



Synthesis of a novel chelating resin and its use for selective separation and preconcentration of some trace metals in water samples

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ABSTRACT

A new chelating resin, poly[N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene], was synthesized and characterized. The resin was used for selective separation, preconcentration and determination of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions in water samples by flame atomic absorption spectrometry. Effects of pH, concentration and volume of elution solution, sample flow rate, sample volume and interfering ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Mn^{2+} , Al^{3+} , Zn^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Cl^- and SO_4^{2-}) on the recovery of the analytes were investigated. The sorption capacity of the resin was 25.6, 19.8, 32.1, 41.3, 38.9, 13.9 and 18.3 mg g^{-1} for Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Mn(II) and Fe(III), respectively. A high preconcentration factor, 100, and low relative standard deviation, $\leq 2.5\%$ ($n=7$) values were obtained. The detection limits ($\mu\text{g L}^{-1}$) were 0.57 for Cu(II), 0.37 for Ni(II), 0.24 for Co(II), 0.09 for Cd(II), 1.6 for Pb(II), 0.19 for Mn(II) and 0.72 for Fe(III). The method was validated by analysing fortified lake water (TMDA-54.4, a trace element fortified calibration standard) and spiked water samples. The method was applied to the determination of the analytes in tap and lake water samples.

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1. Introduction

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of heavy metal ion at trace level in environmental samples is becoming great importance [1]. Cr(III) is considered to be an essential trace element for the maintenance of effective glucose, lipid and protein metabolism in mammals. On the other hand, Cd(II) and Pb(II) even at very low concentrations, are well-known toxic elements. Both metals cause adverse health effects in humans and their widespread presence in the human environment comes from anthropogenic activities [2,3]. Copper is both micro-nutrient as well as toxic element for living beings, depending upon the concentration level. Its deficiency causes the ischemic heart disease, anemia, abnormal wool growth and bone disorders. Severe oral intoxications affect mainly blood and kidneys. Excess of copper enters through into the body as a pollutant present in water, food contamination and some other plant foods rich in copper. Nickel is a moderately toxic element. The most common harmful health effect of nickel in humans is an allergic reaction [4,5].

The toxicity of cobalt is low and its considered as an essential element, which is required in the normal human diet in the form of vitamin B₁₂ (cyanocobalamin). For this reason, Co has been used in the treatment of anemia. Iron is an essential element for all forms of life, i.e. it is a cofactor in many enzymes and essential for oxygen transport and electron transfer. It is potentially toxic in excess concentration because of its pro-oxidant activity. Manganese is a necessity for the proper function of several enzymes and an essential micro-nutrient for the function of the brain, nervous system and normal bone growth. It optimizes enzyme and membrane transport functions [6–8].

The direct determination of trace metals in various samples may not be possible with sufficient sensitivity by also using expensive analytical methods, such as inductively coupled plasma atomic emission spectrometry or electrothermal atomic absorption spectrometry because of low concentrations and/or matrix interferences. The most effective way to avoid these problems is to perform appropriate sample pretreatment prior to analysis aimed at lowering the limits of detection, by both removal of interferences and increasing the concentration of the species of interest. Therefore, a separation/preconcentration technique is necessary, prior to determination of trace metals by an instrumental technique [9,10]. The widely used techniques for the separation and preconcentration of trace metals include coprecipitation [3,11], liquid–liquid

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extraction [12], cloud point extraction [5,6,8,9], electrodeposition [13] and solid phase extraction [1,2,7].

