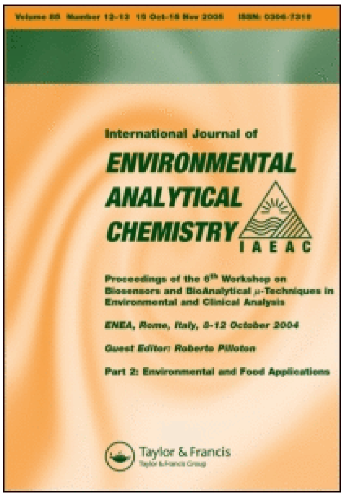

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Selective separation of silver(I) and mercury(II) ions in natural water samples using alumina modified thiouracil derivatives as new solid phase extractors

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To cite this Article Soliman, Ezzat M. and Ahmed, Salwa A.(2009) 'Selective separation of silver(I) and mercury(II) ions in natural water samples using alumina modified thiouracil derivatives as new solid phase extractors', International Journal of Environmental Analytical Chemistry, 89: 6, 389 — 406

To link to this Article: DOI: 10.1080/03067310902719142

URL: http://dx.doi.org/10.1080/03067310902719142

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 6, 15 May 2009, 389–406

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Selective separation of silver(I) and mercury(II) ions in natural water samples using alumina modified thiouracil derivatives as new solid phase extractors

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(*Received 31 August 2008; final version received 2 January 2009*)

A simple and reliable solid-phase extraction (SPE) method has been developed to synthesise two new sorbents: 6-propyl-2-thiouracil and 5,6-diamino-2-thiouracil physically loaded onto alumina surface, phases I and II, respectively. The synthesis of these new phases has been confirmed by IR-spectroscopy. The surface concentrations of the organic moieties were determined to be 0.182 and 0.562 mmol g^{-1} for phases I and II, respectively. The evaluation of the selectivity and metal uptake properties incorporated in these two alumina phases were also studied and discussed for 10 different metal ions: Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) and Ag(I) under different controlling factors. The data obtained clearly indicated that the new SP-extractors have the highest affinity for retention of Hg(II) ions. Selective separation of Hg(II) from Ag(I) as one of the most interfering ion, in addition to the other eight coexisting metal ions under investigation, was achieved successfully using the new sorbents at $\text{pH} = 9.0$ under static conditions. Therefore, Hg(II) exhibits major retention percentage (100.0%) using phase I or II. However, Ag(I) exhibits minor retention percentage equal to 1.33% using phase I and 0.67% using phase II. On the other hand, the retention percentage of the other eight metal ions ranged (0.0–3.08%) using phase I and (0.0–1.54%) using phase II at the same pH. The new phases were applied for separation and determination of trace amounts of Hg(II) and Ag(I) spiked natural water samples using cold vapour atomic absorption spectroscopy and atomic absorption spectroscopy with no matrix interference. The high recovery values of Hg(II) and Ag(I) obtained using phases I and II were ranged 98.9 ± 0.1–$99.2 \pm 0.05\%$ along with a good precision (RSD% 0.01–0.502%, $N = 3$) demonstrate the accuracy and validity of the new sorbents for separation and determination of Hg(II) and Ag(I).

Keywords: alumina; thiouracil; Hg(II); Ag(I); separation; natural water samples

1. Introduction

With the expansion of industrial activities during this century, a large increase in heavy metal quantities has been spread in the environment. The toxicity of these heavy metals is widely recognised due to their adverse effects upon human health. Mercury is a particularly toxic element and a widely distributed environmental pollutant because it is widespread in the lithosphere and in water. Inorganic mercury, especially soluble mercury

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902719142
http://www.informaworld.com

species, can be transformed into methyl mercury by the action of microorganisms and can be accumulated in the tissue of fishes and birds [1,2]. So, its concentration should be kept under permanently controlled conditions. Silver compounds and silver-containing preparations have also found an increasing use in industry and medicine [3,4]. Silver can enter the environment via industrial waters because it is often present as an impurity in copper, zinc, arsenic and antimony ores. Moreover, recent information about the interaction of silver with essential nutrients, especially Selenium, Copper, Vitamin E and Vitamin B_{12} has focused attention on potentially toxic nutrients [5]. Mercury and silver ions are present together in many environmental samples, the separation and determination of which are of great importance. On account of the growing awareness of environmental mercury and silver pollution, there is a need for new and more accurate, efficient, precise and selective methods for simultaneous separation, preconcentration and determination of Hg(II) and Ag(I). In this context, solid-phase extraction (SPE) technique [6–9] is a well-known method of separation which has great advantages [1,10–12] over the other separation tools [13–16]. In fact, in this technique the choice of the organic modifier is a key point in the synthesis of selective SP-extractors, because it can control the analytical parameters such as selectivity, affinity and capacity. On the other hand, the nature of solid support whether organic [17–20] or inorganic [10,21–23] can also control the stability, durability and mechanical properties. The SP-extractors devoted for purposes of separation and preconcentration of inorganic Hg(II) and/or Ag(I) can be outlined under three main categories. In the first category, several papers were directed to study separation of Hg(II) with no mention of Ag(I) as a chief interfering ion; however, few papers included Ag(I) as one of the studied foreign ions [10,12,23–34]. Thus, acetyl and methanesulfonyl sulphonamide resins have been prepared for the selective extraction of mercuric ions [24]. A solid-phase (SP) extractor was prepared from silica gel modified with xylenol orange (SGMXO). It has been used for the preconcentration of Hg(II) in surface, tap and sea water [31]. Alumina modified dimethylsulfoxide (AMDMSO) SP-extractor was used for selective retention of Hg(II) in the presence of the other eight coexisting metal ions [23]. The multifunctional ligand, thiosemicarbazide, was physically loaded on neutral alumina (AM-TSC). It was found to have the highest capacity in selective extraction of Hg(II) from aqueous solutions [10]. Mahmoud and Gohar [12] synthesised different SP-extractors for the extraction of Hg(II). A Sp-extractor, diphenylcarbazone-functionalised silica gel has been synthesised and used to separate and enrich Hg(II) selectively from eight metal ions. The effect of foreign ions including Ag(I) on the determination of Hg(II) was investigated [33]. The second category deals with the synthesis of a number of sorbents and their applications for separation and/or determination of Ag(I) in the presence of different cations and anions. Hg(II) as a main interfering ion was completely absent in these studies [35–39]. However, it was included just as one of the coexisting metal ions in few reports [40–42]. Madrakian *et al.* [36] have used silica gel modified with 2,4,6-trimorpholino-1,3,5-triazin for the separation, preconcentration and determination of silver ions in natural water samples by atomic absorption spectroscopy (AAS). Benzil derivative of polyacrylohydrazide was used as a sorbent for preconcentration of silver ion from aqueous samples [38]. Di(*n*-propyl) thiuran disulfide bonded on silica gel, was applied for separation and preconcentration of silver ion from aqueous samples. The effect of coexisting ions on percent recovery of Ag(I) was studied [41]. The third category represents indirect methods for separation, preconcentration prior to the determination of both Hg(II) and Ag(I) using a non-selective SP extractors. These SP-extractors were able to bind them in one step followed by sequentional separation process in a second step based on using different eluants or different concentration gradients of the same eluant [1,43,44]. Thus, Mondal *et al.* [1] determined both Hg(II) and Ag(I) in environmental samples by AAS using 6-mercaptopurine depending on used different eluants for their separation. A resin incorporating benzimidazolylazo group into a matrix of polystyrene divinylbenzene has been prepared. The exchange capacity of the resin for Hg(II), Ag(I) and Pd(II) as a function of pH has been determined. It is highly selective for these three metal ions and exhibited no affinity for alkali or alkaline earth metals [43]. Recently, Shamsipur *et al.* [44] introduced an application of supported liquid membranes (SLMs) in the simultaneously selective transport of Ag(I) and Hg(II) ions.

