

Article

Highly Efficient Removal of Mercury Ions from Aqueous Solutions by Thiol-Functionalized Graphene Oxide

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Abstract: Mercury ion (Hg(II)) is one of the most prevalent and dangerous heavy metal ions in the environment, and its removal from water sources is a priority for public health and ecosystem conservation policies. Adsorption is a cost-effective and efficient method for removing heavy metal ions from aqueous solutions. In this study, the thiol-functionalized graphene oxide (GO-SH) was synthesized and used for efficient removal of Hg(II) from aqueous solutions. More than 98% of Hg(II) was efficiently removed by GO-SH within 36 h. The Hg(II) removal efficiency by GO-SH treatment was approximately double that by pure GO treatment. The adsorption behavior of Hg(II) on GO-SH was well described by the pseudo-second-order kinetic and the Freundlich isotherm models. Moreover, GO-SH exhibited good stability and reusability in the cycle experiments. Analysis of the adsorption mechanism showed that Hg(II) could be loaded onto the GO-SH surface by reacting with the sulfhydryl groups. This study demonstrates that GO-SH is a promising water purification material with a high efficiency for Hg(II) removal.

Keywords: graphene oxide; sulfhydryl; mercury ion; adsorption



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1. Introduction

Over the past several decades, rapid urbanization and industrialization have resulted in excessive heavy metals levels in aquatic systems [1]. Owing to their being extremely poisonous, carcinogenic, and bio-accumulating in the living body, heavy metals pollution in water is being extensively studied [1–5]. Several industrial processes, including the creation of chlorine and caustic soda, coal and waste combustion, batteries manufacturing, and electrotechnical application, produce Hg(II)-containing wastewater, and their substandard discharge results in their accumulation in living organisms and entry into the food chain [1]. In addition to industrial activities, some drugs that are closely related to human life also cause the emission of heavy metals. For example, Tibetan medicine as a famous traditional national medicine in China has attracted increasing attention owing to its unique curative effect [6,7]. The unique formulation of Tibetan medicine makes it contain high concentrations of the heavy metal mercury [6,7]. However, the absorption rate of mercury in the human body is considerably low (<4%) [6,8], which results in the excretion of a large amount of toxic heavy metal Hg(II) from the body, reaching the aquatic environment in various ways and resulting in high levels of Hg(II) in water [6,8].

Hg(II), which ranks as the sixth most harmful compound among hazardous compounds, is one of the most pervasive and damaging heavy metal ions in the environment [1,3]. Exposure to Hg(II) or its complexes, even at the lowest levels, can lead to human diseases, such as mercury poisoning, which can disrupt vital cellular functions and may lead to serious diseases, such as irreversible damage to the human nervous system, renal insufficiency, Minamata disease, mental retardation, and liver damage [1–4]. Therefore, it is imperative to treat mercury ions in aquatic environments.

Many treatment processes such as chemical precipitation process [9], ions exchange [10], membrane process [11], and adsorption [1,3–5,12,13] have become widely adopted for the removal of the heavy metal mercury ion. The process of chemical precipitation is often accompanied by the production of a large number of wastes [9]. In the process of ion exchange and membrane treatment, the ion exchange resin and membrane are easy to be contaminated, thus affecting the removal effect [10,11]. In contrast, adsorption is an economical and efficient method to remove heavy metal ions from aqueous solutions owing to its advantages, such as easy operation, relatively low cost, and simple equipment [1,3–5,12,13]. In this process, the highly specific surface area or special groups of the adsorbent material are used for physical and chemical adsorptions to effectively remove heavy metals from water [1,3–5,12,13]. Various carbon-based materials adsorbents for heavy metal removal have been developed so far [12,14].

Over the last decade, carbon-based substances like graphene, fullerenes, and carbon nanotubes have garnered particular attention [2–4]. These materials, which are relatively effective in pollutant removal, also have some deficiencies, resulting in a low adsorption rate or being limited in use [3]. Among the carbon allotropes, graphene, a molecular layer of graphite, exhibits remarkable physical, chemical, and biological properties [3]. Owing to their stability and limited solubility in ordinary solvent, graphene-based compounds are excellent catalysts for chemical reaction [2]. However, the direct applicability of graphene is severely hindered due to its poor dispersion in solvents, tends to agglomerate, and has inherent zero band gap energy [3]. In addition, it also lacks sufficient binding sites to interact with heavy metal ions [2–4]. The treatment of graphene materials without impairing their peculiar performances has resulted in advances in chemical modification of graphene materials. Graphene oxide (GO), an important derivative of graphene, is a two-dimensional sheet-structured material with a honeycomb host [2–4,15]. In addition to the large specific surface area of graphene, GO contains a considerable quantity of oxygen-containing functional group, such as carboxyl and hydroxyl groups, between the sheets, which results in good water solubility and easy functionalization characteristics [3,4,15]. However, GO is highly hydrophilic, easily agglomerated in aqueous solutions, and has a single functional group type and low functional group density [3,4,15]. Owing to these properties, GO lacks sufficient binding sites to interact with metal ions, which limits its ability to adsorb heavy metals and its application in wastewater treatment. Therefore, to effectively remove mercury ions from aqueous solutions, further modification to the above-mentioned GO is necessary.

Based on the hard–soft acid–base theory, there is a strong affinity between mercury ions and sulfur-containing functional groups such as sulfhydryl and sulfonic acid groups; therefore, the introduction of sulfur-containing functional groups can endow the material with excellent heavy metal adsorption capacity. Based on this, we aimed to obtain initial information on the adsorption of Hg(II) ions in aqueous solutions using thiol-functionalized graphene oxide (GO-SH) in this study. We developed GO-SH and investigated its adsorption performance for Hg(II) ions in aqueous solutions. The adsorption process was studied by adsorption kinetics and isotherms. In addition, the regeneration of GO-SH was evaluated. Finally, the potential adsorption mechanism of Hg(II) ions by GO-SH was revealed. This study provides theoretical and technical bases for the removal of heavy metal ions from aqueous solutions.

