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Removal of Hg²⁺ 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 Hg²⁺ 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 Hg²⁺ and MeHg, and the removal efficiency could reach up to 92% (0.5 g/L MWCNTs, and 100 µg/L Hg²⁺ and MeHg) which is independent of pH. NOM had complex effects on the adsorption of Hg²⁺ and MeHg to MWCNTs. Cl⁻ inhibited the adsorption of Hg²⁺ and MeHg to MWCNTs. The adsorption of Hg²⁺ 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 Hg²⁺ and MeHg in aqueous environment.

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Hg²⁺; methylmercury;
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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 Hg⁰, Hg²⁺ and methylmercury (MeHg). Hg⁰ and Hg²⁺ 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 Pb²⁺, Cd²⁺, Zn²⁺, Cu²⁺, Ni²⁺, Hg²⁺ 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 adsorbents to removal of Hg²⁺ and MeHg in waters, it is of great importance to understand the effects of NOM and other environmental factors on the sorption of Hg²⁺ and MeHg to functionalized MWCNTs. Although the adsorption of Hg²⁺ by MWCNTs has been extensively studied [17,28–30], the adsorption of MeHg to functionalized MWCNTs especially in the presence of Hg²⁺, has not been reported.

In this study, we studied the removal efficiency of Hg²⁺ 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-NH₂), respectively. The effects of environmentally relevant factors like pH, NOM, and Cl⁻ on the

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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. Milli-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]:

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

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]:

$$q = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

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]:

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{C_e Q_m b} \quad (3)$$

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). Q_m 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]:

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

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]:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (5)$$

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 ($\text{mg}^{1-n} \text{L}^n/\text{g}$) 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]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

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), β is related to the mean adsorption energy, ε is the Polanyi potential, and R (J/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]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

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]:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (9)$$

where $RT/b_T = B_T$, 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_T 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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

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:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) 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 $\sim 2884 \text{ cm}^{-1}$ 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 $\sim 1617 \text{ cm}^{-1}$, which are assigned to stretching vibrations of $\nu(\text{-OH})$ and $\nu(\text{C=O})$ of -COOH [34,39]. The peaks at $\sim 3450 \text{ cm}^{-1}$ corresponded to -NH_2 stretching vibration in the MWCNTs- NH_2 spectrum. In addition, the presence of peaks at ~ 1415 and $\sim 1262 \text{ cm}^{-1}$, originated from N-H in-plane and C-N bond stretching, respectively [39].

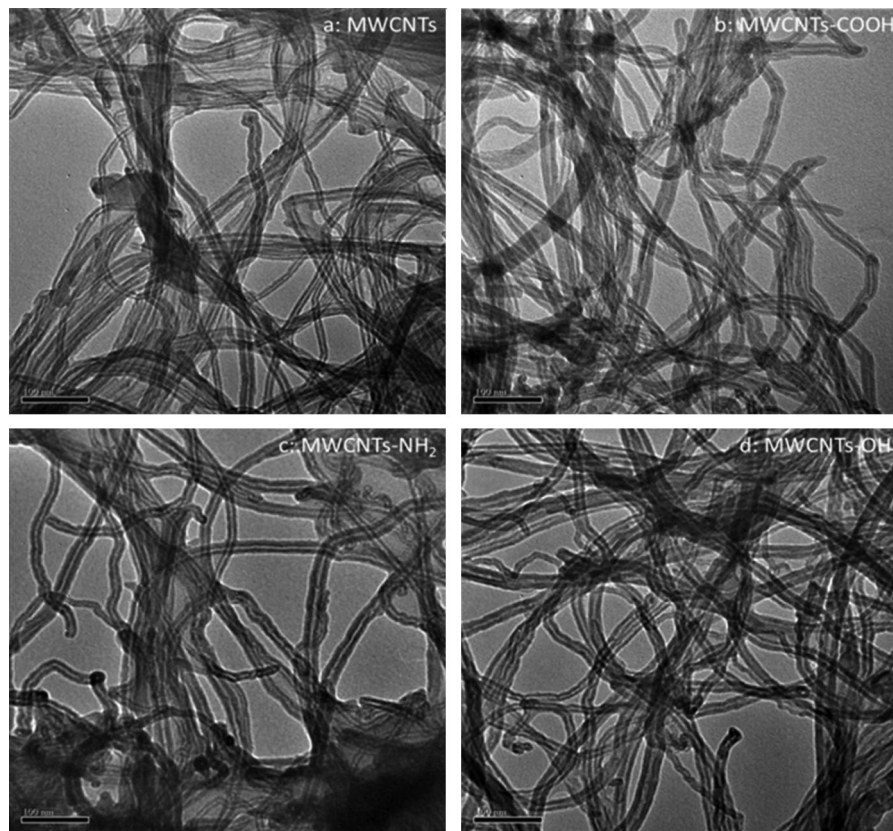


Figure 1. TEM images of pristine and functionalized MWCNTs. (a) MWCNTs; (b) MWCNTs-COOH; (c) MWCNTs-NH₂; (d) MWCNTs-OH.

