Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2019

Supplemental Information for:

## FUNCTIONALIZED ELECTROSPUN POLYMER NANOFIBERS FOR TREATMENT OF WATER CONTAMINATED WITH URANIUM

Adam Johns,<sup>1</sup> Jiajie Qian,<sup>1</sup> Margaret E. Carolan,<sup>1</sup> Nabil Shaikh,<sup>2</sup> Allison Peroutka,<sup>3</sup> Anna Seeger,<sup>1</sup> José M. Cerrato,<sup>2</sup> Tori Z. Forbes,<sup>4\*</sup> and David M. Cwiertny<sup>1,3,5\*</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, University of Iowa, 4105 Seamans Center for the Engineering Arts and Sciences, Iowa City, IA 52242

<sup>2</sup> Department of Civil, Construction & Environmental Engineering, University of New Mexico, Albuquerque, NM 87131

<sup>3</sup>Department of Chemical and Biochemical Engineering, University of Iowa, 4133 Seamans Center for the Engineering Arts and Sciences, Iowa City, IA 52242

<sup>4</sup>Department of Chemistry, University of Iowa, Iowa City, IA 52242

<sup>5</sup>Center for Health Effects of Environmental Contamination, 251 North Capitol Street, Chemistry Building - Room W195, The University of Iowa, Iowa City, Iowa 52242

> \*Co-corresponding authors DMC: Phone (319) 335-1401; e-mail: david-cwiertny@uiowa.edu TZF: (319) 384-1320 tori-forbes@uiowa.edu

Prepared November 24, 2019 for Environmental Science: Water Research & Technology

## SUPPLEMENTAL METHODS

Reagents. All reagents were used as received. Polymers used in electrospinning were polyacrylonitrile (PAN; MW 150,000, Aldrich) and polyvinylidene difluoride (PVDF; MW 180,000, Aldrich). Solvents used to dissolve polymers included N,N-Dimethylacetamide (DMA; 99.8%, Aldrich), N,N-dimethylformamide (DMF; 99.85%, BDH Chemicals), dimethyl sulfoxide (DMSO; ≥99.9%, Fisher Scientific), acetone (≥99.5%, Aldrich), and glacial acetic acid (GAA; ≥99.7%, Fischer Scientific). Surfactants added to precursor solutions were tetrabutylammonium bromide (TBAB; Sigma Aldrich). Aliquat® 336 (Aq; Alfa Aesar), tributyl phosphate (TBP; Sigma Aldrich), diamyl amylphosphonate (DAAP; Sigma Aldrich), CMPO (Carbosynth; 98%), bis(2-ethylhexyl phosphate (HDEHP; 97%, Aldrich), and hexadecyl phosphonic acid (HDPA; 97%, Aldrich). Batch experiments were conducted in 10 mM HEPES buffer (≥99%, Aldrich), calcium chloride dihydrate (99%, Fisher Scientific). Amidoximation of PAN mats used hydroxylamine hydrochloride (98%, Aldrich) and sodium hydroxide (97.0%, Fisher Scientific).

**Electrospinning.** *PAN-PVDF composite.* To enhance the mechanical stability and handling of PAN nanofiber mats, a composite material was created to have a PVDF backbone. For the PVDF layer of the composite material, 12 wt.% PVDF was dissolved in DMA and acetone (3:7 volume ratio) by mixing at 60°C for 2 h at 700 rpm (Eppendorf ThermoMixer C). For the PAN layer of the composite, 7 wt.% PAN was dissolved in DMF by mixing at 60°C for 2 h at 700 rpm. Six mL of the PVDF sol gel was added to a 12 mL plastic syringe (HSW Norm-Ject) that was subsequently loaded onto a syringe drive (New Era Pump Systems, Inc.). A polyethylene (PE) 1/16" female Luer lock fitting was connected to the syringe and a 2.0 mm ID PE tube was

attached to the lock fitting. The tubing was then connected to a metal nozzle adapter (NanoNC Co., Ltd) by another PE 1/16" female Luer lock fitting and a ½" 25G needle attached to the other end of the nozzle. A distance of 10 cm was created between the end of the needle tip and the surface of a 9-5/16" circumference metal drum collector (SPG Co., Ltd; Korea). The metal drum was grounded and covered in Al foil for collection of the electrospun polymer composites. PVDF was electrospun first by passing the polymer solution through the needle at 0.4 mL/h with a positive voltage of 21 kV applied at the needle tip (high voltage AC to DC converter, Acopian) and the grounded collector (Dingtuo Technology) rotating at 500 rpm. After completion of PVDF layer, six mL of the PAN solution was electrospun at 0.3 mL/h and 15 kV, with all other fabrication parameters being identical to those described for PVDF. The resulting material was a composite containing 50 wt.% PAN and 50 wt.% PVDF. The two-layer polymeric composite was removed from the Al foil with tweezers to prevent tearing and used in subsequent processes (e.g., amidoximation) without any additional modification.

