Supplementary Materials

Recent advances in electrochemical decontamination of perfluorinated compounds from water: a review

Fuqiang Liu[1], Shengtao Jiang[2], Shijie You[3,*], Yanbiao Liu[1,*]

1 College of Environmental Science and Engineering, Textile Pollution Controlling Engineering Center of the Ministry of Ecology and Environment, Donghua University, Shanghai 201620, China. E-mail: yanbiaoliu@dhu.edu.cn; Tel: +86 21 67798752.

2 College of Life Science, Taizhou University, Taizhou 318000, China.

3 State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China.

Table S1. A summary of some representative applications of coupled technologies for PFAS removal.

Types	Processes	PFAS	Anodes	pH	Applied voltage /Current density	Time (h)	Removal performance	Reactor configuration	Energy consumption (kWh/m^3)	Ref.
Tandem arrangement	Ion exchange + EO[a]	PFOA (100.5 mg/L)	Ti_4O_7	n/a[c]	10.0 mA/cm^2	17	77.2%	Batch	450.0	(Liang et al., 2018)
	Ion exchange + EO	PFAA (n/a)	BDD	7.7	50.0 mA/cm^2	8	>99.0%	Batch	173	(Maldonado et al., 2021)
	Nanofiltration + EO	PFHxA (774 mg/L)	BDD	7.7	50.0 mA/cm^2	1.47	~100%	Batch	15.2	(Soriano et al., 2017)
	Nanofiltration + EO	PFHxA (204 mg/L)	BDD	~7.0	50.0 mA/cm^2	9	99.0%	Batch	11.6	(Soriano et al., 2019)
	Nanofiltration + EO	GenX (1 mg/L)	BDD	~7.0	50.0 mA/cm^2	4	~60%	Batch	47.5	(Pica et al., 2019)
	Nanofiltration/ + EO	PFAA (70 µg/L)	BDD	6.3	350.0 A/m^2	46.7	99.9%	Cross-flow	26.0	(Soriano et al., 2020)
	EC[b] + EO	PFOA (0.05 µM)	Zn, Ti_4O_7	6.0	10.0 mA/cm^2	1	>95.0%	Batch	0.95	(Shi et al., 2021)
Integration arrangement	Nanofiltration + EO	PFOS (10.0 µM)	Ti_4O_7 REM	7.0	3.6 V	11.3 s	~100%	Flow-through	6.7	(Le et al., 2019)
	Ultrasound + EO	PFOA (60 mg/L)	Ti/SnO_2-Sb/Ce-PbO_2	n/a	15.0 mA/cm^2	3	~100%	Batch	55.3	(Xu et al., 2020)
	Ultrasound + EO	PFOA (100 mg/L)	SnO_2-Sb/CA	n/a	20.0 mA/cm^2	5	91.0%	Batch	n/a	(Zhao et al., 2013)
	Ultrafiltration + EO	PFOA (10 mg/L)	Ti_xO_{2x-1} and Pd/CNT	4.6	4.5 V	480	94.1%	Flow-through	381.0	(Xie et al., 2022)
	PMS activation + EC	PFOS (5 mg/L)	Fe	3.0	60.0 V	1	~100%	Batch	n/a	(Li et al., 2022a)

[a] Electro-oxidation; [b] Electro-coagulation; [c] Not available

Table S2. A summary of some representative applications of electro-oxidation, electro-adsorption, and electro-coagulation technologies for PFAS removal.

