



Thorough removal of inorganic and organic mercury from aqueous solutions by adsorption on *Lemna minor* powder

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ABSTRACT

The adsorption ability of duckweed (*Lemna minor*) powders for removing inorganic and organic mercury (methyl and ethyl mercury) has been studied using cold vapour atomic absorption spectrometry. The optimal adsorption conditions were: (a) the pH value of the solution 7.0 for inorganic and ethyl mercury, 9.0 for methyl mercury, and (b) equilibrium adsorption time 10, 20, and 40 min for inorganic mercury, methyl mercury, and ethyl mercury, respectively. After adsorption by *L. minor* powder for 40 min, when the initial concentrations of inorganic and organic mercury were under $12.0 \mu\text{g L}^{-1}$ and $50.0 \mu\text{g L}^{-1}$, respectively, the residual concentrations of mercury could meet the criterion of drinking water ($1.0 \mu\text{g L}^{-1}$) and the permitted discharge limit of wastewater ($10.0 \mu\text{g L}^{-1}$) set by China and USEPA, respectively. Thorough removal of both inorganic and organic mercury from aqueous solutions was reported for the first time. The significant adsorption sites were C–O–P and phosphate groups by the surface electrostatic interactions with aqueous inorganic and organic mercury cations, and then the selective adsorption was resulted from the strong chelating interaction between amine groups and mercury on the surface of *L. minor* cells.

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1. Introduction

Mercury is well known for its extremely high toxicity. A very low concentration of mercury in water may cause health hazard. The drinking water criterion for mercury established by USEPA is $2.0 \mu\text{g L}^{-1}$ [1], and the permitted discharge limit of wastewater for total mercury is $10.0 \mu\text{g L}^{-1}$ [2]. The World Health Organization (WHO) and China have set the guideline value for inorganic mercury in drinking water at $1.0 \mu\text{g L}^{-1}$ [3]. So it is very important to decrease the residual mercury concentration below the safety limit for organic and inorganic mercury from industrial wastewater, especially from drinking water. Conventional methods for the removal of mercury from waste streams include adsorption [4–6], biosorption [7], ion exchange [8], membrane filtration [9], chelate precipitation [10], precipitation/adsorption [11,12], and photoreduction [13,14]. Polymer adsorbents immobilizing S-contained functional groups were conveniently used for the removal of mercury in water [15]. However, most of these methods require either high energy or large quantities of chemicals. Conventional precipitation methods do not always provide a satisfactory removal rate

to meet pollution control limits; moreover, synthetic ion-exchange resins are often expensive [16], and adsorbents have low mechanical strength, weak hydrothermal stability, or a weak chemical bond with the metals [3]. These methods are ineffective when the mercury concentration was low [17]. Furthermore, most of the researches were limited to the removal of inorganic mercury. Mercury exists in two major forms in aqueous solutions: inorganic mercury and organic mercury, in particular, methyl mercury [18]. The treatment method that could be used for the removing of both inorganic and organic mercury from aqueous solutions has not been reported until now. Therefore, in order to meet the demand of residual concentration lower than $1 \mu\text{g L}^{-1}$ in drinking water purification, it is necessary to explore adsorptive materials with low cost, high adsorption speed, and good removal performance for low concentration of both inorganic and organic mercury.

Lemna minor was chosen as a test subject due to the widespread availability of the plant. It is tolerant of cold weather and can withstand temperatures ranging from 35°F to 95°F . *L. minor*, also known as duckweed, is a voracious grower and it can double its mass within a week under optimum growing conditions [19]. Previous works have shown that *L. minor* possesses excellent removal capabilities of heavy metals, including lead, nickel, cadmium, copper, and chromium [19–22]. For *L. minor* samples in the field and in the laboratory, the mercury levels were all significantly higher as 400–700 times of those in the unexposed samples. Therefore, *L. minor* powder could be used as a potential low-cost adsorbent for

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its excellent heavy metal removal capabilities. The application of *L. minor* powder on mercury removal has not reported until now. The adsorption ability of *L. minor* powders for removing inorganic and organic mercury (methyl and ethyl mercury) was studied by cold vapour atomic absorption spectrometry. The influence factors, such as the pH value of the sample, adsorption time, the usage of duckweed, the initial concentration of three species of mercury, temperature, and the coexistence of ions, on the adsorption ratio have been explored.

2. Materials and methods

2.1. Apparatus

The reduction of mercury was carried out using a Pyrex test tube (diameter 30 mm, length 200 mm, volume ca. 87 mL) equipped with a ball glass filter for the aeration of the solution. A SG 921 mercury analyzer (cold vapor atomic absorption spectrometer; closed circulation system; CV-AAS) was used to measure the concentration of mercury; the relative atomic absorbance at 253.7 nm was indicated in this instrument.

