[Supplementary Information]

Engineered Superparamagnetic Iron Oxide Nanoparticles for Ultra-Enhanced Uranium Separation and Sensing

Wenlu Li,[a,#] John T. Mayo,[b,#] Denise N. Benoit,[b] Lyndsay D. Troyer,[c] Zuzanna A. Lewicka,[d] Brandon J. Lafferty,[e] Jeffrey G. Catalano,[c] Seung Soo Lee,[a] Vicki L. Colvin,[f,*] and John D. Fortner[a,*]

[a] Department of Energy, Environmental, and Chemical Engineering, Washington University in St. Louis, St. Louis, MO, 63130, USA
[b] Department of Chemistry, Rice University, Houston, TX, 77005, USA
[c] Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO, 63130, USA
[d] Department of Electrical and Computer Engineering, Rice University, Houston, TX, 77005, USA
[e] U.S. Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS, 39180, USA
[f] Department of Chemistry, Brown University, Providence, RI, 02912, USA

[#]These authors contributed equally to this work.

*To whom correspondence should be addressed:

Vicki L. Colvin: T: +1-401-863-2321; F: +1-401-863-2594; Email: vicki_colvin@brown.edu

John D. Fortner: T: +1-314-935-9293; F: +1-314-935-5464; Email: jfortner@wustl.edu