Types	Anodes	PFAS	Applied voltage /Current density	pH	Time (min)	Electrolyte type	Removal performance	Reactor configuration	Energy consumption (kWh/m^3)	Removal mechanism	Ref.
EO[a]	BDD	PFOA (1 mg/L)	21.4 mA/cm^2	n/a[d]	240	Na_2SO_4 (14.2 mM)	99.5%	Batch	143.0	n/a	(Uwayezu et al., 2021)
	BDD	PFOA (0.1 mg/L)	75.0 mA/cm^2	~7.0	480	PB[e] (100 mM)	80.0%	Batch	88.0	Cycles II and III	(Pierpaoli et al., 2021)
	N-BDD	PFOA (50 mg/L)	4.0 mA/cm^2	4.8	120	Na_2SO_4 (50 mM)	100%	Batch	n/a	Cycles II and III	(Liu et al., 2019)
	Ti/SnO_2-Sb	PFOA (100 mg/L)	10.0 mA/cm^2	5.0	90	$NaClO_4$ (10 mM)	98.8%	Batch	n/a	Cycles II and III	(Lin et al., 2012)
	SnO_2-Sb/CA	PFOA (100 mg/L)	20.0 mA/cm^2	n/a	300	Na_2SO_4 (100 mM)	>91%	Batch	n/a	n/a	(Zhao et al., 2013)
	Ti/RuO_2	PFOS (0.1 mg/L)	100.0 mA/cm^2	n/a	60	NaCl (5 g/L)	100%	Batch	60.3	Cycles I, II and III	(Barisci and Suri, 2021)
	Ti_4O_7	PFOS (2.0 µM)	4.0 mA/cm^2	n/a	120	Na_2SO_4 (100 mM)	98.3%	Cross-flow	n/a	Cycle II	(Shi et al., 2019)
	Ti_4O_7-Pd	PFOA (120 µM)	10.0 mA/cm^2	7.2	60	Na_2SO_4 (50 mM)	2.02 h^{-1}	Batch	57.1	Cycle II	(Huang et al., 2020)
	Nano-Ti_4O_7	PFOS (2.0 µM)	10.0 mA/cm^2	n/a	840	Na_2SO_4 (100 mM)	99%	Batch	4.7	n/a	(Wang et al., 2022)
	$(Ti_{1-x}Ce_x)_4O_7$	PFOS (20 µM)	20.0 mA/cm^2	n/a	120	Na_2SO_4 (10 M)	100%	Flow-by	13.6	n/a	(Lin et al., 2021)
EA[b]	P(TMA_x-*co*-$TMPMA_{1-x}$)	PFOA (100 µM)	1.0 V	n/a	30	NaCl (20 mM)	>1000 mg/g	Batch	n/a	EI[f]	(Kim et al., 2020a)
	Graphite	PFOA (10 µM)	1.2 V	n/a	0.17	n/a	2.52 mg/g	Flow-by	n/a	EI	(Shrestha et al., 2021)
	CC/PPy	PFOA (5 mg/L)	0.4 V	5.5-6.0	1440	NaCl (10 mM)	~6 mg/g	Batch	n/a	EI	(Tian et al., 2021)
	ACF	PFOA (1 mg/L)	0.5 V	6-7	2880	Na_2SO_4 (10 mM)	~80 mg/g	Batch	n/a	EI	(Saeidi et al., 2021)
	Cu/F-rGA	PFOA (10 mg/L)	0.8 V	6.0	720	Na_2SO_4 (1 mM)	~6.31 mg/g	Batch	n/a	EI and F-F interaction	(Liu et al., 2021)
	CNTs-20% graphene	PFOA (100 µM)	0.6 V	3.6	240	n/a	~2.42 mg/g	Batch	n/a	EI	(Niu et al., 2017)
EC[c]	Al	PFOS (1 mg/L)	12.0 V	7.0	0.17	NaCl (1 g/L)	100%	Batch	n/a	HI[g]	(Bao et al., 2020)
	Zn	PFOA (250 µM)	1.0 V	3.5	45	NaCl (10 mM)	99.8%	Batch	0.14	HI	(Mu et al., 2021)

Al	PFOA (1 mM)	5.0 mA/cm^2	3.0	30	NaCl (10 mM)	100%	Batch	n/a	coagulation	(Li et al., 2022b)
Fe	PFOS (0.25 mM)	25.0 mA/cm^2	5.2	50	NaCl (2 g/L)	99%	Batch	7.4	EI	(Yang et al., 2016)
Fe	PFOA (24 μM)	40.0 mA/cm^2	9.0	360	NaCl (35 mM)	100%	Batch	23.2	coagulation	(Kim et al., 2020b)

[a] Electro-oxidation; [b] Electro-adsorption; [c] Electro-coagulation; [d] Not available; [e] phosphate buffer; [f] Electrostatic interaction; [g] Hydrophobic interaction

Table S3. A summary of advantages and disadvantages of electro-oxidation, electro-adsorption, and electro-coagulation technologies for PFAS removal.

Types	Advantages	Disadvantages
Electro-oxidation	✧ High reactivity due to direct electron transfer ✧ Direct mineralization of PFAS may be achieved ✧ No additional toxic chemicals are required ✧ Modular reactor design and easy automatic control	◊ High energy consumption and low efficiency to the treatment of low concentration PFAS ◊ Electrode fouling and corrosion issues ◊ External supporting electrolyte is needed for wastewater with poor conductivity
Electro-adsorption	✧ Low energy consumption and simple operation ✧ Environment-friendly because no by-product is generated ✧ Electrode can be regenerated when reverse voltage is applied ✧ No additional toxic chemicals are required ✧ Modular reactor design and easy automatic control	◊ Degradation of PFAS cannot be achieved ◊ Low adsorption efficiency to the treatment of high concentration PFAS ◊ Susceptible to interference from the background matrix
Electro-coagulation	✧ Multiple harmful pollutants may be removed simultaneously ✧ No additional flocculants are required ✧ Modular reactor design and easy automatic control	◊ Higher operating costs due to the need for anodic dissolution ◊ A large amount of sludge may be generated ◊ Electrode surface is easily passivated, reducing dissolution efficiency of metal ions ◊ Short lifetimes due to anode sacrifice

Table S4. Current challenges and future research directions of electrochemical technology for removing PFAS.

