Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Supplementary Materials

Electrochemicaly-mediated Remediation of Genx Using Redox Copolymers

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S1. Methods

S1.1 Synthesis of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl-co-4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (PTMA-co-PTMPMA)

Synthesis for PTMA-co-PTMPMA was described in previous work from our group.[1] Radical content obtained was 51%. This result was obtained by UV-vis measurements with TEMPO used as a reference[2], and SEC data obtained from GPC resulted in M_n of 84.7 kg/mol and M_w of 290.0 kg/mol.[2]

S1.2 Electrode preparation

To prepare the PTMA-co- PTMPMA/MWCNT electrodes, we dissolved 80 mg of the polymer in 20 mL of acetone and sonicated for 15 min. Then, 80 mg of MWCNT were added to the solution and dispersed by sonication for 120 min in icy water. After the solution was completed, the electrodes were dipped onto a stainless-steel mesh from McMaster-Carr, stainless steel cloth, 325x325. The stainless-steel mesh was cut into 1 cm x 2 cm and soldered onto a Cu wire (0.0016 inches). The active electrode area was 1cm x 1cm x 2 sides of coating, and the loadings were controlled to be 0.5 mg of the PTMA-co-PTMPMA/MWCNT coating per electrode. Before use, PTMA-co-PTMPMA/MWCNT electrode was activated by carrying out cyclic voltammetry in 0.1 M NaClO4 in the range of 0 – 1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV s-1 for three cycles and then fully reduced for 3 minutes at 0.0 V.

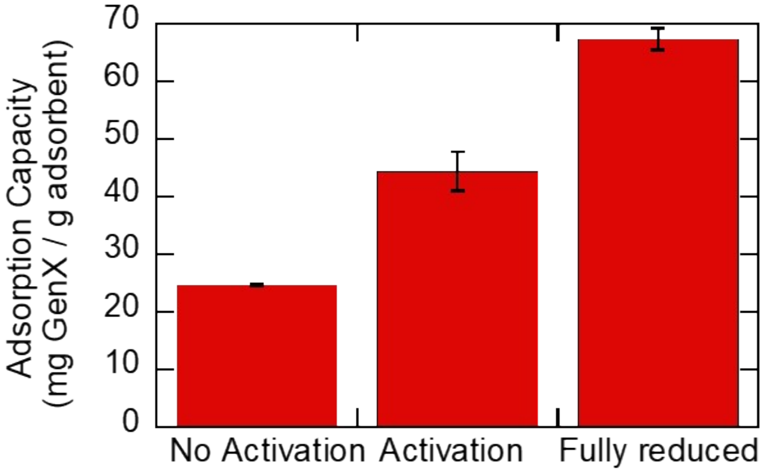


Figure S1: Adsorption uptake of GenX with different electrode pretreatments. Experiment performed with 0.1 mM GenX and 20 mM NaCl at 0.8 V for 30 min.

S1.3 Flow by-cell assembly

The flow cell assembled is composed of a top flowing (TF) acrylic base, TF electrode backing gasket, PTMA-co-PTMPMA/MWCNT electrode, 1/16" middle gasket, 4x4 cm plastic mesh, Ti electrode, which could be switch to a Pt coated/Ti electrode, bottom flowing (BF) backing electrode backing gasket, and BF acrylic base. The flow cell was tightened with 8 M3 nuts and bolts in an aleatory fashion (1,5,2,6,3,7,4,8) to provide stability and prevent leaking by adjusting to a proper seal. This seal was rapidly tested by passing an initial solvent solution without applying any potential and measuring the volume in versus the volume out for one minute.

The PTMA-co-PTMPMA/MWCNT electrode had an active area of 4 cm x 4 cm. A non-conductive tape was placed around the corners of the Ti or Pt coated/Ti plate to obtain a precise coating area of 4 cm x 4 cm. The polymer solution was then dropped cast, and a total volume of 800 uL was injected onto the surface. The solution was dried rapidly in air, and to ensure dryness, we applied forced air onto the surface to enhance the drying. Before experimentation, the electrode was pre-treated by activating it with cyclic voltammetry in 0.1 M NaClO4 in the range of 0 – 1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV/s for three cycles to then fully reduce for 3 minutes at 0.0 V.

To start the experimentation, the stock solution, composed of 0.1 mM Genx and 20 mM NaCl or 0.1 mM PFOA and 20 mM NaCl, is placed on a magnetic stirring plate. A suction side tube, connected to the Longer peristaltic pump, is inserted in the stock solution, and the discharge side tube is connected to the bottom flowing inlet of the flow cell. On the other side of the flow cell, a tube is attached to the output flowing outlet of the flow to collect samples. The electrolyte flowed from the bottom of the Ti side to flow out from the top on the PTMA-co-PTMPMA/MWCNT side. The flow rate of the peristaltic pump is calculated and set to be 1.0 mL/min.

Typical experimental parameters were set as followed:

1. 30 minute adsorption - chronopotentiometry (2 mA)

3. 10 minute mid-rinse - open circuit (0A)

4. 30 minute desorption - chronopotentiometry (-2.0 mA)

During the experiment, the sample collection was set for one sample collection every five minutes of the experimental run. In addition, a 5 ml stock solution is taken directly before and directly after the experiment. The samples were then diluted and analyzed for LC/MS.

S1.4 Sputter coating of a Ti electrode with Pt

For the flow cell, experimental analysis on two electrodes was compared: one containing bare Ti and a Pt/Ti electrode. The Pt coated Ti electrode was sputter-coated (3 x 3 in.) through magnetron sputtering (AJA ORION 3 sputter system with ST20 ORION magnetron sputter gun). The base pressure was 2.5 x 10^{-6} Torr, and argon was used at a process pressure of 3.4 mTorr. Sputtering took place at room temperature, with direct current and 80 W power, ~15 rpm sample rotation, 1 minute pre-sputtering. The recorded sputtering rate was 9.6-10.4 Å/s. The Pt thickness measured by the instrument's quartz crystal microbalance was 251.0 nm.

S1.5 LC/MS parameters

Table S1: LC/MS conditions for the analysis of PFAS

LC/MS conditions	
Instrument	Waters Synapt G2Si with Waters Acquity H-class UPLC system
Column	Aquity UPLC BEH C18 1.7 um
Column temperature	40 °C
Mobile phase	A) H_2O with 5mM ammonium acetate solution B) Acetonitrile
Flow rate	0.4 mL/min
Equilibration time	2 minutes
Gradient elution profile	0–3 minutes: 30–65 % B
	3–4 minutes: 65 % B
	4–5 minutes: 65–100 % B
	5–8 minutes: 100 % B
	8.1 minutes 30% B
	10 minute 30 % B
Ionization mode	ESI negative

Injection volume for each PFAS differed depending on the compound. Longer chain PFAS, PFOA, were rapidly detected and would require a smaller injection volume and lower calibration curve concentrations. Table S2 indicates the summary for each LC/MS standard and injection volume.

