Supporting information

Functional, mesoporous, superparamagnetic colloidal sorbent for efficient removal of toxic metal

Experimental details:

Materials and Reagents. [3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPS), tetraethoxysilane (TEOS), 3-mercaptopropyltrimethoxysilane (MPS), tetramethylamonium hydroxide 25 wt% in methanol (TMAH), ethylenediaminetetraaceticdianhydride (EDTADA) all were purchased from Sigma-Aldrich and used as received. Cetyltrimethylammonium bromide (CTAB) was purchased from Alfa Aesar.

Silane coating of γ-Fe_2O_3 nanoparticles: Purified toluene solution (10 mL) of γ-Fe_2O_3 was mixed with 5 mL toluene solution of AEAPS (0.01M), followed by the addition of 5 mL of methanol solution of TMAH (0.01M) under stirring and heated to 80 ^{0}C for 10 to 15 minutes for complete precipitation. Then the precipitate was washed once with toluene and twice with ethanol. Then the precipitate was dissolved in 10 mL water with the addition of 200 µL 0.1 M acetic acid solution.

Synthesis of amine functionalized MMS and MMS-SH: 10 mL of above silica coated γ-Fe_2O_3 was diluted to 45 mL by distilled water and then 5 mL of CTAB (0.15 M) solution was added to this solution under stirring condition. After 5-10 minutes 1.5 mL 25 % ammonia solution was added to this solution. Next, 10 mL ethanolic solution of TEOS (0.3 mL TEOS dissolved in 10 mL ethanol) was added to above solution. After 15 minutes AEAPS (to prepare MMS) or MPS (to prepare MMS-SH) was added as ethanolic solution (50 µL AEAPS or MPS dissolved in 2.5 mL ethanol) all at a time and stirring was continued for 3 hrs. Particles were precipitated by adding ethanol and washed three times with ethanol and three times with water. In order to remove CTAB, the particles were dispersed in 50 mL ethanolic solution of NH_4NO_3 and heated to 70 ^{0}C for 1 hrs under stirring condition. Particles were then collected by centrifuge. This CTAB removal process was repeated twice. Finally, particles were collected as solids and preserved for further use.

Synthesis of MMS-EDTA: The amine functionalized MMS particles were dissolves in 20 mL DMF and then EDTADA solution (100 mg EDTADA dissolved in 20 mL DMF) was added to this solution under stirring condition and stirring was continued for 6 hrs. Then the particles were collected by centrifuge and washed three times with DMF and three times with water then the particles were dried under vacuum for further use.

Quantification of EDTA in MMS-EDTA: The amount of EDTA present in MMS-EDTA was quantified using conventional complexomeric titration. 5 mg of MMS-EDTA was dispersed in 5 mL water. Next, 1 mL phosphate buffer solution of pH 10 and 2 drops of erichrome black T indicator solution was added to this. This solution was titrated against 0.01 M $CaCl_2$ solution. The concentration of EDTA present in the MMS-EDTA was calculated as $0.8x10^{-3}$ mole/g.

Quantification of thiol in MMS-SH: The amount of thiol present in MMS-SH was quantified using spectrophotmetric method using 5,5’-dithiobis-2-nitrobenzoic acid (DTNB) as the reagent. DTNB reacts with thiol forming a characteristic absorbance peak at 410 nm and the absorbance at 410 nm was used for quantitative estimation of thiols. First, a standard curve was prepared for known concentration of thiols with their respective absorbance after reaction with DTNB. Next, DTNB was reacted with dispersed MMS-SH and respective absorbance at 410 nm was used to determine the amount of thiol. The thiol estimated was ~$2.4x10^{-4}$ mole/g of MMS-SH.

Metal removal study: The removal of Cd and Pb were performed using MMS-EDTA and removal experiment of Hg and As were performed using MMS-SH. Typically, 10 mg solid MMS-EDTA or MMS-SH was added to 10 mL solution of heavy metal salt of varied concentration. Whenever necessary the solution pH was adjusted between 7-8, using the aqueous solution of NaOH. The solution was magnetically stirred for overnight and then particles were separated from solution by bar magnet and finally the supernatant was used for ICP-AES measurement to estimate the metal present.

Recycling experiment for MMS-EDTA: In recycling experiment at first 10 mg of MMS-EDTA were added to 10 mL of Pb solution (20 mg/L) and stirred for overnight. Then the materials were separated by magnet and regenerated by mixing with 10 mL of 0.01 (M) K_2EDTA solution followed by the stirring for two hours. Next, particles were separated by magnet and washed two times with water and dried under vacuum for further separation experiment.

Recycling experiment for MMS-SH: For recycling experiment of MMS-SH at first 10 mg of MMS-SH were added to 10 mL of Hg solution (20 mg/L) and stirred for 5 hrs. Then the particles were separated by magnet and regenerated by mixing with 5 mL of 0.01 (N) HCl solution followed by the stirring 15 mints. Next, the particles were separated by magnet and washed three times with water. After that the particles were dried in vacuum and used for another adsorption experiment.

Instrumentation:

UV-vis spectra were measured on a Shimadzu UV-2550 spectrometer using a quartz cell with 1 cm path length. FEI Technai G2 transmission electron microscope was used for Transmission electron microscopic (TEM) image of sample. Nicolet 6700 FT-IR (thermo scientific) was used for Fourier transform infrared (FTIR) spectra of sample using KBr pallet. Quantachrome Autosorb-1C was used for BET surface area measurement of the sample and pore size distributions were analyzed by Non Local Density Functional Theory (NLDFT). Amount of metal ion before and after separation by functionalized mesoporous silica were estimated by Optima 2100DV inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer). Magnetic measurement was performed using a Cryogenic Physical Property Measurement System (PPMS).

