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Article

Preconcentration of Trace Elements by Using 1-(2-Pyridylazo)-2-naphthol Functionalized Amberlite XAD-1180 Resin and their Determination by FAAS

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Neste estudo foi sintetizada a resina Amberlite XAD funcionalizada por 1-(2-piridilazo)-2-naftol (PAN) e a resina resultante foi usada na pré-concentração dos íons Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) e Pb(II) presentes em baixas concentrações em diferentes amostras. Para isso, o copolímero foi nitrado, reduzido à correspondente amina, convertido ao sal diazonato com nitrito e em reação com PAN produziu a resina complexante XAD-1180-PAN. Para o método descrito, parâmetros analíticos para recuperação dos elementos traço foram avaliados tais como, pH, volume da amostra, quantidade de resina, vazão de retenção e remoção, volume e tipo de eluente. Os metais retidos na resina XAD-1180-PAN foram eluídos com HNO_3 2 mol L^{-1}. A influência dos íons presentes na matriz, ou seja, Na(I), K(I), Ca(II) e Mg(II), sobre a recuperação dos elementos traço também foi avaliada, quando presentes isoladamente ou em conjunto. A repetibilidade do método foi avaliada nas condições experimentais ótimas estabelecidas. Os valores de recuperação, para todos os elementos, exceto o Cr(III), foram ≥92% e os desvios padrão relativos ≤8.5%. Os limites de detecção (3 s_{branco} / coeficiente angular) para Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) e Pb(II) foram 4,1; 0,13; 2,7; 1,2; 0,19; 0,06 e 0,13 μg L^{-1}, respectivamente. O método desenvolvido foi utilizado para a pré-concentração e determinação de Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) e Pb(II) em águas de abastecimento urbano, pluvial e interior, e de Ni(II), Cd(II) e Pb(II) em materiais de referência certificados (RM 8704 sedimento do rio Buffalo) por espectrometria de absorção atômica com chama (FAAS).

In this study, Amberlite XAD-1180 resin functionalized by 1-(2-pyridylazo)-2-naphthol (PAN) was synthesized and the resulting resin was used for preconcentration of Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) and Pb(II) elements present at trace levels in different matrices. For this purpose, the copolymer was nitrated, reduced to the corresponding amine, converted to the diazonium salt with nitrite and reacted with PAN to produce the XAD-1180-PAN chelating resin. For the described method, the effect of some analytical parameters, such as pH, sample volume, resin amount, flow rates of uptake and stripping, volume and type of eluent, on the recovery of the trace elements was investigated. The metals retained on the XAD-1180-PAN resin were eluted by 2 mol L^{-1} HNO_3. The influence of matrix ions, *i.e.*, Na(I), K(I), Ca(II) and Mg(II), on the recovery of trace elements was also examined by using the developed method when they occurred both individually and together. The repeatability of the method at the optimum conditions determined experimentally was investigated. The recovery values for all the elements, except for Cr(III), were found to be ≥92% and the relative standard deviation was ≤8.5%. The 3s/b detection limits for Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) and Pb(II) were found to be 4.1, 0.13, 2.7, 1.2, 0.19, 0.06 and 0.13 μg L^{-1}, respectively. The developed method was utilized for preconcentration and determination of Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) and Pb(II) in tap water, rain water, and stream water, and of Ni(II), Cd(II) and Pb(II) in a certified reference material (RM 8704 Buffalo river sediment) by flame atomic absorption spectrometry (FAAS).

Keywords: Amberlite XAD-1180, PAN, chelating resin, preconcentration, FAAS

Introduction

In the analysis of trace metal ions present in various samples such as natural and waste water, biological and alloy samples, the direct determination with various instrumental methods is not possible owing to matrix effect and low concentration of metal ions in a sample. In trace analysis, therefore, a preconcentration and/or separation of trace elements from the matrix is frequently

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necessary to improve the detection limit and selectivity.[1,2] Various methods used for this purpose are co-precipitation,[3] liquid-liquid extraction,[4] ion exchange,[5] and solid phase extraction.[6,7] The solid phase extraction technique is now routinely used in various research and application areas due to its characteristics and advantages over the classical solvent extraction or other preconcentration techniques. Chelating resin sorption method is one of the most effective multielement preconcentration methods. The chelating resins include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics. Generally, chelating ligands bound to copolymers by covalent bonds are much more resistant to external effects than those immobilized by simple impregnation.[8-10]