Table S2: LC/MS calibration curve standards concentration and injection volume

Compound	Calibration Range (µM)	Injection Volume (µL)
PFOA	0-5	0.5
GenX	0-25	10
PFBS	0-25	10

PFBA	0-25	10
PFHpA	0-5	0.5

S1.6 Water matrixes properties

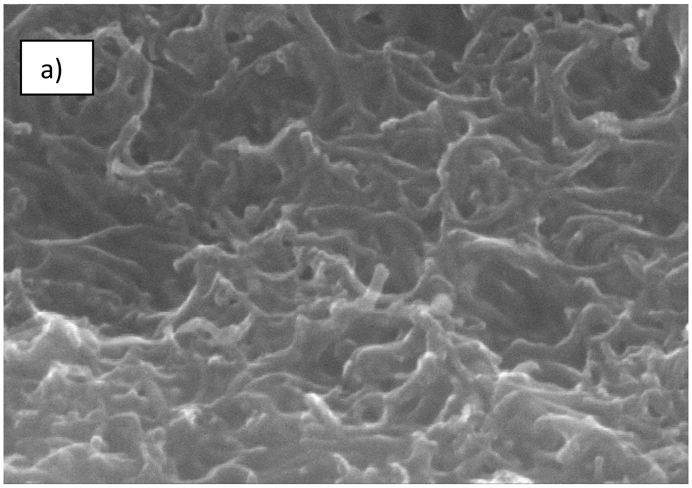
Different water matrices were used to explore our system's behavior in multiple scenarios.

A) 0.1 mM GenX in municipal secondary wastewater effluent
  - Wastewater was obtained from Urbana-Champaign Sanitary District
  - Conductivity of 922 µS/cm
  - Water content:
    i. Biological oxygen demand 4-10 mg/L
    ii. Total suspended solids 3-10 mg/L
    iii. Ammonia 2-8 mg/L
    iv. Phosphorus 1-2.5 mg/L

B) 0.1 mM GenX in tap water
  - Tap water was obtained from the University of Illinois at Urbana-Champaign
  - Conductivity of 330 µS/cm
  - Water content (based on the 2020 water quality report of the University of Illinois at Urbana-Champaign):
    i. Chlorine 2 mg/L
    ii. Haloacetic acids 17-30 µg/L
    iii. Fluoride 0.71 mg/L
    iv. Arsenic 1 µg/L
    v. Manganese 0-19 µg/L

S2. Characterization techniques

S2.1 Scanning electron microscopy (SEM) images.



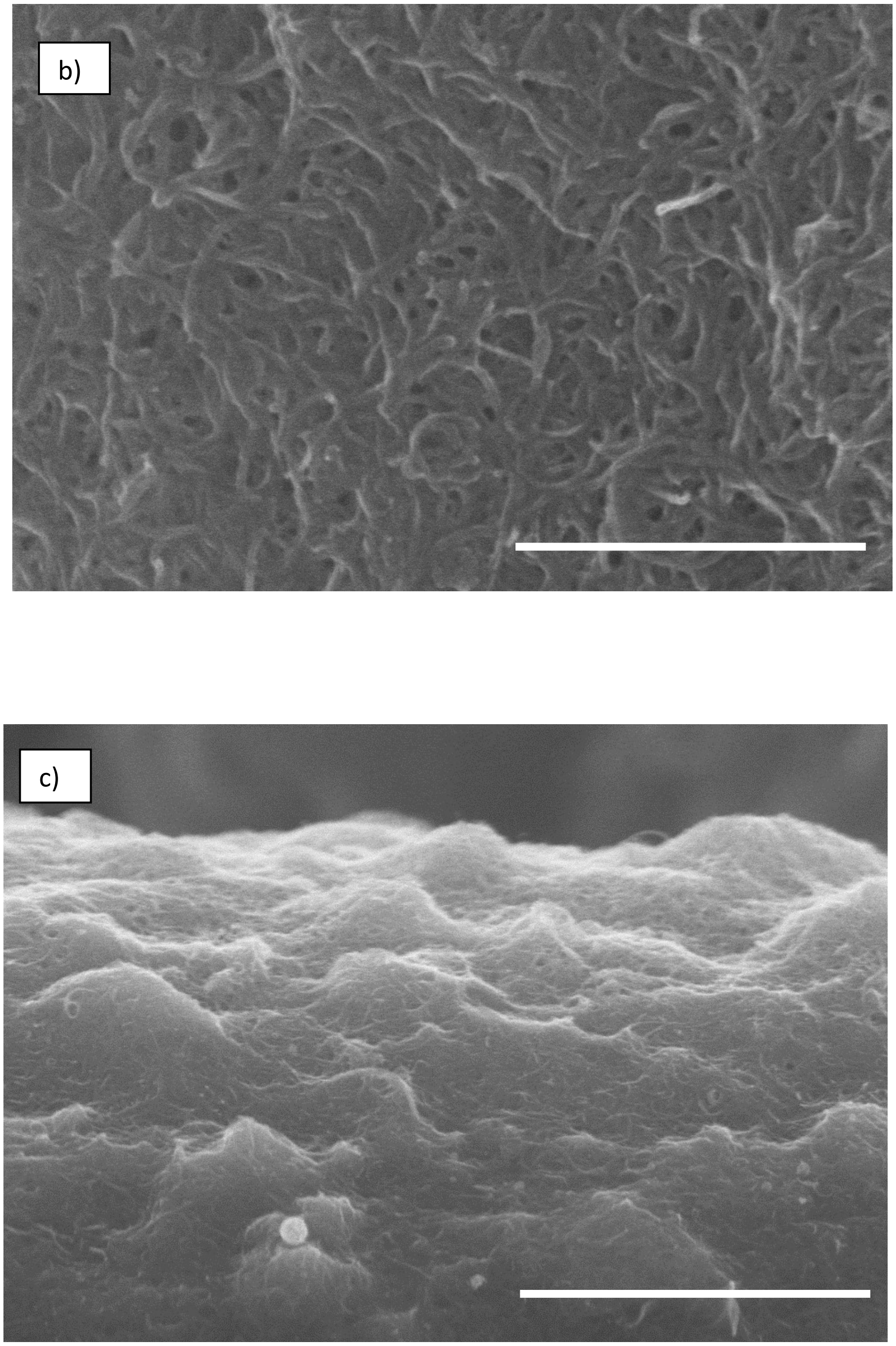


Figure S2: High-resolution SEM images of a PTMA-co-PTMPMA/MWCNT electrode at various magnifications. Scale bars: a) 500 nm, b) 1 µm, and c) 5 µm.

S2.2 Electron paramagnetic resonance behavior of PTMA-co-TMPMA/MWCNT electrodes

Solid spectra for Electron paramagnetic resonance (EPR) spectroscopy were determined to prove the radical behaviour of the copolymer PTMA-co-PTMPMA. The analysis was performed in a 3 mm diameter quartz EPR tube with a dilution of 1 to 9 ratio of high-purity (99.999%) KNO_3. The Bruker EMXPlus spectrometer was used with an X-band frequency of 9.8 GHz along with a Bruker ER4119HS high sensitivity resonator.

