Removal of Hg$^{2+}$ and methylmercury in waters by functionalized multi-walled carbon nanotubes: adsorption behavior and the impacts of some environmentally relevant factors

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**ABSTRACT**

Adsorption of Hg$^{2+}$ and methylmercury (MeHg) to multi-walled carbon nanotubes (MWCNTs) modified, respectively, with hydroxyl, amine and carboxyl groups was studied. The effect of various factors like the initial pH, natural organic matter (NOM), Cl$^-$ and adsorbent dose on the sorption efficiency were evaluated. It was found that amine-modified MWCNTs showed a strong adsorption capacity to Hg$^{2+}$ and MeHg, and the removal efficiency could reach up to 92% (0.5 g/L MWCNTs, and 100 μg/L Hg$^{2+}$ and MeHg) which is independent of pH. NOM had complex effects on the adsorption of Hg$^{2+}$ and MeHg to MWCNTs. Cl$^-$ inhibited the adsorption of Hg$^{2+}$ and MeHg to MWCNTs. The adsorption of Hg$^{2+}$ and MeHg was found to be inhomogeneous and homogeneous chemisorption, respectively. Our results suggested that MWCNTs modified with different functional groups can efficiently adsorb both Hg$^{2+}$ and MeHg in aqueous environment.

1. Introduction

Because of its long distance migration and bioaccumulation, mercury as a global pollutant has been attracting widespread attention [1,2]. Mercury in environment and biological body mainly exists in three forms including Hg$^0$, Hg$^{2+}$ and methylmercury (MeHg). Hg$^0$ and Hg$^{2+}$ can be converted into MeHg by microorganisms [3–6]. MeHg is the most toxic organic mercury and is ubiquitous in the aquatic environment [7]. Mercury pollution comes mainly from industrial production, mercury mine and non-ferrous metals processing factory [8]. Various kinds of methods have been used to remove heavy metals from aqueous solutions including ion exchange, chemical precipitation, biological treatment, membrane filtration and adsorption [9]. Recently carbon nanotubes (CNTs), as adsorbents in the field of environment, have attracted more and more attention, because of their unique structure and chemical properties [10–12].

Multi-walled carbon nanotubes (MWCNTs) as one type of CNTs have been used widely to adsorb heavy metals such as Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Hg$^{2+}$ from aqueous solutions [9,13–17]. The MWCNTs have been experimentally proven to possess cylindrical hollow micro-crystals of graphite which have strong adsorption ability, exceptional mechanical properties, unique electrical property, high chemical and thermal stability, a large specific surface area, and high adsorption capacity [13–15]. Researches have shown that the surface functional groups such as amino [18,19], carboxyl [20,21], hydroxy [20,21] and thiol [19,22–24] on carbon nanotubes can greatly improve their adsorption capacity for metal ions. Moreover, various aqueous environment relevant factors including pH, ionic strength and natural organic matter (NOM) can affect the adsorption of metal ions onto MWCNTs [12,13,20,25–27]. To assess the efficiency of MWCNTs as absorbents to removal of Hg$^{2+}$ and MeHg in waters, it is of great importance to understand the effects of NOM and other environmental factors on the sorption of Hg$^{2+}$ and MeHg to functionalized MWCNTs. Although the adsorption of Hg$^{2+}$ by MWCNTs has been extensively studied [17,28–30], the adsorption of MeHg to functionalized MWCNTs especially in the presence of Hg$^{2+}$, has not been reported.

In this study, we studied the removal efficiency of Hg$^{2+}$ and MeHg from aqueous solution by pristine MWCNTs and MWCNTs modified with carboxylic functional group (MWCNTs-COOH), hydroxyl functional group (MWCNTs-OH), and amino functional group (MWCNTs-NH$_2$), respectively. The effects of environmentally relevant factors like pH, NOM, and Cl$^-$ on the
sorption efficiency were evaluated. In addition, the adsorption isotherms and kinetics were studied by fitting to various models to understand the sorption mechanisms.

