

# Alumina physically loaded by thiosemicarbazide for selective preconcentration of mercury(II) ion from natural water samples

Salwa A. Ahmed

*Chemistry Department, Faculty of Science, El-Minia University, El-Minia, Egypt*

Received 23 October 2007; received in revised form 29 November 2007; accepted 15 December 2007

Available online 23 December 2007

## Abstract

The multifunctional ligand, thiosemicarbazide, was physically loaded on neutral alumina. The produced alumina-modified solid phase (SP) extractor named, alumina-modified thiosemicarbazide (AM-TSC), experienced high thermal and medium stability. This new phase was identified based on surface coverage determination by thermal desorption method to be  $0.437 \pm 0.1 \text{ mmol g}^{-1}$ . The selectivity of AM-TSC phase towards the uptake of different nine metal ions was checked using simple, fast and direct batch equilibration technique. AM-TSC was found to have the highest capacity in selective extraction of Hg(II) from aqueous solutions all over the range of pH used (1.0–7.0), compared to the other eight tested metal ions. So, Hg(II) uptake was  $1.82 \text{ mmol g}^{-1}$  (distribution coefficient  $\log K_d = 5.658$ ) at pH 1.0 or 2.0 and 1.78, 1.73, 1.48, 1.28 and  $1.28 \text{ mmol g}^{-1}$  ( $\log K_d = 4.607, 4.265, 3.634, 3.372$  and  $3.372$ ), at pH 3.0, 4.0, 5.0, 6.0 and 7.0, respectively. On the other hand, the metal ions Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) showed low uptake values in range  $0.009\text{--}0.720 \text{ mmol g}^{-1}$  ( $\log K_d < 3.0$ ) at their optimum pH values. A mechanism was suggested to explain the unique uptake of Hg(II) ions based on their binding as neutral and chloroanionic species predominate at pH values  $\leq 3.0$  of a medium rich in chloride ions. Application of the new phase for the preconcentration of ultratrace amounts of Hg(II) ions spiked natural water samples: doubly distilled water (DDW), drinking tap water (DTW) and Nile river water (NRW) using cold vapor atomic absorption spectroscopy (CV-AAS) was studied. The high recovery values obtained using AM-TSC ( $98.5 \pm 0.5, 98.0 \pm 0.5$  and  $103.0 \pm 1.0$ ) for DDW, DTW and NRW samples, respectively based on excellent enrichment factor 1000, along with a good precision (R.S.D.%  $0.51\text{--}0.97\%$ ,  $n = 3$ ) demonstrate the accuracy and validity of the new modified alumina sorbent for preconcentrating ultratrace amounts of Hg(II) with no matrix interference.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Alumina; Thiosemicarbazide; Mercury(II); Preconcentration; Natural waters

## 1. Introduction

Toxic metals are tending to accumulate in the vital organs of human being where they can act progressively over a long period. Environmental pollution of natural water by toxic metals arises mainly from industrial effluents and wastewater disposal from different sources. Amongst these metals, inorganic and organic mercury compounds which may be present in natural water and may concentrate in various organisms [1,2]. So, their concentration should be kept under permanently controlled conditions. On account of the growing awareness of environmental mercury pollution it is need for new and more accurate, efficient, precise and selective methods for mercury(II) extraction from natural water samples. In fact, two basic steps are necessary to be performed before determination of Hg(II) presents at trace

or ultratrace levels especially in natural matrices. The first step is the removal of interfering matrix components [3], while the second is an efficient preconcentration step to meet its determination requirements by spectrometry modes, viz., CV-AAS or ICP-AES. These two steps can be achieved successfully using selective solid-phase extraction (SPE) technique [4]. It is a well-known technique, which has rapidly become established as the prime means of sample pre-treatment for quantitation of various organic or inorganic analytes [5]. The basic principle of this technique is the transfer of the analyte from the aqueous phase to bind to active sites of adjacent solid phase. The advantages of using SPE technique is versatile [1,6], it is rapid, reproducible, requires only small volumes of solvents or none at all as in the case of solid-phase microextraction device [5]. The solid-phase extractor is arised from the immobilization of organic complexing agents to the surface of organic supports such as polyurethane foams [7], cellulosic derivatives [8,9] and ion exchange resins [10–13] or inorganic as silica gel [14–20] and alumina [21–23].

*E-mail address:* [salwa\\_kasem2003@yahoo.com](mailto:salwa_kasem2003@yahoo.com).

These inorganic supports have the advantages of no swelling, fast kinetics and good mechanical stability as well [18]. In fact, the design of a stable and selective SP-sorbents for separation and preconcentration of a target metal ion [16,24–26] depends on different factors related to the nature of solid support, its surface area and activity [27] as well as other important factors related to the organic complexing agent bound to the solid substrate [28]. The opportunity for chemical surface modification of alumina with organo-functional groups is too limited [29], where it is mainly physically modified via hydrogen bonding [30–33]. A new modification mode was introduced by Hiraide et al. [34]. According to this modification, the selected organic reagent is incorporated in the cores of admicelles of sodium dodecyl sulfate surfactant attached to alumina surfaces at pH 2.0. Consequently, new organic reagents are immobilized on surfactant-coated alumina for separation and enrichment of different metal ions [22,35,36], in addition to polyaromatic hydrocarbon as well [37]. However, modification of alumina surface via physical loading of organic substrates is still attractive due to its great simplicity. In this respect, the most successful SP-extractors for Hg(II) ions are those immobilized basically, sulphur and/or nitrogen containing compounds [38–40]. In fact, thiosemicarbazide (TSC) [ $\text{H}_2\text{N}-\text{HN}-\text{CS}-\text{NH}_2$ ] is a well-known complexing agent able to bind to transition metal ions in solution and solid state [41–45]. It has simple, elastic and aliphatic structure which minimizes steric hindrance. Moreover, it is rich in binding sites, where it is able to bind to alumina via hydrogen bonding from a hand and bind to metal ions from the other hand. So, TSC is expected to satisfy these important requirements needed to achieve a successful and selective physical binding. This manuscript is devoted to the design, synthesis and application of alumina physically immobilized TSC as selective SP-extractors for mercury(II). Strong emphasis is directed to study and evaluate the utility of this new sorbent to act as a selective solid-phase extractor for preconcentration of ultratrace amounts of Hg(II) spiked natural water samples prior to the determination by CV-AAS.

