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[Supporting Information]

Engineered Superparamagnetic Nanomaterials for Arsenic (V) and Chromium (VI) Sorption and Separation: Quantifying the Role of Organic Surface Coatings

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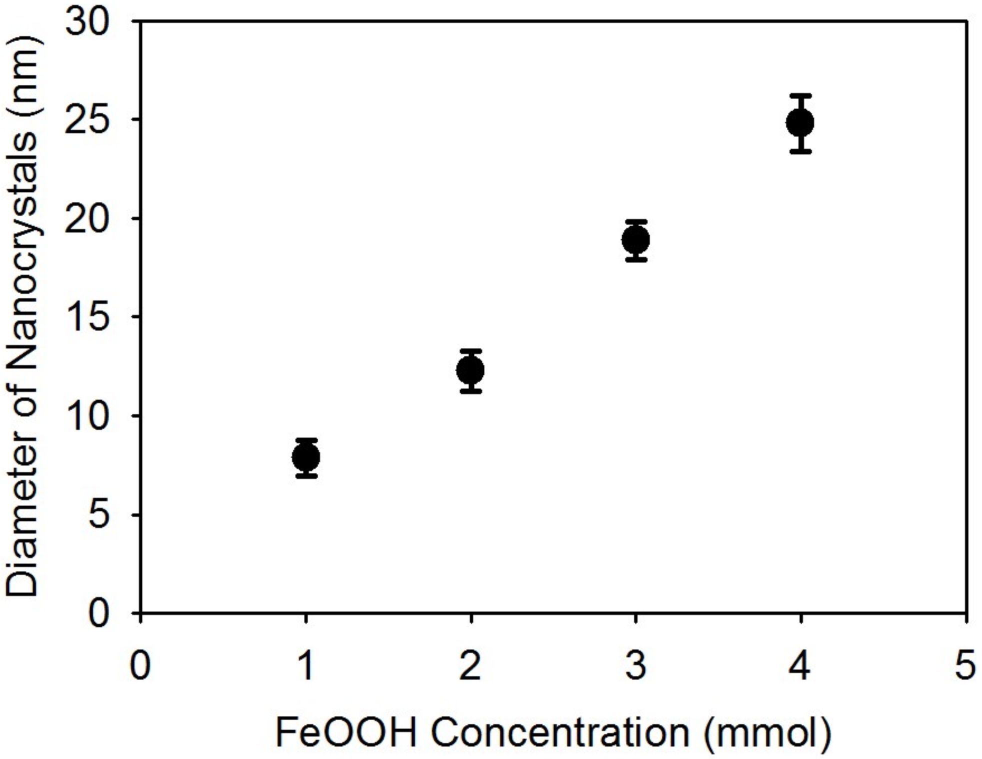

Figure S1. The diameter of synthesized Fe_3O_4 NCs as a function of oxyhydroxide (FeOOH) concentration in 5 g of 1-octadecene as a solvent with the ratio of FeOOH/OA fixed to 1/3.

