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Chemical functionalization of silica gel with 2-((3-silylpropylimino) methyl) phenol (SPIMP) and its application for solid phase extraction and preconcentration of Fe (III), Pb (II), Cu (II), Ni (II), Co (II) and Zn (II) Ions

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Abstract

2-((3-silylpropylimino) methyl) phenol chemically bonded silica gel were successfully applied for the enrichment of trace amount of Fe(III), Pb(II), Cu(II), Ni(II), Co(II) and Zn(II) ion prior to their determination by Flame Atomic Absorption Spectroscopy (FAAS). The influences of the analytical parameters including pH, amount of ligand and solid phase, type and condition of eluent 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 with the low limit of detection (1.4 - 2.6 µg L^{-1}), the enrichment factor of 25.3, 28.2, 24.6, 20.1, 28.2 and 18.6 respectively for Ni^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and Fe^{3+} ions, and relative standard deviation less than 4.0%, especially for their determination in real samples. Graphical correlation of various adsorption isotherm models like, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich have been carried out. The adsorption of these metal ions has been found endothermic and feasible in nature and various thermodynamic parameters such as Gibb's free energy, entropy and enthalpy of the on-going adsorption process has been calculated. The kinetic studies suggest the process following pseudo second order kinetics and involvement of particle diffusion mechanism.

Keywords: Trace metal enrichment, Silica gel, 2-((3-silylpropylimino) methyl) phenol, Atomic absorption spectrometry, Solid phase extraction.

Introduction

Trace level study of elements assumes greater significance from the point of humans health and environmental hygiene (Jamali *et al.*, 2007; Marahel *et al.*, 2011a; Soylak *et al.*, 2011; Jamshidi *et al.*, 2011; Marahel *et al.*, 2011b). Although, flame atomic absorption spectrometry (FAAS) with unique advantages such as high sample throughput, low cost operation, high precision and specificity is an even accessible and low cost instrument. There is a critical need for preconcentration and separation of the trace metals from matrices prior to their determination (Ghaedi *et al.*, 2010; Safavi *et al.*, 2006). Nowadays, solid-phase extraction (SPE) becomes the most common technique for environmental sample pretreatment because of advantages such as high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents over liquid-liquid extraction. In this technique, the choice of appropriate sorbents is a critical factor to obtain full recovery and high enrichment factor. Silica gel with unique advantages such as relative activity, large adsorption capacity, different pore size and high surface area in addition to possibility of surface modification by covalent binding of surface functional groups, is suitable for retaining the analyte (Citak & Tuzen, 2010; Mahmoud *et al.*, 2010; Mahmoud *et al.*, 2004; Osman *et al.*, 2004; Tu *et al.*, 2010; Fan *et al.*, 2007; Jiang *et al.*, 2006; Jal *et al.*, 2004; Soliman *et al.*, 2004; Madrakian *et al.*, 2006; Ghaedi *et al.*, 2009; Edson Luiz da Silva *et al.*, 2004). Chemical modification of silica gel change significantly the wet- ability and adsorption behavior of the parent support by incorporation of certain functional groups. This scheme changes the structure of silica gel, i.e. surface hydroxyl groups transfer to chelating group (Wu *et al.*, 2004; Soliman *et al.*, 2006; Akl *et al.*, 2004; Madrakian *et al.*, 2008; Prado & Airoldi, 2001; Mahmoud 1999). Immobilized silica gel is superior to organic polymers in term of good mechanical and thermal stability, less susceptibility to swelling, shrinking and microbial effects (Abou-El-Sherbini *et al.*, 2002; Pyell & Stork, 1992; Mahmoud & Soliman, 1997; Pu *et al.*, 1998; Goswami *et al.*, 2003; Goswami & Singh 2002a; Goswami & Singh, 2002b; Jal *et al.*, 2004; Liu *et al.*, 2000; Safavi *et al.*, 2004; Soylak & Elci, 2000).

