Removal of Hg\textsuperscript{2+} from desulfurization wastewater by tannin-immobilized graphene oxide

Heng Chen\textsuperscript{1} · Fengjun Liu\textsuperscript{1} · Chenjian Cai\textsuperscript{1} · Hao Wu\textsuperscript{2} · Linjun Yang\textsuperscript{1}

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Abstract
A novel adsorbent consisting of tannic acid (TA) immobilized on graphene oxide (GO) was proposed and used to remove Hg\textsuperscript{2+} from desulfurization wastewater. The morphology and physicochemical properties of tannin-immobilized graphene oxide (TAIGO) were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The characterization results showed that TA was successfully immobilized on GO, and that new functional groups were introduced on TAIGO. The effects of contact time, adsorbent dose, pH, and ion components on removal efficiency were evaluated. The adsorption process was found to be complete within 15 min, and the removal efficiency increased with increasing adsorbent dosage. The pH value affected the protonation of TAIGO and the form of Hg\textsuperscript{2+} in wastewater. High concentrations of Cl\textsuperscript{-} and SO\textsubscript{3}\textsuperscript{2−} hindered the adsorption performance, whereas SO\textsubscript{4}\textsuperscript{2−} and cations had a negligible effect. In addition, the excellent economic benefits of TAIGO were analyzed in an economic evaluation, and the Hg\textsuperscript{2+} removal efficiency remained at 88% after three recycles. A pseudo-second-order kinetic model ($R^2=0.9995$) was used to fit the adsorption process, and the oxygen-containing functional groups and chelation reaction played critical roles in adsorption. TAIGO is a low-cost adsorbent with high Hg\textsuperscript{2+} removal efficiency and could be further used in practical desulfurization wastewater.

Graphical abstract

Keywords Mercury · Desulfurization wastewater · GO · Tannin · Removal efficiency

Introduction
The wet flue gas desulfurization (WFGD) system has been widely used for SO\textsubscript{x} treatment and has a synergistic effect in removing Hg\textsuperscript{2+} from flue gas (Zhang et al. 2019). It was reported that the WFGD system could capture approximately
90% of \( \text{Hg}^{2+} \) and transport it into the desulfurization slurry (Krzyżyńska et al. 2020). However, excessive heavy metals and \( \text{Cl}^- \) that accumulate in the slurry may deteriorate the desulfurization slurry quality, which is a disadvantage for the desulfurization process. Thus, the WFGD system regularly discharges desulfurization wastewater and supplies fresh water to maintain the quality of the desulfurization slurry (Zheng et al. 2019). Coal-fired power plants generate a large amount of desulfurization wastewater, which puts a significant strain on the environment (Zheng et al. 2020). Therefore, it is necessary to treat \( \text{Hg}^{2+} \) in desulfurization wastewater. At present, triplet tank technology is conventionally used for desulfurization wastewater treatment, and heavy metals can be removed by trimethylthiazoline (TMT15) and dithiocarbamate-type chelating resin (DTCR) (Jan et al. 2018). TMT15 is a favored organic sulfide reagent that can co-precipitate heavy metals. However, because of its toxicity, the use of this compound cannot ensure that the water quality conforms to strict regulations. The adsorption method is an effective, economical, and environmentally friendly method of treating \( \text{Hg}^{2+} \) in desulfurization wastewater (Hsu et al. 2020; Taurozzi et al. 2013).