Solid phase extraction (SPE) has become increasingly popular in compared with the classical liquid–liquid extraction method because of its advantages of high enrichment factor, high recovery, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [14]. Numerous substances have been applied as solid phase extraction sorbents for preconcentration of trace metals, such as activated carbon [15], silica gel [16], XAD-resins [17,18], nanomaterial [19,20], and chelating resins [21–23]. The chelating resins are frequently used in analytical chemistry for preconcentration of metal ions and their separation from interfering constituents. The use of these sorbents can provide a better separation of interferent ions, high efficiency and higher rate of process, and the possibility of combining with different determination methods. Chelating resins are typically characterised by functional groups containing O, N, S and P donor atoms which coordinate to different metal ions. Chelating resins are superior in selectivity to solvent extraction and ion exchange due to their triple function of ion exchange, chelate formation and physical adsorption [17,24–27].

In this work, poly N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene (BrPMAAm/AMPS/DVB) chelating resin was synthesized and used as solid phase extractant. Experimental parameters affecting the preconcentration of the metal ions, such as pH of sample, type, volume and concentration of eluent, sample flow rate, sample volume and interfering ions were studied and optimized. The described method was used for the separation and preconcentration of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions present in various water samples.

2. Experimental

2.1. Instruments

A PerkinElmer AAnalyst 800 model flame atomic absorption spectrometer (Waltham, MA, USA) was used for the determination of the metals. The operating parameters for the spectrometer were set as recommended by the manufacturer. The acetylene/air flow rates were 2.0/17 L min⁻¹. A Consort C533 model digital pH meter (Belgium) was used for all the pH measurements. Infrared spectra of the chelating resin were measured on a Jasco 460 Plus FT-IR spectrometer (Jasco Co., Tokyo, Japan). Elemental analyses were carried out by a Leco CHNSO-932 auto microanalyser (USA). The surface morphology of the resin was examined using Leo 440 model scanning electron microscopy (SEM, USA).

2.2. Reagents and solutions

All chemicals used for preparation of solutions were of analytical grade. The metal stock solutions (1000 µg mL⁻¹) were prepared by dissolving the appropriate amounts of their nitrate or chloride salts in doubly distilled water. The working solutions of the metal ions were obtained by appropriate dilution of the stock solutions. The pH of the solutions was adjusted by use of the following solutions. For the pH 1 and 2, a KCl/HCl solution was used. CH₃COOH/CH₃COONH₄ buffer was used to adjust pH in the range of 4–6, while NH₃/NH₄Cl buffer was used for pH 8–10.

N-(4-bromophenyl)-2-methacrylamide (BrPMAAm) monomer was prepared as reported in the literature [28]. 2-Acrylamido-2-methyl-1-propanesulfonic acid (Merck, 99%) was used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform-methanol. Divinylbenzene (DVB),

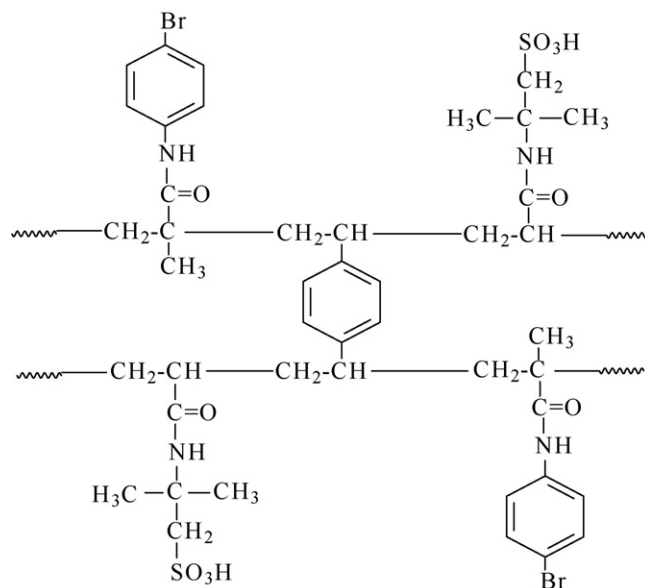


Fig. 1. The structure of the poly[N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene].

N,N-dimethylformamide, diethylether and benzene (Merck) were analytical grade commercial products and used as received unless otherwise noted.

