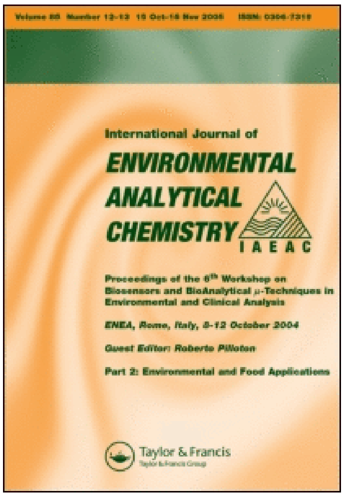

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Reactivity of Thioglycolic Acid Physically and Chemically Bound to Silica Gel as New Selective Solid Phase Extractors for Removal of Heavy Metal Ions From Natural Water Samples

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REACTIVITY OF THIOGLYCOLIC ACID PHYSICALLY AND CHEMICALLY BOUND TO SILICA GEL AS NEW SELECTIVE SOLID PHASE EXTRACTORS FOR REMOVAL OF HEAVY METAL IONS FROM NATURAL WATER SAMPLES

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A method is presented for the immobilization of thioglycolic acid moiety on the surface of active silica gel via a simple and direct synthetic route and based on one step reaction procedure. Two-product solid phase extractors were successfully synthesized according to physical adsorption and chemical immobilization binding techniques, phases (I) and (II), respectively. The mode of interaction between the silanol group and the thioglycolic moiety was also discussed for both phases based on the infrared analysis studies. The thermal stability properties as well as the effect of buffer solutions on the percentage hydrolysis of the two silica gel phases were examined and revealed the high stability and superiority of silica phase (II) in these respects. The evaluation of the selectivity and metal uptake properties incorporated in these two silica gel phases were also studied and discussed for a series of divalent heavy metal ions under different controlling factors. The mmol/g values were found to be higher in case of phase (I). The selective removal and extraction of some heavy metal ions, *viz*. Cu(II), Zn(II), and Hg(II) from natural seawater samples was successfully accomplished with the percentage recovery values for the three tested metal ions in the range of 96.5–98.4 ± 0.2–0.6%. The presence of higher concentrations of Na(I), K(I), Mg(II) and Ca(II) showed insignificant role or no matrix effect on such selective extraction process due to their 0% values of removal by these silica gel phases (I) and (II).

Keywords: Heavy metals; Natural waters; Thioglycolic acid; Solid phase extraction; Bonded silica support

INTRODUCTION

The efficiency of silica gel matrix to act as a solid phase extractor for removal, separation and preconcentration of heavy metal ions is very low due to the weak interaction between these metal ions and surface silanol groups [1,2].

Nevertheless silica gel as inorganic solid support offers some distinct advantages over other types such as active carbon [3], ion-exchange resins [4], and modified waste

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materials [5–7]. Silica gel is characterized by a good mechanical strength, does not swell or strain, can undergo heat treatment as well as is insoluble in either common organic solvents or aqueous medium. Consequently, over the last two decades great interest has been devoted to improve silica gel metal exchange capacity and selectivity properties. This was accomplished via modification of silica gel surface with selective organic complexing agents chemically immobilized to silica gel surface through a linkage of a silylating agent [8–18]. The silica gel phases thus produced are characterized by high stability to acids or buffer solutions [19,20] as well as high resistance to leaching effect during the elution of metal ion sorbed on the phase or the percolating large volumes of samples containing minor concentration of metal ions. However, the preparation of such type of phases is some what complicated, time consuming and the selected chelating agents are limited.

