Selective pre-concentration and solid phase extraction of mercury(II) from natural water by alumina-loaded ammonium pyrrolidine dithiocarbamate phases

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ABSTRACT

Alumina phase loaded with ammonium pyrrolidine dithiocarbamate (APDC)were synthesized based on chemical binding and physical adsorption approaches. The stability of a chemically modified APDC especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of alumina immobilized APDC phase. The application of this alumina for sorption of a series of metal ions was performed by using different controlling factors such as the pH of metal ion solution and the equilibration shaking time by the static technique. This difference was interpreted on the basis of selectivity incorporated in these sulfur containing alumina phases. Hg(II) was found to exhibit the highest affinity towards extraction by these alumina phases. The pronounced selectivity was also confirmed from the determined distribution coefficient (K_d) of all the metal ions, showing the highest value reported for mercury(II) to occur by alumina immobilized APDC phase. The potential applications of alumina immobilized APDC phase for selective extraction of mercury(II) to occur from aqueous solution were successfully accomplished as well as pre- concentration of low concentration of Hg(II) (22 pg ml^{-1}) from natural tap water with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapor atomic absorption analysis. © 2008 Trade Science Inc. - INDIA

INTRODUCTION

The direct determination of trace metals especially toxic metal ions such as mercury, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step[1]. This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest[2]. This can be performed simply in many ways including liquid and solid phase extraction techniques[3,4]. The application of solid phase extraction technique for pre- concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable

chemical form[5].

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams[6], filter paper[7], cellulose[8] and ion exchange resins[9]. Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces[10] of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports[11]. The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes[12]. For this reason, modification of the silica

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gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters[13].

Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place[10].

Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds[14-18]. The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of mercury(II)[19,20] and pre-concentration of various cations [21,23-26] and 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations[22]. Ammonium hexa-hydroazepin-1-dithiocarboxylate(HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry(AAS) and inductively coupled plasma atomic emission spectrometry(ICP-AES) was reported[5]. Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater[23]. Sorption of copper(II) by some sulfur containing complexing agents loaded on various solid supports[24] was also reported. 2-Amino-1-cyclopentene-1-dithiocaboxylic acid(ACDA) for the extraction of silver(I), mercury(II) and palladium(II)[25], 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions[26] as well as thiosemicarbazide for sorption of different metal ions[27] and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water[28] are also sulfur contaning silica gel phases.

This paper describes the applications of alumina phase-impregnated with APDC for selective extraction and solid phase pre-concentration of mercury(II) from aqueous and natural water samples.

EXPERIMENTAL

Reagents and materials

Analytical grade nitrate salts of litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and copper(II) and APDC of reagent grade and alumina were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany, and high purity double distilled deionized water was used throughout the experiments and 3-chloro propyl trimethoxysilane was received from Aldrich Chemical, USA. Organic solvents were dried according to conventional methods. For all solutions double distilled water was used and the buffer solutions were prepared from 1.0M sodium acetate to which different volumes of 1.0M hydrochloric acid were mixed and the pH-value of the resulting solution was adjusted with the use of a pH-meter.

Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of alumina loaded-APDC were carried out from KBr by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except mercury(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Mercury(II) determinations were performed by a Varian Spect AA-10 plus atomic absorption spectrophotometer equipped with VGA-76 vapour generation.

Preparation alomina-loaded APDC phases

Activation of surface alumina was filtered, washed with toluene, ethanol and diethyl ether and dried in an oven at 75°C for 6h. An amount of 20.0g of dry alumina were added to 6.12g (20mmol) APDC already dissolved in 400ml dry and hot toluene in the presence of a few drops of pyridine and the reaction mixture was refluxed for 6h. The resulting phase was filtered, washed with toluene, ethanol and finally with water several times until the filtrate showed no characteristic colour of adsorbed APDC. The phase was then dried in an oven at 70°C for 6h. alumina physically adsorbed APDC phase was prepared by reflux of 20.0g of active alu-

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mina and 10.12g APDC in 400ml toluene for 6h. Phase was also washed and dried as mentioned above.

Stability studies

The stability of alumina phases in different buffer solutions(pH 1-6) and concentrated hydrochloric and nitric acids was studied by batch equilibration. In this procedure, 500mg of the phase was mixed with 50ml of the selected solution in 100ml measuring flask and automatically shaken for 5h. The mixture was filtered, washed with 500ml water and dried in an oven at 80^0C. Around 100mg of the treated phase was added to 10 ml of 0.1M mercury(II) and 9.0 ml of 0.1M sodium acetate and the mixture was shaken for 30 min by an automatic shaker. The percentage of hydrolysis of APDC from the surface of modified alumina phases in different acidic solutions was calculated from the determined $\mu mol\ g^{-1}$ value of each treated phase.