Graphene oxide (GO), a crystalline allotrope of sp²-bonded carbon with honeycomb-shaped two-dimensional nanomaterials, has attracted considerable interest (Yang et al. 2021). GO has been used in a variety of fields (e.g., high-strength materials, sensors, electromagnetism) due to its excellent mechanical and chemical properties (Jankovský et al. 2020; Chinnathambi and Euverink 2021; Zhang et al. 2021). In addition, due to its abundance of functional groups and high specific surface area (2630 m²/g), GO has considerable potential in water treatment (Li et al. 2020; Zhang et al. 2020). Many studies have been performed to investigate the GO adsorption capacity in \( \text{Hg}^{2+} \) containing wastewater. Bao et al. (2013) investigated the \( \text{Hg}^{2+} \) removal performance of magnetite/graphene oxide (MGO), and the results showed that the adsorption capacity of MGO was approximately 20 mg/g under typical working conditions (initial \( \text{Hg}^{2+} \) concentration of 10 mg/L). Palanivel et al. (2020) reported that \( \text{Hg}^{2+} \) ions could be effectively removed by GO/FeSO₄ composite adsorbents, with maximum removal efficiencies of 75% and 87.5% for \( \text{Hg}^{2+} \) and \( \text{Cd}^{2+} \), respectively. The combination of iron oxides and GO was innovative because iron oxide–based adsorbents could be easily separated from wastewater by using an external magnetic force (Qi et al. 2015). However, the lower adsorption efficiency posed a great challenge for iron oxide–based adsorbents. In general, iron oxide composites (e.g., FeSO₄, \( \text{Fe}_3\text{O}_4 \) nanoparticles) are immobilized on graphene oxide via the functional groups on GO, causing the abundant adsorption sites in GO to be consumed (Fu et al. 2015). Thus, such modifications may lead to decreased adsorption performance. In addition, the immobilized iron oxides had a limited effect on \( \text{Hg}^{2+} \) adsorption. That is, GO still played the dominant role in the adsorption process. Another issue is the high cost of GO, which may make it difficult to treat the massive amount of desulfurization wastewater emitted by power plants (Powell and Beall 2015). Thus, there is an urgent need to develop a low-cost adsorbent with high \( \text{Hg}^{2+} \) removal performance.

Tannic acid (TA), a low-cost biomass reagent that can be extracted from plants, has been reported to be an excellent adsorbent of heavy metals due to its abundance of adjacent phenolic hydroxyls (Yue et al. 2019). Taksitta et al. (2020) developed a tannin-based adsorbent for removing \( \text{Cu}, \text{Cd}, \text{Pb} \) from wastewater, and the results showed that the heavy metals could be removed effectively. However, TA exhibits good water solubility and thus cannot be collected from wastewater for reuse, which may have an impact on its further use. To overcome this disadvantage, various matrices have been used to immobilize tannic acid. Fan et al. (2019) fabricated a tannin-based adsorbent immobilized on \( \text{Fe}_3\text{O}_4\@\text{SiO}_2 \), and \( \text{Fe}_3\text{O}_4\@\text{SiO}_2\@\text{PT} \) could be easily separated from wastewater after the adsorption process. Huang et al. (2009) immobilized tannins on collagen fibers and performed adsorption experiments to investigate the \( \text{Hg}^{2+} \) adsorption performance. Wang et al. (2020a, 2020b) reported a graphene oxide–based material that was crosslinked with persimmon tannins through the desired groups for methylene blue removal. It can be inferred that tannin-immobilized graphene oxide (TAIGO) may be a feasible adsorbent for improving the adsorption performance and overcoming the water solubility of TA, and its low cost is favorable.

In this study, TAIGO was fabricated, and the adsorption performance of \( \text{Hg}^{2+} \) in desulfurization wastewater was evaluated. The effects of contact time, TAIGO dosage, pH, and ion components on removal efficiency were investigated. In addition, a possible adsorption mechanism was proposed based on the adsorption kinetics and experimental results. Furthermore, an economic evaluation was conducted to determine the economic viability of TAIGO production.