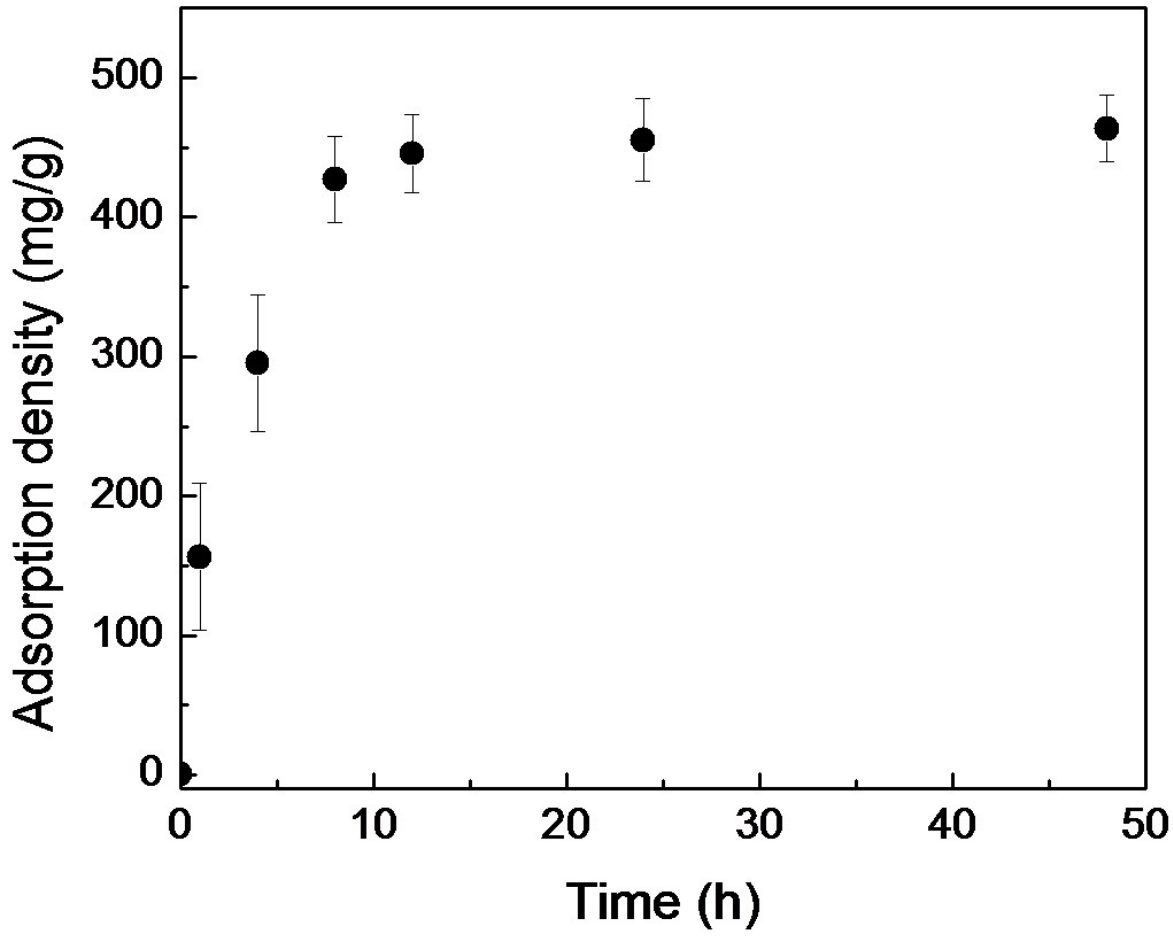


Figure S1. Uranium adsorption density for described engineered IONPs as a function of equilibrium time for a typical uranium sorption experiment at pH 5.6. The concentration of Fe is 20 mg/L and the injected uranium concentration is 20 mg/L. The uranium adsorption density was plotted as a function of time for up to 48 hours and all experiments were conducted in triplicate. Results indicate the systems almost reach equilibrium after 8 hours and thus 24 hours is sufficient for all systems to reach equilibrium.

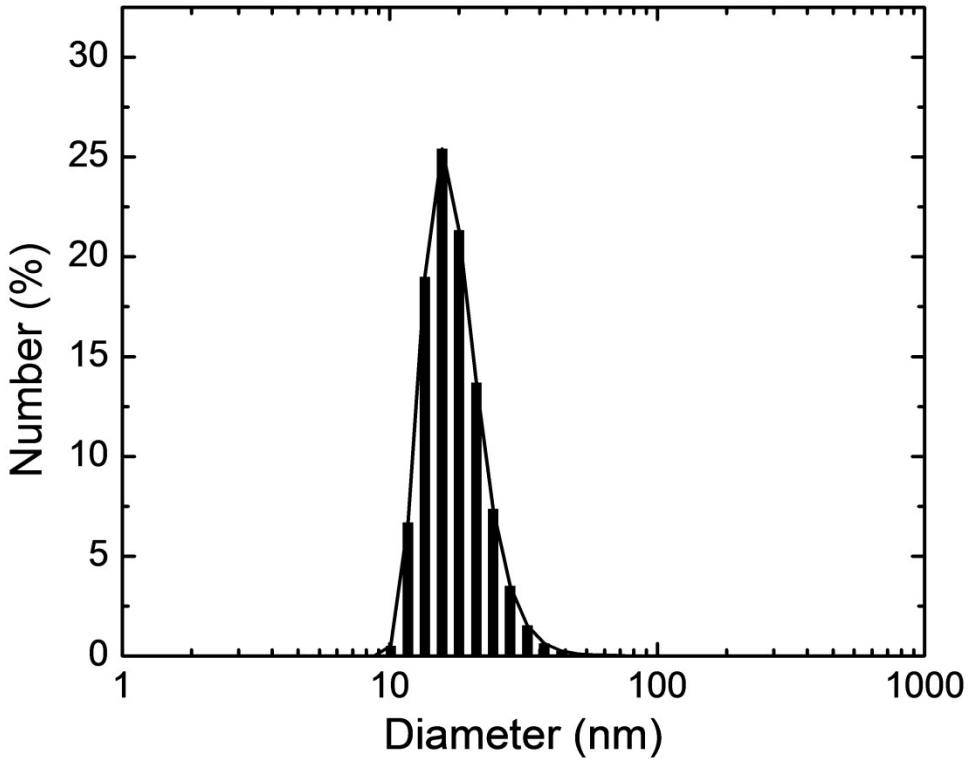


Figure S2. Hydrodynamic diameter of engineered IONPs measured by DLS. Number mean average size distribution of oleic acid bilayer engineered IONPs in water.