A number of supports and chelating ligands have been widely used in the design of chelating resins for the preconcentration and separation of trace metal ions from various matrices. The most prominent among the supports used are Amberlite XAD resins,[11,12] silica gel,[13] activated carbon,[14] activated alumina,[15] sepiolite,[16] and related polymeric supports.[17,18] Some important and recently reported chelating matrices described using such supports are: silica gel modified with purpurogallin,[19] 1-(2-pyridylazo)-2-naphthol,[20] 3-aminopropyltriethoxysilane,[21] 1,8-dihydroxyanthraquinone,[22] 2-aminothiazole,[23] N-propylsalicylaldimine,[24] surfactant coated alumina modified with 1-(2-pyridylazo)-2-naphthol,[15] Amberlite XAD-2 modified with chromotropic acid,[25] alizarin red-S,[26] Nitroso R salt,[27] Amberlite XAD-4 modified with *o*-aminobenzoic acid,[28] N-hydroxyethylenediamine,[29] and Amberlite XAD-16 modified with 1-(2-thiazolylazo)-2-naphthol.[30]

Amberlite XAD 1180 resin (Rohm and Haas Co., Philadelphia, USA) is a non-ionic, hydrophobic, crosslinked polystyrene-divinylbenzene copolymer having a surface area of 650 m^2 g^{-1} and a particle size of 0.3-0.9 mm. It has physical, chemical and thermal stability.[31] Amberlite XAD-1180 resin has been used for the preconcentration and separation of trace metals in various samples in our previous works.[31,32]

1-(2-pyridylazo)-2 naphthol forms stable complexes with many transition metals of interest; it is one of the most extensively used complexing agents for trace element analysis. Essentially it is insoluble in water and in alkaline solutions in which $[OH^-]$ is < 0.01 mol L^{-1}. It is soluble in alcohols, $CHCl_3$, CCl_4 (≈ 0.01 mol L^{-1}) *etc*. Its solutions are stable. In acidic solutions the pyridine nitrogen is protonated and in basic solutions the H of the OH group is ionized. The metal chelates of PAN have the metal atom bonded to O of the OH group, to pyridine N and to azo N.[33,34] Up to now, any information in literature could not found relevant to the usage of Amberlite XAD-1180-PAN chelating resin with the purpose of preconcentrating of trace metal ions from different samples.

In the present study, Amberlite XAD-1180-PAN chelating resin was prepared and characterized by using FTIR. The adsorption and preconcentration capabilities of the resin for Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II), and Pb(II) were ascertained.

Experimental

Apparatus

The concentrations of metal ions were determined by a Perkin Elmer 3110 model atomic absorption spectrometer without background correction, equipped with an air-acetylene burner and hollow cathode lamps of the analytes. The operating conditions such as wavelength, bandwidth, and acetylene/air flow rates were adjusted according to the recommendations of manufacturer's. All pH measurements were made with a Jenko 672 model digital pH meter equipped with a combined pH electrode. Functional groups of the chelating resin synthesized were identified with a Jasco 460 model FTIR spectrometer.

Resin and reagents

Analytical reagent-grade chemicals were used without further purification. Stock solutions containing 1000 mg L^{-1} of Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II), and Pb(II) were prepared by dissolving appropriate amounts of their nitrate salts (purchased from Merck, Darmstadt, Germany) and diluting to 1000 mL with 1% (m/m) HNO_3. Appropriate standard and model solutions of metal ions were prepared by diluting the stock solution prior to use. The buffer solutions used for adjusting pH value of solutions were CH_3COOH/CH_3COO^- buffer for pH 4–6 and NH_3 /NH_4Cl buffer for pH 8–10.

Amberlite XAD-1180 resin (Rohm and Haas Co., Philadelphia, USA) prior to immobilization was successively washed with 4 mol L^{-1} HNO_3 and 1 mol L^{-1} NaOH, distilled water and methanol (99.5%). The Amberlite XAD-1180-PAN chelating resin was dried at 60 °C. Approximately 0.4 g of the resin was suspended in water and packed into a glass column (10 mm i.d. × 100 mm height).

