Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.976766

57 (2016) 1705–1712
January

Taylor & Francis
Taylor & Francis Group

Preconcentration of some heavy metals by Amberlite XAD-4 functionalized with Phenanthroline and investigation of microwave radiation effect on kinetic of adsorption

Hamid Hashemi-Moghaddam*, Hajar Khaton Haghiri

Department of Chemistry, Damghan Branch, Islamic Azad University, P.O. Box 36716-39998, Damghan, Iran,
Tel. +98 23 35225029; Fax: +98 23 35225044; email: h.hashemimoghadam@damghaniau.ac.ir (H. Hashemi-Moghaddam)

Received 18 December 2013; Accepted 8 October 2014

ABSTRACT

Phenanthroline modified Amberlite XAD-4 has been synthesized by coupling it through an azo spacer. The resulting chelating resin, characterized by elemental analysis, thermogravimetric analysis and infrared spectra, was used to preconcentrate Cd, Pb, Fe, Co, Cu and Zn ions. Parameters, such as sorption capacity of the chelating resin, pH and eluent, were evaluated. The effects of electrolytes and cations on the preconcentration were also investigated. Furthermore, effect of microwave power was investigated on adsorption rate of these heavy metals. The obtained results show, time of extraction is reduced significantly by this modification. The detection limit, were found to be 1.4, 4.1, 2.4, 3.9, 3.1, 3.9 μg L^{-1} for Cd, Pb, Fe, Co, Cu and Zn, respectively. The relative standard deviation of the ten replicate determinations was <7%. The procedure was validated by standard addition and comparison of obtained result by GFAAS method. The developed method was utilized for preconcentration of Cd, Pb, Fe, Co, Cu and Zn in wastewater, potato and preconcentration of Pb in lipstick with satisfactory results.

Keywords: Preconcentration; Phenanthroline; Amberlite XAD-4; Microwave assisted extraction; Inductively coupled plasma–atomic emission spectrometry (ICP OES)

1. Introduction

The use of instrumental methods for trace metal quantification frequently requires preconcentration procedures to lower the detection limits [1]. These preconcentration methods include solvent extraction [2, 3], coprecipitation, [4–7] flotation [8–10] and solid phase extraction, [11–17]. Among all the preconcentration methods, chelating resin sorption method is one of the most effective multi element preconcentration methods because, it can provide more flexible working conditions together with good stability, selectivity, high concentrating ability, high capacity of metal ions and simple operation. Moreover, at the same time, demands for trace element determination and concentration using these modified resins are ever increasing. This is because such functional polymers can be employed for the preconcentration in trace metal analysis, particularly for water systems geological and biological samples [18–21]. 1,10-Phenanthroline (phen) is a classic ligand in coordination chemistry, which couples versatility in metal ion binding with peculiar

---

*Corresponding author.

properties of its complexes [22]. In terms of its coordination properties, phen is similar to 2,2´-bipyridine (bipy) [23].

In this work, Amberlite XAD-4 was functionalized with Phenanthroline and it has been investigated in detail for use in preconcentration procedures. The results show that Phenanthroline XAD-4 is a good chelating resin for preconcentration of Cd, Pb, Fe, Co, Cu and Zn. In conventional methods of solid phase extraction, a relatively long time is required to adsorbed analyte to the resin. In a different way, a novel approach has been developed for the extraction of Cd, Pb, Fe, Co, Cu and Zn by assisted of microwave power at atmospheric pressure and time and efficiency of extraction was comprised with conventional extraction method. By this modification, extraction time and efficiency significantly were improved.

Thus a new functionalized resin was synthesized and by applying microwave power a very fast method for effective preconcentration of Cd, Pb, Fe, Co, Cu and Zn in real samples was presented.

2. Experimental

2.1. Apparatus

The Fourier transform infrared (FTIR) spectra were obtained using a Thermo Nicolet FTIR spectrometer (Nicolet 6700, USA). IR spectra were recorded in the range 400–4,000 cm^{-1} by the KBr pellet method. The inductively coupled plasma atomic emission spectrometer ICP OES equipment (Integra XL, GBC, Australia) was used for the determination of metal ions.

Elemental analyses were carried out on a Perkin-Elmer elemental 100 analyzer (Rotkrewz, Switzerland). Thermogravimetric analysis (TGA) analysis was carried out using a TGA-50H instrument (Shimadzu, Kyoto, Japan). A model 3510 Jenway pH-meter was used for pH measurements.

