Synthesis, characterization, and systematic studies of a novel aluminum selective chelating resin

Aminul Islam · Noushi Zaidi · Hilal Ahmad · Sudesh Yadav

Abstract A procedure is detailed for the selective analysis of trace aluminum by flame atomic absorption spectrophotometer coupled with off-line column separation and preconcentration. Chelating resin was synthesized by covalent functionalization of Amberlite XAD-16 by 2-(2-hydroxyphenyl) benzoxazole. The modified resin was characterized using FT-IR spectroscopy, energy dispersive x-ray analysis, elemental analysis, thermogravimetric analysis/differential thermal analysis, and minimum energy run. The optimum sorption was at pH 9±0.1 with corresponding $t_{1/2}$ of only 7 min. Many competitive anions and cations studied did not interfere at all in the selective determination of Al(III), at the optimized conditions. The resin shows maximum sorption capacity of 21.58 mg g^{-1} and can be regenerated up to 75 cycles without any discernible capacity loss. The Langmuir isotherm model provides the better correlation of the experimental data ($r^2 = 0.999$) in comparison to Freundlich isotherm model, while the Scatchard analysis revealed homogeneous binding sites in the chelating resin. Analytical figures of merit were evaluated by accuracy (standard reference materials and recovery experiment), precision (RSD <5 %), and detection limit (2.8 μg L^{-1}). The applicability was demonstrated by analysis of trace aluminum in biological, environmental, and food samples.

Keywords Aluminum · Flame atomic absorption spectrophotometer · 2-(2-Hydroxyphenyl) benzoxazole · Solid phase extraction

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Introduction

Atomic absorption spectrometry (AAS) and inductively coupled plasma–mass spectrometry (ICP-MS) techniques have excellent analytical sensitivity and are the methods of choice for the determination of ultra-trace level elements in various matrices. However, it would be naive to assume that all laboratories that are required to perform trace level estimations are equipped with such sophisticated and expensive instruments. Further, direct determination of metal ions at trace levels by such sophisticated analytical techniques is limited, not only due to insufficient sensitivity but also to matrix interference. To overcome these difficulties, researchers have described various procedures for sample pretreatment. These include liquid–liquid extraction (Carasek 2000), solid-phase extraction (Silva et al. 2004), and cloud point extraction (Paleologos et al. 2005). The separation and preconcentration step is employed prior to the trace metal quantification, as adjuncts to such techniques.

Flame atomic absorption spectrophotometer (FAAS) has been widely used for its advantages of less spectral interferences by concomitants and relatively lower running costs when compared to expensive flameless more sophisticated techniques which are often more sensitive to interferences (Horng and Lin 1997; Ottaway and Pradhan 1973; Bergmann and Hardt 1979; Ejaz et al. 1981; Popova et al. 1991).

Solid-phase extraction offers the advantage of high sensitivity and versatility due to the possibility of performing a simultaneous enrichment step. Chelating resins are superior in selectivity to solvent extraction and ion exchange due to their triple functions (i.e., ion exchange, chelating ability, and physical adsorption) (Dutta and Das 2008). These materials are highly efficient in removing metal ions, and often provide the needed selectivity based on the chelating moiety with an easy on-demand release and reusability. Simple, rapid, and economic solid-phase extraction methods have been developed and applied successfully for the estimation of trace levels of some metal ions in different environmental and biological samples from researcher's laboratory (Islam et al. 2011a; Islam et al. 2012a; Islam et al. 2012b; Islam et al. 2011b; Islam et al. 2013a).

The continually improving technology for the extraction of aluminum from its biologically inert ores accelerates the exposure of non-essential biologically reactive aluminum to human ecology (Exley et al. 2009). Aluminum, which was previously considered benign, has been recently found to be a dementing ion and cause both bone and neurological disorders in humans. The potential toxicity of aluminum to humans and the environment has drawn the attention of many analysts in determination of very low aluminum concentrations (Erdemoglu et al. 2000; Neal et al. 2011; Matus and Kubova 2006).

Many 2-(2-hydroxyphenyl)-benzoxazole (HPB) complexes with aluminum (Hoveyda et al. 1993), gallium (Hoveyda et al. 1993), zinc (Henary and Fahrni 2002; Tian et al. 2008), copper (Zhang et al. 2006), and lithium (Qin et al. 2001) have been investigated so far in aqueous phase. According to the best of our literature knowledge, metal ions complexation with HPB in solid-phase extraction has never been reported. Herein, we report the synthesis and application of a novel aluminum-selective chelating resin by immobilizing HPB on Amberlite XAD-16 through covalent bonding, which tends to be more chemically stable to acidic eluents than those resins prepared by impregnation. This XAD-HPB resin was then characterized and systematically explored for its application in the separation/preconcentration of aluminum, in real samples. The comparative sorption of aluminum on a novel HPB chelating resin with other solid-phase extractants including XAD-GBH (Islam et al. 2013b) (synthesized in our laboratory) is also reported, wherever required.

