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### Separation and Purification Technology



journal homepage: www.elsevier.com/locate/seppur

# Selective adsorption characteristics of g-C<sub>3</sub>N<sub>4</sub> for Hg<sup>0</sup> and HgCl<sub>2</sub>: A DFT study and experimental verification

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#### ARTICLE INFO

Editor: Z. Bao

Keywords: Mercury Graphitic carbon nitride Selective adsorption Weak interaction Polyatomic binding

#### ABSTRACT

The partitioning of  $Hg^0$  and  $HgCl_2$  with selective adsorbent is an essential technology for the mercury continuous emission monitoring system (Hg-CEMS), but the existing adsorbents fail to satisfy the prolonged operational demands of Hg-CEMS due to the irreversible deactivation. This work proposed a novel regenerable selective adsorbent material, g-C<sub>3</sub>N<sub>4</sub>, and delved into the selective adsorption behaviors of  $Hg^0$  and HgCl<sub>2</sub> on the g-C<sub>3</sub>N<sub>4</sub> using DFT calculations and experiments. The results show that g-C<sub>3</sub>N<sub>4</sub> has a strong affinity for HgCl<sub>2</sub>, with the binding energy of -0.843 eV, whereas  $Hg^0$  is only weakly adsorbed. The electronic structure and weak interaction analysis reveal both  $Hg^0$  and HgCl<sub>2</sub> are coupled to g-C<sub>3</sub>N<sub>4</sub> via van der Waals. Further, COHP calculation demonstrates that the adsorption of  $Hg^0$  and HgCl<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> is essentially the consequence of polyatomic cobinding energy. The experiments confirmed the effective capability of g-C<sub>3</sub>N<sub>4</sub> in separating  $Hg^0$  and HgCl<sub>2</sub>, along with its thermal regeneration potential. It maintains a breakthrough rate of over 98 % for  $Hg^0$  and less than 1.6 % for HgCl<sub>2</sub>. This work updates the conventional chemical adsorption-based methods for the separation of  $Hg^0$  and HgCl<sub>2</sub> enhances the comprehension of separating both  $Hg^0$  and HgCl<sub>2</sub> while concurrently broadening the understanding of the interaction between g-C<sub>3</sub>N<sub>4</sub> and small molecules.

#### 1. Introduction

Mercury and its derivatives, possessing atmospheric transportability, neurotoxicity, and bioaccumulation, attract wide concerns because of its destructive damage to both human health and the ecological environment [1,2]. Coal-fired power plants are recognized as one of the prominent sources of anthropogenic mercury emissions, responsible for over 20 % of global anthropogenic mercury emissions into the atmosphere [3]. With the heightened awareness of the need for environmental preservation, worldwide standards for mercury emissions are becoming increasingly stringent, and a series of pertinent rules have been implemented [4]. To effectively expedite the implementation of monitoring and controlling mercury pollution emissions from coal-fired power plants, the sampling and online measuring of mercury in coal-fired flue gas have emerged as an indispensable technical component.

There are two forms of gaseous mercury in coal combustion flue gas, namely elemental mercury  $(Hg^{0})$  and oxidized mercury  $(Hg^{2+})$ ,

whichever possesses unique properties and characteristics [5]. The contrasting physical, chemical, and biological attributes of Hg<sup>0</sup> and Hg<sup>2+</sup> engender dissimilar impacts on the ecological environment and human health. Therefore, it is necessary for Hg speciation measurement [6,7]. Atmospheric mercury emission monitoring techniques are divided into three categories: Ontario hydro method [8] (OHM), EPA Method 30B [9], and the mercury continuous emission monitoring system [10]. The OHM and EPA Method 30B are offline sampling techniques with shared limitations, including cumbersome sampling and analysis processes, substantial reagent consumption, and susceptibility to humaninduced errors. In contrast, Hg-CEMS is a promising approach for automatically continuous monitoring of Hg<sup>0</sup> and Hg<sup>2+</sup>, featuring highly integrated flue gas sampling system, mercury separation and conversion system, mercury analysis module, and calibration module. Since the existing analytical techniques for the detection of mercury are limited to measuring gas-phase Hg<sup>0</sup>, to achieve the speciation measurement of  $Hg^{2+}$  and  $Hg^{0}$ , it is necessary to effectively separate them and convert

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https://doi.org/10.1016/j.seppur.2023.126103

Received 7 October 2023; Received in revised form 3 December 2023; Accepted 16 December 2023 Available online 18 December 2023 1383-5866/© 2023 Elsevier B.V. All rights reserved.  $Hg^{2+}$  into  $Hg^{0}$  [11]. The specific approach in Hg-CEMS works as follows: the separation and conversion module is composed of two paths, one path to selectively capture  $Hg^{2+}$  in the flue gas through the selective adsorbent or alkaline solutions to detect Hg<sup>0</sup> concentration; the other to convert Hg<sup>2+</sup> to Hg<sup>0</sup> through high-temperature reduction or catalytic reduction to detect the total mercury (Hg<sup>T</sup>) concentration [12]. The  $Hg^{2+}$  concentration is calculated by subtracting  $Hg^0$  from  $Hg^T$ . Hence, the selective collection of  $Hg^{2+}$  via effective approaches is vital for the monitoring of mercury speciation concentrations. Solution absorption and solid selective adsorbent [13] are frequent  $Hg^0/Hg^{2+}$  separation techniques. The former involves the absorption of  $Hg^{2+}$  from the gaseous phase into a solution, leaving Hg<sup>0</sup> in the gas phase; and the latter relies on the selective adsorption of  $Hg^{2+}$  onto solid adsorbents. Notably, the technique of solution absorption for separating  $Hg^{2+}$  is commonly accompanied by the concomitant absorption of more reductive SO<sub>2</sub>, which causes enrichment of  $SO_3^{2-}$  in solution and leads to the reduction of  $Hg^{2+}$  to  $Hg^0$  [14,15]. In addition, a substantial volume of wastewater is generated throughout the procedure. Consequently, the separation of Hg<sup>0</sup>/HgCl<sub>2</sub> employing solid selective adsorbent is an advanced approach.

