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Chemically modified nano silica gel with 2-((3silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN) as good and efficient adsorbent for solid phase extraction

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ABSTRACT

A new selective solid phase extractor was prepared based on modification of silica gel with 2-((3silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN). The solid phase extractor is stable in 6 mol/L HCl, common organic solvents, and buffer solutions at pH 2.0–8.0. This new sorbent was successfully applied for the enrichment of trace amount of Fe^{3+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} ions subsequent their determination by flame atomic absorption spectrometry. The influences of the analytical parameters including pH, ratio of aminopropylsilylate to 2-hydroxy-1-naphthaldehyde and amount of solid phase, sample flow rate, eluent solution conditions (type, concentration, and volume), and sample volume on the metal ions recoveries were investigated. The method has high sorption—preconcentration efficiency even in the presence of various interfering ions (recoveries between 98 and 99.4 and detection limits in the range of 1.3–2.8). The proposed method is applicable for understudied analytes with recoveries more than 95% and relative standard deviation < 4.2%, especially for real sample analysis.

Keywords: Silica gel; 2-((3silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN); Atomic absorption spectrometry; Solid phase extraction; Trace metal enrichment

1. Introduction

They have various biological effects as essential and/or toxic element. Generally, metals are potentially toxic to living organisms at variable concentrations. Heavy metals and metalloids are not necessary for metabolic activities, are toxic to the cell even at quite low concentrations [1–3]. The environmental exposure to the heavy metals is a well-known risk factor for human health, plants, and animals [4,5]. Despite high sensitivity of Inductive coupled plasma-mass spectrometry (ICP-MS) being quite sensitive as a measurement analytical technique, the matrix effect may preclude direct analysis by ICP-MS or other techniques. To overcome the conventional problem associated with the real sample (complicated matrices and low level of analyte), generally caring out a separation and preconcentration procedure prior to flame atomic absorption spectrometry (FAAS) is required. Chelating resins as frequently used solid phase procedure provide good stability, high sorption capacity for metal ions and good flexibility in working conditions [6]. Selectivity of the solid phase sorbent towards an analyte depends on the structure of the immobilized

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organic ligands. Nowadays, the solid phase extraction (SPE) method is one of the most effective multielemental preconcentration methods due to advantages such as ease of use, high preconcentration factor, and flexibility in solid-phase selection [7–15]. It is widely used for the isolation and concentration of target analytes and the cleanup of samples (removal of matrix interferences) [5]. An efficient solid phase extractant should consist of a stable and insoluble porous matrix containing suitable active groups (typically organic groups) with unique ability for interaction of metal ions [6]. Thus, selection of an appropriate sorbent has significant importance. Silica gel as the most prominent support has many advantages such as it does not swell, has good mechanical strength and thermal stability as well as quite large surface area. It is the most common applied inorganic solid sorbent in different chromatographic techniques for separating and determination of organic and inorganic species. The surface of silica gel is characterized by the presence of silanol groups, which are responsible for weak or strong adsorption with the analytes. Silica gel surface modifications with certain functional groups generally lead to improvement of physical and chemical properties. Silica gel, due to low acidity of silanol groups (less donor properties) has weak interaction with transition and heavy metal ions [16–23].

Our survey through literature did not show any modification of silica gel surface with Schiff base like chelating agents that be suitable for enrichment of trace amount of metal ions in different samples with complicated matrices. In the present research the intrinsic –OH groups of silica gel were replaced by –N and –OH groups that capable of complexation of more metals ions from the solution.

In this work, via a simple low-cost procedure, the silica gel surface was modified and it was applied for the enrichment of trace amount of Fe^{3+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, $Co^{2+,}$ and Zn^{2+} ions subsequent their determination by FAAS.

2. Experimental

2.1. Instruments

The evaluation of understudy metal ions content was performed using a shimadzu 680 AA atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector at respective wavelengths using an air–acetylene flame according to the instrument parameters recommended by the manufacturer. Adjustment of pH was carried out using a metrohm 691 pH/Ion meter with a combined glass–calomel.