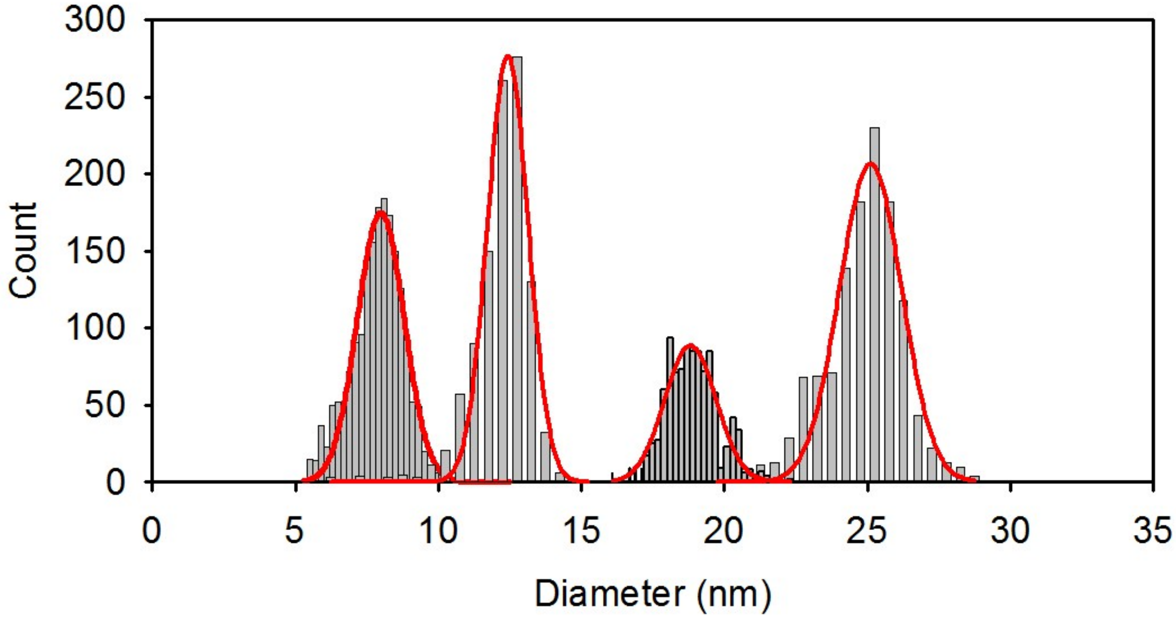

Figure S2. Histograms of the size distribution of synthesized Fe_3O_4 NCs. The average diameter and their standard deviations were 7.9 ± 0.9, 12.3 ± 1.0, 18.7 ± 1.0, and 24.8 ± 1.4 nm. Size and size distribution was analyzed using Image Pro Plus 6.0 with over a thousand NCs counted.

