Preparation of Silica-4-(2-pyridylazo) Resorcinol Chelator for Solid Phase Extraction of Transition Metals from Groundwater

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Summary: The determination of trace heavy metals in environmental samples entails reliable sample preparation method to improve instrument detectability or minimize matrices effect. Solid phase extraction (SPE) using metal chelators is an attractive approach for the selective extraction of trace metals from aqueous media in various applications. In this work, a selective chelating resin was prepared by chemical attachment of the chelating moiety, 4-(2-pyridylazo)resorcinol(PAR) onto silica gel using an eco-friendly chemical transformation. The successfulness of the chemical modification was confirmed by Fourier transform infrared (FTIR), elemental analysis (EA) and scanning electron microscopy (SEM). The separation/preconcentration conditions of the resin including exchange capacity, effect of pH, adsorption kinetics and isotherm for metal extraction, were investigated.At optimum conditions, the resin loading capacity for the metals; Cu^{2+}, Ni^{2+} and Mn^{2+}were 0.121, 0.132 and 0.124 mmolg^{-1}in that order. The material performance as SPE sorbent for trace metals has been assessed usingCu^{2+}, Ni^{2+} and Mn^{2+} in certified reference natural water sample, and real groundwater samples from Almedinah AlMunawarah. The accurate and precise results verify the resin appropriateness for matrix removal/ preconcentration prior to the analysis of heavy metals from this type of matrices.

Keywords: Solid phase extraction, Silica gel PAR, Chelating resin, Heavy/trace metals, Groundwater, AlMedinah AlMunawarh.

Introduction

The environmental pollution with toxic heavy metals is one of the severe challenges facing modern societies everywhere. Although the sources of heavy metals in environment could be natural, various human activities such as rapid industrialization, urbanization and other anthropogenic practices have augmented their concentrations in air, water and soil [1, 2]. The release/emission of heavy metals in the environment is regulated/restricted worldwide because of their potential toxicity, bio accumulative tendency and non-biodegradable nature [3, 4]. Therefore, the accurate determination of heavy metals' concentration in water and environment has become quite essential for reliable environmental assessment [5-7]. The progress in various technologies has enabled the development of many sophisticated instruments for the selective analysis of trace metals. Today, many atomic spectroscopic instruments particularly graphite furnace atomic absorption spectrometry (GFAA) and inductively coupled plasma mass spectrometry (ICP-MS) enable the quantification of many metals at ppt level or lower [8-10]. However, the direct analysis of metal ions at trace/ultra trace levels by these analytical techniques is rather limited; mainly due to the matrix interference that can significantly deteriorate the accuracy and precision of the analytical method. Hence, a preceding preconcentration procedure is required to minimize matrix effects or improve detection limit of the analytical method [11-13].

There are many methods for the preconcentration/extraction of heavy metals such as solvent extraction, coprecipitation, electrodeposition, cloud point extraction, membrane filtration and solid phase extraction [14]. Among the various preconcentration methods, solid-phase extraction with metal chelators has been proven to be an effective method due to the attained high recovery, rapid processing, reduced cost, technical simplicity, lower consumption for harmful organic solvents than liquid–liquid extraction, in addition to the feasibility to synthesize chelating resins for specific applications [14, 15]

4-(2-Pyridylazo) resorcinol (PAR) is aphenolic type complexing analytical reagent capable to form stable complexes with many metals. It behaves as a tetradentate or a bidentate ligand with many transition metal cations. PAR and the other 2-pyridylazo derivatives have been used extensively for many analytical purposes since the early 1960s. They are excellent metallochromic indicators and very useful chromogenic agents for the quantification of over 50 elements at trace levels [16].

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PAR and its derivatives have been exploited extensively as chelating moieties in the synthesis of metal extracting materials by various methods including cross-linked polymerization with styrene monomers [17], physical impregnation onto various polymer substrates such as Amberlite XAD-4, XAD-1180XAD-7 and Dowex ion-exchangers [18, 19], and chemical binding onto polymers [20], silica gel [21] and nanostructured substrates [22, 23]. Among the various synthetic methods for metal chelators, the covalent chemical attachment of chelating agents onto the surface of porous solid substrates; 'post synthesis modification', is a favorable approach due to the availability of wide variety of high surface area and stable materials. Porous silica and glass substrates are much advantageous supports for resin synthesis by post synthesis modification, due to their characteristics large surface area, reactivity, mechanical stability, and the availability of many versatile chemical modification methods [24]. The chemical attachment for PAR onto silica is typically attained making use of Mannich reaction which involves silylation reaction with aminosilane flowed by amino methylation for PAR with aldehyde [21, 25]. Although Mannich reaction can be practiced with simple reaction setup and affordable reagents, it is limited by the lack of selectivity and competitive aldol reactions [26].

Recently, AlSuhaimi and McCready have developed a rapid and eco-friendly chemical transformation for the chemical immobilisation of oxines (e.g., 8-Hydroxyquinoline) moieties onto silica surface [27]. In this work, it was proposed that the method could be adopted for the covalent chemical coupling of chelating agents empathy for diazo coupling. Herein the method was employed to attach PAR moiety onto silica surface. The efficiency of the PAR-Silica cheating resin as SPE material for extraction/precencentration of heavy/transition metals has been investigated using Mn, Cu and Ni (as model ions to prove concept) from groundwater matrix.

