

Article



# **Preconcentration and Solid Phase Extraction of Trace Metal Ions by Chemically Modified Graphene Oxide Nanoconstructs**

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Abstract: The toxicity of arsenic and mercury is highly dependent on their unique chemical forms, mobility, bioavailability, and biological roles. This places a strong demand on specific metal species analysis rather than total quantification. Graphene oxide (GO) is an excellent adsorbent for the extraction of metal ions; however, the functional moieties on the GO surface are not metal ion-specific. In this work, we chemically introduced thioglycolic acid to improve metal ion selectivity after the dual oxidation of graphite to generate graphene oxide (GO) nanosheets. The prepared adsorbent was characterized by various spectroscopic and microscopic techniques. A solid phase extraction method was developed after careful analysis and optimization of the prepared sorbent. The method shows a fairly good quantification limit of 0.20  $\mu$ g L<sup>-1</sup> for As(III) and Hg(II) ions. From diverse water samples, the proposed sorbent preferentially removes As(III) and Hg(II) ions (tap water and groundwater). The remarkable wettability and analyte accessibility that the surface-bonded thiol functionality of GO sheets offers is an exciting feature. In a lesser amount of time, the GO-SH nanosorbent exhibits good extraction of traces of As(III) and Hg(II). The developed method exhibits good reliability and precision in terms of accuracy and relative standard deviation (RSD 3.8%; N = 5) and has low detection limits (0.04  $\mu$ g L<sup>-1</sup>). Real samples that had been spiked to a predefined level were analyzed in order to validate the established procedure.

Keywords: analysis; arsenic; mercury; determination; extraction; water

# 1. Introduction

Arsenic and mercury are two well-known environmental pollutants that have geological and anthropogenic causes and endanger the lives of hundreds of millions of people [1-5]. More poisonous and highly mobile than other arsenic forms, inorganic arsenic (As(III)) is thought to cause health problems in approximately 150 million people worldwide through the intake of food and water. Arsenicosis is the term used to describe a wide range of consequences to human health caused by chronic exposure to low levels of arsenic in food and water [6,7]. Arsenic exposure can result in death through the development of skin lesions, neurological abnormalities, atherosclerosis, and cancers of the skin, liver, kidney, and bladder [8]. A global catastrophe of epic proportions is caused by naturally occurring arsenic in groundwater used for drinking and cooking. Although the amount of arsenic varies, most plants absorb it and store it in sections that are edible. This resulted in a significant pandemic associated with these metals in Asia [3,9–11]. According to estimates, more than 60 million people consume groundwater that has more arsenic than the WHO's limit of 10 ppb (parts per billion) [12]. In Wisconsin, even at levels below 10 ppb, skin cancer rates have increased in correlation with arsenic exposure. Similarly, as a substantial threat to human health, mercury pollution is a significant environmental concern [13–15].



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Mercury species can harm the central neurological and endocrine systems and result in memory loss, Alzheimer's-like dementia, hearing loss, and the loss of muscle coordination [16,17]. The brain, kidneys, and growing fetus all suffer lasting damage as a result of prolonged exposure to high quantities of this metal [18]. The US Environmental Protection Agency has set a 2 ppb limit on the amount of mercury that can be present in drinking water [18,19]. As a result, the World Health Organization (WHO) recognizes environmental monitoring and assessment of such dangerous metals as one of its key goals. Natural water typically has relatively low levels of arsenic and mercury, whereas contaminated natural water is said to have levels as high as several ppb or even ppm along with other organic and inorganic pollutants [20–23]. Since As(III) and Hg(II) are found in real-world samples at trace and ultra-trace levels, and they are proven to be toxic to the human body after prolonged ingestion and cause serious harm. Because of this, it is of great significance to accurately determine their levels in natural waters and/or drinking water sources in order to monitor the environment and evaluate how exposure to the environment affects human health. Despite the accessibility of sophisticated analytical techniques with great sensitivity, the measurement of As(III) and Hg(II) in real samples is problematic due to the low amounts of these substances and the severe influence of the substrates coupled with them. Hence, preconcentrating and separating the matrix components from the analyte ions is a radical method of eliminating the matrix components [24–26]. The employment of a preconcentration step in the determination of such toxic analytes greatly enhances the reliability of analytical data of the final results during analyses.

