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Application of modified alumina coated magnetite nanoparticles as sorbent for separation/preconcentration of mercury trace amounts and its determination by cold vapor atomic absorption spectrometry

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ABSTRACT

A simple and selective method has been developed for rapid extraction and determination of ultra trace amounts of Hg(II) ions using 2-mercaptobenzothiazole (MBT) modified alumina coated magnetite nanoparticles (ACMNPs) for its highly sensitive measurement by cold vapor atomic absorption spectrometry (CVAAS). The effects of various parameters such as pH, reagents concentrations, the standing time, the sample volume, the elution condition and the interfering ions were investigated. Under the optimal experimental conditions, the preconcentration factor, detection limit, linear range and relative standard deviation of Hg(II) were 250 (for 500 mL of sample solution), 0.4 ng mL^{-1}, 2.0 – 80.0 ng mL^{-1} and 3.4% (for 10.0 ng mL^{-1}, n=10), respectively. This method avoided the time-consuming column-passing process of loading large volume samples in traditional solid phase extraction (SPE) through the rapid isolation of MBT/SDS-ACMNPs with an adscititious magnet. The proposed method also was successfully applied for determination of Hg(II) in different water samples.

KEYWORDS

Solid phase extraction;
Alumina-coated magnetite nanoparticles;
Mercury(II);
2-Mercaptobenzothiazole;
Cold vapor atomic absorption spectrometry.

INTRODUCTION

Determination of mercury in environmental samples is of great importance nowadays because mercury is particularly toxic element and a widely distributed environmental pollutant because it is widespread in the lithosphere and in water inorganic mercury, especially soluble mercury species, can be transformed into methyl mercury by the action of microorganisms and can be accumulated in the tissue of fishes and birds[1-3]. So, its concentration should be kept under permanently controlled conditions. Cold vapour atomic absorption spectrometry (CVAAS) is one of the most widely used instruments for determination mercury at trace levels. However, there are some difficult in direct determination of mercury by CVAAS in this quantity levels, therefore, initial separation/preconcentration procedures are often required prior to determination of Hg(II) by this technique. In this context solid phase extraction (SPE)[4-7] is a well-known method of separation/preconcentration which has great advantages[8-11] over the other separation tools[12-15]. In fact, in this technique the choice of the organic modifier is a key point in the synthesis of selective SP-extractors. Using magnetic micro and nanoparticles for separation/preconcentration in analytical chemistry is opening a new method that is rapid, simple and more exact than old ones. A major advantage of using magnetite nanoparticles (MNPs) as solid phase extractor is the possibility of collection of the particles by application of a magnetic field in a batch system. This makes MNPs excellent candidates for combining adsorption properties with ease of phase separation[16]. In this study, a new method using magnetic separation has been developed and applied for the separation and preconcentration of mercury ions. Our study adopted doping method to prepare functional magnetic material for separation and preconcentration of Hg(II). 2-Mercaptobenzothiazole (MBT) was chosen as doping reagent because of its favorable coordination capacity and selectivity for Hg(II). It is concluded from the extraction data that the new sorbent is a promising material for the SPE of mercury. In this paper, we will explore the possibility of MBT/sodium dodecyl sulfate (SDS) immobilized on alumina-coated magnetite nanoparticles (MBT/SDS-ACMNPs) to act as SPE sorbents for the separation/preconcentration of trace level of mercury ions from water samples prior to determination by CVAAS technique.

EXPERIMENTAL

All reagents used were of analytical grade and all solutions were prepared by using triple distilled and deionized water. A stock solution of 1000 μg mL^{-1} mercury (II) was prepared by dissolving 0.1354 g of $HgCl_2$ in 5 mL of concentrate nitric acid and was diluted to 100 mL. Working solutions were obtained by further diluting the stock solution to the required concentrations before use. 2-Mercaptobenzothiazole (MBT), sodium dodecylsulfate (SDS), ferrous chloride ($FeCl_2 \cdot 4H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), aluminum isopropoxide, ethanol, nitric acid, hydrochloric acid, sodium hydroxide, bromic acid and and sodium tetrahydroborate were used without further purification processes. All of the chemicals were obtained from Merck.

