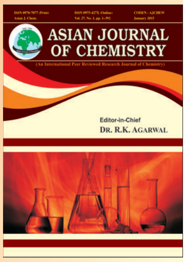
Asian Journal of Chemistry; Vol. 27, No. 9 (2015), 3473-3480

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18911



Separation and Pre-concentration of Some Metals Using Amino-azole Derivatives Supported on Silica

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Received: 6 December 2014; *Accepted*: 20 February 2015; *Published online*: 26 May 2015; AJC-17277

The present study aimed to evaluate the efficiency of amino-azole derivatives supported on silica gel for the separation of some heavy metals *e.g.*, Cu^{2+}, Cd^{2+} and Hg^{2+}. Silica gel was modified by using 3-chloropropyltriethoxysilane and sorption parameters were determined. The newly modified phases were characterized using IR, NMR and elemental analysis and sorption efficiency parameters were determined. The results indicated that the surface coverage and sorption capacity values ranged from 0.48 to 0.54 mmol and 0.03 to 0.45 mmol/g of modified silica, respectively and separation capacity values increased by increasing pH values and did not affected by increasing temperature. Thermal analysis demonstrated non-catalytic degradation effects due to the formation of metals chelates on the silica surface. In addition, it was found that 20-30 min was sufficient to complete sorption and 85-90 % of the sorbed metals occurred within the first 5-10 min. On the other hand, HCl was found to be most potent acid to elute the tested metals at a concentration of 0.2 mol/L. Higher stability and higher distribution coefficient (K_d) of the modified silica were found compared to non-modified silica as well as the possibility of using it is. Real samples collected from industrial areas located at Al-Qassin region, Kingdom of Saudi Arabia illustrated the validity and feasibility of the proposed procedure for the separation and pre-concentration of the selected metals.

Keywords: Amino-azole, Silica gel, Metals, Thermal analysis, Sorption capacity, Distribution coefficient.

INTRODUCTION

One of the most significant environmental problems is the growing discharge of metals from different industries in the soil, water and air. As is the case for most of these metals, even in trace amounts their toxic potential cannot be over emphasized. It therefore becomes imperative that an adequate assessment of the effect of these metals on the environment be carried out. Due to the low concentration levels of these metals in the environment, the use of new analytical methods and techniques with very high sensitivity and selectivity is required for their investigations. Techniques such as flame atomic absorption spectrometry (FAAS)[1], graphite furnace atomic absorption spectrometry (GFAAS)[2], inductively coupled plasma mass spectrometry (ICP-MS)[3,4] and inductively coupled plasma optic emission spectrometry (ICP-OES)[5] have been used for this purpose.

Due to the very low concentration of most of the elements, in environmental samples, their separation and sensitive determination necessitate the use of a preconcentration or trace enrichment method. To overcome these difficulties, researchers have described various procedures for sample pre-treatment such as liquid-liquid extraction (LLE)[6], solid phase extraction (SPE)[7] and cloud point extraction (CPE)[8]. These methods often require a large amount of high purity organic solvents, some of which are harmful to health and cause environmental problems.

Solid-phase extraction (SPE) has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes[9,10]. The basic principle of SPE is the transfer of the analyte from the aqueous phase to bind to active sites of the adjacent solid phase. The advantages of SPE techniques are: higher enrichment factors, safety with respect to hazardous samples, minimal costs due to low consumption of reagents, stability and reusability of the solid phase, easiness of separation and enrichment under dynamic conditions[11]. So, SPE has been widely used for the isolation and enrichment of target analytes and for the clean up of samples in pharmaceutical, clinical, environmental and food chemistry[12]. Among the SPE sorbents used for pre-concentration, metaloxide systems[13], activated alumina[14], nanosized alumina[4], titanium dioxide[15], metallic ions of silica gel chemically modified with zirconium(IV)[3,16] and silica gel with Alizarin violet[17].

The choice of sorbent is a key point in SPE, because it can control the analytical parameters such as selectivity, affinity and capacity[18]. Silica gel presents the advantages of no swelling, fast kinetics, mechanical, thermal and chemical stability under various conditions[19] and used in technology as tailored nano size particles[20,21] with controlled pore structure and high surface area as powerful sorbing agent and important catalytic surface support in chemical chromatographic separations. Therefore, it is a widely used support for various solid-phase extractants. Recently, some chelating reagents have been modified on silica gel as solid-phase extractants for separation/pre-concentration of some metal ions using silica gel modified with glycerol[22], lumogallion[23], aniline formaldehyde condensate[24], polyamidoamine[25], methylthiosalicylate[26,27], 2,4,6-trimorpholino-1,3,5-triazin[28], diphenylcarbazone[17], murexide[29] and 1-f4-[(2-hydroxybenzylidene)amino]phenylgethanone[30].