2.2. Reagents and solutions

All chemicals such as acids, bases, and nitrate salts of cation and potassium salts of anions with the analytical reagent grade were purchased from Merck Dermasdat, Germany and used as received. Double distilled deionized water was used throughout. The element standard solutions (1,000 mg/L) were prepared by weighting and dissolving a required amount of the nitrate salt of all cations. The pH adjustment was done by the addition of diluted nitric acid or sodium hydroxide to the sample solution.

The nano size SiO_2 core was prepared by the sol–gel method proposed through hydrolysis and polycondensation of tetraethoxy silane. 28.6 mL NH_3 H_2O and 58.3 mL absolute ethanol were dissolved into 28 mL deionized water. After preheating for 15 min under 50° C, 22.5 mL TEOS was added, drop by drop, into the solution with a proper agitation to disperse the droplets. Afterward, the mixed solution was stirred for 2 h and aged for 24 h. The resulting dispersions were separated from their mother liquor by centrifugation, the precipitates were washed several times with deionized water and ethanol before drying at 60°C for 12 h. The final SiO_2 nanoparticle was obtained by calcining the above powder at 500°C for 1 h. The SEM of nanosilica gel show that the size of silica gel nanoparticle is lower than 100 nm and the support has homogenous surface.

2.3. Preparation of 2-((3silylpropylimino) methyl) -2-hydroxy-1-naphthol (SPIMHN) bonded to silica gel

The solid phase was prepared according to following procedure. For this purpose SiO_2-supported aminopropyl was synthesized by the reaction of 4.0 g of common SiO_2 powder with 3.6 mL of trimethoxysilylpropylamine in dry dichloromethane (30 mL) for 24 h under reflux as well as severe stirring. The solid was filtered and washed off with distilled water and dried at room temperature. Then 1.8 g of 2-hydroxy-1-naphthaldehyde and 2.1 g of acetic acid (glacial grade) were added to a suspension of silica-supported aminopropyl in methanol (20 mL). Finally, the reaction mixture was refluxed for 24 h to obtain 2-((3silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN) bonded to silica gel (Fig. 1).

2.4. Preconcentration procedure

All SPE experiments were undertaken according to the following procedure. The pH of 250 mL of the sample solution of metal ions (0.01–0.5μg/mL) was adjusted to pH of 5.0 by addition of NaOH and/or HCl solution. This solution was passed through the

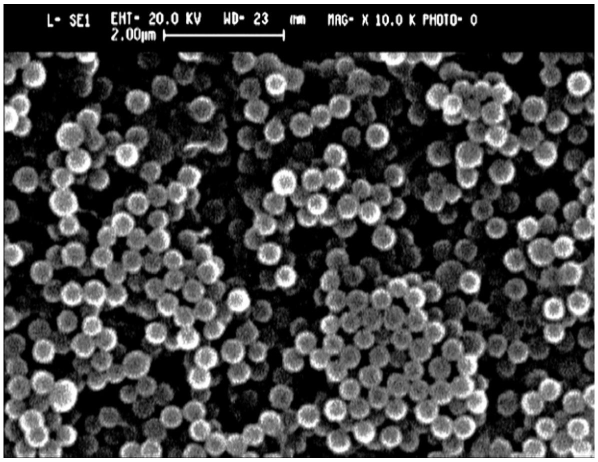

Fig. 1. SEM of nanostructure silica gel.

column containing 0.6 g of SPIMHN bonded to silica gel (SG-SPIMHN) at flow rate of 2.0 mL/min till the metal ions were retained and uptaken by the proposed sorbent quantitatively via chelation. Finally, the retained metal ions were efficiently eluted with 6 mL of 4.0 mol/L nitric acid (with a flow rate of 1 mL/min) and the metal ions content in the eluent were determined by flame atomic absorption spectrometer using standard addition method (see Fig. 1).

3. Results and discussion

To obtain the most suitable data and maximum metal ions recoveries influence of different parameters such as pH, the type, eluent conditions, the ratio of ligand and amount of solid phase on the understudy metal ions recoveries were all examined while the other parameters were kept constant.