A PG 990 flame atomic absorption spectrophotometer (PG Instruments, England) equipped with a mercury hollow cathode lamp as light source and hydride vapor generator (WHG-103 A) was used for mercury generation and absorbance measurements. The mercury compounds were reduced to metallic mercury with sodium tetrahydroborate and the mercury generator was operated with argon as carrier gas. All the measurements were carried out in the cold state under the conditions given in TABLE 1. A Fourier transform infrared spectrometer (IR Perresttige-21, Shimadzu) was used to determine the identity of the as-prepared nanoparticles and to characterize the coated Fe_3O_4 nanoparticles. The surface morphology of the powders was observed by the scanning electron microscope (LEO 1455VP SEM). Magnetic properties of the particles were determined by vibrating sample magnetometer (VSM 7400 Model Lake-Shore). pH measurements were made with a Metrohm Model 780 pH meter with a combination glass electrode. Other instruments used were: ultrasonic bath (S60H Elmasonic, Germany), mechanical stirrer (Heidolph, RZR2020), orbital shaker (Ika, KS130 Basic), an electronic analytical balance (Adam, AA220LA) was used for weighting the solid materials. In addition, for magnetic separations a strong neodymium-iron-boron ($Nd_2Fe_{12}B$) magnet (1.2 T, 2.5cm × 5cm × 10cm) was used.

TABLE 1 : Applied conditions for mercury determination with the WHG-103 A (CV) system

Parameter	Applied condition
Measurement mode	Continuous-flow method
Signal processing	Integrated hold
Integration time/s	10
Argon carrier gas flow rate/mL min^{-1}	80.0
Sample aspiration flow rate/mL min^{-1}	4.5
5.0 M HCl flow rate/mL min^{-1}	2.1
0.5% $NaBH_4$ flow rate/mL min^{-1}	2.0

Preparation of MBT/SDS-ACMNPs

The ACMNPs were prepared according to Karimi *et al.*[17,18]. A MBT/SDS solution was prepared by dissolving 140.0 mg MBTand 200.0 mg SDS in 10 of 0.1 M ammonia diluted to 100 mL with deionized water. Ten milliliters of MBT/SDS solution was added to 10 mL water containing 0.05 g of ACMNPs. The pH of this suspension was adjusted to 2.0 by drop-wise addition of 0.1 M HNO_3 solution. The mixed solution was shaken for 15 min and then separated from the reaction medium under the magnetic field, and rinsed with 10 mL pure water. This product was used as sorbent for nickel ion.

The procedure for the magnetic solid phase extraction of mercury ions is as follows: 10 mL of Hg(II) solution (20 ng mL^{-1}) was added to MBT/SDS-ACMNPs, subsequently the pH value was adjusted to 4.0 with 0.2 M HNO_3 and the solution was shaken for 10 min to facilitate adsorption of the metal ions onto the nanoparticles. Then the magnetite adsorbents was separated easily and quickly using magnet and decanted directly. Subsequently, 2 mL of 0.4 M HBr solution was added as eluent. Finally, the magnet was used again to settle the magnetic nanoparticles and the eluate was separated for CVAAS analysis.

Sample preparation procedure for water and blood

Water samples (i.e., tap water, river and spring water), were filtered through filter paper (Whatman, no. 4) to remove suspended particulate matter after collection and acidified to a pH of about 4.0 with concentrated HNO_3 prior to storage in polyethylene container for use. Subsequently were neutralized with concentrated NH_3 and then pH of solutions were adjusted to 4.0. The SPE procedure was carried out as described in above procedure and then mercury determinate using CVAAS.

Five samples of blood were obtained from healthy human bodies by in the sterile blood collecting tubes containing EDTA as anticoagulant. Four milliliters concentrated HNO_3 was added to 5 mL from each samples and heated for 15 minutes at $80^{?}$C and then 2 mL H_2O_2 was added and heated for 20 minutes again. After filtering and eluting with 2 mL of 0.4 M HBr, the resultant solution was neutralized with concentrated NH_3 and then pH was adjusted to 4.0, and it was analyzed according to the above procedure for extraction and determination of mercury content.