The microwave oven used for extraction provided by Samsung (South Korea) trademark operating at 2,450 MHz. The maximum power of the oven was regulated at 1,000 W. Two power levels, 30% (300 W) and 60% (600 W) were studied in order to examine the effect of microwave power. The dimensions of the interior cavity of the oven were 29 × 37 × 40 cm.

2.2. Chemicals and reagents

Unless otherwise stated, all reagents used were of analytical grade (Merck, Darmstadt, Germany) and all solutions were prepared with ultra-pure water (Millipore). Standard lab ware and glassware were used cleaned with 10% solution of HNO_3 throughout and repeatedly and rinsed with ultra-pure water, according to a published procedure [31].

Stock solutions (1.0 g L^{-1}) of the elements were prepared by dissolving appropriate amounts of nitrate salts in 1.0% HNO_3 and further diluted daily prior to use.

XAD-4 resin (having a surface area in the range of 300–400 m^2 g^{-1} and 40–60 mesh particle size) was procured from Aldrich (Milwaukee, USA). Before use, Amberlite XAD-4 was thoroughly washed according to the sequence of 4.0 mol L^{-1} HCl, distilled water, 1.0 mol L^{-1} NaOH and distilled water successively. Finally, it was washed with 10 mL of methanol and dried in air before further use.

2.3. Synthesis of Phenanthroline-functionalized Amberlite XAD-4 Resin

Procedures described in the literature for similar reagents were used for the synthesis of Phenanthroline-XAD [32,33]. Amberlite XAD-4 beads (5 g) were treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4, and the mixture was stirred at 60˚C for 1 h on an oil bath. The reaction mixture was then poured into 150 mL of ice–cold water. Subsequently, it was filtered, washed repeatedly with distilled water until free from acid, and then treated with a mixture of 40 g of $SnCl_2$, 45 mL of concentrated HCl, and 50 mL of ethanol. The mixture was refluxed for 12 h at 90˚C to reduce the nitrated form of the resin. The solid precipitate was then filtered off and washed with distilled water and 2 mol L^{-1} NaOH to get the free amino polymer.

The amino polymer was treated with 100 mL of 2 mol L^{-1} HCl for 30 min and washed with distilled water to remove the excess HCl. It was then suspended in 150 mL of ice-cold water and mixed with a diazotizing mixture of 1 mol L^{-1} HCl and 1 mol L^{-1} $NaNO_2$ in aliquots of 1 mL each time with constant stirring until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was then filtered, washed with ice–cold water, treated with Phenanthroline solution (0.03 mol in 500 mL ethanol), and stored for 40 h at 0–3˚C. The resulting resin, which appeared as brown-colored beads, was finally washed and filtered.

2.4. Recommended procedure for preconcentration and determination of metal ions

2.4.1. Batch method

The sample solution (100 mL) containing 0.1 mg of one of the six metal ions was taken in a glass container, after adjusting its pH to the optimum value. The 0.1-g of Phenanthroline resin was added to the bottle and the mixture was and stirred for 40 min. The resin was filtered and sorbed metal ion was desorbed with 4 mol L^{-1} HNO$_3$ (25 mL). The concentration of metal ions was determined in the filtrate by ICP OES.

2.4.2. Batch microwave method

The sample solution (100 mL) containing 0.1 mg of one of the six metal ions was taken in a glass container, after adjusting its pH to the optimum value (Fig. 1). The 0.1-g of Phenanthroline resin was added to the bottle and the mixture was placed in microwave oven for 50 s in 300 watt. The resin was filtered and sorbed metal ion was desorbed with 4 mol L^{-1} HNO$_3$ (25 mL). The concentration of metal ions was determined in the filtrate by ICP OES.

3. Results and discussion

3.1. Characterization studies

The TGA plot of the resin shows two-step mass loss up to 329˚C. The 8.1% mass loss up to 120˚C in the first step is due to sorbed water and suggests that approximately one water molecule per repeat unit of polymer is present. The mass loss in the second step was 66%.

The results of elemental analyses suggest that on average one Phenanthroline molecule is present per four repeat unit of the polymeric support.

IR spectrum of Phenanthroline immobilized Amberlite XAD-4 exhibits three additional bands, 1,286, 1,346 and other at 1,629 cm^{-1} which may be contributed by aromatic (C–N and C=N) and –N=N– group, respectively.