Experimental

Chemicals

All chemicals used were of analytical reagent grade (Merck, Mumbai, India). All metal salts were procured from Merck (Mumbai, India) and were standardized by complexometric titration method (Welcher 1958). Working solutions were prepared on a daily basis through serial dilutions of the stock solution with triply distilled water prior to use. The buffer solutions used were hydrochloric acid–glycine, acetic acid–sodium acetate, sodium biphosphate–citric acid, and ammonia–ammonium chloride (Merck, India) for the pH 2.0–3.6, 4.0–5.6, 7.0–7.8, and 8.0–10.0, respectively. Amberlite XAD-16 (particle size 20–60, pore size 100 A°, pore volume 1.82 mL g^{-1}, and surface area 900 m^2 g^{-1}) and HPB were procured from Sigma-Aldrich (Steinem, Germany) and Otto Chemicals Pvt. Ltd. (Mumbai, India), respectively. Standard reference materials (SRMs) were obtained from the National Institute of Environmental Studies (NIES) (Ibaraki, Japan) and National Bureau of Standards (NBS), Department of Commerce (Washington, DC, USA).

Apparatus

A flame AAS (M series, Thermo Electron Corporation, Cambridge, UK) equipped with double beam optics and dual Zeeman correction (conditions for Al: a nitrous oxide-acetylene flame; wavelength, 309.3 nm; lamp current, 100 mA; band pass, 0.5 nm; burner height, 11 mm; and fuel flow rate, 4.3 L min^{-1}) was used for determining metal concentration. For batch studies, a thermostated mechanical shaker (NSW-133, New Delhi, India) was used. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were done on a Shimadzu TGA/DTA simultaneous measuring instrument (DTG-60/60H, Kyoto, Japan). Elemental (CHN) analysis was carried out on an organic elemental analyzer (Flash EA 1112, Thermo Fischer Scientific).

Energy dispersive X-ray analysis (EDAX) was done on a Jeol JSM 6510LV (Japan). A column (1×10 cm), for dynamic studies, was obtained from J-SIL Scientific Industries (Agra, India).

Synthesis of chelating resin XAD-HPB

Five grams of oven-dried AXAD-16 was pretreated with an ethanol–hydrochloric acid–water (2:1:1) solution overnight and then rinsed with triply distilled water until the supernatant liquid became neutral to assure the complete absence of impurities. The modification of the pretreated resin was done by initial nitration and then subsequent amination (by refluxing for 12 h in a reducing mixture containing 40 g of $SnCl_2$, 45 mL of concentrated HCl, and 50 mL of ethanol). The amino compound obtained was washed thoroughly with 2 mol L^{-1} NaOH and then with 4 mol L^{-1} HCl in order to remove the excess $SnCl_2$. Diazotization of the product was done according to the recommended procedure (Saxena and Singh 1997). After amination, the subsequent steps were carried out at a temperature of 0 to 5 (±0.2)°C in order to prevent the degradation of the intermediates. The diazotized product was rapidly filtered off, washed with cold distilled water until neutral, and then subjected to a coupling reaction by treating it with a solution of HPB (2.5 g) in 10 % NaOH mixed with ethanol at a temperature as low as 0 to 5 (±0.2)°C over a period of 24 h. The reddish brown resin was filtered off and thoroughly washed with 2 mol L^{-1} HCl and distilled water until pH 7. Finally, the resin was dried at 50 (±0.2)°C and kept in a desiccator for further use. The synthetic scheme is shown in Fig. 1.

Characterization of XAD-HPB

The resin was characterized on the basis of elemental, IR and EDAX analysis, thermal, and chemical studies.

