

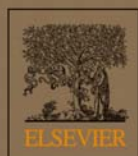


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New generation Amberlite XAD resin for the removal of metal ions: A review

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ABSTRACT

The direct determination of toxic metal ions, in environmental samples, is difficult because of the latter's presence in trace concentration in association with complex matrices, thereby leading to insufficient sensitivity and selectivity of the methods used. The simultaneous removal of the matrix and preconcentration of the metal ions, through solid phase extraction, serves as the promising solution. The mechanism involved in solid phase extraction (SPE) depends on the nature of the sorbent and analyte. Thus, SPE is carried out by means of adsorption, ion exchange, chelation, ion pair formation, and so forth. As polymeric supports, the commercially available Amberlite resins have been found very promising for designing chelating matrices due to its good physical and chemical properties such as porosity, high surface area, durability and purity. This review presents an overview of the various works done on the modification of Amberlite XAD resins with the objective of making it an efficient sorbent. The methods of modifications which are generally based on simple impregnation, sorption as chelates and chemical bonding have been discussed. The reported results, including the preconcentration limit, the detection limit, sorption capacity, preconcentration factors etc., have been reproduced.

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Introduction

Heavy metals are included within the category of environmental toxins: "Materials which can harm the natural environment even at low concentration, through their inherent toxicity and their tendency to accumulate in the food chain and/or have particularly low decomposition rates". Heavy metals are

cumulative poison and are toxic even at low dose (Hu, 2000; Chowdhury and Chandra, 1987). The indication of their importance relative to other potential hazards is their ranking by the U.S. Agency for Toxic Substances and Disease Registry, which lists all hazards present in the toxic waste sites according to their prevalence and severity of their toxicity (Hu, 2005). The first, second, third and sixth hazards on the list are heavy metals:

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lead, mercury, arsenic and cadmium, respectively (Hu, 2005). The other metal ions that pose potential dangers to human lives include chromium, copper, zinc, nickel, cobalt, iron and manganese (Friberg et al., 1986; Martin, 2006; Nelson and Cox, 2000; Stoeppler, 1980).

It is obvious that one of the potential solutions to the serious ecological problems, posed by contamination of environmental samples by heavy metals, is the latter's careful monitoring and determination. However, the presence of these metal ions in very low concentration necessitates their prior preconcentration to an appropriate level that exceeds the detection limit of the analyzing instruments. The most recent trend in preconcentration methods has been the use of solid adsorbents, which facilitates rapid elimination of the interfering elements from the matrix of the samples (Xu et al., 2013; Wang et al., 2012; Zhu et al., 2011; Hajiaghababaei et al., 2012). There has been enormous development in separation techniques since it was first introduced in 1941, by Martin and Synge, as a method of chromatography, where one of the two immiscible liquids was supported on a solid phase. The problem of bleeding of the liquid phase from the solid support leads to the introduction of covalently bonded phases, where the liquid phase was anchored to the solid support (Martin and Synge, 1941). Sorption tendency is dependent on the characteristics of the sorbent, the liquid sample (i.e., solvent) matrix, and the analyte. Higher breakthrough volumes (Ezoddin et al., 2010; Huang et al., 2008; Li et al., 2009), for selected polar analytes, have been observed when the hydrophilic functionalized polymeric resins are used as compared to the classical hydrophobic bonded silicas or nonfunctionalized, apolar polymeric resins. In addition to having a greater capacity for polar compounds, functionalized polymeric resins provide better surface contact with aqueous samples. Using covalent bonding to incorporate hydrophilic character permanently in the sorbent ensures that it would not be leached from the sorbent unlike the common hydrophilic solvents (e.g., methanol, acetonitrile, or acetone) which were used to condition bonded silica sorbents or polymeric resins (Pereira et al., 2010; López-García et al., 2009; Gao et al., 2009). Porous sorbents are designed so as to allow accessibility to selected molecules of certain size into the internal pore structure of the sorbent such that they would be retained. Small molecules are retained by sorption processes in the pores of the sorbent while the large molecules are excluded and eluted at the interstitial volume of the sorbent. This separation leads to size-selective disposal of interfering macromolecular matrix constituents. Porous sorbents vary in pore size, shape, and tortuosity (Henry, 2000) and are characterized by properties such as particle diameter, pore diameter, pore volume, surface areas, and particle-size distribution. In this review, an overview of the recent development made in the modification of solid adsorbent Amberlite XAD resin in context to preconcentration of toxic heavy metals has been discussed.

1. Amberlite XAD-resin

Amberlite XAD adsorbents are very porous spherical polymers based on highly crosslinked, macroreticular polystyrene, aliphatic, or phenol-formaldehyde condensate polymers. On the basis of polymeric matrix, it may be divided into two main groups: i) polystyrene-divinyl benzene based resins including

XAD-1, XAD-2, XAD-4, XAD-16, XAD-1180, XAD-2000 and XAD-2010 and ii) polyacrylic acid ester based resins including XAD-7, XAD-8 and XAD-11. Some characteristic physical properties of these resins have been mentioned in Table 1.

1.1. Nascent polymeric resins as sorbent

Nascent styrene-DVB resins such as Amberlite XAD-1180 (Tokahoglu et al., 1997), XAD-4 (Islam et al., 2010a), and XAD-16 (Elçi et al., 2000; Soylak and Elçi, 2000; Tunçeli and Türker, 2000a, 2000b; Abdullah et al., 2009) have been used directly (without any modification) for the enrichment of inorganic species in the form of their halide or thiocyanate complex. The results reflect that prominent factors, namely the type and quantity of sorbent, hydrophobicity, ionizability of the analytes, sample volume and pH play an interactive role in determining the breakthrough volume. Therefore, it may be inferred that the more hydrophobic the compound is, the larger would be its breakthrough volume and also the larger would be the sample size from which quantitative recovery could be expected (Sabarudin et al., 2007; Çekiç et al., 2004; Sharma and Pant, 2009; Venkatesh and Singh, 2007; Venkatesh and Singh, 2005). The fact that stronger interaction would lead to larger breakthrough volume may hold good for other sorbents as well. Hence, with the objective of acquiring stronger interaction, between analyte and the adsorbent, further modification of these nascent resins has been carried out. Some of these research works, pertaining to the modifications, shall be discussed in the following section.

1.2. Modification of nascent polymeric resins

In addition to the hydrophobic interaction that also occurs with C18-silica, Amberlite XAD series (macroporous hydrophobic resins) allow π - π interactions. The use of surface-modified PS-DVB copolymers with different polar substituent overcomes the following disadvantages suffered by standard silica-based material used for SPE: lack of pH stability under acidic or basic conditions, low breakthrough for polar analytes and they are not wettable by water alone and always need a conditioning step with a wetting solvent, such as methanol (Kantipuly et al., 1990; Camel, 2003; Ferreira et al., 2000a, 2000b). However, in practice, the resins prepared by impregnation of the ligand are difficult to reuse, due to partial leaching of the ligand (thus resulting in poor repeatability). To overcome this problem, the resin may be chemically functionalized. Chemical modification of PS-DVB copolymers has been carried out by immobilizing varying substituents through different bridging groups.

2. Amberlite XAD-2

Amberlite XAD 2, with a high surface area and a large pore size, has been extensively used either as a sorbent or as a solid support in preconcentration. Large surface area of Amberlite XAD-2 is appreciably feasible for quantitative sorption of pollutants. Its chemical stability and low sorption encouraged its further modification with an objective of making it more selective for the target analyte. The various chelating agents which have been used so far for the chemical modification of the resin are summarized in Table 2.

Table 1 – Properties of some Amberlite XAD resins.

Amberlite	Matrix	Surface area (m ² /g)	Particle size (mesh)	Pore size (Å)
XAD-2	Styrene–divinylbenzene	300	20–60	90
XAD-4	Styrene–divinylbenzene	750	20–60	100
XAD-7	Aliphatic ester	500	20–60	450
XAD-8	Acrylic ester	140	40–60	250
XAD-16	Styrene–divinylbenzene	800	20–60	200
XAD-1180	Styrene–divinylbenzene	500	20–60	400
XAD-2000	Styrene–divinylbenzene	600	20–60	45
XAD-2010	Styrene–divinylbenzene	660	20–60	280

2.1. Surface modification of Amberlite XAD-2

One of the most common, easy, simple and even accessible routes for modification of Amberlite XAD-2 sorbents is their surface impregnation by various chelating agents through physical pathway. Chelating resins, namely Amberlite XAD-2 loaded with calmagite reagent (Ferreira et al., 2000a, 2000b) and 2-(2-benzothiazolylazo)-2-*p*-cresol (Ferreira et al., 2001), have been developed in order to determine trace amounts of Cu(II) and Ni(II), respectively. A detection limit (3σ) of 0.15 mg/L and 1.1 µg/L was achieved, respectively. Amberlite XAD-2 resin impregnated with Cyanex272 {bis (2,4,4-trimethylpentyl) phosphinic acid} and Cyanex302 {bis (2,4,4-trimethylpentyl) monothiophosphinic acid}, prepared by Karve and Rajgor (2008), demonstrated poor distribution coefficients for La(III) and Nd(III) but, however, -U(VI) was quantitatively sorbed from 1×10^{-3} mol/L HNO₃ followed by its recovery with 1 mol/L HCl from the solid phase. The proposed method was simple, selective and reproducible for U(VI) determination with a relative standard deviation (RSD) of 0.4%. Later, Karve and Pandey (2012) prepared a chelating resin, Amberlite XAD-2 resin impregnated with Cyanex272, and determined U(VI) in aqueous sample using batch method. The maximum sorption capacity of U(VI) was found to be 0.168 mmol/g. Sorption equilibrium data for U(VI) removal was well fitted with Langmuir and Freundlich isotherm models.

