Asian Journal of Chemistry; Vol. 25, No. 1 (2013), 316-320

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13025

Solid Phase Extraction of Hg(II) from Environmental Samples

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(*Received*: 5 November 2011; *Accepted*: 23 July 2012) AJC-11871

This study investigates application of alizarin violet functionalized silica gel as an adsorbent for solid phase extraction of Hg(II) from enviromental water samples. Hg(II) can be easily separated and pre-concentrated in the presence of common coexisting ions. The influences of analytical parameters including pH of the aqueous solution, amount of the functionalized silica gel, stirring time and flow rates of sample solutions on the quantitative recoveries of Hg(II) were investigated. At the optimum conditions, Hg(II) can be adsorbed with almost 100 % retention, the adsorption equilibration for Hg(II) was achieved within 10 minutes and the adsorption capacity of the sorbent for Hg(II) is 6.38 mmol/g of dry functionalized silica gel. For Hg(II) solution of 10 ng mL^{-1}, the pre-concentration factor is as high as 333 and the recovery is higher than 96 %. The new solid phase extractant has been used for the pre-concentration of low level of Hg(II) in different water samples with high recoveries. The self made chromatographic column can be reused for 50 times and the recovery of Hg(II) is higher than 95 %.

Key Words: Silica gel, Alizarin violet, Solid phase extraction, Separation/pre-concentration, Hg(II).

INTRODUCTION

Mercury is one of the most toxic elements for plants and animals. This metal is so volatile that it could be easily exposed to human environment. Since mercury and their compounds are widely used as chemical materials in modern society, they are widespread in natural waters and soils. Because of low concentration of Hg(II) and complex matrix interferences in water and soil samples, direct determination of Hg(II) is usually insufficient, although atomic absorption spectrometry[1-3] and inductively coupled plasma atomic emission spectrometry[4-6] were often used. Therefore, a separation/pre-concentration step is required.

The traditional separation and pre-concentration methods for metal ions include liquid-liquid extraction, coprecipitation, ion exchange and others. These methods often require large amount of high purity organic solvents, some of which are harmful to health and cause environmental problems. Nowadays, several methods have been used for pretreatment of the samples, solid phase extraction (SPE)[7-12] is one of them. Its advantage[13] include: i) higher enrichment factors; ii) safety with respect to hazardous samples; iii) minimal costs due to low consumption of reagents. So, solid phase extraction has been widely used for the isolation and enrichment of target analytes and for the clean up of samples (eliminate of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry[14].

The choice of sorbent is a key point in solid phase extraction, because it can control the analytical parameters such as selectivity, affinity and capacity[15,16]. Preparation of new material for selective solid phase extraction of analytes is an important trend of solid phase extraction[13]. Reagents can be modified on organic or inorganic support as solid phase extractants. Silica gel presents the advantages of no swelling, fast kinetics, mechanical, thermal and chemical stability under various conditions[17]. Therefore, it is a widely used support for various solid phase extractants. Recently, some chelating reagents have been modified on silica gel as solid phase extractants for separation/pre-concentration of some metal ions[18-24].

Several sorbents have been used for solid phase extraction of Hg(II)[25-27]. They are produced by immobilization of complexing or chelating reagents on different solid surface through physical loading or chemical bonding. Generally speaking, chemical bonding is more stable than physical loading. In the present work, alizarin violet was chemically functionalized on silica gel as a new sorbent for selective solid phase extraction of Hg(II). The utility of the new sorbent for separation and pre-concentration of low level of Hg(II) was evaluated. The results showed that the new sorbent can selectively extract of Hg(II) in the presence of common coexisting metal ions. This new solid phase extractant has been used for separation and pre-concentration of trace amount of Hg(II) from different samples.

EXPERIMENTAL

Analytical reagent-grade chemicals were employed for preparation of all solutions. Doubly distilled water was used for the experiment. Standard solutions of 1 mg mL^{-1} of Cd(II), Ni(II), Co(II), Mn(II), Hg(II), Zn(II) and Cu(II) were prepared by dissolving the corresponding metal salts in 0.03 mol L^{-1} of nitric acid, hydrochloric acid or sulfuric acid.