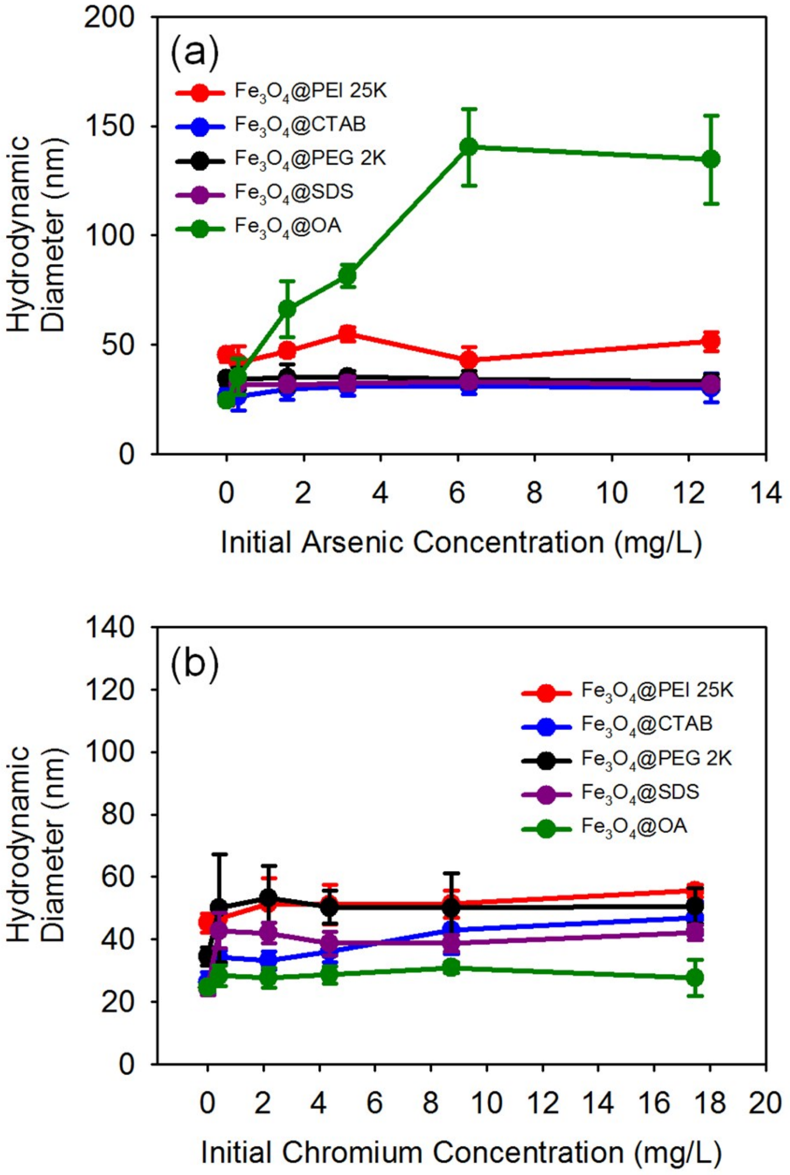

Figure S3. Hydrodynamic diameter of functionalized (PEI (red), CTAB (blue), PEG (black), SDS (purple) and OA (green)) Fe_3O_4 NCs after (a) As(V) and (b) Cr(VI) sorption.

