SUPPLEMENTAL MATERIALS

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Development and Laboratory Scalability of Ultraviolet-Activated Silica-Based Granular Media as an Engineered System for the Degradation of Per- and Polyfluoroalkyl Substances in Concentrated Liquid Waste

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Section S1. Reagent Grade Solutions and Standards

Silica-based granular media was synthesized with tetraethyl orthosilicate (CAS: 78-10-4, Thermo Fisher Scientific), silicic acid (CAS: 1343-98-2, Sigma Aldrich), sodium hydroxide (CAS: 1310-73-2, Sigma Aldrich), and either titanium (IV) oxide, Aeroxide ® P25, ACROS Organics (CAS: 13463-67-7, Thermo Fisher Scientific) or Bismuth (III) oxide (CAS: 1304-76-3, Thermo Fisher Scientific). The bismuth trioxide variation utilized nitric acid (CAS: 7697-37-2, Thermo Fisher Scientific). Perfluorooctanesulfonic acid – 1H, 1H, 2H, 2H (CAS: 27619-97-2, Synquest Laboratories), perfluorooctanesulfonic acid (CAS: 6164-3-08, Synquest Laboratories), perfluorohexanesulfonic acid (CAS: 3871-99-6, Sigma Aldrich), perfluorobutanesulfonic acid (CAS: 375-73-5), perfluorononanoic acid (CAS: 375-95-1, Alfa Aesar), perfluorooctanoic acid (CAS: 335-67-1, Sigma Aldrich), perfluoroheptanoic acid (CAS: 375-85-9, Thermo Fisher Scientific), perfluorohexanoic acid (CAS: 307-24-4, Thermo Fisher Scientific), perfluoropentanoic acid (CAS: 2706-90-3, Thermo Fisher Scientific), and perfluorobutanoic acid (CAS: 375-22-4, Sigma Aldrich) were purchased for PFAS spiked deionized water solutions. Sodium hydroxide (CAS: 1310-73-2, Sigma Aldrich) and sulfuric acid (CAS: 7664-93-9, Thermo Fisher Scientific) were purchased for experimental amendments. Technical grade methanol (CAS: 67-56-1, Thermo Fisher Scientific) was purchased for reactor cleaning and rinsing, along with deionized water.

Dionex AS23 eluent concentrate and Dionex combined seven anion standard II were purchased from Thermo Fisher Scientific for ion chromatography. LC/MS grade water (Cat no: W6-1, Thermo Fisher Scientific), ACS grade methanol (Cat no: A412-1, Thermo Fisher Scientific), LC/MS grade acetonitrile (Cat no: LC015-1, Honeywell), LC/MS grade ammonium acetate (CAS: 631-61-8, Sigma Aldrich) and LC/MS grade acetic acid (CAS: 64-19-7, Sigma Aldrich) were purchased for LC-MS sample preparation and analysis. Wellington standards MPAC MXA and MPFAC-24ES were purchased for internal standards. Wellington PFAC30PAR was purchased for the calibration mix.

Table S1. PFAS Mix Analytes

PFAS Analyte	Concentration (mg/L)
PFOS	4.53
PFNA	5.73
6:2 FTS	1.27
PFOA	4.27
PFHxS	4.87
PFHpA	5.07
PFHxA	9.33
PFPeA	8.67
PFBA	5.2
Total	**48.93**

Section S2 Reactor Configurations

Table S2. UV Lamp Parameters

Lamp Wattage	Radiation Flux at 254 nm (W)	Irradiance at 254 nm ($\mu W/cm^2$)	Radiation Flux at 185 nm (W)
21	7.2	72	-
48	12	120	2.4
57	13	130	-
85	23	230	6

Equation 1. Residence Time

- Residence Time = $\frac{Total\ Treatment\ Time}{\left({Total\ Volume}/{Reactor\ Volume}\right)}$