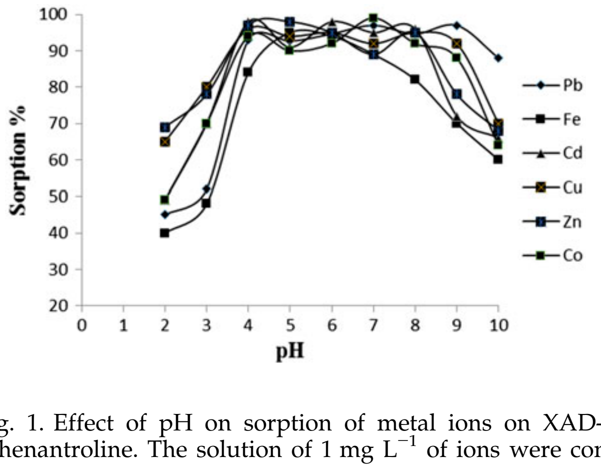

Fig. 1. Effect of pH on sorption of metal ions on XAD-4 -Phenantroline. The solution of 1 mg L^{-1} of ions were contact with 0.1-g of Phenanthroline resin for 40 min.

3.2. Effect of pH on quantitative enrichment

The optimum pH of metal ions uptake was determined using the batch procedure. A suitable aliquot of the metal ion solution (Cd, Pb, Fe, Co, Cu and Zn) was used at varying pHs. The 0.1-g of Phenanthroline resin was added to the bottle and the mixture was stirred for 40 min.

The percentages of sorbed metal were determined in supernatant liquid by ICP OES. The sorption experiments were duplicated for all six metal ions. The optimum pH range is 4–6 for Cd, Cu, Co, Zn, and Fe and for Pb 4–7.0 (Fig. 1). The results by microwave method confirm the obtained results for optimization of pH by simple batch method.

3.3. Kinetics of metal sorption (classic method)

To determine the rate of loading of Cd, Pb, Fe, Co, Cu and Zn on the resin, batch experiments were carried out under the following conditions: 0.5 g resin beads were stirred with 100 mL of feed solution containing 0.1 mg each of Cd, Fe, Co, Zn and 0.2 mg of Pb at room temperature (25˚C). At predetermined intervals, aliquots of 5.0 mL solution were taken out for analysis.

The concentration of metal ions in the supernatant solution was determined and the amount of metal ion loaded on the resin phase was calculated by mass balance (in μg g^{-1} resin). It was observed that an equilibrium time of about 40 min was required for 95–100% sorption.

3.4. Kinetics of metal sorption (microwave method)

To investigate the effect of microwave on loading of Cd, Pb, Fe, Co, Cu and Zn on the resin, batch experiments were carried out under the following conditions: 0.5 g resin beads were mixed with solution containing 0.1 mg each of Cd, Fe, Co, Zn and 0.2 mg each of Pb. Then, the mixture was placed in microwave oven for 10, 20, 40, 70, 90, 120, 150, 180 sec in 300 watt.

Subsequently, the concentration of metal ions in the supernatant solution was determined and the amount of metal ion loaded on the resin phase was calculated by mass balance (in μg g^{-1} resin). It was observed that an equilibrium time decrease significantly as, about 40 s was required for 95–100% sorption in this condition. Higher microwave powers are not suitable because of boiling of the solution. Comparison of sorption time with some of functionalized Amberlite XAD polymers were tabulated in Table 1.

Table 1
Comparison of sorption time

Supporter	Immobilized ligand	Metal	$T_{1/2}$ (min)	Ref.
Amberlite XAD-2	2-Aminothiophenol	Cd, Hg, Ag, Ni, Co, Cu, Zn	40*	[18]
	Aminothiophenol	Cd, Ni, Co, Cu, Zn	30*	[24]
	Thiosalicylic acid	Cd, Co, Cu, Zn	≤2	[25]
		Ni,	13.7	
	Pyrocatechol	Cd(II)*	1.4	[26]
		Co(II)*	4.8	
		Cu(II)*	1.6	
		Fe(III)*	3.3	
		Ni(II)*	2.3	
		Zn(II)*	1.8	
Amberlite XAD-4	**Phenanthroline**	**Cd, Pb, Fe, Co, Cu, and Zn**	**0.67***	**This work**
	2-Hydroxybenzaldehyde Thiosemicarbazone	Cu, Cd	6	[27]
		Pb	8	
	alizarin red-s	Rd(III)	120*	[28]
Amberlite XAD-7	Xylenol Orange	Cd(II)	5.3	[29]
		Co(II)	2.9	
		Cu(II)	3.2	
		Fe(III)	3.3	
		Ni(II)	2.5	
		Zn(II)	2.6	
Amberlite XAD-16	2-hydroxy-3-methoxybenzaldehyde	Zn(II)	9.0	[30]
		Cu(II)	5.0	
		Ni(II)	7.2	
		Cd(II)	13.7	
		Pb(II)	12.2	

*Full Loading time.

