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Fast and efficient removal of mercury from water samples using magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole

H. Parham*, B. Zargar, R. Shiralipour

Chemistry Department, College of Science, Shahid Chamran University, Ahvaz, Iran

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ABSTRACT

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Keywords: Mercury 2-Mercaptobenzothiazole Modified magnetic iron oxide nanoparticles Removal Mercury in the lowest levels of concentrations is dangerous for human health due to its bioaccumulation in body and toxicity. This investigation shows the effective removal of mercury (II) ions from contaminated surface waters by modified magnetic iron oxide nanoparticles (M-MIONPs) with 2-mercaptobenzothiazole as an efficient adsorbent. The proposed method is fast, simple, cheap, effective and safe for treatment of mercury polluted waters. Preparation of adsorbent is easy and removal time is short. Non-modified magnetic iron oxide nanoparticles (MIONPs) can adsorb up to 43.47% of 50 ng mL⁻¹ of Hg (II) ions from polluted water, but modified magnetic ironoxide nanoparticles (M-MIONPs) improved the efficiency up to 98.6% for the same concentration. The required time for complete removal of mercury ions was 4 min. Variation of pH and high electrolyte concentration (NaCl) of the solution do not have considerable effect on the mercury removal efficiency. Loading capacity of adsorbent for Hg ions is obtained to be 590 μ g g⁻¹.

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1. Introduction

Removal of inorganic and organic pollutants from waters has been one of the major investigations in the last few decades. Mercury is one of the most toxic metals known to man. During the 20th century there were several major catastrophes of Hg poisoning through contaminated food [1].

Main contamination sources of surface and waste waters by mercury ions are battery, paper and pulp, chlor-alkali production, oil refinery and paint manufacturing industries. There are some other minor sources of pollution [2,3]. Some aquatic bacteria in the water sediments can convert the mercury ion to the very toxic compound methyl mercury which can readily be absorbed by the human body. Numerous cases of mercury poisoning, or Minamata disease are reported in different countries around the world which resulted due to the consumption of fish and shellfish by humans [4].

Mercury was thought to be environmentally stable until recent decades. But, it can form different salts and complexes with anionic components in water and can also be converted from one form to another in different aquatic environments. Some acute and chronic symptoms which are caused by inorganic mercury are as follows: thirst; metallic taste; inflammation of the mouth; nausea; kidney degeneration; excessive salivation and tremor [1]. The availability of clean water to humans, decreasing the degree of surface and waste waters pollution and contamination of environment by toxic pollutants have emerged as the most serious problems facing global society in the twenty-first century.

Nanotechnology has great potential for providing efficient, costeffective, and environmentally acceptable solutions for improving water quality and increasing quantities of potable water [5]. Introduction of nanomaterials and especially magnetic nanoparticles showed many key physicochemical characteristics that make those substances particularly attractive as separation media for water purification. These special properties offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high extraction capacity, rapid extraction dynamics, and high extraction efficiencies in compare to micrometer-sized particles. Nanoparticles are good building blocks for developing high-capacity sorbents with modification ability to enhance their affinity and selectivity for purification of contaminated waters. Application of nanoparticles (NPs) as novel adsorbents for removal of pollutants is gaining research interest. Recently, magnetic iron oxide nanoparticles (MIONPs) have shown widespread applications as solid phase adsorbent for removal of different types of pollutants such as dyes and heavy metals since no centrifugation or filtration of the sample is needed after treatment (in comparison with non-magnetic adsorbents) [6-12].

Removal of mercury from water samples have been carried out by different solid phase extraction (SPE) techniques, such as: chelating 2-mercaptobenzothiazole loaded resin [13], aminopropylbenzoylazo-2-mercaptobenzothiazole bonded to

^{*} Corresponding author. Tel.: +98 611 3360018; fax: +98 611 3337009. *E-mail address*: hoparham@yahoo.com (H. Parham).

