Uses of 5-Methylresorcin-Bonded Polyurethan Foam as a New Solid Phase Extractor for the Selective Separation of Mercury Ions from Natural Water Samples

N. Burham*

Chemistry Department, Faculty of Science, Fayoum University, Fayoum City, Egypt

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Abstract: In this work, 5-Methylresorcin (MR) bonded to untreated polyurethane foam (PUF) was successfully employed as a sorbent (MR-PUF) for the selective separation and determination of mercury in natural water samples. Mercury can be quantitatively recovered in the pH range of 5-7. The system presented a minicolumn packed with the new sorbent, where the sample solution was passed through it for a period of time and an eluent solution stripped out the retained mercury, which was further determined with dithizone. The new matrix was characterized by using different tools (IR spectra, stability and density). The kinetics of mercury uptake by the new matrix was found to be fast, reaching equilibrium in 20 minutes. A preconcentration factor of 350 was achieved. The proposed preconcentration procedure was applied successfully to the selective separation and determination of trace mercury in natural water samples.

Keywords: 5-Methylresorcin • Polyurethane foam • Column study • Mercury preconcentration • Water analysis

1. Introduction

Solid phase extraction (SPE) is one of the pretreatment methods for separative concentration of trace elements from the matrix. The analyte is separated by being sorbed onto the solid phase. Because many solid phases provide an excellent ability and efficiency to sorb analytes, the method has been widely used in the analysis of various samples [1]. The concentration ratio of the analytes is much larger compared with other separation methods and extraction is possible even outside the context of polluted solvents, leading to various studies to reduce the detection limit and enhance the reliability in the determination of organic and inorganic constituents. The most widely used techniques for the separation and preconcentration of trace metal ions include liquid-liquid extraction [2], solid-phase extraction [3-5], etc. Recently, the solid-phase extraction technique has become increasingly popular compared with the classical liquid-liquid extraction (LLE) method, because of its advantages of high enrichment factor, the ability of combination with different detection techniques in the form of either on-line or off-line mode [6], low consumption of organic solvents, high recovery, rapid phase separation and low cost.

Numerous substances have been proposed and applied as solid phase extractors such as chelating resins [6,7], modified silica [8,9] activated carbon [10] polyurethane foam [11], cellulose [12] and biological substances [13]. Mercury and its compounds are hazardous for humans, plants and animals [14]. Mercury metal, its vapors, and most of its organic and inorganic compounds are protoplasmic poisons. Mercury is a highly dangerous element because of its accumulative and persistent character in the environment and biota [15,16]. It is well known that, the toxicity, biogeochemical behavior and transportation of mercury in the environment are heavily dependent on its chemical form [17,18]. In the last two decades, the development of species-selective analytical methodologies has made possible the identification and quantification of mercury species.
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The most common methods of mercury speciation are gas chromatography (GC) [18, 19] and high performance liquid chromatography (HPLC) coupled with mercury-specific detection [18-20]. It is essential to form volatile, thermally stable derivatives for GC. The detection methods coupled with GC or HPLC for mercury determination include atomic absorption spectrometry (AAS) [18-22], atomic fluorescence spectrometry (AFS) [18, 23-25], microwave-induced plasma atomic emission spectrometry (MIP-AES) [18, 19], inductively coupled plasma atomic emission spectrometry (ICP-AES) [26, 27] and inductively coupled plasma mass spectrometry (ICP-MS) [24, 28, 29]. Although these determination methods are attractive for mercury speciation because of their excellent detection limits and selectivity, their relatively high instrumental and running costs as well as complicated instrument setup, make it difficult to employ these hyphenated techniques for routine speciation analysis, especially in a country in a developing area.

