



REMOVAL OF LEAD (II) WITH POLY 3-(AZA-18-CROWN-6) SILICA BONDED PHASE FROM SUCCINATE MEDIUM AND SAMPLES ANALYSIS

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ABSTRACT

A method was described for the determination of micro amount of lead (II) with Poly 3-(Aza-18-crown-6) Silica bonded phase employed as an ion-pair forming a neutral complex from Sodium succinate medium (0.01 to 3.0 M). The adsorbed ion-pair complex was back eluted with 0.5 M hydrochloric acid and determined spectrophotometrically with PAR. The various parameters like concentration of acid, equilibrium time, back eluting agents, loading capacity were optimized for quantitative adsorption of lead (II). The applicability of the proposed method was successfully applied to the analysis of diverse ions, binary mixture of associated metal ions, ternary mixtures, alloys, ayurvedic samples and water samples and lead (II) was determined with the PAR and results of analysis were confirmed by AAS.

Keywords: Poly 3-(Aza-18-crown-6) Silica bonded phase, Lead (II), Real sample analysis.

1. INTRODUCTION

The separation and determination of trace metals in natural water has increased in the last decades because of the environmental problems and public health studies. Lead deficiency caused anemia and may cause several health problems (cancer, heart disease, arthritis, and diabetes and liver diseases). Lead was restricted to 0.1 mg L⁻¹ by Granular entrapped adsorbents of crown ether-phosphotungstic acid (PW) and crown ether-phosphomolybdic acid (PMA) in polyacrylamide [1, 2]. Due to the very low concentration of iron and the interfering effect of the matrix, its determination demand very sensitive analytical techniques, Removal of lead and nickel from aqueous solutions by SiO₂ doped potassium titanate, XAD7 impregnated resins with organophosphorus extractants [3]. Extraction of Pb(II) by XAD7 impregnated resins with organophosphorus extractants (DEHPA, Biosorption of Cadmium, Lead, Nickel, and Zinc by Algae [4] Adsorption of Pb(II) onto Modified Rice Bran [5]. Separation and pre concentration were applied to overcome these difficulties. Many procedures are well characterized for such a purpose [6-9]. Solid phase extraction (SPE) has attracted a great attention owing to its simple operation, rapid phase separation, no emulsification, high enrichment factor and easy automation. Organic chelating resins [10], polymer inclusion sorbents [11], modified nanometer-sized alumina [12]. Adsorbent selectively adsorbed Pb (II) from

wastewater again interfering ions [13], controlled-pore glass [14], PS-EDTA resin [15]. A novel polyvinyl-tetrazole-grafted resin with high capacity for the adsorption of heavy metal ions was prepared *via* surface-initiated atom transfer radical polymerization (SI-ATRP) of acrylonitrile on chloromethylated cross linked styrene-divinylbenzene resin and a subsequent cyanotetrazole conversion reaction under microwave assistance [16]. nanofibers, polyacrylonitrile, amidoxime polyacrylonitrile, adsorption [17]. A new method for the preparation of an azacrown ether-bonded silica gel stationary phase has been developed by the authors on the basis of a successive reaction pathway to form the crown ether cycle on the surface of the silica gel [18]. This research article describes in detail the sorption study and separation of lead (II) form other associated elements in sodium succinate medium. The concentration of sodium succinate required for quantitative sorption of lead (II) is very low, a clear cut separation was achieved.

