SP70-α-benzoin oxime chelating resin for preconcentration–separation of Pb(II), Cd(II), Co(II) and Cr(III) in environmental samples

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Abstract

In the presented work, α-benzoin oxime immobilized SP70 chelating resin was synthesized for separation and preconcentration of Pb(II), Cd(II), Co(II) and Cr(III). The optimization procedure for analytical parameters including pH, eluent type, flow rate, etc. was examined in order to gain quantitative recoveries of analyte ions. The effects of foreign ions on the recoveries of studied metal ions were also investigated. The detection limits (3σ) were found to be 16.0, 4.2, 1.3, 2.4 $\mu g\,L^{-1}$ for Pb, Cd, Co and Cr, respectively. The preconcentration factor was 75 for Pb, 100 for Cd, Co and Cr. The optimized method was validated with certified reference materials and successfully applied to the waters, crops and pharmaceutical samples with good results (recoveries greater than 95%, R.S.D. lower than 10%).
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Keywords: Chelating resin; Solid phase extraction; Trace metal; Flame atomic absorption spectrometry

1. Introduction

Because of harmful negative effects of trace heavy metal ions for human health, environmental trace heavy metal pollution is one of the most important problems for public health. The necessity of trace heavy metal ions determination in environmental samples is having more importance in recent years [1]. Accurate analysis of trace level metal ions is a complicated and difficult analytical process. In the analysis of trace metal ions present in various samples like natural and wastewater, sediment, and tissue direct determination with some analytical techniques such as atomic absorption methods is not possible because of matrix effect of foreign ions and low concentration of metal ions in the sample and the low selectivity and sensitivity of analytical techniques. It is a necessity to preconcentrate the trace elements before their analysis to enhance the concentration of the analyte ions to be determined [2].

Preconcentration–separation methods including precipitation [3], solvent extraction [4], ion exchange [5], adsorption [6,7], electrochemical deposition [8], membrane separation [9], and other techniques are frequently used for determination of trace metal levels in environmental matrices. Solid phase extraction has been extensively used for enhancing the selectivity and sensitivity of analytical methods for trace metal determination. Different solid phase extraction materials have been experimented with order to carry out the solid phase are activated carbon [10,11], polystyrene-based resins [12], Ambersorb resins [13,14]. In recent years, chelating resins have proved to be very useful in the separation and preconcentration of metal ions at trace levels [15–20]. Amberlite XAD resins are widely used to develop series several chelating materials [16,19]. Sepabeads SP70 is an aromatic type synthetic adsorbent made from highly pure starting material (divinylbenzene). Sepabeads SP70 is designed to efficiently adsorb bitter components such as naringin, limonin, etc., from citrus juice. Sepabeads meets the requirements of FDA (Food and Drug Administration of USA) regulations [21].

α-Benzoin oxime is a spectrophotometric reagent for the heavy metal ions in various media including natural waters and other samples [22,23]. It has been also used on some preconcentration studies including solid phase extraction, solvent extraction, and cloud point extraction as chelating agent [23–28].

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In this study, SP70-α-benzoin oxime chelating resin was synthesized for the separation and preconcentration of some metal ions in crop, pharmaceutical and water samples.

2. Experimental

2.1. Solutions and reagents

Chemicals used for experiments were all in analytical reagent grade. Aqueous solutions of chemicals were prepared with deionized water (Millipore Elix® 5 UV resistant $14\,M\Omega\,cm^{-1}$). The glass equipments kept in HNO_3 10% (v/v) solution overnight and washed with deionized water two times, oven-dried and kept in closed bags before use. Standard solutions of Pb(II), Cd(II), Co(II) and Cr(III) were prepared from the nitrates of these elements each as $1000\,mg\,L^{-1}$. Stock solutions diluted with $1\,mol\,L^{-1}$ HNO_3 for calibration procedures. For model solutions, which were used in optimization of SPE, adequate volumes of stock metal solutions were used.