In the domain of separation science, solid-phase extraction (SPE) has always been significant for isolating the desired analyte from a wide range of sample matrices as well as for preconcentrating the analytes before their detection. Numerous nanomaterials such as graphene oxide (GO) [27], molybdenum disulfide nanosheets ( $MoS_2$ ) [13], functionalized  $ZrO_2$  nanoparticles [28], magnetic iron oxide nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) [29], metal–organic frameworks (MOF) [30], carbon nanotubes (CNTs) [31], activated carbon [32], and cellulose nanoparticles [33] have been actively studied in SPE and have shown significant potential because of their inherent qualities, such as large surface areas, ease of surface functionalization, and high mechanical strength. Among these nanomaterials, the two-dimensional geometrical structure of GO and the abundance of hydroxyl, epoxy, and carboxyl groups on its surface have made it a good sorbent for SPE [27,34–38]. These functional groups with oxygen can effectively bind with heavy metal ions by exchanging a single pair of electrons with those located at their basal plane and edges [39–42]. However, GO's adsorption effectiveness for Hg(II) is extremely low or nonexistent for As (III) [43,44]. The inclusion of particular ligand molecules into GO is necessary to enhance the adsorption performance toward these metal ions [45,46]. These metal-specific ligands increase the metal ion adsorption capability by providing selectivity and forming stable metal ligand complexes.

Since nascent GO has less tendency to complex with Hg(II) and As(III) ions, our aim in this study is to prepare a hydrophilic sorbent that shows high selectivity towards As(III) and Hg(II) ions. To achieve this, herein we incorporate thiol moieties onto the GO sheets' surface and develop a solid phase extraction (SPE) method for the preconcentration of As(III) and Hg(II) from various aqueous matrices. Thioglycolic acid is introduced to the GO surface, and thereby increases the surface's selectivity for As(III) and Hg(II) ions. The oxygen-containing surface functional groups of GO provide hydrophilicity, resulting in the high accessibility of trace metal ions. Before connecting to ICP-OES, the experimental settings are tuned to achieve a high enrichment factor with high sensitivity and better detection limit. The developed method after optimization has been employed for real sample analysis to explore its utility.

## 2. Experimental Section

# 2.1. Reagents and Solution

The chemicals and reagents used were of AR grade. Mercury (II) chloride and arsenic (III) chloride were obtained from Merck (Shanghai, China). Working solution was prepared

by dissolving required amount of metal salts into triply distilled water (TDW). The solid graphite powder was obtained from Chengdu Organic Chemicals (China). All standard and round-bottom flasks were cleaned by soaking and rinsing in 2% HNO<sub>3</sub> before use. Standard solution obtained from Merck (China) was employed for the calibration of ICP-OES.

#### 2.2. Instruments

The surface functional groups were identified using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR; Spectrometer) (Bruker, CA, USA) in the spectral region from 4000 to 400 cm<sup>-1</sup>. After coating the manufactured sorbent with a fine layer of gold to prevent charge interactions during beam (electron) irradiation, the surface morphologies of the sorbent were examined under a scanning electron microscope (SEM, JSM-800F, JEOL, Japan). A TECNAI F30 S-Twin model was used to view the GO–SH picture obtained using transmission electron microscopy (TEM). Prior to TEM characterization, the GO–SH sample was probe-sonicated for dispersion in ethanol. On the Flash EA 1112 Organic Elemental Analyzer, an elemental analysis was performed (Thermo Fischer Scientific, Waltham, MA, USA). To analyze the samples, a Perkin Elmer Avio 200 inductively coupled plasma optical emission spectrometer (ICP-OES, operated in axial mode of viewing plasma) was employed. The following were the instrumental operating parameters: pressure: 3.2 bar, read time: 2 mL min<sup>-1</sup>, wavelengths: 194.168 nm (Hg) and 188.97 nm (As); injector: alumina injector 2.0; plasma gas: Ar (8 L min<sup>-1</sup>); auxiliary gas: (0.2 L min<sup>-1</sup>); nebulizer gas: (0.7 L min<sup>-1</sup>) (As).