### Experimental methods

#### Materials

The reagents sulfuric acid (\( \text{H}_2\text{SO}_4 \)), hydrogen peroxide (\( \text{H}_2\text{O}_2 \)), potassium permanganate (\( \text{K}_2\text{MnO}_4 \)), hydrochloric acid (\( \text{HCl} \)), nitric acid (\( \text{HNO}_3 \)), sodium sulfite (\( \text{Na}_2\text{SO}_3 \)), and tannic acid (TA) were purchased from Nanjing Chemical Reagent Co., Ltd. Graphite was obtained from Sinopharm Chemical Reagent. Desulfurization wastewater was collected from two different coal-fired power plants in Nanjing. The compositions of desulfurization wastewater are listed in Table 1.
Immobilization of tannic acid on GO

In this paper, GO was prepared via the Hummers method, which was divided into three stages: low temperature, medium temperature, and high temperature. First, graphite and NaNO₃ were mixed at a weight ratio of 2:1, and then, a certain amount of H₂SO₄ was added to the solution and reacted in a low-temperature environment. Next, KMnO₄ was added to the solution, and the water bath temperature was maintained below 35 °C. The solution was stirred for 30 min until the solution turned brown. Then, excess deionized water was added to the mixture to ensure that the reaction temperature was below 95 °C. After stirring for 15 min, 30% H₂O₂ was used to remove the excess KMnO₄. Finally, the GO suspension was washed several times with 5% HCl and dried in a drying oven at 50 °C.

The TAIGO was prepared by the co-blending method. The GO and TA powders were mixed into 100 mL deionized water and reacted in a reflux-stirring device at 80 °C. Then, the obtained TAIGO mixture was washed with deionized water several times to remove impurities before being dried at 90 °C.

Characterization of TAIGO

Scanning electron microscopy (SEM, HITACHI S-3000 N, Japan) was used to observe the morphology of TAIGO. Atomic force microscopy (AFM, Bioscope Resolve, USA) was used to observe the structure of TAIGO. The possible adsorption mechanism was investigated by Fourier transform infrared spectroscopy (FTIR, Bruker VERTEX 70, Germany) and X-ray photoelectron spectrum (XPS, ESCALAB XI+, USA). The specific surface area (BET, GAPP V-Sorb2800P, China) was also tested to confirm the physical properties of GO and TAIGO. In addition, the zeta potential (Quantachrome DT-300, USA) was measured as an index to evaluate the adsorbent’s surface charge and charge density.

Adsorption of Hg²⁺ by TAIGO

The adsorption performance evaluation experiments were conducted in a 250 mL conical flask. As shown in Fig. 1, the adsorption experiments were conducted in a stirring apparatus to ensure adequate reaction. Then, the adsorbent was collected from the wastewater by a microfiltration membrane for later use, and the concentration of Hg²⁺ in the wastewater was determined by atomic fluorescence spectrometry (AFS, RGF-6800, China). The pH value of the wastewater was adjusted by adding a certain amount of HCl and NaOH, and then measured by a pH meter (VSTAR10, Thermo Fisher Scientific, USA). All experiments in this work were repeated at least three times, and the adsorption performance was calculated by using Eq. (1) and Eq. (2). The amount of Hg²⁺ adsorbed and the removal efficiency were based on Eq. (1) and Eq. (2), respectively:

\[
q_e = \frac{(C_o - C_e)V}{m} \tag{1}
\]

\[
R = \frac{C_o - C_e}{C_o} \times 100\% \tag{2}
\]

where \(C_o\) and \(C_e\) (mg/L) represent the initial and equilibrium concentrations of Hg²⁺ in wastewater, respectively. \(V\) (L) is the volume of the solution, and \(m\) (mg) is the weight of the adsorbent.

