Electronic Supplementary Information

Are Engineered Nanomaterials Superior Adsorbents for Removal and Pre-concentration of Heavy Metal Cations from Water?

KunYang[a, b*],Wei Wei[a, b], Long Qi[a, b], WenHao Wu[a, a], QingFeng Jing[a, b], DaoHui Lin[a, b]

[a]Department of Environmental Science, Zhejiang University, Hangzhou 310058, China.

[b]Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Hangzhou 310058, China.

[*]Corresponding author(Kun Yang). Tel.:86-571-88982589; Fax:86-571-88982590;

E-mail: kyang@zju.edu.cn

Material and Methods

Materials. Three multi-walled CNTs, i.e., G-CNTs, P-CNTs, and COOH-CNTs, were purchased from Chengdu Organic Chemistry Co., Ltd. (China) and used as-received. The purity, length, outer diameter and inner diameter of these CNTs are >95%, 10-50 μm, 8-15 nm and 3-5 nm, respectively. Nanoscale metal oxides were purchased from Zhejiang HongSheng Material Technology Co., China, and used as-received. These CNTs and nano-oxides were used in our previous studies with their properties measured (Tables S1 and S2). A description of the characterization of these ENMs and the forms of these nano-oxides is also given in the Supporting Information. $Cu(NO_3)_2 \cdot 3H_2O$ (99.5%), $Pb(NO_3)_2$ (99%), $Zn(NO_3)_2 \cdot 6H_2O$ (98%) and $Cd(NO_3)_2 \cdot 4H_2O$ (99%), purchased from Acros organics, were used to prepare the stock metal ion solutions and diluted for the using in the batch sorption experiments.

Precipitation experiments. Six mL of $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Cd(NO_3)_2$ solutions were mixed with 2 mL of HNO_3 or NaOH solution in 8 mL screw-cap vials. The initial Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} concentrations in the vials were all at 30mg/L. The vials were shaken at 150 rpm for 24 h and the final pH of the suspension was measured by a pH-meter (Mettler Toledo). Then, The vials were centrifuged at 3000*g* for 20 min to withdraw the supernatants for the measurement of the residual heavy metal concentrations by a flame atomic absorption spectrophotometer (AAS-700, Perkin-Elmer, USA)at the wavelength of 324.8 nm for Cu^{2+}, 228.8 nm for Cd^{2+}, 283.3 nm for Pb^{2+}, 213.9 nm for Zn^{2+}, respectively, using a mixture of acetylene at a flow of 2.5 L/min and air at 17 L/min. The percent removals of metal ions were calculated from the difference between the initial metal concentrations and the residual metal concentrations.

Sorption experiments. Six mL of $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Cd(NO_3)_2$ solutions were mixed with 2 mL of HNO_3 or NaOH solutions in 8 mL vials. The pH of the mixtures was measured as the initial pH. Then, 10, 50 or 200 mg of CNTs or 5, 25,200 or 500 mg nano-oxides were added into the screw-cap vials. The initial Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} concentrations in the vials were 30or 200 mg/L. The vials were shaken at 150 rpm for 24 h (the previous experiments showed that the equilibrium was reached within 120 min) and the final pH of the suspension was also measured. Then, the vials were centrifuged at 3000*g* for 20 min to withdraw the supernatants for the measurement of the residual heavy metal concentrations by the atomic absorption spectrophotometer. The percent removal values of metal ions were calculated directly from the difference between the initial metal concentrations and the residual metal concentrations.

Description of the forms of Nano-oxides: The TiO_2 group is composed of rutile, anatase, and brookite. The minerals rutile and brookite as well as anatase all have the same chemistry, TiO_2, but they have different structures. Anatase is a polymorph with two other minerals. At higher temperatures, about 915 degrees Celsius, Anatase will automatically revert to the rutile structure. Rutile is the more common and the more well-known mineral of the three, while anatase is the rarest. Anatase shares many of the same or nearly the same properties as rutile such as luster, hardness and density. However, due to structural differences, Anatase and rutile differ slightly in crystal habit and more distinctly in cleavage. More information of TiO_2 can be obtained on http://ruby.colorado.edu/~smyth/min/tio2.html and http://mineral.galleries.com/minerals/oxides/anatase/anatase.htm. Al_2O_3 exists in several forms, the principal being gamma- alumina and alpha-alumina (or corundum). Alpha-Al_2O_3 is the pure form obtained by calcination at high temperature. Beta-Al_2O_3, which contains a small amount of alkali metal oxide, is the compound Na_2O-Al_2O_3.Gamma-Al_2O_3 is stable to about 1000°C and contains traces of water or hydroxyl ions. According to the description of the supplier (http://www.mrnm.com.cn/product_2.htm), porous SiO_2 nano-oxide was called as P-form SiO_2, while spherical SiO_2 nano-oxide was called as S-form SiO_2.