Sorption studies

1. Determination of $\mu mol\ g^{-1}$ values

The determination of metal capacity of 13 metal ions, viz. Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ba(II), Hg(II) and Pb(II) as a function of pH was studied by the static technique. Then 100mg of the dry phase was added to a mixture of 1.0ml of 0.1M metal ion and 9.0ml of the buffer solution(pH 1-6 and 0.1M sodium acetate) in 50ml measuring flask. The mixture was then automatically shaken for 30min, filtered, washed with 50ml water and the unbound metal ion was subjected to complexometric titration using the proper buffer and indicator solutions and/or atomic absorption analysis. The effect of shaking time on the percentage extraction of metal ions was also studied for only Hg(II) by the static technique. In this, 100 mg of the alumina phase was added to 1.0ml of 0.1M Hg(II) and 9.0ml of 0.1M sodium acetate in 50ml measuring flask and automatically shaken for the selected period of time (1,5,10,20 and 25min). The mixture was filtered, washed with 50ml water and the free metal ion was determined as described above.

2. Determination of the distribution coefficient

About 100mg of the alumina phase was mixed with 50 ml of the metal ion(1mgml⁻¹) in a 100ml measuring flask and shaken for 3h by an automatic shaker. The mixture was filtered, washed with water and diluted with 2% nitric acid solution in order to fit in the linear dynamic range of each metal ion. A standard solution for each metal ion was also prepared in a similar way.

3. Percentage removal of mercury(II) from aqueous solutions

One liter of Hg(II) solution, containing 10, 50 and 100ng ml⁻¹ was passed over a column[29] packed with 500 and 1000mg each of alumina. The flow rate was adjusted to 2.0ml min⁻¹. The eluents were collected and 5ml was diluted with 20ml of 2% nitric acid solution and subjected to cold vapour atomic absorption spectrometric analysis(CV-AAS).

4. Pre-concentration of mercury(II) from aqueous and natural tap water

Two liters sample solution spiked with 20pg ml⁻¹ in both DDW and natural tap water were prepared and passed over a column packed with 1000mg of alumina with a flow rate of 2ml min⁻¹. Then 10ml concentrated hydrochloric acid (10.0M) was then passed over the phase and adsorbed metal ion to desorb the bound-mercury(II). The desorbed metal ion was directly determined by CV-AAS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

RESULTS AND DISCUSSION

Stability studies

The stability of the newly synthesized alumina phases was performed in different buffer solutions (pH 1,2,3, 4,5,6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in section 2 revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the alumina phase[14]. The results of this study proved that the alumina -chemically immobilized APDC phase is more resistant than the physically adsorbed analog especially in 1.0, 5.0 and 10.0M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively.

However, the use of nitric acid with different concentration values(1.0,5.0,10.0M) was found to change

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the color of alumina phases from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic APDC modifier via oxidation. In addition, stability of phases was also confirmed from the interaction with 10.0M hydrochloric acid for more than 1 week.

This test proved a reasonable stability of alumina phase compared to non-treated silica gel phases judging from the color change of the two phases as well as the metal capacity values determination of Hg(II) and comparison of these with those of the original non-treated alumina phases.

Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a polymeric matrix[9]. Finally, the alumina phase-loaded APDC phases were also found to be stable over a range of 1 year during the course of this work.

Metal capacity in various controlling factors

The metal capacity values determined in mmol g^{-1} for the alumina phase -loaded-APDC in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the alumina phase. TABLE 1 compiles the μmol g^{-1} values for the 13 tested metal ions, viz) Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II),Cd(II), Hg(II) and Pb(II). Several trends can be observed and outlined from the data given. First, is the strong dependence of mmol g^{-1} extracted values from the metal ion solution for most tested metal ions on the pH-value[20,25].

The maximum value was found to be mainly at higher pH-values (pH 5-6 and 0.10M NaOAc). Second, is the strong affinity of the alumina phase for extraction and removal of Hg(II) from aqueous solution compared to other tested metal ions, as shown by the higher μmol g^{-1} values by alumina phases 250.

This behavior of alumina-loaded sulfur containing compounds for selective extraction and removal of Hg(II) from aqueous and natural water sample is well documented[19,20] and reported based on different governing rules[30]. Third are the notably high μ100 mol g^{-1} values determined for chemically modified alumina phase in comparison with values found as given in TABLE 1. The comparison between the metal sorption properties of chemically and physically-alumina phases has been extensively studied[31] and the results presented in this work are consistent with the surface activity of the donor atoms responsible for metal ion interaction, sorption, extraction and selective removal. APDC is well known to participate in metal binding via the nitrogen and sulfur donor atoms[32]. In the case of the physically adsorbed phase, some of these donor atoms are involved in physical adsorption processes with the active surface, leading to the minimization of the reactivity of such donor atoms for metal interaction and binding processes. In contrast, the chemical binding of APDC was accomplished via direct bond formation between silica modified propylchloride with the thiol-or imino-group[9]. The product, alumina, in this case is tuned with the active donor atoms (N, S) directed on the surface of the modified silica gel with the capability and accessibility for fast and direct interactions with the free metal ion present in solution. Fourth, are the general orders of metal capacity values for all tested metal ions by the two phases which are in many respects consistent and similar. Therefore, the conclusion drawn from this section can be outlined as the high superiority of phase for selective extraction of Hg(II) as well as the higher metal uptake behavior of alumina phase .