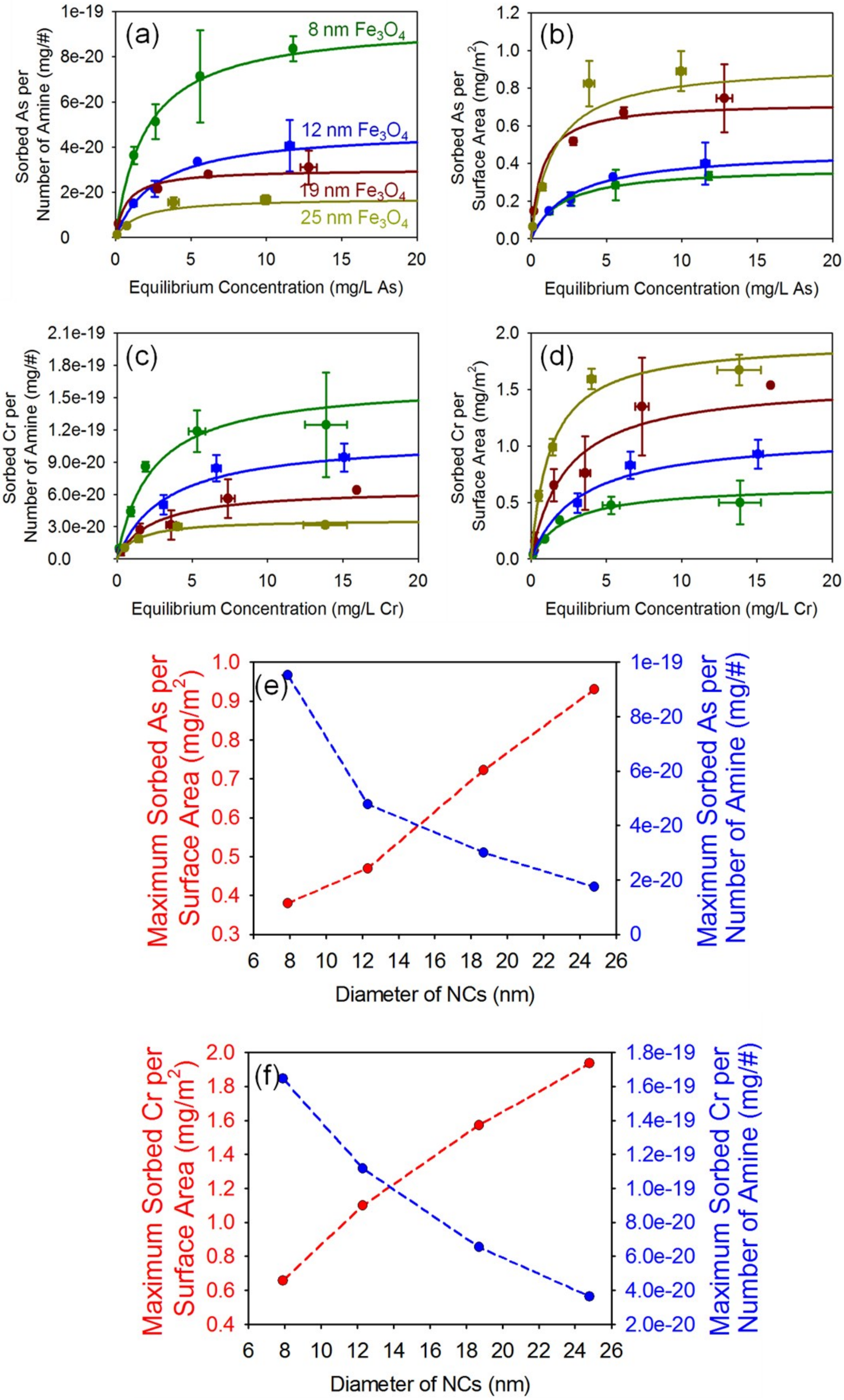

Figure S4. (a-d) Normalized sorption isotherm by number of amine or by surface area of NC as a function of size of NCs (e) Maximum sorbed As per surface area and per number of amine group as a function of size of NCs. (f) Maximum sorbed Cr per surface area and per number of amine group as a function of size of NCs.

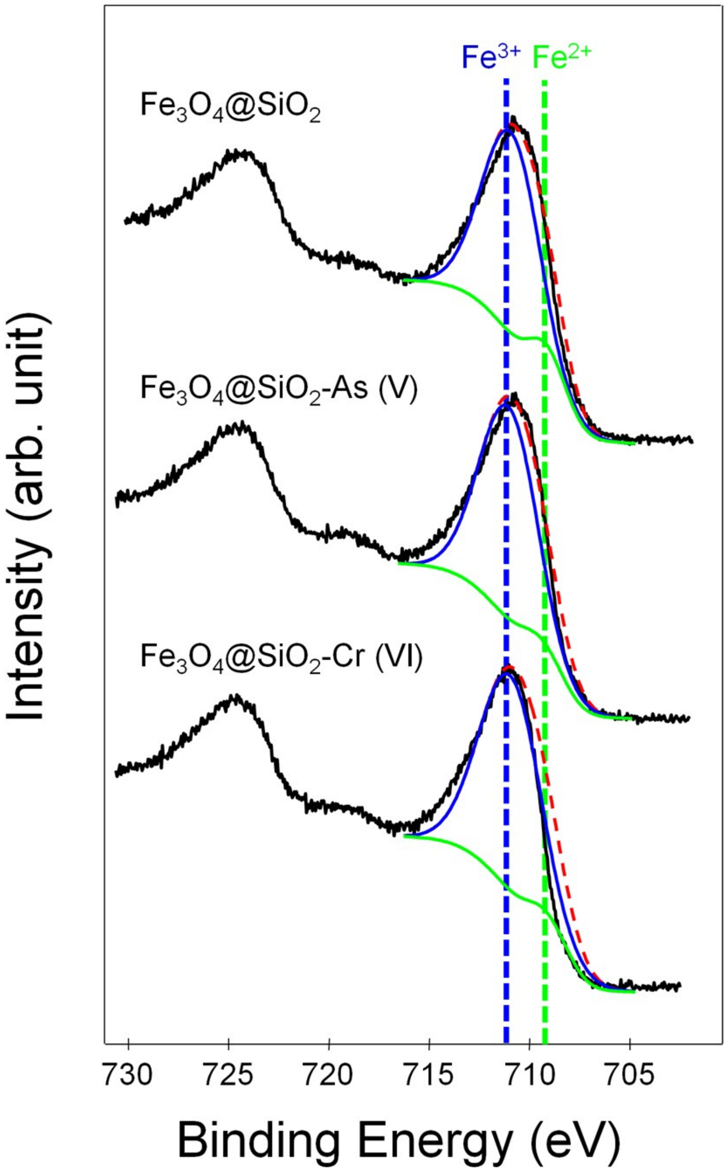

Figure S5. The oxidation states of iron (Fe) of silica coated 8nm iron oxide NCs (Fe_3O_4@SiO_2) before sorption and after As(V) and Cr(VI) sorption were explored using XPS by measuring 2P iron.

