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Alumina modified by dimethyl sulfoxide as a new selective solid phase extractor for separation and preconcentration of inorganic mercury(II)

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Abstract

Dimethyl sulfoxide (DMSO) was simply immobilized to neutral alumina via quite strong hydrogen bonding between sulfoxide oxygen and surface alumina hydroxo groups. The produced alumina-modified dimethyl sulfoxide (AMDMSO) solid phase (SP)-extractor experienced high thermal and medium stability. Moreover, the small and compact size of DMSO moiety permit high surface coverage evaluated to be $2.1 \pm 0.1\,\mathrm{mmol\,g^{-1}}$ of alumina. Hg(II) uptake was $1.90\,\mathrm{mmol\,g^{-1}}$(distribution coefficient $\log K_d = 5.658$) at pH 1.0 or 2.0, $1.68\,\mathrm{mmol\,g^{-1}}$ ($\log K_d = 4.067$) at pH 3.0 or 4.0 while the metal ions Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) showed low values $0.513–0.118\,\mathrm{mmol\,g^{-1}}$ ($\log K_d < 3.0$) in the pH range 4.0–7.0. A mechanism was suggested to explain the unique uptake of Hg(II) ions by binding as neutral and chloroanionic species predominate at pH values ≤ 3.0 of a medium rich in chloride ions. A direct and fast batch separation mode was achieved successfully to retain selectively Hg(II) in presence of other eight coexisting metal ions. Thus, Hg(II) was completely retained; Ca(II), Co(II), Ni(II) and Cd(II) were not retained, while Pb(II), Cu(II), Zn(II) and Fe(III) exhibited very low percentage retention evaluated to be 0.42, 0.49, 1.4 and 5.43%, respectively. The utility of the new modified alumina sorbent for concentrating of ultratrace amounts of Hg(II) was performed by percolating 2 l of doubly distilled water, drinking tap water, and Nile river water spiked with 10 ng/l over 100 mg of the sorbent packed in a minicolumn used as a thin layer enrichment bed prior to the determination by CV-AAS. The high recovery values obtained (98.5 ± 0.5, 98.5 ± 0.5 and 103.0 ± 1.0) based on excellent enrichment factor 1000, along with a good precision (R.S.D.% 0.51–0.97%, $N = 3$) demonstrate the accuracy and validity of the new modified alumina sorbent for preconcentrating ultratrace amounts of Hg(II) with no matrix interference.

Keywords: Alumina; DMSO; Solid phase; Separation; Preconcentration; Natural waters

1. Introduction

Environmental pollution of natural water by toxic inorganic mercury arises mainly from industrial effluents and wastewater disposal from different sources. Moreover, Hg(II) compounds are converted into the more toxic methyl mercury species by the action of aquatic organism [1]. So, its concentration should be kept under permanently controlled conditions. 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, [2] 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 [3]. 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 [4]. 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 this technique is versatile, [5,6] it is rapid, reproducible, requires only small volumes of solvents or not at all as in the case of solid-phase microextraction device [4]. Moreover, it has high preconcentration factors, showed easiness of separation and enrichment under dynamic conditions and able to be combined on line with analytical instruments. The analysis of environmental, clinical, biological and pharmaceutical samples have all benefited

