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Preconcentration and determination of aluminum in water samples by inductively coupled plasma-atomic emission spectroscopy with brilliant green-based anion-exchange solid-phase extraction support

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ABSTRACT

A new chelating resin is produced by coupling a dye brilliant green to Amberlite XAD-2 through an azo spacer. The resulting resin has been characterized by FT-IR, elemental analysis, thermogravimetric analysis, and scanning electron microscopy and studied for the preconcentration and determination of trace Al(III) from solution samples. The optimum pH value for sorption of the aluminate ions was nine. The sorption capacity of functionalized resin is 10.8 mg g^{-1}. A recovery of 94% was obtained for Al(III) when eluted with 0.5 M nitric acid. The equilibrium data of Al(III) adsorption on modified resin were analyzed using Langmuir, Freundlich, and Temkin models. The method was applied for Al(III) assay in environmental samples.

Keywords: Solid phase extraction; BG-Amberlite XAD-2; Immobilization; Isotherm study; Preconcentration

1. Introduction

Aluminum is the third most abundant element in the Earth's crust (8.1% by mass), and is a non-essential element to which humans are frequently exposed [1]. Some studies suggested that Al(III) may be accumulated in the brain via different routes (drinking water, food, and pharmaceutical formulations) and may interfere with the normal activities of the nervous system [2]. Since Al(III) affects humans negatively, determination of low levels of Al(III) in environmental samples has become an important issue. Different techniques for Al(III) preconcentration prior to analysis, such as liquid-liquid extraction [3], single-drop micro extraction [4], solid-phase extraction [5], have been described in the literature. Often Amberlite XAD series (styrene-divinylbenzene copolymer) are used as solid supports and modified with different ligands [6,7]. The merits of Amberlite XAD supports are good physical and chemical properties such as porosity, high surface area available for ligand coupling, durability and purity [8–10].

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Brilliant green (BG) is a cationic dye used as a biological stain [11,12] in veterinary medicine [11], as an additive to poultry feed to inhibit propagation of mold [11,13], intestinal parasites, and fungus [14]. Recently, it has been used as a ligand for grafting on different supports intended for the separation of uranyl ions [15] and for the preconcentration of mercury ions [16].

The goal of the present work is preconcentration—determination of trace amounts of Al(III) from environmental water samples using BG-Amberlite XAD-2 sorbent. The influences of some adsorption parameters including pH and contact time on the quantitative recoveries of the Al(III) were investigated. Trace Al(III) is retained by BG-Amberlite XAD-2 and then eluted with 0.1 M nitric acid prior to determination by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The method developed has good accuracy, providing high recovery and a high preconcentration factor for Al(III).

2. Experimental

2.1. Instruments

ICP-AES Varian, Vista-pro (Salt lake city, Australia); infrared spectra, Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland); Elemental analysis, Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer; thermogravimetric analysis (TGA), TGA-50H (Shimadzu Corporation, Kyoto, Japan) and the SEM micrographs were obtained on a SEM-PHILIPS XL30 scanning electron microscopy.

2.2. Reagents and solutions

All chemical compounds were products of Merck (Darmstadt, Germany). Amberlite XAD-2 resin (surface area 745 $m^2\ g^{-1}$, pore diameter 5 nm, and bead size 0.3–1.0 meshes) was obtained from Serva (Heidelberg, New York).

2.3. Synthesis of BG-functionalized Amberlite XAD-2 resin

Amberlite XAD-2 beads (5 g) were treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4; the mixture was stirred at 60°C for 1 h in an oil bath. The suspension was then poured into 150 mL ice cold water. Subsequently, the resin was filtered, washed repeatedly with distilled water, and then treated with a mixture of 40 g of $SnCl_2$, 45 mL of concentrated HCl, and 50 mL of ethanol. The mixture was refluxed for 12 h at 90°C, to reduce the nitrated form of the resin. The resin was then filtered and washed with distilled water and 2 M NaOH, so as to get the free amino polymer. The amino polymer was treated with 100 mL of 2 M HCl for 30 min and washed with distilled water to remove the excess of HCl. The polymer was then suspended in 150 mL ice cold water and mixed with 1 mL aliquots of diazotizing mixture (1 M HCl and 1 M $NaNO_2$) under constant stirring until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was then filtered, washed with ice cold water, and treated with 0.06 M BG solution and stored for 40 h at 0–3°C. The resulting resin which appeared as green-colored beads was finally filtered and washed with distilled water and dried in air.

