SUPPORTING INFORMATION

Florescent resin- assisted extraction for selective separation and preconcentration of mercury(II) and its online detection.

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File S1:

2.1 Instrumentation: The pH measurements were carried out with a digital pH meter combined with glass electrode (Elico L1-120). The morphology, particle size, surface properties and composition of the synthesized material were observed by using Scanning Electron Microscopy (SEM), transmission electron microscopy (TEM), Brunauer−Emmett−Teller (BET) analysis and Energy Dispersive X-Ray (EDX) Spectroscopy. The EDX and SEM were performed using a Scanning Electron Microscope (ZEISS Supra 55). The TEM images were taken at an accelerating voltage 60-200KV in 50V steps using JEM-2100 microscope. The specific surface area of the synthesized resin was conducted based on an N_2 adsorption−desorption isothermal analysis with BET multipoint measurement model using Quantachrome Nova Win Nova Station A - Data Acquisition and Reduction instrument version 10.01. On the other hand, BJH method was used to calculate the pore size, at the instrumental conditions viz., Analysis Adsorptive: N_2; Analysis Bath Temperature: 350.5°C; measured warm free space 26.4410 cm^3 ; cold free space : 82.1653 cm^3 with sample mass 0.0132 g without thermal correction. Fourier transform infrared (FT-IR) spectra of Resin in its loaded (Resin-Metal complexes) and unloaded forms were scanned over the range of 400−4000 cm^{-1} on Shimadzu FTIR spectrophotometer (Model no. FTIR-8400S) using KBr pellets to identify the chemical interactions occur inside the synthesized resin. The thermal stability and composition of the extracted species has been determined by thermo gravimetric analysis (TGA) at the range of temperature 40°C to 900°C at a heating rate of 25°C/minutes using Perkin Elmer (STA 6000) Simultaneous Thermal Analyzer; under the nitrogen flow of 20 ml/minutes. Fluorescence spectra of nano FSG-EBT in DMSO were recorded on Perkin Elmer LS-55 spectrofluorometer at its varying concentrations (0.0625×10^{-7} – 0.01×10^{-5} (M)). Human blood samples, collected from pathological laboratory, PM Hospital, Visva-Bharati were treated with a multicomponent metal ion mixture containing zinc(II), cadmium(II) and mercury(II). The samples

were centrifuged at 1500 rpm for 20 minutes by using REMI Laboratory centrifuge (R-4C DX) instrument and filtered.

File S2:

2.2 ***Reagents and Chemicals:*** Silica gel (SG) (60-120 Mesh; BDH, Mumbai, India) was functionalized with *m*-nitroaniline (Merck, Mumbai, India) using dimethyldichlorosilane (DMDCS) (BDH, Mumbai, India) as a new silane coupling reagent (FSG). EBT (Merck, Mumbai, India), alkali soluble azo dye containing phenolic –OH groups was immobilized on FSG by chemical binding. Standard stock solutions of zinc(II), cadmium(II) and mercury(II) (4×10^{-2} M) were prepared by dissolving an appropriate amount of metal salts (viz., $ZnSO_4.7H_2O$, $Cd(NO_3)_2$ and $Hg(NO_3)_2$) (E. Merck, Mumbai, India) in de-ionized water and estimated complexometrically using Xylenol orange (XO) as an indicator. Buffers of different pH were prepared by adding hexamine or ammonium chloride / ammonia buffer solution (NH_4Cl: NH_3 = 17.3 g: 142 mL L^{-1}). All reagents were prepared from analytical reagent grade chemicals unless specified otherwise. Double distilled water was used throughout the experiments.

File S3:

2.3 Preparation of the extractor (FSG-EBT):

SG (A) (60-120 mesh/10-20 nm) and *m*-nitro aniline (B) were mixed adequately in toluene in a round bottom flask at 27^0C and DMDCS (C) was added drop wise into the mixture with constant stirring (FSG). Finally, EBT was immobilized on this FSG by diazo coupling reaction (FSG-EBT) (F). The synthesized resin (deep black colored) mass was sequentially washed with 6M HNO_3 and cold distilled water; and dried at room temperature till constant weight. The whole synthesis need only 25-30 minutes. The corresponding nanomaterial (nano-FSG-EBT) was also synthesized using nano SG.