Results and discussion

Characterization

The physicochemical properties of GO and TAIGO were confirmed by SEM, AFM, FTIR, XRD, and XPS. The morphologies of TA, GO, and TAIGO are shown in Fig. 2. TA was smooth and round shaped, whereas GO and TAIGO exhibited layered structures, which could be explained by their polar groups (Mi et al. 2012). The formation of GO and TAIGO was also determined by AFM in the tapping mode (Fig. 3). GO had a height profile with a thickness of 1 nm, while TAIGO had a thickness of 2 nm. The AFM results indicated that GO had been prepared and that TA had been successfully immobilized on GO. The immobilization of TA was induced by SN₂ nucleophilic reactions, in which the epoxy ring on GO was destroyed by the phenolic hydroxyl group on TA (Lei et al. 2011). Other possible formation mechanisms included \(\pi-\pi\) interactions and Van der
Waals forces on aromatic ring sites (Patil et al. 2009; Li et al. 2010).

To further study the changes in the functional groups, the FTIR tests were conducted. As shown in Fig. 4(a), many functional groups were found in GO, including hydroxyl groups at 3429 cm\(^{-1}\), carbonyl groups at 1717 cm\(^{-1}\), and epoxy groups at 1118 cm\(^{-1}\). Some characteristic peaks of TA could be observed in the FTIR spectra of TAIGO, which confirmed that TA was successfully coated on GO. Furthermore, it was found that the signals attributed to epoxy groups were significantly weakened, which was related to the ring-opening reactions of epoxy groups during the synthesis process (Eftekhari et al. 2018). In addition, the crystalline structure of TAIGO was studied using XRD analysis. The XRD patterns of GO, TAIGO, and TA are shown in Fig. 4(b). It was found that GO had a typical diffraction peak at 2\(\theta\) = 12.7\(^{\circ}\), which was shifted to 9.9\(^{\circ}\) after TA immobilization (Sun et al. 2020). This shift could be due
The addition of the functional groups inserted between the GO layers, causing an increase in interval spacing from 7 to 8.9 Å (Jia and Wang 2018). The peak at 23.8° was similar to the typical diffraction of TA, indicating that TA was grafted onto GO.

The XPS was used to investigate the changes in the elemental composition and chemical structure properties of TAIGO before and after Hg$^{2+}$ adsorption. The XPS full spectra of TAIGO showed photoelectron lines with binding energies of approximately 285 and 533 eV attributed to C 1s and O 1s, respectively (Fig. 5(a)). After the Hg$^{2+}$ adsorption process, a peak in the Hg 4f spectrum with a binding energy of about 102 eV appeared in the XPS full spectra of TAIGO. In addition, the Hg 4f spectrum (Fig. 5(d)) had two peaks at 101 eV and 105 eV, corresponding to the spin-orbital components of the Hg4f$_{7/2}$ and Hg4f$_{5/2}$ states, respectively. It was indicated that TAIGO adsorbed Hg$^{2+}$ in the form of surface complexes (Ehrhardt et al. 2015).

The deconvolution of the C 1s peak of TAIGO (Fig. 5(b)) revealed three peaks at 284.8, 286.9, and 288.8 eV, which were assigned to nonoxygenated sp$^2$ carbon domains (C–C), C–O bonds, and O–C=O functional groups, respectively (Zhang et al. 2021). However, after the adsorption process, the binding energies of the C–O and O–C=O bonds were shifted to 287.1 eV and 289 eV, respectively. In contrast, the binding energy of the nonoxygenated sp$^2$ carbon domains was unchanged (Fig. 5(c)). The normalized intensities of the C–O and O–C=O bonds were also changed. All these facts suggested that the oxygen-containing functional groups played a crucial role in the adsorption process. The adsorbed Hg$^{2+}$ would affect the oxygen-containing functional groups in TAIGO. When the Hg$^{2+}$ was adsorbed on the adsorption sites of TAIGO, the electronic density around the oxygen-containing functional groups decreased, causing the binding energy and relative fraction of these specific bonds to change (Huang et al. 2009).