According to this literature survey, it is obvious that the synthesis of a SP extractor which is able to achieve a direct, simple and selective separation of Hg(II) in the presence of Ag(I) represents a great challenge. In this article, two structurally related thiouracil derivatives are chosen; the first is 6-propyl-2-thiouracil. Replacement of the H-atom and the propyl group in position 5,6 by two amino groups produced the second thiouracil derivative, 5,6-diamino-2-thiouracil. These two derivatives, were physically immobilised on neutral alumina as inorganic solid support to produce alumina modified 6-propyl-2-thiouracil (AM-PT, phase I) and alumina modified 5,6-diamino-2-thiouracil (AM-DAT, phase II). It is aimed to explore the effect of the richness of the binding sites incorporated in these thiouracil derivatives on the value of surface coverage, stability and selectivity properties for direct separation of Hg(II) in presence of Ag(I) prior to the determination. Moreover, applications were also emphasised to study their percentage extractions in natural samples to investigate the effect of matrix composition on separation and determination processes.

2. Experimental

2.1 *Apparatus*

IR-spectra of the phases before and after metal ion sorption were obtained from KBr pellets by using Perkin Elmer infrared spectrophotometer model 1430. A Fisher Scientific Accumet pH-meter model 825, calibrated against two standard buffer solutions at pH 4.0 and 10.0, was used for all pH-measurements. Atomic absorption measurements were performed with Perkin Elmer 2380 spectrometry. Hg(II) was determined with a cold vapour technique using Varian Spectr. AA-10 plus with VGA-76 vapour Generation Accessory.

2.2 *Chemicals and reagents*

Highest grade commercially available reagents were used throughout this study without further purification. Neutral alumina of standard grade (150 mesh, 58 Å and surface area $155\,m^2\,g^{-1}$, pH of aqueous suspension is 7.0 ± 0.5), 6-propyl-2-thiouracil and 5,6-diamino-2-thiouracil and metal salts as nitrates or acetate and other chemicals used were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Doubly distilled water (DDW) and portable drinking water (PDW), were used as matrices. Organic solvents used were purchased from Merck (Darmstadt, Germany). The purity of the organic modifier was checked by its melting point and the IR spectral data.

2.3 *Synthesis of alumina physically modified with 6-propyl-2-thiouracil (AM-PT, phase I) and 5,6-diamino-2-thiouracil (AM-DAT, phase II)*

Neutral alumina was first heated in an oven at 150°C for 5 h. Twenty five grams of the dry alumina was refluxed with 30 mmol of each of 6-propyl-2-thiouracil in 200 mL ethanol for 5 h, the second complexing agent 5,6-diamino-2-thiouracil was refluxed in 100 mL ethanol/dimethylsulphoxide, 70/30 v/v mixture for 5 h. Then cooled, filtered, washed with diethyl ether and dried in an oven at 120°C for 2 h.

2.4 *Sorption of metal ions by alumina phases I and II (Batch method)*

2.4.1 *Effect of pH values*

The metal uptake capacities of such new modified alumina phases towards Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) and Ag(I) ions were determined in triplicate under static conditions by the batch equilibrium technique. A total of 50 mg of each of the phases was added to a mixture of 0.5 mL of 0.01 M of the metal ion (the actual concentration of the prepared solution was determined using ethylenediaminetetracetic acid (EDTA) titration) and 24.5 mL of a buffer solution in the pH range of 1.0–10.0, using diluted HNO_3 and NaOH for pH adjustment, except with Fe(III) where the pH used between 1.0–4.0, 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 SP was separated by filtration, washed with DDW and the unretained metal ion in the filtrate was determined by complexometric EDTA titration, AAS and/or CV-AAS technique.

2.4.2 *Effect of shaking time*

The effect of shaking time on the percentage extraction of metal ions was also investigated by the previous static technique using the buffer at the pH of the highest metal ion uptake (optimum pH) [45] 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 of the phases I and II*

2.5.1 *Effect of medium and temperature*

The effect of medium on the stability of the new modified alumina phases I and II was investigated in pH range 1.0–10.0 using HNO_3 and NaOH under static conditions [45]. In this study, 100 mg of each 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 [22] a weight of 100 mg of each of the phase was kept for 1 h at 50, 100, 150, 200, 250, 300 and 350°C in an electric oven, then left to cool. To show the extent of hydrolysis or decomposition of the modified chelate on alumina surface, 50 mg of each medium and thermally treated phases along with untreated one taken as standard, were used to evaluate Hg(II) 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 [22].