Thermal and chemical stability

The thermal stability of the resin was studied by TGA and DTA analysis. Chemical stability was established by determining the sorption capacity after soaking the resin sets of same amount in 25 mL of acid (1–7 mol L^{-1} HCl and HNO_3) and alkaline solution (1–5 mol L^{-1} NaOH) for 48 h. The resin was found to withstand several sample injection/elution cycles without discernible loss of performance.
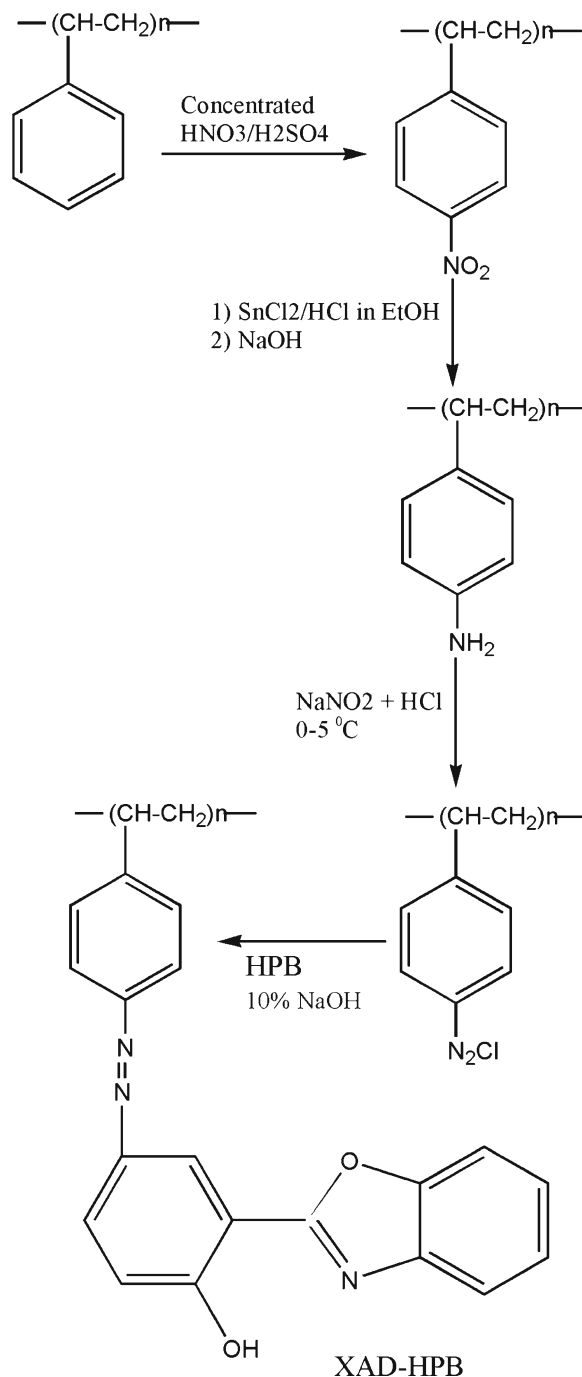

Fig. 1 Immobilization of HPB ligand on Amberlite XAD-16

Water regain value and hydrogen ion capacity

The water regain capacity was calculated as mentioned in an earlier work (Islam et al. 2010a). For hydrogen ion capacity, exactly 0.5 g resin was treated with
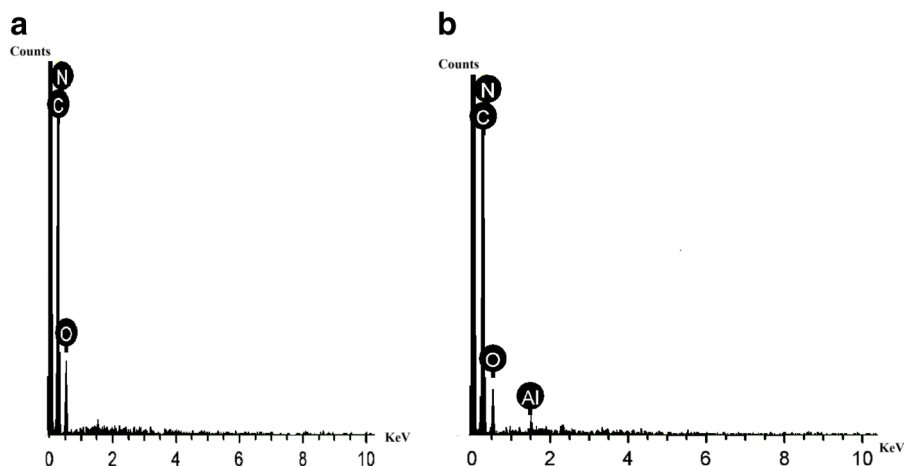
Fig. 2 EDAX spectra showing elemental analysis for the selected area in SEM picture. **a** EDAX spectra of XAD-HPB. **b** EDAX spectra of XAD-HPB complexed with aluminum

4.0 mol L^{-1} HCl filtered off, washed thoroughly with distilled water, and dried at 100 °C for 6 h. The resin in acidic form was equilibrated with 20 mL of 0.1 mol L^{-1} NaOH solutions for 6 h and the excess alkali was estimated with 0.1 mol L^{-1} HCl.

