Preconcentration and separation of trace amount of copper (II) on N[1], N[2]-bis(4-fluorobenzylidene)ethane-1,2-diamine loaded on Sepabeads SP70

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ABSTRACT

A sensitive and simple method for the preconcentration of copper (II) ions has been reported. The method is based on the adsorption of copper ion N[1], N[2]-bis(4-fluorobenzylidene)ethane-1,2-diamine loaded on Sepabeads. The sorbed copper content was eluted by 8 ml of 4 M nitric acid in acetone. The influences of the analytical parameters including pH and sample volume were investigated. The interference effects of matrix ions on the retentions of the copper (II) ions were also examined. The recovery of understudy analyte was generally higher than 95%. The method has been successfully applied to the evaluation of copper contents in some real samples including water samples, vegetable samples and milk samples.

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1. Introduction

Copper is a gastrointestinal tract irritant but is generally not harmful to humans at low concentration. However, in concentration less than $1 \, \text{mg} \, \text{l}^{-1}$ it can be toxic to aquatic plants and some fishes [1–3], so, copper tends to be much more of an environmental hazard than a human hazard. The determination of trace amounts of copper has received considerable attention in many samples especially environmental pollution. The atomic absorption spectrometry (AAS) technique, which offers fast multi-elemental analysis, suffers from poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples [4–9]. This drawback can be overcome by the combination of a suitable preconcentration technique with subsequent AAS determination. Solid-phase extraction (SPE) is preferred on account of the fast, simple and direct application in micro liter volume without any sample loss, higher preconcentration factor, rapid phase separation, time and cost saving [8–12]. The basic principle of SPE of trace metal ions is the transfer of analytes from aqueous phase to the active sites of solid phase. A number of solid phase

and chelating ligands have been widely used for the preconcentration and separation of trace metal ions from various matrices [13–19]. The solid phase extraction of traces heavy metal ions from solutions by sorbents modified with analytical reagents is one of the most promising methods of their determination, especially in environmental objects [16,18–28].

The studies on the synthesis resins by the reaction with a commercial resin and a suitable chelating agent and sorption characterization of chelating resin available for interesting metal ions have been extensively carried out in a number of analytical laboratories because both their sorption capacities and sorption selectivity are superior to those of ion exchangers in trace levels.

In the presented work, a preconcentration scheme is proposed for the preconcentration of copper (II) in the environmental samples.

2. Experimental

2.1. Instruments

The measurements of metal ions were performed with a PerkinElmer 603 (Norwalk, CT, USA) atomic absorption spectrometer equipped with a flame burner. Single element hollow cathode lamp for Cu was used as energy source at respective wavelengths using an air-acetylene flame and a deuterium lamp as background

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corrector. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/Ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH.

2.2. Reagents and solutions

Doubly distilled deionized water was used throughout. All the reagents were of the analytical grades obtained from Merck (Darmstadt, Germany). Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium (Merck). All reagents were of the highest purity and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide solution for preparing the desired pH buffer solution. Sepabeads SP70 is a divinylbenzene copolymer that was purchased from Sigma (St. Louis, USA)). Its surface area is $800\,m^2\,g^{-1}$ with 20–60 mesh, was washed successively with methanol, water, $1\,mol\,l^{-1}$ HNO_3 in acetone, water, $1\,mol\,l^{-1}$ KOH, and water, sequentially.

2.3. Preparation of N^1, N^2-bis(4-fluorobenzylidene)ethane-1,2-diamine (BFBAED):

A solution of ethylenediamine (0.183 g, 3 mmol) in absolute ethyle alcohol (EtOH) (10 ml) was added to a solution of 4-flourobenzaldehyde (0.744 g, 6 mmol) in absolute EtOH (10 ml) and stirred for 2 h. Then cold water (40 ml) was added to the reaction mixture and was kept in the refrigerator for 3 h. After several hours, the product was obtained as white precipitate. The products were filtrated and washed twice with cooled water and dried under air (83% yields).