The goal of this work is the development of simple and less expensive off-line method for the determination of trace mercury from natural water. An important strategy for metal enrichment is the incorporation of complexing agents in solid supports to sorbe, preconcentrate and separate metal ions from solution. The incorporation processes reduce problems resulting from leaching of the ligand from the support in case of loaded foam. Ligands can be coupled on a polymeric sorbent such as open cell polyurethane foam (PUF) [30-32] through several groups, such as azo [33-40]. Immobilization via an azo linkage is one of the most commonly employed methods. A stable chelating resin matrix was prepared by covalently linking 3,5-dihydroxy toluene with PUF (MR-PUF) to be used as a packing material for separation, preconcentration and determination of trace mercury in natural water samples. We have built 5-Methylresorcin azo derivatives in the backbone of the polyurethane foam. This has chelating groups that are used for the retention of the free mercury ions due to the presence of two nitrogen atoms of the azo group adjacent to the two hydroxyl groups of the phenolic 5-Methylresorcin. At higher pH values, the concentration of protons decreases in addition to the easier ionization of the two-hydroxyl groups to form phenoxides, which have negatively charged oxygen. On this basis, an analytical methodology was developed for the retention of free mercury ions. This work demonstrates the potentialities of (MR-PUF) combined with simple UV/VIS spectrophotometric analysis of Hg(II). This combination resulted in a simple, sensitive and inexpensive analytical procedure. The properties of the developed sorbent are suitable for its application in minicolumn preconcentration and separation technique, in addition the large scale availability of PUF all over the world for many industrial applications.

2. Experimental Procedures

2.1. Apparatus and reagents
A Lambda 3B UV/VIS spectrophotometer (Perkin-Elmer, USA) with 10 mm quartz cells was used for the determination of mercury(II) by the dithizone method. The pH measurements were carried out using the microprocessor pH meter BT 500 BOECO, Germany, which was calibrated against two standard buffer solutions at pH 4 and 9. Agitation was achieved by a mechanical shaker with up to 200 rpm (SL 350 Nüve San. Malz. Imal. Ve Tic. A.S., Akyurt, Ankara-Turkey). Doubly distilled water (DDW) was obtained from two successive distillations using a Hamilton laboratory glass instrument (Europe House, Sandwich Industrial Estate, Sandwich Kent, England).

Stock solutions of mercury were prepared by dissolving 1.079 g of analytical reagent grade mercury oxide HgO (Riedel—De Haën AG Seelze, Hannover, Germany) in 0.1 mol L\(^{-1}\) HNO\(_3\) (Panreac, Spain) and the solution diluted as required. Freshly prepared dithizone solution (0.001% in CCl\(_4\), Adwic, El-Nasser Chemicals, Cairo, Egypt) and 5-Methylresorcin hydrated 97% from Aldrich were used for the spectrophotometric determination of metal ions. Sodium nitrite and sodium hydroxide were received from Winlab Company, UK. Hydrochloric acid used was delivered from Merck (Germany). All liquids were used without any further purification.

2.2. Synthesis of MR-PUF
Polyurethane foam (PUF), commercial open-cell polyethertype (25 kg \(m^{-3}\), supplied by the Egyptian Company for Foam Production, Cairo, Egypt) was cut into similar cubes, washed by a 0.1 mol L\(^{-1}\) solution of HCl, followed by doubly distilled water and acetone and then squeezed between clean sheets of filter paper and left to dry at room temperature [37]. Finally, PUF was dried in a stove at 80°C for 1 h and stored in a dark bottle. One-gram foam cubes were soaked in HCl (1:1) for 1 h to liberate the maximum number of free amino groups by the hydrolysis of the free isocyanate groups in the foam. Therewith, the foam was washed with water, placed into a 0.1 mol L\(^{-1}\) HCl solution (100 mL) and then cooled in an ice bath. The foam was diazotized by the dropwise addition of 10 mL of 7 mol L\(^{-1}\) of sodium nitrate to the cold solution containing the foam, and stirred.
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Removal of free dithizone from the combined extracts ceased its color change from dithizone solution, until the last portion of dithizone in a separating funnel by adding are the initial and the following formula:

\[
E\% = \left(\frac{C_i - C_f}{C_i}\right) \times 100,
\]

where \( C_i \) and \( C_f \) are the initial and remaining concentrations (µg L\(^{-1}\)) of the metal ion, respectively.

