Ionic Fluorogels for Remediation of Per- and Polyfluorinated Alkyl Substances from Water

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1. MATERIALS AND INSTRUMENTATION

Materials: All materials were purchased from commercial source and used as received without further purification unless otherwise mentioned. Perfluoropolyether Fluorolink® MD700 (Mwt: 1.8-2.0 kg·mol^{-1}) was purchased from Solvay Solexis. 2-(dimethylamino)ethyl methacrylate, Poly(ethylene glycol) dimethacrylate (average Mn 750), azobisisobutyronitrile (AIBN), humic acid and perfluorooctanoic acid (PFOA) were purchased from Sigma-Aldrich. Trifluoroethanol was purchased Synquest labs. Perfluorohexanoic acid (PFHxA) and GenX were purchased from TCI and Matrix respectively.

For the studies done in Cape Fear River water, analytical standards for PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, and GenX were obtained from Wellington Labs (Guelph, ON, CA). Analytical standards for PFMOAA, PMPA, PEPA, PFO2HxA, PFO3OA, PFO4DA, PFO5DoA, Nafion Byproduct 2, HydroEve, and NVHOS were obtained from The Chemours Company (Wilmington, DE).

Instrumentation:

LCMS: Water samples were stored under refrigeration until analysis. A 196 µL aliquot of sample and 4 µL of stable isotope-labeled analogues (Wellington Labs, Guelph, CA, product numbers MPFAC-C-ES and M3HFPO-DA) were transferred to polypropylene autosampler vials and closed with caps fitted with silicone septa. No other processing was done as per a direct injection method by M. Sun et al.[1]

Analysis of target compounds was performed using an Accela HPLC system coupled to a TSQ-Quantum Ultra triple-quadrupole mass analyzer (Thermo Scientific, San Jose, CA) operated in negative ion mode. Samples were chromatographed on a 3.0 × 50 mm Poroshell C18 2.7 µm column (Agilent Technologies, Santa Clara, CA) with gradient elution at a flow rate of 350 µL per min. Binary mobile phase consisted of 95:5:water:methanol containing 2 mM ammonium acetate (A) and 5:95:water:methanol containing 2 mM ammonium acetate (B). Composition started at 25% B, was held for 0.5 min., increased linearly to 90% B over 2 min., was held at 90% B for 1.5 min., decreased linearly to 25% B over 0.1 min., and held at 25% B for 0.9 min for column equilibration. Mass spectrometer parameters were as follows: spray voltage of 3000 V, vaporizer temperature of 150 ˚C, sheath gas flow rate 40, auxiliary gas flow rate 20, capillary temperature of 225 ˚C, argon collision gas pressure of 1.0 mTorr, 0.05 sec per scan, quadrupole 1 resolution of 0.5 amu, quadrupole 3 resolution of 0.7 amu and collision energy 10 eV. Mass transitions and other compound-specific parameters are listed in Table 1. The limit of detection was 2 pg per 100 µL (20 pg/mL) injection for each analyte. Linear or quadratic calibration curves using the analyte to internal standard ratio were used to calculate analyte amounts. Calibration points were 2, 10, 50, 200, and 1000 pg analyte versus 50 pg internal standard for PFCAs and PFASs.

Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA (Discovery Series) using 5-8 mg of the sample. The samples were heated to 25-600 °C at a temperature ramp rate of 10 °C/min. Infrared (IR) spectra were obtained using PerkinElmer Frontier FT-IR spectrometer.

Deionized water used in this study is a type 1, 18.2 megohm-cm water obtained from Labconco – waterpro PS series. This water was amended with sodium chloride and humic acid if necessary.

Centrifugation was performed using a benchtop centrifuge - Mini mouse II by Denville.

2. BATCH ADSORPTION STUDIES

2.1. Equilibrium adsorption studies

The batch adsorption studies of mixtures of PFAS (PFOA, PFHxA and GenX) was performed in a 1L HDPE bottle equipped with a magnetic stir bar. The mixture was stirred on a stir plate at room temperature and at 700 revolution per minute (rpm).

High Concentration (50μg/L): To a 1L deionized water added sodium chloride (200 mg) and humic acid (20 mg) and stirred overnight. To this mixture added vacuum dried polymer adsorbent (ionic fluorogel) (10 mg L^{-1}) and stirred at room temperature for 3 h with occasional sonication to disperse the adsorbent. A stock solution of PFAS was spiked to the mixture to create an initial concentration of 50 μg L^{-1} of each PFAS. This mixture was stirred for 21 h after which an aliquot of about 10 mL was withdrawn and filtered through either 0.2 μm PTFE or 0.45 μm cellulose acetate filter. The first 5 mL was drained to avoid any electrostatic effect from the filter and the remaining 5 mL was collected for LCMS analysis. Control experiments to account for PFAS losses during handling were performed under identical condition in the absence of adsorbent. This batch experiment was performed once due to the high adsorption observed.

Low Concentration (1μg/L): The batch adsorption studies of PFAS under environmentally relevant concentration (1 μg L^{-1}) was performed under identical condition as detailed above except that the PFAS was spiked to create an initial concentration of 1 μg L^{-1} of each PFAS. This set of experiments were performed in triplicates.

Control adsorbents used in the study granular activated carbon (GAC: Filtrasorb 400), powdered activated carbon (PAC: PicaHydro MP23) and ion-exchange resin (IX: PFA694E) were purchased from commercial sources.

The efficiency of PFAS removal by adsorbents was determined by the following equation

$$\% \text{ PFAS removal} = \frac{C_0 - C_t}{C_0} \times 100$$

C_0 (μg L^{-1}) = Initial concentration of PFAS

C_t (μg L^{-1}) = Residual concentration of PFAS

The amount of PFAS bound to the polymer sorbent is given by the following equation

$$q_t = \frac{C_0 - C_t}{C_A}$$

q_t (mg g^{-1}) = Amount of PFAS adsorbed on the solid phase at time *t* (h)

C_t (μg L^{-1}) = Concentration of PFAS in liquid phase at time *t* (h)