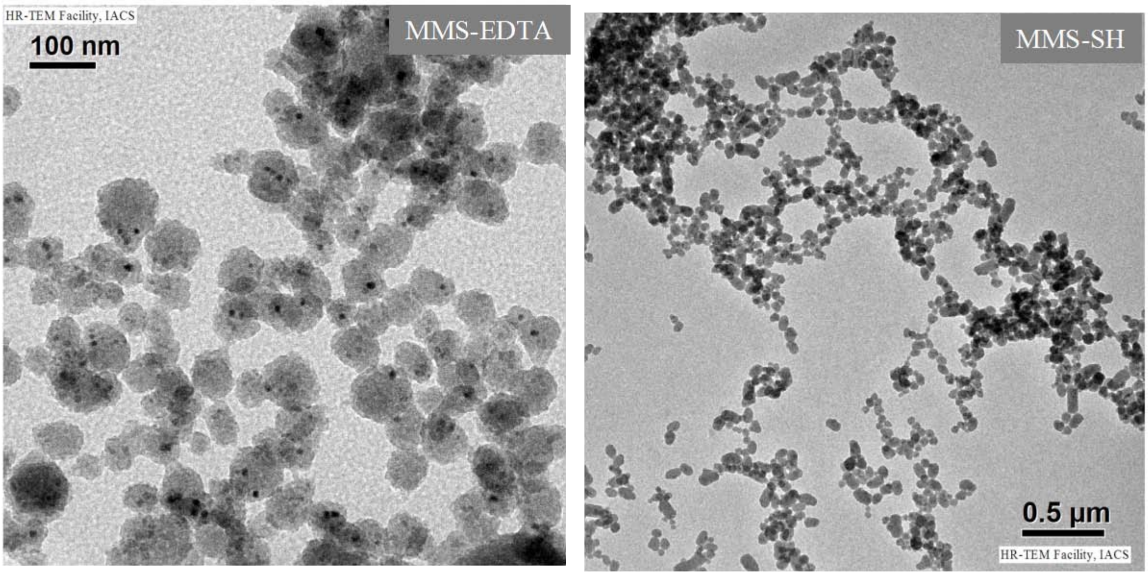

Figure S1. Low resolution TEM image of MMS-EDTA and MMS-SH.

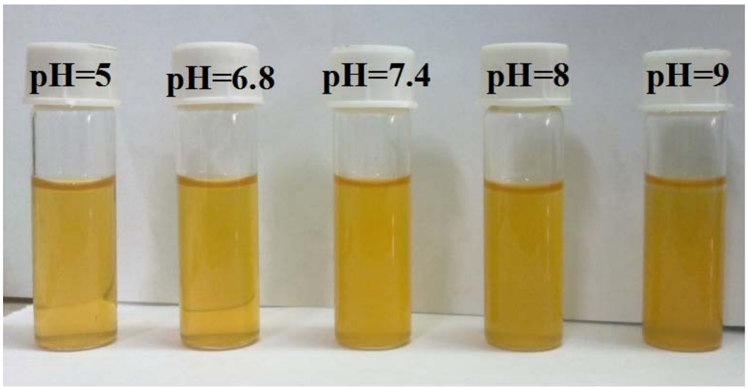

Figure S2. Colloidal dispersion of functional MMS in aqueous phosphate buffers of different pH.

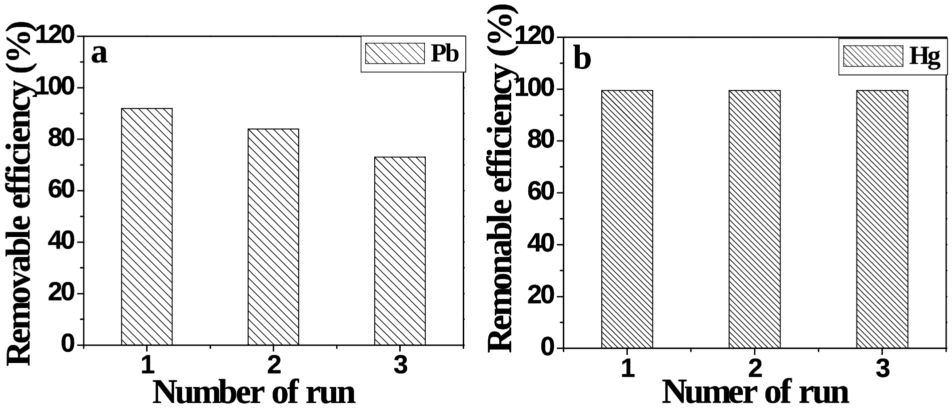

Figure S3. Removal efficiency of re-used MMS. 10 mg of MMS-EDTA was used for 10 mL of Pb solution (20 mg/L) and 10 mg of MMS-SH was used for 10 mL of Hg solution (20 mg/L)

Table S1: Comparative metal removable capacity of different functional MMS. [#]

Functional Materials	Removable capacity (mg of metal removed/gm of the materials)				Reference
	Hg	Cd	Pb	As	
EDTA-MMS and HS-MMS	180	180	160	140	present work[#]
Quaternary ammonium -MMS	20.86				2f
H_2N-magnetic-silica	--	22	80		10
HS-MMS	256	--	--	--	4b
HS-mesoporous silica	380	--	--	8-30	4a
DMSA-Fe_3O_4 and HS-Fe_3O_4	227 and 167	--	--	--	3b

[#] Removal capacity was estimated by using varying concentration of metal ions for fixed amount of MMS and then determined the removal capacity at higher metal ion concentrations (typically ~mM concentration of metal for MMS concentration of 1 mg/mL) where it is highest.