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Preconcentration of mercury(II) from waters using glycidyl methacrylate-methyl methacrylate-divinyl benzene terpolymer with diethylenetriamine tetra acetic acid functions prior to inductively coupled plasma mass spectrometric determination

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ABSTRACT

A novel sorbent, glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-divinylbenzene (DVB) terpolymer functionalized with diethylenetriamine tetraacetic acid (DTTA), has been used for the sorption and preconcentration of Hg^{2+} from waters prior to its determination by inductively coupled plasma mass spectrometry. Various parameters such as solution pH, contact time, and sorbent amount were studied. Optimum sorption conditions were determined as pH of 7, contact time of 60 minutes, and sorbent amount/solution volume ratio of $1.5\ \mathrm{mg\ mL^{-1}}$. Batch-type equilibration studies have shown that the novel sorbent can be employed at a pH range resulting in quantitative sorption (>95%) at pH 4.0–8.0. For the quantitative elution of Hg^{2+} from the sorbent, 1.0 M HCl was used. Langmuir isotherm model was found to characterize the uptake of Hg^{2+} by the novel sorbent. In addition, it was observed that the sorbent effectively removed Hg^{2+} ion even in the presence of several competitor ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cd^{2+}) with ≥99% removal. The validity of the method was verified both through the analysis of certified reference materials (BCR 422 and NIST 1547) and by spike recovery experiments. A recovery of ≥93% was obtained for ultrapure, tap and bottled drinking water samples even with a preconcentration factor of 100. Moreover, a good agreement was found for the results obtained with the proposed method and the certified values.

Keywords: Mercury; Removal; Preconcentration; Inductively coupled plasma mass spectrometry

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Dedicated to Prof. Dr. Emür Henden in honor of his retirement.

1. Introduction

Mercury is one of the global harmful pollutants and it has become widespread in the environment mainly as a result of anthropogenic activities [1–4]. It has been reported that mercury levels in the ocean, land, and atmosphere have increased by a factor of 3–5 due to human activities [5]. In addition, due to its bioaccumulation and biomagnification abilities, mercury at a trace level in aquatic system is harmful to environment and humans [6]. One of the routes of incorporation of mercury into the human body is drinking water. Its presence in living organisms is associated with cancer, birth defects, and other undesirable outcomes [7].

Mercury and its compounds are considered to be pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA). According to USEPA, a maximum contamination level goal and maximum contaminant level are both 2 $\mu g\ L^{-1}$ for drinking water [8]. In drinking water, the World Health Organization recommends a limit of 1 $\mu g\ L^{-1}$ [9]. Hence, control of mercury is becoming increasingly important, especially in water sources. Since mercury concentrations in waters are expected to be very low [10], powerful techniques are required and only few of them show enough sensitivity.

Several analytical techniques have been used for mercury determination including, cold vapor atomic absorption spectrometry (CV-AAS) [11], cold vapor atomic fluorescence spectrometry (CV-AFS) [12,13], inductively coupled plasma atomic emission spectrometry (ICP-OES) [14] and inductively coupled plasma mass spectrometry (ICP-MS) [15], anodic or cathodic stripping voltammetry [16], neutron activation analysis chromatography [17], spectrofluorimetry [18], X-ray fluorescence spectrometry [19], ion selective electrodes [20], and gas chromatography [21].

The development of new methods for separation, preconcentration, and determination of mercury at trace levels in water samples is an important environmental concern due to its important role in our life. In addition, direct determination of trace amounts of mercury in several complex matrices (e.g. hair), various water samples, and the other complicated matrices is usually difficult owing to matrix interferences and/or insufficient detection power. Consequently, a preliminary preconcentration and/or separation step is usually required.

Particularly, polymeric sorbents have recently attracted more attention because of their larger sorption capacities, higher efficiencies, and ease of preparation. In a recent work by Şenkal and Bıçak, glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-divinylbenzene (DVB) terpolymer owing diethylenetriamine tetra acetic acid (DTTA) functions was synthesized and used for the efficient removal of Ca(II) and Mg(II) ions from waters [22]. In this work, GMA-MMA-DVB-DTTA terpolymer sorbent is proposed for the preconcentration and determination of Hg^{2+} at trace levels (ng L^{-1}) for the first time prior to inductively coupled plasma mass spectrometric (ICP-MS) determination. In order to clarify the sorption process with the novel sorbent, the effect of pH, contact time, and sorbent amount was elucidated. The sorption process was then investigated in terms of Langmuir and Freundlich isotherms to characterize the uptake of Hg^{2+} ions by the sorbent. In addition, the affinity of the sorbent to several metal ions, such as Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cd^{2+} were investigated. The developed method was also applied to the determination of Hg^{2+} in ultrapure, tap, and bottled drinking water samples.