2. EXPERIMENTAL

2.1. Apparatus and Reagents

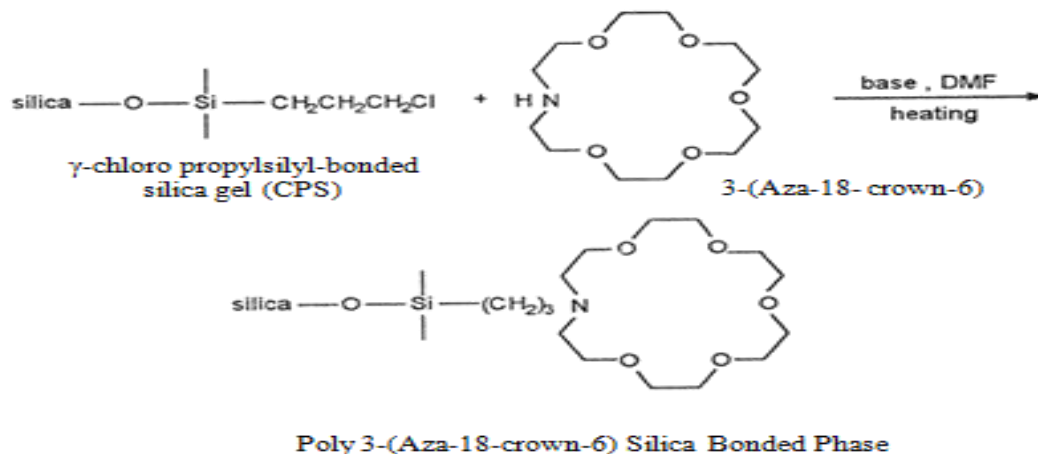
A Ziess Spectrophotometer (German), Digital pH meter (Model LI-120, ELICO, and India) with glass and calomel electrodes and a digital Flame photometer (PI, Model No. 041, and India) were used. A Stock solution of lead (II) was prepared by dissolving 1.59 g of Lead nitrate in 100mL of distilled deionized water and

standardized gravimetrically. The diluted solution containing 100 µg/mL of lead was prepared by appropriate dilution of the stock solution. Sodium succinate solution was prepared by dissolving 1.7612 g in distilled deionized water and diluted to 100 mL. Poly 3-(Aza-18-crown-6) propylsilyl-bonded silica gel was used after screening to 100-200 mesh. A total of 2g of polymer was slurred with distilled deionized water and poured into a pyrex glass chromatographic column (20 x 0.8 cm internal diameter). The column was used after preconditioning with Salicylic acid solution.

2.2. Preparation of bonded stationary phase

Silica gel (10g) was treated with 100mL of 5 M HCl at room temperature for 20 h. After filtration, the silica gel was washed with distilled water to neutrality and then dried at 120°C under reduced pressure for 10 h. The silica gel (10g) was suspended in 120mL anhydrous toluene containing 10mL of γ -chloropropyltriethoxy silane, and three drops of triethylamine were added into

the mixture. The mixture was heated under reflux and stirred under a stream of nitrogen for 20 h. The γ -chloro propylsilyl-bonded silica gel was filtered and washed in sequence with distilled water, methanol, acetone, and ether. Subsequently, γ -chloro propylsilyl-bonded silica gel was dried under a vacuum over P_2O_5 at 100°C overnight. Condensation of γ -chloro propylsilyl-bonded silica gel with 3-(Aza-18-crown-6) ether was allowed to react with NaH in DMF until a complete reaction was attained. After the reaction, the mixture was filtered, and the γ -chloro propylsilyl-bonded silica gel and toluene were added to the filtrate. The mixture was allowed to react while heating and stirring under a nitrogen atmosphere for 12h. Poly 3-(Aza-18-crown-6) Silica Bonded Phase was synthesized using chemical pathways are presented in Figure 1. The Poly 3-(Aza-18-crown-6) Silica Bonded Phase was used as shown in scheme and it is used as adsorbent for column extraction chromatographic separation of lead (II) ion from its real sample analysis.



Scheme: Synthesis of Poly 3-(Aza-18-crown-6) Silica Bonded Phase.