RESULTS AND DISCUSSION

The MNPs, ACMNPs and MBT/SDS-ACMNPs were characterized by vibrating sample magnetometery (VSM), scanning electron microscopy (SEM) and Fourier transform infrared spectrometry (FT-IR). The magnetization curves show that both MNPs and ACMNPs exhibit typical superparamagnetic behavior due to no hysteresis[17,18]. However, these ACMNPs are sufficient for magnetic separation with a conventional magnet. SEM images of NPs and ACMNPs also were showing which the uniform size distribution of the nanoparticles[17,18]. The modified ACMNPs were also confirmed by FT-IR analysis, as shown in Figure 1. As can be seen in Figure 1a, a broad band exists around 588.29 cm^{-1}, assignable to the Fe–O–Fe of the MNPs. The peak at about 1602.85 cm^{-1} can be assigned to the stretching vibration of N_2 adsorbed on the surfaces of the nanoparticles. The flexing vibration peak of hydroxyl, resulting from the adsorbed water, can be observed at 3433.64 cm^{-1}[38]. In Figure 1b, the spectrum of ACMNPs compared with the spectrum of MNPs,after binding alumina, and the broadening of the peak at 644.22cm^{-1} can be assigned to Al–O, that overlapped with Fe–O characteristic peak. Comparison of the FT-IR spectra of ACMNPs and MBT/SDS-ACMNPs (Figure 1c) is also shows a new sharp peak at 1382.96 cm^{-1} appeared, it was due to that the C–S stretching peak of MBT stabilized on ACMNPs. Consequently, the FT-IR data suggest that MBT are successfully immobilized on the ACMNPs surface.

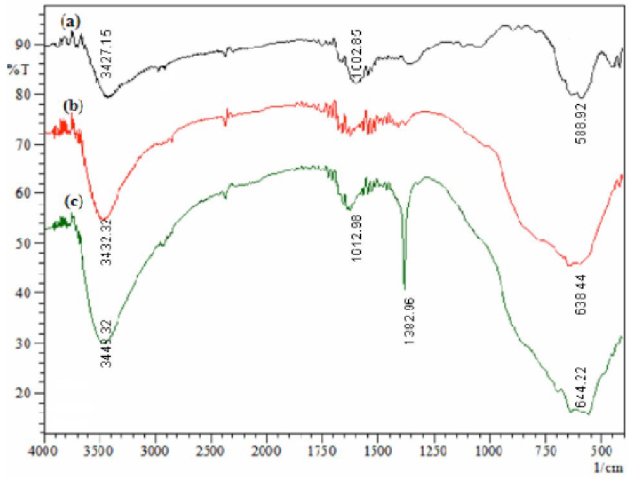

Figure 1 : FTIR spectra of the MNPs (a), ACMNPs (b), and MBT/SDS-ACMNPs (c)

The negatively charged surfactants such as SDS can strongly adsorb on positively charged surfaces of ACMNPs in highly acidic solutions. A concentration of SDS, below its critical micellar concentration (CMC,

8×10^{-3} M), was used. Above this concentration, the excess of SDS would form micelles in the aqueous solution, which were not adsorbed on alumina surfaces. The influence of amounts of SDS/MBT on the adsorption of the mercury ions on ACMNPs was investigated. The results showed that with the increase of SDS concentration, the adsorption increases and a maximum is obtained after the SDS concentration approaches to 2×10^{-3} M and remains constant up to CMC and then decreased, because above this point micelles was formed strongly. Thus, a concentration of 2×10^{-3} M was selected as the optimum SDS concentration for further studies.

In order to study the effect of MBT concentration on the adsorption of Hg(II) on the ACMNPs, ammoniacal solutions of SDS/MBT with constant concentration of SDS and different concentrations of MBT were used to study of Hg(II) ions percent adsorbed on ACMNPs. At MBT concentrations less than 2×10^{-5} M, the amount of MBT molecules immobilized into SDS cores are low. Therefore, 2×10^{-5} M of MBT was selected as the optimum concentration for further studies.

pH is the main investigated factor for the all extraction studies[20-25]. The recovery of mercury(II) with MBT coated alumina was studied at different pH values. For this purpose, a series of Hg(II) solutions with different pH values from 2.0 to 12.0 were used, and the adsorbed mercury was eluted with 2.0 mL of 0.4 M HBr solution. The results are presented in Figure 2. It can be seen from the figure, it is evident that the adsorption of mercury is quantitative (100%) in the pH range of 3.0–6.0. A pH of 4.5, in the middle of the pH range was selected as the optimum pH to avoid any abrupt changes in pH that may occur during adsorbing step and could consequently affect the precision. At the pH values below 3.0, the recovery percent decreased, because the H^+ ion was competed with Hg^{2+} for adsorption on sorbent and in pH values above 6.0, MBT and/or SDS could be washed out from surface of sorbent. Consequently, the load of the sorbent with the adsorbent will be decreased; this gives a lower recovery percent for Hg(II).