C_o (μg L^{-1}) = Average concentration of PFAS in control experiments

C_A (mg L^{-1}) = Concentration of adsorbent

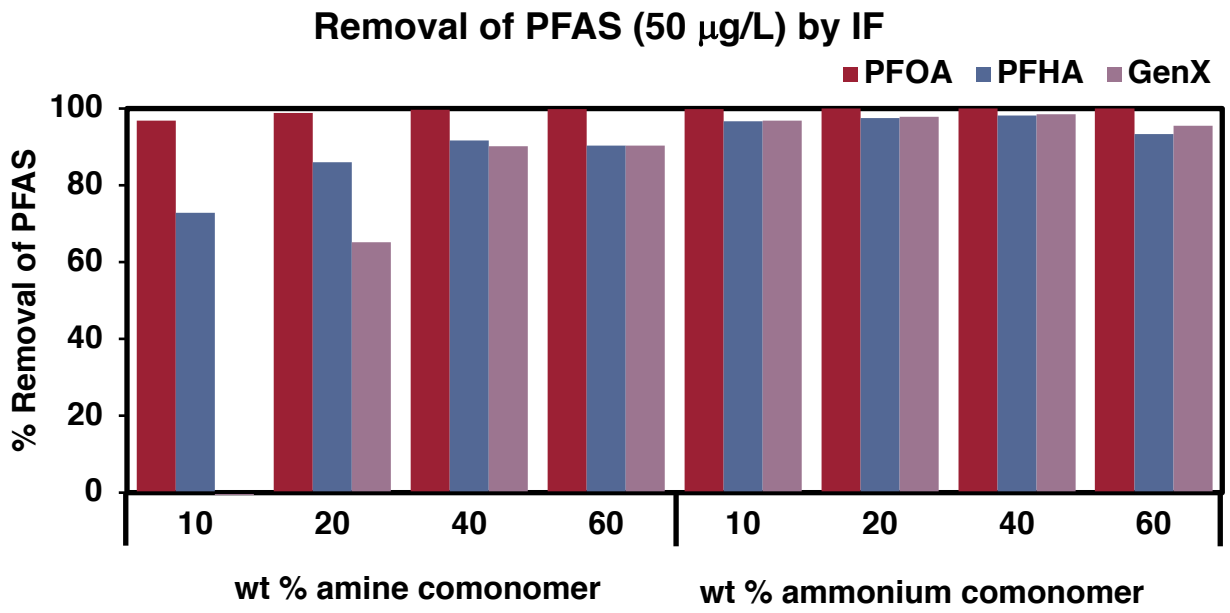

Figure S1: Equilibrium PFAS removal efficiency of different compositions of Ionic Fluorogel in presence of NaCl (200 ppm) and humic acid (20 ppm). PFAS: PFOA, PFHxA and GenX (each 50 μg/L). adsorbent dosage: 100 mg/L. equilibrium time: 21 h.

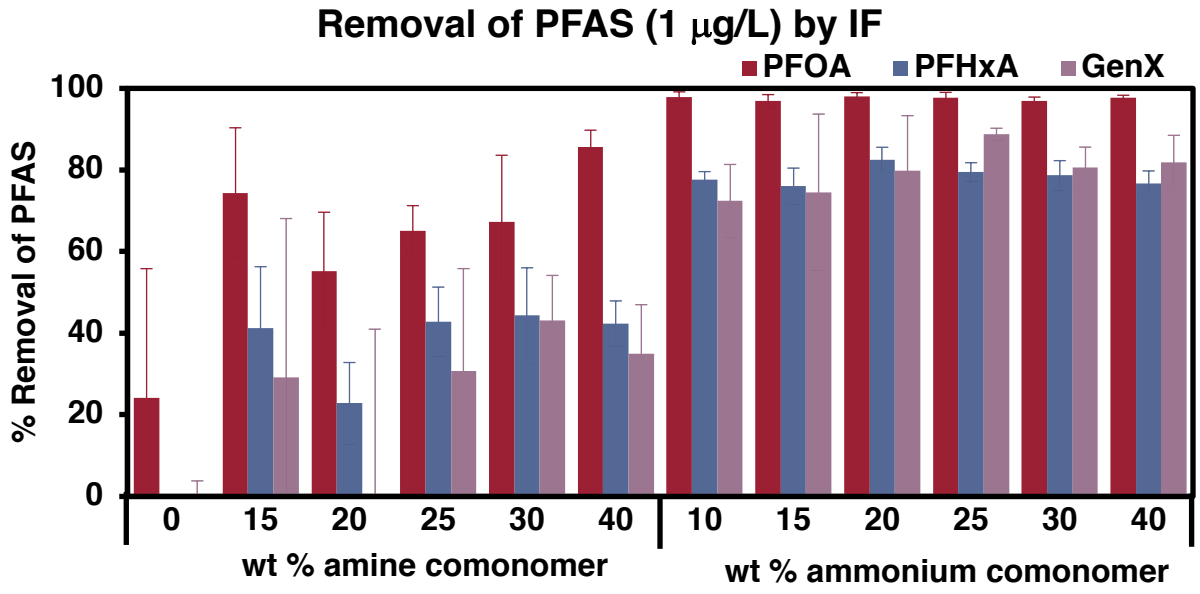

Figure S2: Equilibrium PFAS removal efficiency by various compositions of Ionic Fluorogels in presence of NaCl (200 ppm) and humic acid (20 ppm). PFAS: PFOA, PFHxA and GenX (each 1 μg/L). adsorbent dosage: 10 mg/L. equilibrium time: 21 h. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

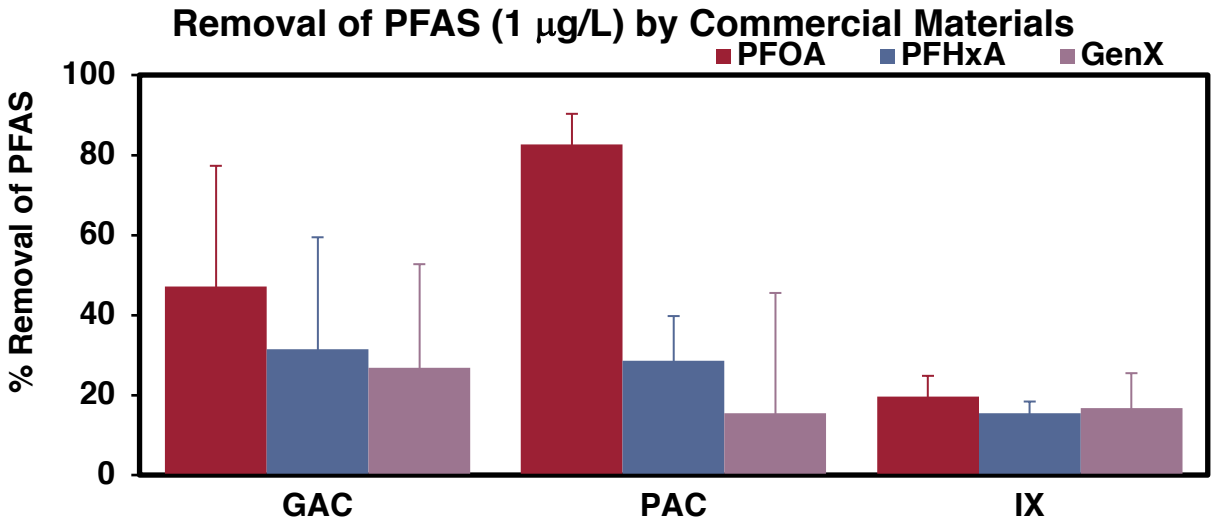

Figure S3: Equilibrium PFAS removal efficiency by granular activated carbon (GAC), powdered activated carbon (PAC) and ion-exchange resin (IX), in presence of NaCl (200 ppm) and humic acid (20 ppm). PFAS: PFOA, PFHxA and GenX (each 1 μg/L). adsorbent dosage: 10 mg/L. equilibrium time: 21 h. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