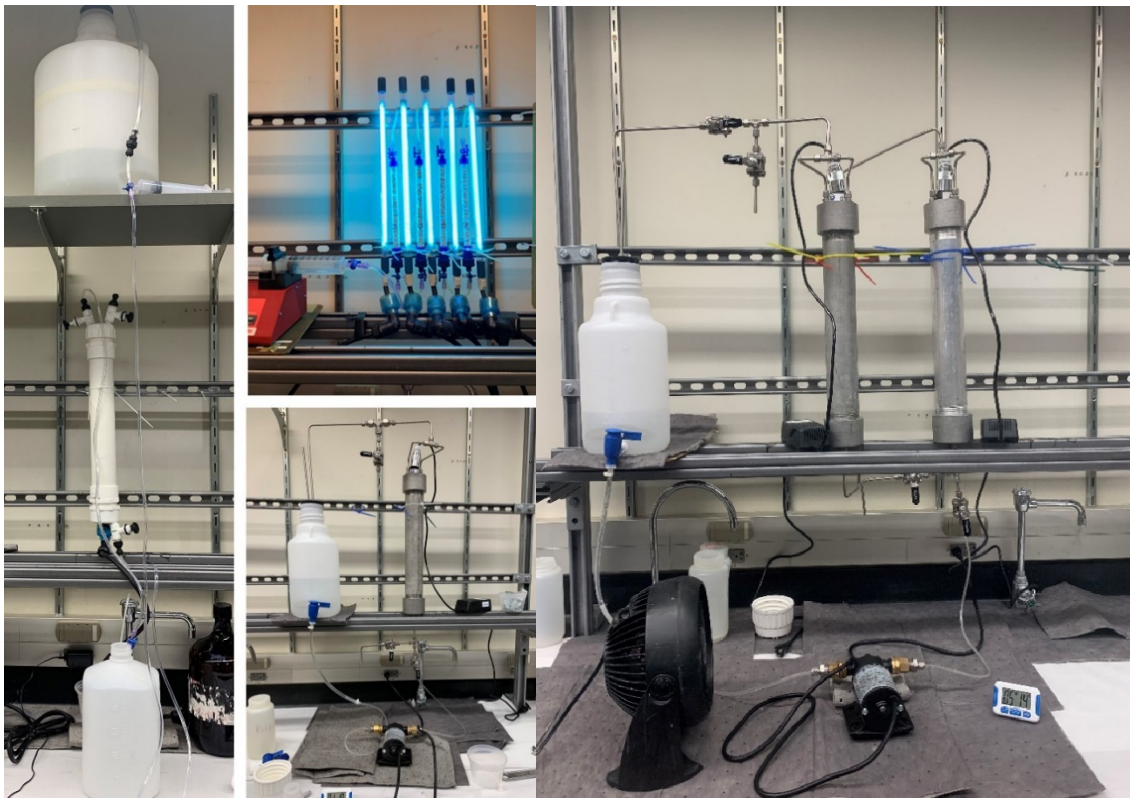

Figure S1. Photographs of various column reactor configurations used for scalability assessment including the flow-through reactor, mini-column reactor, recirculation reactor, and modified recirculation reactor.

Section S3. LC-MS Analysis

Table S3. Gradient

Time (minutes)	Concentration of Channel A (%)	Concentration of Channel B (%)
0	95	5
5	95	5
6.5	75	25
19	20	80
19.5	5	95
20.5	5	95
21	95	5
25	95	5

Table S4. LC-MS Parameters

LC System	Shimadzu Nexera XR (40-Series) UHPLC System	
	System Controller	SCL-40
	Degassing Unit	DGU-405
	Pump	LC-40DX3
	Autosampler	SIL-40CX3
	Column Oven	CTO-40C
Autosampler Temperature	4 °C	
Column Oven Temperature	40 °C	
MS Instrument	Shimadzu 9030 Q-TOF	
m/z Range	40-1000	
Acquisition Time	25 minutes	
Event Time	0.5 second	
Threshold	Low	
Interface Voltage	-5.00 kV	
Corona Needle Voltage	-4.50 kV	
Ionization Interface	Dual Ion Source (DUIS)	
Nebulizing Gas Flow	2 L/minute	
Heating Gas Flow	10 L/minute	
Interface Temperature	175 °C	
Drying Gas Flow	10 L/minute	
Desolvation Line Temperature	250 °C	
Heat Block Temperature	400 °C	

Table S5. Method Limit of Detection

Analyte	**MDL (ng/L)**
PFBA	950
PFPenA	400
PFHexA	400
PFHepA	400
PFOA	400
PFNA	400
PFBS	250
PFHexS	250
PFOS	250
6:2 FTS	100

*Please note this is the limit of the detection for the method and column used and not what the instrument is capable of.