HgCl<sub>2</sub>, as the primary form of oxidized mercury in flue gas, exhibits weak acidity. Based on this trait, the prevailing method for separating HgCl<sub>2</sub> involves supporting the alkaline components (CaO, KCl, and so on) onto the surface of carrier materials with well-established porous structure [16]. This method utilizes chemical adsorption to selectively capture HgCl<sub>2</sub>. Prestbo et al. [17] identified the effective selective binding capacity of KCl/lime sorbents towards Hg<sup>2+</sup>, achieving a selective adsorption efficiency exceeding 90 %. Tang et al. [16] calculated the adsorption behavior of  $Hg^0$  and  $Hg^{2+}$  on typical alkali metal chlorides (KCl, NaCl) and oxides of alkaline-earth metals (CaO, MgO) using density functional theory (DFT). The outcomes suggested that alkali metal adsorbents chemisorbed with HgCl2 and Lewis acid-base interaction was the essence of the bonding of HgCl<sub>2</sub> with the adsorbent. Simultaneously, the physical adsorption of Hg<sup>0</sup> was proved comparably feeble. Li et al. [18], through fixed-bed experiments, also confirmed the favorable Hg<sup>2+</sup> selectivity exhibited by calcium-based adsorbents. However, there exists a significant amount of acid gas in the flue gas, with acidity and concentration far exceeding that of HgCl<sub>2</sub>. These acid gases compete with HgCl<sub>2</sub> for the active sites on the alkaline sorbents, leading to irreversible deactivation of the adsorbents. Sasmaz [19] and Tang [20] confirmed experimentally and theoretically that SO<sub>2</sub> and HgCl<sub>2</sub> undergo intensely competitive reaction on alkaline adsorbent, and the adsorption energy of SO<sub>2</sub> with CaO was -167.55 kJ/mol, substantially greater than that of HgCl<sub>2</sub> (-95 kJ/mol). In addition, the adsorbent is prone to produce CaSO3 in the presence of SO2, and the reducing properties of  $CaSO_3$  are prone to transform  $Hg^{2+}$  to  $Hg^0$ , causing significant interference with the analysis of  $\mathrm{Hg}^{2+}$  sample measurement. The identical  $CaO/\gamma$ -Al<sub>2</sub>O<sub>3</sub> adsorbent as reported by Zheng [21] was prepared and found that the adsorption of  $Hg^{2+}$  exceeded 95 % within the N<sub>2</sub> atmosphere. Regrettably, when subjected to low concentrations of simulated flue gas, the samples completely failed within 12 h in our previous tests. Conclusively, traditional alkali metal adsorbents effectively facilitate the segregation of Hg<sup>0</sup> and Hg<sup>2+</sup>; yet, their performance in the face of intricate flue gas conditions, particularly in the presence of acidic gases, is markedly hindered. The adsorption efficiency is substantially declined, and the operational lifespan is considerably shortened. These limitations are insufficient for Hg-CEMS to operate for long periods. Hence, a novel adsorbent that is unaffected by flue gas components is highly required.

It has consistently adduced in the published papers that the pristine graphitic carbon nitride  $(g-C_3N_4)$  is evinced the feeble adsorption capacity for Hg<sup>0</sup> [22,23] and less adsorption energy with regard to CO<sub>2</sub> [24], H<sub>2</sub>O [25], O<sub>2</sub> [26], SO<sub>2</sub> [27], and other components [28–30], manifesting that it is commendable acid resistance. Additionally, it was confirmed in previous work that g-C<sub>3</sub>N<sub>4</sub> exhibited a well-defined affinity for Hg<sup>2+</sup> [31–33]. These observations highlight the significant potential

of  $g-C_3N_4$  as a selective adsorbent for  $Hg^{2+}$ . However, the inherent adsorption of  $g-C_3N_4$  towards  $Hg^0$  and  $HgCl_2$  remains unclear, and the separation mechanism of  $Hg^0$  and  $HgCl_2$  is yet to be elucidated. Therefore, it is imperative to clarify the adsorption behavior and binding modes of  $g-C_3N_4$  on  $Hg^0$  and  $HgCl_2$ . In this work, the adsorption characteristics of  $Hg^0$  and  $HgCl_2$  on  $g-C_3N_4$  surface were systematically investigated. The adsorption conformation at various adsorption sites was constructed, and the corresponding adsorption energies, deformation energies, and binding energies, were compared to determine the most stable adsorption state. The essence of binding of  $Hg^0$  and  $HgCl_2$  with  $g-C_3N_4$  and the mechanism for selective adsorption were revealed with electronic structure analysis and weak interaction analysis. Experimentally, the performance of  $g-C_3N_4$  as selective adsorbent for the adsorption of  $Hg^0$  and  $HgCl_2$  was confirmed.

#### 2. Method

#### 2.1. Computational method

The first principles calculation of Hg<sup>0</sup>/HgCl<sub>2</sub> adsorption on g-C<sub>3</sub>N<sub>4</sub> surface was performed with Vienna Ab initio Simulation (VASP) Package. The projector-augmented wave (PAW) method was adopted to simulate the Electron-ion interactions, and the exchange-correlation energy was studied using the Perdew-Burke-Ernzerhof (PBE) function with the DFT-D3 correction [34,35]. To prevent undesirable interactions between the slab and periodic structure, a 15 Å vacuum region was embedded. The convergence standards for the self-consistent iteration energy and forces in structural relaxation were set to  $1.0 \times 10^{-5}$  eV, 0.02 eV/Å, respectively, and the plane wave cutoff energy was set to 500 eV [36]. The irreducible Brillion zone sampling was performed with a regular Monkhorst–Pack grid of  $3 \times 3 \times 1$  K-points. The precise density of states (DOS) was obtained using Heyd - Scuseria - Ernzerhof (HSE06) hybrid functional with a Monkhorst–Pack K-point of  $7 \times 7 \times 1$ . The adsorption energy (Eads) of adsorbate molecules on the g-C3N4 system was determined by Equation (1) [37]:

$$E_{ads} = E_{sys} - E_{gas} - E_{sorbent} \tag{1}$$

where  $E_{sys}$ ,  $E_{gas}$ ,  $E_{sorbent}$ , are the total energies of the absorption system, the energy of Hg<sup>0</sup>/HgCl<sub>2</sub> in the calculated supercell, the energy of pristine g-C<sub>3</sub>N<sub>4</sub>, respectively.

The deformation energy  $(E_{def})$  was employed to assess the thermodynamic stability of the adsorbent or adsorbate after involvement in the adsorption process and calculated by **Equation** (2) and **Equation** (3):

$$E_{def}(gas) = E'_{gas} - E_{gas}$$
<sup>(2)</sup>

$$E_{def}(g - C_3 N_4) = E'_{g - C_3 N_4} - E_{g - C_3 N_4}$$
(3)

where  $E_{def}$  (gas) and  $E_{def}$  (g- $C_3N_4$ ) represent the deformation energy of gas molecules and the deformation energy of g- $C_3N_4$ , respectively.  $E'_{gas}$ and  $E'_{g} - C_{3N_4}$  are the energy of the Hg<sup>0</sup> or HgCl<sub>2</sub> gas molecule and the g- $C_3N_4$  surface separated from the optimized adsorption system, respectively, maintaining the same structure [38].  $E_{gas}$  and  $E_{g-C3N_4}$  are the energy of gas molecules in the calculated supercell, the energy of pristine g- $C_3N_4$ , respectively.

 $g-C_3N_4$  tends to bends deforms, which cause a part of the energy to be released in the adsorption process. The adsorption energy fails to take this portion of energy into account, thus rendering it inadequate to accurately describe the binding strength between the adsorbent and the adsorbate. To precisely figure out the strength of the intrinsic interaction between the adsorbent and the adsorbate, the binding energy (E<sub>b</sub>) was adopted as the discriminant criterion, defined as **Equation** (4) [39,40]:

$$E_{b} = E_{ads} - E_{def}(gas) - E_{def}(g - C_{3}N_{4})$$
(4)

In addition, the interaction region indicator (IRI) with promolecular approximation based on the reduced density gradient (RDG) and Quantum Theory of Atoms in Molecules (QTAIM) were derived for uncovering the type and strength of the interaction between the adsorbent and the adsorbate utilizing the Multiwfn 3.7 [41]. Crystal orbital Hamilton population (COHP) was evaluated with lobster-4.1.0, and the plot was exported using VMD 1.9.3 software. The adsorption system of Hg<sup>0</sup> and HgCl<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub> were labeled as g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, respectively.