The new chemically modified silica gel (SPIMHN 50 mg) was shaken with 25 mL of HNO_3 (1–5 mol/L) or NaCl, KCl, $NaNO_3$ (5 mol/L) for 5 h was filtered and washed with distilled water until free from acid or salt. The composition of produced solid phase is constant at all these media. Basic media was excluded due to severe hydrolysis of silica gel, while the modified silica composition and stability is not affected by soaking in DMF, DMSO, acetone, or MIBK for 24 h.

The sorption/desorption was repeated at the same silica gel and the recoveries were estimated after each cycle of operation. It was found that the proposed solid phase is applicable for repeatable recoveries of understudy metal ion for at least five times.

3.1. FT-IR characterization of chemically modified silica with 2- (3-silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN)

IR spectrum of silica gel exhibits some important characteristic vibration frequencies at 3,437(bs), 1,097 (vs), 799(m), and 464(s) cm^{-1} that contributed to stretching vibration of OH, asymmetric stretching vibration of Si–O–Si symmetric stretching vibration of Si–O–Si, and asymmetric Si–O–Si bending, respectively (Fig. 3a). After immobilization of trimethoxysilylpropylamine to the silica gel surface, the absorption intensity of OH is smoothly decreased because of decrease in silica surface, OH functional groups and some additional characteristic absorption bands at 1,634(w), 1,567(w), 1,490(w), and 693(w) cm^{-1} are appeared assigned to bending of NH_2, NH_2-scissoring, CH_2-bending, and CH_2 rocking, respectively, (Fig. 3b). Finally, 2-hydroxy-1-naphthaldehyde is chemically binded to silica-supported aminopropylsilylate via iminic bound to give new chemically functionalized modified silica gel with 2-((3silylpropylimino) methyl) -2-hydroxy-1-naphthol (SPIMHN) as solid phase. IR spectrum well shows some characteristic absorption frequencies related to Schiff base as following: a broad band at 3,400–2,500(m) (phenolic OH), 2,931(w)(CH-aliphatic), 1,636(s) (a sharp strong band belonged to iminic (C=N) group stretching), 1,607(w), 1,546(m), 1,518(m), and 1,492(w) (ring C=C stretching frequen-

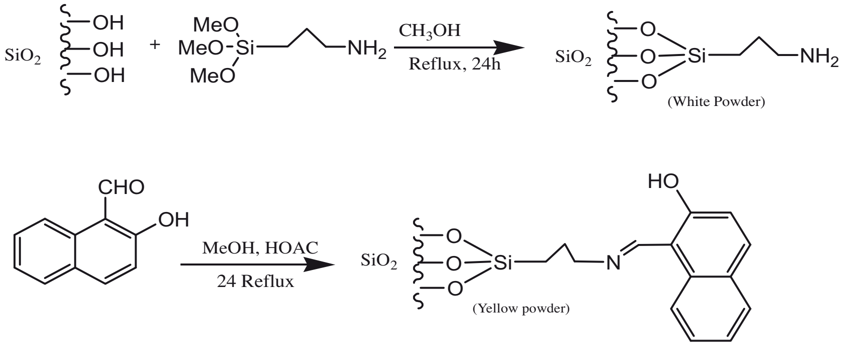

Fig. 2. Schematic diagram of synthesis of proposed sorbent.