Section S4. Ion Chromatography Analysis

The Dionex ion chromatography system (ICS-90) was coupled with an automated sampler (AS40). ICS-90 system contained a 4× 250-mm AS23 analytical standard bore column (part #064149), an AG23 guard

standard column (064147), coupled with an AMMS 300 chemically driven suppressor (064558), and a D5 stabilizer conductivity cell. A 50 µL injection loop was used as a standard for all samples and standards. Chromeleon 6.80 was the software used for analysis.

Section S5. Additional Data

Batch Reactor

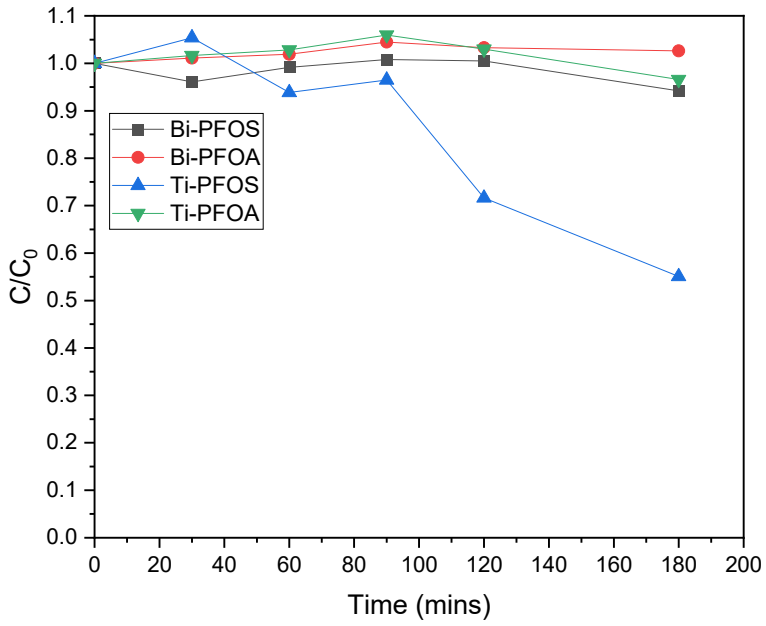

Figure S2. Ti-SGM and Bi-SGM batch reactors, No UV (adsorption control), no amendment