2. Experimental

2.1. Apparatus

The inductively coupled plasma mass spectrometer (ICP-MS) used for mercury ($m/z = 202$, natural abundance of 29.86%) and other diverse ions determination was an Agilent 7700 (Tokyo, Japan) type instrument equipped with a high solid nebulizer, a Peltier-cooled spray chamber (2˚C), and an octopole collision/reaction cell with hydrogen gas pressurization (purity of 99.999%). The ICP-MS operating conditions were as follows: forward power of 1550 W, plasma gas flow of 15.0 L min^{-1}, carrier gas flow of 1.0 L min^{-1}, collision gas flow of 4.5 mL min^{-1}; sample uptake time of 45 sec , and integration time of 100 msec.

In batch sorption studies, Nüve water bath shaker equipped with a controlled thermostat (Turkey) was used to provide efficient mixing. The pH measurements were performed using Orion 4 Star pH meter with a pH/ATC plastic-body electrode.

2.2. Reagents

All reagents and chemicals were of analytical grade. Ultrapure water (18.2 MΩ) was used throughout the study. Glassware and plastic ware were cleaned by soaking in 10% (v/v) nitric acid and rinsed with ultrapure water prior to use. About 1000 mg L^{-1} Hg^{2+} stock solution was prepared by dissolving elemental mercury (Merck) in concentrated (14.3 M) HNO_3 and diluting with ultrapure water. Stock solutions of diverse metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+},

Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cd^{2+}) were prepared from analytical reagent grade (Merck) compounds. Lower concentration standards were prepared daily from their stock standard solutions. All standards and samples contained 1.0% (v/v) HNO_3 corresponding to a HNO_3 concentration of 0.144 mol L^{-1}.

2.3. Sorption/desorption studies

An accurately weighed amount (30.0 mg) of GMA-MMA-DVB-DTTA terpolymer sorbent particles (125–150 μm) was added into 20.0 mL of solutions in a 50-mL falcon tubes containing the specified concentrations of mercury and the mixtures were shaken in a thermostated water bath at 25.0℃ for a fixed period (60.0 minutes). At the end of the shaking period, the solid and solution phases were separated by filtration using Whatman blue ribbon filter paper, and then the filtrate is analyzed for its mercury content by ICP-MS. The same methodology was followed to identify the pH effect, contact time, sorbent amount on sorption, isotherm models, and to understand the effect of any competitive ion on the mercury ion sorption efficiency.

The percentage of mercury sorption, sorption capacity, distribution, and selectivity coefficients of the sorption process were calculated using Eqs. (1)–(4), respectively, where C_i (mg L^{-1}) is the initial, C_e (mg L^{-1}) the equilibrium concentration in the solution, and V (L and mL) the solution volume and W (g) the amount of the sorbent. Moreover, Q (mg g^{-1}) represents the sorption capacity and K_d the distribution coefficient. In addition to these, the selectivity coefficient (k) for the binding of a specific metal ion (M^{m+}) in the presence of competitor species was obtained, where X^{n+} represents Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cd^{2+} ions from the equilibrium binding data according to Eq. (4):

$$\text{Sorption } \% = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$Q = \frac{(C_i - C_e)V}{W} \tag{2}$$

$$K_d = \left[\frac{C_i - C_e}{C_e}\right]\frac{V}{W} \tag{3}$$

$$k = \frac{K_d(M^{m+})}{K_d(X^{n+})} \tag{4}$$

Subsequently, several eluents (EDTA, HCl and HNO_3) were tried for the desorption of Hg^{2+} from the sorbent. For this purpose, 20.0 mL of 400.0 mg L^{-1} Hg^{2+} was prepared and the sorption process was performed with the proposed sorbent, as mentioned above. The recovery of mercury was performed by shaking 10.0 mL of eluent and sorbent for 30 minutes. At the end of this period, the solution was filtered and analyzed by ICP-MS.

