Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Toxic/Heavy Metal Ions Using Ion-Imprinted Aminofunctionalized Silica Gel

R. K. Dey[a]; Usha Jha[a]; Tanushree Patnaik[a]; A. C. Singh[a]; Varun K. Singh[a]
[a] Department of Applied Chemistry, Birla Institute of Technology, Mesra, Ranchi, India

To cite this Article Dey, R. K. , Jha, Usha , Patnaik, Tanushree , Singh, A. C. and Singh, Varun K.(2009) 'Removal of Toxic/Heavy Metal Ions Using Ion-Imprinted Aminofunctionalized Silica Gel', Separation Science and Technology, 44: 8, 1829 — 1850

To link to this Article: DOI: 10.1080/01496390902880115

URL: http://dx.doi.org/10.1080/01496390902880115

Separation Science and Technology, 44: 1829–1850, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390902880115

Taylor & Francis
Taylor & Francis Group

Removal of Toxic/Heavy Metal Ions Using Ion-Imprinted Aminofunctionalized Silica Gel

**R. K. Dey, Usha Jha, Tanushree Patnaik,
A. C. Singh, and Varun K. Singh**
Department of Applied Chemistry, Birla Institute of Technology,
Mesra, Ranchi, India

Abstract: The investigation reports the preparation and evaluation of Cr(III) and Fe(III)-imprinted amino-functionalized silica gel adsorbents (APTS-Cr(III)-Si and APTS-Fe(III)-Si) for selective solid-phase extraction of Cr(III) and Fe(III), respectively, from aqueous solutions. The adsorbent materials were prepared by a surface imprinting technique using 3-aminopropyltrimethoxysilane as the surface modifying ligand. The effects of solution pH, sorption time, temperature, and initial metal ion concentration upon adsorption characteristics were investigated. The adsorption isotherms for Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) were evaluated and the thermodynamics of the adsorption processes were correlated. By optimizing the parameters, the synthesized materials could be used successfully for selective removal of trivalent cations from a mixture of cations in dilute aqueous solution.

Keywords: Adsorption isotherm, aminofunctionalized silica gel, solid-phase extraction (SPE), surface imprinting technique

INTRODUCTION

Pollution due to heavy metals has received wide spread attention in recent years (1,2). Various industrial sources such as leather tanning, electroplating, metal processing, textile, steel fabrication, etc., are the

Received 28 May 2008; accepted 8 January 2009.

Address correspondence to R. K. Dey, Department of Applied Chemistry, Birla Institute of Technology, Ranchi–835 215, India. E-mail: rkdey@rediffmail.com

main contributor to the contamination of water bodies with chromium and iron. In the environment, chromium exists in two stable oxidation states, Cr(III) and Cr(VI), and the trivalent form is relatively innocuous (3). The inter-conversion of Cr(III) to Cr(VI) is controlled by various factors such as concentrations of Cr(III) ion, presence of oxidizing or reducing agents, the electrochemical potentials of the oxidation and reduction reactions, temperature, light, acid–base reactions, complexing agents, etc. (1). Preconcentration and determination of a trace of Fe(III) carries importance due to environmental protection, hydrogeology, and various chemical processes (4,5).

In analytical chemistry, the study of molecularly imprinted materials/ion imprinted materials has received much attention due to high selectivity and easy preparation methodologies (6–8). By adopting a molecular imprinting technique, a molecular memory is imprinted on the prepared material. Thus the prepared materials show selectivity in recognizing and binding the desired molecular target with high affinity and selectivity (9). Such kind of materials find potential applications in solid-phase extractive preconcentration of analytes present in low concentration and/or the separation from other coexisting ions or complex matrix. A number of molecularly imprinted materials, capable of high molecular recognization, have been prepared by various researchers using metal ions such as, Pb(II), Ni(II), Pd(II), and Th(IV) (10–15).

Currently, the use of various precursors of silica and functionalized silica gel in preparation of molecularly-imprinted adsorbent material gains immense importance in adsorption/separation processes. Silica gel is an amorphous inorganic support composed of internal siloxane groups (Si–O–Si) in the bulk and silanol groups (Si–OH) distributed on the surface (16). The active hydrogen atom of the silanol groups of silica gel has the ability to react with agents containing organosilyl functions, to give some organic nature to the precursor inorganic support (17). The direct attachment of organic molecules to inorganic surfaces is difficult due to the relative inertness of silica surfaces. Therefore, organic extractants can be attached to inorganic surface by surface modification procedures (18). Silica gel based molecularly imprinted material (molecularly imprinted silicas, MIS) is well documented in a recently published report (19). Silica based oxide materials, tetralkoxysilanes and organically modified silicas have been imprinted to produce materials with various applications in the areas of development of sensors, catalysts, and new adsorbent materials (20–22).

Recently, Fan et al. (23) prepared Hg(II)-imprinted thiol-functionalized mesoporous sorbent by sol-gel process and the developed material was successfully used to determine trace of mercury in biological and environmental samples. Chang et al. (7) prepared Fe(III)-imprinted aminofunctionalized silica gel sorbent by combining a surface molecular imprinting technique for selective extraction or preconcentration of Fe(III). Compared with the non-imprinted particle, the ion-imprinted one showed higher selectivity and adsorption capacity for Fe(III). A Cr(III)-imprinted silica gel for the speciation of chromium in environmental water samples was prepared by Zhang et al. (24) which was used to enrich and determine both Cr(III) and Cr(VI) from aqueous solution. However, considering the various applications oriented aspects involved in ion-imprinted silica based materials, a number of potential applications as well as the thermodynamics of adsorption processes are yet to be evaluated and various investigations in this aspect are still in developmental stage. The present investigation reports the preparation of Fe(III) and Cr(III)-imprinted silica gel adsorbents using 3-(trimethoxypropylamino) silane (APTS) as a surface modification ligand. The prepared adsorbents were capable of removing the target metal ions from a complex matrix. A number of other heavy metal ions having the same charge-to-radius ratio as that of the targeted metal ions could also be removed from complex matrix in a dilute aqueous solutions. Adsorption of four selected trivalent and divalent metal ions such as, Cr(III), Fe(III), Zn(II), and Mn(II) were investigated in both the competitive and the non-competitive environment with a variation of parameters. A comparative account was drawn regarding the selectivity and efficiency of adsorbents in the removal of the target metal ion as well as the non-target one from aqueous solutions. The thermodynamics of the adsorption processes were also evaluated which can be helpful in finding out a number of possible potential applications of prepared materials in solid phase extraction.

