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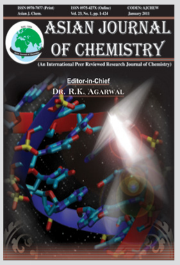

Solid Phase Extraction of Mercury(II) from Natural Water by Octadecyl-Bonded Silica-Loaded Schiff's Base 4,4'-Dimethoxybenzil bisthiosemicarbazone Phases

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Octadecyl-bonded silica phase loaded with 4,4'-dimethoxybenzil *bis*thiosemicarbazone were synthesized based on chemical binding and physical adsorption approaches. The stability of a chemically modified 4,4'-dimethoxybenzil *bis*thiosemicarbazone especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of octadecyl-bonded silica immobilized 4,4'-dimethoxybenzil *bis*thiosemicarbazone. The application of this octadecyl-bonded silica 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 octadecyl-bonded silica phases. Mercury(II) was found to exhibit the highest affinity towards extraction by these octadecyl-bonded silica 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 octadecyl-bonded silica immobilized 4,4'-dimethoxybenzil *bis*thiosemicarbazone phase. The potential applications of octadecyl-bonded silica immobilized 4,4'-dimethoxybenzil *bis*thiosemicarbazone 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) (40 pg mL^{-1}) from natural tap water with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapour atomic absorption analysis.

Key Words: Solid phase extraction, Mercury(II), Octadecyl-bonded silica, 4,4'-Dimethoxybenzil *bis*thiosemicarbazone.

INTRODUCTION

Direct determination of trace metals especially toxic metal ions such as mercury, tin, lead and metalloids arsenic, 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 forms[6], filter paper[7], cellulose[8] and ion exchange resins[9]. Silica gel, carbon active, 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].

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[12-18]. 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[21-25] and 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations[26]. 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[22]. Sorption of copper(II) by some sulfur containing complexing agents loaded on various solid supports[23] was also reported. 2-Amino-

1-cyclopentene-1-dithiocaboxylic acid for the extraction of silver(I), mercury(II) and palladium(II)[24], 2-[2-triethoxysilylethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions[25] as well as thiosemicarbazide for sorption of different metal ions[23] and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water[25] are also sulfur contaning silica gel phases. This paper describes the applications of octadecyl-bonded silica phase-impregnated 4,4'-dimethoxybenzil bisthiosemicarbazone (DBTS) (Fig. 1) for selective extraction and solid phase pre-concentration of mercury(II) from aqueous and natural water samples.

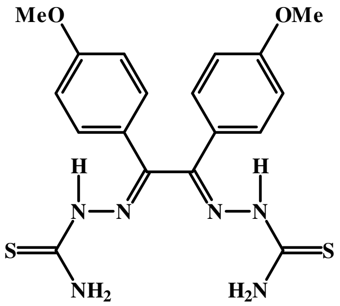

Fig. 1. Structure 4,4'-dimethoxybenzil bisthiosemicarbazone (DBTS)

EXPERIMENTAL

Analytical grade nitrate salts of mercury, manganese, iron, chromium, magnesium, barium, zinc, cadmium, lead, nickel, cobalt and copper of reagent grade and octadecyl-bonded silica were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany and high purity 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 1.0 M sodium acetate to which different volumes of 1.0 M HCl; HNO_3 were mixed and the pH-value of the resulting solution was adjusted with the use of a pH-meter.

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 octadecyl-bonded silica loaded-DBTS 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 octadecyl-bonded silica-loaded 4,4′-dimethoxybenzil bisthiosemicarbazone phases: Activation of surface octadecyl-bonded silica was filtered, washed with toluene, ethanol and diethyl ether and dried in an oven at 70 °C for 6 h. An amount of 20.0 g of dry octadecyl-bonded silica were added to 5.12 g (20 mmol) of DBTS already dissolved in 400 mL dry and hot toluene in presence of a few drops of pyridine and the reaction mixture was refluxed for 6 h. The resulting phase was filtered, washed with toluene, ethanol and finally with water several times until the filtrate showed no characteristic colour of adsorbed DBTS. The phase was then dried in an oven at 60 °C for 7 h. Octadecyl-bonded silica physically adsorbed DBTS phase was prepared by reflux of 20.0 g of active octadecyl-bonded silica and 5.12 g DBTS in 400 mL toluene for 6 h. Phase was also washed and dried as mentioned above.

Stability studies: The stability of octadecyl-bonded silica phases in different buffer solutions (pH 1-6) and concentrated hydrochloric acid and nitric acid was studied by batch equilibration. In this procedure, 500 mg of the phase was mixed with 50 mL of the selected solution in 100 mL measuring flask and automatically shaken for 5 h. The mixture was filtered, washed with 500 mL water and dried in an oven at 80 °C. Around 100 mg of the treated phase was added to 1.0 mL of 0.1 M mercury(II) and 9.0 mL of 0.1 M sodium acetate and the mixture was shaken for 0.5 h by an automatic shaker. The percentage of hydrolysis of DBTS from the surface of modified octadecyl-bonded silica phases in different acidic solutions was calculated from the determined μmol g^{-1} value of each treated phase.