#### 2.2. Experimental method

To validate the reasonableness of the DFT calculated result, a series of experiments were conducted on a fixed bed at the temperature of 120 °C, the experimental setup is shown in Fig. 1.  $Hg^0$  and  $HgCl_2$  are generated through the mercury permeation device (VICI Metronics Inc; USA) placed in a water bath, and the concentration of Hg<sup>0</sup>/HgCl<sub>2</sub> is controlled by modulating the temperature of the water bath, with the concentrations of  $\text{Hg}^0$  and  $\text{HgCl}_2$  being constant at 80  $\mu\text{g/m}^3$  and 160  $\mu g/m^3$ , respectively. The mercury vapor is transported by N<sub>2</sub> at a rate of 200 ml/min to the mixing chamber, where it is blended with 800 ml/ min of balance N<sub>2</sub> and subsequently, it enters the fixed bed reactor. The reactor consists of a heating furnace and a quartz tube with the inner diameter of 8 mm and the outer diameter of 10 mm. For the experiments of Hg<sup>0</sup> adsorption, a single section of the adsorbent weighing 100 mg is positioned on the middle of the quartz tube, with the filling height of approximately 15 mm, and the concentration of Hg<sup>0</sup> is monitored online by automatic mercury online analyzer (Lumex RA-915). As for the experiments of HgCl<sub>2</sub> adsorption, following the EPA Method 30B [9], the adsorbent is stuffed in two segments, with each segment containing 100 mg of the sample, designated as the adsorption section and the breakthrough section, respectively. The content of mercury in the solid adsorbent is detected by Lumex RA-915 attached by a Pyro-915 + solid module. Prior to being expelled, the exhaust gases are treated by activated carbon adsorption. All pipelines maintain at a constant temperature of 120°C to prevent HgCl<sub>2</sub> adsorption during the experiment.

The breakthrough rate for adsorbents was adopted in this work to evaluate the selective adsorption performance of  $Hg^0$  and  $HgCl_2$ . The breakthrough rate of  $Hg^0$  is determined as in **Equation** (5):

$$\eta_{Hg^0} = \frac{C_{out}}{C_{in}} \times 100\% \tag{5}$$

where  $C_{in}$ ,  $C_{out}$  denote the inlet and outlet Hg<sup>0</sup> concentrations of the fixed bed, respectively.

The breakthrough rate of  $HgCl_2$  is determined as in **Equation** (6):

$$\eta_{H_gCl_2} = \frac{m_2}{m_1 + m_2} \tag{6}$$

where  $m_1$ ,  $m_2$  are the mass of mercury in the adsorption and breakthrough sections, respectively.

To study the thermal regeneration potential of the adsorbent, the performance of g- $C_3N_4$  for HgCl<sub>2</sub> adsorption at various temperatures was investigated, and the HgCl<sub>2</sub> adsorption rate is calculated by **Equation** (7):

$$\xi_{ads} = \frac{m_{ads}}{m_{tatal}} \tag{7}$$

where  $m_{ads}$  represents the adsorption mass of HgCl<sub>2</sub> at that temperature,  $m_{tatal}$  is the total mass of HgCl<sub>2</sub>.

#### 2.3. Adsorbent preparation and characterization

The g-C<sub>3</sub>N<sub>4</sub> used in the experiments were prepared by thermal polycondensation, and the preparation procedure was as follows: urea, melamine, dicyandiamide, and thiourea were selected as precursors, and the precursors were calcined in a muffle furnace at 550 °C for 240 min with a heating rate of 2.5 °C/min. After natural cooling, a pale yellow product was obtained, ground into a powder of 40–60 mesh, and placed aside. Since the urea-prepared g-C<sub>3</sub>N<sub>4</sub> was extremely flimsy, it was pressed before grinding.

X-ray diffraction (XRD) was measured on a D8-ADVANCE diffractometer (Bruker, USA) to obtain crystal phase information and to determine the product  $g-C_3N_4$  after thermal polycondensation.

#### 3. Results and discussion

#### 3.1. Optimized structure of pristine $g-C_3N_4$ and adsorption site

Fig. 2(a) demonstrates the outcomes of lattice parameter optimization. Initially, the calculated range of lattice parameters was set to a = b = 6.96-7.20 Å, 2D g-C<sub>3</sub>N<sub>4</sub> presents a planar structure, the lowest energy is obtained at a = b = 7.13 Å, consistent with other calculations results [24,42,43]. However, previous work has shown that the g-C<sub>3</sub>N<sub>4</sub> surface tends to distort and buckle upon adsorption and doping [22,44], resulting in enhancing structural stability. Consequently, the lattice parameters a and b were further reduced. It is discovered that for  $a = b \le 6.95$  Å, the 2D g-C<sub>3</sub>N<sub>4</sub> structure experiences pronounced deformation and buckling, resulting in a further decrease in energy. The minimum energy and the most stabilized structure were identified at a = b = 6.94Å. To compare the two fundamental substrates, both planar and buckled adsorption configurations were calculated in this work. The pristine 2D



Fig. 1. Schematic diagram of fixed bed system for Hg<sup>0</sup>/HgCl<sub>2</sub> adsorption evaluation.



Fig. 2. (a) Lattice parameter optimization; (b) pristine structure of g-C<sub>3</sub>N<sub>4</sub>; Brown, gray spheres: indicate C, N atoms, respectively.

 $g-C_3N_4$  structure was attained by cleaving  $g-C_3N_4$  along the (001) direction of the unit cell [40]. Subsequently, a 2  $\times$  2 supercell was constructed, as depicted in Fig. 2(b).

As illustrated in Fig. 3, based on the  $g-C_3N_4$  cell symmetry, N atoms can be categorized into three types and C atoms into two types, which are designated for convenience as N1, N2, N3, C1, C2. The top, bridge, and hollow sites are the most typical adsorption sites, and thus 11 representative adsorption sites were identified, including five top sites (N1, N2, N3, C1, C2), four bridge sites (midpoint of C-N bonds, labels B1, B2, B3, B4), and two hollow sites (one located at the center C-N sixmembered ring, marked as A1; another situated the center of the gap enclosed by three triplet triazine units, designated as A2).

The model of  $\text{Hg}^0$  molecule adsorbed onto the g-C<sub>3</sub>N<sub>4</sub> surface at various sites, prior to undergoing geometry optimization, is depicted in Fig. **4(a)**. HgCl<sub>2</sub> adsorption is subdivided into vertical and parallel configurations. The parallel models are presented in Fig. **4(b)**, while the vertical conformation is analogous to the Hg<sup>0</sup> adsorption model, with the difference that the Cl atom is at the bottom. The value of "d" in Fig. 4 indicates the distance between Hg<sup>0</sup>/HgCl<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> surface, with d setup 2.5 Å. Moreover, the mean value of all atoms in the y-direction of the buckled structure was picked as the standard plane.