2.2. Chemical modification of Amberlite XAD-2

The commercial availability and high regeneration capacity of Amberlite XAD-2 have resulted in its extensive application for the determination of metal ions in environmental and biological samples. Hence, wide-ranging developments have been carried out in the chemical modification of the resin. Guo et al. (2004a, 2004b) synthesized a resin by covalently bonding Amberlite XAD-2 with 2-(methylthio)aniline and 2-aminoacetylthiophenol through a -N=N-NH- group and applied it for the preconcentration of Cd, Hg, Ag, Ni, Co, Cu and Zn ions. Various experimental parameters, such as the distribution coefficient and sorption capacity of the chelating resin, pH and flow rates of uptake and stripping, and volume of sample and eluent, were evaluated. Applicability of the developed method was tested on tap water and river water samples. The detection limit and limit of quantification (3σ and 10σ) of the chelating resin (Amberlite XAD-2-2-(methylthio)aniline) for Cd, Hg, Ni, Co, Cu and Zn were found to be 0.022, 0.028, 0.033, 0.045, 0.041, 0.064 µg/L and 0.041, 0.043, 0.052, 0.064, 0.058, 0.083 µg/L, respectively, when FAAS

was used for the determination, while detection limits (3σ) of chelating resin (Amberlite XAD-2-2-aminoacetylthiophenol) for Cd, Hg, Ag, Ni, Co, Cu and Zn were found to be 0.10, 0.23, 0.41, 0.13, 0.25, 0.39 and 0.58 µg/L, respectively when determination was done by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Lemos and Baliza synthesized a new sorbent (Amberlite XAD-2-2-aminothiophenol) via azo coupling (-N=N-) (Lemos and Baliza, 2005). The enrichment factors were found to be 28 and 14 for Cd(II) and Cu(II), respectively when preconcentration time was 60 sec, while 74 and 35 for Cd(II) and Cu(II), respectively for preconcentration time of 180 sec. The detection limits, corresponding to the preconcentration time of 180 sec, for Cd(II) and Cu(II), were found to be 0.14 and 0.54 µg/L, respectively. The method was applied for the determination of Cd(II) and Cu(II), in natural, drinking and tap water samples. Functionalized resins, such as Amberlite XAD-2-Nitroso-R salt (Lemos et al., 2003a), Amberlite XAD-2-3,4-dihydroxybenzoic acid (Lemos et al., 2003b) and Amberlite XAD-2-4,5-dihydroxy-1,3-benzenedisulfonic acid (Lemos et al., 2005) have been synthesized. The detection limits were found to be 0.39, 0.27 and 2 µg/L for Co(II), Cu(II) and Ni(II), respectively. The accuracy of the methods was evaluated by analyzing the certified reference material, and their applications were demonstrated with food samples and natural water samples. Later, Lemos et al. (2006) developed a new chelating sorbent using Amberlite XAD-2 resin anchored with pyrocatechol through -N=C- spacer. The enrichment factors for 60 sec preconcentration time were found to be 16, 24, 15 and 19 for Cd(II), Co(II), Cu(II) and Ni(II), respectively, while 39, 69, 36 and 41 were found for Cd(II), Co(II), Cu(II) and Ni(II) at 180 s preconcentration time. Under experimental conditions, the detection limits were reported to be 0.31, 0.32, 0.39 and 1.64 µg/L for Cd(II), Co(II), Cu(II) and Ni(II) respectively. The accuracy of the developed procedure was confirmed by using certified reference materials, namely NIST 1515 apple leaves and NIST 1570a spinach leaves. The method was successfully applied to the analysis of food samples, such as spinach, black tea and rice flour. A new chelating resin was developed by coupling Amberlite XAD-2 with pyrocatechol through an azo spacer by Tewari and Singh (2001) for the monitoring of Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II) by using FAAS. The preconcentration limit for metal ions, with quantitative recovery, was 5, 10, 20, 25, 10 and 10 mg/L for Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II), respectively. The proposed method was applied for the determination of all six metal ions in tap and river water samples (RSD 53.9% and 7.3%, respectively). FAAS determination of Pb(II) onto Amberlite XAD-2 with chromotropic acid (AXAD-2-CA or 1), pyrocatechol (AXAD-2-PC

Table 2 – Chelating agents used for modification of Amberlite XAD-2 resin.

Reagent	Techniques coupled	Metals	Sorption capacity (mg/g)	Reference
Tiron	FAAS	Cu ²⁺ , Cd ²⁺ , Co ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺ , Mn ²⁺ , Fe ³⁺ , UO ₂ ²⁺	14.0, 9.5, 6.5, 12.6, 12.6, 11.1, 10.0, 5.6, 7.7	Kumar et al. (2000a, 2000b)
Thiosalicylic acid	FAAS	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Fe ³⁺ , Ni ²⁺ , Zn ²⁺	22.2, 6.3, 13.9, 3.7, 18.2, 3.1	Tewari and Singh (2000a, 2000b)
Pyrogallol	FAAS	Cu ²⁺ , Cd ²⁺ , Co ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺ , Mn ²⁺ , Fe ³⁺ , U ⁴⁺	4.53, 5.22, 4.10, 4.09, 6.71, 4.54, 4.51, 4.62, 4.49	Kumar et al. (2001)
Calmagite	FAAS	Cu ²⁺	0.1009	Ferreira et al. (2000a, 2000b)
o-Aminophenol	FAAS	Cu ²⁺ , Cd ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Pb ²⁺	3.37, 3.42, 3.29, 3.24, 2.94, 3.32	Kumar et al. (2000a, 2000b)
2-(Methylthio)aniline	FAAS	Cd ²⁺ , Hg ²⁺ , Ni ²⁺ , Co ²⁺ , Cu ²⁺ , Zn ²⁺	23.67, 37.87, 14.07, 10.35, 8.83, 8.46	Guo et al. (2004a)
2-Aminoacetylthiophenol	ICP-AES	Cd ²⁺ , Hg ²⁺ , Ag ²⁺ , Ni ²⁺ , Co ²⁺ , Cu ²⁺ , Zn ²⁺	21.40, 48.70, 37.29, 17.60, 19.19, 24.07, 19.59	Guo et al. (2004b)
2-Aminothiophenol	FAAS	Cd ²⁺ , Cu ²⁺	382.16, 292.10	Lemos and Baliza (2005)
Nitroso R salt	FAAS	Co ²⁺		Lemos et al. (2003a, 2003b)
Azocalix[4]pyrrole A	FAAS	Cu ²⁺ , Zn ²⁺ , Cd ²⁺	20.20, 11.42, 18.86,	Jain et al. (2009)
Azocalix[4]pyrrole B	FAAS	Cu ²⁺ , Zn ²⁺ , Cd ²⁺	27.25, 14.40, 19.63	Jain et al. (2009)
Pyrocatechol	FAAS	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Fe ³⁺ , Ni ²⁺ , Zn ²⁺	4.59, 1.35, 5.87, 4.10, 3.11, 1.85	Tewari and Singh (2001)
Chromotropic acid	FAAS	Pb ²⁺	38.60	Tewari and Singh (2002)
Pyrocatechol	FAAS	Pb ²⁺	21.69	Tewari and Singh (2001)
Thiosalicylic acid	FAAS	Pb ²⁺	18.50	Tewari and Singh (2001)
Xylenol orange	FAAS	Pb ²⁺	3.50	Tewari and Singh (2001)
Palmitoyl quinolin-8-ol	Spectrophotometric	Mn(II)	1.64	Doğutan et al. (2003)
Cyanex272	Spectrophotometric	U ⁶⁺	39.98	Karve and Pandey (2012)
Purpurin	FAAS	Cd ²⁺ , Cr ³⁺ , Pb ²⁺	8.43, 3.54, 17.13	Wongkaew et al. (2008)
Calcein blue	AAS	Cu ²⁺	27.0	Moniri et al. (2011)
Pyrocatechol	FAAS	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Ni ²⁺	4.01, 1.65, 1.99, 1.43	Lemos et al. (2006)

or 2) and thiosalicylic acid (AXAD-2-TSA or 3) through azo spacer was done by Tewari and Singh (2002). The limit of detection and limit of quantification were found to be in the ranges 2.44–7.87 and 2.76–8.64 ng mL⁻¹, respectively. Pb(II) has been determined in river (with RSD of 2.6%–12.8%) and tap (with RSD of 1.8%–7.2%) water samples. Later, Jain et al. (2009) developed a novel azocalix [4] pyrrole Amberlite XAD-2 polymeric chelating resin for extraction, preconcentration and sequential separation of metal ions such as Cu(II), Zn(II) and Cd(II) by column chromatography prior to their determination by UV/Vis spectrophotometry or FAAS or ICPAES. The proposed method was successfully applied for the determination of Cu(II), Zn(II) and Cd(II) in natural and ground water samples. Doğutan et al. (2003) synthesized palmitoyl-8-hydroxyquinoline functionalized Amberlite XAD-2 by a modified procedure through chloromethylation. Column method was used for the preconcentration of trace Mn(II) from artificial and real seawater. The preconcentration factor was found to be 60 with the resin column and detection limits (LOD) of spectrophotometry and FAAS for Mn (i.e., 17 and 12 µg/L, respectively) were significantly reduced. The proposed method was not adversely affected from high ionic strength media for preconcentration of Mn(II) and method is suitable for Mn

determination in seawater. Later, Filik et al. (2004) synthesized Amberlite XAD-2 copolymer resin with palmitoyl quinolin-8-ol for preconcentration and separation of trace amounts of vanadium species in synthetic solutions and seawater. Both V(IV) and V(V) species were sorbed and preconcentrated onto modified resin and quantitatively eluted from column using HCl as stripping agent and analyzed by both spectrophotometrically and FAAS for speciation studies. The detection limits of V(V) were found to be 1.6 and 0.9 µg/L, with spectrophotometry and FAAS. The proposed method showed good agreement with the certified value of certified reference material (IAEA-405). Badrinezhad et al. (2012) has synthesized a chelating resin Amberlite XAD-2 resin with iminodi acetic acid and applied for Cd(II) determination by FAAS after preconcentration in natural water samples. High recovery was achieved up to 90% at pH 7.5 and proposed method gives good accuracy, enrichment factor, preconcentration factor and simplicity. A new polymer support, Amberlite XAD-2 with purpurin through an azo linkage (N=N) was synthesized by Wongkaew et al. (2008) and applied for the extraction of Cd(II), Cr(III) and Pb(II) by batch and column methods in both matrices, leachate from cement-based material and de-ionized water. The proposed method gave a good accuracy in batch system with the

recovery of 86.5% and 89.9% for Cd(II) and Pb(II) and R.S.D. less than 2.3% ($n = 14$). Moniri et al. (2011) synthesized a chelating resin Amberlite XAD-2 coupling with a dye calcein blue through an azo spacer. Sorption capacity of modified resin was 27 mg/g with 10 regeneration cycles without any significant lose in capacity. The method was applied for Cu(II) assay in environmental samples. Table 2 shows some of the sorption capacities reported in the literature.

3. Amberlite XAD-4

Amberlite XAD 4 has a surface area of 750 m²/g and a pore size of 100 Å, thereby making it a promising solid phase extractant. The feasibility that it offers for chemical as well as surface modification has led to its wide ranging development as a selective sorbent. Chelating agents which have been used so far in the modification of Amberlite XAD 4 have been reproduced briefly in Table 3.