2.2. Reagents and *L. minor* powder

All the reagents were of analytical grade and the presence of mercury was not detected within the working range. Stock standard solutions for Hg were: Hg (II), stock standard solution for AAS, Trace CEPT™, 998.0 $\mu\text{g mL}^{-1}$ in 2 mol L⁻¹ HNO₃, (Sigma–Aldrich); methyl mercury or ethyl mercury (200.0 $\mu\text{g mL}^{-1}$ Hg), prepared by dissolving methyl mercury (II) chloride or ethyl mercury (II) chloride, analytical standard, Sigma–Aldrich in 0.1 mol L⁻¹ nitric acid (Ultra pure grade). All standards were stored in PTFE bottles at 4 °C. The working standard solutions were prepared by diluting the stock solution with 0.1 mol L⁻¹ HNO₃ daily. A commercially available sodium hypochlorite solution (Sigma–Aldrich, reagent grade) was used, the concentration of sodium hypochlorite determined by iodometric titration was 12.7% and then diluted to 9.2% (w/v) before using. A solution containing 1000.0 mg L⁻¹ of copper (II) was prepared by dissolving copper (II) sulfate hexahydrate with approximately 0.2 mol L⁻¹ sulfuric acid. A tin (II) chloride solution (10% (w/v)) was prepared by dissolving tin (II) chloride dihydrate with approximately 0.5 mol L⁻¹ sulfuric acid. Diluted HCl (Ultra pure grade) and NaOH (Merck) were used to adjust pH. Ultrapure water (18 M Ω cm) was obtained from a Millipore Continental Water System.

The duckweed was collected from San-xiang River (Zhangzhou, Fujian) and was taxonomically classified as *Lemna minor*. The duckweed was acclimatized to laboratory conditions for one week before starting the experiments. Samples of the *L. minor* were grown in three 8-L polyethylene water tanks (20 cm × 20 cm × 80 cm) to maximize water–air surface area. The *L. minor* was washed twice with running water, followed by once wash with deionized water. The washed biomass was oven-dried at 95 °C for 24 h, crushed with an analytical mill, sieved (size fraction of 0.150–0.125 mm), washed with 2.0 mol L⁻¹ HCl, stirred for 12 h, centrifuged, oven-dried at 95 °C for 24 h, and then stored in polyethylene bottles for later use.

2.3. Adsorption procedure

In order to establish the optimum conditions for thorough removal of inorganic and organic mercury from aqueous solutions with *L. minor* powder as an adsorbent, influence factors of solid phase adsorption of inorganic mercury, methyl mercury, and ethyl mercury were studied by batch isotherm adsorption tests. PTFE bottles containing 500 mg *L. minor* powder were filled with certain

concentration (10.0–120.0 $\mu\text{g L}^{-1}$) mercury wastewater 250 mL at certain solution pH (1.0–11.0). The bottles were shaken periodically for certain times (10–120 min) at different temperatures (283, 293, and 313 K). After adsorption, aqueous samples from the bottles were analyzed for mercury concentration. Control experiments, without adsorbent treatment, were performed at each pH used in the adsorption experiments, simultaneously. The mass of mercury adsorbed on the adsorbent was calculated according to the difference between the initial and final concentration in the solution. The adsorption ratio was calculated based on the mass ratio between the adsorbed mercury on the adsorbent and the total mercury in the initial mercury wastewater samples. The spent adsorbent should be handled according to appropriate disposal procedures and according to applicable safety and transportation regulations.

2.4. Determination of mercury

The concentrations of inorganic mercury, methyl mercury, and ethyl mercury in water sample were determined by CV-AAS, according to the literature [23]. To the water sample (15 mL), 5 mL of a 5.0 mol L⁻¹ sodium hydroxide solution, 1 mL of the sodium hypochlorite solution, and 0.4 mL of the copper (II) solution were added in order. The tin (II) chloride solution (5 mL) was then added, and the atomic absorbance of mercury was immediately measured. A blank, using distilled-deionized water as a sample solution, was also measured; the mercury content obtained was subtracted from the content for each sample solution.

2.5. FT-IR analysis

The FT-IR analysis was used for the determination of the functional groups in *L. minor* powder. KBr pellet were prepared and the proportion of biomass/KBr was 1/100. The background was obtained from the scan of pure KBr. Perkin-Elmer spectrum RX/FT-IR system was used for FT-IR analysis of biomass.

3. Results and discussion

3.1. Analytical performance of CV-AAS

Straight lines, passing through the original point, were obtained over the concentration range of 0.1–33.0 $\mu\text{g L}^{-1}$ Hg of inorganic mercury, methyl mercury, and ethyl mercury in 15 mL of the sample solution. A 15 mL of solution containing 1.0 $\mu\text{g L}^{-1}$ of inorganic mercury, methyl mercury, and ethyl mercury was measured 11 times. The detection limit, defined as three times the standard deviation obtained from eight replicate determinations of a blank, was 0.06 $\mu\text{g L}^{-1}$ Hg in 15 mL of the sample solution. The water samples, including municipal wastewater (MW), experimental wastewater (EW), and their treated water samples by adsorption on *L. minor* powder (AD-MW, AD-EW, respectively) were determined by CV-AAS, the results are shown in Table 1 and 95.0–103.3% of recoveries were obtained from a sample solution spiked with each mercury species.