EXPERIMENTAL

Chemicals and Reagents

Reagents of analytical and spectral purity were used for all experiments. 3-aminopropyltrimethoxysilane (APTS), Aldrich, was used as received. The methanol and ethanol were of reagent grade and methanol was distilled before use. Other solvents such as toluene (reagent grade) was used as received. The doubly distilled water (DDW) was obtained from an ultra-pure Milli-Q 18.2 MΩ system. Solutions of M^{n+} (Fe^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}) were prepared from suitable reagent grade nitrate or chloride salts in DDW. The pH of the medium was adjusted using $0.1\,mol\,L^{-1}$ HNO_3, or $0.1\,mol\,L^{-1}$ ammonia solutions. Silica gel (Fluka) having particle size 0.063 –0.200 mm and pore volume $0.74–0.84\,cm^3\,g^{-1}$ was used to prepare the ion-imprinted and non-imprinted functionalized silica gel sorbents.

Instrumentation

Elemental analysis was done on a Vario EL III, elemental analyzer. The infrared spectra of the samples in KBr pellets were performed by diffuse reflectance by accumulating 35 scan on IR-Prestige 21, in the range of 4000 to 400 cm^{-1}. The amount of cations adsorbed per gram of the adsorbent was determined by the difference between the initial concentration in aqueous solution and that found in the supernatant, by using an Atomic Absorption Spectrophotometer (AAS) (Shimadzu, 680) apparatus. For each experimental point, the reproducibility was checked by at least one duplicate run. The pH of the solution was measured using a pH/Ion Analyzer, model 450 M. Scanning electron microscope (SEM) of the sample materials were taken using JSM-6390LV (Jeol, Japan) and the chemical composition of the sample materials were evaluated using Energy Dispersive Spectra (EDS) (Oxford).

Preparation of Ion-Imprinted Functionalized Silica Gel Sorbent

The silica gel surfaces were activated by refluxing 10 g of silica gel with 500 mL of 5.0 mol L^{-1} HCl with constant stirring for 12 h. Activated silica gel was filtered and washed with DDW to neutral and dried under vacuum at 70°C for 10 h. Fe(III)-imprinted amino-functionalized silica gel was prepared by dissolving 2.27 g of $FeCl_3 \cdot 6H_2O$ in 100 mL of methanol under constant stirring and heating followed by addition of 4.0 mL of APTS to the mixture. The solution was stirred under constant reflux condition for 3 h after which, 6.0 g of activated silica gel was added to the mixture. After 24 h of constant stirring and refluxing, the material, APTS-Fe(III)-Si, was filtered and washed with ethanol. Subsequently, the material was washed with 100 mL of 6.0 mol L^{-1} HCl to ensure the removal of adhered metal ions. The color of APTS-Fe(III)-Si was found to be pale brown. Using identical procedure Cr(III)-imprinted amino-functionalized silica gel, APTS-Cr(III)-Si, was also prepared and the color of APTS-Cr(III)-Si was found to be pale green. The non-imprinted functionalized silica gel adsorbent was prepared using the same procedure without adding the metal salt $FeCl_3 \cdot 6H_2O$ or $CrCl_3 \cdot 6H_2O$

Sorption Experiments

The batch method was used to concentrate M^{n+} (Fe^{3+}, Cr^{3+}, Mn^{2+}, Zn^{2+}) from aqueous solutions in order to obtain the adsorption isotherm. Samples of 100 mg of adsorbent materials were suspended in 50.0 cm^3 of aqueous solutions of each cation with varying concentrations ranging from 10 to 50 mg L^{-1}. The samples were mechanically shaken at (25 ± 2)°C for 24 h, after which the solid was separated by centrifugation. The supernatant was analyzed using AAS.

The adsorption capacity, distribution ratio, and the selectivity coefficient were calculated according to the following equations:

$$Q = V(C_o - C_e)/W \tag{1}$$

$$D = Q/C_e \tag{2}$$

$$\alpha_{Fe/Cr} = D_{Fe}/D_{cr} \tag{3}$$

where, Q is the adsorption capacity (mg g^{-1}), C_o and C_e are the initial and equilibrium concentration of sorbed metal ions (mg L^{-1}), and W is the mass of the solid adsorbent (g) used in the adsorption process and V is the volume of metal solution (L). D is the distribution ratio (mL g^{-1}), $\alpha_{Fe/Cr}$ is the selectivity coefficient.

RESULTS AND DISCUSSION

Characterization

Considering the various stages of reaction for the synthesis of APTS-Fe(III)-Si, the main features of the silica spectrum, as shown in Fig. 1,

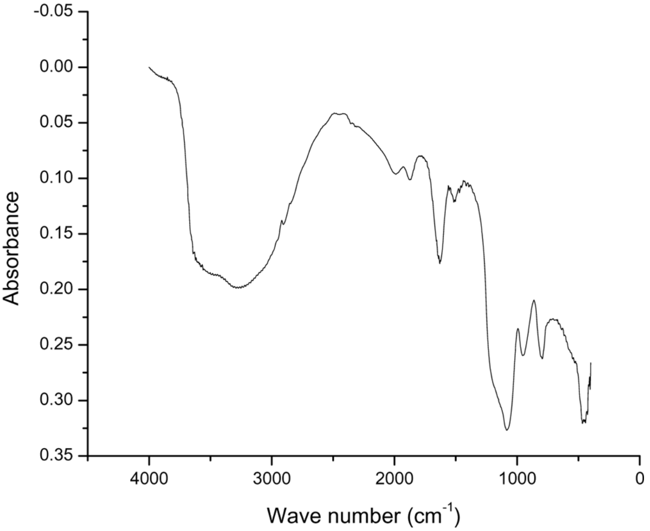
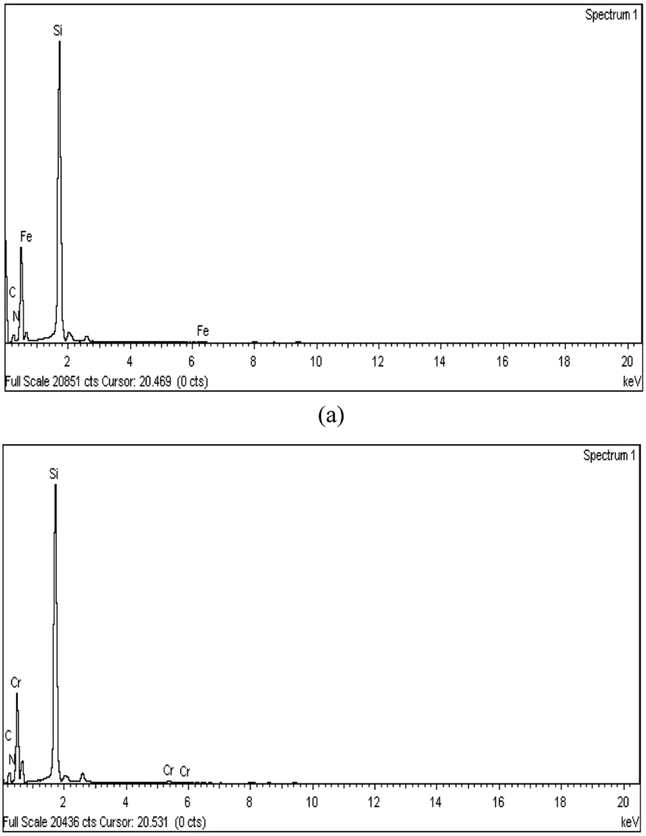