Synthesis of XAD-1180 –PAN chelating resin

The XAD-1180-PAN chelating resin was prepared as described in literature.[30] 5 g of Amberlite XAD-1180 resin was tranferred to a 250 mL of flask containing 40 mL of concentrated HNO_3 and 60 mL of concentrated H_2SO_4. The mixture was heated to 60 °C and the heating procedure maintained for 1 h. Then the reaction mixture containing the nitrated resin was poured into a beaker filled with ice water. The resin was filtered and washed with distilled water until the pH 4–5. The nitrated resin (XAD-1180-NO_2) was reduced by refluxing at 90 °C for 24 h in a mixture of conc. HCl and ethanol (45:50, v/v) containing 50 g of stannous chloride. After cooling to ambient temperature, the product reduced was filtered and washed with a mixture of concentrated HCl and ethanol (45:50, v/v), 2 mol L^{-1} NaOH and distilled water, successively. The aminated polymer was suspended in 200 ml of ice-cold water and then diazotized with ~75 mL of 1 mol L^{-1} $NaNO_2$ and 100 mL of 1 mol L^{-1} HCl at 0-3 °C until the reaction mixture started to change the colour of iodide paper to violet. The diazotized resin was filtered, washed with ice-cold water and reacted with 2.5 g of PAN which was dissolved in a mixture including 100 mL of 10% (m/v) NaOH and 50 mL of methanol and afterwards the mixture was maintained at 0-3 °C for 24 h. After stirring for 30 min, the resulting product was filtered and washed with distilled water and 1 mol L^{-1} HCl until it was free from alkali. Afterwards it was dried at 60 °C over P_2O_5 in vacuum.

Optimized separation and preconcentration procedure

The method was tested using the model solutions prior to its application to the real samples. For this purpose, the pH of the model solution including analyte ions**,** 10 μg (0.2 μg mL^{-1}) each of Ni(II), Fe(III) and Cu(II), 20 μg (0.4 μg mL^{-1}) each of Cr(III) and Pb(II), 2.5 μg (0.05 μg mL^{-1}) of Cd(II), and 5 μg (0.1 μg mL^{-1}) of Mn(II) was adjusted to the desired value (pH 9.0) by using 1 mol L^{-1} of NH_3/NH_4Cl buffer solution, and then the volume of the solution was completed to 50 mL with distilled water. The resulting solution was passed through the column filled with XAD-1180-PAN resin at a flow rate of 2 mL min^{-1}. The column was washed with 5-10 mL of distilled water. The metal ions retained on the resin were eluted by using 20 mL of 2 mol L^{-1} HNO_3. The eluate was evaporated near to dryness on a hot plate and then the moist residue was diluted to 5 mL with 1 mol L^{-1} HNO_3. The Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II), and Pb(II) contents were determined by flame AAS. The chelating resin was used repeatedly after washing with 2 mol L^{-1} HNO_3 and water. The blank analyses were made in the same way.

Analysis of water samples

A tap water sample taken from the laboratory of the University was analysed without pre-treatment. The rain water and stream water samples were collected in pre-washed polyethylene bottles. These samples were filtered through a Millipore cellulose membrane filter of 0.45 μm pore size and then acidified with 5 mL of concentrated nitric acid per liter of sample. The samples were analyzed by the separation/preconcentration procedure mentioned above. For the analysis, the aliquots of 400 mL of tap water and 250 mL of rain water and stream water were used.