2.4. Preconcentration factor

In order to investigate the efficiency GMA-MMA-DVB-DTTA terpolymer sorbent for the enrichment of Hg^{2+} from different concentrations and different volumes (keeping the absolute amount constant), solutions at various volumes (10.0–1000.0 mL) and concentrations (0.010–1.0 μg L^{-1}) were prepared. Appropriate amount of sorbent (proportionally increased with sample volume) was added into each solution and the same sorption/desorption procedure was applied with an eluent volume of 10.0 mL. The preconcentration study was also performed with water samples including ultrapure, tap, and bottled drinking water samples. Tap and bottled drinking water samples were filtered through Whatman blue ribbon filter paper prior to use.

2.5. Sorption isotherm models

Sorption isotherm is a constant–temperature curve that describes the retention of a substance on a solid at various concentrations and is used to predict the mobility of the substance in the environment. The equilibrium conditions of the sorption process can be described using several sorption isotherms. Among these theoretical and empirical sorption models, the Langmuir and Freundlich isotherm models were applied utilizing the linearized equations indicated below:

$$\frac{C_e}{C_s} = \frac{1}{Q_m L} + \frac{C_e}{Q_m} \tag{5}$$

$$\ln C_s = \ln K_F + n_F \ln C_e \tag{6}$$

Here Q_m (mg g^{-1}) and L (L mg^{-1}) are the Langmuir constants, Q_m is the amount of mercury ion sorption corresponding to monolayer coverage, L the affinity of mercury for the sorbent, C_e (mg L^{-1}) is the amount of mercury in the liquid phase at equilibrium, and C_s (mg g^{-1}) the amount of mercury adsorbed on the surface of the sorbent at equilibrium. Moreover, K_F (mg g^{-1}) and n_F are the Freundlich constants [23,24].

3. Results and discussion

3.1. Effect of pH

pH of the working media is a very important factor for the quantitative sorption of Hg^{2+} ions. Therefore, the influence of the pH of the sample solution was investigated separately by adjusting the pH of the solutions. For this purpose, the pH of 20.0 mL portions of 100.0 μg L^{-1} Hg^{2+} was adjusted to 2.0, 4.0, 6.0, and 8.0 using HCl or NaOH at various concentrations (0.01, 0.1, 1.0 M). Then 30.0 mg sorbent was added into these solutions in 50.0-mL falcon tubes and the mixtures were shaken for 2 hours. After separation of liquid and solid phases by filtration, the solutions were analyzed with ICP-MS for their mercury concentrations. The percentage sorption graph for the sorbent as a function of pH is shown in Fig. 1.

The sorption percentage towards Hg^{2+} ion is almost constant (>95%) between the pH range of 4.0–8.0. The decrease in the sorption of Hg^{2+} ion at pH ~2 is due to the higher concentration of H^{+} ions present in the solution that compete with the Hg^{2+} ions for the sorption sites on the sorbent surface. This finding is in accordance with the p_{zpc} (~3.7) value obtained from the experiments (can be inset of Fig. 1). Moreover, at the pH decrease, the ionic strength of the solution increases and as a consequence the effectiveness of Hg^{2+} sorption onto the sorbent decreases. At higher pH values (>2), the increase in pH increases the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between positively charged Hg^{2+} ion and negatively charged sorbent, and results in an increase in the sorption of Hg^{2+}. To be on the neutral side, a pH of ~7 was used in all subsequent experiments.

3.2. Effect of sorbent amount

The sorbent amount is an important parameter because this determines the capacity of a sorbent for a given initial concentration. The dependence of Hg^{2+} sorption on the amount of sorbent was studied for varying amounts of the sorbent from 10.0 to 100.0 mg. For this purpose, separate solutions of 20.0 mL of 100.0 μg L^{-1} Hg^{2+} was shaken at 25.0℃ with the specified amounts of the sorbent for sorption. After the usual filtration step, mercury concentrations in the filtrate were determined with ICP-MS. Fig. 2 indicates the Hg^{2+} sorption behavior with discrete amount of sorbent. It was observed that even with a very small amount of sorbent (30.0 mg) almost ≥99% sorption is observed for the given 20.0 mL of Hg^{2+} concentration. Therefore, a sorbent amount/solution volume ratio of 1.5 mg mL^{-1} is used in the subsequent studies for the quantitative sorption of Hg^{2+}.