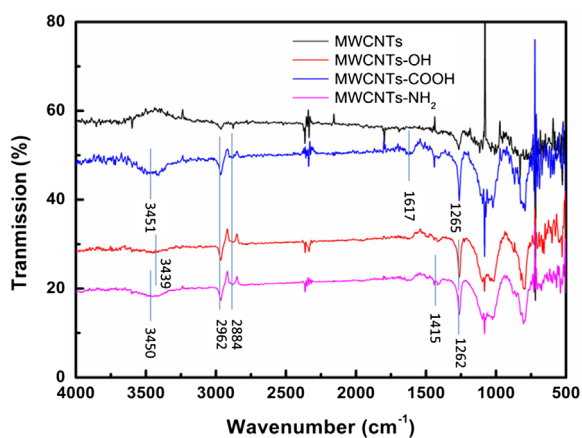


Figure 2. FTIR of pristine and functionalized MWCNTs.

The peaks at ~ 3439 and ~ 1265 cm^{-1} were attributed to -OH stretching vibration in the MWCNTs-OH spectrum [20]. Functional groups on the surface of the carbon nanotubes offered a lot of adsorption sites, which may be useful to increase the adsorption ability of carbon nanotubes.

3.2. Influence of initial pH on adsorption

The pH of solution had a great effect on the adsorption of metal ions [9,10,40]. To evaluate the effect of initial pH on the Hg²⁺ and MeHg adsorption, a series of sample solutions with pHs ranging from 4.0 to 9.0 by phosphate

buffers were adopted. The results shown in Figure 3 indicate that the pH had no significant effect on the removal of Hg²⁺ and MeHg on MWCNTs-NH₂. This is because the adsorption of Hg²⁺ and MeHg onto MWCNTs-NH₂ 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 consistent with the results in Ref. [41].

Figure 3 also shows that for pristine MWCNTs, MWCNTs-OH and MWCNTs-COOH, the removal efficiency of Hg²⁺ 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 Hg²⁺ and MeHg adsorption [17,20]. It should be noted that a slight increase of removal efficiency of Hg²⁺ and MeHg were observed for pH > 8.0. This might be attributed to the fact that when the solution pH is larger than the critical 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 Hg²⁺ and MeHg [40].

3.3. Effect of NOM on adsorption

The impact of NOM on the adsorption of Hg²⁺ and MeHg to MWCNTs seemed very complicated. There are at least

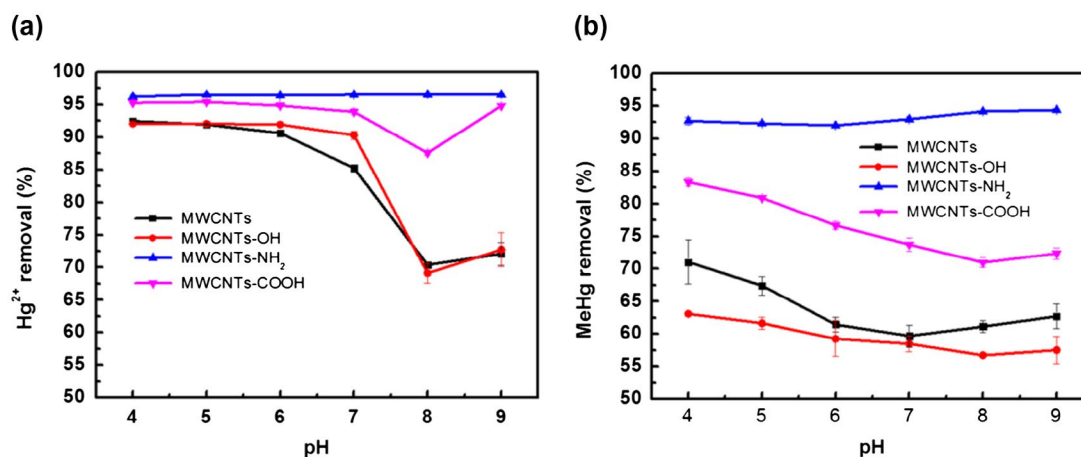


Figure 3. Effect of pH on removal of Hg²⁺ (a) and MeHg (b) by MWCNTs.