River Sediment Digestion (SRM)

A 50 mg of the reference material (RM 8704 Buffalo river sediment, dried at 110 °C for 2 h) was digested in a beaker by adding 10 mL of aqua regia. The mixture was heated on a hot plate until to almost dryness. Then, 10 mL of aqua regia was added again to the residue and the mixture was evaporated to dryness. The insoluble part was filtered through a filter paper with blue band, and the filter paper and beaker were rinsed with hot 1 mol L^{-1} HNO_3. 5 mL of 1 mol L^{-1} NaF was added to the filtrate in order to prevent the precipitation of Fe(III) found in the sample in excess amounts in hydroxy forms. So, Fe(III) ions have been masked by F^- in the solution as $(FeF_6)^{3-}$ anionic complex. The pH of this solution was adjusted to pH 9 by adding NH_3/NH_4Cl buffer. The total volume was made up to 50 mL with water. The column procedure described above was applied to separation and preconcentration of the metal ions from the sample solution. After the elution, the eluate was evaporated near to dryness and completed to 5 mL with 1 mol L^{-1} HNO_3. The determination of the studied metals in the final solution, except for Fe(III), was performed by using FAAS.

Results and Discussion

Characteristics of XAD-1180-PAN chelating resin

Analytical data of the intermediates and synthesized resin were illustrated in Table 1. XAD-1180-NO_2 shows two strong bands at 1526 (asymmetrical stretching) and

1348 cm^{-1} (symmetrical stretching), which describe characteristic nitro groups. In the IR spectrum of XAD-1180-NH$_2$, a band was observed at 1625 cm^{-1} owing to amine groups (N-H bending). The IR spectrum of PAN functionalized Amberlite XAD-1180 was compared with that of pure Amberlite XAD-1180. As it can be seen in Table 1, there are additional bands at 3433 cm^{-1} (O-H stretching) and 1630 cm^{-1} (-N=N- stretching), which appear to originate due to modification of the resin by the ligand and are characteristics of O-H and -N=N- vibrations, respectively. The results obtained are in good agreement with informations given in literature.[2,8,30]

Table 1. Analytical data of the intermediates and synthesized resin

Intermediates and synthesized resin	IR spectrum of functional group (cm^{-1})			
	νN-O	νN-H	νN=N	νO-H
XAD-1180-NO$_2$	1526 1348			
XAD-1180-NH$_2$		1625		
XAD-1180-PAN			1630	3433

Effect of pH on recoveries

The sorption of metal ions on chelating resin is dependent on the pH of a sample solution due to the competitive reaction between chelate forming groups and hydrogen ions in the solutions.[30] 10 μg of Ni(II), Fe(III) and Cu(II), 20 μg of Cr(III) and Pb(II), 2.5 μg of Cd(II), and 5 μg of Mn(II) were spiked to a 50 mL of the model solution. The pH of this solution was adjusted in the range of 4 to 10 using different buffer solutions and then the separation/preconcentration procedure described was applied. As it can be seen in Figure 1, quantitative recoveries (≥ 95%) were obtained for all the elements at pH 9.0. Therefore, the working pH was chosen as 9.0 for the following experiments. In addition, in the column study performed with only the original Amberlite XAD-1180 resin without using PAN reagent, the recovery values for the elements at the pH 9.0, except for Cu which presented a recovery around 95%, were not quantitative.

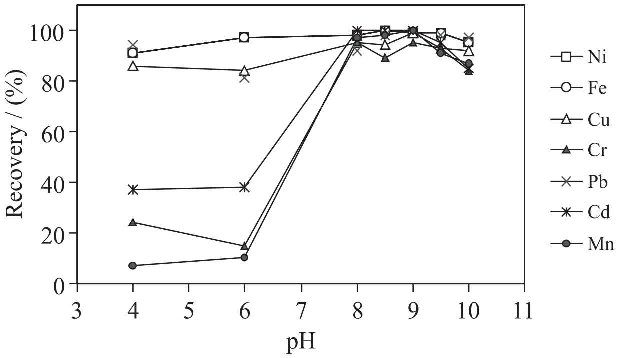

Figure 1. Effect of pH on the recovery of metal ions on XAD-1180-PAN resin.

Effect of resin amount

The resin amount is one of the other important parameters for obtaining quantitative recovery. After adjusting the pH of model solution including trace metal ions to 9.0 by using NH$_3$/NH$_4$Cl buffer solution, the model solutions were passed through the column filled with 100-500 mg of the XAD-1180-PAN resin. The metal ions adsorbed were eluted by 20 mL of 2 mol L^{-1} HNO$_3$. The recovery (%) values for all the elements were found as quantitative for 0.4 g of the resin (Figure 2).