Sample preparation

Fruit juice (3×500 mL), peritoneal dialysis fluid (2× 2,000 mL), and packaged drinking water (3× 1,000 mL) of different batches were collected from the local market of Aligarh, India. The tap water sample was collected from the university campus. The required volume of each sample after mixing all the contents was then pretreated prior to their application to the SPE procedures. The water samples and dialysis fluid (500 mL each) were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size while the fruit juice (500 mL) sample was digested by wet oxidation with 5 mL of conc. HNO_3, $HClO_4$, and 2 mL of 30 % H_2O_2. The residue was dissolved in 5 mL of 0.5 M HNO_3 and finally made up to 50 mL with triply distilled water at the working pH. The sample solutions of 2,000 and 55 mg of rice flour-unpolished NIES-10(a) and citrus leaves NBS-1572, respectively, were similarly prepared as reported in earlier work (Islam et al. 2010b).

Recommended procedure

Batch method

Batch experiments were conducted by equilibrating 50.0 mL of metal solution of suitable concentration at constant pH with 0.1 g XAD-HPB in an Erlenmeyer flask stirred for 3 h at 27±0.2 °C. The metal ions were
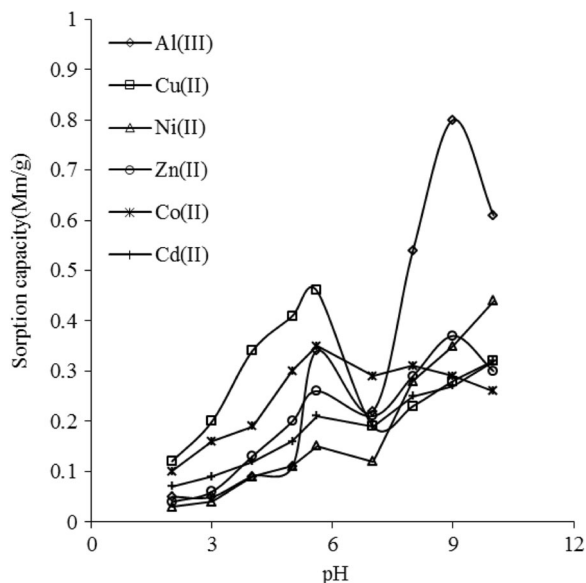

Fig. 3 Dependence of sorption capacity on the pH of the solution. (Experimental conditions: sample volume 50 mL, metal ion 100 μg mL^{-1}, resin amount 0.1 g)

desorbed by shaking with the appropriate eluting agents and measured by FAAS.

Column method

A total of 0.3 g chelating resin was filled into a glass column (10 cm×1.0 cm) fitted with porous disk. Before use, the column was treated with 10 mL of 2.0 mol L^{-1} HNO_3 solutions and washed with double distilled water until the resin was free from acid. Then, the column was preconditioned to the desired pH with buffer solution. The sample solution was permitted to flow through the column under gravity at set optimum conditions. The column was then rinsed thoroughly by triply distilled water. The metal ions were stripped off from the resin bed by using a set volume of eluent and determined by FAAS.

Result and discussion

Characterization of XAD-HPB

The TGA/DTA curve depicted that thermally the degradation of the functionalized resin commences from 270 °C; above which an exothermic peak (at 380 °C) indicating a weight loss of 51 % was observed (Online Resource 1 and 2). The chemical stability was established up to 5 mol L^{-1} of mineral acids and alkali. The water regain capacity was calculated to be 21.63 mM g^{-1} reflecting the high hydrophilic character of the resin which is excellent for column operation (Islam et al. 2010a). The results of elemental analysis of nitrated, aminated (Online Resource 3), and reagent-coupled resin (Online Resource 4) were (C, 67.7; H, 5.9; N, 4.6 %),
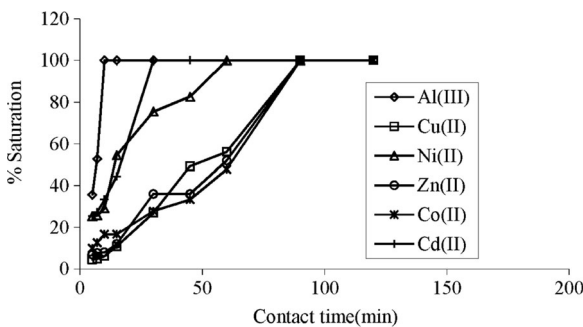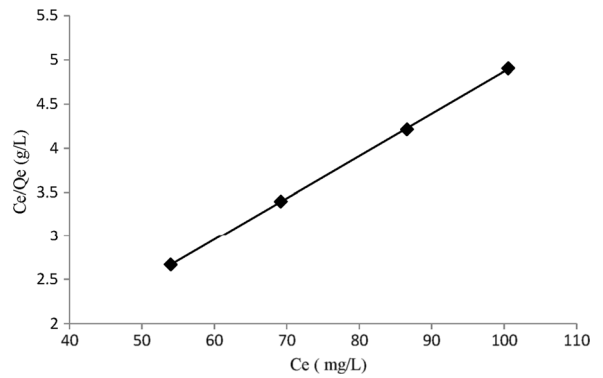
Fig. 5 Langmuir sorption isotherm for Al(III) on XAD-HPB