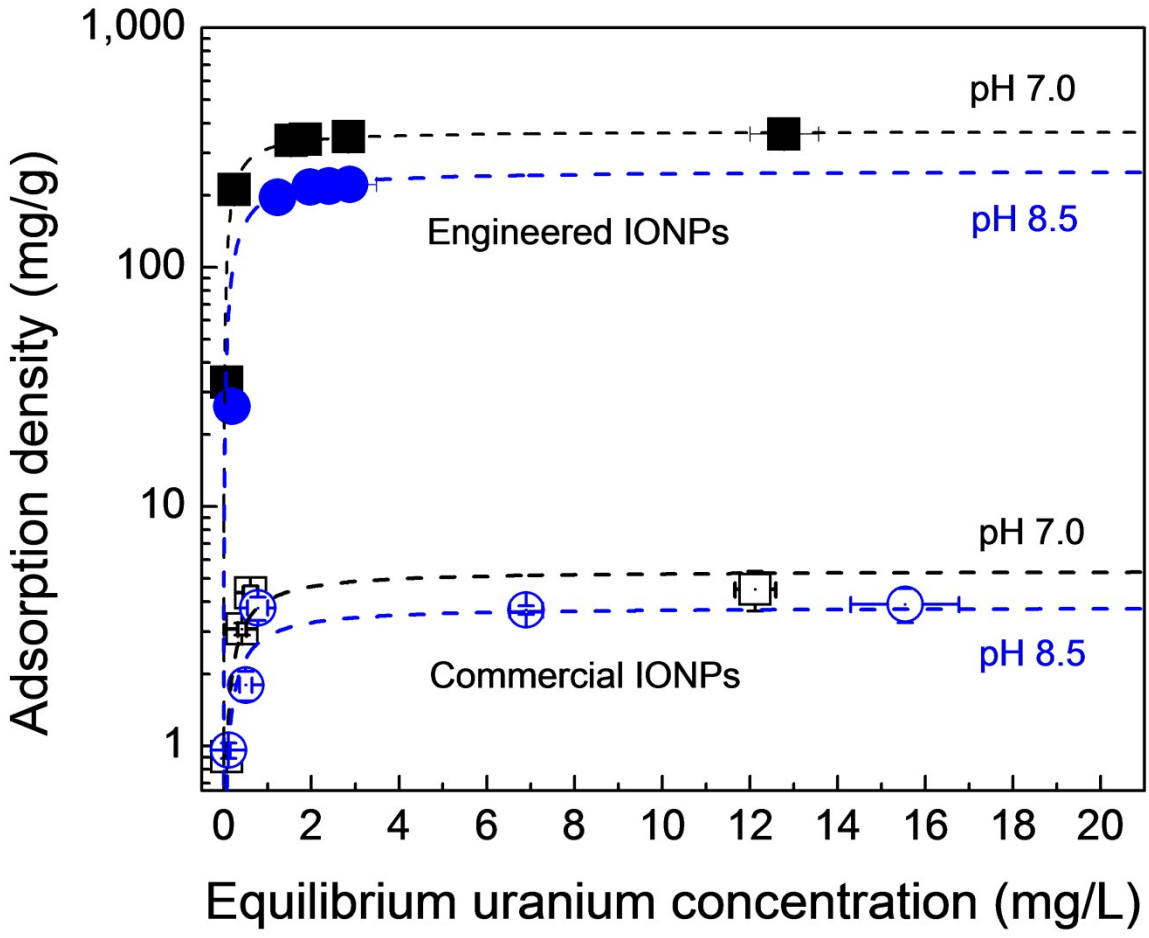


Figure S3. Effect of solution pH on uranium sorption isotherms for commercial and engineered IONPs. pH dependent uranium sorption isotherms of commercial and engineered IONPs at pH 7.0 and pH 8.5. Dashed lines represent Langmuir modeling of the data.