An alternative method for chemical binding is the physical adsorption of the chelating agent to silica surface [21–31]. This may be achieved via direct impregnation process as that reported for selective preconcentration of Co(II) using silica gel physically loaded 1-hydroxy-2-nitroso-naphthol [22], or improved impregnation process which involve the use of Aliquate 336 (methyltricaprylammonium chloride) and organic complexing agents containing sulphonic groups. Several silica gels modified in this way were used for preconcentration, removal and/or separation purposes of different metal ions [23–26]. Terada *et al.* [27,28] described a method for the preparation of 2-mercaptobenzothiazole physically supported on silica gel by simple reflux. The synthesized phase was used for chromatographic enrichment of Cu(II), Cd(II), Zn(II) and Pb(II) in natural water samples. Developments were made to improve the stability of these phases. This include the use of surfactants incorporation of a long chain hydrocarbon moiety (C_{18}-bonded phases) [29–31]. Thus 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone was proposed as a chelating agent supported on silica gel for preconcentration of Co(II), Ni(II) and Cu(II) in solution of sodium chloride samples and tap water [31].

In this manuscript, we describe a direct method for chemical immobilization of thioglycolic acid to silica gel surface without using a link of silylating agent through a simple reaction between its ethyl ester and silica gel in benzene under reflux conditions. The selectivity of this phase as well as a physically loaded one towards extraction of some heavy metal ions such as Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) was investigated and optimized. IR, recycling, medium and thermal stability studies of the new phases were used to differentiate between mode of immobilization of thioglycolic acid to silica surface. Application of the two phases for removal of the free heavy metal ions from seawater showed their selectivity especially in presence of high concentration of alkali and alkaline earth metals but the chemically bonded phase was found to be superior than the physically adsorbed one in this respect.

EXPERIMENTAL

Materials

Silica gel used was of TLC grade (70–230 mesh size and 60 Å pore diameter), purchased from Woelm pharm, Eschwege, Germany. Thioglycolic acid (2-mercaptoacetic acid) and ethylthioglycolate (ethyl-2-mercaptoacetate) were purchased from Aldrich Chemical Company. 0.1 M stock acidified solutions of Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) were prepared by dissolving the respective metal chloride salts in doubly distilled water. pH values were controlled by mixing appropriate volumes of 1.0 M sodium acetate tri hydrate and 1.0 M hydrochloric acid. 1.0 M sodium acetate trihydrate was also used alone. Seawater samples were collected from El-Shatby near shore, Alexandria city, Egypt. Organic solvents used were of spectroscopic grade.

Apparatus

IR-spectra of the two modified silica gel phases before and after metal ion sorption were obtained from KBr pellets by suing Shimadzu 470 infrared spectrophotometer. Fisher Scientific Accumet pH meter Model 810 calibrated against two standard buffer solutions at pH 4.0 and 9.2 was used for all pH-measurements. Atomic absorption measurements were performed with a Perkin–Elmer 2380 spectrophotometer to quantify Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) present in a mixture. Hg(II) spiked in seawater samples was determined with a cold vapor technique using Varian Spectr. AA-10 plus with VGA-76 vapor Generation Accessory. Corning 410 Flame Photometer was used for determination of sodium and potassium ions in seawater. Complexometric EDTA titrations with the proper indicator were also used for metal ion determination in batch experiments.

Synthesis of Silica Gel Immobilized Thioglycolic Acid and Ethyl Thioglycolate Sorbents

Silica gel was first refluxed with concentrated hydrochloric acid for 4 h to remove any contaminating metals such as iron. It was then filtered off and washed thoroughly with doubly distilled water till neutral and dried at 150°C for 6 h. The dried silica gel (5 g) was refluxed with (7 mmol) each of the two-complexing agents: thioglycolic acid and its ethyl ester in benzene (100 ml) and (10 ml) of dioxane for 3 h. Silica gel modified sorbents thus produced were separated by filtration, washed with benzene and dioxane, dried at (40°C) for 1 h and kept in a desicator over P_2O_5.

Metal Capacity as a Function of pH and Shaking Time

The metal capacity values of such modified silica gel phases toward Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) were determined in triplicate under static conditions by the batch equilibrium method. In this method, 30 mg of the phase were added to 1 ml of 0.1 M metal ion and 9 ml of buffer solution, pH 1.75–6.20, and the total volume completed to 30 ml by doubly distilled water in 50 ml flask. This mixture was mechanically shaken for 30 min at room temperature to attain equilibrium. The mixture was then filtered off, washed with doubly distilled water and the unextracted metal ion in the filtrate was determined by complexometric EDTA titrations using the proper buffer and indicator. Acetate buffer as well as 1 M sodium acetate solutions were used to cover the pH range of 1.75–6.20.