Characterization of Sorbents: The C, Hand N contents of dry-weight-based nano-oxides were determined by combusting samples at 980 °C with oxygen using a Perkin-Elmer 2400 CHN Elemental Analyzer (Sheton, CT). Surface areas of all sorbents were calculated from N_2 sorption isotherms by the multi-point BET method. N_2 sorption was conducted at 77 K using a NOVA 1000e instrument (Quantachrome). All samples were out-gassed at 105 °C for 16 h before N_2 adsorption and elemental analysis. Zeta potential values were measured with a Zeta sizer nano ZS (Malvern Instruments, UK) at 25°C, using suspensions containing 50 mg/L of solids in solution. Measurements were performed after 24 h shaking of the suspensions for which the pH was pre-adjusted by NaOH and HCl. The Zeta potential values of a given ENMs in a range of pH from 2.0 to 12.0 were used to identify the pH_{zpc}. Surface acidic group (i.e., carboxyl, hydroxyl and lactonic groups) contents and surface oxygen/carbon atomic percents of CNTs were characterized by Boehm titration method (Boehm, *Carbon***1994**, 32, 759-769) and X-ray photoelectron spectroscopy (XPS) technique (Cho,*et al.Environ. Sci. Technol.* **2008**, 42, 2899-2905), respectively. These ENMs were from the same batch as the one used in our previous studies(Wu,*et al.Environ. Sci. Technol.* **2012**, 46 (10), 5446–5454.; Yang, *et al.Langmuir***2009**,25, 3571-3576).

Table S1. Selected Properties of Carbon Nanotubes[a]

CNTs	Surface atomic percent (XPS)		Surface acidic group content (mmol/g)				pH_{zpc}	pH4.0[b]	pH6.0[b]	S_{BET} (m^2/g)
	C%	O%	Hydroxyl groups	Carboxyl groups	Lactonic groups	Total acidic groups				
G-CNTs	100	ND[c]	0.009	0.012	ND	0.021	6.2	6.2	6.4	114
P-CNTs	98.1	1.9	ND	0.018	0.010	0.028	5.7	6.5	6.6	127
C-CNTs	94.0	6.0	0.079	0.138	0.038	0.255	3.0	6.5	6.8	161

[a]Data cited from Wu,*et al. Environ. Sci. Technol.* **2012,**46 (10), 5446–5454.

[b]The final pH values of 8 mL water at initial pH of 4.0 or 6.0 after mixed with 200mg ENMs.

Table S2.Selected Properties ofNano-oxides

Nano-oxides	**diameter[a] (nm)**	**Purity[a] (%)**	N%	C%	H%	S_{BET} **(m²/g)**	**pH$_{zpc}$**	**pH4.0[b]**	**pH6.0[b]**	**Notation[a]**
nano-SP1-SiO_2	20±5	≥99.5	0.026	0.041	2.402	570	0.35	4.2	5.3	P form, Surface Hydroxyl Content >45%
nano-DP1-SiO_2	20±5	≥98.0	0.007	0.861	2.116	675	0.62	3.8	4.7	P form, Surface Hydroxyl Content >15%
nano-SS1-SiO_2	30±5	≥99.5	0.013	0.043	1.408	191	0.06	6.1	6.2	S form, Surface Hydroxyl Content >19%
nano-DS1-SiO_2	30±5	≥98.0	0.087	3.005	1.386	221	0.50	6.0	6.2	S form, Surface Hydroxyl Content >10%
nano-TiO_2	50±5	>99.0	0.237	0.034	1.367	324	5.90	6.0	6.7	Anatase form
nano-α-Al_2O_3	150±5	≥99.9	0.020	0.019	0.062	4.73	5.50	6.1	6.8	α form
nano-γ-Al_2O_3	60±5	≥99.9	0.116	0.186	1.210	208	7.10	5.8	6.1	γ form

[a] Data cited from the description of the supplier (http://www.mrnm.com.cn/product_2.htm).