Citric acid buffers $(0.1\,mol\,L^{-1})$ of pH 2 and 3, ammonium acetate buffers $(0.1\,mol\,L^{-1})$ of pH 4–6, phosphate buffer $(0.1\,mol\,L^{-1})$ for pH 7, and ammonium chloride buffer solutions $(0.1\,mol\,L^{-1})$ were prepared of pH 8–10.

Sepabeads SP70 was purchased from Sigma (St. Louis). Its surface area is $700\,m^2\,g^{-1}$. Certified reference materials (Stream Sediment GBW 07310, GBW 07603 Bush Branches and Leaves, GBW 07605 Tea, BCR 144 R Sediment) were obtained from National Research Centre for Certified Reference Materials (NRCCRM), China.

2.2. Apparatus

A Shimadzu AA 6501 F and Varian AA240 model flame atomic absorption spectrometers was used for applications. An air/acetylene flame was used for measurements. The operating parameters for working elements are given in Table 1. IR spectrums were recorded on a Jasco 300 FTIR spectrometer. These spectra were studied using to potassium bromide. In pH measurements Inolab pH Level 1 model digital pH meter was used. For dry ashing procedure Elektro-mag 1813 model oven and for sample drying Heraeus D 6450 model oven were used. A Shinko Denshi 150 model analytical balance was used for all mass measurements. In the solid phase applications, 0.8 cm of diameter, 10.0 cm long glass adsorption columns were used.

2.3. Synthesis of SP70-α-benzoin oxime resin

The procedure given by Venkatesh and Singh, [19] with some modifications was applied to the synthesis of the SP70-
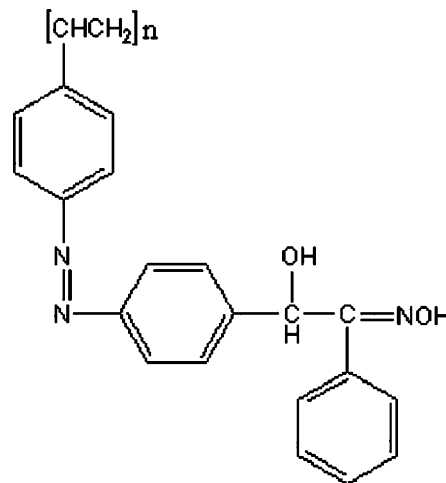
Fig. 1. Structure of SP70-α-benzoin oxime chelating resin.

α-benzoin oxime chelating resin. A 5.0 g of SP70 resin was treated with a nitrating mixture, containing 20 mL of concentrated nitric acid and 50 mL of concentrated sulphuric acid and stirred for 1 h at 60 °C on a water bath. This reaction mixture was poured into ice-cold water. Subsequently, it was filtered, washed repeatedly with deionized water until free from acid. Then it was reduced with $SnCl_2$ (40 g), concentrated hydrochloric acid (45 mL), ethanol (60 mL) and refluxed for 12 h at 50 °C. The solid precipitated was filtered off and washed with mixture of HCl/ethanol, water and $2\,mol\,L^{-1}$ NaOH, so as to get the free amino polymer. The amino polymer was treated with 50 mL of $2\,mol\,L^{-1}$ HCl for 30 mL, washed with distilled water, in order to remove excess of HCl and suspended in 150 mL of ice-cold water and mixed with $1\,mol\,L^{-1}$ HCl and $1\,mol\,L^{-1}$ $NaNO_2$ in aliquots of 2.0 mL each time with constant stirring. The diazotised resin was filtered and washed with ice-cold water. The resin was treated with 50 mL of α-benzoin oxime (1.0% in ethanol) at room temperature for 1 h. Proposed structure of the new chelating resin was given in Fig. 1.

2.4. Enrichment procedure

Adequate volumes of stock solutions containing 12.5–25.0 μg analyte ions were added into a beaker and 5 mL of pH 8 buffer solution were added on. The solution was diluted to 50 mL with distilled water and carefully shaked. Model solution was passed through the column at $7\,mL\,min^{-1}$ flow rate. Then, the column was washed firstly with the deionized water and retained analyte ions were eluted with 5 mL $1\,mol\,L^{-1}$ nitric acid in acetone. Acetone in eluent solution was carefully evaporated near to dryness. Final solution diluted to 2 or 5 mL with $1\,mol\,L^{-1}$ HNO_3 and metal concentrations determined with flame atomic absorption spectrometer. The concentrations were determined from calibration curves.