Experimental

Chemical reagents

All chemicals used in the synthesis of chelator throughout analytical process were of analytical grade. The solid substrate silica gel (mesh size 70–230, of surface area 300 m^3/g) and sodium nitrite ($NaNO_2$) were obtained from LobalCheme (Gujarat, India), silylation coupler (p-Aminophenoxy)propyltrimethoxysilane was purchased from Fluorochem Ltd.(Hadfield, UK). The mineral acids; hydrochloric acid, nitric acid, anhydrous toluene and ethanol were ordered from Scharlau (Barcelona, Spain). The standard metal solutions were prepared from single element standard solutions of each metal ion (1 mg/ml; Across Organics, Geel, Belgium). The natural water reference samples, NIST SRM 1643f, was purchased from National Institute of Standards and Technology (Gaithersburg, MD, USA). Ammonium acetate, aqueous ammonium hydroxide solution which were used for pH adjust of solutions were obtained from Fisher Scientific (Waltham, MA, USA). The buffer solutions were passed through a glass column packed with the chelating resin; Chelex-100 (BioRad, CA, USA) to remove any trace metals residual. All solution preparations as well as washing were performed using high purity Millipore water.

All plastic/glassware's used in all work were precleared with water, washed thoroughly using Fairy® liquid detergent and soaked overnight in 10% HNO_3, and rinsed carefully with high-purity water immediately before use.

Instrumentation, apparatus and measurements

Instrumentation, apparatus and measurements

The elemental analysis was performed using a 2400 CHNS/O Elemental Analyzer, Perkin Elmer (Waltham, MA, USA) and FTIR spectra were obtained using a Fourier transform infrared instrument, Thermo NICOLET 380 FTIR with aattenuated total reflection (ATR) accessory (Thermo-Fisher Scientific, Waltham, MA, U.S.A). The morphology of resin surface elemental composition were inspected by a scanning electron microscope (SEM ssx 550, Shimadzu, Kyoto, Japan). The measurement of solutions pH was taken with a Basis pH meter, Denver Instrument Company (Bohemia, NY, USA). A 12-way standard SPE manifold (Ato Science, China) operated with Welch Vacuum - Gardner Denver vacuum pump model WOB-L Pump 2534 (Mount Prospect, IL, USA) was used for the solid-phase extraction procedure. All metal ions analysis were performed using inductively coupled plasma mass spectrometer, ICP-MS 7500 series, Agilent Technologies (Santa Clara, CA, USA) at standard operating conditions stated by manufacturer.

Preparation of Silica-PAR chelator

The resin was prepared using a modified method adapted previously in our laboratory for covalent chemical attachment of 8-hydroxyquiniline onto silica surfaces [27]. In summary, 10 g of silica powder heated in 10% HNO_3 solution (70° C)for 45 min to activate the surface, then filtered, washed thoroughly with distilled water, and oven dried at 120◦ C for 4 hrs. The silica beads were left to cool to room temperature then silanized with a 2.5% (p-aminophenoxypropyl)trimethoxysilane solution in anhydrous toluene for 5 hrs. After that, the salinized silica beads were filtered, rinsed with toluene and ethanol, and placed into an oven at 110 °C to dry for 12 hrs to guarantee complete curing. The cured phenoxyamine-silica powder was cooled at room temperature and treated with 2% sodium nitrite in 2 M HCl at 0-4°C for 45mintto form diazonium salt-silica intermediate which was rapidly filtered, washed with three 10 ml portions of cold distilled water and 10 ethanol. The resin was then added to 50 ml aqueous solution containing 1 g of PAR and stirred for about5hrs for complete diazocoupling that can be observed from the appearance of deep red coloring reaction system. The resulting resin was filtered, washed thoroughly with ethanol and water to remove any unreacted PAR molecules. The resin was dried at 75° C for 8hrs, then allowed to cool to room temperature and stored in a desiccator until later use. The synthesis steps are shown in the reaction scheme (Fig. 1).