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from the rapid growth in the use of SPE where it has largely replaced solvent-extraction technique [4]. In fact, several selective SP-sorbents have been synthesized for uptake of inorganic mercury Hg(II). These sorbents are produced by immobilization of complexing or chelating compounds through physical loading or chemical binding to different solid surfaces such as organic polymeric resins [6–11] or inorganic silica gel [12–18] and alumina [19–21]. Generally, the design of a stable and selective SP-sorbents for separation and preconcentration of a target metal ion depends on different factors related to the nature of solid support, its surface area and activity [22] as well as other important factors related to the organic complexing agent bound to the solid substrate. These factors include the structure of the immobilized organic compound as a whole, the nature of the incorporated donor atoms (O, N, P and S), the positioning of the functional groups along the surface of the solid support and the steric requirements of the complex formed after uptake of the desired metal ion [23]. The most successful SP-extractors for Hg(II) and other soft metal ions are those immobilized basically, sulfur and nitrogen or phosphorous containing compounds [24]. Nevertheless, the inorganic sorbents have the advantages of no swelling, fast kinetics and good mechanical stability as well [15]. In this context, a large number of silica gel sorbents functionalized organic moieties have been produced in the last 3 decades, their utility for separation and extractive concentration have been recently reviewed [25]. The great success of silica gel surface modification, may be argued to the strong covalent siloxane ≡Si–O–Si≡ bond formed on its reaction with different silylating agents to produce selective sorbents [12,26]. These silylating agents can also be used as linkers to bind to other selected organic reagents [14,23]. Regarding alumina, the opportunity for its chemical surface modification with organo functional groups is too limited as so recently appeared [27], where it is mainly physically modified via hydrogen bonding [28–31]. A new modification mode was introduced by Hiraide et al. [32]. The organic reagent is incorporated in the cores of admicelles of sodium dodecyl sulfate SDS surfactant attached to alumina surfaces at pH 2.0. According to this improvement, new organic reagents are immobilized on surfactant-coated alumina for separation and enrichment of different metal ions [33–35], and recently polyaromatic hydrocarbon as well [36]. In fact, modification of alumina surface via physical loading of organic substrates is still attractive due to its great simplicity. New sorbents may be obtained with quite strong hydrogen bonding if we take into consideration the strength of proton-acceptor nature of the selected organic modifier [37].

Dimethyl sulfoxide (DMSO) is expected to fulfil this requirement. It has a polar nature and quite strong hydrogen bond acceptor [37], in addition to its small and compact structure. It associates with biological molecules (proteins, carbohydrates and nucleic acids). When it is free (not bind to a solid support), it can coordinate with hard and soft metal ion via its own O and S donor sites [38,39], also used as potential eluant for column chromatographic separation of metal ions [40]. The main objective of this paper is to employ the high surface polarity of alumina along with the combined advantage of DMSO for designing a new modified alumina sorbent. Strong emphasis is devoted to study and evaluate the utility of the new sorbent to act as a selective solid phase extractor for separation and preconcentration of ultratrace amounts of Hg(II) spiked natural water samples prior to the determination by CV-AAS.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO) and neutral alumina of standard grade (150 mesh, 58 Å and surface area 155 m^2/g, pH of aqueous suspension is 7.0 ± 0.5) were purchased from Aldrich Chemical Company, USA. Metal salts as chloride or acetate and other chemicals used were of analytical grade. River water samples were collected from El-Nile River at El-Minia governorate, Egypt, as well as drinking tap water and doubly distilled water which were used as matrices.

2.2. Apparatus

IR-spectra of the phases before and after metal ion sorption were obtained from KBr pellets by using Perkin-Elmer 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 Perkin-Elmer 2380 spectrometry. Hg(II) was determined by a Perkin-Elmer MHS-10 mercury hydride generation system, that permits the determination of mercury and metallic hydride forming elements by AAS.

2.3. Synthesis of alumina physically loaded with dimethyl sulfoxide

Neutral alumina was heated first in an oven at 150 °C for 5 h. Then, 25 g of the dry alumina was added to 100 ml of DMSO. The reaction mixture was heated under reflux with stirring for 5 h, then cooled, filtered, washed with benzene, diethylether and dried in an oven at 120 °C for 2 h.

2.4. Metal uptake capacity of the new alumina-modified dimethyl sulfoxide (AMDMSO) phase as a function of pH and shaking time

The metal uptake capacities of such new AMDMSO 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 doubly distilled water (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 CV-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. Moreover, The effect of contact time on metal uptake was determined under the same batch conditions, but at different equilibrium periods (2, 5, 10, 20 and 30 min) and at the pH of the highest metal ion uptake (optimum pH) [23].

2.5. Medium and temperature effects on the stability of the new AMDMSO phase

Medium effect on the stability of the new phase was investigated in acetate buffer, pH 1.0–6.0 and ammonia buffer 8.0, 10.0 under static conditions [23]. In this study, 100 mg of the phase was treated with 25 ml of the selected buffer in 50 ml measuring flask for 10 h, then mechanically shaken for another 30 min. The treated phase was separated by filtration, washed and dried.