3.5. Total sorption capacity

The sorption capacity of the resin was determined by the batch process, by equilibrating 1.0 g of the resin sample with 100 mL of 50 μg L^{-1} metal ion solution (Cd, Pb, Fe, Co, Cu and Zn) for 24 h at their selected pH at 30˚C. The sorption capacity of the resin for each metal ion was calculated from the difference between the metal ion concentrations before and after desorption. The values are 167.2, 231.7, 274.6, 305.2, 349.1 and 288.4 μmol g^{-1} for Cd, Pb, Fe, Co, Cu and Zn, respectively.

3.6. Effect of temperature

The temperature is an effective factor in the context of sorption on solid adsorbent and has two major effects on the sorption process. Increasing the temperature causes to change the equilibrium constant and sorption capacity of the adsorbent for a particular solute. In addition, changing temperature will increase the rate of diffusion of the solute molecules, or ions, across the external boundary layer and in the internal pores of the adsorbent particles, owing to decrease in the viscosity of the solution and, also, increase in the solute mobility in the solution.

In the present study, the effect of temperature on the sorption was studied in the range of 288–328 K under the selected agitation time (1 h), the volume of solutions (100 mL) and 0.50 g of Phenanthroline resin. The sorption capacity of Phenanthroline resin was increased with increasing the temperature. The increase in the sorption capacity may be due to an increased equilibrium constant for sorption at higher temperature. In addition, the increase in the sorption capacity, qe, with the increase in the temperature, indicates that sorption is endothermic nature.

3.7. Selection of eluent

The effect of different eluents (HCl, HNO_3, H_2SO_4 and EDTA) on desorption of these heavy metals were investigated with 10–25 mL of different eluents with several concentrations. The obtained results show that 2 mol L^{-1} HNO_3 is suitable for desorption of these metals, Thus desorption of heavy metals took place with 25 mL of 2 mol L^{-1} HNO_3 solution.

3.8. Effect of matrix ions on preconcentration

The effect of NaCl, KBr, KI, $NaNO_3$, Na_3PO_4, Na_2SO_4, humic acid, sodium citrate and cations such as Ca and Mg on the sorption of these six metal ions was studied. The results show in Table 2 that the tolerance limits of the investigated electrolytes or cations are very high. The reported tolerance limit is defined as the ion concentration causing a relative error < ± 5%.

3.9. Limit of detection

The detection limit, defined as by IUPAC [34] were found to be 1.4, 4.1, 2.4, 3.9, 3.1, 3.9 μg L^{-1} for Cd, Pb, Fe, Co, Cu and Zn, respectively. The relative standard deviation of the replicated (preconcentration procedure) was <7%.

3.10. Application

3.10.1. Determination of metal ions in potato

The preconcentration procedures were applied for determination of Co (II), Pb(II), Fe(III), Cd (II), Cu (II), and Zn (II) in potatoes.

Potato was purchased from local markets in Damghan city, Iran during 2014. The 1 g sample of potatoes of 0.5 mm grain size, dried previously to the constant air dry mass was mineralized by adding 10 mL of HNO_3 and H_2O_2 (t~190°C) in a mineralizer. Then, the obtained solution was diluted to a volume of about 50 mL. Table 3 shows the results of determination of heavy metals in a sample of potatoes after preconcentration on functionalized XAD resin.