## 2. Experimental

### 2.1. Materials

Neutral alumina of standard grade (150 mesh, 58 Å and surface area  $155 \text{ m}^2 \text{ g}^{-1}$ , pH of aqueous suspension is  $7.0 \pm 0.5$ ), thiosemicarbazide and metal salts as chloride or acetate and other chemicals used were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). River water samples were collected from El-Nile River at El-Minia governorate, Egypt, as well as drinking tap water, doubly distilled water (DDW) and natural mineral water, which are used as matrices. Organic solvents used were purchased from Merck (Darmstadt, Germany).

### 2.2. Apparatus

IR-spectra of the phase before and after metal ion sorption were obtained from KBr pellets by using PerkinElmer 1430, infrared spectrophotometer. A Fisher Scientific Accumet pH-meter, Model 825 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 PerkinElmer 2380 spectrometry. Hg(II) was determined by a PerkinElmer MHS-10 mercury hydride generation system, which permits the determination of mercury where an electrically heated quartz T-tube was used as an alternative to flame heating. The volatile specie of mercury was generated by merging the acidified sample and sodium tetrahydroborate(III) in a continuous flow system. The gaseous analyte was subsequently introduced via a stream of Ar carrier into the atomizer device.

### 2.3. Synthesis of alumina physically loaded with thiosemicarbazide

Neutral alumina was first treated by heating in an oven at  $150^\circ\text{C}$  for 5 h. Then, 25 g of the treated alumina was refluxed with 30 mmol of thiosemicarbazide in 200 ml ethanol for 5 h, then cooled, filtered, washed with diethyl ether and dried in an oven at  $120^\circ\text{C}$  for 2 h.

### 2.4. Sorption studies of the newly alumina-modified thiosemicarbazide (AM-TSC) phase

#### 2.4.1. Effect of pH values

The metal uptake capacities of such new AM-TSC phase towards Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) ions were determined in triplicate under static conditions by the batch equilibrium technique. Fifty milligrams of the phase was added to a mixture of 1.0 ml of 0.1 M of the metal ion (the actual concentration of the prepared solution was determined using EDTA titration) and 24 ml of a buffer solution of pH 1.0–10.0 except with Fe(III) where the pH used between 1.0 and 4.0. The total volume was completed to 50 ml by DDW in a 100 ml measuring flask. This mixture was mechanically shaken for 30 min at room temperature to attain equilibrium. Then the solid phase was separated by filtration, washed with DDW and the unretained metal ion in the filtrate was determined by complexometric EDTA titration and/or atomic absorption spectrometry AAS, Hg(II) was determined by borohydride generation AAS technique. Metal chloride solutions were prepared in 0.1 M hydrochloric acid to avoid hydrolysis. Mixed known volumes of equimolar concentrations (1.0 M) of each of hydrochloric acid and sodium acetate, 1.0 M sodium acetate and ammonia buffer were used to cover the pH range 1.0–10.0 [28].

#### 2.4.2. Effect of shaking time

The effect of shaking time on the percentage extraction of metal ions was also investigated for some metal ions by the static technique. In this, 50 mg of the phase was added to 1 ml of 0.1 M of the metal ion and 24.0 ml buffer at the pH of the highest metal ion uptake (optimum pH) [28]. The total volume was completed to 50 ml by DDW in 100 ml measuring flask and automatically shaken for the selected period time 2, 5, 10, 20 and 30 min. The mixture was filtered, washed with DDW several times and the free metal ions were determined as described above.

## 2.5. Stability studies of the newly alumina-modified thiosemicarbazide (AM-TSC) phase

### 2.5.1. Effect of buffer and temperature treatment on the stability of AM-TSC phase

The effect of medium on the stability of the new modified alumina phase was investigated in acetate buffer, pH 1.0–6.0 and ammonia buffer 8.0, 10.0 under static conditions [28]. In this study, 100 mg of the phase was treated with 25 ml of the selected buffer in 50 ml measuring flask for 1 h, then mechanically shaken for another 30 min. The treated phase was separated by filtration, washed and dried. To investigate the temperature effects [17] a weight of 100 mg of the phase was kept for 1 h at 50, 100, 150, 200, 250 and 300 °C in an electric oven, then left to cool. To show the extent of decomposition or hydrolysis of the modified chelate on alumina surface, 50 mg of medium and thermally treated phases along with untreated one taken as standard, were used to evaluate Hg(II) ion sorption capacity under the same conditions previously described for batch experiments and pH of the highest uptake. Then comparing the Hg(II) uptake values obtained with that of the standard untreated one [17].

### 2.6. Determination of the surface coverage value of AM-TSC phase by the thermal desorption method

One hundred milligram of the modified alumina phase was weighed in a dry porcelain crucible and this was gradually heated in an oven to 700 °C to determine the concentration of thiosemicarbazide physically loaded to neutral alumina surface. The sample was maintained at this degree for 1 h to ensure the completion of the desorption process, then left to cool to room temperature. The weight loss due to thiosemicarbazide desorption was evaluated by difference. Blank sample of dry unmodified neutral alumina was subjected to the same treatment for comparison.

### 2.7. Selective preconcentration of mercury(II) from natural water samples

River water samples were collected from El-Nile river (NRW) at El-Minia governorate, Egypt, as well as drinking tap water

(DTW) and DDW were used as matrices to validate the efficiency of the AM-TSC phase to act as selective and efficient preconcentrators for Hg(II) ions. Thus, the water samples were filtered through filter paper and spiked with 10 ng l<sup>-1</sup> adjusted to pH 2.0 by HCl. Then, 2.0 l of the spiked water sample were passed through a minicolumn (length 10.0 cm, i.d. 1.65 cm, attach to a glass reservoir of 1.0 l volume) [16] packed with 100 mg of the phase used as thin layer enrichment bed, at a flow rate of 5 ml min<sup>-1</sup>. The mercury retained on the column was eluted slowly using 2.0 ml of concentrated HNO<sub>3</sub> (flow rate 0.4 ml min<sup>-1</sup>) and subjected to analysis by hydride generation AAS technique.

