Electronic Supplemental Information for

Hematite decorated multi-walled carbon nanotubes (α-Fe_2O_3/MWCNTs) as sorbents for Cu(II) and Cr(VI): Comparison of hybrid sorbent performance to its nanomaterial building blocks

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Supplemental Information contains the full list of reagents, protocols for CNT oxidation and hematite nanoparticle synthesis, and details of materials characterization. Also included are additional experimental data including result of Cu(II) adsorption on all nanomaterials and hybrids.

SUPPLEMENTAL MATERIALS AND METHODS

Reagents. MWCNTs synthesized by chemical vapor deposition (CVD) were acquired from CheapTubes.com. These MWCNTs have a vendor-reported purity of >95%, with an outer diameter (OD) of ~20-30 nm, an inner diameter (ID) of 2-5 nm, a length of 10-30 μm, and a specific surface area of 500 m^2/g. Ferric nitrate nonahydrate (Fisher; 100%) was used as an iron precursor in the synthesis of hematite nanoparticles and hematite-coated MWCNTs. Adsorption experiments were conducted with hexavalent chromium [Cr(VI)] prepared from potassium chromate (K_2CrO_4; Fisher; reagent grade) and copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$; Acros Organics; 98%). Reagents used for CrO_4^{2-} colorimetric analysis included diphenyl carbazide (Fisher; Certified ACS grade) and sulfuric acid (H_2SO_4, Acros Organics; 95-98%). Zincon monosodium salt (Fluka Analytical) was utilized for measurement of aqueous Cu(II) concentration. Colorimetric analysis of aqueous Fe(III) utilized 1,10-phenanthroline (Aldrich, 99+%), ammonium acetate (Sigma-Aldrich; >98%), hydroxylamine hydrochloride (Sigma-Aldrich; 99%) and glacial acetic acid (Fisher; ACS grade). Sodium chloride (NaCl; ACS reagent; ≥99.0%) was used to poise ionic strength and all solutions were prepared in deionized water (Milipore, Q-Grad 2). Solution pH was adjusted via hydrochloric acid (Fisher, trace metal grade) and sodium hydroxide (NaOH; 97+%; ACS reagent grade).

Oxidation of MWCNTs. As received MWCNTs were treated prior to use with concentrated (70%) HNO_3 according to established protocols.[1, 2] Briefly, 100 mg of as received MWCNTs was dispersed in 250 mL of 70% HNO_3 and sonicated for 1 h. The dispersed suspension was then refluxed for 1.5 h at 140 °C in a temperature controlled oil bath while stirring. After cooling overnight, the acid-treated CNTs were then collected on a 0.2 μm nitrocellulose filter and washed extensively with deionized water until the wash solution reached pH 5. Washed MWCNTs were then dried at 80 °C overnight and ground via mortar and pestle prior to suspending in DI water at a final concentration of 1 g/L. Suspensions were then sonicated for 20 h to promote oxidized MWCNT dispersion prior to use in synthesis.

Preparation of hematite nanoparticles. Hematite nanoparticles were synthesized according to "Method 4" in Schwertmann and Cornell.[3] Adapted from the work of Sorum,[4] this approach is known to produce unidimensional crystals with diameters between 7-10 nm. Briefly, 60 mL of 1 M ferric nitrate solution was added drop-wise via peristaltic pump (rate of 0.5 mL/min) into 750 mL of boiling water that was well-mixed with a magnetic stirrer. At early stages of ferric nitrate addition, the boiling water was red in color but transparent. Eventually the solution thickened to form a suspension with red particles. After the drop-wise addition was completed, the nanoparticle suspension was removed from the hot plate and allowed to cool overnight. Once cool, the suspension was loaded into dialysis tubing (MWCO of 3500) and dialyzed against DI water, with the DI water being exchanged 3-4 times a day over a period of 4 days. After dialysis, the suspension was dried in air via partitioning suspension aliquots into several plastic weight boats. After drying, the particles were ground with mortar and pestle and passed through a 53 μm sieve.