*Amidoximation of PAN nanofibers*. This protocol was originally reported in Horzum et al.<sup>1</sup> and optimized by varying temperature (20 or 30 °C), reaction time (24 or 48 hours), and solution exchanges (reacted in either one or two fresh solutions). A PAN-PVDF mat (2 g/L of mat, 1 g/L of PAN, ~0.65 cm<sup>2</sup>/mL) was placed into a glass dish containing a solution of 15 g/L hydroxylamine hydrochloride (0.216 M) and sodium hydroxide (0.375 M) with the PAN side of the mat on the surface of the solution. A lid was placed on the glass dish, which was then placed into a 30°C water bath for 24 hours. Afterwards, the mat was rinsed extensively with DI water to remove any remaining salts; all mats were rinsed until the samples of the wash water were at the same pH of DI water. Mats were then left to dry for 12 hours in air prior to use in any experiments.

Nanofiber Characterization. Nanofiber morphology and diameter were determined through imaging with Scanning Electron Microscopy (SEM; S-4800, Hitachi). Prior to imaging, pieces of nanofiber mats were sputter coated with a thin layer of Au/Pd (Emitech Sputter Coater K550). Average nanofiber diameters (with standard deviation) were determined from the diameter distribution of at least 100 nanofibers, sized using the software ImageJ. Fourier Transform Infrared Spectroscopy (FTIR; Nicolet<sup>™</sup> iS<sup>™</sup> 50 FTIR Spectrometer) was used to examine all functionalized nanofiber formulations to confirm the presence of PAN and the binding agent. For FTIR analysis, a piece of the nanofiber mat was loaded into the sample chamber and purged with dry air and nitrogen. Spectra were collected using 128 single beam scans at a resolution of 2 cm<sup>-1</sup>, which were compared to a single baseline (no mat) scan. Mat pore volume and specific surface area were determined by N<sub>2</sub>-BET adsorption isotherms on a Quantachrome NOVA 4200e Analyzer. Samples were degassed for at least 12 hours prior to analysis. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra spectrometer to characterize the near surface region (~top 5-10 nm) of the functionalized nanofibers before and after U<sup>6+</sup> uptake experiments. A monochromatic Al source was used at 150 W power to obtain elemental composition from survey scans and explore the U binding environment based on the U 4f high resolution spectra. Shirley background subtraction was used to process the background noise.

## SUPPLEMENTAL RESULTS AND DISCUSSION

**Timescales of Uranium Uptake.** The rate of U uptake was explored for each material at the optimal pH regime identified from initial uptake studies (Figure 1, main text) and subsequent pH edge experiments (Figure 3, main text), specifically pH 2 for HDEHP and HDPA and pH 6.8 for AO-PAN and Aq-containing PAN. All materials showed relatively rapid uptake, with the majority of U binding occurring over the first ~2 h (**Figure S1**). Notably, the time necessary to achieve equilibrium varied for each material; Aq and HDEHP mats reaching equilibrium at 2 hours and AO-PAN achieving steady-state near 16 hours. HDPA followed a much slower period of uptake and never reached equilibrium during the course of the experiment. At pH 2 and after 16 hours, the sorbed fraction of U bound to HDPA-containing mats exceeded that for HDEHP (~90% versus 45%, respectively). At pH 6.8, AO-PAN far exceeded the performance of Aq-containing materials, with approximately 75% U removal versus 25%, respectively.

Generally, these trends in the rate and relative extent of uptake match expectations from prior studies with analogous binding agents or materials. Prior studies with AO-PAN nanofibers showed similar uptake rates (1 g mat L<sup>-1</sup>; initial uranium concentration of 100 mg/L; pH 4) in batch systems, with rapid uptake in the first 1.3 h, followed by equilibration after 3 hours.<sup>2</sup> Similarly, phosphate functionalized polyethylene nanofibers also had similar uptake rates compared to our HDPA-functionalized materials (0.2 g mat L<sup>-1</sup>; initial uranium concentration of 50 mg/L; pH 8.2), with rapid uptake in the first 6 hours and maintained sorption percent at any longer reaction periods.<sup>3</sup>

**Table S1.** Surface associated atomic percentages on electrospun mats from XPS survey scans (n.d. = not detected). Data are shown for control (as synthesized) nanofibers and for nanofibers after equilibration with a solution containing initially 10  $\mu$ M of U<sup>6+</sup>. All XPS characterization results pertain to optimal nanofiber formulations (i.e., those containing 2 wt.% Aq, 0.5 wt.% HDPA, 1 wt.% HDEHP, as well as AO-PAN).