[b] The final pH values of 8 mL water at initial pH of 4.0 or 6.0 after mixed with 200mg ENMs.

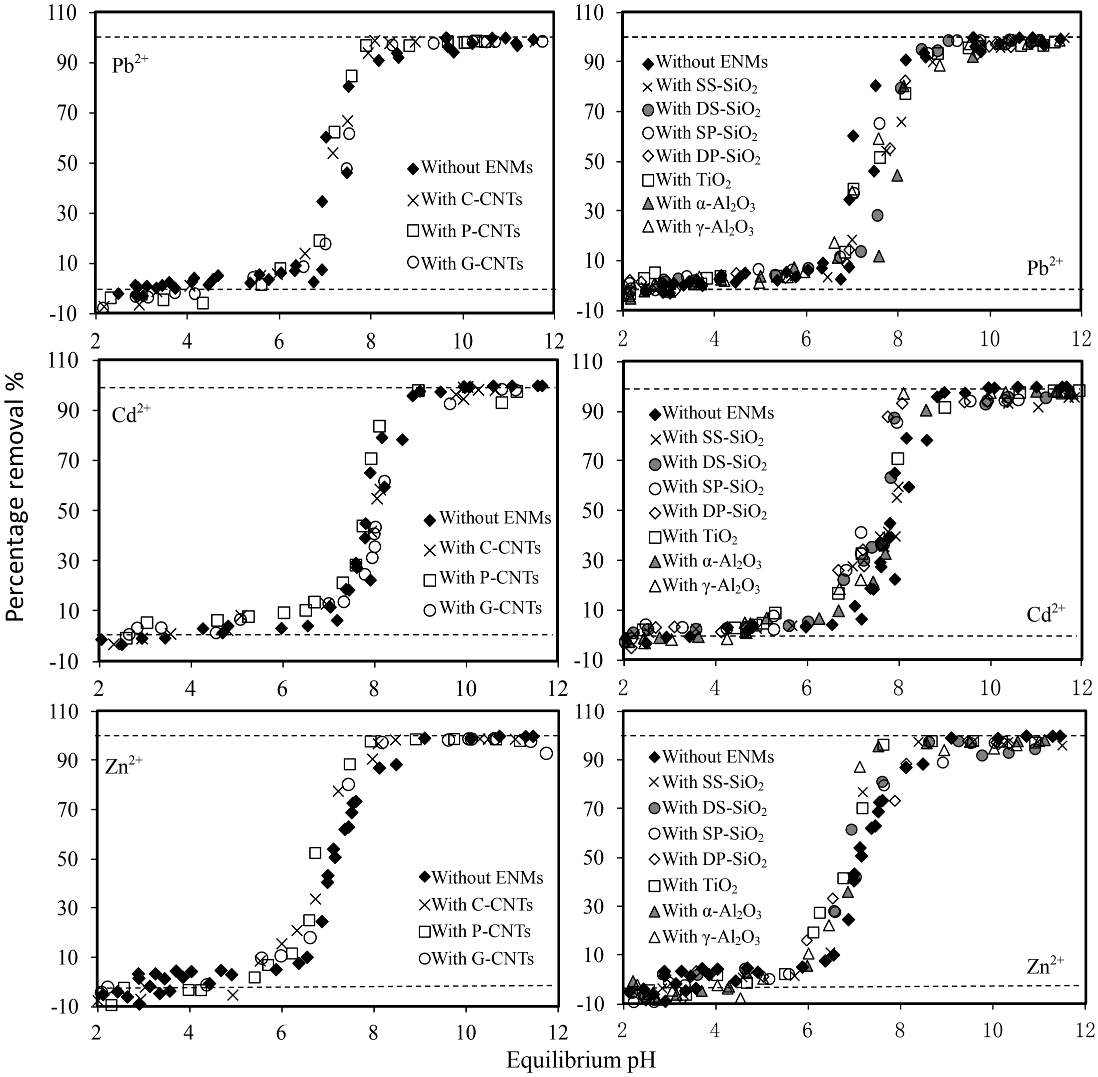

Figure S1. The pH-dependent percentage removal curves of 30mg/L Pb^{2+}, Cd^{2+} and Zn^{2+} in the presence of 200mg CNTs (i.e., C-CNTs, P-CNTs, and G-CNTs) or 200 mg nano-oxides including nano-SiO_2 (i.e., SS-SiO_2, DS-SiO_2, SP-SiO_2, and DP-SiO_2), nano-TiO_2 and nano-Al_2O_3 (i.e., α-Al_2O_3 andγ-Al_2O_3) in 8 mL solution. The pH-dependent percentage removal curves of Pb^{2+}, Cd^{2+} and Zn^{2+} without engineered nanomaterials (ENMs), i.e., the precipitation curve, is also plotted as a reference.