The effect of shaking time on metal exchange capacity was determined under the same batch conditions at different equilibrium time periods (2, 5, 10, 20 and 30 min) at the selected optimum pH of maximum uptake.

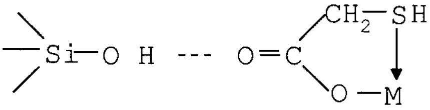
Recycling of the newly synthesized silica gel phases after first use was carried out by treating about 150 mg of the phase after maximum sorption of Hg(II) with excess 0.01 M EDTA solution. This mixture was automatically shaken for 1 h, filtered, washed with doubly distilled water and dried as usual, then checked for another Hg(II) uptake.

Buffer and Temperature Effects on the Stability of the Phases

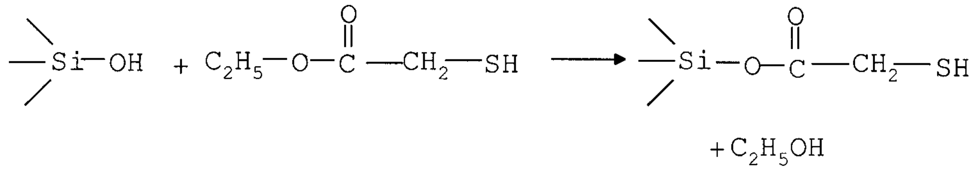
Prolonged medium effects on the stability of the modified silica gel phases (I and II) were investigated in acetate buffer, pH (1.0–6.0) and ammonia buffer (pH 10.0), under static conditions. In this study, 100 mg of the phase was treated with 25 ml of the selected pH buffer in 50 ml flask, then mechanically shaken for 1 h. The treated phase was separated by filtration, washed and dried. To investigate the temperature effects, four weights of 50 mg each of the phase were kept for 1 h at 50–125°C, respectively in an electric oven, then left to cool. To show the extent of ligand decomposition or hydrolysis (i.e. stability of the phase), 30 mg of thermally or medium treated phase along with untreated one taken as standard, were used to evaluate the metal ion sorption capacity for Hg(II), under the same conditions previously described for batch experiments and at pH of maximum uptake, then comparing metal capacity values obtained with that of the standard untreated phase.

RESULTS AND DISCUSSION

Silica gel physically and chemically bond thioglycolic acid moiety, (SG-PBT, phase I) and (SG-CBT, phase II) respectively, are white in color and when they were used as solid phase extractors for uptake of metal ions from solution they showed a color change due to complex formation. For example, (SG-PBT, phase I) changed to green, buff, yellowish white, dark gray and pale brown after sorption of Ni(II), Cu(II) or Zn(II), Cd(II), Hg(II) and Pb(II) ions, respectively at optimum pH values, while (SG-CBT, phase II) showed pale green, pale buff, pale orange, pale gray and pale orange on sorption of the above metal ions, respectively at optimum pH values. The colored metal complexes explain the earlier use of thioglycolic acid for spot tests [32] and recently for spectrophotometric determinations [33]. IR spectra of (SG-PBT, phase I) confirms its immobilization to silica gel surface due to the presence of a new strong band located at 1635 cm^{-1} assigned to the antisymmetrical stretching vibration of carboxylate moiety [34]. In addition, there is a weak band located at 1660 cm^{-1} according to the absorption frequency of the carbonyl group involved in intermolecular hydrogen bond with silanol groups [34]. However, the weak (–OH) stretching vibration of the carboxylic group could not be detected since it merged with strong characteristic band of the silanol groups of silica gel at 3400 cm^{-1} [15]. Moreover, the region below 1400 cm^{-1} which involve stretching frequencies of (–S–C–), ($-S-CH_2-$) as well as symmetrical carboxylate moiety is completely obscured due to the strong absorption by silica gel matrix [34]. The sorption of the metal ion, Hg(II), by the silica gel phases was found to affect the carboxylate stretching vibration band where it splits into two bands at 1637 and 1550 cm^{-1} indicating its participation in binding to Hg(II) ions. Based on these spectral data the physical immobilization of thioglycolic acid to silica gel surface and its binding to metal ions via carboxylate oxygen and thiol sulfur atoms (O, S) may be given as follows:

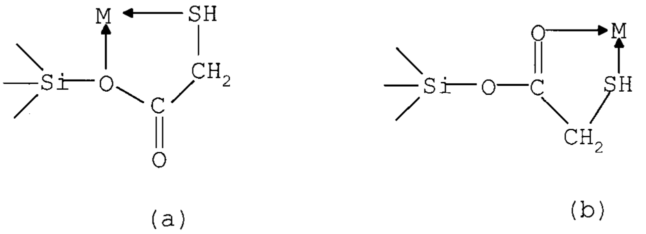


IR spectra of (SG-CBT, phase II) showed no bands attributed to ν(C–H) stretching vibrations of ethyl group indicating that thioglycolic acid immobilized chemically to silica surface with the formation of (≡Si–O–CO–) covalent bonds through the loss of the ethanol molecule as shown below:



$$\equiv Si-OH + C_2H_5-O-\overset{O}{\overset{\|}{C}}-CH_2-SH \longrightarrow \equiv Si-O-\overset{O}{\overset{\|}{C}}-CH_2-SH + C_2H_5OH$$

This assumption was reinforced by the presence of a new absorption frequency band of moderate intensity at 1720 cm^{-1} due to the carbonyl group of the type (Si–O–CO–). On the other hand, binding to metal ion may be occurred via one of the two ways where the band at 1720 cm^{-1} became weak and shifted to ≅ 1700 cm^{-1}.



SCHEME 1 (a) Binding to metal ion in (SG-CBT) via thiol sulfur and ether oxygen; (b) thiol sulfur and carbonyl oxygen.

Although, the mode of bonding of (SG-PBT, phase I) and (SG-CBT, phase II) to metal ion is the same through sulfur and oxygen donor atoms but the nature of the functional group incorporated oxygen donor atom is different. However, the structure (a) is very similar to that of (SG-PBT, phase I). This is inconsistent with the same color obtained for a given metal sorbed by the two phases. On the other hand, the surface concentration of thioglycolic acid physically and chemically bound to silica gel surface was found to be 0.81 and 0.51 mmol/g based on probe method [35].

Characteristics of (SG-PBT, Phase I) and (SG-CGT, Phase II) as Solid Phase Extractors for Metal Ion from Aqueous Media

i) Metal Ion Uptake as a Function of pH

The pH value is one of the most important factors controlling the extraction of metal ions from solution. Table I complies the metal uptake capacities (mmol/g) determined

TABLE I Metal uptake capacities (mmol/g) of the phases I and II at different pH values[a]

Metal ion	*pH*	*SG-PBT (phase I)*	*SG-CBT (phase II)*
Ni(II)	1.75	0.227	0.243
	1.95	0.390	0.211
	2.55	0.373	0.373
	4.25	0.390[b]	0.308
	4.75	0.308	0.308
	6.10	0.373	0.385[b]
Cu(II)	1.95	0.091	0.042
	2.25	0.173	0.156
	2.90	0.254	0.075
	4.55	0.467	0.271
	5.10	0.528[b]	0.393[b]
	6.60	0.303	0.385
Zn(II)	1.80	0.165	0.292
	1.95	0.334	0.292
	3.00	0.524	0.325
	4.25	0.465	0.292
	4.80	0.512	0.276
	6.35	0.526[b]	0.422[b]
Cd(II)	1.75	0.373	0.325
	2.05	0.373	0.356[b]
	2.80	0.292	0.162
	4.50	0.503	0.162
	5.05	0.568	0.243
	6.45	0.629[b]	0.260
Hg(II)	1.90	0.633	0.307
	2.15	0.650	0.370
	2.60	0.698	0.465
	4.65	0.633	0.402
	5.10	0.698	0.509
	6.40	0.808[b]	0.509[b]
Pb(II)	2.15	0.292	0.260
	2.95	0.406	0.195
	3.80	0.373	0.178
	4.65	0.503	0.351[b]
	5.05	0.528[b]	0.276
	6.20	0.243	0.146