2. Materials and Methods

2.1. Adsorbent Preparation

In this study, GO, obtained by oxidative intercalation, deep purification, dilution, and ultrasonic stripping, was prepared using the modified Hummers method, as previously reported [15]. GO-SH was prepared according to the method of Chua and Pumera [16]. In a nutshell, 80 mL of a 4 mg/mL GO solution was combined with 5 mL of hydrobromic acid, and the mixture was then stirred at 30 °C for 2 h. The mixture was then agitated for 24 h while 5 g of thiourea was added and the temperature raised to 80 °C. After stirring,

the mixture was allowed to cool to room temperature, 50 mL of 4 mol/L sodium hydroxide solution was added, and the mixture was stirred for 30 min. The solid–liquid separation was then achieved, followed by multiple rounds of washing alternatively with ethanol and ultrapure water. Finally, GO-SH was produced by lyophilizing the obtained solid for 24 h in a vacuum freeze-dryer.

2.2. Batch Experiment

To evaluate the suitability of the obtained GO-SH as an adsorbent for Hg(II) removal, a batch experiment was performed in a 250 mL Erlenmeyer flask as the reaction container. Thirty milligrams of the sorbent and 150 mL of aqueous solution containing Hg(II) were mixed well in a conical flask. The initial concentration of Hg(II) was set at 10 mg/L. The conical flask was shaken at a constant temperature of 25 ± 2 °C with a rolling speed of 170 rpm to reach equilibrium. The samples were collected within the set adsorption time, and the impurities in the collected samples were removed through a 0.45 µm filter for further analysis. Additionally, GO adsorption experiments were carried out as a control to determine the adsorption performance of the functionalized material. The final results were averaged over all three iterations of each experiment.

The adsorption efficiency and capacity of Hg(II) were calculated using Equations (1) and (2), respectively:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 (mg/L) denotes the starting concentration of Hg(II) in the solution, C_t (mg/L) represents the residual concentration of Hg(II) in the solution at a specified time, V (L) is the volume of the Hg(II) solution used, m (g) is the mass of the adsorbent used, $R(\%)$ is the removal efficiency, and q_t (mg/g) is the adsorption capacity of Hg(II).

2.3. Adsorption Kinetics

To investigate the effect of contact time on Hg(II) adsorption, kinetic tests were conducted at 25 ± 2 °C. Throughout this procedure, the samples were collected at different intervals until the concentration of Hg(II) in the solution was constant. The adsorption kinetics of Hg(II) were also described using two common dynamic models, the pseudo-first-order (Equation (3)) and the pseudo-second-order (Equation (4)) models. The relevant equations used are shown below.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where k_1 (h^{-1}) and k_2 ($\text{g}(\text{mg h})^{-1}$) indicate the adsorption rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively, and q_e (mg/g) indicates the equilibrium adsorption capacity.

To learn more about the mechanism of adsorption and potential rate-controlling step, such as mass transfer and diffusion-controlled process, the internal diffusion model was utilized to predict the rate control steps, whose equation (Equation (5)) was expressed as follows:

$$q_t = k_i t^{0.5} + C \quad (5)$$

where k_i ($\text{mg/g h}^{-1/2}$) represents the diffusion rate constant, and C is the intercept.

2.4. Adsorption Isotherm Experiments

To establish the adsorption isotherm curve, the temperature was changed to 15 °C, 25 °C, and 35 °C by shaking at 170 rpm with initial Hg(II) concentrations ranging from 1 mg/L to 100 mg/L. Two classical adsorption isotherm models, the Langmuir (Equation (6)) and Freundlich isotherm model (Equation (7)), were used to mathematically describe Hg(II) adsorption. In terms of monolayer adsorption with a constrained number of adsorption sites on the surface, the Langmuir isotherm model is one of the most effective. The Freundlich model is an adaptation of the Langmuir model that can be used to describe the isotherms of pollutant adsorption on heterogeneous or rough adsorption surfaces with multiple adsorption sites.

$$q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \quad (6)$$

$$q_e = k_F C_e^{1/n} \quad (7)$$

where C_e (mg/L) is the equilibrium concentration of pollutants in the aqueous phase, Q_m (mg/g) represents the maximum monolayer adsorption capacity, k_L and k_F (L/g) represent constants related to the Langmuir and Freundlich isotherms, respectively, and n represents the nonlinear coefficient, which is a measure of the energy distribution of the adsorbent site.

2.5. Analytical Methods

The residual concentrations of Hg(II) were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Fisher iCAP PRO).

The surface morphology and elemental distribution were evaluated using a scanning electron microscope (SEM, FEI Scios 2 HiVac) coupled with an energy dispersive spectrometer (EDS). The samples' crystal structures were analyzed by X-ray diffraction (XRD, Bruker D8 Advance, Germany) using a Cu K α source, with a scan step of 1°/min and a scan range between 5° and 90°. The functional groups of the materials were identified using a Fourier transform infrared spectroscopy (FTIR, Nicolet iN10, Thermo Scientific, USA) at the wave numbers ranging between 400 and 4000 cm⁻¹. The surface components and their valance distributions of the materials were investigated using an X-ray photoelectron spectrometer (XPS, ESCALAB Xi+, Thermo Scientific, USA) at a vacuum pressure of approximately 8×10^{-10} Pa with Al K α X-rays ($h\nu = 1486.6$ eV) as the excitation source.