Determination of the sorbent capacity was carried out by the sorption of Hg(II) ions from aqueous solutions. Typically, 0.2 g of the modified foam was equilibrated with 200 µg metal ion solution adjusted to the optimum pH in a 25 mL volumetric flask, which was automatically shaken for 60 min at room temperature. After equilibration, the mixture was filtered and the remaining metal ion in the filtrate was determined. The sorption capacity per gram PUF \((Q, \mu g g^{-1})\) was calculated from the equation:

\[
Q = \left(\frac{(C_0 - C_f)V}{m}\right)
\]

where \( V \) is the sample volume in liters and \( m \) is the weight of PUF in grams. These experiments were repeated several times with similar results.

3.2. Dynamic measurements

Glass columns (10 cm long and 1.0 cm diameter) were packed with 1.0 g of 5-Methylresorcin PUF using the vacuum method as previously reported [42]. The column was successively rinsed with 20 mL of water, 5 mL of a 3 mol L\(^{-1}\) solution of HCl, and finally with distilled water until the effluent was free from any acid.

Breakthrough capacity was studied as follows: a 200 mL volume of the metal ion solution (2 mg metal ion) was percolated through the column at a flow rate of 3 mL min\(^{-1}\). Five milliliter portions of the effluent were collected and analyzed. Saturation of the foam was reached when the concentration of metal ion in the effluent aliquot was the same as in the original solution loaded onto the column.

Preconcentration of the studied metal ions was investigated from model solutions prior to the determination in the real samples. 1750 ml of a solution containing 20 µg of Hg(II) were passed through the column after adjusting to the optimum pH value and a flow rate. The stripping of the metal ions from the foam column was carried out by 3.0 mol L\(^{-1}\) hydrochloric acid solution and the amount of mercury ions in the eluent was determined by the recommended method. The concentration factor (CF) could be calculated from the ratio of the initial volume of the sample to the final volume after concentration.

Effect of the flow rate of the suitable eluting agents on the recovery of mercury ions was investigated. Packed columns loaded with 50.0 mL solutions containing the mercury metal adjusted to the pH 6.0 and at a loading rate varied from 1 - 4 mL min\(^{-1}\) was investigated. The amount of metal ion remained in the effluent was determined by the recommended method. The desorption flow rate was examined at 2 and 4 mL min\(^{-1}\) for the elution of Hg(II) from 5-Methylresorcin PUF.

The effect of diverse ions on the recovery of the studied metal ions from the column was investigated. Solutions containing 20 µg of Hg(II) were added to solutions containing interfering ions and adjusted to the optimum uptake pH then passed through the column at a flow rate of 3 mL min\(^{-1}\). The metal ions held to the sorbent were desorbed by 3.0 mol L\(^{-1}\) hydrochloric acid.

Typically, 0.2 g of the modified foam was equilibrated with 20 µg of Hg(II) free from Au, Pt and Pd, were placed in an acidic medium (1 mol L\(^{-1}\) HCl). Mercury was extracted out by the sorption of Hg(II) ions from aqueous solutions, were shaken with 0.2 g of foam for 1 h. The pH of the metal ion solution was adjusted before equilibration with the foam over the range of 1–8. After equilibration, the remaining Hg ions were determined by the recommended method.

The effect of shaking time on the extraction efficiency of Hg(II) was studied using the batch experiment. For that purpose, 0.2 g of foam was added to 25 mL of samples containing 20 µg of metal ions at the optimum pH 6 and automatic shaking for different time intervals. The percentage of extraction \((E\%)\) was determined by using the following formula:

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E\% = \left(\frac{C_i - C_f}{C_i}\right) \times 100,
\]

where \( C_i \) and \( C_f \) are the initial and remaining concentrations (µg L\(^{-1}\)) of the metal ion, respectively.

The optimum pH of metal ion uptake was determined by using the batch equilibration technique, 25 milliliters of metal ion solutions containing 20 µg of Hg(II), from aqueous solutions, were shaken with 0.2 g of foam for 1 h. The pH of the metal ion solution was adjusted before equilibration with the foam over the range of 1–8. After equilibration, the remaining Hg ions were determined by the recommended method.