The selectivity of the immobilized surface towards metal ions depends on various factors such as size of the modifier, activity of the loaded group and characteristic of the hard-soft acid-base. Due to the presence of many reactive sites on silica gel large number of organic molecule could be immobilized on its surface to improve its sorption behavior. The synthetic pathway of modified silica gel was similar to the reaction of organosilane with silanol groups on silica gel, while the types of chelating molecules which selectively chelate to metal ions in different way. In despite of un-reactivity of silica gel silanol group it easily react with 2-((3-silylpropylimino)methyl)phenol (SPIMP) to yield the siloxan bind and amino groups that is capable to react with ketone and/or aldehyde to yield the Schiff's base compound. A new sorbent in this research was produced and efficiently applied for trace metal enrichment.

Experimental

Instruments

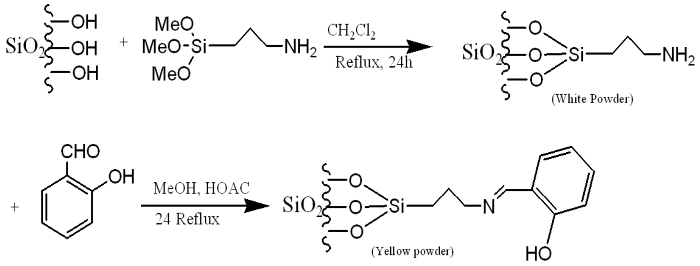
The measurements of metal ions were performed with a Shimadzu 680 AA atomic absorption spectrometer

(Norwalk, CT, USA) equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/Ion meter (Herisau, Switzerland) with a combined glass-calomel electrode was used for adjustment of test solution pH.

Reagent and solutions

All applied chemicals were of analytical reagent grade and were used without further purification. Double deionized water was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1:9) and were rinsed with distilled water prior to use. Stock solutions of diverse elements were prepared from high purity nitrate salts. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg L^{-1} of the given element supplied by Merck (Darmstadt, Germany).

Scheme 1. Schematic diagram of solid phase preparation



Preparation of SPIMP bonded to silica gel

The modified silica gel was prepared according to following procedure as shown in Scheme 1. For this purpose SiO_2-supported aminopropyl was prepared by refluxing 2.0 g commonly SiO_2 powder with 2.2 mL of trimethoxysilylpropylamine in dry dichloromethane (30 mL) for 24 h. The solid was filtered and washed off with distilled water and dried at room temperature. 1.3 mL of salicylaldehyde and 2.1 g of acetic acid (glacial grade) were added to the suspension of silica-supported aminopropyl in methanol (20 mL) and the reaction mixture was refluxed for 24 h to make a bonded silica gel SPIMP.

Column preparation

A short glass column with an inner diameter of 0.5 cm and a length of 50 cm, equipped with porous frits was filled up to height of about 1.0 cm with a suspension of 0.8 g of SPIMP bonded silica gel. SPIMP bonded silica gel was preconditioned by the 1 mol L^{-1} HNO_3 as blank solution prior to each use and after using, the column was rinsed with water and stored for the next experiment.

Test procedure

250-2000 mL of 0.2 µg mL^{-1} of all samples containing understudy metal ions at pH= 2.0-9.0 were passed through 0.8 g of solid phase at a flow rate of 4 mL min^{-1} to effect the deposition of analyte and the retained metal ions. The retained metal ion were then eluted with 6 mL 4 mol L^{-1} nitric acid with a flow rate of 1 mL $min^{-1}$and their contents was determined by FAAS.

Batch adsorption experiments

To study the influence of initial metal ions concentration, time and temperature on the efficiency of removal of metal ions, batch experiments were conducted. In this regard, in each experiment, 100 mL of metal ions solution with known concentration and pH in the presence of known amount of the modified silica gel were taken in a 250 mL erlenmeyer flask. This mixture was agitated on stirrer at a constant speed at a fixed temperature or at fixed initial metal ion concentration and different temperature. Similar experiments were undertaken at different time intervals (0-60 min) and kinetics of adsorption was determined by analyzing of remaining metal ions concentration from aqueous solution at optimum pH=5. The initial solution pH was adjusted by addition of dilute aqueous solutions of HNO_3 (1 mol L^{-1}) or KOH (1 mol L^{-1}). The percentage removal of metal ions was calculated using the following relationship:

$$\text{Removal (\%)} = ((C0 - Ct)/ C0) \times 100 \qquad (1)$$

where C0 and Ct (mg L^{-1}) are the initial metal ions concentration and concentration at time t, respectively. For investigating the adsorption isotherms, metal ions solutions with different concentrations (1-20 mg L^{-1}) at different temperatures (10-60 °C) were agitated with known amounts of modified silica gel till reaching the equilibrium. Equilibrium adsorption capacity was calculated from the following relationship

$$qe = (C0 - Ce)\, V/W \qquad (2)$$

where qe (mg g^{-1}) is the equilibrium adsorption capacity, Ce is the metal ions concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

Pretreatment of real samples

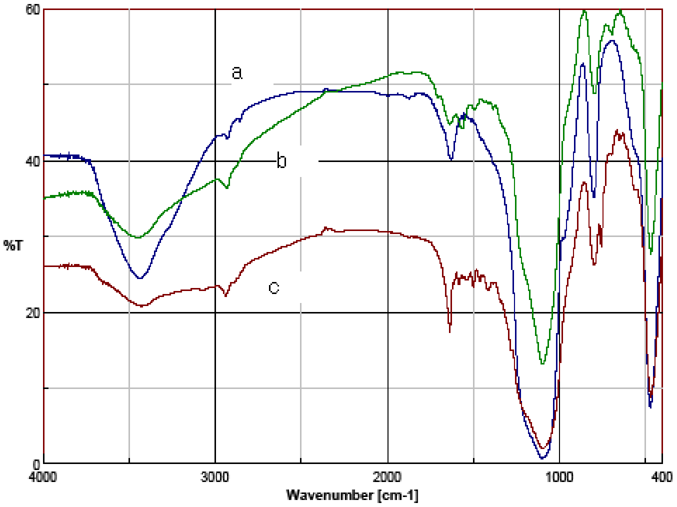
Twenty grams of homogenized biscuit sample was weighed accurately and in a 200 mL beaker was digested with addition of 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70% and then heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value (5.0) and diluted to mark with de-ionized water. Then the preconcentration-separation procedure above was performed.

A 20 g sample of rice, tomato, grapes and vegetable sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to a furnace at 650 ºC for overnight. The cooled residue was treated with 10.0 mL of concentrated nitric acid and 3 mL 30% H_2O_2 (w/w) and again kept in a furnace for 2 h at 650 ºC. The final residue was treated with 3 mL concentrated hydrochloric acid and 2 to 4 mL of 70 wt% perchloric acid and heated to expel the fumes. The dissolved solid residue in water was filtered and distilled water was added to bring up the volume of each sample to 250 mL and its pH was adjusted to 5.0 by the addition of KOH and

HCl and preconcentration procedure mentioned above was applied.

For the microwave, digestion of fish samples 5.0 g of sample was digested with 4 ml of concentrated HNO_3 and 2 ml of concentrated H_2O_2 in microwave system. After completing the digestion, the volume of sample was made up to 250 ml with distilled water. Blanks were prepared in the same way as the sample omitting the real samples and the preconcentration-separation procedure above was applied.

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



Results and discussion

The support material in SPE should be thermally and chemically stable during the reaction process and its active sites must be well dispersed on its surface and be easily accessible. Thus the chemical modification of silica gel is recommended.