2.3. Synthesis of chelating resin

The synthesis of the BrPMAAm/AMPS/DVB resin was carried out with a radical initiator in dimethylformamide solution. To a polymerization flask, the two appropriate monomers (BrPMAAm and AMPS), the crosslinking reagent (DVB), and the initiator (AIBN) were added. The system was kept under N₂ for 3 h at 70.0 ± 0.1 °C. Subsequently, the resin was filtered and washed with about 200 mL of diethylether and dried under vacuum at 50 °C until a constant weight was obtained. The conversion of monomer to polymer was determined by a gravimetric method. The structure of the chelating resin is illustrated in Fig. 1.

2.4. Characterization of chelating resin

The morphology of the BrPMAAm/AMPS/DVB resin was investigated by SEM (Fig. 2). The porous surface structure and cauliflower-like structure in pristine resin can be seen easily in the figure. Platelet adhesion and aggregation involve the whole polymer surface. The surface area of the resin is quite wide and it has high adsorption capacity as expected.

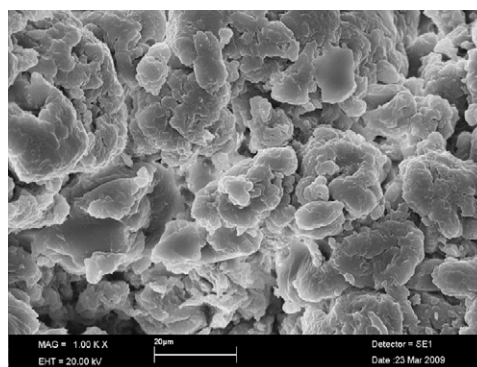


Fig. 2. Scanning electron micrograph of the BrPMAAm/AMPS/DVB resin.

Table 1Effect of volume and concentration of HCl and HNO₃ on the recovery of the analytes (sample volume: 50 mL, pH 2).

Concentration of eluent	Volume (mL)	Recovery (%) ^a						
		Cu(II)	Ni(II)	Co(II)	Cd(II)	Pb(II)	Mn(II)	Fe(III)
1 mol L ⁻¹ HCl	10	98 ± 1	94 ± 2	98 ± 2	83 ± 6	105 ± 4	99 ± 3	93 ± 3
	20	95 ± 2	95 ± 4	94 ± 0	97 ± 1	99 ± 2	98 ± 1	95 ± 1
2 mol L ⁻¹ HCl	10	95 ± 3	93 ± 1	93 ± 2	96 ± 2	95 ± 4	97 ± 2	91 ± 3
	20	107 ± 2	105 ± 4	108 ± 2	105 ± 2	105 ± 4	109 ± 3	111 ± 6
1 mol L ⁻¹ HNO ₃	10	96 ± 1	93 ± 1	94 ± 2	91 ± 2	97 ± 5	93 ± 3	83 ± 1
2 mol L ⁻¹ HNO ₃	5	97 ± 3	94 ± 3	92 ± 2	94 ± 1	98 ± 2	96 ± 3	90 ± 5
	10	99 ± 1	98 ± 2	100 ± 2	99 ± 0	100 ± 3	101 ± 2	94 ± 1

^a $\bar{x} \pm s$, s: standard deviation, n = 3.

The elemental analysis results of the resin are as follows: found (%): C, 55.76; H, 5.50; O, 13.87; S, 5.58; N, 5.16; calculated (%): C, 56.15; H, 5.37; O, 14.10; S, 5.62; N, 5.12. The results have shown that there is a good agreement between experimental and theoretical values.