3.1. Surface modification of Amberlite XAD-4

Surface modification of Amberlite XAD resin is an easy and economical choice for the separation and preconcentration of heavy metal ions from aqueous samples. Liu et al. developed methods, based on determination by FAAS, by immobilizing complexing ligands, namely acetylmercaptophenyldiazoaminoazobenzene (Liu et al., 2005) and DHDAA (Liu et al., 2007), onto Amberlite XAD-4. The former resin exhibited a detection limit of 0.028, 0.064, 0.042, 0.023 and 0.16 mg/L and the quantification limit of 0.043, 0.11, 0.099, 0.044 and 0.29 mg/L for Cd(II), Co(II), Cu(II), Ni(II) and Zn(II), respectively, while the latter resin offered detection limits of 0.1, 0.5, 0.3, and 0.2 mg/L, respectively for Cd(II), Co(II), Cu(II), and Zn(II). A standard reference material (GBW 08301) was analyzed as a part of validation in both the methods. A surface modified Amberlite XAD-4 resin was introduced by Ramesh et al. (2002) wherein, ammonium pyrrolidine dithiocarbamate (APDC) and piperidine dithiocarbamate (pipDTC) were applied as coating. The detection limits for Cd(II), Cu(II), Mn(II), Ni(II), Pb(II), Zn(II) are 0.1, 0.4, 0.3, 0.4, 0.6, 0.5 µg/L, respectively, for resin coated with APDC and 0.7, 1.0, 0.8, 0.9, 1.7 and 1.2 µg/L for resin coated with pip DTC. The method was applied for the determination of trace metal ions in artificial sea water and natural water sample with extraction AAS method. A surface modification method for the on-line preconcentration of Cd(II), based on its complex formation with the ammonium salt of O,O-diethyldithiophosphate (DDTP), was developed by dos Santos et al. (2005) using Amberlite XAD-4 resin as the solid support. Cd(II) was detected by FAAS. The method was validated by analyzing five biological certified samples. The relative standard deviation was around 3%, which reflects a good precision method. A unique separation method, for determining U(VI), was developed by Singh and Maiti (2006) wherein, Amberlite XAD-4 resin was modified with 8-hydroxy quinoline (Oxine) by equilibrating the former with methanol solution of the reagent. The U(VI) retained in the column could be eluted with methanol-HCl mixture and subsequently determined spectrophotometrically using arsenazo(III) as the chromogenic reagent. Kocaoba and Ansoy (2011) introduced a biologically

modified resin for trace metal determination. Herein, a white rot fungus (*Pleurotus ostreatus*) was used to immobilize on XAD-4. Maximum adsorption of Cr(III), Cd(II) and Cu(II) ions took place in the pH range 4–5. They produced remarkable results on the determination of trace metals. Afzali and Mohammadi (2011) reported an economical method for separation and preconcentration of the trace amounts of Cu(II), Ni(II), Co(II) and Mn(II) in water samples using modified XAD-4 resins. Selected elements were determined by FAAS. The detection limits were 9.2, 28.6, 12.3 and 5.7 ng/mL for Cu(II), Ni(II), Co(II) and Mn(II), respectively. Shahtaheri et al. (2007) did remarkable work in determining trace toxic metal of Pb(II) with FAAS. In this work, mini columns filled with XAD-4 resin were developed for SPE. The obtained recoveries of metal ions were greater than 92%. A very sensitive and selective flow injection online determination method of Th(IV) preconcentration was developed by Ali et al. (2011). Minicolumn having XAD-4 resin impregnated with N-benzoylphenylhydroxylamine was described. The preconcentration factors obtained were 32 and 162, detection limits of 0.76 and 0.150 µg/L. The method was also applied on certified reference material IAEA-SL1 (Lake Sediment) for the determination of Th(IV) and the results were in good agreement with the reported values. A flow injection on-line determination of U(VI), after preconcentration in a minicolumn filled with Amberlite XAD-4 resin impregnated with dibenzoylmethane (DBM), was described by Shahida et al. (2011). The detection limits were 0.9 and 0.232 µg/L. The proposed method was applied on water (spiked tap, well and sea water) and biological samples and good recovery was obtained. An Amberlite XAD-4 resin column was developed by Rajesh et al. (2008) for the SPE of chromium(VI), whose concentration was subsequently determined by using visible spectrophotometry. A detection limit of 6 µg/L was reported.

3.2. Chemical modification of Amberlite XAD-4

The main focus of extensive research on chelating resins is the preparation of functionalized polymers, which can provide more flexible working conditions together with good stability, selectivity, high concentrating ability, high capacity of metal ions and simple operation (Kantipuly et al., 1990; Kantipuly and Westland, 1988; Myasoedova et al., 1986; Warshawsky, 1982; Warshawsky, 1998). Metilda et al. (2005) synthesized a chelating resin Amberlite XAD-4 with succinic acid through acetylation. Quantitative sorption of U(VI) was done in both batch and column modes. Spectrophotometer has been used for preconcentrative separation of U(VI) from host of other inorganic species. The detection limit, corresponding to three times the standard deviation of the blank, was found to be 2 µg/L when the procedure was tested by analyzing reference material, such as marine sediment (MESS-3) and soil (IAEA soil-7). Azotization was used for immobilization of o-vanillinsemicarbazone onto a nonionic polymeric adsorbent styrene divinylbenzene Amberlite XAD-4 resin (Jain et al., 2001) and this chelating resin were utilized for selective column separation, pre-concentration and trace determination of lanthanum(III) (La(III)), cerium(III) (Ce(III)), thorium(IV) (Th(III)) and uranium(VI) (U(VI)) by spectrophotometry and their simultaneous confirmation of the results by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and graphite furnace-atomic absorption spectrometry (GF-AAS).

Table 3 – Chelating agents used for modification of Amberlite XAD-4 resin.

Reagent	Techniques coupled	Metals	Sorption capacity (mg/g)	Reference
8-Hydroxyquinoline (Oxine)	Spectrophotometry	UO ₂ ²⁺	–	Singh and Maiti (2006)
o-Aminobenzoic acid	FAAS	Pb ²⁺ , Cd ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺	12.22, 8.99, 5.36, 7.10, 7.58	Çekiç et al. (2004)
2,3-Dihydroxy-naphthalene	ICP-AES	Cu ²⁺ , Ni ²⁺ , Co ²⁺ , Cd ²⁺		Hemasundaram et al. (2009)
Ammoniumpyrrolidine-Dithiocarbamate	ICP-AES	Cd ²⁺ , Cu ²⁺ , Mn ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺	9.47, 11.08, 8.62, 7.21, 10.25, 10.62	Ramesh et al. (2002)
Piperidine dithiocarbamate (pipDTC)	ICP-AES	Cd ²⁺ , Cu ²⁺ , Mn ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺	9.18, 10.76, 8.17, 7.46, 9.86, 10.28	Ramesh et al. (2002)
2-Acetylmercapto-Phenyldiazoaminoazobenzene	FAAS	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Ni ²⁺ , Zn ²⁺	20.23, 5.89, 6.03, 9.97, 3.92	Liu et al. (2005)
2,6-Dihydroxyphenyl-Diazoaminoazobenzene	FAAS	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Zn ²⁺	20.23, 9.42, 12.38, 10.46	Liu et al. (2007)
Diethyldithiocarbamates	FAAS	Cu ²⁺ , Fe ²⁺ , Pb ²⁺ , Ni ²⁺ , Cd ²⁺ , Bi ²⁺		Uzun et al. (2001)
1-Hydrazinophthalazine	AAS	Cu ²⁺ , Ni ²⁺ , Co ²⁺ , Zn ²⁺ , Cd ²⁺ , Pb ²⁺ , Fe ³⁺ , Cr ³⁺	78.74, 48.12, 50.09, 48.38, 107.90, 178.10, 73.70, 32.23	Lemos et al. (2008a, 2008b)
1-(2-Pyridylazo)-2-naphthol	FI-FAAS	Cu ²⁺		Yebra et al. (2001)
1-(2-Pyridylazo)-2-naphthol	AAS	Cd ²⁺ , Cu ²⁺ , Ni ²⁺ , Pb ²⁺ , Cr ³⁺ , Mn ²⁺		Tuzen et al. (2005)
Salen	AAS	Cu ²⁺ , Pb ²⁺ , Bi ²⁺	17.3, 26.9, 39.5	Kim et al. (2005)
Succinic acid	Spectrophotometry	U ⁶⁺	12.3	Metilda et al. (2005)
Schiff bases	FI-FAAS	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Ni ²⁺ , Pb ²⁺		Kara et al. (2009)
O,O-diethyldi-thiophosphate	FI-FAAS	Cd ²⁺	–	dos Santos et al. (2005)
m-Phenylendi-amine	ICP-AES	Rh ³⁺	26.34	Panahi et al. (2009)
2,3-Diamino-naphtalene		Se ⁶⁺	3.4	Depecker et al. (2009)
2-Aminothiophenol	FAAS	Cd ²⁺ , Ni ²⁺	3.20, 1.39	Lemos et al. (2008a, 2008b)
Maleic acid	AAS	Cr ³⁺	3.90	Yalçin and Apak (2004)
<i>Bacillus subtilis</i>	FAAS	Cu ²⁺ , Cd ²⁺	1.88, 3.93	Dogru et al. (2007)
Diphenylcarbazine complex	UV-vis spectrophotometer	Cr ³⁺	0.85	Rajesh et al. (2008)
Aliquat-336	spectrophotometer	La ³⁺ , Gd ³⁺	4.73, 4.44	El-Sofany (2008)
Salicylic acid	FAAS	Pb ²⁺ , Cu ²⁺ , Ni ²⁺ , Co ²⁺ , Zn ²⁺	78.12, 74.04, 72.99, 73.20, 74.07	Khazaeli et al. (2013)
Catechol	ICP-AES	Cd ²⁺ , Cu ²⁺ , Ni ²⁺ , Pb ²⁺	2.89, 5.69, 2.87, 6.25	Bernard et al. (2008)
Monoaza dibenzo 18-crown-6-ether	ICP-AES	La ³⁺ , Nd ³⁺ , Sm ³⁺	9.17, 9.05, 8.08	Dave et al. (2010)
<i>A. tumefaciens</i>	FAAS	Mn ²⁺ , Co ²⁺	1.20, 1.70	Baytak and Türker (2005)
Allyl phenol	FAAS	Cu ²⁺	106.38	Nezhati et al. (2010)
<i>N,N</i> -bis(salicylidene) cyclohexanediamine	FAAS	Cu ²⁺ , Pb ²⁺ , Ni ²⁺	22.74, 28.77, 11.93	Topuz and Macit (2011)
1-(2-Thiazolylazo)-2-naphthol	NAA	Cu ²⁺	8.0	Goodwin et al. (2013)
<i>Geobacillus thermoleovorans</i> subsp. <i>stromboliensis</i>	FAAS	Cd ²⁺ , Ni ²⁺	4.19, 3.26	Özdemir et al. (2010a, 2010b)
<i>Bacillus</i> sp.	UV-vis spectrophotometry	Th	17.24	Özdemir et al. (2010a, 2010b)