3.3. Effect of contact time

Contact time is one of the important parameters for successful use of the sorbents for practical applications and rapid sorption is among the desirable parameters. To determine the optimum contact time for the sorption of Hg^{2+} using GMA-MMA-DVB-DTTA terpolymer sorbent, 30.0 mg of sorbent was added on to 20.0 mL of a 100.0 μg L^{-1} Hg^{2+} solution and the mixtures were shaken for 5.0, 10.0, 30.0, 60.0, and 120.0 minutes. At the end of the shaking period the solid and solution phases were separated by filtration. The concentration of mercury in the supernatant solution was determined by ICP-MS. The sorption yield of Hg^{2+} increased considerably with increasing contact time up to 60.0 minutes and after that,

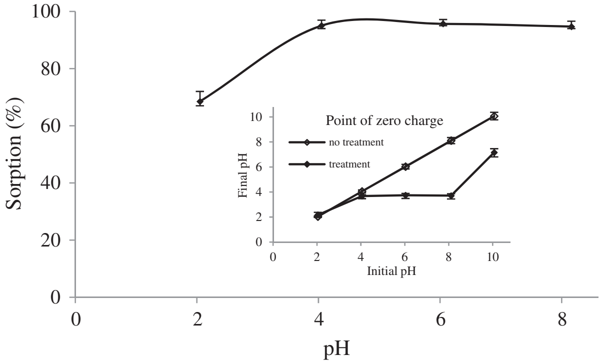

Fig. 1. Effect of pH on the sorption of Hg^{2+} towards GMA-MMA-DVB-DTTA terpolymer sorbent (100 μg L^{-1} Hg^{2+} solution, 20.0 mL sample volume, 2 hours contact time, 30.0 mg sorbent at 25℃ sorption temperature).

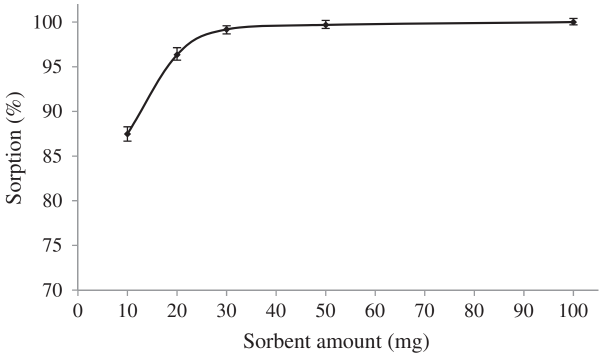

Fig. 2. Effect of GMA-MMA-DVB-DTTA terpolymer sorbent amount on sorption (100 μg L^{-1} Hg^{2+} solution, 20.0 mL sample volume, pH 6.0, 60 min contact time, at 25℃ sorption temperature).

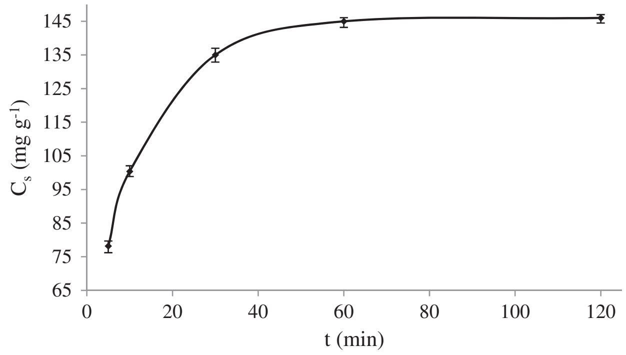

Fig. 3. Effect of contact time on the sorption of Hg^{2+} towards GMA-MMA-DVBDTTA terpolymer sorbent (100 µg L^{-1} Hg^{2+} solution, 20.0 mL sample volume, pH 6.0, 30.0 mg sorbent at 25°C sorption temperature).