IR (KBr, cm^{-1}): 3435 (m), 3035 (w), 2927 (w), 2907 (m), 2848 (s), 1651 (s), 1595 (vs), 1506 (vs), 1459 (m), 1414 (m), 1373 (m), 1298 (m), 1283 (m), 1260 (w), 1230 (vs), 1213 (s), 1152 (s), 1096 ((m), 1019 (s), 984 (m), 968 (m), 936 (w), 874 (m), 845 (vs), 818 (m), 804 (m), 780 (w), 580 (s), 531 (s), 470 (m), 417 (m). UV–vis ($CHCl_3$): 251 (ε = 37,857), 276 (ε = 15,746), 287 (ε = 11,864) nm. ^1H NMR (DMSO-d_6): 8.31 (s, 2H), 7.74 (dt, 4H, J = 6.11 Hz, J = 5.98 Hz and J = 2.05 Hz), 7.22 (t, 4H, J = 8.80 Hz and J = 8.75 Hz), 3.84 (s, 4H) ppm.

2.4. Preparation of BFBAED coated Sepabeads SP70

As a solid phase composed of 0.5 g of modified Sepabeads SP70 in water suspension. Was incorporated in a Pyrex glass column with 40 cm long and 0.75 cm in internal diameter. The bed height in the column was approximately 1 cm. The Sepabeads SP70 (500 mg) was impregnated with BFBAED by percolating 3 ml of 1% (w/v) BFBAED solution through the column packed with Sepabeads SP70 at a flow rate of $4\,ml\,min^{-1}$. The filtrate was collected and analyzed for unadsorbed BFBAED with the UV–vis spectrophotometer at optimum wavelength. The column was then washed twice with 5 ml water and the filtrates were analyzed for ligand that was released. The retained amount of BFBAED on the Sepabeads SP70 column was $110\,mg\,g^{-1}$.

2.5. Preconcentration procedure

The pH of the solution (250–2000 ml) was adjusted to 7.0 with hydrochloric acid or KOH and passed through the BFBAED loaded on Sepabeads SP70 column at a flow rate of $4\,ml\,min^{-1}$ with the aid of a suction pump. The analyte was then eluted with 8 ml of 2 M nitric acid in acetone. The metal ion content of the eluent was measured by flame-AAS.
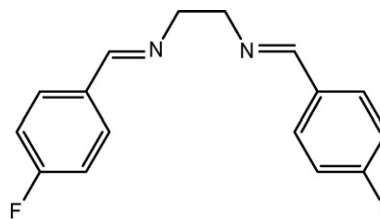
Scheme 1. Structure of ligand (BFBED).

2.6. Applications

Leaves of lettuce tree were purchased from Firouzabad, Iran. Afterwards, they were dried and were taken in small mesh. A 40 g leaf of lettuce was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 ml concentrated nitric acid and 3 ml 30% H_2O_2 was again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 ml concentrated hydrochloric acid and 2–4 ml 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water filtered and made up to 250 ml in volumetric flask. The pH of solution was kept 7.0 by dilute KOH. Then the procedure given above was applied.

10 ml of milk sample was placed in a 100 ml beaker and 10 ml of 65% HNO_3 and 3 ml of 30% of H_2O_2 were added. The contents in the beaker were heated on a hot plate at 100 °C for 40 min, then the semiresidue mass was dissolved in 10 ml of 1 M HCl. The obtained clear solution was neutralized by adding dilute KOH and diluted up to 25 ml in volumetric flask. A duplicate 10 ml portion of final solution was analyzed according to prescribed procedure.

Bread (1 g) was dried to constant weight at 150 °C, then ashed in a muffle furnace at 450 °C. Ashed samples were dissolved in dilute HCl and diluted to 25–100 ml in volumetric flask depending on metal ion content. Duplicate of 5 ml of each diluted sample was subjected to procedure given above.

Rose water samples were collected from Firouzabad, Iran. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm. The organic content of the water samples was oxidized by H_2O_2 and concentrated nitric acid (1:2) ratio and heated on hot plate for 1 h. After oxidation process the rose water samples were stored in polyethylene bottles.

For the preconcentration procedure, pH of the 800 ml of water samples was adjusted to 7.0 and the sample passed through the column at flow rate of $4\,ml\,min^{-1}$. The copper ions retained on column were eluted with 4 M HNO_3 in acetone. Then the preconcentration procedure given above was applied.