Notes: In the solutions were spiked with 0.5 g/L different MWCNTs, and 100 µg/L Hg²⁺ and MeHg, respectively. The solution pH was adjusted by using 10 mmol/L phosphate buffer.

four adsorbing processes in the solution: (i) NOM could combine with Hg²⁺ and MeHg [25,43]; (ii) MWCNTs could adsorb Hg²⁺ and MeHg [17,21,29,37,44–46]; (iii) MWCNTs could adsorb NOM and form MWCNTs-NOM complexes [47]; and (iv) NOM could stabilize the dispersion of MWCNTs [26,27]. Depending on the characteristics of MWCNTs and NOM, as well as the aqueous chemistry parameters, these four processes showed different strength and therefore resulted in varied removal efficiency of Hg²⁺ and MeHg.

The effect of NOM concentration on the adsorption of Hg²⁺ and MeHg was studied at pH 7.0. As shown in Figure 4(a), the removal efficiency of Hg²⁺ decreased gradually when the NOM concentration increased from 0 to 20 mg/L DOC. The influence of NOM on the adsorption of Hg²⁺ can be understood from the following three aspects. Firstly, MWCNTs could adsorb NOM and Hg²⁺ at the same time, which generated the competitive adsorption. Secondly, NOM occupied the binding sites on the MWCNTs, reducing the adsorption of Hg²⁺. Lastly, free NOM in the solution could increase the distribution of Hg²⁺ in water, which could lead to reduced adsorption of Hg²⁺.

Figure 4(b) shows that when the NOM concentration increased from 0 to 20 mg/L DOC, the removal efficiency of MeHg varied depending on the functional groups modified on MWCNTs. For MWCNTs and MWCNTs-OH, due to their relatively weak binding to MeHg, when low concentration of NOM was present, the NOM adsorbed on MWCNTs enhanced the adsorption and therefore removal of MeHg. For MWCNTs-NH₂ and MWCNTs-COOH that showed relatively strong combination with MeHg, when NOM was present, the NOM adsorbed on MWCNTs could not increase the adsorption of MeHg on MWCNTs; in contrast, the competitive binding of NOM to MeHg in the solution slightly reduced the removal efficiency of MeHg by MWCNTs.

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 lead 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

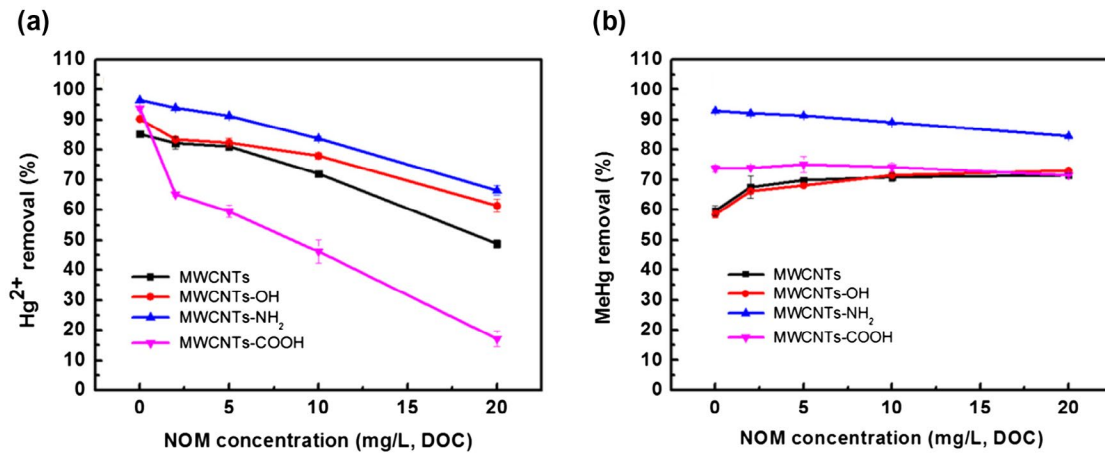


Figure 4. Effect of NOM on the removal of Hg^{2+} (a) and MeHg (b) by MWCNTs.

Notes: In the solutions were spiked with 0.5 g/L different MWCNTs, and 100 $\mu\text{g/L}$ Hg^{2+} and MeHg, respectively. The solution pH was adjusted to pH 7.0 by using 10 mmol/L phosphate buffer.