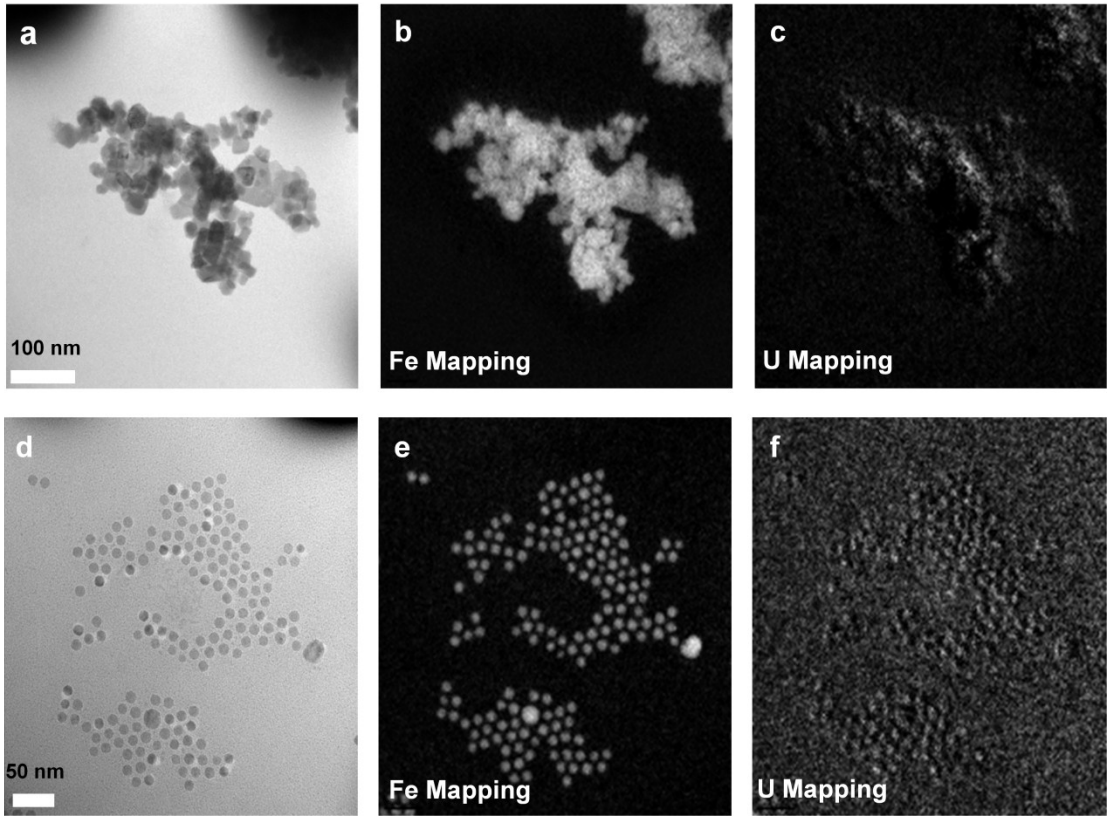


Figure S4. Images of IONPs before and after uranium exposure. (a) FEG-TEM image of the commercial IONPs. (b) Fe mapping using GIF imaging on commercial IONPs. (c) U mapping using GIF imaging on commercial IONPs. (d) FEG-TEM image of oleic acid bilayer stabilized engineered IONPs. (e) Fe mapping using GIF imaging on oleic acid bilayer stabilized engineered IONPs. (f) U mapping using GIF imaging on oleic acid bilayer stabilized engineered IONPs.