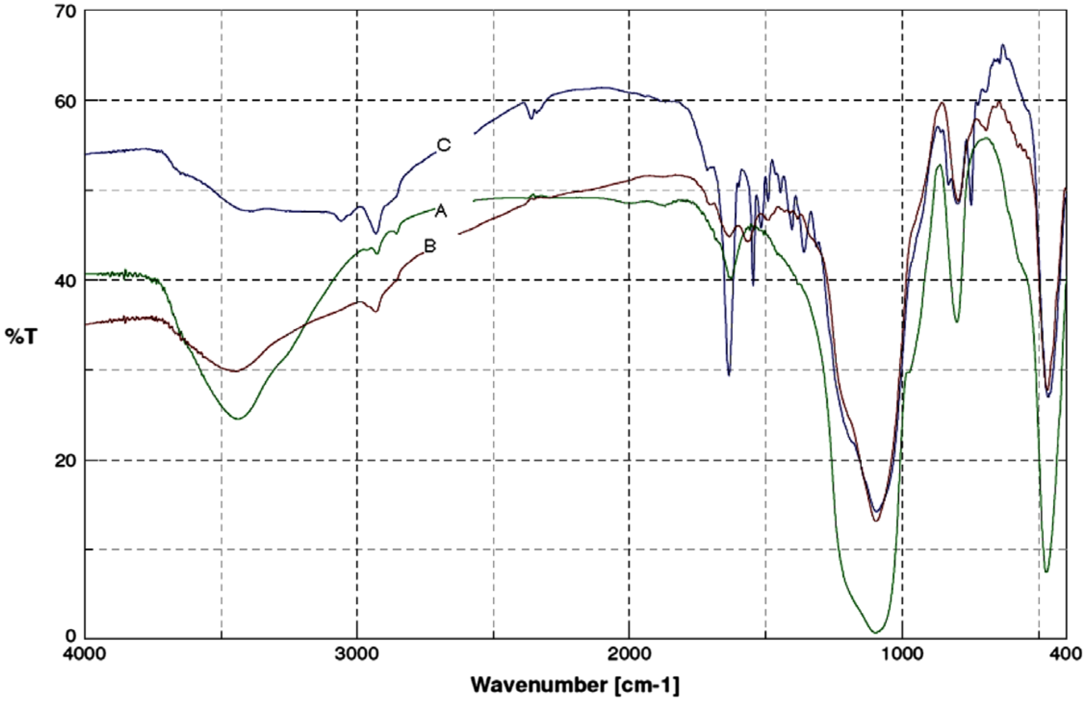

Fig. 3. FT-IR spectra of silica gel(a), silica-supported aminopropylsilylate(b), modified silica gel with 2-((3silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN)(c).

cies), 1,404(m), 1,361(m), and finally 797(s), and 747(s) cm^{-1} (out of plain bending of phenolic OH) (Fig. 3c). The new vibration frequencies at spectrum C with respect to B and A well confirm the formation of chemically modified silica gel.

3.2. Thermal analysis of solid phase

Thermogravimetric analysis is required to obtain some information about its thermal stability and existence of water molecules. Thermal decomposition studies of the sorbent were evaluated at temperature in the range of 100–1,000°C with the heating rates of 5 (°C/min) under oxygen atmosphere (Fig. 4). The lack of mass loss under 200°C show the absence of crystalline water molecules in the sorbent. Above 200°C, the sorbent is subjected to decomposition at three steps and losses 1.07, 2.87, and 5.56% weight as shown in Table 1. The thermodynamic activation parameters of decomposition processes of sorbent including activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*), and Gibbs free energy change of the decomposition (ΔG^*) can be estimated graphically by employing the Coats–Redfern relation (Eq. (1)) [25].

$$\log[\log\{W_{\mathrm{f}}/(W_{\mathrm{f}} - W)\}/T^2] = \log[AR/\Theta E^*(1 - 2RT/E^*)] - (E^*/2.303RT) \qquad (1)$$

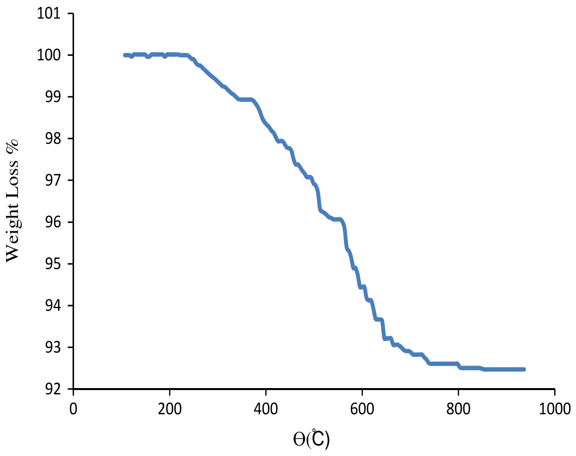

Fig. 4. TG graph of solid phase at range of 100–1,000°C.