Characterization of adsorbent

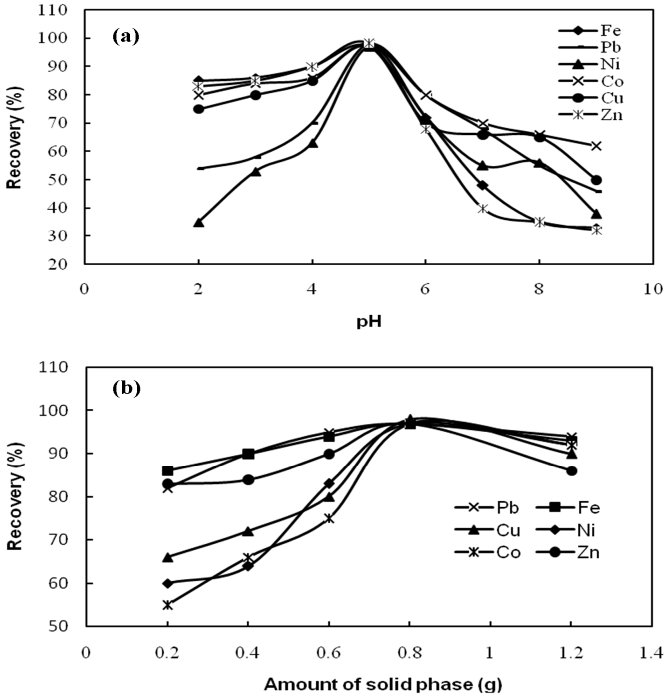
IR spectrum of silica-gel shows some important characteristic vibrational frequencies at 3437(bs), 1097(vs), 799(m) and 471(s) cm^{-1} assigned to stretching vibration of OH, asymmetric stretching vibration of Si-O-Si, symmetric stretching vibration of Si-O-Si, and asymmetric Si-O-Si bending respectively (Fig. 1(a)). After loading of trimethoxysilylpropylamine on silica-gel surface as in experimental section, the absorption intensity of OH is smoothly decreased indicating the decreasing of OH groups on silica surface. Some additional characteristic absorption bands at 1635(w), 1567(w), 1490(w) and 693(w) cm^{-1} are appeared in IR spectrum of silica supported aminopropylsilylate that can be related to bending of NH-bending, NH_2-scissoring, CH_2-bending and CH_2-rocking respectively (Fig. 1(b)). Finally salicylaldehyde is bounded to silica supported aminopropylsilylate via an iminic bound to obtain a chemically modified silica gel with 2-((3-silylpropylimino) methyl) phenol (SPIMP) as extractor. IR spectrum well exhibits some characteristic peaks at 3422(m), 3020-3070(w), 2936(w), 1634(s), 1460-1583(m), and 755(s) cm^{-1} assigning to OH-phenolic, CH-aromatic, CH-aliphatic, C=C stretching and out of plain bending of phenolic OH (Fig. 1(c)).

Selectivity studies of the new solid phase as a function of pH

It is well known that the nature of the function groups toward agent immobilized on the surface of solid support influence its affinity and selectivity of certain metal (Soylak & Tuzen, 2008; Ghaedi *et al.*, 2007). Due to hydrogen ions themselves are strongly compete with metal ions for binding to ligands, the sample acidity affect the protonate binding sites of the chelating molecules at low pH while at high pH hydroxide may hinder complex formation and lead to formation of hydroxide precipitate of metals ions. Both of these phenomena lead to decrease in metal ions recoveries.

Fig. 2 (a) shows the effect of sample pH on the metal ions sorption within the range of 2-9 at room temperature, 0.8 g of solid phase and 6 mL of HNO_3 4 mol L^{-1} with a flow rate of 4 mL min^{-1}. As it can be seen in acidic medium a weak complexation and sorption occurs, which is explained by competition between metal ions and hydrogen ions for the binding to functional groups or atoms of sorbent. On the other hand, by increasing the pH the active sites and functional group of chelating agent deprotonated and its tendency for binding of ligand to metal ion increased and consequently the metal ions sorption increased. The sorption capacities increased with increasing pH reaching plateau values at around

Fig. 2. Effect of pH (a) and amount of solid phase (b) on metal ions recoveries



pH=5. pH higher than 5, due to the precipitation of metal ions as $M(OH)_n$ or mixed charged hydroxo complexes, the contamination of sorbents surface and hence a slight decline of the retention efficiency was achieved. Therefore, the pH=5 was chosen throughout the subsequent experiments.