2.5. Analysis of real samples

One hundred milligrams of sediment standard reference material (GBW 07310 Stream Sediment and BCR 144 R

Table 1
Conditions for flame atomic absorption spectrometer

Parameter	Pb	Cd	Co	Cr
Wavelength, nm	217.0	228.8	240.7	357.9
Slit width, nm	1.0	0.5	0.2	0.2
Lamp current, mA	5	4	7	7

Sediment) were digested with a combination of dry ashing and wet digestion procedure. For this purpose, 100 mg SRM sediment sample was weighed into a porcelain plate and ashed in a laboratory oven at 450 °C for 12 h. Then, the ashed material transferred into a glass beaker and 3 mL of concentrated HNO_3 (65%), 9 mL of concentrated HCl added. The solution heated at 120 °C until dryness and this applied two times. A 20 mL of distilled water was added on and pH of the solution adjusted to 5–6 with 0.5 mol L^{-1} ammonia solution. pH of the solution adjusted to 8 with 5 mL of NH_3/NH_4Cl buffer. Finally, the recommended preconcentration procedure applied to the final solution.

About 250 mg of certified reference material (GBW 07603 bush branches and GBW 07605 food products) was taken into a glass beaker and 10 mL of nitric acid (65%) added on. The mixtures were boiled for 30 min to oxidize easily oxidizable materials. After cooling, 5 mL $HClO_4$ (70%), and 1 mL H_2SO_4 (98%) were added on then the mixtures were boiled until dryness and same procedure applied two times [29]. A 20 mL of distilled water were added on to clear solutions. pH of the solutions adjusted to 5–6 with 0.5 mol L^{-1} ammonia solution and pH adjusted to 8 with 5 mL of NH_3/NH_4Cl buffer.

Wheat, barley, corn, bean, lentil and chickpea samples were purchased from Nigde city. Samples were air-dried for 48 h and then were dried for 12 h at 105 °C in oven. Dried samples were grinded in a porcelain mortar and particle size of powdered samples fixed with a 200 mesh sieve. About 1.0 g of each crop sample was taken into a glass beaker and 10 mL of nitric acid (65%) added on. The mixtures were boiled for 30 min. After cooling, 5 mL $HClO_4$ (70%), and 1 mL H_2SO_4 (98%) were added on then the mixtures were boiled until dryness and same procedure applied two times [29]. Then, the preconcentration procedure given above was applied.

The presented procedure was also applied to tannery wastewater and mineral water from Nigde, Turkey. pH of 100 mL of water samples were adjusted to 8 and then the preconcentration procedure given above was applied.

Cobalt content of Benexol® drug (250 mg B_1, 250 mg B_6 and 1 mg B_{12} in one pill) was also determined by the presented procedure. For that purpose, Benexol® was digested. About 1.0 g of Benexol® was taken into a glass beaker and 10 mL of nitric acid (65%) added on. The mixtures were boiled for 30 min. After cooling, 5 mL $HClO_4$ (70%), were added on then the mixtures were boiled until dryness and same procedure applied two times. Then, the preconcentration procedure given above was applied.