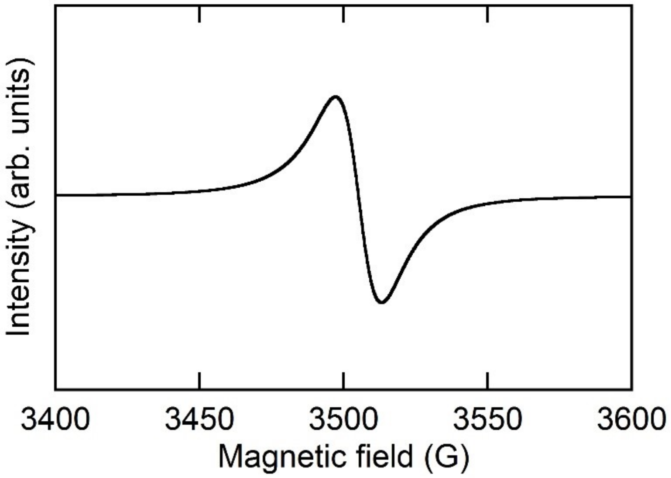


Figure S3: Solid EPR spectra for PTMA-co-PTMPMA.

S2.3 XPS analysis

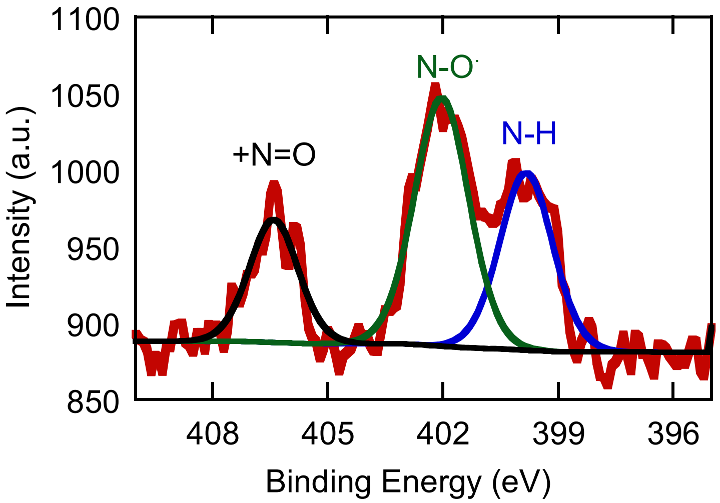


Figure S4: High magnification XPS of N1s spectra for PTMA-co-PTMPMA electrode. Three nitrogen states can be observed.

S2.4 Contact Angle

Contact angle measurements were performed in a Rame-Hart 250 Standard Goniometer. The program used for angle analysis was DROP Image Advanced. The contact angle experiment was performed on top of a PTMA-co-PTMPMA electrode with 0.1 mM GenX + 20 mM NaCl as the droplet.

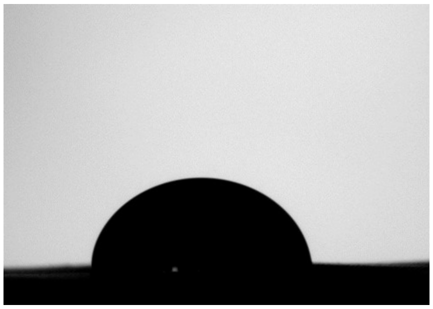


Figure S5: Contact angle of PTMA-co-PTMPMA with 0.1 mM GenX + 20 mM NaCl.

S2.6 Electrode stability testing

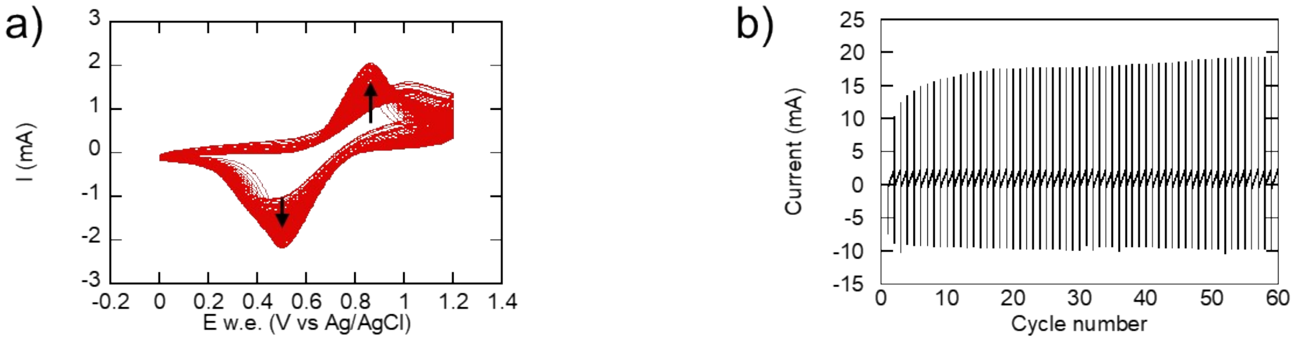


Figure S6: a) cyclic voltammogram of PTMA-co-PTMPMA after 100 cycles, scan rate of 10 mV/s in a range from 0.0 to 1.2 V vs. Ag/AgCl, b) potentiometric charge/discharge of PTMA-co-PTMPMA after 60 cycles, adsorbing for 5 minutes at 0.8 V vs. Ag/AgCl and desorbing in the 0.1 Mm GenX solution for 5 minutes.

S3. Adsorption Isotherms

All adsorption isotherms were performed under different equilibrium concentrations: 0.05, 0.1, 0.25, 0.5 and 0.75 mM GenX and 20 mM NaCl. Both Langmuir and Freundlich adsorption isotherms were analyzed using their respective equations:

$$\frac{1}{Q_e} = \frac{1}{Qm} + \frac{1}{C_e Q_m b} \; (Eq.\, S1)$$

$$Q_e = GenX \; adsorbed \; at \; equilibrium \left[\frac{mg}{g}\right]$$

$$Q_m = maximum \; adsorption \; capacity \; for \; GenX \left[\frac{mg}{g}\right]$$

$$C_e = equilibrium \; concentration \; of \; GenX \left[\frac{mg}{L}\right]$$

$$b = equilibrium \; constant \left[\frac{L}{mg}\right]$$

$$Q_e = KC_e^{\frac{1}{n}} \; (Eq.\, S2)$$

$$Q_e = GenX \; adsorbed \; at \; equilibrium \left[\frac{mg}{g}\right]$$

$$K = Freundlich \; constant$$

$$n = Affinity \; of \; adsorptive \; distribution$$

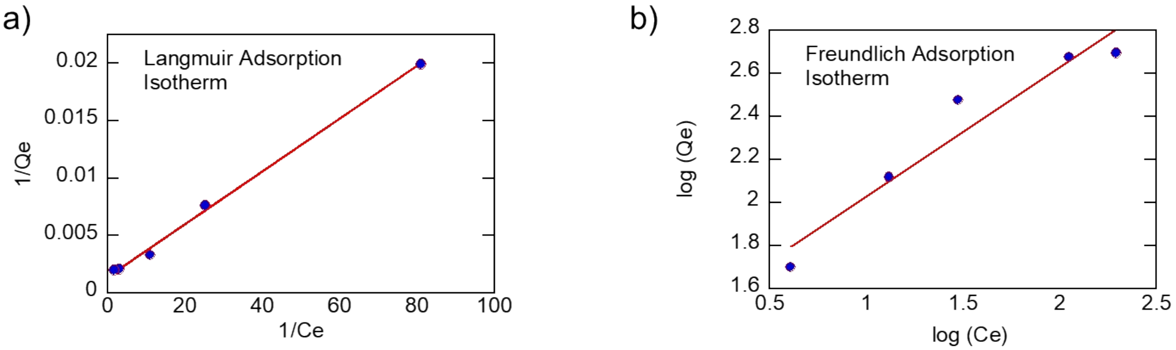


Figure S7: Isotherm curve-fit lines for a) Langmuir adsorption model and b) Freundlich adsorption model.