## 3.2. Adsorption energy, deformation energy, binding energy, electron transfer

The calculated adsorption energy, deformation energy, binding



Fig. 3. Schematic diagram of adsorption sites, Brown, gray spheres: indicate C, N atoms, respectively.

energy, and electron transfer of the designed Hg<sup>0</sup>/HgCl<sub>2</sub> adsorption model are detailed in Table 1. Notably, it is found that most stabilized adsorption sites are all A2. To interpret the optimal adsorption sites, color-filled maps of the electrostatic potential (ESP) distribution on the surface of the planar and buckled structures were plotted, as depicted in Fig. 5. For Hg<sup>0</sup>, which is electrically neutral, whereby, the ideal adsorption sites are either the B1 site (blue region) with the strongest electrostatic potential or the A2 position (red region) with the weakest electrostatic potential. For HgCl2, the Hg atom with positive ESP inclines to adsorb at the A2 point where the ESP is negative, in accordance with the geometry optimization results. In the aforementioned adsorption configurations, as shown in Fig. 6, the structures of g-C<sub>3</sub>N<sub>4</sub> are all distorted to varying degrees following geometry optimization, suggesting that their propensity to deform and form more stable structure during the adsorption process. Noticeably, the observations imply that the planar structure is not the most stable conformation, and partial energy might be released during the adsorption process. Moreover, from Table 1, the absorption energy and binding energy of all the configurations exhibit negative values, indicating that Hg<sup>0</sup>/HgCl<sub>2</sub> adsorption on the g-C<sub>3</sub>N<sub>4</sub> surface is exothermic. In the case of planar structures, the deformation energies of all g-C<sub>3</sub>N<sub>4</sub> are noted to be negative, consistent with the observed deformations after geometry optimization, suggesting the release of energy from g-C<sub>3</sub>N<sub>4</sub> during the adsorption process, which accounts for the fact that the adsorption energy is invariably higher than the binding energy. Conversely, in all models of the buckled structure, the deformation energies of g-C<sub>3</sub>N<sub>4</sub> are positive, due to the fact that the buckled g-C<sub>3</sub>N<sub>4</sub> is the most stable structure, and the deformation of the g-C<sub>3</sub>N<sub>4</sub> structure absorbs part of the energy during the adsorption process, resulting in lower adsorption energy compared to the binding energy. The difference in binding energy between planar and buckled structures is within 0.04 eV, reflecting that the essential binding capacity of both structures for Hg<sup>0</sup> or HgCl<sub>2</sub> is approximately equivalent. Also, a comparison of the binding energies of g-C<sub>3</sub>N<sub>4</sub> for Hg<sup>0</sup> and HgCl<sub>2</sub> with those of conventional alkaline adsorbents was performed, as shown in Table 2. The selective adsorption capacity of g-C<sub>3</sub>N<sub>4</sub> is almost comparable to CaO and exceeds those of MgO, KCl, NaCl. The binding energy between  $Hg^0$  and  $g-C_3N_4$  is -0.314 eV, and combined with the Bader charge transfer analysis, little to no electron transfer occurs with Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>, confirming the typical physisorption. The binding energy for the vertical adsorption mode of HgCl<sub>2</sub> is -0.248 eV, significantly inferior to that of the parallel one. Moreover, the binding energy of HgCl<sub>2</sub> to g-C<sub>3</sub>N<sub>4</sub> is -0.843 eV, with strongly intensity, which falls under the category of strong binding interaction. However, there is no distinct charge transfer between HgCl<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, implying a possible absence of chemical bonding interactions. Therefore, further investigations are



**Fig. 4.** Adsorption configuration (a) Hg<sup>0</sup> and HgCl<sub>2</sub> vertical configuration (b) HgCl<sub>2</sub> parallel configuration.

required to gain deeper insights into these phenomena, which will be elucidated in subsequent sections through electronic structure analysis and weak interaction analysis.

#### 3.3. Electronic structure analysis

To further unravel the adsorption properties of  $g-C_3N_4$  on  $Hg^0/$ HgCl<sub>2</sub>, 3D differential charge density (EDD) plots, and density of states (DOS) analysis were conducted. EDD is available from the disparity of the 3D-spatial electron density across the adsorbed system and its two separated components, Hg<sup>0</sup>/HgCl<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. The electron depletion and accumulation zones are depicted in cyan and yellow, respectively.  $\Delta \rho = \rho_{sys} - \rho_{gas} - \rho_{g-C_3N_4}$  is defined as the transfer of electrons among the fragments in the system [46]. From Fig. 7(a, d), it is evident that merely a tiny portion of the electron cloud appears on the  $0.002 \text{ e/bohr}^3$  isosurface (Van der Waals surface), signifying virtually no electron transfer with Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>, which is consistent with the electron transfer in Table 1. For g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> absorption system, as showcased in Fig. 7(b, e), the Hg atom undergoes electron loss, while the Cl atoms experience electron gain, collectively, HgCl2 obtains a net electron from the g-C3N4 surface with 0.052e. Moreover, the electron cloud is not pronounced on the  $0.002 \text{ e/bohr}^3$  isosurface, indicating that chemical bonding is not the dominant bonding mode. To more visually characterize the electron transfer between the adsorbent and the adsorbate, EDD plots of lower isosurfaces (0.0006 e/bohr<sup>3</sup>) were developed. Notably, the Cl atom shows slight overlapping of the electron cloud with the adjacent C atoms, and N atoms, implying the potential for bonding interactions between the Cl atoms and the g-C<sub>3</sub>N<sub>4</sub> surface. This underlying bonding capability of the Cl atoms might be the contributing factor to the higher binding energy of g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>.

Fig. 8 delineates the DOS for the pristine  $g-C_3N_4$ , isolated  $Hg^0/HgCl_2$  molecule, and  $g-C_3N_4$  system with adsorbed  $Hg^0/HgCl_2$ . Since the

serious underestimation of the band gap energy using the GGA-PBE method, accurate results were obtained employing the HSE06 hybrid function. Remarkably, the DOS profiles of both  $Hg^0$  and  $HgCl_2$  with g-C<sub>3</sub>N<sub>4</sub> in the adsorption configuration exhibit minimal discrepancy compared to that of pristine g-C<sub>3</sub>N<sub>4</sub>. Furthermore, the absence of apparent hybridization of molecular orbitals is observed in g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, the similar findings were found in the g-C<sub>3</sub>N<sub>4</sub> system with O<sub>2</sub>, CO<sub>2</sub> adsorption [24].