Where W_{f} is the mass loss at the completion of the reaction step, W is the mass loss up to temperature T; R is the gas constant, E^* is the activation energy in kJ/mol, is the heating rate (5°C/min). A graph of the left hand side of Eq. (1) against $1/T$ gives a slope and intercept equal to E^* and A (Arrhenius constant), respectively. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*), and the free energy change of activation (ΔG^*) are calculated using the following equations:

Table 1
Thermo-kinetic parameters of the thermal decomposition of solid phase

$\Delta\Theta$ (°C)	E^* (kJ/mol)	A^*	ΔS^*	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	Weight loss (%)
230–350	63.87	1.25×10^3	-1.91×10^2	59.19	1.67×10^2	1.07
400–540	38.73	5.53	-2.38×10^2	32.63	2.07×10^2	2.87
540–750	45.55	5.20	-2.39×10^2	39.28	2.19×10^2	5.56

$$\Delta S^* = 2.303[\log(\mathrm{A}h/kT)R] \tag{2}$$

$$\Delta H^* = E^* - \mathrm{RT} \tag{3}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{4}$$

As it can be seen from the summarized data in Table 1, the high value of activation energies of decomposition (in the range of 38.73–63.87 kJ/mol), reflect the thermal stability of sorbent, while negative values ΔS^* indicate that the decomposition reactions proceed with a lower rate reaction with positive ΔS^*. ΔH^* and ΔG^* values are positive and found to be 32.63–59.19 and $(1.67–2.19) \times 10^2$ kJ/mol, respectively.

3.3. Effect of pH

The acidity of a solution is one of the most important factors affecting the adsorption process. It seems, proton in the acidic solution via protonation of the binding site of the chelating molecules and hydroxide in basic solution by complexation and precipitation of many metal ions to respective hydroxide hinder from their sorption [26,27].

By elevating the pH until five the functional group of proposed sorbent deprotonated and the sorption/recoveries of understudy metal ions increased. The binding of metal ions to the chelating agents (either in solution or loaded on solid support) depends on factors such as nature, charge, and size of the metal ions, nature of the donor atoms and acidity or basicity of chelating agent and the. To evaluate the suitability of the newly synthesized SG-SPIMHN for uptake of metal ions the pH influence on the metal ions sorption and recoveries was examined as follows:

250 mL of 0.2 μg/mL of Fe^{3+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} ions in the in the range of the 2–8 was passed through the column and respective results are presented in Fig. 5. As it can be seen, maximum metal ions recoveries were achieved at pH = 5 and further value recoveries significantly decreased.

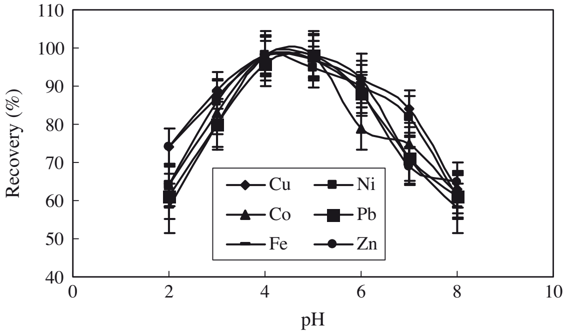

Fig. 5. Effect of pH on metal ions recoveries.

3.4. Effect of ratio of aminopropylsilylate to 2-hydroxy-1-naphthaldehyde and amount of solid phase on metal ion recovery

In this research, silica gel surface was modified with 2-(3silylpropylimino) methyl)-2-hydroxy-1-naphthol (SPIMHN) to improve hydrophobic nature and stability. On the other hand, chemical functionalization of silica gel which lead to replacement of silanol group with new Schiff base-like chelating agent can be seen from Scheme 1, the formation of proposed solid phase is based on reaction of aminopropylsilylate (TMSPA) and 2-hydroxy-1-naphthaldehyde (2-HNA). Therefore, various solid phases based on different ratios of these species have been prepared and for this study, 250 mL of sample solution containing 50 μg/mL of understudy metal ions at pH 5.0 is passed through 0.6 g solid phase and results are presented in Table 2. As it can be seen, solid phase composed of 3.6 mL TMSPA and 1.8 g of 2-HNA high recoveries was obtained. Hence, this ratio was selected for subsequent works.