Table S3: Isotherm parameters for the removal of GenX with PTMA-co-PTMPMA. a) Langmuir Isotherm parameters. b) Freundlich isotherm parameters.

a) Langmuir isotherm parameters:

Intercept	**Slope**	**Qm (mg/g)**	**b (L/mg)**	**R²**

0.00141	2.29E-04	709.21986	6.14E+00	0.99737

b) Freundlich isotherm parameters:

Intercept	**Slope**	**1/n**	**K ((mg/g)(L/mg)$^{1/n}$)**	**R^2**
1.43002	0.59854	0.59854	26.91659	0.93353

S4. Kinetic study

The kinetics study was performed at open circuit and at 0.8 V vs. Ag/AgCl under 2.5 mL total volume of 0.1 mM GenX and 20 mM NaCl. To obtain the rate constants of our experimental data, we used two different kinetic models for comparison. Lagergren pseudo-first-order model (equation Eq. S3) was used as well as the pseudo-second-order model (Eq. S4).[3, 4]

$$ln(q_e - q_t) = ln(q_e) - k_1 t \quad \textbf{(Eq. S3)}$$

$$q_e = equilibrium\ uptake\ \left[\frac{mg}{g}\right]$$

$$q_t = uptake\ at\ a\ specific\ time\ \left[\frac{mg}{g}\right]$$

$$k_1 = rate\ constant\ \left[\frac{1}{min}\right]$$

$$t = time\ [min]$$

$$\frac{t}{q_t} = \frac{1}{\left(k_2 {q_e}^2\right)} + \frac{t}{q_e} \quad \textbf{(Eq. S4)}$$

$$k_2 = rate\ constant\ \left[\frac{g}{mg\ min}\right]$$

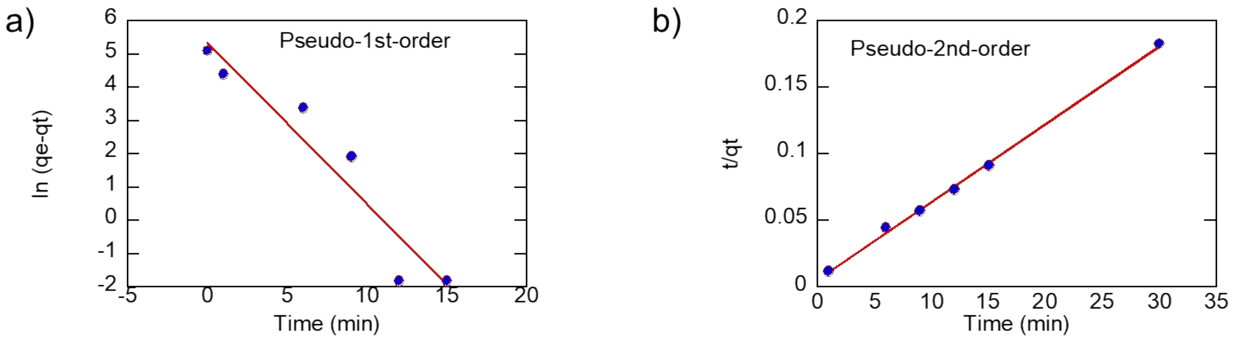


Figure S8: Kinetics curve-fit lines for the removal of GenX using PTMA-co-PTMPMA while applying 0.8 V for 30 minutes: a) Pseudo-first-order kinetic model and b) Pseudo-second-order kinetic model.

Table S4: Kinetic parameters for the removal of GenX using PTMA-co-PTMPMA while applying 0.8 V for 30 minutes for a) the pseudo-first-order kinetic model and b) pseudo-second-order kinetic model.

a) Pseudo-first-order kinetic model

Intercept	**Slope**	**q_e (mg/g)**	**k_1 (1/min)**	**R^2**
5.35042	-0.48624	210.6968	0.01621	0.89644

b) Pseudo-second-order kinetic model

Intercept	**Slope**	**q_e (mg/g)**	**k_2 (g/(mg*min))**	**R^2**
0.00396	0.00595	168.0672	0.00894	0.99762

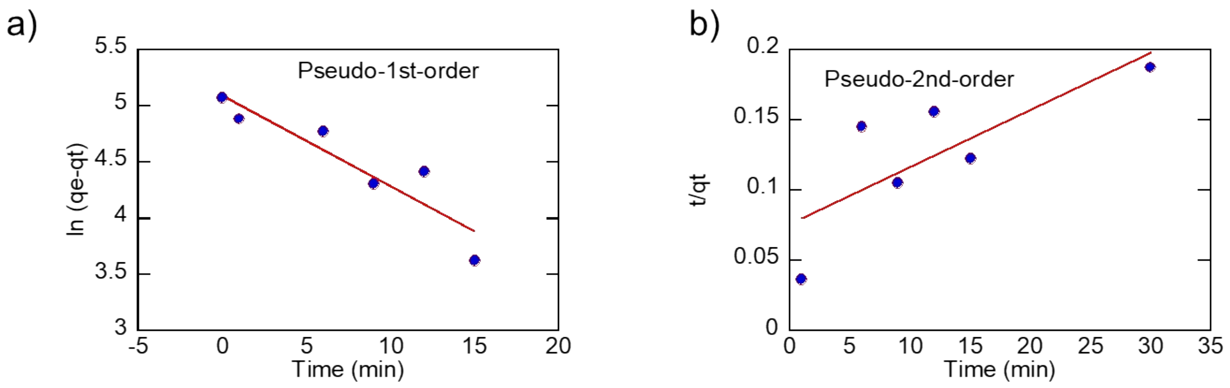


Figure S9: Kinetics curve-fit lines for the removal of GenX using PTMA-co-PTMPMA at open circuit for 30 minutes: a) Pseudo-first-order kinetic model and b) Pseudo-second-order kinetic model.