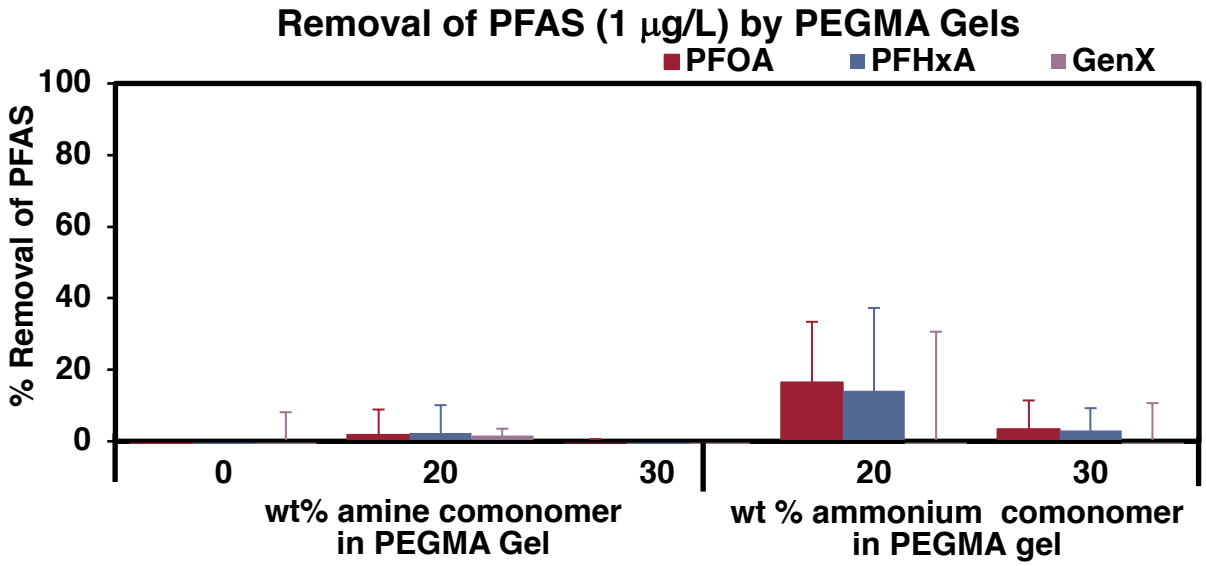

Figure S4: Equilibrium PFAS removal efficiency by gel made from polyethylene glycol diacrylate (PEGDA, Mn 750) in presence of NaCl (200 ppm) and humic acid (20 ppm). PFAS: PFOA, PFHxA and GenX (each 1 μg/L). adsorbent dosage: 10 mg/L. equilibrium time: 21 h.

2.2. GenX adsorption kinetics

High concentration (200 μg/L): The adsorption kinetic experiments were performed in 125 mL polypropylene bottle equipped with a magnetic stir bar. The experiments were performed at room temperature on a multi-position stirrer at 500 rpm. The adsorbent dose was set at 10 mg/L with total operating volume of 100 mL. The fluorogel and water mixture was stirred for 3 h with occasional sonication to disperse the adsorbent before being spiked with GenX stock to create an initial concentration of 200 μg/L. About 1 mL aliquot was taken at each predetermined time intervals (0.5, 1, 5, 10, 30, 60, mins and 21, 48 and 72 h). The aliquots were centrifuged for 15 minutes and the supernatant was analyzed by LCMS to determine the residual GenX concentration. Control experiments to account for GenX losses during handling were performed under identical condition in the absence of adsorbent. This batch kinetics experiment was performed in triplicates.

Low concentration (1 μg/L): About 5 mg of Ionic fluorogel was taken in an 8 mL vial, followed by addition of DI water to create a concentration of 1 mg/mL. The mixture was subjected to series of vortex and sonication to completely disperse ionic fluorogel. 1 mL of this mixture was taken while under constant mixing and added to 99 mL of water in a polypropylene bottle (125 mL) equipped with a magnetic stir bar. The mixture was stirred at 500 rpm for 3 h before being spiked with GenX stock to create an initial concentration of 1 μg/L. About 1 mL aliquot was taken at each predetermined time intervals (0.5, 1, 3, 5, 10, 20, 30, 60, 120, 240 mins and 21, 48 and 72 h). The aliquots were centrifuged for 15 minutes and the supernatant was analyzed by LCMS to determine the residual GenX concentration. Control experiments to account for GenX losses during handling were performed under identical condition in the absence of adsorbent. This batch kinetics experiment was performed in triplicates.

The kinetics of adsorption can be described with Ho and McKay's linearized form of pseudo-second-order adsorption model given by following equation[2]

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{obs} q_e^2}$$

q_e (mg g^{-1}) = Amount of GenX adsorbed on the solid phase at equilibrium
k_{obs} (g mg^{-1} h^{-1}) = Rate of adsorption
q_t (mg g^{-1}) = Amount of GenX adsorbed on the solid phase at time *t* (h)

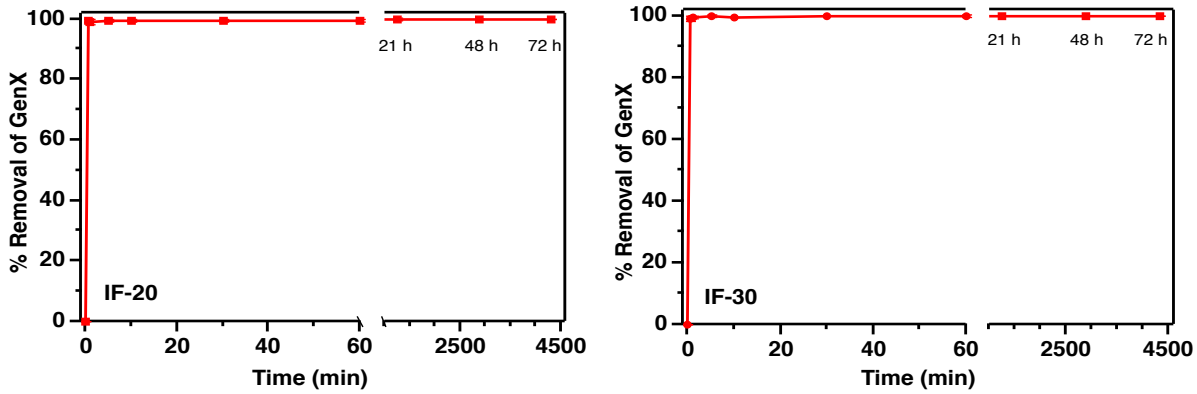

Figure S5: Kinetics of GenX (200 μg/L) adsorption by Ionic Fluorogel with 20 wt% quaternized DMEAMA (left) and Ionic Fluorogel with 30 wt% quaternized DMEAMA (right). Adsorbent dosage: 100 mg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

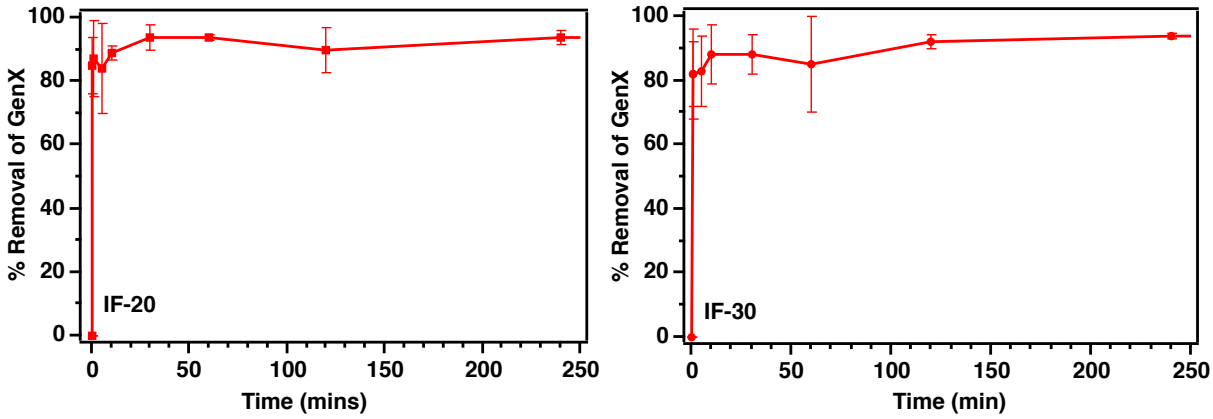

Figure S6: Kinetics of GenX (1 μg/L) adsorption by Ionic Fluorogel with 20 wt% quaternized DMEAMA (left) and Ionic Fluorogel with 30 wt% quaternized DMEAMA (right). Adsorbent dosage: 10 mg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