To investigate the temperature effects [15] 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 explore the extent of hydrolysis or decomposition of the physically loaded DMSO on alumina surface (i.e. stability of the phase), 50 mg of each medium and thermally treated phases along with untreated one taken as standard, were used to evaluate their Hg(II) sorption capacity under the same conditions previously described for batch experiments and at the optimum pH, then comparing the resulted Hg(II) uptake values with that of the standard untreated one [15].

2.6. Determination of the surface coverage value of AMDMSO phase by thermal desorption method

To determine the concentration of DMSO physically loaded to neutral alumina surface, 100 mg of the dry phase was weighed in a clean and dry porcelain crucible and gradually heated in an oven to 500 °C. The sample was maintained at this degree for 1 h to ensure the completion of the desorption process, then left to cool up to room temperature. The weight loss due to DMSO 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 doubly distilled water (DDW) were used as matrices to validate the efficiency of the new AMDMSO phase to act as selective and efficient preconcentrator for Hg(II) ions. Thus, the water samples were filtered through filter paper and spiked with 10 ng/l adjusted to pH 2.0 by HCl. Then, 2.0 l of the spiked water sample were passed trough a minicolumn (length 10.0 cm, i.d. 1.65 cm, attach to a glass reservoir of 1.0 l volume) [14] packed with 100 mg of the phase as thin layer enrichment bed, at a flow rate of 5 ml/min. The mercury retained on the column was eluted slowly using 2.0 ml of concentrated HNO_3 (flow rate 0.4 ml/min) and subjected to analysis by hydride generation AAS technique.

3. Results and discussion

3.1. IR-spectra and surface coverage

The IR-spectra of the pure unmodified alumina displayed a broad band at 3450 cm^{-1} [28] which may be attributed to hydrogen bonded surface hydroxo groups. Moreover, there is an intense broad band located in the vicinity of 560 cm^{-1} was argued to Al–O stretching vibration [28]. The loading of DMSO moiety to alumina surface was confirmed by IR-spectral analysis for the new synthesized phase, where new bands not present in the parent unmodified alumina were appeared. Two medium bands at 1440, 1420 cm^{-1} due to ν(S–C) in addition to a strong band at ≅1025 cm^{-1} due to ν(S–O) involved in hydrogen bonding with alumina surface hydroxo groups [38]. Nevertheless, both asymmetric and symmetric C–H stretching frequency bands due to DMSO-methyl groups around 3000 and 2918 cm^{-1} [38], respectively, could not be detected since they were merged with the strong characteristic band centred at 3450 cm^{-1} to look more wider than the parent alumina. On the other hand, comparing the IR-spectra of the modified alumina phase after metal ion sorption with the metal free one clearly demonstrate that the sulfoxide sulfur atom is the main active donating site to metal ions. This is based on: (i) the absence of stretching frequency bands around 930 ± 25 cm^{-1} characteristic to metal ion binding to sulfoxide oxygen [38] and (ii) the appearance of stretching frequency bands at 1097–1040 cm^{-1} characteristic to metal ion binding to sulfoxide sulfur [38].

These results for the linkage to metal ion support the physical loading of DMSO to alumina surface via hydrogen bonding formation between sulfoxide oxygen and alumina surface hydroxo group hydrogen [29].

The amount of DMSO loaded to alumina surface as determined by the thermal desorption method indicates a fairly high surface coverage value equal 2.1 ± 0.1 mmol g^{-1}. This may be account for the small size and compact structure of DMSO molecule compared to other organic modifiers [7].

3.2. Selectivity studies incorporated AMDMSO phase for uptake of metal ions as a function of pH and shaking time

The pH value is one of the most important factors controlling the extraction of metal ions from solution [14]. Fig. 1 represents the relation between the metal uptake capacities (mmol g^{-1}) determined based on the batch equilibrium technique for the AMDMSO phase with Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) at different pH values. Just one look to this figure, one can deduce the following: the uptake of Hg(II) by the new modified alumina phase is uniquely different from the other eight metal ions. Hg(II) is quantitatively sorbed (99.78%) at low pH values. Hg(II) uptake was 1.90 mmol g^{-1}