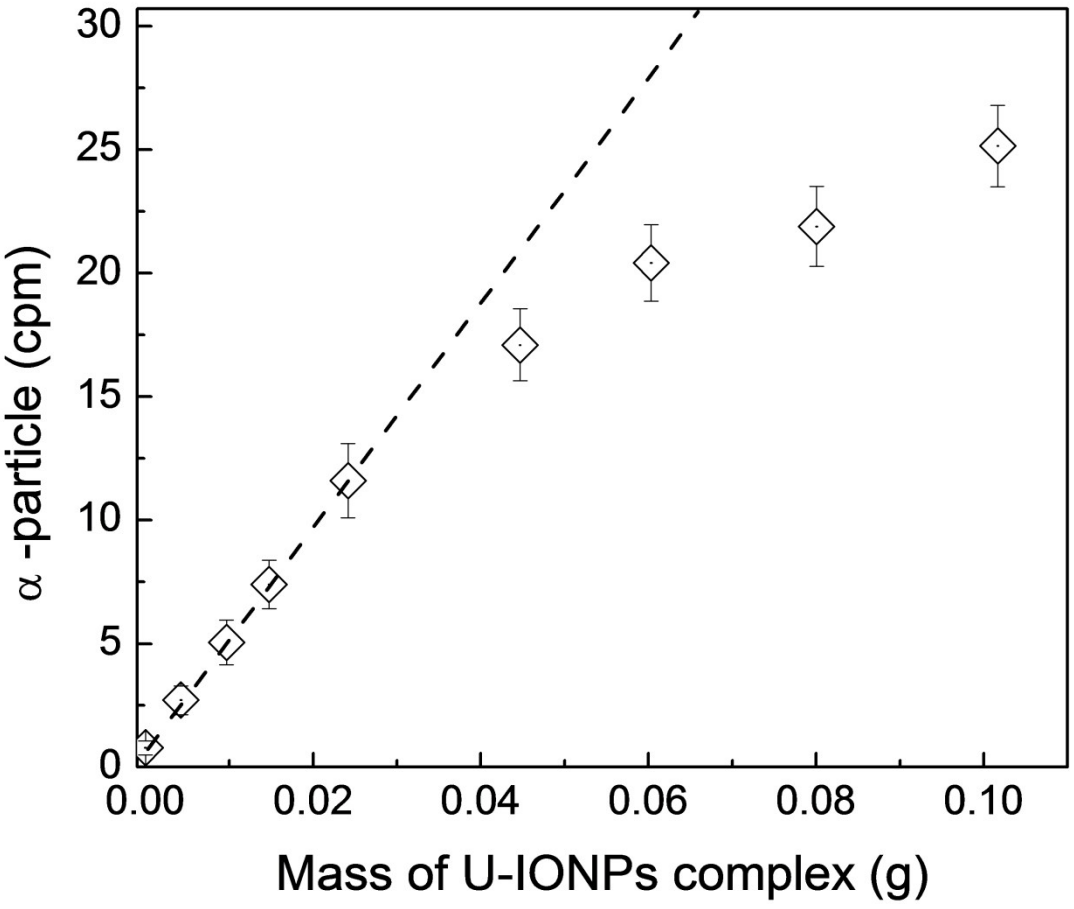


Figure S5. Commercial U-IONPs α-particle detection analysis. This experiment was designed to observe particle shielding. The U-IONPs concentrations were held at the set ratio but were added at higher total mass to the film (i.e. thicker deposits). Thus α-particle detection should increase linearly, until α-particle blocking is observed.