The detection limit of these metal ions was 100 ng/cm³ with recovery of up to 96%–98%. This method was successfully applied for their determination in monazite sand and some

standard geological materials. Çekiç et al. (2004) functionalized Amberlite XAD-4 resin with o-aminobenzoic acid (ABA) via azo spacer and employed it for the preconcentration of various

heavy metals Pb(II), Cd(II), Ni(II), Co(II) and Zn(II) from weakly acidic or neutral aqueous sample. The retained metals were eluted with 1.0 mol HNO₃ from the resin column followed by the determination of concentration with FAAS. The developed method was successfully applied to the analysis of a synthetic metal mixture solution, a certified reference material (CRM) of coal sample, and brackish lake water. Lemos et al. (2008b) reported a 2-aminothiophenol functionalized Amberlite XAD-4 (AT-XAD) resin that was synthesized by covalent coupling of the ligand with the copolymer through a methylene group. Here, in this work SPE method combined with flow injection (FI) on-line FAAS was used for the determination of Cd(II) and Ni(II) in tobacco samples. With the consumption of 21.0 mL of sample solution, the detection limits (3 sec) of 0.3 and 0.8 µg/L for Cd(II) and Ni(II) were achieved at a sample throughput of 18 hr⁻¹. The amount of Cd(II) and Ni(II) in the certified reference material (NIST 1570a, spinach leaves) determined by the present method was in good agreement with the certified value. Kara et al. (2009) used Amberlite XAD copolymer resins functionalized through Schiff base reactions. These resins were used to preconcentrate transition and other trace heavy metal analytes from soil and sediment samples after digestion in nitric acid. Three different Amberlite XAD resins were modified with 4-phenylthiosemicarbazide, 2,3-dihydroxybenzaldehyde and 2-thiophenecarboxaldehyde. The analytes Cd (II), Co(II), Cu(II), Ni(II) and Pb(II) were preconcentrated from acid extracts of certified soil/sediment samples and then eluted with 0.1 mol/L HNO₃ directly to the detection system. FAAS was used as a means of detection during the studies. The efficiency of the chelating resin and the accuracy of the proposed method were evaluated by the analysis of soil (SO-2) and sediment (LGC 6157 and MESS-3) certified reference materials. Recently, Amberlite XAD-4 was used by Khazaeli et al. (2013) to anchor salicylic acid through an azo linkage (–N=N–) for the preconcentration of Pb (II), Cu(II), Ni(II), Co(II), and Zn(II) in water samples. The determination of the metal ions was carried out on FAAS. Developed new method, gave a good accuracy in batch system as indicated by the recovery of ≥93% for the extraction of all metal ions and R.S.D. Kim et al. (2005) used chemically modified XAD-4 for separation of metal ion from aqueous solution. The distribution coefficient at various pH values and adsorption capacities was obtained with respect to Cu(II), Pb(II) and Bi(III). Trace elements were pre-concentrated on the synthesized XAD-4-salen by batch method for AAS determination. XAD-4-salen was synthesized by diazonium coupling reaction of salen [N,N'-bis(salicylidene) ethylenediamine] and Amberlite XAD-4 resin. This material was applied for the determination of Cu(II), Pb(II) and Bi(III) in real samples of five kinds of river water, using a standard calibration curve method. Panahi et al. (2009) developed a new chelating resin by coupling Amberlite XAD-4 with metaphenylenediamine through an azo spacer and studied for preconcentration Rh (III) using ICP-AES for Rh(III) monitoring. The optimum pH value for sorption of the metal ion was 6.5 (recovery 100%). The sorption capacity was found 0.256 mmol/g of resin for Rh(III). The positive value of the enthalpy change (2.48 kJ/mol) indicates that the adsorption was an endothermic process. The method was applied for Rh(III) ion determination from tap water sample. A new chelating sorbent has been prepared by grafting 2,3-diaminonaphthalene (DAN) on

Amberlite-XAD-4 resin beads via a diazo bridge (Depecker et al., 2009). This synthesis was first carried out at a molecular level to optimize experimental conditions and to facilitate characterization of solid sorbent by FTIR. SPE for cationic elements is a promising approach for water treatment or for analysis applications. However, supports that allow the selective extraction and/or preconcentration of metalloid species are still not widespread. A method was proposed by Uzun et al. (2001) for the preconcentration of Cu(II), Fe, Pb(II), Ni(II), Cd(II) and Bi as their diethyldithiocarbamate chelates by using a column filled with Amberlite XAD-4 resin. The relative standard deviations of the determinations were below 95%. The limits of detection (3 sec, *n* = 20) for analytes were found to be between 4 and 23 mg/L. This proposed method was applied to the analysis of some waste waters from the organized industrial region. Nezhati et al. (2010) were prepared a new chelating resin by coupling Amberlite XAD-4 with phenol through an azo spacer, then modified by allyl bromide for preconcentration of Cu(II) using FAAS for metal monitoring. The chelating resin can be reused for 15 cycles of sorption–desorption without any significant change in sorption capacity. The method was applied for the Cu(II) determination from industrial wastewater sample. A maleic acid-functionalized XAD sorbent was used by Yalçın and Apak (2004), for the preconcentration of Chromium, that may exist in environmental waters as Cr(III) and Cr(IV) and was coupled to AAS or diphenylcarbazide (DPC) spectrophotometry for determination. Karadaş et al. (2011) introduced an off-line column preconcentration technique using a micro-column, packed with 2,6 diacetylpyridine functionalized Amberlite XAD-4 resin, automated to an ICP-MS. In this method, they evaluated sea water to determine rare earth elements (REEs), namely La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. The sorption capacities for the resin were found to range between 47.3 µmol/g (for Lu) and 136.7 µmol/g (for Gd). Limits of detection (36), without any preconcentration, ranged from 2 to 10.3 ng/L (for Tm and Lu respectively). Lemos and Gama (2010) introduced the β-nitroso-α-naphthol functionalised Amberlite XAD-4 resin for the preconcentration and determination of uranium. The limit of detection and the preconcentration factor were 1.8 µg/L and 10, respectively. The eluate was measured spectrophotometrically at 650 nm using Arsenazo III as a colorimetric reagent. A chemically modified Amberlite XAD-4 was introduced by Topuz and Macit (2011) which was used for the selective separation, preconcentration, and determination of Cu(II), Pb(II), and Ni(II) ions in water samples using FAAS. This Amberlite XAD-4 loaded N,N-bis(salicylidene)cyclohexanediamine (SCHD) resin, demonstrated a sorption capacity of 1.38×10^{-1} and 3.58×10^{-1} mmol/g. The detection limits of the method were found to be 0.11, 1.91, and 0.43 µg/L for Cu(II), Pb(II), and Ni(II), respectively. In year 2011, Islam et al. developed a chemically modified Amberlite XAD-4 resin for the preconcentration of alkali and alkaline earth metals, present in varying concentrations, from different matrices. 1-(2-Pyridylazo)-2-naphthol loaded Amberlite XAD-4 resin showed high preconcentration factor of 160–400 and a low preconcentration limit of 10 µg/L was achieved for almost all the metals. Chromatographic separation of metal ions in binary mixtures was also accomplished. A new chelating resin was prepared by coupling Amberlite XAD-4 with alizarin red-s through an azo spacer (Kalal et al., 2012). In this work, preconcentration of Rh(III), using

ICP-AES, was performed. A recovery of 88% was obtained for the metal ion with 1.5 M HCl as the eluting agent. Goodwin et al. (2013) introduced a method for the determination of trace levels of Cu(II) in natural waters including seawater with an absolute detection limit of 0.106 μg . The method involves the preconcentration of Cu onto Amberlite XAD-4 resin coated with 1-(2-thiazolylazo)-2-naphthol using reversed phase extraction chromatography (RPEC). Amberlite XAD-4 as the solid support and a Schiff base (pyridine-2-carbaldehyde thiosemicarbazone, PCTSC), as a chromogenic reagent, the solid-phase extraction of Fe (III) and Cr (III) ions was performed in the column procedure (Baytak et al., 2006). The detection limits for Fe (III) and Cr (III) were 4.1 and 3.72 $\mu\text{g/L}$, respectively. Kocaoba and Arisoy (2007) introduced Amberlite XAD-4 loaded with white rot fungi (*Pleurotus ostreatus*) for the separation and preconcentration of Cr(III), copper(II) and Cd(II). The proposed method promises a cheap, simple, highly sensitive, accurate, and selective procedure for enrichment analysis. A procedure has been developed by Bezerra et al. (2007) for the simultaneous determination of trace amounts of Cd(II), Cu(II), Cr(III), Ni(II) and Pb(II) in digested vegetable samples. The procedure includes Amberlite XAD-4 resin, modified with dihydroxybenzoic acid (DHB), and ICP-OES as the detecting instrument. The reported detection limits ($3\sigma_B$) were 0.02, 0.23, 0.58, 0.060 and 0.54 g/L for Cd(II), Cu(II), Cr(III), Ni(II) and Pb(II), respectively. The procedure was applied for the determination of metals in samples of guarana and cabbage. Dogru et al. (2007) proposes the use of *Bacillus subtilis* immobilized on Amberlite XAD-4 as new biosorbent in trace metal determination. The procedure was based on the biosorption of Cu(II) and Cd(II) ions in a column of Amberlite XAD-4 resin loaded with dried, dead bacterial components prior to their determination by FAAS. The sorption capacity of the resin was 0.0297 and 0.035 mmol/g for Cu(II) and Cd(II), respectively. El-Sofany (2008) proposed a method for the removal of La(III) and Gd(III) from nitrate medium using Aliquat-336 impregnated Amberlite XAD-4. The capacity of the impregnated resin for both La(III) and Gd(III) was found to be 4.73 and 4.44 mg/g . Lemos et al. (2008a, 2008b) functionalized Amberlite XAD-4 with 3,4-dihydroxybenzoic acid (XAD4-DHB) packed in a minicolumn was used as sorbent material. The proposed material used for on-line preconcentration of Cd(II), Cu(II) and Zn(II) was determined by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). The detection limits were 28, 100, and 77 ng/L for Cd(II), Cu(II) and Zn(II) in 60 sec preconcentration time, at a sample flow rate of 7.0 mL/min . A bioadsorbent was prepared by immobilizing *Geobacillus thermoleovorans* subsp. *stromboliensis* on to Amberlite XAD-4, as reported by Özdemir et al. (2010a), for preconcentrating Cd(II) and Ni(II) from the natural water, which were determined by FAAS. The detection limits were 0.24 $\mu\text{g/L}$ for Cd(II) and 0.3 $\mu\text{g/L}$ for Ni(II). In another report, Özdemir et al (2010b) immobilized *Bacillus* sp. on Amberlite XAD-4 resin and used it in SPE of thorium prior to UV-vis spectrometry determination. The loading capacity was found to be 17.2 mg/g . Özdemir and Kilinc (2012) made a combined effort in employing *G. thermoleovorans* immobilized Amberlite XAD-4 resin as a biosorbent for SPE of U(VI) followed by its determination using UV-vis spectrophotometer. The limits of detection and quantification are 2.7 and 9.0 $\mu\text{g/L}$, respectively. The method was applied to the determination of U(VI) in a certified reference sample (NCS ZC-73014; tea leaves) and in natural water samples.