## 3. Results and discussion

### 3.1. Infrared spectral studies and surface coverage

The surface modification of solid sorbents, such as alumina with organic modifier, can be mainly interpreted based on infrared spectrophotometric analysis. The new physically modified alumina phase has a white color. An obvious color change occurred after metal ion sorption by this phase due to the complex formation. For example, the color of the phase changed from white to dark brown, orange, blue, dark yellow, pale yellow and yellowish brown after sorption of Fe(III), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) ions, respectively at optimum pH values (maximum metal ion uptake) (Table 1). The IR-spectra of the pure unmodified alumina displayed a broad band at 3450 cm<sup>-1</sup> [30] which may be attributed to hydrogen bonded surface hydroxo groups. Moreover, there is an intense broad band located in the vicinity of 560 cm<sup>-1</sup> was argued to Al–O stretching vibration [30]. The loading of thiosemicarbazide to alumina surface was confirmed by IR-spectral analysis, where new bands not present in the parent unmodified alumina were appeared. A strong band at 1200, 1050 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{S})$  in addition to a weak bands at 3550, 3300 cm<sup>-1</sup> due to  $\nu(\text{N}-\text{H})$  and  $\nu(\text{NH}_2)$  involved in hydrogen bonding with alumina surface hydroxo groups [46]. These bands cannot be detected clearly, since they were merged with the strong characteristic band centred at 3450 cm<sup>-1</sup> to look wider than the parent alumina. On the other hand, comparing the IR-spectra of the modified alumina

Table 1  
Metal uptake capacities (mmol g<sup>-1</sup>) of the AM-TSC phase at different pH values  $\phi$

Metal ion	mmol g <sup>-1</sup> values in different buffer solutions								
	pH 1.0	pH 2.0	pH 3.0	pH 4.0	pH 5.0	pH 6.0	pH 7.0	pH 8.0	pH 10.0
Hg(II)	1.820 <sup>a</sup>	1.820 <sup>a</sup>	1.780	1.730	1.480	1.280	1.280	–	–
Ca(II)	0.009	0.009	0.058	0.067	0.058	0.144	0.154	0.200 <sup>a</sup>	0.150
Fe(III)	0.278	0.278	0.634	0.720 <sup>a</sup>	–	–	–	–	–
Co(II)	0.086	0.134	0.086	0.058	0.182 <sup>a</sup>	0.048	0.029	0.100	0.010
Ni(II)	0.019	0.019	0.009	0.069	0.069	0.069	0.078	0.100 <sup>a</sup>	0.009
Cu(II)	0.118	0.392 <sup>a</sup>	0.392 <sup>a</sup>	0.363	0.363	0.392 <sup>a</sup>	0.392 <sup>a</sup>	0.010	0.020
Zn(II)	0.086	0.086	0.086	0.048	0.086	0.125	0.298 <sup>a</sup>	0.110	0.010
Cd(II)	0.009	0.009	0.106 <sup>a</sup>	0.106 <sup>a</sup>	0.058	0.009	0.106 <sup>a</sup>	0.100	0.010
Pb(II)	0.106	0.154	0.106	0.125	0.106	0.154	0.202 <sup>a</sup>	–	–

$\phi$  values are based on  $n = 3$  with maximum S.D. of 0.008.

<sup>a</sup> Maximum metal uptake values (mmol g<sup>-1</sup>).

phase after Hg(II) sorption with the metal free phase clearly demonstrate that the sulphur atom is the main active donating site to Hg(II). This is based on the appearance of stretching frequency bands at 1097–1040  $\text{cm}^{-1}$  characteristic to metal ion binding to sulphur atom [39,46]. This result for the linkage to metal ion support the physical loading of thiosemicarbazide to alumina surface via hydrogen bonding formation between amino nitrogen and alumina surface hydroxo group hydrogen [31].

The concentration of TSC in mmol on alumina surface in g (surface coverage  $\text{mmol g}^{-1}$ ) is determined based on the thermal desorption method [47] and found to be  $0.437 \pm 0.1 \text{ mmol g}^{-1}$ .

### 3.2. Equilibration studies of the AM-TSC phase for uptake of metal ions as a function of pH and shaking time

Binding of the metal ion to the chelate compounds in the solution, is heavily dependent on the pH of the metal ion solution as well as the nature of the metal ion, charge, size and the chelate compounds [38]. This is mainly attributed to the favoured conditions for complex formation between the hydrated metal ion in aqueous solution and the active functional groups participating in such bond formation. Table 1 compiles the  $\text{mmol g}^{-1}$  values determined on the basis of the batch equilibrium technique for nine tested metal ions, viz. Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) Cd(II), Hg(II) and Pb(II) in different acetate buffer solutions. The study was performed at constant shaking time (30 min). It is noteworthy that a strong dependence of the metal ion capacity values on the pH of the tested metal ion solution is observed. This can be easily noticed by the significant increase in the  $\text{mmol g}^{-1}$  value on going from pH 1.0 to 6.0 for most metal ions such as Ca(II), Fe(III), Co(II), Cu(II), Zn(II) and Pb(II). On the other hand, metal ions such as Ni(II) and Cd(II) showed only slight dependence on the pH values (Fig. 1). Hg(II) was found to exhibit decrease in the  $\text{mmol g}^{-1}$  value on going from pH 1.0–6.0 and it exhibit the maximum metal capacity,  $1.82 \text{ mmol g}^{-1}$  at pH 1.0 and 2.0. Comparison between the  $\text{mmol g}^{-1}$  values and those of the surface coverage ascertain the richness of TSC as a metal-binding molecule incorporated more than one binding site are available for binding to mercury atoms selectively. However, Ca(II) and Cd(II) extraction by phase were less than that for Hg(II), based on

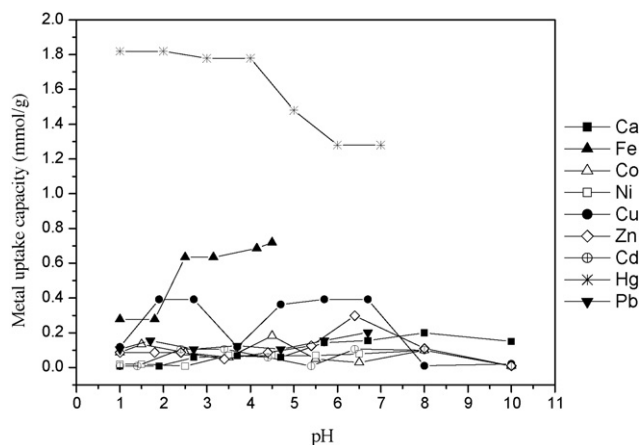


Fig. 1. Effect of pH on metal uptake capacities ( $\text{mmol g}^{-1}$ ) using AM-TSC phase.

the determined  $\text{mmol g}^{-1}$  value, which were  $0.009 \text{ mmol g}^{-1}$  at pH 1.0 and 2.0. It is important to mention here that, the small molecular size of the used organic modifier contained S and N donor sites may account for the high values of Hg(II) uptake. This will consequently lead to the use of small amounts of this new solid-phase extractor for packing columns in preconcentration or separation processes comparing to other modified phases [19,48,49]. Finally, the general order for maximum metal uptake and  $\log K_d$  values of all tested metal ions along with the optimum buffering conditions for AM-TSC phase is summarized in Tables 1 and 2, respectively.