2.4. Batch method

A sample solution of 50 mL containing 0.5 $\mu g\ mL^{-1}$ of Al(III) and 10 mL of 0.1 M potassium iodide was taken in a glass-stoppered bottle and the pH was adjusted to the required value. BG-Amberlite XAD-2 (0.05 g) was added to the bottle and the mixture was shaken for the required time. The resin was filtered, and adsorbed Al(III) was eluted with 0.5 M nitric acid (10 mL). The Al(III) concentration in the eluate was determined using ICP-AES.

3. Results and discussion

3.1. Characterization of modified Amberlite

The comparison of FTIR spectra of BG-Amberlite XAD-2 with that of parent Amberlite XAD-2 indicate two additional bands at 1,622 and 1,372 cm^{-1} which appear to originate due to the groups N=N, C=C, and CH_3, respectively. There is an additional band at 1,706–1,717 cm^{-1} corresponding C=N vibration in the molecular structure of the ligand. The elemental analysis of BG-Amberlite XAD-2 (found: C, 91.10, H, 7.70; N: 3.02%, calculated for $(C_8H_7)14\ C_{27}H_{36}\ N_4$: C, 89.77; H, 7.21; N, 3.02%) shows that on average one BG molecule is present for each 14 repeated units of the monomer.

TGA of BG-Amberlite XAD-2 showed two-step weight loss up to 510°C. The weight loss up to 130°C was due to desorption of polymer bound water. The major weight loss after 290°C was due to the detachment of chemically immobilized moiety from the polymeric matrix.

The surface morphology and internal structure of polymer beads were investigated by SEM (Fig. 1). As

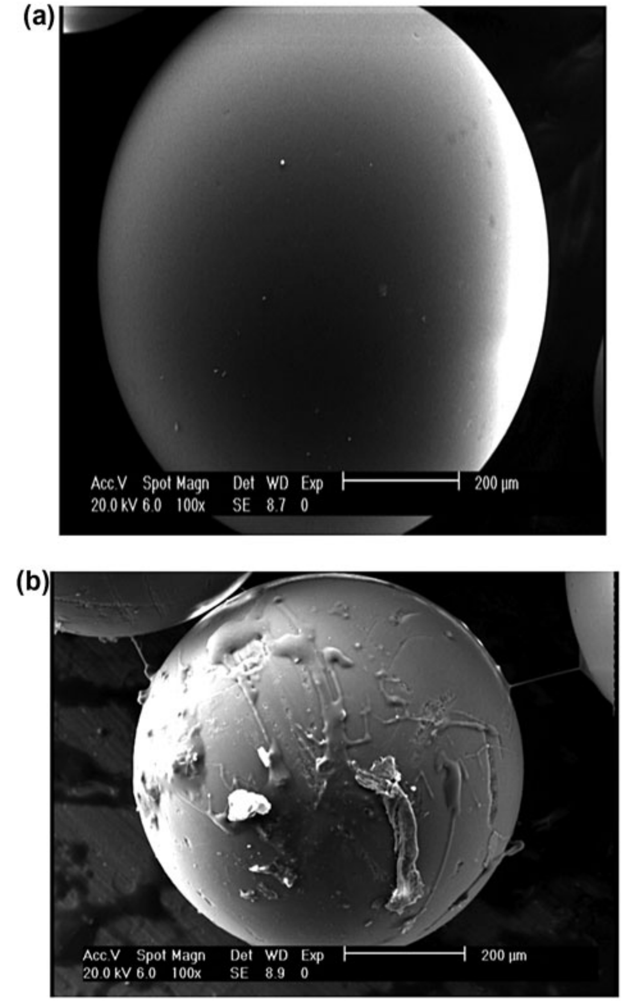

Fig. 1. SEM photograph of Amberlite XAD-2 (a) and BG-Amberlite XAD-2 (b).

clearly seen here, Amberlite XAD-2 is comprised of homogeneous and smooth small particles. In comparison with the unmodified Amberlite, surface of the modified resin was more coarse and grooved, most probably due to partial matrix degradation during the harsh chemical treatment used for BG immobilization.