Table 2
Tolerance limits of electrolytes (n = 3)

	Electrolytes or metal ions (mol L^{-1})								
Metal ions	NaCl	KBr	KI	$NaNO_3$	Na_3PO_4	Na_2SO_4	Sodium citrate	Ca	Mg
Cd	0.04	0.01	0.05	0.3	0.2	0.2	0.005	0.02	0.02
Pb	0.05	0.05	0.005	0.2	0.1	0.1	0.005	0.02	0.02
Fe	0.1	0.05	0.05	0.3	0.2	0.2	0.001	0.04	0.04
Co	0.05	0.05	0.05	0.3	0.2	0.2	0.001	0.04	0.04
Cu	0.1	0.05	0.005	0.3	0.2	0.2	0.001	0.04	0.04
Zn	0.05	0.05	0.05	0.3	0.2	0.2	0.001	0.02	0.02

Table 3
Metal contents (mg kg^{-1} wet wt.) in potato sample

Ion	Added (mg kg^{-1})	Mean[a] ± SE (mg kg^{-1})	Recovery %
Cd	0	0.39 ± 0.06	–
	5	5.14 ± 1.12	95.36
	10	9.33 ± 1.48	89.79
Pb	0	2.04 ± 0.17	–
	5	6.69 ± 0.67	94.6
	10	11.45 ± 1.15	95.09
Fe	0	87.21 ± 1.03	–
	5	88.22 ± 2.42	95.67
	10	91.34 ± 1.60	93.96
Co	0	0.44 ± 0.11	–
	5	5. 07 ± 0.37	93.19
	10	9.47 ± 1.32	90.7
Cu	0	0.5 ± 0.09	–
	5	5.02 ± 1.24	91.27
	10	9.29 ± 1.98	88.47
Zn	0	4.6 ± 0.12	–
	5	8.91 ± 1.34	92.81
	10	13.16 ± 2.25	90.13

[a] The results are reported as the average value from five sample measurements.

3.10.2. Determination of metal ions in wastewater

Samples were collected from the final effluents of the wastewater treatment plant of Ravand factory (Mashhad, Iran). The Ravand factory produces sodium hydroxide by an electrochemical method. The wastewater samples were acidified by HNO$_3$, filtered through 0.45-mm Millipore membrane filters, and mix with resin as mentioned in Section 2.4.2.

Along with wastewater sample, the samples were spiked with two amounts of stock solutions of Cd, Pb, Fe, Co, Cu and Zn to examine the reliability of the method. The results and the standard deviations are shown in Table 4.

3.10.3. Determination of lead in lipstick

Lipstick was purchased in retail store. It was imported from China. A weighed sample of 0.2 g lipstick was placed into a Teflon vessel and reacted with 8 mL concentrated nitric acid, left at room temperature for 4 h then placed in the oven overnight at 85˚C. After digestion, the sample was allowed to cool to room temperature. Furthermore, after adding 5 mL of 30% hydrogen peroxide, the sample solutions were heated at 85˚C for another hour. The clear supernatant was transferred to a polypropylene tube and it was diluted to 50 mL, with deionized water. Then lead content was separate and preconcentrate with microwave extraction by Phenanthroline resin. Finally, concentration of lead was determined by ICP OES. Lead content was expressed as part per million wet weight (mg kg^{-1} wet wt.)The validity of the proposed method was confirmed by comparing the results obtained from the sample analysis with those obtained by GFAAS method, without out preconcentration step. (Table 5) Each analysis replicates three times.

Table 4
Determination of metal ions in wastewater

Ion	Added (mg L^{-1})	Mean[a] ± SE (mg L^{-1}) ±	Recovery %
Cd	0	2.21 ± 0.67	–
	5	6.74 ± 0.63	93.9
	10	10.64 ± 1.24	87.14
Pb	0	1.18 ± 0.65	–
	5	5.86 ± 0.87	94.82
	10	9.78 ± 1.45	87.47
Fe	0	39.49± 1.90	–
	5	43.13 ± 1.23	96.94
	10	48.09 ± 1.56	97.17
Co	0	0.23 ± 0.19	–
	5	4. 61 ± 0.95	88.14
	10	9.47 ± 1.12	92.57
Cu	0	8.09 ± 1.09	–
	5	12.13 ± 1.35	92.66
	10	17.07 ± 1.97	94.36
Zn	0	78.14 ± 1.65	–
	5	78.98 ± 1.23	94.99
	10	85.98 ± 1.14	97.54

[a] The results are reported as the average value from five sample measurements.

Table 5
Lead contents (mg L^{-1} wet wt.) in various lipstick samples

Brand	Color	Lead content (mg kg^{-1}) Proposed method*	Lead content (mg kg^{-1}) GFAAS*
1	Shimmering pink	1.2 ± 0.6	1.2 ± 0.4
2	Orange	17.2 ± 0.9	18.1 ± 0.5
3	Brown	9.5 ± 1.8	8.6 ± 1.1

*Each analysis replicates three times.