3. Results and discussions

As shown in Scheme 1, due to the existence of donating nitrogen atom as well as NH group in BFBAED was expected to increase both the stability and selectivity of its Cu^{2+} ion complex over other metal ions, especially alkali and alkaline earth cations. It is occurred to us that the presence of some constituents with non-cyclic sulfur-containing ligand and hydroxyl group in addition to the electrons results in selective interaction with Cu^{2+} ion while oxygen atoms of the ligands mostly interact with this ion as a soft acid through ion–dipole interactions, while all resulting in fast complexation and higher sensitivity.

In preliminary experiments typical complexation between Cu^{2+} ion and BFBAED was examined using cyclic voltammetry. In order to confirm this result and ascertain the nature and structure of the extracted species, to the fixed amount of BFBAED different mole
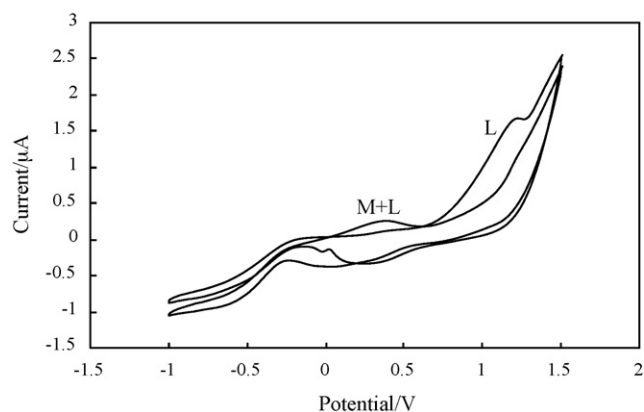
Fig. 1. Cyclic voltamogram of copper (II) ions with BFBAD (1×10^{-3} M) with Cu^{2+} (1×10^{-3} M) in water: ethanol ($T = 25\,°C$ and $I = 0.05$ M).

Fig. 3. Effect of amount of ligand ($N = 3$).

ratio of copper (II) ion was added and corresponding cyclic voltamogram was presented in Fig. 1. As it can be seen, a reversible wave that is an indication of strong and reversible complexation occured which indicating the association of two BFBAED molecules with the one molecule of copper (II) ion. This reagent has sufficient hydrophobicity to be used as a complexing agent in cloud point extraction.

Therefore, for obtaining the high efficiency in short time with low consumption of material the influence of effective variables such as pH, ligand and solid phase amount, shaking time and condition of eluting solution on ions recovery were optimized.

3.1. Effect of pH

As known in literature, pH is a critical parameter on the recoveries of analytes on solid phase extraction works [26–30]. The effect of pH on the preconcentration of metals on Sepabeads SP70 loaded with BHAPED was studied by determination of copper content. 50 μg of this ion was preconcentrated in the pH range of 1.0–11.0 by introducing 30 mg of BHAPED on the 0.5 g Sepabeads SP70. The results were shown in Fig. 2. The results obtained indicated that the copper ion could be retained quantitatively by the modified Sepabeads SP70 at the pH range of 6.5–7.0. The decrease in signal at pH > 7.0 is probably due to the precipitation of ions as their related hydroxide and at pH < 6.5 may be due to competition of hydronium ion toward complexation with BHAPED, which led to the decrease in the recovery. To achieve high efficiency and good selectivity, a pH of 7.0 was selected for subsequent work.
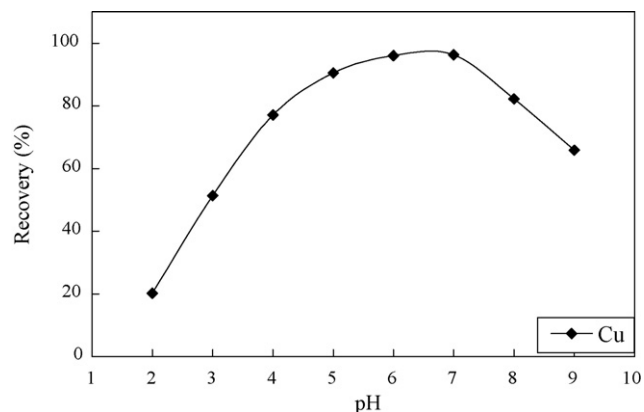
3.2. Effect of ligand concentration

Effects of the quantity of BFBAED as a chelating agent were also studied. In order to determine this, quantities of BFBAED on the retention were examined .0 to 50.0 mg (Fig. 3). Without BFBAED the preconcentration yields of copper (II) ions are 21%. By addition of BFBAED up to 25 mg recovery of trace ions was quantitative and further addition has no significant change on recovery of ions. 40 mg of BFBAED is recommended for subsequent works.