2. Materials and methods

2.1. Materials

Four kinds of multi-walled carbon nanotubes (MWCNTs > 95% in purity and special surface area, SSA > 140 m²/g), including unmodified MWCNTs, and MWCNTs-COOH (–COOH group content 2.56%, m/m and SSA > 130 m²/g), MWCNTs-OH (–OH group content 5.58%, m/m and SSA > 233 m²/g), and MWCNTs-NH₂ (–NH₂ group content 0.45%, m/m and SSA > 233 m²/g) were purchased from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). They have the same outer diameter (8–15 nm), length (~50 μm) and numbers of walls (6–12). Stock solutions of 1000 mg/L Hg²⁺ (as Hg) in 5% HNO₃ and 60 mg/L MeHg (as Hg) in methanol were purchased from National Institute of Metrology (Beijing, China). All stock solutions were stored in darkness at 4 °C. Mili-Q deionized water was used for all experiments. Serial dilutions of the stock solutions were obtained with deionized water. The working standard solutions were prepared daily. L-cysteine was obtained from Sigma Aldrich Co. (St. Louis, MO, USA). Suwannee River natural organic matter (SRNOM) (Lot No. 2R101N) was obtained from the International Humic Substance Society (St. Paul, MN, USA). One g/L stock solutions of SRNOM were prepared in deionized water and shaken for 12 h at room temperature under the darkness. Then the solution was filtered through 0.22 μm cellulose nitrate membrane. A HPLC system (Agilent 1200 series, Agilent Technologies, Palo Alto, CA) was coupled to the ICP-MS instrument (Agilent 7700cs) by directly connecting the column outlet to the cross-flow nebulizer of ICP-MS through a commercial polytetrafluoroethylene (PTFE) connector. The mobile phase for the HPLC-ICP-MS system consisting of 1 g/L L-cysteine and 0.06 mol/L ammonium acetate was prepared daily.

2.2. Characterization of MWCNTs

The morphology and size of MWCNTs were characterized by transmission electron microscope (TEM, Hitachi, Japan). Ten mg pristine and functionalized MWCNTs were added into 20 mL deionized water to form aqueous solution respectively. Then 20 μL sample of pristine and functionalized MWCNTs were dropped on carbon membrane copper net, drying in vacuum oven at room temperature for 12 h.

The surface functional groups of pristine and functionalized MWCNTs were detected by Fourier transform infrared spectroscopy (FT/IR-6100, JASCO, Japan). A transparent thin sheet was pressed and scanned from 400 to 4000 cm⁻¹, which the MWCNTs to KBr quality ratio was 1–100.

2.3. Adsorption experiments

The experiments were performed in 40 mL glass bottles with caps. The total volume of the solution was 20 mL, and Hg²⁺ and MeHg working standard solutions were spiked into glass bottles to reach a final concentration of 100.0 μg/L Hg, respectively. After adding 10 mg MWCNTs, the solutions were placed on the oscillator to shake at 245 rpm and 20 °C for 90 min to reach adsorption equilibrium.

After achieving the equilibrium, 2 mL solution was taken out from each bottle and filtered through 0.22 μm PTFE membrane. The HPLC-ICP-MS hyphenated system was used to determine Hg²⁺ and MeHg in the filtered solutions, and the detailed instrumentation and procedure could refer to our previous study [31].

To evaluate the influence of initial pH on adsorption, the pH of the solution was adjusted to 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0, respectively, by using 10 mmol/L phosphate buffer. The effects of other factors, including Cl⁻ (0–800 mmol/L), NOM (0–20 mg/L, DOC) and adsorbent dose (0–3 g/L), on the adsorption were tested at pH 7.0. For each experiment, three parallel samples were prepared.

The removal efficiency of Hg²⁺ or MeHg was calculated according to the equation [32]:

\[ R = \frac{C_0 - C_e}{C_0} \times 100\% \]  

where \( R \) is the removal efficiency of Hg²⁺ or MeHg, \( C_0 \) is the initial concentration of Hg²⁺ or MeHg (mg/L), and \( C_e \) is the equilibrium concentration of Hg²⁺ or MeHg (mg/L).

The adsorption capacity of adsorbent at equilibrium was calculated by the following equation [21]:

\[ q = \frac{(C_0 - C_e) \times V}{m} \]  

where \( q \) is the adsorption capacity of adsorbent (mg/g), \( C_0 \) is the initial concentration of Hg²⁺ or MeHg (mg/L), and \( C_e \) is the equilibrium concentration of Hg²⁺ or MeHg (mg/L). \( m \) is the adsorbent weight (g), \( V \) is the volume of solution (L).

2.4. Adsorption isotherm models

To reveal the adsorption process and evaluate adsorption capacity, adsorption isotherms were studied. The Hg²⁺ and MeHg adsorption isotherms for MWCNTs, MWCNTs-OH, MWCNTs-NH₂, MWCNTs-COOH were modeled by various isotherms.

The Langmuir model is used to describe homogeneous monolayer adsorption on the surface generally. The linear form of the model is given as [33]:

\[ \frac{q}{C_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \]
\[
\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{C_e Q_m b}
\]

where \(q_e\) is the equilibrium adsorption capacity of adsorbent (mg/g), \(Q_m\) is the equilibrium concentration of Hg\(^{2+}\) or MeHg (mg/L), \(Q_e\) and \(b\) are Langmuir constants indicating the capacity and energy of adsorption, respectively, and can be calculated from the intercept and slope value of the linear plot, \(1/q_e\) vs. \(1/C_e\).