## 2.3. Material Synthesis

The Hummers method's step I oxidation of graphite powder was followed by second step oxidation to enhance the number of oxygen groups on the GO surface [39,47]. To avoid agglomeration, 2.5 g of graphite powder and 1.0 g of NaNO<sub>3</sub> were added to 150.0 mL of 95%  $H_2SO_4$  while being vigorously stirred. A total of 15.0 g of oxidant (KMnO<sub>4</sub>) was gradually added while being stirred and reduced the reaction temperature down to 10  $^\circ$ C. For next 2 h, the reactants were stirred at 37 °C. The paste was gradually filled with 350.0 mL of TDW while being continuously stirred and heated to 95 °C. After agitating the suspension for 2 h at 95 °C, the mixture was dried at 80 °C in an air oven. The solid product was then washed with deionized water until neutral pH. The resultant grey powdered graphite oxide was centrifuged at 5000 rcf (g) to eliminate unexfoliated graphite oxide and exfoliated to GO sheets by dispersion in deionized water using bath sonication (250 W, 20 kHz) for 3 h. In the next step, 1.5 g of GO sheets were reacted with 15 mL of thionyl chloride for 6 h; thionyl chloride was used to activate the produced GO sheets at reaction pH of 4 and temperature of 80 °C. The activation of GO by thionyl chloride incorporated chloro groups for further functionalization. For further immobilization of the thioglycolic acid, the resulting GO-Cl suspension prepared in 25 mL deionized water was mixed with 25 mL of thioglycolic acid along with 5 mL of triethanolamine to capture the released HCl. The whole reaction mixture was heated at 60 °C for 8 h. The resultant product was separated from the solution using centrifugation and washed with deionized water to remove unbound ligand molecules. A schematic representation of synthesis is shown in Scheme 1.

#### 2.4. Optimized SPE Procedure

A total of 30.0 mg of GO–SH was packed in a glass column of length 10 cm and diameter 1 cm with a bed thickness of 0.4 cm. A total of 50.0 mL of sample solution of metal ions, set at pH value 6.0, was percolated across the adsorbent bed at flow rate of 6 mL min<sup>-1</sup>. The uptaken metal ion was desorbed with 5 mL of 0.2 M thiourea in 10% HCl (strippant) and subsequently determined by using ICP-OES.



Scheme 1. A schematic diagram illustrating the synthesis steps of GO–SH adsorbent.

## 3. Results and Discussion

# 3.1. Choice of Material

The dual oxidation of the graphite powder was used to synthesize GO–SH, which was then surface-functionalized using thioglycolic acid. Dual oxidation increases hydrophilicity by introducing several functional groups containing oxygen. The added thiol groups enable the specific binding of As(III) and Hg(II). Additionally, the presence of intercalated water molecules enhances the interlayer distance within GO–SH nanosheets, which results in high hydrophilicity and provides the accessibility of chelating sites to analyte ions.

## 3.2. Characterization

The surface morphology of GO–SH was characterized by ATR-FTIR, elemental analysis, and SEM and TEM analysis. In the ATR-FTIR spectra of GO, the peaks at 3200  $cm^{-1}$ correspond to O-H (-COOH and -COH) stretching vibrations. In GO-SH, the presence of characteristic peaks associated with S-H and C-SH stretching vibrations appeared at 620 and 2905 cm<sup>-1</sup>, respectively, confirming the successful immobilization of thioglycolic acid (Figure 1A) [48]. The broad peak appeared at 3200 cm<sup>-1</sup>, corresponding to O–H (–COOH and -COH) stretching vibrations of GO, and the band at 1647 cm<sup>-1</sup> was assigned to the stretching of C=O bonds of the –COOH functional group [48]. Further, in the elemental analysis (C, H, N, O and S) of GO–SH, the percent ratio of sulfur obtained (2.96 %) was fairly good, indicating the successful incorporation of thioglycolic acid equivalent to 1.85 mmol  $g^{-1}$ , onto the GO surface (Table 1). The SEM images of GO and GO–SH (Figure 1B,D) depict a wrinkled GO surface with a structure resembling crushed silk waves. Similarly, in the TEM image a single to a few layers of GO (Figure 1C) and GO–SH Sheets (Figure 1E) were clearly observed, indicating the least aggregation of sheets and a high degree of functionalization. Furthermore, the energy-dispersive X-ray analysis (EDS) spectra of GO and GO–SH (Figure 1F,G) showed the constituent elemental peaks of GO (C and O) and GO–SH (C, O and S), indicating the successful functionalization of ligand molecules. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses (Figure 2A,B) were carried out to analyze the surface area, pore size, and pore volume distribution of GO and GO-SH. The results are presented in Table 2. X-ray diffraction (XRD) studies for GO were carried out and the characteristic diffraction pattern (001) observed at  $2\theta$  (10) indicates the successful oxidation of graphite (Figure 2C).