Effects of amounts of solid phase

To investigate the optimum amount of SPIMP bonded silicagel for the quantitative extraction of the investigated metal ions by the chemically modified silica gel, their extraction was conducted using solid phase containing various amount of solid phase from 0.2 to 1.2 g at pH=5 and 6 mL of HNO_3 4 mol L^{-1} with a flow rate of 4 mL min^{-1}. The results expressed in Fig. 2 (b) show that with increasing amount of SPIMP bonded silicagel up to 0.8 g causes an increase in recoveries and at further value mentionable change in efficiency was not obtained. Quantitative recoveries for the analytes were obtained after 0.8 g of SPIMP bonded silicagel and subsequent studies were carried using 0.8 g of SPIMP bonded silicagel.

Condition of eluent

The choice of a suitable eluent is very important for the successful computable of a preconcentration system to measurement system (Tuzen *et al.*, 2007; Tuzen & Soylak, 2009). A satisfactory eluent should effectively elute the analytes ion with small volume to obtain a high enrichment factor and simultaneously affect the accurate determination of the analytes and destroy life time and reusability of solid phase. The effect of Eluent on the metal ions sorption was investigated at the condition of pH=5, 0.8 g of solid phase and flow rate of 4 mL min^{-1}. The experimental results in Fig.2 (a), shows that the adsorption of these metal ions was negligible at pH <3. For this reason, different solutions of acids including HCl, H_2SO_4 and HNO_3 were attempted to be used as the eluent (Table 1). Quantitative recoveries for all metal ions were obtained only with 4 mol L^{-1} of HNO_3, while lower recoveries were obtained using other eluent. The acid concentration was an important factor because at lower proton concentration it may be not enough to protonate the chelation site, while high acid concentration affect the determination step due to the contamination from applied acid. To achieve high preconcentration factor, metal ions in large sample volume desorbed by small stripping volume. This was examined by varying of 4 mol L^{-1} nitric acid volumes in the range of 2-12 mL and various nitric concentrations in the range of 1-5 mol L^{-1}. It was found that quantitative recoveries could be obtained with 6 mL of HNO_3 4 mol L^{-1}. Therefore, 6.0 mL of HNO_3 4 mol L^{-1} was used for the subsequent experiments to obtain high enrichment factor.

Table 1. Effect of type and concentration of eluting agent on recovery of analytes

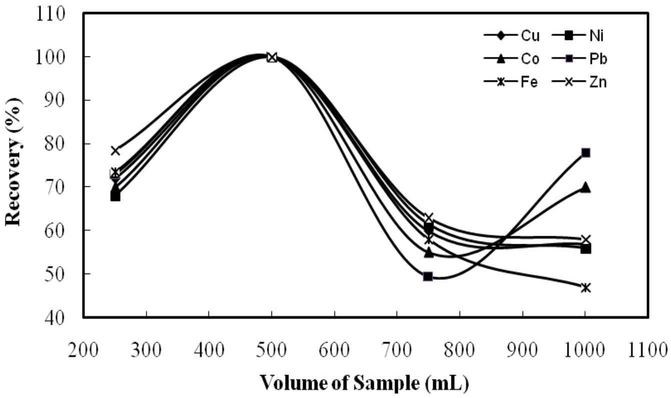
Condition of eluting Solution	Cu	Ni	Co	Pb	Fe	Zn
HCl [a]	44	36	47	51	55	60
H_2SO_4 [a]	50	50	45	40	47	50
2 mL HNO_3 [a]	72	72	75	82	82	85
4 mL HNO_3 [a]	97	80	82	94	90	95
6 mL HNO_3 [a]	100	100	100	100	100	100
8 mL HNO_3 [a]	98	97	97	98	97	99
12 mL HNO_3 [a]	95	94	92	94	93	97
1.0 mol L^{-1} HNO_3 [b]	64	66	59	70	83	91
2.0 mol L^{-1} HNO_3 [b]	77	84	74	87	90	97
3.0 mol L^{-1} HNO_3 [b]	96	95	91	94	94	95
4.0 mol L^{-1} HNO_3 [b]	100	100	100	100	100	100
6.0 mol L^{-1} HNO_3 [b]	92	91	90	88	88	92

a) All solutions are 4.0 mol L^{-1}; b) all volumes are 6 mL.