Analytical methods. Total dissolved iron was quantified using the 1,10-phenanthroline method.[5, 6] Briefly, 40 μL of acidified supernatant from digestion of hematite-MWCNT nanostructures was diluted with 1 mL of DI water. For colorimetric analysis, 20 μL of a 10 g/L hydroxylamine solution was first added to the diluted sample to reduce all Fe(III) to Fe(II). Then, 200 μL of a 1 g/L solution of 1,10-phenanthroline, which complexes Fe(II), and 200 μL of a 100 g/L ammonium acetate buffer were added to the sample. The mixture was allowed to sit in the dark for ~30 min prior to analysis. Absorbance measurements were then performed on a Shimadzu UV-visible spectrophotometer at λ=510 nm. Standards for Fe(II) were prepared from anhydrous beads of ferrous chloride ($FeCl_2$, 99.9%, Sigma-Aldrich).

Dissolved concentrations of Cr(VI) were determined colorimetrically with the reagent diphenylcarbazide.[7] Briefly, 80 μL of filtered sample was diluted with 1 mL of deionized water and then combined with 40 μL of 5 N sulfuric acid and 40 μL of a solution prepared by dissolving 250 mg of diphenylcarbazide in 50 mL acetone. The mixture was allowed to react for 30 min in the dark, over which time a pink color developed if Cr(VI) was present above the detection limits (~36 μg/L). The solutions were analyzed on a Shimadzu UV/visible spectrophotometer at λ=540 nm. Standards of Cr(VI) were made from potassium chromate and were prepared for analysis in a manner identical to the experimental samples.

Dissolved concentrations of Cu(II) were measured colorimetrically with 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (also known as Zincon).[8] The procedure called for 0.130 g of Zincon powder to be dissolved in 2 mL of 1 M sodium hydroxide and subsequently diluted to a final volume of 100 mL with DI water, yielding a final Zincon concentration of 0.002 M. The solution was deep red in color and tests showed it to be stable for one week. A 60 μL aliquot of the Zincon solution was added to 940 μL of filtered sample, and the mixture was allowed to react for 40 min in the dark, over which time color developed if Cu(II) was present above the method detection limit (~0.1 mg/L). The color of the sample changed from red to dark brown with increasing dissolved Cu(II) concentrations. The samples were analyzed on a Shimadzu UV/visible spectrophotometer at $\lambda = 600$ nm. Standards of Cu(II) from copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) were prepared for UV/vis analysis in a fashion identical to the experimental samples.

SUPPLEMENTAL RESULTS AND DISCUSSION

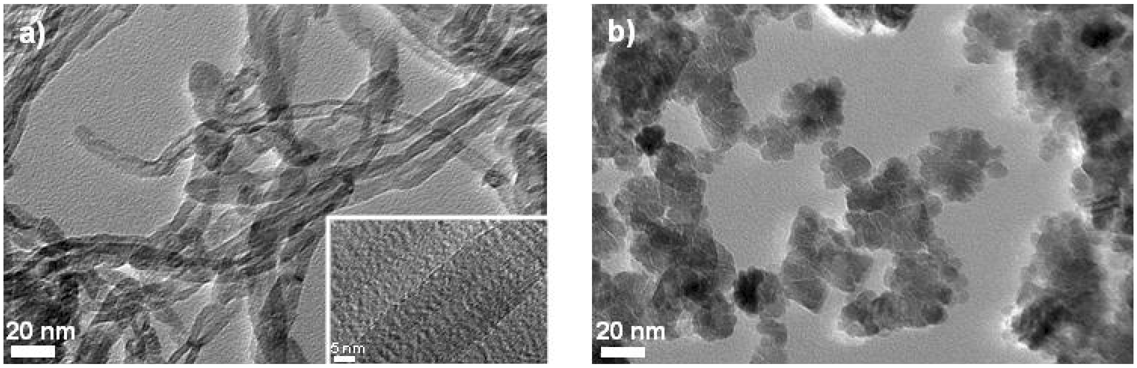

Figure S1: TEM images of (a) oxidized MWCNTs (with inset of a single MWCNT at high magnification and (b) aggregated hematite (α-Fe_2O_3) nanoparticles synthesized from the hydrolysis of ferric nitrate.