2.3. General procedure

Hundred µg of lead (II) was mixed with Sodium succinate in the concentration range of 0.1M to 2 M in a total volume of 10mL. The solution was then passed through Poly 3-(Aza-18-crown-6) column, preconditioned with same concentration of sodium succinate as that of the sample solution at flow rate of 0.5mL/min. The column was then washed with the same concentration of Sodium succinate. The sorbed lead(II) was then eluted with different eluting agents at the flow rate of 0.5mL/min. 5.0 mL fractions were collected and lead(II) content was determined Spectrophotometrically with 4-(2-pyridyl-lazo) resorcinol at 520 nm.

The concentration of lead (II) was calculated from a calibration graph.

3. RESULTS AND DISCUSSION

3.1. Sorption of lead (II) on Poly 3-(Aza-18-crown-6) as a function of Sodium succinate concentration

Sorption of Lead (II) on Poly 3-(Aza-18-crown-6) as a function of Sodium succinate concentration sorption studies of lead (II) were carried out from Sodium succinate medium. The concentration of sodium succinate varied from 0.002M to 2M. After sorption, the elution of lead (II) was carried out with 0.5M hydro-

chloric acid. It was found that there was quantitative (100%) sorption of lead (II) from 0.1 M to 2 M Sodium succinate. The results are shown in table 1 and fig.1. The subsequent sorption studies of lead (II) were carried out with 0.2 M sodium succinate.

Table 1: Sorption of Pb(II) as a function of Sodium succinate concentration

Sodium succinate Concentration M	Adsorption of Pb(II)%
0.002	20
0.004	30
0.006	65
0.008	77
0.01	86
0.04	95
0.06	98
0.08	100
0.1	100
0.2	100
0.4	100
0.6	100
0.8	100
1.2	100
1.4	100
1.6	100
1.8	100
2	100

The results showed that lead (II) was quantitatively eluted with 2.0 M to 8.0 M hydrochloric acid, 1.0 M to 8.0 M Nitric acid where as sodium acetate, ammonium nitrate, acetic acid was found to be an inefficient eluent for lead (II) (Table 2). Further elution studies of lead (II) were carried out with 4.0 M hydrochloric acid.

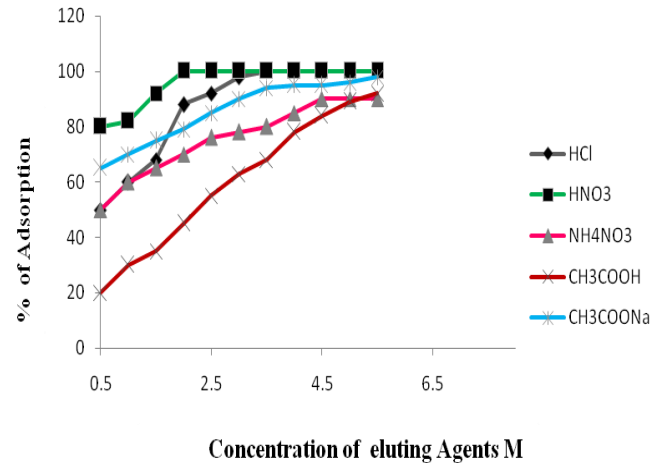
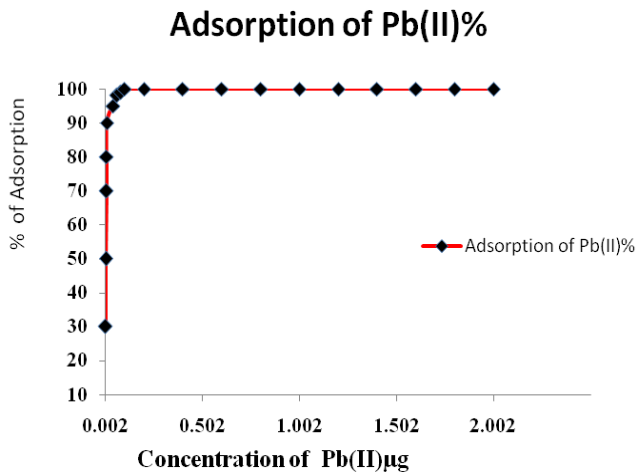