(C, 58.9; H, 4.6; N, 4.0 %), and (C, 73.2; H, 5.9; N, 4.0 %), respectively. The relative nitrogen percent calculated on comparing theoretical and experimental CHN data resulted in 83, 74, and 45 % efficient conversion for the subsequent steps depicted in Fig. 1, respectively. This inferred that there was an incorporation of one group or reagent molecule per two monomer units. The overall hydrogen ion capacity amounts to 1.7 mM g^{-1} of resin. This affirmed the incorporation of 0.85 mM reagent g^{-1} resin, taking into account that 1 mol of reagent is equivalent to 2 mol of replaceable hydrogen ions. To validate the proper synthesis, IR spectra of nitrated (Online Resource 5), aminated (Online Resource 6), and HPB-functionalized AXAD-16 (Online Resource 7) were compared. A peak at 3,380 cm^{-1} due to –N–H– stretch was observed only in aminated AXAD-16 and was absent in both nitrated and HPB-functionalized AXAD-16. The HPB-functionalized AXAD-16 gave visible peaks at 1,450, 1,708, and 3,417 cm^{-1} in the IR spectrum,
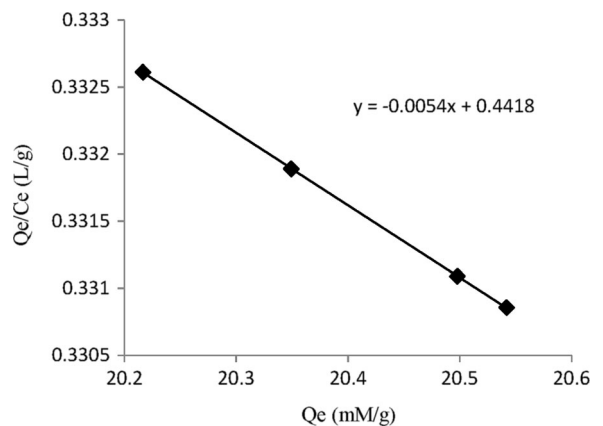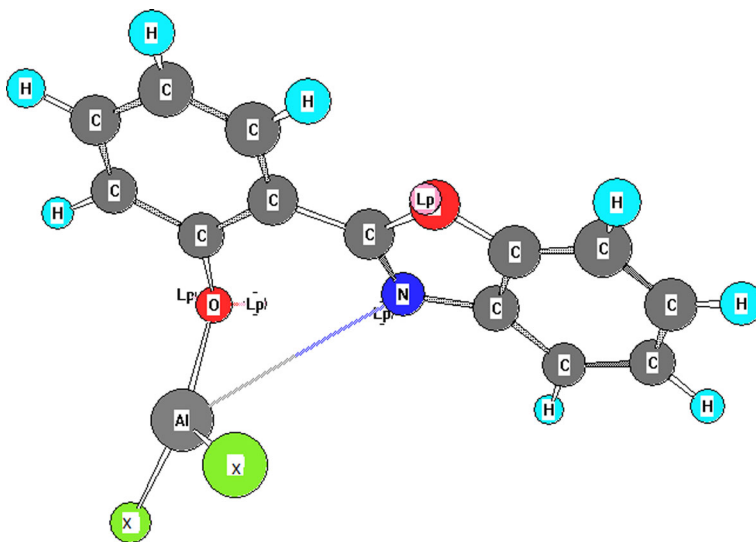
Fig. 4 Sorption kinetics for Al(III) complexation on XAD-HPB

Fig. 6 Scatchard plot for Al(III) on XAD-HPB

Fig. 7 CS Chem 3D ultra model of Al(III) complexation on XAD-HPB

which were ascribed to –N=N–, –C=N–, and phenolic –OH group, respectively, whereas non-functionalized AXAD-16 did not offer any such peaks. Complexation of Al(III) with the synthesized chelating resin was analyzed by EDAX in the range of 0–20 keV. The absence and presence of Al(III) in uncomplexed and complexed XAD-HPB was confirmed by the observations depicted in panels a and b of Fig. 2, respectively.