2.6 *Determination of the surface coverage value of alumina phases by the thermal desorption method*

One hundred milligrams of each of the modified alumina phases was weighed in a dry porcelain crucible and this was gradually heated into a furnace from 50 to 700°C. The ignition was completed in 1 h and the remaining alumina phase was left to cool in a desiccator and weighed to determine the mass of desorbed organic compound.

2.7 *Applications*

2.7.1 *Studying the separation of Hg(II) in presence of high concentrations of Ag(I) spiked natural samples*

The validity of the proposed thiouracil phases for separation of Hg(II) from high concentrations of Ag(I) in natural water samples, DDW and PDW, were examined under the optimised conditions using batch technique. For this purpose, a range (0.001–0.01 mmol) of Ag(I) were mixed with 0.001 mmol of Hg(II) in 50.0 mL solutions at pH 9.0 for phases I and II. Hg(II) adsorbed was eluted with 2.0 mL concentrated HNO_3 at an elution rate of 1.0 mL min^{-1}. Hg(II) concentration in the eluent and Ag(I) concentration in the effluent after dilution to the linear limit of detection were determined by CV-AAS and AAS, respectively.

2.7.2 *Effect of foreign metal ions on the recovery of Hg(II) and Ag(I)*

A glass minicolumn (length 10.0 cm, i.d. 1.65 cm, attach to a glass reservoir of 1.0 l volume) [21] was prepared by careful filling 100 mg of each phase I and II used as thin layer enrichment bed. In the standard procedure, an aliquot of 100 mL contains 1.0 ppm of each of Hg(II) and the other following cations: Ag(I), Ca(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were spiked to DDW and PDW samples which contains: the cations [Ca(II) 5.2 ppm, Mg(II) 13.2 ppm, Na(I) 14.5 ppm and K(I) 0.8 ppm] and the anions [HCO_3^{-1} 6.0 ppm, SO_4^{-2} 65.0 ppm, Cl^{-1} 17.0 and SiO_4^{-4} 2.0 ppm] and passed through the column at a flow rate of 5.0 mL min^{-1}. The pH of the sample solutions were adjusted to 9.0 by the drop-wise addition of diluted NaOH solution. Mercury (II) adsorbed on the column was eluted with 2.0 mL concentrated HNO_3 at an elution rate of 1.0 mL min^{-1}. The Hg(II) and Ag(I) concentrations were determined under the conditions described previously, Section 2.7.1.

3. Results and discussion

3.1 *Infrared spectral analysis*

The IR-spectra of the pure unmodified alumina displayed a broad band at 3450 cm^{-1} [46] 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} which was argued to Al–O stretching vibration [46]. The loading of 6-propyl-2-thiouracil and 5,6-diamino-2-thiouracil moieties to alumina surface was confirmed by IR-spectral analysis for the new synthesised phases I and II. So, new bands that were not present in the parent unmodified alumina were appeared. For phases I and II, two medium bands appeared at 1660, 1540 and 1620, 1600 cm^{-1} due to ν(C=N), in addition to a band at ≅2800–2600 cm^{-1} due to ν(S–H). The bands which related to ν(–OH) groups in both phases were disappeared, ensuring that the binding sites with alumina surface is due to the formation of hydrogen bond between thiouracil hydroxyl oxygen and alumina surface hydroxo group hydrogen [47]. Nevertheless, both asymmetric and symmetric ν(C–H) stretching frequency bands were due to thiouracil ethyl and methyl groups around 3000 and 2918 cm^{-1} [47], respectively; and the two amino groups in phase II 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 demonstrates that, the thiouracil sulfur atom is one of the active donating site to metal ions. This is based on changing the position and the shape of ν(–SH) band from 2600 to 2620 cm^{-1} and 2610 cm^{-1} for using phases I and II, respectively. Also, it was found that, the bands related to pyridine nitrogen were disappeared indicating that the pyridine nitrogen atoms are also from the binding sites to metal ions. Moreover, an obvious colour change occurred after metal ion sorption by the phases, for example the colour of phase I 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 pH of maximum uptake. This colour change may be taken as criteria to support metal binding via complex formation [45].

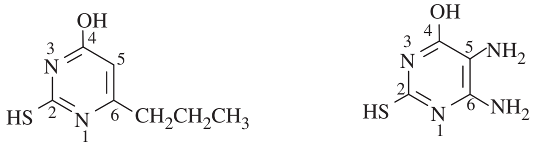
3.2 *Surface coverage – organic modifier structure relationship*

The concentration of organic modifier onto alumina surface (mmol g^{-1}, surface coverage) are determined on the basis of the thermal desorption method [48]. These values were found to be 0.182 and 0.562 mmol g^{-1} for phases I and II, respectively. The higher surface coverage of phase II than phase I is in accordance with the increasing number of binding sites in compound **2** over compound **1** by its two additional amino groups Figure 1. Taking into consideration that the physical binding of the two thiouracil derivatives via hydrogen bond formation with alumina hydroxo groups is more favourite according to the following sequence of binding sites: (–OH ··· O), (–OH ··· N) and (–OH ··· S) [49]. This situation increases the probability of compound **2** via its additional amino groups for binding to alumina surface which reflects its higher surface coverage than compound **1**.

3.3 *Equilibration studies of the physically loaded phases for uptake of metal ions as a function of pH and contact time*

3.3.1 *Percentage extraction of Hg(II) and Ag(I) as a function of pH values*

The percentage extraction values for the two new sorbents in different pH values were studied to evaluate the pH effect of metal ion solutions on their extractability.



Compound **1**
4(6)-propyl-2- thiouracil

Compound **2**
5,6-diamino-2- thiouracil

Figure 1. Structures of the two thiouracil derivatives.