Table 1
Desorption of Hg(II) by different eluents from the GMA-MMA-DVB-DTTA sorbent, (n = 3)

Eluent	Concentration (M)	Recovery (%)
HCl	0.01	35 ± 1.3
	0.1	55 ± 2.0
	1.0	97 ± 1.9
	4.0	97 ± 2.1
HNO_3	0.01	32 ± 1.5
	0.1	54 ± 1.8
	1.0	92 ± 2.2
	4.0	96 ± 2.5
EDTA	0.01	70 ± 2.1

it was nearly constant. A quantitative sorption (~93%) was obtained even in 30.0 minutes, but, to be on the safe side, a sorption time of 60.0 minutes was used throughout the study (Fig. 3).

3.4. Desorption from the sorbent

The efficiency/feasibility of quantitative desorption of Hg^{2+} from GMA-MMA-DVB-DTTA terpolymer sorbent was studied using several eluents (Table 1). At first, a strong complexing agent (0.01 M EDTA) was tried to extract Hg^{2+} ions from the sorbent. Quantitative results (~70%) were not obtained. As a second route, various concentrations of HCl (0.01, 0.1, 1.0, and 4.0 M) and HNO_3 (0.01, 0.1, 1.0, and 4.0 M) were tried. It was found that 1.0 M HCl was sufficient for quantitative elution of Hg^{2+} (>97%) from the sorbent. This evaluation is possibly due to the fact that by acidifying solution with acids, the exchange sites of the sorbent are protonated, and the mercury compounds are detached from these sites.

Table 2
Percent sorption, K_d and k values of Hg^{2+} with respect to diverse metal ions

Ion	Sorption (%)	K_d	k
Hg^{2+}	99	65999	–
Cu^{2+}	99	65999	1.0
Zn^{2+}	99	65999	1.0
Pb^{2+}	98	32666	2.0
Fe^{3+}	89	5500	12.0
Al^{3+}	63	1142	57.8
Ba^{2+}	55	796	82.9
Co^{2+}	50	668	98.8
Mn^{2+}	45	548	120.4
Mg^{2+}	39	419	157.5
Ni^{2+}	37	383	172.3
Cd^{2+}	30	290	227.6
Ca^{2+}	26	231	285.7

3.5. Selectivity study

Sorption selectivity for Hg^{2+} against the diverse ions, Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cd^{2+} were studied. For this purpose 20.0 mL of 100.0 µg L^{-1} Hg^{2+} and these competitor ion solutions (20.0 mL of 100.0 µg L^{-1}) were added onto 30.0 mg sorbent, and they were shaken for 60.0 minutes at 25°C. After the sorption equilibrium, the concentrations of mercury and competitor ions in the remaining solutions were measured by ICP-MS. Finally, the percent of sorption, distribution coefficients (K_d), and selectivity coefficients (k) of $Hg^{2+}$and these diverse ions were calculated using Eqs. (1), (3) and (4). As can see from Table 2, the sorbent removed Hg^{2+} ions in the presence of these competitor ions with ≥99% removal. The order of decreasing selectivity toward the sorbent at 100.0 µg L^{-1} is $Hg^{2+} \approx Cu^{2+} \approx Zn^{2+} \approx Pb^{2+} > Fe^{3+} > Al^{3+} > Ba^{2+} > Co^{2+} > Mn^{2+} > Mg^{2+} > Ni^{2+} > Cd^{2+} > Ca^{2+}$. Moreover, the distribution coefficient of Hg is 12–286 folds larger than Fe^{3+}, Al^{3+}, Ba^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}, and Ca^{2+} ions. In addition, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} were almost completely removed from the solutions. This promising sorption behavior of the novel sorbent toward the abovementioned ions has also boosted further studies in the authors' laboratory for the separation/determination of these ions.

3.6. Isotherms and sorption capacity

The sorption capacity of sorbent for Hg^{2+} was determined by a batch method. The sorbent (30.0 mg) was added to 20.0 mL of Hg^{2+} solutions, varying from 50.0 to 500.0 mg L^{-1}. The concentration of Hg^{2+} in the

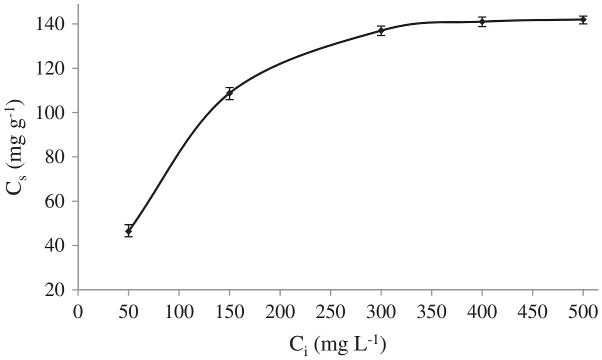

Fig. 4. Variation in the amount of Hg^{2+} sorbed with the initial concentration of Hg^{2+} solution (20.0 mL sample volume, pH 6.0, 60 min contact time, at 25˚C sorption temperature).