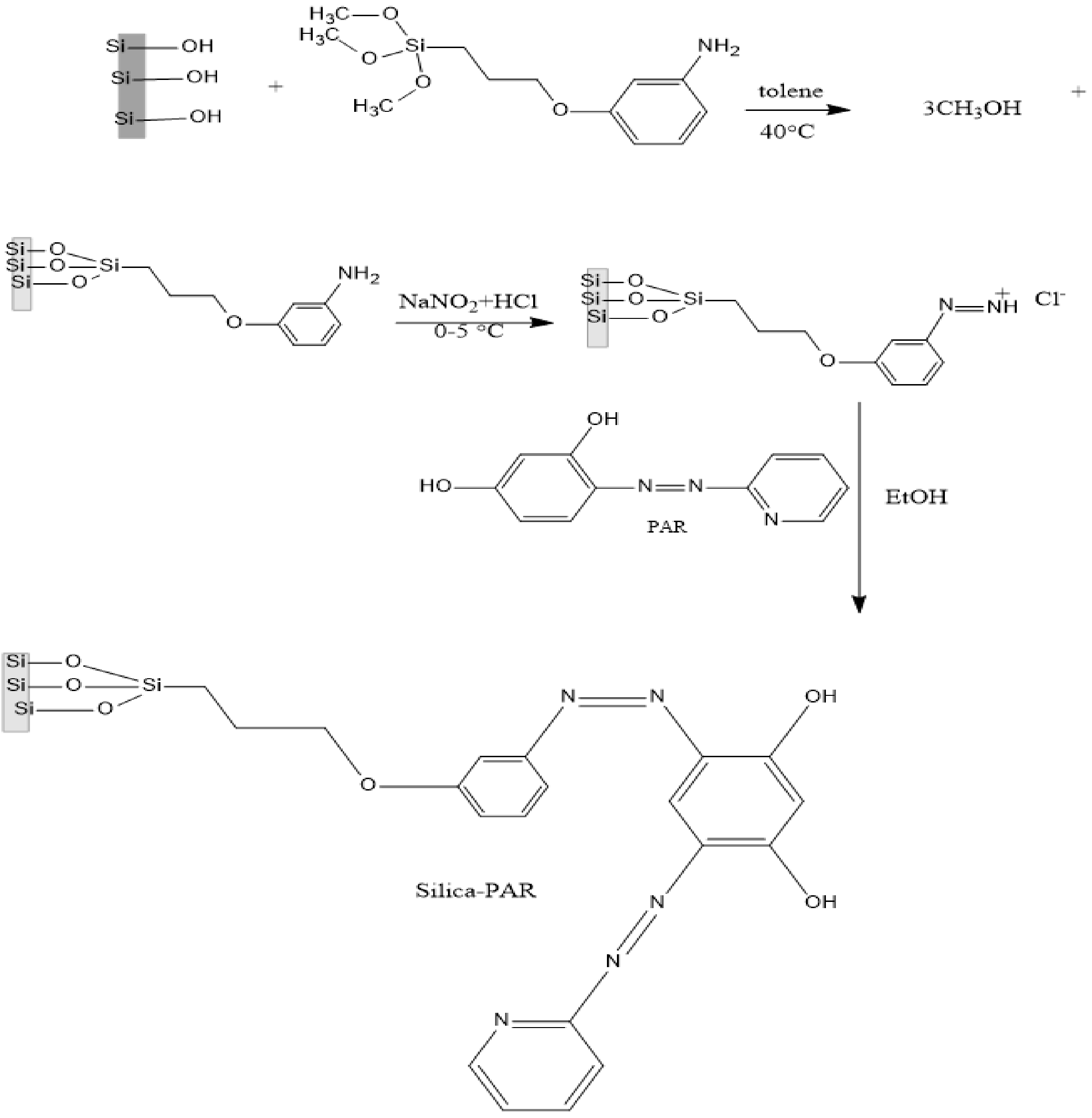


Fig. 1: The reaction sequence for the synthesis of silica –PAR chelator.

Extraction studies

Batch extraction experiments

The most significant parameters influencing chelator efficiency to chelate ions from aqueous solutions; pH, loading capacity and kinetic of sorption were estimated using batch method reported in the literature [28, 29]. In short, 50 mg portions of the dry silica-PAR chelator were added to 10 mL of metal solutions containing the anticipated concentrations (for each test) of the examined metal ions and stirred at room temperature. After that, the resin was centrifuged at 3500 rpm for 5 min to separate resin from solution. The ions concentration remained in the supernatant was analyzed with ICP-MS against the initial concentrations. All experiments were performed in triplicate measurements.

Solid phase extraction experiments

For the solid-phase extraction process, 200–300 mg portions of the silica-PAR chelating resin were packed into empty SPE cartridges (Biotage AB. Uppsala, Sweden) to make discs of 5–10 mm height, sandwiched between two porous Teflon filters. The SPE experiments were performed using standard SPE manifold and executed in the following sequence. The SPE cartridges were firstly conditioned with 10 ml of buffer solution passing at 0.5 mL/min, and then the samples were loaded at 0.5 ml/min. After that cartridges were flushed with 5 ml water to eliminate the non-chelated metal ions and matrices. The sequestered metal ions were then eluted with 5 ml of 2 M nitric acid at 2 ml/min into 15 ml PTFE sample tubes for subsequent an offline ICP-MS quantification. Similar procedure was employed for all standards and certified water and real groundwater samples.

Groundwater samples collection and analysis

Groundwater samples were collected from 4 operating narrow mouth wells near Ambar Ali industrial zone (10 km to the west of AlMedinah AlMunararh) in 1 L acid washed polyethylene bottles. The samples were filtered in site, acidified with drops of HNO_3, then transported into ice boxes to the laboratory and processed (prepared) using SPE manifold as detailed in SPE experiments.

Results and Discussion

Resin synthesis and characterization

The chemical modification adapted in this work for the covalent attachment of PAR chelating agent onto silica surface is schematically presented in Fig. 1. Briefly, the silane coupler, 3-aminphenoxy-propyltrimethoxysilane was used to anchor aryl amine groups onto the silica surface via the usual silylation reaction in dry toluene. Subsequently, the amino functional groups were converted into silica-diazouniun salt intermediate to allow diazotization coupling of PAR moieties. The successfulness of synthesis can be evidenced optically with naked eye from the appearance of the eminent deep red color of the azo dye. The obtained resin has been characterized using FTIR, CHN and SEM.