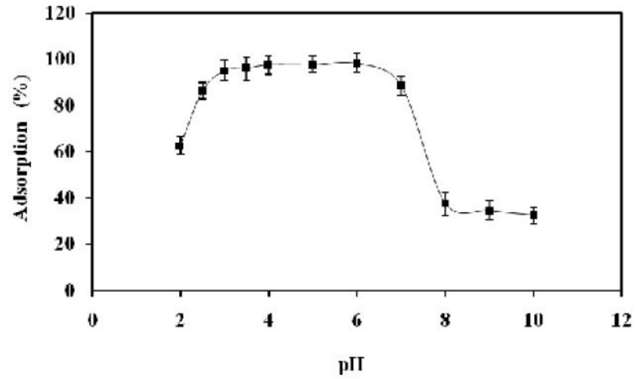

Figure 2 : Effect of pH on adsorption of Hg(II). Conditions: ACMNPs (0.05 g), SDS (10 mL, 2×10^{-5} M), MBT (10 mL, 2×10^{-5} M), Hg(II) solution (10 mL, 20.0 ng mL^{-1}).

In the SPE procedure, we found that the standing time had obvious effect on the target analyte extraction. When the MNPs were isolated immediately without a standing process, the recovery of Hg(II) was only 45 %. However, when the standing time were adjusted to 2, 5 and 10 min, recoveries improved to 80, 91 and 98 %, respectively. 10 min was sufficient to achieve satisfactory adsorption and better recovery of Hg(II). Meanwhile, in the experiment, MBT/SDS-ACMNPs possessed superparamagnetism properties and large saturation magnetization, which enabled them to be completely isolated at the least time (less than 1 min) by a strong magnet.

A variety of eluents were tested in order to elute the adsorbed mercury from the sorbent. Different eluents of thiourea, thiosulphate, HBr, HNO_3 HCl at various concentrations were examined so that the most effective eluent for the quantitative recovery of Hg(II) could be chosen. It was found that 2.0 mL of Hbr with a concentration of 0.4 M was sufficient for quantitative recovery of adsorbed Hg(II).

In order to perform SPE procedure on water samples leading to high enrichment factor, the sample volume need to be optimized. In this case the effect of sample volume on the adsorption of mercury ions on MBT/SDS-ACMNPs was investigated. The solutions in the range 0f 50–700 mL containing 20 ng mL^{-1} of mercury ion were operated according to the general procedure and eluted using 2.0 mL of 0.4 M. At sample volumes higher than 500 ml, the recovery percent decreased. The recoveries of the analyte ions were quantitative until 500 mL. In this study, the final solution volume of eluate for analysis was 2.0 mL, therefore the preconcentration factors was 250.

The recovery of 10.0 ng mL^{-1} of mercury ions was investigated in binary mixtures containing Hg(II) and one of the foreign ions. The following excess of ions did not interfere the reaction (i.e., caused a relative error of less than 5%): more than a 1000-fold amount of Na$^+$, Ca^{2+}, Mg^{2+}and K$^+$; a 500-fold amount of Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, K$^+$, Cr^{3+}, Fe^{3+}, Bi^{3+}, Pd^{2+} and NH$_4^+$; a 200-fold amount of, NO$_3^-$ and CH$_3$COO$^-$, a 100-fold amount of SO$_4^{2-}$, PO$_4^{3-}$, C$_2$O$_4^{2-}$, Ag$^+$, Pb^{2+} and a 50-fold amount of I$^-$, F$^-$, Cl$^-$ and Br$^-$. The results showed that most of the investigated ions do not interfere in the adsorption–desorption and determination of traces of mercury ion in water samples.

The adsorption capacity study used here was adapted from the recommended method by Maquieira *et al.*[26]. The static adsorption capacities of MBT/SDS-ACMNPs were found to be 21.7 mg g^{-1} for mercury ions.

Regeneration is one of the key factors for evaluating the performance of the adsorption material. In this work, it was found that the ACMNPs can be reused up to five times without loss of analytical performance. This reusable number is suitable because 4.0 g of ACMNPs could be prepared in one batch and only 0.05 g of ACMNPs was used for one extraction operation.

In order to show the validation of the proposed method, under the optimal experimental conditions, the analytical features of the method such as limit of detection (LOD), linear range of the calibration curve and precision were examined. The LOD of the proposed method based on three times the standard deviation of the blank (3S$_b$), was 0.4 ng mL^{-1} (n = 10). The linear range of calibration curve for Hg(II) was 2.0-80.0 ng ml^{-1} with a correlation coefficient of 0.997. The regression equation for the line was $A = 0.091\ C_{Hg} + (4.6 \times 10^{-3})$ (n=8), where C_{Hg} is the concentration of Hg(II) in ng mL^{-1} and A is the absorbance. The relative standard deviation (RSD) for 10 replicate measurements of 10.0 ng mL^{-1} of mercury ions was 3.4%.