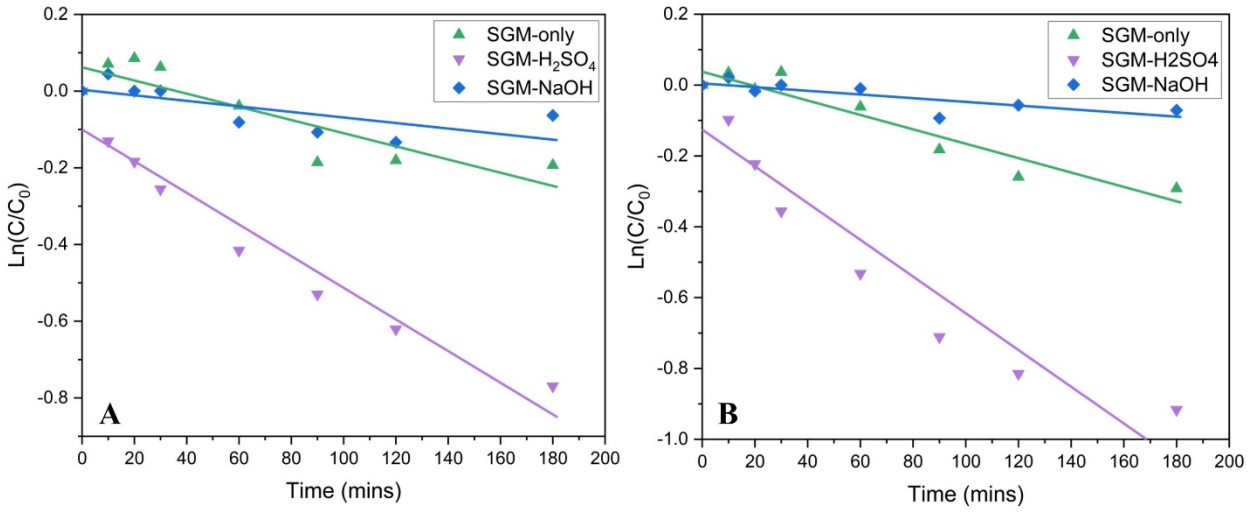

Figure S3. Degradation kinetics of UV/SGM batch reactors under various pH conditions

Table S6. Ti-SGM and Bi-SGM Reactor Kinetics

Treatment	**$\ln(C/C_0) = kt + b$**	**R^2**	**k (min^{-1})**
Ti-SGM-Only	$\ln(C/C_0) = -0.002t + 0.062$	0.77	-0.002
Bi-SGM-Only	$\ln(C/C_0) = -0.002t + 0.038$	0.91	-0.002
Ti-SGM-H_2SO_4	$\ln(C/C_0) = -0.004t - 0.10$	0.95	-0.004
Bi-SGM-H_2SO_4	$\ln(C/C_0) = -0.005t - 0.13$	0.91	-0.005
Ti-SGM-NaOH	$\ln(C/C_0) = -0.0007t + 0.0036$	0.52	-0.0007
Bi-SGM-NaOH	$\ln(C/C_0) = -0.0005t + 0.0048$	0.65	-0.0005

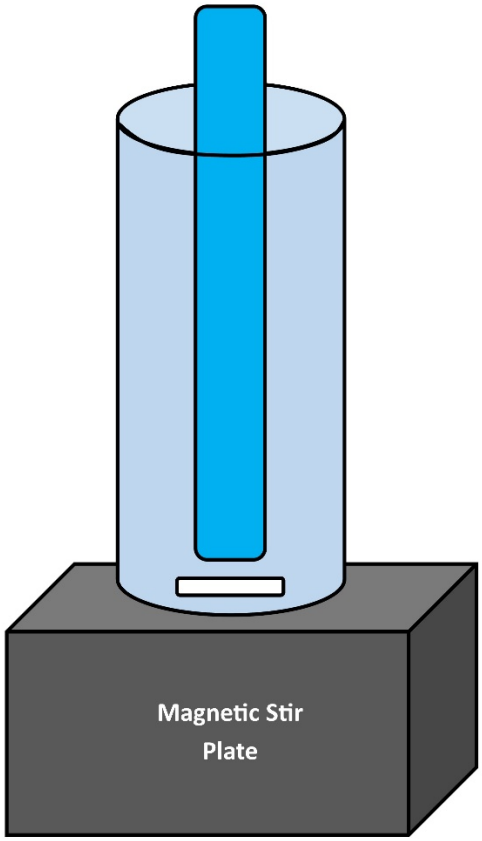

Figure S4. UVC/VUV experimental reactor

Table S7. Reactor Configuration Kinetics

Reactor Configuration	**$\ln(C/C_0) = kt + b$**	**R^2**	**k (min^{-1})**
Batch Reactor	$\ln(C/C_0) = -0.0041t - 0.1$	0.95	-0.0041
Flow-Through Reactor	$\ln(C/C_0) = -0.017t - 0.1$	0.92	-0.017
Recirculation Reactor	$\ln(C/C_0) = -0.0069t - 0.1$	0.88	-0.0069

