Supporting Information

Mitigation of Harmful Algal Blooms by Electrochemical Ozonation: From Bench-scale Studies to Field Applications

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Table S1. Composition of the supporting electrolyte and lake water.

Component	PBS	Lake Neatahwanta	Oneida Lake
Chl-a (μg/L)	100	105 ± 36	5.4 ± 1.4
MC-LR (μg/L)	1	3 ± 0.8	BDL
TOC (mg/L)	--	8.60	4.23
pH	7.7	7.8	8.3
Conductivity (μS/cm)	329	801.5	377.2
Cl^- (mg/L)	--	46.5	32.7
Br^- (mg/L)	--	BDL	BDL
NO_3^- (mg/L)	--	11.0	1.8
SO_4^{2-} (mg/L)	--	13.2	43.4
PO_4^{3-} (mg/L)	150	BDL	BDL

BDL: below detection limit. The detection limit of Br^- and PO_4^{3-} is 0.04 mg/L. The detection limit of MC-LR is 0.041 μg/L.

Table S2. Toxicity evaluation of influent (INF) and effluent (EFF) samples relative to the lab controls (CON) based on the fecundity of *Ceriodaphnia dubia* (invertebrate) and growth of *Pimephales promelas* (fish). Samples were collected during the treatment of lake Neatahwanta water. The treatment system was operated at 7 and 10 mA/cm^2. Test dates and sample collection times were provided.

Acute & Chronic Test Results	7 mA/cm^2; Aug 11, 2021					10 mA/cm^2; Aug 10, 2021				
	CON	INF 9:00 AM	EFF 9:00 AM	INF 12:00 PM	EFF 12:00 PM	CON	INF 9:00 AM	EFF 9:00 AM	INF 12:00 PM	EFF 12:00 PM
48 h Invertebrate Survival; n=10	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
6 d Invertebrate Survival; n=10	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
6 d Invertebrate Reproduction; n=10	18.1 ± 7.5	*12.7 ± 3.8	13.4 ± 4.6	*10.1 ± 3.2	*9.9 ± 5.4	19.4 ± 6.3	*7.20 ± 3.0	*2.90 ± 2.1	*8.10 ± 2.8	*4.00 ± 3.4
48 h Fish Survival; n=4	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
7 d Fish Survival; n=4	100%	100%	100%	100%	100%	95%	100%	100%	97.5%	100%
7 d Fish Growth (mg); n=4	0.729 ± 0.085	0.683 ± 0.44	0.687 ± 0.035	0.665 ± 0.085	0.774 ± 0.073	0.694 ± 0.069	0.637 ± 0.061	0.729 ± 0.049	0.692 ± 0.060	0.730 ± 0.071

* The data is significant at p=0.05 versus lab controls. The lower reproduction in INF may be attributed to existing toxicity in the HAB-impacted lake water.

Table S3. Toxicity evaluation of influent (INF) and effluent (EFF) samples relative to the lab controls (CON) based on the fecundity of *Ceriodaphnia dubia* (invertebrate) and growth of *Pimephales promelas* (fish). Samples were collected during the treatment of Oneida Lake water. The treatment system was operated at 6 and 7 mA/cm^2. Test dates and sample collection times were provided.

Acute & Chronic Test Results		6 mA/cm2; Aug 22, 2022		7 mA/cm2; Aug 22, 2022	
	CON	INF 8:50 AM	EFF 8:50 AM	INF 7:00 AM	EFF 7:00 AM
48 h Invertebrate Survival; n=10	100%	100%	100%	100%	100%
6 d Invertebrate Survival; n=10	100%	100%	100%	100%	100%
6 d Invertebrate Reproduction; n=10	16.2 ± 4.6	13.9 ± 8.2	16.2 ± 8.4	*9.2 ± 7.0	17.2 ± 8.8
48 h Fish Survival; n=4	100%	100%	100%	100%	100%
7 d Fish Survival; n=4	100%	100.0%	100%	82.5%	100%
7 d Fish Growth (mg); n=4	0.754 ± 0.040	0.976 ± 0.066	0.986 ± 0.058	0.570 ± 0.19	0.894 ± 0.071

* The data is significant at p=0.05 versus lab controls. The lower reproduction in “INF 7:00 AM” sample may be attributed to existing toxicity in the HAB-impacted lake water.