The effect of shaking time on the percentage extraction of metal ions at various equilibration time inter-

TABLE 1 : Metal capacity values determined in μmol g^{-1a}

pH	Hg(II)	Pb(II)	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
NaOAc	221	51	55	10	-	16	54	60	20	40
6	203	40	32	40	-	35	45	93	35	62
5	121	31	24	50	-	28	42	72	22	30
4	20	20	18	45	54	20	33	60	11	20
3	32	15	10	25	33	13	33	45	5	21
2	23	14	9	12	21	10	20	20	00	5
1	11	3	5	10	4	5	10	5	00	00

[a] **Values are based on n=3 with standard deviation of 4**

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vals (1,5,10,15,20,25min) was also studied and evaluated as μmol g^{-1} and correlated to that determined at 30min shaking time. Figure 1 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between alumina phase and Hg(II). One minute shaking time was found to be sufficient to establish 84% of the determined μmol g^{-1} value at 30min whereas 10min shaking time led to 98% extraction. The data and results presented in this section reveal the superiority of alumina phase as previously declared in the stability studies (Section 1).

The distribution coefficient (K_d) data of the tested metal ions with the two newly alumina-loaded APDC phase are summarized in TABLE 2. It is evident that Hg(II) is the strongest sorbed metal ion by alumina-loaded APDC phase. The distribution coefficient values of Hg(II) by the loaded APDC phase were found to be much higher than those reported for ion exchange resins containing APDC derivatives[9]. In addition, the K_d values for Cu(II) by alumina-loaded APDC phase were found to come on the second place after Hg(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and sulfur donor atoms present in APDC for binding with Cu(II)[19,20]. On the other hand, the various tested metal ions as shown in TABLE 2 were found to exhibit lower tendency to bind with alumina-loaded APDC phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher K_d value for Hg(II) and the lower ones for the other metal ions, except Cu(II), provide an additional evidence for the suitability of these two newly alumina-loaded APDC phase for selective extraction of Hg(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K_d values by alumina -loaded APDC phase is consistent with the reported data.

Percentage removal of Hg(II) from aqueous solution

The use of a column technique is a common procedure for extraction, separation and selective extraction of metal ions from various aquatic systems[10]. The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes[14-16]. This property enables the pre-concentration of metal ions at

very low trace levels. The percentage removal of metal ions from aqueous solutions is essential for the evaluation of the method described and suggested here. This is mainly dependent on several well known factors such as the type and amount of packing stationary and mobile phases and the flow rate of the mobile phase[21]. In this study, we attempted to evaluate the percentage recovery of Hg(II) with different spiked concentrations, namely 10,50 and 100 ng ml^{-1} from 1 l of 0.1M NaOAc solution by the application of two different amounts (500 and 1000mg) of alumina-loaded APDC phase packing. The results of the percentage removal of Hg(II) from aqueous solutions are presented in TABLE 3 which clearly demonstrate the suitability and validity of alumina immobilized APDC phase for removal and extraction of Hg(II). In addition, the effect of packing amount of silica gel phase is also evident in TABLE 3, where the near completion of Hg(II) removal was accomplished by the use of 1000 mg phase.

Selective pre-concentration of Hg(II) from natural water for off-line CV-AAS

This study was undertaken in order to evaluate the potential application of alumina immobilized APDC phase for pre-concentration of trace levels of Hg(II) in
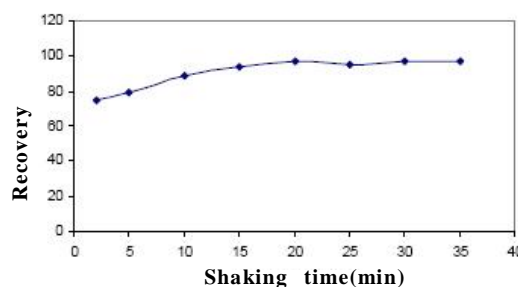

Figure 1 : Effect of shaking time (min) on the percentage extraction of Hg(II) by the alumina phases

