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Electronic Supplementary Information for:

Porous Polymeric Electrospun Nanofibers with Surface-Active Iron Oxide Nanoparticles: Composite Filtration Materials for Removal of Metal Cations

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3 Tables, 14 Figures, and 20 Pages

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Electrospinning. Precursor solutions were loaded into a 12 mL plastic syringe (HSW Norm-Ject) connected to 2.0 mm ID polyethylene (PE) tubing via a PE 1/16" female luer lock fitting (NanoNC Co., Ltd). The tubing was connected to a metal nozzle adapter (NanoNC Co., Ltd) via a PE 1/16" male luer lock fitting, and a 25G 1/2" needle was attached to the other end of the nozzle adapter. The needle tip was located a distance of 10 cm from the surface of a 9-5/16"-circumference metal drum collector (SPG Co., Ltd; Korea), which was coated in Al foil and grounded. Electrospinning conditions included a temperature and relative humidity of 28°C and 16%, respectively, pumping rate of 0.3 mL/h (New Era Pump Systems, Inc.), a positive 15 kV voltage applied at the needle tip (Acopian), and a drum collector rotation speed of 500-rpm (Dingtuo Technology). Electrospinning was typically carried out for 8 h.

Nanofiber Characterization. The morphology of electrospun nanofiber mats was investigated using a field-emission scanning electron microscope (SEM; S4800, Hitachi) at an acceleration voltage of 1.5 kV. All samples were sputter-coated with a thin layer of gold/palladium (60:40 Au:Pd) prior to SEM imaging. Average fiber diameters were developed from measurement of >100 nanofibers in ImageJ software. Nanoparticles were examined using high resolution transmission electron microscopy (HRTEM; JEOL JEM 2100 F with Schottky FEG Emission-Zr/W). Samples were prepared via sonication in deionized water, and a droplet was allowed to dry on a grid prior to imaging (#01824 UC-A on holey 400 mesh Cu; Ted Pella, Inc.). Cross sectional images of nanofiber composites were obtained using transmission electron microscopy (TEM; JEOL JEM-1230) at an operating voltage of 120 kV. Samples were prepared via embedding nanofiber mats in EPONTM resin (Hexion) and sectioning at 80 nm on an ultramicrotome (Leica UC6). Sections were placed on a grid for imaging (#01814-F C-B 400 mesh Cu; Ted Pella, Inc). Surface area and pore volumes were determined by N₂-BET analysis using a Quantachrome NOVA 4200e Analyzer. Nanoparticle samples and nanofiber materials were degassed at 90°C for 12 h and 35°C for 12 h, respectively, prior to analysis. Surface composition was analyzed with a custom Kratos Axis Ultra X-ray photoelectron spectroscopy

(XPS) system equipped with a monochromatic Al K α X-ray source. XPS was used to collect full spectrum survey scans, as well as to examine Fe 2p regions (prior to sorption) and Pb 4f regions (after sorption). An extensive description of this system can be found elsewhere.^{1,2} After sorption of lead, copper, and cadmium (10 mg/L initial concentrations; pH 6 for Cu and Pb; pH 7 for Cd) on rinsed Fe2-SDS1 composites, composites were air-dried at room temperature and analyzed via X-ray diffraction (XRD; Rigaku MiniFlex II, cobalt X-ray source). Samples were prepared for XRD by placing a ~2 cm by ~2 cm piece of nanofiber mat (or a compact layer of nanoparticles) on a slide with a well depth of 0.2 mm. Samples were analyzed from 10° to 80° with an interval of 0.02°.

Rinsing Procedure for SDS Removal. To remove SDS from the composite matrix prior to characterization and/or performance assessment, 5 mg of the nanofiber mat was rinsed twice for 3 h in 15 mL of DI water (water exchanged between each rinse), followed by an 18 h rinse in 15 mL of the buffer in which sorption was to be performed (e.g., 10 mM HEPES, MES, or AMPSO). Rinsed nanofiber mats were used directly for performance assessment, or allowed to dry prior to characterization.

Analytical Methods. Soluble iron concentration was quantified via the phenanthroline colorimetric method,³ which used 1 mL sample, 30 μ L 100 g/L hydroxylamine hydrochloride, 200 μ L 1 g/L 1,10-phenanthroline, 200 μ L ammonium acetate buffer; 20 minute reaction time; and measurement at 510 nm on UV-vis spectrophotometer. Iron standards were made by dilutions of ferrous ammonium sulfate in 0.1 N H₂SO₄.