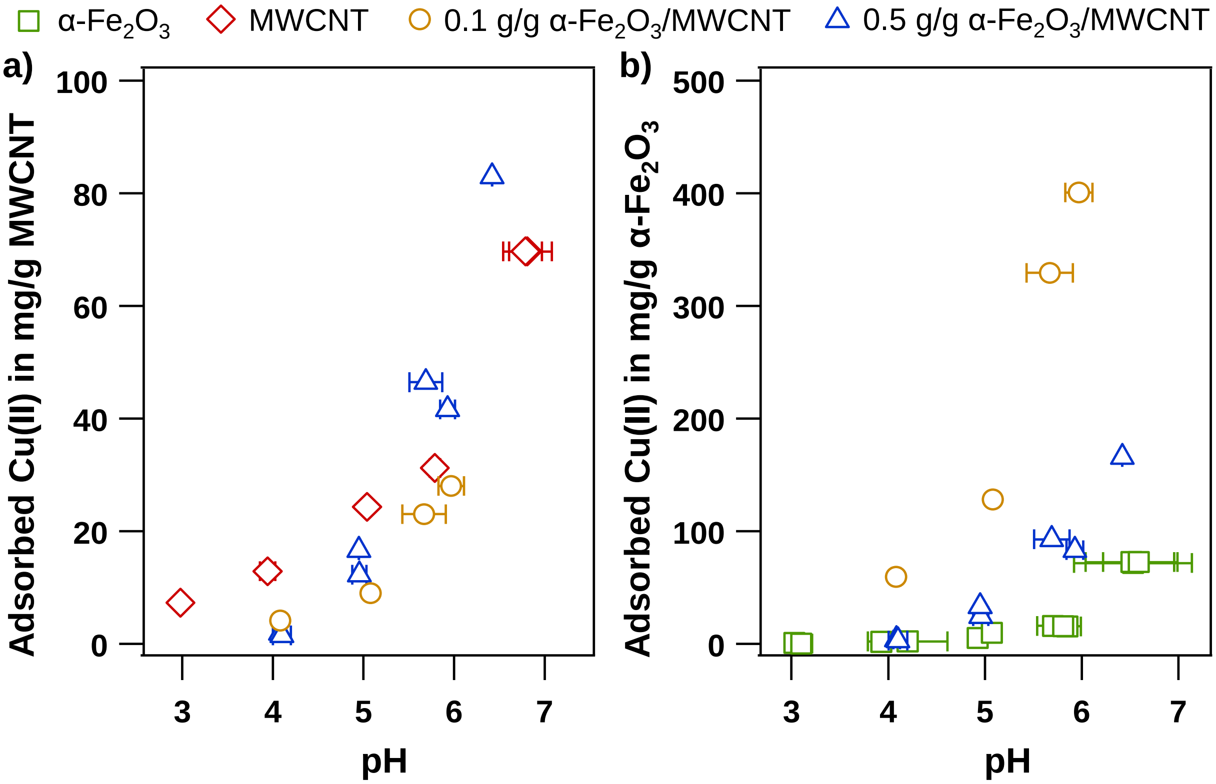

Figure S2. Adsorption of Cu(II) as a function of pH in suspensions of oxidized MWCNTS, a-Fe$_2$O$_3$ nanoparticles and 0.5 g/g a-Fe$_2$O$_3$/MWCNT hybrid nanostructures. Adsorbed concentrations of Cu(II) are presented after normalization by the total mass of (a) MWCNT and (b) hematite in suspension. Experiments were conducted in 25 mM NaCl without pH buffer. pH values represent the average value over the duration of the adsorption experiment based upon measurements at the start and end of reaction. The uncertainties associated with these average pH value represent the standard deviation associated with the initial and final pH value measured in the adsorption experiment. Experiments used an initial Cu(II) concentration of 80 mM (5.1 mg/L), and suspensions concentrations of 0.05 g/L for MWCNT and a-Fe$_2$O$_3$/MWCNT and 0.05 and 0.1 g/L for a-Fe$_2$O$_3$ nanoparticles .