In further experiments, the influence of amount of solid phase on metal ions recoveries was assessed by conducting similar experiments at the held constant of optimum value of all variables and various amounts of solid phase in the range 0.4–1.2 g and results are shown in Fig. 6. Results show that maximum recoveries were achieved using 0.6 g of solid phase, while both raising and decreasing the SP lead to significant

Table 2
Effect of ratio of 2-HNA to TMSPA on metal ion recovery

Ratio of 2-HNA to TMSPA	Cu	Ni	Co	Pb	Fe	Zn
1.8–3.6	98 ± 1.5	99 ± 1	98 ± 2.0	94 ± 2.0	99 ± 2.0	98 ± 1
2–4	82 ± 3.0	78 ± 4	83 ± 2.0	73 ± 4.0	76 ± 3.8	78 ± 2
2.4–4.8	94 ± 3.0	96 ± 2	98 ± 2.0	98 ± 2.0	98 ± 2	97 ± 2
2.6–5.2	89 ± 1.5	96 ± 1	96 ± 2.0	96 ± 2.0	92 ± 3	90 ± 2

decrease in metal ions recoveries. At higher amount of solid phase, probably due to insufficiently of eluent, the recoveries decreased. At lower SP amount, the extent of complexation and retention of metal ions on the loaded solid phase is low and hence the recovery was decreased.

3.5. Effect of eluent conditions on metal ions recovery

To select the most effective eluent for quantitative elution of retained metal ions from adsorbent surface, a series of selected eluents (different acids) were used and the respective results are shown in Table 3. As it was found, maximum metal ions recoveries were achieved using HNO_3 as eluent. Since, the proposed solid phase is stable in the presence of HNO_3, this eluent was selected for subsequent work. The volume of eluent is important to obtain the high concentration factor. The effect of eluent volume and concentration on the recoveries of the analytes was also studied by using various volumes of 4 mol/L HNO_3 and 6 mL of different concentration of HNO_3. It was found that maximum recoveries were obtained using 6.0–8.0 mL of 4 mol/L HNO_3 that was selected for the subsequent work.

3.6. Metal ion sorption as a function of temperature

Temperature is an important parameter in the context of adsorption on solid phase. In the present case, solution temperature was varied between 283 and 323 K. Respective results show temperature rising leads to increase in the removal and recoveries percentage and metal ions behave similarly. The increase in percentage uptake maybe thought as either due to an increased equilibrium constant for complexation at higher temperature or due to the activation of the adsorbent surface. The recoveries were found to be increase until 323 K that was selected for the subsequent work.

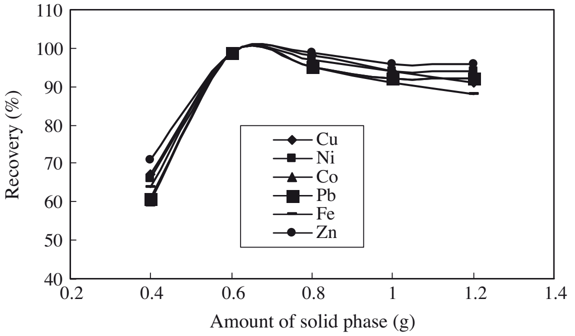

Fig. 6. Effect of the amount of solid phase on metal ions recoveries.

3.7. Effect of the sample flow rate

The retention of elements on adsorbent depends upon flow rate of the sample solution. Therefore, the influence of sample flow rate in the range of 1–5 mL/min on metal ions sorption was examined by passing 250 mL of sample solution through the column controlled with a stop check. It was found that the Fe^{3+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} ions recoveries were not affected obviously by flow rate until 4 mL/min.