Optimization studies on the Al(III) ion uptake

Effect of loading solution pH

The effect of pH on the sorption showed that the maximum uptake of Al(III) occurs at pH 9±0.1 (Fig. 3). This is attributed to the involvement of –O⁻ in chelate formation with the Al(III) as a result of the deprotonation of phenol moiety of the reagent (Pearson 1968; Pearson 1963), and to the competition between the hydrogen and

aluminum ions on the sorption sites, at low pH (Abdelwahab 2007). For subsequent experiments, pH 9±0.1 was selected as the working pH.

Effect of contact time

The contact time of the sorption reaction are one of the important characteristic in defining Al(III) sorption. The results indicated that the solid-phase extraction is very rapid for the highly hydrophilic XAD-HPB: $t_{1/2}$ of merely 7 min (Fig. 4). The fast sorption kinetics is an obvious advantage for the preconcentration studies; a time of 10 min (100 % saturation) was then set in all further experiments.

Sample flow rate and desorption of Al(III) ions

High sample flow rate is desirable to achieve the highest preconcentration factor in the shortest time. Observations indicated that metal retention on the

Table 1 The effect of sample volume on the sorption of Al(III) ion (amount of Al(III)—3 μg; eluent volume—5 mL)

Sample volume (mL)	Preconcentration limit (μg L^{-1})	Preconcentration factor	Recovery (%)
300	10.0	60	100.2
600	5.0	120	100.1
900	3.3	180	103.3
1,100	2.7	220	100.1
1,200	2.5	240	98.3

resin was optimum at a flow rate of 5 mL min^{-1}. In the elution studies, >98 % recovery of the sorbed metals from the resin could be achieved at a flow rate of 2 mL min^{-1}. The percent recovery for aluminum by using 5 mL each of 2 M HCl, 2 M HNO$_3$, and 2 M H$_2$SO$_4$ were found to be 98.9±1, 72±3, and 68±2, respectively. In consequence, the sorption flow rate of 5 mL min^{-1}, the elution flow rate of 2 mL min^{-1}, and 5.0 mL of 2 M HCl as eluent were set in all further dynamic operations.

Physical studies

Langmuir and Freundlich sorption isotherm equilibrium models were used for the analysis of the present sorption system (Langmuir 1918). The Langmuir sorption isotherm model, to evaluate the monolayer sorption phenomena, is depicted in the equation.

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_b} + \frac{C_e}{q_m} \qquad (1)$$

where q_e is the analyte uptake per unit weight of sorbent (mg g^{-1}), C_e is the concentration of analyte in aqueous phase at equilibrium (mg L^{-1}), and q_m and K_b are Langmuir constants related to the sorption capacity and sorption energy, respectively. The constants can be evaluated from the intercept and the slope of the linear plots of C_e/q_e vs. C_e (Fig. 5). The experimental data shows a straight line with a good correlation coefficient ($r^2=0.999$) indicating the applicability of the model for the present sorption. The essential characteristics of the Langmuir isotherm can be expressed in terms of either a dimensionless constant separation factor or equilibrium parameter

$$R_L = \frac{1}{1 + K_b \cdot C_o} \qquad (2)$$

Where R_L is a dimensionless separation factor, C_0 is the initial analyte concentration (mg L^{-1}), and K_b is the Langmuir constant (L mg^{-1}). The calculated R_L values ($0 < R_L > 1$) indicate the favorable sorption of Al(III) onto XAD-HPB. The linear Freundlich equation is

$$\ln q_e = \ln k + \frac{1}{n} \cdot \ln C_e \qquad (3)$$

Where k and n are Freundlich constants indicating the sorption capacity and intensity, respectively. Theoretical linear plots, $\ln q_e$ vs $\ln C_e$ with low

Table 2 Effect of interfering ions on the recovery of Al(III) (resin amount 300 mg, sample volume 100 mL, amount of Al(III) loaded 5 μg, $N=3$)