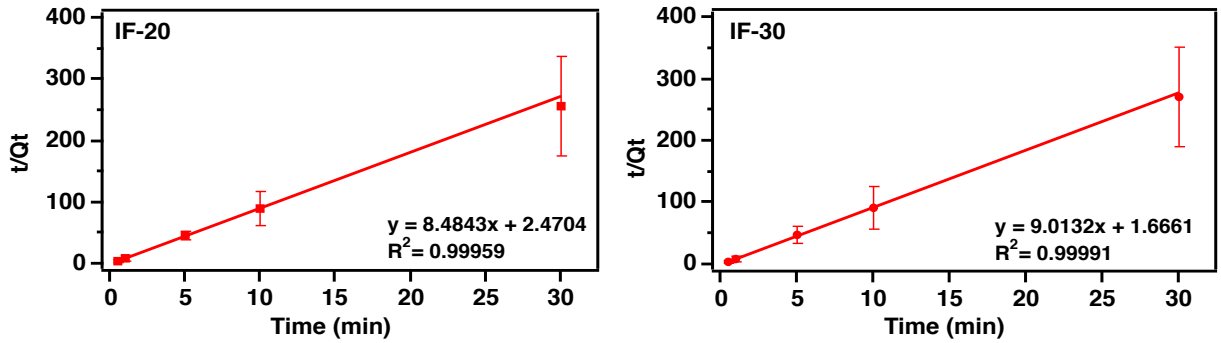

Figure S7: Pseudo second order plots of Ionic Fluorogel with 20 wt% quaternized DMEAMA (left) and Ionic Fluorogel with 30 wt% quaternized DMEAMA (right). Adsorbent dosage: 10 mg/L; GenX: 1 μg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

2.3. Binding isotherm studies

The batch isotherm studies were performed in 125 mL polypropylene bottles (100 mL operating volume) containing a magnetic stir bar on a multi-position stirrer at 23-25 °C at 500 rpm. The deionized water containing the ionic fluorogel adsorbent (100 mg/L) was stirred for 3 h before the GenX addition. A stock solution of GenX was spiked to create initial concentrations of 0.2, 1, 5, 10, 20, 30 and 50 mg/L. The suspension was stirred for 21 h to reach equilibrium and an aliquot was taken in a centrifuge tube. The aliquots were centrifuged for 15 minutes and the supernatant from the top was taken for LCMS analysis. High concentration samples were serially diluted (5-10 mg/L diluted 20x and 20-50 mg diluted 100x) before LCMS analysis. Control experiments in the absence of adsorbent were performed under identical conditions to account for handling losses. All the batch experiments were carried out in triplicate.

Langmuir adsorption and Freundlich isotherm fits were generated by Non-linear Least Square Regression of the following equation.

Langmuir adsorption isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + C_e q_m K_L}$$

q_e (mg g^{-1}) = Amount of PFAS adsorbed on the solid phase at equilibrium
q_m (mg^{-1} g) = Maximum adsorption capacity of adsorbent at equilibrium
C_e (mg^{-1} L^{-1}) = Residual PFAS concentration at equilibrium
K_L (mg^{-1} L^{-1}) = Equilibrium constant

Freundlich adsorption isotherm:

$$q_e = K_F C_e^{\frac{1}{n}}$$

q_e (mg g^{-1}) = Amount of PFAS adsorbed on the solid phase at equilibrium
C_e (mg^{-1} L^{-1}) = Residual PFAS concentration at equilibrium
K_F (mg g^{-1})(L $mg^{-1})^{1/n}$ = Freundlich constant.
n is the intensity of adsorption

Note: A preliminary fit was generated using linearized equations of Langmuir ($1/q_e$ vs $1/C_e$) and Freundlich (ln q_e vs ln C_e) adsorption isotherm and the obtained values were used as a starting point for non-linear least square regression analysis. We used a Microsoft excel spreadsheet template obtained from USA-ARS website.[3]

Table S1: Langmuir and Freundlich parameters derived from linearized plots of the GenX binding isotherm

Fluorogel	Langmuir Fit			Freundlich Fit		
	K_L (M^{-1})	Qm (mg/g)	R^2	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
IF-20	5.9×10^6	278	0.99	141	2.2	0.93
IF-30	1.5×10^7	217	0.99	152	2.2	0.95

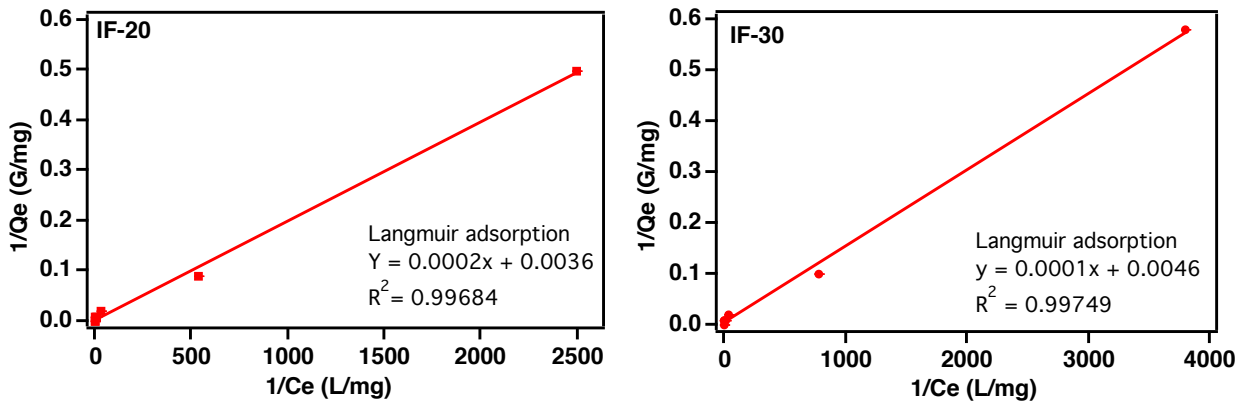

Figure S8: GenX adsorption isotherm linear fitted to Langmuir model for Ionic Fluorogel with 20 wt% quaternized DMEAMA (left) and Ionic Fluorogel with 30 wt% quaternized DMEAMA (right). Adsorbent dosage: 100 mg/L; [GenX]: 0.2-50 mg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