Purification of industrial effluents loaded with heavy metal ions is one of the major problems on wastewater treatment because of their toxicity and they cannot be degraded by means of chemical or biological ways in nature. Therefore, it is necessary to research more effective and low cost methods to eliminate heavy metal ions from effluents. In this study, we report the synthesis of of amino-azole derivatives bonded on the surface of silica gel as a new solid-phase extractant and as a selective sorbent for traces of Cu(II), Cd(II) and Hg(II) as well as analysis of real water samples collected from industrial area located in Al-Qassim region of Kingdom of Saudi Arabia, by atomic absorption spectrometry (AAS) and/or inductive coupled plasma (ICP).

EXPERIMENTAL

All chemicals were of analytical grade and obtained from either BDH, Merk, Aldrich or Fulka companies. Double distilled water (DDW) was used throughout all the experiments to prepare all solutions. Standard Labware and glassware were acid washed and rinsed with double distilled water. Stock solutions. Standard solutions of 1,000 mg/mL of Cu^{2+}, Cd^{2+} and Hg^{2+} were prepared by dissolving the corresponding metal salts in 0.03 mol/L of nitric acid, hydrochloric acid or sulfuric acid and further diluted daily prior to use.

A Shimadzu model AA-6300 flame atomic absorption spectrometry (FAAT) (Shimadzu, Japan) was used for determination of the concentration of metal ion of Cd^{2+} and Cu^{2+}, while an ICPA 6000 series inductively coupled plasma atomic emission spectrometry (ICAP-AES) (Thermo Scientific, UK) was used for Hg^{2+} determination. The instrument's performance was assessed daily prior to its usage. Argon 99.996 % was used. The instrumental parameters and the program used in the flow system in case of FAAT and ICAP are shown in Tables 1 and 2, respectively.

Synthesis of pyrazole derivatives: Four new pyrazole derivatives, namely, 4-[(2-carboxyphenyl)hydrazono]-3-amino-1H-pyrazol-5-one (CPHPY), 4-[(4-carboxy-3-hydroxyphenyl)hydrazono]-3-amino-1H-pyrazol-5-one (HCPHPY), 5-amino-2-(4-antipyrinylazo)phenol (HPHPY) and 2-amino-4-(4-antipyrinylazo)-4-methyl-thiazole (MTHPY) were prepared by adding 0.01 mol of sodium nitrite to 0.01 mol of either antharnilic acid, 4-aminosalicylic acid, 4-aminoantipyrine, or 4-aminoantipyrine, respectively, dissolved in concentrated HCl at 0-5 °C. The resultant was added to either 0.01 mol of sodium cyanoacetate, sodium cyanoacetate, 4-aminosalicylic acid, or 2-amino-4-methylthiazole, respectively, in the presence of ethanol and sodium acetate, sodium cyanoacetate. The mixture was vigorously mixed for 2 h at room temperature, cooled, filtrated and then dried. The purity of the obtained compounds was tested by thin layer chroma-tgtaphy and characterized by IR, NMR and elemental analysis. All other chemicals and solution preparation were found elsewhere.

TABLE-1
OPTIMUM OPERATIONAL PARAMETERS FOR DETERMINATION OF Cu^{2+} AND Cd^{2+} BY FAAS

Parameter	Cu^{2+}	Cd^{2+}
Absorption line	324.8 nm	228.8 nm
Slit widths	0.7 nm	0.70 nm
Lamp currents	6 mA	8 mA
Type of flame	Air/acetylene	Air/acetylene
Flow rate of acetylene	1.80 L/min	1.80 L/min
Flow rate of air	15.0 L/min	15.0 L/min

TABLE-2
OPTIMUM OPERATIONAL PARAMETERS FOR DETERMINATION OF Hg^{2+} BY ICP-AES

RF power	1150 kw
Signal measurement	Peak area
Replicate	3
Resolution	0.7 amu (at 10 % peak height)
Auto lens	on
Gas flow rates	
Pressure of argon	60 Pi
Principal	12.0 L/min
Intermediate	0.5 L/min
Nebulizer	0.7 L/min
Dead time	35 ns
Dwell time	25 ns

The pH measurements were controlled with a pHs-HQ30 digital pH meter (HACH Company, USA) was used for the pH measurements. Infrared spectra (4000-400 cm^{-1}) in KBr were recorded on a Nicolet NEXUS 670 FT-IR apparatus (USA). A YL-110 peristaltic pump (The general research academy of coloured metal, Beijing, China) was used in the process. Parking station and glass microcolumn (10 mm × 3.2 mm i.d.) were obtained from Restek Company, USA.