Figure 1. FTIR spectra of APTS-Fe(III)-Si.

contains: (a) a large broad band between 3400–3200 cm^{-1} attributed to the presence of O–H stretching frequencies of silanol groups and also the adsorbed water molecule. (b) siloxane stretching $\nu_{(Si-O-Si)}$ and $\nu_{(Si\text{-}OH)}$ stretching vibration are noticed at 1100 and 900 cm^{-1}, respectively. The band at 1650 cm^{-1} characterizes the angular vibration of the water molecule. Adsorption bands at 3344, 1090, and 850 cm^{-1} characterize the presence of N–H stretching. The presence of the band at 2950 cm^{-1} is assigned to the C–H stretching of tetrahedral carbon, thus confirming the anchoring of the organic molecule to the silica surface (25). Similar observations were noted in case of APTS-Cr(III)-Si. The EDS spectra (Fig. 2) of the sample materials showed the elemental



(a)

(b)

Figure 2. (a) EDS spectra of APTS-Fe(III)-Si, showing the presence of iron in the moiety. (b) EDS spectra of APTS-Cr(III)-Si, showing the presence of chromium in the moiety.

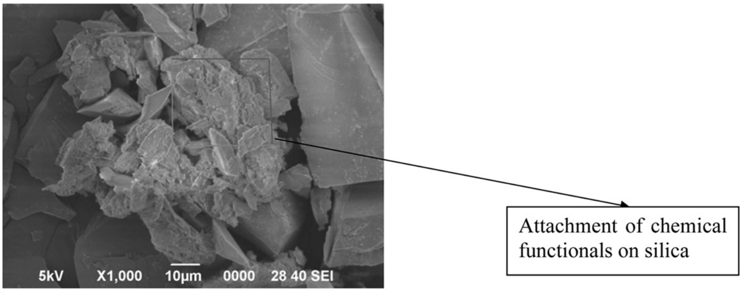


Figure 3. Scanning Electron Micrograph of APTS-Fe(III)-Si showing the development of new particles in modified silicas.

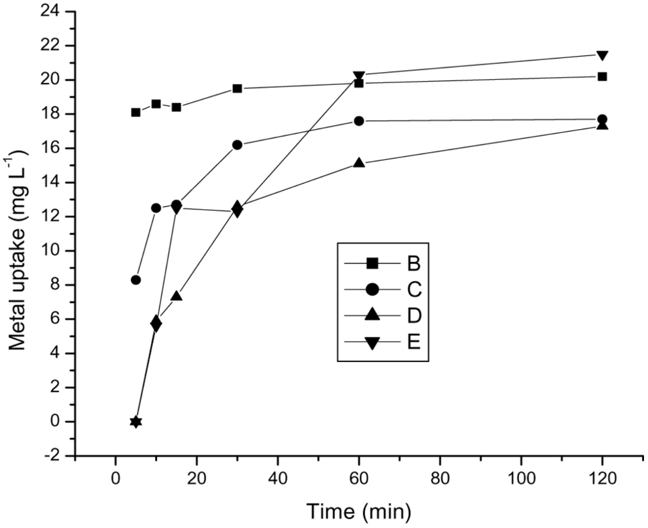
composition of the adsorbent material. The incorporation of Fe(III) and Cr(III) in APTS-Fe(III)-Si and APTS-Cr(III)-Si, respectively, supported the evidence towards appropriate chemical modification of silica.

Figure 3 shows the scanning electron micrograph (SEM) of APTS-Fe(III)-Si, which confirm the morphology of the particles of modified silicas. The attachment of chemical functionalities, characterized by the presence of microstructures on the surface of silica, was observed in case of modified silica. Such morphology was not present in case of unmodified silica. The microstructures on the surface of modified silica, however, did not affect the reproducibility of the binding process during continuous use of the material for metal uptake experiment.

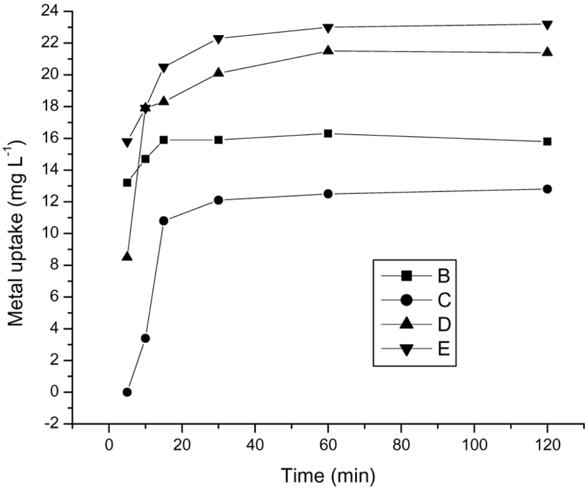
Analytical Studies

Equilibrium Time Period

Metal sorption capacities were determined as a function of time (Fig. 4) to determine the optimum contact time for the sorption of heavy metal ions such as Fe^{3+}, Cr^{3+}, Mn^{2+}, and Zn^{2+}. In case of APTS-Cr(III)-Si, the equilibrium time period for Cr^{3+}, shown in Fig. 4 (a), was reached within a time period of 10–20 minutes. An equilibrium time period of 60 minutes was noted for all other metal ions, indicating the efficient removal of Cr^{3+} in comparison to other metal ions. However, maximum metal uptake was observed both for Cr^{3+} and Fe^{3+} in comparison to divalent Mn^{2+} and Zn^{2+}. In case of APTS-Fe(III)-Si, as shown in Fig. 4(b), a higher uptake was observed for Fe^{3+} and the metal uptake follows the order $Fe^{3+} > Cr^{3+} > Zn^{2+} > Mn^{2+}$. For all metal ions, the equilibrium time period was found to be reached within a time period of 20–30 minutes.



(a)



(b)

Figure 4. (a) Effect of contact time variation. For APTS-Cr(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. Amount of adsorbent materials, 100 mg; concentration of solution, 50 mg L^{-1}, pH, neutral; total volume of solution, 50 mL; temperature, 25 ± 2°C. (b) Effect of contact time variation. For APTS-Fe(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. Amount of adsorbent materials, 100 mg; concentration of solution, 50 mg L^{-1}, pH, neutral; total volume of solution, 50 mL; temperature, 25 ± 2°C.

Analysis of data indicated that APTS-Cr(III)-Si showed more preference towards Cr^{3+}, whereas, APTS-Fe(III)-Si showed more preference towards Fe^{3+} in solution. The reason could be attributed to the coordination-geometry selectivity where the Fe(III)/Cr(III)-imprinted silica gel sorbent may be able to provide the ligand groups arranged in a suitable way required for coordination of Fe(III)/Cr(III) ions.