The character of the Langmuir isotherm can also be expressed by adopting a dimensionless equilibrium parameter, \(R_L\) which is defined as [33]:

\[
R_L = \frac{1}{1+bC_0}
\]

where \(b\) is the Langmuir constant (L/mg) and \(C_0\) is the initial concentration of Hg\(^{2+}\) or MeHg (mg/L). The \(R_L\) value indicates the shape of isotherm. \(R_L\) values between 0 and 1 indicate favorable adsorption, while \(R_L > 1\), \(R_L = 1\), and \(R_L = 0\) indicate unfavorable, linear, and irreversible adsorption isotherms, respectively.

The Freundlich model describes the heterogeneity adsorption system and can be expressed as the following equation [28,33,34]:

\[
\ln(q_e) = \frac{1}{n} \ln(C_e) + \ln K_f
\]

where \(q_e\) is the equilibrium adsorption capacity of adsorbent (mg/g), \(C_e\) is the equilibrium concentration of Hg\(^{2+}\) or MeHg (mg/L), \(K_f\) (mg\(^{-1}\) L\(^n\)/g) and \(n\) are Freundlich constants indicating the relative adsorption capacity and adsorption intensity. \(1/n\) and \(\ln K_f\) are the slope and intercept value of the linear Freundlich equation, respectively.

The Dubinin-Redushkevich (D-R) model is related to adsorption energy and can be expressed as the following equation [33,35]:

\[
\ln q_e = \ln q_m - \beta \varepsilon^2
\]

\[
\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)
\]

where \(q_e\) is the equilibrium adsorption capacity of adsorbent (mg/g), \(q_m\) is the maximum adsorption capacity, \(C_e\) is the equilibrium concentration of Hg\(^{2+}\) or MeHg (mol/L), \(\beta\) is related to the mean adsorption energy, \(\varepsilon\) is the Polanyi potential, and \(R\) (L/mol/K) and \(T\) (K) are gas constant and the temperature, respectively. \(E\) (kJ/mol) is the mean adsorption energy of adsorption per molecule of adsorbent, when it is transferred from infinity in the solution to the solid surface [33]:

\[
E = \frac{1}{\sqrt{2\beta}}
\]

The Temkin isotherm model is based on a hypothesis that the adsorption energy decreases linearly with the surface coverage. The Temkin isotherm can be expressed as the following equation [33]:

\[
q_e = \frac{RT}{\beta_f} \ln A_f + \frac{RT}{\beta_f} \ln C_e
\]

where \(RT/\beta_f = B_T\) \(q_e\) is the equilibrium adsorption capacity of adsorbent (mg/g), \(q_m\) is the maximum adsorption capacity, \(C_e\) is the equilibrium concentration of Hg\(^{2+}\) or MeHg (mg/L), \(A_f\) and \(B_T\) are the constants of the linear plot \(q_e\) vs. \(\ln C_e\).

### 2.5. Kinetic models

The adsorption kinetic of Hg\(^{2+}\) and MeHg was studied according to pseudo-first-order and pseudo-second-order adsorption equations [35–37]. The pseudo-first-order equation is given as:

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

where \(q_t\) is the amount of adsorption at time \(t\) (mg/g), \(q_e\) is the equilibrium adsorption capacity (mg/g), and \(k_1\) (min\(^{-1}\)) is the pseudo-first-order rate constant.

The pseudo-second-order equation is shown as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

where \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order rate constant.

### 3. Results and discussion

#### 3.1. Physical characterization

**3.1.1. Characterization of MWCNTs with TEM**

Figure 1 shows the TEM images of four kinds of MWCNTs, in which no distinct changes in surface morphology was observed for the functionalized MWCNTs in comparison to the pristine MWCNTs.