Influence of sample volume

Applicability of every proposed SPE depend to its ability for enrichment of low concentrations of trace metals from larger sample volume to smaller volumes of eluent to obtain high preconcentration factor. The break through sample volume was investigation by preconcentration of a fixed amount (µg) of understudy metal ions from various samples in the range of 250-1000 mL at pH=5 and their subsequent and recoveries via 6 mL of HNO_3 4 mol L^{-1} with a flow rate of 1 mL min^{-1}. The results show that the recoveries of the analytes were increase until 500 mL and decreased at sample volume above this value (Fig. 3). In this study, the eluent solution volume was 6.0 mL; therefore the preconcentration factors were 83 for all analytes.

Fig. 3. Effect of sample volume on metal ions recoveries



Effect of flow rate of sample and eluent solutions

The sample and eluent flow rate significantly affect the whole preconcentration and analysis time and thereby provide useful information about the rate of adsorption and complexation of metal ions with the solid phase. The influences of the sample and eluent flow rates on the recovery of metal ions were separately examined in the flow rates range of 1-6 mL min^{-1} with the model solutions of 250 mL. It was observed that the recovery was not changed significantly up to 4.0 mL min^{-1}, which was selected for further experiments. In the eluent volume lower than 1.0 mL min^{-1}, the recoveries of the analytes were not quantitative and after this value, the recoveries of the analytes were not quantitative.

Adsorption equilibrium study

Adsorption isotherms relationship between the amount of retained metal ion by the adsorbent and the remained concentration remaining in solution is necessary to explain the nature of interaction between adsorbate and the adsorbent. The experimental data was fitted different conventional isotherm models like Langmuir and Freundlich equations and their constant elucidate the adsorption process. The Langmuir equation (valid for monolayer adsorption onto homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules) is represented in the linear form as follows:

$$Ce/qe = 1/kLQm + Ce/Qm \qquad (3)$$

where KL is the Langmuir adsorption constant (Lmg^{-1}) and Qm is the theoretical maximum adsorption capacity ($mg\ g^{-1}$). The adsorption isotherms of all metal ions at experimental condition (pH=5, 0.8 g of solid phase and 6.0 mL of HNO_3 4 mol L^{-1} with a flow rate of 4 mL min^{-1}) were found to be linear and the correlation coefficients were extremely high ($R^2 > 0.99$). The values of Qm increase with temperature increases that show the process is endothermic.

Interference

To assess the possible analytical applications of the recommended procedure, the effect of some foreign ions which interfere the preconcentration of metal ions or/and often accompany analyte ions in various real samples was examined with the optimized conditions above (pH=5, 0.8 g of solid phase and 6.0 mL of HNO_3 4 mol L^{-1} with a flow rate of 4 mL min^{-1}). To evaluate tolerance limit, a fixed amount of metal ions in the presence of different amounts of foreign ions was subjected to recommended procedure and recoveries of understudy metal ions was examined. The recoveries of metal ions in these studies were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of the proposed SPE and the FAAS methods. The results are summarized in Table 2 show that large numbers of alkaline, alkaline earth and transition metal ions used have no considerable effect on the determination of analyte ions.

Table 2. Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Ion	Added as	Tolerance limits mass fold
Na^+	NaCl	1000
K^+	KCl	1000
Cl^-	NaCl	1000
SO_4^{2-}	$(NH_4)_2SO_4$	850
Mg^{2+}	$MgCl_2$	800
HCO_3^-	$NaHCO_3$	800
PO_4^{3-}	Na_3PO_4	900
Cd^{2+}, Ba^{2+}, Ca^{2+}, Ag^+, Al^{3+}, Hg^{2+}		1000 250

Analytical features

The limit of detection (LOD), defined as the lowest analyte concentration that produces a response detectable above the noise level of the system is based on general definition of $3SD_b/m$ (n=10)) was 2.4, 1.6, 2.0, 2.8, 2.0 and 1.4 μg L^{-1} for Fe^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+} ion respectively.