The FT-IR spectrum of resin shows a strong band at 3432 cm⁻¹ which is attributed to ν_{NH} . The peak at 3050 cm⁻¹ corresponds to the C–H stretching of the aromatic system. The symmetrical and asymmetrical stretchings, due to the methyl and methylene groups, are observed at 2981, 2940 and 2865 cm⁻¹. The absorption at 1662 cm⁻¹ could be assigned for a complex stretching vibrations of N–C=O and C–N. The broad band at 1440 cm⁻¹ could be due to the C–N scissoring vibration of the –N–C=O group. The ring breathing vibrations of the aromatic nuclei are observed at 1600, 1505 and 1470 cm⁻¹. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1390 and 1369 cm⁻¹. A strong band at 1038 cm⁻¹ can be attributed to ν_{SO} . The C–H and C=C out of plane bending vibrations of the aromatic nuclei are observed at 790 and 565 cm⁻¹, respectively. The absorption at 624 cm⁻¹ could be assigned to the C–Br of the BrPMAAm units.

2.5. Column preparation

The synthesized polymer was washed successively with 1 mol L⁻¹ HNO₃ and distilled water and then dried in an oven at about 45 °C. A glass column (100 mm l. × 10 mm i.d.) with a small amount of glass-wool on the disk was used. A 0.65 g of polymer was put into the column. A small amount of glass-wool was placed on top of the resin to avoid disturbance during sample passage. The column was washed thoroughly with distilled water and then pre-conditioned to the desired pH before passing the appropriate metal ion containing solutions over it.

2.6. General procedure

An aliquot of 50 mL of model solutions containing 25 µg of Cu(II), Ni(II), Co(II) and Fe(III), 50 µg of Pb(II) and Cr(III), 5 µg of Cd(II) and 10 µg of Mn(II) was placed in a beaker and the pH adjusted to 2 with a KCl/HCl solution. The column was preconditioned by passing the related solution. The resulting solution was passed through the column at a flow rate of 4 mL min⁻¹. The retained metal ions were eluted with 10 mL of a 2 mol L⁻¹ HNO₃ solution. The concentrations of metal ions in the eluate were determined by FAAS. The column could be used repeatedly after regeneration with distilled water.

2.7. Sample preparation

Tap water samples were taken from our laboratory and analysed without pre-treatment. The lake water from Adana was collected in pre-washed polyethylene bottles, filtered through a Millipore cellulose membrane filter with a 0.45 µm pore size and acidified to pH 2 with HNO₃.

3. Results and discussion

3.1. Effect of pH

pH is a very important factor for metal-chelate formation and solid phase extraction processes. For this purpose, the pH values of 50 mL of each of the model solutions, containing 25 µg of Cu(II), Ni(II), Co(II) and Fe(III), 50 µg of Pb(II) and Cr(III), 5 µg of Cd(II) and 10 µg of Mn(II) were adjusted to a range of pH 1–10 using related buffer solutions and the described pre-concentration procedure was applied. The results are shown in Fig. 3. The recoveries for all the metal ions investigated in the range of pH 1–10 were quantitative, except for Fe(III) at pH 6. This wide pH working range

Table 2Effect of some foreign ions on the recovery of the analytes (pH 2, eluent: 10 mL of 2 mol L⁻¹ HNO₃, sample volume: 50 mL, n = 3).