For the determination of Hg(II), the dithizone method [41] was applied as follows: not more than 40 µg of Hg(II) free from Au, Pt and Pd, were placed in an acidic medium (1 mol L\(^{-1}\) HCl). Mercury was extracted in a separating funnel by adding small portions of the dithizone solution, until the last portion of dithizone ceased its color change from green to yellow-orange. Removal of free dithizone from the combined extracts was carried out by shaking it with dilute NH\(_3\) solution, then with 2 mol L\(^{-1}\) CH\(_3\)COOH. This was followed by the dilution of the yellow-orange solution by CCl\(_4\) in a 25 mL volumetric flask, and measuring the absorbance at 485 nm against CCl\(_4\).

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3. General procedures

3.1. Batch measurements

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where \( V \) is the sample volume in liters and \( m \) is the weight of PUF in grams. These experiments were repeated several times with similar results.

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3.3. Recovery of spikes
A volume of natural water sample (1750 mL) was spiked with 20.0 µg of standard solution of mercury ions and the pH was adjusted to 6.0 ± 0.2 with NaOH, then the solution was passed through the column at an appropriate flow rate. The columns were rinsed with 20 mL of doubly distilled water and the Hg ions were eluted by 3 mol L⁻¹ HCl. The concentration of Hg metal ions was determined by the recommended method. The recovery (R) percentage for Hg ions was calculated from the amount of metal ion added to the sample and the amount found by the elution.

3.4. Optimum condition of the separation / preconcentration of mercury using MR-PUF
4.2. Batch procedure
Batch experiment technique was used to determine the optimum uptake conditions such as pH, shaking time, capacity of the new sorbent and the effect of foreign ions.

4.2.1. Effect of pH
The experiments are carried out using Hg(II) solution 20 µg / 25 ml at different initial pH values 1-8, maintaining all other conditions constant to determine the equilibrium metal ion uptake. From Fig. 1, it is obvious that extraction percentage is zero at pH 1, because the Hg ions would be repelled by the positive charge on the new modified PUF, and the percentage uptake increases within the polymer backbone. This chemical stability enables the possibility of application of this foam in different media and various conditions. In addition, the sorbent was stable for several months if stored in a black polyethylene bag.
with increasing solution initial pH. It is apparent that using solution with an initial pH 5 - 7 gives essentially quantitative extraction, the highest extraction values are at pH 6 - 7. These results reveal that controlling the pH could play an important role in enhancing the selectivity of the tested metal ion uptake. Considering the strong affinity of MR-PUF in addition to the azo group, there are good chelating centers for Hg ions.

### 4.2.1.2. Effect of shaking time

The variations of the amount of mercury ions sorbed by MR-PUF as a function of time are shown in Fig. 2, from which it is obvious that the sorption percentage of Hg is found to be much more rapid and attains a constant value after 25 min shaking. This rapid uptake reflects the fact that the extraction is a chelating phenomenon and that this surface is readily accessible to the mercury ions in solution. Fig. 2 indicates that, after only 5 min shaking, about 76.7% of the Hg was extracted. This behavior can be attributed to the rapid utilization of the most readily available chelating sites on the foam surface, which reflects a better accessibility of the mercury ions to the chelating sites in the bonded PUF, and strong bond formation with 5-Methylresorcin ligand.

Therefore, it is evident that the new extractor offers two important advantages, *i.e.*, low cost of foam and rapid uptake, which is favorable in a column as well as for the static method. The contact time between the mercury ions and the new foam is generally short. Thus, it is comparable to those presented by other methods described in the literature [43]. These results also demonstrate the suitability of this sorbent for the matrix removal / preconcentration step. Additionally, the applicability of the new sorbent in SPE cartridges is possible. To ensure attainment of equilibrium, shaking time for one hour was applied in the subsequent studies with the batch method.