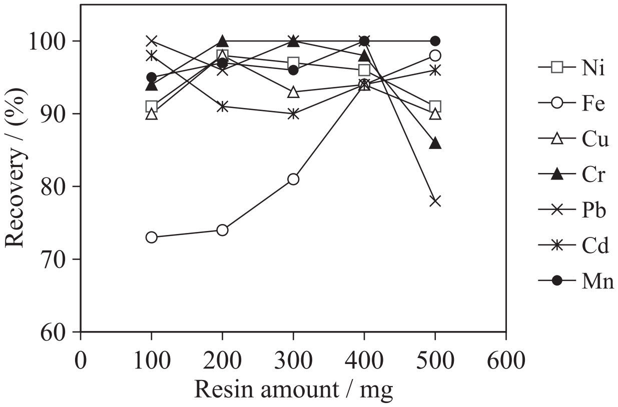

Figure 2. Effect of the amount of the chelating resin on the recovery of the elements.

Effect of type, concentration and volume of eluent

The elution of the retained metals from the XAD-1180-PAN resin was studied by using various eluting agents and different eluent volumes. As seen in Table 2, 20 mL of 2 mol L^{-1} HNO$_3$ was found to be the most adequate eluent for quantitative recoveries of all the elements examined.

Effect of sample and eluent flow rate

The effect of flow rates of the sample and eluting solutions on metal sorption and desorption, respectively, was investigated for the flow rates of 1.0, 2.0, 2.5 and 3.5 mL min^{-1} under the optimum conditions. It was found that the retention of all metal ions, except for Fe(III) and Cr(III), was not affected from the flow rate up to 3.5 mL min^{-1}. The effect of eluent flow rate on the recovery was examined for the flow rates of 1.0, 2.0 and 3.5 mL min^{-1}. The optimum flow rate for the elution of all the elements was found as 2.0 mL min^{-1}.

Table 2. Effect of type, concentration and volume of eluents on the recovery (n=3)

Eluent type and concentration	Volume (mL)	Recovery (%)						
		Ni(II)	Fe(III)	Cu(II)	Cr(III)	Pb(II)	Cd(II)	Mn(II)
1 mol L^{-1} HNO_3	10	87	89	83	80	77	98	96
	20	96	96	94	100	95	90	94
2 mol L^{-1} HNO_3	10	87	89	83	80	77	98	96
	20	96	94	94	98	100	94	100
3 mol L^{-1} HNO_3	20	94	96	100	82	95	97	100
1 mol L^{-1} HCl	10	67	66	34	78	73	81	92
	20	87	95	62	81	90	85	92
2 mol L^{-1} HCl	20	90	64	79	70	79	92	96

Effect of sample volume

In the analysis of real samples using a preconcentration procedure, the sample volume is one of the important parameters for obtaining high preconcentration factors. For that reason, the volumes of model solutions containing 10 μg each of Ni(II), Fe(III) and Cu(II), 20 μg each of Cr(III) and Pb(II), 2.5 μg of Cd(II), and 5 μg of Mn(II) were varied from 50 to 750 mL to determine the maximum applicable volume of sample solution for natural water samples. The metals were preconcentrated on the XAD-1180-PAN resin by applying the proposed procedure. The effect of the sample volume on the recovery was illustrated in Figure 3. The recoveries for Cu(II), Ni(II) and Fe(III) were quantitative up to the sample volume of 750 mL. Breakthrough volume for Cr(III) was 400 mL and almost 750 mL for Mn (94%) and Cd (92%), and also 500 mL for Pb (91%). If the volume of final solution is down to 5 mL, thus an enrichment factor of 100 for Cu(II), Ni(II), Fe(III) and Pb(II), of 80 for Cr(III), of 150 for Cd(II), and Mn(II) can be acquired.