The calibration curves for analyte ions were drawn after setting recommended value of parameters of FAAS including wavelength, slit width and lamp current. The optimum concentration ranges and regression equations for analytes were given in Table 3. The statistical calculations are based on the average of triplicate readings for standard solutions of the analyte ions. The precision of the method was investigated by using the model solutions containing the spiked elements on the optimal conditions of the method (Table 3). Consumptive index (CI) as indication of preconcentration performance (is the ratio of volume of analyte solution (V, mL) to the experimental preconcentration factor (EPF) ratio (CI= V/EPF) is the required volume to obtain one unit of enrichment factor. It is important to emphasize that CI value obtained in the present study (3.5 mL) is lower than that of the most procedure (Table 3). The preconcentration factor as the phase volume ratio was 291 for all ions. The enrichment factor, defined as the ratio of the slopes of linear section of the calibration graphs before and after the preconcentration which give the same absorbance, were 25.3 for Ni^{2+}, 28.2 for Zn^{2+} ion, 24.6 for Ni^{2+}, 20.1 for Pb^{2+} ion 28.2 for Cu^{2+} ions and 18.6 for Fe^{3+} ions (Jamshidi *et al.*, 2011; Marahel *et al.*, 2011 Ghaedi et al,. 2010).

Table 3. Specification of presented method at optimum conditions for each element

Parameters	Fe	Cu	Ni	Pb	Co	Zn
L. R.^{a}	20-510	12-420	15-385	28-318	18-458	10-350
D. L.^{b}	2.4	1.6	2.0	2.8	2.0	1.4
RSD (%)	2.5	1.9	2.4	2.6	2.3	2.1
Recovery (%)	97.8	96.1	95.6	96.2	97.8	98.0
L. C.^{c}	87.6	86.9	82.4	69.8	80.4	90.0

a) Linear range (μg L^{-1}); b) detection limit (μg mL^{-1}); c) loading capacity (mg g^{-1})

Application to environmental samples

The feasibility of the proposed methodology for the preconcentration and determination of ions in different environmental matrices by standard addition method have been explored. Reliability was checked by spiking experiments and independent analysis. Therefore, the proposed method was applied for analysis of real samples such as rice, biscuit, tomato, grapes and vegetable samples and results are shown in Table 4. The recovery of spiked samples is satisfactorily reasonable and was confirmed using standard addition method.

Table 4. Recovery of analytes from spiked samples by using proposed method (N=3)

Ion	Added ($\mu g\ mL^{-1}$)	Found ($\mu g\ mL^{-1}$)	RSD (%)	Recovery (%)	Found ($\mu g\ mL^{-1}$)	RSD (%)	Recovery (%)
		Rice			Fish		
Fe	0	3.19	3.9	---	0.170	3.3	---
	0.2	3.40	3.0	105.0	0.376	2.9	103.0
Cu	0	2.06	4.3	----	0.214	4.2	----
	0.2	2.25	3.3	95.0	0.422	2.9	104.0
Zn	0	1.97	3.3	---	0.149	4.2	-----
	0.2	2.18	2.9	98.0	0.356	3.0	103.5
Pb	0	0.166	4.1	----	0.250	4.2	---
	0.2	0.371	3.7	102.5	0.458	3.4	104.0
Co	0	0.297	4.0	-----	0.260	3.3	----
	0.2	0.505	3.2	104.0	0.471	2.1	105.5
Ni	0.0	0.683	3.8	----	0.144	3.3	-----
	0.2	0.890	3.1	103.5	0.352	2.9	104.0
		Grapes			Tomato		
Fe	0.0	24.32	3.8	---	10.33	3.6	---
	0.5	25.34	3.3	98.0	10.80	3.1	94.0
Cu	0.0	1.26	4.0	---	0.69	4.0	---
	0.5	1.74	3.6	96.0	1.21	3.4	104.0
Zn	0.0	8.89	3.5	---	8.05	3.8	---
	0.5	9.43	3.0	102.0	8.54	3.0	98.0
Pb	0.0	0.19	3.7	---	0.11	3.9	---
	0.5	0.72	3.4	98.0	0.53	3.5	104.0
Co	0	0.42	3.6	---	0.56	3.4	---
	0.5	0.95	2.9	106.0	1.04	2.8	96.0
Ni	0.0	2.92	3.6	---	2.99	3.6	--
	0.5	3.44	3.0	104.0	3.52	2.9	106.0
		Biscuit			Vegetable		
Fe	0	27.24	3.6	---	0.28	3.8	--
	0.5	27.65	3.0	104.0	0.80	3.1	104.0
Zn	0	3.31	2.6	---	2.43	2.6	---
	0.5	3.79	2.1	96.0	2.95	2.1	104.0
Pb	0	1.04	2.5	---	0.36	2.5	---
	0.5	1.51	2.0	94.0	0.85	2.0	98.0
Ni	0	3.21	3.8	--	4.23	3.8	---
	0.5	3.74	3.3	106.0	4.74	3.3	102.0
Cu	0	0.00	---	--	0.02	3.5	---
	0.2	0.24	3.5	---			
	0.5	0.56	3.0	106.7	0.53	3.0	102.0
Co	0	2.76	4.4	--	2.94	4.2	---
	0.5	3.28	3.8	104.0	3.42	3.9	96.0