### 3.3. Optimization of SPE Procedure

The optimization of important experimental variables such as (a) sample pH value (Figure 3A); (b) column flow rate (Figure 3C); (c) eluent type and concentration (Figure 4); and (d) interference ion effect parameters were all tuned. The experimental setups studied

were discovered to produce the best outcomes: the optimum sorption of As(III) and Hg(II) was observed at a sample pH of 6.0; a column flow rate of 6 mL min<sup>-1</sup> was optimized; 5 mL of 0.2 M thiourea+10% HCl was used as an eluent. Varying concentrations of As(III) and Hg(II) were used to optimize the varying experimental processes.





**Figure 1.** (**A**) The FTIR spectra of GO and GO–SH sorbent; (**B**,**D**) SEM image of GO and GO–SH with wrinkled structure; (**C**,**E**) TEM image of GO and GO–SH depicts layered nanosheets; (**F**,**G**) EDS spectra of GO and GO–SH.

Table 1. Elemental analysis of GO-SH.

Elements	GO Nanosheet (%)	GO–SH Nanosheet (%)
Carbon	62.446	65.687
Hydrogen	4.646	5.216
Öxygen	32.908	26.135
Sulfur	-	2.962



Figure 2. (A,B) The BJH plot of GO and GO-SH nanosheets; (C) XRD spectra of GO nanosheets.

	Parameters	GO Nanosheet	GO-SH Nanosheet	
_	Surface area (m <sup>2</sup> /g)	772.494	1351.371	
	Pore volume $(cc/g)$	1.288	1.214	
_	Pore size (nm)	1.458 (microporous)	0.866 (microporous)	
Sorphion Capacity, mMg Sorphion Capacity, mMg	(B) 15 pHz 10 5 6 7 (B) 15 pHz 10 5 5 0 2 4 pH 2 4 pH	(C) 100 % 95 00 90 85 80 2	As(III) Hg(II) 4 6 8 10 Flow rate, mL/min	

Table 2. The BET analysis data of GO and GO-SH.

**Figure 3.** (**A**) pH of GO–SH sorbent; (**B**) pHz of GO–SH sorbent; (**C**) Effect of sample flow rate on the sorption of As(III) and Hg(II) ions.



Figure 4. Optimization of stripping agent.

# 3.4. Effect of Sample pH

The distribution of the charge density of the metal ion species and the GO–SH extractant in the aqueous medium is influenced by the pH of the solution. As a result, the pH of the sample is crucial for the adsorption of the metal ions. In this work, we examined the adsorption of As(III) and Hg(II) over the pH range of 1–7. The Hg(II) precipitation prevented the pH from becoming too basic (8–10). To investigate the effect of pH, a succession of aqueous solutions (50 mL) comprising 50 mg  $L^{-1}$  of analyte ions were pumped across the column using a peristaltic pump. The amount of As(III) and Hg(II) that had been adsorbed and the metal ion content in the filtrates were both assessed using ICP-OES. Figure 3A displays the information that was gathered. It can be seen that As(III) adsorbs very consistently over the entire pH range of the material under investigation. The chemisorption of Hg(II) ions is steady between pH 5–7 and significantly increases between pH 1 and 5 for the sample. The maximum Hg(II) adsorption occurred at pH 7, which was chosen as the ideal pH for the subsequent experiments. As the pH levels of the sample changed, there was no discernible difference in the As(III) adsorption onto GO–SH adsorbent. It was demonstrated that the adsorption performance of Hg(II) reduces at low pH values of 1–4; this may be caused by electrostatic repulsion between the positively charged GO–SH surface and the positively charged Hg (II). However, as the pH of the sample rises, the surface of the sample becomes negatively charged, encouraging the innersphere complex formation of Hg(II) with the GO–SH surface. As a consequence of the