The 2-Acetylmercaptophenyldiazoaminoazobenzene (AMPDAA) impregnated Amberlite XAD-4 resin, introduced by Liu et al. (2005) was used for the preconcentration of Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) ions in natural water samples, which were subsequently determined by FAAS. The detection limit for Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) was 0.028, 0.064, 0.042, 0.023 and 0.16 mg/L , respectively. Shahida et al. (2012) introduced the online preconcentration of uranium that consists of a minicolumn packed with Amberlite XAD-4 resin impregnated with nalidixic acid. In this work, spectrophotometer was used for the determination of uranium from water, biological, and ore samples in association with a flow injection system coupled to SPE. This method presented a detection limit of 1.1 $\mu\text{g/L}$. Preconcentration of metal ions through chelation on a synthesized resin containing O,O donor atoms for quantitative analysis of environmental and biological samples has been developed by Islam et al. (2013a, 2013b). The maximum sorption of Ni(II), Mn(II), Cu(II), Zn(II), Cd(II), Cr(III), and Co(II) was observed at pH 5.5–8.0 and detection limits, for FAAS, were found to be 0.62, 0.60, 0.65, 0.75, 0.72, 0.84, and 0.85 $\mu\text{g/L}$, respectively. As reported by Kaur and Agrawal (2005), a crosslinked polystyrene resin, Amberlite XAD-4, was functionalised with a new chelating agent, namely bis-2[(O-carbomethoxy) phenoxy] ethylamine, for the chromatographic separation of La(III) and Nd(III), Nd(III) and Sm(III) from their mixtures. Following a different approach, Bernard et al. (2008), prepared a new chelating resin by grafting catechol on Amberlite XAD-4. Sorption capacity of 2.5 $\mu\text{mol/g}$ for Cd(II), 8.4 $\mu\text{mol/g}$ for Cu(II), 10.5 $\mu\text{mol/g}$ for Ni(II) and 1.6 $\mu\text{mol/g}$ for Pb(II) were observed at a pH range of 2 to 9, using ICP-AES. Dave et al. (2010) chemically modified Amberlite XAD-4 with monoaza dibenzo 18-crown-6 ether and investigated its potential for the preconcentration and separation of La (III), Nd (III) and Sm (III) in synthetic solution. The limits of detection ($n = 5$) and limits of quantification ($n = 5$) for La(III), Nd(III) and Sm(III) were found to be 3.9, 4.2 and 7.4 $\mu\text{g/L}$ and 13, 15 and 26 $\mu\text{g/L}$, respectively. The eluted metal ions were determined by ICP-AES. An immobilization of *Agrobacterium tumefaciens* on Amberlite XAD-4, as performed by Baytak and Türker (2005), resulted in a biosorbent that was applied for the metal ion determination in water samples, alloy samples, infant foods and certified samples, such as whey powder (IAEA-155), and aluminum alloy (NBS SRM 85b). FAAS analysis of Fe(III), Co(II), Mn(II) and Cr(III) was done following their enrichment with the biosorbent. Amberlite XAD-4 underwent chemical modification by coupling, through azo-linking, with p-hydroxybenzoic acid (Islam et al., 2010a), 1-(2-pyridylazo)-2-naphthol (Islam et al., 2010b), salicylic acid (Islam et al., 2012a) and o-Hydroxybenzamide (Islam et al., 2012b) for studying the sorption behavior of several metal ions which were subsequently determined by FAAS. The detection limit was found to be in the range of 0.47–1.37, 0.65–1.40, 0.42–1.41, 0.39–1.10 $\mu\text{g/L}$, respectively. All the above methods have been successfully applied in the analysis of natural water, multivitamin formulation, infant milk substitute, hydrogenated oil, urine, and fish.

4. Amberlite XAD-16

Amberlite XAD 16 promises to be a good sorbent by virtue of its appreciable surface area of 800 m^2/g and a pore size of 200 Å.

Besides, it also offers a high chemical stability that favors its further modification both chemically as well superficially. Table 4 represents the numerous works reported using different chelating agents.

4.1. Surface modification of Amberlite XAD-16

Traces of metal ions have been enriched on Amberlite XAD-16 resin beads through surface adsorption of their chelates. Wuilloud et al. (2002) prepared a chelating resin, namely 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) loaded on the XAD-16 resin, for the determination of lead by ICP-AES that was associated to flow injection (FI) with ultrasonic nebulization (USN). The enhancement factor and detection limit of Pb(II) was found to be 150 and 0.2 ng mL⁻¹, respectively using ICP-AES. The developed method was successfully applied for the determination of lead in drinking water samples. A chelating resin, 3-((2,6-dichlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (DCPIMI) loaded onto Amberlite XAD-16, was developed by Ghaedi et al. (2010) for the determination of Cu(II), Zn(II) and Mn(II) ions in real samples by FAAS. Various parameters, such as reversible uptake, elution of metal ions, flow rates of eluent and sample solution, ligand concentration and amount of surfactant and condition of elution solution were studied. Preconcentration factor was achieved to 225 and limit of detection (LOD) was found to be 1.9, 1.5 and 2.6 ng mL⁻¹ for Cu(II), Zn(II) and Mn(II) ions, respectively. A simple and reliable method for the determination of Pb(II) in trace amount has been developed by using chelating resin Amberlite XAD-16 modified with phthalic acid (Memon et al. (2005). Different parameters were investigated for sorption study of metal such as pH, shaking speed, and contact time between the two phases. Preconcentration limit for quantitative recovery was achieved to 5.8 ng/cm³ with a preconcentration factor of 850. Kinetics was well fitted with the first order rate equation and the sorption equilibrium data of Pb(II) followed the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms at all investigated temperatures. This method was successfully applied for the determination of Pb(II) in automobile exhaust particulates by AAS using direct and standard addition methods. To investigate the removal of metal ions including, Co(II), Ni(II), Cu(II) and Cd(II) ions on SDS coated Amberlite XAD-16 modified with new resorcinarenes derivative (Ghaedi et al., 2009). The adsorbed analytes were eluted with 6 mL of 3 mol HCl in acetone solution, which then were analyzed by AAS. Various analytical parameters, including pH, ligand amount and solid phase ingredient, eluting solution conditions and sample volume were studied. Modified resin showed excellent stability towards acid and bases and a high preconcentration factor of 208 was observed. The accuracy of the method was estimated by using different real samples. Tunçeli and Türker (2000a, 2000b) modified Amberlite XAD-16 resin with thiocyanate solution (a complexing agent) for the determination of silver by FAAS. Various factors such as pH, the nature of complexing agent, sample volume, flow rate, and the type and concentration of elution solution were investigated. High recovery, of 99.20% ± 0.07% at the 95% confidence level, of silver was obtained from nitric acid solution (pH 2). Preconcentration factor and detection limit of silver were found to be 70

and 0.047 mg/L, respectively. Adsorption follows Langmuir equation with a maximum adsorption capacity of 4.66 mg/g (0.043 mmol/g) and the proposed method was successfully applied for the determination of silver in standard alloy with a relative error of 6.25%. Tokahoglu et al. (2002) developed Amberlite XAD-16 resin, using hexamethylenammonium-hexamethylenedithiocarbamate (HMA-HMDTC) as a chelating agent, and used it to separate and preconcentrate the Cu(II), Pb(II), Ni(II), Cd(II), Mn(II) and Fe(III). The relative standard deviation (RSD) and the detection limit (LOD) were found to be in the range of 0.8%–2.9% and 0.006–0.277 µg/mL, respectively. At optimum conditions, more than 95% recovery was obtained by the column method. The proposed method was successfully applied for the determination of metal ions in seawater and wastewater samples.

N,N-dibutyl-N1-benzoylthiourea (DBBT) loaded onto a polymeric matrix, Amberlite XAD-16 that was packed into a column, to prepare a chelating resin for preconcentrating Ag(I) (Ayata et al., 2009). The optimum pH range for quantitative sorption was 2–5 while an elution with 1 mol/L thiourea in 1 mol/L HCl resulted in a quantitative recovery of Ag(I). The sorption capacity of resin was 0.115 mmol Ag(I)/g resin. The relative standard deviation and detection limit were 3.1% (for 1 µg Ag⁺ mL⁻¹ solution) and 0.11 µg/L, respectively. The method was used for the determination of silver in geological water samples. Merdivan et al. (2001) impregnated N, N-dibutyl, N'-benzoylthiourea (DBBT) on Amberlite XAD-16 by surface modification and used it for the determination of U(VI) in real samples. The sorption capacity of resin for U(VI) was found to be 0.90 mmol/g. Quantitative recovery of U(VI) was achieved by stripping with 0.1 mol/L HNO₃. The method was applied to the determination of U(VI) in synthetic samples. The precision of the method was 2.4 RSD% in a concentration of 1.20 µg/mL for ten replicate analysis. Tunçeli and Türker (2002) developed a chelating resin Amberlite XAD-16 by complexing with 1,5-diphenylcarbazone and applied this resin for the speciation, separation and preconcentration of Cr(VI) and Cr(III) in tap water by FAAS. Various parameters, such as the effect of acidity, amount of adsorbent, eluent type and flow rate of the sample solution were investigated. The recovery of Cr(VI) was 99.7 ± 0.7 at 95% confidence level. The highest preconcentration factor was 25 for a 250 mL sample volume. The detection limit of Cr(VI) was observed at 45 µg/L. The adsorption capacity of the resin was found as 0.4 mg/g for Cr(VI). As reported by Özdemir et al. (2012), a *Pleurotus eryngii* immobilized Amberlite XAD-16 was used for the determination of Cd(II) and Co(II) by ICP-OES. The optimum extraction conditions were determined as follows: a pH of 6.0 for Cd(II) and 5.0 for Co(II); a sample flow rate of 2.0 mL/min; 200.0 mg of biosorbent; and 5.0 mL of 1.0 mol/L HCl as eluent. The capacities of the biosorbent for metal uptake were found to be 11.3 and 9.8 mg/g for Cd(II) and Co(II) ions, respectively. Limit of quantifications (LOQs) were found to be 0.67 and 0.82 ng/mL, respectively, for Cd(II) and Co(II). The developed method was successfully applied to NCSZC-73014 (a certified reference tea sample). Relative standard deviations (RSD) were lower than 5.0%. The Cd(II) and Co(II) concentrations in the different parts (leave, root, stem, and fruit) of purslane, onion, rocket, okra, and aubergine were determined after microwave digestion and solid-phase extraction with the biosorbent.