3.2. Al(III) sorption by BG-Amberlite XAD-2

The degree of Al(III) sorption at different pH values was determined by batch equilibration technique (Fig. 2). The maximum adsorption of 94% was achieved at pH 9, where Al(III) exist mainly as aluminate ions. At moderate acidic pH values, there is another albeit less maximum in the Al(III) adsorption. Probably at these pH values, the immobilized ligand may act as chelating agent adsorbing cationic forms of Al(III) in solution. The extraction recovery was defined as the percentage of the total Al(III) which was extracted into the solid phase and subsequently into eluent.

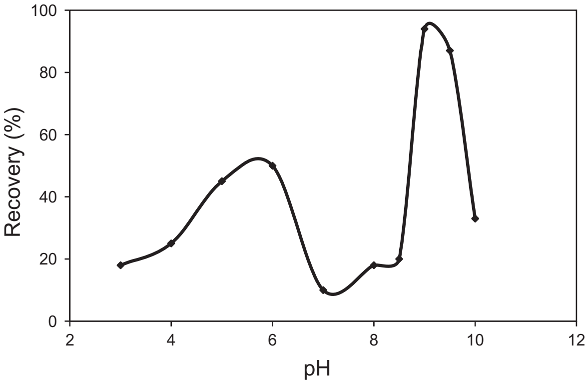

Fig. 2. Effect of pH sorption of Al(III) onto BG-Amberlite XAD-2. Volume of each 50 mL containing 0.5 μg mL^{-1} of Al(III) and 10 mL of 0.1 M potassium iodide. Their pH values were adjusted with buffer solutions. The 0.05 g of BG-Amberlite XAD-2 was added to each solution and the mixture was shaken for 30 min. The adsorbed Al(III) was eluted with 10 mL 0.5 M nitric acid.

The sorption capacity was around 10 mg g^{-1} at Al(III) concentrations of 100 μg mL^{-1} (Fig. 3). The profile of Al(III) uptake by the resin reflects good accessibility of the anion exchanging sites in the resin. Less than 5 min was sufficient for maximal adsorption (Fig. 4). Nitric acid at 0.5 M provided the best recovery (94%) of bound Al(III). The Al(III) was adsorbed and desorbed on the BG-Amberlite XAD-2 several times. It was found that sorption capacity of BG-Amberlite XAD-2 after five cycles of its equilibration with Al(III), changes less than 10%. Therefore, repeated use

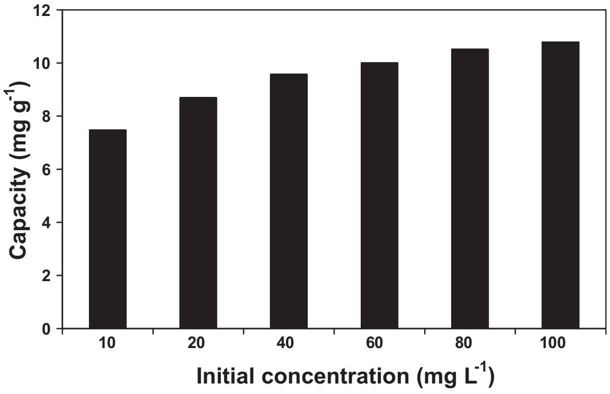

Fig. 3. Effect of initial concentration of the aluminum in the solution on sorption capacity of Al(III) onto BG-Amberlite XAD-2.

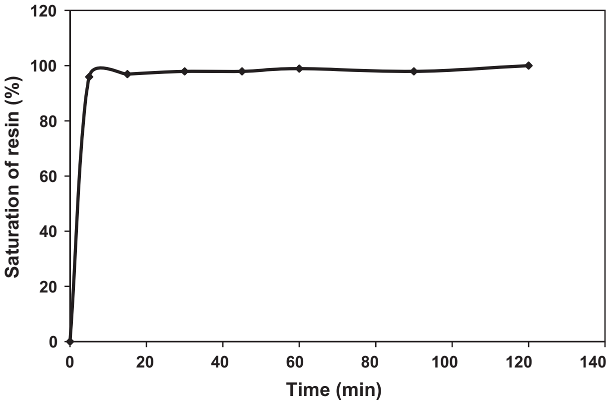

Fig. 4. Kinetics of aluminum sorption on BG-Amberlite XAD-2. Volume of each 50 mL containing 60 μg mL^{-1} of Al(III) and 10 mL of 0.1 M potassium iodide. The 0.05 g of BG-Amberlite XAD-2 was added to each solution and the mixture was shaken for different lengths of time at pH 9.

of the BG-Amberlite XAD-2 is feasible. The BG-Amberlite XAD-2 after loading it with samples can be readily regenerated with nitric acid 1 M.