[a] Standard deviation values are in the range of 0.000–0.007 based on $N = 3$.
[b] Maximum metal capacity values at 30 min shaking time.

based on batch equilibrium technique for the two phases with Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) ions at different pH values. Generally, the metal capacity values in (mmol/g) for (SG-PBT, phase I) are higher than those values for (SG-CBT, phase II), as detemined to be (0.808, 0.509), (0.629, 0.356), (0.528, 0.393), (0.528, 0.351), (0.526, 0.422) and (0.390, 0.385) for uptake of Hg(II), Cd(II), Cu(II), Pb(II), Zn(II) and Ni(II) using the phases I and II, respectively. This behavior reflects the high concentration of thioglycolic acid physically loaded on silica surface as previously indicated. Moreover, the order of decreasing divalent ions uptake by (SG-PBT, phase I) phase is as follows:

$$\mathrm{Hg(II)} > \mathrm{Cd(II)} > \mathrm{Cu(II)} = \mathrm{Pb(II)} \cong \mathrm{Zn(II)} > \mathrm{Ni(II)}$$

The highest affinity of silica phase I was found to be towards Hg(II) extraction and the lowest for Ni(II) ions. This is in agreement with Person principle [36] for soft and hard acids and bases as well as formation constants values (log β_2) for Hg(II) and Ni(II) complexes with thioglycolic acid determined as 43.82 and 13.53, respectively [34]. The order of metal capacity values for (SG-CBT, phase II) with the metal ions under investigations was found to be:

Hg(II), 0.509 > Zn(II), 0.422 > Cu(II), 0.393 > Ni(II), 0.385 > Cd(II), 0.356 > Pb(II), 0.351

which also showed the greatest affinity towards Hg(II) extraction in comparison with the other metal ions, where, there is insignificant difference between their metal capacity values.

ii) *Metal Ion Uptake as a Function of Shaking Time*

Modification of silica gel surface with organic complexing agents results in producing metal ion extractors need only few minutes to complete the metal ion extraction processes in comparison with other organic adsorbents [4] and this represents one of the advantages of using silica gel as inorganic solid support for immobilization of chelating compounds. Moreover, the relative fastness of extraction of different metal ions can be used for the selective separation of metal ion from mixture containing other interfering metal ions. To account for the fastness of metal ion sorption using silica gel physically and chemically bound thioglycolic acid, phases I and II, respectively. Metal capacity values were determined using batch method at different shaking times (2, 5, 10, 20 and 30 min) to determine the time needed to attain equilibrium. The percentage extraction for each metal ion was calculated at each time interval relative to the maximum uptake at 30 min shaking time. It is evident from using (SG-PBT, phase I), that the extraction of Hg(II) was the fastest judging from only 5 min contact time. The percentage extraction of the metal ions were found to be 100, 96.7, 72.5, 71.2, 64.9 and 54.1% for uptake of Hg(II), Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II). This order obeys satisfactorily the order of maximum metal uptake. On the other hand, extraction of Hg(II), Cd(II), Pb(II) using phase I was always faster than using phase II. Moreover, Hg(II) was the fastest metal ion to extracted either by using phase I or II.

iii) *Buffer and Temperature Effects on the Stability of Silica Gel Phases* (*I*) *and* (*II*)

The study of medium and temperature effects on the stability of the newly synthesized phases I and II seems to be important from practical application point of view. On the other hand, the result obtained regarding (SG-CBT, phase II) supported its covalently bonding to silica gel surface. This can be explained as follows:

SG-CBT, phase II showed pronounced stability after prolonged treatment in the pH range from 3.00 to 10.5 where no decreases in Hg(II) uptake occurred. However, a decomposition or hydrolysis of the chemically bound thioglycolic acid was found at high hydrogen ion concentration judging from the percentage decrease of efficiency of metal ion uptake as found to be 22.9 and 7.5% at pH 1.4 and 2.00, respectively.