remaining solutions was measured by ICP-MS and the experimental capacity of the sorption process was calculated using Eq. (2). As can be seen from Fig. 4, the amount of Hg^{2+} sorbed per unit mass of sorbent (the sorption capacity) increased with the initial concentration of Hg^{2+} and reached a plateau value (141.5 mg g^{-1}), where the sorption capacity could be determined. In addition, a comparison of the Langmuir and Freundlich sorption models was made for the sorption of Hg^{2+} onto sorbent using Eqs. (5) and (6). Linearized forms of the models were used for the calculations of the coefficients. The correlation coefficient for the Freundlich isotherm was only 0.9477, and the Langmuir isotherm appeared to be linear within the range of 0–500 mg L^{-1} Hg^{2+} with a high correlation coefficient of 0.9997. This evaluation also certified that the Langmuir isotherm excellently describes the monolayer adsorption process. A high total sorption capacity value was obtained from the Langmuir equation (14 mg g^{-1}), which is in accordance with the experimental value obtained from Eq. (2).

3.7. Analytical performance

Under the optimized experimental conditions, the limit of detection ($LOD = (3\sigma)/k$) and limit of

Table 3
Comparison of the proposed method with some studies in literature for Hg^{2+} preconcentration

Sorbent	Elution agent	Detection method	LOD (ng L^{-1})	Enrichment factor	Matrix	Refs.
YPA4 chelating resin	Thiourea	GF-AAS	200	100	Lake and tap water	[25]
Mercapto-grafted graphene oxide–magnetic chitosan	Mixture of HCl and thiourea	CV-AAS	60	80	Tap water, sea water	[26]
Dithizone-functionalized-Fe_3O_4 nanoparticles	Mixture of HCl and thiourea	CV-AAS	50	250	Water, salt, tea, vegetable, cosmetic	[27]
Hg(II)-imprinted thiol-functionalized mesoporous sorbent	HNO_3	ICP-OES	390	150	Sea and river water samples	[28]
L-cysteine functionalized cellulose fiber	HNO_3	CV-AFS	1	9.8	Sea, river, lake water, seaweed, cosmetic	[29]
4-bpdb functionalized octadecyl silica	HNO_3	CV-AAS	1.87	70	Sea and tap waters, fish, milk, sausage	[30]
1-acylthiosemicarbazide-modified activated carbon	$CS(NH_2)_2$ and HCl	ICP-OES	120	100	River and tap water	[31]
Staphylococcus aureus loaded Dowex Optipore V-493 micro-column	HCl	CV-AAS	2500	25	Sea and tap waters, fish samples	[32]
Poly(acrylamide) grafted onto cross-linked poly(4-vinyl pyridine)	HNO_3	CV-AFS	2	20	Sea and estuarine waters	[13]
Aminopropyl-controlled pore glass functionalized with [1,5-bis (2 pyridyl)-3-sulphophenyl methylene thiocarbonohydrazyde]	Thiourea	CV-AAS	10	28	Sea food, biological samples	[33]
Glycidyl methacrylate-methyl methacrylate–divinylbenzene terpolymer with diethylenetriamine tetraacetic acid functions	HCl	ICP-MS	0.74	100	Tap and bottled drinking waters	This work

Table 4
Recovery results for ultra pure, tap, and bottled drinking water samples

Sample	Hg^{2+} spike (μg L^{-1})	Initial volume	Final volume	Enrichment factor	Recovery (%)
Ultra pure water	0.01	1000	10	100	96.5 ± 1.3
	0.1	100	10	10	93.3 ± 2.6
	0.2	50	10	5	98.0 ± 3.2
	1.0	10	10	1	97.4 ± 2.1
Tap water	0.01	1000	10	100	92.7 ± 1.9
	0.1	100	10	10	97.4 ± 0.8
	0.2	50	10	5	98.0 ± 2.2
	1.0	10	10	1	98.5 ± 1.6
Bottled drinking water	0.01	1000	10	100	92.9 ± 2.6
	0.1	100	10	10	96.2 ± 1.5
	0.2	50	10	5	99.5 ± 3.1
	1.0	10	10	1	98.5 ± 2.8