Sorption studies

Determination of metal capacity values (μmol g^{-1}): The determination of metal capacity of 13 metal ions, *viz.* Ba(II) Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II) as a function of pH was studied by the static technique. Then 100 mg of the dry phase was added to a mixture of 1.0 mL of 0.1 M metal ion and 9.0 mL of the buffer solution (pH 1-6 and 0.1 M sodium acetate) in 50 mL measuring flask. The mixture was then automatically shaken for 0.5 h, filtered, washed with 50 mL 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 octadecyl-bonded silica phase was added to 1.0 mL of 0.1M Hg(II) and 9.0 mL of 0.1 M sodium acetate in 50 mL measuring flask and automatically shaken for the selected period of time (1, 5, 10, 20, 25, 30 and 35 min). The mixture was filtered, washed with 50 mL water and the free metal ion was determined as described above.

Determination of the distribution coefficient: About 100 mg of the octadecyl-bonded silica phase was mixed with 50 mL of the metal ion (1 mg mL^{-1}) in a 100 mL measuring flask and shaken for 3 h 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.

Percentage removal of mercury(II) from aqueous solutions: 1 L of Hg(II) solution, containing 10, 50 and 100 ng mL^{-1} was passed over a column[27] packed with 500 and 1000 mg each of octadecyl-bonded silica The flow rate was adjusted to 2.0 mL min^{-1}. The eluents were collected and 5 mL was diluted with 20 mL of 2 % nitric acid solution and subjected to cold vapour atomic absorption spectrometric analysis.

Pre-concentration of mercury(II) from aqueous and natural tap water: 2 L sample solution spiked with 20 pg mL^{-1} of Hg (II) in both double distilled water and natural tap water were prepared and passed over a column packed with 1000 mg of octadecyl-bonded silica with a flow rate of 2 mL min^{-1}. Then 10 mL concentrated hydrochloric acid (10.0 M) was then passed over the phase and adsorbed metal ion to desorb the bound-mercury(II). The desorbed metal ion was directly determined by cold vapour atomic absorption spectrometry. 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 octadecyl-bonded silica phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in 'metal capacity in various controlling factor' revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the octadecyl-bonded silica phase[14]. The results of this study proved that the octadecyl-bonded silica -chemically immobilized DBTS phase is more resistant than the chemically adsorbed analogue especially in 1.0, 5.0 and 10.0 M 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, 10.0 M) was found to change the colour of octadecyl-bonded silica phases from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic DBTS modifier *via* oxidation. In addition, stability of phases was also confirmed from the interaction with 10.0 M hydrochloric acid for more than 1 week.

This test proved a reasonable stability of octadecyl-bonded silica phase compared to non-treated silica gel phases judging from the colour 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 octadecyl-bonded silica 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 octadecyl-bonded silica phase -loaded DBTS 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 μmol g^{-1} for the octadecyl-bonded silica phase-loaded-DBTS in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the octadecyl-bonded silica 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), Ba(II), Ca(II), Mg(II) and Pb(II). Several trends can be observed and outlined from the data given. First, is the strong dependence of μmol g^{-1} extracted values from the metal ion solution for most tested metal ions on the pH-value[20,24].

The maximum value was found to be mainly at higher pH-values (pH 5-6 and 0.10 M NaOAc). Second, is the strong affinity of the octadecyl-bonded silica 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 octadecyl-bonded silica phases[24].

This behaviour of octadecyl-bonded silica-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[17]. There are the notably high μmol g^{-1} values determined for chemically modified octadecyl-bonded silica phase in comparison with values found as given in Table-1. The comparison between the metal sorption properties of chemically and physically-octadecyl-bonded silica phases has been extensively studied[21] 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. 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 DBTS was accomplished *via* direct bond formation between silica modified propylchloride with the thiol-or imino-group[9]. The product, octadecyl-bonded silica, 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. 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 behaviour of octadecyl-bonded silica phase.

TABLE-1
METAL CAPACITY VALUES DETERMINED (μmol g^{-1})*

pH	Hg(II)	Pb(II)	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ca(II)	Mg(II)	Ba(II)
NaOAc	240	59	52	20	–	14	43	63	19	40	23	20	30
6	210	45	36	58	–	35	64	91	39	68	21	28	38
5	137	33	23	69	10	50	69	75	20	39	35	29	29
4	58	25	15	50	44	25	38	60	10	25	30	15	20
3	39	12	10	28	30	14	38	45	5	19	25	10	13
2	22	7	8	18	26	10	25	25	00	5	15	5	6
1	10	3	3	13	6	5	14	14	00	2	2	00	2

*Values are based on n = 3 with standard deviation of 4.