Based on the preceding analysis of the electronic structure, the adsorption of  $Hg^0$  and  $HgCl_2$  on  $g-C_3N_4$  is likely attributed to noncovalent interactions. To further investigate this, an intriguing test was accomplished to calculate the binding energies with and without DFT-D3 correction, as demonstrated in Fig. 9. Under the two conditions, the binding energy of  $g-C_3N_4$  to  $Hg^0/HgCl_2$  exhibits substantial disparities, and all binding energies involving non-bonding interactions are substantially higher than that without considering the DFT-D3 correction. In the absence of DFT-D3 correction, the binding energies of  $g-C_3N_4@Hg^0$  and  $g-C_3N_4@HgCl_2$  are merely -0.052 eV and -0.310 eV, respectively, suggesting that the contributions of weak interactions to the binding energy of  $g-C_3N_4@Hg^0$  and  $g-C_3N_4@HgCl_2$  might be dominant.

#### 3.4. Weak interaction analysis

In order to accurately elucidate the types and properties of the interactions between  $Hg^0/HgCl_2$  and g-C<sub>3</sub>N<sub>4</sub>, QTAIM analysis was conducted, which investigates the electron density distribution in molecules by employing the principle of topological analysis in mathematics to determine the critical points of electron density distribution. Then, according to the nature of these critical points [47,48], the chemical structure of the molecule and the nature of the chemical bonds are identified. The bond critical point (BCP, (3, -1) points) exists between

#### Table 1

Adsorption energy, deformation energy, binding energy, electron transfer of Hg/HgCl2 on g-C3N4 at different adsorption sites.

A 1	· · · · · · · · · · ·		P	F (10)	E (- C N ) (-V	F	<b>M</b> /-
Adsorption con	nguration		Eads	E <sub>def</sub> (IVI)	E <sub>def</sub> (g-C <sub>3</sub> N <sub>4</sub> )/ev	E <sub>b</sub>	M <sub>charge-</sub> transfer/e
			/ev	/ev		/ev	
Planar	Hg <sup>0</sup>	N1	-1.399	0.000	-1.208	-0.191	-0.009
	0	N2	-2.088	0.000	-1.799	-0.289	0.009
		N3	-1.480	0.000	-1.275	-0.205	0.001
		C1	-1.931	0.000	-1.647	-0.284	0.009
		C2	-1.870	0.000	-1.647	-0.223	-0.005
		B1	-1.872	0.000	-1.648	-0.224	-0.005
		B2	-2.088	0.000	-1 798	-0.290	0.008
		B3	-2.087	0.000	_1 799	-0.290	0.009
		B4	-1.870	0.000	-1.648	-0.200	-0.005
		Δ1	-1.871	0.000	-1 647	_0.220	-0.006
		A1 A2	1 500	0.000	1 208	-0.224	-0.000
	HaCl	N1	-1.300	0.000	-1.200	-0.292	0.007
	ngGl <sub>2</sub>	NI	-1.292	0.000	-1.210	-0.082	0.009
	-vertical	N2	-2.016	0.000	-1.798	-0.218	0.004
		N3	-1.292	0.000	-1.209	-0.083	0.074
		CI	-1.8/6	-0.001	-1.647	-0.228	0.004
		C2	-1.831	0.000	-1.649	-0.183	0.004
		BI	-1.731	0.000	-1.564	-0.166	0.003
		B2	-0.064	0.003	-0.049	-0.018	0.007
		B3	-1.828	0.000	-1.648	-0.180	0.002
		B4	-1.808	0.000	-1.648	-0.160	0.006
		A1	-1.839	0.000	-1.647	-0.192	0.004
		A2	-1.457	0.000	-1.209	-0.248	0.007
	HgCl <sub>2</sub>	N1	-1.930	0.002	-1.647	-0.284	0.009
	-parallel	N2	-2.478	0.083	-1.784	-0.777	0.035
		N3	-1.859	0.003	-1.309	-0.553	0.023
		C1	-2.481	0.092	-1.784	-0.789	0.036
		C2	-2.480	0.085	-1.784	-0.781	0.035
		B1	-2.209	0.049	-1.633	-0.625	0.047
		B2	-2.479	0.090	-1.784	-0.785	0.035
		B3	-2.479	0.091	-1.785	-0.785	0.035
		B4	-1.860	0.004	-1.311	-0.554	0.020
		A1	-2.344	0.099	-1.630	-0.812	0.045
		A2	-2.364	0.109	-1.630	-0.843	0.044
Buckled	Ho <sup>0</sup>	N1	-0.234	0.000	0.000	-0.234	-0.02
Ducincu		N2	-0.302	0.000	0.003	-0.305	0.003
		N3	-0.192	0.000	0.001	-0.193	-0.016
		C1	-0.310	0.000	0.004	-0.314	-0.003
		C2	-0.255	0.000	0.003	-0.258	-0.015
		81	-0.300	0.000	0.000	-0.300	0.004
		B2	0.311	0.000	0.000	0.314	0.004
		B2	0.026	0.000	0.613	0.314	0.004
		B3	-0.920	0.000	-0.013	-0.313	0.004
		A1	-0.230	0.000	0.002	-0.236	0.004
		Al	-0.203	0.000	0.003	-0.200	0.001
	11-01	AZ	-0.310	0.000	0.004	-0.314	-0.022
	rigCi <sub>2</sub> -parallel	NI	-0.473	0.01	0.015	-0.498	-0.004
		N2	-0.615	0.056	0.017	-0.688	-0.065
		N3	-0.589	0.056	0.017	-0.662	0.005
		CI	-0.629	0.047	0.015	-0.691	-0.01
		C2	-0.584	0.018	0.017	-0.619	0.024
		B1	-0.607	0.026	0.017	-0.65	0.048
		B2	-0.627	0.102	0.017	-0.78	0.035
		B3	-0.627	0.045	0.017	-0.689	-0.019
		B4	-0.584	0.013	0.017	-0.614	0.027
		A1	-0.650	0.062	0.015	-0.727	0.045
		A2	-0.686	0.101	0.017	-0.804	0.052



Fig. 5. The electrostatic potential in the 0.002 e/bohr<sup>3</sup> isosurface of (a) Planar structure of g-C<sub>3</sub>N<sub>4</sub>, (b) Hg<sup>0</sup>, (c)HgCl<sub>2</sub>, (d) Buckled structure of g-C<sub>3</sub>N<sub>4</sub>.



Fig. 6. Optimized structure of (a) planer g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, (b) planer g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, (c) bucked g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, (d) bucked g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>.

Table 2 g-C<sub>3</sub>N<sub>4</sub> vs. conventional alkaline adsorbents.