3.2. Functional groups of *L. minor* powder

The IR spectra of *L. minor* powder before and after the adsorption of inorganic mercury, methyl mercury, and ethyl mercury are shown in Fig. 1. The band at 3399–3375 cm⁻¹ is O–H stretching of polymeric compounds, 2927–24 cm⁻¹ and 2856–2850 cm⁻¹ is symmetric vibration of CH₂, 2375–2370 cm⁻¹ and 2339–2346 cm⁻¹ are the stretching vibration of COO,

Table 1

Inorganic mercury (Hg^{2+}), methyl mercury (MeHg^+), and ethyl mercury (EtHg^+) in municipal wastewater (MW), experimental wastewater (EW), and their treated water samples by adsorption on *Lemna minor* powder (AD-MW, AD-EW, respectively) ($\mu\text{g L}^{-1}$, $n=3$).

Samples	Mercury added			Mercury found			Recovery (%)		
	Hg^{2+}	MeHg^+	EtHg^+	Hg^{2+}	MeHg^+	EtHg^+	Hg^{2+}	MeHg^+	EtHg^+
Municipal wastewater (MW)	0.00	0.00	0.00	7.7 ± 0.1	5.3 ± 0.1	3.2 ± 0.1	–	–	–
	8.00	5.00	3.00	15.6 ± 0.2	10.1 ± 0.1	6.2 ± 0.1	98.7 ± 2.5	96.0 ± 2.0	99.9 ± 3.0
Experimental wastewater (EW)	0.00	0.00	0.00	20.0 ± 0.1	15.0 ± 0.1	10.0 ± 0.2	–	–	–
	20.00	15.00	10.00	40.3 ± 0.5	29.8 ± 0.4	19.8 ± 0.1	101.5 ± 2.5	98.7 ± 2.7	98.0 ± 1.0
AD-MW	0.00	0.00	0.00	0.5 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	–	–	–
	1.0	1.0	1.0	1.5 ± 0.1	1.3 ± 0.1	1.1 ± 0.1	95.0 ± 5.0	95.0 ± 5.0	95.0 ± 5.0
AD-EW	0.00	0.00	0.00	2.4 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	–	–	–
	3.0	2.0	1.0	5.5 ± 0.1	3.5 ± 0.1	2.5 ± 0.1	103.3 ± 3.3	95.0 ± 5.0	95.0 ± 5.0

$1727\text{--}1720\text{ cm}^{-1}$ is C=O stretching, $1656\text{--}1652\text{ cm}^{-1}$, $1543\text{--}1540\text{ cm}^{-1}$, and $1530\text{--}1518\text{ cm}^{-1}$ are the band of amide, $1459\text{--}1443\text{ cm}^{-1}$ is of C=O stretching of carboxylates, $1407\text{--}1400\text{ cm}^{-1}$ and $1386\text{--}1372\text{ cm}^{-1}$ are CH bending, 1315 cm^{-1} is the stretching vibration of C–O, $1232\text{--}1233\text{ cm}^{-1}$ band is vibration of COO, $1161\text{--}1056\text{ cm}^{-1}$ is vibration of C–O–C and C–O–P. In the finger print zone, the bands $779\text{--}607\text{ cm}^{-1}$ is phosphate functional groups. After adsorption of inorganic mercury, methyl mercury, and ethyl mercury onto *L. minor* powder, the peaks for amide, C–O–P, and phosphate, were much stronger and get a little red-shift, implying the participation of amide, C–O–P, and phosphate groups in binding of these three species of mercury on *L. minor* powder. The functional groups, including amide, C–O–P, and phosphate, could be able to react with mercury in aqueous solution [21,24]. No a notable change could be seen among the IR spectra of *L. minor*–inorganic mercury, *L. minor*–methyl mercury, and *L. minor*–ethyl mercury, so the adsorption mechanism was same for these three species of mercury.