### 4.2.1.3. Total sorption capacity

The capacity of MR-PUF is an important factor to determine the amount of foam required to remove a specific metal ion quantitatively from the solution. The loading capacity was determined by the batch process at optimum pH 6 with the result 1125.8 µg g⁻¹ of the sorbent expressed in Fig. 3. The amount of mercury(II) retained onto the MR-PUF from the bulk aqueous solution was found to depend on its initial concentration. Therefore, the sorption profile of mercury over a relatively wide range of equilibrium concentrations was determined.
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At low or moderate mercury concentration, the amount of metal ion retained on the MR-PUF varied linearly with that which remained in the bulk solution. It is well known that oxygen and nitrogen donor atoms are poor for complex formation with mercury, because these atoms form more stable complex with low ionic diameter metals such as Fe(III), Zn(II), Mn(II) etc. However, the new foam has a greater affinity for mercury as a hard acceptor atom with the possibility and ease of binding with the two soft donor oxygen atoms in the (OH) groups and the nitrogen atoms of the azo group in the new foam. This means that the donor atoms are accessible for complex formation process with the high ionic diameter mercury(II) under this condition.

4.2.1.4. Foam reuse
The foam stability was tested by subjecting the resin to several loading and elution batch and column operations. The MR-PUF is highly stable and can be used repeatedly. There is no decrease in the uptake capacity under the static and dynamic conditions even after 17 cycles of operation without decrease in the performance. It is important to mention here that because the modified foam contained two oxygen and two nitrogen donor sites, that may account for the higher service coverage of the foam and for the high values of mercury uptake. This will consequently lead to the use of this solid phase extractor for packing columns in the preconcentration or separation processes, and only 0.2 g is required by the static method. Such a behavior strongly supports the fact that the ligand is strongly chemically bonded to the foam backbone.

4.2.1.5. Selective extraction of mercury
The results taken from the extraction of mercury as a function of shaking time and the pH have prompted a selective extraction study of mercury from mixtures containing different interfering ions in order to validate the use of the newly synthesized bonded foam as a selective solid phase extractor. Table 1 reports the recovery percentage in excess of different foreign ions. The recovery values demonstrate that only Hg(II) was separated from the mixture containing all other interfering ions.

The reported tolerance limit is defined as the ion concentration causing a relative error ≥ ± 5%. These results prove the suitability and validity of the newly synthesized phase for application in the selective extraction of mercury in the presence of different interfering cations and anions by the solid phase technique. The data given in Table 1 indicate that 95% of Hg(II) was extracted in the presence of 15000 mg L⁻¹ Cl⁻ ions, which indicates the insignificant contribution of Cl⁻ concentration in the process. In addition, the use of masking agents such as phosphate, citrate and oxalate ions have no effect on the selective extraction of mercury. This study leads to an application of the methodology to determine trace mercury in the presence of different interfering cations and anions.

4.2.2. Column Procedure
4.2.2.1. Breakthrough curve
The capacity of the foam column containing 1 g of MR-PUF could be determined from the curves obtained by plotting the amount of metal ion that emerged from the column versus the volume of effluent collected (see Fig. 4). The column was saturated after a flow of 100 mL solution. The breakthrough capacity of mercury ions per 1 g of MR-PUF was calculated according to the equation given in [44] for the uptake [uptake = (V₅₀% Cₒ)/m] and found to be 630 μg g⁻¹. Compared with the isotherm capacity of mercury ions, it is obvious that the breakthrough capacity is about half the batch capacity, because the breakthrough capacity is not the total capacity; it is the working capacity of the column.
4.2.2.2. Elution
Three acids HNO\textsubscript{3}, HCl and H\textsubscript{2}SO\textsubscript{4} were tested as eluents, it is interesting to note that all the acids at different concentration are able to elute Hg(II) ions, however HCl was adopted as eluent.

4.2.2.3. Effect of flow rate
The effect of the sample flow rate on the Hg (II) extraction through the minicolumn was studied by varying the flow rate from 1 to 4 mL min\textsuperscript{-1} at the optimal pH established in the previous experiment. The results in Fig. 5 indicate that the efficiency of mercury retention on the MR-PUF extractor reached its maximum at a flow rate of 3 mL min\textsuperscript{-1}. All further studies were preformed at the sample and eluent flow rates of 3 mL min\textsuperscript{-1}.