The effect of shaking time on the percentage extraction of metal ions is considered to be of significant importance to determine the possible discrimination order in the behaviour of the AM-TSC phase towards the different metal ions. This factor is studied to determine the equilibration rate and the most suitable shaking time or flow rate for further study in the coming sections. Two representative metal ions, viz. Hg(II) and Fe(III), were selected because of their high metal capacity values to study metal uptake (as  $\text{mmol g}^{-1}$ ) and percentage extraction in different shaking times, viz. 2, 5, 10, 20 and 30 min. It is evident from the results that the equilibrium between Hg(II) and the phase is very rapid judging from the 98.4% extraction of Hg(II) after only 2 min of shaking, while only a 10–20 min

Table 2  
Distribution coefficient (expressed as  $\log K_d$ ) for the uptake of metal ions at different pH-values using AM-TSC phase

Metal	pH									
	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	10.0	
Hg(II)	5.658	5.658	4.607	4.265	3.634	3.372	3.372	–	–	
Ca(II)	0.781	0.781	1.604	1.669	1.604	2.026	2.058	2.187	2.046	
Fe(III)	2.239	2.239	2.706	2.706	2.759	2.793	–	–	–	
Co(II)	1.666	1.870	1.666	1.489	2.015	1.404	1.181	1.735	0.714	
Ni(II)	0.995	0.995	0.668	1.567	1.567	1.567	1.622	1.735	0.668	
Cu(II)	1.806	2.398	2.398	1.806	2.357	2.398	2.398	0.709	1.013	
Zn(II)	1.685	1.685	1.685	1.423	1.685	1.858	2.280	1.798	0.733	
Cd(II)	0.673	0.673	1.767	1.767	1.493	0.673	1.767	1.739	0.719	
Pb(II)	1.757	1.931	1.757	1.833	1.757	1.931	2.060	–	–	

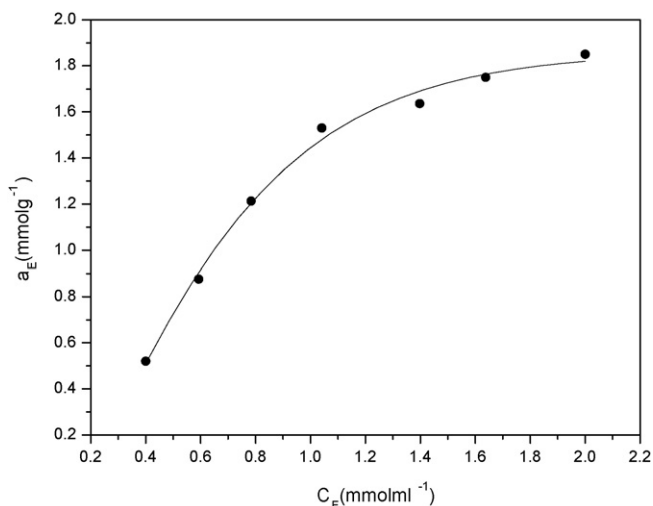


Fig. 2.  $a_E$  vs.  $C_E$  relationship for isotherm curve of Hg(II) uptake using AM-TSC phase.

shaking time was sufficient to obtain complete extraction of Hg(II) by the phase. Thus, it is evident from the study of the effect of shaking time that this newly alumina phase is superior in its efficiency for the extraction of Hg(II) rather than Fe(III).

### 3.3. Langmuir isotherms of the new physically loaded AM-TSC phase

The sorption isotherms for the uptake of the metal ions under investigation with alumina phase were determined by the batch technique at the pH of maximum uptake of each metal ion. Thus, solutions of metal ion in the concentration range ( $4.0 \times 10^{-4}$  to  $2.0 \times 10^{-3}$  M) were shaken for 30 min with a constant weight 0.05 g of the phase. The analysis of the isotherm data is important in order to develop an equation that accurately represents the results. The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of identical sites [50,51] (Fig. 2). An equilibrium model able to identify chemical mechanism involved the Langmuir equilibrium equation is represented as

$$\frac{C_E}{a_E} = \frac{1}{KA_S} + \frac{C_E}{A_S}$$

where  $K$  and  $A_S$  are the binding constant and maximum metal ion sorption capacity, respectively;  $C_E$  the unsorbed metal ion in the filtrate ( $\text{mmol ml}^{-1}$ ) when sorption equilibrium is attained and  $a_E$  the sorbed metal ion by the phase in  $\text{mmol g}^{-1}$ . The linear plots of  $C_E/a_E$  against  $C_E$  (Fig. 3) showed that the Langmuir equation gives a fairly good fit to the adsorption isotherms. These plots were employed to give the value of maximum metal ion sorption capacity  $A_S$  and binding constant  $K$  from the slope and intercept of the plot. It is evident that the new alumina phase has the highest binding constants  $K \times 10^{-4}$  (21.862) and maximum uptake ( $1.85 \text{ mmol g}^{-1}$ ), towards Hg(II) sorption. The other metal ions have smaller  $K$  and  $A_S$  values at their optimum pH values. Generally, the very high binding constants support

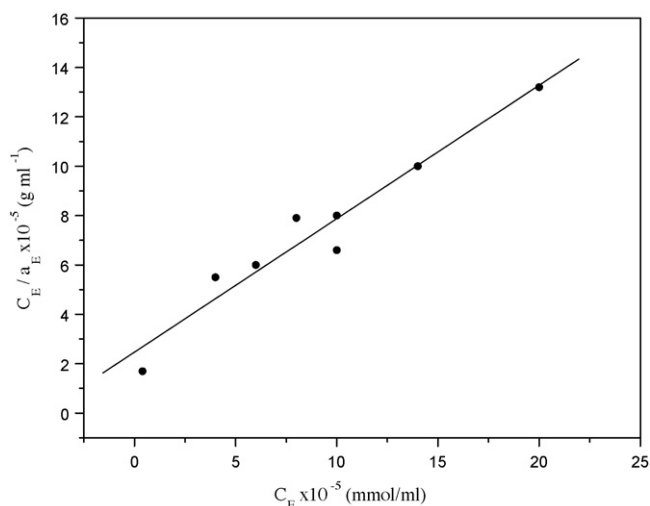


Fig. 3.  $C_E/a_E$  vs.  $C_E$  relationship for binding constant and maximum Hg(II) uptake using AM-TSC phase.

the sorption of metal ion from solution by the solid phase via strong binding with S and N donor sites [52].