soft-acid-soft base association, adsorption effectiveness rises. Moreover, the zeta potential of GO–SH as a function of the solution pH (Figure 3B) showed that the isotropic electric point (pH<sub>z</sub>) of GO–SH was observed at pH 3.8, indicating that the surface was negatively charged beyond pH 3.8, which favored the adsorption of Hg(II) by both the electrostatic attraction and the formation of inner-sphere complexes. Below the pH<sub>z</sub>, the GO–SH surface became positively charged, and therefore showed a decrease in the complexation of Hg(II) ions due to electrostatic repulsion. On the other hand, the adsorption trend for As(III) was observed differently compared to Hg(II) for the entire studied pH range of 1–7, with more or less constant adsorption capacity. It was observed that the variation in the surface charge of GO–SH upon altering the solution pH does not have much effect on As(III) adsorption and the adsorption of As(III) remains constant. This might be due to the fact that As(III) forms direct inner- and outer-sphere complexes with the functional groups of adsorbent rather than the electrostatic interaction between the neutral H<sub>3</sub>AsO and GO–SH.

In summary, the binding of As(III) and Hg(II) with the sulfur and carboxylic group atoms on GO–SH adsorption sites is the underlying mechanism of the adsorption phenomena.

## 3.5. Effect of Sample Flow Rate

The sample drift in the column tests alters the metal ions' adsorption onto the packed adsorbent. To reach equilibrium between both the functional groups and the analyte ions, the sample flow must be perfect. To maximize the adsorption flow rate, a sequence of samples (volume 50 mL; metal ion 50 mg L; pH 6.0) were fed across the column at a flow range between 2 and 10 mL min<sup>-1</sup>. The data are presented in Figure 3C. The quantitative recovery of As(III) and Hg(II) was unchanged through a flow of 6 mL min<sup>-1</sup>. The GO–SH adsorbent's great hydrophilicity, which is brought on by the abundance of hydroxyl groups on its surface, is evidenced by the high sample flow. Above 6 mL min<sup>-1</sup>, the extraction of both As(III) and Hg(II) ions steadily dropped by 8–15%. The lack of appropriate interaction between the metal ions and the adsorption sites of the adsorbent may be the cause of this drop in adsorption at higher sample flows. Therefore, for the column adsorption experiment, a sample flow rate of 6 mL min<sup>-1</sup> was chosen and used.

#### 3.6. Eluent Type and Concentration

Reusing the solid phase extraction column requires the appropriate stripping of the sorbed metal ions. Only the proper striping agent can accomplish this. Different mineral acids (CH<sub>3</sub>COOH, HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) were evaluated separately and in conjunction with thiourea in a variety of concentrations in order to discover the appropriate eluent type (3 and 5 mL). The results are shown in Figure 4. Hg(II) is recovered fully (recovery > 97%) when used with eluents of the right volume and concentration. Adsorbed Hg(II) showed incomplete elution at reduced low eluent strength, with significantly low recovery of less than 90%. Therefore, 5.0 mL of 0.2 M thiourea + 10% HCl was utilized as the eluting mixture to extract the uptaken As(III) and Hg(II) using the GO–SH column. The results for acetic acid used as an eluent were not particularly significant; acetic acid at concentrations of 0.5 and 1.0 M gives extremely low recoveries (less than 35%) of Hg(II) and As(III) and therefore is not a suitable stripping agent.

#### 3.7. Interference and Selectivity Studies

The quantitative sorption and recovery of As(III) and Hg(II) allow GO–SH utility in analytical determination, which in turn prescribes its prospective applicability. In genuine environmental samples, trace levels of As(III) and Hg(II) invariably coexist with other matrix ions, which may significantly obstruct the recovery or identification of analyte ions. Herein, a suitable amount of sample solution (volume 50 mL) comprising As(III) and Hg(II) and Hg(II) and variable amounts of inorganic and organic ions was passed under ideal circumstances in order to evaluate the liberality of GO–SH in the process of analyte recovery in the presence of various concomitant ions. The obtained results are presented in Table 3. According to the findings, no notable intrusion in the extraction of As(III)

and Hg(II) was found for any of the added ions up to considerable concentrations. In the presence of these potentially interfering ions, the analyte ion recovery rate was substantially above 97%. As a result, GO–SH demonstrated the selective determination of As(III) and Hg(II) in the presence of possibly interfering ions under optimal experimental conditions.