**3.1.2. FTIR spectroscopic characterization of MWCNTs**

The FTIR spectrum were used to characterize the surface functional groups of MWCNTs, and the results were shown in Figure 2. While no major functional group was identified for the pristine MWCNTs, symmetric and asymmetric methylene stretching bands appeared at ~2962 and ~2884 cm\(^{-1}\) were detected in functionalized MWCNTs. Generally these functional groups located on the surface defect of the carbon nanotubes [38]. In the MWCNTs-COOH spectrum the characteristic peaks appeared at the ~3451 and ~1617 cm\(^{-1}\), which are assigned to stretching vibrations of ν(OH) and ν(C=O) of –COOH [34,39]. The peaks at ~3450 cm\(^{-1}\) corresponded to -NH\(_2\) stretching vibration in the MWCNTs-NH\(_2\) spectrum. In addition, the presence of peaks at ~1415 and ~1262 cm\(^{-1}\), origin from N-H in-plane and C-N bond stretching, respectively [39].
buffers were adopted. The results shown in Figure 3 indicate that the pH had no significant effect on the removal of Hg$^{2+}$ and MeHg on MWCNTs-NH$_2$. This is because the adsorption of Hg$^{2+}$ and MeHg onto MWCNTs-NH$_2$ is very strong that is independent of the initial pH. It is very important that the stability constant of the compounds of amino group and mercury can reach $10^{18}$ [41]. It was found that the maximum removal efficiency is up to more than 92%, which is consist with the results in Ref. [41].

Figure 3 also shows that for pristine MWCNTs, MWCNTs-OH and MWCNTs-COOH, the removal efficiency of Hg$^{2+}$ and MeHg decreased gradually with the increase of pH. This is because with the increase of solution pH, the Hg(OH)$^+$ or MeHgOH compounds could be generated, which is stable in the water and reduced the Hg$^{2+}$ and MeHg adsorption [17, 20]. It should be noted that a slight increase of removal efficiency of Hg$^{2+}$ and MeHg were observed for pH > 8.0. This might be attributed to the fact that when the solution pH is larger than the critial value pH$_{pzc}$, mostly in the range of 4–6 [9,42], the negative charge surface, which can provide electrostatic interactions, enhances the absorption of Hg$^{2+}$ and MeHg [40].

3.3. Effect of NOM on adsorption

The impact of NOM on the adsorption of Hg$^{2+}$ and MeHg to MWCNTs seemed very complicated. There are at least
3.4. Effect of Cl⁻ on adsorption

The effect of Cl⁻ on adsorption of Hg²⁺ and MeHg at pH 7.0 was shown in Figure 5, in which Cl⁻ exhibited a strong inhibitory effect on the adsorption of Hg²⁺ and MeHg. With the increase of Cl⁻ concentration from 0 to 800 mmol/L, the removal efficiency of Hg²⁺ and MeHg decreased sharply except MWCNTs-NH₂, in which case the removal efficiency decreased gradually due to the strong adsorption of Hg²⁺ and MeHg on MWCNTs-NH₂.

It is well known that Hg²⁺ and MeHg inclined to bind to Cl⁻ to form complexes, which could reduce their sorption to MWCNTs. While HgCl₂ was the main existing form for Cl⁻ concentration in the range of 5−115 mmol/L, HgCl₄²⁻ dominated when the concentration increased from 115 to 800 mmol/L (Figure S1). High concentration of Cl⁻ in solution could also promote the formation of very stable MeHgCl complex which showed lower sorption than MeHg to MWCNTs. These results agreed with those of previous studies [20,48]. de Diego et al. [48] found that a high concentration NaCl could led to declined adsorption rates of mercury species. Chen et al. [20] revealed that the adsorption of Hg²⁺ dropped drastically from 94.3% to 1.5% as the increase of Cl⁻ concentration from 0 to 1.0 mol/L and as the pH increasing from 4.3 to 10.5.

3.5. Effect of adsorbent dose

Figure 6 shows the effect of adsorbent dose on the adsorption of Hg²⁺ and MeHg at pH 7.0. The strong sorption of Hg²⁺ to MWCNTs make it requires low dose of MWCNTs to remove Hg²⁺, and high (>90%) and almost equal removal efficiencies were obtained in the studied range of MWCNTs concentration (0.5−2.0 g/L) for all the four MWCNTs. Due to the relatively weak sorption of MeHg to MWCNTs, the removal efficiency
3.6. Adsorption isotherms

Adsorption isotherm was conducted by varying the initial concentration of Hg$^{2+}$ and MeHg from 10–500 μg/L (Figures S2-S5), and obtained isotherm parameters of MeHg increased with the MWCNTs dose. The maximum value of removal efficiency was observed at 1.0 g/L MWCNTs-NH$_2$ for the strong complex between the -NH$_2$ and MeHg, and at about 2.0 g/L of the other three MWCNTs.

3.6. Adsorption isotherms

Adsorption isotherm was conducted by varying the initial concentration of Hg$^{2+}$ and MeHg from 10–500 μg/L (Figures S2-S5), and obtained isotherm parameters...
were shown in Tables 1 and 2. The $R^2$ values in Tables 1 and 2 indicate that the Freundlich model and Dubinin-Radushkevich model can describe the Hg$^{2+}$ adsorption very well, while the Langmuir and Dubinin-Radushkevich models showed the best fit to the MeHg adsorption.