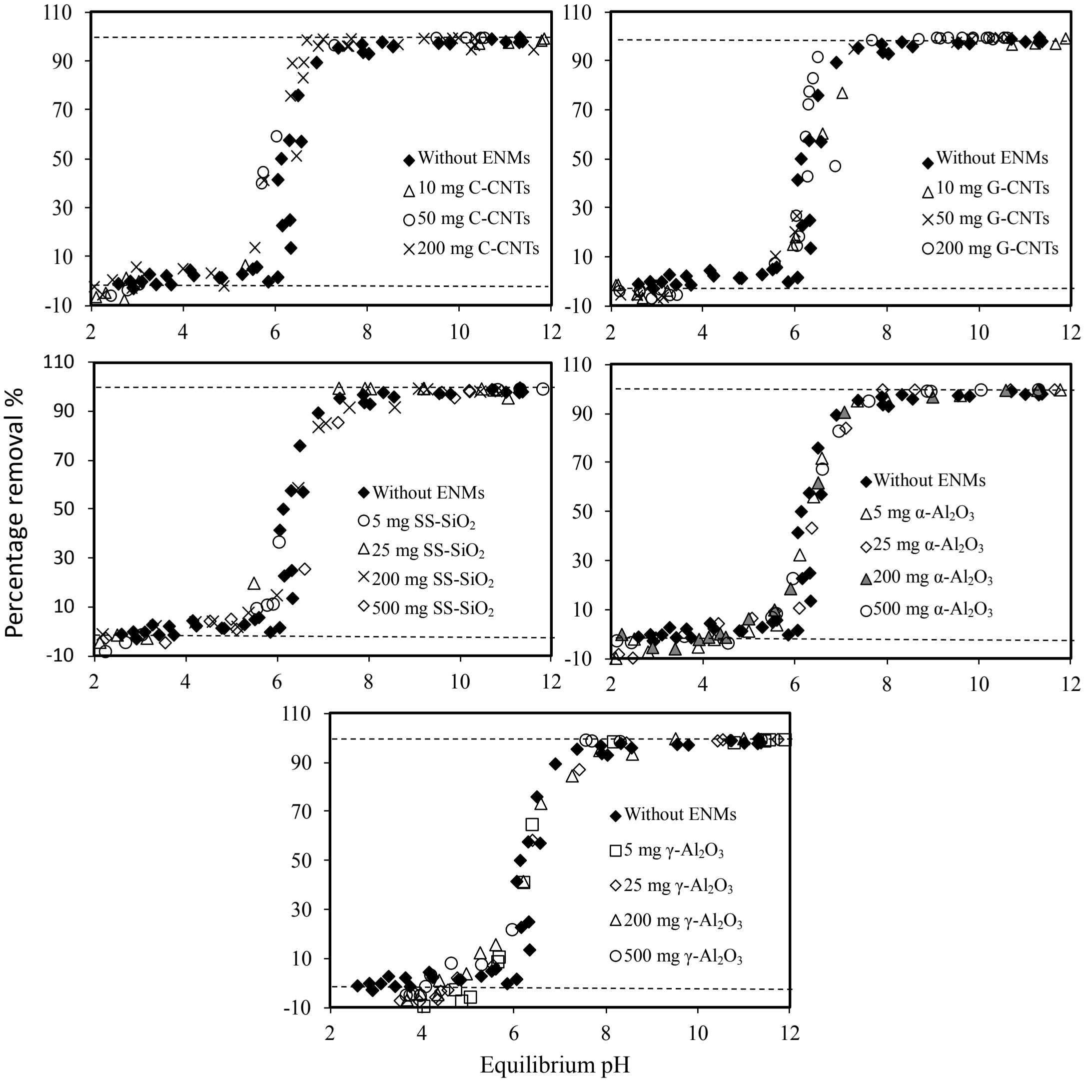

Figure S2. The pH-dependent percentage removal curves of Cu^{2+} (30 mg/L) with variation of the loading of CNTs or nano-oxides in 8 mL solution. The precipitation curve of Cu^{2+} (i.e., without ENMs) is also plotted as a reference.