3.3. Amount of SDS

In order to conduct an efficient and repeatable solid phase extraction the composition of solid phase must be optimized. In this regard solid phase composed of 50 mg of various surfactants including SDS, Triton X-100 and Triton X-114, CTAB and DTAB at fixed value of ligand (30 mg) and 0.5 g Sepabeads SP70 have been prepared then procedure described in Section 2.5 has been carried out at pH 7.0 and respective results are presented in Table 1. Quantitative results were obtained with SDS. In all optimization sections the volume of sample solution is 250 ml. This result is probability due to the fact that expected neutral complex could be efficiently trapped in to the interior core of micelles or ad-micelled coated on the surface of Sepabeads SP70.

As can be seen in Fig. 4, by using 60 mg of SDS, complete and reversible uptake-elution of metal ions could be achieved. The retention of metal ions on hemi-micelles, which have a hydrophobic surface, was clearly dependent on analyte complex polarity. The formation of minute amounts of ad-micelles was essential to achieve complete adsolubilization of these ions as respective complex (which probably are neutral). At surfactant concentrations higher than about $100\,mg\,g^{-1}$ Sepabeads SP70, a decrease in the percentage of ions recovery was observed. Probably at surfactant value higher than $100\,mg\,g^{-1}$ the amount of eluting solution is not sufficient for reversible elution of the retained metal ions.

Fig. 2. Effect of pH on recovery of copper ions ($N = 3$).

Table 1
Effect of surfactant type on recovery of copper ions.

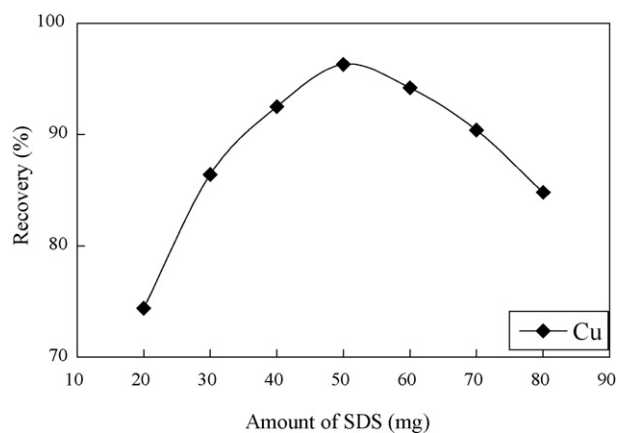| Surfactant	Recovery of copper, %
Without	56
SDS	98
DTAB	50
CTAB	52
Triton-X114	76
Triton-X100	73

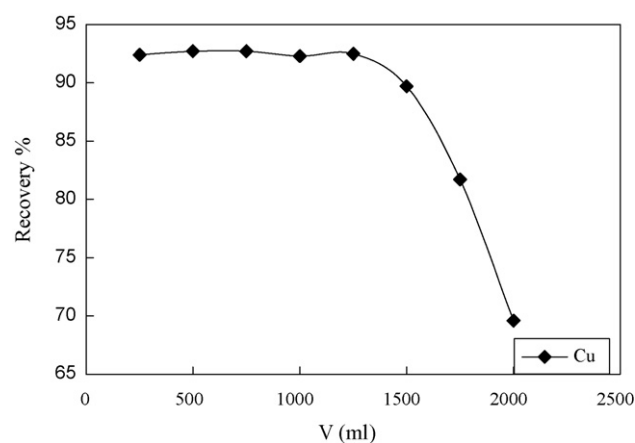**Fig. 4.** Effect of amount of SDS on the recoveries of copper (II) ions ($N = 3$).

Fig. 5. Effect of sample volume ($N = 3$).