### Adsorption performance

To compare the differences in removal efficiency between GO and TAIGO, adsorption experiments in actual desulfurization wastewater were conducted. As shown in Fig. 6, the removal efficiencies of GO and TAIGO in desulfurization wastewater A were 80.23% and 90.39%, respectively, and those in desulfurization wastewater B were 65.44% and 78.06%. TAIGO had a better adsorption performance than GO due to the induced abundance of adjacent phenolic hydroxyl groups on TA. The specific surface area and zeta potential results, shown in Table 2, indicated that TAIGO exhibited a larger specific surface area and higher charge properties, which may improve its removal performance of Hg$^{2+}$ in wastewater. Additionally, the leaching of TA should
be considered due to its high water solubility. According to Xu's work, the detection of free TA was carried out by using FeCl₃ solution (Xu et al. 2017). The results showed that TAIGO exhibited excellent stability in the adsorption process, with no TA leakage detected.

**Effect of operation parameters**

To better understand the factors affecting adsorption performance, simulated desulfurization wastewater prepared by Hg²⁺ solution was used instead of actual wastewater in the following experiment.

**Effect of contact time**

Figure 7 shows the effect of reaction time on the Hg²⁺-removal efficiency. The removal efficiency increased quickly in the initial 10 min, and the adsorption process was completed within 15 min. It can be inferred that the adsorption process was quick and that complete adsorption took a short time. At the initial adsorption stage, the Hg²⁺ concentration in the desulfurization wastewater was relatively high, which caused the adsorption driving force to increase. Furthermore, a large number of adsorption sites of TAIGO were available within 15 min. After a while, the adsorption sites became occupied, leading to a slow increase in removal efficiency.

**Table 2** The specific surface area and zeta potential of GO and TAIGO

| Material | Specific surface area (m²·g⁻¹) | Zeta potential (mV) |
|----------|--------------------------------|--------------------|
| GO       | 430                            | −42.8              |
| TAIGO    | 562                            | −48.5              |
Effect of TAIGO dosage

The amount of adsorbent was a critical metric for industrial applications. The effect of adsorbent dosage was studied by adding different amounts of TAIGO into a 250 mL Hg\(^{2+}\)-containing solution. The reaction time was set to 120 min to ensure that the adsorption process was completed. As shown in Fig. 8, as the dosage of TAIGO increased from 5 to 10 mg, the Hg\(^{2+}\)-removal efficiency increased from 56.28 to 92.1%, and the removal efficiency gradually stabilized as the dosage of TAIGO was further increased to 20 mg. As the adsorbent amount increased, the number of adsorption sites of Hg\(^{2+}\) gradually increased, increasing the likelihood of binding between TAIGO and Hg\(^{2+}\). However, no remarkable changes in removal efficiency were observed as the adsorbent dosage was increased further. It can be inferred that the adsorption process reached a saturation point and that the surface of TAIGO adsorption sites overlapped, restricting further improvement in the removal efficiency.

Effect of pH

The pH value of the wastewater affects the existence of functional groups in the adsorbent and changes the form of Hg\(^{2+}\) in the desulfurization wastewater (Wang et al. 2015). Thus, it is essential to investigate the effect of pH on the adsorption performance of Hg\(^{2+}\). As presented in Fig. 9, as the pH value increased from 3 to 12.3, the removal efficiency first increased and then decreased. The optimal removal efficiency was obtained at a pH of 9. This phenomenon could be explained by the following reasons. When the pH value of wastewater was lower than 7, most of the mercury ions in the desulfurization wastewater were in the valence state of Hg\(^{2+}\), and the excess H\(^+\) ions would bind to the adsorption sites of TAIGO, resulting in a decrease in adsorption capacity toward Hg\(^{2+}\). It was noted that the adjacent phenolic hydroxyl groups on TA were sensitive to the presence of H\(^+\), and the lower pH value was conducive for chelating Hg\(^{2+}\) in desulfurization wastewater (Huang et al. 2009). As the pH value increased to 9, the ionization degree of phenolic hydroxyl groups located in TA increased, leading to enhanced chelation and electrostatic effects between TAIGO and Hg\(^{2+}\) (Sun et al. 2020; Ma et al. 2006). However, as the pH value further increased above 9, the Hg\(^{2+}\) in the desulfurization wastewater was easily converted into insoluble Hg(OH)\(_2\), which was directly related to the decrease in adsorption capacity.
Effect of ion components