**Table 3.** Interference studies on the recovery of As(III) and Hg(II) (sample pH 6; flow rate 6 mL min<sup>-1</sup>; N = 3).

Foreign Ions	Amount Added	% Recovery		
	Added as	(μg L <sup>-1</sup> )	As(III) RSD)	Hg(II) (RSD)
Cl-	NaCl	$7.5  imes 10^3$	99.5 (3.82)	97.0 (4.20)
$\mathrm{Br}^-$	NaBr	$8.0 imes10^3$	99.0 (2.89)	98.6 (3.85)
$PO_{4}^{2-}$	Na <sub>2</sub> HPO <sub>4</sub>	$5.4 imes10^3$	95.6 (4.10)	98.5 (3.65)
$NO_3^-$	NaNO <sub>3</sub>	$7.5 imes10^3$	100.0 (2.87)	99.8 (3.30)
CO3 <sup>2-</sup>	Na <sub>2</sub> CO <sub>3</sub>	$5.8 imes10^2$	100.0 (3.18)	99.4 (2.97)
$SO_4^{2-}$	$Na_2SO_4$	$5.5 imes10^2$	99.5 (3.88)	99.2 (2.95)
Na <sup>+</sup>	NaCl	$7.5 imes10^3$	99.6 (3.85)	99.3 (2.52)
$K^+$	KCl	$6.0 imes10^3$	99.2 (3.85)	99.5 (2.96)
Ca <sup>2+</sup>	CaCl <sub>2</sub>	$3.0 imes10^3$	97.5 (4.02)	99.2 (3.45)
Mg <sup>2+</sup>	MgCl <sub>2</sub>	$3.0 imes10^3$	98.7 (3.95)	98.0 (3.68)
$Zn^{2+}$	$ZnCl_2$	$2.5 imes10^2$	98.6 (4.04)	99.2 (3.15)
Cd <sup>2+</sup>	CdCl <sub>2</sub>	$2.0  imes 10^2$	98.6 (3.98)	99.2 (3.81)
Ni <sup>2+</sup>	$Ni(NO_3)_2$	$2.4 imes10^2$	96.8 (3.87)	98.4 (3.78)
Cu <sup>2+</sup>	$Cu(NO_3)_2$	$2.0 imes10^2$	98.3 (4.20)	98.7 (3.68)
Co <sup>2+</sup>	$Co(NO_3)_2$	$3.0  imes 10^2$	97.8 (4.42)	98.6 (4.26)
Humic acid	-	35	95.5 (3.88)	96.2 (3.87)
Fulvic acid	-	35	96.0 (2.98)	95.8 (3.66)

# 3.8. Reusability Test

The reusability experiment was carried out by extracting 10  $\mu$ g of analyte ions (As(III) and Hg(II)) from 50 mL of numerous sets of model solution, using the same GO–SH packed column. For the sequential separation-desorption, a complete adsorption cycle under optimal conditions was performed. According to Figure 5, the prepared GO–SH is a stable solid phase sorbent for the selective extraction of As(III) and Hg(II) and can be reused multiple times because there was no discernible change in the sorbent's performance up to 35 cycles (recoveries more than 95%).



**Figure 5.** Reusability test for the sorption of As(III) and Hg(II) ions (sample volume 50 mL; metal ion 10  $\mu$ g; sample pH 6; sample flow 6 mL min<sup>-1</sup>; sorbent amount 30 mg).

# 3.9. Effect of Adsorbent Amount

In SPE, it is important to optimize the adsorbent amount in order to efficiently extract the analyte of interest. Herein, a bench of experiments was conducted by passing the sample solution (50 mL) with an analyte concentration of 10 mg L<sup>-1</sup> through a column packed with varying amounts of adsorbent (10 mg, 20 mg, 30 mg, 40, and 50 mg). The adsorbed amount of metal ions was eluted and subsequently determined by ICP-OES. It was observed that on increasing the adsorbent amount from 10 mg to 30 mg, the extraction efficiency of As(III) and Hg(II) increases from 70% to 99.9% and becomes saturated for 40 mg and 50 mg. Hence, a 30 mg adsorbent amount was optimized and used for column studies.