FTIR

FTIR spectra is a useful technique to distinguish the chemical structure of resins by identification of certain functional groups. Commonly, the FTIR spectra of the modified substrate are compared with that of pure one. Attenuated Total Reflectance (ATR) is more adequate method for the surface analysis of powdered samples than traditional infrared analysis with KBr. The ATRFTIR spectra of plain and modified silica powder are presented in Fig. 2. Obviously, there are three notable broad peaks observed at 1050, 954 and 766 cm^{-1} in both samples confirming the existence of the silanol groups; Si-O-Si and S-OH. Apparently, the intensities of these bands have diminished in the modified silica due to the coverage of some of the silanol groups by the anchored PAR moieties. The presence of the anchored PAR moieties can be demonstrated from the four bands at 2922, 2852, 1745 and 1465cm^{-1} which are assigned for the CH_2 C=C (aromatic) and C-O functional groups correspondingly (Fig. 2b). The reason that the intensities of IR bands originate from the attached organic moieties usually appear relatively weak because the mass of the bonded chelators in comparison to the bulk mass of silica is quite low [29].

Elemental Analysis

The comparison of theoretical C/N ratio with that obtained from CHN elemental analysis is an appropriate method to trace the functionalization process. As demonstrated in Table-1, the C/N ratio computed (estimated) from the formula weight was about 3.43, and that found from the CHN examination was 3.37. The insignificant difference between two ratios is anticipated, because the yield of such reactions is not expected to reach 100%. Commonly, and the number of methoxy groups in silane coupler that hydrolyzed and involved in the reaction cannot be estimated precisely. However, the matched ratios confirm the addition of PAR moieties to the silica surface.

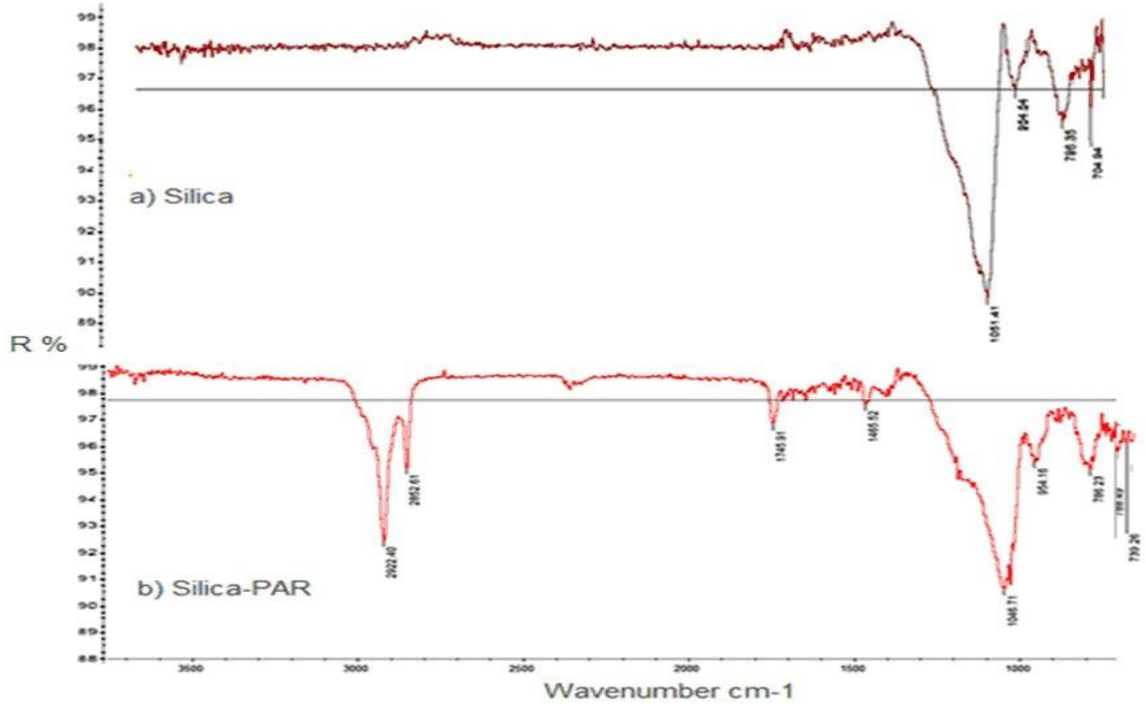


Fig. 2: ATR-FTIR for (a) plain silica and (b) Silica-PAR chelator.

Table-1: Comparison of C/N ratio of Si-PAR chelating resin.