4.2.2.4. Preconcentration and recovery
The experiments on the preconcentration were carried out using 1750 ml of mercury solution as an initial volume. The column technique under optimum extraction conditions was used. Owing to the limited sensitivity of the many instrumental analyses such as spectrophotometry and AAS and to the low mercury concentration levels in natural samples, mercury determination frequently requires a preconcentration step. In addition, the high dissolved solid content as in saline waters such as lake water, results in poor precision and sensitivity, unless a preconcentration or separation procedure is applied to these samples. The results of enrichment of 20 µg of Hg(II) spiked in the DDW that were eluted in 5 ml 3 mol L\textsuperscript{-1} HCl are given in Table 2; the percentage of recovery (R %) is 100% with a concentration factor (CF) 350.

4.2.3. Accuracy and applications
In order to establish the validity of the proposed procedure, the method has been applied to the determination of mercury in standard reference material (Primary Drinking Water Metals - Mercury, Perkin Elmer NO: N930-0216). The determined value was not significantly different from the certified value (see Table 2). The proposed method was applied to the determination of Hg(II) ions in real samples, with different matrices containing varying amounts of a variety of diverse ions, and applied to the separation and recovery of mercury ions from different matrices such as tap water, Yussof seawater and Qaroun lake water. Spiking experiments using the standard addition method was used to check the reliabilities. The percent of recoveries and relative standard deviation for mercury in the spiked real samples are given in Table 2. As may be seen, the results of the analyses of each sample show that, in all cases, the Hg ion recoveries are quantitative with R.S.D < 6%. The results also indicate the suitability of the present sorbent for the quantitative preconcentration of

| Ion       | Added as   | Conc. (mg L\textsuperscript{-1}) | Recovery (%) |
|-----------|------------|-----------------------------------|--------------|
| Br\textsuperscript{-} | NaBr      | 100                              | 100          |
| Cl\textsuperscript{-} | NaCl      | 15000                           | 95.0         |
| I\textsuperscript{-}  | NaI       | 100                             | 99.2         |
| SO\textsubscript{4}\textsuperscript{2-} | Na\textsubscript{2}SO\textsubscript{4} | 100 | 98.3 |
| PO\textsubscript{4}\textsuperscript{3-} | Na\textsubscript{3}PO\textsubscript{4} | 50   | 100 |
| Citrate   | Na-Citrate | 50                             | 100          |
| Oxalate   | Na-Oxalate | 50                             | 100          |
| Cu        | CuSO\textsubscript{4} | 2.0                              | 98.3         |
| Zn        | ZnSO\textsubscript{4} | 2.0                            | 95.8         |
| Cd        | CdSO\textsubscript{4} | 2.0                             | 97.5         |
| Ni        | NiCl\textsubscript{2} | 2.0                             | 100          |
| Fe        | FeCl\textsubscript{3} | 2.0                             | 96.7         |
| Mn        | MnSO\textsubscript{4} | 2.0                             | 100          |
| Cr        | Cr\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} | 2.0 | 100 |

Table 1. Selective extraction of Hg(II) in the presence of different interfering ions average of 3 detection.

Figure 5. Effect of flow rate on the recovery of Hg(II) onto MR-PUF average of three determinations.
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Table 2. Determination of Hg (II) from different real water samples average of 6 detection.

| Water sample                  | Added µg L⁻¹ | Initial volume ml | Found µg L⁻¹ | Final volume ml | Recovery % | R.S.D % | Material source                  |
|-------------------------------|--------------|------------------|--------------|----------------|------------|---------|----------------------------------|
| Certified reference material  | 20           | 25               | 20.1         | 5              | 100.5      | 1.3     | Perkin Elmer NO: N930-0216       |
| (Primary Drinking Water Metals – Mercury) |              |                  |              |                |            |         |                                 |
| DDW                           | 20           | 1750             | 20           | 5              | 100.0      | 1.5     | DDW                              |
| Tap water                     | 20           | 1750             | 20.1         | 5              | 100.5      | 2.4     | Faculty of science, Fayoum city  |
| Qaroun lake water             | 20           | 1750             | 19.8         | 5              | 99.0       | 4.5     | Fayoum city                      |
| Yussof seawater               | 20           | 1750             | 19.9         | 5              | 99.5       | 5.1     | Fayoum city                      |