6	Unrinsed Materials: Copper			Rinsed Materials: Copper		
Material	K_L (L/mg)	C _{sorb} (mg/g mat)	C _{sorb} (mg/g np)	K _L (L/mg)	C _{sorb} (mg/g)	C _{sorb} (mg/g np)
Fe ₂ O ₃ nanoparticles	0.32 ± 0.04		38.7 ± 1.4			
PAN		1.9 ± 1				
Fe1	0.27 ± 0.07	3.3 ± 0.2	26.0 ± 1.74			
Fe2	0.32 ± 0.05	3.8 ± 0.2	17.0 ± 0.7			
Fe3	0.41 ± 0.1	3.9 ± 0.3	13.0 ± 1.1			
SDS1		<1		0.39 ± 0.14	1.72 ± 0.18	
Fe0.1-SDS1				0.37 ± 0.2	2.1 ±0.2	164 ± 16
Fe0.25-SDS1				0.06 ± 0.05	4.0 ±1.7	131 ± 54
Fe0.5-SDS1	0.47 ± 0.16	2.7 ± 0.2	47 ± 3.6	0.13 ± 0.05	5.4 ± 0.8	94.0 ± 14
Fe1-SDS1	0.28 ± 0.09	5.3 ± 0.5	48 ± 4.3	0.14 ± 0.04	7.9 ± 0.9	72.0 ± 8.3
Fe1.5-SDS1	0.22 ± 0.05	8.0 ± 0.6	51.0 ± 3.6	0.17 ± 0.04	8.9 ± 0.8	56.8 ± 5.3
Fe2-SDS1	0.29 ± 0.05	8.4 ± 0.4	42.0 ± 2.0	0.16 ± 0.04	11.7 ± 1.2	58.6 ± 6.0
Fe2.5-SDS1	0.32 ± 0.07	10.7 ± 0.6	44.3 ± 2.7	0.22 ± 0.05	11.9 ±0.9	49.6 ± 3.8
Fe3-SDS1	0.39 ± 0.1	11.2 ± 0.9	41.9 ± 3.3	0.28 ± 0.05	11.5 ±0.07	43.0 ± 2.4
Fe3-SDS3	0.39 ± 0.06	10.9 ± 0.5	46.9 ± 2.2	0.17 ± 0.06	10.9 ± 0.5	47.1 ± 2.1

Table S1. Langmuir model fits for Cu isotherms.

8	Unrinsed Materials: Lead			Rinsed Materials: Lead		
Material	K _L (L/mg)	C _{sorb} (mg/g mat)	C _{sorb} (mg/g np)	K _L (L/mg)	C _{sorb} (mg/g)	C _{sorb} (mg/g np)
Fe ₂ O ₃ nanoparticles	0.27 ± 0.06		106 ± 5.8			
PAN		1.7 ± 0.9				
Fe1	0.14 ± 0.04	12.6 ± 1.0	100 ± 8.0			
Fe2	0.10 ± 0.02	19.2 ± 1.0	86.4 ± 4.5			
Fe3	0.18 ± 0.05	18.2 ± 1.2	61.2 ± 4.2			
SDS1		<1		0.10 ± 0.09	1.6 ± 0.5	
Fe0.5-SDS1	0.75 ± 0.1	6.0 ± 0.1	104 ± 2.0	0.27 ± 0.08	5.8 ± 0.4	102 ± 6.3
Fe1-SDS1	0.66 ± 0.2	11.0 ± 0.5	100 ± 4.9	0.18 ± 0.05	12.9 ± 0.8	117 ± 7.2
Fe1.5-SDS1	0.60 ± 0.1	17.8 ± 0.6	114 ± 4.1	0.19 ± 0.05	18.8 ± 1.2	119 ± 7.6
Fe2-SDS1	0.50 ± 0.1	26.3 ± 0.9	132 ± 4.5	0.22 ± 0.05	25.6 ± 1.4	128 ± 7
Fe2.5-SDS1	0.60 ± 0.07	29.1 ± 0.6	121 ± 2.6	0.23 ± 0.07	28.7 ± 1.9	119 ± 7.8
Fe3-SDS1	0.53 ± 0.09	35.1 ± 1.1	131 ± 4.1	0.31 ± 0.06	31.4 ± 1.3	117 ± 4.8

Table S2. Langmuir model fits for Pb isotherms.