	Element theoretical F. Wt calculated (g/M)	Mass obtained with CHN analysis (mg)
C	**240**	**2.57**
N	**70**	**0. 75**
Ratio C/N	**3.43**	**3.37**

SEM-EDX

In a scanning electron microscope (SEM) test, a beam of electrons is focused onto sample substrate to produces images revealing detailed surface topographic features. The technique is a useful tool to inspect resin surface topography and also to identify major elemental composition [29-31].The micrographs (Fig. 3) displays the SEM images of the bare silica gel (image A) and PAR-Silica resin, (image B) show obvious changes in the surface topography of silica due to the immobilization of PAR. Meanwhile the surface of plain silica appeared smooth and uniform, the surface of silica-PAR resin beads seemed rough covered with high density microstructures. This indicates that PAR moieties have been grafted onto silica surface. Electron microscopy with energy dispersive X- ray analysis (SEM/EDX) also a convenient tool to confirm the functionalization by the identification of elemental composition substrate surface. Fig. 4 show the EDX spectrum and the elemental composition of bare silica and the modified. The presence of carbon (3.4 %) proves the success of PAR immobilization. However, EDX for metal loaded resin showed weak peaks with metal ratios around 0.03-0.04 % because the surface scanned for signal acquisition only 20 µm^2 .

Study of pH effect

The pH and ionic strength of solution have remarkable influence on the extent of complexation, which regulates the fraction of the retained metals by the chelator [32]. Typically, a plot of pH versus recovery percentages is adequate tool to evaluate pH effect on metal sorption by chelating resins.

Herein, the impact of pH of 0.2 M ammonium acetate solution on the recovered percentage of the tested metal ions; Cu^{+2}, Ni^{+2} and Mn^{+2} was investigated in the range 2-8. It is clear from the results presented in Fig. 5 that the virtual amount of metal sequestered by resin increases as the solution shifted from acidic to basic medium. The optimum pH values for the extraction of studied metal ions were ranged between pH5 and pH7 (Fig. 5). At this pH, the retrieval values were 89 % for Ni^{+2}, 96% for Mn^{+2} and 102% for Cu^{+2}.

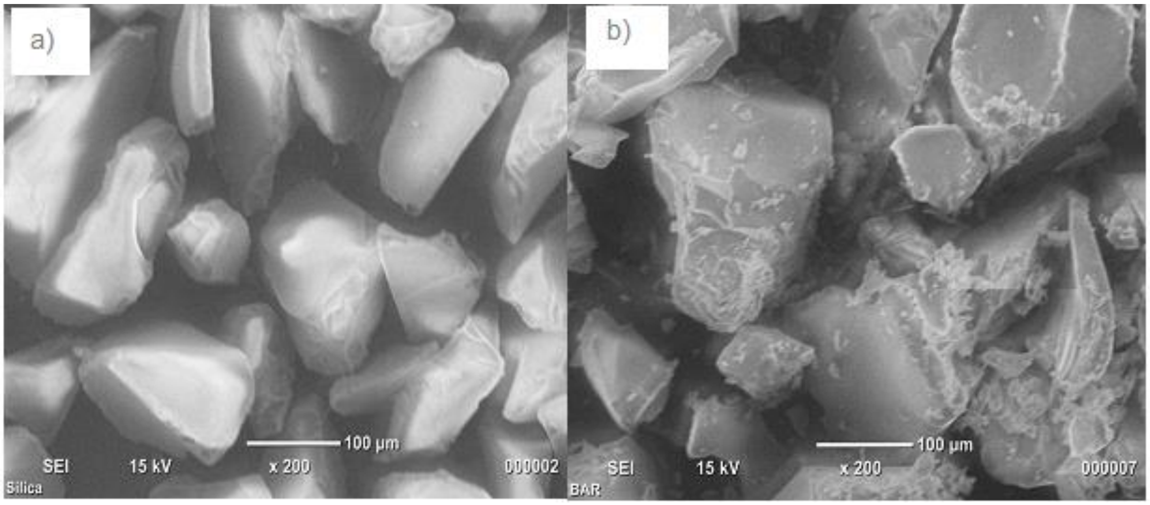
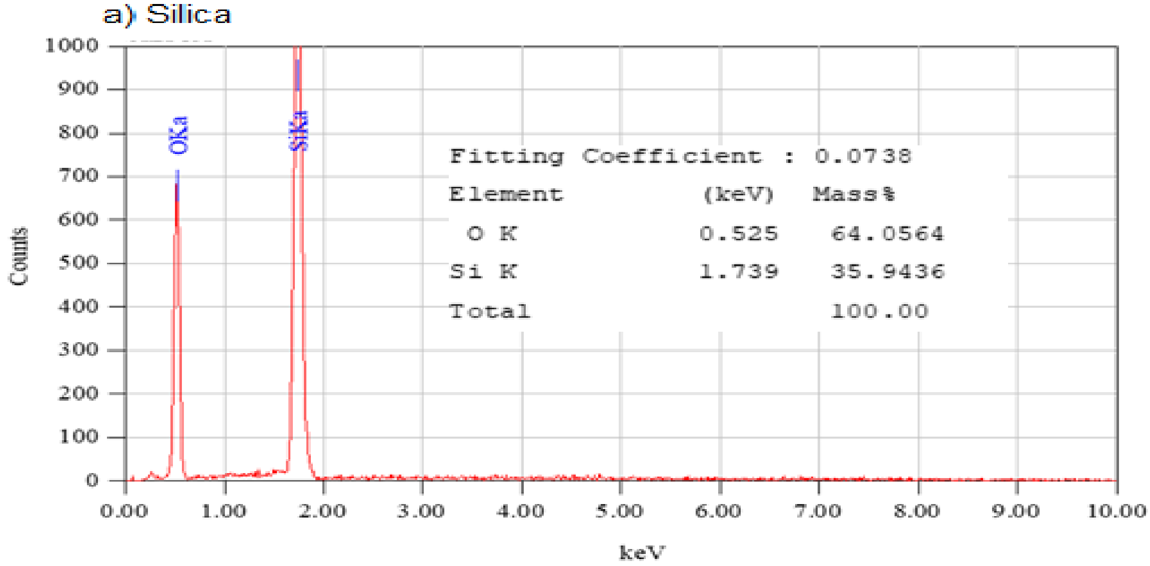
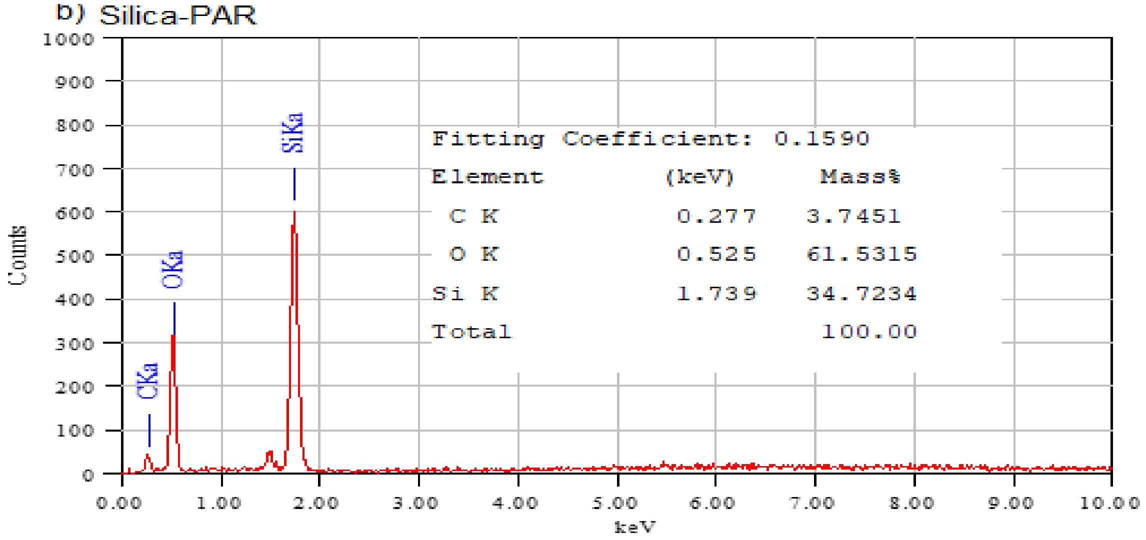