Figures 2 and 3 compile the values for the ten tested metal ions, namely Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) and Ag(I). Based on these values it can be deduced that, all the phases showed low efficiency towards extraction of metal ions from aqueous solutions at low pH values due to protonation of chelation sites in the ligands which inhibit their binding to metal ions [50] where, at acidic media the nitrogen

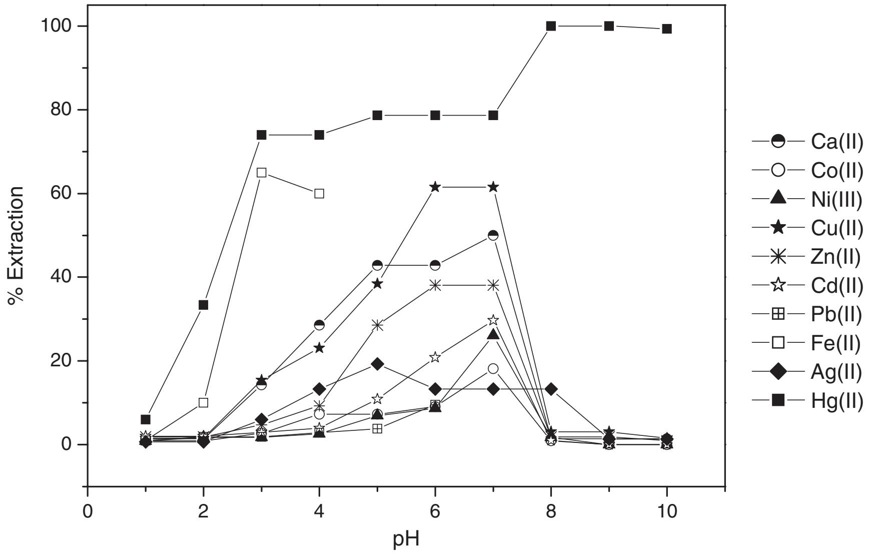


Figure 2. Percentage extraction of Hg(II) and different metal ions using batch technique with AM-PT, phase I at different pH values.

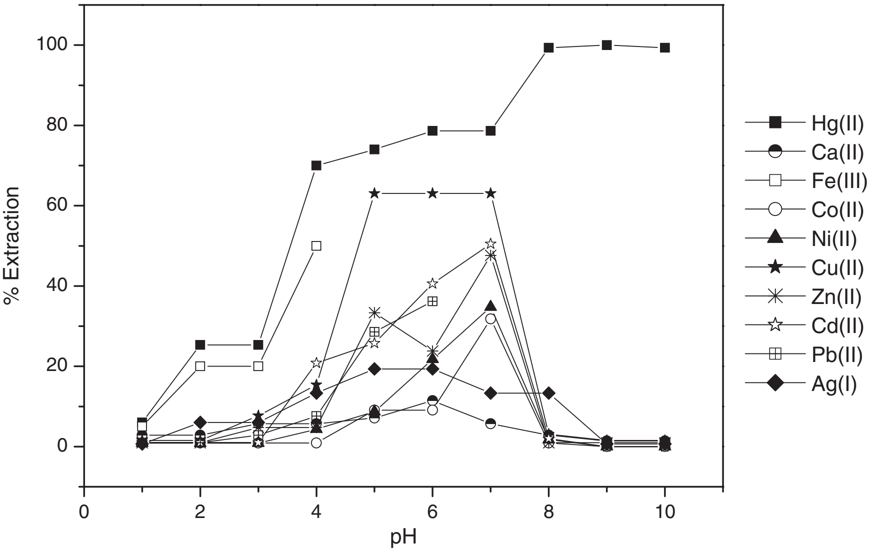


Figure 3. Percentage extraction of Hg(II) and different metal ions using batch technique with AM-DAT, phase II at different pH values.

atom could be protonated and at basic media the thiol proton dissociates [37]. This reveals that the mechanism of metal uptake is pH dependent. The two new sorbents have the highest affinity all over the pH range 1.0–10.0 towards Hg(II) and lowest one towards Pb(II) Tables 1 and 2. At pH 6.0, phases I and II show high percentage extractions for most tested metal ions (Figures 2 and 3). These values decreased obviously at the pH range 8.0–10.0 except for Hg(II), its percentage extraction increased to the maximum value in this range. So, it is clearly indicated that it can be easily separated Hg(II) from the other investigated metal ions at this range of pH especially at pH 9.0, Tables 1–4 and Figure 4. Focusing attention to the behaviour of percentage extraction values of Hg(II) and Ag(I) (Figures 5 and 6), it was found that, the two newly synthesised alumina immobilised thiouracil derivatives with N and S binding sites, phases I and II show very poor affinity towards uptake of Ag(I) compared to other sorbents [35–41]. Its percentage extraction does not exceed 20% at pH 6.0. This percentage decreases either in strong acid

Table 1. Distribution coefficient (expressed as $\log K_d$) for the uptake of metal ions at different pH values using alumina phase I.

pH / Metal	$\log K_d$									
	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Hg(II)	1.805	2.699	3.454	3.454	3.567	3.567	3.567	9.176	9.176	5.173
Ca(II)	1.161	1.161	2.222	2.602	2.875	2.875	3.000	1.161	1.161	1.161
Fe(III)	1.004	2.046	3.269	3.176	–	–	–	–	–	–
Co(II)	0.962	0.962	1.448	1.895	1.895	2.000	2.347	0.962	0.00	0.00
Ni(II)	0.943	1.248	1.248	1.428	1.874	1.979	2.548	1.248	0.00	0.00
Cu(II)	1.194	1.194	2.259	2.477	2.796	3.204	3.204	1.502	1.502	1.194
Zn(II)	1.288	1.288	1.699	2.022	2.602	2.789	2.789	1.288	1.288	0.983
Cd(II)	1.305	1.305	1.486	1.615	2.087	2.419	2.626	1.000	0.00	0.00
Pb(II)	0.983	1.288	1.288	1.468	1.598	2.022	–	–	–	–
Ag(I)	0.827	0.827	1.805	2.187	2.379	2.187	2.187	2.187	1.131	1.131

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

pH / Metal	$\log K_d$									
	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Hg(II)	1.805	2.530	2.530	3.368	3.454	3.567	3.567	5.173	9.176	5.173
Ca(II)	1.468	1.468	1.782	1.782	1.886	2.111	1.782	1.468	1.161	1.161
Fe(III)	1.721	2.398	2.398	3.000	–	–	–	–	–	–
Co(II)	0.962	0.962	0.962	0.962	2.000	2.000	2.669	0.962	0.00	0.00
Ni(II)	0.943	0.943	0.943	1.657	1.979	2.444	2.727	1.248	0.00	0.00
Cu(II)	1.194	1.194	1.921	2.259	3.232	3.232	3.232	1.502	1.194	1.194
Zn(II)	0.983	0.983	1.699	1.699	2.699	2.495	2.959	0.983	0.983	0.983
Cd(II)	1.000	1.000	1.000	2.419	2.539	2.835	3.009	1.305	0.00	0.00
Pb(II)	0.983	0.983	1.468	1.916	2.602	2.754	–	–	–	–
Ag(I)	0.827	1.805	1.805	2.187	2.379	2.379	2.187	2.187	0.827	0.827