Table 4 – Chelating agents used for modification of Amberlite XAD-16 resin.

Reagent	Techniques coupled	Metals	Sorption capacity (mg/g)	Reference
1,6-Bis(2-carboxy aldehydephenoxy)butane	FAAS	Cu ²⁺ , Cd ²⁺	5.38, 4.43	Oral et al. (2011)
2,6-Dichlorophenyl-3,3-bis(indolyl)methane	FAAS	Cu ²⁺ , Zn ²⁺ , Mn ²⁺	70.6, 64.3, 60.1	Ghaedi et al. (2010)
Gallic acid	FAAS	Cr ³⁺ , Mn ²⁺ , Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺	11.22, 9.88, 22.50, 16.55, 14.67, 21.84	Sharma and Pant (2009)
4-[(2-Hydroxyphenyl)imino]methyl-1,2-benzenediol	FAAS	Zn ²⁺ , Mn ²⁺ , Ni ²⁺ , Pb ²⁺ , Cd ²⁺ , Cu ²⁺ , Fe ³⁺ , Co ²⁺	10.98, 6.09, 13.20, 21.75, 6.29, 26.35, 18.98, 14.49	Venkatesh and Singh (2007)
Acetylacetone	AAS	Cr ³⁺ , Cr ⁶⁺	779.84, 977.41	Memon et al. (2009)
3,4-Dihydroxy benzoyl methyl phosphonic acid	FAAS	U ⁶⁺ , Th ⁴⁺	395.11, 350.36	Maheeswari and Subramanian (2005)
Phthalic acid	AAS	Pb ²⁺	40.0	Memon et al. (2005)
N,N-dibutyl-N-benzoylthiourea	Spectrophotometry	U ⁶⁺	214.21	Merdivan et al. (2001)
(Bis-2,3,4-trihydroxybenzyl) ethylene diamine	Spectrophotometry	U ⁶⁺ , Th ⁴⁺ , Pb ²⁺ , Cd ²⁺	340.36, 276.11, 209.27, 87.67	Prabhakaran and Subramanian (2003)
Thiocyanate	FAAS	Ag ²⁺	4.66	Tunçeli and Türker (2000a, 2000b)
1,5-Diphenylcarbazone	FAAS	Cr ⁶⁺	0.40	Tokaloğlu et al. (2009)
Nitrosonaphthol	AAS	Ni ²⁺ , Cu ²⁺	605.79, 352.14	Memon et al. (2007)
Iodide complex	FAAS	Pd ²⁺	35.6	Tunçeli and Türker (2000a, 2000b)
(Salicylaldehyde calix[4]resorcinarenes)	AAS	Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Cd ²⁺	68.5, 61.9, 61.9, 62.5	Ghaedi et al. (2009)
2-[[1-(3,4-Dihydroxyphenyl)methylidene]amino]benzoic acid	FAAS	Zn ²⁺ , Mn ²⁺ , Ni ²⁺ , Pb ²⁺ , Cd ²⁺ , Cu ²⁺ , Fe ²⁺ , Co ²⁺	12.94, 9.77, 15.78, 26.52, 10.90, 29.71, 28.75, 13.02	Venkatesh and Singh (2005)
Pleurotus eryngii	ICP-OES	Cd ²⁺ , Co ²⁺	11.3, 9.8	Özdemir et al. (2012)
N,N-dibutyl-N1-benzoylthiourea	AAS	Ag ⁺	12.40	Ayata et al. (2009)
3-Hydroxyphosphinoyl-2-oxo-propyl)phosphonic acid dibenzyl ester	Spectrophotometer and fluorescence spectrophotometer	U ⁶⁺ , Th ⁴⁺ , La ³⁺	328.46, 308.59, 104.25	Prabhakaran and Subramanian (2004a, 2004b)
Glyoxal-bis(2-hydroxyanil)	FAAS	Al ³⁺	24.28	Islam et al. (2013a, 2013b)
2-(2-Hydroxyphenyl) benzoxazole	FAAS	Al ³⁺	21.58	Islam et al. (2014)

4.2. Chemical modification of Amberlite XAD-16

Chemical modification of Amberlite XAD-16, modified with organic moieties via chemical route has gained appreciable interest. The chemical route of azotization was taken to functionalize Amberlite XAD-16 with gallic acid for the determination of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. The synthesized resin was characterized on the basis of thermogravimetric analysis (TGA), infrared (IR) spectra and BET analysis (Sharma and Pant, 2009). Various parameters like the effect of solution pH, effect of sample volume, effect of contact time, and flow rate of sample were studied. Sorption capacity and preconcentration factors for Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were found to be 216, 180, 403, 281, 250 and 344 $\mu\text{mol/g}$, and 300, 200, 400, 285.7, 300 and 400 respectively. The method was successfully applied for the determination of metal ions present in river water and industrial area aqueous samples. Memon et al. (2009) synthesized a polymeric Amberlite XAD-16 with acetyl acetone and applied it for the speciation of chromium in industrial water samples. Two forms of chromium showed different exchange capacities at different pH values, wherein Cr(III) was selectively retained at pH 5–7 while Cr(VI) at pH 1. Detection limits of Cr(III) and Cr(VI) were found to be 0.02 and 0.014 $\mu\text{g mL}^{-1}$, respectively, with high enrichment factor of 100 and 140. Oral et al. (2011) reported the synthesis of 1,6-bis(2-carboxy aldehyde phenoxy) butane functionalized polystyrene-

divinyl benzene co-polymer, Amberlite XAD-16 via C=N- spacer. The synthesized resin was applied for preconcentration of Cu(II) and Cd(II) prior to their determination by FAAS. The detection limits of Cu(II) and Cd(II) were observed at 0.33 and 1.19 $\mu\text{g/L}$, respectively, while the recoveries were achieved up to 100 ± 2.15 and 100 ± 1.40 . The proposed method was successfully applied for the determination of Cu(II) and Cd(II) ions in real samples and the accuracy was checked with certified reference material (NCS-DC 73350). Prabhakaran and Subramanian (2003) developed a new ion-selective chelating polymer using Amberlite XAD-16 (AXAD-16), as the polymer support, and functionalized with (bis-2,3,4-trihydroxy benzyl) ethylene diamine (BTBED) through an azo spacer. Investigation of various physio-chemical parameters, such as pH, metal exchange kinetics, metal loading capacity, diverse ion tolerance and sample breakthrough volume was carried out. High sorption capacities of U(VI), Th(IV), Pb(II) and Cd(II) were found to be 1.43, 1.19, 1.01, and 0.78 mmol/g, respectively. High preconcentration factor was achieved for all the analytes and chelating resin showed high resistivity towards various complexing species. A new chelating ion-exchanger, namely AXAD-16-3,4-dihydroxy benzoyl methyl phosphonic acid was applied for the selective extraction of U(VI) and Th(IV) by Maheeswari and Subramanian (2005). Chelating resin was characterized on the basis of FT-IR spectroscopy, CHNPS elemental analysis and TGA followed by the optimization of various physio-chemical parameters by both static and dynamic

methods. A high sorption capacity of 1.66 and 1.51 mmol/g was achieved for U(VI) and Th(IV), respectively and the saturation point could be reached within 5 min. A high enrichment factor of 333 was achieved, with the lower concentration limits at 10 ng/cm for both U(VI) and Th(IV). The developed method was applied for the determination of U(VI) and Th(IV) in nuclear reprocessing mixture, synthetic seawater, real water and monazite sand samples. The Amberlite XAD 16 resin was functionalized, using azo linker, with 2-[[1-(3,4-Dihydroxyphenyl)methylidene] amino]benzoic acid (Venkatesh and Singh, 2005) and 4-[[2-(hydroxyphenyl) imino]methyl]-1,2-benzenediol (Venkatesh and Singh, 2007) for the determination of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II). Sorption capacity was in the range of 97–515 $\mu\text{mol/g}$ and 56–415 $\mu\text{mol/g}$, while the preconcentration factors were of 100–450 and 150 to 300, respectively. The values of limit of detection (blank +3 s) are 1.12, 1.38, 1.76, 0.67, 0.77, 2.52, 5.92 and 1.08 $\mu\text{g/L}$ and 1.72, 1.30, 2.56, 2.10, 0.44, 2.93, 2.45 and 3.23 $\mu\text{g/L}$, respectively, for Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II), respectively. Memon et al. (2007) synthesized nitrosonaphthol-functionalized Amberlite XAD-16 resin and determined Ni(II) and Cu(II). Various parameters were optimized with respect to the sorptive medium (pH), shaking speed and equilibration time between liquid and solid phases. The sorption data followed Langmuir, Freundlich, and D-R isotherms. The variation of sorption with temperature gives thermodynamic quantities of $\Delta H = -58.9 \pm 0.12$ and -40.38 ± 0.11 kJ/mol, $\Delta S = -83 \pm 10$ and -30 ± 8 J/(mol·K) and $\Delta G = -0.4 \pm 0.09$ and -2.06 ± 0.08 kJ/mol at 298 K for Ni(II) and Cu(II) ions, respectively. Proposed method was successfully applied for the determination of Ni(II) and Cu(II) in tea, vegetable oil, hydrogenated oil (ghee) and palm oil by AAS using direct and standard addition methods. A new chromatographic extraction method was developed using Amberlite XAD-16 with (3-hydroxyphosphinoyl-2-oxo-propyl) phosphonic acid dibenzyl ester (POPDE) by chemical modification Prabhakaran and Subramanian (2004a, 2004b). Modified resin was characterized on the basis of ^{13}C CPMA and ^{31}P solid-state NMR, Fourier Transform-NIR-FIR-Raman spectroscopy, CHNPS elemental analysis, and TGA. The kinetic data revealed that 10 min was sufficient to achieve complete metal ion extraction, while the maximum sorption capacity was found to be 1.38, 1.33, and 0.75 mmol/g for U(VI), Th(IV), and La(III), respectively. Applicability of the synthesized resin was investigated with synthetic mixtures mimicking nuclear spent fuels, seawater compositions and real water and geological samples with the RSD value lying within 5.2%, whereby favoring the reliability of the developed method. Ruhela et al. (2012) functionalized 2-acetyl pyridine on Amberlite XAD-16 by coupling it with 2-chloro pyridine after acetylation. The chelating resin was applied for the preconcentration and separation of palladium and other metal ions present in high level waste solution. During sorption studies, 30–45 min was enough to reach the equilibrium. The pseudo-second order kinetics model yielded the best fit for the experimental data and adsorption isotherm data fitted well with Langmuir as well as Freundlich models. The maximum sorption capacity of the resin was found to be 8 mg/g. Islam et al. (2011a, 2011b) developed a chelating resin, namely Amberlite XAD-16-salicylanilide through an azo spacer and applied for separation and preconcentration of trace metal

ions. The breakthrough capacities for Cu(II), Co(II), Ni(II), Zn(II), Cr(III), Cd(II), and Pb (II) were found to be 697.91, 641.83, 629.32, 551.38, 531.72, 249.11 and 125.36 mmol/g, with low detection limits of 0.56, 0.64, 0.65, 0.70, 0.75, 0.88 and 1.17 mg/L, respectively. Modified resin was successfully applied for the determination of trace metal ions in natural water, mango pulp, leafy vegetables and fish. Later, a styrene-divinylbenzene based resin was functionalized with 2-hydroxy-3-methoxybenzaldehyde and applied for the preconcentration of Zn(II), Cu(II), Ni(II), Cd(II), and Pb(II), in trace amount in various real matrices (Ahmad et al., 2013). The synthesized resin was able to preconcentrate at low concentration level up to 5.55–8.33 $\mu\text{g/L}$. This method was successfully applied to the determination of the heavy metals in natural waters as well as food samples.