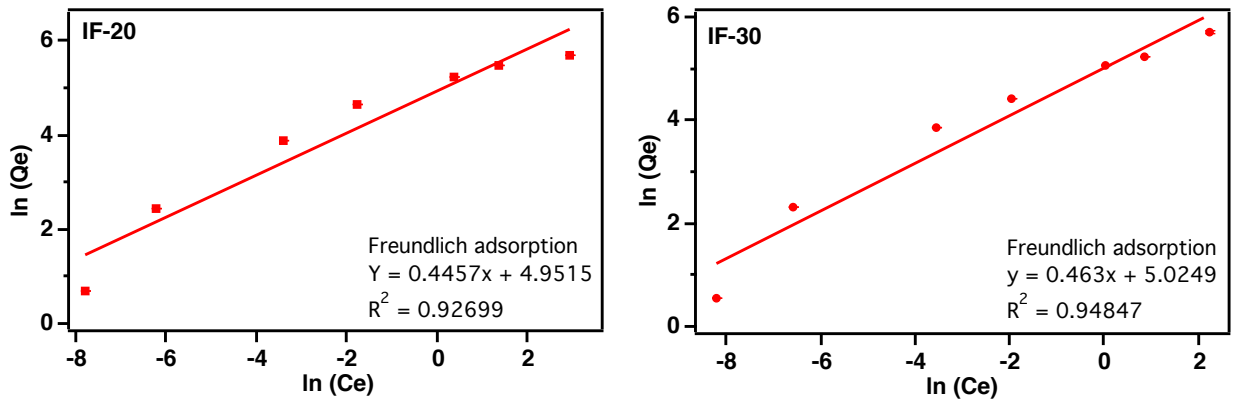

Figure S9: GenX adsorption isotherm linear fitted to Freundlich model for Ionic Fluorogel with 20 wt% quaternized DMEAMA (left) and Ionic Fluorogel with 30 wt% quaternized DMEAMA (right). Adsorbent dosage: 100 mg/L; [GenX]: 0.2-50 mg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

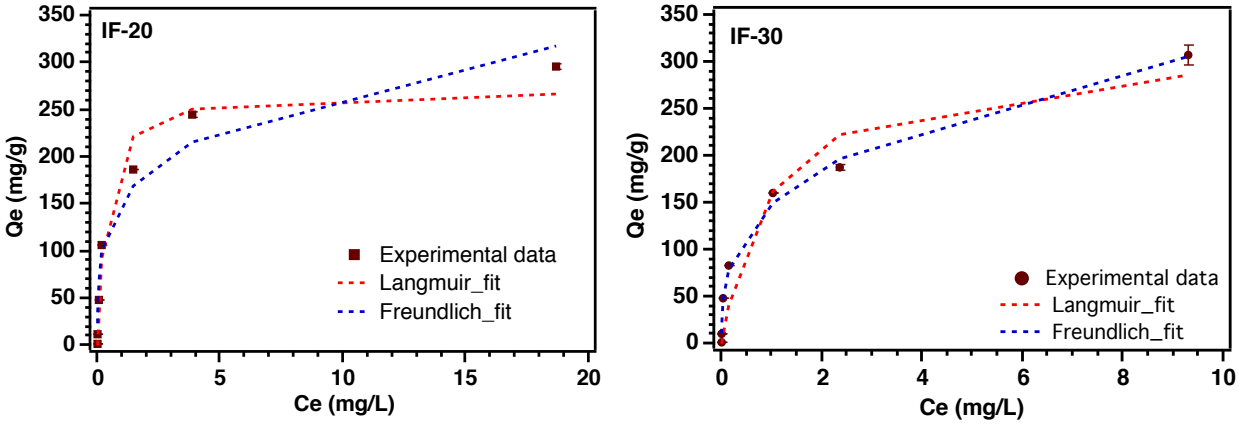

Figure S10: GenX adsorption isotherm for Ionic Fluorogel with 20 wt% quaternized DMEAMA (left) and Ionic Fluorogel with 30 wt% quaternized DMEAMA (right). Dotted lines represent fit to Langmuir (red) and Freundlich (blue) models. Adsorbent dosage: 100 mg/L; [GenX]: 0.2-50 mg/L. The data points in the figure are an average of 3 experiments and the error bar show their standard deviation.

2.4. Real water studies

The adsorption kinetic experiments were performed in 500mL polypropylene bottles equipped with a magnetic stir bar. The experiments were performed at room temperature on magnetic stirrers. The adsorbent dose was set at 100 mg/L with a total operating volume of 400mL. The fluorogel was soaked in 5ml of water for 3 days with occasional sonication to disperse the adsorbent before being adding to the 1 ug/L PFAS spiked water. About 10 mL aliquot was taken at each predetermined time intervals (0, 30, 60 and 120 mins). The aliquots were filtered through pre-washed 0.45um glass fiber syringe filter and the filtered solution was analyzed by LCMS to determine the residual PFAS concentration. Two control experiments to account for PFAS losses and PFAS contaminations during handling were performed under an identical condition in the absence of adsorbent and Deionized water. This batch kinetics experiment was performed in duplicate. Settled water was obtained from the Sweeney Water Treatment Plant (TOC = 1.3 mg/L, pH = 6.2).

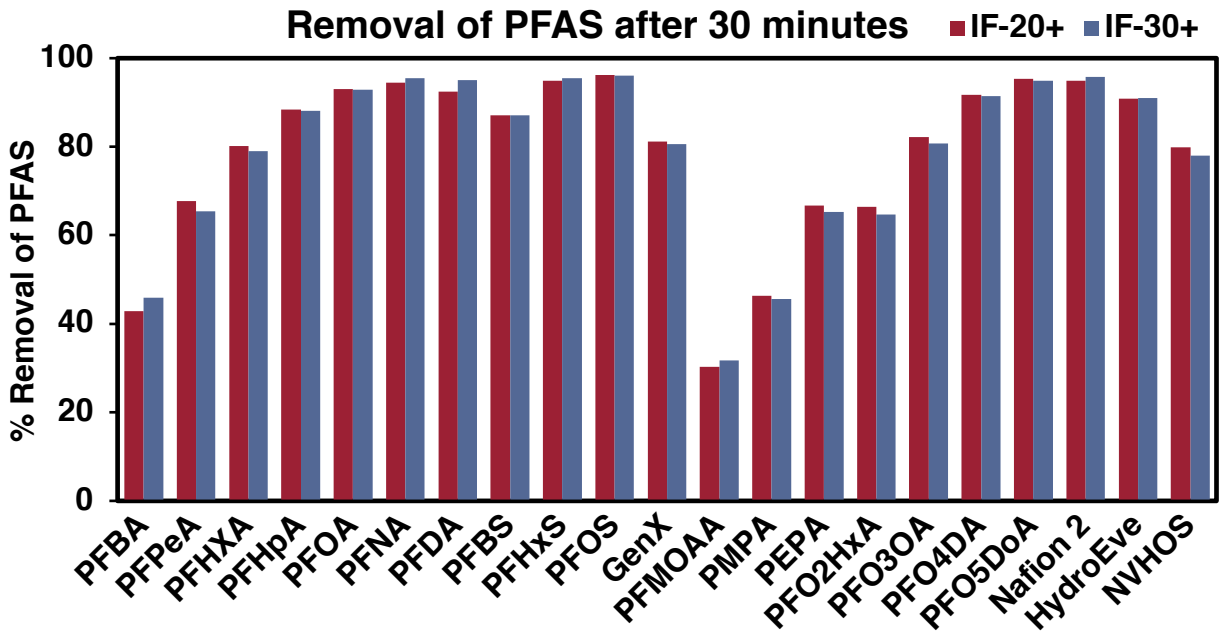

Figure S11: 21 PFAS absorption by **IF-20+** (red) and **IF-30+** (blue) after 30 minutes. Adsorbent dosage: 100 mg/L; [PFAS]: 1 μg/L each. Nafion 2 = Nafion byproduct 2. The data shown are an average of duplicate experiments.