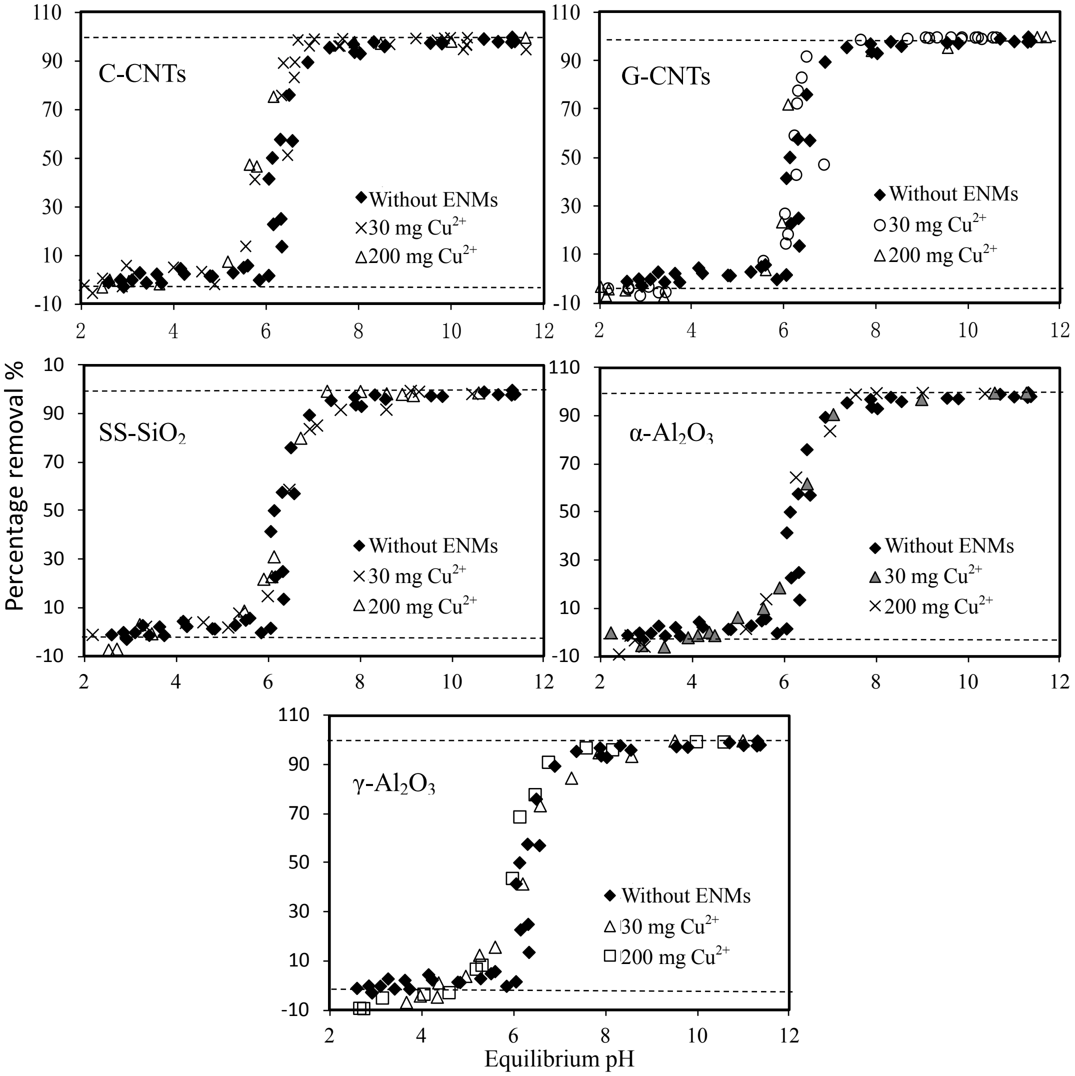

Figure S3. The pH-dependent percentage removal curves of Cu^{2+} at 30 mg/L and 200 mg/L in the presence of CNTs or nano-oxides in 8 mL solution. The precipitation curve of Cu^{2+} (i.e., without ENMs) is also plotted as a reference.