Table S5: Kinetic parameters for the removal of GenX using PTMA-co-PTMPMA at open circuit for 30 minutes for a) the pseudo-first-order kinetic model and b) pseudo-second-order kinetic model.

a) Pseudo-first-order kinetic model

Intercept	**Slope (1/min)**	**q_e (mg/g)**	**k_1 (1/min)**	**R^2**
5.09252	-0.08051	162.7996	0.00268	0.81692

b) Pseudo-second-order kinetic model

Intercept (min*g/mg)	**Slope (g/mg)**	**q_e (mg/g)**	**k_2 (g/(mg*min))**	**R^2**
0.05201	0.00534	187.2659	0.000548	0.59065

S5. Electrochemical Experiments

S5.1 Chronopotentiometry screening

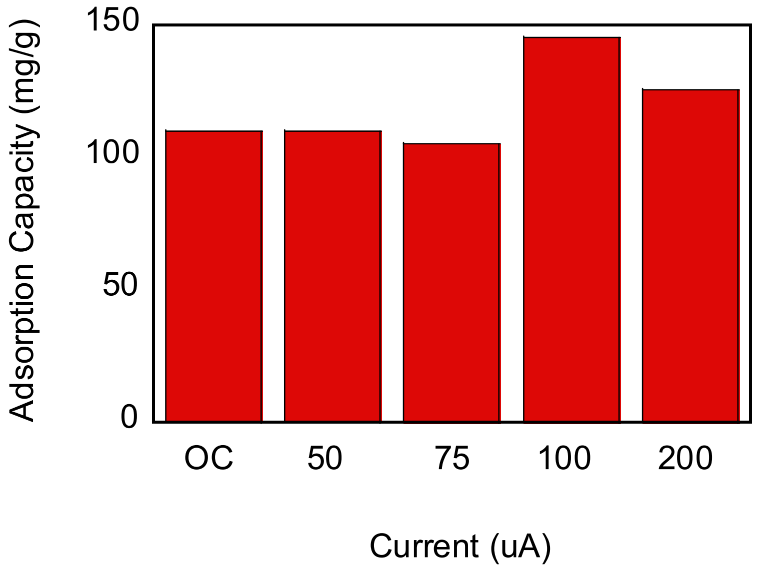


Figure S10:. Adsorption capacity of PTMA-co-PTMPMA/MWCNT electrode during chronopotentiometry with different currents in 0.1 mM GenX and 20 mM NaCl for 30 min.

S5.2 Desorption screening

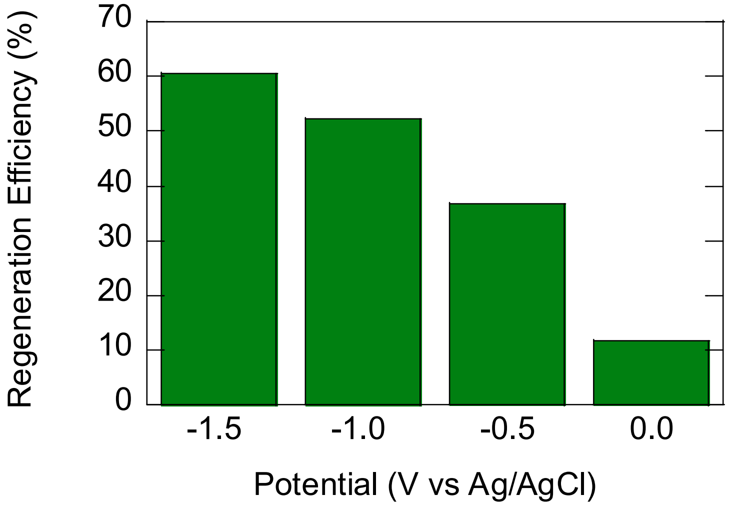


Figure S11: Regeneration efficiency of PTMA-co-PTMPMA/MWCNT electrodes. Adsorption was carried out in 0.1 mM GenX and 20 mM NaCl at +0.8 V for 30 min. Various regenerative potentials were applied for 1 hour in 20 mM NaCl.

S5.3 Control experiment

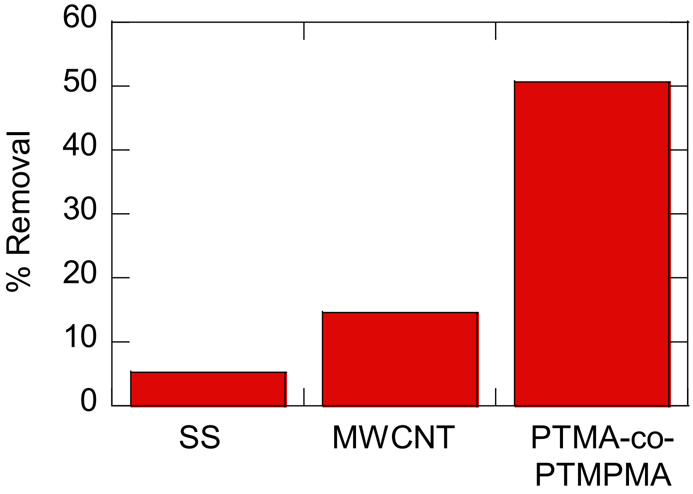


Figure S12: Percent removal of 0.1 mM GenX + 20 mM NaCl while applying 0.8 V vs Ag/AgCl using different electrodes after 30 min of adsorption: (a) bare stainless-steel mesh, (b) MWCNT, and (c) PTMA-co-PTMPMA

S5.4 Energy comparison for Chronoamperometry screening versus chronopotentiometry screening.

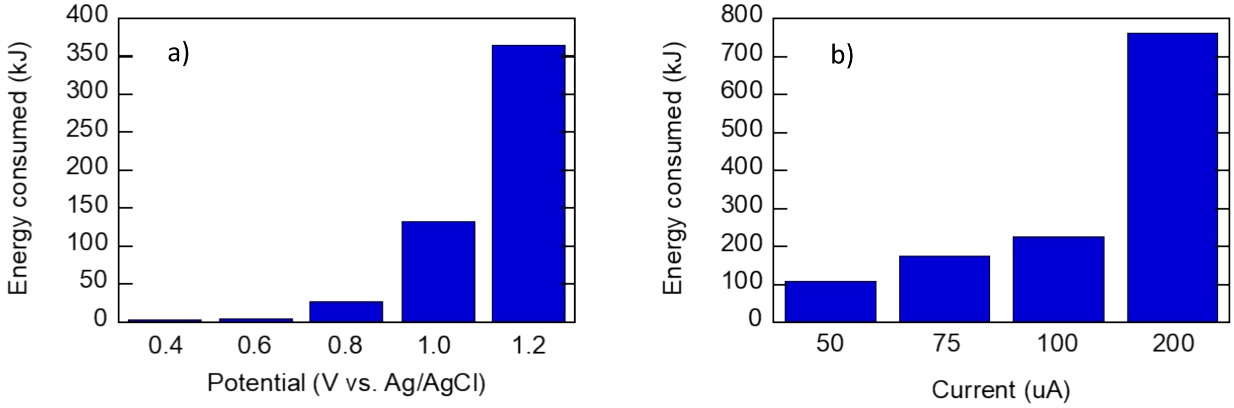


Figure S13: Energy comparison for a) chronoamperometry and b) chronopotentiometry experiments performed for 30 min in 0.1 mM GenX and 20 mM NaCl.