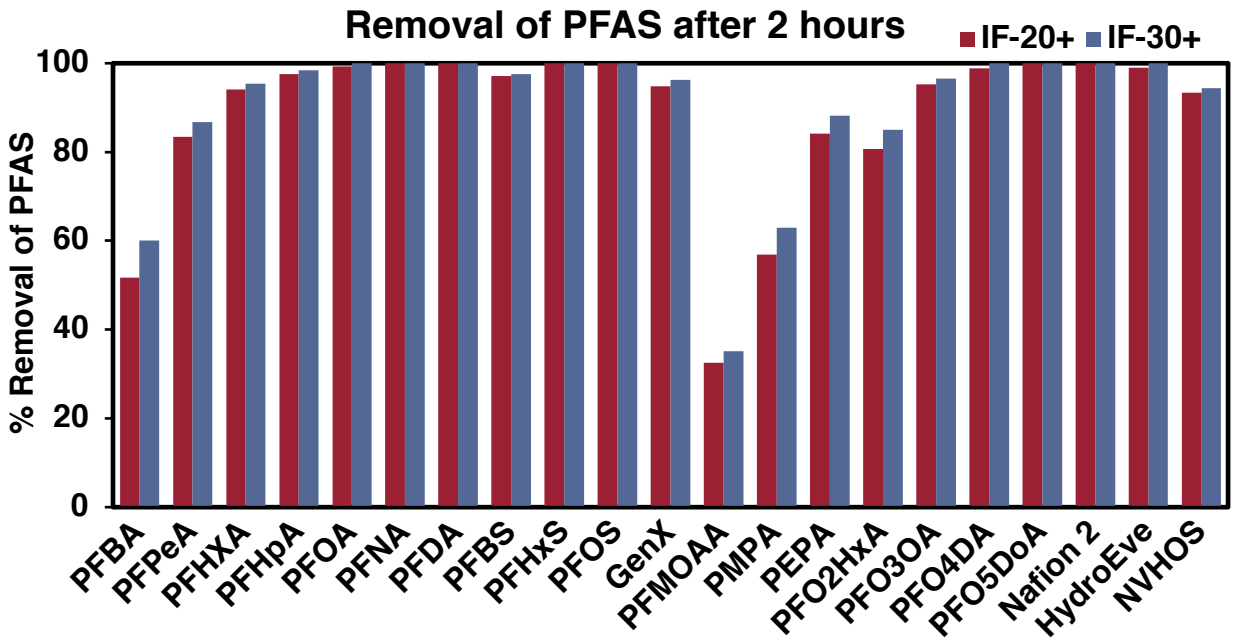

Figure S12: 21 PFAS absorption by **IF-20+** (red) and **IF-30+** (blue) after 2 hours. Adsorbent dosage: 100 mg/L; [PFAS]: 1 μg/L each. Nafion 2 = Nafion byproduct 2. The data shown are an average of duplicate experiments.

Fifteen of the 21 PFAS are listed by abbreviation at the following link:

https://cen.acs.org/sections/pfas.html

The other 6 are given in Figure S13.

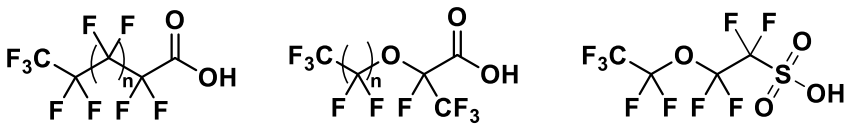

Figure S13. Emerging PFAS analyzed which are not available on the Chemical & Engineering News PFAS information page.

3. ADSORPTION AND REGENERATION STUDIES

Low Concentration (10mg/g): *Adsorption experiment:* Ionic Fluorogel **IF-20+** (20 mg) was suspended in deionized water (5 mL) followed by series of sonication and vortexing for 5 mins to disperse the adsorbent. The resulting suspension was passed through 20 mL syringe fitted with 0.45 μm PTFE filter (25 mm), additional water was used if necessary. The **IF-20+** thus created a packed bed of resin on top of the PTFE filter through which subsequent water had to flow through in order to exit the syringe. A solution of GenX (10 mg L^{-1}, 20 mL) was passed through the filter over 2 mins and the resultant filtrate was collected in a polypropylene tube. The PTFE filter was washed by passing through deionized water (20 mL) to remove any trace of GenX solution. The change in GenX concentration in the filtrate was measured by LC-MS.

Desorption experiment: The PTFE filter containing GenX was extracted by passing through 20 mL of a methanolic solution containing 400 mM ammonium acetate over 2 minutes. The concentration of extracted GenX was analyzed by LC-MS. The PTFE filter was washed by passing through deionized water (20 mL) to remove any trace of methanolic solution left over and the residual deionized water was removed by vacuum suction.

The adsorption-desorption cycle was extended to 5 cycles to demonstrate the recyclability of the ionic fluorogel without the loss of efficiency.

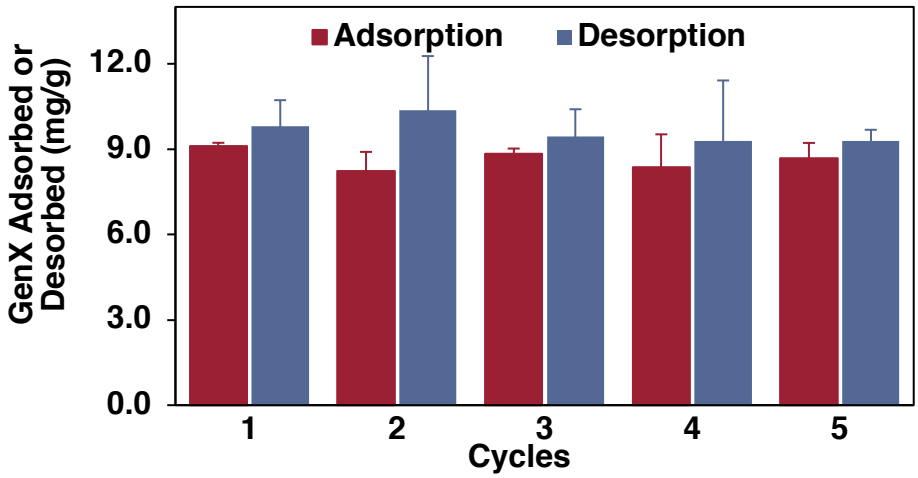

Figure S14: Regeneration and reuse of ionic fluorogel **IF-20+** with 400 mM methanolic ammonium acetate. Adsorbent dosage: 20 mg; [GenX]: 10 mg/L, 20 mL. Extraction: **IF-20+** was extracted with 400 mM methanolic ammonium acetate over 2 minutes.