Added ion	Concentration (µg mL ⁻¹)	R (%) ± s						
		Cu(II)	Ni(II)	Co(II)	Cd(II)	Pb(II)	Mn(II)	Fe(III)
Na ⁺	5000	99 ± 1	98 ± 2	91 ± 7	67 ± 5	96 ± 7	99 ± 2	101 ± 0
K ⁺	1000	98 ± 4	98 ± 3	93 ± 6	96 ± 5	96 ± 5	97 ± 4	97 ± 5
Ca ²⁺	100	97 ± 1	97 ± 2	97 ± 2	95 ± 1	95 ± 2	96 ± 1	99 ± 1
	250	94 ± 1	98 ± 3	91 ± 2	85 ± 3	96 ± 1	82 ± 1	87 ± 6
Mg ²⁺	100	98 ± 0	98 ± 3	98 ± 2	99 ± 1	100 ± 0	101 ± 0	95 ± 2
	250	83 ± 1	84 ± 1	80 ± 2	76 ± 1	96 ± 1	81 ± 2	91 ± 1
Cl ⁻	2500	96 ± 3	98 ± 1	99 ± 3	90 ± 4	98 ± 4	97 ± 2	96 ± 1
SO ₄ ²⁻	250	97 ± 2	96 ± 4	97 ± 3	95 ± 1	100 ± 6	99 ± 4	96 ± 5
Fe ³⁺	10	98 ± 3	95 ± 3	91 ± 1	91 ± 2	98 ± 2	96 ± 3	–
Mn ²⁺	10	86 ± 2	85 ± 1	82 ± 7	83 ± 2	85 ± 4	–	83 ± 3
Al ³⁺	10	97 ± 1	98 ± 2	91 ± 3	92 ± 5	98 ± 4	96 ± 1	97 ± 5
Zn ²⁺	10	91 ± 4	86 ± 4	88 ± 2	81 ± 2	98 ± 4	92 ± 1	82 ± 2
Pb ²⁺	10	100 ± 3	102 ± 2	100 ± 3	98 ± 4	–	101 ± 3	96 ± 3
Cu ²⁺	10	–	98 ± 2	98 ± 2	96 ± 2	97 ± 3	96 ± 1	97 ± 4
Ni ²⁺	10	99 ± 2	–	100 ± 1	98 ± 1	100 ± 1	99 ± 0	100 ± 1
Cd ²⁺	10	99 ± 3	98 ± 3	99 ± 2	–	93 ± 3	99 ± 3	101 ± 4

Table 3
Precision of the method and its DL values.

	Cu(II)	Ni(II)	Co(II)	Cd(II)	Pb(II)	Mn(II)	Fe(III)
$(R\% \pm \frac{R\%}{\sqrt{N}})$	100 ± 1	100 ± 1	101 ± 1	101 ± 1	99 ± 2	100 ± 1	95 ± 2
R.S.D. (%)	0.9	1.6	1.3	1.4	2.5	1.0	1.7
DL ($\mu\text{g L}^{-1}$)	0.57	0.37	0.24	0.09	1.6	0.19	0.72

R.S.D.: relative standard deviation; DL: detection limit.

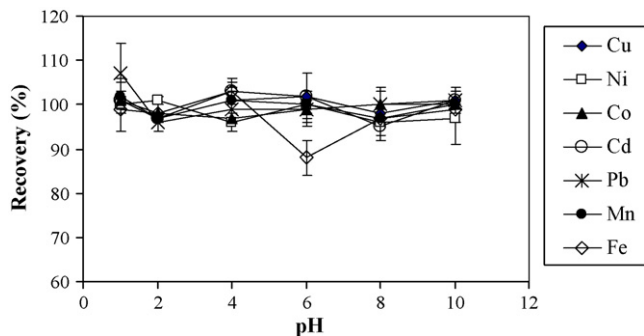


Fig. 3. Effect of pH on the recovery of analytes (sample volume: 50 mL; chelating resin: 0.65 g; eluent: 10 mL of 2 mol L⁻¹ HNO₃).

(1–10) for all the elements is one of the most important advantages of the proposed method. A pH of 2 was selected for subsequent studies.

3.2. Effect of elution conditions

The elution of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Mn(II) and Fe(III) from the chelating resin was examined by using 5–20 mL volumes of 1 and 2 mol L⁻¹ HCl and HNO₃ solutions. As can be seen in Table 1, 10 mL of 2 mol L⁻¹ HNO₃ solution was found to be satisfactory for elution of all the analytes ($R\% \geq 94$).