File S4:

2.4 3-D Structural Optimization of the synthesized extractor: Single crystal XRD analysis was beyond our scope, as the central core of the material was amorphous in nature. Therefore, as an alternative using Gaussian 09 revision D.0134 package, density functional theory (DFT) computation was made. Along with the three-dimensional optimized structure it generates different inherent chemical qualities viz., hard−soft character, position, and energy of the highest occupied and lowest unoccupied molecular orbital (HOMO−LUMO), placement of various functional groups.[1] The calculations were carried out using the B3LYP hybrid functional STO-3G basis set. [2, 3] In addition, neutral bond order (NBO) calculations of the optimized structures were performed to find the molecular orbital. The energies of the optimized structures were calculated after the ZPE (zero point energy) and thermal corrections.

File S5:

Adsorption kinetics:

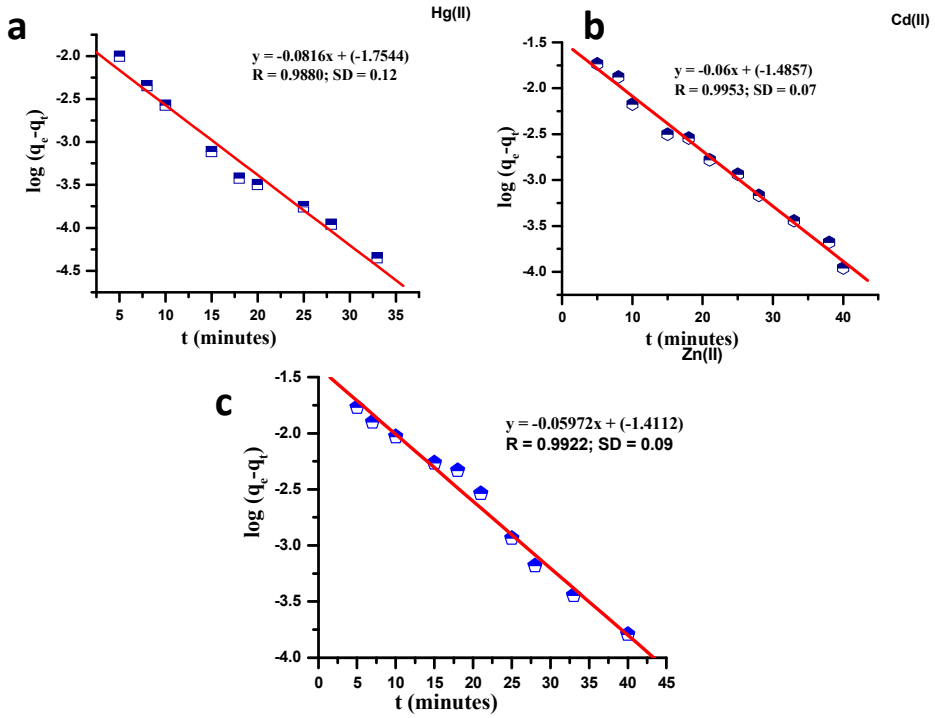

Figure S1. Plot of (log (q_e–q_t) vs. t) for (a) mercury(II); (b) cadmium(II); (c) zinc(II).

REFERENCES:

(1) Mandal, B.; Barman, M. K.; Srivastava, B. Extraction Chromatographic Method of Preconcentration, Estimation and Concomitant Separation of Vanadium (IV) with Silica Gel-Versatic 10 Composite, *J. Chromatogr. Sci.* **2013**, 52, 1135-1144.

(2) Srivastava, B.; Barman, M. K.; Chatterjee, M.; Mandal, B. EBT anchored SiO_2 3-D microarray: A simultaneous entrapper of two different metal centers at High and Low oxidation states using its respective highest occupied and lowest unoccupied molecular orbital. *RSC Adv.* **2015**, 5, 55686–55703 and references therein.

(3) Srivastava, B.; Barman, M. K.; Chatterjee, M.; Roy, D.; Mandal, B. Solid phase extraction, separation and preconcentration of rare elements thorium(IV), uranium(VI), zirconium(IV), cerium(IV) and chromium(III) amid several other foreign ions with Eriochrome black T anchored to 3-D networking silica gel, *J. Chromatogr. A* **2016**, 1451, 1–14.