High Concentration (200mg/g): *Adsorption experiment:* Ionic Fluorogel **IF-20+** (5 mg) was suspended in deionized water (4.67 mL) in a 20mL glass vial followed by stirring 18hours to disperse the adsorbent. The solution was spiked with 33 μL 30 mg/mL GenX (final concentration 200 mg/L), and the solution was stirred 2 hours. The mixture was transferred to a 15mL centrifuge tube and centrifuged at 3000 rpm for 3 minutes.

An aliquot of the supernatant was used to determine the change in GenX concentration in the filtrate via LC-MS.

Desorption experiment: The pellet was transferred from the centrifuge tube to the glass vial, and 5 mL methanolic ammonium acetate (400mM) was added. The mixture was stirred 4 hours, after which the centrifugation process was repeated. The concentration of extracted GenX was analyzed by LC-MS.

The adsorption-desorption cycle was extended to 2 cycles to demonstrate the recyclability of the ionic fluorogel without the loss of efficiency.

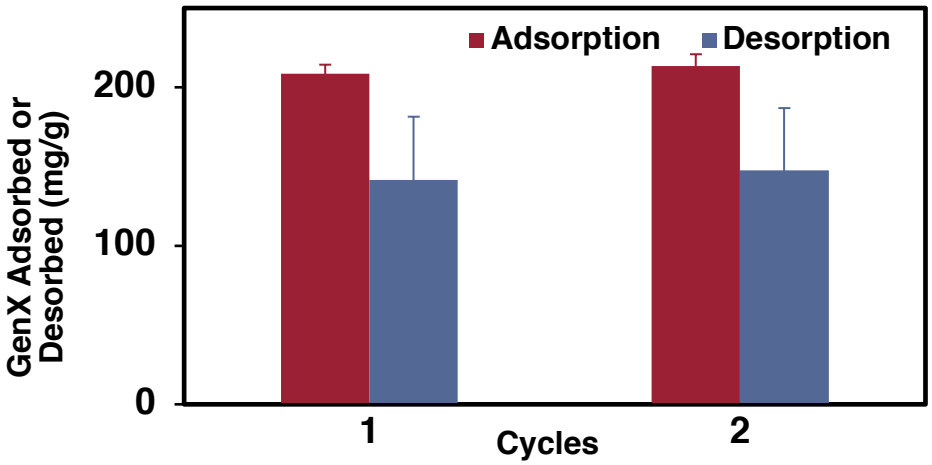

Figure S15: Regeneration and reuse of ionic fluorogel **IF-20+** with 400 mM methanolic ammonium acetate. Adsorbent dosage: 40 mg; [GenX]: 200 mg/L, 5 mL. Extraction: **IF-20+** was extracted with 400 mM methanolic ammonium acetate (5 mL).

4. SYNTHESIS OF IONIC FLUOROGELS

Illustrative procedures for the synthesis of Ionic Fluorogel **IF-20** and **IF-20+** are given below:

Thermally-initiated copolymerizations:

To a 20 mL scintillation vial with green top cap equipped with magnetic stir bar was added Fluorolink MD700 (1.6 g, 80 wt%), 2-(dimethylamino)ethyl methacrylate (0.4 g, 20 wt%), azobisisobutyronitrile (20 mg, 1 wt%) and trifluoroethanol (2.0 g). The vial was closed, nitrogen was passed through the solution for 5 minutes, and the solution was heated at 70 °C for 5 h while stirring at 200-300 rpm. Within 15 mins, gel particles were observed and within 1 h the entire mixture gelled. After the reaction, the mixture was cooled to room temperature and the gel was ground to fine powder. To this powder, additional trifluoroethanol (10 mL) and iodomethane (2 mL) was added and the mixture was stirred at room temperature for 24 h. The content of the vial was transferred to teabag using ethanol as a transfer solvent. The gel was washed with ethanol using a Soxhlet extraction set up for 24 h. Finally, the gel was dried in a vacuum oven at 50 °C for 24 h. The dried gel was passed through 125 μm and 75 μm sieves to collect particles in the size range of 75 – 125 μm. The ionic fluorogel **IF-20+** was obtained as a pale-yellow powder in 2.2 g yield.

To obtain fluorogel **IF-20** (tertiary amine derived), the methylation step was not performed. Instead, after grinding, the fluorogel was directly place in teabag and purified using Soxhlet apparatus.

Other formulations of fluorogel (**F**) or ionic fluorogel (**IF**) containing varying amount of amine/ammonium derivatives were prepared by adding appropriate amount of amine and Fluorolink MD700 using the procedure above. For instance, to make **IF-30+**, 1.4 g of Fluorolink MD 700 and 0.6 g of 2-(dimethylamino)ethyl methacrylate (0.4 g, 20 wt%) was used (yield: 2.3 g).

Photoinitiated copolymerizations:

To a 20mL scintillation vial was added Fluorolink MD700 (400 mg, 80 wt%), 2-(dimethylamino)ethyl methacrylate (100 mg, 20 wt%), 1-hydrocyclohexyl phenyl ketone (10 mg, 2 wt%) and trifluoroethanol (25 mg). The solution was vortexed 1 minute to ensure homogeneity. The solution was pipetted onto a glass slide which had been pre-treated with Rain-X, and washed with water, then acetone, and dried. The film was cured 1 hour under 365nm irradiation under N_2 atmosphere. The film was removed from the slide with a razor blade, then 8 mm discs were punched using 8 mm biopsy punches. The resulting **IF-20** gels were then soaked in DI water 24 hours, changing the water every 8 hours.

To obtain **IF-20+**, instead of soaking in water, the discs were submerged in 2M iodomethane in trifluoroethanol solution 24 hours. Then the discs were washed via soaking in water.

Synthesis of control PEG gel: PEG gels were obtained using the same procedure as mentioned above. The Fluorolink MD 700 was replaced by poly(ethylene glycol) dimethacrylate (average Mn 750). This particular molecular weight was chosen to mimic the number of atoms in the backbone between the dimethacrylate functionality of fluorolink.

5. WATER UPTAKE OF IONIC FLUOROGELS

Photocured discs of Ionic Fluorogels were swollen in DI H_2O 24 hours, massed, then dried under vacuum and massed again. This analysis was completed in triplicate for each IF formulation. Swelling of the IF was determined using the swelling ratio:

$$Swelling\ Ratio = \frac{mass\ of\ swollen\ disc}{mass\ of\ dried\ disc}$$

As the wt % DMAEMA increased, no significant trend was observed in swelling ratio. Likewise, no difference was observed between tertiary and quaternary formulations. (Figure S13)