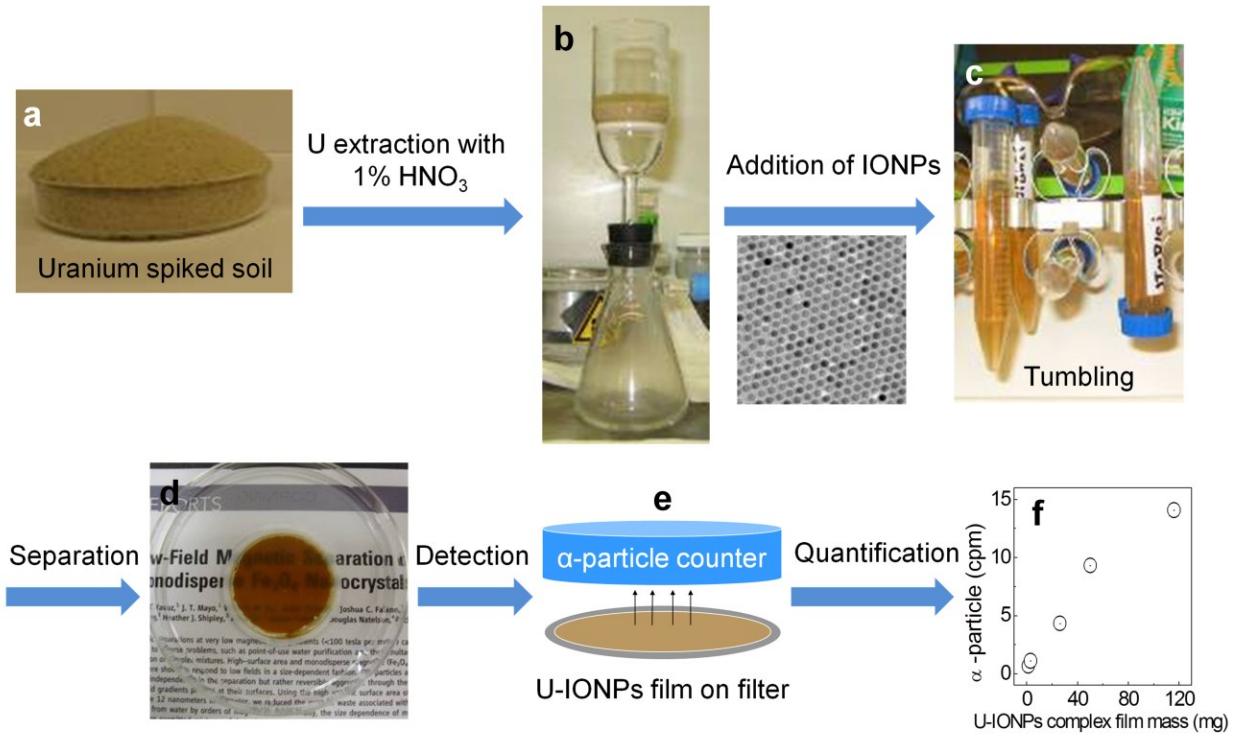
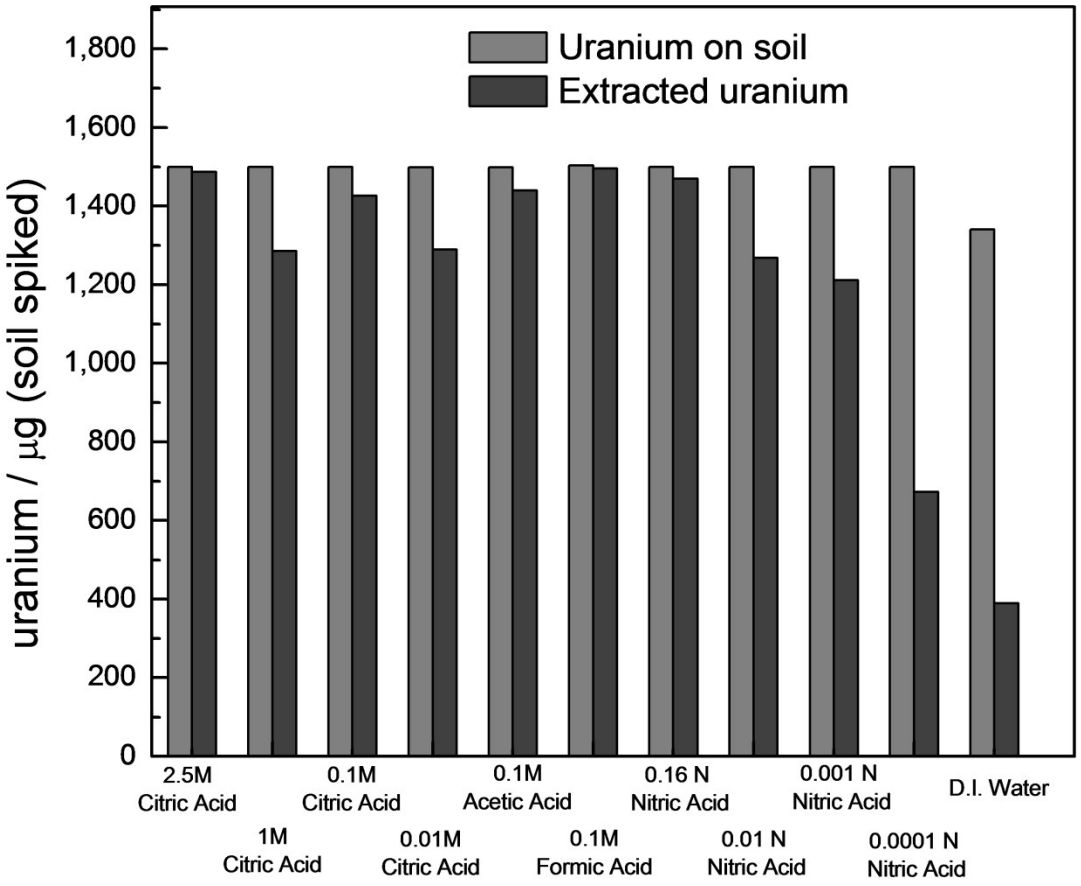


Figure S6. General process schematic. (a) Uranium laden soil (sand). (b) Soil extraction, dissolving bound uranium. (c) Addition of IONPs suspension and equilibrating suspension (uranium-IONPs sorption). (d) Resulting thin film formation. (e) α-particle detection of uranium via U-IONPs film. (f) Example of quantified α-particle counts as a function of uranium loading onto the film.



57

58 **Figure S7.** Soil extraction efficiencies for varying aqueous extraction solutions. Sample
59 preparation included washed sea sand (Fisher scientific) with uranium spiked as dissolved uranyl
60 nitrate stock which was allowed to dry under slight vacuum and then homogenized. Background
61 uranium soil concentration was determined to be 150.7 ± 5.6 μg U/g sand for all systems except
62 for the D.I. water extracted (134.1 ± 3.2 μg U/g sand). Uranium extraction efficiencies with
63 different aqueous chemistries resulting in higher extraction efficiencies (25 - 99 %). For each, 10
64 g of spiked sand was extracted with 20 mL total extractant solution (2 x 10 mL steps). All
65 systems were under oxic conditions.