3. Results and Discussion

3.1. Characterization of the Prepared Materials

In order to understand the morphology and elemental composition of the obtained adsorbents, the obtained adsorbents were characterized by SEM and EDS, respectively, and the characterization findings are shown in Figure 1. The SEM image of GO (Figure 1a) showed the aggregated and closely associated graphene oxide layers. The surface structure of GO was wrinkled and wavy, which may be attributed to the interactions between hydrophilic oxygen-containing functional groups [3]. By comparison, GO-SH presented graphene oxide layers without agglomerates and wrinkles (Figure 1c). This result indicates that the introduction of functional groups effectually prevents the aggregation of GO, resulting in an increased number of available active sites, which subsequently increases the adsorption capacity.

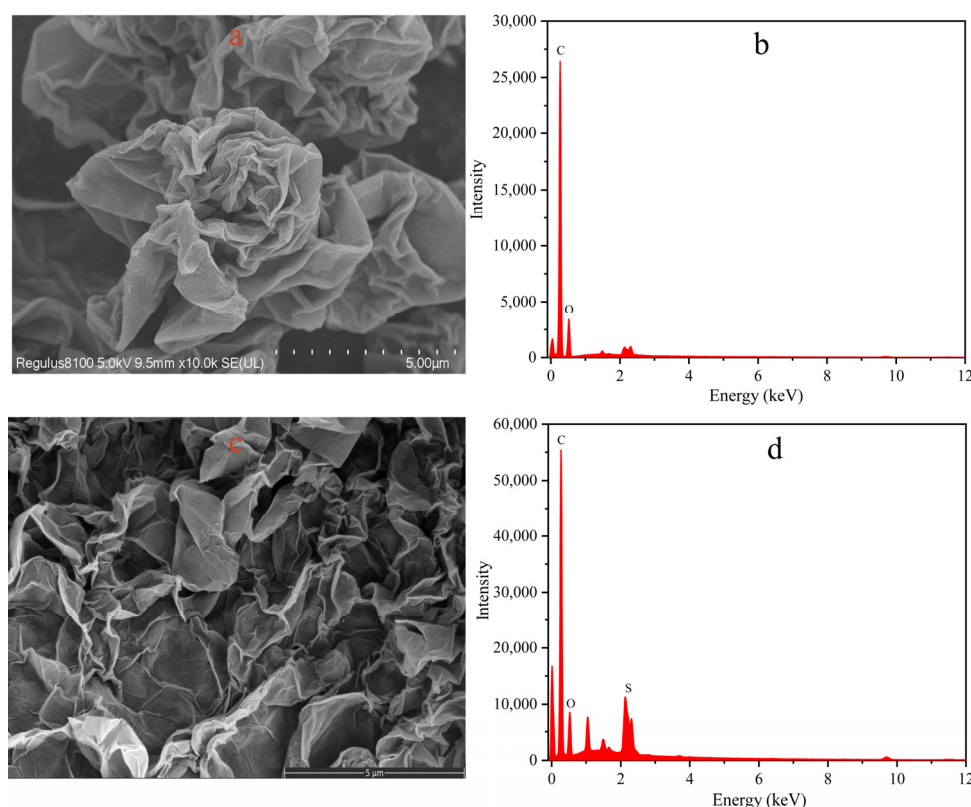


Figure 1. SEM image (a) and EDS spectra (b) of GO; SEM image (c) and EDS spectra (d) of GO-SH.

The EDS spectra showed that the elemental compositions of GO and GO-SH were significantly different. The EDS spectrum of GO (Figure 1b) showed only carbon and oxygen, indicating that the anchoring functional groups on the GO sheet consisted of carbon and oxygen containing groups. A peak of sulfur appeared in GO-SH (Figure 1d), confirming the presence of functionalized sulfur groups on the GO surface. Further analysis of the EDS results revealed that the carbon element in GO-SH slightly increased, whereas the oxygen element significantly decreased. This may be due to the partial reduction of graphene oxide and the conversion of hydroxyl groups on the surface of graphene oxide to sulfhydryl groups during the sulfhydryl functionalization step. These results indicate that the sulfhydrylation modification of graphene oxide was successful.

The XRD spectrum of graphene oxide (Figure 2a) reveals the stronger diffraction peaks at approximately $2\theta = 11.4^\circ$ and $2\theta = 26.5^\circ$, of which $2\theta = 11.4^\circ$ is a characteristic peak of graphite oxide, which was assigned to its (001) crystal plane with an interlayer space of 0.79 nm. The characteristic peak of natural graphite at $2\theta = 26.5^\circ$ corresponds to the (002) crystal plane, with an interlayer space of 0.34 nm. The comparison of the interlayer spacing of graphite oxide and natural graphite revealed that the graphite is oxidized and transformed into graphite oxide, and the interlayer spacing was increased, indicating the exfoliation of graphite. The larger layer spacing of the GO layers may also be attributed to the generation of oxygen-containing functional groups between the structural sheet, the formation of GO nanosheets, and the adsorption of interlayer water molecules captured between the hydrophilic GO layers [3,17]. The diffraction peak of the graphite oxide (001) crystal plane at approximately $2\theta = 11.4^\circ$ completely disappeared after the chemical modification of GO. There was a wide diffraction peak at approximately $2\theta = 24.7^\circ$, which was close to the diffraction peak position of graphite. These results indicate that the graphene oxide reduction process occurred during the functionalization step.