On the other hand (SG-CBT, phase I) showed less resistance to buffer effect compared to (SG-CBT, phase II) under the same experimental conditions where there is a decrease in metal capacity values relative to a non-treated standard phases

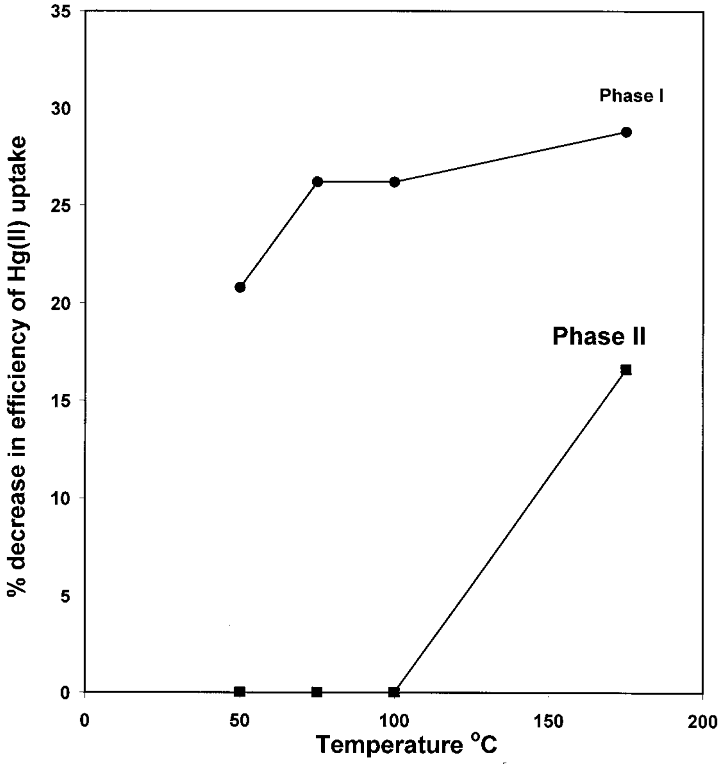


FIGURE 1 Effect of thermal treatment on efficiency of Hg(II) uptake using phases (I) and (II).

and consequently the percentage decreased in Hg(II) uptake were found to be 14.3, 28.6, 7.4, 7.4, 0.00, and 14.3% at the pH value of 2.00, 3.00, 4.00, 5.00, 6.25 and 10.5, respectively.

The study of thermal effects on the efficiency of the phases toward metal ion uptake is too important, not only to indicate their relative stabilities but also can be used as a criteria to differentiate between the mode of bonding (physical or chemical binding) of the complexing agent to adsorbent surface. In this context, the results of these studies introduced an additional proof that ethylthioglycolate (ethyl ester of thioglycolic acid) not physically adsorbed to silica gel surface but chemically bonded with the loss of ethanol molecule. This proof based on the fact that the boiling point of ethylthioglycolate is 54°C and the results of thermal stability studies after keeping phase II for 1 h at 50, 75, 100 and 125°C followed by evaluating the change in its metal capacity comparing to a standard sample revealed that no loss of phase II efficiency for the investigated Hg(II) uptake at 50, 75, 100°C (Fig. 1). However, there is a decrease in efficiency at 125°C found to be 16.6%. Thus, if thioglycolate is physically adsorbed, so it is expected to be decomposed near 50°C and consequently the decrease in phase efficiency will start at this temperature. On comparing these results with that obtained for phase I (thioglycolic acid, B.P. 125°C, physically loaded to silica surface) where the percentage decrease in efficiency of Hg(II) uptake evaluated to be 20.9, 26.3, 26.3 and 28.8% at 50, 75, 100 and 125°C, respectively, clearly prove that phase I is thermally unstable due to its physical immobilization.