To evaluate the adsorption performance of TAIGO in the complex wastewater component, the adsorption experiments in the presence of different ion components were conducted. In actual desulfurization wastewater, the concentration of Cl\(^-\) ranged widely from 4000 to 20,000 mg/L, which may affect the adsorptive capacity for Hg\(^{2+}\). The effect of chloride ions (Cl\(^-\)) on the adsorption efficiency is shown in Fig. 10(a). TAIGO showed excellent adsorption performance (88.2%) at a low concentration of Cl\(^-\) (12,000 mg/L). However, as the chloride ion concentration increased, the adsorption efficiency of TAIGO gradually decreased. This result could be attributed to excess chloride ions in the slurry were likely to accumulate on the surface of TAIGO, resulting in a decrease in adsorbent surface charge. In addition, it was reported that Hg\(^{2+}\) tended to form Hg(OH)\(_2\) and to further form HgCl(OH) and HgCl\(_2\)\(^{2-}\) in a solution containing chloride ions, which may further hinder the adsorption performance (Castro et al. 2011).

Furthermore, the effect of SO\(_3\)\(^{2-}\) was investigated in this work. Although the concentration of SO\(_3\)\(^{2-}\) in desulfurization wastewater was relatively low, it may cause the migration and conversion of Hg\(^{2+}\) (Wu et al. 2019). Figure 10(b) shows the effect of the concentration of SO\(_3\)\(^{2-}\) on the removal efficiency. As the concentration of SO\(_3\)\(^{2-}\) increased to 700 mg/L, the removal efficiency remained at 88.2%. When the concentration exceeded 700 mg/L, the inhibitory effect of SO\(_3\)\(^{2-}\) on the adsorption efficiency gradually increased, and the adsorption efficiency was reduced to 75.6%. It was reported that SO\(_3\)\(^{2-}\) was an essential factor in reducing Hg\(^{2+}\) in desulfurization wastewater to Hg\(^0\) and releasing it into the atmosphere (Ma et al. 2018). However, due to the relatively low wastewater temperature (room temperature of 20\(^\circ\)C) in this work, Hg-S(IV) decomposition was difficult, resulting in limited mercury re-emission (below 2%); the mercury re-emission was measured by using a mercury vapor monitor, Mercury Instruments, Germany). With the addition of SO\(_3\)\(^{2-}\), the Hg\(^{2+}\) in wastewater reacts with the abundant SO\(_3\)\(^{2-}\) to form HgSO\(_3\) and Hg(SO\(_3\))\(_2\)\(^{2-}\) (Eqs. (3) and (4)) (Hsu et al. 2021). In addition, Hg\(^{2+}\) accelerates the free radical reactions, causing SO\(_3\)\(^{2-}\) to be oxidized to SO\(_4\)\(^{2-}\) (Wu et al. 2004). As a result, less Hg\(^{2+}\) can be involved in the chemical adsorption reaction, which may cause a low adsorption efficiency.

\[
\text{Hg}^{2+} (\text{aq}) + \text{SO}_3^{2-} (\text{aq}) \rightarrow \text{HgSO}_3 (\text{aq})
\] (3)
HgSO₃(aq) + SO₃²⁻(aq) → Hg(SO₃)₂⁻(aq) \quad (4)

In addition, with the development of desulfurization wastewater concentration technology, the concentrations of Ca²⁺, Mg²⁺, and Na⁺ can vary extensively. Therefore, the effect of Ca²⁺, Mg²⁺, and Na⁺ concentrations was considered, and the results are displayed in Fig. 11. As the concentrations of Ca²⁺, Mg²⁺, and Na⁺ increased from 2000 to 6000 mg/L, there was no significant decrease in the adsorption efficiency. The main reason is that the lack of d or f electron orbitals may cause the interaction force between Hg²⁺ and ions to weaken. In other words, the interaction between Hg²⁺ and TAIGO was stronger than that between Ca²⁺ and Mg²⁺, and the presence of Ca²⁺, Mg²⁺, and Na⁺ did not affect the adsorption efficiency of TAIGO (Sun et al. 2014).