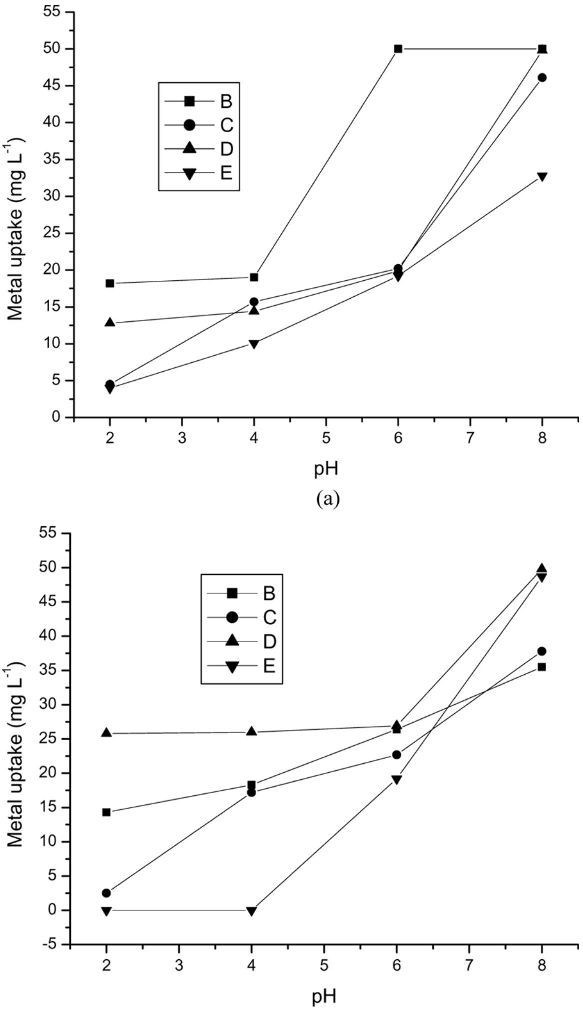
Effect of pH

The pH of the medium is one of the most important factors controlling the sorption of metal ions by adsorbent materials. The sorption of metal ions uptake at different pH of the medium, as shown in Fig. 5, was examined in a pH range of 2 to 8. Further increase in pH of the medium was discouraged due to possible hydrolysis of cations and degeneration of silica gel in strong alkaline medium (26). Adsorption of metal ions increased with increase in pH of the medium. It could be attributed to the fact that at low pH, the competition between the metal ion and the H^+ ion favors H^+, thus resulting in decrease in metal uptake quantities. However, at a higher pH of the medium, the adsorption surface becomes less positive, favoring electrostatic attraction between the metal ions and sorbent surface (15). In case of APTS-Cr(III)-Si, (Fig. 4(a)), at low pH almost no significant increase Cr^{3+} uptake was observed, but Cr^{3+} adsorption increases progressively within a pH range of 4.0–6.0 along with adsorption of Fe^{3+}. The adsorption of Zn^{2+} remained almost constant within a pH range of 6.0–8.0. Similarly, APTS-Fe(III)-Si showed no uptake of Fe^{3+} at low pH (2.0–4.0) of medium (Fig. 5(b)). However, adsorption of Fe^{3+} increased gradually within pH range of 4.0–8.0 along with adsorption of Cr^{3+}.

The above observation indicated that with change in pH of the medium, ion-imprinted adsorbent materials showed more preference towards trivalent metal ion in a particular pH range. Therefore, by optimizing the parameters, it may be possible to separate a mixture of metal ions using these adsorbent materials.

Variation of Sorbent Quantity

The variation of sorbent quantity is illustrated in Fig. 6. With increase in quantity of adsorbent material, metal sorption increases gradually for both APTS-Fe(III)-Si and APTS-Cr(III)-Si. However, for APTS-Cr(III)-Si, no significant adsorption for Mn^{2+} was noted within the range of study. For all other metal ions, the adsorption characteristics showed a gradual increase.



(a)

(b)

Figure 5. (a) Effect of pH of the medium. For APTS-Cr(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. Amount of materials, 100 mg; concentration of the solution, 100 mg L^{-1}; total volume of the solution, 50 cm^3; time of contact, 24 h. (b) Effect of pH of the medium. For APTS-Fe(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. Amount of materials, 100 mg; concentration of the solution, 100 mg L^{-1}; total volume of the solution, 50 cm^3; time of contact, 24 h.

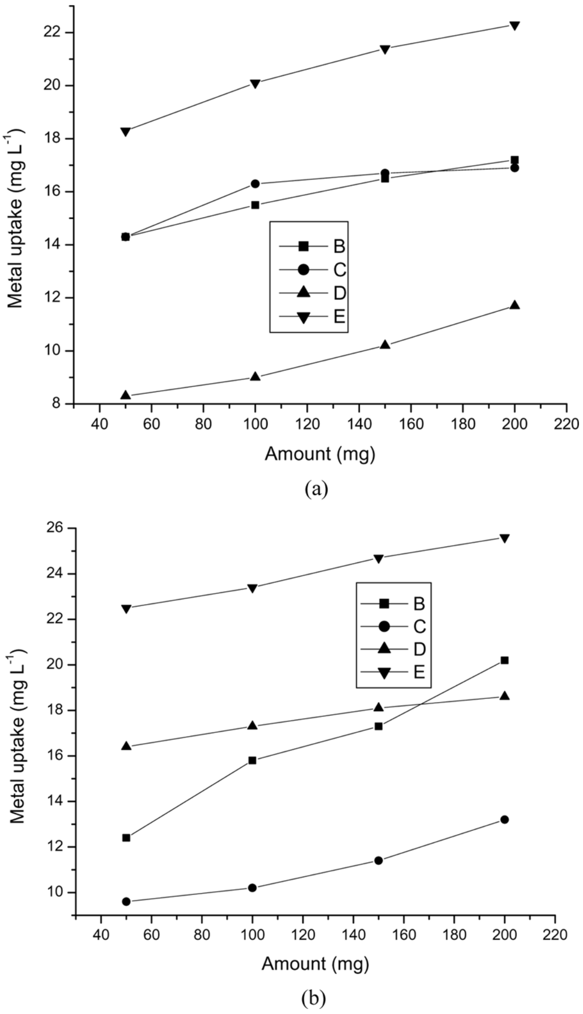


Figure 6. (a) Effect of variation in amount of adsorbent. For APTS-Cr(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. concentration of the solution, 50 mg L^{-1}; total volume of the solution, 50 cm^3; time of contact, 24 h. (b) Effect of variation in amount of adsorbent. For APTS-Fe(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. concentration of the solution, 50 mg L^{-1}; total volume of the solution, 50 cm^3; time of contact, 24 h.

In case of APTS-Fe(III)-Si, adsorption of Fe^{3+} remains higher in comparison to all other metal ions. Additionally, higher adsorption of Cr^{3+} was also noted with an increase in the sorbent quantity. For Zn^{2+}, no significant increase in adsorption quantity was observed.