The suitability of the proposed method for seperation/preconcentration and determination of mercury in spiked water and human's blood samples. The results tabulated in TABLES 2 and 3. As the results show, the proposed method is suitable for the separation/preconcentration of Hg(II) at the ng mL^{-1} level in real samples.

TABLE 2 : Recoveries results of real water samples spiked with mercury ions.

Sample	Hg(II) (ng mL^{-1}) Added	Found	Recovery (%)
Tap water (Sirjan)	0.0	-	-
	10.0	9.7 (±0.2)	97
	20.0	20.2 (±0.4)	101
River water (Hajiabad, Hormozgan Province)	0.0	-	-
	10.0	9.9 (±0.3)	99
	20.0	20.4 (±0.3)	102
Spring water (Koran, Sirjan)	0.0	-	-
	10.0	9.8 (±0.1)	98
	20.0	20.0 (±0.2)	100

TABLE 3 : Mercury contents in various blood samples

Sample no.	Hg(II) (ng mL^{-1})		Recovery (%)
	Added	Founded	
1	0.0	3.4 (±0.4)	-
	5.0	8.6 (±0.3)	105.8
2	0.0	7.5 (±0.6)	-
	5.0	12.3 (±0.5)	96.0
3	0.0	4.3 (±0.7)	-
	5.0	9.4 (±0.2)	102.3
4	0.0	2.7 (±0.3)	-
	5.0	7.9 (±0.4)	107.4
5	0.0	8.3 (±0.5)	-
	5.0	13.2 (±0.6)	98.7

CONCLUSION

It has been demonstrated that the MBT immobilized on modified ACMNPs provides a new and fast route for separation/preconcentration and determination of Hg(II) using CVAAS technique in different samples. This sorbent was successfully applied for convenient, fast, simple and efficient enrichment of trace amounts of mercury ions from tap water, spring water, river water and and human's blood samples. The main benefits of this methodology are: no use of toxic organic solvent(s), simplicity and high capacity of sorbent, preconcentration factor, good stability, fast adsorption and low cost. Furthermore, it avoids the time-consuming column passing (about 1 h in conventional SPE method) and filtration operation, and no clean-up steps were required. TABLE 4 shows a comparison of

TABLE 4 : Comparison of the proposed method with other reported SPE methods for separation/preconcentration of mercury ions

Adsorbent	Detection method	Enrichment factor	RSD (%)	Linear range (ng mL$^{?1}$)	Detection Limit (ng mL$^{?1}$)	Reference
2,6-Pyridine dicarboxylic acid/nanometer silica	ICP-AES^{a}	175	3.0	-	0.09	[27]
Dithizone/alumina	Spectrophotometry	100	2.5	-	4.0	[28]
2-Mercaptobenzimidazole/agar	CVAAS	100	2.6	0.04-2.4	0.02	[29]
Dithizone/alumina	CVAAS	100	1.7	0.6-5.0	0.11	[30]
N-(2-Chlorobenzoyl)-N-phenylthiourea Loaded/sulfur	CVAAS Spectrophotometry	333	3.9	0.02-1.20	0.012	[31]
Dithizone/cellulose	Spectrophotometry	33	3.5	0-2	2.0	[32]
Dithizone/silica gel	CVAAS	500	3.0	1.0-1500	0.9	[33]
1,5-Bis (2 pyridyl)-3-sulphophenyl methylene thiocarbonohydrazyde/Resin	CV-ETAAS^{b}	28	3.4	0.1-30.0	0.01	[34]
		42	3.5	0.009-1.5	0.006	
1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene/ octadecyl silica cartridge	CVAAS	128	2.4	0.13-25.0	0.05	[35]
MBT/SDS-ACMNPs	CVAAS	250	3.5	0.2-80.0	0.005	This work

[a] Inductively coupled plasma - atomic emission spectrometry; [b] Cold vapor-electrothermal atomic absorption spectrometry

the proposed method with other reported SPE methods. It could be seen that some obtained values for the proposed method such as sorbent capacity and preconcentration factor are as or better than some of the previously reported methods.

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