Interfering ions	Added as	Amount added ($\times 10^3$ μg)	Al(III) Recovery (%)	RSD
Na$^+$	NaCl	500.0	100.43	1.15
		1,000.0	100.37	1.53
K$^+$	KCl	100.0	100.47	0.76
		200.0	100.10	0.85
Ca^{++}	CaCl$_2$	50.0	100.43	1.65
		100.0	97.27	0.87
Mg^{++}	MgCl$_2$	50.0	100.33	1.42
		100.0	100.03	0.85
Cr^{3+}	CrCl$_3$	0.125	100.06	0.64
Co^{2+}	Co(NO$_3$)$_2$	0.125	100.00	0.60
Mn^{2+}	Mn(NO$_3$)$_2$	0.125	100.00	0.90
Ni^{2+}	Ni(NO$_3$)$_2$	0.125	99.98	0.75
Cu^{2+}	Cu(NO$_3$)$_2$	0.125	100.04	0.84
Zn^{2+}	ZnCl$_2$	0.125	99.97	0.73
Pb^{2+}	Pb(NO$_3$)$_2$	0.125	100.06	0.64
Cl$^-$	NaCl	750.0	100.03	0.85
		1,500.0	99.70	1.60
Br$^-$	NaBr	25.0	100.00	0.40
		50.0	98.60	0.73
I$^-$	NaI	25.0	100.10	0.70
		50.0	100.20	1.06
F$^-$	NaF	25.0	100.80	1.88
		50.0	97.50	1.80
PO$_4^{---}$	Na$_2$HPO$_4$	5.0	98.33	2.72
		10.0	97.60	1.08
SO$_4^-$	Na$_2$SO$_4$	50.0	96.43	1.38
		100.0	95.87	0.42
CO$_3^-$	Na$_2$CO$_3$	50.0	96.90	0.98
		100.0	98.53	2.78
C$_2$O$_4^-$	Na$_2$C$_2$O$_4$	25.0	100.00	0.72
		50.0	99.80	0.87
CH$_3$COO$^-$	CH$_3$COONa	50.0	99.47	1.39
		100.0	99.80	0.70
C$_6$H$_5$O$_7^{---}$	Na$_3$C$_6$H$_5$O$_7$	5.0	98.87	1.44
		12.5	99.10	1.53
C$_4$H$_4$O$_6^-$	Na$_2$C$_4$H$_4$O$_6$	5.0	99.67	0.88
		12.5	97.87	0.66

correlation coefficient ($r^2=0.884$) indicates the non-applicability of Freundlich sorption isotherm (Online Resource 8).

Table 3 Validation of proposed separation/preconcentration method by analysis of SRMs for Al concentration

SRM	Certified value ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)± standard deviation	Calculated Student's t value[b]
Rice flour NIES 10(a)[c]	3.0	2.92±0.08	1.69
Citrus leaves NBS-1572[d]	92±15	90.77±1.59	1.34

[a] $N=3$

[b] At 95 % confidence level

[c] Al as minor component

[d] Al as major component

The Scatchard plot analysis is also used to investigate the sorption process and nature of binding sites in solid phase. The Scatchard equation is represented as (Gezici et al. 2007)

$$\frac{q_e}{C_e} = q_m K_b - q_e K_b \qquad (4)$$

where q_m and K_b are the sorption isotherm parameters related to the slope and intercept of q_e/C_e vs q_e (Fig. 6). The type of the interactions of analyte with sorbent is related to the shape of the Scatchard plot. The presence of a deviation from linearity on a plot based on Scatchard analysis usually points to the presence of more than one type of the binding sites, while the linearity of the Scatchard plot observed here indicated that the binding sites are identical and independent. The coordination mode shown in Fig. 1 was further explored by running MM2 of CS Chem 3D Ultra 7.0.0 software for the minimum energy run (7.9) of aluminum ligand complex (Fig. 7).

Preconcentration and recovery of metal ions

For the determination of trace elements in large volume of real samples, the analyte should be preconcentrated in smaller volume. Preconcentration improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results, offers a high degree of selectivity, and facilitates calibration (Mizuike 1983; Pyrzynska and Trojanowicz 1999). Under optimized conditions, the preconcentrating ability of the chelating resin along with lower limit of quantification was investigated by diluting the aluminum ion solution and keeping the total amount of loaded metal at 3 μg. Table 1 reflects the preconcentration ability of XAD-HPB with the highest preconcentration factor of 240 when the final volume was 5 mL, thus indicating the resin's ability to extract analyte quantitatively even from large sample volumes. The detection limit and limit of quantification evaluated as 3 s and 10s (Long and Winefordner 1983) of the

Table 4 Determination of Al(III) in spiked real samples after column preconcentration (resin amount 300 mg, sample volume 500 mL) on XAD-HPB by FAAS

Samples	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)	RSD
PDW[a]	0	23.15	–	3.97
	4	27.02	96.74	3.62
	10	33.00	98.54	2.91
Tap water	0	35.46	–	2.93
	4	39.44	99.35	2.77
	10	45.31	98.45	2.92
Fruit juice	0	588.31	–	0.55
	10	598.05	97.39	0.51
	20	607.94	98.14	0.49
Dialysis fluid	0	25.01	–	3.84
	4	29.04	100.66	3.58
	10	34.99	99.76	3.86