3.8. Effect of interferences

Two types of interference affect the performance of pre-concentration and/or detection step [8]. In this regard, the influence of several common ions frequently accompany understudying metal ions in real samples was examined by conducting similar SPE procedure at different mass ratio concentrations on the and recoveries of understudy metal ions from 250 mL solution containing 50 μg/L of each analytes. The presence of interferences cause and produced variation in the absorbance and recoveries more than 5%. The effect of some interfering ions which obstruct the determination and/or preconcentration of trace amount of the target ions and/or often accompany analyte ions in various real environmental samples was examined with the optimized conditions and the results are given in Table 4. As it can be seen, the proposed method has reasonably tolerance limits for common interfering ion (which commonly found in saline real samples). Therefore, the proposed method can be successfully applied for extraction of metal ions from such systems.

Table 3
Effect of eluent condition

Condition of eluent	Cu	Ni	Pb	Co	Fe	Zn
6 mL of HCl (4.0 mol/L)	59	49	46	47	47	53
6 mL of HNO_3 (4.0 mol/L)	99	98	98	98	98	99
6 mL of CH_3COOH (4.0 mol/L)	44	43	38	47	41	47
6 mL of H_3PO_4 (4.0 mol/L)	49	46	40	41	42	52
6 mL of HNO_3 (2.0 mol/L)	63	52	47	49	49	67
6 mL of HNO_3 (3.0 mol/L)	98	98	96	95	95	96
6 mL of HNO_3 (5.0 mol/L)	94	92	92	93	92	95
6 mL of HNO_3 (6.0 mol/L)	94	91	90	92	91	93
2 mL of HNO_3 (4.0 mol/L)	63	56	50	53	51	68
4 mL of HNO_3 (4.0 mol/L)	79	80	75	77	74	87
8 mL of HNO_3 (4.0 mol/L)	92	94	98	98	96	98

3.9. Effect of sample volume

Breakthrough volume evaluation (represents the sample volume that can be preconcentrated without the loss of analyte during elution) was tested by dissolving 75 µg of metal ions while increasing the sample volume from 250 to 1,000 mL and performing SPE procedure.

The eluted metal ions content was evaluated by FAAS. It was found that the metal ions recoveries have not significantly affected unite 1,000 mL sample solution. Enrichment of understudy metal ions to final eluent volume (6 mL) causes a preconcentration factor of 166 (1,000/6). Sorption capacity (ability of sorbent to enrich traces amounts of metal ions from different sample solution) was determined by batch method. Therefore, 250 mL of 200 µg/mL of analytes was shaken for 1 h at pH 5 via 400 rpm till saturation of sorbent. The solid phase filtered and concentration of metal ions in the diluted filtrate were determined by FAAS. The amount of sorbed analytes the difference of metal ion concentration before and after sorption, show the uptake of metal ions and the results are presented in Table 5.

3.10. Analytical features

At optimum experimental conditions, the proposed method was applied to the solution containing various amounts of analytes and blank. The experimental preconcentration factors—the slope ratio calibration graph with and without preconcentration was 28.9, 24.3, 25.1, 19.5, 20.5, and 30.6 for Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}, and Zn^{2+} ions, respectively while the preconcentration factor as the volume of initial solution (1,000/6 mL) was 166. The limit of detection (LOD) (three times the standard deviation of the blank ($n = 10$) based on $3SD_b/m$) was 1.5, 2.5, 2.2, 2.8, 2.5, and 1.3 for Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}, and Zn^{2+} ions, respectively. The empirical limit of quantification (LOQ) based on $10\,SD_b/m$, was

Table 4
Effects of the matrix ions on the recoveries of the examined metal ions ($N = 3$)

Ion	Added As	Tolerance limit (mg/L)
Na^+	NaCl	1,000
K^+	KCl	
Cl^-	NaCl	
SO_4^{2-}	$(NH_4)_2SO_4$	800
CH_3COO^-	CH_3COO Na	800
Mg^{2+}	$MgCl_2$	700
HCO_3^-	$NaHCO_3$	850
PO_4^{3-}	Na_3PO_4	900
Sr^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, Mn^{2+}	Nitrate salt	1,000
Ag^+, Al^{3+}, Hg^{2+}		250

Table 5
Specification of the presented method at optimum conditions for each element