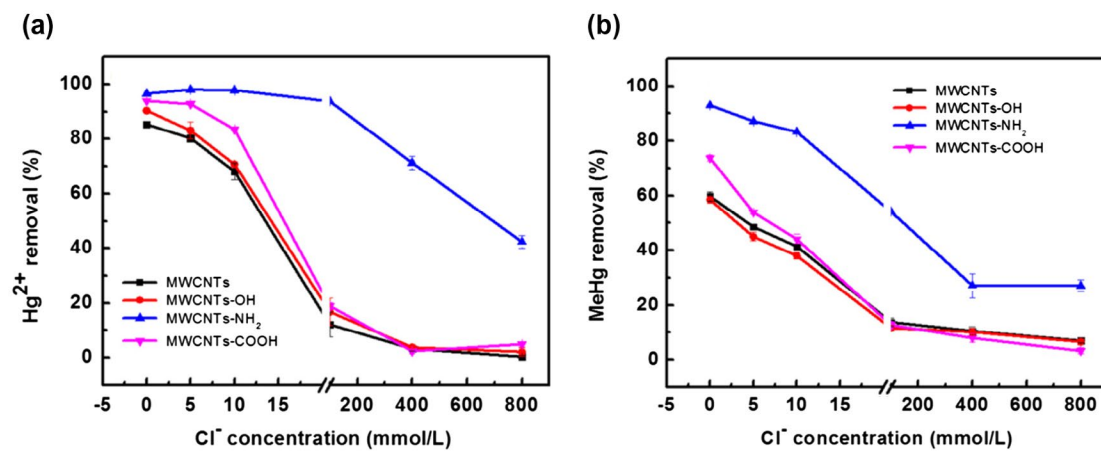


Figure 5. Effect of Cl^- on the removal of Hg^{2+} (a) and MeHg (b) by MWCNTs.

Notes: In the solutions were spiked with 0.5 g/L different MWCNTs, different concentration of Cl^- , and 100 $\mu\text{g/L}$ Hg^{2+} and MeHg, respectively. The solution pH was adjusted to pH 7.0 by using 10 mmol/L phosphate buffer.

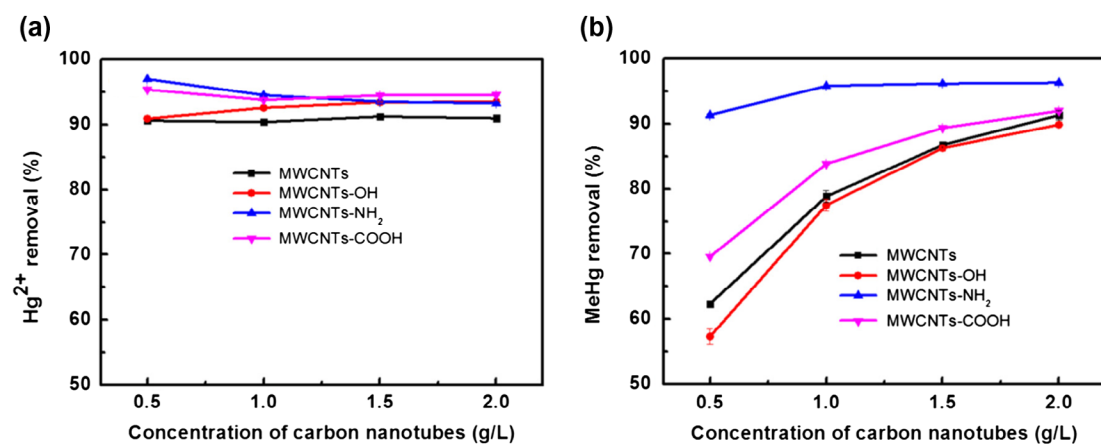


Figure 6. Effect of adsorbent dose on removal of Hg^{2+} (a) and MeHg (b).

Notes: In the solutions were spiked with 100 $\mu\text{g/L}$ Hg^{2+} and MeHg, respectively. The solution pH was adjusted to pH 7.0 by using 10 mmol/L phosphate buffer.

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 $-\text{NH}_2$ 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 $\mu\text{g/L}$ (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-NH₂ > MWCNTs-COOH > MWCNTs-OH > MWCNTs. For the initial concentration of 100 $\mu\text{g/L}$ Hg^{2+} and MeHg, the values of R_L were between 0 and 1, indicating the favorable adsorption onto the four kinds of MWCNTs. The R^2 of MeHg was closer to one than that

of Hg^{2+} , which indicated that the adsorption of MeHg agreed more closely with Langmuir isotherms. The Q_m of MWCNT-COOH for Hg^{2+} was 133.5 mg/g. The result was higher than that in the literature [20].