Fig. 2: Elution study of lead (II) with various eluting agents

3.3. Effect of varying concentration of lead (II)

In order to find out the capacity of Poly 3-(Aza-18-crown-6), the concentration of lead(II) varied from 100-1500 µg of lead(II)/10mL of solution in 0.2M sodium succinate. The results showed that the sorption of lead (II) was quantitative up to 1100 µg/10mL (Table 3). The sorption of lead (II) decreases with increase in concentration of lead (II) and is as shown in fig. 3. The capacity of Poly 3-(Aza-18-crown-6) for lead (II) was found to be 1.06±0.01 mmol/g of azacrown polymer.



3.2. Elution study of lead (II) with various eluting agents

Hundred µg/mL of lead (II) in 0.2 M Sodium succinate was sorbed on the Poly 3-(Aza-18-crown-6) column. After sorption, lead (II) was eluted with various eluents such as hydrochloric acid; the concentration of eluting agent varied from 0.5 M to 8 M. The elution profile of lead (II) with various eluting agents is shown in fig. 2.

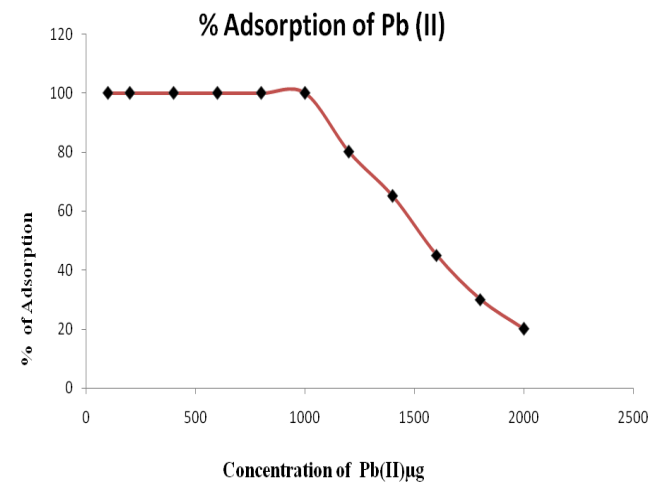


Fig. 3: Effect of varying concentration of lead (II)

Table 2: Elution study of lead (II) with various eluting agents

Conc Molar	% Eluting Agents				
	HCl	HNO ₃	NH ₄ NO ₃	CH ₃ COOH	CH ₃ COONa
0.5	50	80	50	20	65
1.0	60	82	60	30	70
1.5	68	92	65	35	75
2.0	88	100	70	45	79
2.5	92	100	76	55	85
3.0	98	100	78	63	90
3.5	100	100	80	68	94
4.0	100	100	85	78	95
4.5	100	100	90	84	95
5.0	100	100	90	89	96
5.5	100	100	90	92	98

Table 3: Effect of varying concentration of lead (II)

Concentration of Pb(II) µg	% Adsorption of Pb (II)
100	100
200	100
400	100
600	100
800	100
1000	100
1200	80
1400	65
1600	45
1800	30
2000	20

3.4. Separation of lead (II) from binary mixtures

An aliquot of solution containing 100 µg/mL of lead (II) was mixed with foreign ions and sodium succinate acid was added so that its concentration was 0.2 M in total volume of 10 mL. The tolerance limit was set as the amount of foreign ions required to cause $\pm 2\%$ deviation in the recovery of metal ion. The solution was passed through a Poly 3-(Aza-18-crown-6) column at a flow rate of 0.5 mL/min. Subsequently the column was washed with 15 mL of 0.2 M sodium succinate. Various foreign ions were not sorbed and hence passed through the column. The effluent was collected and analyzed for foreign ion content. The alkali and alkaline earth metals showed high tolerance limit except rubidium (I), cesium (I) and beryllium (II). Most of the p-block and d-block elements shows high tolerance limit. Amongst the inner transition elements, uranium (VI), thorium (IV), cerium (III) and lanthanum (III) shows high tolerance limit and sorbed quantitatively. The anions of inorganic and organic acids showed high tolerance limit. The tolerance

limits of various foreign ions are as given in table 4.