Effect of Concentration

The effect of the initial concentration on metal ion sorption was investigated by varying the initial concentration of the metal ions (Fig. 7). With an increase in initial concentration of the metal ion, a quantitatively higher adsorption of metal ions was noted. This result could be explained

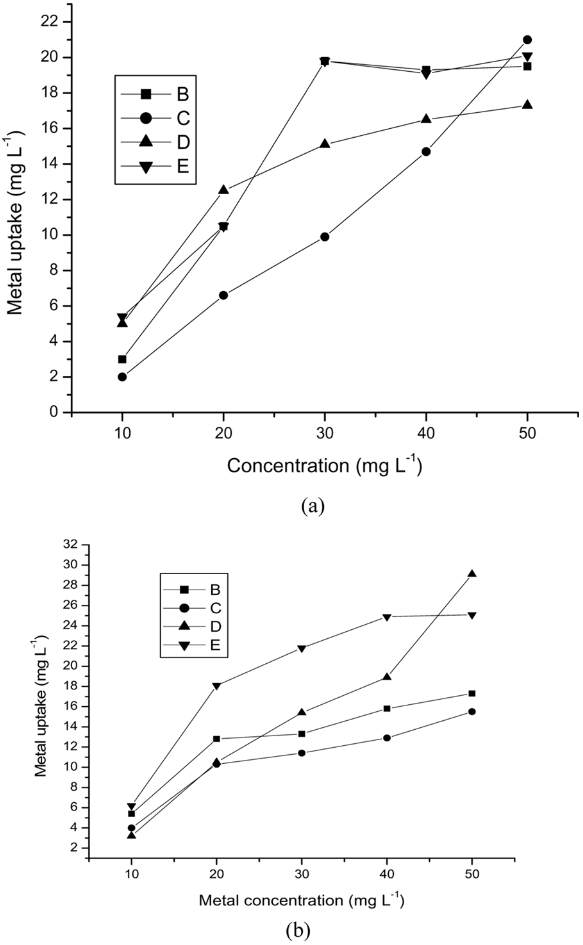


Figure 7. (a) Effect of variation in concentration of metal ions. For APTS-Cr(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. Amount of adsorbent, 100 mg; total volume of the solution, 50 cm^3; time of contact, 24 h. (b) Effect of variation in concentration of metal ions. For APTS-Fe(III)-Si: B, Cr^{3+}; C, Mn^{2+}; D, Zn^{2+}; E, Fe^{3+}. Amount of adsorbent, 100 mg; total volume of the solution, 50 cm^3; time of contact, 24 h.

on the basis of a high driving force for mass transfer (27), where the increase in concentration of metal ions increase the competition to occupy all the available coordination sites in the adsorbent material. To test and compare the adsorption isotherms, experimental data obtained from the effect of variation in initial concentration of a trivalent cation (Cr^{3+}) and divalent cation (Zn^{2+}) were tested for the sorption capacity of adsorbent APTS-Cr(III)-Si. The results were fitted to Langmuir, Freundlich, and D-R isotherm. The following linearized forms of equations representing the models were used for the method validation purpose:

Langmuir Isotherm

The Langmuir adsorption isotherm model (Eq. 4), is valid for monolayer adsorption onto a surface containing a finite number of identical sites (28). The equation can be written as:

$$C_e/q_e = C_e/Q_o + 1/bQ^o \tag{4}$$

Where, q_e is the amount of solute adsorbed on the surface of the adsorbent (mmol g^{-1}), C_e is the equilibrium concentration in the solution (mmol L^{-1}), Q_o is the maximum surface density at monolayer coverage, and b is the Langmuir adsorption constant (L $mmol^{-1}$). When C_e/q_e is plotted against C_e, as shown in Fig. 8(a), for adsorption of Zn^{2+} upon the surface of adsorbent material APTS-Cr(III)-Si, a straight line with slope $1/Q_o$ and intercept $1/bQ^o$ was obtained for which the R^2 value was found to be 0.9988. However, for Fe^{3+} and Cr^{3+}, the R^2 values were found to be 0.9256 and 0.8938, respectively. Comparison of R^2 values indicated a better fitment of curve in case of Zn^{2+}.

Similarly for the adsorption of trivalent cation (Fe^{3+}) and divalent cation (Mn^{2+}) onto the adsorbent material APTS-Fe(III)-Si, the data were fitted to the Langmuir adsorption model (Fig 8 (b)) for which the R^2 values were found to be 0.9938, and 0.9593, respectively.

Freundlich Isotherm

The Freundlich adsorption isotherm (Eq. 5) (29) can be expressed as:

$$\ln q_e = \ln K_F + 1/n(\ln C_e) \tag{5}$$

where, q_e is the equilibrium solute concentration (mmol g^{-1}) on the adsorbent material, C_e is the equilibrium concentration of the solute

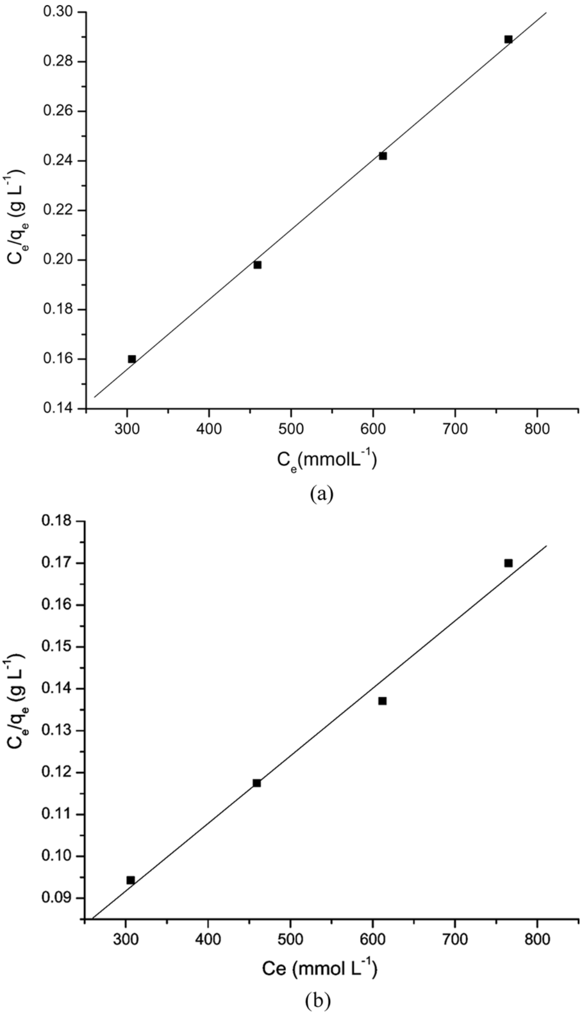


Figure 8. (a) Verification of Langmuir adsorption isotherm. For adsorbent material APTS-Cr(III)-Si: metal ion, Zn^{2+}; time of contact, 24 h; temperature, 25 ± 2°C. (b) Verification of Langmuir adsorption isotherm. For adsorbent material APTS-Fe(III)-Si: metal ion, Fe^{3+}; time of contact, 24 h; temperature, 25 ± 2°C.