S5.5 Complementary Electrochemical experiments

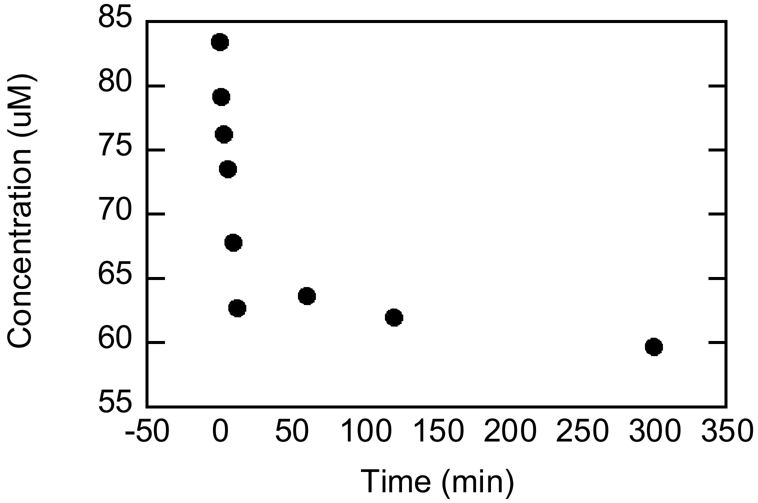


Figure S14: Kinetics of GenX at 0.8 V in 0.1 mM GenX and 20 mM NaCl with 5 mL volume.

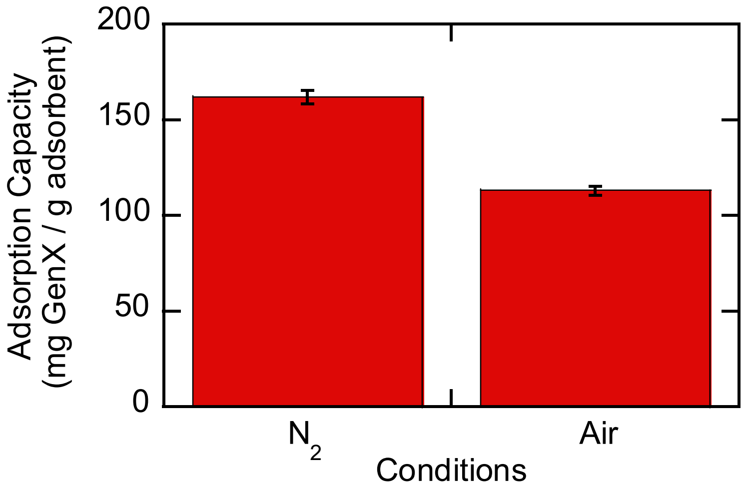


Figure S15: Adsorption changes at +0.8 V in 1 mM GenX and 20 mM NaCl for 30 min under inert conditions with N_2 purge versus when adsorbing without N_2 purge.

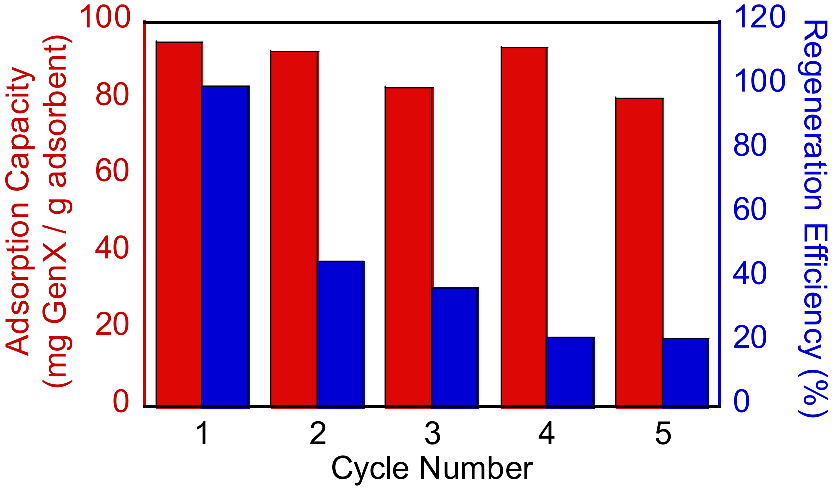


Figure S16: Adsorption uptake for five adsorption-regeneration cycles of 0.1 mM GenX and 20 mM NaCl. Adsorption was performed for 30 minutes with 0.8 V vs. Ag/AgCl, and desorption was done by releasing in 20 mM NaCl and applying -1.0 V vs. Ag/AgCl for 1 hour.

S6. Electrochemical Measurements

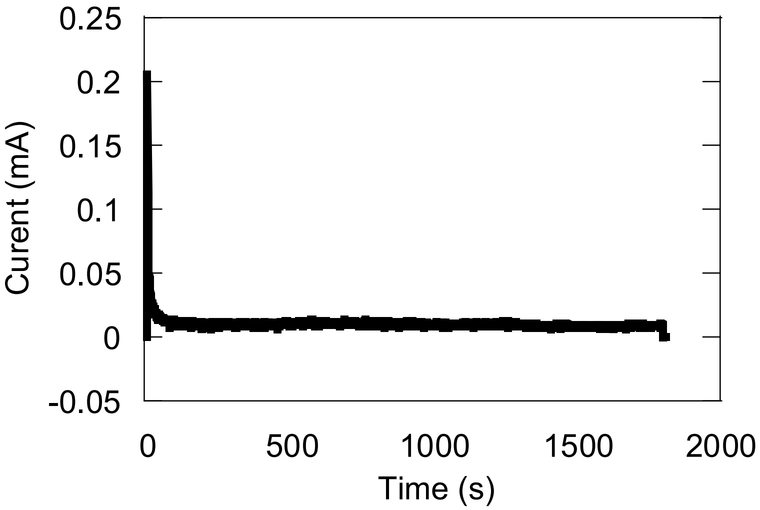


Figure S17: Typical current behavior during adsorption via chronoamperometry with PTMA-co-TMPMA/MWCNT electrode. This adsorption experiment was under chronoamperometry at +0.8 V for 30 min in 0.1 mM GenX and 20 mM NaCl.