3.5. Separation of lead (II) from Multicomponent mixtures

When mixture containing magnesium (II), uranium (VI) and Lead (II) was passed through Poly 3-(Aza-18-crown-6) column at 0.2 M Sodium succinate medium, the magnesium (II) was not adsorbed and hence passed through the column, where as uranium (VI)/ Lead (II) were sorbed. The magnesium (II) content was analyzed spectrophotometrically. The sorbed uranium (VI) was eluted with 0.2 M ammonium carbonate at this condition lead (II) remains on the column. Lead was eluted with 0.5 M Nitric Acid and determined spectrophotometrically with 4-(2-pyridylazo) resorcinol at 520 nm. When mixture containing Calcium (II), uranium (VI) and Lead (II) was passed through Poly 3-(Aza-18-crown-6) column at 0.2 M Sodium succinate medium, the Calcium (II) was not adsorbed and hence passed through the column, where as uranium (VI)/ Lead (II) were sorbed. The Calcium (II) content was analyzed spectrophotometrically. Under this condition, Mixture containing Strontium (II)/ Barium (II)/ Uranium (VI)/Lead (II) was achieved. The results are given in the table 5.

3.6. Determination of lead in real sample (Ayurvedic sample)

The known amount of Rhumayog tablets was treated with concentrated nitric acid. The solution was heated to moist dryness, extracted with distilled deionized water and filtered to remove residue. The filtrate and washings were diluted to 100mL. An aliquot sample solution was analyzed as per the general procedure and the amount of lead (II) in Rhumayog tablet was found against by AAS as shown in table 6.

Table 4: Separation of lead (II) from binary mixtures

Ions	Added as	Tolerance Limit (mg)	Ions	Added as	Tolerance Limit (mg)
Na ⁺	NaCl	25	Cr ³⁺	Cr(NO ₃) ₃ .9 H ₂ O	25
Be ²⁺	BeSO ₄ .4H ₂ O	05	Ce ³⁺	CeCl ₃ .6H ₂ O	1
Mg ²⁺	MgCl ₂ .6H ₂ O	35	Zr ⁴⁺	Zr(NO ₃) ₄ .4H ₂ O	3
Ca ²⁺	CaCl ₂	20	V ⁴⁺	VOSO ₄ .4H ₂ O	5
Sr ²⁺	Sr(NO ₃) ₂	25	Cr ⁶⁺	K ₂ Cr ₂ O ₇	7
Ba ²⁺	Ba(NO ₃) ₂	15	Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	4
Cu ²⁺	CuCl ₂ .2H ₂ O	0.5	W ⁶⁺	Na ₂ WO ₄ .4H ₂ O	30
Ni ²⁺	NiCl ₂ .6H ₂ O	2	La ³⁺	LaCl ₃	6
Mn ²⁺	MnCl ₂ .4H ₂ O	1.5	Al ³⁺	Al(NO ₃) ₃ .9 H ₂ O	3
Zn ²⁺	ZnCl ₂	30	SCN ⁻	NaSCN	75
Cd ²⁺	Cd(NO ₃) ₂	20	ClO ₄ ⁻	ClO ₄	10
Fe ³⁺	FeCl ₃ .6H ₂ O	25	CH ₃ COO ⁻	CH ₃ COOH	35