From the Langmuir model, the maximum adsorption capacities $Q_m$ of Hg$^{2+}$ and MeHg are in the order of MWCNTs-NH$_2$ > MWCNTs-COOH > MWCNTs-OH > MWNTs. For the initial concentration of 100 μg/L Hg$^{2+}$ and MeHg, the values of $R_l$ were between 0 and 1, indicating the favorable adsorption process. The Freundlich isotherm also indicated that the adsorption presented in the surface of absorbents for Hg$^{2+}$ was heterogeneity with the regression coefficient 0.862 to 0.960.

Table 1. Parameters of isotherms for Hg$^{2+}$ adsorption on MWCNTs (mean ± SD, n = 3).

| Model                  | Parameter | MWCNTs  | MWCNTs-OH | MWCNTs-COOH | MWCNTs-NH$_2$ |
|------------------------|-----------|---------|-----------|-------------|---------------|
| Langmuir               | $Q_m$ (mg/g) | 71.1 ± 7.3 | 78.9 ± 4.7 | 134 ± 20 | 205 ± 10 |
|                        | $R_l$ ($C_i = 0.1$ mg/L) | 0.13 ± 0.01 | 0.13 ± 0.03 | 0.06 | 0.03 |
|                        | $b$ (L/mg) | 0.07 ± 0.01 | 0.07 ± 0.02 | 0.17 | 0.30 ± 0.01 |
|                        | $R^2$     | 0.719 | 0.935 | 0.914 | 0.865 |
| Freundlich             | n         | 0.84 ± 0.01 | 0.57 ± 0.03 | 0.81 ± 0.05 | 0.60 ± 0.02 |
|                        | $K_f$ (mg$^{-1}$ L$^n$/g) | 8.63 ± 0.82 | 18.3 ± 0.3 | 33.9 ± 0.3 | 48.0 ± 0.3 |
|                        | $R^2$     | 0.862 | 0.960 | 0.956 | 0.931 |
| Dubinin-Radushkevich  | $E$ (kJ/mol) | 9.13 ± 0.08 | 9.97 ± 0.21 | 9.29 ± 0.29 | 8.15 ± 0.17 |
|                        | $β$ (mol$^{-1}$/kJ) | 0.006 | 0.005 | 0.006 | 0.006 |
|                        | $R^2$     | 0.977 | 0.969 | 0.977 | 0.805 |
| Temkin                 | $b_j$ (kJ/mol) | 12.6 ± 0.6 | 10.6 ± 0.1 | 10.1 ± 0.6 | 7.79 ± 0.27 |
|                        | $A_j$ | 2.67 ± 0.05 | 1.49 ± 0.15 | 1.18 ± 0.16 | 1.44 ± 0.11 |
|                        | $R^2$     | 0.944 | 0.849 | 0.790 | 0.695 |

Table 2. Parameters of isotherms for MeHg adsorption on MWCNTs (mean ± SD, n = 3).

| Model                  | Parameter | MWCNTs  | MWCNTs-OH | MWCNTs-COOH | MWCNTs-NH$_2$ |
|------------------------|-----------|---------|-----------|-------------|---------------|
| Langmuir               | $Q_m$ (mg/g) | 184 ± 8 | 237 ± 12 | 265 ± 38 | 334 ± 11 |
|                        | $R_l$ ($C_i = 0.1$ mg/L) | 0.24 ± 0.02 | 0.17 ± 0.01 | 0.27 ± 0.02 | 0.16 ± 0.02 |
|                        | $b$ (L/mg) | 0.03 | 0.03 | 0.05 | 0.05 ± 0.01 |
|                        | $R^2$     | 0.997 | 0.995 | 0.998 | 0.964 |
| Freundlich             | n         | 1.47 ± 0.04 | 1.60 ± 0.04 | 1.34 ± 0.01 | 1.28 ± 0.02 |
|                        | $K_f$ (mg$^{-1}$ L$^n$/g) | 9.40 ± 0.12 | 10.5 ± 0.1 | 10.6 ± 0.1 | 23.9 ± 0.4 |
|                        | $R^2$     | 0.996 | 0.997 | 0.997 | 0.922 |
| Dubinin-Radushkevich  | $E$ (kJ/mol) | 11.8 ± 0.2 | 12.4 ± 0.1 | 11.4 ± 0.1 | 11.1 ± 0.1 |
|                        | $β$ (mol$^{-1}$/kJ) | 0.004 | 0.003 | 0.004 | 0.004 |
|                        | $R^2$     | 0.999 | 0.999 | 0.998 | 0.997 |
| Temkin                 | $b_j$ (kJ/mol) | 36.4 ± 2.5 | 30.2 ± 1.6 | 21.6 ± 0.5 | 14.1 ± 0.2 |
|                        | $A_j$ | 3.44 ± 0.21 | 3.01 ± 0.15 | 3.16 ± 0.17 | 1.59 ± 0.03 |
|                        | $R^2$     | 0.838 | 0.829 | 0.806 | 0.936 |