3.3. Effect of sample flow rate

The flow rate of the sample solution is a very important parameter for controlling the time of adsorption and analysis. The effect of flow rate of the sample solution on the metal ion sorption was investigated by varying flow rates in the range of 2–6 mL min⁻¹ under optimum conditions (pH 2, eluent: 10 mL of 2 mol L⁻¹ HNO₃). The results are given in Fig. 4. For flow rates above 4 mL min⁻¹, the recovery of Fe(III) was not quantitative and a flow rate of 4 mL min⁻¹ was subsequently selected in further experiments for all the analytes.

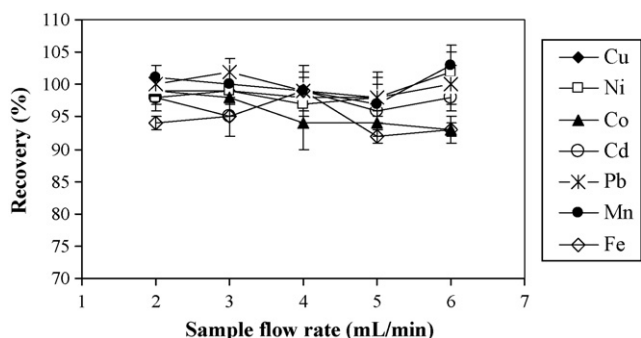


Fig. 4. Effect of flow rate of sample solution on the recovery of analytes ($n=3$).

Table 4
Determination of analytes in certified reference material ($\mu\text{g L}^{-1}$).

Element	Certified ^a	Found ^b	Recovery (%)
Cu(II)	443 ± 4	427 ± 5	96
Ni(II)	337 ± 3	330 ± 11	98
Co(II)	309 ± 3	299 ± 20	97
Cd(II)	158 ± 2	145 ± 4	92
Pb(II)	514 ± 5	527 ± 24	103
Mn(II)	275 ± 2	281 ± 11	102
Fe(III)	382 ± 5	384 ± 18	101

^a At 95% confidence level.

^b $\bar{x} \pm s, n=3$.

3.4. Effect of sample volume

The effect of sample volume on the recoveries of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Mn(II) and Fe(III) was examined by using model solutions in the volume range of 50–1000 mL. The described preconcentration method was applied to the model solutions containing 25 μg of Cu(II), Ni(II), Co(II) and Fe(III), 50 μg of Pb(II) and Cr(III), 5 μg of Cd(II) and 10 μg of Mn(II). The results are depicted in Fig. 5. The recoveries for all the metal ions were quantitative for volumes of 50–1000 mL. For an elution volume of 10 mL, a preconcentration factor of 100 was achieved.

3.5. Effect of foreign ions

The effect of foreign ions, usually found at high concentrations in water samples, on the recovery of analytes was investigated. The foreign ions were added to model solutions as their nitrate

Table 5
Determination of analytes in water samples (sample volume: 50 mL).

Element	Added (μg)	Tap water		Lake water	
		Found ^a (μg)	R (%)	Found ^a (μg)	R (%)
Cu(II)	–	<DL	–	<DL	–
	20	19.8 ± 0.5	99 ± 2	20.6 ± 0.5	103 ± 3
	40	40.8 ± 0.6	102 ± 2	40.1 ± 0.7	100 ± 2
Ni(II)	–	<DL	–	<DL	–
	20	20.1 ± 0.3	101 ± 2	19.0 ± 0.5	95 ± 3
	40	39.7 ± 1.3	99 ± 3	37.6 ± 1.3	94 ± 3
Co(II)	–	<DL	–	<DL	–
	20	20.2 ± 0.3	101 ± 1	18.2 ± 0.3	91 ± 2
	40	39.7 ± 0.1	99 ± 1	35.8 ± 0.6	90 ± 1
Cd(II)	–	<DL	–	<DL	–
	4.0	4.0 ± 0.1	100 ± 3	3.8 ± 0.1	95 ± 3
	8.0	7.8 ± 0.1	98 ± 1	7.1 ± 0.2	89 ± 3
Pb(II)	–	<DL	–	<DL	–
	40	40.4 ± 0.6	101 ± 2	39.8 ± 1.0	100 ± 3
	80	81.3 ± 2.1	102 ± 3	79.2 ± 1.4	99 ± 2
Mn(II)	–	<DL	–	<DL	–
	10	9.9 ± 0.3	99 ± 3	9.4 ± 0.3	94 ± 3
	20	19.4 ± 0.1	97 ± 1	18.4 ± 0.5	92 ± 2
Fe(III)	–	<DL	–	<DL	–
	20	20.0 ± 0.3	100 ± 1	19.9 ± 0.5	100 ± 3
	40	38.9 ± 1.1	97 ± 3	39.3 ± 0.5	98 ± 1