Table 3. Separation parameters (α) and (S) of Hg(II) and different metal ions using phases I at pH 8.0, 9.0 and 10.0.

	pH = 8.0		pH = 9.0		pH = 10.0	
Phase I	$\alpha \times 10^8$	S	$\alpha \times 10^8$	S	$\alpha \times 10^4$	S
Ca(II)	1.035	8.015	1.035	8.015	1.028	4.012
Co(II)	1.637	8.214	14.99	9.176	14.89	5.173
Ni(II)	0.847	7.928	14.99	9.176	14.89	5.173
Cu(II)	0.472	7.674	0.472	7.674	0.953	3.979
Zn(II)	0.773	7.888	0.773	7.888	1.549	4.190
Cd(II)	1.499	8.176	14.99	9.176	14.89	5.173
Ag(I)	0.097	6.989	1.109	8.045	1.101	4.042

Table 4. Separation parameters (α) and (S) of Hg(II) and different metal ions using phases II at pH 8.0, 9.0 and 10.0.

	pH = 8.0		pH = 9.0		pH = 10.0	
Phase II	$\alpha \times 10^4$	S	$\alpha \times 10^8$	S	$\alpha \times 10^4$	S
Ca(II)	0.507	3.705	1.035	8.015	1.028	4.012
Co(II)	1.625	4.211	14.99	9.176	14.89	5.173
Ni(II)	0.841	3.925	14.99	9.176	14.89	5.173
Cu(II)	0.469	3.671	0.959	7.982	0.953	3.979
Zn(II)	1.549	4.190	1.559	8.193	1.549	4.190
Cd(II)	0.738	3.868	14.99	9.176	14.89	5.173
Ag(I)	0.097	2.986	2.233	8.349	2.218	4.346

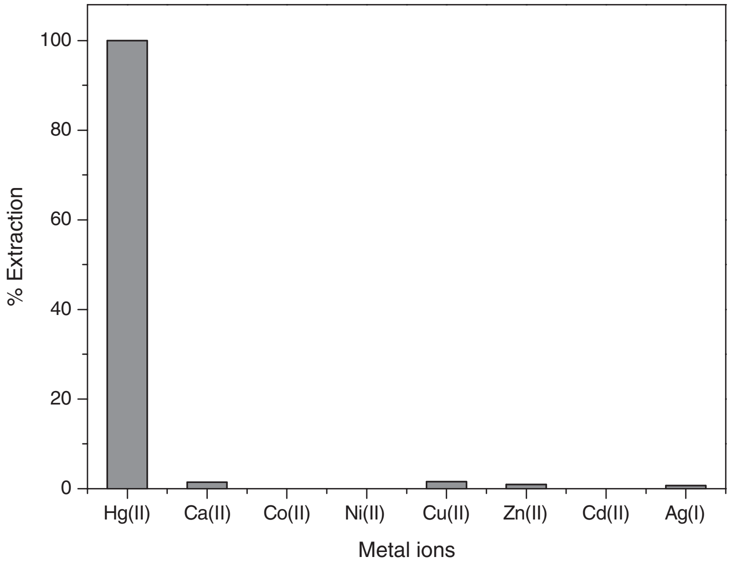


Figure 4. Percentage extraction of Hg(II) and different metal ions using batch technique with AM-DAT, phase II at pH 9.0.

medium due to protonation of coordination sites or in moderate or high basic conditions due to the formation of different nonadsorable complexes of silver with hydroxyl ion $Ag(OH)_n^{(n-1)-}$ [41]. So, the percentage extraction values of Ag(I) were 1.33% and 0.67% for both phases I and II, respectively, at pH 9.0. In contrast, phases I and II showed the

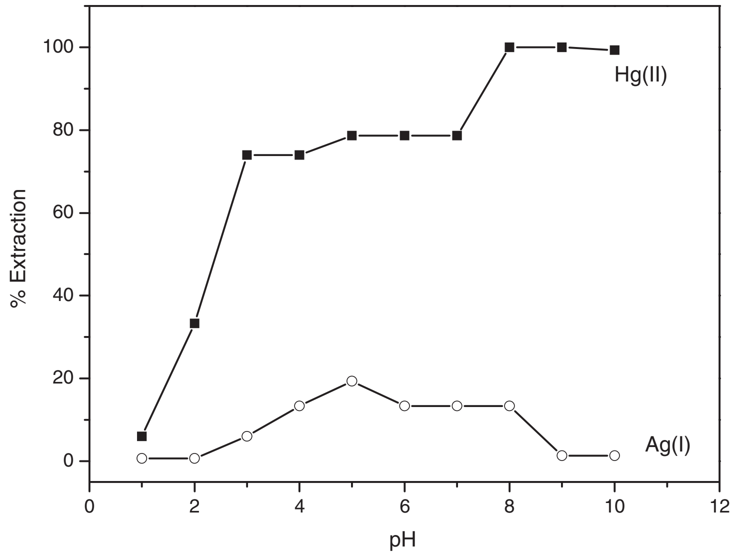


Figure 5. Percentage extraction of Hg(II) and Ag(I) using batch technique with AM-PT, phase I at different pH values.

