Supporting Information

Effects of Anodic Potential and Chloride Ion on

Overall Reactivity in Electrochemical Reactors

Designed for Solar-Powered Wastewater Treatment

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Number of pages: 9 (including the cover page)

Number of figures: 4

Number of tables: 2

Experimental Section

Electrochemical methods. Before all electrochemical experiments, the electrodes were rinsed with acetone and large amount of Milli-Q water. The electrode module was allowed to equilibrate with the electrolyte solution in an open circuit for 30 minutes while monitoring the open circuit potential of anode and cathode. As a routine procedure, the pH, conductivity and the ohmic resistance between anode and reference electrode (R) were measured before and after the electrochemical experiments. The pH and conductivity of the samples were monitored using a pH meter (Mettler Toledo, USA) and a portable conductivity meter (VWR International, USA). As shown in Figure S1, the conductivity increased while R decreased monotonically as the added chloride concentration increased. The anodic potentials were converted into NHE scale using E_a (NHE) = E_a (Ag/AgCl) + 0.197 V.

Prototype PV-powered Wastewater Electrolysis. The solar panel had a peak power output of 180 W with an open circuit voltage of 25.9 V, a short circuit current of 6.95 A, and an active surface area of 1.50 m^2 (0.95 m × 1.57 m), respectively. Incident solar irradiation was measured using a pyranometer (Apogee, USA) which ranged from 1,000 W m^{-2} (noontime) to 600 W m^{-2} depending on the solar zenith angle. A 12 V rechargeable battery that was regulated using a charge controller was used to store excess solar energy. The voltage of the battery was controlled in order to adjust the cell voltage to be 3.9 V. The main oxidants at this cell voltage should be free chlorine species (HOCl considering the bulk pH ~ 6) since the actual anodic potential was not high enough to generate chlorine radicals. In scaling-up the WEC, an inevitable increase of ohmic voltage loss caused a reduction in current density when compared to the bench-top experiment. In these circumstances, an adjustment of electrode configuration was required to

keep the free chlorine generation rate. In particular, the electrolyte volume-to-electrode surface area ratio was adjusted to 2.5 cm (20,000 cm^3 / 8,000 cm^2) while the distance among electrodes was reduced to 2 mm, to achieve a current per unit electrolyte volume comparable with laboratory WEC (L50).

Analysis of total and fecal coliform concentration. In our sampling procedure, a 0.45 μm membrane filter was used to collect a microbial sample. The filter membrane is then placed on a 'mEndo' agar LES media for total coliform and a 'mFC' agar for fecal coliform for selective growth. The media plates were incubated at 35 °C for total coliform and 44.5 °C for fecal coliform for 24 hours in order to promote discrete colonies. The concentration of total and fecal coliform bacteria in the wastewater was estimated in terms of CFU 100 mL^{-1} (Colony Forming Units per 100 mL).

Table S1. Composition of residential-strength wastewater used in this study.

Constituent	Mean	COV (%)
pH	6.6 – 7.3	–
COD (mg L^{-1})	180	6.02
TN (mM N)	2.594	7.96
NH$_4^+$ (mM)	1.910	5.19
NO$_3^-$ (mM)	< 0.01	–
Cl$^-$ (mM)	3.880	–
ClO$_3^-$ (mM)	< 0.01	–
Mg^{2+} (mM)	0.6387	1.96
Ca^{2+} (mM)	1.287	1.38

COV: Coefficient of Variation.

Table S2. Reduction potential (E) at pH 7 and standard reduction potential (E^0) at pH 0 for several redox couples involved in the electrochemical reactions.