^a $\bar{x} \pm s, n=3$.

Table 6
Comparison of the described method with the some other solid phase extraction methods.

Element	Chelating matrix/detection technique	PF	DL ($\mu\text{g L}^{-1}$)	AC (mg g^{-1})	R.S.D. (%)	References
Pb, Cu, Cd, Ni	Gallic acid-modified silica gel/FAAS	100–200	0.58–0.92	4.62–15.38	0.41–0.96	[29]
Cu, Zn, Pb	<i>P. digitatum</i> immobilized on pumice stone/FAAS	50	1.3–5.8	<3	<3	[30]
Cu, Cd, Co, Ni, Zn, Pb	<i>o</i> -Aminophenol-XAD-2/FAAS	40–100	2–25	2.94–3.42	1.9–5.8	[31]
Zn, Mn, Ni, Pb, Cd, Cu, Fe, Co	2,3-Dihydroxypyridine loaded AXAD-2/FAAS	100–300	0.30–13.88	5.11–25.9	0.4–7.6	[32]
Cd, Co, Cu, Zn	DHDAA impregnated AXAD-4/FAAS	28–42	0.1–0.5	9.4–12.4	2.4–4.3	[33]
Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Chromotropic acid coated alumina/ICP-AES	50–100	0.14–0.62	10.3–16.8		[34]
Cu, Fe, Pb	Methylthymol blue–methyltriethyl ammonium chloride supported on naphthalene/FAAS	100	0.54–4.5	0.1–0.3	0.62–3.4	[35]
Cd, Pb	Thioureasulfonamide resin/STAT-FAAS	20	0.021, 0.15	21.9, 48.5	11,12	[36]
Co, Ni	5,7-Dichloroquinoline-8-ol embedded styrene-EDGMA/FAAS	200	2.0, 2.0	11.46, 7.05	2.52, 2.25	[37]
Cu, Ni, Co, Cd, Pb, Mn, Fe	BrPMAAm/AMPS/DVB chelating resin/FAAS	100	0.09–1.6	13.9–41.3	0.9–2.5	This work

FAAS: flame atomic absorption spectrometry; DHDAA: 2,6-dihydroxyphenyl-diazoaminoazobenzene; EDGMA: ethylene glycol dimethacrylate; AC: adsorption capacity; PF: preconcentration factor.

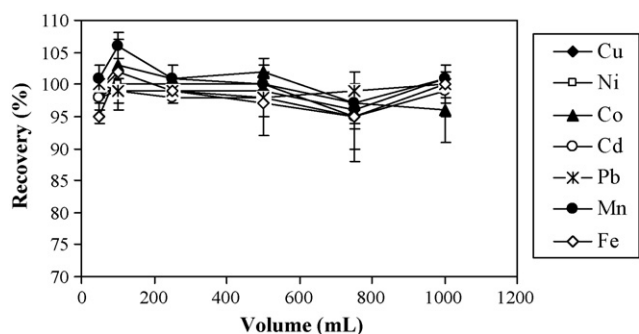


Fig. 5. Effect of the volume of sample solution on the recovery of metal ions (sample flow rate: 4 mL min^{-1} ; elution solution: 10 mL of $2 \text{ mol L}^{-1} \text{ HNO}_3$).