3.4. Effect of eluent type and volume

Various eluting solutions were used to identify the best eluent for the adsorbed metal-BHAPED chelates on modified Sepabeads SP70. The results were summarized in Table 2. Among the solvents studied, especially the acids with acetone provided higher recovery efficiency compared to the acids in aqueous and alcoholic solutions and therefore the highest recoveries were obtained for nitric acid in acetone. Finally, 4 M HNO_3 in acetone was specified as the eluent for desorption of metal chelates from modified Sepabeads SP70 and was used for the optimization of the other parameters. The effects of 4 M HNO_3 solutions in acetone with volumes 5.0–10 ml were investigated and quantitative recoveries were obtained after 8 ml of the eluent. The optimum eluent volume is specified as 8–10 ml for the subsequent studies.

3.5. Effect of sample volume

Due to the low concentrations of trace metals in real samples, by using samples with large volumes, the trace metals in these volumes should be taken into smaller volumes for high preconcentration factor. Hence, the maximum sample volume was optimized by the investigation of the recovery of copper ions in various sample volumes in the range 250–2000 ml. The recoveries from different volumes of aqueous solutions containing the same amounts of the metal ions are shown in Fig. 5. The recovery of copper ion was found to be stable until 1500 ml and was chosen as the largest sample volume to work.

3.6. Effect of the amount of Sepabeads SP70

The amount of solid phase filled to column is the main parameter for the quantitative recoveries of analytes ions [22,30–36]. The efficiency of the BFBAED-Sepabeads SP70 column for the sorption of copper ions was studied by using 500 mg of BFBAED-Sepabeads

Table 2
Effect of type and concentration of eluting agent on recovery of copper ions.

Recovery of Cu (%)	Eluent
55.6	10 ml 1 mol l^{-1} HNO$_3$
95.9	10 ml 4 mol l^{-1} HNO$_3$
64.2	5 ml 4 mol l^{-1} HNO$_3$
96.1	8 ml 4 mol l^{-1} HNO$_3$
93.5	10 ml 6 mol l^{-1} HNO$_3$
88.5	10 ml 4 mol l^{-1} HCl
93.3	10 ml 6 mol l^{-1} HCl
72.3	8 ml 4 mol l^{-1} H$_3$PO$_4$
65.4	8 ml 4 mol l^{-1} H$_2$SO$_4$

Table 3
Effect of amount of Sepabeads SP70 on the recovery of copper (II).

Recovery %	Amount of Sepabeads SP70 (g)
41.7	0.2
77.4	0.4
96.3	0.5
96.3	0.6
96.2	0.8
96.2	1.0

SP70 in comparison with 500 mg of Sepabeads SP70 for preconcentration of this ion in a model solution, starting with 50 μg of copper ions in 250 ml of solution, the quantity of metals ion in the eluent was determined by FAAS and respective results are presented in Table 3. The BFBAED-Sepabeads SP70 can retain this ion while the untreated Sepabeads SP70 cannot quantitatively retain copper ion. Evidently, the preconcentration of the copper ion with the untreated Sepabeads SP70 is not suitable. Therefore, BFBAED-Sepabeads SP70 seems to be a better sorbent in sorption of the copper ion. As it can be seen from Table 3, using modified Sepabeads SP70 more than 0.5 g high and efficient ions recovery could be achieved which was selected for subsequent work.

Sepabeads SP70 in the column used for preconcentration can be used approximately 10 times. After 10 times, the recoveries of the metal-chelates were not quantitative.

3.7. Effect of flow rate on copper ion recovery

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise

Table 4
Effects of the interferences ions on the recovery of the copper ions.

Ion[a]	Interference/analyte amount	Recovery (%) Cu
Pb^{2+}	1000	98.3
Ba^{2+}		93.0
Ag$^+$		92.4
Mg^{2+}	1000	92.4
Bi^{3+}		92.5
Ba^{2+}		93.0
Hg$^+$		93.2
Li$^+$		93.1
Na$^+$	1000	92.6
Ca^{2+}	1000	93.1
K$^+$		92.6
Mn^{2+}		92.4
Cl$^-$		93.1
I$^-$		93.2
Br$^-$		92.7

Table 5
Kinetic investigation of enrichment of copper ion on Sepabeads SP70.