Bind energy (eV)	This work	CaO [45]	MgO [16]	KCl [16]	NaCl [16]	
Hg <sup>0</sup> HgCl <sub>2</sub>	$-0.314 \\ -0.843$	$-0.274 \\ -0.812$	$-0.118 \\ -0.725$	$-0.097 \\ -0.794$	$-0.089 \\ -0.678$	

interacting atoms, and the topological parameters at BCP provide a reflection of the property and strength of the interaction being studied. The distribution of bond diameter and the positions of BCP of the g-C<sub>3</sub>N<sub>4</sub>@ Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> system were calculated, as shown in Fig. 10. The results reveal the presence of BCPs between Hg atoms and multiple N atoms within  $g-C_3N_4@Hg^0$ , indicating that the interaction between Hg atom and N atoms is the primary binding mode of the g- $C_3N_4@Hg^0$  absorption system. For g- $C_3N_4@HgCl_2$ , BCPs are observed between Hg atom, Cl atoms, and g-C<sub>3</sub>N<sub>4</sub>, signaling that both Hg atom and Cl atoms are involved in the binding process. Further, the quantity of BCPs exceeds four, implying that the adsorptions of Hg<sup>0</sup> and HgCl<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> are attributed to polyatomic co-binding. Topological parameters for the above BCPs were calculated and listed in Table 3, including electron density ( $\rho$ , reflects the strength of the chemical bond,  $\rho > 0.1$  a. u is covalent bonding,  $\rho < 0.1$  a.u is closed-shell interactions, such as hydrogen bonding, van der Waals, the lower the value, the weaker the bond), Laplacian of electron density at BCPs ( $\nabla^2 \rho$ ,  $\nabla^2 \rho > 0$  means

electron divergence, corresponding to non-covalent interaction, such as hydrogen bonding, van der Waals, etc.;  $\nabla^2 \rho < 0$  means electron aggregation, corresponding to covalent interaction), Potential energy density (V), Lagrangian kinetic energy (G), Energy density (H, indicators of chemical bonding properties in terms of energy, H > 0 (<0) for (noncovalent) covalent interaction). From Table 3, the electron density, Laplacian of electron density, and energy density of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> are all exceeding 0, while electron density is considerably less than 0.1. This suggests that the interactions between Hg<sup>0</sup> and HgCl<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub> are non-covalent and bound with weak interaction, consistent with the findings from electronic structure analysis. This is consistent with the findings that g-C<sub>3</sub>N<sub>4</sub> binds to small molecules, such as O2, CO2, via van der Waals force. In addition, a significantly higher electron density is observed for g-C3N4@HgCl2 compared to g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, which explicates the superior binding energy of g- $C_3N_4@HgCl_2$  than that of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>. Moreover, the presence of BCPs of Cl...N and Cl...C underscores that the combination of Cl atoms and g-C<sub>3</sub>N<sub>4</sub> for the weak interaction was non-negligible.

The topological parameters of BCPs are effective in distinguishing chemical bonds and non-covalent interactions. However, they fall short in characterizing the type, strength, and spatial region of weak interactions. To further investigate the nature of the adsorption of Hg<sup>0</sup>/HgCl<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub> and expand upon the findings of QTAIM, the Interaction Region Indicator (IRI) [49,50] was introduced to investigate the non-covalent interaction of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>. With



**Fig. 7.** Maps of differential charge densities of  $Hg^0/HgCl_2$  being absorbed on (a-c) planar g- $C_3N_4$  structure, (d-f) buckled g- $C_3N_4$  structure. The cyan and yellow colors represent charge depletion and accumulation, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Density of states of  $Hg^0/HgCl_2$  after and before adsorption, (a)planar g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, (b)planar g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, (c)buckled g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, (d) buckled g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>.



Fig. 9. Binding energy with and without considering DFT-D3 correction.

processing the IRI function, the region of weak interactions associated with the molecules can be explicitly displayed, and the essence of the weak interaction was intuitively identified through visualization. The weak interaction types are obtained by the sign of the second largest eigenvalue of the electron density Hessian matrix  $\lambda_2$  (sign( $\lambda_2$ )),  $\lambda_2 > 0$ ,  $\lambda_2 \approx 0$ ,  $\lambda_2 < 0$  represent repulsive interaction(red portion of Fig. 11(e)), van der Waals interaction(green portion of Fig. 11(e)), attractive interaction(blue portion of Fig. 11(e)), respectively. From the IRI of

Fig. 11, it is evident that between the  $Hg^0/HgCl_2$  and  $g-C_3N_4$  surface are dominantly shown in green color with slight brown shading, corresponding to van der Waals, indicating that both Hg<sup>0</sup> and HgCl<sub>2</sub> binding to g-C<sub>3</sub>N<sub>4</sub> depend predominantly on van der Waals. Interestingly, the weak interaction region of g- $C_3N_4@Hg^0$  is closed for the planar structure but not for the buckled one, chiefly owing to the fact that Hg atom is not in the center of three triplet triazine units in the buckled structure, and the distance between the Hg atom and the C/N atoms far exceeds the van der Waals radius of both. Compared with g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, the weak interaction region of g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> is broader, with both Hg atom and Cl atoms binding to the g-C<sub>3</sub>N<sub>4</sub> surface, in agreement with the findings of QTAIM analysis. Further analysis of the scatter plot reveals that the ground gradient spikes of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> are focused on the range -0.005 a.u. to 0.01 a.u., which is the attraction of  $g-C_3N_4$ and Hg<sup>0</sup>/HgCl<sub>2</sub>. The density of spikes in g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> is noticeably higher than that of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, which is consequence of the joint action of Hg atom and Cl atoms. Additionally, a peak value at 0.009 a.u. is observed in g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, surpassing the peak value at 0.007 a.u. in g- $C_3N_4@Hg^0$ , indicating that the attraction of g- $C_3N_4@HgCl_2$  is more intense. In addition, the blue region in Fig. 11 is mainly the binding interaction between C atoms and N atoms in g-C<sub>3</sub>N<sub>4</sub> through chemical bonding, and the red region is the occurrence of stronger repulsion in the center of C-N six-membered ring and three triplet triazine units. Furthermore, upon comparing the sizes of Hg<sup>0</sup> and HgCl<sub>2</sub> molecules, an intriguing observation was made. Hg<sup>0</sup> exists as a monatomic molecule with a kinetic diameter of 3.40 Å (twice the van der Waals radius). In contrast, HgCl<sub>2</sub> adopts a linear molecular configuration, presenting a maximum molecular interaction diameter of 8.16 Å (equivalent to twice the sum of the Hg-Cl bond length and the van der Waals radius of Cl). The central ring diameter of g-C<sub>3</sub>N<sub>4</sub> is approximately 4.7 Å, falling



**Fig. 10.** Absorption system of (a)planar g- $C_3N_4@Hg^0$ , (b)planar g- $C_3N_4@HgCl_2$ , (c)buckled g- $C_3N_4@Hg^0$ , (d) buckled g- $C_3N_4@HgCl_2$ ; the small orange points are BCPs and the lines were bond paths. Brown, gray, green, and milky white spheres: indicate C, N, Cl, and Hg atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3 Topological parameters at BCP of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> (unit: a.u).