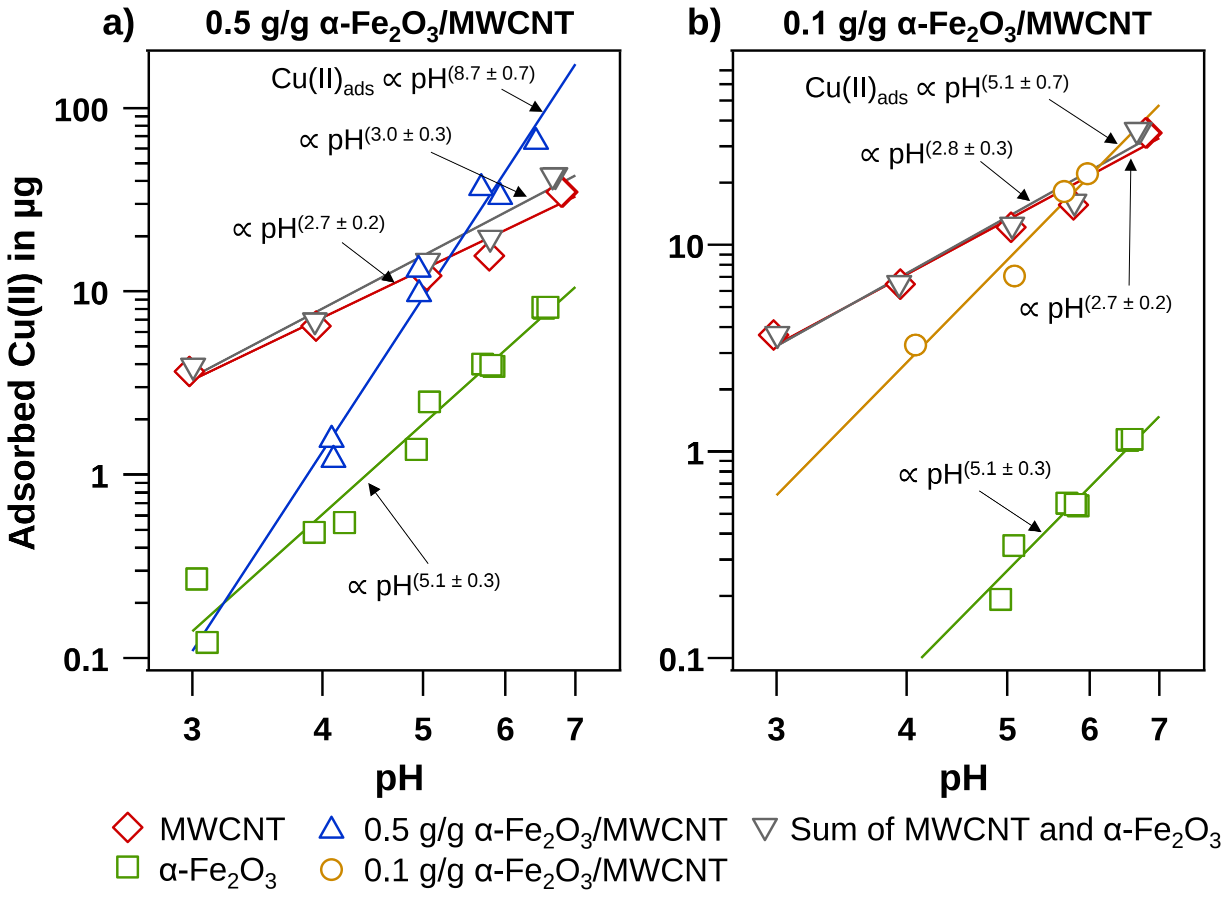

Figure S3. Adsorption of Cu(II) as a function of pH in suspensions of oxidized MWCNTS, α-Fe_2O_3 nanoparticles and α-Fe_2O_3/MWCNT hybrids; also included is the sum of uptake measured independently with MWCNTs and α-Fe_2O_3 for total sorbent masses equal to either (a) 0.5 or (b) 0.1 g/g α-Fe_2O_3/MWCNT. To facilitate comparison between systems, absorbed Cu(II) concentrations are presented on a log-log basis. Experiments were conducted in 25 mM NaCl, and used initial Cu(II) concentration of 80 μM (5.1 mg/L) and suspension concentrations of 0.05 g/L for MWCNT and α-Fe_2O_3/MWCNT (based on total MWCNT mass) and 0.1 g/L for α-Fe_2O_3 nanoparticles.