### 3.4. Buffer and temperature treatment on the stability of the phases

The study of prolonged medium (pH 1.0–10.0) and temperature ( $50$ – $300^\circ\text{C}$ ) effects on the stability of the new phase is important from practical application point of view [28]. The results of medium effects showed that AM-TSC phase experienced pronounced stability. Since hydrolysis not exceed than 34.6% at all pH range 1.0–10.0 (Fig. 4). On the other hand, results of thermal stability studies of the phase maintained its efficiency for Hg(II) uptake at  $50$  and  $100^\circ\text{C}$  where no decomposition occurred. However, the decrease in its Hg(II) sorption was recorded as follows: at  $150$ ,  $200$ ,  $250$  and  $300^\circ\text{C}$  values of 0.5, 5.4, 5.4 and 21.6%, respectively (Fig. 5).

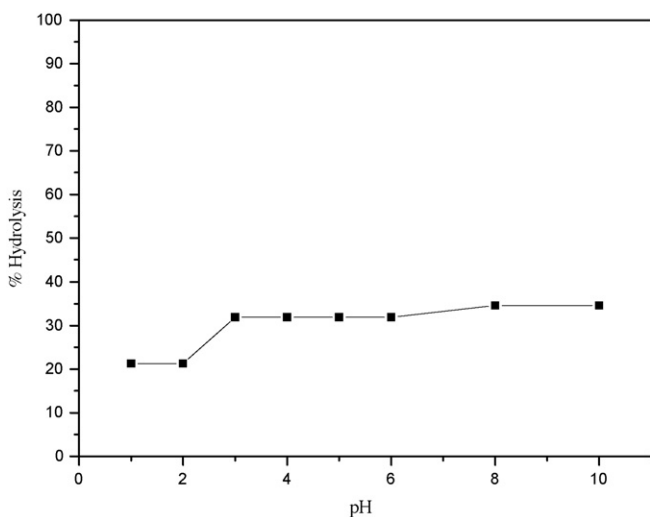


Fig. 4. Effect of medium at different pH values on efficiency of Hg(II) uptake using AM-TSC phase.

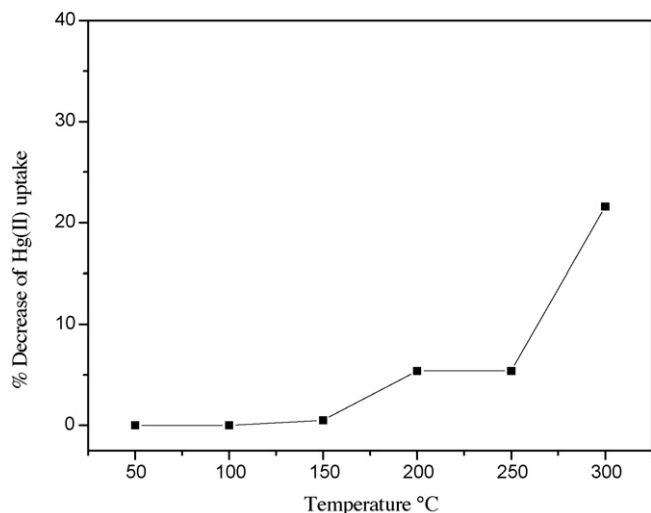


Fig. 5. Effect of thermal treatment on efficiency of Hg(II) uptake using AM-TSC phase.

### 3.5. Suggested mechanism for selective retention of Hg(II) at pH 2.0 in presence of chloride ions by the new phase

It is very clear from the previous results that the binding mode taking place between eight of the metal ions under investigation and the new AM-TSC sorbent are highly favoured in the pH range 4.0–10.0 of contact solutions. On the other hand, Hg(II) is showing reverse behaviour where it is completely retained at low pH values 1.0 or 2.0 [Hg(II) uptake  $1.82 \text{ mmol g}^{-1}$ ]. This can be well understood on dealing with the conditions used for the sorption of the metal ions, where the buffer solutions used in acidic medium (pH 1.0–7.0) were prepared from 1.0 M sodium acetate adjusted to the appropriate pH with 1.0 M hydrochloric acid. At low pH values for example, at  $\text{pH} \leq 2.0$  where the medium is rich in chloride ions Hg(II) are present as neutral  $\text{HgCl}_2$  and chloroanionic  $\text{HgCl}_3^{1-}$ ,  $\text{HgCl}_4^{2-}$  complexes [16,53]. At this working pH, it is suggested that Hg(II) chloroanionic complexes were retained via electrostatic attraction with the available positive sites produced by protonation of alumina surface hydroxyl groups in acidic medium [22]. In addition to a selectively coordinative binding of TSC, sulphur atom to the neutral  $\text{HgCl}_2$  species [14,28]. The synergetic effect played by S atom for binding  $\text{HgCl}_2$  was further proved by increasing values of Hg(II) uptake from 1.45, 1.40 and  $1.35 \text{ mmol g}^{-1}$  at pH 1.0, 2.0 and 3.0, respectively on using alumina only to 1.82, 1.82 and  $1.78 \text{ mmol g}^{-1}$  on

Table 4

Percentage recovery of Hg(II) spiked natural portable water<sup>a</sup> contains different concentrations of cations and anions under batch conditions<sup>b</sup>

Sample	Conc. of Hg(II) spiked (mmol)	% recovery	R.S.D.%
1	$2 \times 10^{-4}$	$99.25 \pm 1.1$	1.11
2	$6 \times 10^{-4}$	$99.2 \pm 1.1$	1.11
3	$1 \times 10^{-3}$	$98.6 \pm 0.7$	0.71

<sup>a</sup> Natural portable water sample contains: Ca(II) (5.2 ppm), Mg(II) (13.2 ppm), Na(I) (14.5) and K(I) (0.8 ppm) and anions as  $\text{HCO}_3^-$  (6.0 ppm),  $\text{SO}_4^{2-}$  (65.0 ppm),  $\text{Cl}^-$  (17.0) and  $\text{SiO}_4^{4-}$  (2.0 ppm).

<sup>b</sup> Experimental conditions: mass of the phase 50 mg, volume of solution 50 ml, contact time 30 min, pH 2.0.

using the AM-TSC phase at the same pH values and under the same experimental condition. Moreover, the potential participation of chloride ions in binding of Hg(II) as chloroanionic species was also ensured based on the obtained values of Hg(II) uptake on using this new phase in acidic medium (pH 1.0–7.0) adjusted by  $\text{HNO}_3$  only with no source of chloride ions and under the same batch conditions. Values of Hg(II) uptake in this medium was  $0.450 \text{ mmol g}^{-1}$  at pH 1.0 and increased gradually to reach a maximum value of  $1.00 \text{ mmol g}^{-1}$  at pH 7.0 supporting the Hg(II) uptake as complex formation [6].