S7. Other experimentations

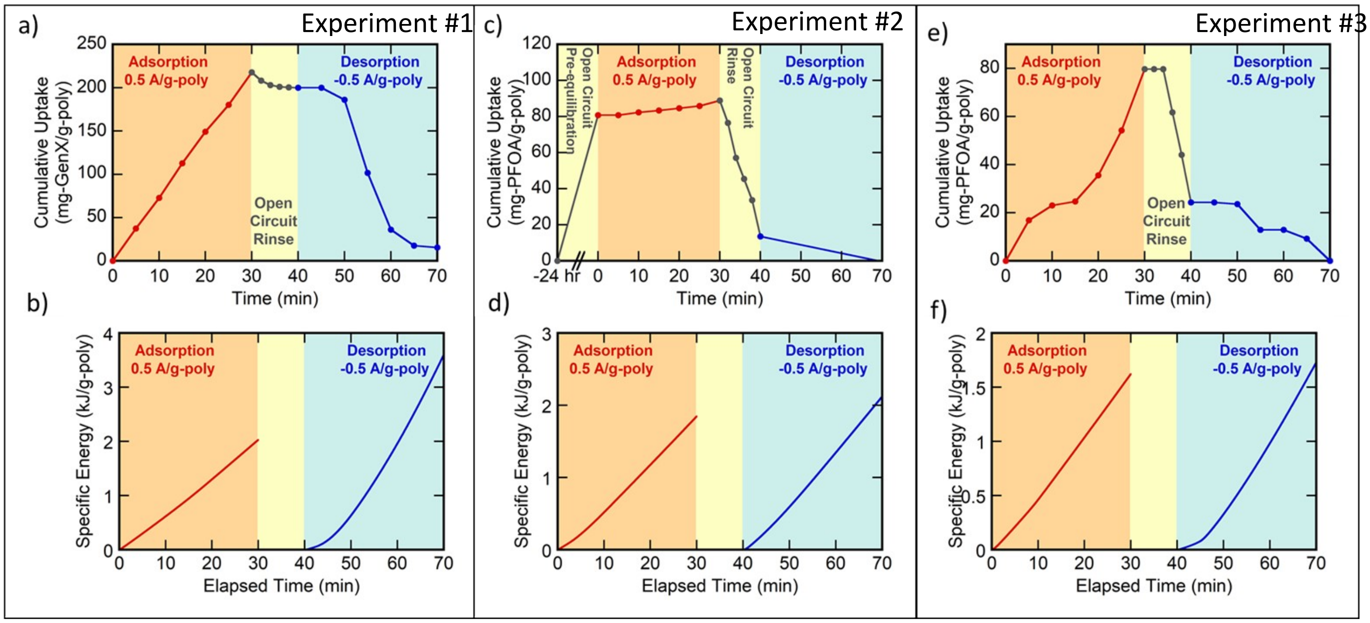


Figure S18: (a),(c), and (e) Flow cell adsorption experiments. Uptake is determined based only on the polymer mass load. (b), (d), and (f) Flow cell energy analysis determined with the polymer mass load. (a) adsorption-release of GenX after pre-treating the PTMA-co-PTMPMA electrode and pre-equilibrating for 8 hours. The counter electrode was Ti for this experiment. (c) adsorption and release of PFOA after pre-treating the PTMA-co-PTMPMA electrode and pre-equilibrating for 8 hours. (e) adsorption and release of PFOA after only activating the PTMA-co-PTMPMA electrode. The counter electrode in this case was Pt coated/Ti plate

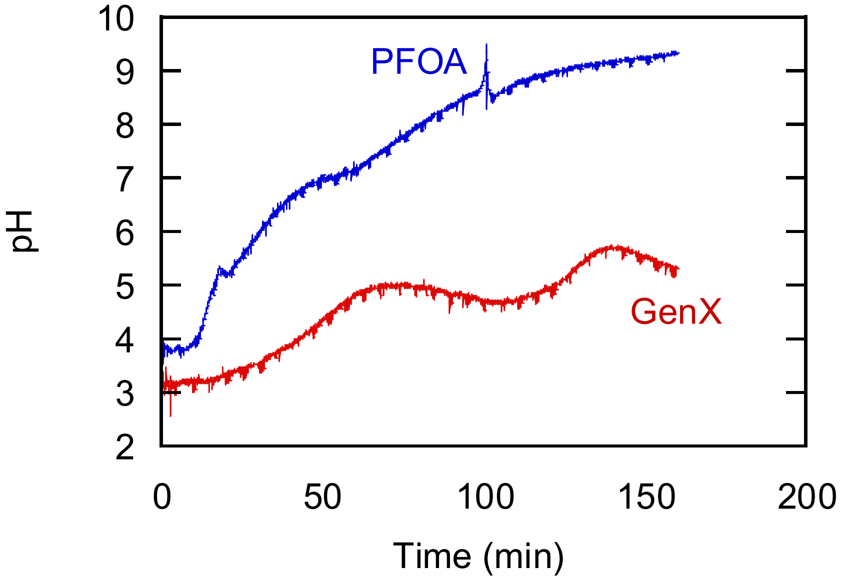


Figure S19: pH performance with PTMA-co-TMPMA/MWCNT electrode. This adsorption experiment was under chronoamperometry at +0.8 V for 30 min in 0.1 mM GenX and 20 mM NaCl.

S7.1 Possible fragmentation

A possible route for fragmentation occurrence was detected after six desorption cycles. Further analysis must be implemented to fully quantify LC spectra with detectable trace peaks.

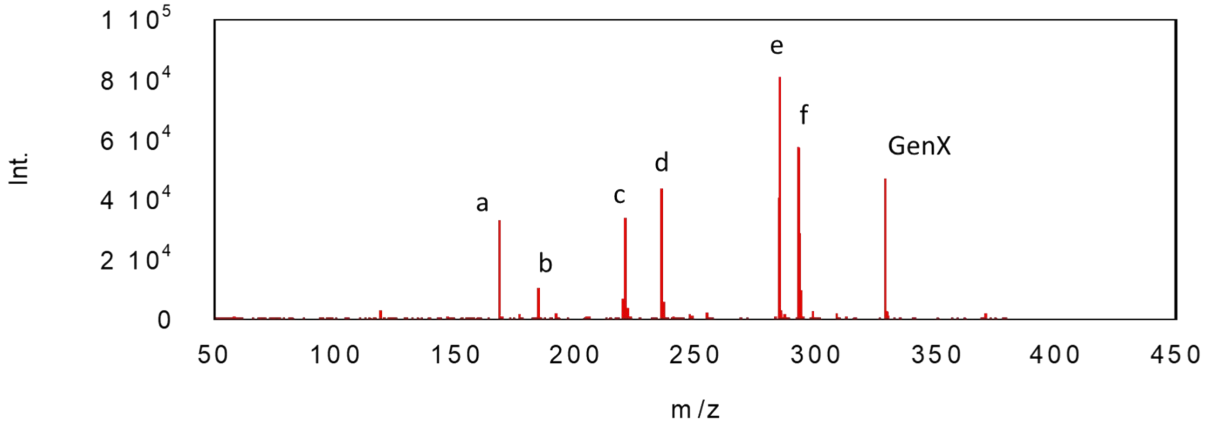


Figure S20: Electron ionization mass spectrum for GenX desorption after six cycles.