Fig. 3: SEM immages for (a) plain silac and (b).silica-PAR resin.



Fitting Coefficient : 0.0738

Element	(keV)	Mass%
O K	0.525	64.0564
Si K	1.739	35.9436
Total		100.00



Fitting Coefficient: 0.1590

Element	(keV)	Mass%
C K	0.277	3.7451
O K	0.525	61.5315
Si K	1.739	34.7234
Total		100.00

Fig. 4: EDX scan and elemental composition of a) plain silica and b) silica PAR resin.

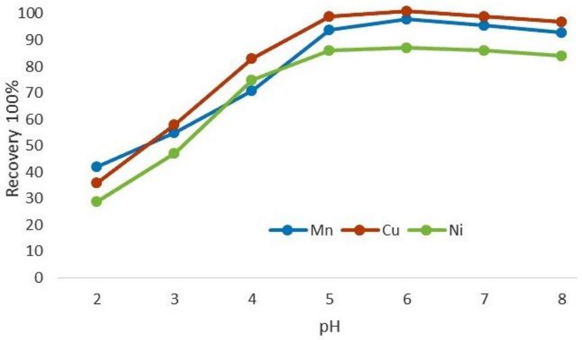


Fig. 5: pH effect on metal extraction by silica-PAR chelator.

It is believed that the sorption of metal ions on chelators take place through complexation by the active groups and this process is a pH dependent. At certain pH values, metal ion starts to replace hydronium ions (H^+) on the resin and the competence reaches maximum rate at pH value at which all ion exchange sites participate in the reaction, and the functional groups able to form stable chelate rings with metal cations [33, 34]. However, as the medium shift to be alkaline the ions prefer to form hydroxides (and might be precipitated) rather than complexed with the chelator, therefore the adsorption start to decrease.

Sorption capacity study

The sorption capacity (SC) is a valuable measure to estimate the required mass of chelating resin to preconcentrate the targeted ions from a given solution with quantitative fraction. The capacity study was determined for Cu^{2+}, Mn^{2+} and Ni^{2+}following Nelms el. al.' batch procedure [28] by the addition of 50 mg portions of the dry resin to 10 ml solution contains 100mg/l of each metal prepared in ammonium acetate solution (1.0 M, pH 6).