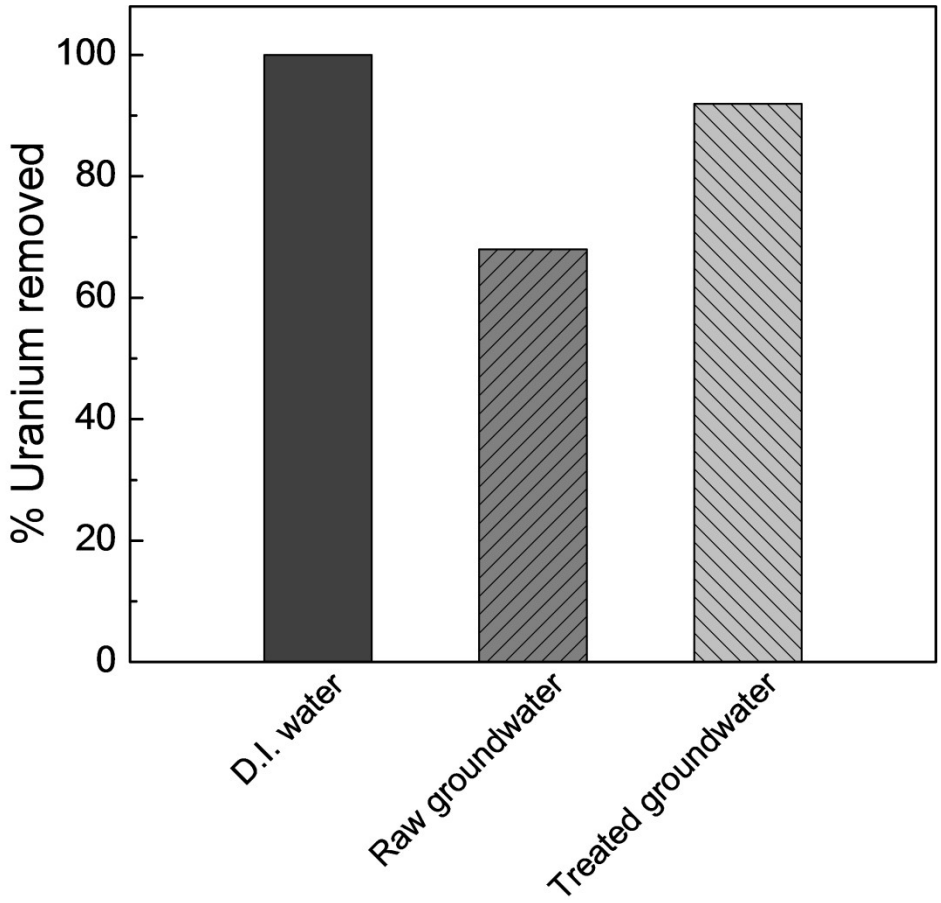


Figure S8. Interfering constituents: uranium sorbed in a complex media (groundwater) relatively compared to D.I. water. Raw ground water was taken from a local well (at 500 ft below the surface) and only filtered with 0.45 μm PES filter to remove solids. Treated groundwater was acidified at 1 % nitric acid and allowed to equilibrate with the atmosphere (removing carbonates). Percent numbers are relative to D.I. water control, pH 5.5. Results indicate that carbonate interactions retarded uranium sorption when untreated (68 % removal efficiency), but when treated with acid effectively removing carbonates, uranium could effectively sorb to available IONPs (92 %). For these studies a 100 ppb uranium solution was exposed to 1 mg/L engineered IONPs.

Table S1. The maximum uranium sorption capacity (q_{max}) and the sorption constant (k) for engineered and commercial IONPs derived by the Langmuir equation.

	Engineered IONPs			Commercial IONPs		
pH	5.6	7.0	8.5	5.6	7.0	8.5
q_{max} (mg/g)	500.0	370.4	250.0	5.7	5.4	3.8
k (L/mg)	1.5	5.4	3.1	2.3	3.0	3.1

Table S2. Percent removal of IONPs using 0.02 μm filtration or magnetic separation (0.35 T, 48 hours).

Material	Separation	% IONPs Removal	Separation	% IONPs Removal
Commercial IONPs	20 nm Filter	99.9	Magnetic	99.9
Engineered IONPs	20 nm Filter	98.9	Magnetic	93.3