NMR spectra were measured on a JEOL ECLIPSE 400 spectrometer (Thermo Scientific Company, USA) at 400 MHz for ^1H and at 100 MHz for ^{13}C and measured in ppm downfield from TMS with coupling constants reported in Hz. Elemental analysis (C. H, N, S and O) was determined using a Perkin Elmer 2400 analyzer (series II CHNS/O analyser 2400, USA). The thermogravimetric analysis was performed using a Mettler Toledo TG/DSC 1 Star System (Swizerland) cooled with a PolyScience 107A00647 cryostat at 22 °C, equipped with GC200 Star System Gas Controller and DSC sensor HSS2.

Activation and preparation of silica gel modified with 3-chloropropyltriethoxysilane: In order to remove any adsorbed metal ions and increase the content of –OH, silica gel (SG) was activated by dipping in 6 mol/L of hydrochloric acid for 2 days, then filtered and washed repeatedly with distilled water until no detectable Cl^- can be found in the filtrate. The treated silica gel was dried in an oven at 160 °C for 8 h to remove any adsorbed water on the surface.

The process for the preparation of 3-chloropropyltriethoxysilane functionalized silica gel was synthesized according to the following procedure: 3-chloropropyltriethoxysilane was dissolved in 50 mL of toluene (Merk) and 9 g of activated silica gel was added into a sealed flask. The mixture was stirred and refluxed in a condenser for 12 h. The solution was left to cool, filtered and washed with toluene, ethanol and diethyl ether to remove unreacted 3-chloropropyltriethoxysilane and finally dried in an oven at 60 °C for 6 h. The loading of CPHPY, HCPHPY, HPHPY and MTHPY on 3-chloropropyltriethoxysilane functionalized silica gel is got by adding 4 g of functionalized silica gel and 0. 5 g of the organic compound in the presence of 50 of dimethyl formamide and 1 mL triethyl amin. The mixture was heated for 12 h, then filtrate, washed many times with 20 mL ethanol and dried.

Stability of the modified silica gel: The stability of the modified silica gel was carried out by stirring 100 mg of functionalized silica gel with 50 mL of buffer solution, pH 8.5 for 1 h. The mixture was filtrated, washed with double distilled water, then dried at 150 °C for 1 h and then weighted.

Batch experiments: 3-Chloropropyltriethoxysilane functionalized silica gel was stirred in a solution with suitable amount of metal ion for a fixed period of time (30 min) at room temperature. The supernatants were taken form the unextracted metal ions measurements by either FAAS or ICP-AOS.

Column experiments: For the column experiment, 500 mg of modified silica gel (Si-CPHPY, Si-HCPHPY, Si-HPHPY and Si-MTHPY) was packed in a glass column (10 cm × 3.2 i.d.) and 20 mL of HCl at a flow rate of 2 mL/min followed by 10 mL of double distilled water at a flow rate of 2 mL/min were passed through the column. A solution containing of 10 mg/L of the tested metal ions was adjusted to pH 6.0 and passed through the column at a flow rate of 2 mL/min. Metal ion retained on the column was eluted with 0.3 mol/L of HCl at a lower flow rate and its concentration was determined by FAAS or ICP-AOS

Effect of stirring times: The stirring time taken for the adsorption of the metal ion by the functionalized silica gel and the attainment of the equilibrium conditions are of considerable importance. The effect of stirring times on the retention of the selected metals was studied by the batch experiments. For this purpose, 50 mg of the functionalized silica gel was added in 50 mL of solution containing 20 mg of metal ions, stirred for different times (5-30 min) at room temperature and appropriate pH, filtrated and then the unextracted metal ions in the supernatants were determined by either FAAS or ICP.

Influence of sample pH: The pH value is one of the important factors controlling the extraction of metal ions from aqueous solutions. In order to obtain optimum extraction condition, the adsorption of metal ions on the functionalized silica gel was examined with different solutions pH by the batch mode experiments. The study of the pH influence on the retention of the analytes was carried out between pH 2.0 and 9.0 using an appropriate buffer. For this purpose, 50 mg of the functionalized silica gel was added in 50 mL of solution containing 20 mg of metal ions, stirred for 30 min, filtrated and then the unextracted metal ions in the supernatants were determined by either FAAS or ICP.

Effect of temperature: The effect of temperature on the retention of the tested metals was studied by the batch experiments. For this purpose, 50 mg of the functionalized silica gel was added into 50 mL of solution containing the appropriate amount of metal ions, stirred for 30 min at different temperatures (25, 40 and 60 °C), filtrated and then the unextracted metal ions in the supernatants were determined by either FAAS or ICP.

Capacity of the sorbent: The capacity of the sorbent is an important factor that determines how much sorbent is required to quantitatively remove a specific amount of metal ion from the solution. For investigation of the adsorption capacity of metal ion in solution at the appropriate pH, the same volumes of metal ion solution with different concentrations was stirred with the same amount of the modified silica (50 mg) for 30 min, then the concentrations of metal ion in the solutions were determined. Change in the adsorption of Cu^{2+}, Cd^{2+} and Hg^{2+} by the modified silica gel was measured. The adsorption capacity of metal ion by modified silica gel and the extraction percentage was calculated by eqns. 1 and 2, respectively.