The estimated sorption capacity for the three ions were 0.132, 0.124 and 0.121mMg^{-1} for Cu^{2+}, $Mn^{2+}$and Ni^{2+}individually**.** These SC values are quite comparable with other silica based chelators of similar particle size [27, 28]. However, higher value (0.276 mmolg^{-1} of Hg(II)), has been obtained using SiO_2nanoparticle modified with PAR [25]. This difference is attributed to the large surface area of the nanostructured particles.

Adsorption isotherm

There are several adsorption isotherm models designed to evaluate the capacity of the adsorbent and adsorbate. Ordinarily, the ratio between the quantity adsorbed and the amounts remain in solution at stable temperature at equilibrium, is employed to define isotherm [35] In this study, the adsorption isotherm study was conducted at room temperature using 50 mg of the chelating resin mixed with different concentrations of the tested ions in the rang 0.2-1.5 mg/l (prepared in ammonium acetate buffer at pH 6). Samples were mechanically shaken then centrifuged and the remained metals in the supernatant were analyzed by the ICP-MS. As shown in Fig. 6, the amount of the extracted ions by the resin increases steadily at low concentrations but the extraction rate was reached a plateau statue at high concentration. The curve approach optimum values near 1mg/l. At this value, the reactive chelating sites on the resin are saturated by the adsorbed metal ions. The shape of grave designates a monolayer adsorption pattern.

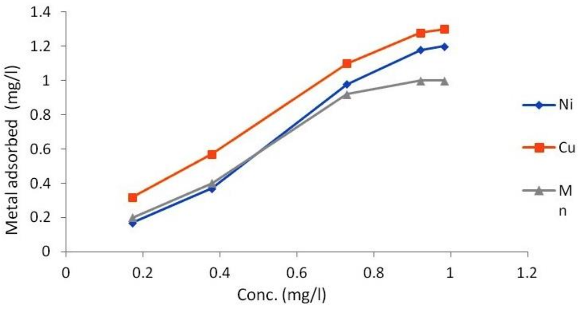


Fig. 6: Isotherm for the extraction of metals silica-RAR chelator.

Kinetic of metal sorption

Studying kinetic of metal sorption is quite significant in SPE because the effectiveness of the sorption process of analytes by the chelator from aqueous solutions governed by the sorption dynamics [36].The sorption of the examined metal ions carried out with portions of 50 mg of resins added to 50 ml of a metal ion solution containing 5 mg/L and agitated mechanically for different time intervals (2, 5, 10, 15, 30and 60 min). The concentration of metal ions remained in the supernatant solution was determined by ICP-MS after an appropriate dilution. The results are presented as recovery percentage versus time in Fig. 7. Observably, the adsorption of metal ions often increased as a function of shaking time [37]. An equilibration time of 10 min seemed to be sufficient for the chelating resin to retain about 60% of the all ions. Meanwhile, at an equilibration time of 15 min the resin is capable to uptake more than 90% of Cu^{2+}, $Mn^{2+}$and 80%of Ni^{2+}. This finding however is comparable with previous results reported for silica-oxin chelating resin [31].

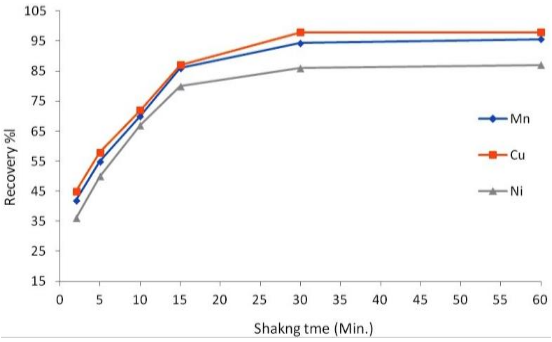


Fig. 7: Kinetics of metal sorption by silica-PAR chelator.

Kinetics models are used to examine the rate of the adsorption process and potential rate controlling step. In the present work, the kinetic data have been analyzed by using pseudo-second-order model.

$$t/q_t=1/\ k_2q_e^2 + t/q_e \qquad (1)$$

where, q_e is the amount of metal adsorbed at equilibrium per unit weight of sorbent (mg·g–1); q_t is the amount of metal adsorbed at any time (mg^{-1}) and h ($k_2q_e^2$) is the initial sorption rate (mg/ g min) and k_2 is the rate constant of pseudo-second order kinetics (g/mg min). The slope and intercept of plot of t/q_t against (t) were used to determine q_e and k_2 respectively [38]

The kinetics of metal adsorption on silica-PAR chelator were better described by pseudo-second order kinetic model (Fig. 8). The linearity of the plot also showed the applicability of the pseudo-second order kinetic model, which has average regression coefficient of R_2^2 (0.9982, for Cu and Mn, and of 0.994 for Ni.). The value of $q_{e(exp)}$ obtained with the pseudo-second order kinetic model was close to $q_{e(cal)}$ (0.463 mg/g for Ni, 0.556 mg/g for Cu and 0.554 mg/g for Mn)./g for Ni, 0.556 mg/g for Cu and 0.554 mg/g for Mn).