Parameters	Cu	Ni	Co	Pb	Fe	Zn
Linear range (μg/mL)	0.01–0.24	0.015–0.26	0.013–0.27	0.02–0.21	0.02–0.20	0.01–0.17
Correlation coefficient (R^2)	0.996	0.998	0.995	0.993	0.994	0.996
Detection Limit (ng/mL)	1.5	2.5	2.2	2.8	2.5	1.3
RSD (repeatability) (%)	3.1	3.3	3.1	3.2	3.4	2.8
Recovery (repeatability) (%)	99.2	99.4	99.6	99.1	99.0	98.9
RSD (reproducibility) (%)	2.6	2.8	2.6	2.9	2.6	2.5
Recovery (reproducibility) (%)	98.9	99.0	99.0	99.2	99.3	99.1
Loading capacity (mg/g)	45.6	42.5	41.2	41.8	48.4	38.7
Enrichment factor	25.9	22.4	23.1	20.1	21.9	28.6
Preconcentration factor	166					

Table 6
Recovery of analytes from spiked samples by using the proposed method ($N = 3$)

		Lentil			Mushroom		
Ion	Added	Found	RSD	Recovery (%)	Found	RSD	Recovery (%)
Ion	0	33.4	3.8	–	25.3	3.8	–
	10	43.7	3.2	104.0	35.7	3.3	104.0
Fe	0	2.35	4.0	–	2.38	3.7	–
	10	12.74	3.5	103.9	12.68	3.0	103.0
Ni	0	23.31	3.6	–	22.41	3.2	–
	10	33.09	3.1	97.8	32.73	2.6	103.2
Zn	0	0.45	3.0	–	1.08	2.9	–
	10	10.51	3.5	100.6	10.98	2.7	99.0
Pb	0	19.6	3.7	–	21.82	3.9	–
	10	29.3	3.3	97.0	32.09	3.3	102.7
Cu	0	0.58	3.4	–	1.06	3.1	–
	10	11.45	3.0	100.1	11.56	2.9	100.2

Table 7
Levels of analyte ions in the real samples ($N = 3$)

		Carrots			Turnip		
Ion	Added	Found	RSD	Recovery	Found	RSD	Recovery
Fe	0	9.81	3.9	–	12.3	3.8	–
	10	19.25	3.3	94.4	22.6	3.2	104.0
Ni	0	7.06	4.1	–	8.9	4.2	–
	10	17.25	3.5	101.9	18.7	2.9	103.0
Zn	0	11.97	3.3	–	14.6	4.6	–
	10	22.35	2.9	103.8	24.8	3.8	103.2
Pb	0	0.17	4.1	–	0.62	4.2	–
	10	10.16	3.7	99.9	10.54	3.4	99.0
Cu	0	1.6	3.8	–	1.44	3.5	–
	10	11.4	3.3	98.0	11.69	3.0	102.7
Co	0	0.18	4.2	–	0.68	3.4	–
	10	11.15	3.9	99.9	12.22	2.9	100.2

between 8 and 10 μg/L for all understudy metal ions. Characteristic performances of the proposed SPE procedure are shown in Table 5.

Consumptive index (CI) (volume of analyte solution (V, mL) to experimental preconcentration factor (EPF) ratio (CI = V/EPF)) was calculated and presented in Table 5. The required volume to obtain one unit of enrichment factor for analytes was between 4.4 and 8.3.

The accuracy of the proposed preconcentration methodology was evaluated by means of analyte determination in different real samples including the Lentil, Mushroom, Carrots, and Turnip sample and respective results are shown in Tables 6 and 7. As it can be seen, the proposed method due to its high recoveries and low RSD is suitable for preconcentration and determination of understudy metal ions from such real samples with complicated matrices. The analytical results for the spiked samples were confirmed by the standard addition method.

4. Conclusions

In this research, a new sorbent was prepared with a simple and relatively rapid procedure by a chemical reaction between silica gel and organic compounds according to scheme 1 and efficiently characterized by FT-IR spectroscopy. This new sorbent with high efficiency has been applied for the preconcentration and subsequent determination of metal ions such as Fe^{3+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} ions. The proposed method has enrichment factor in the range of 20.8–29.2 and low detection limit between 1.0–2.6 ng/mL with relative standard deviation of 2.9–3.4.

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