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

$$E\ (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

where Q represents the adsorption capacity (mg/g), C_o and C_e are the initial and equilibrium concentrations of metal ions (μg/mL), W is the mass used of SG3-chloroproyltriethoxysilane functionlized silica gel (g), V is the volume of metal ion solution (mL) and E (%) stands for the extraction percentage.

Determination of distribution coefficient: For investigation of the distribution coefficient of metal ions, 20 mL of metal ion of different concentrations (10-50 mg/L) with pH 8.0 was stirred with 100 mg of the modified silica for 60 min, filtrated into a volumetric flask containing 10 mL HCl (1 M) and completed with double distilled water to 50 mL. The concentrations of metal ion in the solutions were determined and distribution coefficient (K_d) was calculated by eqn. 3.

$$K_d = ((C_0 – C_e)/m/C_e)/V \tag{3}$$

Choice of eluent: Fifty milliliters of solution containing 20 μg of metal ion at pH 6 was stirred at the optimum conditions for 30 min and then filtrated. Metal ion retained in the column was eluted by different volumes (5, 10 and 15 mL) and different concentration (0.10, 0.20 and 0.50 M) of either HCl, HNO_3 or H_2SO_4 with a flow rate of 0.5 mL/min. The eluted metal ions in the supernatants were determined by either FAAS or ICP.

Effect of flow rate: The sample flow rate is a very important operational parameter for the pre-concentration, efficiency and it determines the sample volume to be used. For the column experiment, 500 mg of modified silica (Si-CPHPY, Si-HCPHPY, Si-HPHPY and Si-MTHPY) gel was packed in a glass column (10 cm × 3.2 i.d.) and 20 mL of HCl followed by 10 mL of double distilled water and then 10 mL of buffer solution at a flow rate of 2 mL/min were allowed to pass through the column at the optimized conditions. 40 mL of a solution containing 20 mg/L of the tested metal ions was passed through the column, employing different flow rates (in the range of 1.0-4.0 mL/min). Metal ion retained on the column was eluted with 0.3 mol/L of HCl at a constant flow rate and its concentration was determined by FAAS or ICP-AOS. It was observed that the adsorption efficiency of the serpent was not altered up to a sample flow rate of 4 mL/min. However, at higher run, there was a reduction in the percentage adsorption of metal ion. This could be probably due to the insufficient contact time between the sample solution and solid sorbent.

Breakthrough capacity of the functionalized silica gel column: Glass column (10 cm × 3.2 i.d.) was packed with 500 mg of modified silica gel (Si-CPHPY, Si-HCPHPY, Si-HPHPY and Si-MTHPY) and 20 mL of HCl followed by 10 mL of double distilled water and then 10 mL of buffer solution at a flow rate of 2 mL/min were allowed to pass through the column at the optimized conditions. 100 mL of a solution containing about 10 mg/L of the tested metal ions was passed through the column at a flow rate 2.0 mL/min and the percentage of each metal in every 5 mL interval of the effluent was determined by FAAS or ICP-AOS after elution with 0.3 mol/L of HCl at a constant flow rate. From the variation of metal percentage in the effluents with the solution volumes passed through the column, the breakthrough volume and the volume needed to reach the saturation for the mercury can be determined.

Effect of interfering ions: The effect of different cations and anions was investigated on percent recovery of metal ion by aforementioned optimized conditions. A fixed amount of analyte (20 mL of 50 µg/L) was taken with different amounts of foreign ions and recommended procedure was followed.

Regenerability of the functionalized silica gel golumn reuse: The regenerability of the functionalized silica gel column was tested by loading 100 mL of Cu^{2+} of 10 mg/L at a flow rate of 2 mL/min and pH 8.0. Four milliliters of eluent was collected after elution with 0.2 mol/L of HCl at a constant flow rate and the concentration of metal ions in the eluent were determined by AAS.

Real water sample: Water samples used in the present work include lake water and industrial wastewater located at Al-Qassim region Kingdom of Saudi Arabia. The samples were filtered through 0.45 µm cellulose membrane (Millipore) and stocked in PTFE flasks under refrigeration at 4 °C until the analysis. Thus, 250 mL of each water sample was adjusted to pH 8 and passed through the column. Four milliliters of eluent was collected after elution with 10 mL of 0.2 mol/L of HCl at a constant flow rate and the concentration of metal ions in the eluent were determined by AAS.

RESULTS AND DISCUSSION

For grafting aromatic group onto the silica surface, the use of intermediate reagent such as 3-chloropropyl trimethoxysilane is necessary[31] and can be used as adsorbents for SPE, in a pre-concentration of organic compounds with environmental interest[32,33]. In the present study, IR, TGA and NMR were used to characterize the organic grafting processes. The molecular formula, m.p. and elemental analysis of aminoazole derivatives are presented in Table-3.