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silica gel [14], 2-mercaptobenzimidazole-clay [3], polyacrylamidegrafted iron (III) oxide [15], resin functionalized with a 1,2-bis(o-aminophenylthio)ethane moiety [16], synthetic mercury (II) chelating ligand [17], stabilized iron sulfide nanoparticles [18], hybrid silica-polyacrylamide aerogels [19], carbon nanoparticleconjugated polymer nanocomposites [20], carbonaceous sorbent chemically prepared from rice husk[21], TiO₂ nanoparticles [22], silica coated magnetite particles [23], polyaniline/humic acid nanocomposite [24], synthesized TiO₂ nanoparticles [25], papain immobilized on alginate bead [26], DNA condensation [27], dithiocarbamate-anchored polymer/organosmectite composites [28], o-benzenedithiol modified cellulose resin [29], charcoalimmobilized papain [30], camel bone charcoal [31], aminated chelating fiber [32], chitosan based ceramic membranes [33], silica-titania composites [34] and silver nanoparticle-based adsorbent [35]. Removal of inorganic mercury, methyl mercury and other heavy metal ions from surface waters are also reported [36-39]. New SPE techniques based on the use of magnetic or magnetizable adsorbents called magnetic solid-phase extraction (MSPE) have been introduced [40,41]. A distinct advantage of this technology is that magnetic materials can be readily and shortly isolated from sample solutions by the application of an external magnetic field. Generally, most of the dissolved environmental contaminants are nonmagnetic, and thus do not respond to magnetic field. Magnetic nanoparticles possess large surface areas and have unique magnetic properties. Selective removal of toxic target compounds from complex environmental matrices can be obtained when certain special functional ligands with affinities for target molecules are bounded onto these magnetic nanoparticles [42].

Present work introduces an efficient removal of Hg (II) ion from polluted water using modified magnetic iron oxide nanoparticles with 2-mercaptobenzothiazole (MBT) that can form strong complex with Hg (II) ion [43–46]. The proposed method shows high potential for effective removing of traces of Hg (II) ion from water solution in a short time via an easy procedure and lowers the concentration of this ion close to the standard healthy levels announced by the World Health Organization (WHO), that declared there is no safe level of mercury for human beings, in other words, mercury is so poisonous that no amount of mercury absorption is safe.

2. Experimental

2.1. Instrumental

A Varian 240AAFS (Australia) atomic absorption spectrophotometer equipped with a mercury hallow cathode lamp (Varian, Australia) at the wavelength 253.7 nm was used for the determination of mercury in sample solutions. A Varian vapor generation accessory model VGA-77 (Australia) with a T-quartz cell was used for the cold generation of mercury vapor and its determination in water, respectively. An infrared spectrum was obtained using a Fourier Transform-Infrared Spectrometer (FT-IR, Perkin Elmer, spectrum 100) to identify the functional groups and chemical bonding of the coated materials. Transmission electron microscopy (TEM) was performed using a Field emission TEM (TEM, 906E, LEO, Germany) operating at 200 kV to measure the particle size and shape. The structure analysis of the MIONPs and M-MIONPs was carried out using an X-ray Diffractometer (XRD, Brucker D8 Discover, Germany). FRITSCH Laser particle sizer ANALYSETTE 22 nanotech plus (Germany) was used for measuring the size distribution of both Fe₃O₄ and MBT@Fe₃O₄. A Jenway pH meter model 3510 (UK), a Jenway hotplate and stirrer model 1000 (UK) and a magnet $(1.2 \text{ T}, 10 \text{ cm} \times 5 \text{ cm} \times 2 \text{ cm})$ were used during the experiments.

2.2. Reagents

All solutions were prepared by double distilled de-ionized water with electric conductivity below $1.5 \ \mu S \ cm^{-1}$.

The Hg^{2+} stock solution (100 µg mL⁻¹) was prepared daily from $HgCl_2$ (Merck, Darmstadt, Germany). More diluted mercury solutions were prepared using step-by-step dilution of concentrated mercury solutions.

FeCl₃ (96%, w/w), FeCl₂·4H₂O (99.9%, w/w), and ammonia solution (25%, w/w), hydrochloric acid (37%, w/w), phosphoric acid (96%, w/w), sodium hydroxide and Tin (II) chloride dihydrate were purchased from Merck (Darmstadt, Germany). 2-Mercaptobenzothiazole (Fluka, Swiss) was used as modifier for MIONPs.

2.3. Preparation of modified iron oxide magnetic nanoparticles

MIONPs were prepared according to method represented by Jang et al. [47]. The transmission electron microscope (TEM) image and graph of size distribution of the MIONPs (average size of particles is about 40-50 nm) is shown in Fig. 1A. In order to coat the iron oxide nanoparticles with 2-mercaptobenzothiazole (MBT), 3 mL of MBT solution (5%, w/v, in acetone) was added to 20 mL of damped nanoparticles (equivalent to 0.66 g of dried MIONPs) and the mixture was diluted to 50 mL with acetone. The solution mixture was stirred for 25 min with a glass rod at 30 °C. After complete mixing, the beaker was placed on the magnet and M-MIONPs were collected at the bottom of beaker. Based on this procedure MBT is coated on MIONPs possibly via physical adsorption. The supernatant solution was decanted to eliminate the excess amount of the MBT and the modified ferrofluid was washed with distilled water for several times. The TEM image and graph of size distribution of MBT-coated MIONPs are given in Fig. 1B.