3. Results and discussion

3.1. Characterization of the new chelating resin

In order to characterization of the new chelating resin, Infrared spectrum of the chelating resin was compared with that IR spectrum of the free SP70 resin. Additional peaks in the IR spectrum of the resin that do not appear in the spectrum of the free Sepabeads SP70 are at 3440, 1700, 1630 and 1375 cm^{-1}, which appear to originate due to modification of resin by the ligand and are characteristic of O–H, N=N, C=N
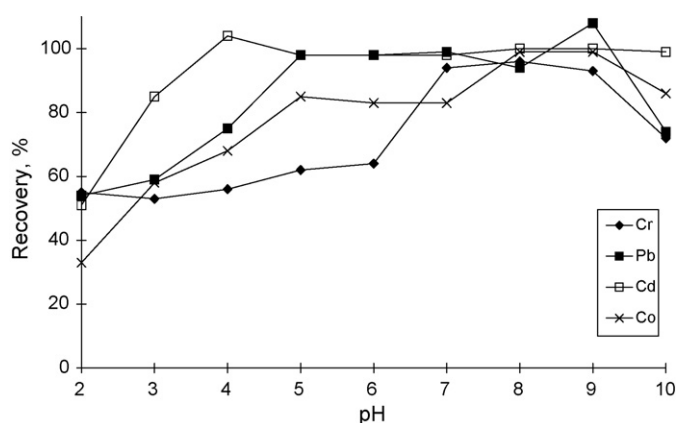

Fig. 2. The effects of pH on the recoveries of metal ions on SP70-α-benzoine oxime resin (eluent: 1 mol L^{-1} nitric acid, sample and eluent flow rates: 5 mL min^{-1}, $N = 4$).

and C–OH vibrations, respectively. These results are agreed with the results of the some chelating resin with the same structure [30,31].

3.2. Influences of pH

Because of the pH of aqueous solution is a critical parameter for adsorption metal ions on a solid phase, the influences of the pH on the retentions of lead(II), cadmium(II), cobalt(II), and chromium(III) on SP70-α-benzoin oxime chelating resin were investigated in the pH range of 2–10. The pH adjustments were made by different buffer solutions given in Section 2. The results were given in Fig. 2. Cadmium(II) was quantitatively recovered in pH 4–10 range. The recoveries of lead(II), chromium(III) and cobalt(II) were quantitative in the pH range of 5–9, 7–10 and 8–9, respectively. For all-further studies were performed at pH 8.

3.3. Effects of eluent type and volume

Desorption studies of investigated metal ions on SP70-α-benzoin oxime chelating resin were tested by using 50 mL of model solutions containing 12.5–25.0 μg of metal ions at pH 8. The results were given in Table 2. Recoveries of all metal ions were quantitative with 1 mol L^{-1} HNO_3 in acetone and this solution preferred as eluent.

Table 2
Effect of eluent type on the desorption of investigated metal ions (eluent volume: 5 mL, $N = 4$)

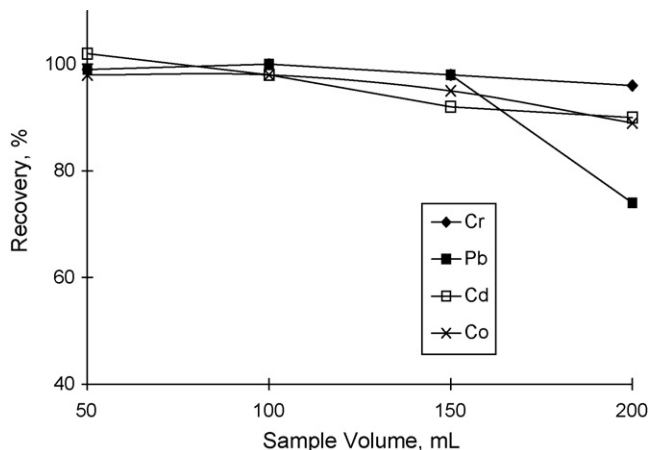| Eluent	Recovery (%)			
	Pb	Cd	Co	Cr
1 mol L^{-1} HNO_3 in acetone	100 ± 5	101 ± 2	101 ± 4	99 ± 3
2 mol L^{-1} HNO_3 in acetone	86 ± 3	78 ± 5	78 ± 2	76.7 ± 6
1 mol L^{-1} HCl in acetone	101 ± 4	94 ± 4	103 ± 4	97.6 ± 3
2 mol L^{-1} HCl in acetone	92 ± 5	100 ± 2	99 ± 3	107 ± 2
1 mol L^{-1} HNO_3	87 ± 2	54 ± 2	49 ± 4	48 ± 2
2 mol L^{-1} HNO_3	70 ± 4	52 ± 3	68 ± 4	56 ± 3
1 mol L^{-1} HCl	88 ± 4	50 ± 1	48 ± 3	38 ± 3
2 mol L^{-1} HCl	87 ± 4	53 ± 1	58 ± 2	38 ± 3

Fig. 3. Effects of sample volume on the recoveries of metal ions on SP70-α-benzoine oxime resin ($N = 4$).