The reagent of 5×10^{-3} mol L^{-1} of 1-(2-pyridylazo)-2-naphthol (PAN) was used for Hg(II) determination. The following buffer solutions (0.2 mol L^{-1}) were used for pH adjustment: pH 1-2 (HCl-KCl), pH 3-6 (CH_3COONa-CH_3COOH), pH 6-8 (KH_2PO_4-Na_2HPO_4), pH 6-9 (KH_2PO_4-NaOH). 110-125 μm diameter particles of silica gel (Qingdao Haiyang Chemical Factory, Qingdao, China), aminopropyltrieth-oxysilane (Sigma Chemical Co., St Louis, MO, USA), alizarin violet (ShangHai SSS Reagent Co., Ltd., Shanghai, China), and *N,N'*-dicyclohexylcarbodiimide (Shanghai Medpep Co., Ltd., Shanghai, China). A glass tube of Φ3 × 20 mm was washed with 6 mol L^{-1} HCl, 95 % ethanol and doubly distilled water and then used as a chromatographic column.

A 752 spectrophotometer (Shang Hai precision scientific Instrument Co. Ltd., Shang Hai, China) was used for the determination of absorbance at a given wavelength. For the spectrophotometer, the determination wavelength is 550 nm and the pH of the solution was adjusted to 9.3. A pHS-3C digital pH meter (Shang Hai precision scientific Instrument Co. Ltd., Shang Hai, China) was used for the pH measurements.

Preparation of the alizarin violet functionalized silica gel: In order to remove any adsorbed metal ions and increase the content of -OH, silica gel (SG) was activated by dipping in 6 mol L^{-1} of hydrochloric acid for two days, then filtered and washed repeatedly with distilled water until no detectable Cl^- can be found in the filtrate. Such treated silica gel was dried in an oven at 110 ºC to remove any adsorbed water on the surface. The process for the preparation of alizarin violet functionalized silica gel was showed in **Scheme-I**. Step (I) was performed according to the method described in literature[28]. 10 g of dried silica gel was mixed with 10 mL of aminopropyltriethoxysilane in anhydrous toluene incubated in a sealed flask at 70 ºC, the reaction was completed within 7 h and the product aminopropyl silica gel (APSG) was filtered, washed with acetone and dried under vacuum. The dried aminopropyl silica gel was added in a flask, then added 50 mL of tetrahydrofuran and 8.3 g of *N,N'*-dicyclohexylcarbodiimide and 13 g of alizarin violet, stirred at room temperature for 24 h, the resulting solid phase was filtered, washed with ethanol and water until the filtrate showed no characteristic colour of alizarin violet. The solid was then dried at 80 ºC for 6 h to obtain the alizarin violet functionalized silica gel.

Batch experiments: Alizarin violet functionalized silica gel was stirred in a solution with suitable amount of metal ion for a fixed period of time at room temperature. The supernatants were taken for the un-extracted metal ions measurements by spectrophotometry. This method was used to study the effects of pH and stirring time on the retention of metal ions on the alizarin violet functionalized silica gel and to determinate the maximum adsorption capacity of Hg(II) on the functionalized silica gel.

Column experiments: For the column experiment, alizarin violet functionalized silica gel was packed in a glass column, a solution containing metal ions was adjusted to pH = 7 and passed though the column at a certain flow rate. Metal ion retained on the column was eluted with 0.3 mol L^{-1} of $HClO_4$ at a lower flow rate and its concentration was determined by spectrophotometry.