Challenges	◊ Reports on the effect of operation parameters (*e.g.*, pH and current density) on electrochemical decontamination of PFAS are not consistent; ◊ The degradation pathway of PFAS by electro-oxidation technology is still unclear; ◊ The reported removal mechanism of PFAS by electro-coagulation is sometimes contradictory; ◊ The reported PFAS removal performance may be overestimated since most studies were conducted in synthetic wastewater.
Outlook	✧ Novel electrode materials to minimize the competition effects of the coexisting species are highly demanded; ✧ Characteristics and toxicity of degradation intermediates should be focused on; ✧ Effectiveness of electrochemical methods for removing short-chain PFAS needs to be further evaluated; ✧ Long-term experiments and on-site demonstration tests of electrochemical methods should be carried out; ✧ Electrochemical coupling technology for PFAS removal should be continuously developed; ✧ Electrodialysis with excellent selectivity should be explored for PFAS removal; ✧ The TEA and LCA of electrochemical technologies need to be carried out.

References

Bao J, Yu W J, Liu Y, Wang X, Liu Z Q, Duan Y F (2020). Removal of perfluoroalkanesulfonic acids (PFSAs) from synthetic and natural groundwater by electrocoagulation. Chemosphere, 248: 125951

Barisci S, Suri R (2021). Electrooxidation of short- and long-chain perfluoroalkyl substances (PFASs) under different process conditions. Journal of Environmental Chemical Engineering, 9(4): 105323

Huang D H, Wang K X, Niu J F, Chu C H, Weon S, Zhu Q H, Lu J J, Stavitski E, Kim J H (2020). Amorphous Pd-loaded Ti_4O_7 electrode for direct anodic destruction of perfluorooctanoic acid. Environmental Science & Technology, 54(17): 10954-10963

Kim K, Medina P B, Elbert J, Kayiwa E, Cusick R D, Men Y J, Su X (2020a). Molecular tuning of redox-copolymers for selective electrochemical remediation. Advanced Functional Materials, 30(52): 2004635

Kim M K, Kim T, Kim T K, Joo S W, Zoh K D (2020b). Degradation mechanism of perfluorooctanoic acid (PFOA) during electrocoagulation using Fe electrode. Separation and Purification Technology, 247: 116911

Le T X H, Haflich H, Shah A D, Chaplin B P (2019). Energy-efficient electrochemical oxidation of perfluoroalkyl substances using a Ti_4O_7 reactive electrochemical membrane anode. Environmental Science & Technology Letters, 6(8): 504-510

Li M, Jin Y T, Yan J F, Liu Z, Feng N X, Han W, Huang L W, Li Q K, Yeung K L, Zhou S Q, Mo C H (2022a). Exploration of perfluorooctane sulfonate degradation properties and mechanism via electron-transfer dominated radical process. Water Research, 215: 118259

Li Y F, Hu C Y, Lee Y C, Lo S L (2022b). Effects of zinc salt addition on perfluorooctanoic acid (PFOA) removal by electrocoagulation with aluminum electrodes. Chemosphere, 288(132665)

Liang S T, Pierce R, Lin H, Chiang S Y, Huang Q (2018). Electrochemical oxidation of PFOA and PFOS in concentrated waste streams. Remediation Journal, 28(2):

127-134

Lin H, Niu J F, Ding S Y, Zhang L L (2012). Electrochemical degradation of perfluorooctanoic acid (PFOA) by Ti/SnO_2-Sb, Ti/SnO_2-Sb/PbO_2 and Ti/SnO_2-Sb/MnO_2 anodes. Water Research, 46(7): 2281-2289

Lin H, Xiao R L, Xie R Z, Yang L H, Tang C M, Wang R R, Chen J, Lv S H, Huang Q G (2021). Defect engineering on a Ti_4O_7 electrode by Ce^{3+} doping for the efficient electrooxidation of perfluorooctanesulfonate. Environmental Science & Technology, 55(4): 2597-2607

Liu L F, Liu Y L, Che N J, Gao B, Li C L (2021). Electrochemical adsorption of perfluorooctanoic acid on a novel reduced graphene oxide aerogel loaded with Cu nanoparticles and fluorine. Journal of Hazardous Materials, 416: 125866

Liu Y M, Fan X F, Quan X, Fan Y F, Chen S, Zhao X Y (2019). Enhanced perfluorooctanoic acid degradation by electrochemical activation of sulfate solution on B/N codoped diamond. Environmental Science & Technology, 53(9): 5195-5201

Maldonado V Y, Becker M F, Nickelsen M G, Witt S E (2021). Laboratory and semi-pilot scale study on the electrochemical treatment of perfluoroalkyl acids from ion exchange still bottoms. Water, 13(20): 2873