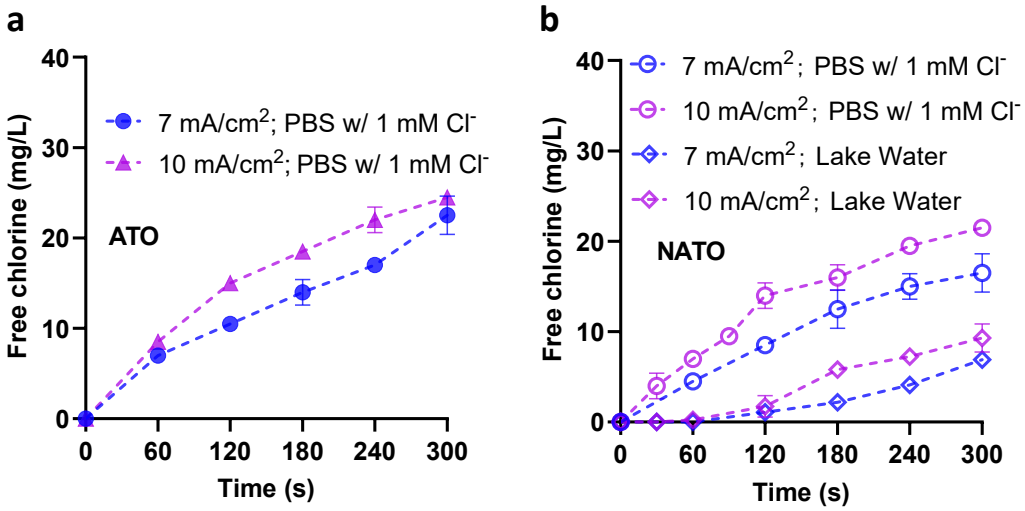

Figure S1. Evolution of free chlorine during electrolysis by (a) ATO and (b) NATO anodes in PBS containing 1 mM Cl^- and lake water collected from Lake Neatahwanta.

Given that the formation of free chlorine/ozone increased linearly with electrolysis time, the free chlorine and ozone evolution rate was calculated in mmol/m^2/s by the following equation,

$$Chlorine\ or\ Ozone\ Evolution\ Rate = (C \times V)/(A \times t) \quad (1)$$

where C is the concentration of free chlorine or ozone after electrolysis duration t, V is the electrolyte volume, and A is the geometric surface area of the anode.

The current efficiency (CE) was calculated by the chlorine or ozone production rates,

$$CE = \frac{nFVdC}{Idt} \times 100\% \quad (2)$$

Where $n = 2$ for chlorine evolution from Cl^- and $n = 6$ for O_3 from oxidation of water, F is the Faraday constant (96486 C/mol), V is the electrolyte volume (L), C is the concentration of chlorine or O_3 (mol/L), I is the current (A), and t is the electrolysis time (s).