	Unrinsed Materials: Cadmium			Rinsed Materials: Cadmium		
Material	$K_L (L/mg)$	C _{sorb} (mg/g mat)	C _{sorb} (mg/g np)	K _L (L/mg)	C _{sorb} (mg/g)	C _{sorb} (mg/g np)
Fe ₂ O ₃ nanoparticles	0.37 ± 0.09		13.3 ± 0.7			
PAN		0.7 ± 0.4				
Fe1	0.30 ± 0.21	3.6 ± 0.6	28.5 ± 4.5			
Fe2	0.37 ± 0.13	5.0 ± 0.4	22.4 ± 1.7			
Fe3	0.17 ± 0.06	5.1 ± 0.51	17.1 ± 1.7			
SDS1	0.27 ± 0.08	1.3 ± 0.1		0.11 ± 0.02	3.5 ± 0.27	
Fe0.5-SDS1	0.36 ± 0.1	2.4 ± 0.2	42.0 ± 3.2	0.16 ± 0.06	3.3 ± 0.4	56.0 ± 6.7
Fe1-SDS1	0.64 ± 0.3	2.0 ± 0.1	18.0 ± 1.3	0.1 ± 0.04	5.8 ± 1.0	52.7 ± 8.7
Fe1.5-SDS1	0.14 ± 0.04	4.9 ± 0.5	31.5 ± 3.3	0.11 ± 0.04	6.1 ± 0.9	39.1 ± 5.6
Fe2-SDS1	0.45 ± 0.2	3.7 ± 0.3	18.3 ± 1.7	0.19 ± 0.05	5.2 ± 0.4	26.2 ± 1.9
Fe2.5-SDS1	0.3 ± 0.1	4.6 ± 0.4	18.9 ± 1.6	0.13 ± 0.04	7.6 ± 0.8	31.6 ± 3.2
Fe3-SDS1	0.4 ± 0.1	4.5 ± 0.2	16.6 ± 0.9	0.24 ± 0.07	6.5 ± 0.5	24.2 ± 1.9

Table S3. Langmuir model fits for Cd isotherms.



Figure S1. (a) HRTEM image and (b) XRD spectra of as-received ~ 3 nm Fe₂O₃ nanoparticles (Alfa Aesar), showing that nanoparticles are amorphous hematite.



Figure S2. Effect of SDS concentration (1 vs. 3 wt%) on Cu isotherms. Data are shown for unrinsed and rinsed composites containing a 3 wt% Fe_2O_3 nanoparticle loading (Fe3-SDS1 vs. Fe3-SDS). Experimental conditions: 0.5 g/L mass loading; 10 mM MES buffer, pH 6; 2-30 mg Cu/L.



Figure S3. Results of composite digestion in strong acid (5N H₂SO₄; 0.25 g/L composite mass loading) for 24 h. Data are shown for PAN-Fe and PAN-Fe-SDS composites containing 1, 2 and 3 wt% Fe₂O₃ and 1 wt% SDS. (a) Total experimental Fe content (as mg Fe/g mat) and (b) fraction of theoretical Fe content based on the theoretical Fe₂O₃ nanoparticle loading in the composite and the Fe content of Fe₂O₃ nanoparticles (625 ± 14 mg Fe/g nanoparticle, determined via 24 h digestion in 5N H₂SO₄; 0.125 g/L nanoparticle loading).



Figure S4. Nanofiber diameter histograms and representative SEM images of nanofiber composites, including unmodified PAN, SDS1, Fe1, Fe2, Fe3, Fe0.5-SDS1, Fe1-SDS1, Fe1-SDS1, Fe2-SDS1, Fe2-SDS1, Fe2-SDS1, Fe3-SDS1, and Fe3-SDS3. Average nanofiber diameters (from measurement of n > 100 nanofibers in ImageJ® software) are noted on each histogram. Inclusion of 3 wt% Fe₂O₃ nanoparticles yielded a slight, but not statistically significant, decrease in nanofiber diameter relative to unmodified PAN, while inclusion of 1 wt% SDS yielded a slight increase in nanofiber diameter. Limited differences relative to SDS1 were observed with inclusion of both Fe₂O₃ nanoparticles and 1 wt% SDS in nanofiber composites, although the inclusion of both 3 wt% Fe₂O₃ and 3 wt% SDS yielded significantly larger nanofiber diameters (presumably due to increased viscosity at the higher SDS concentration).



Figure S5. Representative SEM images of Fe2-SDS1, showing nanofiber uniformity and surface roughness due to Fe₂O₃ nanoparticle aggregates at or near the nanofiber surfaces.



Figure S6. XPS survey scans of (a) Fe3 and (b) Fe3-SDS1 composites, with C 1s, N 1s, O 1s, and Fe 2p peaks labeled.



Figure S7. Dissolution of PAN-Fe and PAN-Fe-SDS composites in dilute acid ($0.1N H_2SO_4$; 0.25 g/L composite mass loading). Data of dissolve Fe over time are shown (a) as mg Fe / g mat and (b) normalized to the theoretical Fe loading in the composite (based on theoretical Fe₂O₃ nanoparticle loading and Fe content of Fe₂O₃ nanoparticles). Normalized rate of dissolution from PAN-Fe-SDS composites is ~2.5 times that from PAN-Fe materials due to improved solution phase accessibility of Fe₂O₃ nanoparticles upon inclusion of SDS.