Redox Couple	at pH 7 (V NHE)	at pH 0 (V NHE)
O_2/H_2O	0.82	
Cl_2/Cl^-	1.36	1.36
$HOCl/Cl^-$		1.48
ClO^-/Cl^-		0.81
$Cl\cdot/Cl^-$		2.4
$Cl_2^-\cdot/Cl^-$		2.0
ClO_3^-/Cl_2	0.97	
$ClO_3^-/HOCl$	0.92	
ClO_3^-/ClO^-	0.94	
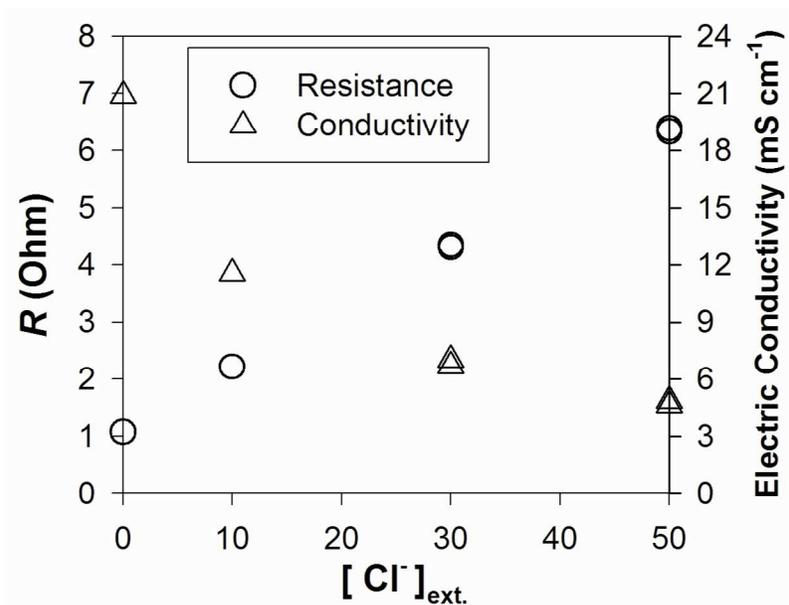
Figure S1. Ohmic resistance between anode and reference electrode (R) and electric conductivity of bulk electrolyte as functions of added Cl⁻ concentration ([Cl⁻]$_{ext.}$) in bench-top electrolysis experiments using domestic wastewater samples.
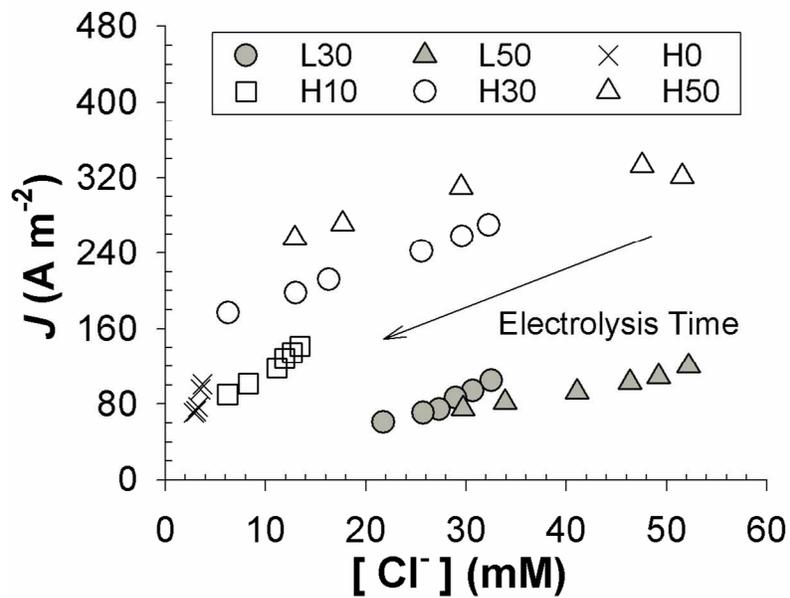
Figure S2. Evolution of current densities along with variations in Cl$^-$ concentration under variable applied anodic potential (L: 2.2 V, H: 3.0 V NHE) and added Cl$^-$ concentration (0, 10, 30, 50 mM) in