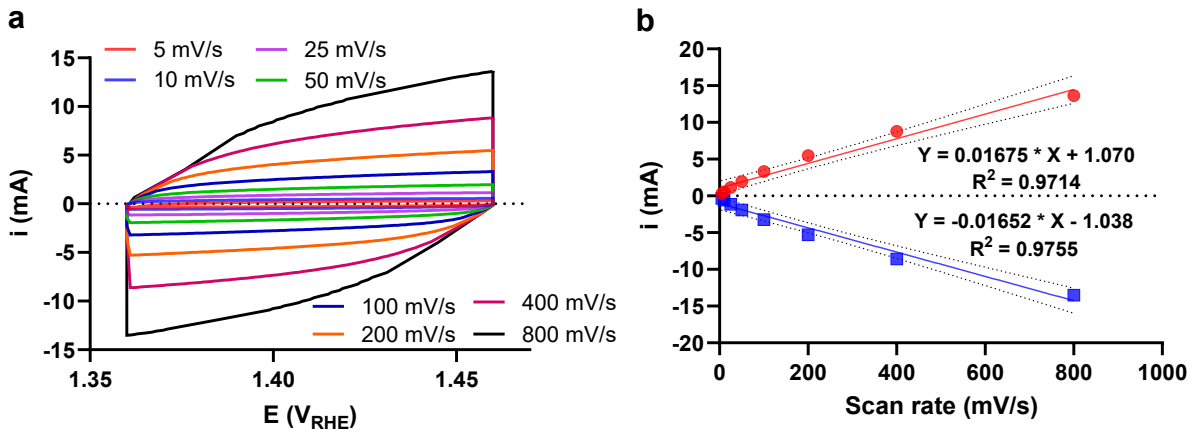

Figure S2. Electric double-layer capacitance measurement for NATO mesh electrode (5 cm x 5 cm). (a) Continuous cyclic voltammograms in a window of open circuit potential ± 0.05 V (non-Faradaic region) at different scan rates (5 – 800 mV/s). CVs were conducted in 100 mM $NaClO_4$ electrolyte. (b) Anodic (red line) and cathodic (blue line) charging currents (i) obtained from Figure S2(a) as a function of scan rates (v).

The double-layer capacitance (C_{DL}) can be calculated by following equation,[1]

$$C_{DL} = i/v \tag{3}$$

which is the average slope in Figure S2(b), determined as 16.64 mF. The electrochemical active surface area (ECSA) can be further calculated by measured double-layer capacitance (C_{DL}) and specific capacitance ($C_S = 0.0375\ mF/cm^2$).[1]

$$ECSA = C_{DL}/C_S \tag{4}$$

The ECSA of mesh NATO anode is calculated as 443.6 cm^2, which is 8.9 times larger than the geometric surface area (50 cm^2).

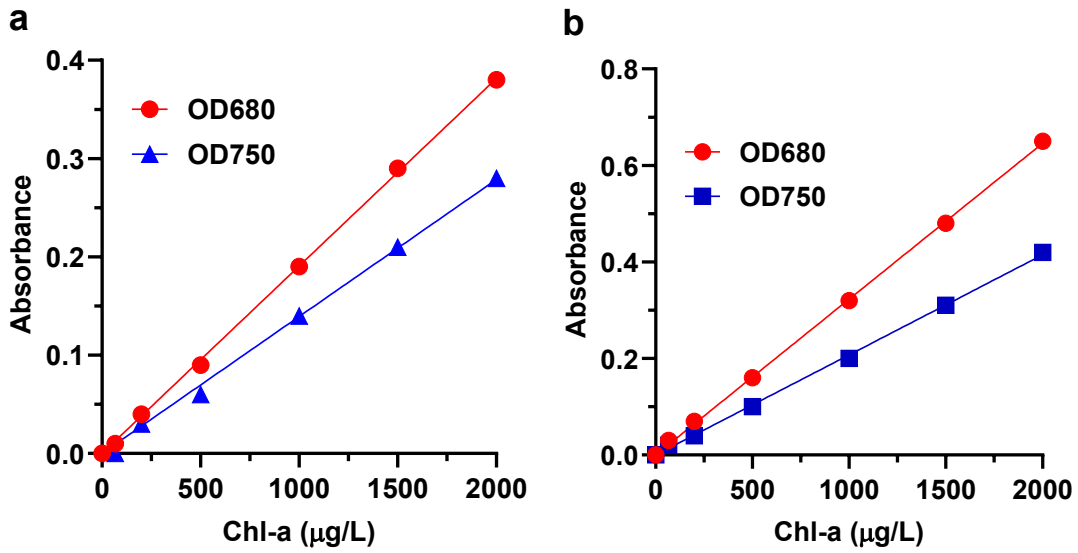

Figure S3. Correlation between optical density (OD) and chlorophyll-a (Chl-a) concentrations for (a) *Microcystis aeruginosa* and (b) *Synechococcus* cultures.