Table 5: Separation of lead (II) from Multicomponent mixtures

Sr. No	Mixture	Taken µg	Found µg	Recovery %	Eluents
1	Mg(II)	100	100	100	NAPC
	U(VI)	100	100	100	0.2 M ammonium carbonate
	Pb(II)	100	100	100	0.5 HNO ₃
2	Ca (II)	100	100	100	NAPC
	U(VI)	100	100	100	0.2 M ammonium carbonate
	Pb(II)	100	100	100	0.5 HNO ₃
3	Sr (II)	100	100	100	NAPC
	U(VI)	100	100	100	0.2 M ammonium carbonate
	Pb(II)	100	100	100	0.5 HNO ₃
4	Ba(II)	100	100	100	NAPC
	U(VI)	100	100	100	0.2 M ammonium carbonate
	Pb(II)	100	100	100	0.5 HNO ₃

Table 6: Determination of lead in real sample (Ayurvedic sample)

Ayurvedic	Pb(II) found by Proposed method	Pb(II) found by AAS, (µg/gm)	Recovery* (%)	R.S.D (%)
Rhumayog	78.00	78.18	99.76	0.24
Mahalakshmi	298.21	299.87	99.40	0.60
Maha Sudarshan Churma	38.92	39.87	98.65	1.35

3.7. Determination of lead (II) in alloys samples

An alloy samples (0.1 g) was dissolved in 5 mL hot nitric acid, followed by the addition of two 5mL portions of conc nitric acid and solution was evaporated to moist dryness. The residue was extracted into 50 mL of water. The solution was boiled to dissolve the insoluble matter. The solution was filtered through Whatman filter no 1 to remove insoluble silica if any. The filtrate was diluted to 100 mL with water and used

for analysis of lead (II) by the proposed method. The certified samples such as tin base white metal (BCS-178/2), non-ferrous alloy (Brass) were not available at this working place, therefore synthetic mixtures corresponding to the composition of alloys were prepared and lead(II) was extracted and determined by proposed method (table 7). The results were in close agreement with those of the values obtained by the AAS.

Table 7: Determination of lead (II) in alloys samples

Alloy samples and its Composition in, (%)	Pb(II) found by Proposed Method *m (%)	Pb(II) found by AAS, (%)	R.S.D, (%)
Solder alloy Pb, 40; Sn, 60.	99.4	99.7	0.7
Gun metal alloy Pb, 2.31; Cu, 84.95; Sn, 4.89	99.2	99.6	0.6
Tin base whitmetal (BC 178/2)-Sn, 82.2; Sb, 9.45; Cu, 4.58; Pb, 3.18; Nib, 0.17; As, 0.15; Cda, 0.14; Bi, 0.11; Zn, 0.04.	99.7	99.9	0.4
Leaded Bronze (ITA lab, 4016)- Cu, 60.04; Zn, 33.02; Pb, 5.75; Al, 0.37; Sn, 0.30; Nib, 0.03; Fe, 0.18; Sb, 0.02; P, 0.02.	99.5	99.6	0.3
Leaded Bronze (BCS 364) Cu, 8.06; Nib, 0.28; As, 0.065; Fe, 0.002; Bi, 0.007; Sb, 0.181; P, 0.056; Co, 0.002; Pb, 9.35; Zn, 0.04.	99.3	99.8	0.6
5 g Non-ferrous alloy (Brass) Pb, 2.0; Cu, 65; Zn, 30.0; Sn, 1.0.	99.6	99.8	0.4

4. CONCLUSION

This work focused on the study of removal of lead (II) from foreign ions, associated metal ions, synthetic mixtures, alloy samples, ayurvedic samples and water samples by using Poly 3-(Aza-18-crown-6) Silica bonded phase. The various parameters were studied to observe the optimum conditions. The extractant, Poly 3-(Aza-18-crown-6) Silica bonded phase was sensitive towards lead (II), separation took place rapidly, low reagent concentration was required for quantitative adsorption of lead (II). The extraction of ion-pair complex was carried out at room temperature and required one step for quantitative extraction of lead (II). The results obtained by proposed method were compared with AAS and in good agreement with the amount taken of lead (II) for extraction. The method is simple, easy for operation, good accuracy and precision, low cost and a good enrichment factor.

Conflict of interest

There is no conflict of Interest

5. REFERENCES

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