TABLE 2 : Distribution coefficient (K_d) values of various metal ions

Metal ions	K_d
Cr(III)	130
Mn(II)	83
Fe(III)	35
Co(II)	72
Ni(II)	62
Cu(II)	850
Zn(II)	450
Cd(II)	90
Hg(II)	19700
Pb(II)	130

natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water (DDW) to evaluate and investigate the matrix effect. Both drinking tap water and DDW (2 l) were spiked with 22pg ml⁻¹ of Hg(II). Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl[9] as well as ethylenediaminetetraacetic acid[27]. However, some of these reagents are usually characterized by adsorption on the surface of alumina which lead to severe change in the nature of packing material as well as non reproducible results if the column used in future applications. The efficiency of metal ion pre-concentration especially Hg(II), by 10.0M HCl acid is found to be high without causing any notable change to the chemical nature of the organic APDC modifier. Therefore, 10.0ml of 10.0M HCl was used for the elution of the adsorbed Hg(II) from the column bed. The pre-concentration factor targeted from this study is 200 as given in TABLE 4 . As the results indicate, the off-line detection results of the eluted and pre-concentrated Hg(II) are very good with a satisfactory pre-concentration factor which can be further increased to 500-fold by simply increasing the water sample volume to 5 l instead of 2 l. Moreover, natural tap water sample was found to give very close results to that reported for DDW sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic

matters played an insignificant role in the aimed selective extraction, removal and pre-concentration of Hg(II) by alumina immobilized APDC phase

REFERENCES

[1] D.E.Leyden, G.H.Luttrell, W.K.Nonidez, D.B.Werho;Anal.Chem., **48**, 67 **(1976)**.
[2] J.S.Jones, D.E.Harrington, B.A.Leone, W.R. Bramdstedt; Atom.Spectrosc., **4**, 49 **(1983)**.
[3] D.C.Nambiar, N.N.Patil, V.M.Shinde; J.Fresenius. Anal.Chem., **360**, 205 **(1998)**.
[4] C.Caroli, A.Alimanti, F.Petrucci, Zs.Horvath; Anal. Chim.Acta, **248**, 241 **(1991)**.
[5] A.Alexandrova, S.Arpadjan; Analyst, **118**, 1309 **(1993)**.
[6] S.Arpadjan, L.Vuchkova, E.Kostadinova; Analyst., **122**, 243 **(1997)**.
[7] D.E.Leyden, G.H.Luttrell; Anal.Chim., **47**, 1612 **(1975)**.
[8] M.C.Gennaro, C.Baiocchi, E.Campi, E.Mentasti, R.Aruga; Anal.Chim.Acta, **151**, 339 **(1983)**.
[9] M.Grote, A.Kettrup; Anal.Chim.Acta, **175**, 239 **(1985)**.
[10] K.Unger; 'Porous Silica', Elsevier, Amsterdam, **(1979)**.
[11] S.P Boudreau, W.T.Cooper; Anal.Chem., **61**, 41 **(1989)**.
[12] R.J.Kvitek, J.F.Evans, P.W Carr; Anal.Chim.Acta, **144**, 93 **(1982)**.
[13] M.L.Bruening, D.M.Mitchell, J.S.Bradshaw, R.M.Izatt, R.L.Bruening; Anal.Chem., **63**, 21 **(1991)**.
[14] M.E.Mahmoud; Talanta, **45**, 309 **(1997)**.
[15] M.E.Mahmoud, E.M.Soliman; Talata, **44**, 15 **(1997)**.
[16] M.E.Mahmoud, E.M.Soliman; Talanta, **44**, 1063 **(1997)**.
[17] A.Tong, Y.Akama, S.Tanaka; Anal.Chim.Acta, **230**, 179 **(1990)**.
[18] V.Dadler, L.F.Lindoy, D.Sallin, C.W.Schlaepfer; Aust.J.Chem., **40**, 1557 **(1987)**.

TABLE 3 : Percentage removal of Hg(II) from aqueous solutions by alumina-loaded APDC phase[a]

Hg(II) spiked (ng ml⁻¹)	Phase (mg)	Percentage removal
10	500	92±2
50	500	89±3
100	500	96±1.5
10	1000	100±2
50	1000	98±2
100	1000	97±2

[a]Values are based on triplicate analysis.

TABLE 4 : Preconcentration of Hg(II) from DDW and natural tap water samples[a].

Phase (mg)	Sample volume(mL)	Hg(II)spiked (pg ml⁻¹)	Preconcentra tion reagent	Preconcentration factor	Hg(II)detected[a] (ng ml⁻¹)	Percentage removal
1000	2000 Tap water (Saveh)	20	10.0ml of 10.0M HCl	200	3.93? 1.8	99.1? 0.9
1000	2000 DDW	20	10.0ml of 10.0 M HCl	200	3.92? 1.9	99.2? 0.8

[a] Values are corrected for blank concentration of water samples and based on triplicate analysis.