Complex		BCP	ρ	$\nabla^2 \rho$	G	V	Н
Planar	Hg <sup>0</sup>	BCP-1 <sub>(HgN)</sub>	0.00671	0.02016	0.00415	-0.00325	0.00089
		BCP-2(HgN)	0.00674	0.02024	0.00416	-0.00327	0.00090
		BCP-3 <sub>(HgN)</sub>	0.00639	0.01925	0.00394	-0.00307	0.00087
		BCP-4 <sub>(HgN)</sub>	0.00684	0.02052	0.00423	-0.00334	0.00090
		BCP-5(HgN)	0.00687	0.02062	0.00426	-0.00336	0.00090
		BCP-6(HgN)	0.00639	0.01925	0.00394	-0.00307	0.00087
	HgCl <sub>2</sub>	BCP-1 <sub>(HgN)</sub>	0.01418	0.04303	0.00983	-0.00891	0.00092
		BCP-2 <sub>(HgN)</sub>	0.00511	0.01627	0.00319	-0.00232	0.00087
		BCP-3(HgN)	0.00724	0.02296	0.00471	-0.00369	0.00103
		BCP-4 <sub>(ClN)</sub>	0.00871	0.03004	0.00614	-0.00476	0.00137
		BCP-5 <sub>(ClC)</sub>	0.00839	0.02962	0.00585	-0.00429	0.00156
Buckled	Hg <sup>0</sup>	BCP-1 <sub>(HgN)</sub>	0.00591	0.01664	0.00343	-0.00271	0.00073
		BCP-2 <sub>(HgN)</sub>	0.00604	0.01761	0.00363	-0.00286	0.00077
		BCP-3(HgN)	0.00704	0.02059	0.00425	-0.00335	0.00090
		BCP-4(HgN)	0.00691	0.02028	0.00418	-0.00328	0.00089
	HgCl <sub>2</sub>	BCP-1 <sub>(HgN)</sub>	0.00857	0.02481	0.00526	-0.00432	0.00094
		BCP-2 <sub>(HgN)</sub>	0.00546	0.01648	0.00336	-0.00259	0.00077
		BCP-3(HgN)	0.00761	0.02221	0.00462	-0.00368	0.00094
		BCP-4(HgN)	0.00432	0.01290	0.00253	-0.00183	0.00070

between the kinetic diameters of  $Hg^0$  and  $HgCl_2$ . This suggests that the physical interaction between g-C<sub>3</sub>N<sub>4</sub> and HgCl<sub>2</sub> would be significantly greater than that of  $Hg^0$ , aligning with the aforementioned analysis of QTAIM and IRI.

From the foregoing analytical results, it can be concluded that the binding of both  $Hg^0$  and  $HgCl_2$  to  $g-C_3N_4$  is predominantly governed by weak interactions, and both Hg atom and Cl atoms in  $HgCl_2$  possess the capability to bind with  $g-C_3N_4$ . Additionally, the polyatomic binding effect contributes to the larger binding energy of  $HgCl_2$ . Nevertheless, it fails to reveal the strength of the interplay of individual atoms of  $g-C_3N_4$  with  $Hg^0/HgCl_2$ . In the following, COHP [51,52] will be exploited to investigate the bonding and antibonding states of  $g-C_3N_4@Hg^0$  and  $g-C_3N_4@HgCl_2$ . Subsequently, the curve of COHP will be integrated into the Fermi energy level to obtain integrated-crystal orbital Hamilton population (ICOHP), and to quantitatively estimate the net binding ability and effectiveness of the interaction of each atom in  $g-C_3N_4$  to both Hg atom and Cl atoms. The calculations are summarized in Fig. 12.

In the planar g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, a notable binding affinity is observed between Hg and specific atoms, namely N11, N14, N26, N28, N29, N31, C22, and C24. However, in the buckled g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup>, numerous atoms exhibit weak binding to Hg atom. It is associated with the interaction distance of the atom pairs. Notably, in the g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, the binding strength of each atom in g-C<sub>3</sub>N<sub>4</sub> to HgCl<sub>2</sub> is significantly higher than that of Hg<sup>0</sup>. This enhanced binding can be attributed to the overlapping effect resulting from the interactions of Hg and Cl atoms. Further, an intriguing analysis was conducted by cumulatively summing the -ICOHP values between Hg<sup>0</sup>, Cl, C, and N atoms, roughly comparing the binding intensity of Hg and Cl atoms to g-C<sub>3</sub>N<sub>4</sub>, as listed in Table 4. For g- $C_3N_4@Hg^0$ , the interaction between N atoms and Hg atoms was found to make a substantial contribution to the overall binding. In the case of g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, the -ICOHP of Cl atoms with g-C<sub>3</sub>N<sub>4</sub> was 0.473 eV and 0.364 eV in the planar and buckled structures, respectively, even exceeding the -ICOHP value of g-C<sub>3</sub>N<sub>4</sub> with Hg atom, indicating that the contribution of Cl atoms to the binding is non-negligible. This



**Fig. 11.** Scatter and IRI plots of adsorption configurations of (a) planar  $g-C_3N_4@Hg^0$ ; (b) planar  $g-C_3N_4@HgCl_2$ ; (c) buckled  $g-C_3N_4@Hg^0$ ; (d) buckled  $g-C_3N_4@HgCl_2$ , (e) color bar of scatter of plots. Brown, gray, green, and milky white spheres: indicate C, N, Cl, and Hg atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. -ICOHP of each atom in  $g\text{-}C_3N_4$  to Hg atom and Cl atoms.

Table 4		
-ICOHP of $g$ -C <sub>3</sub> N <sub>4</sub> to Hg atom and	Cl	atoms

		Hg-C	Hg-N	Cl1-C	Cl2-C	Cl1-N	Cl2-N
Planar	Hg <sup>0</sup>	0.056	0.192	-	-	-	-
	HgCl <sub>2</sub>	0.117	0.212	0.142	0.151	0.083	0.097
Buckled	Hg <sup>0</sup>	0.122	0.143	-	-	-	-
	$HgCl_2$	0.143	0.298	0.068	0.109	0.084	0.103

polyatomic superposition effect is the essence of the binding between  $Hg^0$  and  $HgCl_2$  on g-C<sub>3</sub>N<sub>4</sub> surface. The triatomic parallel structure of  $HgCl_2$ , facilitates binding with more atoms in g-C<sub>3</sub>N<sub>4</sub>, resulting in a more stable g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub> system. This is an impressive factor in attaining the selective separation of  $Hg^0$  and  $HgCl_2$ .