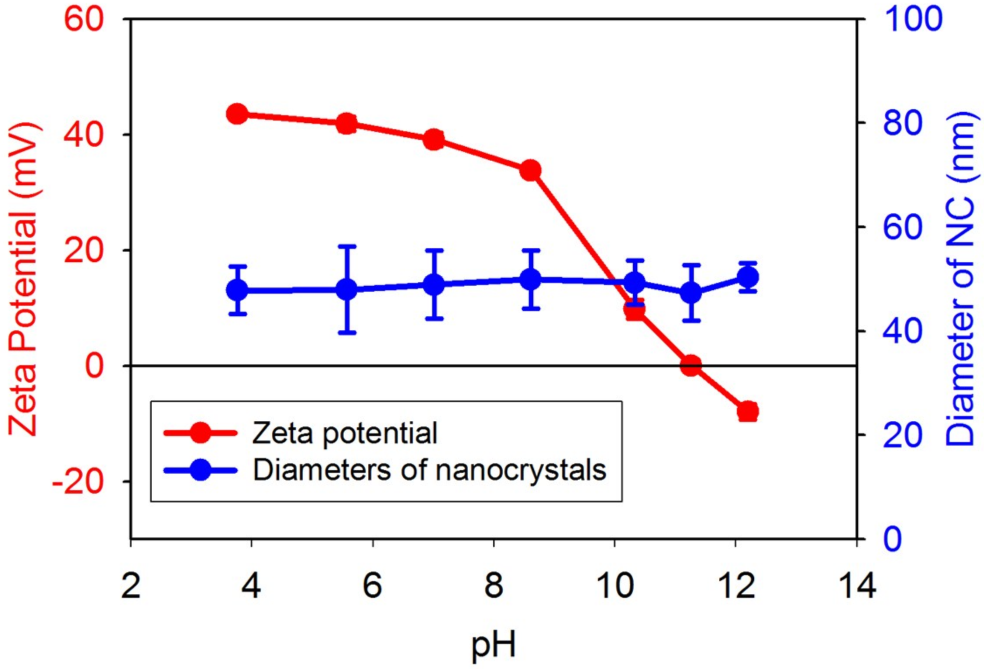

Figure S6. Hydrodynamic diameter (blue) and zeta potential (red) of PEI coated 12 nm Fe_3O_4 NCs as a function of pH.