The adsorption capacity and extraction percentage were calculated, respectively, by the following equations:

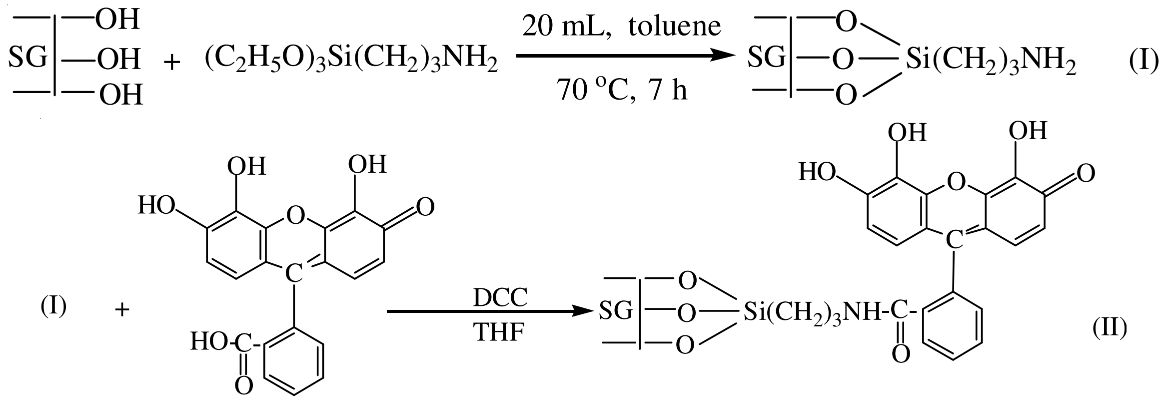
$$Q = \frac{(C_0 - C_e)\,V}{W} \qquad (1)$$

$$E\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

where, Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e are the concentrations of metal ions before and after pre-concentration(μg mL^{-1}), W is the mass of the dry functionalized silica gel (g) and V is the volume of metal ion solution (L); E (%) stands for the extraction percentage.

RESULTS AND DISCUSSION

Analysis of the IR spectrum of the functionalized silica gel: IR absorption bands found for the silica gel at 3448, 1636 and 1081 cm^{-1} are assigned to the streching vibration for -OH, bending vibration for -OH and absorption band for -Si-O-, respectively. The bands at 971, 807 and 472 cm^{-1} are assigned to the absorption bands for the background of the silica gel.



Scheme-I: Preparation of alizarin violet functionalized silica gel

Comparison of the IR spectrum between the silica gel and the functionalized silica gel reveals a new band at 1616 cm^{-1}, which is the bending vibration for -C-N-O.

Stability of the functionalized silica gel: 0.2 g of the functionalized silica gel was added in some organic solvents (ethanol, acetone and chloroform), 6 mol L^{-1} of HCl, 6 mol L^{-1} of H_2SO_4 and aqueous solutions with pH 1-9, respectively. The systems were stirred for 30 min and the supernatants were found to be colourless. The solid was filtered, washed with water and then added into 20 mL of solution containing 80 µg of Hg(II). The mixture was stirred for 30 min, the Hg(II) in the supernatant was determined by spectrophotometry. The adsorption of Hg(II) is almost 100 %, the functionalized silica gel is thus fairly stable in these media. Such a behaviour strongly supports the fact that alizarin violet is chemically functionalized on the silica gel.

Effect of pH on the adsorption of metal ions: The pH value is one of the important factors controlling the extraction of metal ions from aqueous solutions. In order to obtain optimum extraction condition, the adsorption of metal ions on the functionalized silica gel was examined with different solutions pHs by the batch mode experiments. For this purpose, 0.2 g of the functionalized silica gel was added into 20 mL of solution containing 80 µg of Hg(II) at different pHs. The mixture was stirred for 30 min and then the unextracted metal ions in the supernatants were determined by spectrophotometry. Fig. 1 showed that the retention of Hg(II) varies significantly with change in the pH. At low pHs, the retention of Hg(II) is low, few of Hg(II) can be absorbed on the functionalized silica gel. With the increase of pH, the retention of Hg(II) was also increased, Hg(II) in solution can be easily absorbed on the functionalized silica gel. The possible mechanism for this is suggested bellow: at low pHs, few of Hg(II) can chelate with the functionalized silica gel because of the protonation of alizarin violet; with the increase of pH, the protonation of the alizarin violet functionalized silica gel become weak, which enhances the chelation and absorption of Hg(II). At pH > 9.0, the retention of Hg(II) decreased because of the hydrolyze of Hg(II). Therefore, pH = 7 was chosen for the separation and preconcentration of Hg(II) in the following studies.