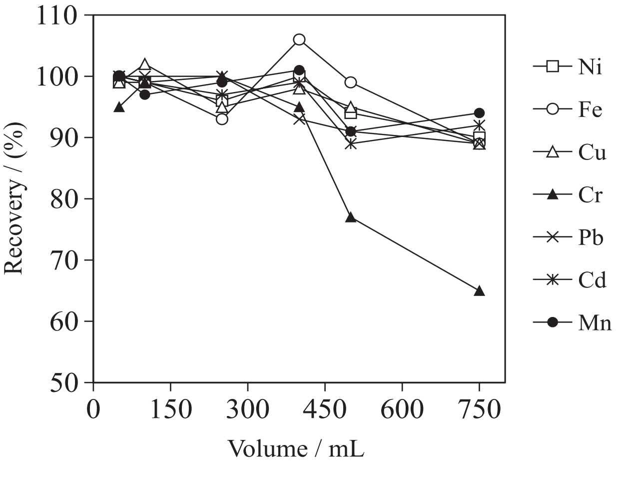

Figure 3. Effect of sample volume on the recovery of the elements.

Effect of matrix elements with and without using the preconcentration procedure

The effect of Na(I), K(I), Ca(II), Mg(II), Cl^- and NO_3^- ions on the signals of the metals was examined both with the proposed method and without it. When the influence of matrix components without using the enrichment procedure proposed was investigated, it was seen that especially the concentrations of both 500 mg L^{-1} and 1000 mg L^{-1} of Ca(II), and Mg(II) ions had a decreasing effect on Fe(III), Cd(II), Cr(III) and Mn(II) absorbance signals. When the concentrations of Na(I) and K(I) ions were 500 mg L^{-1}, any interference on the elements studied was observed, except for Cd(II), at the concentration of 500 mg L^{-1} K(I). While the model solution containing 500 mg L^{-1} of each of Na(I), K(I), Ca(II) and Mg(II) ions shows a decreasing effect on Ni(II), Fe(III), Cr(III) and Pb(II) signals, the solution containing 1000 mg L^{-1} of matrix ions has an important decreasing effect on the signals of all the elements. These results show that a separation procedure is requisite for the determination of analytes in a complex matrix medium prior to their measurements by FAAS.

Because of the decreasing influence of the matrix ions on the metal signals, the separation procedure is necessary. For this purpose, the metal ions at appropriate amounts were added to the model solutions of 50 mL containing the

Table 3. Influence of matrix ions on the retention of metal ions on the Amberlite XAD-1180-PAN chelating resin (n=3)

Interfering ion (Salt added)	Concentration (µg mL^{-1})	Recovery (%)						
		Ni(II)	Fe(III)	Cu(II)	Cr(III)	Pb(II)	Cd(II)	Mn(II)
Na(I): (NaCl)	500	96	100	98	100	100	92	96
	1000	96	100	99	100	100	100	92
	5000	98	95	94	96	96	97	100
K(I): (KNO$_3$)	500	100	103	103	95	99	91	100
	1000	94	88	96	96	99	96	104
	5000	96	80	100	96	98	95	94
Ca(II): (CaCl$_2$)	500	97	95	97	90	94	100	95
	1000	100	92	96	90	94	98	81
	5000	100	95	91	83	90	100	79
Mg(II): (Mg(NO$_3$)$_2$)	500	100	109	96	98	100	92	96
	1000	98	100	96	92	100	96	89
	5000	95	96	97	86	83	88	75
Na(I), K(I), Ca(II), Mg(II)	500	105	98	96	96	106	100	108
	1000	100	93	97	98	106	92	99
	5000	102	97	94	84	110	89	96

matrix ions [Ca(II), Mg(II), K(I) and Na(I)] at increasing concentrations. The pH of the solutions was adjusted to 9.0. The results showed that the recovery of the metal ions studied was not affected by the solution containing the matrix ions at high concentrations (see Table 3).

Repeatability and detection limit of the method

The repeatability of the method was examined under the optimum experimental conditions described above by using the model solutions. For this purpose, the analyses were performed by applying the proposed method at three consecutive days (totally eleven replicates). The first three runs were performed at the first day while the others (four runs for each day) were performed at the second and the third days. The contents of the elements in the elution solution were determined by FAAS. The repeatability of the described method was evaluated by monitoring the changes in the recoveries of the analytes (R±s%), 103±3 for Ni(II), 98±5 for Fe(III), 97±2 for Cu(II), 94±5 for Cr(III), 97±5 for Pb(II), 106±8 for Cd(II), and 94±8 for Mn(II).