3.3. Influence of pH on the adsorption ratio of mercury

The pH value of the solution is an important parameter for the adsorption experiments. The influence of pH on the adsorption of mercury by 500 mg L. minor powder was studied in the range of 1.0–11.0. A series of 250 mL standard solutions containing $100.0\text{ }\mu\text{g L}^{-1}$ of inorganic mercury, methyl mercury, and ethyl mercury, respectively (i.e., $25.0\text{ }\mu\text{g Hg}$) was added to polyethylene beaker, stirred for 30 min to adsorb Hg, then centrifuged. The centrifugal liquid was used for determining the concentration of Hg by CV-AAS. The adsorption mass of mercury on the adsorbent was the product of sample volume (250 mL) and the concentration difference between initial sample solution and the centrifugal liquid. The adsorption ratio was the mass ratio between the adsorption mass of mercury on the adsorbent and $25\text{ }\mu\text{g}$. Fig. 2 indicates the pH value played a determining role with respect to the mercury adsorption on *L. minor* powder. The medium pH affects the physicochemical state of those mercury species in solution, the ionization state of the

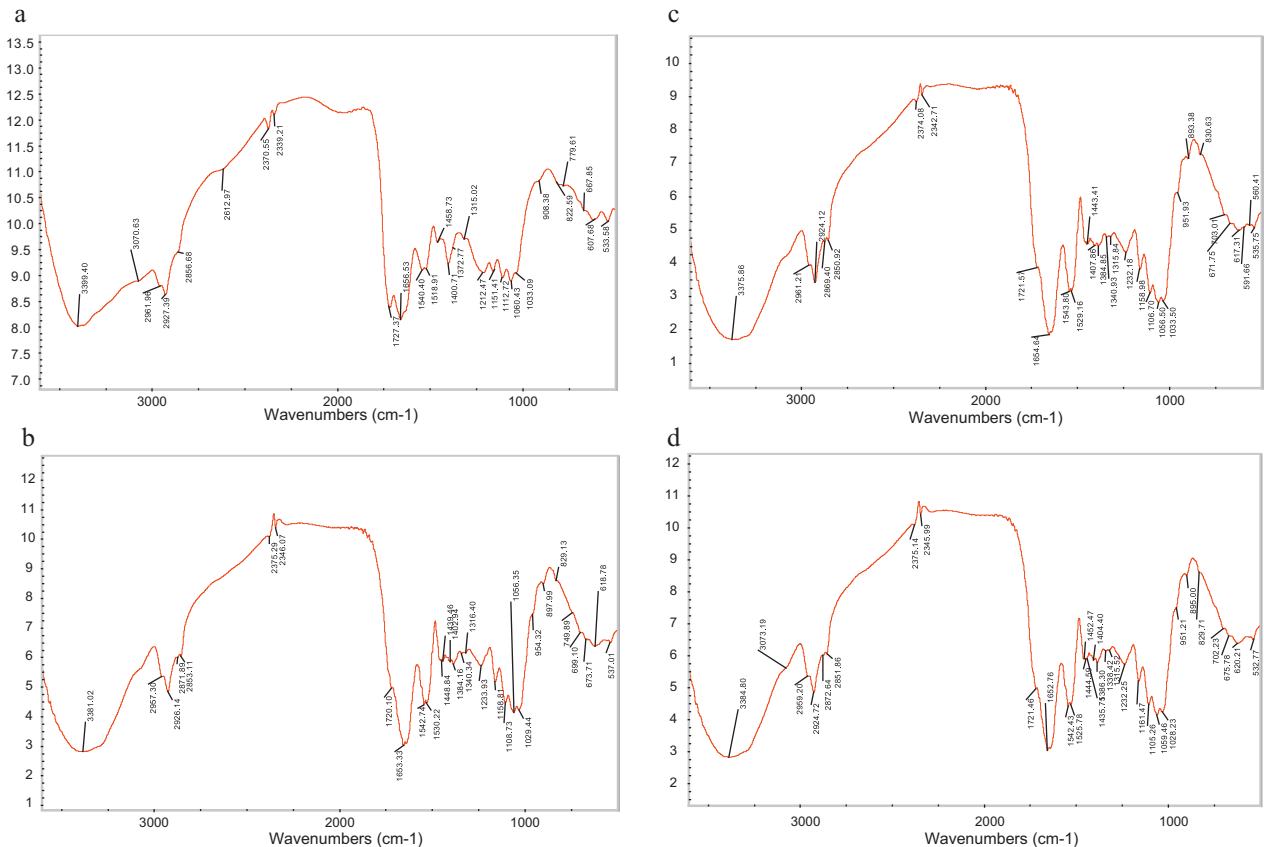


Fig. 1. FT-IR spectra of *L. minor* powder before (a) and after the adsorption of inorganic mercury (b), methyl mercury (c), and ethyl mercury (d).

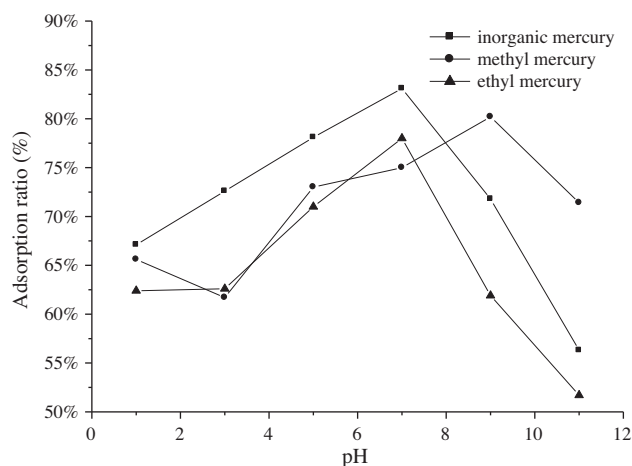


Fig. 2. Effect of the initial solution pH value on the adsorption ratio of mercury ($100.0 \mu\text{g L}^{-1}$) by *L. minor* powder.