### 3.6. Selective preconcentration of mercury(II) from natural water samples

This study was undertaken in order to evaluate the potential application of AM-TSC phase for preconcentration of trace levels of Hg(II) in natural water samples. The results of enrichment of 10 and  $25 \text{ ng l}^{-1}$  of Hg(II) spiked in three water samples, namely: DDW, DTW and NRW using 100 mg of each phases packed in a minicolumn and used as a thin layer enrichment bed showed in Table 3. The results demonstrate the validity and accuracy of the phases for preconcentration of the spiked ultra concentrations of Hg(II) with no matrix effect. The efficiency of metal ion preconcentration especially Hg(II) by concentrated  $\text{HNO}_3$  acid is found to be high without causing any notable change to the chemical nature of the organic alumina modifier. The high recovery of Hg(II) from the DDW, DTW and NRW samples as determined to be  $98.5 \pm 0.5$ ,  $98.0 \pm 0.5$  and  $103.0 \pm 1.0$ , respectively with excellent preconcentration factor (1000), using a small mass of the phase account for the high metal capacity values for Hg(II) uptake using the new phase. On the other hand, the highest recovery of Hg(II) from the NRW

Table 3  
Selective preconcentration of Hg(II) from water samples spiked with ultratrace amounts of Hg(II) using AM-TSC phase

Water sample	Spiked Hg(II) ( $\text{ng l}^{-1}$ )	Mass of the phase (g)	Sample volume (l)	Eluent ml of conc. $\text{HNO}_3$	% recovery <sup>a</sup>
Doubly distilled water	10.0	0.1	2.0	2.0	$98.5 \pm 0.5$
	25.0	0.1	2.0	2.0	$98.4 \pm 0.5$
Drinking tap water	10.0	0.1	2.0	2.0	$98.0 \pm 0.5$
	25.0	0.1	2.0	2.0	$98.0 \pm 0.6$
El-Nile river water	10.0	0.1	2.0	2.0	$103.0 \pm 1.0$
	25.0	0.1	2.0	2.0	$102.0 \pm 0.8$

<sup>a</sup> Average of three triplicate runs.

Table 5  
Comparison of AM-TSC with some recent sorbents used for Hg(II) separation and preconcentration

Sorbent	Metal uptake (mmol g <sup>-1</sup> )	Equilibrating time (min)	Enrichment factor	pH range of Hg(II) uptake	Weight of sorbent (mg)	Simplicity of sorbent synthesis		Reference
						Synthesis steps	Time needed for synthesis (h)	
1,5-Diphenylcarbazine functionalized sol-gel material	0.028	30	560	6.0	50	Multisteps	Complex	[54]
Diphenylcarbazine-functionalized silica gel	–	40	500	6.0–9.0	300	Multisteps	Complex	[55]
Hg(II)-imprinted diazaminobenzene–vinylpyridine copolymers	0.205	60	200	5.0–8.0	50	Multisteps	Complex	[56]
TAN-functionalized AC	0.011	10	–	6.0 ± 0.2	200	One step	Complex	[57]
Xylenol orange-modified silica gel	0.018	3	333	1.0–9.0	200	Multisteps	Complex	[58]
Alumina-modified thiosemicarbazide	1.820	2	1000	1.0–7.0	50	One step	Simple	This work

sample may denote to the enrichment of the predominant inorganic mercury species present in river water and able to bind to the phase at the working hydrogen ion concentration [2,14].

### 3.7. Determination of mercury(II) spiked natural portable water

Percentage recovery of Hg(II) was determined by spiking three different standard concentrations ( $2.0 \times 10^{-4}$ ,  $6.0 \times 10^{-4}$ , and  $1.0 \times 10^{-3}$  mmol) into 50 ml natural portable water sample using batch technique and under the same conditions previously described. The natural portable water sample contains interferences from different cations as calcium (5.2 ppm), magnesium (13.2 ppm), sodium (14.5) and potassium (0.8 ppm) and anions as bicarbonates (6.0 ppm), sulphates (65.0 ppm), chlorides (17.0) and silicates (2.0 ppm). The results obtained in Table 4 support the validity of AM-TSC as a new selective sorbent for separation and preconcentration of inorganic mercury.

## 4. Comparison with alternative sorbents

The proposed method was compared to a variety of recent sorbents reported in literature for the separation and preconcentration of Hg(II). The distinct features are summarized in Table 5.

## 5. Conclusion

The unique properties of TSC, with its simple, elastic aliphatic structure and richness in binding sites, enable to prepare simply new and selective sorbent by its physical loading to alumina surface AM-TSC. This new sorbent has the following advantages: (i) it has the highest capacity in selective extraction of Hg(II) from aqueous solutions all over the range of pH used (1.0–7.0), compared to the other eight tested metal ions; (ii) it can be used for selective preconcentration of Hg(II) from different natural water samples using small amounts of it for packing column in preconcentration processes; (iii) the preconcentration procedure is selective and simple with high enrichment factor and low analytical cost as well.

## References

- [1] B.C. Mondal, D. Das, A.K. Das, Application of a new resin functionalised with 6-mercaptapurine for mercury and silver determination in environmental samples by atomic absorption spectrometry, *Anal. Chim. Acta* 450 (2001) 223–230.
- [2] F.W. Fifield, P.J. Haines, *Environmental Analytical Chemistry*, second edition, Blackwell Science Ltd., 2000.
- [3] C.J. Kantipuly, A.D. Westland, Review of methods for the determination of lanthanides in geological samples, *Talanta* 35 (1988) 1–13.
- [4] G. Seeber, P. Brunner, M.P. Bunchmeiser, G.K. Bonn, Poly(7-oxanorborn-2-ene-5,6-dicarboxylate)-coated silica prepared by ring-opening metathesis polymerization for the selective enrichment of radioactive lanthanides, *J. Chromatogr. A* 848 (1999) 193–202.
- [5] D. Kealey, P.J. Haines, *Instant Notes Analytical Chemistry*, first edition, BIOS Scientific Publishers Limited, UK, 2002.