Table S6: LC/MS peak analysis of figure S.11

Peak	**Molecular weight (Da)**	**Molecular fragment**
a	168.9892	$C_3F_7^-$
b	184.9836	$C_3HF_7O^-$
c	221.15	$C_4H_2F_7NaO^-$
d	236.1	$C_4HF_9O^-$
e	284.9771	$C_5HF_{11}O^-$
f	293.1751	$C_5F_9Na_2O^-$

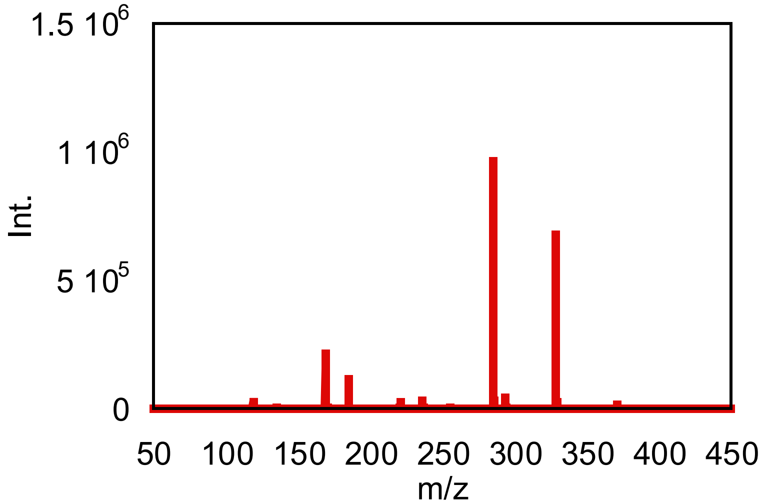


Figure S21: Electron ionization mass spectrum for GenX stock solution of 0.1 mM GenX and 20 mM NaCl. Mass spectra was analyze on m/z = 328.967 +/- 0.05 Da.

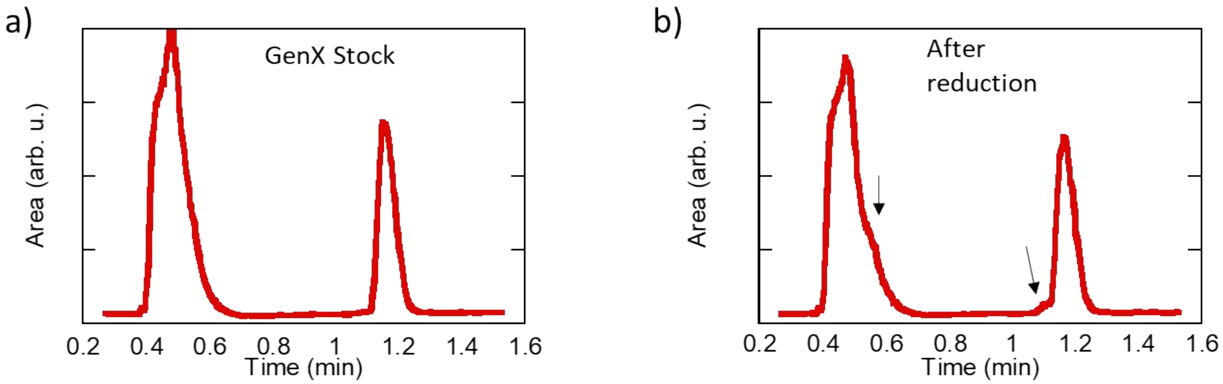


Figure S22: (a) LC/MS Chromatogram of GenX stock (0.024 mM GenX + 20 mM NaCl) and (b) LCMS chromatogram of a sample after being reduced for one hour on 0.024 mM GenX + 20 mM NaCl.

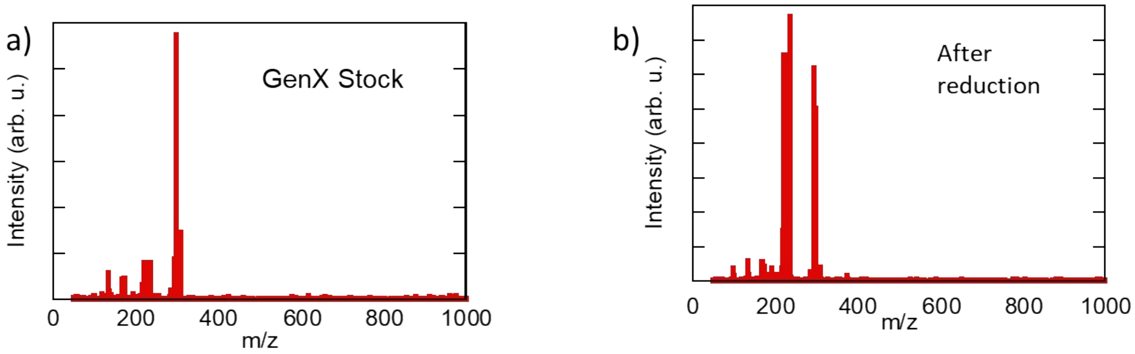


Figure S23: (a) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl stock. (b) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl being reduced for 1 hour at -1 V vs Ag/AgCl with PTMA-co-PTMPMA. Both spectrums are being analyzed at 1.097 min. Notable peaks at 98.9473 and 220.8866 +/- 0.0500 Da have been generated. These peaks could correspond to $C_2HFNaO_2^-$ and $C_4H_2F_7NaO^-$, respectively.

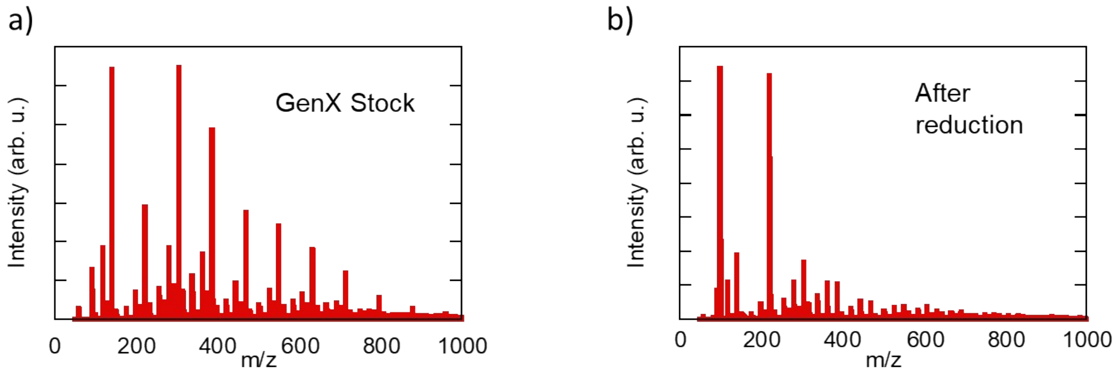


Figure S24: (a) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl stock. (b) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl being reduced for 1 hour at -1 V vs Ag/AgCl with PTMA-co-PTMPMA. Both spectrums are being analyzed at 0.537 min. Notable peaks at 221.1531, 236.1041, and 293.1749 +/- 0.0500 Da have been generated. These peaks could correspond to $C_4H_2F_7NaO^-$, $C_4HF_9O^-$, and $C_5F_9Na_2O^-$, respectively.

References

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4. Y. S. Ho and G. McKay, Pseudo-second order model for sorption processes, *Process Biochemistry*, 1999, **34**, 451-465.