#### 3.10. Adsorption Isotherms

The individual study of the Langmuir and Freundlich isotherms was used to assess the adsorption behavior of the proposed GO–SH adsorbent towards As(III) and Hg(II). To study this, a 30 mg GO–SH was equilibrated with varying concentrations in the range (200–400 mg L<sup>-1</sup>) of As(III) and Hg(II) in an Erlenmeyer flask for 24 h. The force that overcomes the resistance of mass transfer between the two phases is the initial concentration of sorbate. The linearized forms of both the Langmuir and Freundlich isotherm models were used for the experimental data. It was observed that, for both analytes, the Langmuir plots (Figure 6A) with a correlation coefficient value (R<sup>2</sup>) > 0.99 are better fit, in contrast to the Freundlich plots with significantly lower R<sup>2</sup> values (Figure 6B). The Langmuir fit to the available data implies the monolayer adsorption of As(III) and Hg(II) onto the GO–SH surface.



Figure 6. (A) Langmuir and (B) Freundlich isotherm models.

## 3.11. Analytical Figures of Merits

The analytical features of the proposed solid phase extraction method developed for the enrichment of trace As(III) and Hg(II) under optimal conditions using ICP-OES are shown in Table 4. The linearity of the calibration plot for As(III) and Hg (II) was observed by preconcentrating a series of solutions (50 mL) in the concentration range of 1–1000  $\mu$ g L<sup>-1</sup>, using a GO–SH packed column. The sorbed metal ions were recovered with 5 mL of stripping agent (corresponding to 0.01–10  $\mu$ g L<sup>-1</sup>), and it was discovered that the calibration curve produced using the least squares method has good linearity and correlation coefficient. In accordance with the IUPAC method [49], the LOD and LOQ were evaluated as three times and ten times (3 S/m and 10 S/m) the standard deviation of the mean blank signal proportional to the slope of the calibration equation, respectively.

The proposed ICP-OES method's limit of detection and limit of quantification were determined to be 0.04 and 0.2  $\mu$ g L<sup>-1</sup> for 10 replicate blank runs, respectively. Multiple analyses of As(III) and Hg(II) on the same day and on various days under ideal experimental conditions showed that the method had good precision (RSD 3.8–4.2%). For five consecutive measurements of 0.5  $\mu$ g of analyte ions in 50 mL, the coefficient of variation was less than 5%. Our investigation shows that the LOD and LOQ results for ICP-OES are similar to

those for ICP-MS. It is clear that the LOD and LOQ of the ICP-OES and the ICP-MS are both more than a hundred times lower than those of the FAAS instrument.

Parameters	As(III)	Hg(II)	
Calibration range	$1-1000 \ \mu g \ L^{-1}$	$1-1000 \ \mu g \ L^{-1}$	
Regression equation	$A = 13.9562 X_{As} + 0.0547$	$A = 107.4142 X_{Hg} + 4.0685$	
Coefficient of variation	0.9989	0.9998	
LOD ( $\mu g L^{-1}$ )	$0.04\pm0.01$	$0.04\pm0.01$	
$LOQ (\mu g L^{-1})$	$0.20\pm0.02$	$0.20\pm0.02$	
Precision (RSD)	3.894	4.203	

Table 4. Analytical figures of merits of the proposed SPE method.

### 3.12. Application of the Method

By examining samples of both groundwater and municipal tap water collected from the local area, the applicability of the devised approach for usage in practice was evaluated. Following the optimized solid phase extraction process, the contents of As(III) and Hg(II) in all water samples (1 L) were preconcentrated and determined with a 95% confidence limit. The preconcentration factors for real samples (1000 mL) were equal to 200 after eluting the analyte with 5 mL of stripping agent. After spiking real environmental samples with two levels of known amounts of As(III) and Hg(II), recovery tests were carried out to check the method's accuracy. Table 5 provides the findings of the As(III) and Hg(II) content measurements together with the recoveries for the spiked samples. The accuracy of the procedure is demonstrated by the mean percentage recoveries, which are in good accordance with the spiked quantity and range from 100.1 to 101.4% for the spiked quantity with a relative standard deviation (RSD) < 5%. The student's *t*-test values at a 95% confidence level for the observed data were found to be less than the critical *t*-value of 4.304.