functional groups, and the total charge produced on the surface of *L. minor* cells. The lowest metal uptake values were determined at pH 1.0 for inorganic and ethyl mercury, and pH 2.0 for methyl mercury. At lower pH, more protons will be available to protonate of three species of mercury and the active functional groups (amide, C–O–P, and phosphate) on *L. minor* powder surface, and then the adsorption would be depressed by the electrical repulsion. The optimal adsorption initial pH values of the solutions were 7.0 for inorganic and ethyl mercury, and 9.0 for methyl mercury, because: (a) more negative charge could be developed from phosphate groups which have pK_2 (the second dissociation constant of phosphoric acid) values of 7.0–8.0 and would favour the surface electrostatic interactions with aqueous mercury cations or surface mercury adsorption; (b) according to stability constant calculations, the main species of inorganic mercury, methyl mercury, and ethyl mercury at a higher pH range was $\text{Hg}(\text{OH})_2$, CH_3HgOH , $\text{C}_2\text{H}_5\text{HgOH}$, but no significant change of dissolved mercury at pH range of 1–12 with a initial concentration lower than 120 mg L^{-1} in the absence of the adsorbent [25], furthermore, the mercury adsorption could accelerate the species transformation of mercury from $\text{Hg}(\text{OH})_2$ to Hg^{2+} , from CH_3HgOH to CH_3Hg^+ , and from $\text{C}_2\text{H}_5\text{HgOH}$ to $\text{C}_2\text{H}_5\text{Hg}^+$. These optimal pH values were chosen for the subsequent experiments. In the case of Hg biosorption by *L. minor* cells, the pH dependence is slightly different to that observed for other metals [23], these three species of mercury present an \wedge -shape curve, Cd(II) as an example presents an S-shape curve, and the maximum uptake of Cd(II) was at pH 4.5, because: (a) amide group is unique for selective mercury binding because nitrogen atom in this group is a very weak electron donor and does not form coordinative linkages with transition metal ions but the amide nitrogen could form a covalent linkage with mercury in ordinary conditions to give mono or diamido mercury compounds [26] and (b) the adsorption functional groups for Cd(II) might be carboxylate groups that have pK values of 4.0–5.0 [27].

3.4. Influence of adsorption time on the adsorption ratio

Because rapid adsorption was of great importance in water treatment, the study of the adsorption equilibration time was performed. Under the best pH value condition and initial mercury concentration $100.0 \mu\text{g L}^{-1}$, the effect of adsorption time of 10, 20, 30, 40, 60, 80, 100, and 120 min on the adsorption ratio was studied and the results are shown in Fig. 3. The adsorption ratio of mercury was increased with the increasing of the adsorption time until reaching the adsorption equilibrium time of inorganic mercury

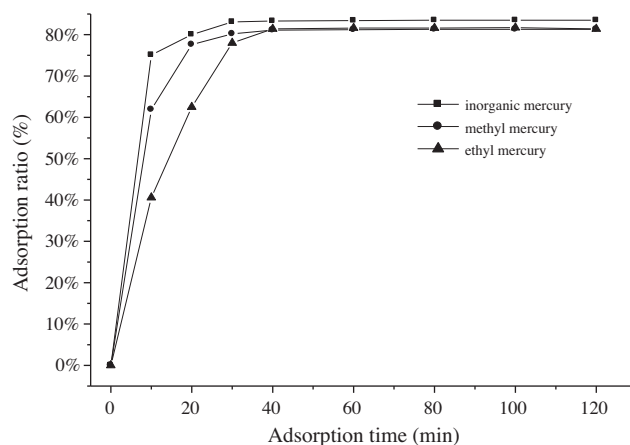


Fig. 3. Effect of the adsorption time on the adsorption ratio of mercury ($100.0 \mu\text{g L}^{-1}$).

(10 min), methyl mercury (20 min), and ethyl mercury (40 min). The adsorption rate of mercury could be calculated from the slopes of the plots, following the rate order: inorganic mercury > methyl mercury > ethyl mercury. Both the adsorption ratio and rate were controlled by the species of mercury. So the reasonable adsorption time for removal mercury in Hg-containing wastewater was 40 min and this adsorption time was used in the following experiment.

