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Electronic Supporting Information

Acetoacetanilide functionalized Fe₃O₄ nanoparticles for selective and cyclic removal of

Pb²⁺ ions from different charged wastewaters.

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by Pb²⁺ removal sequence.

Experimental Section

- Materials: Acetoacetanilide, ferric sulphate and ferrous sulphate were procured from Sisco Research Laboratory. APTES and tetraethoxyorthosilicate (TEOS) were obtained from Fluka. A 1000.0 mgL⁻¹ Pb²⁺ stock solution (as lead nitrate) was procured from Merck, while high purity analytical grade metal salts (Merck) were used for other studies. The double deionized water was used throughout the studies. All other reagents of analytical grade were purchased from Spectrochem. Pvt. Ltd.
- 2. Instrumentation: Powder X-ray diffraction patterns (XRD) of the nanosamples were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, bundesland, Germany) using graphite monochromatized Cu-Ka radiation at a scanning rate of 4° min⁻¹ in the 20 interval of 10–80° (λ =1.54056 nm, 40 kV, 40 mA). The size and morphology of the nanoparticles were examined on a transmission electron microscope (TEM, JEM-2010, JEOL, Japan) operated at 200 kV, equipped with an energy-dispersive X-ray spectrometer (EDS) and on a high resolution transmission electron microscope (HR-TEM, FEI TECNAIF 30) with a TECNAI F20 microscope operating at 300 kV with a point-to-point resolution of 0.24 nm. Sampling was done by dipping carbon coated copper grid into sample suspension, subsequently putting it on the filter paper to remove excessive solution from the grid. Electron micrographs were taken for the particles retained on the film. Energy dispersive spectroscopy (EDS) analysis was performed using an adjacent Oxford INCA system. Surface imaging of the samples was performed using focused ion beam-scanning electron microscopy (FIB/SEM) on Gemini Ultra 55 (Zeiss) instrument. Initially, double-sided tape was applied to metal stubs and then, the sample was placed onto the tape. Excess sample was removed using pressurized air. The sample was then sputter-coated with a 10 nm gold layer with the help of a Cressington-208 HR Sputter Coater. A Fischer

Scientific FS60H sonication bath was used for all other sonication purposes. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (EV-9, Microsense, ADE) in the magnetic field range of -20,000 Oe to 20,000 Oe at room temperature. The Fourier transform infrared (FTIR) spectra were obtained on a Perkin-Elmer spectrometer at room temperature using KBr pellet technique in the range of 4000–400 cm⁻¹ under the atmospheric conditions with a resolution of 1 cm⁻¹. Digestions were performed in Anton Paar multiwave 3000 microwave reaction system equipped with pressure and temperature sensor. The pH and potential measurements were carried out with ELICO LI 120 pH meter, India. LABINDIA AA 7000 Flame atomic absorption spectrophotometer (FAAS) was used for the determination of metal concentrations.

3. Synthesis of NH₂-Si@MNPs: For the synthesis of magnetic nanoparticles (MNPs), FeCl₃.6H₂O (6.0 g) and FeCl₂.4H₂O (4.2 g) were dissolved in 250 mL of deionized water at 60 °C to form a homogeneous solution. Then, 15 mL of 25% NH₄OH was added slowly under the intensive stirring conditions. In this process, colour of the bulk solution immediately turned black from yellowish orange. The stirring was continued for another 30 min at the same temperature. The black precipitates formed were separated magnetically and washed several times with deionized water and ethanol. Then, in order to form the outer silica shell, MNPs were redispersed in a new portion of ethanol (200 mL) and deionized water (50 mL) followed by the addition of 0.1 M HCl (2.2 mL). Thereafter, the successive addition of 5 mL of 25% NH₄OH and 1 mL of TEOS was performed, and the obtained reaction mixture was stirred for 6 h at 60 °C. The as-synthesized Si@MNPs were separated by an external magnet, washed with ethanol and dried under vacuum. Further, to introduce terminal amino groups on the silanol surface, 0.5 mL of 3-aminopropyltriethoxysilane (APTES) was

added to the dispersion containing 0.1 g of Si@MNPs in ethanol (100mL). The mixture was stirred for 6 h at 50 °C, and the devised aminopropylated silica coated magnetic nanoparticles (NH₂-Si@MNPs) were separated, washed several times with ethanol to remove the unreacted silylating agent and dried