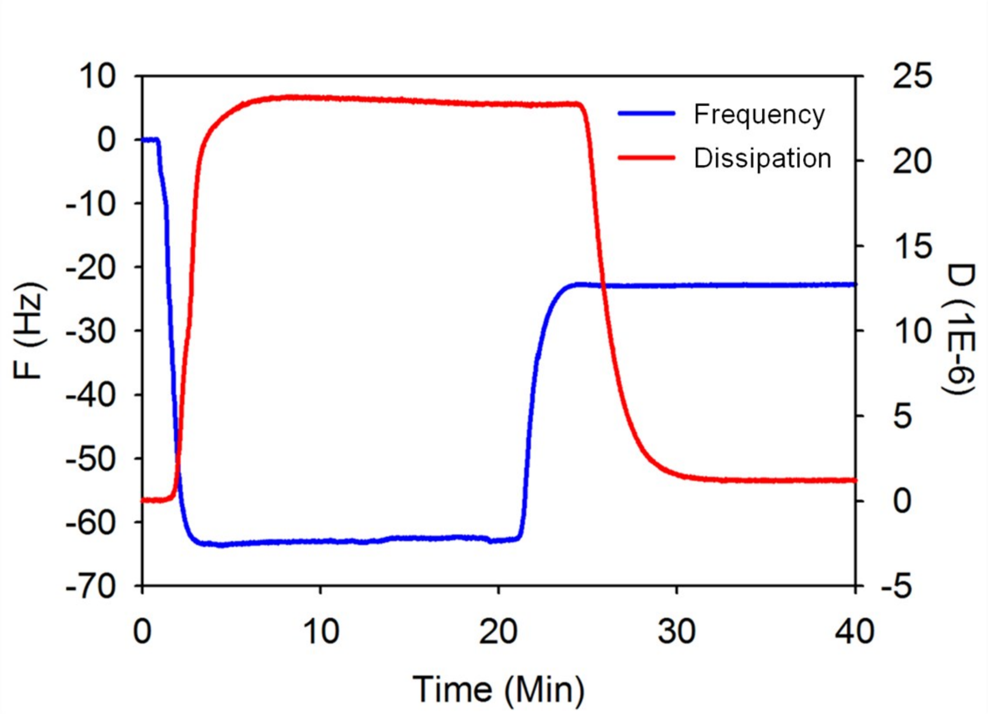

Figure S7. Time dependent frequency (blue) and dissipation (red) responses for PEI coating on Q-sensor with overtone (n = 3). DI stabilized Q-sensor was coated by PEI solution (1 min to 3 min) and further stabilized for 20 min, and then PEI coated Q-sensor was restabilized with DI water at pH7 (22 min to 40 min).

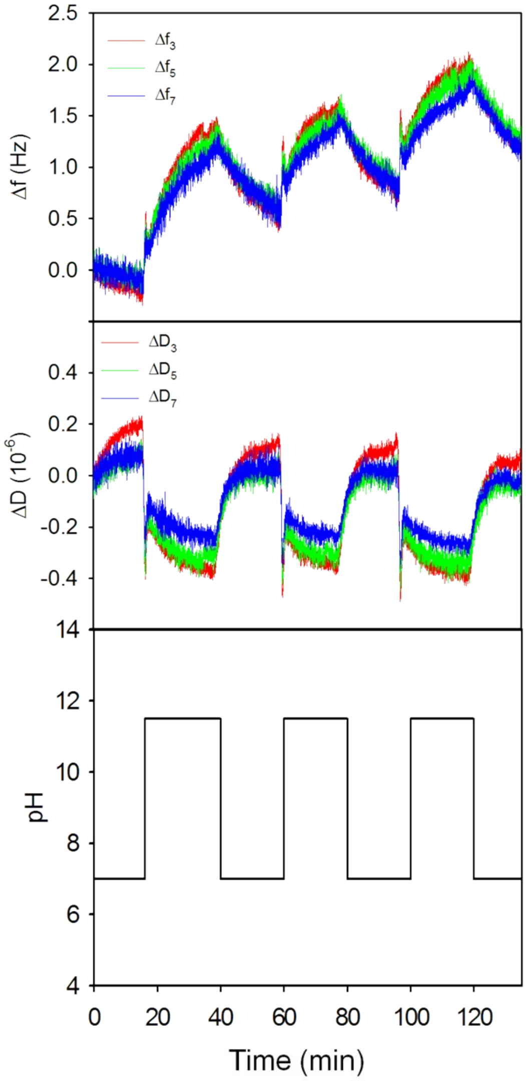

Figure S8. Frequency and dissipation shifts of PEI coated sensors as a function of pH between 7 and 11.5 with the overtone n = 3 (red), 5 (green) and 7 (blue). Low frequency (high dissipation) at pH 7 indicates that water molecules adsorbed with the charged functional groups of PEI and adsorbed water molecules are released via the charge neutralization of PEI functional groups at pH 11.5 (point of zero charge).