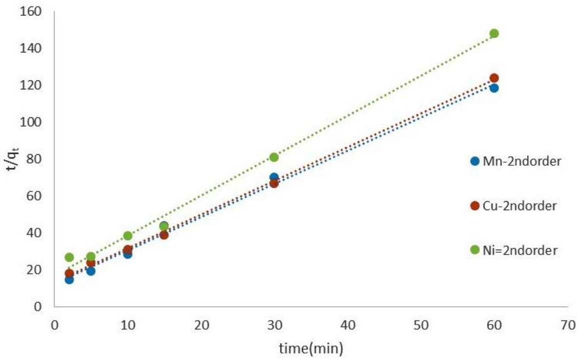


Fig. 8: Kinetics of metals adsorption on silica-PAR chelator.

Method validation: Analysis of reference natural water

Method validation has a considerable importance in trace analysis and very essential to verify the accuracy and precision of the proposed method. For this reason, natural certified reference water 1643f was processed using the developed SPE manifold according to the SPE protocol detailed in the experimental work, prior to the determination of the investigated ions by ICPMS. The determined concentrations of the analyzed metal ions in reference natural water were well compared with the certified values (Table-2). The RSD% of the method was lower than 4.0 %.

Table-2: Analysis of certified reference materials (Natural water, 1643f after SPE with Silica-PAR resin (Mean concentration ± RSD in µg/l, n = 3).

Certified	Measured (Recovery %)	Metals
37.14± 0.602	35.72 ± 0.21 (96.10%)	Mn
59.8 ± 1.4	53.17± 0.02 (89.83%)	Ni
21.66 ± 0.71	22.24± 0.08 (102.32%)	Cu

Method application: The analysis of groundwater samples

To test resin applicability to extract trace metals from real samples, the developed method was used for the determination of trace metals in groundwater real samples (TDS 634–820 mg/l) collected from four narrow mouth wells (with depth 80-160 m) in AlMedinah Almunawwara, Abar Ali industrial zone. The samples were buffered offline with 0.2 M ammonium acetate buffer and treated following the SPE protocol, and the concentrations of the eluted metal ions were quantified with ICPMS. The results are presented in Table-3. The recoveries as estimated from spiking groundwater samples with 10 µg/l were in the range of 96–103%, 95-99 % and 81-90 % for Cu^{2+}, $Mn^{2+}$and Ni^{2+}respectively. Thus, the resin is a useful sorbent material for the development of SPE sample pretreatment procedure for the simultaneous analysis of heavy/transition elements in groundwater and other environmental real samples.

Resin stability and reusability

The synthesized chelating resin exhibited excellent stability when used as packed chelator in SPE cartridges. It has been used for more than 50

SPE cycles, using metal solutions and 1M nitric acid eluent solution, without apparent drop in its sorption capacity. The resin also suspended into acidic (1 M nitric acid) and basic (M ammonium hydroxide pH 9) solutions to evaluate its stability in harsh environment. Although no change was observed even in 3 M nitric acid, yellow coloration was noticeable when the resin was agitated in basic media (pH 11) for 3 hours. The yellow coloration indicates that the boding of chelator moieties to the support might be cleavage or due to the partial dissolution of silica in alkaline solutions. However, the resin performance did not change during storing for more than one year.

Table-3: Metal concentrations in groundwater samples after SPE with silica-PAR resin (mean ±RSD µg/l, n=3).

	Meta ions		
Sampling sites	**Mn**	**Cu**	**Ni**
GW1 ▪(3)	**8.56 ± 1.27**	**31.17±3.08**	**3.83 ± 1.61**
GW1 spiked	**18.74 ± 1.31**	**39.56±3.12**	**12.32 ± 2.27**
Recovery %	**102**	**95**	**82**
GW2 (3)	**9.20 ± 2.02**	**23.06±3.64**	**2.32 ± 0.87**
GW2 spiked	**18.83 ± 1.41**	**32.71±2.82**	**11.87 ± 1.73**
Recovery %	**96**	**98**	**81**
GW3 (3)	**8.52 ± 1.68**	**21.68±2.26**	**3.24 ± 1.08**
GW3 spiked	**18.82 ± 1.27**	**31.47±2.45**	**12.93 ± 2.07**
Recovery %	**103**	**99**	**90**
GW4 (3)	**9.97 ± 2.17**	**23.72±2.25**	**2.63 ± 1.14**
GW4 spiked	**19.58 ± 2.13**	**32.81±3.46**	**12.17 ± 2.91**
Recovery %	**96**	**96**	**82**

▪ (replicates), the symbols GW for groundwater. To all spiked samples 10 µg/l of ion added

Conclusion

The work reported in this article has demonstrated the feasibility of the adapted chemical transformation to graft silica surface with PAR chelating agent and similar moieties. The synthesized chelating resin has demonstrated an adequate performance as SPE material for the extraction/preconcentration of Cu^{2+}, Ni^{2+} and Mn^{2+}ions from water samples at the examined conditions. The chelator exhibited high affinity, good stability and proved to be convenience for the studied metal ions. The efficiency of the resin has been verified by its application for sample pretreatment by SPE standard manifold prior the analysis of trace metals from groundwater CRM and real samples by ICPMS.

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