#### 3.5. Experimental verification

In order to verify the correctness of the above DFT calculations and identify the ability of g-C<sub>3</sub>N<sub>4</sub> to selectively adsorb mercury, Hg<sup>0</sup>, and HgCl<sub>2</sub> adsorption experiments were conducted on the fixed bed, with the results shown in Fig. 13. From Fig. 13(a), The four samples exhibit two characteristic peaks of g-C<sub>3</sub>N<sub>4</sub> near 13.2° and 27.5°, corresponding to the (100) crystalline plane of the sequential stacking in the unit face of the tri-s-triazine ring and the (002) crystalline plane of the periodic interlayer stacking in the graphite-like structure, respectively, indicating that the primary phase of the products after calcination of the four precursors are g-C<sub>3</sub>N<sub>4</sub> [53]. The breakthrough curves of Hg<sup>0</sup> in the adsorbent are shown in Fig. 12(b), where the experimental temperature was 120 °C. The passage of  $\text{Hg}^0$  in the g-C\_3N\_4 adsorbent prepared from four precursors is instantaneous, and the breakthrough rate is sustained at over 98 %. In addition, the recovery assays of Hg<sup>0</sup> were performed on the post-test adsorbent samples, and the recovery rate of Hg<sup>0</sup> in Fig. 12 (c) is less than 1.6 %, similarly verifying that Hg<sup>0</sup> can not be caught by the adsorbent, corresponding with the results of the preceding DFT calculation. The adsorption performance of the four g-C<sub>3</sub>N<sub>4</sub> adsorbents on HgCl<sub>2</sub> is illustrated in Fig. 12(d), compared to the apparent penetration behavior of Hg<sup>0</sup>, the g-C<sub>3</sub>N<sub>4</sub> adsorbent exhibits efficient adsorption ability for HgCl<sub>2</sub>, virtually all of the HgCl<sub>2</sub> in the gas phase is trapped by the g-C<sub>3</sub>N<sub>4</sub> adsorbent particles in the adsorption section, and only less than 2 % of the HgCl<sub>2</sub> penetrates into the breakthrough section. The adsorbent with the pinnacle of capture performance is g-C<sub>3</sub>N<sub>4</sub>-Urea with 99 % adsorption, which might be attributed to the developed

specific surface area.

From the weak interaction analysis, the binding of  $HgCl_2$  to  $g-C_3N_4$  relies primarily on van der Waals, which is unstable and susceptible to desorption at high temperatures. Hence, the adsorption temperature



Fig. 14. Experimental assessment of  $\mathrm{HgCl}_2$  adsorption over  $\mathrm{g}\text{-}\mathrm{C}_3\mathrm{N}_4$  under different temperatures.



**Fig. 13.** Experimental verification of selective adsorption of  $g-C_3N_4$  absorbent. (a) XRD Spectrum of  $g-C_3N_4$  prepared from different precursors, (b) HgCl<sub>2</sub> adsorption performance of  $g-C_3N_4$ , (c) Hg<sup>0</sup> adsorption performance of  $g-C_3N_4$ , (d) Hg<sup>0</sup> recovery rate.

experiment was undertaken, and the outcomes are illustrated in Fig. 14. It can be observed that the g-C<sub>3</sub>N<sub>4</sub> adsorbent possesses positive adsorption performance with the adsorption efficiency of over 94 % at temperatures below 300°C, as the temperature exceeds 400°C, the adsorption efficiency declines significantly, and is only 0.7 % at 500°C. This implies that thermal regeneration of the deactivated g-C<sub>3</sub>N<sub>4</sub> can be achieved by heating sample at 500 °C with N<sub>2</sub> as the carrier gas. From Table 1, the adsorption of g-C<sub>3</sub>N<sub>4</sub> with HgCl<sub>2</sub> is exothermic. As the temperature increases, the harder adsorbent bound to the adsorbate and the ease of desorption. Almost complete desorption of the sample at 500°C, implies that the adsorbent might be regenerated by heating.

#### 4. Conclusion

In this work, g-C<sub>3</sub>N<sub>4</sub> was theoretically investigated as a potential  $Hg^0/HgCl_2$  selective adsorbent based on DFT theory, and the selective adsorption performance of g-C<sub>3</sub>N<sub>4</sub> was experimentally investigated, and the reliability of the DFT results was verified. Diverging from conventional alkaline adsorbents, this work introduced a novel approach for separation of  $Hg^0$  and  $HgCl_2$  via physical adsorption, offering a new perspective on the selective adsorption of  $HgCl_2$ . Simultaneously, it revealed a multi-atomic co-binding effect between g-C<sub>3</sub>N<sub>4</sub> and  $Hg^0/HgCl_2$ , enriching the understanding of the adsorption mechanism of g-C<sub>3</sub>N<sub>4</sub> with small molecules. The conclusions are as follows:

- (1) A novel Hg<sup>0</sup>/HgCl<sub>2</sub> selective adsorbent is developed. The principle of selective absorption is the difference in binding energy of g-C<sub>3</sub>N<sub>4</sub>@Hg<sup>0</sup> and g-C<sub>3</sub>N<sub>4</sub>@HgCl<sub>2</sub>, the former with the binding energy of -0.314 eV, considerably less than the latter with -0.843 eV.
- (2) The electronic structure analysis reveals that there is no significant electron transfer between both Hg and HgCl<sub>2</sub> with  $g-C_3N_4$ , and the electron cloud is not remarkably overlapped. Furthermore, there is the absence of significant orbital hybridization during the adsorption process of Hg<sup>0</sup> and HgCl<sub>2</sub>, indicating that no stable chemical bond forms between the adsorbent and both Hg<sup>0</sup> and HgCl<sub>2</sub>.
- (3) QTAIM calculations display that  $Hg^0$  and  $HgCl_2$  are bound to  $g-C_3N_4$  predominantly through non-covalent interactions, and visualization of the weak interactions by IRI finds that the binding of  $Hg^0$  and  $HgCl_2$  with  $g-C_3N_4$  is primarily dependent on van der Waals.
- (4) The COHP study confirms that the adsorption of  $g-C_3N_4$  with  $Hg^0$  and  $HgCl_2$  is multi-atom superposition binding process, namely, multiple C atoms and N atoms on  $g-C_3N_4$  are bound with both Hg atoms and Cl atoms to different degrees. The triatomic parallel structure of  $HgCl_2$ , which could bind to more atoms in  $g-C_3N_4$ , is an impressive factor in attaining the selective separation of  $Hg^0$  and  $HgCl_2$ .
- (5) The results of the experiments on the selective adsorption of Hg and HgCl<sub>2</sub> by g-C<sub>3</sub>N<sub>4</sub> show that the breakthrough rate of Hg<sup>0</sup> exceeds 98 %, while that of HgCl<sub>2</sub> is only less than 1.6 %. Moreover, g-C<sub>3</sub>N<sub>4</sub> fails to adsorb HgCl<sub>2</sub> under high-temperature conditions, indicating that g-C<sub>3</sub>N<sub>4</sub> possesses a potential for thermal regeneration.
- (6) The present study elucidates the selective adsorption mechanisms of  $g-C_3N_4$  towards  $Hg^0$  and  $HgCl_2$  from DFT perspective. Future research can further explore the separation mechanisms through experimental and characterization methods, such as employing XAS, to delve deeper in-sight into the contributions of different functional groups on the adsorption of the metal ions.

#### CRediT authorship contribution statement

Haiyang Li: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. Xiaoshuo Liu: Validation, Investigation.

Haitao Hu: Funding acquisition, Supervision. Yu Shang: Validation. Jiangyi Tong: Writing – review & editing. Ao Shen: Data curation. Yuxing Zhou: Investigation. Baotian Wang: Software. Yufeng Duan: Writing – review & editing, Supervision, Project administration, Funding acquisition. Weijie Yang: Conceptualization, Investigation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgments

This study was supported by the National Key Research and Development Program of China (2016YFC0201105), Youth Innovation Promotion Association CAS (2021017), Graduate Student Research and Innovation Program of Jiangsu Province (KYCX23\_0245).

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#### H. Li et al.

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#### Separation and Purification Technology 335 (2024) 126103

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