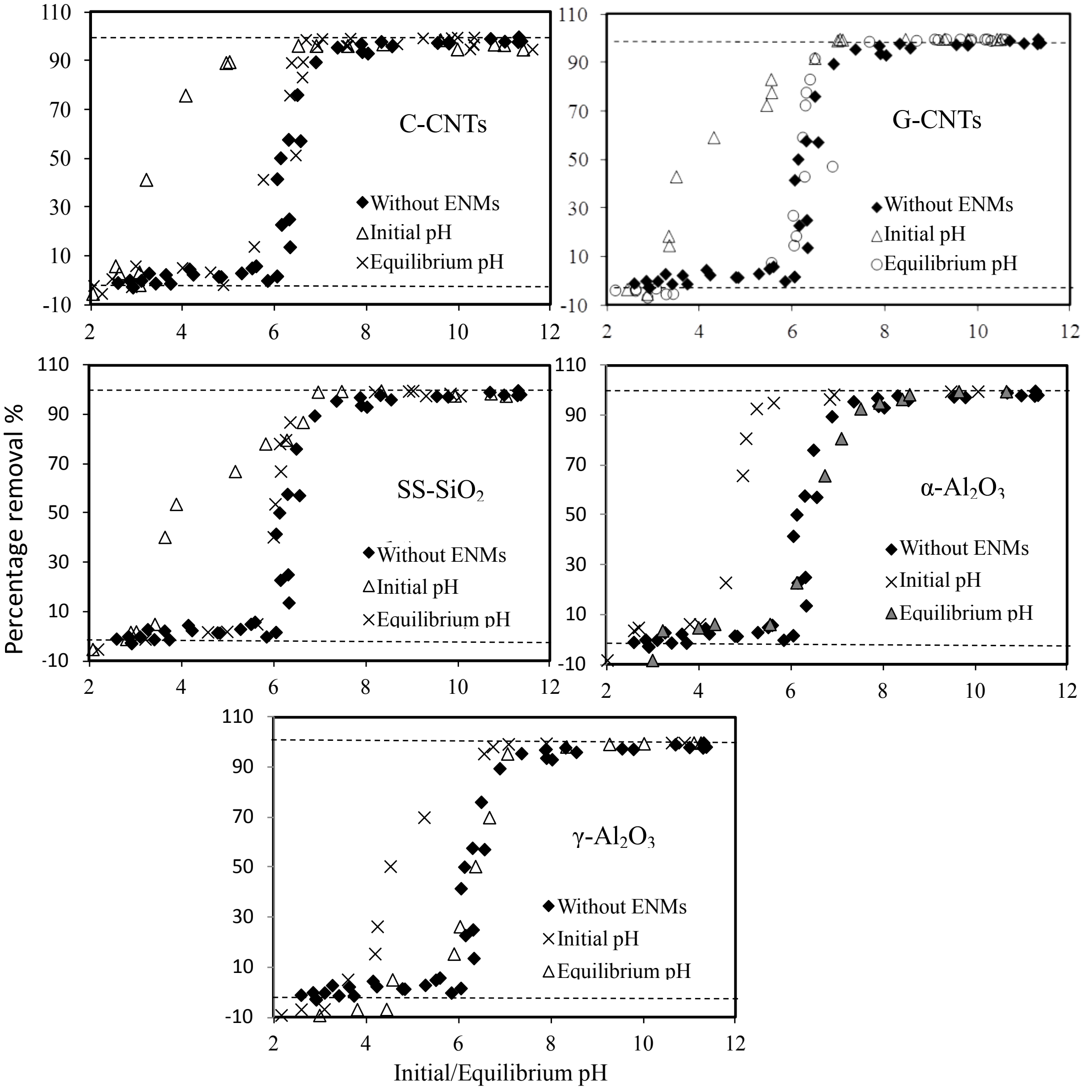

Figure S4. Percentage removal of Cu^{2+} (30 mg/L) versus initial/equilibrium pH in the presence of CNTs or nano-oxides in 8 mL solution. The precipitation curve of Cu^{2+} (i.e., without ENMs) is also plotted as a reference.