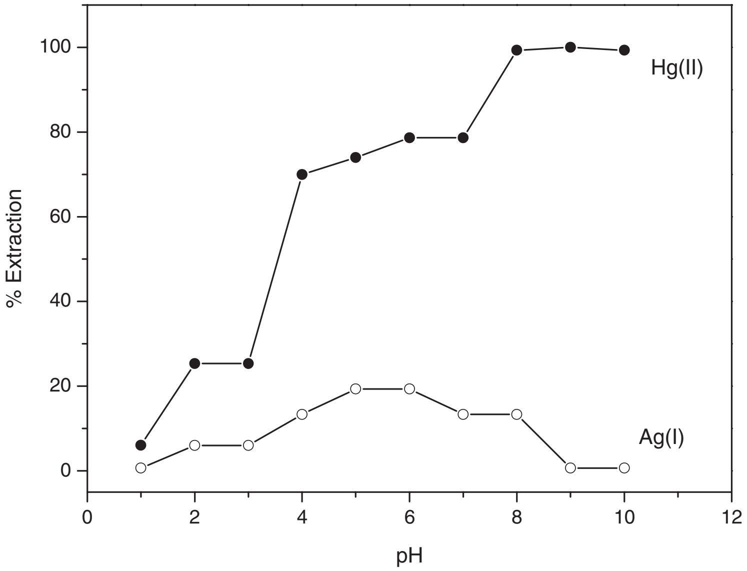


Figure 6. Percentage extraction of Hg(II) and Ag(I) using batch technique with AM-DAT, phase II at different pH values.

highest percentage extraction for Hg(II) at pH 9.0 which equals 99.5% and 100.0%, respectively. The results obtained regarding these high values in the pH range 8.0–10.0 agree with the recent studied devoted for separation of Hg(II) in the pH 6.0–12.0 using organic modifiers incorporating different donor sites as N [27], N, S [26,28], N, O [25,33], N, O, S [31] or biosorbents [32] due to complex formation involving coordination of amino groups to soluble $Hg(OH)_2$ species [27]. On the other hand, these results ascertain the fundamental relationship between the pH of maximum metal ion uptake and the nature of the coordinating sites incorporated in the organic modifier used. This variation in the pH of maximum uptake allows the uptake of the target metal ion Hg(II) in presence of other coexisting metal ions, especially Ag(I). In this context, the remarkable high values of separation factor (α) 1.109×10^8 and 2.233×10^8 and selectivity (S) 8.045 and 8.349 for Hg(II) and Ag(I) at pH 9.0 using phases I and II, respectively ($\alpha = K_{dHg(II)}/K_{dAg(I)}$, $S = \text{Log}\, L_{dHg(II)} - \text{Log}\, K_{dAg(I)}$), support the separation process (Tables 3 and 4).

3.3.2 *Metal ion uptake as a function of shaking time*

Modification of alumina 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 [51], and this represents one of the advantages of using alumina as inorganic solid support for immobilisation of chelating compounds. Moreover, the relative fastness of extraction of different metal ions can be used for the selective separation of metal ion from a mixture containing other interfering metal ions [22]. To account for the fastness of metal ion sorption using alumina phases I and II, 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. It is evident that the extraction of Hg(II) was the fastest judging from only less than 20 min contact time. The percentage extraction of the Hg(II) was found to be: 98.0%, 99.0%, 99.5% for phase I and 98.4%, 98.9%, 100.0% for phase II at contact time 2, 5 and 10 min, respectively. On the other hand, for Ag(I) the values did not exceed 0.7% at 30 min and this behaviour reflects the easiness in separation of Hg(II) from Ag(I).

3.4 *Stability of the phases I and II*

The study of prolonged medium (pH 1.0–10.0) and temperature (50–350°C) effects on the stability of the new phases is important from practical application point of view [45]. Comparing the results of medium effects for phases I and II, it was found that the phase II showed pronounced stability after prolonged treatment compared to phase I (Figures 7 and 8). In fact, no hydrolysis occurred at pH 1.0 and 2.0 and low hydrolysis was experienced at pH values between 1.06% and 4.25%. Phase I showed less resistance to buffer effect under the same experimental conditions where there is a decrease in metal capacity values relative to a non-treated standard phases, and consequently the percentage decrease in Hg(II) uptake were found to be 20.4% at pH 1.0 and 2.0, 31.2% at pH 3.0–5.0 and 20.4% at pH 6.0–10.0.

The study of thermal effects on the efficiency of the phases towards metal ion uptake is too important, not only to indicate their relative stabilities but also to be used as criteria to differentiate between the differences of functional groups in organic modifier which bond to adsorbent surface [22]. In this context, results of thermal stability studies of phase I maintained its efficiency for Hg(II) uptake at 50, 100, 150 and 200°C and phase II at 50, 100, 150, 200, 250 and 300°C where no decomposition occurred. However, the decrease in their Hg(II) sorption were recorded as follows: at 250, 300 and 350°C values of 3.3, 6.9 and 6.9%, respectively, and at 350°C a value of 3.3% for the two phases I and II, respectively (Figures 9 and 10). The previous results clearly proved that phase II is thermally stable than phase I and this is agreed with the surface coverage studies, Section 3.2.

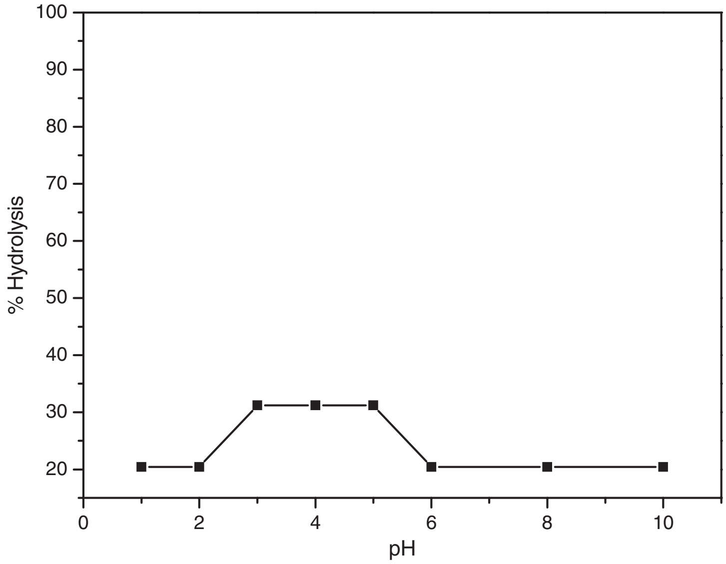


Figure 7. Effect of medium at different pH values on efficiency of Hg(II) uptake using phase I.