2.4. Removal procedure

A batch procedure was applied for the removal process. The adsorption of Hg ions by modified magnetic iron oxide nanoparticles (M-MIONPs) was carried out in a pH 9 solution at 25 °C. In General, 3 mL of solution containing M-MIONPs (equivalent to 0.1 g of dried M-MIONPs) was added to a 50 mL solution of Hg²⁺ ions (25 ng mL⁻¹) adjusted to pH 9 using dilute solutions of NaOH and HCl. After mixing for 4 min with a stirring speed of 400 rpm, magnetic nano-adsorbents were separated magnetically from solution by the magnet. Removal percent and adsorbed amount of Hg were determined by cold vapor atomic absorption spectrophotometric (CVAAS) measurement of the sample solution before and after removing process. The effects of MIONPs on the mercury ion removal before and after modification with 2-mercaptobenzothiazole were compared.

2.5. Sampling

Water samples were collected from four main sources: (1) tap water from Ahvaz (Khuzestan, Iran) drinking water. (2) Karoon river passing through Ahvaz City. (3) Industrial wastewater of sugar factory in southern Ahvaz. (4) Industrial wastewater of a paper manufacturing factory placed in northern Ahvaz. All the samples were prepared freshly prior to analysis. No matrix modification had been done on the water samples before removal process and analysis.



Fig. 1. TEM image and graph of size distribution of the synthesized MIONPs and M-MIONPs.

3. Results and discussion

3.1. Characterization of the M-MIONPs

An infrared spectrum was obtained using a Fourier Transform-Infrared Spectrometer (FT-IR, Perkin Elmer, spectrum 100) to identify the functional groups and chemical bonding of the coated materials. Fourier infrared spectrum (Fig. 2a–c) shows the characteristic peaks of MIONPs (a), MBT (b) and MBT@Fe₃O₄ (c). The double peaks of S–H were found at 2358 and 2345 cm⁻¹ (Fig. 2b for MBT and Fig. 2c for MBT@Fe₃O₄,) which are typically very weak due to the aggregation of mercapto groups within the monolayer



Fig. 2. FT-IR spectrum of MIONPs (a), MBT (b) and MBT@Fe₃O₄ (c). the left arrows shows S-H stretching for both MBT and MBT@Fe₃O₄ and right arrows show Fe-O stretching for both Fe₃O₄ and MBT@Fe₃O₄.



Fig. 3. X-ray diffraction pattern of (a) MIONPs and (b) MBT@Fe₃O₄.

and hydrogen binding effects. The presence of S–H double peaks in 2358 and 2345 cm⁻¹ in MBT@Fe₃O₄ spectrum shows that the adsorption of MBT on MIONPs is mainly due to physical interaction. The absorption bands at 570–640 cm⁻¹ are usually attributed to the Fe–O stretches [48,49]. These bands are overlapped with sharp bands of MBT at the same region and in Fig. 2c stronger mixed bands are seen which are shifted to 600–670 cm⁻¹.

The XRD spectra of naked MIONPs is compared with MBTcapped particles, the XRD pattern of this nanoparticles agrees well with that of the unmodified nanoparticles (as shown in Fig. 3a), the result shows that the reflection peaks can be seen in an XRD pattern at 30.1, 35.5, 43.2, 53.5, 57.0 and 62.7. These peaks correspond to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes. The XRD pattern of the MIONPs exactly matched the JCPDS reference no. 19-629. The X-ray diffraction pattern of MBT-coated MIONPs is shown in Fig. 3b. It can be seen that the intensities of peaks are decreased due to caption of MIONPs by MBT.

3.2. Effect of modification of MIONPs on mercury removal

In order to investigate the influence of modification of MIONPs by 2-mercaptobenzothiazole on mercury removal from water samples, different mercury contaminated solutions in the concentration range of $5-200 \text{ ng mL}^{-1}$ of Hg ion were tested by magnetic iron oxide nanoparticles with and without modification. The results are presented in Table 1. According to the obtained results, the modification of MIONPs strongly improved the adsorption ability of the adsorbent.