3.5. Adsorption isotherms

The adsorption capacity was the maximum metal quantity taken up by 1 mg of adsorbent and given by $\text{ng mercury mg}^{-1}$ adsorbent. The adsorption isotherm was defined as the plot of the adsorbed amount on *L. minor* powder (q_e) against the equilibrium concentration of mercury (C_e) in an aqueous solution. At different temperatures (283, 293, and 313 K), the test solutions 250 mL containing 20.0, 40.0, 60.0, 80.0, 100.0, and $120 \mu\text{g L}^{-1}$ of inorganic mercury, methyl mercury, and ethyl mercury, respectively, were added *L. minor* powder 500 mg, stirred for 40 min, and centrifuged. The content in the centrifugate, i.e., the free concentration of mercury after reaching the adsorption equilibrium, was determined, and then the adsorption isotherm of mercury could be constructed, shown in Fig. 4.

A declined trend of q_e , especially for q_m , was observed for a raise in temperature from 283 to 313 K, revealing the exothermic nature of the adsorption process. Isotherms were modeled with the two most commonly used equilibrium models, namely, Freundlich and Langmuir.

The Freundlich isotherm is an empirical equation used for non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption and is derived by assuming an exponentially decaying adsorption site energy distribution, which can be expressed as:

$$\ln q_e = \frac{1}{n} \times \ln C_e + \ln K_F$$

where K_F and n are the Freundlich constants denoting adsorption capacity and intensity of adsorption, respectively. However, the Freundlich equation fails to obey the Henry's law at lower concentrations non-complying to the fundamental thermodynamic principles. The Langmuir isotherm derived from simple mass action kinetics is based on the assumptions that molecules are adsorbed as a saturated monolayer of one molecule thickness with no transmigration in the plane of the surface, and interaction between adsorbed molecules are negligible with energy of adsorption remaining constant. The non-linear form of the Lang-

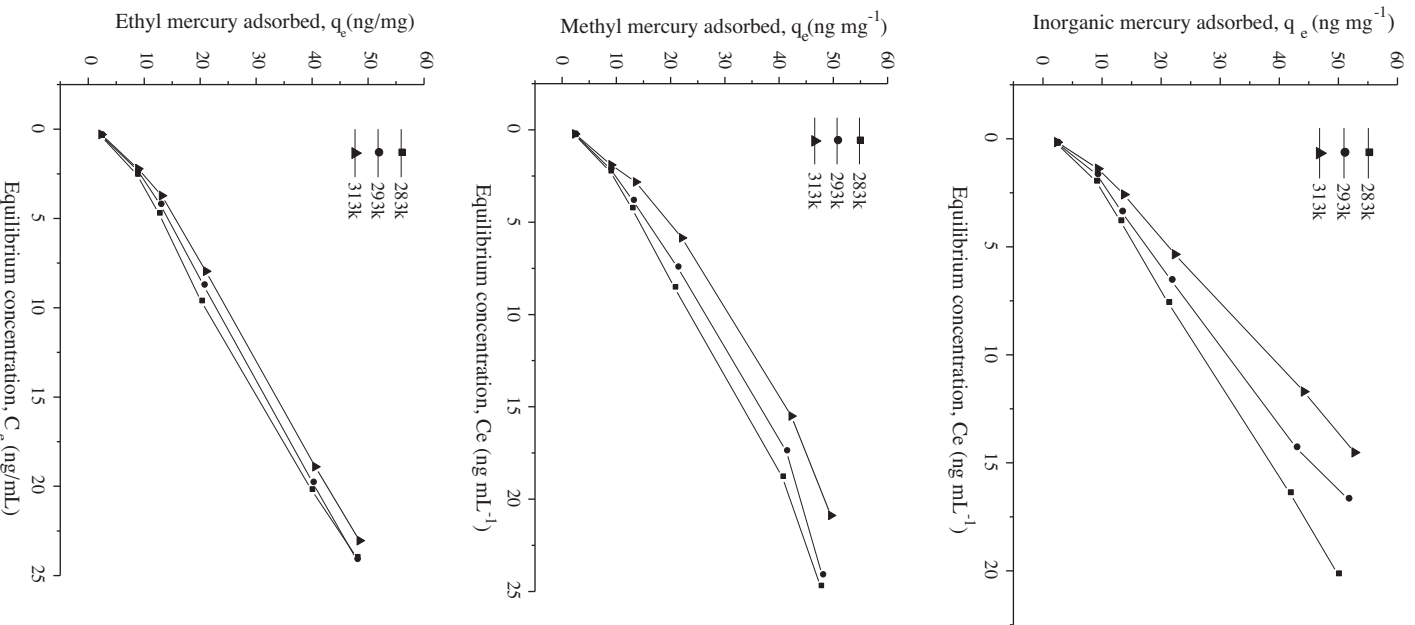


Fig. 4. Adsorption isotherm of inorganic mercury, methyl mercury, and ethyl mercury on *L. minor* powder.

Langmuir equation is given by:

$$\frac{1}{q_e} = \frac{1}{q_m b} \times \frac{1}{C_e} + \frac{1}{q_m}$$

where q_m and b represent the maximum adsorption capacity and energy of adsorption (equilibrium constant), respectively.