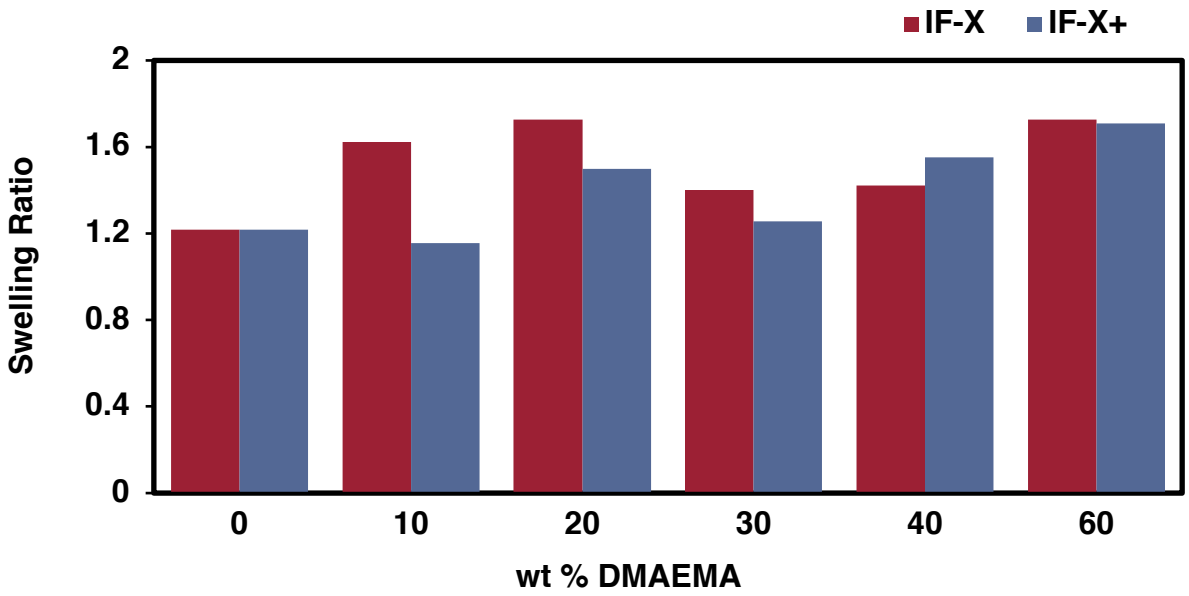

Figure S16. Swelling ratios of Ionic Fluorogels in DI H_2O.

6. CHARACTERIZATION

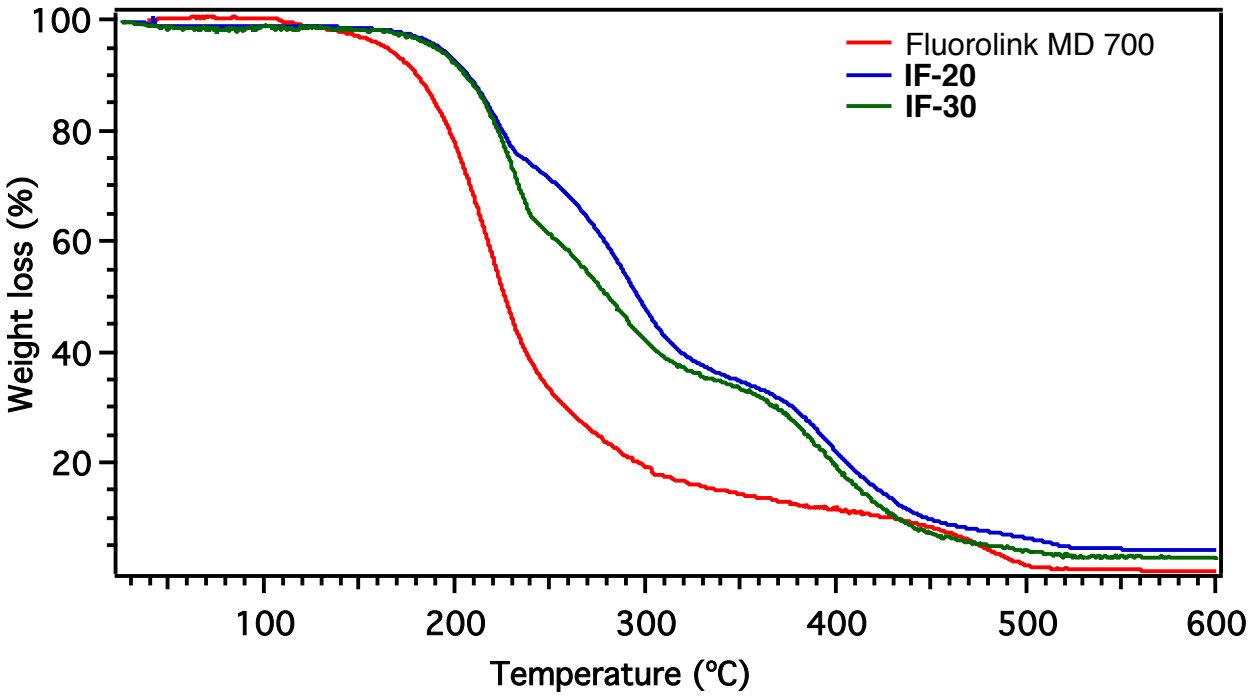

Figure S17: Thermogravimetric analysis (TGA) of Fluorolink MD700 (red), ionic fluorogel **IF-20** (blue) and **IF-30** (green).

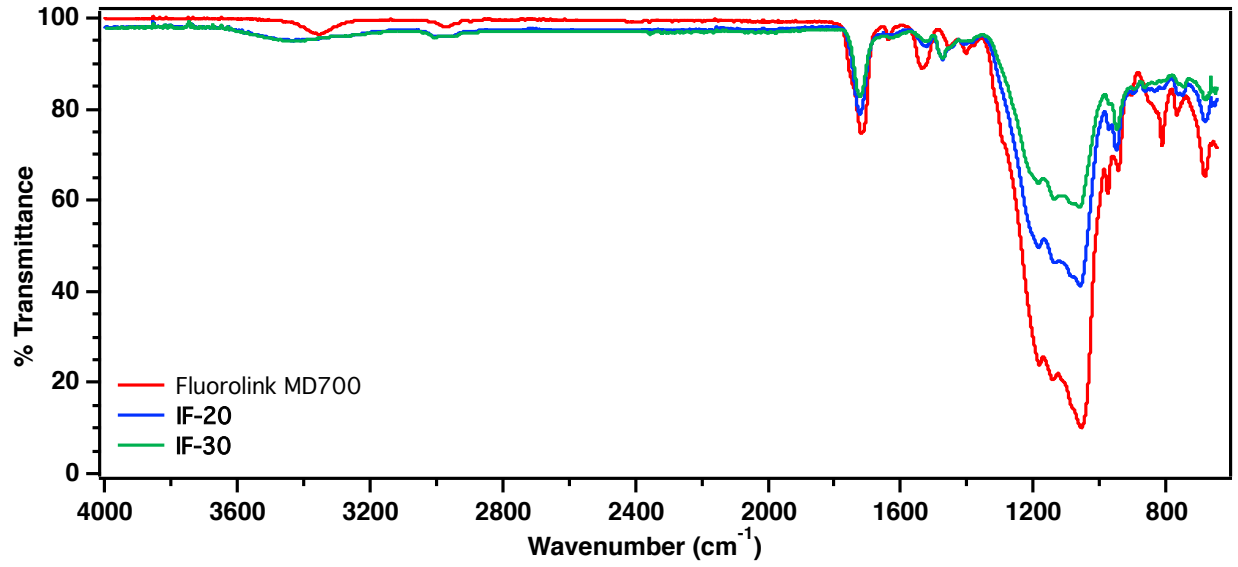

Figure S18: Fourier transform-infrared (FTIR) spectra of Fluorolink MD700 (red) and ionic fluorogel **IF-20** (blue) and **IF-30** (green).

7. REFERENCES

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