Characterization of the four new silica gel modified phases using IR, NMR and elemental analysis data: The IR for the four organic reagents were characterized by the presence of IR absorption bands at 3473, 3312, 3222 cm^{-1} assigned to NH and NH_2 groups, hydrogen bond of hydroxyl groups at 2924 cm^{-1} and strong absorption band at 1624 cm^{-1} assigned to a C=O group. The IR spectra for silica modified with 3-chloropropyltriethoxysilane is characterized by the presence of absorption bands at 948, 798 cm^{-1} and the appearance of new bands of about 3000 cm^{-1} assigned for aliphatic (C-H). The IR spectra of modified silica phases are characterized by the following the disappearance of the bands assigned to NH_2 groups in the (3473-3201 cm^{-1}) region and appearance of new band at 3446 cm^{-1}. Some bands are noticed in the 1660-1200 cm^{-1} region, which are not present in the chloro-silica IR spectra. The modified silica loaded with metal ions reveals the additional absorption band in the regions 560-500 cm^{-1} and 490-440 cm^{-1}which were attributed to ν(M-O) and ν(M-N) bonds, respectively.

The data of NMR illustrated singlet signal assigned to NH_2 at (δ 6.6 p.m., triplet signals for aromatic hydrogen atom at (δ 7.2-7.6 ppm. Signals at (δ 10.4 ppm was assigned for OH, while 11.2 and 11.8 were assigned to NH groups. The assignment of all other newly synthesized organic reagents are also given.

Determination of surface coverage values for modification silica gel phases: The surface coverage values for modification silica gel phases were found to be 0.54, 0.48, 0.52 and 0.50 mmol for Si-CPHPY, Si-HCPHPY, Si-HPHPY and Si-MTHP, respectively (Table-4). Also, the surface coverage was calculated by comparing the elemental analysis of nitrogen content loaded on the silica and that present in the organic moieties. Results are adjacent to those calculated using the thermal desorption method. The surface immobilization of silica gel was confirmed by the presence of carbon and nitrogen in the modified materials, which were primarily absent in activated silica. The presence of organic moieties covalently attached to the silica backbone reduces the access of nitrogen to the skeleton base, which results in a gradual decrease in its surface area[30].

TABLE-3
ELEMENTAL ANALYSIS FOR AMINOAZOLE DERIVATIVES

Organic compound	m.f.	m.p. (°C)	Elemental analysis (%): Theorical (Practical)			
			C	H	N	S
CPHPY	$C_{10}H_9N_5O_3$	240-242	44.58 (48.76)	3.67 (3.73)	28.33 (28.12)	–
HCPHPY	$C_{10}H_9N_5O_4$	205-206	45.63 (45.46)	3.45 (3.52)	26.61 (26.44)	–
HPHPY	$C_{17}H_{17}N_5O_2$	176-177	63.15 (63.32)	5.30 (5.36)	21.66 (21.44)	–
MTHPY	$C_{15}H_{16}N_6OSI$	210-212	54.86 (54.95)	4.91 (4.84)	25.59 (25.67)	9.76 (9.59)

TABLE-4
DETERMINATION OF ORGANIC COMPOUNDS MOUNTED ON MODIFIED SILICA GEL BY THERMO AND NITROGEN ANALYSIS TECHNIQUES

Phase	Thermo analysis	Nitrogen analysis		
	Amount (nmol)	% of N in aminoazole	% of N in modified silica gel	Amount (mmol)
Si-CPHPY	0.54	28.2	3.8	0.51
Si-HCPHPY	0.48	26.4	3.3	0.45
Si-HPHPY	0.52	21.4	2.9	0.46
Si-MTHP	0.50	25.7	3.9	0.50

Thermal analysis: The thermogravimetric analysis (TGA) and DTA curves were carried out from room temperature to 1000 ºC for modified silica solid phases which showed three catalytic degradation steps appeared at separate mid points and ranged from 110-140 ºC and were attributed to the loss of humidity water contaminated with modified silica (the weight loss in this step was generally within 2-3 %). The midpoints of the 2nd degradation steps ranged from 290-390 ºC and were attributed to the partial decomposition of the organic moiety, while the third degradation steps recorded in the range of 500-580 ºC and were assigned to complete decomposition of organic matter leaving silicon dioxide residue.

For modified silica phases loaded with metal ions weight loss were generally occurred in three degradation steps. Thermal analysis measurements were carried for some representative samples for cover for Cu-Si-HCPHPY. The total weight loss was 10.985 %, which was lower than that of free HCPHPY phases (11.854 %) indicating that the non catalytic degradation effect due to the metal chelates formed on the surface of silica dispersed metal oxides. It was found that the stability of modified silica binding with aminoazol as following: Si-MTHP > Si-CPHPY > Si-HCPHPY > Si-HPHPY (Table-5). These data indicate that absorbents that have been synthesized have good thermal stability.