**Adsorption kinetics**

Adsorption kinetics provided vital information about the mechanism of Hg²⁺ adsorption onto TAIGO, which was necessary to determine the adsorption behavior of TAIGO.

In this study, pseudo-first-order and pseudo-second-order kinetic models were used to fit the adsorption process. The pseudo-first-order and pseudo-second-order kinetic models were represented by the following equations:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

\[
\frac{1}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

where \(q_e\) and \(q_t\) (mg/g) are the ions adsorbed at the equilibrium state and time \(t\) (min). The \(k_1\) and \(k_2\) (g/(mg-min)) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively.

Figure 12 shows the fitting curves for the adsorption of Hg²⁺ with TAIGO at natural pH. The correlation coefficient \((R^2 = 0.9995)\) of the pseudo-second-order kinetic model was larger than that of the pseudo-first-order kinetic model, which indicated that chemical adsorption played a significant role in the adsorption of Hg²⁺ and that physical adsorption promoted the adsorption performance (Anbia and Amirmahmoodi 2016).
In addition, the parameters $k_1$ and $k_2$ were essential indices for evaluating the adsorbent performance. Table 3 lists the adsorption rate constants based on the pseudo-first-order and pseudo-second-order kinetic models for $\text{Hg}^{2+}$ adsorption. Furthermore, a comparative analysis between TAIGO and other reported GO-based materials was performed. Table 4 shows that TAIGO had superior adsorption performance when compared to other materials, as well as a shorter equilibrium adsorption time.

The probable $\text{Hg}^{2+}$ removal mechanism is shown in Fig. 13. For TAIGO, in desulfurization wastewater, the considerable surface area of GO acted as a large net to capture $\text{Hg}^{2+}$ and served as the carrier for TA. Additionally, the functional groups in GO could improve the $\text{Hg}^{2+}$ removal performance. Furthermore, TA’s multiple ortho-position phenolic hydroxyl structure functioned as a multibase ligand for complex reactions with $\text{Hg}^{2+}$. A stable five-membered chelate ring with $\text{Hg}^{2+}$ formed, which further improved the removal efficiency. Thus, GO and TA were both involved in the adsorption process, and $\text{Hg}^{2+}$ was effectively removed from desulfurization wastewater.

### Economic evaluation

An economic evaluation was conducted in this work, including regeneration performance and cost analysis. For the regeneration performance, a strongly acidic environment was prepared, and 0.1 mol/L HCl was used to elute the adsorbent. The removal efficiency remained at 88% after three recycles, as shown in Fig. 14. As discussed regarding the effect of pH, excess $\text{H}^+$ resulted in protonation of TAIGO and replacement of $\text{Hg}^{2+}$, thereby achieving excellent desorption efficiency. However, the decomposition of adsorbents occurred during the elution process, leading to a slight decrease in efficiency in the third adsorption step compared to that in the first adsorption step.