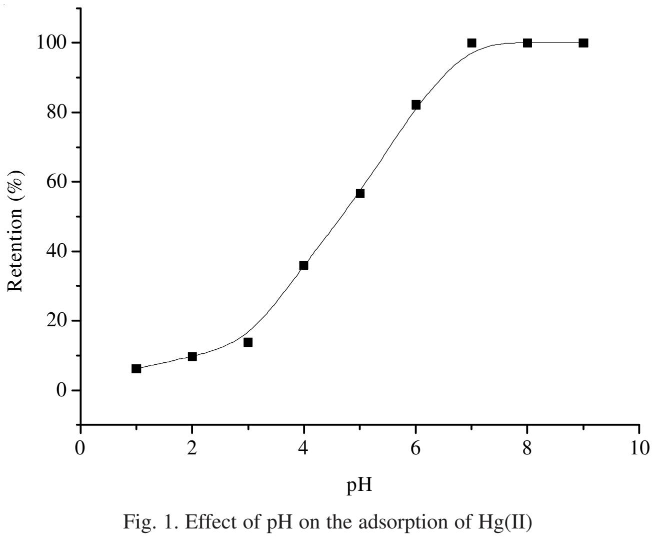


Fig. 1. Effect of pH on the adsorption of Hg(II)

Effect of the amount of the functionalized silica gel: The effect of the amount of the functionalized silica gel on absorption of Hg(II) was examined by a batch mode experiment. For this purpose, 20 mL of solution containing 80 µg of Hg(II) at pH = 7 was stirred for 30 min with different amount of the functionalized silica gel added and then the Hg(II) concentration in the supernatants was determined by spectrophotometry. 0.2 g of the functionalized silica gel was sufficiency for 100 % retention of Hg(II). Therefore, not less than 0.2 g of the functionalized silica gel was used in the following experiment.

Effect of stirring time: The stirring time taken for the adsorption of the metal ion by the functionalized silica gel and the attainment of the equilibrium conditions are of considerable importance. Effect of stirring time on the retention of Hg(II) was studied by the batch experiments. As can be seen from Fig. 2, 10 min of the stirring time is necessary for the adsorption equilibrium of Hg(II). This confirmed the fact that modification of silica gel surface with organic chelate reagent results in metal ion extractants, which need only a few minutes to complete extraction processes[29]. This is one of the advantages of using silica gel support for immobilization of chelating compounds.

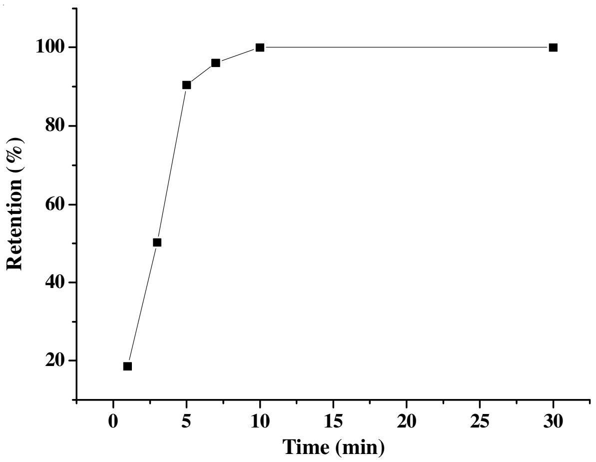


Fig. 2. Effect of stirring time on the retention of Hg(II)

Adsorption capacity of Hg(II) on the functionalized silica gel: The adsorption capacity of the functionalized silica gel is an important parameter for determining how much functionalized silica gel is required to quantitatively adsorb a specific amount of metal ion from solution[30]. For investigation of the adsorption capacity of Hg(II) at pH = 7, the same volumes of Hg(II) solutions with different concentrations was stirred with 0.5 g of the functionalized silica gel for 30 min, then the concentration of Hg(II) in solutions were determined. Concentration change in the adsorption of Hg(II) by the functionalized silica gel was measured. It can be seen in Fig. 3 that the amount of Hg(II) adsorbed by the functionalized silica gel increased linearly with increasing concentration of Hg(II) in aqueous solutions over a wider range of concentration. From this adsorption curve, the maximum adsorption capacity of Hg(II) by the functionalized silica gel was found to be 6.38 mmol g^{-1}.