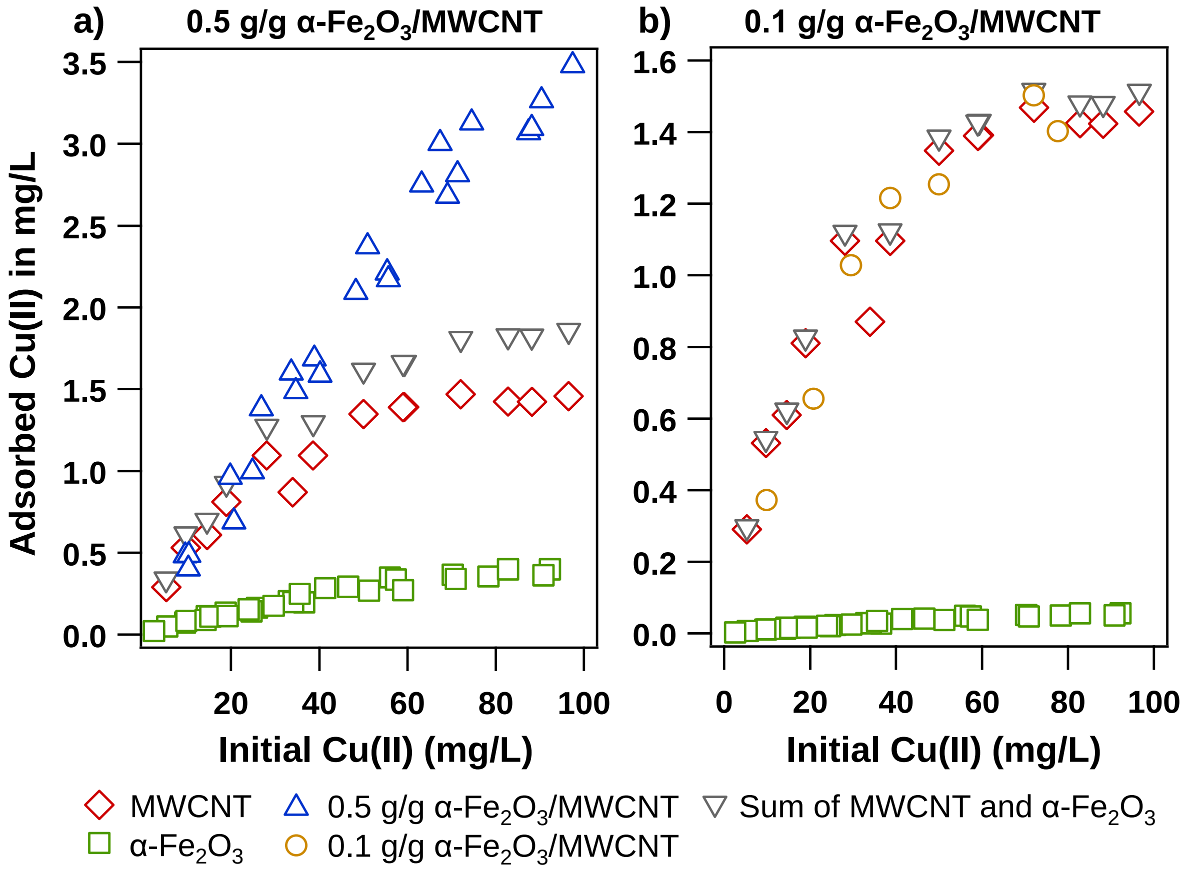

Figure S4. Adsorption of Cu(II) as a function of initial Cu(II) concentration in suspensions of oxidized MWCNTS, α-Fe_2O_3 nanoparticles and α-Fe_2O_3/MWCNT hybrids; also included is the sum of uptake measured independently with MWCNTs and α-Fe_2O_3 for total sorbent masses equal to either (a) 0.5 or (b) 0.1 g/g α-Fe_2O_3/MWCNT. Experiments were conducted in 25 mM NaCl without pH buffer at suspension concentrations of 0.05 g/L for MWCNTs and α-Fe_2O_3 /MWCNTs hybrids and 0.05 and 0.1 g/L for α-Fe_2O_3 nanoparticles.

Table S1. Summary of reported sorbent capacities for Cu(II) and Cr(VI) using various iron and carbon based sorbent materials.

Sorbent	Isotherm Model Fit	Capacity (mg/g)	Temp (°C)	pH	Ref
Cu(II)					
MWCNT	Langmuir	30	20	6	This work
α-Fe_2O_3	Langmuir	25	20	6	This work
0.1 g/g α-Fe_2O_3/MWCNT	Langmuir	30[a]/470[b]	20	6	This work
0.5 g/g α-Fe_2O_3/MWCNT	Langmuir	110[a]/220[b]	20	6	This work
Apricot stone-derived Activated Carbon	NA	24.21	Room	6	9
o-MWCNTs	Langmuir	24.49	Room	5	10
o-MWCNTs	Langmuir	3.3	20	6	11