The adsorption behaviors of inorganic mercury, methyl mercury, and ethyl mercury on *L. minor* powder were coincided with both Freundlich and Langmuir adsorption isothermal and the results are shown in Table 2. These phenomena indicated that two adsorption mechanisms might be coexisted, including: (a) surface

Table 2
Modeled adsorption isotherm equation, isotherm parameters, and thermodynamic parameters for the adsorption of inorganic mercury, methyl mercury, and ethyl mercury on *L. minor* powder at different temperatures.

	Inorganic mercury			Methyl mercury			Ethyl mercury		
	283 K	293 K	313 K	283 K	293 K	313 K	283 K	293 K	313 K
Langmuir model									
Isotherm equation	$1/q_e = 0.0591 \times (1/C_e) + 0.0355$	$1/q_e = 0.0748 \times (1/C_e) + 0.0362$	$1/q_e = 0.0888 \times (1/C_e) + 0.037$	$1/q_e = 0.0876 \times (1/C_e) + 0.0335$	$1/q_e = 0.0955 \times (1/C_e) + 0.0352$	$1/q_e = 0.1139 \times (1/C_e) + 0.0359$	$1/q_e = 0.1175 \times (1/C_e) + 0.0312$	$1/q_e = 0.1362 \times (1/C_e) + 0.0324$	$1/q_e = 0.1489 \times (1/C_e) + 0.0334$
R^2	0.9839	0.9838	0.9834	0.9862	0.9835	0.9863	0.9882	0.9904	0.9890
q_m (ng mg ⁻¹)	28.169	27.624	27.027	29.851	28.409	27.855	32.051	30.864	29.940
b (mL ng ⁻¹)	0.601	0.484	0.417	0.382	0.369	0.315	0.266	0.238	0.224
Freundlich model									
Isotherm equation	$\ln q_e = 0.6752 \ln C_e + 2.0658$	$\ln q_e = 0.6787 \ln C_e + 1.9012$	$\ln q_e = 0.675 \ln C_e + 1.7800$	$\ln q_e = 0.6789 \ln C_e + 1.8623$	$\ln q_e = 0.6648 \ln C_e + 1.7432$	$\ln q_e = 0.6784 \ln C_e + 1.6457$	$\ln q_e = 0.6900 \ln C_e + 1.6679$	$\ln q_e = 0.7022 \ln C_e + 1.5780$	$\ln q_e = 0.7157 \ln C_e + 1.4966$
R^2	0.9942	0.9909	0.9929	0.9979	0.9971	0.9968	0.9988	0.9982	0.9947
n	1.481	1.473	1.481	1.473	1.504	1.474	1.449	1.424	1.397
K_F (mL ⁿ ng ¹⁻ⁿ mg ⁻¹)	7.892	6.694	5.930	6.439	5.716	5.184	5.301	4.845	4.466
Thermodynamic parameters									
ΔG° (J mol ⁻¹)	11.275	11.146	11.519	10.379	10.659	10.977	9.671	9.746	10.257
ΔH° (J mol ⁻¹)	8.587			4.900			3.995		
ΔS° (mJ mol ⁻¹ K ⁻¹)	9.204			19.481			19.901		

Table 3
Effect of the initial mercury concentrations on the adsorption ratio (%) and the residual concentration (V: 250 mL).

Initial concentration ($\mu\text{g L}^{-1}$)	Inorganic mercury		Methyl mercury		Ethyl mercury	
	Adsorption rate (%)	Residual concentration ($\mu\text{g L}^{-1}$)	Adsorption rate (%)	Residual concentration ($\mu\text{g L}^{-1}$)	Adsorption rate (%)	Residual concentration ($\mu\text{g L}^{-1}$)
10.0	95.1	0.5	93.7	0.6	93.6	0.6
12.0	93.8	0.74	92.9	0.9	92.5	0.9
20.0	90.4	1.9	92.5	1.5	86.7	2.7
50.0	87.2	6.4	88.8	5.6	81.8	9.1
100.0	83.1	16.9	81.1	18.9	81.4	18.6

electrostatic interactions between significant adsorption sites in *L. minor* powder (C–O–P and phosphate groups) and aqueous mercury cations; (b) the strong chelating interaction between amine groups and mercury on the surface of *L. minor* cells.