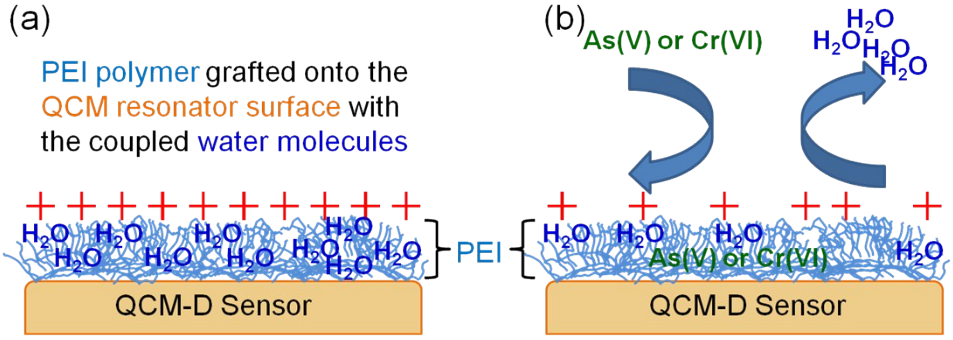

Figure S9. Conceptual depiction of arsenate and chromate binding on PEI grafted sensor. (a) Water molecules adsorbed with positively charged functional groups of PEI grafted sensor. (b) The positively charged PEI functional group is neutralized via anion contaminants (As(V) and Cr(VI)) sorption and then adsorbed water molecules are released from the sensor surface. As(V) and Cr(VI) speciation are dependent on solution pH.

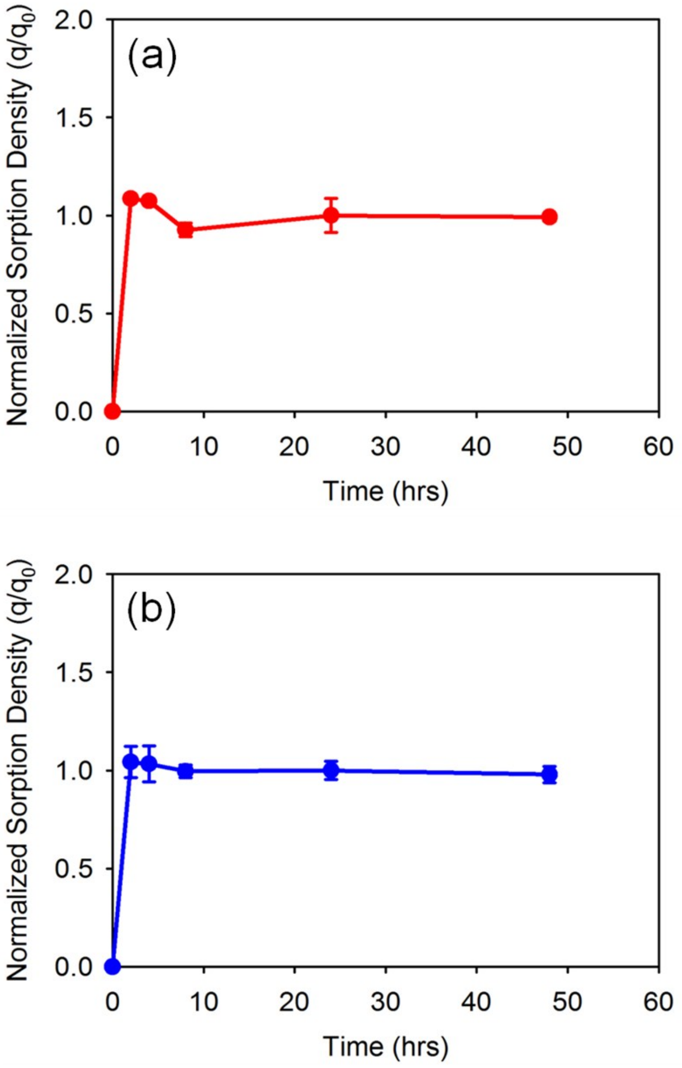

Figure S10. Time dependent normalized sorption density for 1 mM (a) arsenate (red) and (b) chromate (blue) using PEI coated 12 nm Fe_3O_4 NCs at pH7.