Effect of flow rate on retention of Hg(II): In the column experiment, 0.5 g of the functionalized silica gel was conditioned with an appropriate solution and packed in a glass column and then 20 mL of solution containing 80 μg of Hg(II) was passed through the column. The flow rate of solution is an important factor affecting the retention of Hg(II), it is necessary to choose an appropriate flow rate that ensures a higher mecury uptake. Hence, the influence of flow rate on species retention was studied in the range from 0.2 to 3 mL min^{-1}. 100 % of Hg(II) was adsorbed by the functionalized silica gel when the flow rate is less than 2 mL min^{-1}. However, when the flow rate is up to 3 mL min^{-1}, the retention of Hg(II) is only 73.6 %. It is known that when the flow rate is too fast, Hg(II) can not be adsorbed sufficiently by the functionalized silica gel in the column. Therefore, we choose 1.5 mL min^{-1} as sample flow rate in the following experiments.

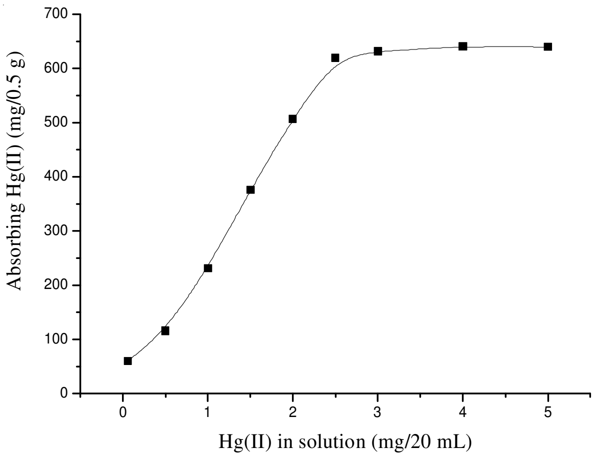


Fig. 3. Adsorption isotherm of Hg(II): 0.5 g of the functionalized silica gel at pH 7

Elution curve for Hg(II): 20 mL of solution containing 20 μg of Hg(II) at pH = 7 was passed through the column with a flow rate of 1.5 mL min^{-1}. Hg(II) retained in the column was eluted by 0.3 mol L^{-1} of $HClO_4$ with a flow rate of 0.5 mL min^{-1}. 6 mL of the eluent was collected in two aliquots, the concentration of Hg(II) in the eluent was determined and the total recovery of 100 % of Hg(II) was obtained. Hence, a flow rate of 0.5 mL min^{-1} and 6 mL of the eluent were selected for the following studies.

Pre-concentration and recoveries of Hg(II): The pre-concentration and recovery of Hg(II) were performed by the column method. Solutions containing 20 μg of Hg(II) but in different volumes were made up and passed through the column. The Hg(II) retained in the column was eluted and its content was determined. As in Table-1, it is found that the recovery of 96.6 % and the pre-concentration factor of 333 were obtained even when the concentration of Hg(II) is as low as 10 ng mL^{-1}. Therefore, it is possible to enrich low level of Hg(II) from aqueous solutions by the functionalized silica gel.

Effect of common cations and anions on the recovery of Hg(II): To assess the possibility of analytical applications for the proposed procedure, the effects of some foreign ions, which interfere with the determination of Hg(II) and often accompany with Hg(II) in various real samples, were examined under the optimum conditions. For this purpose, different amount of each ions were mixed with 20 μg of Hg(II) in 20 mL of solution at pH = 7. These mixtures were passed through the column, then the Hg(II) retained in the column was eluted with 6 mL of $HClO_4$ and the concentration of Hg(II) in the eluent was determined. The permit ratios of ions were given in Table-2 as the relative error is less than 5 %. It is clear that ions which often co-existed with Hg(II) in various real samples did not interfere with the recoveries and the determination of Hg(II). This suggests that the new solid phase extractant has good selectivity for recovery of Hg(II).