TABLE-5
STABILITY OF MODIFIED SILICA GEL BINDING WITH AMINOAZOLE

Phases	Weight before shaking (mg)	Weight after shaking (mg)
Silica	100	91.3
Si-CPHPY	100	97.0
Si-HCPHPY	100	94.4
Si-HPHPY	100	95.6
Si-MTHP	100	98.1

Factors affecting the sorptivity of metal ions on the modified silica solid phases

Effect of pH: The effect of pH on the separation and preconcentration of the investigated metal ions indicated the increase of the separation capacity values by increasing the pH of the sorption media. The maximum pH for sorption of all metal ions was in the range of 7-9. For Cu^{2+}, the high capacity was achieved at pH = 8, but for Cd^{2+} pH 9 was preferred for all modified silica solid phases. The sorption of Hg was at pH = 7 for 1st and 2nd silica phase and at 9 of 3rd and 4th phases. At higher pH, lower loadings efficiencies of metal ion were observed, which could be attributable to the precipitation of targeted ion[34].

Effect of stirring times: The study of time needed for quantitative sorption of metal ions on the modified silica is very important for establishing the possibility of applying the column operation, fast equilibrium reaction makes the resin suitable for packing and using in a column. It was found that a time of 20-30 min is sufficient for complete sorption of the investigated metal ions and at least 85-90 % of these metal ions were sorbed within 5-10 min of the interaction with the resin depending on the concentration of metal ion. Thus the sorption rate is considered rapid enough for separation in a column. This confirmed the fact that the modification of silica gel surface with organic chelate reagent results in metal ion extractants, which need only a few minutes to complete extraction processes[35]. This is one of the advantages of using silica gel support for immobilization of chelating compounds.

Effect of eluting agent: The use of HCl, HNO_3 and H_2SO_4 acids for stripping the metal ions after their sorption on the modified silica phases at optimum conditions was studied. The present results indicated the elution depends on the concentration of eluent (0.1-0.5 M) and 95-98 % of the sorbed metal ions were completely stripped except for mercury where as the recovery was between 88 and 90 %. Moreover, HCl with concentration of 0.2 mol/L was foud to be the best eluting agent. The present study is parallel with the results of Kumar[36] who found that 0.2 mol/L of HCl or HNO_3 can be used without interfering of sulfate ions

Effect of temperature: The effect of temperature on the uptake of metal ions was studied in water bath at temperatures 25, 40 and 60 °C. It was noticed that the quantitative uptake was not affected by increasing temperature, however, results obtained indicated that higher temperatures fasted the equilibrium and shorted the shaking time, where 10 min was enough to reach the maximum sorption at 60 °C.

Determination of stability of modified silica gel phases and analytical parameters: To reuse the modified silica, it was important to study the effect of modification on the stability of silica gel. Special care must be noticed when working with silica in alkaline solution where silica is hydrolyzed easily at higher pH values. Studies were elaborated to compare the weight loss of silica gel and modified silica after soaking in buffer solution at pH 8.5 for 1 h. Results presented in Table-5 indicate that the modified silica has relatively higher stability (94.4-98.1 %) compared to silica gel (91.3 %). The sorption and desorption was repeated on the same modified silica phases and the amount of metal eluted was estimated. The reduction in the sorption capacity of metal ions was within 0-5, 1.3-16.5 and 1.8-18 % for Cu^{2+}, Cd^{2+} and Hg^{2+}, respectively after repeating use for 10 cycles (Table-6). Thus the multiple use of the modified silica as a column is feasible.

TABLE-6
EFFECT OF AMOUNT OF MODIFIED SILICA GEL A BINDING WITH AMINOAZOLE DERIVATIVES ON METAL ABSORPTION

Ion	Weight (g)	Concentration (ppm)	Concentration of extracted metal (ppm)			
			Si-CPHPY	Si-HCPHPY	Si-HPHPY	Si-MTHPY
Cu^{2+}	0.05	30	28.5	29.4	29.7	29.4
	0.10		29.5	29.9	29.9	29.7
	0.15		29.8	30.0	30.0	29.9
Cd^{2+}	0.05	7.9	6.6	7.8	7.0	7.2
	0.10		7.1	7.8	7.5	7.7
	0.15		7.4	7.8	7.7	7.8
Hg^{2+}	0.05	5.6	4.9	4.7	4.6	5.4
	0.10		5.2	5.1	4.7	5.4
	0.15		5.2	5.1	5.0	5.5