Microcystis aeruginosa and *Synechococcus* cultures were diluted by PBS electrolyte to reach different Chl-a concentrations. Light absorbance of these serially diluted samples was measured at 680 nm and 760 nm. The optical density at 680 nm (OD680) measures the direct absorbance of light by intracellular chlorophyll-a (Chl-a) molecules in live algae. Plotting the OD680 values (y-axis) against the Chl-a concentrations obtained after cell extraction (x-axis; see Methods section for details) reveals a linear correlation, thereby validating the accuracy of the Chl-a measurement method for quantifying viable algae cells. The optical density measurement at 750 nm (OD750) primarily represents the scattering of light by the cells rather than absorption by cellular pigments.[2] OD750 has been widely used to estimate algae cell density. The strong linear correlations between Chl-a concentrations and OD750 readings further validate that Chl-a can serve as a reliable proxy for representing cell density.

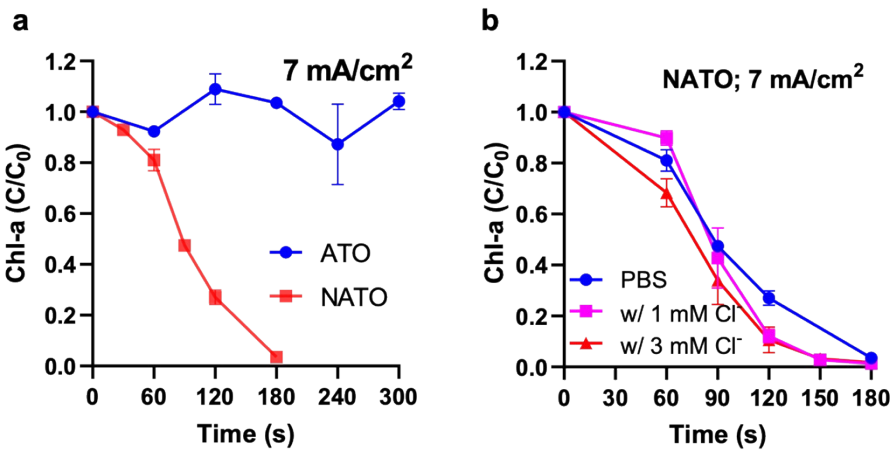

Figure S4. (a) Inactivation of *Synechococcus* by ATO and NATO electrodes in PBS electrolyte. (b) Effect of Cl^- content on the destruction of Chl-a on NATO anode. All tests were conducted at 7 mA/cm^2, the PBS electrolyte volume is 95 mL.

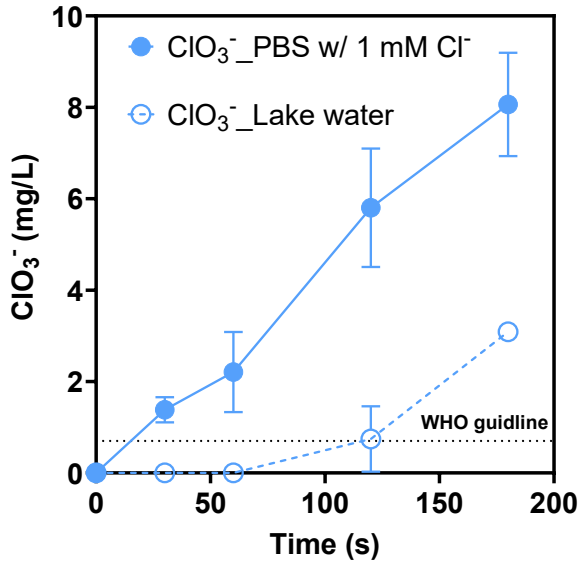

Figure S5. Chlorate (ClO_3^-) formation during electrolysis in PBS solution spiked with 1 mM Cl^- and lake water by NATO anode at 7 mA/cm^2.