**Table 5.** Analysis of environmental water samples after column preconcentration (column parameters: sample pH 6; flow rate 6 mL min<sup>-1</sup>; eluent volume 5 mL and eluent flow rate 1 mL min<sup>-1</sup>; N = 3).

Identity	Spiked Value	Value Found (µg L <sup>-1</sup> ) $\pm$ Standard Deviation (% Recovery of Added Amount; RSD) (Values of <i>t</i> -Test)	
-	(µg) –	As(III)	Hg(II)
Tap water	0	Not detected	Not detected
	5	$5.01\pm0.05$	$5.05\pm0.12$
	5	(100.1; 2.37) (1.15)	(101; 4.03) (1.09)
Ground water	0	$1.50\pm0.08$	$2.32\pm0.21$
	5	$6.56 \pm 0.20$	$7.82 \pm 0.32$
		(101.2; 2.35) (1.52)	(100; 1.88) $(1.82)$

# 4. Comparison of Present Studies with Other Methods

The poor sorption of As(III) and Hg(II) by GO due to the lack of specific functional groups is one of the reasons for the development of a column approach for trace As(III) and Hg(II); preconcentration is therefore made easier by the surface modification of GO. Even though the calculated value of GO–SH sorption capacity for As(III) and Hg(II) is equivalent to that of other sorbents, it is nevertheless important given that GO–SH is more selective for As(III) and Hg(II) than unmodified GO. Graphene oxide, on the other hand, lacked the specific functional groups needed to bind As(III) and Hg(II); hence, it failed to demonstrate any sorption capacity for these metal ions. Our suggested technique is contrasted with several earlier SPE efforts based on the separation/preconcentration of As(III) and Hg(II) (Table 6). Comparative results show that our work is superior to that of others, particularly in terms of the system's sorption capacity, detection limit, and preconcentration factor, in addition to the inherent benefits of column operation and reusability.

Sorbent	Sorption Capacity (mmol g <sup>-1</sup> )	Preconcentration Factor	Detection Limit (μg L <sup>-1</sup> )	Ref.
GO-SH	As: 0.62 Hg: 0.64	As/Hg: 200	As/Hg: 0.04	This work
MoS <sub>2</sub> nanocomposite	Hg: 0.58	Hg: 150	Hg: 0.09	[25]
Cellulose/ZrO <sub>2</sub> MWCNT C18	Hg: 0.60 - -	Hg: 200 As: 125 Hg: 52.5	Hg: 0.05 As: 0.008 Hg: 0.007	[28] [50] [51]

Table 6. Comparative data of proposed work with previous studies.

## 5. Conclusions

The objective in developing a novel solid phase extractant is to establish a column preconcentration/separation technique that is safe for the environment, with the purpose of determining the degree of contamination by dangerous environmental pollutants. Pure graphene oxide (GO) with numerous epoxy (-COC), hydroxyl (-OH), carbonyl (-CO), and carboxyl (-COOH) groups at the surface leads to the development of a highly hydrophilic character and active sites for metal ion complexation, making it a potential SPE sorbent and substitute for other carbon-based sorbents. However, these oxygen-containing moieties are not sufficient to selectively form complexes with As(III) and Hg(II) ions. Therefore, we chemically introduce sulfur containing functional groups onto the GO surface for the selective sorption of As (III) and Hg(II) ions. Due to the ideally strong S-As and S-Hg interactions, the produced GO–SH nanosheets exhibit remarkable selectivity and good sorption efficiency towards As(III) and Hg(II) ions. It is interesting to note that As(III)and Hg(II) ions can be successfully preconcentrated and extracted for quantitative analysis from solutions with high ionic strength and low analyte concentrations. The minimum contamination levels for As(III) and Hg(II) identified in drinking water, as stipulated by the WHO and USEPA recommendations, are well above the quantification limits of the proposed SPE/ICP-OES technique and can be easily determined. Because GO-SH effectively extracts As(III) and Hg(II), it can be utilized precisely and without spectrum interferences to measure these analyte ions in a high-salt matrix. As a result, the application of SPE and ICP-OES analyses is greatly enhanced.

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