TABLE-7
ADSORPTION CAPACITY AND DISTRIBUTION COEFFICIENT OF MODIFIED SILICA GEL AND BINDING WITH AMINOAZOLE DERIVATIVES

Phases	Absorption capacity (mmol/g)			Distribution coefficient (mmol/g)		
	Cu^{2+}	Cd^{2+}	Hg^{2+}	Cu^{2+}	Cd^{2+}	Hg^{2+}
Si-CPHPY	0.45	0.10	0.06	458	53	57
Si-HCPHPY	0.32	0.12	0.05	8342	653	41
Si-HPHPY	0.30	0.13	0.03	1062	151	29
Si-MTHPY	0.25	0.16	0.12	546	536	305
Activated silica	–	–	–	72	29	13

Determination of distribution coefficient: The distribution coefficient values (K_d) for Cu^{2+} were found to give maximum values of 548, 8432, 1062 and 546 for with for Si-CPHPY, Si-HCPHPY, Si-HPHPY and Si-MTHP, respectively (Table-7). For Cd^{2+} the values ranged between 53 and 653, whereas for Hg^{2+} the K_d values were between 29 and 305. These values are high compared to those reported for silica gel indicating the priority of N donating atoms for complexing metal ions compared to silanol group. This result indicates that the sorbent has excellent selectivity for Cu^{2+} and could be used to enrich the Cu^{2+} selectively in the presence of Cd^{2+} and Hg^{2+}. It seems the complex formation plays a key role for uptake of these metals by this new sorbent.

Effect of the amount of the functionalized silica gel: The effect of the amount of the functionalized silica gel on absorption of Cu^{2+}, Cd^{2+} and Hg^{2+} was examined by a batch mode experiment. 20 mL of solution each containing 30, 7.9 and 5.6 ppm, respectively, at pH 6.0 was stirred for 30 min with different amount of the functionalized silica gel added (0.05, 0.10 and 0.15 g). 0.05 g of the functionalized silica gel was sufficient for 83-99 % retention of the tested metals (Table-6). Therefore, not less than 0.05 g of the functionalized silica gel was used in the following experiment.

Column technique

Effect of flow rate: The sample flow rate is a very important operational parameter for the pre-concentration efficiency and affecting the retention of metal ions and it is necessary to choose an appropriate flow rate that ensures a higher metal uptake. In general, for on-line systems the sample flow rate is limited by its pressure and/or sorption efficiency. So, the degree of metal ion sorption on the modified silica packed mini column was studied at various flow rates (1, 2, 3 and 4 mL/min) of the metal ion solution. The effluent received after an elapsed time was fractionated into 5 mL portions and the metal ion was determined. Results obtained indicates 1mL/min in all cases was that the most suitable flow rate. However, the increasing in the flow rate resulted in decreasing the percentages of sorption. This may be due to insufficient contact time of the sample sorption with the sorbent, probably because the metal ions do not equilibrate sufficiently the modified silica phases. By comparing the results obtained, it was clear that the effect of flow rate was varied from metal ion metal ion; for example, in case of mercury this effect is relatively inefficient, but for copper and cadmium higher flow rates caused an efficient decrease in sorbitivity of metal ions.

Breakthrough curves: The breakthrough capacity gives the actual working capacities of the resin in a column breakthrough capacities and is defined as the capacity at the moment when the analyte starts to appear in the effluent. The study was performed by packing the column with 0.5 g of the modified silica and passing solution of 5 × 10^{-3}, 1.8 × 10^{-3} and1. 3 × 10^{-3} M of Cu^{2+}, Cd^{2+} and Hg^{2+}, respectively, with a flow rate of 2mL/min at the optimum pH. The effluent was fractionated into 5 mL portions and each portion was subjected to either AAS or ICP analysis. Results obtained indicates that the sorption capacity was between 0.06-0.12 mmol/g for Hg^{2+}, 0.13-0.16 mmol/g of dry functionalized silica gel for Cd^{2+} and 0.30-0.45 mmol/g for Cu^{2+} (Table-8). These results are more or less in the same range as those calculated from batch experiments.

TABLE-8
ADSORPTION CAPACITY (mmol/g) OF MODIFIED SILICA GEL BINDING AND BINDING WITH AMINOAZOLE DERIVATIVES

Ion	Si-CPHPY	Si-HCPHPY	Si-HPHPY	Si-MTHP
Cu^{2+}	0.35	0.30	0.45	0.30
Cd^{2+}	0.141	0.13	0.16	0.15
Hg^{2+}	0.08	0.08	0.06	0.12