4. Conclusion

A chelating resin was prepared by coupling of Phenanthroline to Amberlite XAD-4 in order to separate and preconcentrate of Cd, Pb, Fe, Co, Cu and Zn.

In this work for the first time, effect of microwave power at atmospheric pressure on extraction of these heavy metals was investigated. The extraction time for this method is significantly less than conventional approaches (simple solid phase extraction) and extraction efficiency improve significantly.

The modified procedure has some benefits such as very faster rate of equilibrium, higher sorption rate. The obtained results show that the modified procedure has good potential for rapid trace enrichment of these heavy metals.

Acknowledgments

We are grateful to the Pars material research and testing (PMRT) for valuable technical assistance.

References

[1] R. Sturgeon, S. Berman, J. Desaulniers, A. Mykytiuk, J. McLaren, D. Russell, Comparison of methods for the determination of trace elements in seawater, Anal. Chem. 52 (1980) 1585–1588.

[2] P.L. Malvankar, V.M. Shinde, Ion-pair extraction and determination of copper (II) and zinc (II) in environmental and pharmaceutical samples, Analyst 116 (1991) 1081–1084.

[3] R. Shukla, G. Rao, Solvent extraction of metals with potassium-dihydro-bispyrazolyl-borate, Talanta 57 (2002) 633–639.

[4] R.E. Santelli, M. Gallego, M. Valcarcel, Atomic absorption determination of copper in silicate rocks by continuous precipitation preconcentration, Anal. Chem. 61 (1989) 1427–1430.

[5] S. Kagaya, Y. Araki, K. Hasegawa, Flame atomic absorption spectrometric determination of lead in waste water and effluent after preconcentration using a rapid coprecipitation technique with gallium phosphate, Fresenius' J. Anal. Chem. 366 (2000) 842–845.

[6] E.A. Boyle, J.M. Edmond, Determination of copper, nickel, and cadmium in sea water by APDC chelate coprecipitation and flameless atomic absorption spectrometry, Anal. Chim. Acta 91 (1977) 189–197.

[7] Z. Fang, M. Sperling, B. Welz, Flame atomic absorption spectrometric determination of lead in biological samples using a flow injection system with on-line preconcentration by coprecipitation without filtration, J. Anal. At. Spectrom. 6 (1991) 301–306.

[8] H. Hashemi-Moghaddam, A selective flotation-spectrophotometric method for the determination of nickel using dimethylglyoxime, J. Braz. Chem. Soc. 22 (2011) 1056–1060.

[9] M.S. Hosseini, H. Hashemi-Moghaddam, Sensitized extraction spectrophotometric determination of Hg (II) with dithizone after its flotation as ion-associate using iodide and ferroin, Talanta 67 (2005) 555–559.

[10] M.S. Hosseini, H. Hashemi-Moghaddam, Flotation-Spectrophotometric Determination of Ag (I) at the 10Γ7 mol LΓ1 level using iodide and ferroin as an ion-associate, Bull. Korean Chem. Soc. 26 (2005) 1529.

[11] T. Kiriyama, R. Kuroda, Anion-exchange enrichment and spectrophotometric determination of traces of gallium in natural waters, Fresenius' Zeitschrift für analytische Chemie 332 (1988) 338–340.

[12] J. Kubová, V. Nevoral, V. Streško, Determination of rare earth elements in mineral waters by inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 9 (1994) 241–243.

[13] H. Hashemi-Moghaddam, H.A. Panahi, M.N. Nezhati, Synthesis and application of new resin functionalized by brilliant green for spectrophotometric determination of mercury in environmental samples, Anal. Lett. 42 (2009) 1911–1922.

[14] A. Duran, M. Tuzen, M. Soylak, Preconcentration of some trace elements via using multiwalled carbon nanotubes as solid phase extraction adsorbent, J. Hazard. Mater. 169 (2009) 466–471.

[15] M. Tuzen, K.O. Saygi, C. Usta, M. Soylak, *Pseudomonas aeruginosa* immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions, Bioresour. Technol. 99 (2008) 1563–1570.

[16] M. Tuzen, K.O. Saygi, M. Soylak, Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes, J. Hazard. Mater. 152 (2008) 632–639.