For the determination of detection limit of the method, 50 mL of blank solution was passed through the column (n=20). The detection limit was calculated as the ratio of the three standard deviations of the blank to the slope of the calibration curve. When an enrichment factor of 100 for Cu(II), Ni(II), Fe(III) and Pb(II); 80 for Cr(III); and 150 for Cd(II) and Mn(II) is considered, the following detection limits: 4.1, 0.13, 2.7, 1.2, 0.19, 0.06 and 0.13 µg L^{-1} can be acquired for Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) and Pb(II), respectively.

Table 4. Determination of Ni(II), Pb(II) and Cd(II) in the certified reference material (RM 8704 Buffalo river sediment) by FAAS after preconcentration on the Amberlite XAD-1180-PAN chelating resin (n=7)

Element	Concentration (µg g^{-1}) $(\bar{x} \pm t \times s / \sqrt{n})^{a}$		Recovery (%)
	Certified	Found	
Ni(II)	42.9 ± 3.7	41.1 ± 9.6	95.8
Pb(II)	150 ± 17	143 ± 35	95.3
Cd(II)	2.94 ± 0.29	2.92 ± 0.48	99.3

[a] At 95% confidence limit; t: student constant; s: standard deviation.

Table 5. The recovery of the elements added to the tap water and rain water samples after preconcentration on the Amberlite XAD-1180-PAN chelating resin (in triplicates for each concentration)

Element	Added (µg mL^{-1})	Tap water	Rain water	Tap water	Rain water
		Found (µg mL^{-1})		Recovery(%)	
Ni(II)	1	0.98	1.02	98	102
Fe(III)	1	0.94	0.94	94	94
Cu(II)	1	0.96	0.97	96	97
Cr(III)	2	1.48	1.44	74	72
Pb(II)	2	2.00	2.00	100	100
Cd(II)	0.5	0.49	0.48	98	96
Mn(II)	0.5	0.46	0.48	92	96

Table 6. Determination of Ni(II), Fe(III), Cu(II), Pb(II), Cd(II) and Mn(II) in the water samples by FAAS after preconcentration on the Amberlite XAD-1180-PAN chelating resin

	Concentration, $\bar{x} \pm s$ (μg L^{-1})		
Element	Tap water	Rain water	Stream water
Ni(II)	5.59 ± 0.95 (n=7) [a]	< LOD[b]	4.49 ± 0.88 (n=6)
Fe(III)	7.29 ± 1.50 (n=7)	12.0 ± 0.6 (n=3)	55.4 ± 5.6 (n=4)
Cu(II)	3.44 ± 0.70 (n=4)	3.63 ± 0.77 (n=7)	2.54 ± 0.32 (n=7)
Pb(II)	< LOD	< LOD	< LOD
Cd(II)	0.60 ± 0.10 (n=7)	< LOD	3.37 ± 0.88 (n=6)
Mn(II)	1.52 ± 0.31 (n=6)	3.75 ± 0.58 (n=6)	13.6 ± 2.2 (n=7)

[a] Number of replicates, [b] Limit of detection.

The accuracy of the method

As no standard reference material for water sample was available in our laboratory, the accuracy of the described separation/preconcentration method was tested in the recovery studies by adding known amounts of the elements to the water samples of 50-100 mL and also by analyzing of a standard reference material (RM 8704 Buffalo river sediment). The results obtained from the certified reference material and the water samples are depicted in Table 4 and 5, respectively. The recovery values obtained from the water samples were satisfactory, except for Cr(III). The results obtained from the described method were in good agreement with the analysis of the certified reference material for Ni(II), Pb(II) and Cd(II), except for Mn(II) and Cr(III). The reason of the exception for Mn(II) and Cr(III) may be interferences of some matrix components in the sediment sample, such as silicate and aluminum.