The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and evaluated as μmol g^{-1} and correlated to that determined at 0.5 h shaking time. Fig. 2 represents the percentage extraction *versus* shaking time in min and clearly reflects the rapid exchange equilibrium between octadecyl-bonded silica phase and Hg(II). 1 min shaking time was found to be sufficient to establish 84 % of the determined μmol g^{-1} value at 0.5 h whereas 10 min shaking time led to 88 % extraction. The data and results presented in this section reveal the superiority of octadecyl-bonded silica phase as previously declared in the stability studies (stability constant section).

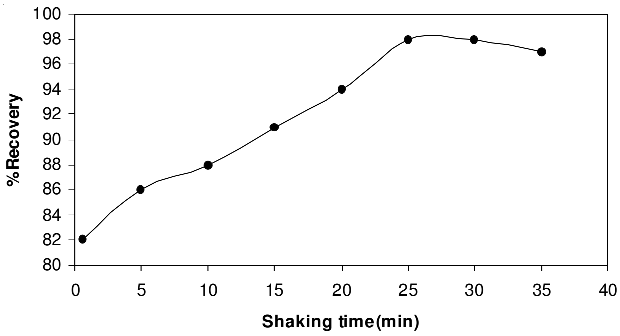

Fig. 2. Effect of shaking time (min) on the percentage extraction of Hg(II) by the octadecyl-bonded silica phases

The distribution coefficient (K$_d$) data of the tested metal ions with the octadecyl-bonded silica-loaded DBTS phase are summarized in Table-2. It is evident that Hg(II) is the strongest sorbed metal ion by octadecyl-bonded silica- loaded DBTS phase. The distribution coefficient values of Hg(II) by the loaded DBTS phase were found to be much higher than those reported for ion exchange resins containing DBTS derivatives[9]. In addition, the K$_d$ values for Cu(II) by octadecyl-bonded silica-loaded DBTS phase were found to come on the second place after Hg(II) which behaviour can be interpreted on the basis of the affinity of both nitrogen and hidroxil donor groups present in DBTS 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 octadecyl-bonded silica-loaded DBTS 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 octadecyl-bonded silica-loaded DBTS 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 octadecyl-bonded silica-loaded DBTS phase is consistent with the reported data.

TABLE-2
DISTRIBUTION COEFFICIENT (K_d) VALUES OF VARIOUS METAL IONS

Metal ions	K$_d$
Cr(III)	160
Mn(II)	79
Fe(III)	89
Co(II)	70
Ni(II)	90
Cu(II)	710
Zn(II)	420
Cd(II)	145
Hg(II)	11600
Pb(II)	130

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 0.1 M NaOAc solution by the application of two different amounts (500 and 1000 mg) of octadecyl-bonded silica-loaded DBTS 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 octadecyl-bonded silica immobilized DBTS 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.

TABLE-3
PERCENTAGE REMOVAL OF Hg(II) FROM AQUEOUS SOLUTIONS BY OCTADECYL-BONDED SILICA-LOADED DBTS PHASE*

Hg(II) spiked (ng mL^{-1})	Phase (mg)	Percentage removal
10	500	93 ± 3
50	500	95 ± 6
100	500	94 ± 5
10	1000	97 ± 6
50	1000	97 ± 4
100	1000	98 ± 5

*Values are based on triplicate analysis.

Selective pre-concentration of Hg(II) from natural water for off-line cold vapour atomic absorption spectrometry: This study was undertaken in order to evaluate the potential application of octadecyl-bonded silica immobilized DBTS phase for pre-concentration of trace levels of Hg(II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water to evaluate and investigate the matrix effect. Both drinking tap water and double distilled water (2 L) were spiked with 20 pg 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 acid and nitric acid, thiourea HCl[9] as well as ethylenediaminetetraacetic acid[24]. However, some of these reagents are usually characterized by adsorption on the surface of octadecyl-bonded silica which

TABLE-4
PRE-CONCENTRATION OF Hg(II) FROM DOUBLE DISTILLED WATER AND NATURAL TAP WATER SAMPLES*

Phase (mg)	Sample volume (mL)	Hg(II) spiked (pg mL^{-1})	Pre-concentration reagent	Pre-concentration factor	Hg(II) detected* (ng mL^{-1})	Removal (%)
1000	2000 Tap water (Saveh)	20	10.0 mL of 10.0 M HCl	200	3.96 ± 2.6	99.6 ± 2.9
1000	2000 Double distilled water	20	10.0 mL of 10.0 M HCl	200	3.94 ± 2.9	98.4 ± 3.9

*Values are corrected for blank concentration of water samples and based on triplicate analysis.

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 10.0 M HCl acid is found to be high without causing any notable change to the chemical nature of the organic DBTS modifier. Therefore, 10.0 mL of 10.0 M 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 close results to that reported for double distilled water 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 octadecyl-bonded silica immobilized DBTS phase.

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