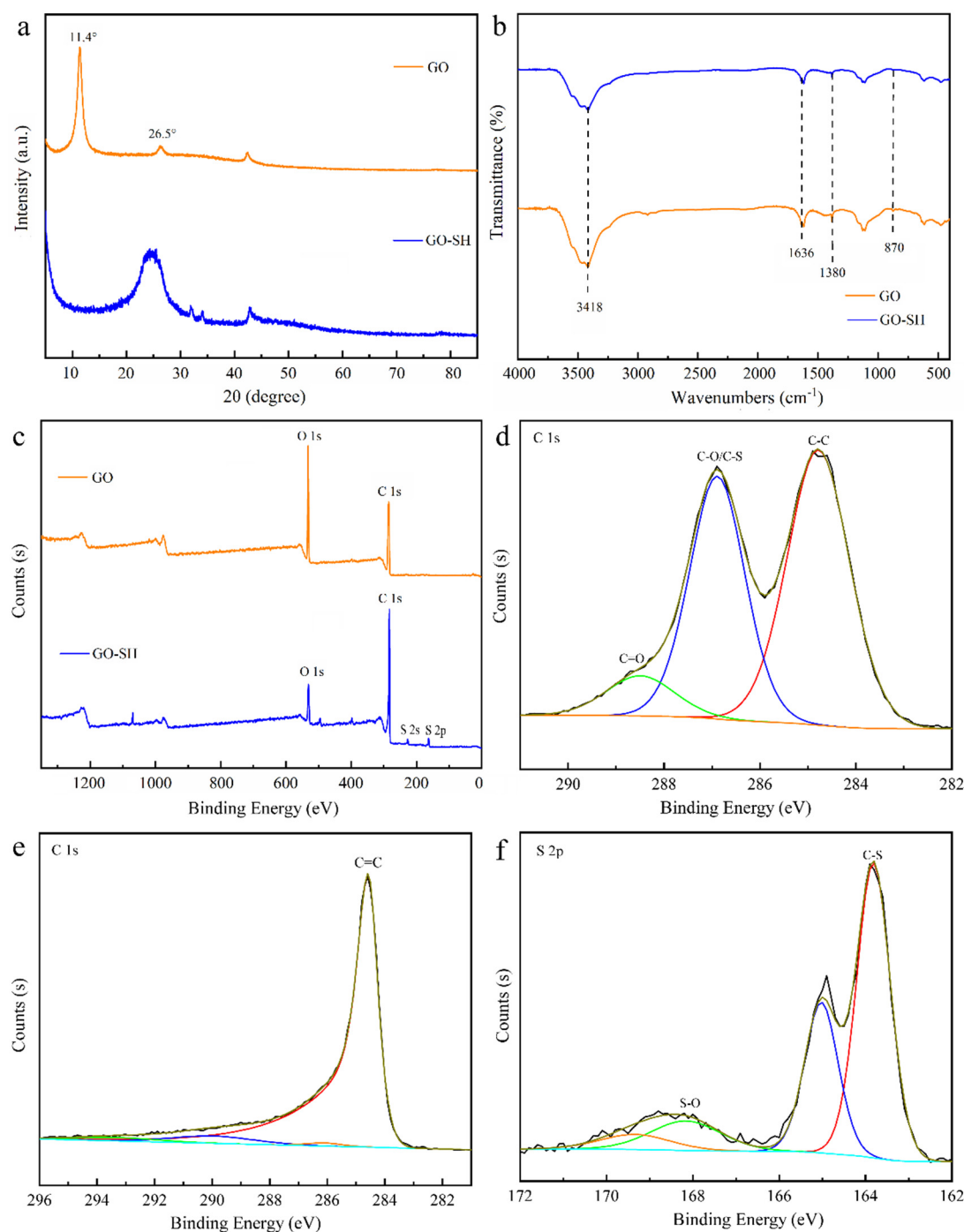


Figure 2. XRD patterns of GO and GO-SH (a), FT-IR spectra of GO and GO-SH (b), XPS survey spectra of GO and GO-SH (c), high-resolution C 1s of GO (d), high-resolution C 1s of GO-SH (e), and high-resolution S 2p of GO-SH (f).

FTIR analysis (Figure 2b) shows that the absorption peak at 3418 cm^{-1} corresponds to the stretching vibration absorption peak of O-H, the absorption peak at 1636 cm^{-1} is the vibration mode of C=O, the absorption peak at 1380 cm^{-1} belongs to the vibration mode of C-OH, and the absorption peak at 870 cm^{-1} is assigned to the bending vibration mode of the epoxide. The graph shows that the peaks of O-H and epoxides decreased slightly after chemical modification. It has been reported that the vibration band of S-H is approximately $2400\text{--}2500\text{ cm}^{-1}$ [16,18]. Although early XPS and EDS analyses were performed, the expected S-H vibrational bands were not apparent. This may be caused by

the inherently weak vibrational mode in the S–H bond and the small number of S–H bonds in the modified material. Additionally, S–H vibrational bands are possibly masked by the strong O–H absorbance. These observations are not unique, and previous work on sulfur-functionalized graphene also failed to detect the S–H peak using FTIR spectroscopy [16,18].

XPS analysis further confirmed the characteristics and composition of the prepared material. The XPS full spectrum scanning provided an overview of the composition of elements on the material surface. The survey scan of GO in the range of 0–1400 eV is shown in Figure 2c. The peaks of C 1s and O 1s, respectively, may be found at binding energies of 284.5 eV and 532.4 eV. Additionally, the survey scan of GO showed that GO comprises 71.48 at.% carbon and 26.87 at.% oxygen while that of GO-SH revealed it to comprise 83.35 at.% carbon and 10.96 at.% oxygen. It is clear that GO and GO-SH have carbon oxygen atom ratios of 2.66 and 7.60, respectively. A more effective reduction process during functionalization, including epoxide ring-opening and nucleophilic replacement on the hydroxyl group, is suggested by the greater carbon–oxygen atom ratios of GO-SH [16]. The survey scan of GO-SH (Figure 2c) also revealed that in addition to the characteristic peaks of C 1s and O 1s, GO-SH has a significant characteristic peak of S 2s at 226.5 eV and S 2p at approximately 162.5 eV, which reinforces the existence of sulfur. This is in line with the EDS findings, demonstrating that sulfur was successfully incorporated into graphene oxide, indicating successful functionalization.