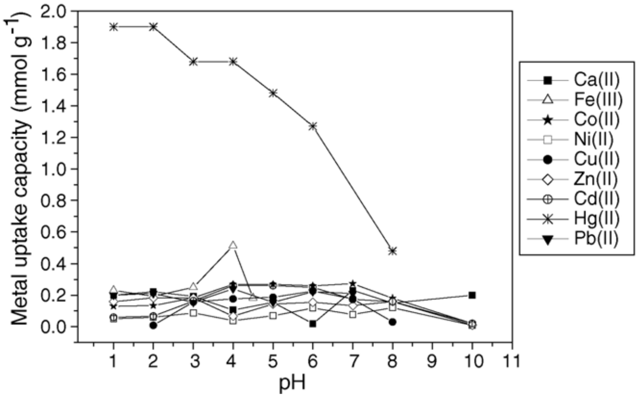

Fig. 1. Effect of pH on metal uptake capacities (mmol g^{-1}) using AMDMSO phase.

at pH 1.0 or 2.0. This value gradually decreases by decreasing acidity to be 1.68 at pH 3.0 or 4.0 then, 1.48 and 1.27 mmol g^{-1} at pH 5.0 and 6.0, respectively, and finally reached a minimum value for Hg(II) sorption equal 0.48 mmol g^{-1} at pH 8.0. Furthermore, values of Hg(II) uptake are always higher than the uptake of any other metal ion under investigation all over the range of pH used. On the other hand, the affinity of the sorbent for the uptake of these metal ions can be arranged according to metal capacity values in mmol g^{-1} at the pH of highest uptake as follows: Hg(II) 1.90 > Fe(III) 0.513 > Co(II) 0.273 > Cd(II) 0.250 > Ca(II) 0.230 > Cu(II) 0.225 > Pb(II) 0.221 > Zn(II) 0.154 > Ni(II) 0.118. This order of metal capacity values exhibited by AMDMSO SP-extractor showed the greatest affinity towards Hg(II) extraction in comparison with the rest of metal ions. This affinity was further strengthed based on the obtained distribution coefficient values [14] as compiled in Table 1, for the uptake of metal ions under investigation at different pH values using the new modified alumina sorbent.

Shaking time is another important factor in the process of evaluation of the new phase. The relative fastness of extraction of a given metal ion can be used for its selective separation from a mixture containing other coexisting metal ions [15]. To account for the fastness of metal ion sorption using the AMDMSO SP-extractor phase, metal capacity values were determined using the 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 maximum uptake at 30 min [15]. It was found that at 2 min contact time, the percentage extraction was 97.3% for uptake of Hg(II) and 49% for Fe(III) as the most interfering metal ion. At 15 min contact time, where Hg(II) extraction reached (99.0%), the percentage extraction of Fe(III) not exceed 59%. So, it is evident that the extraction of Hg(II) is faster than the most interfering metal ion.

3.3. Medium and thermal stability of the phases

The stability of the AMDMSO SP-extractor was performed in different buffer solutions pH 1.0–10.0 for 10 h contact time in order to assess the possible leaching or hydrolysis processes [23]. On the other hand, the study of temperature (50–300 °C) effects on the stability of the new phase is important from practical application point of view [23]. The results of medium effects proved that the phase experienced significant stability all over the wide range of pH used, where no loss in its efficiency for Hg(II) uptake was observed. This strongly support that neither leaching nor hydrolysis has been occurred for the DMSO ligand binds to alumina surface. On the other hand, results of thermal stability studies (Fig. 2) indicated that the new phase maintained its efficiency for Hg(II) uptake at 50, 100, 150 and also at 200 and 250 °C which are higher than DMSO bp at 189 °C, where no decomposition occurred. However, at 300 °C a value of 2.8% decrease in its efficiency for Hg(II) sorption was recorded. In fact, This pronounced stability although DMSO is physically loaded to alumina surface may account for the formation of quite strong hydrogen bond between alumina as one of the most polar solid adsorbents [22] to act as proton donor and DMSO to act as strong proton acceptor judging from the high value of its proton acceptor strength parameter $H' = 2.53$ [41]. Moreover, the stability of this phase along with its high surface coverage support its application for purposes of separation and preconcentration, especially at low pH values [20].