Sample Name	C 1s %	N 1s %	O 1s %	P 2p %	U 4f %
As synthesized electrospun nanofibers					
PAN Control	79.3±0.2	17.3±0.1	3.4±0.2	n.d.	n.d.
HDPA Control	78.5±1.2	15.1±2.1	6.2±1.2	0.2±0.1	n.d.
Aq Control	78.0±1.1	14.0±1.2	7.5±0.3	0.5±0.0	n.d.
AO-PAN Control	70.5±0.2	13.9±0.3	15.6±0.3	n.d.	n.d.
HDEHP Control	83.8±0.1	10.1±0.0	6.0±0.1	0.1±0.1	n.d.
After equilibration with 10 $\mu$ M initial U <sup>6+</sup>					
PAN Reacted	79.1±0.7	15.3±1.6	5.7±0.9	n.d.	n.d.
HDPA Reacted	78.4±0.6	12.3±2.1	8.1±1.5	1.2±0.0	0.05±0.01
Aq Reacted	82.0±0.4	6.8±0.8	9.5±0.5	1.6±0.5	0.05±0.01
AO-PAN reacted	72.2±1.0	7.8±1.3	19.9±0.4	n.d.	0.14±0.02
HDEHP reacted	80.2±0.3	8.8±0.9	9.1±0.6	1.6±0.2	0.32±0.02



**Figure S1.** Sorbed uranium concentration as a function of time. Data are shown for optimal nanofiber formulations (i.e., those containing 2 wt.% Aq, 0.5 wt.% HDPA, 1 wt.% HDEHP, as well as AO-PAN). All materials were tested at an initial concentration of 10  $\mu$ M U. Aq-containing PAN and AO-PAN experiments were conducted in 10 mM HEPES at pH 6.8, while experiments with HDEHP- and HDPA-containing nanofibers were conducted in water acidified to pH 2 with HNO<sub>3</sub>. Uncertainties represent one standard deviation from duplicate experiments. Mass loadings used were 0.25 g L<sup>-1</sup>.



Figure S2. Schematic of flow through filtration system used in simulated point of use treatment of  $U^{6+}$  containing water.



**Figure S3**. Histogram of nanofiber dimensions (bin size of 10 nm) analyzed by ImageJ with images taken via SEM. During analysis  $\geq$ 100 nanofibers were measured with the average and standard deviation reported. Data are shown for PAN and functionalized PAN materials investigated herein (with wt.% of each ingredient relative to the total mass of the sol gel as indicated in the material name; e.g., PAN7-Aq3 is produced via a sol gel with 7 wt.% PAN and 3 wt.% Aq)



**Figure S4**. FTIR spectra of synthesized polymer mats. Key spectral features associated with each material are identified. Spectra are shown for PAN, as well as the optimal formulations for functionalized PAN nanofibers (i.e., those containing 2 wt.% Aq, 0.5 wt.% HDPA, 1 wt.% HDEHP, as well as AO-PAN).



**Figure S5.** Speciation diagram for  $U^{6+}$  with total concentration of (top) 1.0  $\mu$ M and (bottom) 10  $\mu$ M UO<sub>2</sub><sup>2+</sup> between pH 2-7. Speciation diagrams were constructed using the Hydra data base with log*K* data at 25 °C and visualized with the Medusa software [Puigdomenech, I. Chemical Equilibrium Diagrams, Available at: sites.google.com/site/chemdiagr/ (Accessed September 18, 2019)].



**Figure S6.** High-resolution U 4f XPS spectra for reacted electrospun PAN nanofibers containing (a) 0.5 wt.% HDPA; (b) 1 wt.% HDEHP; (c) 2 wt.% Aq; and (d) AO-PAN. Spectra were collected on samples equilibrated with an initial solution of 10  $\mu$ M U<sup>6+</sup> from isotherm experiments shown in Figure 4 of the main text.



**Figure S7**. Normalized concentration (effluent concentration divided by influent concentration) of U as a function of the volume treated in a dead-end filtration setup with AO-PAN (26 m filter). Results are shown for a larger volume of influent treated (to 240 mL), with all effluent values below the limits of analytical detection. Experiments used an influent concentration of 1  $\mu$ M in 10 mM HEPES (pH 6.8) and a flowrate of 0.8 mL/min (160 LMH).



**Figure S8.** Cumulative mass of  $U^{6+}$  removed as a function of dead end filter run time (as volume of water treated) for 0.5 wt.% HDPA-functionalized PAN. Experiments used an influent concentration of 1  $\mu$ M in 10 mM HEPES (pH 6.8) and a flowrate of 0.8 mL/min (160 LMH). Data from four replicate trials (1 through 4) with 20 mg filters are shown. In all cases, the amount of  $U^{6+}$  removed per volume of water treated increases after 40-60 mL of influent has been passed through the filter (behavior most evident for Trials 1 and 2).

## Literature Cited

- 1. Horzum, N.; Shahwan, T.; Parlak, O.; Demir, M. M., Synthesis of amidoximated polyacrylonitrile fibers and its application for sorption of aqueous uranyl ions under continuous flow. *Chemical Engineering Journal* **2012**, *213*, 41-49.
- 2. Hu, L.; Yan, X.-W.; Yao, C.-G.; Deng, S.-Y.; Gao, X.-M.; Zhang, X.-J.; Shan, D., Preparation of amidoximated coaxial electrospun nanofibers for uranyl uptake and their electrochemical properties. *Separation and Purification Technology* **2016**, *171*, 44-51.
- 3. Shao, D. D.; Li, Y. Y.; Wang, X. L.; Hu, S.; Wen, J.; Xiong, J.; Asiri, A. M.; Marwani, H. M., Phosphate-Functionalized Polyethylene with High Adsorption of Uranium(VI). *ACS Omega* **2017**, *2*, 3267-3275.