3.6. Thermodynamic aspects

The equilibrium constant (b) values derived from the Langmuir modeling of isotherms at different temperatures (283, 293, and 313 K) were used to determine thermodynamic parameters like changes in enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) according to the following equation:

$$\Delta G^\circ = -RT \ln Ke$$

$$\ln Ke = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K) and Ke (L mol^{-1}) is the product of Langmuir constant b (mL mg^{-1}) and molar weight of inorganic mercury, methyl mercury, and ethyl mercury (200.59, 215.62, $229.65 \text{ g mol}^{-1}$). The thermodynamic parameters are shown in Table 2. Under different temperatures (283, 293, and 313 K), the negative ΔG° values of 11.275, 11.146, $11.519 \text{ J mol}^{-1}$ for inorganic mercury, 10.379, 10.659, $10.977 \text{ J mol}^{-1}$ for methyl mercury, and 9.671, 9.746, $10.257 \text{ J mol}^{-1}$ for ethyl mercury, respectively, indicated the spontaneous nature of inorganic mercury, methyl mercury, and ethyl mercury adsorption by *L. minor* powder. The magnitude of ΔG° increased along with increasing temperature, implying an increased degree of spontaneity at a higher temperature for its advantage of the chelating interaction between amine groups and mercury. From the van't Hoff plot ($\ln Ke$ versus $1/T$; plot not shown), the negative ΔH° values of (8.587, 4.900, and 3.995 J mol^{-1} for inorganic mercury, methyl mercury, and ethyl mercury, respectively) confirmed the exothermic nature of mercury adsorption, while the negative values of ΔS° (9.204, 19.481, $19.901 \text{ mJ mol}^{-1} \text{ K}^{-1}$ for inorganic mercury, methyl mercury, and ethyl mercury, respectively) revealed the decreased randomness (orderliness) at the solid/solution interface.

3.7. Influence of initial concentration of mercury on the adsorption ratio

Under the optimal adsorption conditions, including the pH value, adsorption time, and *L. minor* powder amount (500 mg), the influence of the initial concentration of mercury solution with same volume (250 mL) on the adsorption ratio and the residual concentration was studied and the results are shown in Table 3.

With the increasing of the initial concentration of three species of mercury from $10.0 \mu\text{g L}^{-1}$ to $100.0 \mu\text{g L}^{-1}$, the adsorption ratio was decreased. When the initial concentration of three species of mercury was not more than $12.0 \mu\text{g L}^{-1}$, after adsorption by *L. minor* powder, the residual concentrations of organic and inorganic mercury were under $1.0 \mu\text{g L}^{-1}$ that can meet the criterion of drinking

water set by China, USEPA, and WHO. When the initial concentration of three species of mercury was not more than $50.0 \mu\text{g L}^{-1}$, the residual concentrations of organic and inorganic mercury were under $10.0 \mu\text{g L}^{-1}$, i.e., below the permitted discharge limit of wastewater established by USEPA and China. Thorough removal of both inorganic and organic mercury from aqueous solutions was reported for the first time.

3.8. Application to removal of mercury in model and real wastewater samples

The performance of adsorption removal of inorganic and organic mercury in real and model wastewater samples by *L. minor* powder and the influence of coexisting ions on the adsorption ratio of mercury have been tested and the results are shown in Table 1. As real wastewater sample, the municipal wastewater (MW) was collected from Zhangzhou Wastewater Treatment Co., in Fujian Province, Zhangzhou city, China. The concentrations of inorganic mercury, methyl mercury, and ethyl mercury in MW were 7.7, 5.3, and $3.2 \mu\text{g L}^{-1}$, respectively, the total mercury in it could be reduced from $16.2 \mu\text{g L}^{-1}$ to $1.2 \mu\text{g L}^{-1}$ by our technology, and the adsorption ratio of total mercury in MW was 92.6%. In experimental wastewater (EW), $45.0 \mu\text{g L}^{-1}$ mercury (including $20.0 \mu\text{g L}^{-1}$ inorganic mercury, $15.0 \mu\text{g L}^{-1}$ methyl mercury, and $10.0 \mu\text{g L}^{-1}$ ethyl mercury) was added together with 50 mg L^{-1} of usual ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) and 5 mg L^{-1} of heavy metal (Mn^{2+} , Cr^{3+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+}) and then was used as model wastewater sample. After adsorption by *L. minor* powder, the total mercury in EW was removed from $45.0 \mu\text{g L}^{-1}$ to $5.5 \mu\text{g L}^{-1}$ and the adsorption ratio of total mercury in EW was 87.8%. The influence of coexisting ions in real and model wastewaters, especially heavy metal ions, on the adsorption ratio of mercury was not obvious. Because the C–O–P and amide groups in *L. minor* powder are soft basic, which could bind selectively mercury cations as soft acid.

4. Conclusions

L. minor powder could be used as a potential low-cost adsorbent for its excellent removal capability of both inorganic and organic mercury. The adsorption behaviors of inorganic mercury, methyl mercury, and ethyl mercury on *L. minor* powder were coincided with the Langmuir adsorption isothermal. For a sample, whose initial concentrations of inorganic and organic mercury are under $12.0 \mu\text{g L}^{-1}$ and $50.0 \mu\text{g L}^{-1}$, respectively, after adsorption by *L. minor* powder for 40 min, the residual concentrations of mercury could meet the criterion of drinking water and the permitted discharge limit of wastewater set by China and USEPA, respectively.

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