Table 3. Comparison of the preconcentration factors CF.

| Chelating agent/solid phase extractor | Method                  | CF | Eluent                  | References |
|--------------------------------------|-------------------------|----|-------------------------|------------|
| 4-Hydroxytoluene/polyurethane foam   | Spectrophotometry       | 100| 3 mol L⁻¹ HCl           | [37]       |
| β-Naphthol/polyurethane foam         | Atomic absorption spectrophotometry | 50 | 0.1 mol L⁻¹ HNO₃       | [45]       |
| Dithizone/silica gel                 | CV-AAS                  | 200| 10 mol L⁻¹ HCl          | [46]       |
| HgI₄²⁻/Aliquat-336/naphthalene       | Anodic stripping voltammetry | 80 | Tetraphenyl-borate     | [47]       |
| DuoliteGT-73 resin                   | ICP-AES                 | 40 | H₂SO₄·H₂O₄ mixture      | [48]       |
| Dithioacetal/SiO₂                    | CV-AAS                  | 5  | Water                   | [49]       |
| Dithizone/neutral alumina            | Spectrophotometry       | 100| Polyethylene glycol     | [50]       |
| 1,5-Diphenylcarbazone/SDS coated alumina | CV-AAS               | 100| 1 mol L⁻¹ HBr          | [51]       |
| 1,5-Bis(2-pyridyl)-3 sulfophenylmethylene)thiocarbonohydrazide/Dowex anion exchange resin | ICP-AES                  |      | HNO₃                  | [7]        |
| 2-Mercaptobenzoxazole/chromosorb     | CV-AAS                  | 300| 2 mol L⁻¹ HNO₃ in acetone| [52]       |
| 4-(2-Pyridyl azo)resorcinol/nano-sized SiO₂ | CV-AAS                  | 50 | 6 mol L⁻¹ HCl          | [53]       |
| Bis(2-mercaptophenyl) ethanediamide/silica gel | Spectrophotometry | 50 | Acetone                 | [54]       |
| 5-Methylresorcin/polyurethane foam  | Spectrophotometry       | 350| 3 mol L⁻¹ HCl           | This work  |

CV-AAS - Cold Vapor Atomic Absorption Spectrometry; ICP-AES - Inductively Coupled Plasma Atomic Emission Spectrophotometry;

Table 2. Determination of Hg (II) from different real water samples average of 6 detection.

5. Conclusion

The proposed system with off-line preconcentration by minicolumn packed with one gram 5-Methylresorcin PUF is a good alternative for Hg preconcentration, separation and determination in natural water samples. This method proved to be simple, rapid, and reliable, with low instrumental requirement and easy operation for the selective separation of mercury from complex matrix samples. By using common techniques and reagents such characteristics are very important and of practical interest for Hg analysis in routine laboratories equipped only with UV/VIS spectrophotometry. In addition, the proposed procedure has analytical performance comparable to other procedures for mercury determination described on the literature. In addition, the dynamic uptake study has shown that the new sorbent can take 90% of Hg ions in 15 min; these rapid kinetics are promising in terms of the applicability of this sorbent in solid phase extraction cartridges.

4.2.4. Comparison with other solid phase extractors

One of the promising chelating matrixes reported to enrich Hg ions in the recent past is the chelating resin [37], which provides a preconcentration factor of the order 100. The present matrix is also capable of achieving a better preconcentration factor for Hg(II), it has a superior CF of 350, also very good reusability and stability. The preconcentration factor of MR-PUF is superior to that of most modified extractors listed in Table 3; also the acid concentration required for the desorption is moderate with the present foam. This combines the high preconcentration factor and low cost.

Mercury from natural water samples. Precision for six determinations of mercury ions varied from 2.4 to 5.1% R.S.D, which is good for this kind of matrix.
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