Table 3. Kinetic parameters for adsorption of Hg$^{2+}$ onto MWCNTs.

| Model                  | Parameter | MWCNTs  | MWCNTs-OH | MWCNTs-COOH | MWCNTs-NH$_2$ |
|------------------------|-----------|---------|-----------|-------------|---------------|
| Pseudo-first order     | $k_1$ (min$^{-1}$) | 0.0146 | 0.0412 | 0.0287 | 0.0314 |
|                        | $q_e$ (mg/g) | 5.96 | 85.9 | 47.0 | 45.0 |
|                        | $R^2$     | 0.564 | 0.938 | 0.862 | 0.962 |
| Pseudo-second order    | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.0321 | 0.00210 | 0.000537 | 0.00572 |
|                        | $q_e$ (mg/g) | 46.0 | 93.9 | 120 | 140 |
|                        | $R^2$     | 0.999 | 0.999 | 0.997 | 0.994 |

Table 4. Kinetic parameters for adsorption of MeHg onto MWCNTs.

| Model                  | Parameter | MWCNTs  | MWCNTs-OH | MWCNTs-COOH | MWCNTs-NH$_2$ |
|------------------------|-----------|---------|-----------|-------------|---------------|
| Pseudo-first order     | $k_1$ (min$^{-1}$) | 0.00867 | 0.00815 | 0.00880 | 0.0117 |
|                        | $q_e$ (mg/g) | 4.89 | 5.43 | 4.85 | 3.67 |
|                        | $R^2$     | -0.101 | 0.564 | 0.204 | 0.835 |
| Pseudo-second order    | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.0161 | 0.0115 | 0.0428 | 0.0229 |
|                        | $q_e$ (mg/g) | 20.2 | 28.1 | 40.2 | 91.6 |
|                        | $R^2$     | 0.986 | 0.992 | 0.990 | 0.995 |
In the Dubinin-Radushkevich model, the mean free energy value \( E_{\text{DR}} \) is used to identify adsorption mechanism. The \( E_{\text{DR}} \) value is between 8 kJ/mol and 16 kJ/mol for the chemical adsorption process, and below 8 kJ/mol for physical adsorption [37]. As the \( E_{\text{DR}} \) values ranged from 8.15 to 12.37 kJ/mol, the adsorption of Hg\(^{2+}\) and MeHg to the four MWCNTs is the chemical adsorption. From the Temkin model, the adsorption energy \( B_T \) shows the biggest value in the adsorption of Hg\(^{2+}\) and MeHg on MWCNTs-NH\(_2\), suggesting that Hg\(^{2+}\) and MeHg could adsorb to MWCNTs-NH\(_2\).

### 3.7. Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetics models were adopted to describe the adsorption kinetics of Hg\(^{2+}\) and MeHg to the MWCNTs (Figures S6 and S7), and the regression coefficients and the parameters of the kinetic models are shown in Tables 3 and 4. Since the \( R^2 \) values of the pseudo-second-order kinetic model are closer to one than that of the pseudo-first-order kinetic model, the pseudo-second-order kinetic model is more suitable to describe the adsorption processes of the Hg\(^{2+}\) and MeHg.

### 4. Conclusions

This work demonstrated that MWCNTs-NH\(_2\), MWCNTs-COOH, MWCNTs-OH and MWCNTs are very efficient adsorbents for removal of Hg\(^{2+}\) and MeHg from aqueous solution, with the order of adsorption capacity as MWCNTs-NH\(_2\) > MWCNTs-COOH > MWCNTs-OH > MWCNTs. For all the four MWCNTs, the adsorption of Hg\(^{2+}\) and MeHg is pH dependent, and NOM and Cl\(^-\) concentration also plays an important role. Increase of NOM concentration caused a significant reduction of the removal efficiency of Hg\(^{2+}\), while Cl\(^-\) produced a strong inhibiting effect on the adsorption of Hg\(^{2+}\) and MeHg. The adsorption isotherm model of Hg\(^{2+}\) agreed with the Freundlich and Dubinin-Radushkevich isotherms very well, suggesting it is the heterogeneity and chemical sorption. The MeHg adsorption followed the Langmuir andDubinin-Radushkevich isotherms, which belongs to the homogeneity and chemical adsorption.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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### References

[1] Tang W, Cheng J, Zhao W, et al. Mercury levels and estimated total daily intakes for children and adults from an electronic waste recycling area in Taizhou, China: key role of rice and fish consumption. J Environ Sci. 2015;34:107–115.