The C 1s core-level spectra with high resolution showed these changes as well. The typical C 1s core-level spectra of GO is shown in Figure 2 deconvoluted by Lorentz and Gaussian functions, where carbon is bonded by C–C (284.8 eV), C–O/C–S (286.9 eV), and C=O (288.5 eV) [5]. During the transition from GO to GO-SH, a noticeable drop in C–O peak intensity was seen at a binding energy of approximately 286 eV. This might be caused by the epoxide's ring opening and the previously mentioned nucleophilic replacement on the hydroxyl group. Notably, a clearer and well-defined C=C signal on GO-SH implied improved properties of the aromatic system. This effect was attributed to the reduction of graphene oxide to graphene during the experiment. A high-resolution S 2p core-level spectrum was acquired in order to better clarify the nature of the chemical bond types of sulfur since the binding energy of the C–S bond in the C 1s core-level spectrum is identical to that of the C–O bond. With an energy difference of roughly 1.16 eV, the S 2p core level spectrum is separated into S 2p_{3/2} and S 2p_{1/2} spin-orbit splitting peaks. According to the S 2p_{3/2} peak energy position and peak shape characteristics, S can be divided into two chemical states. The binding energy at 163.8 eV is mainly attributed to the C–S bond whereas that at approximately 168 eV is mainly attributed to the S–O bond. The largest peak arising from the C–S bond indicates that the sulfhydryl groups are mainly attached to the graphene carbon lattice. In conclusion, these results strongly support the success of thiol-functionalized graphene oxide.

3.2. Adsorption Performance

The adsorption efficiency of GO-SH was examined at an initial Hg(II) concentration of 10 mg/L. As shown in Figure 3a, the removal efficiency of Hg(II) by GO-SH was 98.7% within 36 h, which was considerably higher than its removal efficiency of 52.8% in GO, suggesting that the use of thiol-modified graphene oxide as an adsorption material considerably improves Hg(II) removal efficiency. As shown in Figure 3b, the trends of the two adsorption curves are similar, and the entire adsorption process consists of two stages, namely, an initial fast adsorption process and a late slow equilibrium process. In the initial stage, the adsorption capacity of Hg(II) on GO and GO-SH increased rapidly within the first 4 h. After this fast adsorption phase, the rate of adsorption slowed down and no further increase in adsorption capacity was detected after 6 h. The equilibrium adsorption capacities of Hg(II) by GO and GO-SH were 26.48 mg/g and 49.68 mg/g, respectively, indicating that the adsorption performance of GO-SH is better than that of GO. To determine the adsorption effect of GO-SH on Hg(II), we compared the Hg(II) adsorption performance of GO-SH to that of other advanced carbon-based adsorbents

(Table 1). The results revealed that GO-SH has a good adsorption performance compared to the other materials [15,19–21]. In fact, some pure carbon materials, such as ACs and GOs, only exhibit a low capacity for heavy metal ions adsorption owing to their abundant porosity and high physical adsorption surface area [19]. Therefore, in order to improve their adsorption capacity, the adsorbents need to be modified. Collectively, these results indicate that GO-SH prepared in this study is undoubtedly a good candidate.

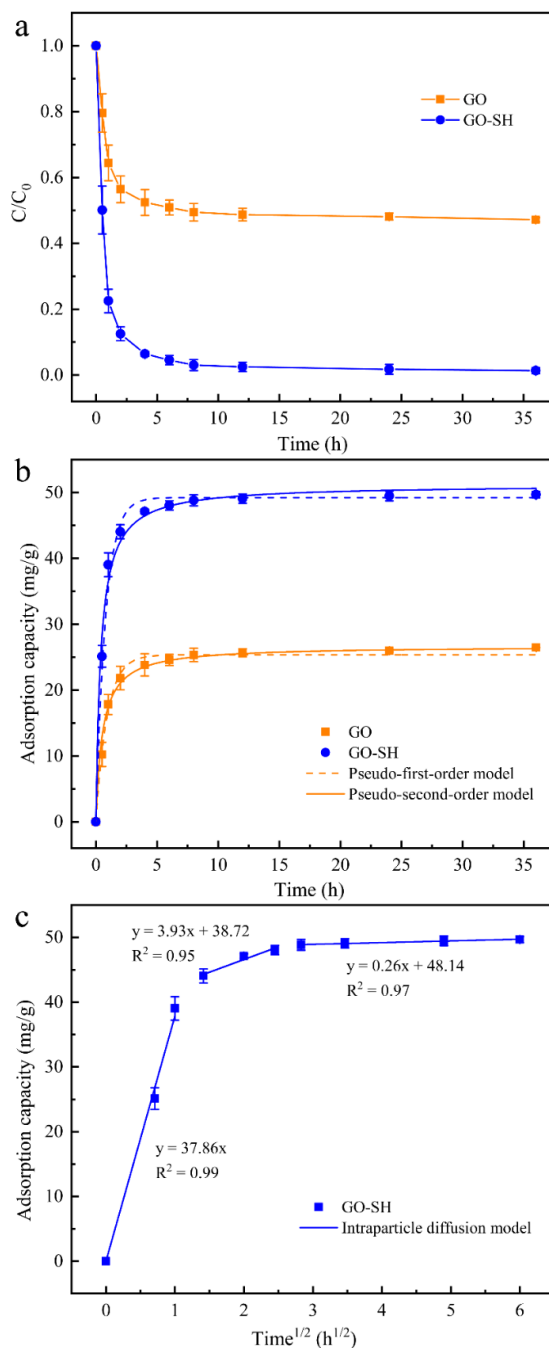


Figure 3. Removal efficiency of Hg(II) by GO and GO-SH (a), kinetic model fitting curves for Hg(II) removal by GO and GO-SH (b), and intraparticle diffusion model fitting curves by GO-SH (c).