		y	R^2	Slope		
P-first order	$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t$	$-0.0129x - 0.6081$	0.9274	-0.0129	$k_1 = 0.0297$	$q_e = 0.246$
Adsorption capacity of resin	$\frac{c_e}{q_e} = \left(\frac{c_e}{q_{max}}\right) + \frac{1}{a_1 q_{max}}$	$1.022x$	1	1.022	$q_{max} = 0.978$	$a_1 = \infty$
Langmuir	$\frac{c_e}{c_{ads}} = \frac{1}{k_1 b} + \frac{c_e}{k_1}$	$1.2977x - 0.0156$	0.9981	1.2977	$k_1 = 0.771$	$b = 83.186$
Frendlich	$\log c_{ads} = \log k_f + \frac{1}{n} \log c_e$	$-0.1176x - 0.1701$	0.9595	-0.1176	$n = -8.50$	$k_f = 0.676$
P-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t$	$1.0221x + 2.9347$	0.9963	1.0221	$q_e = 0.978$	$k_2 = 0.356$

Table 6
Results of determination of copper in real samples spiked with copper (II) (sample volume 100 ml, eluting solution volume 6 ml) $N = 3$.

Added	Bread			Lettuce			Milk			Rose water		
	Found	RSD %	Recovery %	Found	RSD %	Recovery %	Found	RSD %	Recovery %	Found	RSD %	Recovery %
0.0	0.454	3.6	–	1.035	4.1	–	0.081	4.1	–	0.152	3.8	–
0.1	0.515	3.1	102.75	1.065	3.0	104.17	0.154	3.7	104.1	0.254	3.1	102.33

between completion of extraction and efficient separation of phases. Flow rate has a great effect on extraction efficiency, because lower flow rate leads to increasing residence and retention time of analyte in column, and so increasing interaction (complexation) between ions and sorbents. Therefore, different flow rates were examined, that until 4 ml min^{-1} recovery is constant and after that gradually reduced. Therefore, flow rate of 4 ml min^{-1} was used for further studies.

3.8. Effect of divers ions

In the atomic absorption spectrometric determinations of heavy metal ions, levels of diversions is an important problem [22,28–35]. In order to assess the possible analytical applications of the recommended speciation–preconcentration procedure, the effect of some foreign ions which interfere with the determination of trace of these ions or/and often accompany analyte ions in various real environmental samples was examined with the optimized conditions. The results are summarized in Table 4. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% by the combination of the column solid phase extraction and atomic absorption spectrometric determination methods.

3.9. Adsorption isotherms

The adsorption isotherms values were investigated with some experiments. For this purpose 100–5000 μg of copper ion was loaded to the column containing 500 mg of modified solid phase and recoveries were investigated. The results are summarized for adsorption isotherms in Table 5.

3.10. Analytical features

By employing the optimum experimental conditions, the calibration graphs obtained for copper after preconcentration were given as, $A = 4.128$ [Cu mg l^{-1}] $+ 0.263$ ($R^2 = 0.997$, $n = 4$), in the range of 0.0–0.75 μg ml^{-1} for copper (II) ions. The experimental preconcentration factors [28,29], calculated as the ratio of the slope of the calibration graph with and without preconcentration was 33, while the preconcentration factor as the volume of initial solution (1500 ml) to the volume of eluting solution (8 ml) for all ions is 188. The limit of detection (LOD) of a method is the lowest analyte concentration that produces a response detectable above the noise level of the system, typically, three times the standard deviation (s) of the blank ($n = 10$), were found to be 1.6 μg l^{-1} for copper ion. The empirical limit of quantification (LOQ) is the lowest level of analyte

that can be accurately and precisely measured, were found to be 8 μg l^{-1} for this ion.

3.11. Accuracy and applications

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of copper ions from different matrices such as lettuce tree, milk, bread and rose water. Spiking experiments using standard addition method checked reliabilities. The percent of recoveries and relative standard deviation for each element in spiked vegetable, water samples are given in Table 6. As seen, the results of three analyses of each sample show that, in all cases, the copper ions recovery is almost quantitative with a low RSD.

4. Conclusion

The presented method is simple, time saving, and economical. The possible interference of alkaline and earth alkaline ions to the analysis was investigated and since an important interference was not encountered. The preconcentration factor achieved with presented procedure is superior to some coprecipitation methods and other preconcentration techniques [14–20,39–45]. The detection limits of analytes are superior to those of preconcentration techniques [37–45]. The method is relatively rapid as compared with previously reported procedures for the enrichment of analytes.

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