- [6] M.E. Mahmoud, G.A. Gohar, Silica gel-immobilized-dithioacetal derivatives as potential solid phase extractors for mercury(II), *Talanta* 51 (2000) 77–87.
- [7] Y. Toker, M. Eral, U. Hicsönmez, Recovery of uranium from aqueous solutions by trioctylamine impregnated polyurethane foam, *Analyst* 123 (1998) 51.
- [8] M. Muroi, S. Imai, A. Hamaguchi, Sorption of uranium by cellulose derivatives, *Analyst* 110 (1985) 1083.
- [9] V. Gurnani, A.K. Singh, B. Venkataramani, Cellulose based macromolecular chelator having pyrocatechol as an anchored ligand: synthesis and applications as metal extractant prior to their determination by flame atomic absorption spectrometry, *Talanta* 61 (2003) 889–903.
- [10] A.K. Singh, S.K. Dhingra, Application of Dowex-2 loaded with sulfonaphthalen dyes to the preconcentration of copper(II) and cadmium(II), *Analyst* 117 (1992) 889.
- [11] P.K. Tewari, A.K. Singh, Amberlite XAD-2 functionalized with chromotropic acid: synthesis of a new polymer matrix and its applications in metal ion enrichment for their determination by flame atomic absorption spectrometry, *Analyst* 124 (1999) 1847.
- [12] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma-atomic emission spectrometry, *Talanta* 62 (2004) 207.
- [13] P. Pohl, B. Prusisz, Pre-concentration of Cd, Co, Cu, Ni and Zn using different off-line ion exchange procedures followed by the inductively coupled plasma atomic emission spectrometric detection, *Anal. Chim. Acta* 502 (2004) 83–90.
- [14] A. Walcarius, M. Etienne, C. Delacote, Uptake of inorganic Hg<sup>II</sup> by organically modified silicates: influence of pH and chloride concentration on the binding pathways and electrochemical monitoring of the processes, *Anal. Chim. Acta* 508 (2004) 87–98.
- [15] M.E. Mahmoud, M.M. Osman, M.E. Amer, Selective pre-concentration and solid phase extraction of mercury(II) from natural water by silica gel-loaded dithizone phases, *Anal. Chim. Acta* 415 (2000) 33–40.
- [16] E.M. Soliman, M.B. Saleh, S.A. Ahmed, New solid phase extractors for selective separation and preconcentration of mercury(II) based on silica gel immobilized aliphatic amines 2-thiophenecarboxaldehyde Schiff's bases, *Anal. Chim. Acta* 523 (2004) 133–140.
- [17] E.M. Soliman, M.E. Mahmoud, S.A. Ahmed, Reactivity of thioglycolic acid physically and chemically bound to silica gel surface as new selective solid phase extractors for removal of heavy metal ions from natural water samples, *Int. J. Environ. Anal. Chem.* 82 (2002) 403–413.
- [18] F. Xie, X. Lin, X. Wu, Z. Xie, Solid phase extraction of lead(II), copper(II), cadmium(II) and nickel(II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry, *Talanta* 74 (2008) 836–843.
- [19] X. Zhu, X. Chang, Y. Cui, X. Zou, D. Yang, Z. Hu, Solid-phase extraction of trace Cu(II), Fe(III) and Zn(II) with silica gel modified with curcumin from biological and natural water samples by ICP-OES, *Microchem. J.* 86 (2007) 189–194.
- [20] W. Ngeonate, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II), *Talanta* 71 (2007) 1075–1082.
- [21] M. Hiraide, J. Iwasawa, H. Kawaguchi, Collection of trace heavy metals complexed with ammonium pyrrolidine thiocarbamate on surfactant-coated alumina sorbents, *Talanta* 44 (1997) 231–237.
- [22] M. Hiraide, J. Hori, Enrichment of metal-APDC complexes on admicelle-coated alumina for water analysis, *Anal. Sci.* 15 (1999) 1055–1058.
- [23] J.L. Manzoori, M.H. Sorouraddin, A.M. Haji Shabani, Determination of mercury by cold vapour atomic absorption spectrometry after preconcentration with dithizone immobilized on surfactant-coated alumina, *J. Anal. Atom. Spectrom.* 13 (1998) 305.
- [24] M. Soylyak, Au. Kanatepe, L. Elci, M. Dogan, Column preconcentration/separation and atomic absorption spectrometric determinations of some heavy metals in table salt samples using Amberlite XAD-1180, *Turkish J. Chem.* 27 (2) (2003) 235–242.
- [25] I. Narin, M. Soylyak, L. Elci, M. Dogan, Separation and enrichment of chromium, copper, nickel and lead in surface seawater samples on a column filled with Amberlite XAD-2000, *Anal. Lett.* 34 (11) (2001) 1935–1947.
- [26] M. Soylyak, L. Elci, M. Dogan, Determination of trace amounts of cobalt in natural water samples as 4-(2-thiazolylazo) resorcinol complex after adsorptive preconcentration, *Anal. Lett.* 30 (3) (1997) 623–631.
- [27] R.P. Budhiraja, Separation Chemistry, New Age International Publishers, New Delhi, 2004.
- [28] E.M. Soliman, M.E. Mahmoud, S.A. Ahmed, Synthesis, characterization and structure effects on selectivity properties of silica gel covalently bonded diethylenetriamine mono- and bis-salicylaldehyde and naphthaldehyde Schiff's bases towards some heavy metal ions, *Talanta* 54 (2001) 243–253.
- [29] V. Smuleac, D.A. Butterfield, S.K. Sikdar, R.S. Varma, D. Bhattacharyya, Polythiol-functionalized alumina membranes for mercury capture, *J. Membr. Sci.* 251 (2005) 169–178.
- [30] M.E. Mahmoud, Study of the selectivity characteristics incorporated into physically adsorbed alumina phases. II. Mercaptionicotinic acid and potential applications as selective stationary phases for separation, extraction, and preconcentration of lead(II) and copper(II), *J. Liq. Chrom. Rel. Technol.* 25 (2002) 1187–1199.
- [31] A.R. Bowers, C.P. Huang, Adsorption characteristics of polyacetic amino acids onto hydrous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, *J. Colloid Interf. Sci.* 105 (1985) 197–215.
- [32] A.R. Bowers, C.P. Huang, Adsorption characteristics of metal-EDTA complexes onto hydrous oxides, *J. Colloid Interf. Sci.* 110 (1986) 575–590.
- [33] Y. Mao, B.M. Fung, A study of the adsorption of acrylic acid and maleic acid from aqueous solutions onto alumina, *J. Colloid Interf. Sci.* 191 (1997) 216–221.
- [34] M. Hiraide, M.H. Sorouraddin, H. Kawaguchi, Immobilization of dithizone on surfactant-coated alumina for preconcentration of metal ions, *Anal. Sci.* 10 (1994) 125.
- [35] G. Absalan, M.A. Mehrdjardi, Separation and preconcentration of silver ion using 2-mercaptobenzothiazole immobilized on surfactant-coated alumina, *Sep. Purif. Technol.* 33 (2003) 95–101.
- [36] S. Dadfarnia, A.M.H. Shabani, M. Gohari, Trace enrichment and determination of silver by immobilized DDTc microcolumn and flow injection atomic absorption spectrometry, *Talanta* 64 (2004) 682–687.
- [37] T. Saitoh, S. Matsushima, M. Hiraide, Concentration of polyaromatic hydrocarbons in water to sodium dodecyl sulfate- $\gamma$ -alumina admicelle, *J. Chromatogr. A* 1069 (2005) 271–274.
- [38] M. Ghaedi, M. Reza Fathi, A. Shokrollahi, F. Shajarat, Highly selective and sensitive preconcentration of mercury ion and determination by cold vapor atomic absorption spectroscopy, *Anal. Lett.* 39 (2006) 1171–1185.
- [39] E.M. Soliman, M.B. Saleh, S.A. Ahmed, Alumina modified by dimethyl sulfoxide as a new selective solid phase extractor for separation and preconcentration of inorganic mercury(II), *Talanta* 69 (2006) 55–60.
- [40] G.M. Golzar Hossain, A.J. Amoroso, A. Banu, K.M.A. Malik, Syntheses and characterization of mercury complexes of sulfadiazine, sulfamerazine and sulfamethazine, *Polyhedron* 26 (2007) 967–974.
- [41] V.M. Leovac, L.S. Jovanovic, V. Divjakovic, A. Pevec, I. Leban, T. Armbruster, Transition metal complexes with thiosemicarbazide-based ligands. Part LIV. Nickel(II) complexes with pyridoxal semi-(PLSC) and thiosemicarbazone (PLTSC). Crystal and molecular structure of [Ni(PLSC)(H<sub>2</sub>O)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> and [Ni(PLTSC-H)py]NO<sub>3</sub>, *Polyhedron* 26 (2007) 49–58.
- [42] V.M. Leovac, L.S. Jovanovic, V.S. Jevtovic, G. Pelosi, F. Bisceglie, Transition metal complexes with thiosemicarbazide-based ligand—Part LV. Synthesis and X-ray structural study of novel Ni(II) complexes with pyridoxal semicarbazone and pyridoxal thiosemicarbazone, *Polyhedron* 26 (2007) 2971.
- [43] S.B. Novaković, G.A. Bogdanović, V.M. Leovac, Transition metal complexes with thiosemicarbazide-based ligands. Part L. Synthesis, physicochemical properties and crystal structures of Co(II) complexes with acetone S-methylisothiosemicarbazone, *Polyhedron* 25 (2006) 1096–1104.
- [44] E. Mohamed, Mahmoud, Comparison of metal uptake properties of silica gel-bound ion exchangers and some amine derivatives, *Anal. Lett.* 29 (1996) 1791–1804.