[2] Yan H, Rustadbakken A, Yao H, et al. Total mercury in wild fish in Guizhou reservoirs, China. J Environ Sci. 2010;22(8):1129–1136.

[3] Fleming EJ, Mack EE, Green PG, et al. Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium. Appl Environ Microbiol. 2006;72(1):457–464.

[4] Gilmour CC, Henry EA, Mitchell R. Sulfate stimulation of mercury methylation in freshwater sediments. Environ Sci Technol. 1992;26(11):2281–2287.

[5] Wu H, Ding Z, Liu Y, et al. Methylmercury and sulfate-reducing bacteria in mangrove sediments from Jiulong River Estuary, China. J Environ Sci. 2011;23(1):14–21.

[6] Amde M, Yin YG, Zhang D, et al. Methods and recent advances in speciation analysis of mercury chemical species in environmental samples: a review. Chem Speciation Bioavail. 2016;28(1–4):51–65.

[7] Mergler D, Anderson HA, Chan LHM, et al. Methylmercury exposure and health effects in humans: a worldwide concern. Ambio. 2007;36(1):13–11.

[8] Wang S, Zhang L, Wang L, et al. A review of atmospheric mercury emissions, pollution and control in China. Front Environ Sci Eng. 2014;8(5):631–649.

[9] Stafilej A, Pyrzynska K. Adsorption of heavy metal ions with carbon nanotubes. Sep Purif Technol. 2007;58(1):49–52.

[10] Rao GP, Lu C, Su F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review. Sep Purif Technol. 2007;58(1):224–231.

[11] Upadhyayula VKK, Deng S, Mitchell MC, et al. Application of carbon nanotube technology for removal of contaminants in drinking water: a review. Sci Total Environ. 2009;408(1):1–13.

[12] Ihsanullah, Abbas A, Al-Amer AM, et al. Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. Sep Purif Technol. 2016;157:141–161.

[13] Li YH, Ding J, Luan Z, et al. Competitive adsorption of Pb\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) ions from aqueous solutions by multiwalled carbon nanotubes. Carbon. 2003;41(14):2787–2792.

[14] Li YH, Wang S, Luan Z, et al. Adsorption of cadmium(Ill) from aqueous solution by surface oxidized carbon nanotubes. Carbon. 2003;41(5):1057–1062.

[15] Li YH, Wang S, Wei J, et al. Lead adsorption on carbon nanotubes. Chem Phys Lett. 2002;357(3–4):263–266.

[16] Lu C, Chiu H, Liu C. Removal of zinc(II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. Ind Eng Chem Res. 2006;45(8):2850–2855.

[17] Shabad MJ, Mohibb A, Soltani A. Mercury(II) removal from aquatic systems by adsorption on multi-walled carbon nanotubes. Korean J Chem Eng. 2011;28(4):1029–1034.

[18] Vukovic GD, Marinkovic AD, Skapin SD, et al. Removal of lead from water by amino modified multi-walled carbon nanotubes. Chem Eng J. 2011;173(3):855–865.

[19] Jiang L, Li S, Yu H, et al. Amino and thiol modified magnetic multi-walled carbon nanotubes for the simultaneous removal of lead, zinc, and phenol from aqueous solutions. Appl Surf Sci. 2016;369:398–413.
[20] Chen PH, Hsu CF, Tsai DDW, et al. Adsorption of mercury from water by modified multi-walled carbon nanotubes: adsorption behaviour and interference resistance by coexisting anions. Environ Technol. 2014;35(15):1935–1944.

[21] Yaghmaeian K, Khosravi Mashizi R, Nasseri S, et al. Removal of inorganic mercury from aquatic environments by multi-walled carbon nanotubes. J Environ Health Sci Eng. 2015;13(1):1–9.

[22] Lim JK, Yun WS, Yoon MH, et al. Selective thiolation of single-walled carbon nanotubes. Synth Met. 2003;139(2):521–527.

[23] Hu J, Shi J, Li S, et al. Efficient method to functionalize carbon nanotubes with thiol groups and fabricate gold nanocomposites. Chem Phys Lett. 2005;401(4–6):352–356.

[24] Kim YT, Mitani T. Surface thiolation of carbon nanotubes as supports: a promising route for the high dispersion of Pt nanoparticles for electrocatalysts. J Catal. 2006;238(2):394–401.

[25] Feyte S, Tressier A, Gobeil C, et al. In situ adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments. Appl Geochem. 2010;25(7):984–995.