Goethite NPs	Langmuir	149.25	25	5	12
α-Fe_2O_3 NPs	Langmuir	84.46	25	5	13
α-Fe_2O_3 NPs	Langmuir-Freundlich	21.3	NA	8	12
Magnetic iron oxide MWCNT	Langmuir	19	Room	6	12
Cr(VI)					
MWCNT	Langmuir	ND	20	6	This work
α-Fe_2O_3	Langmuir	90	20	6	This work
0.5 g/g α -Fe_2O_3/MWCNT	Langmuir	ND[a]/60[b]	20	6	This work
Apricot stones activated carbon	Langmuir	7.86	Room	6	14
Activated carbon (Acticarbone)	Langmuir	32.4	25	6	15
SWNTs	Langmuir	20.3	20	4	16
MWNTs	Langmuir	2.48	20	4	16
MnO_2/Fe_3O_4/o-MWCNTs	Langmuir	120	25	6	16
o-MWCNTs	Langmuir	1	20	2	17
o-MWCNTs	Langmuir	1	NA	3	17
Raw CNTs	Langmuir	20.56	NA	7.5	17
Ceria nanoparticles supported on aligned carbon nanotubes	Langmuir	31.55	NA	7	17
α-Fe_2O_3	Langmuir	2.299	Room	8	18
α-Fe_2O_3 NPs	Langmuir	6	25	3	19
Hazelnut shell activated carbon	Langmuir	48.64	20	6	20

[a] Normalized to MWCNT mass; [b] normalized to α-Fe_2O_3 mass; NA = not available; ND = not detected; MWCNT = multi-walled carbon nanotubes; SWCNT = single-walled CNT; o-MWCNT = oxidized MWCNT.

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