3.4. Suggested mechanism for the selective retention of Hg(II)

It is very noticeable from the previous results that the binding mode taking place between eight of the metal ions

Table 1
Distribution coefficient (expressed as log K_d) for the uptake of metal ions at different pH-values using AMDMSO phase

Metal	pH								
	1.0 log K_d	2.0 log K_d	3.0 log K_d	4.0 log K_d	5.0 log K_d	6.0 log K_d	7.0 log K_d	8.0 log K_d	10.0 log K_d
Hg(II)	5.658	5.658	4.067	4.067	3.634	3.360	3.000	2.553	ppt.
Ca(II)	2.174	2.154	2.154	1.869	2.046	1.097	2.244	2.033	2.174
Fe(III)	2.124	2.036	2.165	2.549	–	–	–	–	–
Co(II)	1.828	1.842	1.986	2.177	2.177	2.158	2.184	1.981	0.991
Ni(II)	1.400	1.474	1.654	1.289	1.544	1.788	1.599	2.285	0.646
Cu(II)	0.642	0.642	1.916	1.970	1.997	2.088	1.970	ppt.	1.169
Zn(II)	1.959	2.020	2.020	1.558	1.909	1.940	1.875	1.959	0.719
Cd(II)	1.481	1.531	1.939	2.164	2.164	2.145	1.967	1.929	0.996
Pb(II)	2.027	2.055	1.903	2.115	1.903	2.075	2.053	ppt.	ppt.

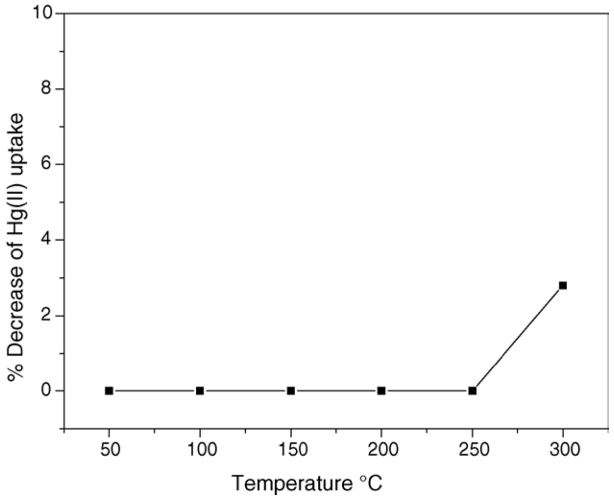

Fig. 2. Effect of thermal treatment on efficiency of Hg(II) uptake using AMDMSO phase.

Table 2
Selective retention of Hg(II) present in a mixture with other eight coexisting metal ions (0.05 mmol each) by direct batch mode using 100 mg of the new AMDMSO SP-extractor at pH 2.0 and 15 min contact time, along with the calculated separation factor α (expressed as log α)

Metal ion	(%) Retained metal ions	Log α
Ca(II)	0.00	3.50
Fe(III)	5.43	3.60
Co(II)	0.00	3.70
Ni(II)	0.00	4.00
Cu(II)	0.49	3.70
Zn(II)	1.40	3.60
Cd(II)	0.00	3.72
Pb(II)	0.42	3.76
Hg(II)	100.00	–

under investigation and the new AMDMSO sorbent are highly favored in the pH range 4.0–7.0 of contact solutions. Hg(II) in the other hand is showing reverse behavior where it is completely retained at low pH values 1.0 or 2.0 (Hg(II) uptake 1.90 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 1.0–6.0) 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 pH $\leq$ 2.0 where, the medium is rich in chloride ions Hg(II) are present as neutral $HgCl_2$ and chloroanionic $HgCl_3{}^{1-}$, $HgCl_4{}^{2-}$ complexes [14,42]. 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 hydroxo groups in acidic medium [20]. In addition to a selectively coordinative binding of DMSO sulfur to the neutral $HgCl_2$ species [12,23] as illustrated in Fig. 3. The synergetic effect played by S atom for binding $HgCl_2$ was further proved by evaluating the efficiency of the parent unmodified alumina, for Hg(II) uptake at pH 2.0 to be 1.40 mmol g^{-1}. 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 1.0–6.0) adjusted by HNO_3 only with no source of chloride ions and under the same batch conditions. Values of Hg(II) uptake in this medium was very low 0.08 mmol/g at pH 1.0 and increased gradually to reach a maximum value of 0.8 mmol g^{-1} at pH 6.0 supporting the Hg(II) uptake as complex formation [5].