Table 3
Effect of sample flow rate on the recovery of investigated metal ions (eluent volume: 5 mL, $N = 4$)

Sample flow rate (mL min^{-1})	Recovery (%)			
	Pb	Cd	Co	Cr
2	100 ± 2	100 ± 3	100 ± 3	105 ± 5
3	96 ± 5.6	99 ± 1	102 ± 3	105 ± 4
4	98 ± 4.4	101 ± 1	101 ± 2	103 ± 6
5	103 ± 3.5	98 ± 2	102 ± 3	104 ± 3
6	100 ± 2	98 ± 1	96 ± 3	99 ± 5
7	96 ± 6	94 ± 1	100 ± 3	101 ± 4
8	99 ± 5	94 ± 3	101 ± 4	102 ± 6
9	97 ± 5	94 ± 2	102 ± 3	102 ± 6

The influences of eluent volume for desorption of analytes from SP70-α-benzoin oxime chelating resin were investigated in the eluent volume range of 1–7 mL with 1 mol L^{-1} HNO$_3$ in acetone. Quantitative recoveries were obtained between 5 and 7 mL of 1 mol L^{-1} HNO$_3$ in acetone. All further studies were performed with 5 mL of eluent. Acetone in the eluent was evaporated near dryness after elution, and then the final volume was completed 2 or 5 mL with 1 mol L^{-1} HNO$_3$.

3.4. Effect of sample volume

In order to application of the presented solid phase extraction procedure for natural water samples, the sample volume is important and critical parameter to obtain satisfactory preconcentration factors and detection limit. The effect of sample volume for retention behaviors of investigated metal ions on α-benzoin oxime immobilized SP70 chelating resin was investigated. The results were given in Fig. 3. The recoveries of Cd, Co and Cr were quantitative up to 200 mL. Lead was quantitatively recovered till 150 mL.

The preconcentration factor is calculated by the ratio of the highest sample volume (150 mL for Pb and 250 mL for Cd, Co

and Cr) and the lowest final volume (2 mL). The preconcentration factor of system was 75 for Pb, 100 for Cd, Co and Cr.

3.5. Effect of sample flow rate

Flow rate is an important parameter to obtain quantitative retention of analytes on chelating resin. The flow rates of the solutions controlled by using the stopcock of the column. The effects of the sample flow rate on the recovery of investigated metal ions were examined in flow rate ranges between 2 and 9 mL min^{-1}. The results for retentions of metal ions on the solid phase were quantitative up to 7 mL min^{-1} (Table 3). Further studies performed at 7 mL min^{-1} flow rate for sample.

3.6. Effect of matrix ions on recovery

For application of recommended solid phase extraction to real samples, effects of some interfering ions on the recoveries of metal ions have been investigated with the optimized procedure above. Obtained results from these studies were given in Table 4. Analyte metal ions recoveries were up to 93.9%. The tolerable limits of interfering ions were also determined. Therefore, all of investigated foreign ions have no interfering effect on the recommended solid phase extraction procedure.

Table 4
Effect of some matrix ions on the recoveries of metal ions on SP70-α-benzoine oxime resin (sample volume: 40 mL, pH: 8, $N = 4$)