3.3. Adsorption isotherms

The Langmuir equation was given in the following form [17]:

$$C_e/q_e = (1/q_{\max}.K_L) + (C_e/q_{\max}) \tag{1}$$

where q_e (mg g^{-1}) is the amount of Al(III) at equilibrium, C_e (mg L^{-1}) is the liquid phase concentrations of Al(III) at equilibrium, $q_{\max}$ is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}). Good fitting of experimental data by Langmuir isotherm indicates the homogeneous nature of Al(III)-binding sites on BG-Amberlite XAD-2 resin (Table 1).

The Freundlich equation is an empirical equation employed to the heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written as [18]:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{2}$$

where K_F is the Freundlich constant (mg g^{-1}) (L $mg^{-1})^{1/n}$ and $1/n$ is the heterogeneity factor. The Freundlich equation predicts that the Al(III) concentration on the adsorbent will increase as long as there is an increase in the Al(III) concentration in the liquid.

The Temkin isotherm has been generally applied in the following form:

$$q_e = B \ln A + B \ln C_e \tag{3}$$

where $B = RT/b$ and b is the Temkin constant related to heat of sorption (J mol^{-1}). A is the Temkin isotherm constant (L g^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln (C_e) + \ln (B) \tag{4}$$

It has three isotherm constants, namely, A, B, and g ($0 < g < 1$), which characterize the isotherm.

Table 1 demonstrates that the values of g were close to unity, indicating that the isotherms are approaching the Langmuir form and not the Freundlich isotherm.

Table 1
Isotherm parameters

Langmuir isotherm model				
Temperature	$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
25˚C	10.98	40.22	2.48×10^{-4}	0.9980
Freundlich isotherm model				
Temperature	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	n	R^2	
25˚C	6.78	9.8	0.9978	
Temkin isotherm model				
Temperature	A (L g^{-1})	B	b (J mol^{-1})	R^2
25˚C	1,215	0.9196	2,695	0.9918
Redlich–Peterson isotherm model				
g	B (dm^3 mg^{-1})g	A (dm^3 g^{-1})	R^2	
1.00	0.86	9	0.9990	

Table 2
Effect of foreign ions on Al(III) sorption by BG-Amberlite XAD-2

Interfering ion	Amount of adsorbed Al(III) (mg L^{-1})	Loss of adsorption (%)	Extraction percentage (%)	Distribution ratio
–	6.64	0	33.2	0.497
Ba (II)	5.88	11.44	29.4	0.416
Zn (II)	6.64	0	33.2	0.497
Ca (II)	6.61	0.45	33.0	0.494
Pb (II)	6.51	1.96	32.5	0.483
Ag (I)	6.05	8.88	30.2	0.434
Mg (II)	6.64	0	33.0	0.497
Cu (II)	6.60	0.60	33.2	0.493
Ni (II)	6.61	0.45	33.0	0.494
Co (II)	6.60	0.60	33.2	0.493
K (I)	6.64	0	33.2	0.497
Na (I)	6.64	0	33.2	0.497

Scatchard analysis was employed to analyze further the binding isotherms. Equilibrium dissociation constant and the maximum adsorption amount for the affinity binding sites were calculated as 0.122 and 404 μmol g^{-1}, respectively.

3.4. Effect of other cations

In order to evaluate the selectivity of the preconcentration system, the effect of some metal ions at the concentration 20 mg L^{-1} on the sorption behavior of Al(III) (20 mg L^{-1}) was investigated. Table 2 indicates the Al(III) adsorption by BG-Amberlite XAD-2 which is mostly affected by Ag(I) and Ba(II), whereas the effects of other ions at given concentrations are negligible allowing for quantitative Al(III) determination in environmental samples.

3.5. Application of the method

The data available in the literature on preconcentration of Al(III) by various methods are compiled in Table 3. The sorption capacity of the BG-Amberlite XAD-2 resin is superior in comparison to all other matrices. The developed method has been successfully applied to the analysis of trace aluminum ions in natural water sample.