or chloride salts. The interference effect of analytes on each other was also studied. The concentration of analytes was fixed and concentration of foreign metal ions was adjusted in the range of $10\text{--}10,000 \mu\text{g mL}^{-1}$. The results are given in Table 2. The tolerance limits of foreign ions on the analytes were quite high. $5000 \mu\text{g mL}^{-1} \text{ Na}^+$ interfered with the determination of Cd(II) only. The most significant interferences result from $10 \mu\text{g mL}^{-1} \text{ Mn(II)}$, $250 \mu\text{g mL}^{-1} \text{ Mg(II)}$ (except for Pb and Fe), $250 \mu\text{g mL}^{-1} \text{ Ca(II)}$ (except for Cd, Mn and Fe) and $10 \mu\text{g mL}^{-1} \text{ Zn(II)}$ (except for Cu, Pb and Mn). The reasons for interferences arising from these ions are probably that they retain stronger than related analyte on the chelating resin.

3.6. Sorption capacity of the resin

The adsorption capacity of the chelating resin for the analyte ions was studied using batch technique. The 0.2 g chelating resin was equilibrated in the excess of metal ion solution (10 mg in 50 mL) by shaking for 30 min at $\text{pH } 2$. The mixture was filtered and the filtrate was diluted 20–100 fold. Concentrations of metal ions in the filtrate were determined by FAAS. Adsorption capacities (mg g^{-1} , $n=3$) were: 25.6 ± 2.1 for Cu (II), 19.8 ± 0.6 for Ni(II), 32.1 ± 0.2 for Co(II), 41.3 ± 0.1 for Cd(II), 38.9 ± 1.0 for Pb(II), 13.9 ± 0.4 for Mn(II), 18.3 ± 2.9 for Fe(III).

3.7. Analytical performance

In order to determine the detection limit (DL) of the described method, a 50 mL of blank solutions ($n=13$) was passed through the column under the optimal experimental conditions. The DLs were calculated as three times the standard deviation of the blank solutions divided by the slope of the calibration curve. In the calculation of DL values of the method, the 100-fold preconcentration factor (PF) was taken into consideration. The precision of the method under the optimum conditions ($25 \mu\text{g}$ of Cu(II), Ni(II), Co(II) and

Fe(III), $50 \mu\text{g}$ of Pb(II) and Cr(III), $5 \mu\text{g}$ of Cd(II) and $10 \mu\text{g}$ of Mn(II), $\text{pH } 2$, flow rate of sample: 4 mL min^{-1}) was estimated by performing seven successive retention and elution cycles. The relative standard deviation of the recoveries was calculated. The obtained data are illustrated in Table 3.

3.8. Accuracy and applications of the method

A certified reference material (TMDA-54.4) was used for the validation of the proposed separation/preconcentration method. The results in Table 4 show that the described method was in a good agreement with the certified values. In addition, the accuracy of the method was tested performing the recovery studies for the tap and lake water samples. The known amounts of the metal ions were added to aliquots of 50 mL of the water samples (Table 5). The recoveries of the analytes in water samples were in the range of 89–103%. The results show the applicability of the method for the analyses of tap and lake water samples.

4. Conclusion

A new chelating resin was synthesized, characterized and applied for the determination of Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions in water samples. Of the synthesized resin 0.65 g was used throughout all the work without any loss in recovery values of the trace metal ions. Table 6 shows the comparison of the described method with other solid phase extraction methods reported in the literature for the determination of some trace metal ions. The metal ion sorption capacities of the chelating resin are much higher than the other chelating matrices. The detection limit and the relative standard deviation values of the method are lower and/or comparable to those of the other solid phase extraction methods. The method has a high preconcentration factor and its accuracy is quite satisfactory. The other advantages of the method are acidic working pH, elution in acidic medium and good tolerance towards many interfering ions.

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