TABLE-1
PRE-CONCENTRATION AND RECOVERIES OF Hg(II)

Volume (mL)	Hg(II) in elution(μg)	Recovery (%)	Concentration factor
20	20.0	100	3.3
50	20.0	100	8.3
250	19.8	99.0	42
500	19.7	98.5	83
1000	19.7	98.5	167
2000	19.3	96.5	333

TABLE-2
EFFECT OF THE COMMON CATIONS AND ANIONS ON THE RECOVERY OF Hg(II)

Metal ion	Permit ratio	Metal ion	Permit ratio
Ca^{2+}	1350	K^{+}	2250
NH_4^{+}	350	Cd^{2+}	40
Co^{2+}	70	SO_4^{2-}	90
Bi^{3+}	100	CO_3^{2-}	1200
Mg^{2+}	1680	As^{3+}	50
Ag^{+}	40	Mo^{6+}	260
Al^{3+}	37	Mn^{2+}	75
Ni^{2+}	60	Sr^{2+}	95

Analysis of environmental water samples[31]**:** Water samples used in the present work include surface water in campus of Luoyang Institute of Science and Technology, tap water in our chemistry laboratory and in the student's dormitory and a simulate seawater sample consisting of 19.10 g kg^{-1} of $Cl^{–}$, 2.66 g kg^{-1} of $SO_4^{2–}$, 10.62 g kg^{-1} of Na^{+}, 0.4 g kg^{-1} of Ca^{2+}, 0.38 g kg^{-1} of K^{+}, 1.28 g kg^{-1} of Mg^{2+}.

A solution containing 500 mL of different water sample was adjusted to pH = 7 and passed though the column. 6 mL of eluent was collected and the content of Hg(II) in the eluent were determined. Because of the very low concentration, Hg (II) in different samples can not be detected by the present method. So, we added a known amount of Hg(II) in different samples. Following the procedure used above, 500 mL of water sample containing 50 μg of Hg(II) at pH = 7 was passed through the column and then eluted, the content of Hg(II) in the eluent was measured by spectrophotometry. The recovery data of Hg(II) in different samples are included in Table-3, the high recoveries of Hg(II) confirmed the validity of this new solid phase extractor. It is also noted from Table-3 that even the samples have complex matrix, Hg(II) still can be enriched and separate selectively by the functionalized silica gel.

Regenerability of the functionalized silica gel: The self made chromatographic column can be reused for 50 times and the recovery of Hg (II) is higher than 95 %. The experimental can still be reproduced after the functionalized silica gel is kept in a desiccator for five months, demonstrating the regenerability and stability of the functionalized silica gel.

TABLE-3
RECOVERIES OF Hg (II) FOR DIFFERENT SAMPLES

Sample	Direct determination	Amount of the functionalized silica gel	Added (µg)	Found (µg)	Recovery (%)	RSD (%) (n=3)
Surface water	Not detect	0.2g	50	49.75	99.6	1.1
Tap water in chemistry laboratory	Not detect	0.2g	50	49.73	99.46	1.8
Dormitory tap water	Not detect	0.2g	50	49.38	98.75	1.6
A simulate sea water sample	Not detect	0.2g	50	49.41	98.82	1.5

Conclusion

A selective and sensitive method was established for separation and pre-concentration of trace level of Hg(II) in natural water samples based on alizarin violet functionalized silica gel as a solid phase extractant. This solid phase extractant has the following advantages: (i) can be used for selective separation and pre-concentration of Hg(II) in the presence of common coexisting metal ions; (ii) can be used to eliminate the interference of complex matrix; (iii) the separation/pre-concentration produce is simple, rapid and low cost; (iv) has high pre-concentration factor and can be reused for many times.

ACKNOWLEDGEMENTS

The work was supported financially by Luoyang Institute of Science and Technology.

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