[a] Packaged drinking water

Table 5 Summary of some previous solid phase extraction studies about aluminum

Adsorbent	Complexing media	pH	Capacity (mg g^{-1})	PF	DL (µg L^{-1})	RSD	References
AXAD-16	HPB	9	21.58±0.24	220	2.8	<5	Present work
Vinyl polymer gel	8-Hydroxy quinoline	5–5.5	–	–	0.004	–	Resing and Measures (1994)
AG l-X8	Chromotrope 2B	7	–	–	10	10.7	Martin-Esteban et al. (1995)
8-Q-CPG	8-Quinolinol	9.3	–	–	15.40	4	Yuan and Shuttler (1995)
XAD-4	Salicylic acid	4	4.4±0.3	–	–	–	Boudenne et al. (2002)
XAD-7	8-Hydroxy quinoline	8.5	–	50	0.23	2.4	Sombra et al. (2000)
Controlled-pore glass	8-Hydroxy quinoline	10	–	76	3.00	<10	Mohammad et al. (1992)
Activated carbon	Cupferron	5	–	150	–	–	Yaman (2001)
Chelex-100	–	7–8	–	–	2.22	–	Pesavento et al. (2003)
Silica gel	8-Hydroxy quinoline	5–8	–	–	0.2	4.2	Chen et al. (2004)
201×8 anion exchange resin	Tiron	4–6	5.6	20	0.3	<10	Luo and Bi (2003)
AXAD-16	GBH	9	24.28±0.24	300	1.3	<5	Islam et al. (2013b)

mean blank absorbance for 20 replicate measurements (100 mL each), after preconcentration were 2.8 (absorbance=−0.0017) and 9.2 µg L^{-1}, respectively. The enhanced lower limit of aluminum detection value indicates the high sensitivity of the developed method.

Interference

The preconcentration procedures can be substantially affected by various potential concomitants through precipitate formation, redox reactions, or competing complexation reactions, either of interferent anions with the analyte metal ion or of the metal ions in matrix with the sorbent. The aluminum preconcentration was not significantly affected by the most common matrix anions and even in the presence of alkali and alkaline earth metals and few other investigated metal cations (Table 2). This unique selectivity of XAD-HPB towards Al(III), at the optimized conditions, can be interpreted in terms of the smaller ionic radius and higher charge density of the Al(III). The smaller radius of the Al(III) permits suitable coordination geometry for the chelating resin and the larger charge density allows strong coordination ability between XAD-HPB and Al(III).

Analytical figures of merit

The bias of the outlined separation/preconcentration method was estimated by the analysis of trace amount of Al(III) present as major and minor component in studied SRMs. The mean concentration values for Al(III) obtained by the proposed method (Table 3) were statistically insignificant from the certified values indicating absence of systematic method errors. The method also had good precision for the analysis of trace Al(III) in sample solutions, as the coefficient of variation for five replicate measurements of 5 µg of Al in 100 mL was <5 %. The calibration curve with the regression equation and correlation coefficient (r^2) for Al(III) determination, after SPE, obtained by the method of least squares, was $A=0.0043C+0.0001$ ($r^2>0.99$), where A is the absorbance and C is the metal ion concentration (mg L^{-1}). The linearity of the calibration curve is apparent from the correlation coefficient (r^2) which lies well above 0.99.

Application of the method

The preconcentration factor of the presented Al(III) separation/preconcentration is superior in comparison to various matrices shown in Table 5. The samples were analyzed at optimized conditions followed by subsequent determination of eluent in FAAS. To rule out the presence of constant errors, by varying the sample size, the proposed method was applied to the determination of Al(III) in the pretreated sample solutions spiked with known amount of Al(III) in 500 mL of sample solution. Table 4 attested the applicability of the procedure for aluminum determination with good recovery (>95 %).

Conclusion

In this article, HPB-functionalized AXAD-16 chelating resin was synthesized by a simple procedure and was employed as a selective solid-phase extraction material for separation/preconcentration of aluminum in real samples prior to its determination by flame atomic absorption spectrophotometer (Table 5). A brief description of characteristics of the synthesized chelating resin followed by description of application in the selected pretreated real samples is reported. The prepared sorbent offered a fast kinetics for the sorption and desorption of aluminum. The resin could be recycled many times (75 cycles) without affecting its sorption capacity of 21.58 mg g^{-1}. The elution was easily achieved using 5.0 mL of 2 M HCl. Under the optimized conditions, the presence of the major matrix anions and alkali and alkaline earth metals ions did not interfere with the analysis even when interferent cations (Co^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, and Zn^{2+}) are 25 times the analyte concentration and, therefore, it was concluded that this analysis could be considered as aluminum selective at optimized condition. The detection limit of 2.8 μg L^{-1} with the relative standard deviation of less than 5 % ($C=0.05$ μg mL^{-1}, $n=5$) for aluminum was obtained. To validate the proposed method, certified reference materials were analyzed and the determined values were in a good agreement with the certified values. The developed method offers rapidity, selectivity, sensitivity with high preconcentration factor, and good analyte recovery (>95 %).

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