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)			
			Pb	Cd	Co	Cr
Na$^+$	NaCl	10,000	101 ± 5	103 ± 3	97 ± 3	91 ± 3
K$^+$	KCl	1,000	92 ± 2	101 ± 3	96 ± 4	96 ± 3
Ca^{2+}	Ca(NO$_3$)$_2$	500	104 ± 3	99 ± 2	99 ± 5	101 ± 3
Mg^{2+}	Mg(NO$_3$)$_2$	250	105 ± 2	101 ± 5	97 ± 1	96 ± 4
Cl$^-$	NaCl	10,000	100 ± 2	104 ± 2	100 ± 3	96 ± 4
SO$_4^-$	Na$_2$SO$_4$	500	98 ± 3	104 ± 4	106 ± 2	98 ± 2
Fe^{3+}	FeCl$_3$	5	95 ± 3	94 ± 1	97 ± 2	95 ± 4
Al^{3+}	Al(NO$_3$)$_3$	50	101 ± 3	94 ± 4	97 ± 1	98 ± 5
Zn^{2+}	ZnSO$_4$	100	98 ± 4	97 ± 3	98 ± 1	96 ± 4
Mn^{2+}	MnSO$_4$	50	102 ± 5	104 ± 3	101 ± 4	97 ± 5
Ni^{2+}	Ni(NO$_3$)$_2$	50	102 ± 4	100 ± 4	95 ± 3	100 ± 6

Table 5
The levels of Pb(II), Cd(II), Co(II) and Cr(III) in the standard reference materials after application of presented procedure ($N = 3$)

	Pb		Cd		Co		Cr	
	Certified value ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Certified value ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Certified value ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Certified value ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)
GBW 07310	27	31.4 ± 1.5	1.12	BDL	15.3	17.9 ± 2.6	136	127.5 ± 10.1
Stream sediment								
GBW 7603 tea	47	42.7 ± 7.0	–	–	6.6	BDL	2.6	BDL
GBW 07605 bush	14	BDL	0.057	BDL	0.18	BDL	0.8	BDL
Branches and leaves								
BCR 144 R sediment	96	88.7 ± 2.4	1.84	2.5 ± 0.2	13.3	13.2 ± 1.2	90	73.1 ± 3.9

BDL, below detection limit.

Table 6
Addition–recovery tests in the experiments for Pb(II), Cd(II), Co(II) and Cr(III) in different food samples, sample volume 50 mL ($N = 3$)

Sample	Metal											
	Pb			Cd			Co			Cr		
	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Recovery (%)	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Recovery (%)	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Recovery (%)	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Recovery (%)
Wheat	0	BDL		0	0.9 ± 0.1		0	1.7 ± 0.3		0	3.0 ± 0.1	
	25.0	11.9 ± 0.6	48	12.5	14.2 ± 0.4	113	25.0	24.2 ± 1.2	90	25.0	29.6 ± 1.5	107
Green lentil	0	BDL		0	0.4 ± 0.1		0	1.25 ± 0.2		0	BDL	
	25.0	26.2 ± 1.6	104	12.5	14.0 ± 0.3	109	25.0	23.5 ± 1.9	89	25.0	24.7 ± 0.5	99
Corn	0	BDL		0	0.6 ± 0.1		0	BDL		0	4.1 ± 0.4	
	25.0	21.1 ± 0.9	84	12.5	13.0 ± 0.6	99	25.0	24.0 ± 2.2	96	25.0	26.9 ± 2.6	91
Lentil	0	BDL		0	BDL		0	2.1 ± 0.4		0	2.6 ± 0.4	
	25.0	18.8 ± 1.9	75	12.5	12.6 ± 1.3	101	25.0	23.9 ± 0.4	87	25.0	27.2 ± 1.0	98
Chickpea	0	BDL		0	0.6 ± 0.1		0	BDL		0	2.3 ± 0.8	
	25.0	18.1 ± 2.2	72	12.5	13.3 ± 0.7	102	25.0	23.9 ± 0.8	96	25.0	25.4 ± 0.7	92
Bean	0	BDL		0	BDL		0	BDL		0	1.6 ± 0.3	
	25.0	12.4 ± 1.3	50	12.5	12.7 ± 0.7	102	25.0	23.9 ± 2.1	96	25.0	28.6 ± 0.6	108

BDL, below limit of detection.

3.7. Figures of merit

The limits of detection (LOD) of the proposed method for the determination of investigated elements were studied under optimal experimental conditions by applying the procedure for blank solutions. The detection limits (LOD) was established by analyzing 21 blank solutions (3σ). The detection limits of Pb, Cr, Cd and Co were calculated 16.0, 2.4, 4.2, 1.3 $\mu g\,L^{-1}$, respectively.