3.3. Effect of pH

The effect of pH on the adsorption of Hg ions $(50 \text{ mL}, 25 \text{ ng mL}^{-1})$ by 3 mL of M-MIONPs solutions at 25 °C is shown in Fig. 4. The

Table 1

Removal efficiency for different concentrations of Hg ions using modified and nonmodified MIONPs with MBT.

Adsorbent	Conc. of Hg (ng mL $^{-1}$)	Removal% RSD	
MIONPs	5	62.3	4.5
	10	67.9	4.1
	20	64.8	3.9
	50	43.4	4.0
	100	35.0	3.7
M-MIONPs	5	92.4	2.9
	10	94.4	2.8
	20	98.6	2.8
	50	98.6	2.1
	100	97.8	2.4
	200	96.2	2.9



Fig. 4. The effect of pH of the solution for quantitative removal of Hg ions using M-MIONPs at 25 $^\circ\text{C}.$

results show that the removal of Hg ions remains constant in a wide pH range from 2.5 to 11. The pH of working solutions was adjusted to 9 (using dilute NaOH solution) for further works due to its positive effect (shortening the time needed for separation of adsorbent particles) on settlement time for M-MIONPs.

3.4. Effect of contact time

Different contact times between M-MIONPs (100 mg) and Hg ion solutions were investigated from 1 up to 30 min. Results are shown in Fig. 5. The contact time of 4 min with a stirring speed of 400 rpm is enough for complete removal of mercury ions from 50 mL solution (25 ng mL⁻¹). It must be mentioned that for larger solution volumes (>100 mL) more contact times are needed for complete removal of Hg ions with a fixed amount of M-MIONPs.

3.5. Effect of 2-mercaptobenzothiazole as modifier of MIONPs

The amount of 2-mercaptobenzothiazole for modification of MIONPs and its effect for the removal of Hg ions from 50 mL solutions of mercury ion (25 ng mL^{-1}) at optimized pH value and contact time were investigated. According to the results (Fig. 6), the optimized amount of 2-mercaptobenzothiazole for coating of MIONPs in 3 mL of colloidal solution (equivalent to 0.1 g of dried MIONPs) is 23 mg. Higher amounts of 2-mercaptobenzothiazole did not improve removal efficiency any more.

3.6. Effect of the amount of M-MIONPs

The optimum amount of the adsorbent required for quantitative removal of Hg (25 ng mL⁻¹) from 50 mL solutions, was obtained by investigating the effect of different volumes of pretreated modified (M-MIONPs) ranging from 0.1 to 4.0 mL (equivalent to 3–120 mg of dried M-MIONPs). As shown in Fig. 7, maximum removal



Fig. 5. The effect of contact times between M-MIONPs and Hg ions solutions for quantitative removal of the analyte.



Fig. 6. The effect of 2-mercaptobenzothiazole amount for modification of MIONPs (100 mg) for quantitative removal of Hg ions from 50 mL solutions of mercury ion (25 ng mL^{-1}) at optimized pH value and contact time.

percentage is obtained when 3 mL of M-MIONPs (equivalent to 0.1 g of dried M-MIONPs) was used.

3.7. Adsorption isotherm

The capacities of M-MIONPs for adsorption of Hg ions were examined by measuring the initial and final concentrations of Hg ions in the test solution (pH 9, 25 °C and contact time of 4 min) in a batch system. Different test solutions with Hg ion concentration ranging from 2 to 4000 ng mL⁻¹ were examined with fixed amount of M-MIONPs (100 mg). Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The results showed that Langmuir model fitted better ($R^2 = 0.9944$) than the Freundlich model ($R^2 = 0.9635$), demonstrating that the adsorption of Hg (II) ion onto MBT@Fe₃O₄ can be considered to be a monolayer adsorption process. This may be due to the formation of a monolayer strong complex between the coated MBT on the surface of MIONPs and Hg (II) ion [42-46] which covers the surface of MIONPs and no more complex molecules can form on the first layer. The Langmuir isotherm equation was used to describe the relationship between the amount of Hg adsorbed and its equilibrium concentration in solutions (Fig. 8).

$$\frac{C}{q} = \frac{1}{Kq_m} + \frac{C}{q_m}$$

where $C(\text{mg }L^{-1})$ is the equilibrium concentration of the Hg ions in the solution, q(mg Hg/g adsorbent) is the equilibrium adsorption amount of Hg, q_m is the maximum adsorption amount of Hg per milligram of adsorbent ($\text{mg }g^{-1}$) and K is the Langmuir adsorption equilibrium constant in liter per mg of adsorbent (Lmg^{-1}).