electrolysis experiments using domestic wastewater samples. The arrow indicates an arbitrary varying direction as a function of time.
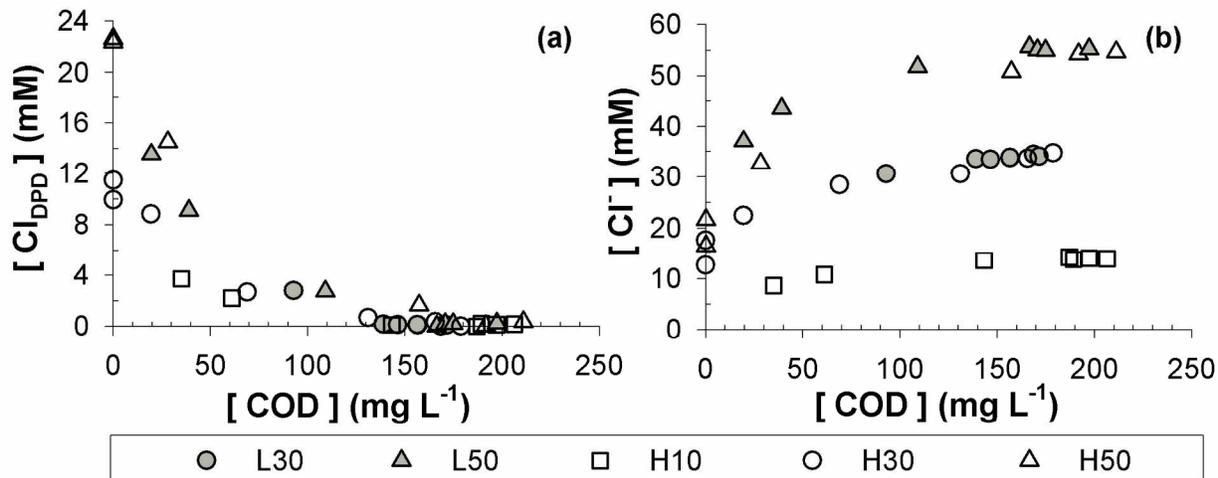
Figure S3. Evolutions of (a) total chlorine (Cl_{DPD}) and (b) Cl^- concentration as a functions of variations in COD concentration under variable applied anodic potential (L: 2.2 V, H: 3.0 V NHE) and added Cl^- concentration (10, 30, 50 mM) in electrolysis experiments using domestic wastewater samples.
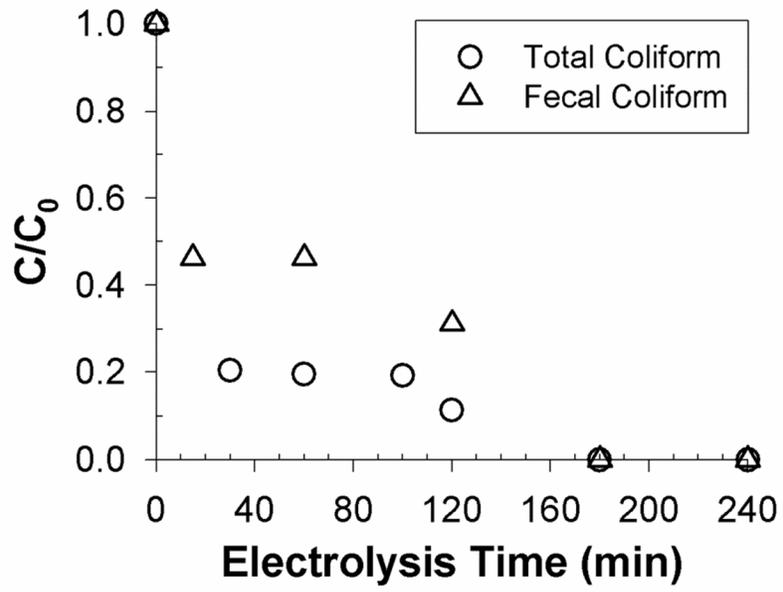
Figure S4. Time profiles for normalized concentration of total and fecal coliform during photovoltaic-powered wastewater electrolysis cell (PWEC, 20 L) experiment using domestic wastewater (cell voltage: 4.9 V, added Cl^- concentration: 50 mM).