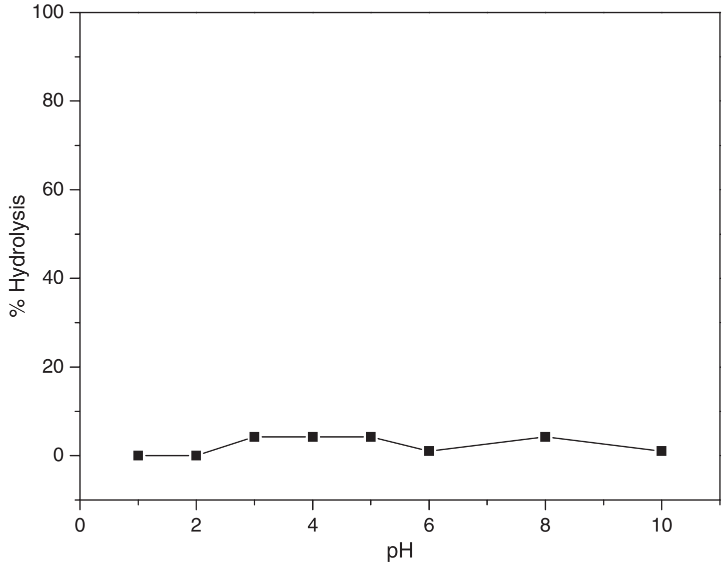


Figure 8. Effect of medium at different pH values on efficiency of Hg(II) uptake using phase II.

On the other hand, comparing the melting points of the free thiouracil derivatives, 218°C for compound **1** and >300°C for compound **2** with the beginning of decomposition of phases I and II at 250°C ad 350°C, respectively, could be taken as an additional proof to the immobilisation of thiouracil derivatives to alumina surface. Finally, the stability of sorbents was excellent where, on storing for more than 2 years their adsorption properties and sorption capacities do not change significantly.

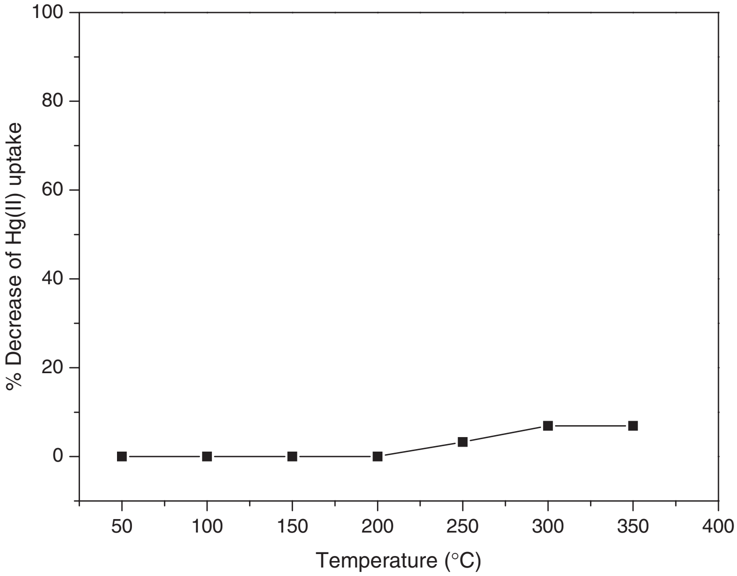


Figure 9. Effect of thermal treatment on efficiency of Hg(II) uptake using phase I.

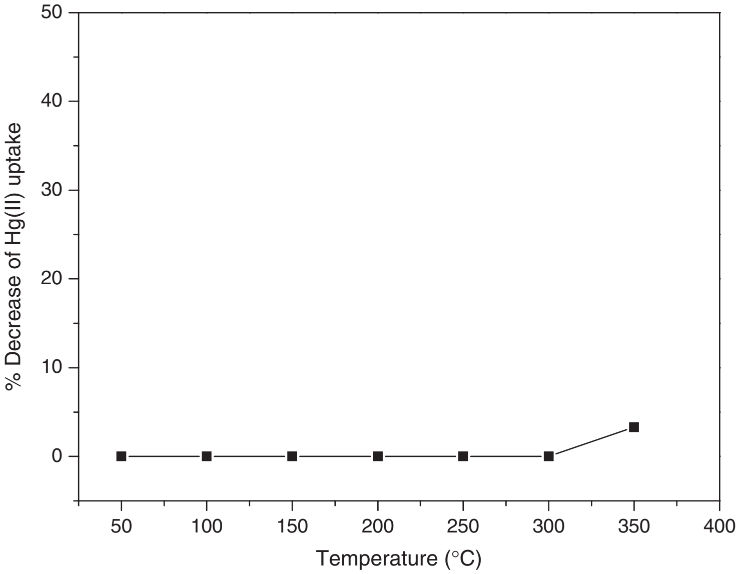


Figure 10. Effect of thermal treatment on efficiency of Hg(II) uptake using phase II.

3.5 *Regeneration of modified alumina phases I and II*

The application of these phases for further extraction of metal ions after first use requires an efficient method for their regeneration. In fact, regeneration using acid or base treatment as in ion-exchangers is not adequate for alumina modified organic complexing agents, due to the great possibility of protonation of active donor centres 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 EDTA to back-extract the metal ion from metal chelate formed modified alumina phase in the regeneration process. Thus, 150.0 mg of each Hg(II)-phase I and Hg(II)-phase II complexes were mixed with excess (0.1 M-EDTA) solution and shaken for 60 min, filtered off, washed with double distilled water and dried. The results of metal capacity determined

Table 5. Effect of interference of Ag(I) ions and matrix ions on the percentage recovery of Hg(II) using AM-PT, phase I and AM-DAT, phase II.

Sample	Phase	Molar ratio of mixing Hg(II) and Ag(I)	% Recovery of Hg(II)	RSD%	%Recovery of Ag(I)	RSD%
DDW	Phase I	1 : 1	100.0 ± 0.1	0.1	100.0 ± 0.1	0.1
		1 : 2	100.0 ± 0.5	0.5	100.0 ± 0.15	0.15
		1 : 5	100.0 ± 0.15	0.15	100.0 ± 0.2	0.2
		1 : 10	100.0 ± 0.15	0.15	100.0 ± 0.5	0.5
PW[b]	Phase I	1 : 1	100.0 ± 0.2	0.2	100.0 ± 0.1	0.1
		1 : 2	99.0 ± 0.15	0.15	97.5 ± 0.2	0.2
		1 : 5[a]	–	–	–	–
DDW	Phase II	1 : 1	100.0 ± 0.1	0.1	100.0 ± 0.2	0.2
		1 : 2	100.0 ± 0.2	0.2	100.0 ± 0.15	0.15
		1 : 5	100.0 ± 0.15	0.15	100.0 ± 0.15	0.15
		1 : 10	100.0 ± 0.2	0.2	100.0 ± 0.1	0.1
PW	Phase II	1 : 1	100.0 ± 0.1	0.1	100.0 ± 0.2	0.2
		1 : 2	99.0 ± 0.2	0.2	99.5 ± 0.15	0.15
		1 : 5[a]	–	–	–	–

Notes: Experimental conditions: Concentration of Hg(II) (2×10^{-5} M) and Ag(I) in concentration range: (2×10^{-5}–2×10^{-3} M) spiked doubly distilled water (DDW) and portable drinking water (PDW) samples, weight of phase 50 mg and the sample volume 50 mL at pH 9.0.