The presented results indicate the capability of the proposed system for the determination of understudy metal ions. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Comparison with literature

A comparison of the proposed system with preconcentration procedures based on other sorbents is given in Table 5 (Ghaedi *et al.*, 2007; Ngeontae *et al.*, 2007; Kumar *et al.*, 2001; Lemos & Baliza 2005). The proposed preconcentration system shows good enrichment factors with reasonable preconcentration time over other preconcentration methods. Consumptive index (CI) is another efficient way to evaluate the performance of preconcentration system. CI is expressed by ratio of volume of analyte solution (V, mL) to experimental preconcentration factor (CI = V/EPF), indicate the necessary volume to obtain one unit of enrichment factor (Jamshidi *et al.*, 2011; Marahel *et al.*, 2011b; Soylak *et al.*, 2011). As seen from the Table 5, the detection limit for proposed method is comparable to those given by many methods.

Conclusions

In the presented study a new simple and low cost and environmentally friendship solid phase extraction technique based on chemical functionalization of silica gel has been reported for the preconcentration of Ni(II), Co(II), Cu (II), Fe (III), Zn (II) and Pb(II) ions. The determination of analyte ions yields quantitative recoveries. Chemically modified silica gel was used as high as greater than 20 experiments without any loss in its sorption behavior. The system was successful in preconcentration of analytes from large sample volume (500 mL). The high enrichment factor and

Table 5. Comparative data for preconcentration of simultaneous preconcentration of some metal ions using chemically modified sorbents and detection by FAAS.

Metal	Sorbent	BTV[a] (mL)	LOD ($\mu g\ L^{-1}$)	C.I[b] (mL)	Preconcentration time	Ref
Cu, Ni, Pb, Co	DHMP[c]	1300	2.9,3.5,8.4,3.4	5.0	75 min	38
Pb, Cu, Ni , Co, Cd	Silica gel	25-100	22.5,1.0,2.9,0.95,1.1	-	10 min	41
Cu, Cd, Co, Pb, Zn, Mn	XAD-2[d]	1000	2.0,1.3,5.0, 1.5, 1.0,1.6	10.0,20.0,25.0, 20.0,10.0,15.4	-	42
Cu, Fe, Zn	B. T. I. [e]	250	1.14, 2.01, 0.14	0.18, 0.57	1-3 min	43
Pb, Cu, Ni, Co, Fe, Zn	SPIMP	500	1.6-2.8	3.5	62 min	This work

[a)] Break Trough Volume [b)] Cumulative index, [c)] DHMP loaded activated carbon; [d)] Quinalizarin XAD-2;
[e)] Bacillus thuringiensis israelensis

good figures of merit for method could be achieved. The present work revealed that the new modified solid phase was the promising materials for the removal of metal ions from aqueous solutions.

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