Table 1. Comparison of adsorption capacities with various adsorbents for Hg(II) ions.

Absorbent	Initial Concentration (mg/L)	Equilibrium Time (min)	Adsorption Capacity (mg/g)	Reference
Modified activated carbons	24	500	2.226	[19]
Partially reduced graphene oxide	150	20	110.21	[21]
Tannin-immobilized graphene oxide	1	15	23.81	[15]
EDTA functionalized graphene oxide nanoparticles	1.2	160	18.6392	[20]
GO-SH	10	360	49.68	This study

3.3. Adsorption Kinetics

The adsorption kinetics can offer crucial information for studying the mechanism of Hg(II) adsorption by GO-SH, which is the necessary condition for determining the adsorption behavior of GO-SH. Therefore, in order to better illustrate the removal process of Hg(II) by GO and GO-SH, the obtained experimental results were fitted using pseudo-first-order kinetics and pseudo-second-order kinetic models. In Figure 3b, the fitting result of the pseudo-second-order kinetic model ($R^2 = 0.991$) for GO-SH was better than that of the pseudo-first-order kinetic model ($R^2 = 0.988$), and the rate constant k_2 was 0.05 h^{-1} . The pseudo-first-order kinetic model for GO, however, had a better fitting result ($R^2 > 0.99$) than the pseudo-second-order kinetic model, and the rate constant k_1 was 1.08 h^{-1} . This indicates that the removal of Hg(II) by GO is primarily caused by the physical adsorption under electrostatic action, whereas the rate-limiting process of Hg(II) removal by GO-SH is a chemical process.

Although the pseudo-second-order kinetic model successfully described the adsorption process of Hg(II) by GO-SH, the identification of the adsorption process as a one-step binding process was limited in accuracy [22]. The intraparticle diffusion model can provide more detailed information on the adsorption rate control procedure by organizing the adsorption process into stages [23]. Figure 3c presents the relationship between q_t and $t^{1/2}$ based on the intraparticle diffusion model. The figure clearly shows three linear parts, and this multiple linearity further indicates the complexity of the adsorption process. The quick adsorption step, which made up the first linear stage, may have been brought on by Hg(II) migration from the solution to the outer surface of the GO-SH. Moreover, chemical adsorption also occurs in this stage. The slow adsorption procedure, in which intraparticle diffusion in the pore structure regulates the adsorption rate, made up the second linear component. The third stage was the final equilibration stage, in which Hg(II) diffused slowly from larger pores to smaller pores. In addition, the rate constants of the different adsorption stages obtained by the intraparticle diffusion model were $k_1 (37.86 \text{ mg/g h}^{-1/2}) > k_2 (3.93 \text{ mg/g h}^{-1/2}) > k_3 (0.26 \text{ mg/g h}^{-1/2})$, indicating that the adsorption rate is the highest in the first stage and lowest in the third stage. In other words, the external adsorption rate of the adsorbent exceeded its internal adsorption rate. If the fitted line crosses the origin, the diffusion within the particle is the only rate-controlling process; otherwise, the external mass transfer process controls the adsorption rate to a certain extent [24]. In our study, the fitting results indicated that only the first stage traverses the origin, whereas the subsequent stages do not. Therefore, it can be concluded that in addition to chemical nonequilibrium, intraparticle diffusion also participates in the Hg(II) adsorption process.

3.4. Adsorption Isotherms

Adsorption isotherm models are mathematical models that elucidate the interactions between the adsorbates and adsorbents. The equilibrium process of Hg(II) adsorption by GO and GO-SH was fit using Langmuir and Freundlich adsorption isotherm models based on the equilibrium adsorption data. Compared to the Langmuir model, the Freundlich model can

better fit the experimental results for GO and GO-SH (Figure 4). The correlation coefficient R^2 of the Freundlich model of GO was all above 0.99 whereas that of GO-SH lay between 0.91 and 0.99. The Langmuir model is based upon the formation of a uniform monolayer adsorption layer on the surface of the adsorbent, whereas the Freundlich model posits that the adsorption happens on a heterogeneous surface and the surface adsorption heat distribution is not uniform [4,25]. Therefore, our results indicate that the surface of the modified GO-SH adsorbent was less homogeneous than that of GO. Moreover, the adsorption performance initially sharply increased and then increased moderately as Hg(II) concentrations grew. The interactions between the sulfur groups and Hg(II) to generate complex adsorption may be the cause of the improved adsorption effectiveness at low concentrations [5]. The adsorption capacity is correlated with the Freundlich constant, k_F . During the adsorption process of Hg(II) by GO-SH, the value of k_F showed an evident increase with the increase in temperature (Table 2). At 35 °C, the maximum value of k_F was 28.23 L/g (Table 2), indicating that the adsorption process is endothermic. In addition, a greater temperature promotes the hydrolysis of Hg(II) to form $\text{Hg}(\text{OH})_2$ or HgO precipitation, which results in high apparent adsorption [5]. The Freundlich constant, n , is closely linked to the adsorption strength. The fitting results of the Freundlich model showed that the n values ranged from 1.43 to 1.54 at different temperatures (Table 2), indicating that GO-SH had a high capacity for Hg(II) adsorption in the experimental temperature range. Notably, the adsorption isothermal curves indicated that adsorption saturation was not reached for Hg(II) at the initial Hg(II) concentrations (1–100 mg/L) and temperature range (15–35 °C), indicating that Hg(II) did not form a complete monolayer on the GO and GO-SH surfaces.