3.8. Application to real samples

Standard reference material (GBW 07310 Stream Sediment and Com. Bureau BCR 144 R Sediment), GBW 07603 bush branches and GBW 07605 food products reference materials were analyzed by developed method. The results are given in Table 5. The results show that the results are good agreement with the certified values for the investigated analyte ions.

The proposed method was applied to a wheat sample, a green lentil sample, a corn sample, a lentil sample, a chickpea sample, and a bean sample. In additional, these food samples were added analyte ions for proposed method accuracy. The results were given Table 6. Proposed solid phase extraction method for determination of trace metal in some food samples were applied successfully except lead(II) ion. Recovery value of lead(II) not can be quantitatively except only sample (green lentil).

Table 7
Pb(II), Cd(II), Co(II) and Cr(III) contents of wastewater sample and a mineral water sample ($\mu g\,L^{-1}$, N: 4)

Sample	Pb	Cd	Co	Cr
Tannery waste water	46.0 ± 2.1	GSA	20.0 ± 4.9	154.5 ± 11.1
Mineral water	51.0 ± 4.2	10.5 ± 2.1	17.0 ± 4.2	13.0 ± 4.2

$X_{\text{mean}} \pm t\,s\sqrt{N}$.

Table 8
Comparison of some chelating resins in literature with the chelating resin proposed in the presented work

Chelating agent	Adsorbent	Metals	Enrichment factor	Detection limits (μg L^{-1})	Precision (%)	Reference
2-(6-Methyl-2-benzothiazolylazo) chromotropic acid (Me-BTANC)	Polyurethane foam	Cd, Pb	22, 37	2.04, 0.80	2.0, 3.1	[32]
2-[2′-(6-Methyl-benzothiazolylazo)]-4-aminophenol (Me-BTAP)	Amberlite XAD-2	Co, Cu, Ni	19, 12, 12	0.34, 0.87, 0.81	–	[33]
Cibacron blue F3-GA	Poly(hydroxyethylmethacrylate)	Pb, Cd, Ni	42, 52, 63	12.01, 1.34, 28.73	8.9, 3.7, 3.5	[18]
2,3-Dihydroxypyridine	Amberlite XAD-2	Zn^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+}	250, 200, 250, 300, 200, 250, 100, 150	3.88, 5.37, 8.72, 13.88, 4.71, 1.24, 0.59, 0.30	–	[34]
o-Aminobenzoic acid	Amberlite XAD-4	Pb(II), Cd(II), Ni(II), Co(II), Zn(II)	400, 400, 150, 200, 400	2.5, 2.5, 6.5, 5.0, 2.5	–	[35]
Xylenol orange	Amberlite XAD-7	Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Zn(II)	50, 100, 50, 200, 100, 100	10, 40, 10, 25, 25	2.0, 1.5, 1.6, 1.1, 1.1, 0.5	[36]
α-Benzoin oxime	Sepabeads SP70	Pb, Cd, Co, Cr	75, 100, 100, 100	16.0, 4.2, 1.3, 2.4	5.4, 5.3, 4.8, 6.2	Present study

The method presented was also employed for determination of cobalt in a multi vitamin tablet (Benoxol B12). The determination of Co(II) in Vitamin B12 combination it has been found that 41.6 μg for one pill. When considering that one pill contains 43.5 μg Co (according to prospectus), finally the recovery of Co(II) is 95.6%.

The method was applied to a wastewater sample and a mineral water sample. The results were given Table 7.

4. Conclusion

For the separation and preconcentration of Pb(II), Cr(II), Cd(II) and Co(II) ions in real samples such as some food sample, water sample and multivitamin tablet sample, SP70-α-benzoine oxime resin is an effective adsorbent. Using SP70-α-benzoine oxime resin for many times in adsorption–elution process of investigations proves that the resin has a great chemical stability. The comparison of proposed method with other solid phase extraction methods is summarized in Table 8. The preconcentration factor of proposed solid phase extraction method was generally high than some literature [18,32–39].

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