(mmol L^{-1}), K_F is the Freundlich constant (mmol g^{-1}), which indicates the adsorption capacity and n is the surface heterogeneity factor. The Freundlich equation is basically empirical in nature and it assumes that the adsorption occurs on heterogeneous surfaces. A plot of ln q_e against

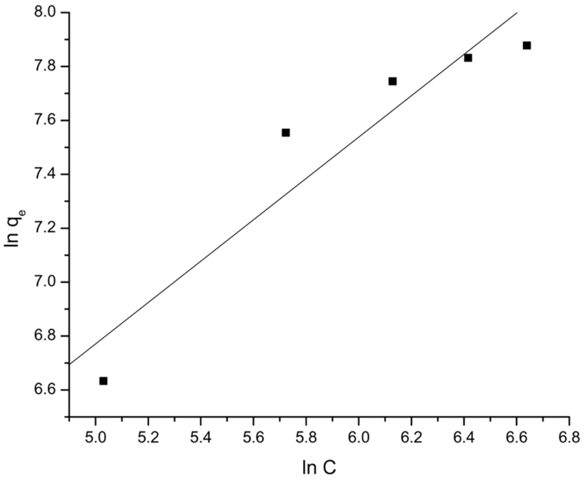


Figure 9. Verification of Freundlich adsorption isotherm. For adsorbent material APTS-Cr(III)-Si: metal ion, Zn^{2+}; time of contact, 24 h; temperature 25 ± 2°C.

ln C, for adsorption of Zn^{2+} on APTS-Cr(III)-Si as shown in Fig. 9, yielded the R^2 value as 0.9454. However, for the trivalent cation Cr^{3+}, the R^2 value was found to be 0.9440. On comparison, it can be concluded that for adsorption of Zn^{2+} on APTS-Cr(III)-Si, Langmuir equation represents a better fit to the experimental data than Freundlich equation.

Similarly in case of APTS-Fe(III)-Si, the adsorption data for Fe^{3+} and Mn^{2+} were fitted into the Freundlich model for which the obtained R^2 values were 0.9392 and 0.9564, respectively, indicating a better fit of experimental data in the Langmuir model.

Dubinin-Radushkevich (D-R) Isotherm

The D-R isotherm is more general than the Langmuir equation. The equation does not assume a homogenous surface or constant sorption potential (30). The linearized form of the D-R isotherm can be written as:

$$\ln q_e = \ln q_m - k\varepsilon^2 \qquad (6)$$

where, ε (Polanyi potential) is [RT ln $(1+(1/C_e))$], q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), k is the constant related to the adsorption energy ($mol^2\ kJ^{-2}$) and q_m is the adsorption capacity (mol g^{-1}). The plot of ln q_e versus ε^2 (Fig. 10) gives the values of q_m and k calculated from the intercept and the slope of the plot.

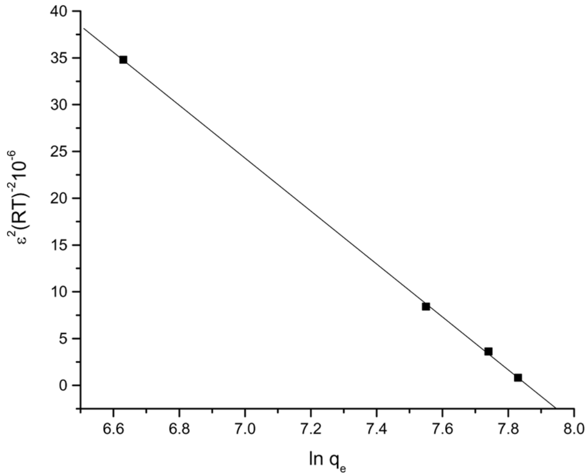


Figure 10. Verification of D-R isotherm. For adsorbent material APTS-Cr(III)-Si: metal ion, Zn^{2+}; time of contact, 24 h; temperature 25 ± 2°C.

The mean free energy of adsorption (E) was calculated from the k values using the following equation:

$$E = (-2k)^{-1/2} \tag{7}$$

The magnitude of E is useful for estimating the type of sorption reaction, i.e., an energy range from about 8 to 16 kJ mol^{-1} indicates electrostatic process (ion-exchange). In the case of E less than 8 kJ mol^{-1}, physical force such as vander Waal's and hydrogen bonding may affect the sorption mechanism. In this study, E value was calculated to be 12.609 for adsorption of Zn^{2+} upon APTS-Cr(III)-Si, indicating a possible ion-exchange process to operate.

Effect of Temperature

The effect of temperature on the adsorption processes was tested for the adsorption of a trivalent cation Fe^{3+} upon the adsorbent material APTS-Fe(III)-Si. The temperature was varied from 25 to 50°C. The obtained result showed that increase in temperature favors the adsorption process. Adsorption of metal ion increased quantitatively up to a temperature range of 40–45°C. However, further increase in temperature decreases the metal removal from aqueous solution. The result suggested that the adsorption process could involve chemical bond formation through

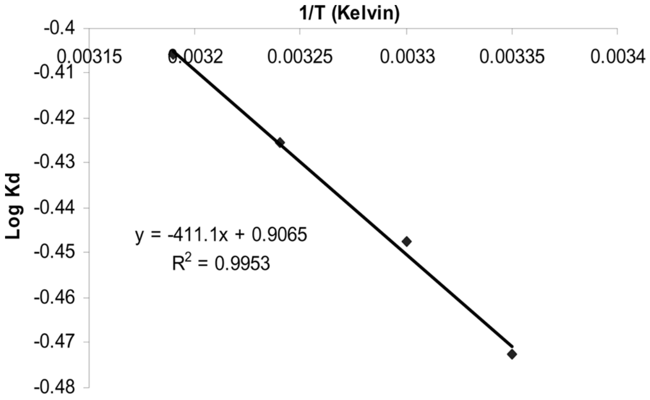


Figure 11. Log K_d Vs. 1/T graph for the sorption of Fe^{3+} onto APTS-Fe(III)-Si: time of contact: 30 min; amount of adsorbent, 100 mg; concentration of metal ion, 50 mg L^{-1}; volume of solution, 50 mL.

ion-exchange mechanism (31). Thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were determined using the following equations:

$$\Delta G^0 = -RT \ln K_d \tag{8}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

$$\log K_d = \Delta S^0/2.303R - \Delta H^0/2.303RT \tag{10}$$

where, ΔG^0 = change in free energy (kJ mol^{-1}), ΔH^0 = change in enthalpy (kJ mol^{-1}), ΔS^0 = change in entropy (kJ mol^{-1} K^{-1}), T = absolute temperature (K), R = gas constant, K_d = equilibrium constant.