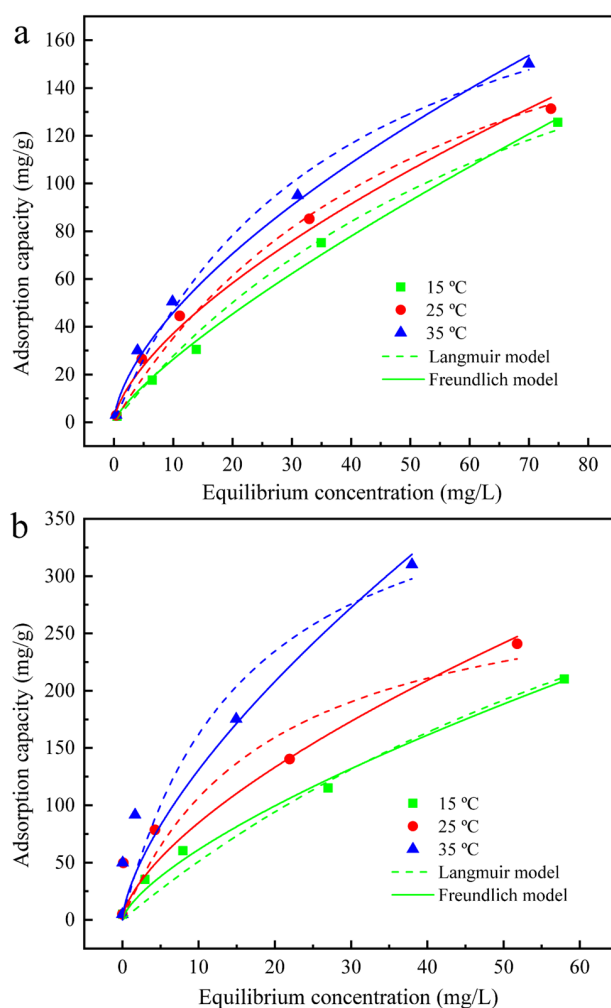


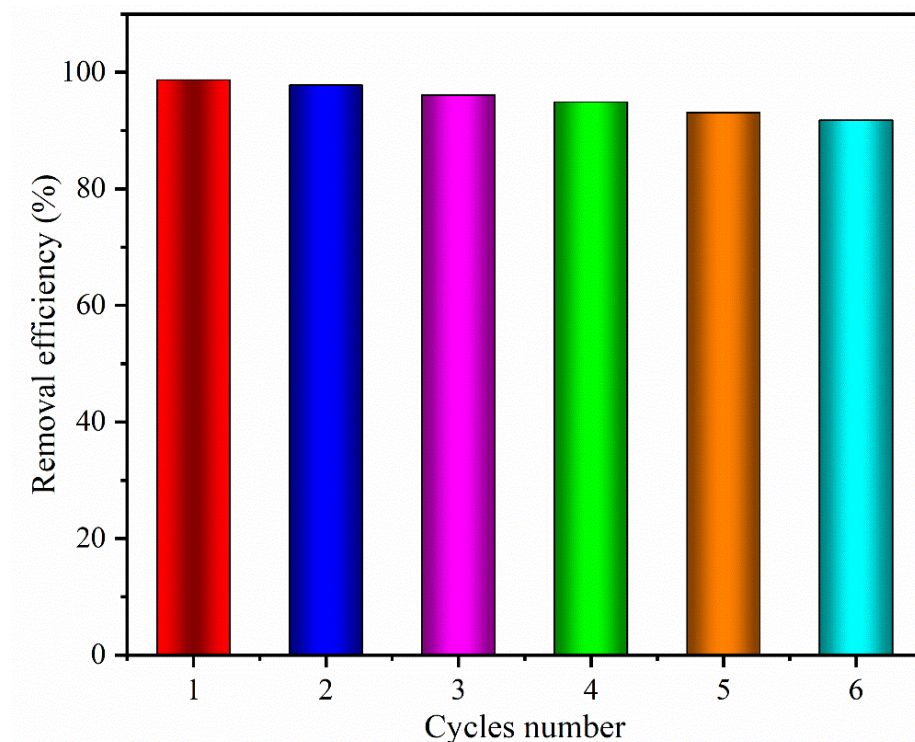
Figure 4. Hg(II) adsorption isotherms on GO (a) and GO-SH (b) at different temperatures.

Table 2. Adsorption isotherm constants for Hg(II) adsorption at different temperatures according to Freundlich and Langmuir.

Absorbent	Temperature (°C)	Freundlich Model			Langmuir Model		
		k_F (L/g)	$1/n$	R^2	Q_m (mg/g)	K_L (L/g)	R^2
GO	15	4.35	0.78	0.99	259.01	0.01	0.99
	25	8.33	0.65	0.99	236.61	0.02	0.98
	35	10.98	0.62	0.99	228.82	0.03	0.98
GO-SH	15	12.36	0.70	0.99	618.27	0.01	0.96
	25	18.99	0.65	0.91	312.41	0.05	0.89
	35	28.23	0.67	0.91	424.75	0.06	0.89

3.5. Regeneration and Recyclability

Figure 5 shows the elimination effectiveness of Hg(II) after six cycles using GO-SH. As shown in Figure 5, the removal efficiency of Hg(II) was 98.7% after the first cycle using the adsorbent and slightly decreased to approximately 96.1% and 94.9% after the third and fourth cycles, respectively. The steady loss of material and functional groups on the GO-SH surface, which are loosely linked to the GO surface, may be the cause of the gradual decline in the Hg(II) removal efficiency. The fact that the Hg(II) on the material surface is not completely liberated and is still occupying the adsorption sites could be another factor. The Hg(II) removal efficiency remained above 91.8% in the sixth cycle, indicating that GO-SH is mechanically stable and suitable for Hg(II) adsorption in wastewater.

