): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **85** (12), 13 (September 2021); Full paper: http://short.pfonline.com/NASF21Sep1.
3. Quarter 2 (April-June 2021): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **86** (3), 18 (December 2021); Full paper: http://short.pfonline.com/NASF21Dec2.
4. Quarter 3 (July-September 2021): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **86** (6), 16 (March 2022); Full paper: http://short.pfonline.com/NASF22Mar2.
5. Quarter 4 (October-December 2021): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **86** (9), 21 (June 2022); Full paper: http://short.pfonline.com/NASF22Jun2.

6. Quarter 5 (January-March 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **86** (12), 22 (September 2022); Full paper: http://short.pfonline.com/NASF22Sep2.

7. Quarter 6 (April-June 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (3), 17 (December 2022); Full paper: http://short.pfonline.com/NASF22Dec1.

8. Quarter 7 (July-September 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (6), 19 (March 2023); Full paper: http://short.pfonline.com/NASF23Mar2.

9. Quarter 8 (October-December 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (9), 19 (June 2023); Full paper: http://short.pfonline.com/NASF23Jun1.

10. Quarter 9 (January-March 2023): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (12), 17 (September 2023); Full paper: http://short.pfonline.com/NASF23Sep2

11. Quarter 10 (April-June 2023): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **88** (5), 19 (February 2024); Full paper: http://short.pfonline.com/NASF24Feb2

6. About the principal investigator
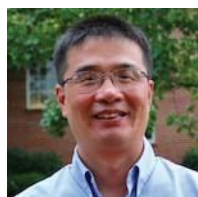
Qingguo (Jack) Huang is Professor in the Department of Crop and Soil Sciences, University of Georgia, Griffin Campus. He holds a B.S. in Environmental Science (1990) and a Ph.D. in Chemistry (1995) from Nanjing University, China as well as a Ph.D. in Environmenal Engineering from the University of Michigan, Ann Arbor, Michigan. Dr. Huang's research interest focuses on catalysis involved in the environmental transformation of organic pollutants, and development of catalysis-based technology for pollution control and environmental remediation and management. His laboratory has been actively involved in several cutting-edge research topics:

• Enzyme-based technology for water/wastewater treatment and soil remediation
• Electrochemical and reactive electrochemical membrane processes in wastewater treatment
• Catalysis in biofuel production and agro-ecosystem management
• Environmental fate and destructive treatment methods of PFASs
• Environmental application and implication of nanomaterials

He has published over 170 peer-reviewed journal articles, five book chapters and had six patents awarded. He has taught three courses at the University Georgia: *Introduction to Water Quality*, *Environmental Measurement* and *Advanced Instrumental Analysis in Environmental Studies*.