When log K_d is plotted against 1/T (Fig. 11), a straight line is obtained with slope $-\Delta H^0/2.303\,R$ and the values of ΔH^0 and ΔS^0 were obtained from the slope and intercept of van't Hoff plots. The values for ΔH^0 and ΔS^0 for above plot was found out to be 7.871 kJ mol^{-1} and 0.0173 kJ $K^{-1}mol^{-1}$, respectively.

Selectivity of the Imprinted Sorbent

Cr(III) and Fe(III) ions have same charge and similar ionic radius. Therefore, Fe(III) was chosen as the competitive species with Cr(III) for comparing the competitive adsorption upon the adsorbent APTS-Fe(III)-Si. The result is illustrated in Table 1(a/b). Comparing the adsorption of

Table 1 (a). Competitive loading of Fe(III) and Cr(III)

	Metal solution (mg L^{-1})		Capacity (mg g^{-1})		D (mL g^{-1})		
Adsorbent	Fe(III)	Cr(III)	Fe(III)	Cr(III)	Fe(III)	Cr(III)	α
APTS-Fe(III)-Si	50	0	12	–	480	–	–
	50	25	11	5	440	400	1.1
	50	50	9	6.5	360	260	1.3

Table 1 (b). Competitive loading of Fe(III) and Mn(II)

	Metal solution (mg L^{-1})		Capacity (mg g^{-1})		D (mL g^{-1})		
Adsorbent	Fe(III)	Mn(III)	Fe(III)	Mn(III)	Fe(III)	Mn(III)	α
APTS-Fe(III)-Si	50	0	12.5	–	500	–	–
	50	25	11.5	2	460	160	2.8
	50	50	11.0	3	220	120	1.8

both Fe(III) and Cr(III) upon the adsorbent APTS-Fe(III)-Si, as shown in Table 1(a), no significant difference in adsorption properties was observed. The result could be attributed to the fact that since ions of similar sizes and charges possesses almost equal affinity toward the ligand, therefore, Fe(III)-imprinted adsorbent material (APTS-Fe(III)-Si) could exhibits almost equal affinity towards both Fe(III) and Cr(III). However, the higher selectivity for extraction of Fe(III) in presence of other metal ions could be attributed to the hole-size theory (32), which emphasizes upon the size of Fe(III) that exactly fits the cavity of the Fe(III)-imprinted sorbent. On the other hand, comparing the adsorption of trivalent Fe(III) and divalent Mn(II) onto the adsorbent APTS-Fe(III)-Si, as shown in Table 1(b), preferential adsorption of Fe(III) was noted. The selectivity coefficient for the adsorption of Fe(III) in the presence of both Cr(III) and Mn(II) was calculated from which it may be concluded that it is possible to selectively separate Fe(III) from a mixture of divalent cation like Mn(II). However, it may be noted that for a mixture of metal ions containing the same charge and ionic radius, higher selectivity could be favorable at low concentration of competitive metal ions. At higher concentration, competition between the metal ions plays a vital role in achieving selectivity.

Table 2. Effect of diverse foreign ions

Chelating materials ions[b]	Metalions	Conc. of metal ions/mg L^{-1}	Recovery[a], %	Recovery in the presence of mixture of diverse 20 mg L^{-1} each
APTS-Fe(III)-Si	Fe^{3+}	20	98.9	96.2
	Mn^{2+}	20	78.9	75.1
	Cr^{3+}	20	88.8	86.9
APTS-Cr(III)-Si	Fe^{3+}	20	97.5	94.1
	Mn^{2+}	20	82.4	75.2
	Cr^{3+}	20	98.3	97.7

Amount of adsorbent material, 0.1 g; time of contact, 24 h; each reading was an average of three close/concordant values.

[a] RSD factor varies between 0.31–0.42%.

[b] RSD factor varies between 0.22–5.16%.

Effect of Coexisting Alkali and Alkaline Earth Metal Ions

The analytical preconcentration procedure for trace heavy metal ions can be strongly influenced due to matrix constituents: e.g., alkali and alkaline earth elements. Therefore, the effect of matrix constituents was examined in the presence of sulphate, nitrate, chloride, NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}, which are common ionic species in natural water. A high concentration of studied species was chosen to magnify their interference effect. The results (Table 2) indicated that the coexisting ions had little effect on the overall adsorption of metal ions. The effects of anions like citrate and oxalate were also examined in case of APTS-Fe(III)-Si to discover the effect of organic species upon the recovery of Fe^{3+} only (20 mg L^{-1}). It was found that the presence of citrate and oxalate reduces the metal recovery to 76% and 72%, respectively. The effects of some other organic species are currently under investigation.

CONCLUSION

This investigation reports the preparation of two new adsorbent materials of Cr(III) and Fe(III) imprinted silica gel (APTS-Cr(III)-Si and APTS-Fe(III)-Si) using 3-aminopropyltrimethoxysilane as the surface modifying ligand. The elemental compositions of the adsorbents were evaluated using energy dispersive spectra. The metal adsorption properties in case of APTS-Fe(III)-Si follows the order $Fe^{3+} > Zn^{2+} > Cr^{3+} > Mn^{2+}$. All the adsorbent materials were efficient in the removal of both divalent as well as trivalent cations from aqueous medium. However, the preferential selectivity of the adsorbents APTS-Cr(III)-Si and APTS-Fe(III)-Si towards Cr^{3+} and Fe^{3+} removal from dilute aqueous solution in a competitive condition favors the usefulness of adsorbents in selective separation processes in solid phase extraction. Both the Langmuir and Freundlich adsorption models were compared for a number of trivalent and divalent cations for which the Langmuir model represented a better fit of experimental data. The mean energy of adsorption (E) for the sorption of Zn^{2+} upon APTS-Cr(III)-Si was evaluated using D-R isotherm and found to be 12.609, indicating a possible ion-exchange process to operate. Experimental data obtained in a competitive condition for the adsorption of Fe^{3+} upon APTS-Fe(III)-Si indicated the efficiency and selectivity of the adsorbent in the separation of the trivalent cation from a mixture of a divalent cation. Alkali and alkaline earth metal ions had little effect upon the adsorption characteristics in aqueous solution. The analytical results obtained in this investigation suggested the future potential applications of developed adsorbent materials in solid phase extraction and separation processes.

ACKNOWLEDGEMENT

RKD is thankful to UGC, New Delhi, for research grant.