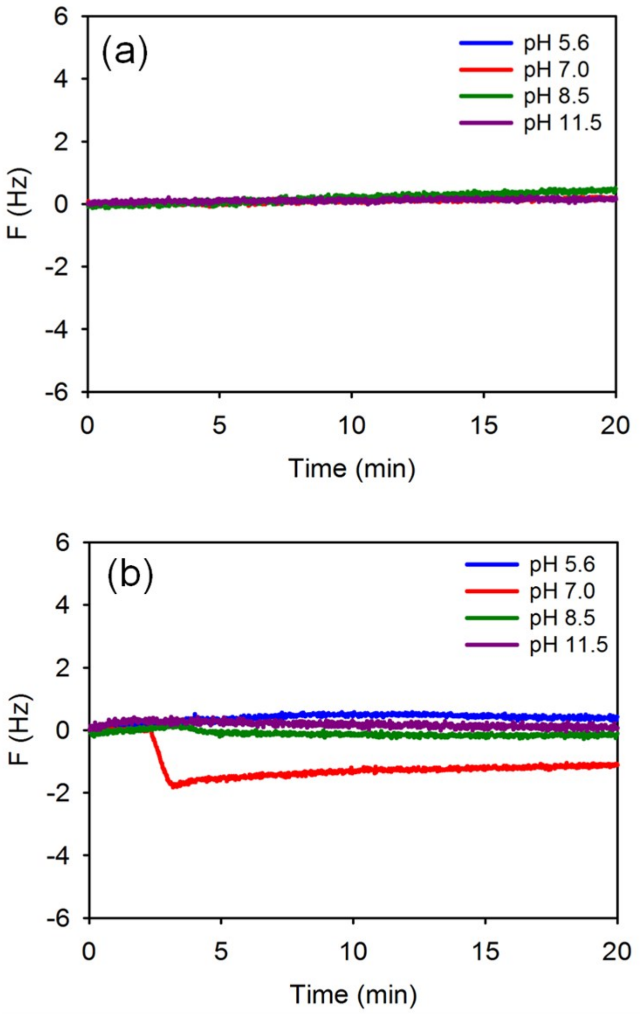

Figure S11. The frequency responses (overtone is 3) of (a) arsenate and (b) chromate adsorbed PEI coated Q-sensor after applying a pH 11.5 solution.

Table S1. Organic loading of surface of NC

Nanocrystals	**Molecular Weight of Coating Material**	**Total Organic Carbon (ppm of carbon)**[α]	**Number of carbon per nanocrystal**	**Number of amine groups per carbon**[β, γ]	**Number of amine group per nanocrystal**	**Number of molecules per nanocrystal**
8 nm Fe_3O_4@CATB	364.45	21.7 ± 4.5	21,172	0.037[α]	784	784
12 nm Fe_3O_4@CATB		34.3 ± 3.5	126,198	0.037	4,674	4,674
19 nm Fe_3O_4@CATB		55.2 ± 10.8	713,203	0.037	26,415	26,415
25 nm Fe_3O_4@CATB		92.0 ± 11.3	2,771,424	0.037	102,645	102,645
12 nm Fe_3O_4@PEI	25000	64.5 ± 0.5	236,989	0.5[β]	118,495	204

α. Total organic carbon (TOC) for organic coated iron oxide NCs (50 ppm Fe)

β. Number of amine groups per carbon of CTAB functionalized NCs was calculated based on an assumption of full CTAB surfactant encapsulation.

γ. Number of amine groups per carbon of 12 nm Fe_3O_4@PEI was obtained by considering repeat unit of multi branched PEI structure (Mw = 25000).

Table S2. Maximum sorption capacity per surface area of NC and per number of amine

Nanocrystals	**Maximum As sorption capacity per surface area of NC (mg/m^2)**	**Maximum As sorption capacity per number of amine**	**Maximum Cr sorption capacity per surface area of NC (mg/m^2)**	**Maximum Cr sorption capacity per number of amine**
8 nm Fe_3O_4@CATB	0.38	9.51×10^{-20}	0.66	1.65×10^{-19}
12 nm Fe_3O_4@CATB	0.47	4.78×10^{-20}	1.10	1.12×10^{-19}
19 nm Fe_3O_4@CATB	0.72	3.00×10^{-20}	1.57	6.54×10^{-20}
25 nm Fe_3O_4@CATB	0.93	1.75×10^{-20}	1.94	3.64×10^{-20}