The coefficient K_f in the Freundlich model, representing the adsorption capacity, shows the same order as the Langmuir coefficient Q_m . The n values ranged between 0 and 10 for all the adsorbents, revealing the favorable adsorption process. The Freundlich isotherm also indicated that the adsorption presented in the surface of adsorbents 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 \pm SD, $n = 3$).

Model	Parameter	MWCNTs	MWCNTs-OH	MWCNTs-COOH	MWCNTs-NH ₂
Langmuir	Q_m (mg/g)	71.1 \pm 7.3	78.9 \pm 4.7	134 \pm 20	205 \pm 10
	R_L ($C_0 = 0.1$ mg/L)	0.13 \pm 0.01	0.13 \pm 0.03	0.06	0.03
	b (L/mg)	0.07 \pm 0.01	0.07 \pm 0.02	0.17	0.30 \pm 0.01
	R^2	0.719	0.935	0.914	0.865
Freundlich	n	0.84 \pm 0.01	0.97 \pm 0.03	0.81 \pm 0.05	0.60 \pm 0.02
	K_f ($\text{mg}^{1-n} \text{L}^n/\text{g}$)	8.63 \pm 0.82	18.3 \pm 0.3	33.9 \pm 0.3	48.0 \pm 0.3
	R^2	0.862	0.960	0.956	0.931
Dubinin-Radushkevich	E (kJ/mol)	9.13 \pm 0.08	9.97 \pm 0.21	9.29 \pm 0.29	8.15 \pm 0.17
	β (mol^2/kJ)	0.006	0.005	0.006	0.008
	R^2	0.977	0.969	0.977	0.805
Temkin	b_T (kJ/mol)	12.6 \pm 0.6	10.6 \pm 0.1	10.1 \pm 0.6	7.79 \pm 0.27
	B_T (kJ/mol)	194 \pm 9	229 \pm 2	242 \pm 14	313 \pm 11
	A_T	2.67 \pm 0.05	1.49 \pm 0.15	1.18 \pm 0.16	1.44 \pm 0.11
	R^2	0.944	0.849	0.790	0.695

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

Model	Parameter	MWCNTs	MWCNTs-OH	MWCNTs-COOH	MWCNTs-NH ₂
Langmuir	Q_m (mg/g)	184 \pm 8	237 \pm 12	265 \pm 38	334 \pm 11
	R_L ($C_0 = 0.1$ mg/L)	0.24 \pm 0.02	0.17 \pm 0.01	0.27 \pm 0.02	0.16 \pm 0.02
	b (L/mg)	0.03	0.03	0.05	0.05 \pm 0.01
	R^2	0.997	0.995	0.998	0.964
Freundlich	n	1.47 \pm 0.04	1.60 \pm 0.04	1.34 \pm 0.01	1.28 \pm 0.02
	K_f ($\text{mg}^{1-n} \text{L}^n/\text{g}$)	9.40 \pm 0.12	10.5 \pm 0.1	10.6 \pm 0.1	23.9 \pm 0.4
	R^2	0.996	0.997	0.997	0.922
Dubinin-Radushkevich	E (kJ/mol)	11.8 \pm 0.2	12.4 \pm 0.1	11.4 \pm 0.1	11.1 \pm 0.1
	β (mol^2/kJ)	0.004	0.003	0.004	0.004
	R^2	0.999	0.999	0.998	0.917
Temkin	b_T (kJ/mol)	36.4 \pm 2.5	30.2 \pm 1.6	21.6 \pm 0.5	14.1 \pm 0.2
	B_T (kJ/mol)	67.2 \pm 4.6	80.9 \pm 4.4	112 \pm 2	173 \pm 2
	A_T	3.44 \pm 0.21	3.01 \pm 0.15	3.16 \pm 0.17	1.59 \pm 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 ($\text{g mg}^{-1} \text{min}^{-1}$)	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 ($\text{g mg}^{-1} \text{min}^{-1}$)	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_{DR} is used to identify adsorption mechanism. The E_{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_{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-NH₂, suggesting that Hg^{2+} and MeHg could adsorb to MWCNTs-NH₂.

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-NH₂, 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-NH₂ > 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 and Dubinin-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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