### Table 3 Kinetic parameters for the adsorption on TAIGO adsorbent

| Kinetic model | $K_1$ (mg/g) | $q_e$ (mg/g) | $R^2$ |
|--------------|-------------|-------------|-------|
| Pseudo-first order | 0.111 | 10.08 | 0.691 |
| Pseudo-second order | 0.047 | 23.81 | 0.9995 |

### Table 4 Comparison of adsorption capacities with various adsorbents for heavy metals

| Adsorbents | Target pollutant | Kinetic | Adsorption capacity (mg/g) | Equilibrium time (min) | Ref |
|------------|-----------------|---------|---------------------------|------------------------|-----|
| Thiol-functionalized silica-coated magnetite | $\text{Hg}^{2+}$ | PSO | 9.5 | 15 | Hakami et al. (2012) |
| EDTA functionalized graphene oxide nanoparticles | $\text{Hg}^{2+}$ | PSO | 18.6392 | 160 | Sun et al. (2020) |
| Magnetic nanoparticle–graphene oxide | $\text{Se}^{4+}$ | - | 4.99 | 0.2 | Fu et al. (2015) |
| Persimmon tannin/graphene oxide composites | $\text{Ge}^{4+}$ | - | 117.38 | - | Zhang et al. (2019) |
| Magnetite/reduced graphene oxide nanocomposites | $\text{Pb}^{2+}$ | PSO | 13.87 | 180 | Qi et al. (2015) |
| Tannin-immobilized graphene oxide | $\text{Hg}^{2+}$ | PSO | 23.81 | 15 | This paper |
Furthermore, a cost analysis was performed to evaluate the economic viability of TAIGO production. Based on Aladdin Reagent Company’s data, the price of GO was 326.8 USD per gram, while the price of TA was only 0.2 USD per gram. That is, tannin-immobilized graphene oxide could reduce the cost of raw materials by at least 30%. Therefore, due to its excellent regeneration performance and relatively low cost, TAIGO is a potential candidate for large-scale production.

**Conclusion**

In this work, a novel adsorbent based on tannin-immobilized graphene oxide was proposed, and the adsorption performance of TAIGO was evaluated under different conditions.

The prepared TAIGO exhibited an excellent adsorption performance for Hg\(^{2+}\) in desulfurization wastewater, which was attributed to the functional groups in GO and TA. The pseudo-second-order kinetic model fits the adsorption process well. In addition, the removal efficiency of Hg\(^{2+}\) was influenced by many factors, such as the contact time, adsorbent dosage, pH, and ion components. The experimental results showed that the adsorption process was completed within 15 min and that increasing the adsorbent dosage increased the removal efficiency. The pH value affected the protonation process of TAIGO and the form of Hg\(^{2+}\) in wastewater. The optimal removal efficiency was obtained at a pH of 9. In terms of the ion component, high concentrations of Cl\(^-\) and SO\(_3\)\(^{2-}\) hindered adsorption, while SO\(_4\)\(^{2-}\) and cations had a negligible impact. In addition, the excellent economic benefits of TAIGO were analyzed in an economic evaluation experiment, indicating that TAIGO is a cost-effective adsorbent that could be further used in practical desulfurization wastewater.

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**Author contribution**

Heng Chen: Conceptualization, methodology, formal analysis, investigation, resources, writing original draft, writing—review and editing.

Fengjun Liu: Methodology, investigation, review and editing.

Chenjian Cai: Methodology, resources, writing—review and editing.

Hao Wu: Conceptualization, writing—review and editing, supervision.

Linjun Yang: Conceptualization, writing—review and editing, supervision.

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**Availability of data and materials**

All data generated or analyzed during this study are included in this published article.

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*Fig. 13* The probable Hg\(^{2+}\) removal mechanism

*Fig. 14* The regeneration performance of TAIGO (C\(_0\)=1 mg/L, V=0.25 L, m=10 mg, natural pH, reaction time = 120 min, eluted by HCl)
Declarations

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

Ethics approval Not applicable.

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Authors and Affiliations

Heng Chen1 · Fengjun Liu1 · Chenjian Cai1 · Hao Wu2 · Linjun Yang1

1 Key Laboratory of Energy Thermal Conversion and Control of Ministry Education, School of Energy and Environment, Southeast University, Nanjing, China

2 School of Energy & Mechanical Engineering, Nanjing Normal University, Nanjing, China