4. Sample collection and digestion: River water was taken from Yamuna, while rain water was collected in the month of September, 2013. Fly-ash samples were procured directly from TERI. These samples were originally gathered from different sections of mycorrhizal treated fly-ash dykes around the two major fertilizer and thermal power plants of North India. A total four samples were collected from each site in a random manner. These ash dump lands have been undertaken by TERI for the reclamation using Mycorrhizal based technology. Microwave assisted acid digestion of fly-ash samples were performed as per the EPA recommended method 3052. The obtained filtrate was made up to 100 mL with deionized water in a calibrated flask. An appropriate aliquot of different sample solutions was taken, and the proposed procedure was applied for Pb²⁺ determination. For validation of the method, the samples were further spiked with the appropriate amount of the analyte ions and the quantitative recoveries were analyzed.

Supporting Figures



Figure S1. Magnetic separation of AAA-NH₂-Si@MNPs.



Figure S2. SEM micrographs of (a) MNPs (b) Si@MNPs and (c) AAA-NH₂-Si@MNPs.



Figure S3. Powder XRD patterns of (a) MNPs, (b) Si@MNPs and (c) AAA-NH₂-Si@MNPs.



Figure S4. pH effect on zeta potential of AAA-NH₂-Si@MNPs.



Figure S5. Linearized Langmuir adsorption isotherm of Pb²⁺ adsorption on AAA-NH₂-

Si@MNPs.



Figure S6. Linearized Freundlich adsorption isotherm of Pb²⁺ adsorption on AAA-NH₂-

Si@MNPs.



Figure S7. Van't Hoff plot for the adsorption of Pb²⁺ on AAA-NH₂-Si@MNPs.



Figure S8. TEM and SEM image of the recovered AAA-NH₂-Si@MNPs.



Figure S9. Magnetization curve obtained by VSM at room temperature for the recovered AAA-

NH₂-Si@MNPs.

Table S1. Recovery of Pb^{2+} ions bound to nanoadsorbent after desorption with variable amounts and concentrations of different eluents and their mixtures (Conditions: initial Pb^{2+} concentration: 400 mgL⁻¹, pH: 5.0, adsorbent dose: 1 gL⁻¹, contact time: 30 min, desorption time: 5 min, reaction temperature: 298 K).

Eluent type	Concentration	Volume (mL)	Recovery (%)
	$(molL^{-1})$		
CH ₃ COOH	0.1	10	54.7
CH ₃ COOH: HCl	0.05: 0.05	10	70.0
HCl	0.1	10	90.6
HCl	0.5	10	96.3
HCl: HNO ₃	0.05: 0.05	10	87.7
HNO ₃	0.05	10	92.9
HNO ₃	0.1	10	99.7
HNO ₃	0.1	6	99.6
HNO ₃	0.1	4	99.4
HNO ₃	0.1	2.5	94.8

Metal ions	Ionic radius (pm)	Electronegativity (Pauling)
Pb ²⁺	120	2.33
Ni ²⁺	69	1.91
Zn^{2+}	74	1.65
Cu^{2+}	72	1.90
Co ²⁺	72	1.88
Cd^{2+}	99	1.69
Fe ³⁺	60	1.83
Al ³⁺	53	1.61
Cr ³⁺	62	1.66

Table S2. Physiochemical properties of the studied heavy metal ior	ns.
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FTIR spectrum of MNPs



FTIR spectrum of Si@MNPs



FTIR spectrum of NH₂-Si@MNPs



FTIR spectrum of AAA-NH₂-Si@MNPs





FTIR spectrum of Pb²⁺ adsorbed AAA-NH₂-Si@MNPs



Scheme 1. Schematic illustration of the synthetic route of AAA-NH₂-Si@MNPs followed by Pb²⁺ removal sequence.