Table 5
Analysis of standard reference materials using the proposed methodology

Sample	Certified value (μg g^{-1})	Found (μg g^{-1})	Recovery (%)
BCR 422	0.559 ± 0.016	0.538 ± 0.018	96.2
NIST 1547	0.031 ± 0.007	0.030 ± 0.006	96.8

quantification ($LOQ = (10\sigma)/k$) where σ is the relative standard deviation of the measures of a blank solution and k is the slope of the analytical curve used for quantification were found to be as 0.74 and 2.45 ng L^{-1} with a preconcentration factor of 100, respectively. The relative standard deviations (RSDs) for ten replicate determinations of 10 μg L^{-1} Hg^{2+} was 1.6%. The working range of the method is 1.0–100.0 μg L^{-1} ($y = 16127x - 1166$) with a correlation coefficient (R^2) of 0.9987.

In addition, a comparison of the represented method with other reported methods for Hg^{2+} is shown in Table 3. The comparison of the proposed method with the previously reported procedures indicates that the present procedure has similar, comparable, and sometimes better LODs than many other analytical determinations of Hg^{2+}. High sorption efficiency and preconcentration factor, lower detection limit, and good RSD values are some of the advantages of the proposed method.

3.8. Applications

The proposed methodology was checked via spike recovery experiments with ultra pure, tap, and bottled drinking water samples. Aliquots of sample (10.0, 50.0, 100.0, and 1,000.0 mL) were spiked with an appropriate amount of Hg^{2+} (0.01, 0.1, 0.2 and 1.0 μg L^{-1}) and were added into containers with the sorbent. After the usual sorption step, the elution was assessed with 10.0 mL of 1.0 M HCl. Blank samples were also prepared and analyzed by ICP-MS in the same manner and all were below the detection limit. As can be seen from Table 4, the proposed methodology works efficiently for ultra pure, tap, and bottled drinking water samples for preconcentration factors of 5, 10, and 100 (recovery % ≥ 93). These results demonstrated the applicability of the method to water samples.

In addition to the spike recovery tests mentioned above, the performance of the method was realized through the analysis of standard reference materials (BCR 422 and NIST 1547). For this purpose, standard reference materials were decomposed using microwave oven acid digestion. After a simple pH adjustment, 10.0 mL aliquots of the digested samples were taken, processed by the proposed method, loaded onto sorbent, and eluted with 10.0 mL of 1.0 M HCl. Finally, Hg^{2+} levels in the eluates were analyzed by ICP-MS. As can be seen from Table 5, the results obtained with the proposed methodology are in accordance with the certified values.

4. Conclusions

It has been shown that, a novel sorbent, glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-divinylbenzene (DVB) with diethylenetriamine tetraacetic acid (DTTA) functions can be applied for the quantitative (>95%) sorption of Hg^{2+} from the waters within pH ranges 4.0–8.0. ICP-MS is used for the determination of mercury due to its high sensitivity, high selectivity, and high sample throughput. Optimized sorption parameters for the batch system were as follows: solution pH of 7, sorbent amount/solution volume ratio of 1.5 mg mL^{-1}, and contact time of 60 minutes. The quantitative elution of Hg^{2+} from the sorbent was realized with 1.0 M HCl. Hg^{2+} adsorption onto sorbent followed the Langmuir isotherm model. The novel sorbent efficiently removes Hg^{2+} ion also in the presence of the several competitor ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Mn^{2+}, and Cd^{2+}) with a sorption percent of ≥99%. Sorption/desorption studies were performed with preconcentration factors of 5, 10, and 100 for ultrapure, tap, and bottled drinking water samples and it is examined that the proposed method has been successfully applied to the real samples for the preconcentration of Hg^{2+} acceptable accuracy and precision. The performance of the method was also realized through the analysis of a standard reference materials and it was found that the results obtained with the proposed method are in accordance with the certified values. The use of the novel sorbent via batch-type equilibration has demonstrated its potential for use in water treatment which would result in a solution to reduce an environmental problem.

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