- [45] S.B. Novaković, G.A. Bogdanović, V.M. Leovac, Transition metal complexes with thiosemicarbazide-based ligands. XLIV. The supramolecular arrangement in the Ni(II) complexes of S-methylisothiosemicarbazide, *Inorg. Chem. Commun.* 8 (2005) 9–13.
- [46] F.A. Cotton, R. Francis, W.D. Horrocks Jr., Sulfoxides as ligands. II. The infrared spectra of some dimethyl sulfoxide complexes, *J. Phys. Chem.* 64 (1960) 1534–1540.
- [47] M.A.H. Hafez, I.M.M. Kenawy, M.A. Akl, R.R. Lashein, Preconcentration and separation of total mercury in environmental samples using chemically modified chloromethylated polystyrene-PAN (ion-exchanger) and its determination by cold vapour atomic absorption spectrometry, *Talanta* 53 (2001) 749–760.
- [48] L. Roman, E. Florean, R. Safndulescu, S. Mirel, Preconcentration of Pb(II), Cd(II), Cu(II) and Hg(II) with 2-mercapto-5-phenylamino-1,3,4-thiadiazole impregnated on silica gel, *J. Pharm. Biomed. Anal.* 14 (1996) 1003–1006.
- [49] A.R. Ghiasvand, R. Ghaderi, A. Kakanejadifard, Selective preconcentration of ultra trace copper(II) using octadecyl silica membrane disks modified by a recently synthesized glyoxime derivative, *Talanta* 62 (2004) 287–292.
- [50] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [51] H.B. Senturk, A. Gundogdu, V.N. Bulut, C. Duran, M. Soyulak, L. Elci, M. Tufekci, Separation and enrichment of gold(III) from environmental samples prior to its flame atomic absorption spectrometric determination, *J. Hazard. Mater.* 149 (2007) 317–323.
- [52] N.L. Dias Filho, Y. Gushikem, W.L. Polito, J.C. Moreira, E.O. Ehirim, Sorption and preconcentration of metal ions in ethanol solution with a silica gel surface chemically modified with benzimidazole, *Talanta* 42 (1995) 1625–1630.
- [53] C.F. Baes Jr., R.E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1976, p. 311.
- [54] A. Khan, F. Mahmood, M.Y. Khokhar, S. Ahmed, Functionalized sol-gel material for extraction of mercury(II), *React. Funct. Polym.* 66 (2006) 1014–1020.
- [55] J. Fan, Y. Qin, C. Ye, P. Peng, C. Wu, 2007. Preparation of the diphenylcarbazone-functionalized silica gel and its application to on-line selective solid-phase extraction and determination of mercury by flow-injection spectrophotometry, *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2007.04.111.
- [56] Y.W. Liu, X.J. Chang, D. Yang, Y. Guo, Sh.M. Meng, Highly selective determination of inorganic mercury(II) after preconcentration with Hg(II)-imprinted diazoaminobenzene-vinylpyridine copolymers, *Anal. Chim. Acta* 538 (2005) 85–91.
- [57] A.M. Starvin, T. Prasada Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, *J. Hazard. Mater. B* 113 (2004) 75–79.
- [58] J. Fan, C. Wu, Y. Wei, C. Peng, P. Peng, Preparation of xylenol orange functionalized silica gel as a selective solid phase extractor and its application for preconcentration–separation of mercury from waters, *J. Hazard. Mater.* 145 (2007) 323–330.