[17] M. Tuzen, M. Soylak, Multiwalled carbon nanotubes for speciation of chromium in environmental samples, J. Hazard. Mater. 147 (2007) 219–225.

[18] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma–atomic emission spectrometry, Talanta 62 (2004) 207–213.

[19] M. Soylak, M. Dogan, Separation and enrichment of zinc, copper, iron, cadmium, cobalt, and nickel from urine with Amberlite XAD-16 resin, Trace Elem. Electrolytes 13 (1996) 130–132.

[20] M. Soylak, U. Şahin, L. Elçi, Spectrophotometric determination of molybdenum in steel samples utilizing selective sorbent extraction on Amberlite XAD-8 resin, Anal. Chim. Acta 322 (1996) 111–115.

[21] M. Soylak, L. Elçi, M. Doğan, Spectrophotometric determination of trace amounts of tungsten in geological samples after preconcentration on Amberlite XAD-1180, Talanta 42 (1995) 1513–1517.

[22] A. Bencini, V. Lippolis, 1, 10-Phenanthroline: A versatile building block for the construction of ligands for various purposes, Coord. Chem. Rev. 254 (2010) 2096–2180.

[23] J.A. McCleverty, T.J. Meyer, Comprehensive Coordination Chemistry II: From Biology to Nanotechnology, Elsevier, Pergamon, 2004.

[24] M. Kumar, D. Rathore, A.K. Singh, Amberlite XAD-2 functionalized with *o*-aminophenol: Synthesis and applications as extractant for copper (II), cobalt (II), cadmium (II), nickel (II), zinc (II) and lead (II), Talanta 51 (2000) 1187–1196.

[25] P.K. Tewari, A.K. Singh, Thiosalicylic acid-immobilized Amberlite XAD-2: Metal sorption behaviour and applications in estimation of metal ions by flame atomic absorption spectrometry, Analyst 125 (2000) 2350–2355.

[26] P.K. Tewari, A.K. Singh, Synthesis, characterization and applications of pyrocatechol modified amberlite XAD-2 resin for preconcentration and determination of metal ions in water samples by flame atomic absorption spectrometry (FAAS), Talanta 53 (2001) 823–833.

[27] D.A. Chowdhury, M.I. ul Hoque, Z. Fardous, Solid phase extraction of copper, cadmium and lead using Amberlite XAD-4 resin functionalized with 2-hydroxybenzaldehyde thiosemicarbazone and its application on green tea leaves, Jordan J. Chem. 8(2) (2013) 90–102.

[28] H.S. Kalal, H.A. Panahi, H. Hoveidi, M. Taghiof, M.T. Menderjani, Synthesis and application of Amberlite xad-4 functionalized with alizarin red-s for preconcentration and adsorption of rhodium (III), Adsorption 9 (2012) 13.

[29] P.K. Tewari, A.K. Singh, Amberlite XAD-7 impregnated with Xylenol Orange: A chelating collector for preconcentration of Cd (II), Co (II), Cu (II), Ni (II), Zn (II) and Fe (III) ions prior to their determination by flame AAS, Fresenius' J. Anal. Chem. 367 (2000) 562–567.

[30] A. Ahmad, A. Khatoon, M. Laskar, A. Islam, A. Mohammad, N. Yong, Use of 2-hydroxy-3-methoxybenzaldehyde functionalized amberlite xad-16 for preconcentration and determination of trace metal ions by flame atomic absorption spectrometry, Der Pharma Chemica 5(1) (2013) 12–23.

[31] D.P. Laxen, R.M. Harrison, Cleaning methods for polythene containers prior to the determination of trace metals in fresh water samples, Anal. Chem. 53 (1981) 345–350.

[32] H. Hashemi-Moghaddam, Z. Noshiri, Removal of cyanide and zinc–cyanide complex with malachite green functionalized amberlite XAD-4 resin from electroplating wastewater, Desalin. Water Treat. (2013) 1–8.

[33] H.A. Panahi, A.R. Feizbakhsh, Z. Tafazoli, E. Moniri, M.N. Nezhati, H. Hashemi-Moghaddam, S.R. Kelahrodi, New anion-exchange solid-phase extraction support used for preconcentration and determination of lead in water samples by flame atomic absorption spectrometry, J. AOAC Int. 93 (2010) 1616–1624.

[34] G.L. Long, J.D. Winefordner, Limit of detection. A closer look at the IUPAC definition, Anal. Chem. 55 (1983) 712A–724A.