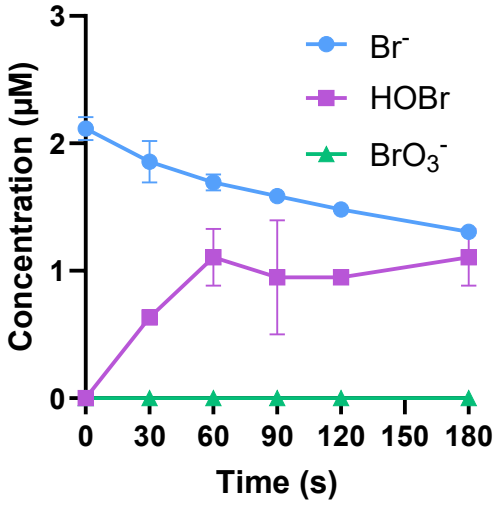

Figure S6. Transformation of Br^- in the electrolysis by NATO in PBS electrolyte amended with 0.2 mg/L KBr at 7 mA/cm^2. Bromate (BrO_3^-) was not detected (detection limit = 10 μg/L) throughout the reaction.

Figure S7. Pictures of the intake screen.

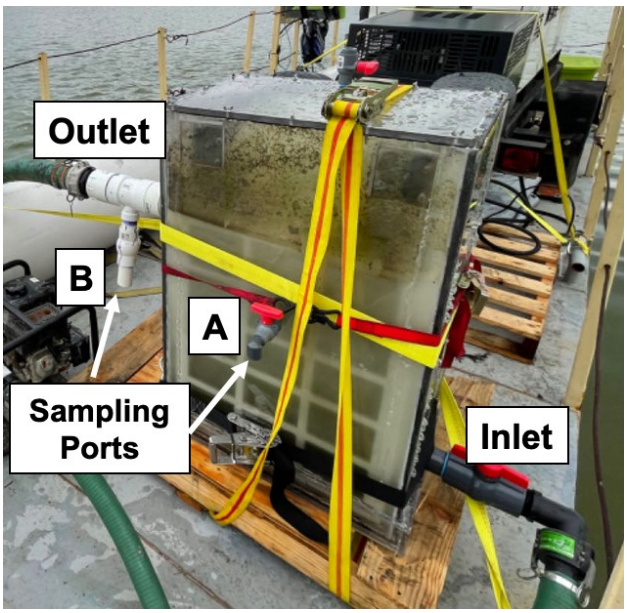

Figure S8. Picture of the full-scale ECO reactor. Samples from port A represent the bulk concentration in the reactor. Samples from port B are considered treated effluent.

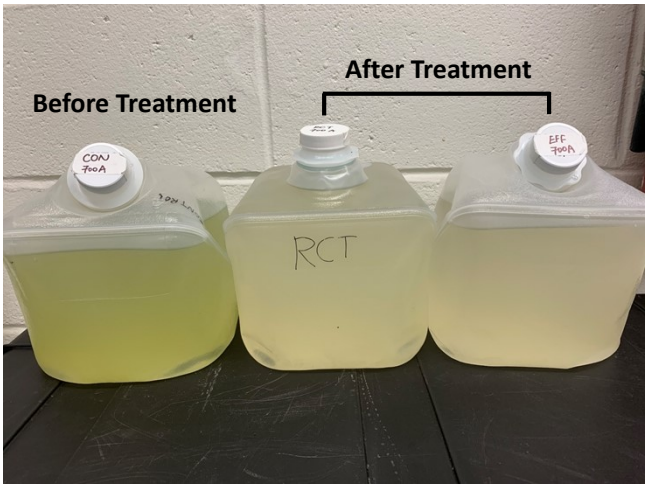

Figure S9. Pictures of influent and treated effluent water samples collected from the full-scale ECO treatment of Lake Neatahwanta water at a current density of 7 mA/cm^2.