5. Other XAD Amberlite

Amberlite XAD 7 and XAD 8 offer itself as a suitable sorbent for quantitative retention in preconcentration. Amberlite XAD 1180 has found extensive application as a sorbent in SPE by virtue of its large surface area of 500 m^2/g and a pore size of 400 Å. The different techniques coupled to resins, which were modified with different chelating agents, have been represented in Table 5.

5.1. Surface modification of other XAD aberlite

Amberlite XAD resins as the backbone for the impregnation of chelating ligands have physical superiorities such as high surface area, porosity, uniform pore size distribution, durability and chemical stability towards acids, bases and oxidizing agents. Surface modification method using impregnation of organic moieties can significantly enhance the capacities of adsorbents to adsorb heavy metals from aqueous medium. Hosseini-Bandegharai et al. (2010) presents a novel support for Cr(VI) sorption and its removal from wastewaters. Toluidine blue o (as an extractant) was impregnated onto Amberlite XAD-7 beads. The maximum sorption of Cr(VI) on TBO-impregnated XAD-7 occurs at pH range of 3.0–4.0, when measured spectrophotometrically. Quinolin-8-ol and Amberlite XAD-7 were developed by Vicente et al. (1998) for on-line preconcentration of Eu, Tb, Ho, Tm and Lu. The arrangement for determination constituted ICP-MS automated to a flow injection system. Kirgöz et al. (2005) developed a novel Centri-voltammetry method, wherein XAD-7 resin was used as the carrier material and the parameters related to the carrier material and medium characteristics as well as the centrifugation settings were investigated. The sensitivity of the method was found comparable to that of the stripping techniques and the detection limit for lead ions was calculated as 5.2×10^{-9} mol with mercury coated gold sphere electrode. Amberlite XAD-8 resin was used for the spectrophotometric determination of traces of molybdenum by Soylak et al. (1996). The procedure was applied to the determination of molybdenum in steel with satisfactory results (recovery > 95%; relative error < 3%; relative standard deviation < 5% in the concentration range of 0.006%–0.024%; IUPAC detection limit, 60 $\mu\text{g/L}$ in solution). A novel SPE procedure, consisting of Amberlite XAD-1180, was developed for the

speciation of Cr(III), Cr(VI) by Narin et al. (2008). The procedure is based on the adsorption of Cr(III)–diphenylcarbazone complex on Amberlite XAD-1180 resin followed by FAAS determination of chromium. The detection limits (LOD) based on three times sigma of the blank ($N = 21$) for Cr(VI) and total chromium were 7.7 and 8.6 $\mu\text{g/L}$, respectively. Rajesh and Manikandan (2008) introduced a simple methodology for the determination of Pb(II) spectrophotometrically after preconcentration of its diphenylthiocarbazone complex on an Amberlite XAD-1180. The limit of detection of Pb(II) was found to be 3.5 $\mu\text{g/L}$.

A simple and sensitive SPE procedure on Amberlite XAD-1180 resin, as reported by Soyak et al. (2003), was used for the determination of Cr, Co(II), Mn(II) and Ni(II) at trace levels by atomic absorption spectrometry. The detection limits for Cr, Co(II), Mn(II) and Ni(II) were 0.27, 0.11, 0.13 and 0.086 $\mu\text{g/g}$, respectively. A SPE method was developed by Elci et al. (2008) for the determination of iron, lead and chromium (in various water samples) by atomic absorption spectrometry using Amberlite XAD-2000 column. The detection limit, based on three standard deviations of the blank, was found to be 0.32, 0.51 and 0.81 $\mu\text{g/L}$, for Fe, Pb and Cr, respectively. A new method for the preconcentration of some trace metals (Co(II), Ni(II), Cu(II), and Cd(II)) was developed by Duran et al. (2009). In this work, a mini-column filled with Amberlite XAD-2000 resin was used for the retention of the metal ions as complexes of ammonium pyrrolidone dithiocarbamate (APDC). Metal contents were determined by FAAS. The method was successfully applied to some samples of stream waters and mushroom samples from eastern black sea region (Trabzon city) of Turkey. A FAAS, for the determination of the trace Pb(II) in aqueous medium following SPE using Amberlite XAD-2000 resins, was proposed by Qingbin et al. (2011). The detection limit, calculated as three sigma, was 3.0 $\mu\text{g/L}$ ($n = 10$). The above procedure was applied for the determination of trace Pb(II) in tap, phreatic and river water with satisfactory results. Bulut et al. (2007a, 2007b) developed a speciation procedure for Cr(III) and Cr(VI), based on column SPE using Amberlite XAD-2010, followed by their determination by FAAS. The detection limit (corresponding to three times the standard deviation of the blank) and the enrichment factor for Cr(VI) were found to be 1.28 $\mu\text{g/L}$ and 25, respectively.

5.2. Chemical modification of other XAD Amberlite

Amberlite XAD is a cross linked polystyrene macroporous structure having high surface area which imparts excellent physical, chemical and thermal stability. After incorporation of organic moieties with different spacer, it is a good choice for the removal of a variety of metal ions. Extraction chromatography of thorium ion by solid phase impregnated resins, containing bi-functional organic extractants, was performed by El-Dessouky and Borai (2006). The maximum uptakes of Th^{4+} were found to be 62.9%, 66.7% and 92.6% for DB18C6, 18C6 and 15C5, respectively. The resin comprising of cyanex-301 impregnated with 15C5 could be utilized for selective separation and preconcentration of thorium ion. The work was performed by Ciftci et al. (2010), wherein the determination of trace amounts of Ni(II) in environmental samples was accomplished. In this study, Ni(II) was preconcentrated as diamino-4-(4-nitro-phenylazo)-1H-pyrazole (PDANP) chelates (Ni-PDANP) from sample solutions using a column containing Amberlite XAD-7 and then

determined by FAAS. Amberlite XAD-7 resin impregnated with trioctylphosphine oxide (Cyanex 921), as introduced by Navarro et al. (2009), was used for the extraction of Fe(III), wherein the latter was removed from HFeCl_4 through direct binding on the resin or by extraction with Cyanex 921 involving a solvation mechanism. Hosseini et al. (2009) developed a new chelating polymeric sorbent, as an extractant-impregnated resin (EIR), comprising brilliant green (BG) and Amberlite XAD-7 resin. Resin showed superior binding affinity for Cr(VI) in the presence of many co-existing ions. Yilmaz and Kartal (2012) established a new chelating resin by immobilizing 1-(2-thiazolylazo)-2-naphthol through the $-\text{N}=\text{N}-$ group on Amberlite XAD-1180 for the preconcentration of Cd(II), Co(II), Cu(II), Mn(II), Ni(II), and Pb(II) ions followed by their determination by FAAS. The detection limits were in the range of 0.1–3.6 $\mu\text{g/L}$. A new method for the separation and preconcentration of trace amounts of Cu(II), Ni(II), Pb(II), Cd(II) and Mn(II) ions in various matrices was proposed by Tokaloğlu et al. (2009). This method includes an Amberlite XAD-1180 resin impregnated with 1-(2-thiazolylazo)-2-naphthol (TAN) that was automated to FAAS. The detection limit values were in the range of 0.03 and 1.19 $\mu\text{g/L}$. Belkhouche and Didi (2010) impregnated Di(2-ethylhexyl)phosphoric acid (D2EHPA) on Amberlite XAD-1180 solid support by extractant impregnated resin technique (EIR). The extraction yield of bismuth was determined as 98.5%, equivalent to 490.7 mg of Bi/g of resin. The increase in the immersion aqueous volume results in the slight decrease in the sorption of Bi(III). Tokaloğlu and Livkebabcı (2009) developed a novel column SPE method for the determination of Cu(II) and Fe(III) in various samples using FAAS following their preconcentration as their N-benzoyl-N-phenylhydroxylamine complexes on Amberlite XAD-1180 resin. Detection limits reported in this method were 0.82 $\mu\text{g/L}$ for Cu(II) and 1.05 $\mu\text{g/L}$ for Fe(III). The method was applied for the determination of the analytes in water (sea water, dam water, lake water and waste water), vegetable, rice and spices samples. Narin et al. (2004) developed a chelating resin, pyrocatechol violet (PV) immobilized on an Amberlite XAD-1180 and used it for the determination of Al(III) in environmental samples by graphite furnace atomic absorption spectrometry. The capacity of sorbent was $6.45 \pm 0.59 \text{ mg/g Al(III)}$ XAD-1180-PV. In the method, as proposed by Duran et al. (2007b), the determination of Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II), constituting environmental samples, was based on the retention of their complexes, with 8-hydroxyquinoline(HQ), on a column packed with Amberlite XAD-2000 resin prior to subjection to FAAS. The enrichment factor was calculated as 100 and the limit of detection was in the range of 0.3–2.2 $\mu\text{g/L}$ ($n = 20$, blank + 3s). Bulut et al. (2007a, 2007b) proposed a method, for the preconcentration of some transition elements at trace level, in which a column filled with diethyldithiocarbamate chelates of Amberlite XAD-2000 resin, was used. The determination of the above metal ions was done by FAAS. The detection limit ($N = 20$, 3 sigma) for Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) was found as 0.20, 0.35, 0.25, 0.20, 0.20, 0.15, 0.45 and 0.25 $\mu\text{g/L}$, respectively. The proposed method was applied to natural waters and kale vegetable (*Brassica oleracea* var. *acephala*). Seyhan et al. (2008) used an o-phenylene dioxydiacetic acid impregnated Amberlite XAD resin for the separation and preconcentration of U(VI) and Th(IV). The above resin exhibited a high chemical stability, good reusability and fast equilibration. The method was used for the determination of U(VI) and Th(IV) in synthetic

Table 5 – Chelating agents used for modification of other Amberlite XAD resin.