**Figure 5.** The reusability of GO-SH for Hg(II) adsorption.

3.6. Proposed Mechanism for Adsorption

Figure 6 displays the outcomes of an XPS study that was carried out on the GO-SH adsorbent both before and after adsorption in order to better understand the adsorption mechanism of GO-SH. Following the adsorption of Hg(II), the peak of Hg 4f may be clearly seen from the survey scan of GO-SH. The appearance of the Hg 4f signal unmistakably demonstrated that Hg(II) had been successfully adsorbed. The peaks with binding energies

at 101.1 eV and 105.1 eV were identified as Hg 4f_{7/2} and Hg 4f_{5/2}, respectively, based on the high-resolution spectra of Hg 4f following adsorption. This suggests that Hg exists as a Hg(II) species rather than in its metal form [26]. These findings imply that redox reactions are not involved in the Hg(II) adsorption on GO-SH. S 2p on GO-SH is deconvoluted into two distinct peaks at 163.82 eV and 165.02 eV in Figure 6c, which are associated with S 2p_{3/2} and S 2p_{1/2}, respectively. These peaks are assigned to C–S bonds with similar binding energies [5,26]. The high binding energy of S 2p somewhat decreased after the adsorption of Hg(II), indicating electron transfer from the S of the C–S bond to Hg(II). This agrees with the outcomes mentioned by Tran et al. [27]. These observations suggest that Hg(II) can be loaded onto the GO-SH surface through sulfhydryl group reactions.

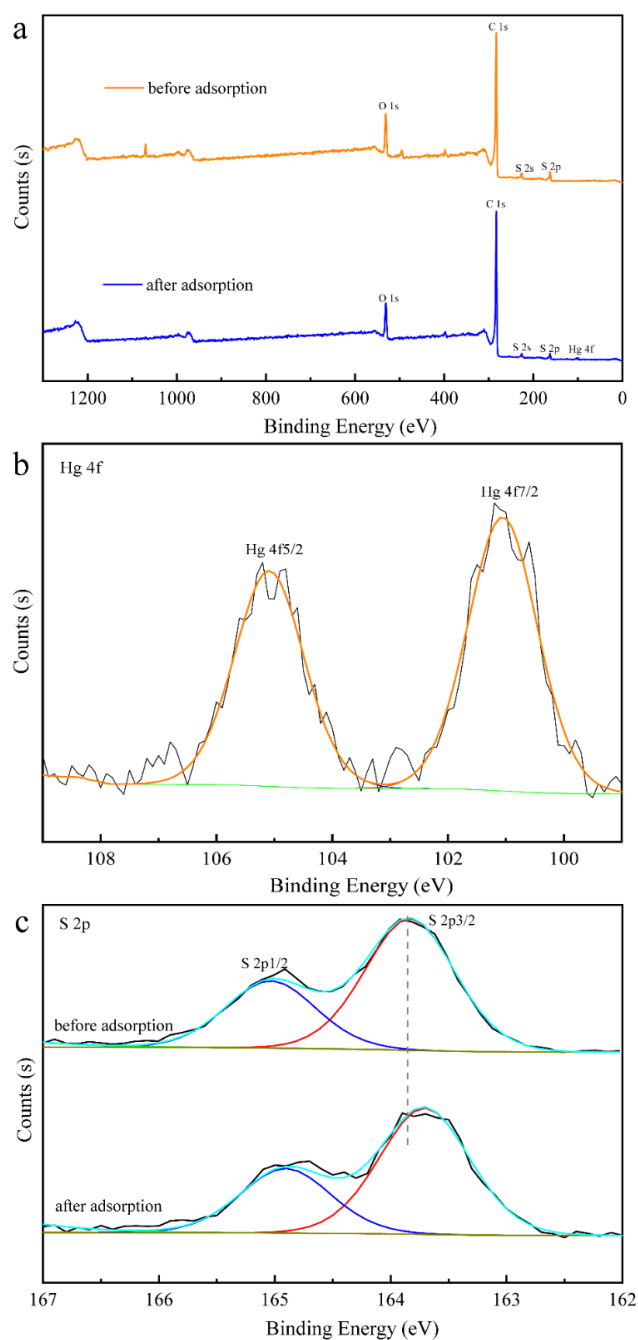


Figure 6. The survey scan before and after adsorption of Hg(II) (a), high-resolution Hg 4f after adsorption of Hg(II) (b), and high-resolution S 2p before and after adsorption of Hg(II) (c).

4. Conclusions

The thiol-functionalized graphene oxide (GO-SH) was developed and successfully used in this study to effectively remove Hg(II) from aqueous solutions. Most Hg(II) was removed within 36 h in the presence of GO-SH. The adsorption behavior of GO-SH for Hg(II) coincides with that of the Freundlich isotherm model and pseudo-second-order kinetic model. Furthermore, the presence of three linear segments in the intraparticle diffusion model indicates that intraparticle diffusions and liquid film diffusion are two different types of diffusion processes that can occur during the adsorption process. The high removal efficiency of Hg(II) was maintained after the recycling of GO-SH, demonstrating the longevity and reusability of GO-SH. This study provides a theoretical basis and technical support for the removal of heavy metal ions from aqueous solutions. However, further research is needed to optimize process variables for practical applications. The study of such adsorbents is important for the removal of actual wastewater containing heavy metals.

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