Modified Recirculation Reactor

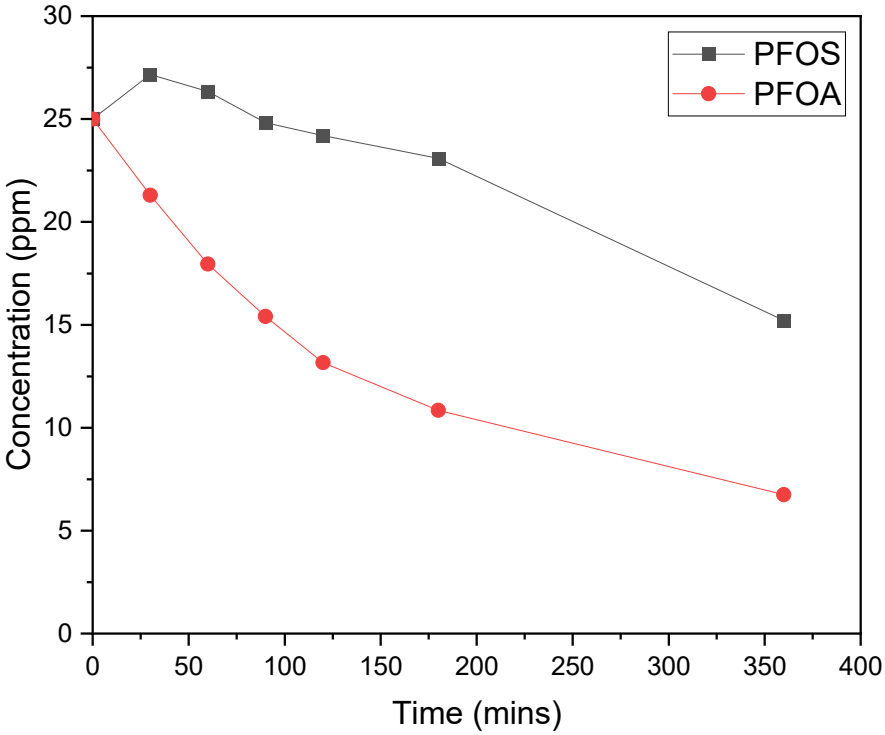

Figure S5. Degradation of PFOS/PFOA solution in the recirculation reactor with two 85-Watt lamp columns in series and 5% H_2SO_4 amendment. One column was packed with SGM and the other column contained no SGM (photolysis only column).

Table S8. Comparison of treatment type on PFOS and PFOA degradation with the recirculation reactor at 180 minutes

Treatment Type	PFOS	PFOA	Total PFOS/PFOA
Photocatalysis – Acidic	64%	70%	67%
Photocatalysis – Basic	60%	35%	48%
Photolysis - Acidic	22%	86%	54%
Photolysis - Basic	13%	75%	44%
Photocatalysis/Photolysis - Acidic	40%	74%	57%
Photocatalysis/Photolysis - Basic	61%	85%	73%

Equation 2. EE/O Calculation

$$EE/O = \frac{P}{-\log(C/C_0)\left(\frac{V}{t}\right)(3600)}$$

Where:

EE/O – electrical energy per log order reduction (kWh/m^3)

P – power/wattage of UV lamp(s) (kW),

C/C_0 – ratio of PFAS removal, specified as individual or total

V – treated volume (m^3)

t – time (s)

Table S9. UV/SGM scenarios for linear treatment scale-up

Scenario	Treatment Volume	Number of Columns	Lamps per Column	Wattage per Lamp	Total Wattage
Real	1.3	1	1	85	85
Projected	100	76	1	85	6460
Projected	100	38	1	155	5890*
Projected	100	10	4	155	6200

*By doubling the length of the column, a reduction of 570 watts could be achieved considering the longer lamps have a slightly lower wattage but an 8% higher UVC/VUV output

Table S10. Comparison of pilot demonstrations for the degradation of PFAS against UV/SGM. Values are linearly extrapolated from the experimental results to treat 100 gallons of solution to give a comparison baseline.

	Real					**Projected**	
Treatment Technology	**Volume (Gallons)**	**Wattage**	**Treatment Time (hours)**	**Flowrate**	**PFAS Removed (%)**	**Volume Projected (Projected)**	**Wattage (Projected)**
UV/SGM	1.3	85	24	3.8	93	100 Gallons	6,460
UV/Sulfite	15.6	1,320	23	3.8	97	100 Gallons	8,461
Electrochemical Oxidation	5	300	80	1	99*	100 Gallons	6,000

*PFOS Only