BG-Amberlite XAD-2 preconcentration followed by ICP-AES was used for the determination of Al (III) in the water samples from the Persian Gulf (Boshehr, Nuclear Power Plant, Iran). The solid-phase extractions at optimum conditions were performed for spiked environmental sample and human plasma as extractant sample without any pretreatments. The results

Table 3
Comparison of the methods for Al(III) preconcentration

Sorbent + Immobilized ligand	C	P. F	M. D	*R*	D. L	Ref
Silica-bonded glycerol	4	500	FAAS	>98	2	[5]
Activated silicagel-quinaldine	–	100	SPF/FAAS	>95	0.25	[2]
Controlled pore glass-L-methionine	–	160	USN-ICP OES	98–100	0.025	[19]
Salicylic acid grafted on Amberlite XAD-4	–	–	GF-AAS	>95	–	[20]
Silica gel modified with Lumogallion	–	–	DRS	–	30	[21]
Amberlite XAD-1180/ Pyrocatechol violet chelating	6.45	150	GF-AAS	>95	0.021	[6]
Anion exchange resin-Tiron	5.6	20	ESR-S	100	0.3	[22]
Chelex 100	–	–	ET-AAS	–	2.22	[23]
Amberlite XAD-4 -Salicylic acid	4.4	–	–	–	–	[24]
Amberlite XAD-7 and Chelex 100	–	–	FAAS	95	–	[25]
Chelex-100	–	2	ET-AAS	86–106	0.5	[26]
BG-Amberlite XAD-2 (our method)	10.8	10	ICP-AAS	94	2.19	–

Notes: C: Capacity (mg g^{-1}), PF: Preconcentration factor, M.D: Method of detection, R: Recovery (%), D.L: Detection limit, Ref: Reference, Spectrofluorometry: SPF, flame atomic absorption spectrometry: FAAS, inductively coupled plasma optical emission spectrometer associated to an ultrasonic nebulization system: USN-CP OES, Graphite-furnace atomic absorption spectrometry: GFAAF, Diffusion reflectance spectroscopy: DRS, ECR spectrophotometry: ECR-S, electrothermal atomic absorption spectroscopy: ET-AAS.

Table 4
Al(III) determination in sea water sample

Added		The Persian Gulf water		Added		Plasma	
(μg mL^{-1})	Found (μg L^{-1})	Recovery (%)	Preconcentration factor	(μg mL^{-1})	Found (μg L^{-1})	Recovery (%)	Preconcentration factor
0	0.083 ± 0.005	–	5	0	0	–	2.5
0.05	0.128 ± 0.007	90	5	0.2	0.108 ± 0.005	54	2.5
0.08	0.154 ± 0.009	89	5	0.4	0.242 ± 0.006	60	2.5

Note: Average of three determinations.

Table 5
Al(III) determination in household water sample

Temperature (˚C)	Time (min)	Preconcentration factor	Al(III) (μg L^{-1})[a]
100	20	10	111 ± 9
100	40	10	281 ± 8
100	60	10	418 ± 7

[a] For three determinations

presented in Table 4 demonstrate the applicability of the procedure for aluminum determination in samples.

Adsorption of Al(III) by BG-Amberlite XAD-2 from human plasma was also studied batch-wise. The moderate recovery (Table 4) indicates a rather strong competition of plasma components for Al(III) binding or a blockage of binding sites on the resin by plasma components.

Utensils made of metallic aluminum are widely used all over the world with the possibility of Al(III) release into food. In this investigation, 1 L of deionized water was poured in aluminum dishes and incubated for different times at different temperatures. The amount of Al(III) released in the water was assayed using the developed method (Table 5) indicating pretty significant release of Al(III) into boiling water within a typical cooking time of about 1 h.

4. Conclusion

A new chelating sorbent is prepared by coupling a dye brilliant green to Amberlite XAD-2 through an azo spacer. The resin has a good potential for enrichment of trace amount of Al(III) from large sample volumes. The Al(III) is adsorbed as aluminate ions to BG-Amberlite XAD-2 at alkaline pH. Preconcentration using BG-Amberlite XAD-2 combined with ICP-AES can be applied for the determination of trace amounts of Al(III) in sea water and household water samples with satisfactory results.

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