Figure S8. Representative TEM images of (a) Fe3 and (b) Fe3-SDS1 composites, showing comparable dispersion of Fe_2O_3 nanoparticles regardless of SDS inclusion.



Figure S9. Sorption isotherms for (panels a,d, and g) Cu (pH 6), (panels b,e, and h) Pb (pH 6) and (panels c, f, and i) Cd (pH 7). Data are shown for (panels a-c) unmodified PAN, PAN-Fe, and PAN-SDS composites, as well as both (panels d-f) unrinsed and (panels h-i) rinsed PAN-Fe-SDS composites. Experimental conditions: 0.5 g/L composite mass loading; 10 mM MES for pH 6, 10 mM HEPES for pH 7.



Figure S10. Reversibility of rinsed Fe2-SDS1 composites for uptake of (a) Cu (pH 6), (b) Pb (pH 6), and Cd (pH 7). To test reversibility, reactors at sorption equilibrium were perturbed by replacement of the metal-containing aqueous phase with fresh, metal-free buffer. This was followed by a second 24 h equilibration period. Partial reversibility was observed for Cu, while composites exhibited near-complete irreversibility for uptake of Pb and Cd. Experimental conditions: 0.5 g/L composite mass loading; 10 mM MES for pH 6, 10 mM HEPES for pH 7.



Figure S11. Analysis of a representative material (Fe2-SDS1-R) after sorption of Cu, Pb, or Cd to determine if metal surface precipitation was contributing to uptake. (a) XRD patterns of dried Fe2-SDS1-R after sorption of Cu (blue), Pb (green) or Cd (pink). Also shown is a control sample analyzed after mixing the mat at equivalent conditions in the absence of an added metal (black). Stars indicate features that appeared after sorption, and suggest the presence of metal precipitates. XPS spectra of the (b) Pb 4f and (c) Cd 3d regions are shown for Fe2-SDS1-R composites after sorption of Pb or Cd, respectively. Sorption of Cu and Pb was performed in 10 mM MES at pH 6; sorption of Cd was performed in 10 mM HEPES at pH 6; 0.5 g/L mat mass loading; 10 mg/L Cu, Pb, or Cd initial concentration. XRD analysis of dried samples suggested precipitation of all targets due to appearance of new diffraction lines not observed on a control material (e.g., Fe2-SDS1-R exposed to a solution without metals). Unfortunately, the corresponding lattice spacings were not characteristic of any known oxides or hydroxides. Additional characterization with XPS revealed the Cu 2p signal to be insufficient to determine its surface chemical state. Likewise, features from the Cd 3d region were inconclusive, as negligible binding energy shifts are expected for different Cd species including surface solid phases. A shift in the Pb 4f region of the XPS spectra to higher binding energies (137.7 eV, relative to 137.0 eV for Pb) is consistent with co-precipitation of lead oxide.⁴ However, sample drying for XRD and the ultra-high vacuum (UHV) conditions of XPS analysis may have altered the surface chemistry of the reacted material. Although these characterization results are suggestive of co-precipitation, we note that we did not observe any corresponding changes to isotherm shape to suggest multi-laver precipitation.



Figure S12. Base titration of dispersed Fe_2O_3 nanoparticles and the Fe2-SDS1 composite by addition of NaOH. Solutions contained a background electrolyte of 5 mM NaCl, and were titrated with either 0.1 or 0.01 M NaOH. Suspensions of Fe_2O_3 nanoparticles were 0.5 g/L, whereas a 2 cm × 2 cm piece of composite was used (~0.25 g/L). The dashed lined indicates the pH at which both the composite and nanoparticles exhibited the greatest buffering capacity (where the titration curve changes from concave down to concave up), and roughly estimates the surface pKa of both materials.



Figure S13. (a) Arsenic (arsenate) sorption isotherms at pH 7 on Fe_2O_3 nanoparticles, Fe2-SDS1-R, and Fe2. (b) pH-dependent uptake of arsenic by Fe_2O_3 nanoparticles and Fe2-SDS1-R, with capacity normalized to nanoparticle loading for composite materials.



Figure S14. XPS spectra of the Pb 4f region for Fe2-SDS1 composites after batch removal of 10 mg/L Pb (10 mM MES, pH 6; green), flow-through removal of 300 μ g/L Pb (10 mM MES, pH 6; red), and flow-through removal of 300 μ g/L Pb (tap water, pH 9.9; blue). The shifts seen for batch removal and flow-through removal from tap water to binding energies >137.0 eV are indicative of Pb (hydr)oxide/hydroxycarbonate precipitation.

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