Mu T H, Park M, Kim K Y (2021). Energy-efficient removal of PFOA and PFOS in water using electrocoagulation with an air-cathode. Chemosphere, 281: 130956

Niu Z J, Wang Y J, Lin H, Jin F Y, Li Y, Niu J F (2017). Electrochemically enhanced removal of perfluorinated compounds (PFCs) from aqueous solution by CNTs-graphene composite electrode. Chemical Engineering Journal, 328: 228-235

Pica N E, Funkhouser J, Yin Y M, Zhang Z Y, Ceres D M, Tong T Z, Blotevogel J (2019). Electrochemical oxidation of hexafluoropropylene oxide dimer acid (GenX): Mechanistic insights and efficient treatment train with nanofiltration. Environmental Science & Technology, 53(21): 12602-12609

Pierpaoli M, Szopinska M, Wilk B K, Sobaszek M, Luczkiewicz A, Bogdanowicz R, Fudala-Ksiazek S (2021). Electrochemical oxidation of PFOA and PFOS in landfill leachates at low and highly boron-doped diamond electrodes. Journal of

Hazardous Materials, 403: 123606

Saeidi N, Kopinke F D, Georgi A (2021). Controlling adsorption of perfluoroalkyl acids on activated carbon felt by means of electrical potentials. Chemical Engineering Journal, 416: 129070

Shi H H, Chiang S Y, Wang Y Y, Wang Y F, Liang S T, Zhou J, Fontanez R, Gao S X, Huang Q G (2021). An electrocoagulation and electrooxidation treatment train to remove and degrade per- and polyfluoroalkyl substances in aqueous solution. Science of the Total Environment, 788: 147723

Shi H H, Wang Y Y, Li C G, Pierce R, Gao S X, Huang Q G (2019). Degradation of perfluorooctanesulfonate by reactive electrochemical membrane composed of magneli phase titanium suboxide. Environmental Science & Technology, 53(24): 14528-14537

Shrestha B, Ezazi M, Ajayan S, Kwon G (2021). Reversible adsorption and desorption of PFAS on inexpensive graphite adsorbents via alternating electric field. RSC Advances, 11(55): 34652-34659

Soriano A, Gorri D, Urtiaga A (2017). Efficient treatment of perfluorohexanoic acid by nanofiltration followed by electrochemical degradation of the NF concentrate. Water Research, 112: 147-156

Soriano A, Gorri D, Urtiaga A (2019). Membrane preconcentration as an efficient tool to reduce the energy consumption of perfluorohexanoic acid electrochemical treatment. Separation and Purification Technology, 208: 160-168

Soriano A, Schaefer C, Urtiaga A (2020). Enhanced treatment of perfluoroalkyl acids in groundwater by membrane separation and electrochemical oxidation. Chemical Engineering Journal Advances, 4: 100042

Tian Y H, Xing J Y, Huyan C X, Zhu C Z, Du D, Zhu W L, Lin Y H, Chowdhury I (2021). Electrically controlled anion exchange based on a polypyrrole/carbon cloth composite for the removal of perfluorooctanoic acid. ACS ES&T Water, 1(12): 2504-2512

Uwayezu J N, Carabante I, Lejon T, Van Hees P, Karlsson P, Hollman P, Kumpiene J (2021). Electrochemical degradation of per- and poly-fluoroalkyl substances using boron-doped diamond electrodes. Journal of Environmental Management, 290: 112573

Wang Y Y, Li L, Wang Y F, Shi H H, Wang L, Huang Q G (2022). Electrooxidation of perfluorooctanesulfonic acid on porous Magnéli phase titanium suboxide Anodes: Impact of porous structure and composition. Chemical Engineering Journal, 431: 133929

Xie J Z, Zhang C Y, David Waite T (2022). Integrated flow anodic oxidation and ultrafiltration system for continuous defluorination of perfluorooctanoic acid (PFOA). Water Research, 216: 118319

Xu L, Qian X B, Wang K X, Fang C, Niu J F (2020). Electrochemical mineralization mechanisms of perfluorooctanoic acid in water assisted by low frequency ultrasound. Journal of Cleaner Production, 263: 121546

Yang B, Han Y N, Yu G, Zhuo Q F, Deng S B, Wu J H, Zhang P X (2016). Efficient removal of perfluoroalkyl acids (PFAAs) from aqueous solution by electrocoagulation using iron electrode. Chemical Engineering Journal, 303: 384-390

Zhao H Y, Gao J X, Zhao G H, Fan J Q, Wang Y B, Wang Y J (2013). Fabrication of novel SnO_2-Sb/carbon aerogel electrode for ultrasonic electrochemical oxidation of perfluorooctanoate with high catalytic efficiency. Applied Catalysis B: Environmental, 136: 278-286