[a] Little turbidity due to formed AgCl by trace Cl^- present in portable drinking water

[b] Portable drinking 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: HCO_3^- 6.0 ppm, SO_4^{-2} 65.0 ppm, Cl^- 17.0 and SiO_4^{-4} 2.0 ppm.

Table 6. Percentage recovery of 1.0 ppm Ag(I) and 1.0 ppm Hg(II) spiked DDW and PDW samples in presence of 1.0 ppm of each of (Ca(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) by column technique at pH 9.0 using Phases I and II.

Samples	Phase	% Recovery Hg(II)	RSD%	% Recovery Ag(I)	RSD%
DDW	Phase I	100.0 ± 0.2	0.200	99.5 ± 0.5	0.502
PDW		99.0 ± 0.1	0.101	98.9 ± 0.1	0.101
DDW	Phase II	100.0 ± 0.01	0.010	99.5 ± 0.1	0.100
PDW		99.2 ± 0.05	0.050	99.0 ± 0.1	0.101

Table 7. Comparison of (AM-PT, phase I) and (AM-DAT, phase II) with some recent sorbents used for Hg(II) separation and determination.

Sorbent	Metal uptake (μmol g^{-1})	Equilibrating time (min)	pH range of Hg(II) uptake	Weight of sorbent (mg)	Simplicity of sorbent synthesis			Mode of column separation	Separation parameter with Ag(I) $\alpha = \log K_{dHg(II)}/\log K_{dAg(I)}$ $S = \log K_{dHg(II)} - \log K_{dAg(I)}$	Dist. Coeff. value of Hg(II)
					Synthesis steps	Nature of organic modifier	Time needed for synthesis (h)			
Polystyrene-divinylbenzene functionalized with 6-mercaptopurine [1]	1740	56	5.0–6.5	100	Multisteps	Complex	24	Indirect[a]	–	–
Polystyrene-divinylbenzene incorporated benzimidazolylazo [43]	830	1440	4.0–6.0	100	Multisteps	Complex	216	Indirect	–	–
Silica gel modified with xylenol orange [31]	18.26	3	1.0–9.0	200	Multisteps	Complex	>72	–	–	894.08
Hg(II)-imprinted diazaminobenzene-vinylpyridine copolymers [27]	205	60	5.0–8.0	50	Multisteps	Complex	>40	–	–	–
Alumina modified 6-propyl-2-thiouracil [our work]	150	<20	1.0–10.0	50	One step	Simple	5	Direct[b]	$\alpha = 1.109 \times 10^8$ S = 8.045	1.5×10^9
Alumina modified 5,6-diamino-2-thiouracil [our work]	150	<20	1.0–10.0	50	One step	Simple	5	Direct	$\alpha = 2.233 \times 10^8$ S = 8.349	1.5×10^9

Notes: [a] Indirect means Hg(II) and Ag(I) are retained followed by sequential separation using different eluants or different conc. of the same eluant. [b] Direct means Hg(II) retained while Ag(I) not retained.

after the second extraction using phase I was $147 \pm 0.1\,\mu\mathrm{mol\,g^{-1}}$, which is very close to metal capacity found in the first one, $150\,\mu\mathrm{mol\,g^{-1}}$, with percentage decrease in efficiency equal to 2.0%. On the other hand, in phase II the percentage decrease was 0.0% where the original metal capacity was $150\,\mu\mathrm{mol\,g^{-1}}$ and after regeneration became $150 \pm 0.2\,\mu\mathrm{mol\,g^{-1}}$.

4. Applications

4.1 *Studying the separation of Hg(II) in the presence of high concentrations of Ag(I) spiked natural samples*

Based on differences of equilibration time between fast uptake of Hg(II) relative to Ag(I) (Section 3.3.2), application was performed at 15 min to minimise the interference by Ag(I). The results as compiled in Table 5 support the validity of using the newly synthesised phases I and II for separation of Hg(II) in the presence of Ag(I) with no matrix interferences.

4.2 *Effect of foreign metal ions on the recovery of Hg(II) and Ag(I)*

The presence of foreign ions influences the sorption of metal ions on the solid surface because of competition for the sorption sites of targeted ions by foreign ions. In order to evaluate the selectivity of sorbent, the sorption of Hg(II) was measured in the presence of the most interfering metal ion Ag(I) and different cations as Ca(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in two different samples DDW and PDW. The results are given in Table 6. These results showed that the proposed method is suitable for the separation of Hg(II) from Ag(I) at the parts per million level in real samples of water. The results also indicated the presence of different cations even though silver ions did not interfere with separation and determination of Hg(II) ions.

5. Comparison with alternative sorbents

The proposed method was compared to a variety of recent sorbents reported in literature for the separation and/or preconcentration of Hg(II). The distinct features are summarised in Table 7. The modified alumina phases I and II described in our work showed high affinity and selectivity of Hg(II) (values of equilibrating time, weight of sorbent, distribution coefficient and separation parameters). This is in addition to the direct mode of separation and the simplicity of sorbent synthesis.

6. Conclusion

In the present study, a SPE technique was developed based on two new SP extractors alumina physically modified with 6-propyl-2-thiouracil (AM-PT, phase I) and 5,6-diamino-2-thiouracil (AM-DAT, phase II) for a selective separation and determination of Hg(II) and Ag(I). The proposed method has the advantages of the good selectivity and simplicity, as there is no need for an additional elution step. This method can selectively separate mercury ions from other metal ions and especially from much higher concentrations of silver ions. The method can be successfully applied to the separation and determination of mercury and silver ions in different natural water samples.

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