[26] Hyung H, Kim JH. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters. Environ Sci Technol. 2008;42(12):4416–4421.

[27] Hyung H, Fortner JD, Hughes JB, et al. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. Environ Sci Technol. 2007;41(1):179–184.

[28] Bandaru NM, Reta N, Dalal H, et al. Enhanced adsorption of mercury ions on thiol derivatized single wall carbon nanotubes. J Hazard Mater. 2013;261:534–541.

[29] Tawabin B, Al-Khaldi S, Atieh M, et al. Removal of mercury from water by multi-walled carbon nanotubes. Water Sci Technol. 2010;61(3):591–598.

[30] Sheela T, Nayaka YA, Viswanatha R, et al. Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. Powder Technol. 2012;217:163–170.

[31] Wang ZH, Yin YG, He B, et al. L-cysteine-induced degradation of organic mercury as a novel interface in the HPLC-CV-AFS hyphenated system for speciation of mercury. J Anal At Spectr. 2010;25(6):810–814.

[32] Zhao XH, Jiao FP, Yu JG, et al. Removal of Cu(II) from aqueous solutions by tartaric acid modified multi-walled carbon nanotubes. Colloid Surf A-Physicochem Eng. 2015;476:35–41.

[33] Gupta A, Vidyarthi SR, Sankararamakrishnan N. Enhanced sorption of mercury from compact fluorescent bulbs and contaminated water streams using functionalized multiwalled carbon nanotubes. J Hazard Mater. 2014;274:132–144.

[34] Hadavifar M, Bahramifar N, Younesi H, et al. Adsorption of mercury ions from synthetic and real wastewater aqueous solution by functionalized multi-walled carbon nanotube with both amino and thiolated groups. Chem Eng J. 2014;237:217–228.

[35] Xu D, Tan X, Chen C, et al. Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes. J Hazard Mater. 2008;154(1–3):407–416.

[36] Zabibi M, Ahmadpour A, Asl AH. Removal of mercury from water by carbonaceous sorbents derived from walnut shell. J Hazard Mater. 2009;167(1–3):230–236.

[37] Moghaddam HK, Pakizeh M. Experimental study on mercury ions removal from aqueous solution by MnO2/CNTs nanocomposite adsorbent. J Ind Eng Chem. 2015;21:221–229.

[38] Scheibe B, Borowiak-Palen E, Kalenczuk RJ. Oxidation and reduction of multiwalled carbon nanotubes – preparation and characterization. Mater Charact. 2010;61(2):185–191.

[39] Vuković G, Marinković A, Obradović M, et al. Synthesis, characterization and cytotoxicity of surface amino-functionalized water-dispersible multi-walled carbon nanotubes. Appl Surf Sci. 2009;255(18):8067–8075.

[40] Ren X, Chen C, Nagatsu M, et al. Carbon nanotubes as adsorbents for environmental pollution management: a review. Chem Eng J. 2011;170(2–3):395–410.

[41] Ma Y, La P, Lei W, et al. Adsorption of Hg(II) from aqueous solution using amino-functionalized graphene nanosheets decorated with Fe3O4 nanoparticles. Desalin Water Treat. 2016;57(11):5004–5012.

[42] Pillay K, Cukrowska EM, Coville NJ. Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. J Hazard Mater. 2009;166(2–3):1067–1075.

[43] Hintelmann H, Welbourn PM, Evans RD. Measurement of complexation of methylmercury(II) compounds by freshwater humic substances using equilibrium dialysis. Environ Sci Technol. 1997;31(2):489–495.

[44] Kushwaha S, Sreedhar B, Padmaja P. Sorption of phenyl mercury, methyl mercury, and inorganic mercury onto chitosan and barbital immobilized chitosan: spectroscopic, potentiometric, kinetic, equilibrium, and selective desorption studies. J Chem Eng Data. 2010;55(11):4691–4698.

[45] Kushwaha S. Sudhakar PP. Adsorption of mercury(II), methyl mercury(II) and phenyl mercury(II) on chitosan cross-linked with a barbital derivative. 2011;86(2):1055–1062.

[46] Jeong HY, Klaue B, Blum JD, et al. Sorption of mercuric ion by synthetic nanocrystalline mackinawite (FeS). Environ Sci Technol. 2007;41(22):7699–7705.

[47] Lu C, Su F. Adsorption of natural organic matter by carbon nanotubes. Sep Purif Technol. 2007;58(1):113–121.

[48] de Diego A, Tseng CM, Dimov N, et al. Adsorption of aqueous inorganic mercury and methylmercury on suspended kaolin: influence of sodium chloride, fulvic acid and particle content. Appl Organomet Chem. 2001;15(6):490–498.