Fig. 7. The effect of different amounts (3–120 mg) of pretreated modified M-MIONPs for quantitative removal of Hg ions from 50 mL solutions of mercury ion (25 ng mL⁻¹) at optimized pH value and contact time.



Fig. 8. The plot of $q_e (\mu g g^{-1})$ versus $C(\mu g L^{-1})$ at 25 °C and pH = 9.0 with Langmuir model fit of the data.

Table 2

Effect of some interfering ions on the removal process of Hg ions by M-MIONPs.

lons	Tolerance ratio
SO ₄ ^{2–} , NO ₃ [–] , Cl [–]	4000
Ca ²⁺ , Mg ²⁺	2000
Ba ²⁺ , Cr (VI), Pb ²⁺ , Mo (VI), Fe ²⁺ , Fe ³⁺ , Cd ²⁺ , NO ₂ ⁻ ,	1000
SO ₃ ^{2–} , B ₄ O ₇ ^{2–} , NH ₄ ⁺ , CH ₃ COO [–]	
As ³⁺	1
Cu ²⁺	0.4

The linear relationship between C/q and C (y = 0.008 + 0.0054) shows the applicability of the Langmuir model. The experiments resulted in 1.46 for K (as Langmuir adsorption equilibrium constant, $L \text{ mg}^{-1}$) and 0.125 for q_m (as the maximum adsorption amounts of mercury per gram of adsorbent, $\text{mg} \text{ g}^{-1}$), respectively.

3.8. Effect of electrolyte

The effect of electrolyte concentration (adjusted by NaCl) on the adsorption and removal of Hg ions (50 mL, 25 ng mL⁻¹) was studied. It was observed that the removal of Hg ions remained almost constant within the concentration range of 0.02–1.00 mol L⁻¹ of NaCl in the test solution. This implied that the complex formation between 2-mercaptobenzothiazole ligand that is on the M-MIONPs and Hg ions in the test solution was not affected significantly even by high NaCl concentration under the examined conditions.

3.9. Effect of interfering ions

The optimum experimental conditions which have been described were used to study the effect of some ions on the removal

Table 3

Removal of Hg²⁺ (spiked) from different water samples using M-MIONPs.

Water samples	Hg ²⁺ Conc. (spiked)	Removal% (RSD%) (ng mL ⁻¹)
Ahvaz (Khuzestan,	0	-
Iran) drinking water	5	98.7 (2.8)
	10	98.5 (2.5)
	20	99.0 (2.0)
Karoon river	0	-
	5	99.0 (3.1)
	10	99.5 (2.9)
	20	99.2 (2.6)
Wastewater of sugar	0	-
refinery industries	5	97.0 (2.9)
(Ahvaz)	10	97.5 (2.8)
	20	98.2 (3.0)
Wastewater of a paper	0	-
industries (Haft Tapeh)	5	97.4 (2.8)
	10	97.5 (3.2)
	20	98.2 (2.7)

Table 4

Comparison of the removal efficiency of the proposed method with some of the reported methods in literature.

Adsorbent type	Conc. range examined	Contact time (min)	Removal efficiency	Ref.
2-Mercaptobenzimidazole-clay	25–100 mg L ⁻¹	480	>99%	[3]
Polyacrylamide-iron(III) oxide	$50-200 \text{ mg } \text{L}^{-1}$	240	95%	[8]
1,3-Benzendiamidoethanethiol	65–188 μg L ^{–1}	15	99.99	[10]
Sulfuric acid treated rice husk	$200 \mathrm{mg}\mathrm{L}^{-1}$	≥1000	>95%	[16]
Metal-based coagulants	$0.002 \mu g L^{-1}$	60	97%	[18]
Silica coated magnetite	$50 \mu g L^{-1}$	1200	74%	[23]
Polyaniline/humic acid	50 mg L ⁻¹	200	95%	[24]
TiO ₂ nanoparticles	$100 \mathrm{mg}\mathrm{L}^{-1}$	30	65%	[25]
Papain immobilized-alginate	10 mg L ⁻¹	8	99%	[26]
DNA condensation	$0.02 - 100 \text{ mg } \text{L}^{-1}$	15	95%	[27]
Dithiocarbamate-anchored	50 mg L ⁻¹	60	40%	[28]
O-benzenedithiol on cellulose	$2 \mathrm{mg}\mathrm{L}^{-1}$	10	100%	[29]
Charcoal-immobilized papain	20 mg L ⁻¹	2	99%	[30]
Camel bone charcoal	10 mg L ⁻¹	30	71%	[31]
Aminated chelating fiber	1 mg L ⁻¹	1440	99.9%	[32]
Chitosan based ceramic	$500 \mu g L^{-1}$	120	99.9%	[33]
Silver nanoparticle-adsorbent	$1 { m mg}{ m L}^{-1}$	1440	68%	[35]
M-MIONPs	$5-200 \mu g L^{-1}$	4	92-99.0%	This