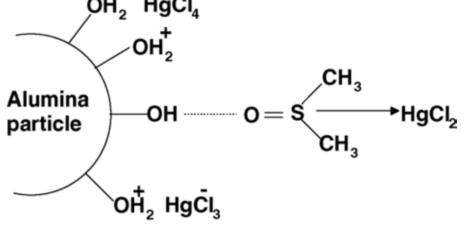

Fig. 3. A suggested binding mode of inorganic Hg(II) to alumina-modified DMSO phase in acid medium (pH 1.0 or 2.0) rich in chloride ions.

3.5. Selective separation of Hg(II) using the newly synthesized AMDMSO SP-extractor

In fact, there is a good anticipation regarding the potential use of this new sorbent to act as a selective SP-extractor for the extraction of inorganic Hg(II) ions in presence of other coexisting and interfering metal ions. This anticipation is based on the following: (i) results of metal uptake capacity-pH relation ship as shown in Fig. 1, (ii) the extremely high distribution coefficients for the uptake of Hg(II) at pH 1.0 or 2.0 (log $K_d = 5.658$) and the high values at pH 3.0 or 4.0 (log $K_d = 4.067$). However, the other metal ions under investigation showed low ones (log $K_d < 3.0$) in the pH range 4.0–7.0 as shown in Table 1, (iii) the high magnitude of the calculated Hg(II) separation factor α (10^5–10^4) especially at pH 2.0 [4], ($\alpha = K_{d\,(Hg)}/K_{d\,(CM)}$, where $K_{d\,(Hg)}$ distribution coefficient of Hg(II) as a target metal ion to be separated and $K_{d\,(CM)}$ distribution coefficient of the coexisting metal ion), so, it is expressed as log α as shown in Table 2. Accordingly, we are involved to examine the utility of AMDMSO phase to retain selectively Hg(II) in presence of other metal ions by performing a direct and fast batch separation mode [22]. So, 50 ml solution containing equimolar concentrations (0.05 mmol) of nine metal ions including Hg(II) (adjusted at pH 2.0 by fine addition of concentrated HCl) was left to compete for binding with small mass (100 mg) of AMDMSO phase for only 15 min contact time. Then, the solution separated by filtration was diluted and subjected to AAS determination for each metal ion. The results compiled in Table 2 demonstrate the achievement of a fast and selective separation process. Thus, Hg(II) was completely retained; Ca(II), Co(II), Ni(II) and Cd(II) were not retained, while Pb(II), Cu(II), Zn(II) and Fe(III) exhibited very low percentage retention evaluated to be 0.42, 0.49, 1.4 and 5.43%, respectively. In this respect, this SP-extractor is more selective than our silica gel phase chemically grafted 2-thiophenecarboxaldehyde [14].

Table 3
Selective preconcentration of Hg(II) from water samples spiked with ultratrace amounts of Hg(II) using AMDMSO SP-extractor phase

Water sample	Spiked Hg(II) (pg/ml)	Mass of the phase (g)	Sample volume (l)	Eluent ml of conc. HNO_3	(%) Recovery[a]
Doubly distilled water (DDW)	10.0	0.1	2.0	2.0	98.5 ± 0.5
Drinking tap water (DTW)	10.0	0.1	2.0	2.0	98.5 ± 0.5
El-Nile river water (NRW)	10.0	0.1	2.0	2.0	103.0 ± 1.0

[a] Average of three triplicate runs.

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

The results of enrichment of 10 ng/l of Hg(II) spiked in three water samples namely: doubly distilled water (DDW), drinking tap water (DTW) and El-Nile river (NRW) using 100 mg of AMDMSO phase packed in a minicolumn and used as a thin layer enrichment bed are compiled in Table 3. The results demonstrate the validity and accuracy of the phase for preconcentration of the spiked ultra concentrations of Hg(II) with no matrix effect. The high recovery of Hg(II) from the DDW, DTW and NRW samples as determined to be 98.5 ± 0.5, 98.5 ± 0.5 and 103.0 ± 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 river water (NRW) 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 [1,12].

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