REFERENCES

1. Gode, F.; Pehlivan, E. (2007) Sorption of Cr(III) onto chelating b-DAEG-sporopollenin and CEP-sporopollenin resins. *Biores. Technol.*, *98*: 904–911.
2. Ghimire, K.N.; Inoue, K.; Hayashida, Ohto T. (2007) Adsorptive separation of metallic pollutants onto waste sea weeds *PorphyraYezoensis*, and *Ulva Japonila*. *Sep. Sci. Technol.*, *42*: 2003–2018.
3. Bishnoi, N.R.; Bajaj, M.; Sharma, N.; Gupta, A. (2004) Adsorption of Cr(VI) on activated rice husk carbon and activated alumina. *Biores. Technol.*, *91*: 305–307.
4. Kara, D.; Alkan, M. (2001) Selective preconcentration, separation and speciation of ferric iron in different samples using N, N′-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane. *Talanta*, *55*: 415–423.
5. Jacques, R.A.; Bernardi, R.; Caovila, M.; Lima, E.C.; Pavan, F.A.; Vaghetti, J.C.P.; Airoldi, C. (2007) Removal of Cu(II), Fe(III) and Cr(III) from aqueous solution by aniline grafted silica gel. *Sep. Sci. Technol.*, *42*: 591–609.
6. Nicholls, I.A.; Rosengren, J.P. (2001) Molecular imprinting of surfaces. *Bioseparation*, *10*: 301–305.

7. Chang, X.; Jiang, N.; Zheng, H.; He, Q.; Hu, Z.; Zhai, Y.; Cui, Y. (2007) Solid phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique. *Talanta*, *71*: 38–43.
8. Skrdla, P.J.; Shnayderman, M.; Wright, L.; O'Brien, T.P. (2006) GC-MS study of the formation of alkoxysilanes from a sol-gel precursor in a hydrophobic solution: A potential new route to hybrid molecularly imprinted polymers. *J. Non-Cryst. Solids*, *352*: 3302–3309.
9. Tóth, B.; Pap, T.; Horvath, V.; Horvai, G. (2007) Which molecularly imprinted polymer is better? *Anal. Chim. Acta*, *591*: 17–21.
10. Bae, S.Y.; Southard, G.L.; Murray, G.M. (1999) Molecularly imprinted ion-exchange resin for purification, preconcentration and determination of UO_2^{2+} by spectrophotometry and plasma spectrometry. *Anal. Chim. Acta*, *397*: 173–181.
11. Garcia, R.; Pinel, C.; Madic, C.; Lemaire, M. (1998) Ionic imprinting effect in gadolinium/lanthanum separation. *Tetrahedron Lett.*, *39*: 8651–8654.
12. Yang, Y.; Long, Y.; Cao, Q.; Li, K.; Liu, F. (2008) Molecularly imprinted polymer using β-cyclodextrin as functional monomer for the efficient recognition of bilirubin. *Anal. Chim. Acta*, *606*: 92–97.
13. Ersöz, A.; Say, R.; Denizli, A. (2004) Ni(II) ion-imprinted solid phase extraction and preconcentration in aqueous solutions by packed-bed columns. *Anal. Chim. Acta*, *502*: 91–97.
14. Daniel, S.; Gladis, J. M.; Prasad Rao, T. (2003) Synthesis of imprinted polymer material with palladium ion nanopores and its analytical application. *Anal. Chim. Acta*, *488*: 173–182.
15. Büyüktiryaki, S.; Say, R.; Ersöz, A.; Birlik, E.; Denizli, A. (2005) Selective preconcentration of thorium in the presence of UO_2^{2+}, Ce^{3+}, and La^{3+} using Th(IV) imprinted polymer. *Talanta*, *67*: 640–645.
16. Hatay, I.; Gup, R.; Ersöz, M. (2008) Silica gel functionalized with 4-phenylacetophenone 4-aminobenzoylhydrazone: synthesis of a new chelating matrix and its application as metal ion collector. *J. Hazardous Mater.*, *150*: 546–553.
17. Dey, R.K.; Airoldi, C. (2008) Designed pendant chain covalently bonded to silica gel for cation removal. *J. Hazard. Mater.*, *156*: 95–101.
18. Jal, P.K.; Patel, S.; Mishra, B.K. (2004) Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta*, *62*: 1005–1028.
19. Guardia, L.; Badía-Laíño, R.; Díaz-García, M.E.; Ania, C.O.; Parra, J.B. (2008) Role of surface adsorption and porosity features in the molecular recognition ability of imprinted sol-gels. *Biosens. Bioelectron.*, *23*: 1101–1108.
20. Olwill, A.; Hughes, H.; Riordain, M.O'.; McLoughlin, P. (2004) The use of molecularly imprinted sol-gels in pharmaceutical separations. *Biosens. Bioelectron.*, *20*: 1045–1050.
21. Kunitake, T.; Lee, S.-W. (2004) Molecularly imprinting in ultrathin titania gel films via surface sol-gel process. *Anal. Chim. Acta*, *504*: 1–6.
22. Komiyama, M.; Takeuchi, T.; Mukawa, T.; Asanuma, H.. (2002) *Molecular imprinting: From fundamentals to applications*; Wiley-VCH: New York.

23. Fan, Z. (2006) Hg(II)-imprinted thiol-functionalized mesoporous sorbent micro-column preconcentration of trace mercury and determination by inductively coupled plasma optical emission spectrometry. *Talanta*, *70*: 1164–1169.
24. Zhang, N.; Suleiman, J.S.; He, M.; Hu, B. (2008) Chromium (III)-imprinted silica gel for speciation analysis of chromium in environmental water samples with ICP-MS detection. *Talanta*, *75*: 536–543.
25. Prado, A.G.S.; Airoldi, C. (2001) The pesticide 3-(3,4-dichlorophenyl)-1, 1-dimethyl urea (Diuron) immobilized on silica gel surface. *J. Colloid Interface Sci.*, *236*: 161–165.
26. Prado, A.G.S.; Tosta, A.H.; Airoldi, C. (2004) Adsorption, separation and thermochemical data on the herbicide picloram anchored on silica gel and its cation interaction behavior. *J. Colloid. Interface Sci.*, *269*: 259–264.
27. Ünlü, N.; Ersöz, M. (2006) Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. *J. Hazard. Mater.*, *136*: 272–280.
28. Gad, H.M.H.; Awwad, N.S. (2007) Factors affecting on the sorption/desorption of Eu(III) using activated carbon. *Sep. Sci. Technol.*, *42*: 3657–3680.
29. Dey, R.K.; Jha, U.; Singh, A.C.; Samal, S.; Ray, A.R. (2006) Extraction of metal ions using chemically modified silica gel covalently bonded with 4,4′-Diaminodiphenylether and 4,4′-Diaminodiphenylsulfone-salicylaldehyde Schiff bases. *Anal. Sci.*, *22*: 1105–1110.
30. Khalid, N.; Ali, S.; Iqbal, A.; Pervez, S. (2007) Sorption potential of styrene-divinylbenzene copolymer beads for the decontamination of lead from aqueous media. *Sep. Sci. Technol.*, *42*: 203–222.
31. Ghazy, S.E.; Ragab, A.H. (2007) Removal of lead from water samples by sorption onto powdered limestone. *Sep. Sci. Technol.*, *42*: 653–667.
32. Fang, G.-Z., Tan, J.; Yan, X.-P. (2005) An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol-gel process for selective solid-phase extraction of cadmium (II). *Anal. Chem.*, *77*: 1734–1739.