Reagent	Techniques coupled	Metals	Sorption capacity (mg/g)	Reference
XAD-7				
Toluidine blue o	Spectrophotometry	Cr ⁶⁺	20.62	Hosseini-Bandegharai et al. (2010)
Diamino-4-(4-nitro-phenylazo)-1H-pyrazole	FAAS	Ni ²⁺	7.2	Ciftci et al. (2010)
Brilliant green	Spectrophotometry	Cr ⁶⁺	5.45	Hosseini et al. (2009)
XAD-1180	–	–	–	–
1-(2-Thiazolylazo)-2-naphthol	FAAS	Cu ²⁺ , Ni ²⁺ , Cd ²⁺ , Mn ²⁺	0.77, 0.41, 0.57, 0.30	Tokaloğlu et al. (2009)
Di(2-ethylhexyl)phosphoric acid	UV-visible spectrophotometer	Bi ³⁺	490.7	Belkhouche and Didi (2010)
Pyrocatechol violet	GFAAS	Al ³⁺	0.59	Narin et al. (2004)
XAD-2000				
Diethyldithiocarbamate	FAAS	Cu ²⁺ , Fe ³⁺ , Zn ²⁺ , Mn ²⁺ , Cd ²⁺ , Pb ²⁺ , Ni ²⁺ , Co ²⁺	5.63, 5.40, 4.80, 4.76, 4.41, 6.42, 3.80, 6.08	Bulut et al. (2007a, 2007b)
o-Phenylene dioxydiacetic acid	UV-vis spectrophotometer	U ⁶⁺ , Th ⁴⁺	28.80, 26.21	Seyhan et al. (2008)
Ammonium pyrrolidinedithiocarbamate	FAAS	Co ²⁺ , Cu ²⁺ , Cd ²⁺ , Ni ²⁺	6.1, 6.4, 6.2, and 6.3	Duran et al. (2009)
α-Benzoin oxime	Spectrophotometry	U(VI), Th(IV), and Zr	3.6, 3.3, 2.6	Ghasemi and Zolfonoun (2010)
XAD-2010				
Sodium diethyldithiocarbamate	FAAS	Cr ⁶⁺	4.40	Bulut et al. (2007a, 2007b)
Sodium diethyldithiocarbamate	FAAS	Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Cd ²⁺ , Pb ²⁺	5.9, 6.0, 6.1, 6.3, 6.0, 5.7	Duran et al. (2007a, 2007b)

samples and rock samples. Ghasemi and Zolfonoun (2010) developed a new SPE method for the separation and preconcentration of trace amounts of U(VI), Th(IV) and Zr(IV) in water samples. The procedure is based on the adsorption of U(VI), Th(IV) and Zr(IV) ions on a column of Amberlite XAD-2000 resin loaded with α-benzoin oxime prior to their simultaneous spectrophotometric determination. The detection limits found for U(VI), Th(IV) and Zr(IV) were 0.50, 0.54, and 0.48 µg/L, respectively. Gundogdu et al. (2007) proposed a simple and sensitive system for simultaneous preconcentration of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and Cd(II) at trace level by FAAS. 8-Hydroxyquinoline chelates of Amberlite XAD-2010 packed in a column were used as sorbent. The detection limits, corresponding to three times the standard deviation of the blank, were found to be in the range of 0.10–0.40 µg/L. A new method using a column packed with Amberlite XAD-2010 resin as a solid-phase extractant was developed by Duran et al. (2007a, 2007b) for the multi-element preconcentration of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) ions, based on their complex formation with the sodium diethyldithiocarbamate (Na-DDTC) prior to FAAS determinations. The limits of detection (LOD) of the analytes were found in the range 0.08–0.26 µg/L.

6. Binding mechanism of metal ions onto modified Amberlite XAD

Amberlite XAD resin modified with organic ligands containing significantly different chemical donor functionalities (–N, –P, –O, –S) find increasing interest in sorption of heavy metal ions. Different types of ligands such as hydroxyl, carboxylic, sulphonic, phosphonic, azo and amine play an important role for donating the electron pair towards metal

ions. A schematic diagram is provided in Fig. 1 which shows the chelating sites for binding of metal ions. Although the interplay between electronic and steric properties has long been recognized as essential in determining the chemical or physical properties of a complex, the prediction remains very difficult because the considerable diversity encountered within different metal centers towards the same ligand or different ligand can completely modify the chemistry of a given metal. This has gained increased acceptance and been found to be very useful in explaining the properties of metal complexes and in the designing of new donor systems that can bestow the resulting complex with interesting and useful properties. Sorption behavior of chelating resin generally influences the solution conditions, nature of adsorbent adsorbate, size of adsorbent and adsorbate, charge of the adsorbate and adsorbent surface, pH and temperature of solution and so forth (Yang and Xing, 2010; Kumar and Ahmad, 2011). Different types of forces and interaction such as hydrogen bonding, electrostatic interaction, surface complexation and van der Waal forces, ion exchange, and so forth are responsible for the sorption of metal ions onto modified Amberlite XAD chelating resin. The carboxylic and phenolic are the major groups that participate in the sorption of metal ions by the proton exchange. Based on the electron donating nature of the oxygen containing groups in chelating resin and the electron accepting nature of metal ions, the ion exchange mechanism could be preferentially considered (Kumar et al., 2014; Liu et al., 2013).

7. Conclusion and future prospect

In the above mentioned works, the main focus has been the improvement in the important parameters, namely

preconcentration limits, preconcentration factors, sorption capacity, detection limits and so on. An estimation of the magnitude of error was done to validate the results. The enormous developments have revealed that the determination of metal ions can be approached in more than one way. The designing of the preconcentration procedure would depend on the sample, the matrix, and the concentration level at which the analysis needs to be carried out. The applicability of SPE method depends on the following important properties/parameters.

(1) Selectivity, i.e., the ability to extract the material of interest in preference to other interfering material; (2) *high distribution coefficient* to minimize the solvent-to-feed ratio; (3) *solute solubility*, which is usually related to polarity differences between the two phases; (4) *ability to recover the extracted material*. Thus the formation of emulsions and other deleterious events must be minimized; (5) *capacity*, the ability to load a high amount of solute per unit of solvent; (6) *nonreactive*. In some instances, such as ion exchange extractions, known reactivity in the extracting fluid is used. In addition to being nonreactive with the feed, the solvent should be nonreactive with the extraction system (e.g., noncorrosive) and should be stable; (7) *inexpensive*. Cost considerations should emphasize the energy costs of an extraction procedure, since, for a given extraction method, capital costs are relatively constant.

In this context, solid phase extraction represents a good method for the determination of metal ions in samples such as natural waters, foods and beverages. However, this method is not very favorable for biological fluids. In such specific cases, where sample volume is small, cloud point extractions could be useful. Again, conventional liquid–liquid extractions are normally avoided due to the extensive use of toxic solvents. Coprecipitation and precipitation procedures may lead to high preconcentration capacity, but are unfavorable because of the use of large amount of substances in the reaction medium. Electrochemical devices, when adopted in metal preconcentration, may offer sensibility and selectivity. Thus, matrices containing many potential interferents (for example, in seawater) can be satisfactorily analyzed by choosing the best electrodepositing potential. On-line systems are usually preferred due to the minimized number of steps, as well as for their lower sample and reagent consumptions. Flame atomic absorption and inductively coupled plasma optical emission spectrometers have found larger number of applications with on-line preconcentration systems, because of their continuous operation mode, in contrast to the GFAAS in which discontinuous heating program is involved.

The low solubility of complex-forming ligands and their ability to form complexes with a large number of metal cations, still offer a vast scope for developing new, more sensitive

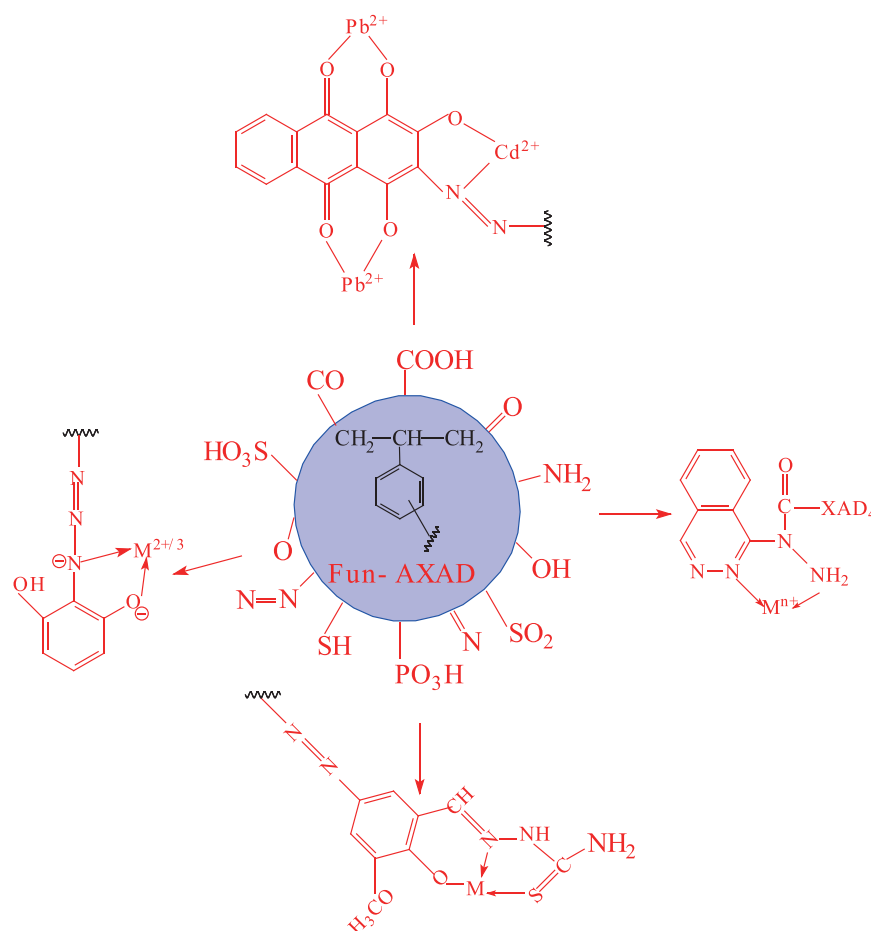


Fig. 1 – Co-ordination of heavy metals with the functionalized Amberlite XAD resins.

determination methods based on systems with multi-element detection, such as ICP-OES, ICP-MS, XRF and FAAS. Introduction of smaller and selective chelating resins would lead to better incorporation in terms of free steric hindrance and density, whereby increasing the sorption capacity of the modified resin that would lead to the improvement of other parameters, namely lower detection limit, preconcentration limit, and preconcentration factors. However, the key to the future prospects of SPE lies in adopting the emerging techniques pertaining to the fields of nanotechnology and detection technology (such as miniature laser sources and light detection techniques), which could be applied to highly sensitive and specific biological and chemical detection.

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