Recycling of Modified Silica Gel Phases I and II

The application of these phases for further extraction of metal ions after first use requires an efficient method for their recycling. In fact, regeneration using acid or base treatment as in ion-exchangers is not adequate for silica gel modified organic complexing agent, due to the great possibility of protonation of active donor centers in the ligand, also because acid or base treatment may increase the chance of hydrolysis of the bound complexing agent. Therefore, we selected to use another strong complexing agent such as ethylenediaminetetracetic acid (EDTA) to back-extract the metal ion from metal chelate formed modified silica gel phase in the pale orange recycling process. Thus Hg(II)-phase I (dark gray) and Hg(II)-phase II (pale gray) complexes were mixed with excess (0.1 M-EDTA) solution and shaken for 30 min, filtered off, washed with double distilled water and dried. It was firstly observed that original color of the phases were restored and the results of metal capacity determined after the second extraction using phase II was (0.490 ± 0.010 mmol/g) which is very close to metal capacity found in the first one (0.509 mmol/g) with percentage decrease in efficiency equal 3.7%. However, with physically loaded thioglycolic, phase I the percentage decrease was 14.4% where the original metal capacity was 0.808 mmol/g and after recycling became 0.690 ± 0.010, due to leaching of physically adsorbed ligand.

Application of the Newly Synthesized Phases for Removal of Heavy Metal Ions from Seawater

It is well known that conventional anion and cation exchange sorbents appear of limited use for removal of trace heavy metal ions from saline solutions such as seawater due to the high concentrations of Na(I), K(I) and Ca(I) ions. However, the use of metal chelate forming sorbents makes it possible to concentrate heavy metal ions from brine solutions and separate them from the major components of the natural aquatic system [37]. It is shown that mercury, zinc and copper are selectivity retained by phases I and II based on the results of percentage recovery compiled in Table II. The selectivity of these sorbents is illustrated by their high preference for Hg(II),

TABLE II Percentage recovery of heavy metal ions after percolating 1.0 l of sea water spiked with Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) on a column packed with 250 mg of (SG-PBT, phase I) and (SG-CBT, phase II) with a flow rate of 2 ml/min

Metal ion	*Conc.* (mg/l)	*% Recovery*[a]	
		Phase I	*Phase II*
Hg(II)	1.180	61.0 ± 0.4	98.4 ± 0.2
Zn(II)	0.641	55.7 ± 0.4	97.3 ± 0.6
Cu(II)	0.762	61.7 ± 0.3	96.5 ± 0.4
Cd(II)	0.831	00.0	00.0
Pb(II)	0.660	45.4 ± 0.2	00.0
Ni(II)	0.764	00.0	00.0
Na(II)	11800.000	00.0	00.0
K(I)	300.000	00.0	00.0
Mg(II)	1640.000	00.0	00.0
Ca(II)	400.000	00.0	00.0

[a] Average of three determinations.

Zn(II) and Cu(II) ions ($\log K_d = 3.19$, 3.09 and 3.20 for phase I; 4.78, 4.56 and 4.46 for phase II, respectively) over such cations as Na(I), K(I), Mg(II) and Ca(II). The high affinity of these sorbents (especially phase II) to act as solid phase extractors for these metal ions make them very useful for removal, preconcentration, separation and analysis of these heavy metal ions in presence of large amounts of alkali and alkaline earth metal ions. On the other hand, the data obtained from recovery of heavy metal ions Table II support the chemical immobilization of thioglycolic acid (phase II) with it higher stability and resistance to leaching process than phase I. This is also realized from the quantitative recovery of mercury ($99.1 \pm 0.4\%$) which was achieved on the percolating 1.0 l of seawater spiked with 1.2 mg/l of Hg(II) alone though a column packed with phase II. However, on using phase I, there is 38% decrease in efficiency relative to phase II due to leaching phenomenon.

CONCLUSION

The tested silica gel phase chemically bound thioglycolic acid (II) was experienced with the general attractive features: An ease of preparation in a one step reaction procedure without the need of a silylating reagent as reported in other silica gel phases [16,17]. It affords a simple chelating sorbent with a high thermal stability and resistance to hydrolysis and leaching by acids and buffer solutions. It shows a good reproducibility in the metal capacity values as well as the metal uptake properties. Finally, it can be applied as a good selective solid phase extractor for removal of free heavy metal ions from natural seawater samples and other industrial waste samples as well.

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