TABLE-9
EFFECT OF INTERFERING IONS ON RECOVERY PERCENTAGES OF METAL IONS

Interfering ion	Concentration (ppm)	Si-CPHPY			Si-HCPHPY			Si-HPHPY			Si-MTHPY		
		Cu^{2+}	Cd^{2+}	Hg^{2+}	Cu^{2+}	Cd^{2+}	Hg^{2+}	Cu^{2+}	Cd^{2+}	Hg^{2+}	Cu^{2+}	Cd^{2+}	Hg^{2+}
Acetate	200	95	100	90	96	98	99	98	92	96	94	92	96
Oxalate	200	98	97	91	94	93	99	92	98	93	95	91	96
Citrate	200	95	99	85	91	93	99	96	94	88	97	93	91
Sluphate	200	99	99	85	94	93	87	92	92	89	97	95	90
Phosphate	100	96	98	95	91	94	90	93	92	96	98	96	91
Chloride	100	99	96	98	91	94	89	99	91	95	97	93	92
Amonia	100	98	98	68	99	99	92	98	97	93	97	94	96
Potasium	100	100	99	99	96	94	88	97	95	90	93	96	95
Sodium	50	100	98	93	91	96	94	96	97	94	92	95	95
Magnesium	50	98	97	96	90	95	96	96	94	96	89	91	93
Calcium	100	99	96	96	94	96	92	97	92	98	89	92	96

*Average of three determinations.

Effect of interfering ions: The reliability of the tested pre-concentration procedure was examined in the presence of the possible matrix elements usually found as common ionic species in natural water samples. The results obtained indicated that some of these ions have some decreasing effects on the recovery of the studied metal ions and others have no considerable on determination of analyte ions up to reasonable amounts (Table-9). The results indicated that high concentrations of all the ions tested did not interfere with the separation and determination of the tested materials. This suggests that the new solid-phase extraction has good selectivity for recovery of Cu^{2+}, Cd^{2+} and Hg^{2+}.

Application of modified silica phases for pre-concentration of metal ions from wastewater samples: Determination of the trace elements in aqueous environmental samples is difficult not only due to the low analyte concentrations present, but also due to the complexity of the samples. Therefore, water samples collected from oxidation lakes and painting factory present in industrial zone of Qassim region of Kingdom of Saudi Arabia as well as spiked were subjected to the same pre-concentration and separation procedures using the modified silica solid phases.

TABLE-10
PROPERTIES OF INDUSTRIAL WATER SAMPLES

Properties	Oxidation lake water sample	Painting factory water sample
Temperature (°C)	24.5	26.0
pH	7.35	7.46
EC (mS/m)	2.73	1.30
Total disolved salts (mg/L)	1370	632
Turbidity (nephelometric turbidity units (NTU)	319	797
Cu^{2+} (mg/L)	0.087	0.03
Mn^{2+} (mg/L)	0.146	0.04
Zn^{2+} (mg/L)	0.0448	0.0175
Cd^{2+} (mg/L)	0.00	0.00
Hg^{2+} (mg/L)	0.006	0.006

TABLE-11
COMPARISON BETWEEN AMMONIUM PYRROLIDINE DITHIOCARBAMATE METHOD USING SOLVENT EXTRACTION AND PROPOSED METHOD FOR METAL ANALYSIS

Metal (mg/L)	AADC	The present study
Cu^{2+}	0.041 ± 0.01	0.042 ± 0.01
Cd^{2+}	0.068 ± 0.04	0.101 ± 0.02
Hg^{2+}	0.006 ± 0.0001	0.0054 ± 0.0002

In accordance with the requirement of routine water analysis procedures, the evaluation of general parameters such as pH, total dissolved salt (TDS), electrical conductivity and alkalinity of water is very important for assessment of the general pollution level or quality of water. The properties of these samples can be seen in Table-10. The pH values of the analyzed water samples were found to lie in the weak base range due to the presence of soluble salts and ammonia, while the samples contained higher concentration of total soluble salts and electrical conductivity values. Also, the results revealed that the samples were free of Cd^{2+}, while it contained detected amount of Mn^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+}. This attributed to anthrogenic activities. However, these results still lie within the permissible limits[34]. Recoveries of Cd^{2+} were found between 90 and 110 %, indicating that matrix effects were negligible. A comparison between the results obtained using the proposed pre-concentration procedure and the ammonium pyrrolidine dithiocarbamate method (AADC) using solvent extraction technique shown in Table-11. The values of inestigated ions found in the proposed pre-concentration procedure are in accordance with AADC method. Further the analysis of the effluents after passing a column packed with modified silica solid phases indicated the complete absence of metal ions from the effluents, which reflect the validity of the proposed procedure.

Conclusion

New solid phase extractors, amino-azole derivatives functionalized silica gel have been prepared and properly characterized. These solid phase extractors have the following advantages:

- can be used for selective separation and preconcentrate of Cu^{2+}, Cd^{2+} and Hg^{2+}.
- can be used to remove the interference of complex matrix.
- the separation/preconcentration produce is simple, rapid and of low analytical cost.
- has high preconcentration factor and can be reused for many times.

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