process of Hg ions by M-MIONPs. To this end removal of Hg ions was performed in the presence of co-existing ions. The maximum acceptable error was chosen $\pm 5\%$. The obtained results in Table 2 show that most of the investigated ions do not interfere with the removal of Hg²⁺ from the water solutions. But As³⁺ and Cu²⁺ strongly interfered during the removal process even at the same concentration as that of Hg²⁺. The interference of these cations is due to their interaction with MIONPs and MBT, respectively [50–57].

3.10. Reusability

The reusing ability of the adsorbent in several successive adsorption processes was tested. The obtained results showed that the modified magnetic iron oxide nanoparticles can be reused for three times without a considerable loss in their adsorption efficiency.

3.11. The effect of solution volume on mercury removal

Maximum applicable sample solution volume was determined by increasing the dilution of the mercury ions solution, while keeping the total weight fixed at $1.25 \,\mu$ g of Hg. Different feed volumes between 25 and 200 mL were tested. The obtained results (Fig. 9) showed that the removal of Hg ions were quantitative up to 100 mL of sample volume (removal >95%). At volumes higher than 100 mL, the analyte was not adsorbed effectively which is probably due to the lower magnetic field strength at higher dilutions (more dilutions causes an increase in height of test solutions in the beaker and so the strength of magnetic field decreases toward far points near the top of the solution).



Fig. 9. Effect of sample volume tolerance limit on the quantitative removal of $1.25 \,\mu\text{g}$ of Hg²⁺. Conditions: pH 9; contact time 4 min; 3 mL of damped M-MIONPs.

3.12. Loading capacity

The loading capacity of adsorbent was determined under optimized conditions (pH = 9, 25 °C, contact time = 4 min, stirring speed = 400 rpm) by batch method. The adsorbent (3 mL of solution containing M-MIONPs which is equivalent to 0.1 g of dried nanoparticles) was added to a 100 mL solution containing 1 mg mL⁻¹ of Hg ion and stirred for 1 h. Removal percent and adsorbed amount of Hg was determined by cold vapor atomic absorption measurement of the sample solution before and after removing process. The loading capacity was determined to be 590 μ g g⁻¹.

3.13. Real samples

The proposed magnetic solid phase extraction (MSPE) method was applied to the removal of Hg ions from different water samples. To examine the reliability and accuracy of the method, several 100 mL solutions of Hg ion (spiked and final concentrations were of 5, 10 and 20 ng mL⁻¹) were prepared using different water samples and removal process was carried out at optimum conditions. The results are given in Table 3. The removal percent of analyte ions were evaluated using CVAAS method and the results showed the capability of the method to real samples with no need to extra matrix modification before removal process.

4. Conclusion

A fast, simple and low cost magnetic solid phase removal of mercury ions from aqueous solution has been successfully developed with MIONPs modified by 2-mercaptobenzothiazole (MBT) as an adsorbent. The adsorbent could be manipulated magnetically and exhibited high adsorption capacity and fast adsorption rates for the removal of Hg ions due to the complexation with coated MBT on MIONPs, high specific surface area and the absence of internal diffusion resistance. The adsorption behavior could be described by Langmuir isotherm. The adsorbent may also be useful for the removal of other heavy metal ions from aqueous solutions. The whole removal (adsorption) processes can be completed within 4 min. In addition the proposed procedure offered higher removal percents from solutions containing very low level of the Hg ion and also shorter adsorption times compared with most of the previously reported methods. Table 4 shows a comparison between the main parameters of the previously reported methods and adsorbents [3,8,10,16,18,23-32,35] and the proposed method. Proposed method shows high potential for fast removal of Hg ion from water and wastewater with high efficiency.

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