Table 7. Comparison of detection limits (LOD, μg L^{-1}) and enrichment factors (EF) of some metal ions using the chelating resins prepared with different ligands and supports

Support	Immobilized ligand		Metal ion							Reference
			Cr(III)	Mn(II)	Fe(III)	Ni(II)	Cu(II)	Cd(II)	Pb(II)	
Amberlite XAD-1180	1-(2-Pyridylazo) -2-naphthol	LOD	4.1	0.13	2.7	1.2	0.19	0.06	0.13	This work
		EF	80	150	100	100	100	150	100	
Amberlite XAD- 2	Chromotropic acid	LOD								25
		EF			120	200	100	100		
	Alizarin red-S	LOD								26
		EF				40		40	40	
	1-(2-Pyridylazo)-2-naphthol	LOD								35
		EF					50	50	50	
	1-(2-Pyridylazo)-2-naphthol	LOD								
		EF				50				11
	Tiron	LOD		2.5	5.0	4.0	2.0	1.3	24	9
		EF		65	80	150	200	50	25	
	2-(Methylthio)aniline	LOD				0.033	0.041	0.022		2
		EF				400	100	300		
Amberlite XAD-4	o-Aminobenzoic acid	LOD								28
		EF				200		400	400	
Amberlite XAD-7	Xylenol Orange	LOD								36
		EF			200	100	50	50		
Amberlite XAD-16	2-{[1-(3,4-Dihydroxyphenyl) methylidene]amino} benzoic acid	LOD		1.38	5.92	1.76	2.52	0.77	0.67	37
		EF		250	450	100	300	250	250	
Silica gel	Purpurogallin	LOD								19
		EF			500					
	2-Aminothiazole	LOD				2.3	1.7			23
		EF				10	10			
	1,8-Dihyroxy-anthraquinone	LOD						0.62	0.45	22
		EF						200	200	

Also, the standard reference material was directly analysed by digesting the sample with aqua regia without using the described separation/ preconcentration procedure. Nickel, Pb and Cd were determined by FAAS. The obtained recovery values were acceptable for Pb (93%) and Cd (106%), except for Ni (75%). For this reason, the described separation/preconcentration procedure was applied to the analysis of the reference material, including Al (6.10%), Ca (2.64%), C (3.35%), Fe (3.97%), Mg (1.20%), K (2.00%), and Na (0.55%, m/m).

Application of the method

The proposed method was applied to the certified river sediment and the natural water samples such as tap water, rain water and stream water. The results obtained for the certified sediment and the water samples are shown in Tables 4 and 6, respectively. As it can be seen in Table 6, the concentration of Pb(II) could not be determined in the water samples because of its low concentrations. The RSD values calculated varied from 5% (Fe in rain water) to 26% (Cd in stream water). Because of the concentrations of metals studied in the water samples are fairly low, the RSDs are generally high for these elements.

Comparison with other solid phase extraction methods

The detection limit (μg L^{-1}) and enrichment factors (EF) of the present method were comparable to those obtained by the other methods described in the literature (see Table 7). The LODs of the present method for all the elements are lower than the other solid phase extraction methods given in Table 7, except for the reference 2, for Ni(II), Cu(II) and Cd(II). The EFs for the metal ions with Amberlite XAD-1180-PAN resin are better[11,23,26,35] than or comparable[9,25,36] to the other chelating resins.

Conclusions

The proposed preconcentration method consists of a simple and low cost procedure which permits the quantitative recovery of the elements Mn(II), Fe(III), Ni(II), Cu(II), Cd(II), and Pb(II) from waters, except for Cr(III) and the certified reference sediment sample (except for Cr(III) and Mn(II)). Owing to the synthesized chelating resin having high affinity for the metal ions, the selective determination of the metal ions is possible. The chelating resin has been used along all the experiments performed for this study. Because of that, it has a superior reusability and stability.

The recovery values for all the elements except for Cr(III) were found to be ≥92% and the relative standard deviation was ≤8.5%. The LODs for Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Cd(II) and Pb(II) were found to be 4.1, 0.13, 2.7, 1.2, 0.19, 0.06, and 0.13 μg L^{-1}, respectively. The method has an enrichment factor of 100 for Cu, Ni, Fe and Pb, 80 for Cr, 150 for Cd and Mn. The LOD values are lower than those of other studies,[9,23,37] and enrichment factors are higher than those of the studies given[11,23,26,35] in the literature.

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